

面向21世纪高等理工科重点课程辅导丛书

有机化学考研辅导

李小瑞 主编



化学工业出版社
教材出版中心

·北京·

目 录

第一部分 专题总结

专题总结 I —— 有机反应的分类	1
一、取代	1
1. 自由基取代	1
2. 亲电取代	1
3. 亲核取代	3
二、加成反应	8
1. 催化加氢	8
2. 自由基加成	9
3. 亲电加成	9
4. 硼氢化反应	10
5. 羟汞化-脱汞反应及烷氧汞化-脱汞反应	10
6. 共轭加成	10
7. 亲核加成	11
8. 安息香缩合——极翻转的概念	12
三、消除反应	12
1. 卤代烃的消除及 E1、E2	12
2. 热消除反应	16
四、氧化反应	18
1. KMnO_4 氧化	18
2. 铬酸氧化	19
3. 丙酮十异丙醇铝氧化 (Oppenauer 氧化)	20
4. HIO_4 氧化	20
5. MnO_2 氧化	20
6. H_2O_2 及过酸氧化	21
7. Tollens 氧化及 Fehling 氧化	22
8. Br_2 水氧化	22
9. 空气氧化	22
五、还原反应	23
1. 催化加氢	23
2. Na/NH_3 (或 $\text{NaNH}_2/\text{液 NH}_3$) 还原	23
3. NaBH_4 、 LiAlH_4 、 $[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$ 还原	24

4. 重要的特殊还原反应	24
5. 醛和酮的还原	25
六、歧化反应 (Cannizzaro 反应)	26
七、重排反应	26
1. 酸性条件下发生的重排	26
2. 碱性条件下发生的重排	31
3. 加热条件下发生的重排	32
八、与活泼亚甲基有关的反应	34
九、降解反应	34
1. Hofmann 降解	34
2. 臭氧化	34
3. 卤仿反应	35
4. 邻二醇氧化	35
5. 脱羧	35
6. 羧基分解	35
十、周环反应	36
1. 环化加成	36
2. 电环化反应	37
3. Claisen 重排和 Cope 重排	38
专题总结 II —— 与活泼亚甲基有关的反应	38
1. 酮的卤化	38
2. 卤仿反应	38
3. 脂肪酸的 α -卤代	38
4. 羧醛缩合	38
5. Perkin 反应	39
6. Knoevenagel 反应	39
7. Claisen 酯缩合反应和 Diekmann 反应	40
8. β -二羰基化合物的烃基化和酰基化	41
9. Michel 加成	41
10. Darzen 反应	43
11. Reformasky 反应 —— 制 β -羟基酸 (酯)	44
12. Mannich 反应 (胺甲基化反应)	44
13. 羰基化合物经烯胺的酰基化或烃基化	45
14. Reimer-Tiemann 反应	46
完成反应式练习题 (I)	46
参考答案 (I)	50
完成反应式练习题 (II)	52
参考答案 (II)	56
完成反应式练习题 (III)	58
参考答案 (III)	61

专题总结 III——基础有机化学中的合成题	63
一、引言	63
1. 设计合成路线的 3 个指标	63
2. 设计合成路线的步骤和方法	63
二、增长碳链的方法 (形成碳-碳键的方法)	66
1. 亲核取代	66
2. 亲核加成	66
3. 芳环上亲电取代	67
4. 其他方法	68
三、环的形成和变化	68
1. 卤代酮、腈、酯的分子内 S_N2 反应	68
2. 二卤代物脱卤	69
3. 丙二酸酯法	69
4. 分子内缩合	69
5. Robinson 并环反应	69
6. 己二酸、庚二酸脱羧脱水	70
7. 芳烃与环酐的 Friedel-Crafts 反应	70
8. 周环反应	71
9. 卡宾法	71
10. 环的扩大与缩小	71
四、重要的有机合成反应	71
1. 格氏反应——制醇或者多一个碳的羧酸	71
2. 苯环上亲电取代反应——制一系列芳香族化合物	71
3. $C=C$ 与 $C\equiv C$ 的转化	72
4. Williamson 法制醚	72
5. 甲基化制氯苄衍生物	73
6. Gattermann-Koch 合成——在苯环上引入甲酰基	73
7. 酮的双分子还原——制不对称酮	73
8. 磺化碱熔法制酚	73
9. 异丙苯氧化法制酚	74
10. 卤仿反应——制少一个碳的羧酸	74
11. Rosenmund 还原——由酰氯制醛	74
12. 由 RX 制酸	74
13. Mannich 反应 (胺甲基化反应)——间接制备 α,β -不饱和醛、酮	74
14. Wittig 反应——制备烯烃	74
15. Darzen 反应——在羰基碳上引入醛基	74
16. Reimer-Tiemann 反应——在酚羟基的邻位上引入醛基	74
17. Perkin 反应制——由芳醛制 α,β -不饱和酸	74
18. Reformatsky 反应——制 β -羟基酸 (酯)	74
19. Gabriel 法制伯胺	74

20. Hofmann 降解制伯胺	75
21. 由三乙制甲基酮	75
22. 由丙二制取代乙酸	75
23. Beayer-Villiger 氧化——由酮制备酯	75
24. 羰基化合物经烯胺的酰基化或烃基化——在羰基的 α -位上引入酰基或 烃基	75
25. Michel 加成——制 1,5-二羰基化合物	75
26. 重氮盐的放氮反应——制一系列芳香族化合物	75
27. 重氮盐的偶联反应——制一系列有颜色的化合物	76
28. 氨基酸的特殊制法——丙二合成法与 Gabriel 合成法联用	76
29. Skrap 合成法——制喹啉类化合物	76
五、重要的工业合成反应	77
1. 异丙苯氧化法制苯酚	77
2. 甲基丙烯酸甲酯的制备	77
3. 乙酸乙烯酯的制备	77
4. 己内酰胺的制备	78
5. 聚对苯二甲酸乙二醇酯的制备	78
合成练习题 (I)	78
参考答案	81
合成练习题 (II)	91
参考答案	92
专题总结 IV——某些反应的立体化学	95
1. S_N1 反应中, C^+ 中心碳原子为平面构型, 产物是外消旋化的	95
2. E2 反应为反式消去	95
3. 催化加氢是顺式加成	95
4. $C=C$ 加卤素是反式加成	95
5. 硼氢化反应是顺式加成	95
6. $C=C$ 环氧化是顺加, 环氧化物开环为反式开环	95
7. 环化加成 (双烯合成) 是顺式加成	95
8. α, β 不饱和醛酮的共轭加成是反式加成	95
9. 醛酮被 $LiAlH_4$ 还原或与 $R''MgX$ 加成时的立体化学为	96
10. α -氯代醛酮与 $R'MgX$ 加成时的立体化学为	96
11. Hofmann 降解时, 手性碳的构型保持不变	96
12. $SOCl_2$ 与含有手性碳的醇反应时, 手性碳的构型保持不变	96
13. Beayer-Villiger 重排中, 手性碳的构型保持不变	96
14. ROH 与 PBr_3 反应为 S_N2 , 构型翻转	97
15. Hofmann 热消除的立体化学为反式消除	97
16. 醋酸酯热消除是顺式消除	97
17. 氧化叔胺的热消除是顺式消除	97
专题总结 V——常用波谱数据	97

1. 红外光谱	97
2. 核磁共振谱	98
专题总结 VI——反应历程总结	99
1. 自由基取代	99
2. 自由基加成	99
3. 亲电加成	99
4. 亲电取代 (苯环上“四化”)	100
5. 亲核取代	100
6. 消除反应	100
7. 羟醛缩合反应历程	101
8. 卤代及卤仿反应历程	101
9. 缩醛的形成	102
10. 酯化反应历程	102
11. 羧酸衍生物的亲核取代 (加成-消除) 反应历程	102
12. 酸催化酯的水解反应历程	103
13. 碱催化酯的水解反应历程	103
14. 克莱森酯缩合反应历程	103
15. 重氮盐放氮反应历程	103
16. 重氮盐偶联反应历程	103
练习题	104
专题总结 VII——鉴别用试剂	109
1. $\text{Br}_2/\text{H}_2\text{O}$ 或 Br_2/CCl_4	109
2. KMnO_4	109
3. 顺丁烯二酸酐 (顺酐) ——检验共轭双烯	109
4. Lucas 试剂 ——区别 1° 、 2° 、 3°ROH	110
5. $\text{AgNO}_3/\text{醇}$ ——检验 1° 、 2° 、 3°RX	110
6. FeCl_3 ——检验酚羟基、“稳定的”烯醇式结构	110
7. 饱和 NaHSO_3 溶液	110
8. 苯肼和 2,4-二硝基苯肼 ——检验羰基	110
9. NH_2OH ——检验羰基	111
10. Tollens 试剂和 Fehling 试剂 ——检验醛	111
11. $\text{I}_2 + \text{NaOH}$ ——检验甲基酮、乙醛、“甲基醇”	111
12. 5% NaHCO_3 和 5% NaOH ——检验有酸性的有机化合物	111
13. 对甲苯磺酰氯、 NaOH (Hinsberg 反应, 鉴别胺)	111
14. CHCl_3/KOH (异脎反应) ——检验伯胺	111
15. 漂白粉 ——检验苯胺	111
16. 水合茚三酮 ——检验 α -氨基酸	112
17. HIO_4 、 AgNO_3 ——检验邻二醇	112
18. HCl -松木片 ——区别五元杂环化合物	112
专题总结 VIII——有机化合物的命名	112

1. 系统命名法	112
2. 桥环化合物的命名	113
3. 螺环化合物的命名	113

第二部分 模拟试题

模拟试题 1	115
参考答案	118
模拟试题 2	121
参考答案	125
模拟试题 3	129
参考答案	131
模拟试题 4	134
参考答案	137
模拟试题 5	140
参考答案	142
模拟试题 6	145
参考答案	118
模拟试题 7	152
参考答案	155
模拟试题 8	158
参考答案	161
模拟试题 9	164
参考答案	167
模拟试题 10	171
参考答案	175
模拟试题 11	178
参考答案	182
模拟试题 12	186
参考答案	188
模拟试题 13	192
参考答案	194
模拟试题 14	197
参考答案	200
模拟试题 15	202
参考答案	205
模拟试题 16	209
参考答案	213
模拟试题 17	216
参考答案	220

模拟试题 18	222
参考答案	224
模拟试题 19	227
参考答案	230
模拟试题 20	233
参考答案	236
模拟试题 21	238
参考答案	241
模拟试题 22	244
参考答案	248
模拟试题 23	251
参考答案	253
模拟试题 24	256
参考答案	259
模拟试题 25	261
参考答案	266
模拟试题 26	270
参考答案	274
模拟试题 27	277
参考答案	282
模拟试题 28	286
参考答案	290
模拟试题 29	294
参考答案	296
模拟试题 30	298
参考答案	302
模拟试题 31	305
参考答案	310
模拟试题 32	314
参考答案	317
模拟试题 33	320
参考答案	324
模拟试题 34	327
参考答案	330
模拟试题 35	332
参考答案	336
模拟试题 36	339
参考答案	342
模拟试题 37	345
参考答案	350

模拟试题 38	353
参考答案	357
模拟试题 39	361
参考答案	364

第一部分 专题总结

专题总结 I —— 有机反应的分类

有机反应的类型有：取代、加成、消除、氧化、还原、歧化、缩合、降解、重排以及其他反应。

一、取代

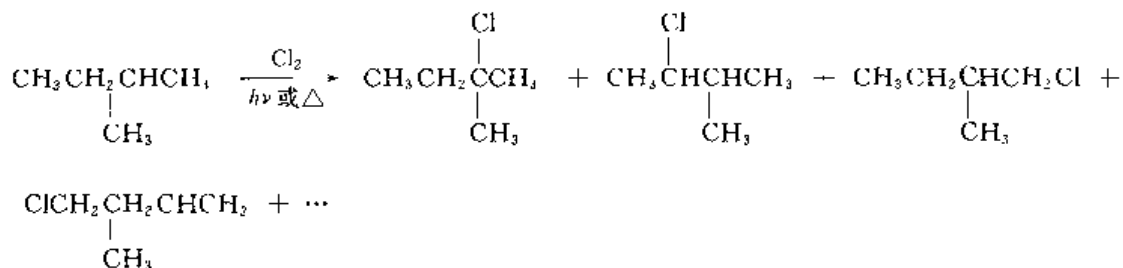
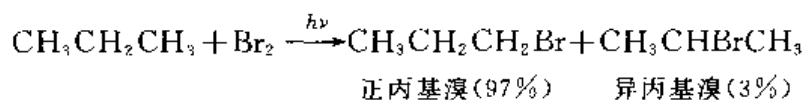
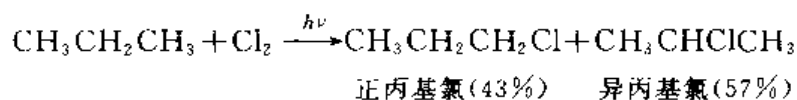
根据反应历程可分为：自由基取代、亲电取代、亲核取代。

1. 自由基取代

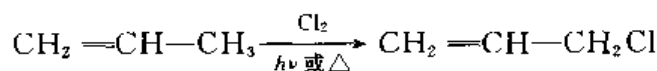
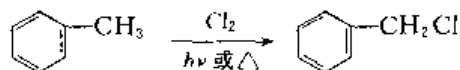
【特点】 有自由基参与，在光照、加热或过氧化物存在下进行。

【举例】

① 烷烃的卤代—氯代选择性差，溴代选择性好。



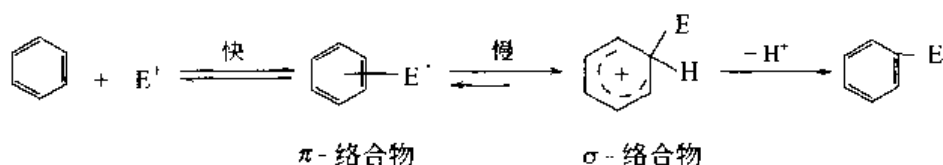
② 烯烃或芳烃的 α -卤代—选择性较好。



2. 亲电取代

芳环上的“四化”反应——卤化、硝化、磺化、烷基化或酰基化。

【特点】 亲电试剂 (E^+) 首先进攻。



【讨论】

① 定位规律 苯环上已有一个取代基之后，新引入的取代基的位置取向受原有取代基的性质的影响。原有基团分为以下两类。

第一类：致活基，新引入基团在它的邻、对位。属于这类基团的有 $-\text{O}^-$ 、 $-\text{NR}_2^-$ 、 $-\text{NHR}^-$ 、 $-\text{OH}$ 、 $-\text{OCH}_3$ 、 $-\text{NHCOCH}_3$ 、 $-\text{OCOR}$ 、 $-\text{C}_6\text{H}_5$ 、 $-\text{R}$ [CH_3 、 $-\text{C}_2\text{H}_5$ 、 $(\text{CH}_3)_2\text{CH}$]、 $-\text{H}$ 、 $-\text{X}$ 等。

【特点】 负电荷，孤对电子，饱和键。

第二类：致钝基，新引入的基团上间位。属于这类基团的有 $-\text{N}^+\text{R}_3$ 、 $-\text{NO}_2$ 、 $-\text{CN}$ 、 $-\text{COOH}$ 、 $-\text{SO}_3\text{H}$ 、 $-\text{CHO}$ 、 $-\text{COR}$ 等。

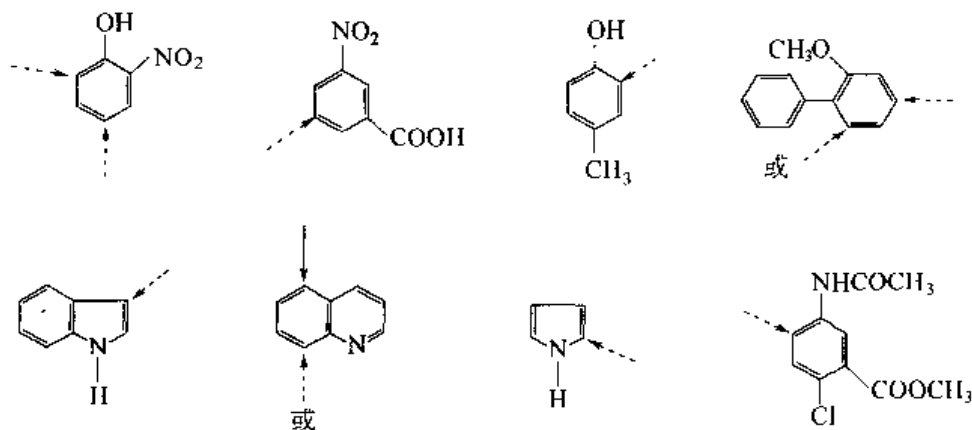
【特点】 正电荷，不饱和键。

上述两类定位基定位能力的强弱是不同的，其大致次序如上所述。

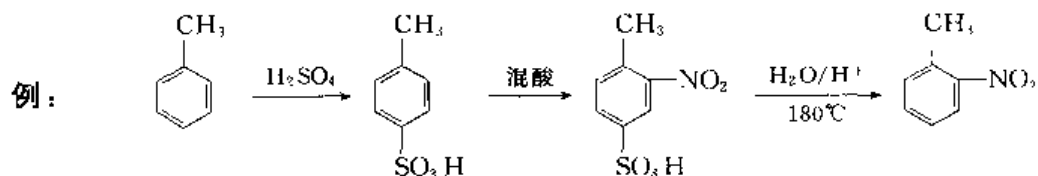
② 取代苯的定位规则 当苯环上已有两个取代基时，第三个基团进入苯环位置主要由原来的两个取代基的性质决定。

(a) 原有基团是同类时，以强者为主。

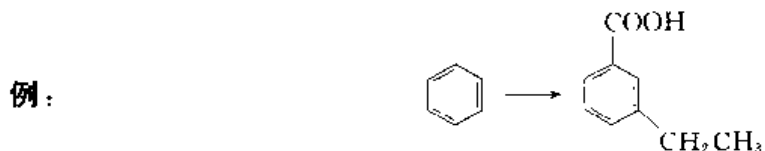
(b) 原有基团不同类时，以第一类为主（不管 II 类有多强，I 类有多弱），因为反应类型是亲电取代反应。

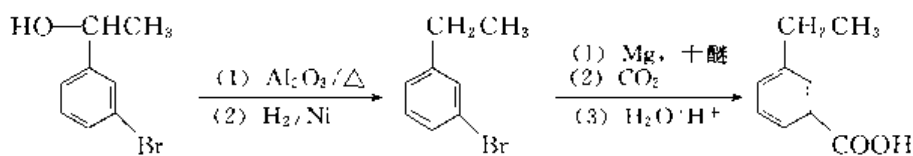
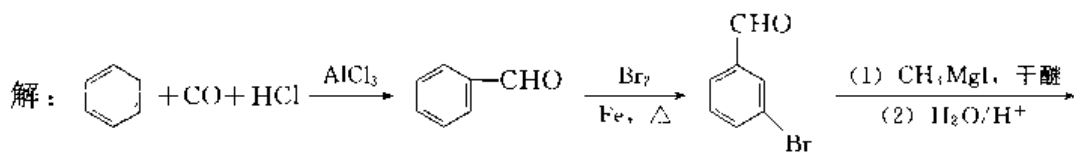


③ 磺化反应可逆 有机合成中常利用磺化反应可逆性，来进行占位。

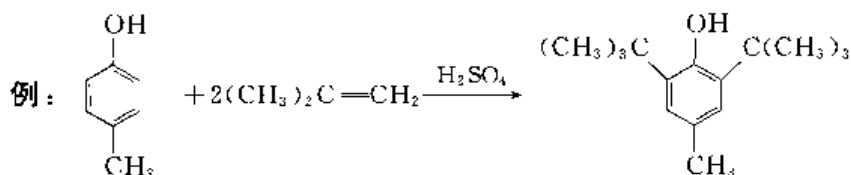
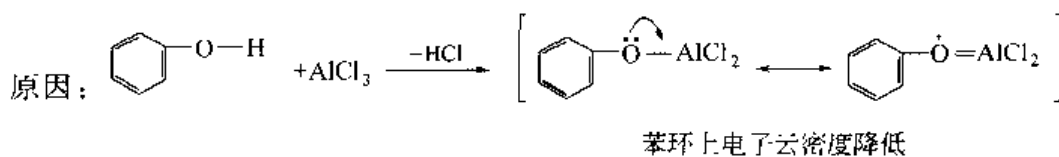


④ 芳环上有吸电子基取代时（如 PhNO_2 、 PhCN 、 PhCOOH 、 PhSO_3H 等）不发生付氏反应。

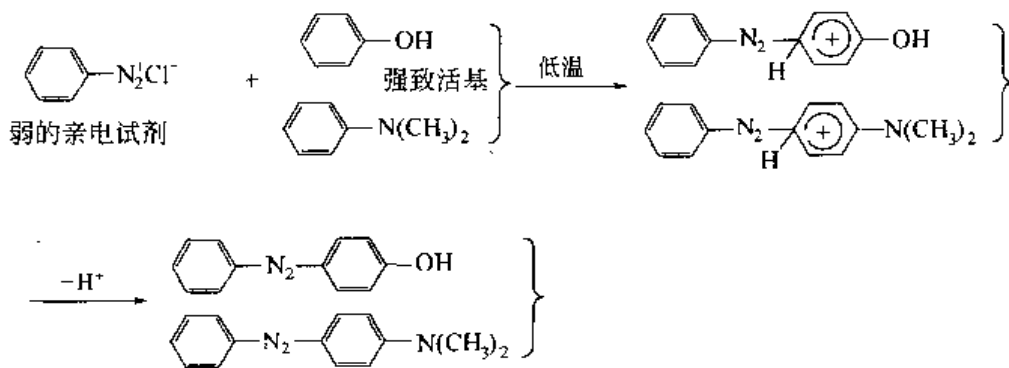




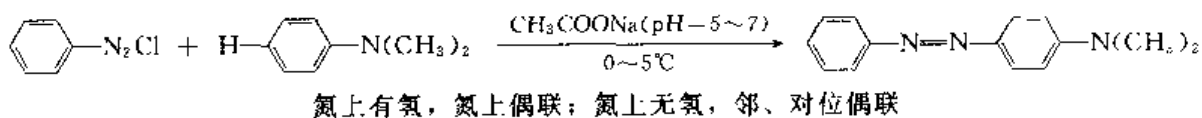
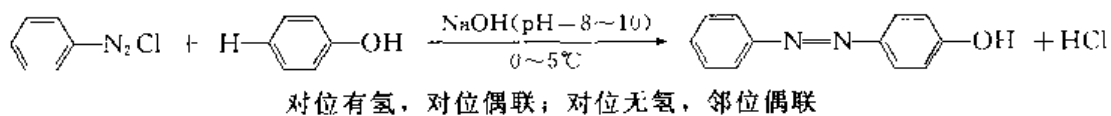
⑤ 酚的付氏反应特殊，一般用质子酸催化。



⑥ 偶联反应的本质也是亲电取代反应。

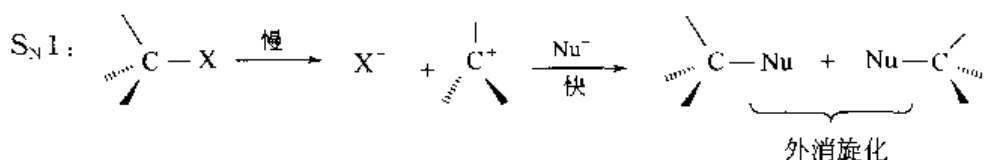


例:



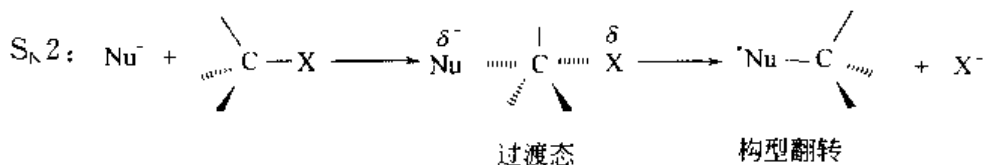
3. 亲核取代

(1) $\text{S}_{\text{N}}1$ 和 $\text{S}_{\text{N}}2$



C⁺的稳定性: 3° > 2° > 1° C⁺

S_N1 反应速率: 3° > 2° > 1° RX



Nu 从背面进攻 α-C 时, 空间障碍: 1° < 2° < 3° RX

S_N2 反应速率: 1° > 2° > 3° RX

【讨论】

S_N1 和 S_N2 是一对相互竞争的反应, 究竟以何种历程进行取决于 RX 的结构、试剂的亲核性、溶剂的极性、离去基团的性质等因素。

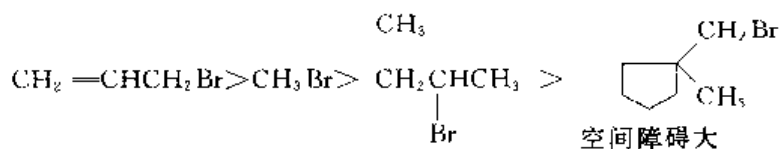
① 3°RX 易进行单分子反应 (3° C⁺ 稳定); 1°RX 易进行双分子反应 (1°RX 空间障碍小); 烯丙型卤代烃既易于 S_N1, 又易于 S_N2。

② 亲核性强的试剂有利于 S_N2, S_N1 基本不受试剂亲核性的影响。

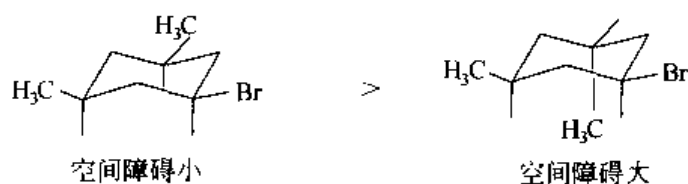
③ 极性大的溶剂有利于 S_N1; 极性小的溶剂有利于 S_N2。

④ 易于离去的基团有利于 S_N1 和 S_N2。

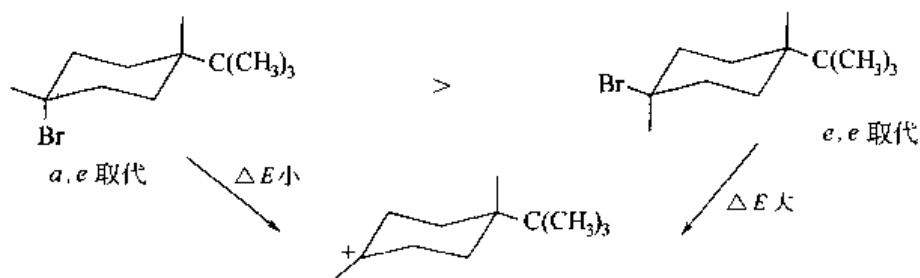
例 1: S_N2 速率:



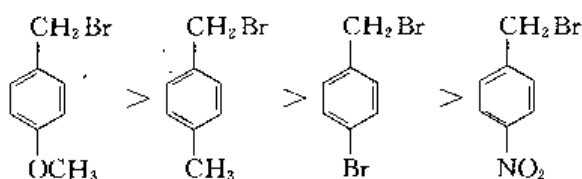
例 2: S_N2 速率:




例 3: S_N1 速率:

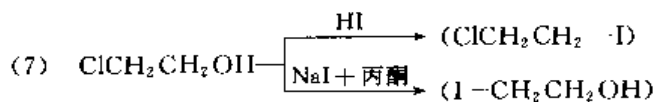
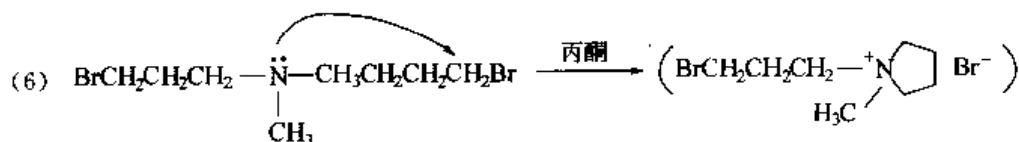
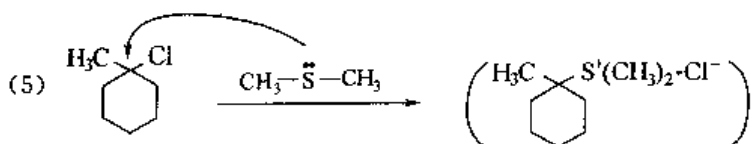
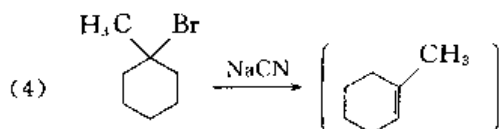
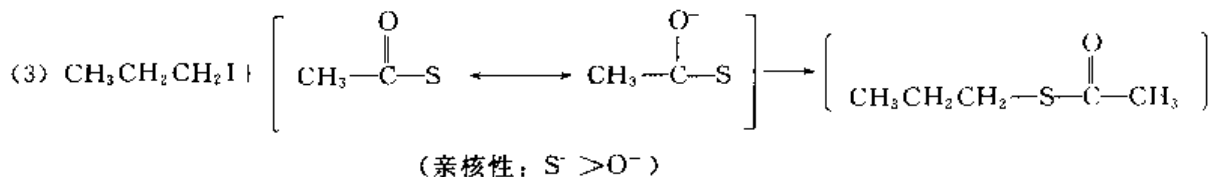
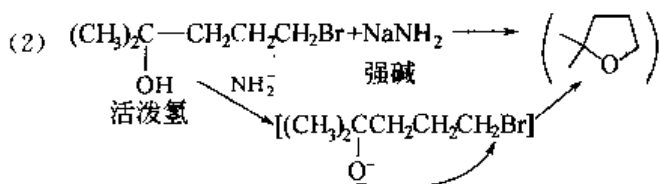
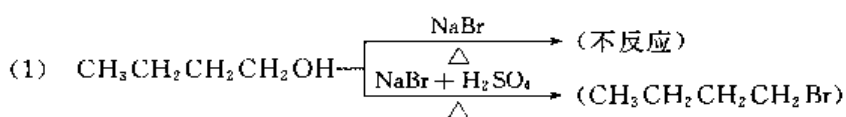


例 4: 与 AgNO_3 -醇的反应速率

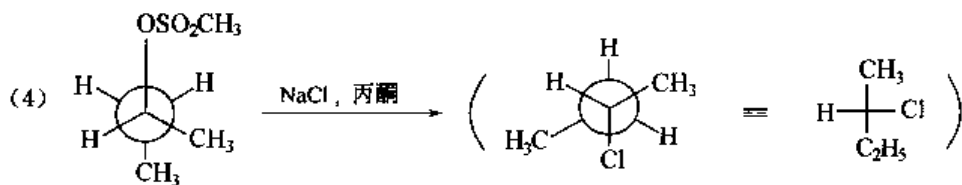
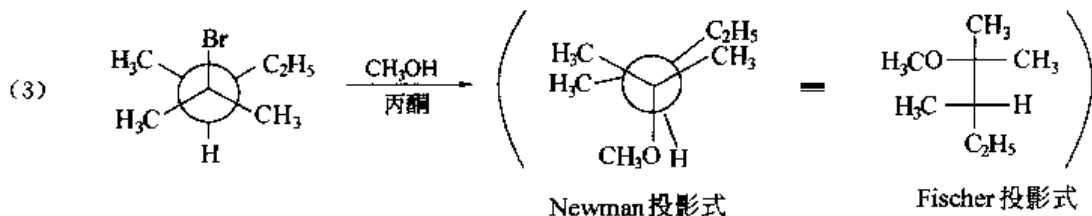
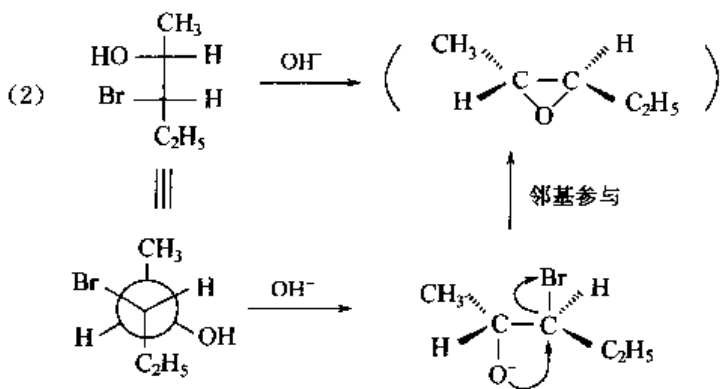
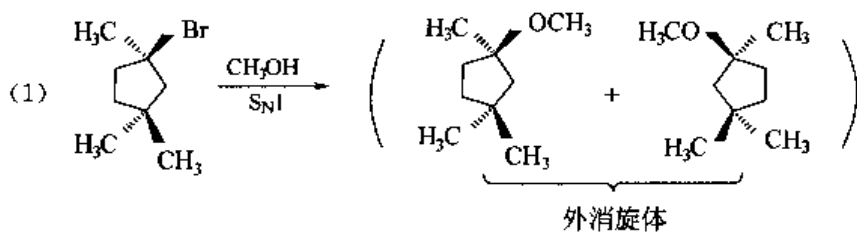


 练习

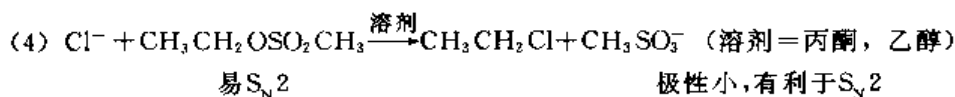
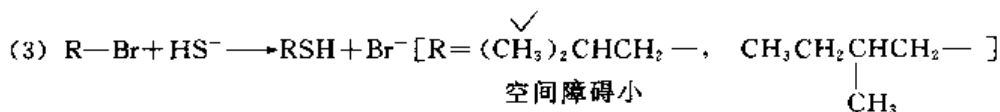
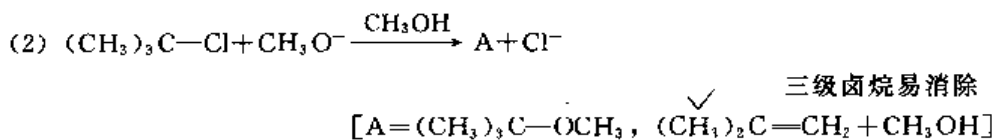
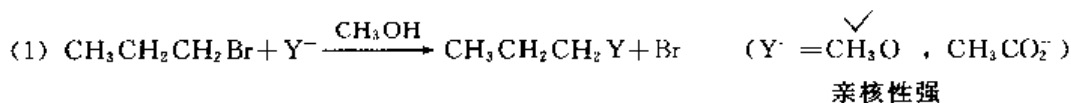
1. 预测下列反应的主要产物。

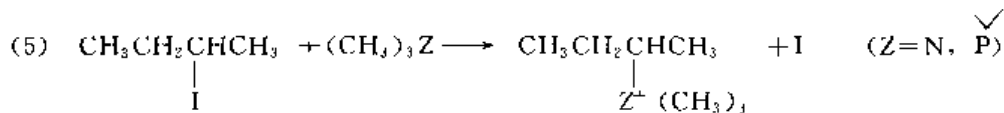


2. 写出下列反应的产物及其构型。

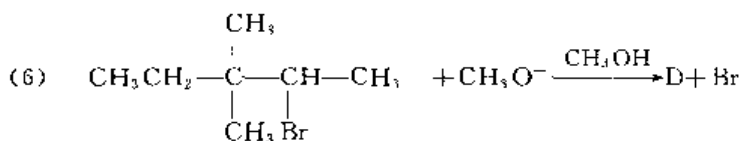


3. 选择有利的反应条件。

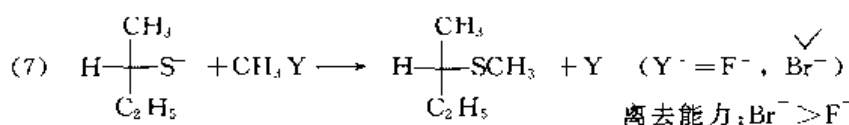
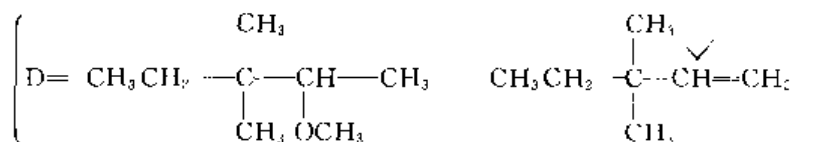




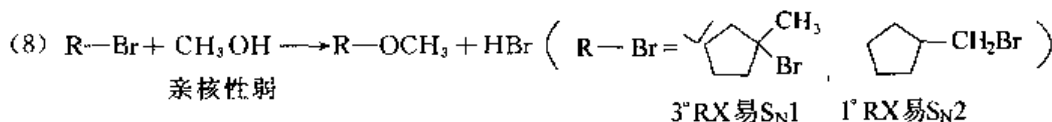
磷的电负性小于氮，孤对电子容易给出去



二级卤烃在碱性介质中易消除



离去能力: $\text{Br}^- > \text{F}^-$



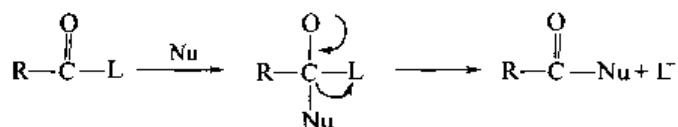
亲核性弱

3°RX 易 $\text{S}_{\text{N}}1$ 1°RX 易 $\text{S}_{\text{N}}2$

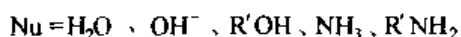
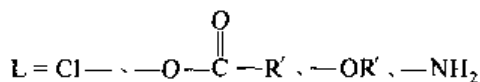
$\text{S}_{\text{N}}1$: 不受试剂亲核性的影响。

$\text{S}_{\text{N}}2$: 试剂亲核性增加, $\text{S}_{\text{N}}2$ 速率增加。

(2) 亲核加成-消除反应 这类反应主要是指羧酸及其衍生物的水解、醇解和氨解。

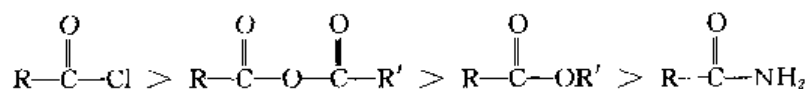


(R 与 R' 可以相同, 也可以不同)



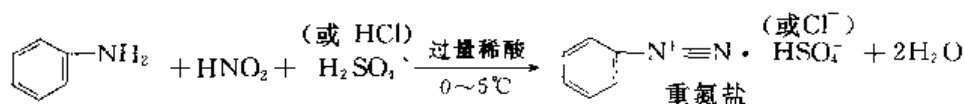
【讨论】 羰基碳越正, 反应速率越快; L 越容易离去, 反应速率越快。

所以, 水解、醇解、氨解速率:

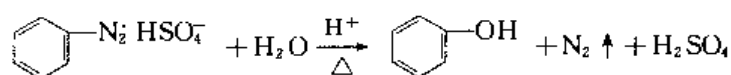


(3) 重氮盐放氮

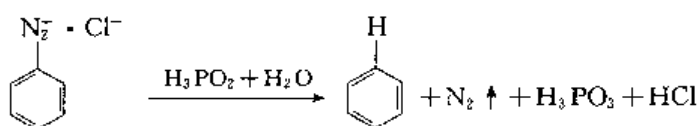
重氮化反应:



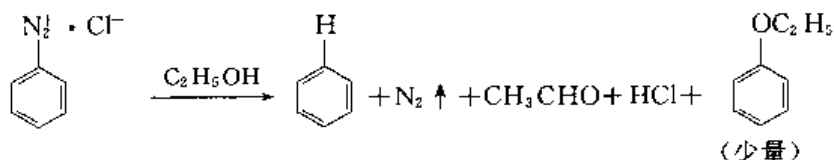
重氮基被羟基取代:



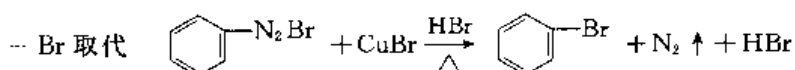
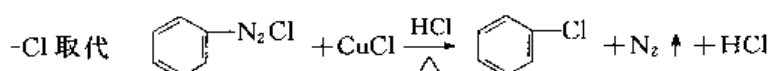
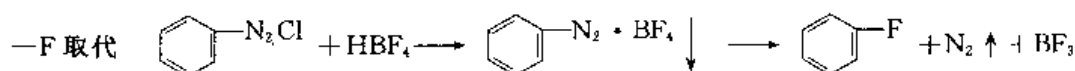
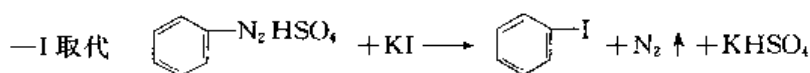
被氢取代:



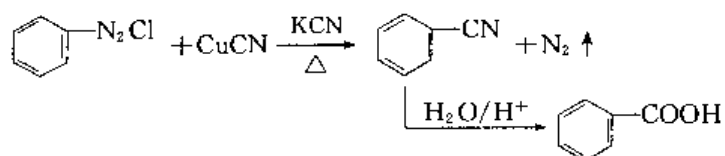
或



被卤素取代:



被氰基取代:



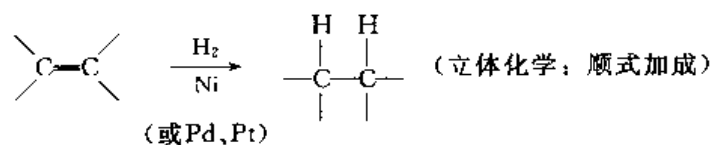
【特点】 低温下，强酸性介质中进行。

【用途】 制备一系列芳香族化合物。

二、加成反应

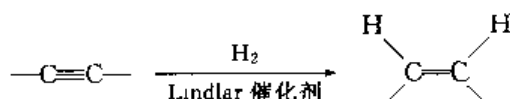
类型：催化加氢、自由基加成、亲电加成、亲核加成。

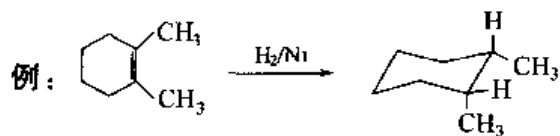
1. 催化加氢



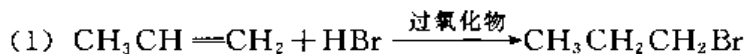
吸附速率: $\text{C}=\text{C} > \text{C}=\text{C}$

所以



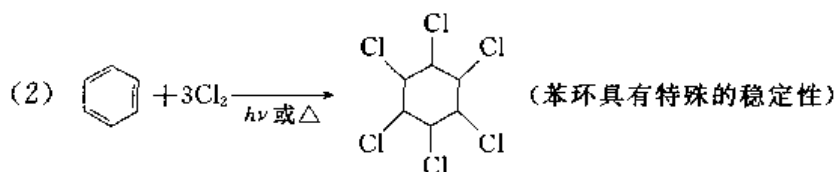


2. 自由基加成



【特点】

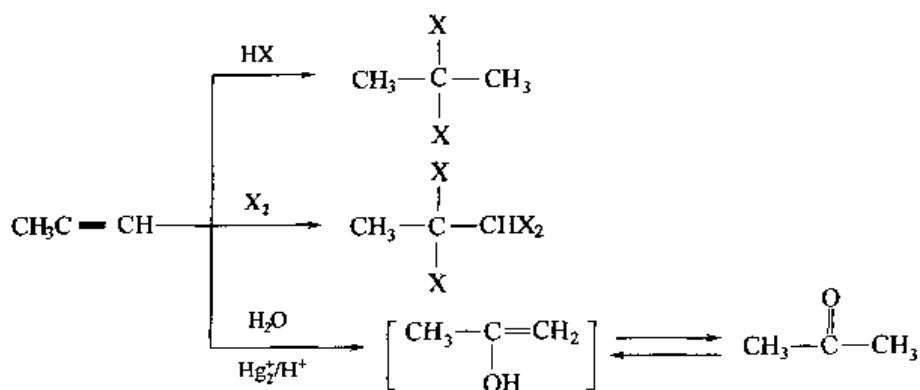
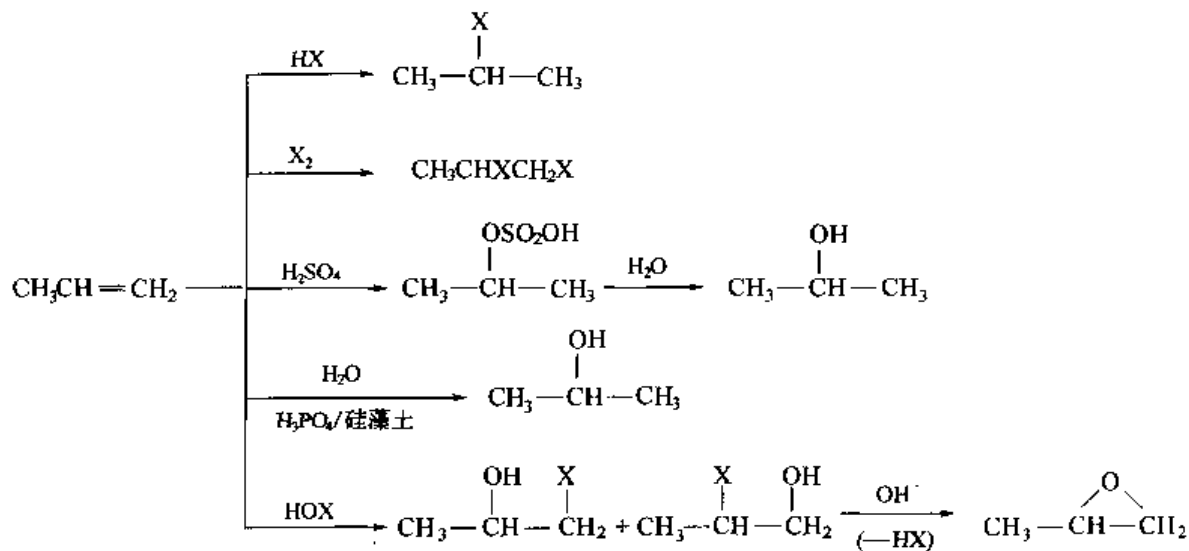
- ① 加成方向违反马氏规则;
- ② 只有 HBr 与烯烃反马式加成。

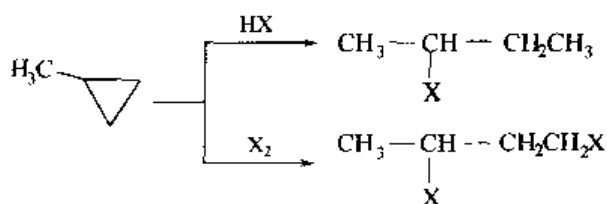


3. 亲电加成

【特点】由 E^+ 首先进攻, 在重键或小环上进行, 遵循马氏规则。

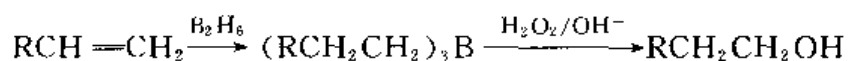
【举例】烯烃的亲电加成。





4. 硼氢化反应

相当于在双键上间接、顺式加成一分子水。

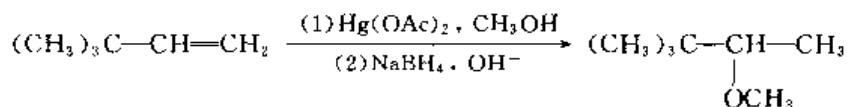
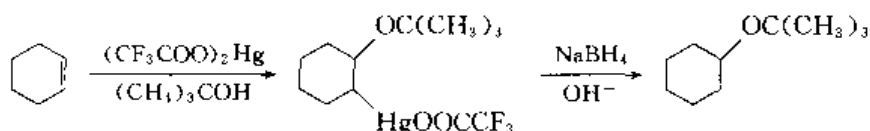
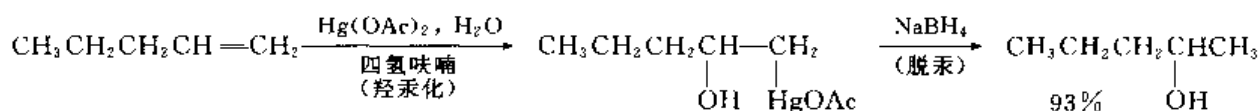


【特点】 顺式加成、反马氏加成、不重排。

【用途】 制伯醇的好办法。

5. 羟汞化-脱汞反应及烷氧汞化-脱汞反应

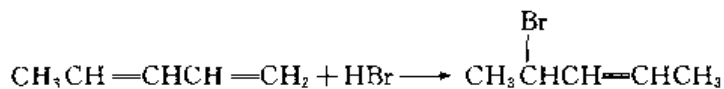
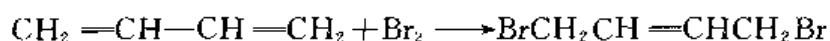
相当于在双键上间接、按马氏规则加成一分子水或醇。



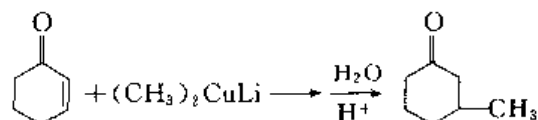
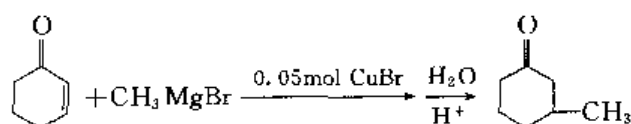
【特点】 反应速率快、条件温和、不重排、产率高 (>90%)。

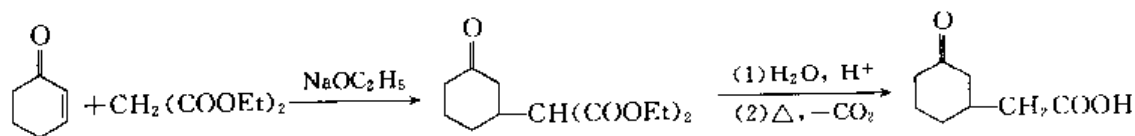
6. 共轭加成

亲电加成：

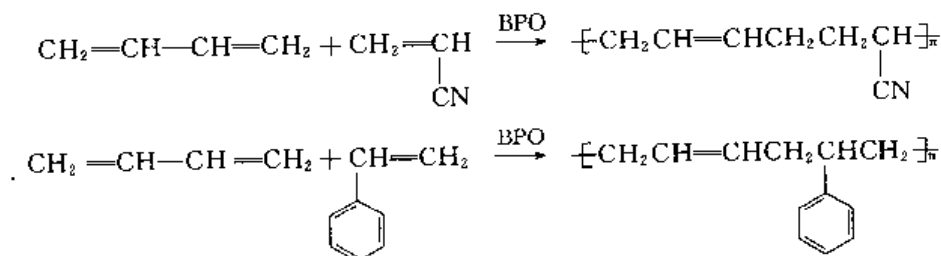


亲核加成：



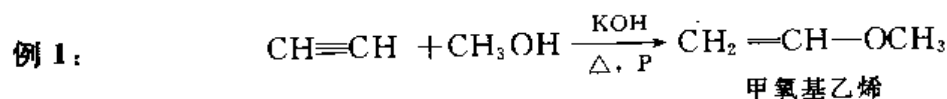


自由基加成:

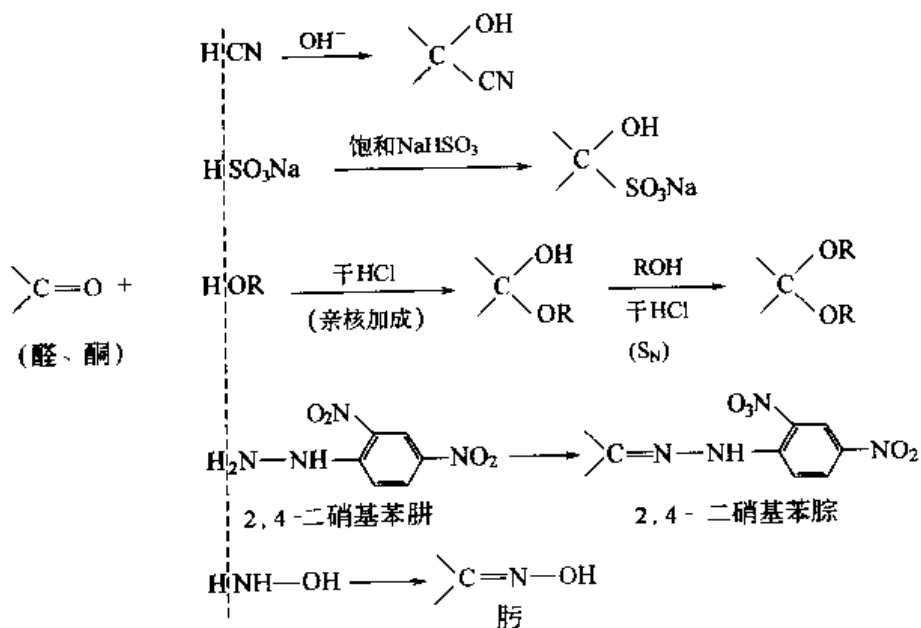


7. 亲核加成

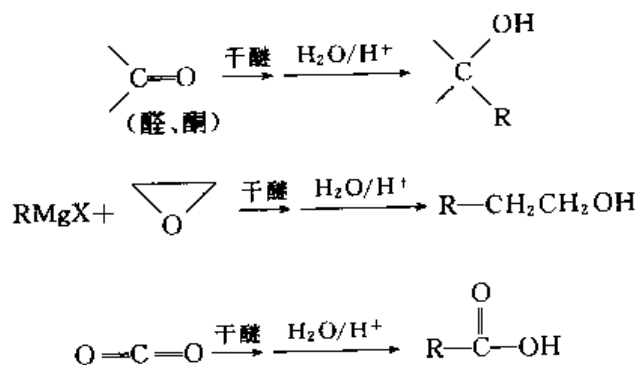
由 Nu 首先进攻，在 C=O、C≡C、小环上进行。



例 2:

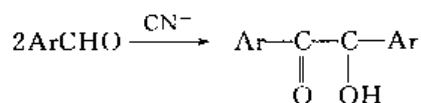


例 3:

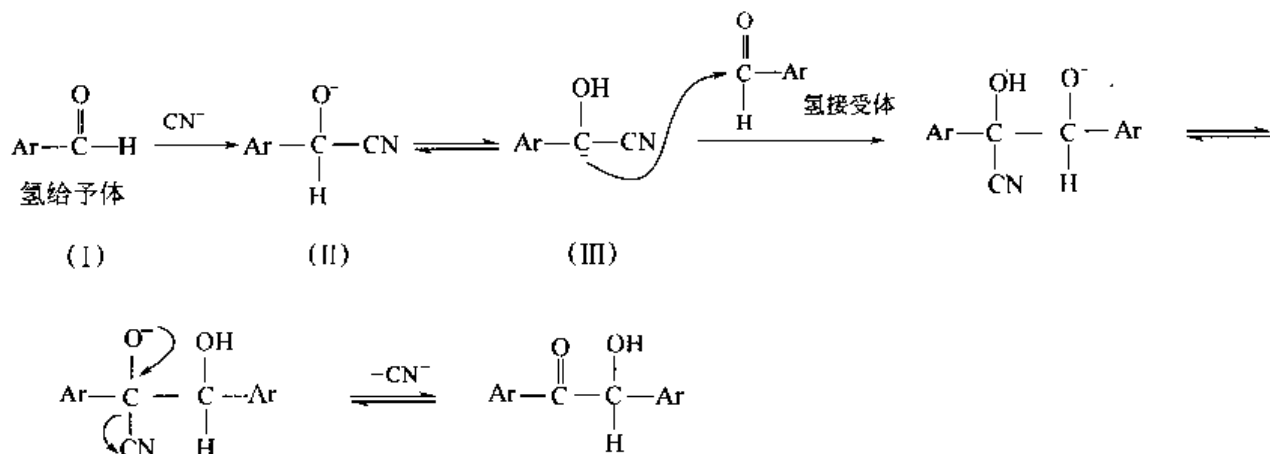


8. 安息香缩合——极翻转的概念

芳香醛在氰离子催化作用下发生双分子缩合，生成 α -羟基酮的反应。



反应历程如下所示。

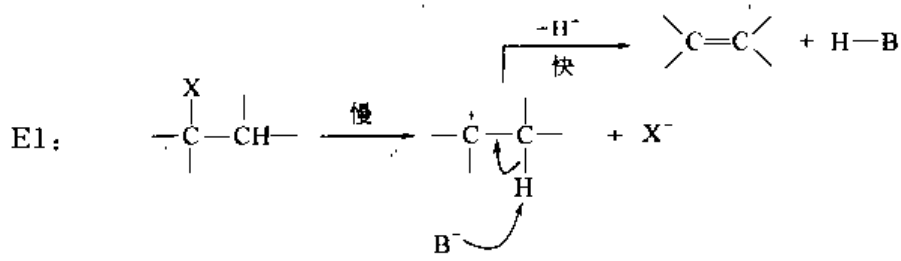


该反应只能在氰离子的催化下进行。其中 CN^- 的作用有 3 点：①与 $\text{C}=\text{O}$ 亲核加成；②加成后吸引电子，使原来醛基中的质子离去，转移到氧原子上；③最后作为离去基团离去。

在反应中 (I) 中羰基碳呈正电性，具有亲电的特性，而 (I) 与 CN^- 加成后经质子转移形成的 (III) 呈负电性，具有亲核性。这种现象称为极翻转。

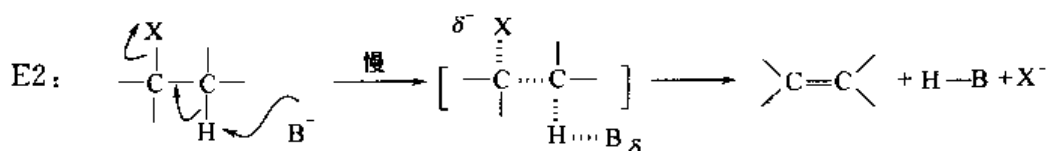
三、消除反应

1. 卤代烃的消除及 E1、E2



C^+ 稳定性： $3^\circ > 2^\circ > 1^\circ \text{C}^+$

反应速率： $3^\circ > 2^\circ > 1^\circ \text{RX}$ (3°RX 易消除)

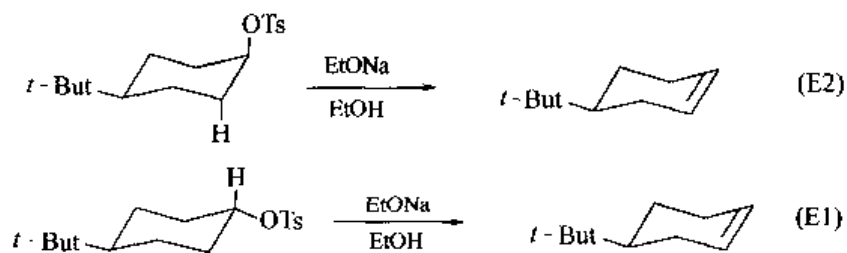


过渡态，负电荷分散在 5 个原子上

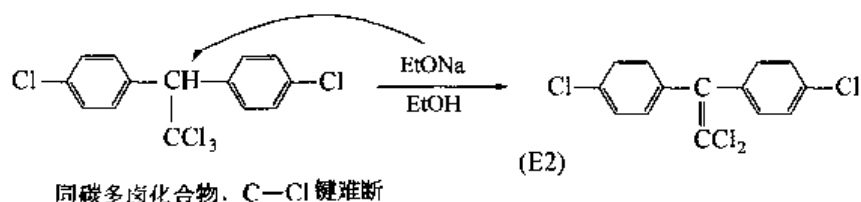
(立体化学：反式共平面)

例 1：反应速率：(1) > (2)

(*t*-But 代表叔丁基)



例 2: 下列反应的机理为 E2。



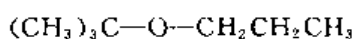
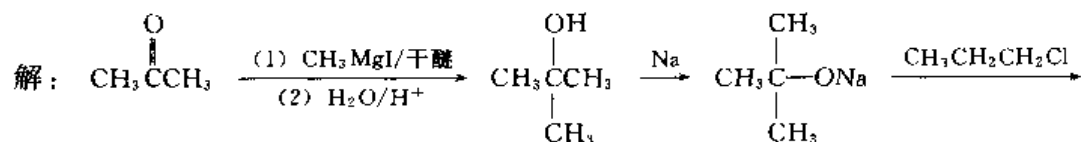
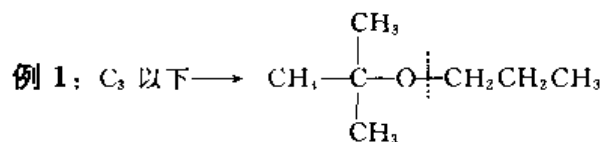
练习

何者与 KOH/醇脱 HX 的速度快?

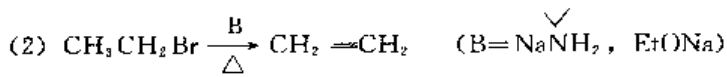
- (1) Br Br (三级卤代烃易消除)
- (2) Br (空间障碍小, β -H 多) Br
- (3) Cl (产物稳定) Cl
- (4) Cl Cl (符合反式共平面)

【讨论】 消除与取代之间的竞争

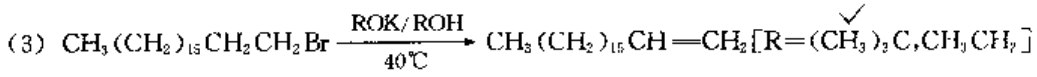
① 3°RX 易消除, 1°RX 易取代; β -H 多者易消除, β -H 少者易取代。



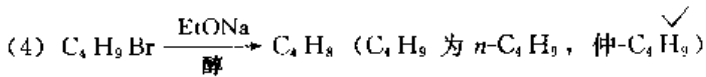
温度升高有利于消除，因为消除需断两个键。



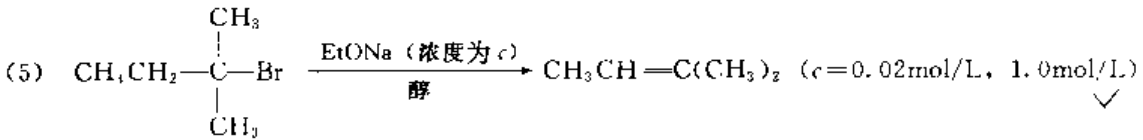
碱性强的试剂有利于消除。



碱性强的试剂有利于消除。

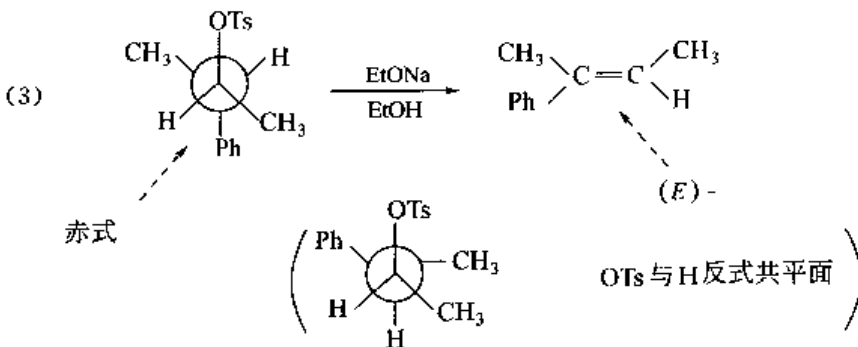
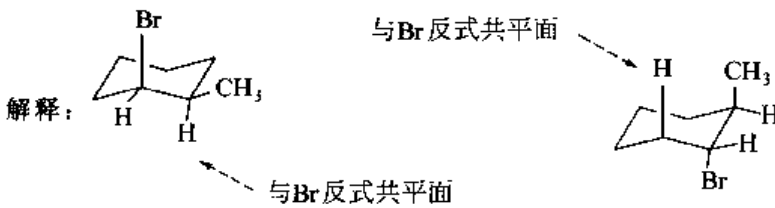
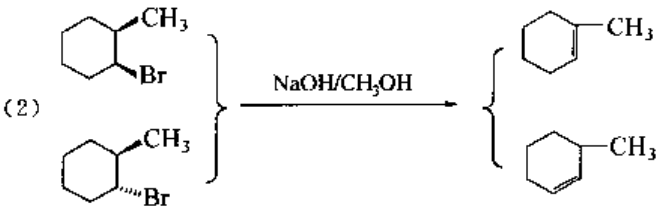
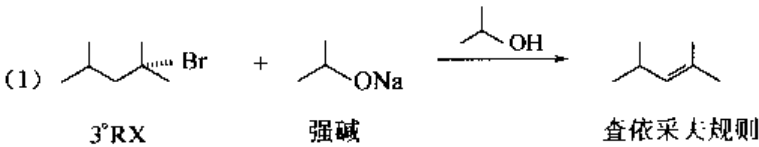


2°卤烃比1°卤烃更容易发生消除反应。



碱的浓度增加，有利于E2(该反应在醇中进行，为E2历程)。

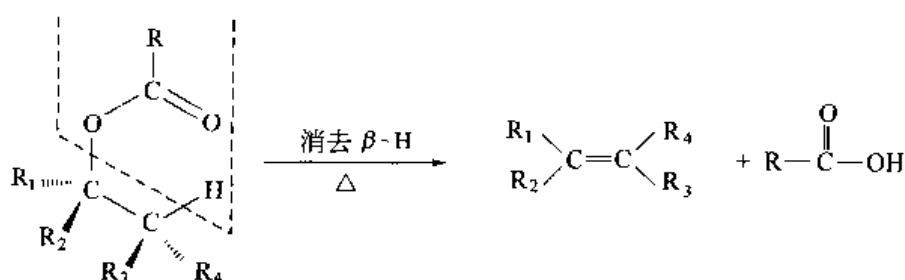
3. 写出下列反应的产物。



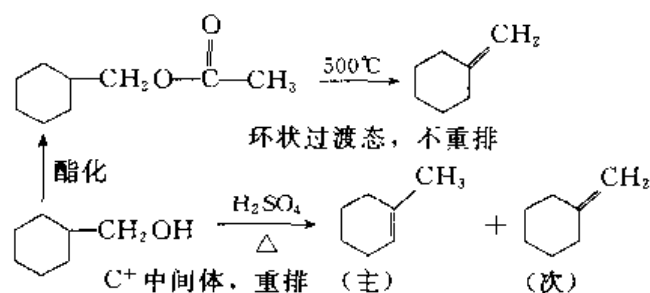
2. 热消除反应

酯、季铵盐、氧化叔胺都可发生热消除。

(1) 酯的热消除

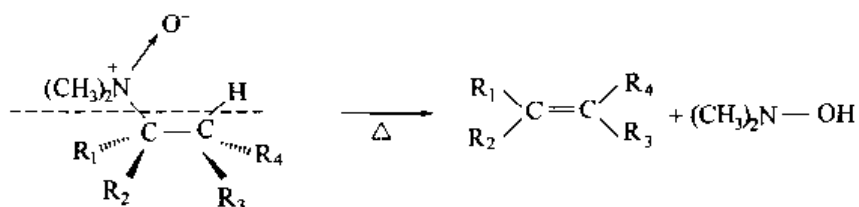


【特点】 加热下进行，环状过渡态。顺式消除酸性大、空间障碍小的 β -H，产物不重排。



所以，酯的热消除反应相当于醇的间接脱水反应。

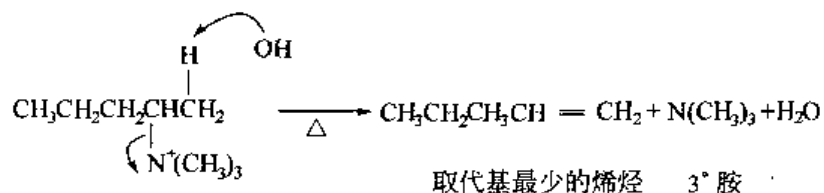
(2) 氧化叔胺的热消除



【特点】 环状过渡态，顺式消除。

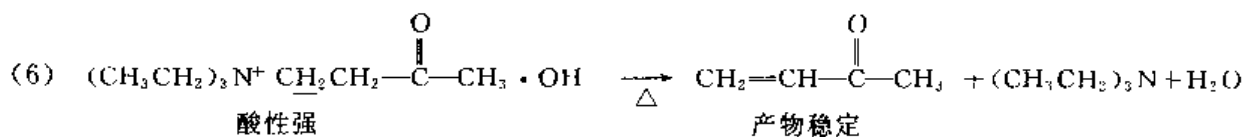
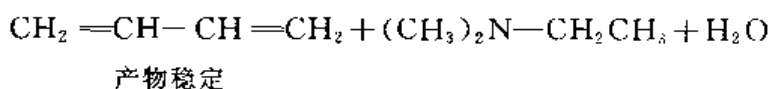
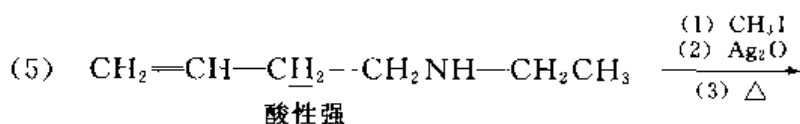
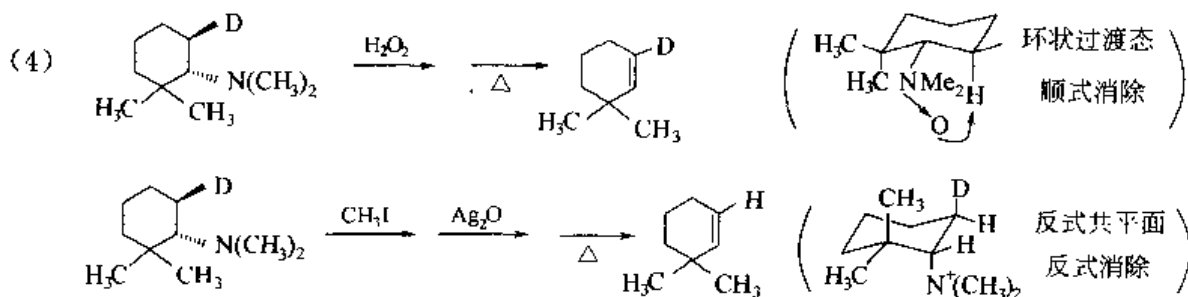
【用途】 ①合成烯烃；②除去 N 原子。

(3) 季铵碱的热消除 (Hofmann 消除)



Hofmann 规则：季铵碱消除时，消去酸性大、位阻小的 β -H，得到取代基最少的烯烃。

【特点】 加热条件下进行，反式消除 (E2 机理要求反式共平面)，消除方向遵循 Hofmann 规则。



【小结】

- ① 卤代烃脱卤化氢是反式消除；
- ② 季铵盐热消除是反式消除；
- ③ 羧酸酯热消除是顺式消除；
- ④ 氧化叔胺热消除是顺式消除。

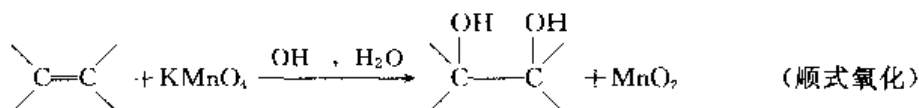
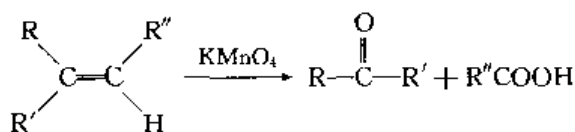
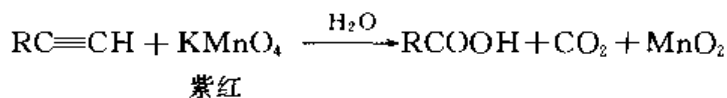
四、氧化反应

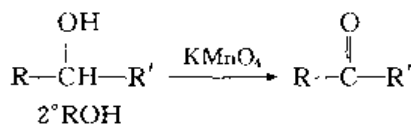
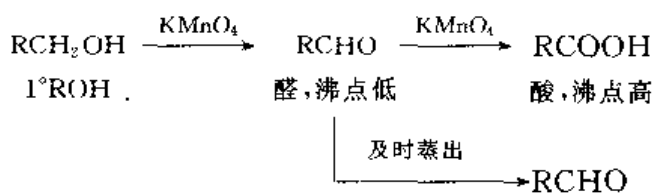
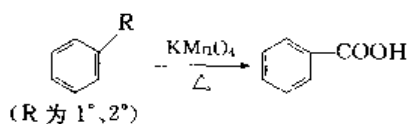
常用氧化剂有 KMnO_4 、浓 HNO_3 、 $\text{K}_2\text{CrO}_7 + \text{H}_2\text{SO}_4$ 、 $\text{CrO}_3 + \text{HOAc}$ 、 $\text{CrO}_3 + \text{乙酐}$ 、 $\text{CrO}_3 + \text{吡啶}$ 、 $\text{CH}_3\text{COCH}_3 + \text{Al}(\text{CHMe}_2)_3$ 、 HIO_4 、 MnO_2 、 H_2O_2 、 RCO_3H (有机过酸)、Tollen's、Fehling's、 Br_2 水等。

1. KMnO_4 氧化

【特点】 氧化性强，通用。

例：



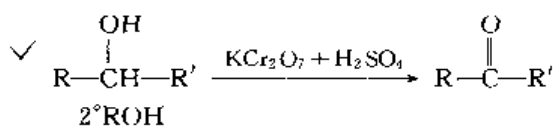
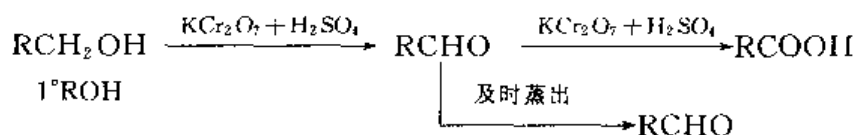


2. 铬酸氧化

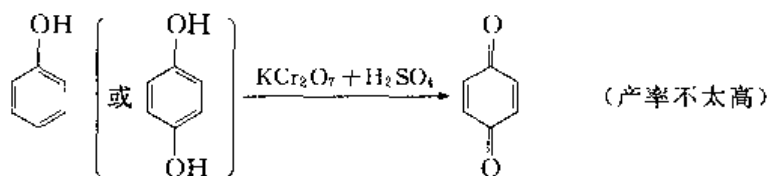
(1) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$

【特点】 通用氧化剂，氧化性强。

例：



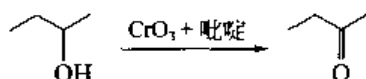
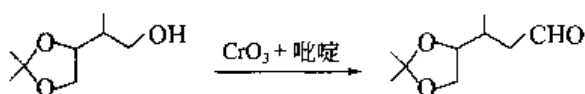
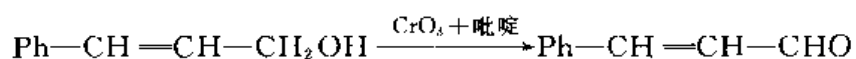
用 $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ 氧化仲醇，速率快、产率高，是由仲醇制备酮的好办法。



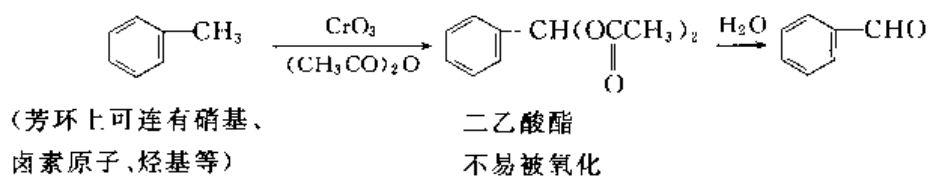
(2) $\text{CrO}_3 + \text{吡啶}$

【特点】 适宜氧化醇 → 醛、酮。产物专一性好，不氧化双键，对分子其他部分影响极小。

例：

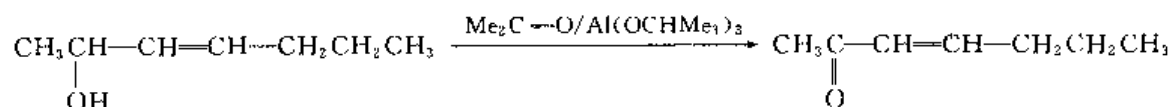
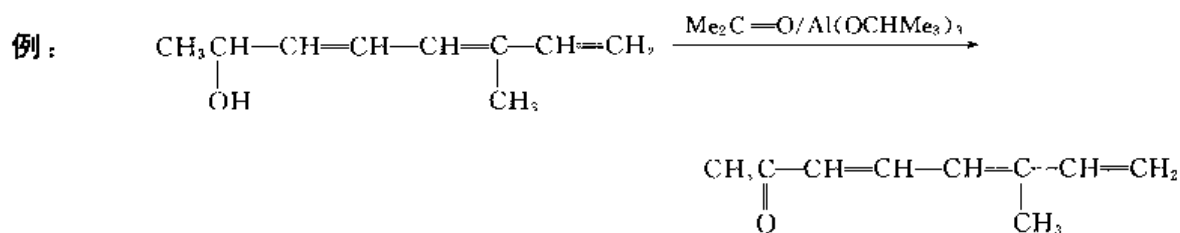
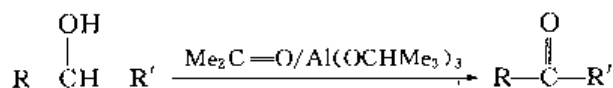


(3) CrO₃ + 乙酐



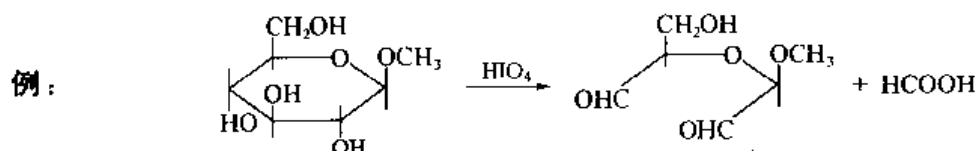
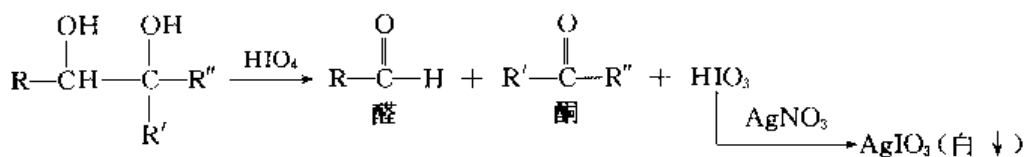
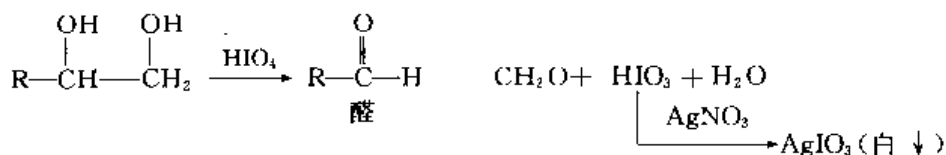
3. 丙酮 + 异丙醇铝氧化 (Oppenauer 氧化)

又称为 Oppenauer 氧化, 其特点是不氧化双键。



4. HIO₄ 氧化

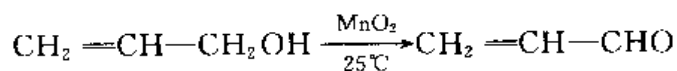
氧化邻二醇, 生成醛或酮。

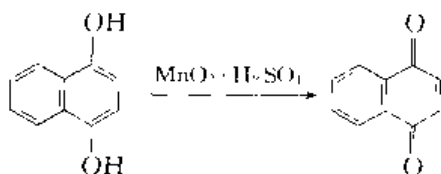
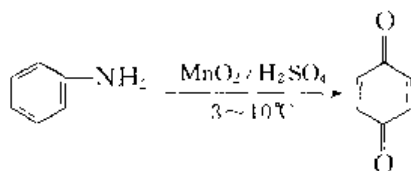


5. MnO₂ 氧化

氧化性较温和, 不氧化双键。

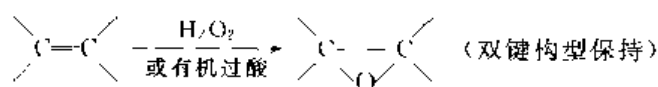
例:



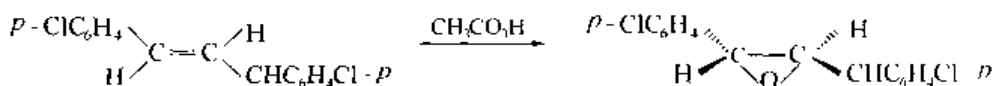
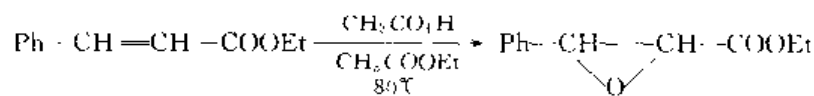
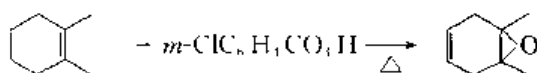


6. H₂O₂ 及过酸氧化

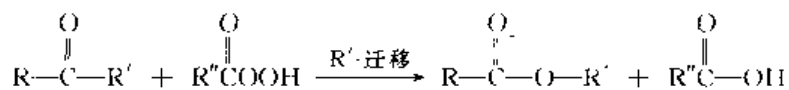
(1) 氧化双键



例:

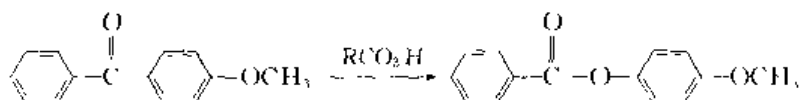
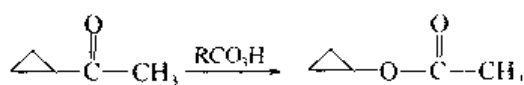
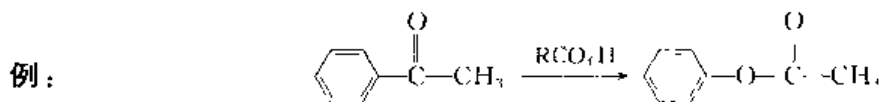


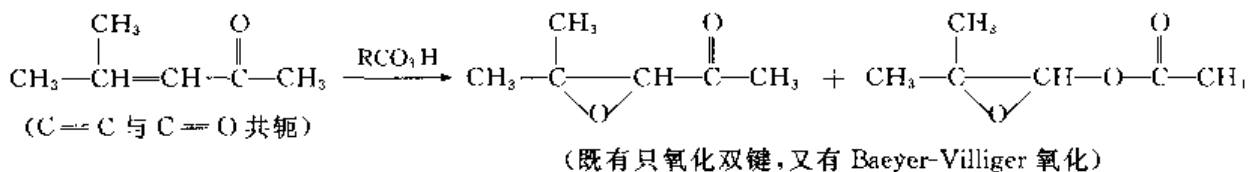
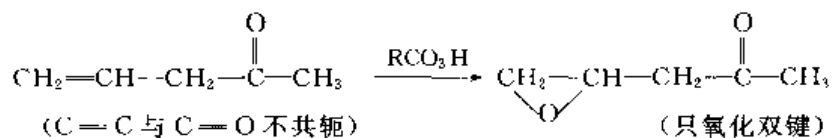
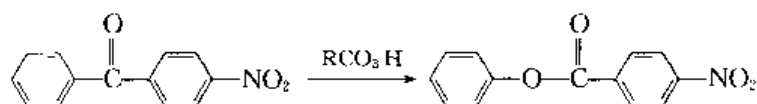
(2) 氧化酮——Beayer-Villiger 氧化 有机过酸与酮反应生成酯。因反应过程中碳架发生变化，又称为 Beayer-Villiger 重排。



迁移优先次序：叔烷基 > 仲烷基 > 环己基 > 苄基 > 苯基 > 伯烷基 > 甲基。

立体化学：迁移过程不改变 R' 的立体构型。





7. Tollens 氧化及 Fehling 氧化

【特点】弱氧化剂, 将醛基氧化成羧基, 均不氧化双键。

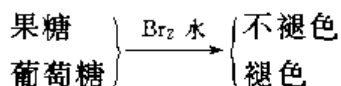
【区别】Tollens 试剂 (硝酸银的氨溶液) —— 氧化所有的醛;

Fehling 试剂 (硫酸铜与酒石酸钾钠的混合液) —— 只氧化脂肪醛, 不氧化芳香醛。

8. Br₂ 水氧化

弱氧化剂只氧化醛糖, 不氧化酮糖。

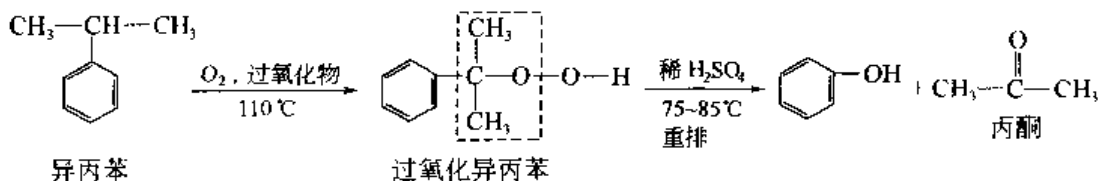
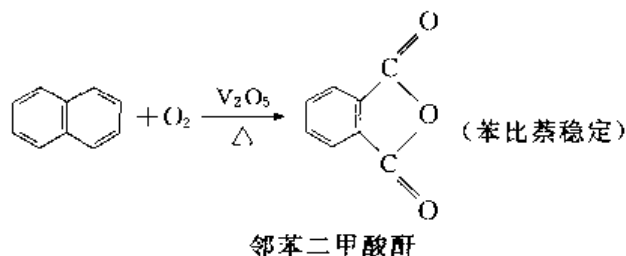
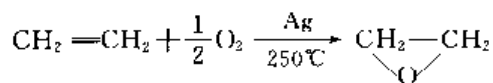
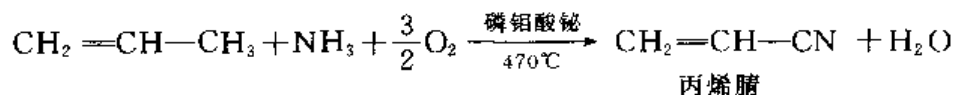
例:



9. 空气氧化

氧化产物取决于催化剂。

例:



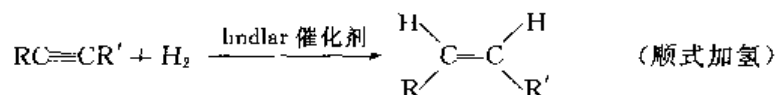
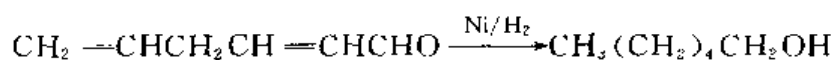
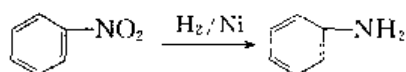
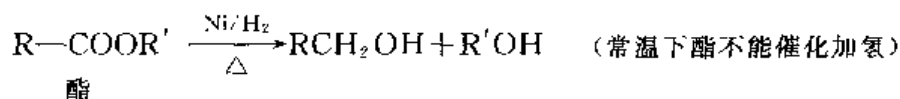
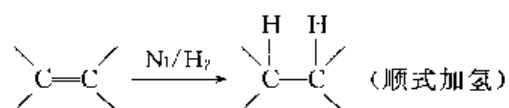
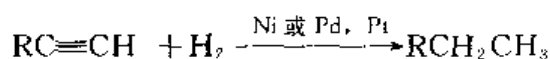
五、还原反应

常用还原剂： H_2/Ni 、 $Na/液 NH_3$ 、 $NaBH_4$ 、 $LiAlH_4$ 、 $[(CH_3)_2CHO]_3Al$ 、 $Fe+HCl$ 、 $Na+EtOH$ 、 $Zn-Hg/HCl$ （克莱门森还原）、 NH_2NH_2 、 $NaOH/三乙二醇醚$ （黄鸣龙还原）、 $H_2/Pd-BaSO_4$ （Rosenmund 还原）等。

1. 催化加氢

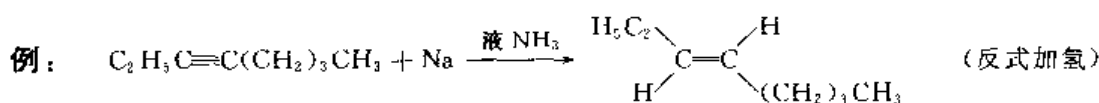
【特点】 a. 顺式加氢； b. 无选择性； c. 特殊催化剂可停留在双键阶段。

例：

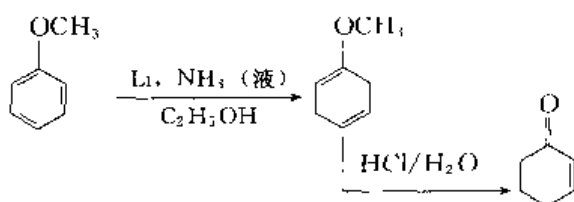
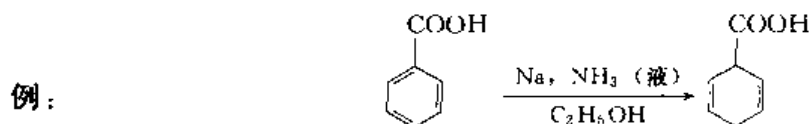


2. Na/NH_3 （或 $NaNH_2/液 NH_3$ ）还原

将叁键还原为反式双键。



将芳环部分氢化生成 1,4-二氢化物（Birch 还原）。

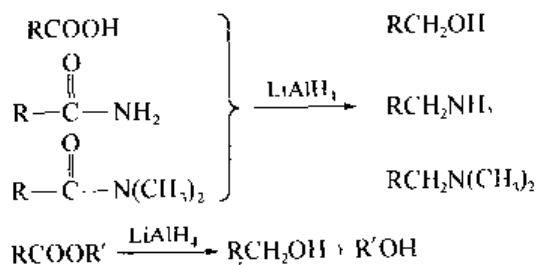
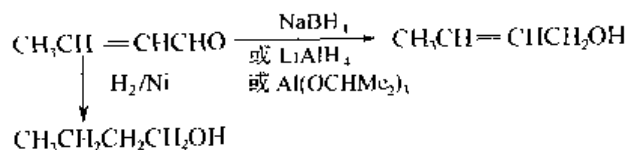


3. NaBH_4 、 LiAlH_4 、 $[(\text{CH}_3)_2\text{CHO}]_2\text{Al}$ 还原

将羰基还原为羟基。

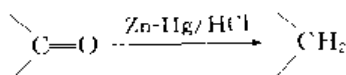
【特点】 不还原双键，其中 LiAlH_4 还原性特别强。

例：



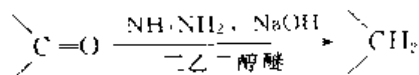
4. 重要的特殊还原反应

(1) 克莱门森还原 在酸性条件下，把羰基还原成亚甲基：



【特点】 操作方便、产率高，但不适用于对酸敏感的化合物。

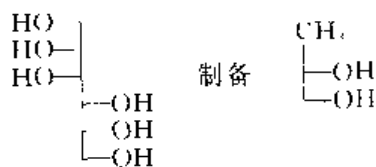
(2) Wolff-Kishner-黄鸣龙还原 碱性条件下，把羰基还原成亚甲基：



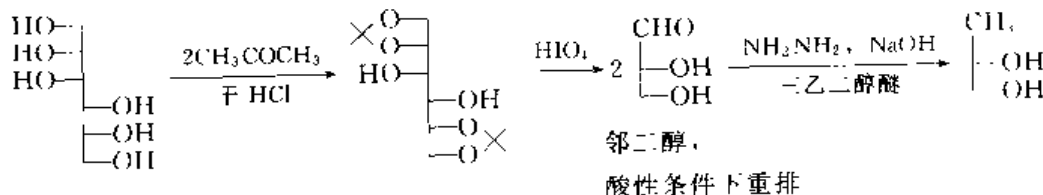
【特点】 操作方便、产率高，可与克莱门森还原相媲美，但不适用于对碱敏感的化合物。

例：

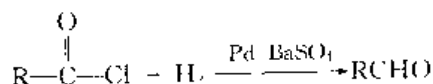
由



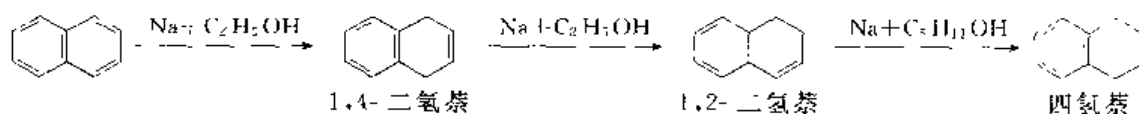
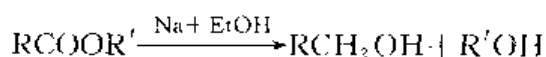
解：



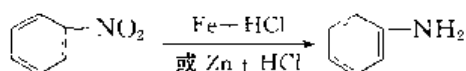
(3) 罗森门德还原



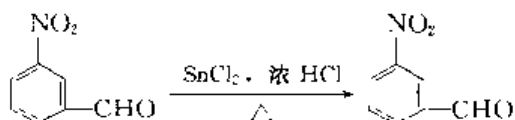
(4) Na+EtOH 还原



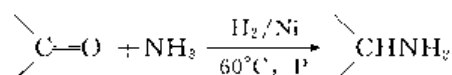
(5) Fe+HCl (或 SnCl₂+HCl) 还原



若芳环上有易被还原的羰基时, 用 SnCl₂+HCl 还原较好。



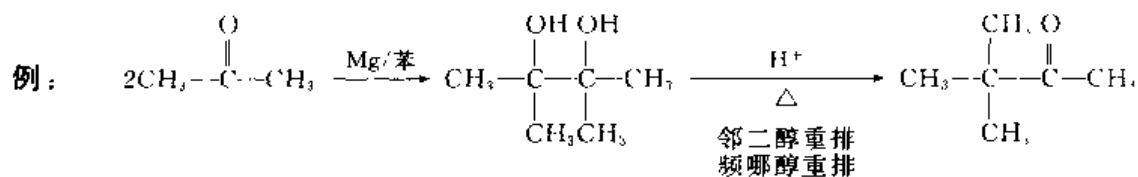
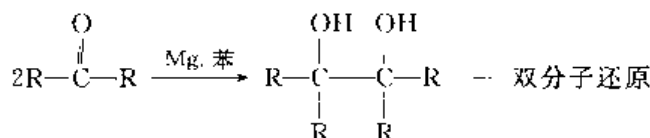
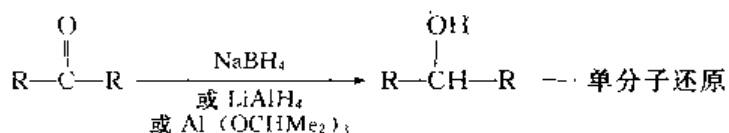
(6) 羰基化合物的还原胺化



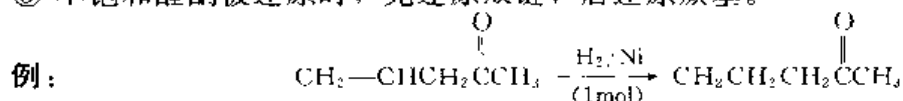
5. 醛和酮的还原

① 一般情况下, 醛比酮容易还原。

② 还原产物: 醛还原得到伯醇; 酮单分子还原得仲醇, 双分子还原得邻二醇。

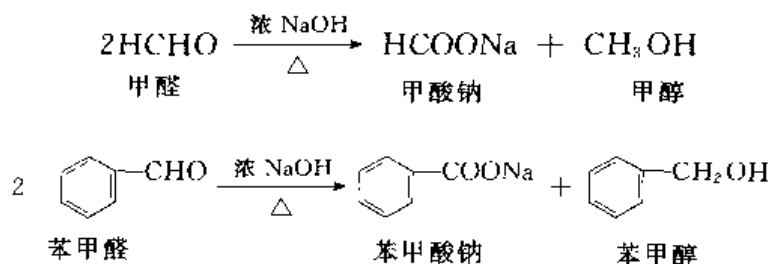


③ 不饱和醛酮被还原时, 先还原双键, 后还原羰基。

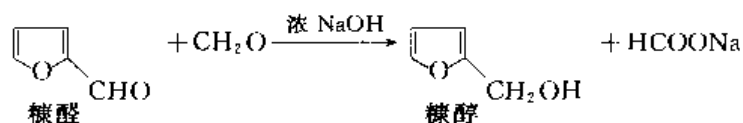
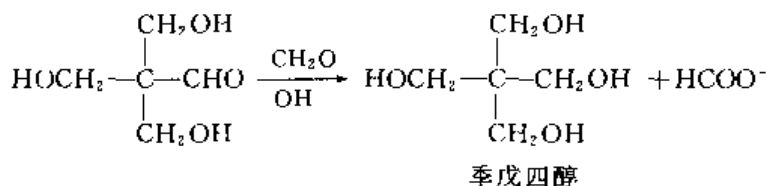
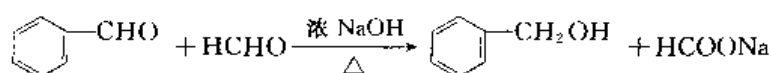


六、歧化反应 (Cannizzaro 反应)

无 α -H 的醛，在浓碱催化下进行。



甲醛与另一种无 α -H 的醛在一起进行歧化反应，一定是甲醛被氧化。

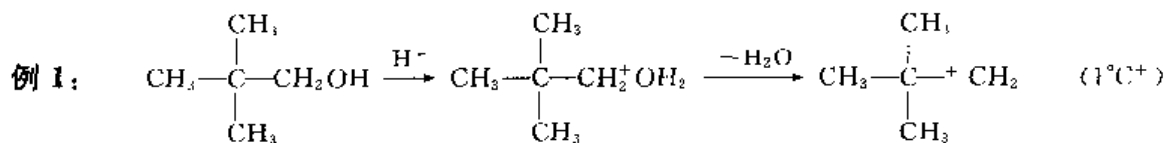


七、重排反应

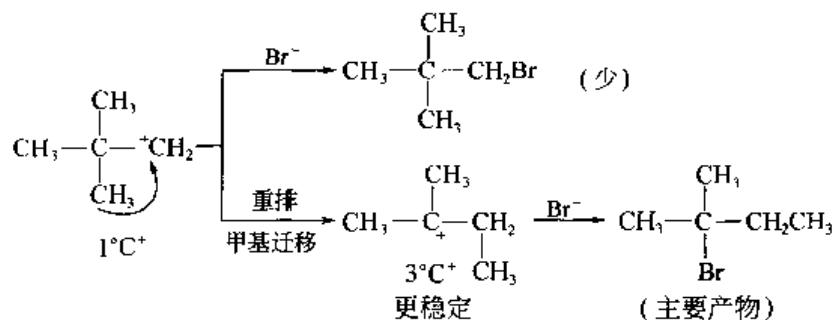
1. 酸性条件下发生的重排

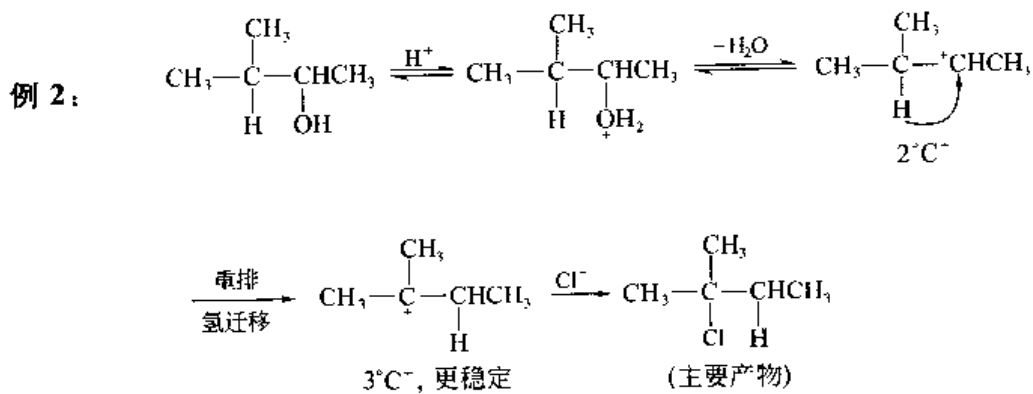
比较常见的有：Wagner-Meerwein 重排，烯丙基重排、Pinacol 重排、Baekmann 重排、Baeyer-Villiger 重排、Fries 重排、联苯胺重排等。

(1) Wagner-Meerwein 重排 醇与酸反应时 C^+ 的重排。

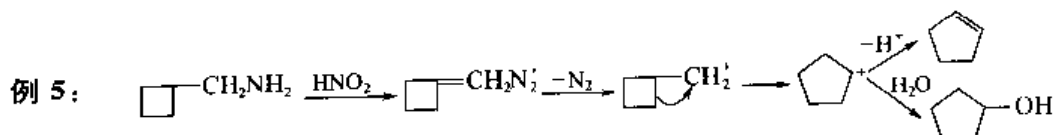
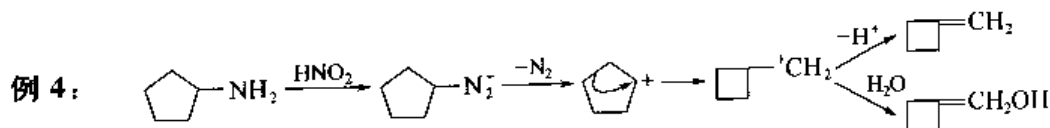
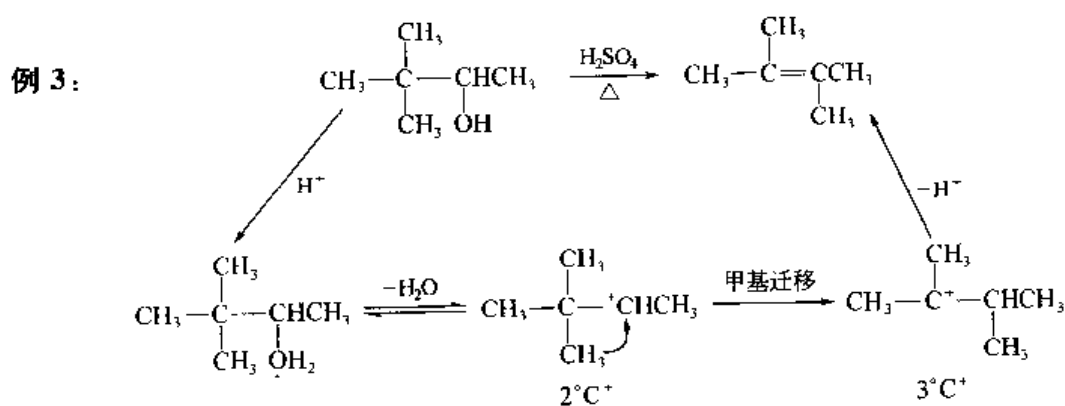


α -C 上有大的 R,
不利于 $\text{S}_{\text{N}}2$

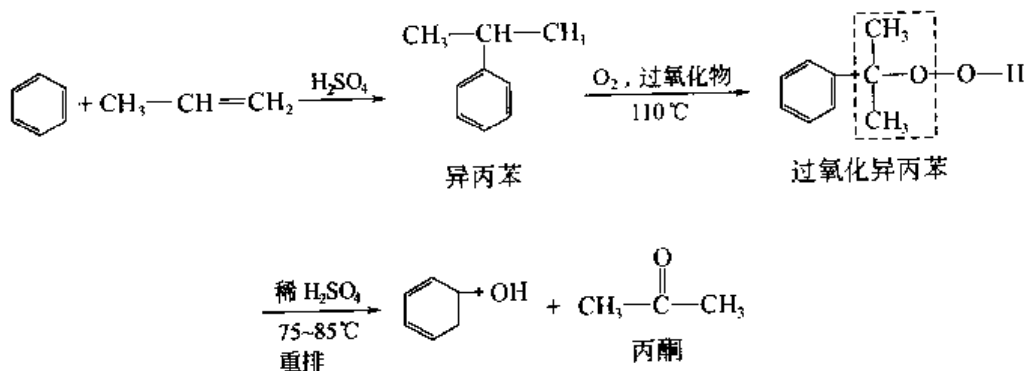




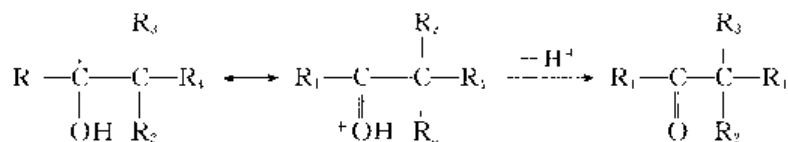
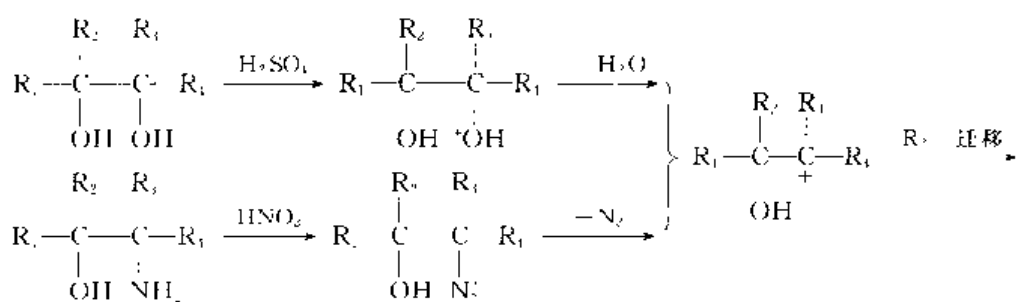
所以, Lucas 试剂试剂 (ZnCl_2/HCl) 只能用来检验伯醇、仲醇、叔醇, 不能用来制备卤代烃。



(2) 异丙苯氧化法制苯酚



(3) Pinacol 重排 (邻二醇重排)

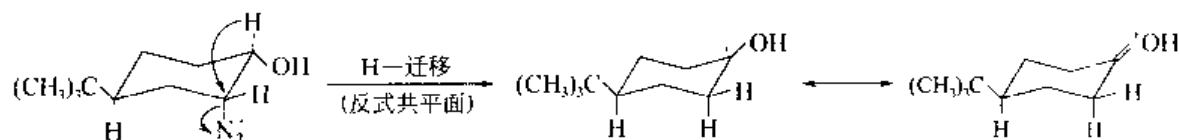
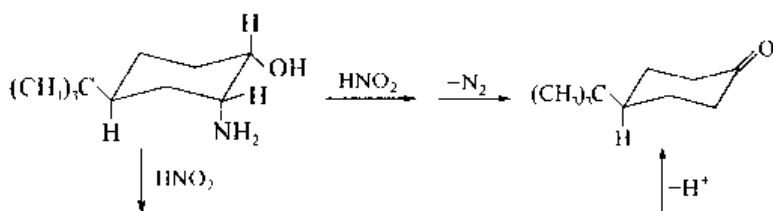


【讨论】

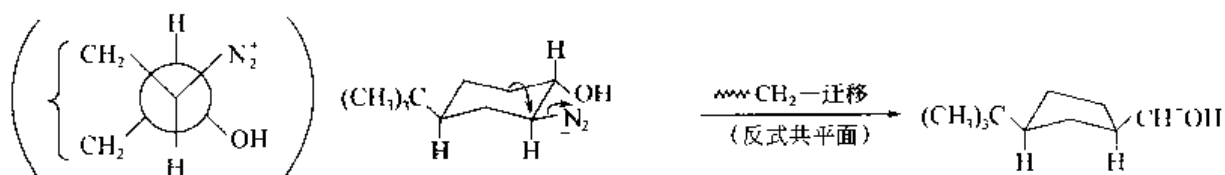
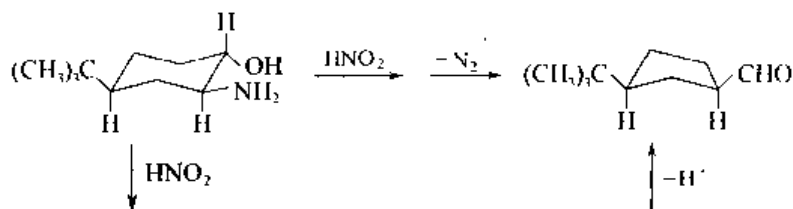
① 碳正离子的形成与基团的迁移是一个协同过程，迁移基团 (R_2) 与离去基团处于反式共平面。

② 基团的迁移倾向与其亲核性一致：苯基 > 叔丁基 > 乙基 > 乙基 > 甲基 > 氢。

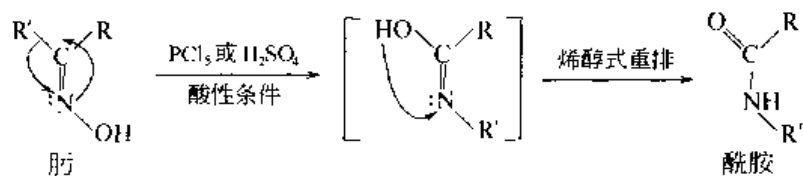
例 1:



例 2:

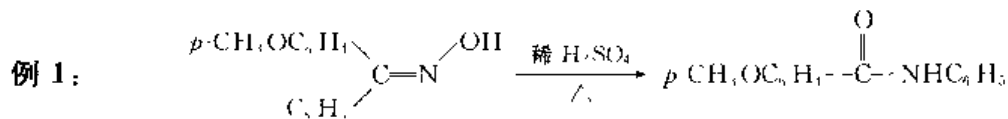


(1) Beckmann 重排 脎在质子酸或 Lewis 酸催化下重排生成酰胺。

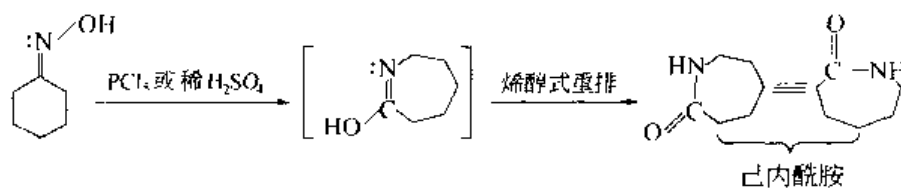


【立体化学】 反式重排， OH 与反式位上 R 互换位置。

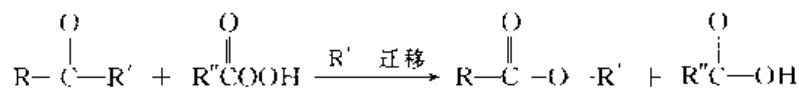
【重排结果】 与 -OH 同侧的烃基在羰基上，与 -OH 异侧的烃基在氨基上。



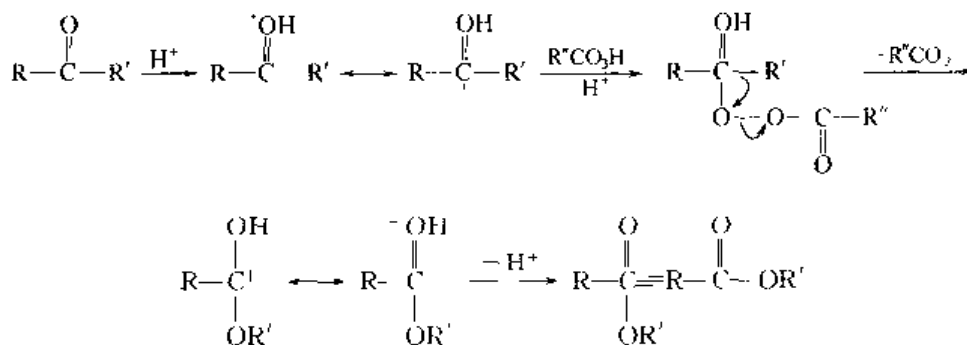
例 2:



(5) Bayer-Villiger 重排 有机过酸与酮反应，生成酯。

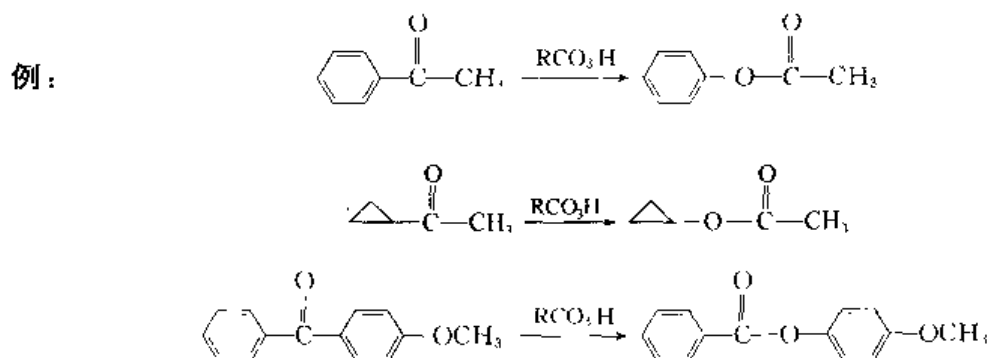


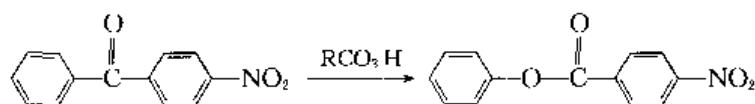
反应历程如下所示。



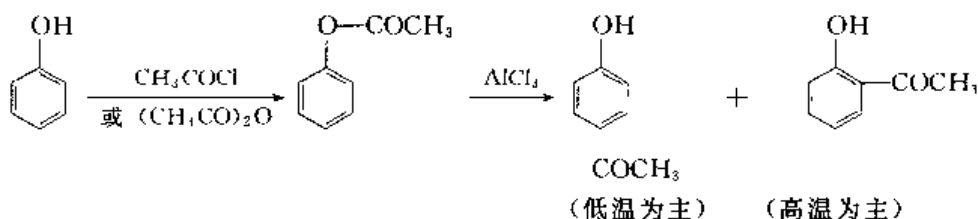
迁移优先次序：叔烷基 > 仲烷基 > 环己基 > 苄基 > 苯基 > 伯烷基 > 甲基。

立体化学：迁移过程不改变 R' 的立体构型。

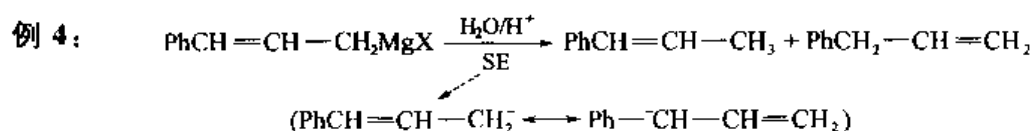
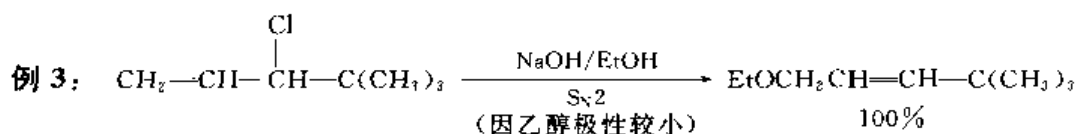
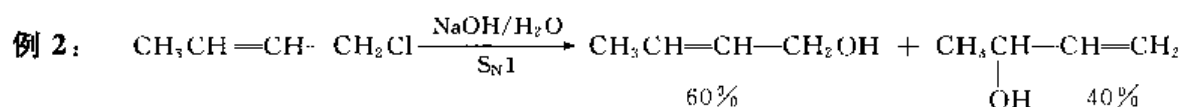
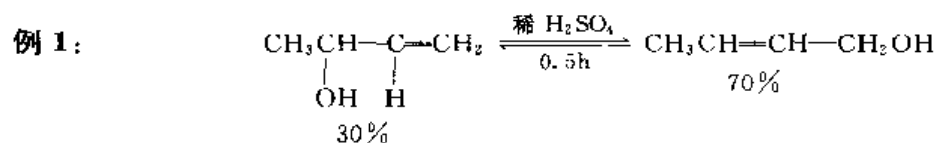




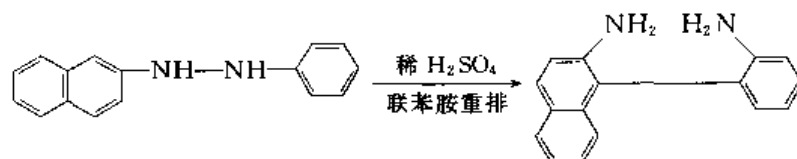
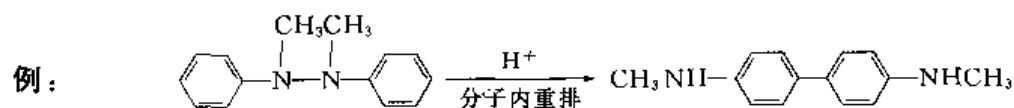
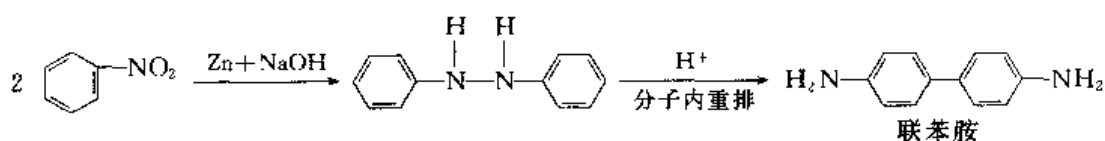
(6) Fries 重排



(7) 烯丙位重排 烯丙基化合物在外界作用下发生双键位移的反应都叫做烯丙基重排 (其机理可以是 S_N1、S_N2、SE、自由基等, 情况复杂)。

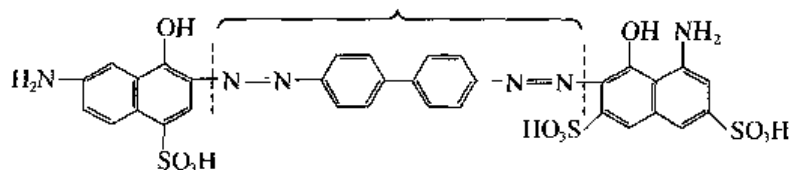


(8) 联苯胺重排



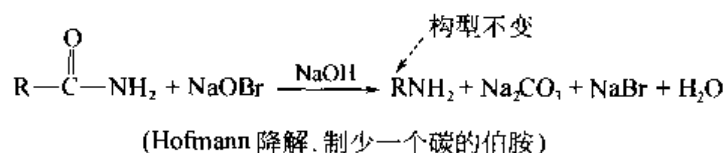
【用途】 制染料。

例：偶氮苯经联苯胺重排后重氮化得

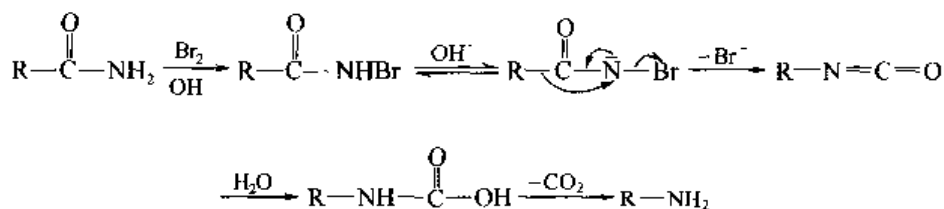


2. 碱性条件下发生的重排

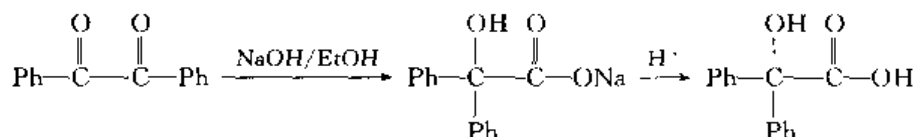
(1) Hofmann 重排



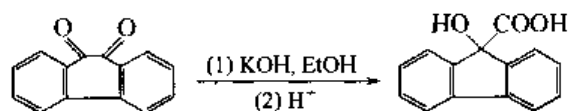
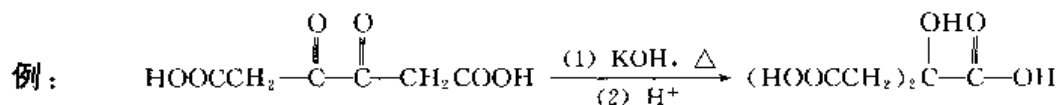
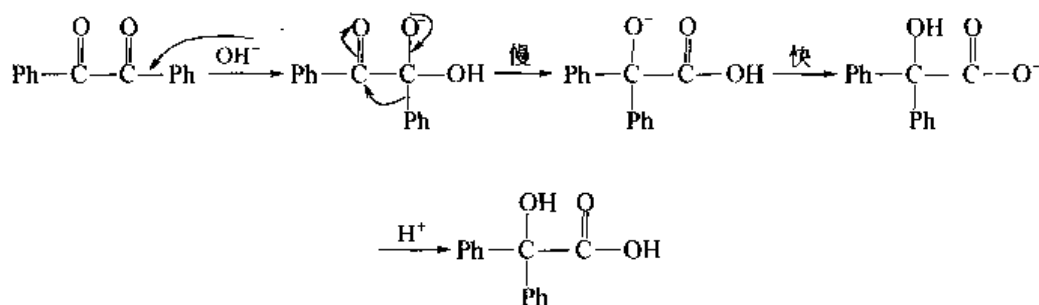
反应历程如下所示。

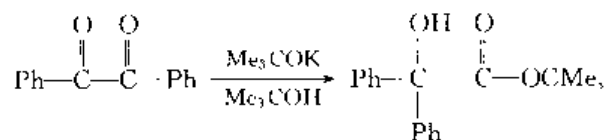


(2) 二苯乙二酮重排



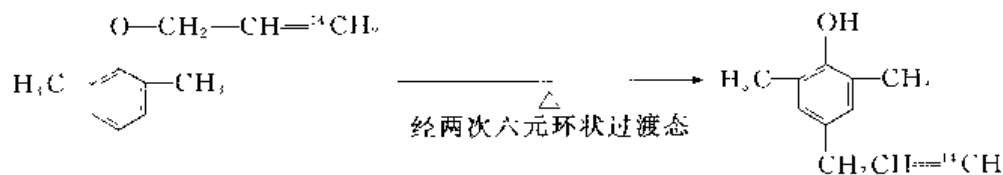
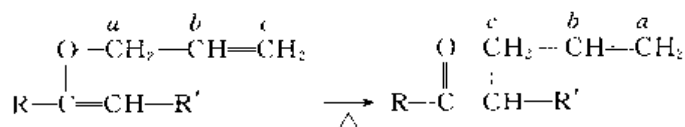
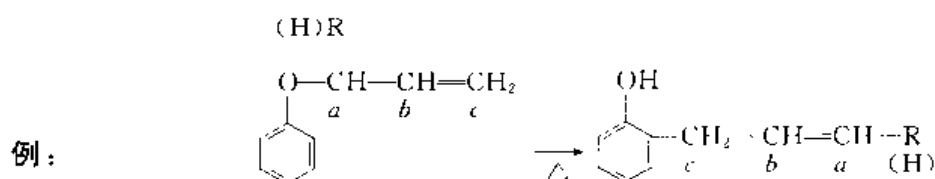
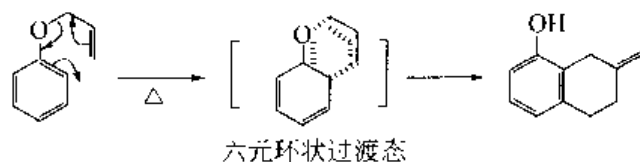
反应历程如下所示。



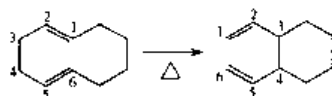
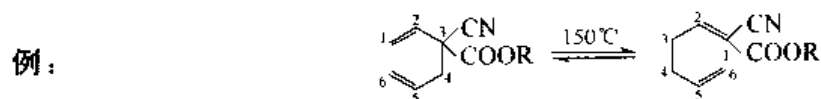
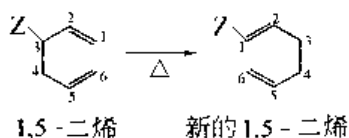


3. 加热条件下发生的重排

(1) Claisen 重排 酚或烯醇的烯丙醚加热时，经六元环过渡态生成 C-烯丙基酚或酮的重排。

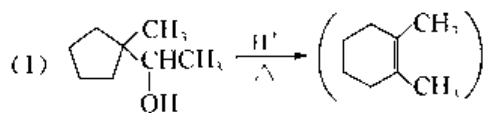


(2) Cope 重排

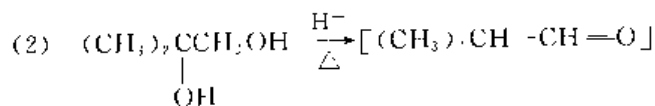
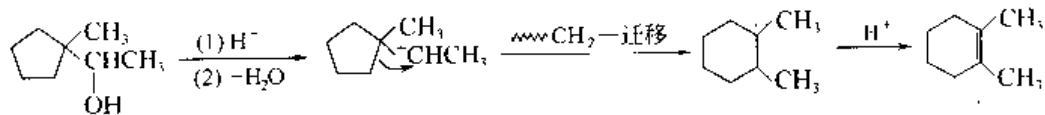


练习

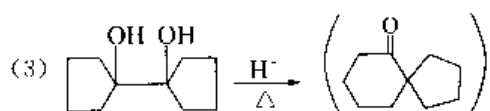
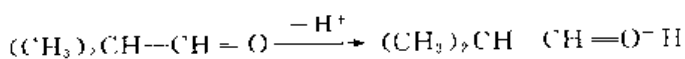
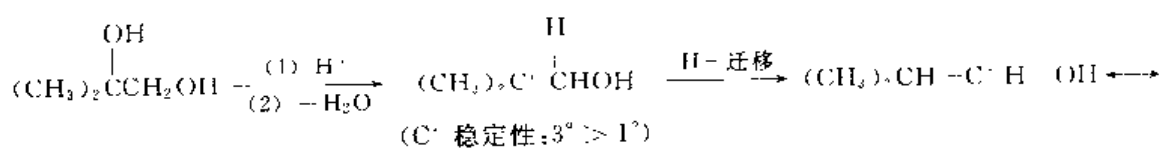
预料下列反应的产物，并提出合适的机理。



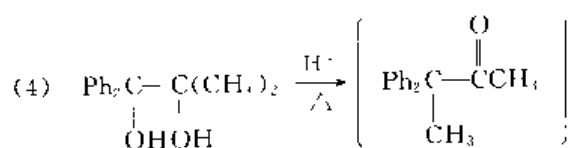
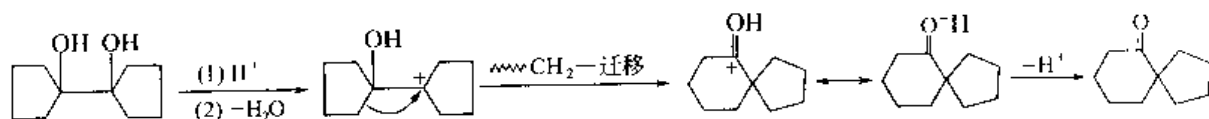
历程:



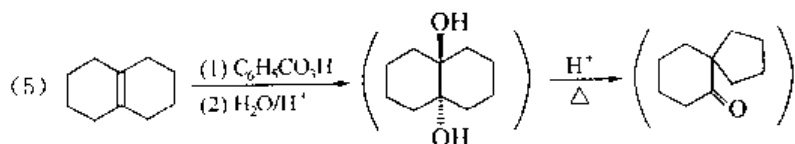
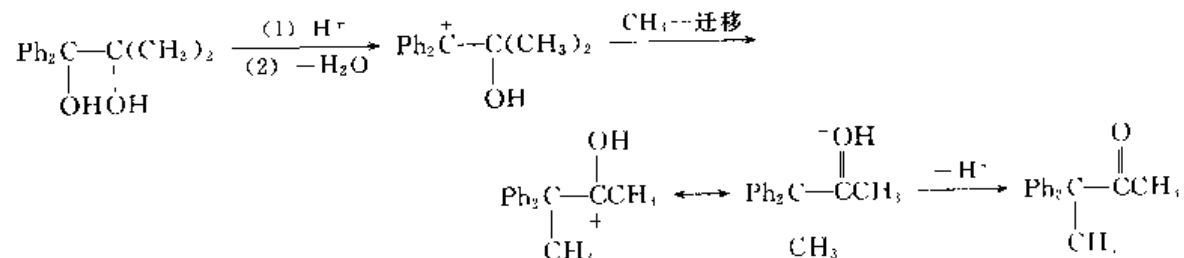
历程:



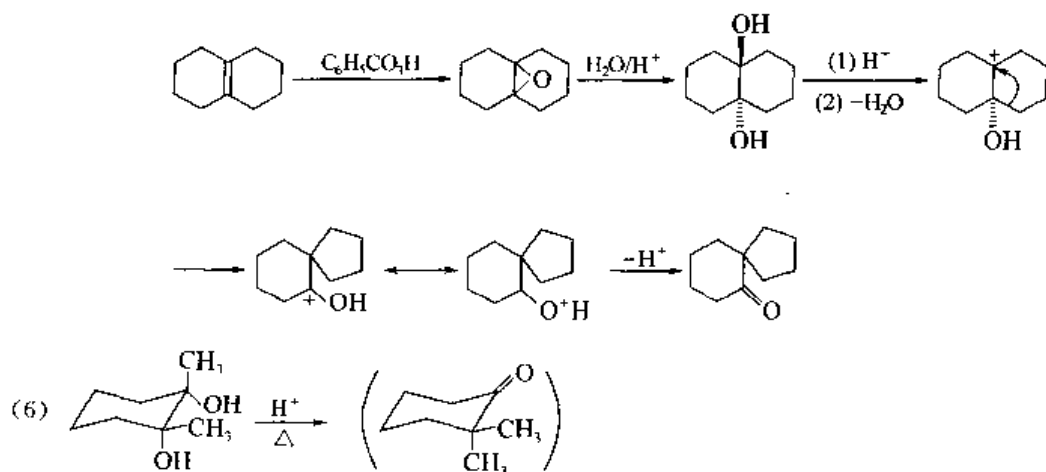
历程:



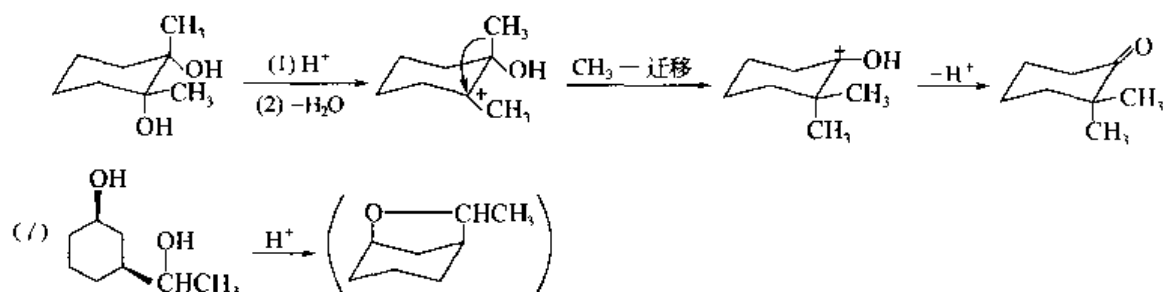
历程:



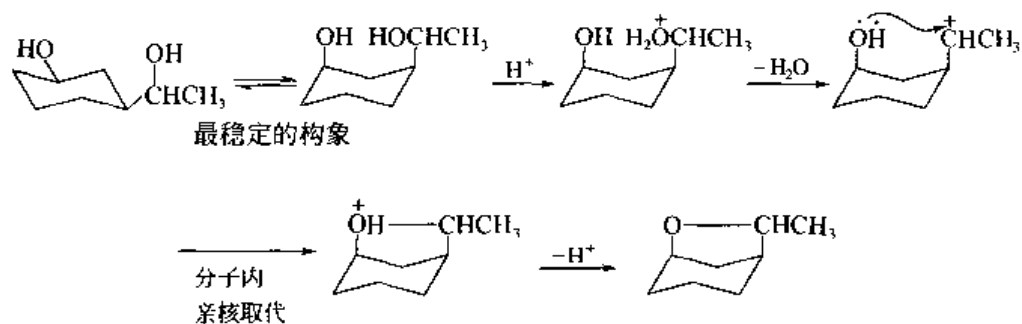
历程：



历程：



历程：



八、与活泼亚甲基有关的反应

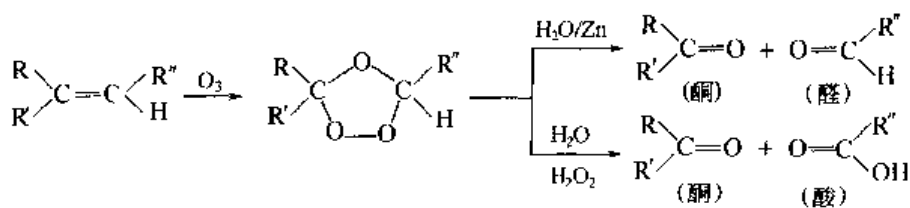
这类反应有：酮的卤化、卤仿反应、脂肪酸的 α -卤代、羟醛缩合、Perkin 反应、Knoevenagel 反应、Claisen 酯缩合反应、 β -二羰基化合物的烃基化和酰基化、Michael 加成、Darzen 反应、Reformatsky 反应、Mannich 反应（胺甲基化反应）、羰基化合物经烯胺的酰基化或烃基化、Reimer-Tiemann 反应等。详见“与活泼亚甲基有关的反应”专题小结。

九、降解反应

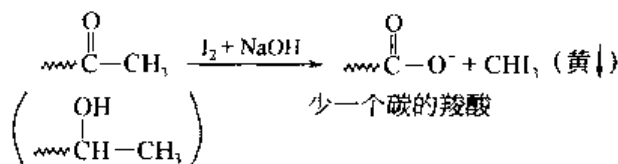
1. Hofmann 降解

见“专题总结 I”中“七、2. 碱性条件下发生的重排”。

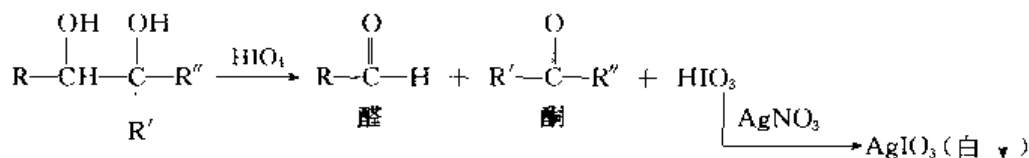
2. 臭氧化



3. 卤仿反应

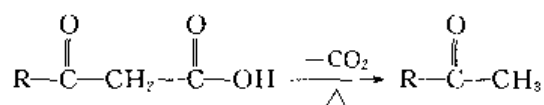


4. 邻二醇氧化



5. 脱羧

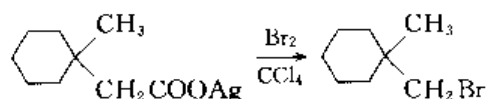
(1) β-羧基酸脱羧



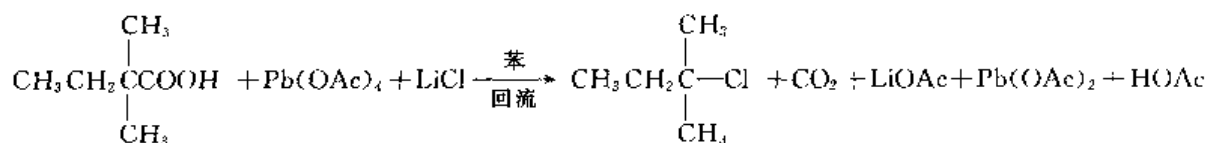
例：三乙或取代三乙 $\xrightarrow{\text{水解}} \xrightarrow{\text{酸化}} \xrightarrow[\Delta]{-CO_2}$ 丙酮或甲基酮

丙二或取代丙二 $\xrightarrow{\text{水解}} \xrightarrow{\text{酸化}} \xrightarrow[\Delta]{-CO_2}$ 乙酸或取代乙酸

(2) 汉斯狄克 (Hunsdiecker H) 脱羧 用羧酸的银盐在无水的惰性溶剂 (如四氯化碳) 中与一分子溴回流失去二氧化碳而形成比羧酸少一个碳的溴代烷。

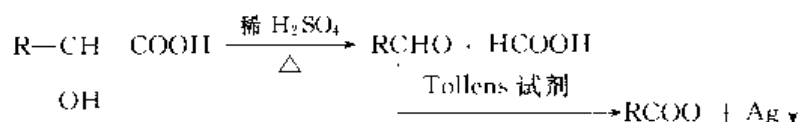


(3) 柯齐 (Kochi J K) 脱羧 用四乙酸铅、金属卤化物 (钾、锂、钙的卤化物) 和羧酸反应, 脱羧卤化而得卤代烷。



6. 羟基酸分解

α -羟基酸与稀硫酸共热，分解为少一个碳的醛。



十、周环反应

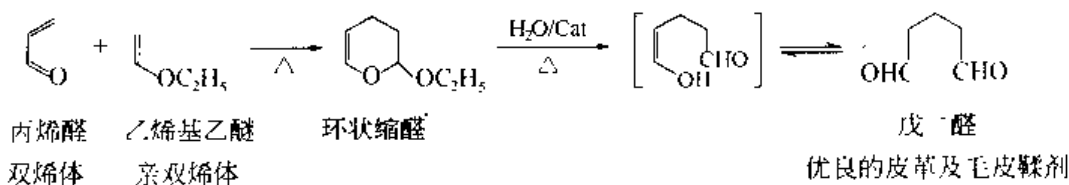
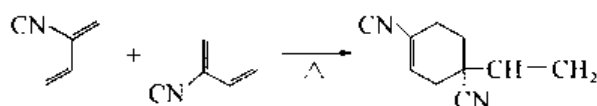
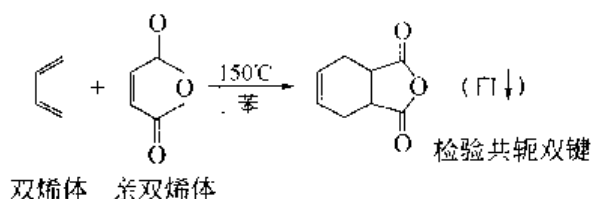
这类反应的特点是经环状过渡态一步完成，并具有高度的区域选择性和立体专一性。

1. 环化加成

【特点】

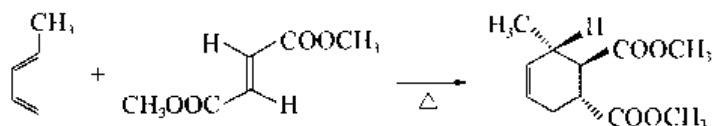
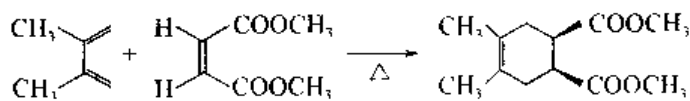
① 成环与加成一步完成，协同进行。当双烯体上有给电子基、亲双烯体上有吸电子基时，更有利于环化加成反应的发生。

例：



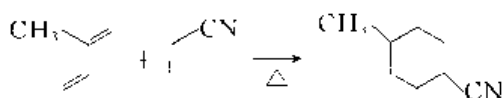
② 顺式加成，亲双烯体的构型保持不变。

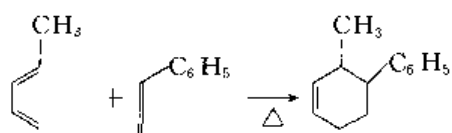
例：



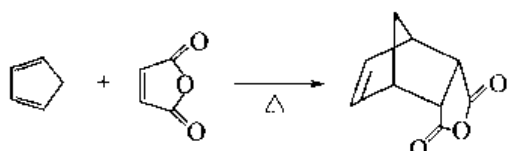
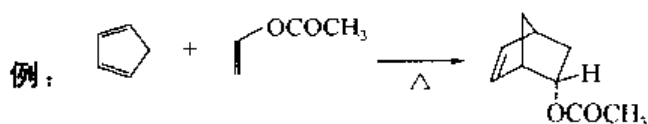
③ 当双烯体和亲双烯体上有取代基时，一般生成邻、对位产物，极少有间位产物的生成。

例：



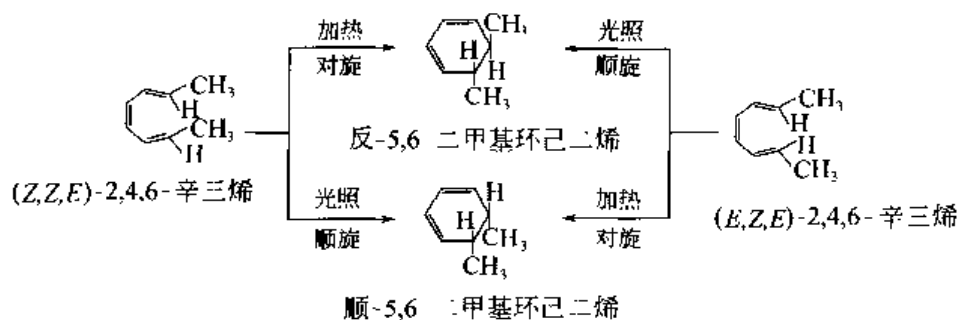
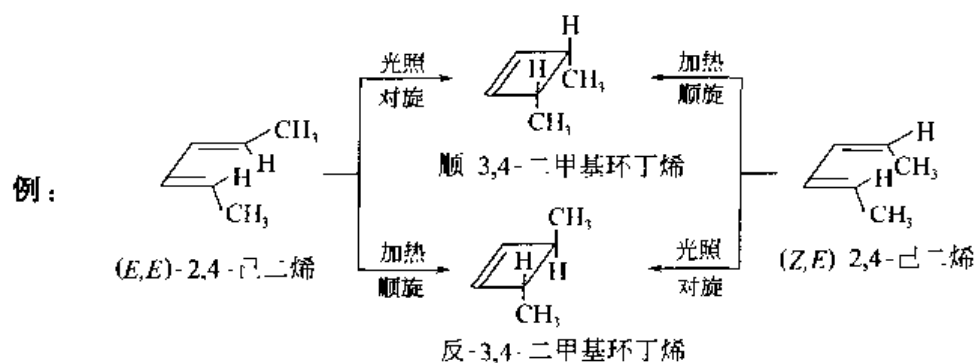


④ 环状共轭二烯反应时，主要生成内型产物。



2. 电环化反应

开链共轭烯烃关环生成环烯烃及其逆反应都叫电环化反应。



热反应只与基态有关，在反应中起关键作用的是 HOMO。光照情况下分子发生跃迁，处于激发态。此时，分子的 HOMO 是基态时的 LUMO。电环化反应规律如下所示。

共轭 π 电子数	反应实例	热反应	光照反应
$4n$		顺旋 允许	对旋 允许
$4n+2$		对旋 允许	顺旋 允许

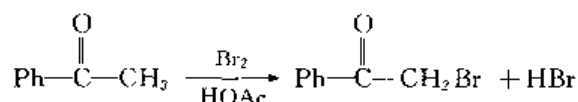
3. Claisen 重排和 Cope 重排

它们都属于 [3,3] 迁移反应，其特点是在加热条件下进行，有六元环状过渡态。详见“专题总结 I 一七、3. 加热条件下进行的重排”。

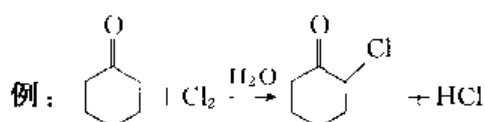
专题总结 II ——与活泼亚甲基有关的反应

这类反应主要有：酮的卤化、卤仿反应、脂肪酸的 α -卤代、羟醛缩合、Perkin 反应、Knoevenagel 反应、Claisen 酯缩合反应、 β -二羰基化合物的烃基化和酰基化、Michael 加成、Darzen 反应、Reformatsky 反应、Mannich 反应（胺甲基化反应）、羰基化合物经烯胺的酰基化或烃基化、Reimer-Tiemann 反应等。

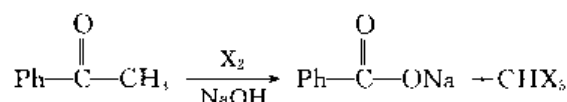
1. 酮的卤化



【特点】 低温，酸性或中性条件下进行，可停留在一元取代阶段。

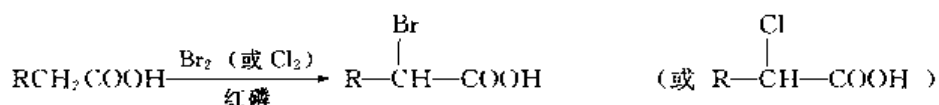


2. 卤仿反应



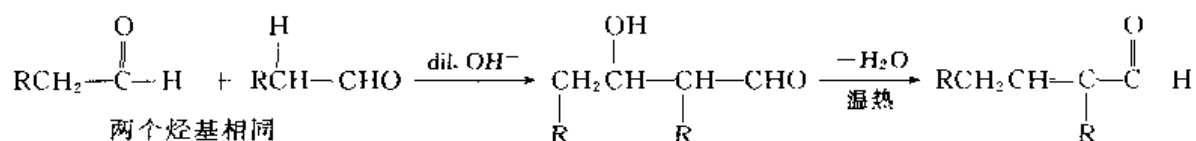
【特点】 碱性条件下进行，不可停留在一元取代阶段。

3. 脂肪酸的 α -卤代

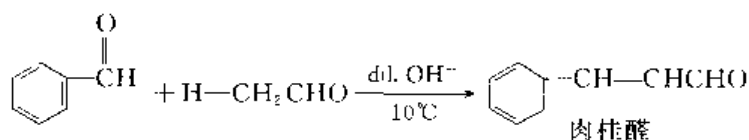


【特点】 必须在红磷催化下进行，只限于氯代或溴代。反应历程经过酰卤阶段，因而酯不能进行类似的反应。

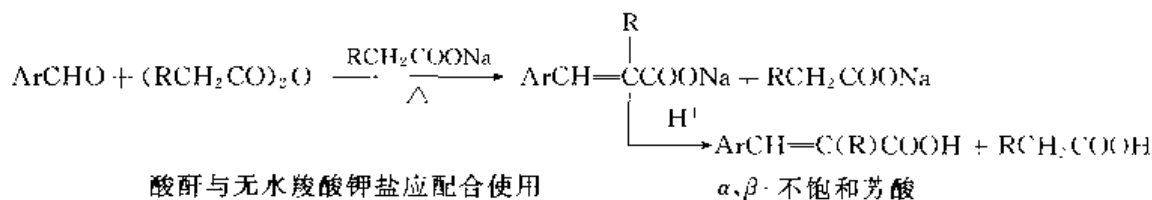
4. 羟醛缩合



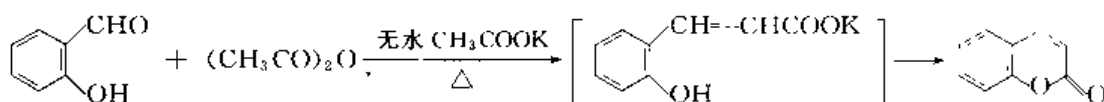
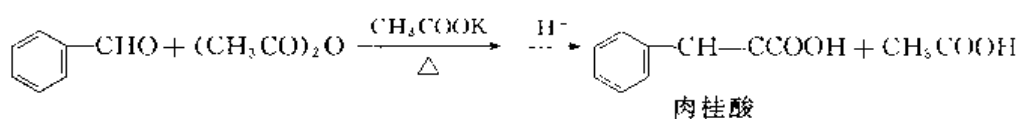
交错羟醛缩合 (Claisen-Schmid 反应)：



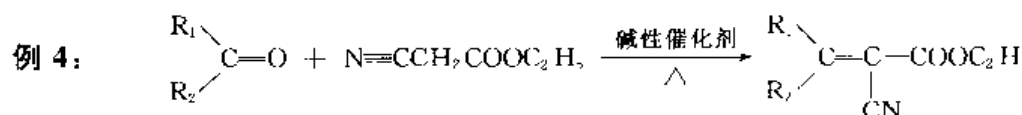
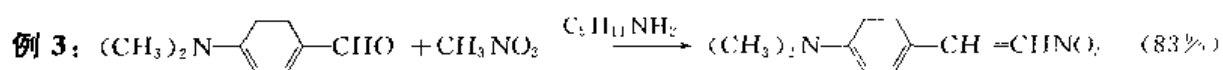
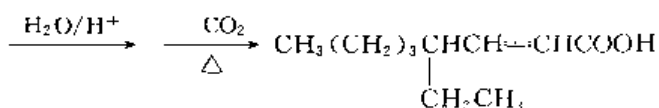
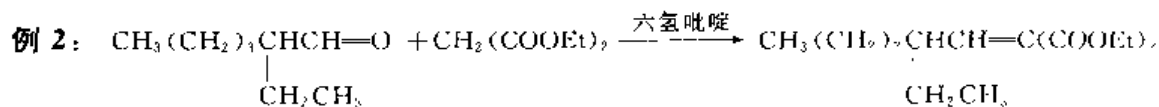
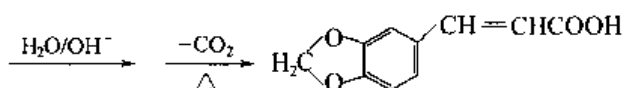
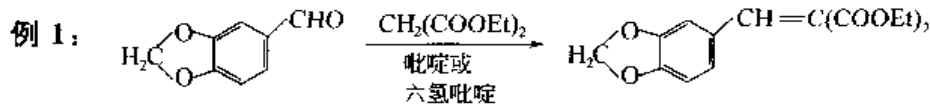
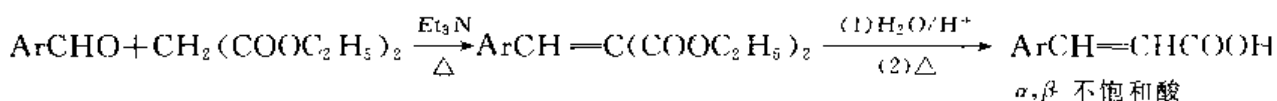
5. Perkin 反应



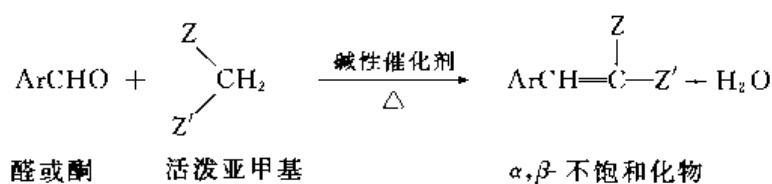
例:



6. Knoevenagel 反应

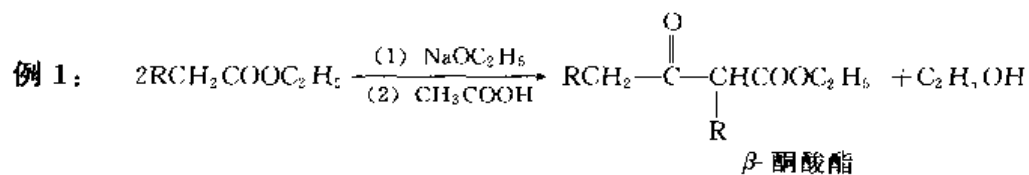


【小结】

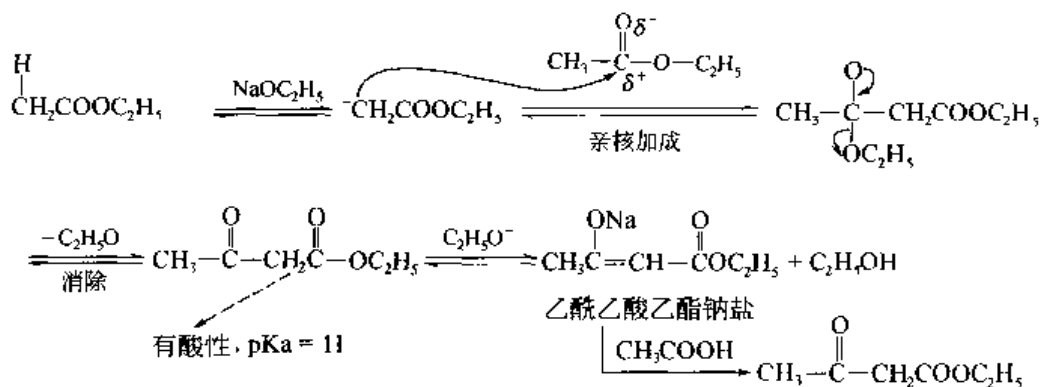


7. Claisen 酯缩合反应和 Dieckmann 反应

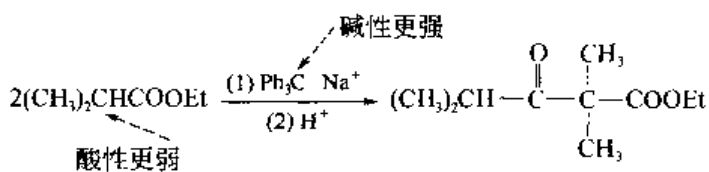
(1) Claisen 酯缩合反应



反应历程如下所示。

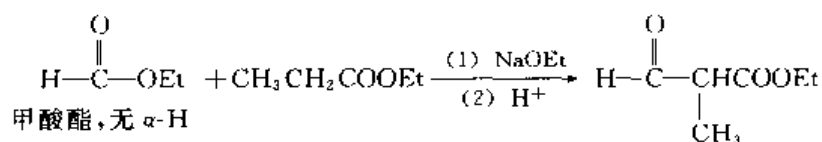


例 2:

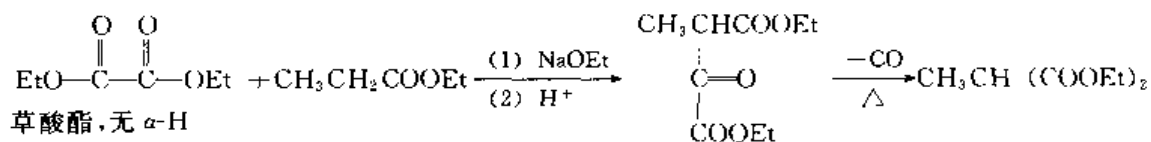


(2) 混合酯缩合

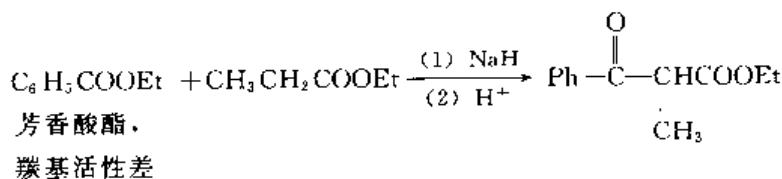
例 1:



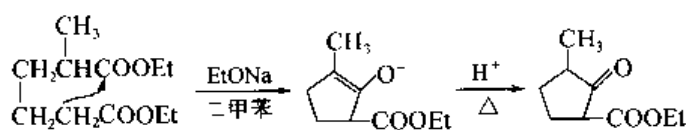
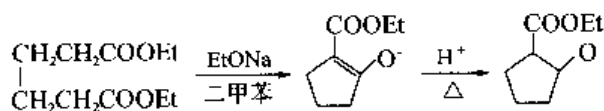
例 2:

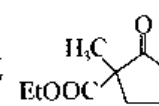
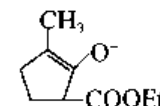
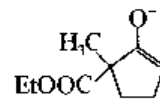


例 3:

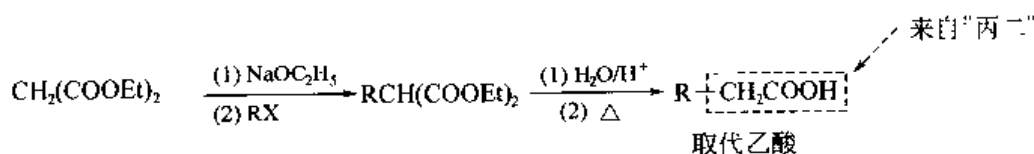
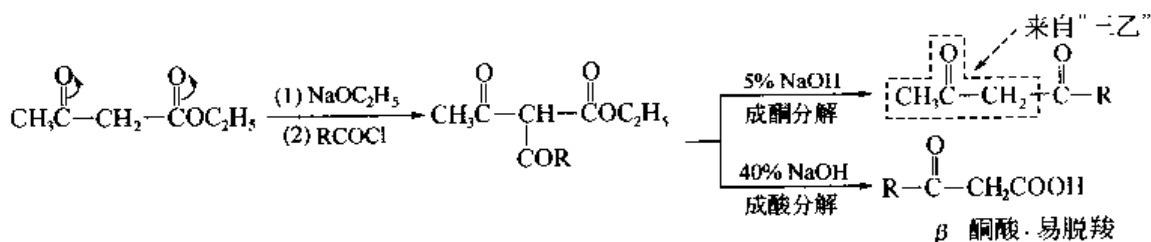
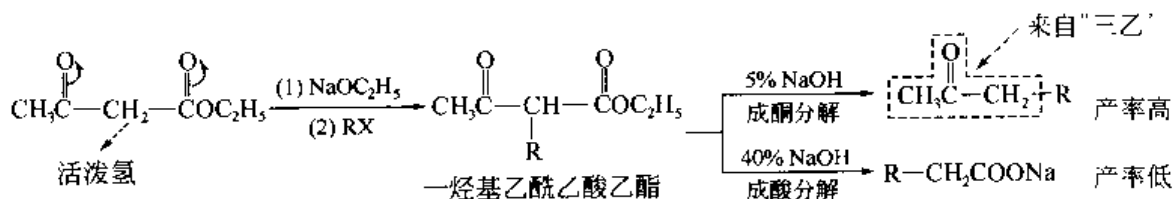


(3) 分子内的酯缩合反应 (Dieckmann 反应)

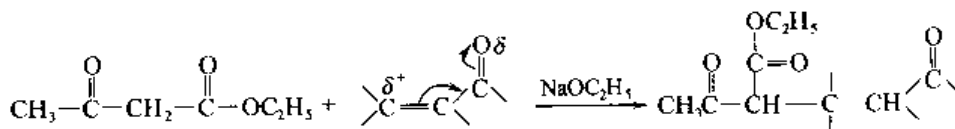


不生成  的原因： 比  更稳定。

8. β -二羰基化合物的烃基化和酰基化



9. Michel 加成

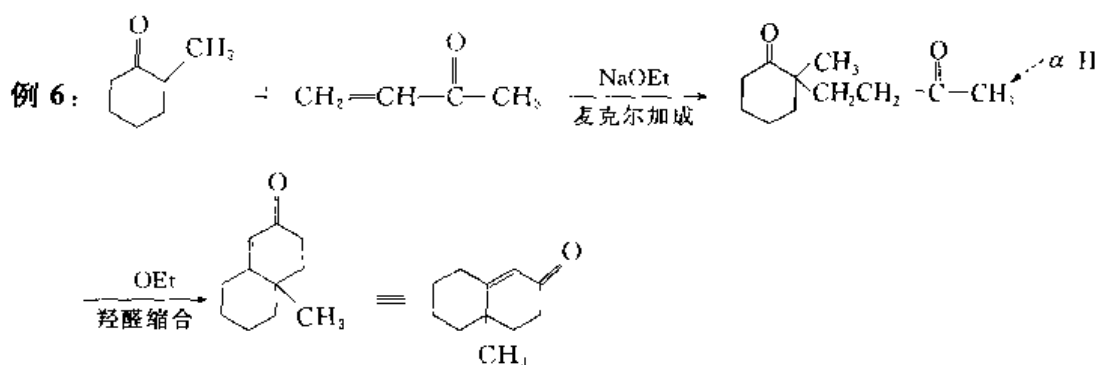


【讨论】 Michel 加成与 Dickmann 反应的结果不同，但原因却都是由烯醇式负离子的稳定性所致。

Michel 加成：共轭加成发生在取代基较多的 α -C 上；

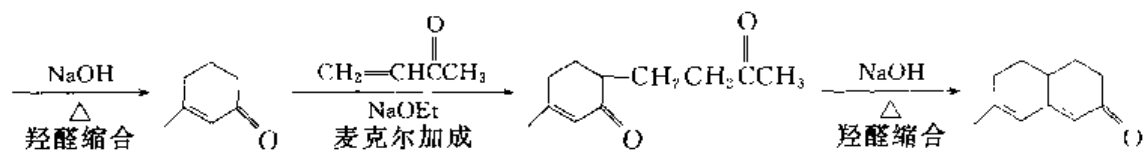
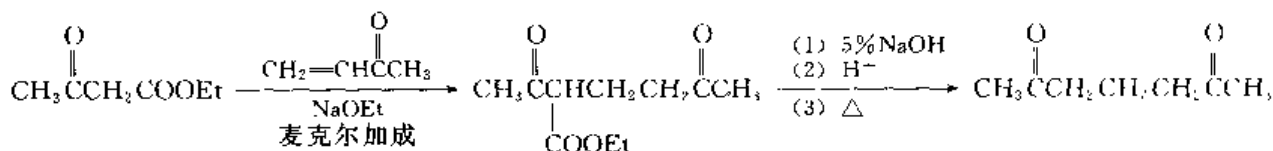
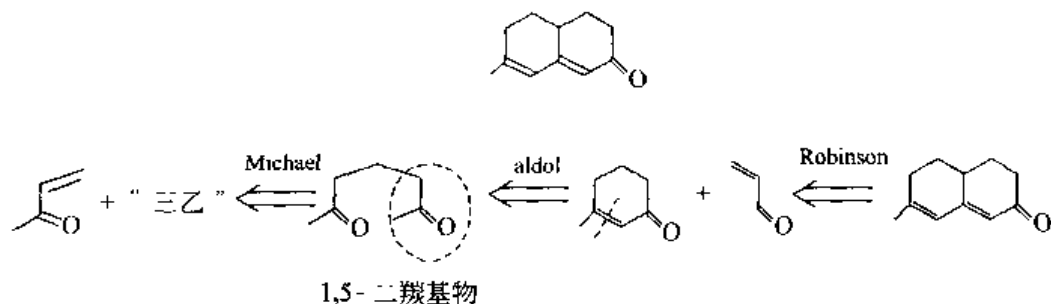


Dickmann 反应：分子内缩合发生在取代基较少的 α -C 上。



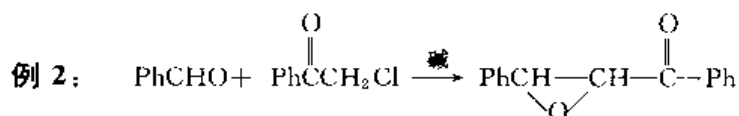
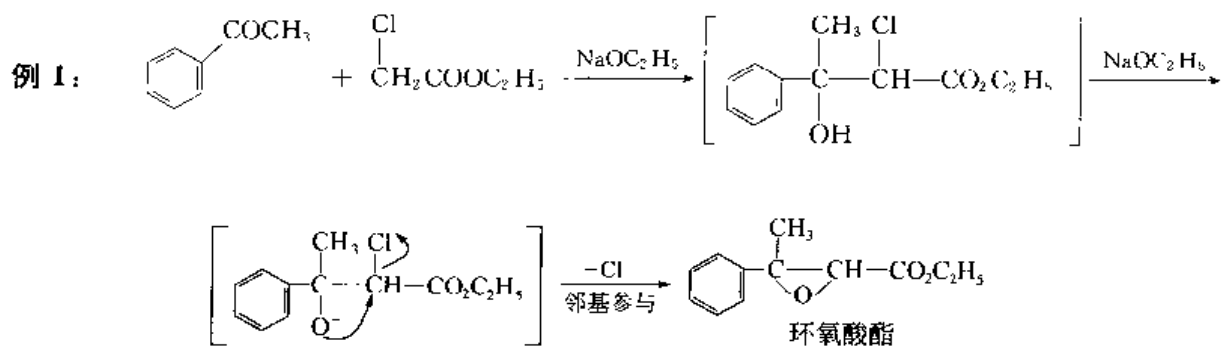
以上的方法称为 Robinson 关环法。

例 7：由 C_2 或 C_4 以下有机物合成



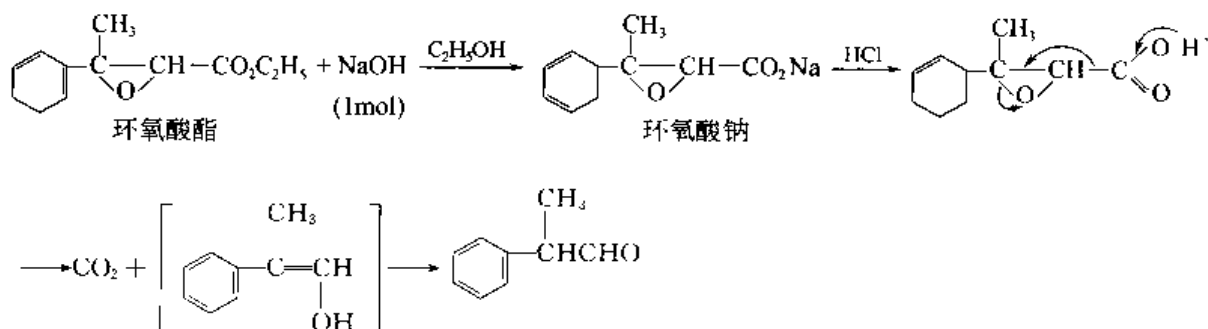
10. Darzen 反应

α -氯代酸酯在醇钠存在下与醛或酮发生的羟醛缩合。

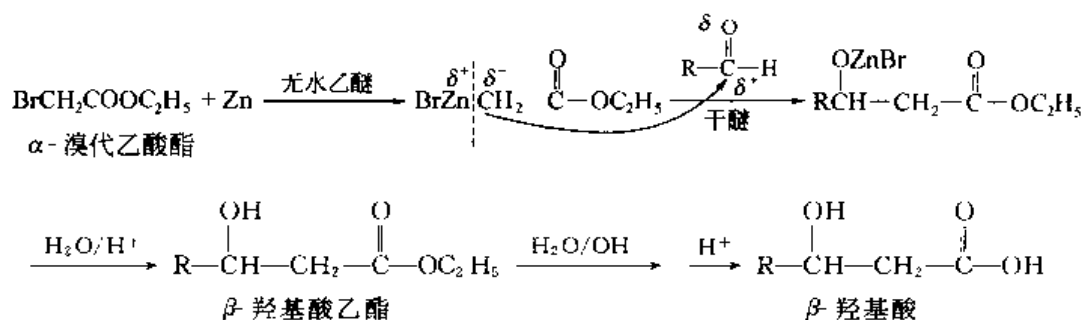


【用途】 合成在羰基碳上多一个碳的醛。

例:

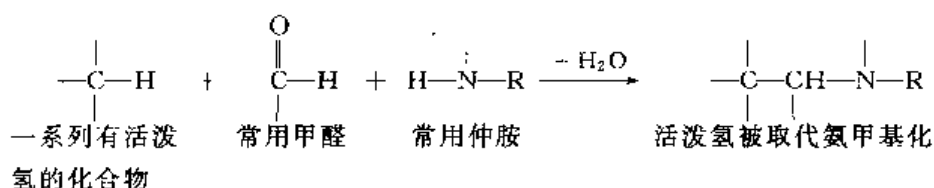


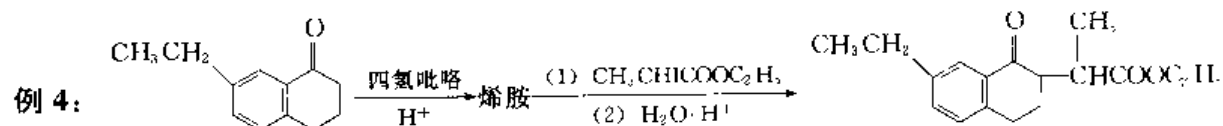
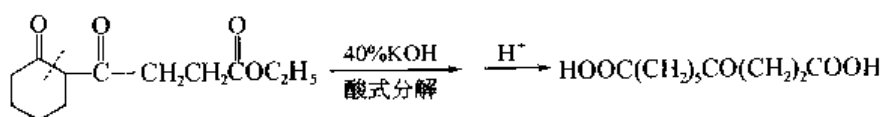
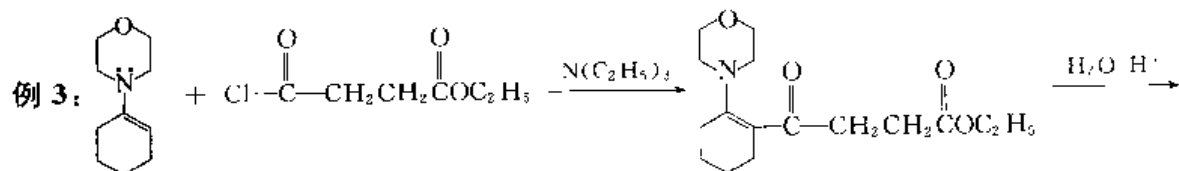
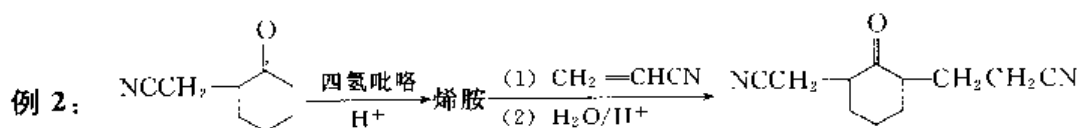
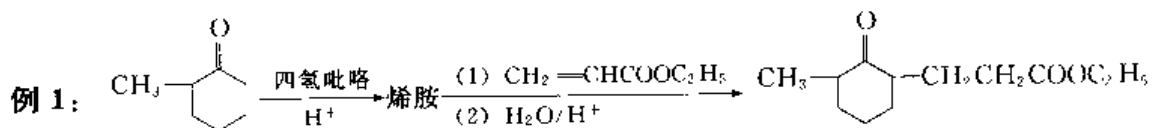
11. Reformasky 反应——制 β 羟基酸 (酯)



12. Mannich 反应 (胺甲基化反应)

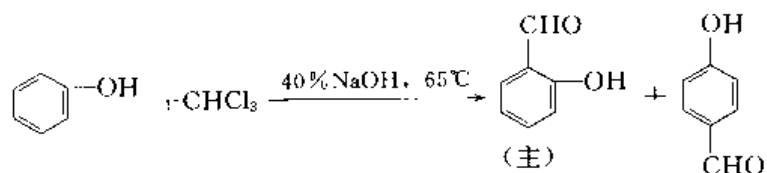
氨、伯胺、仲胺的盐酸盐与醛、酮或其他具有活泼氢的化合物发生缩合，活泼氢原子被氨基或取代氨基所置换的反应称为 Mannich 反应。



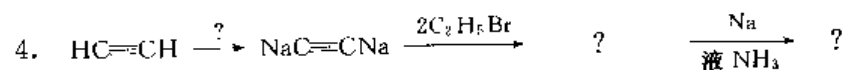
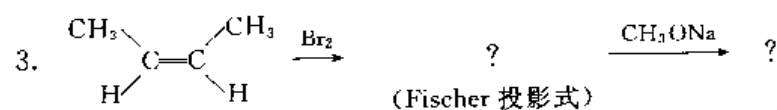
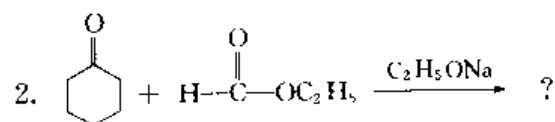
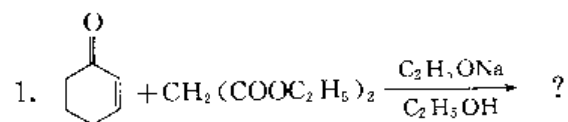


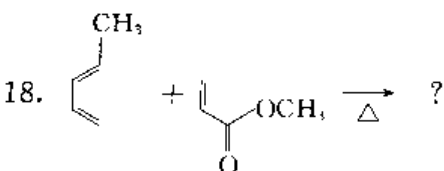
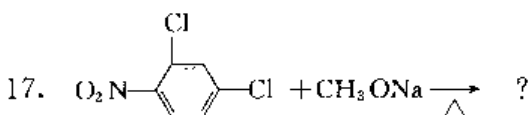
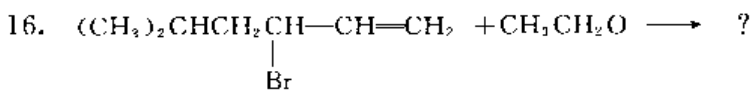
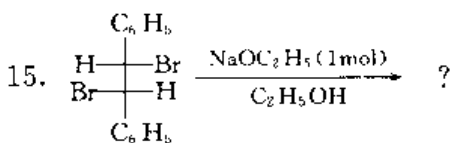
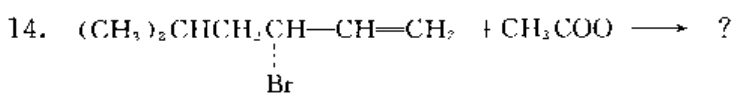
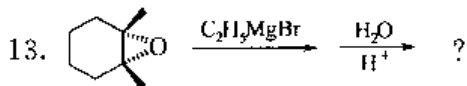
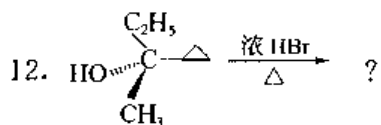
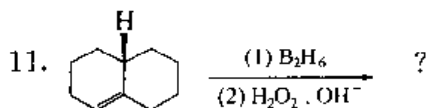
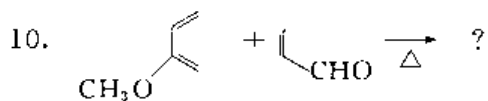
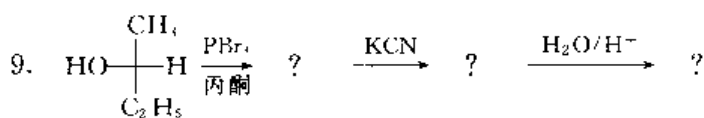
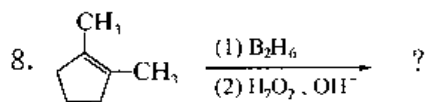
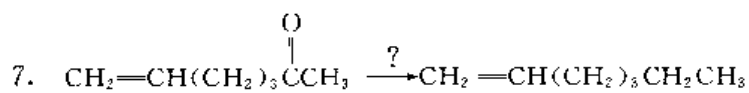
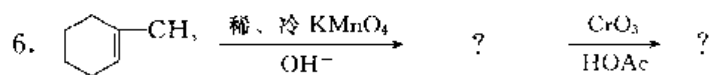
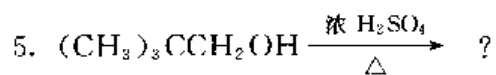
14. Reimer-Tiemann 反应

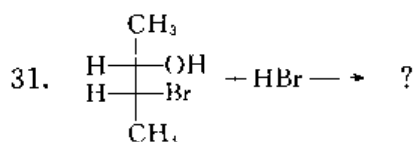
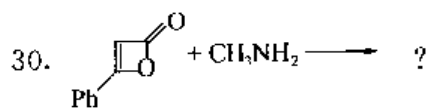
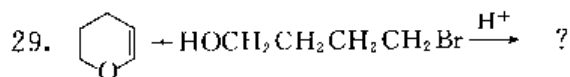
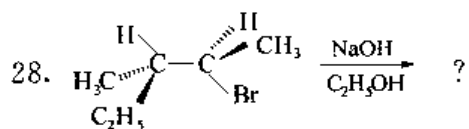
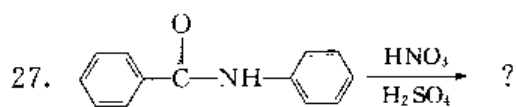
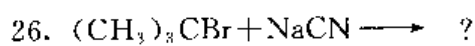
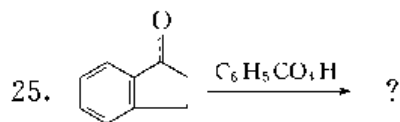
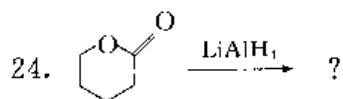
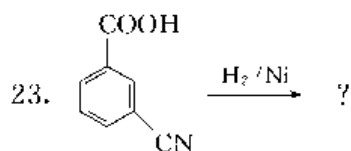
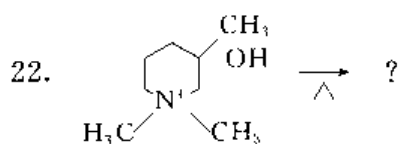
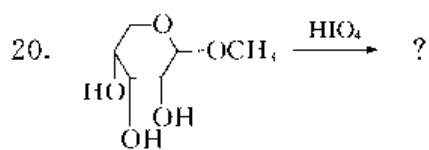
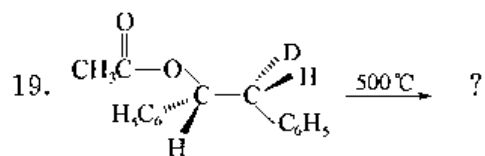
苯酚或烷基苯酚在浓碱中与 CHCl_3 发生放热反应，在酚羟基的邻位引入醛基。

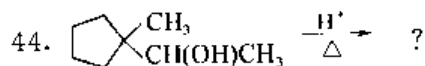
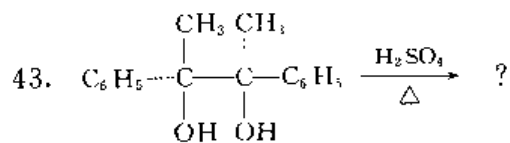
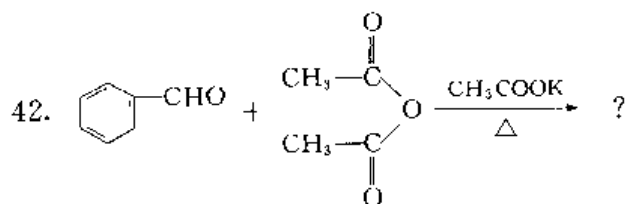
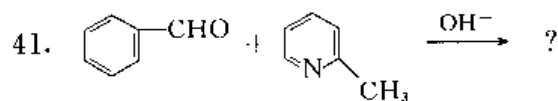
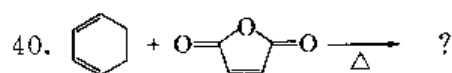
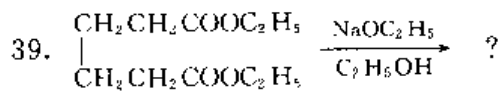
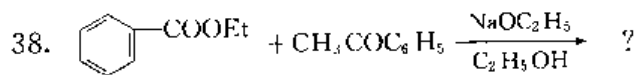
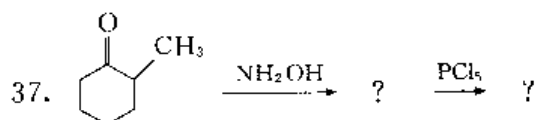
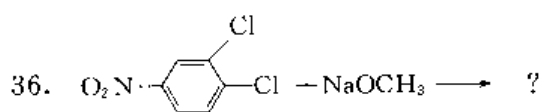
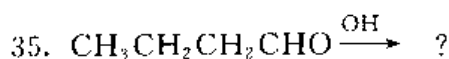
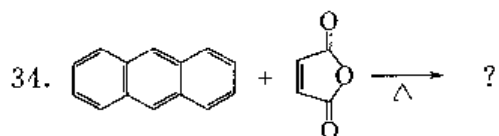
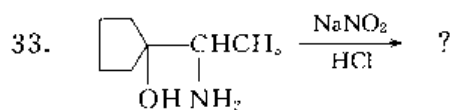
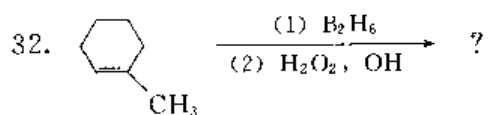


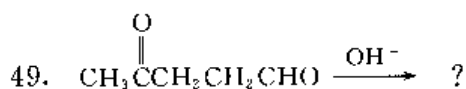
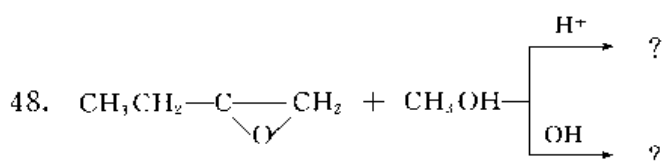
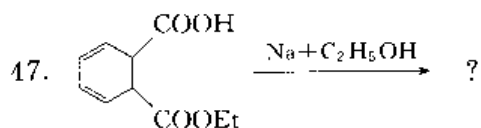
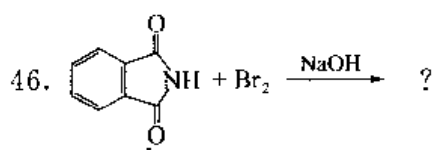
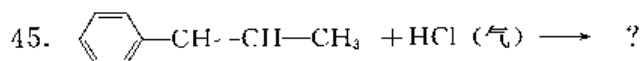
完成反应式练习题 (I)



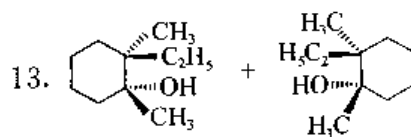
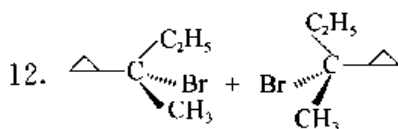
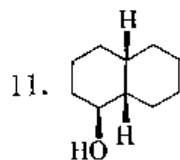
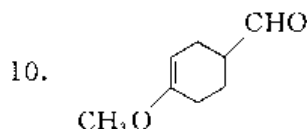
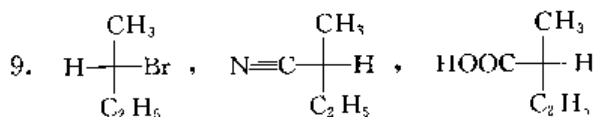
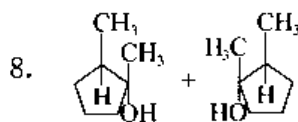
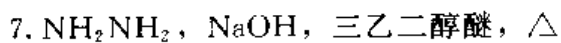
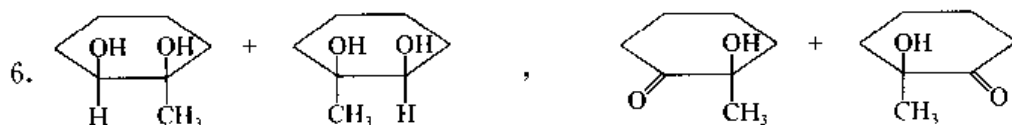
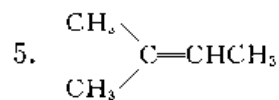
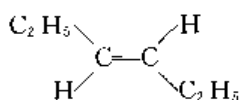
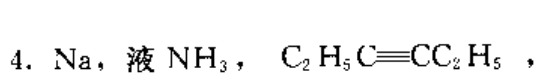
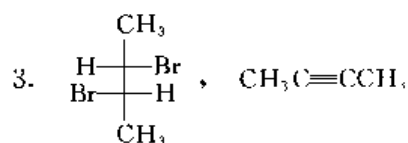
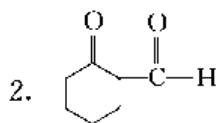
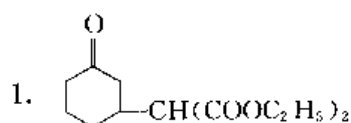


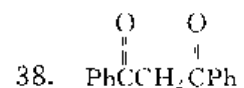
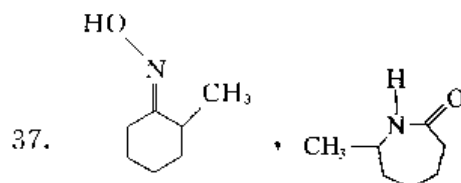
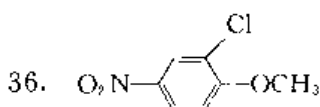
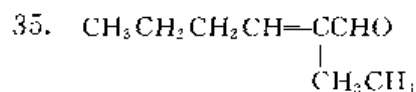
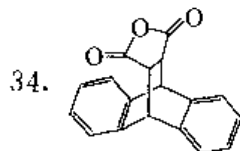
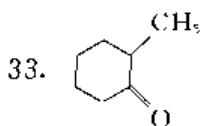
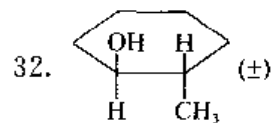
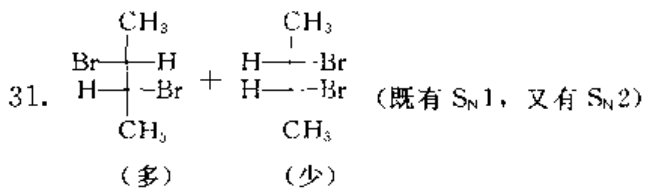
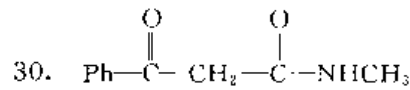
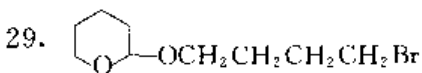
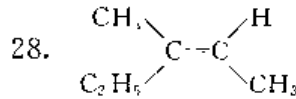
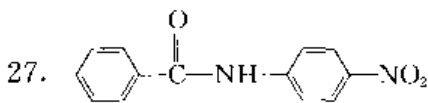
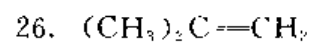
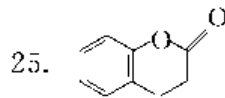
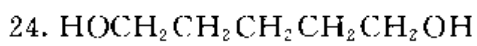
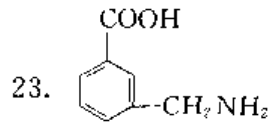
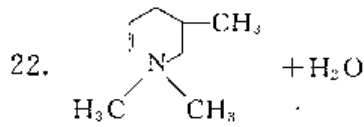
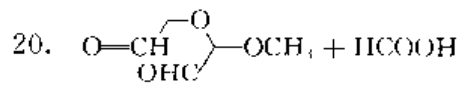
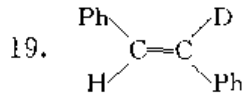
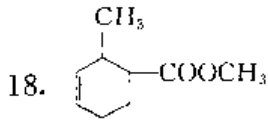
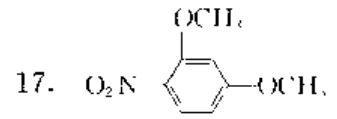
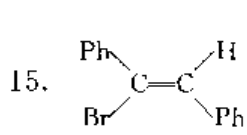
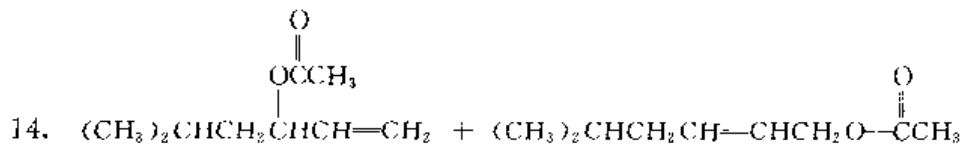


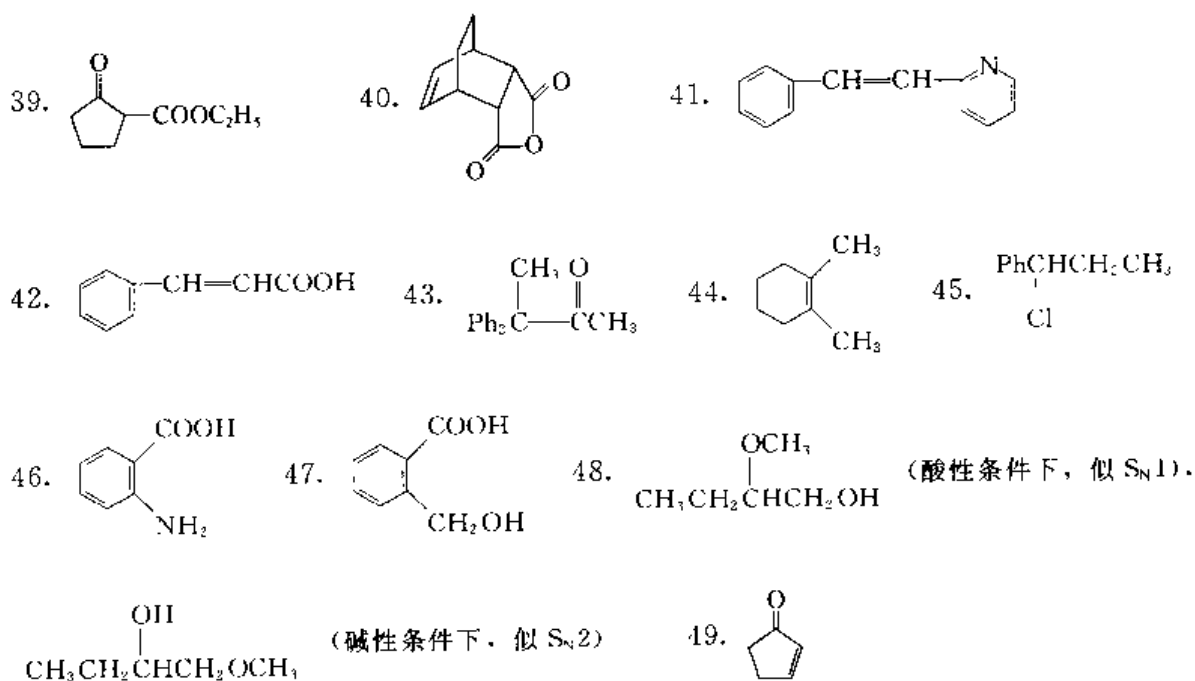




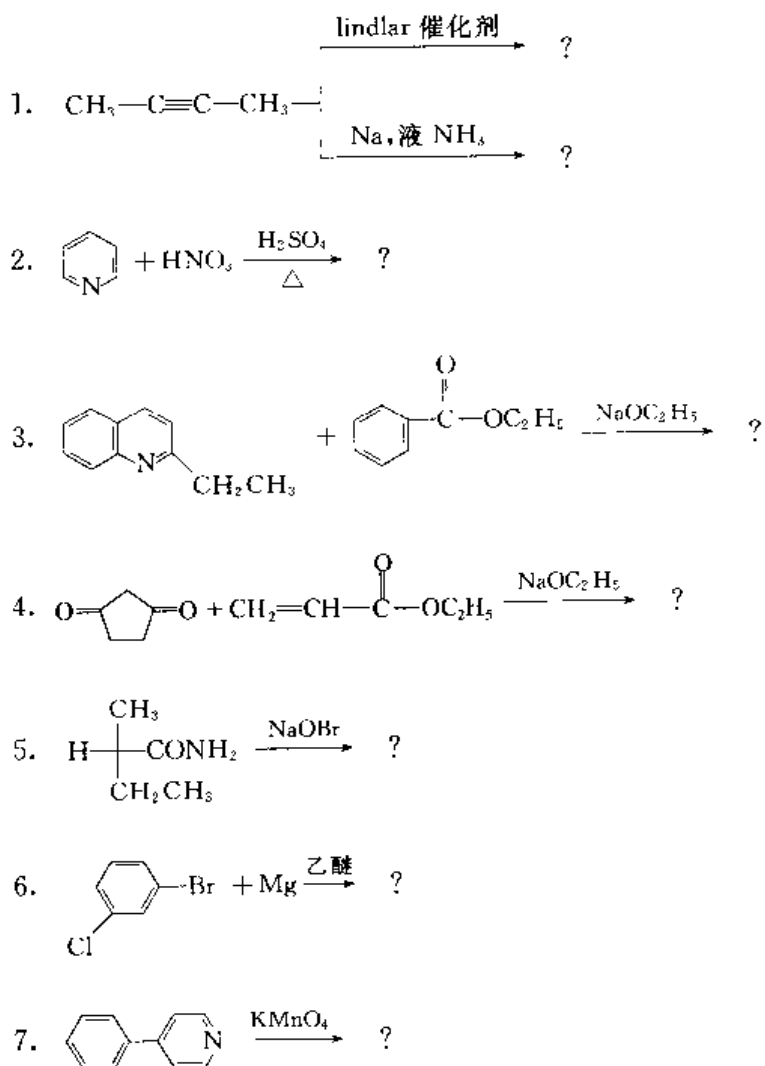
参考答案 (I)

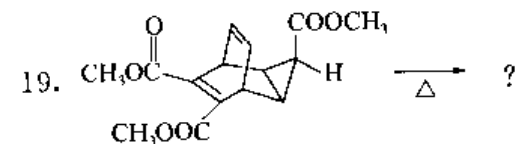
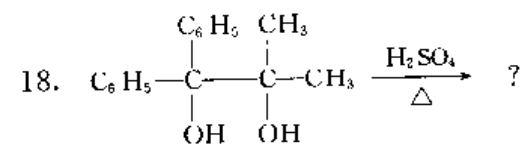
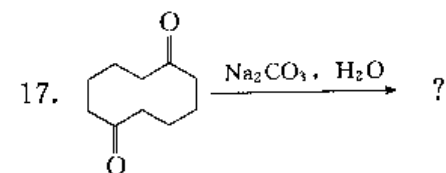
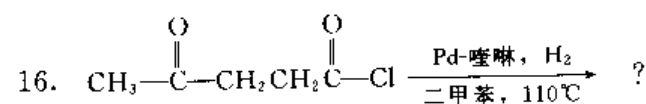
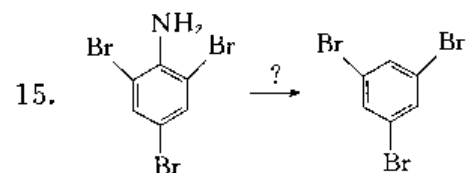
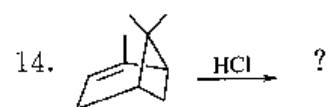
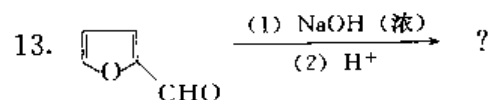
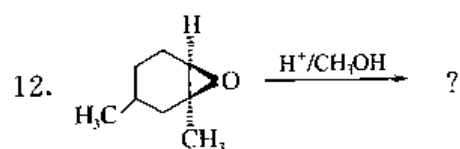
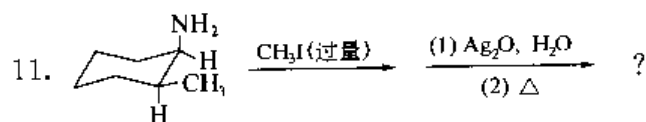
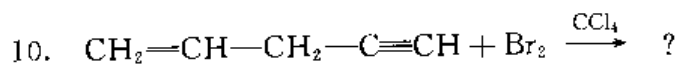
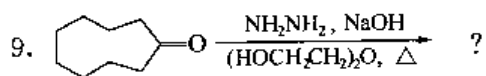
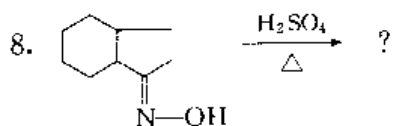


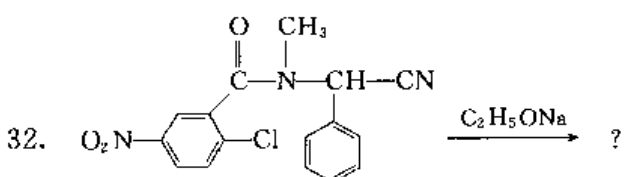
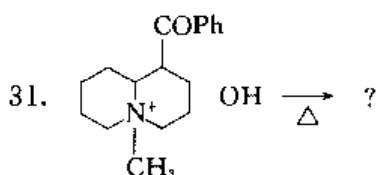
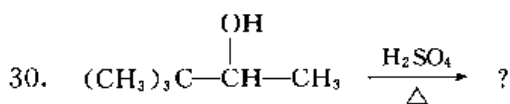
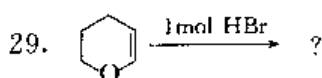
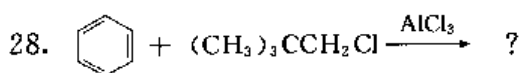
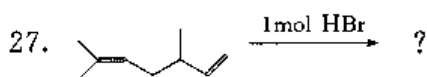
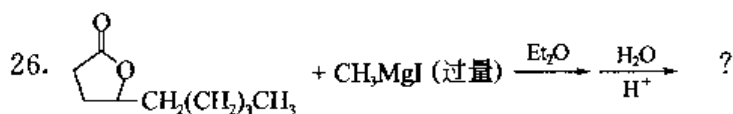
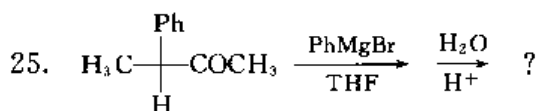
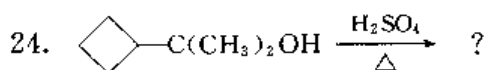
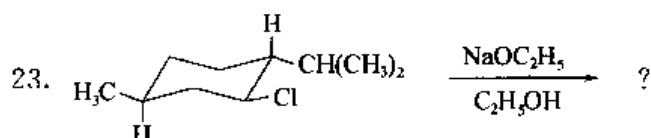
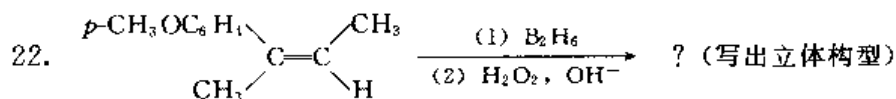
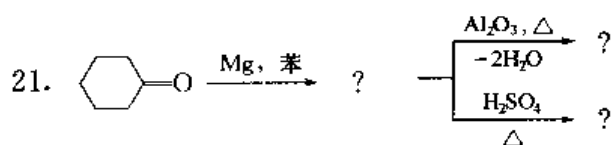
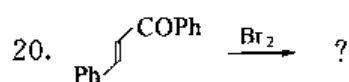


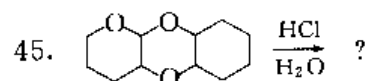
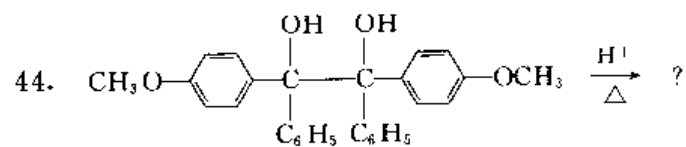
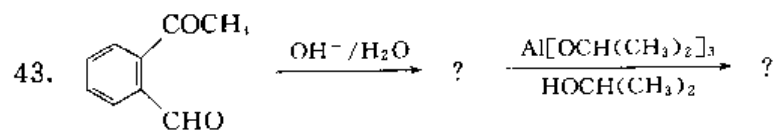
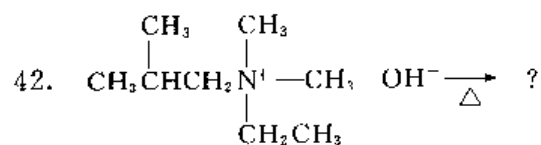
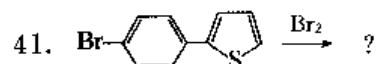
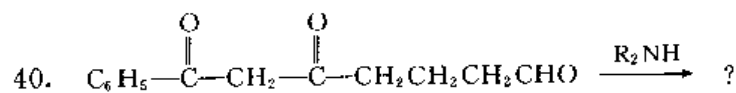
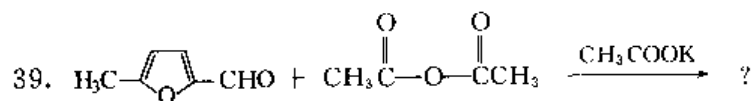
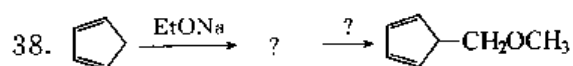
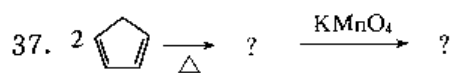
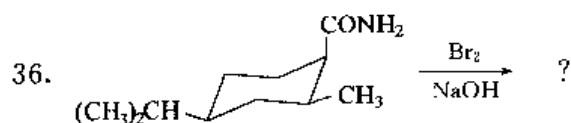
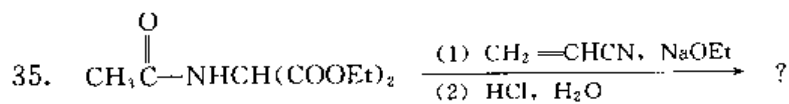
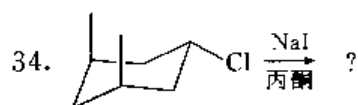
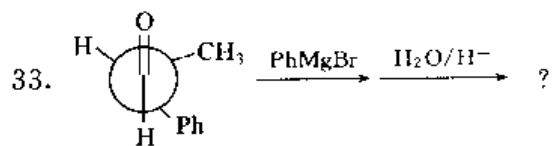


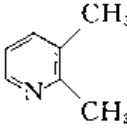
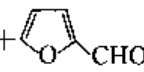
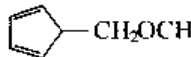
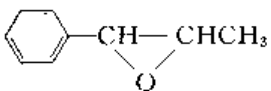
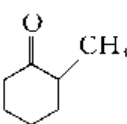
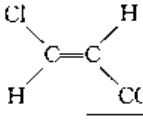
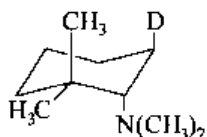
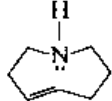
完成反应式练习题 (II)



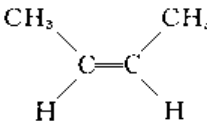
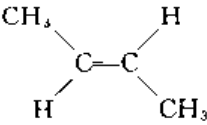
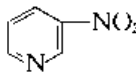
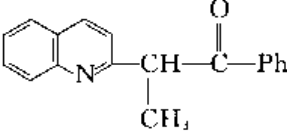
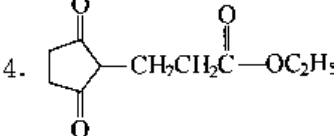
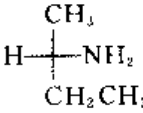
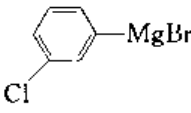
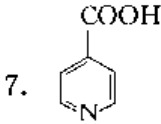
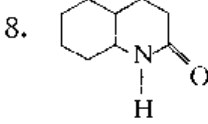
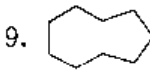
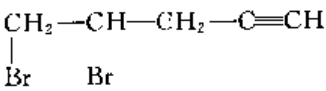
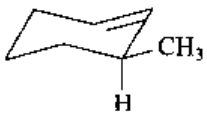
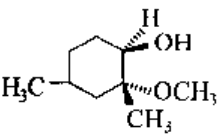


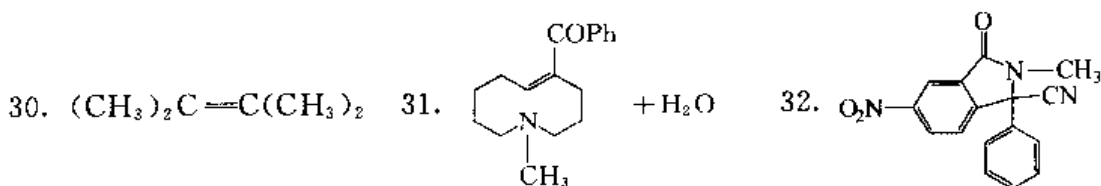
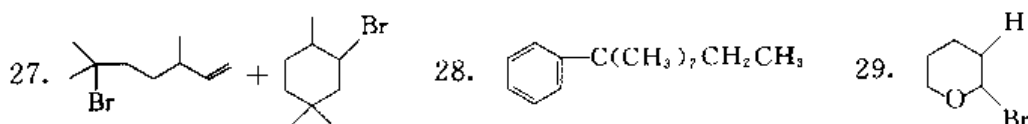
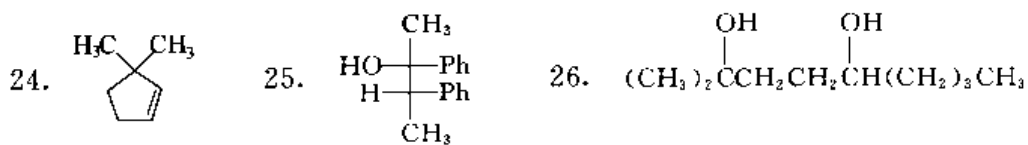
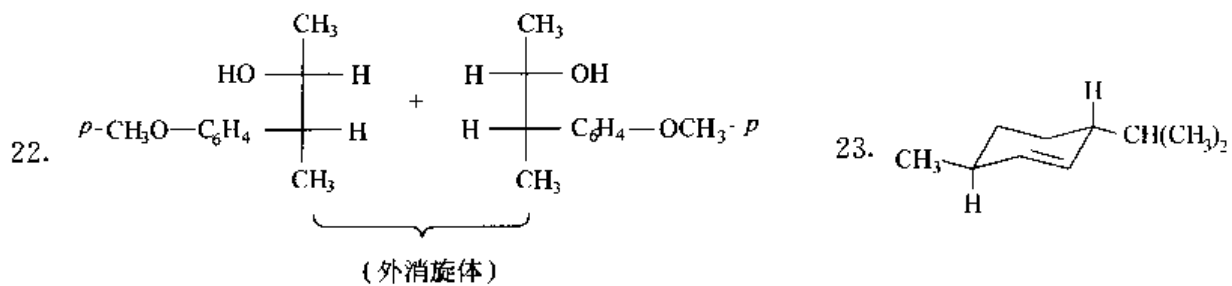
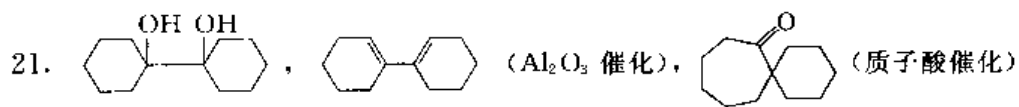
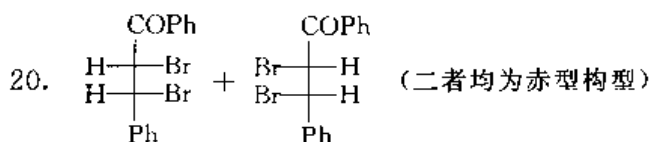
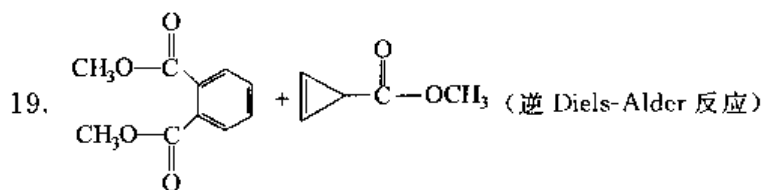
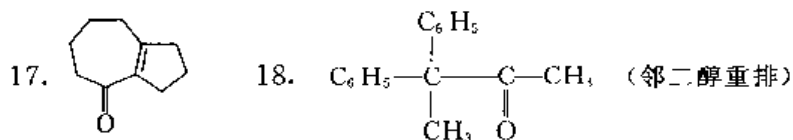
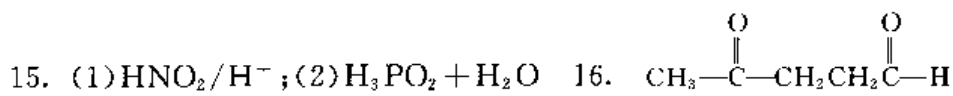
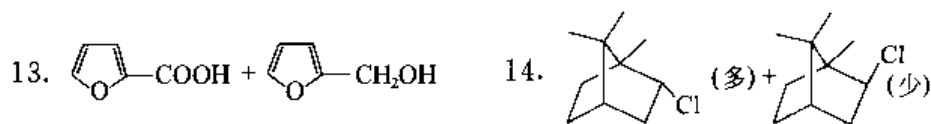


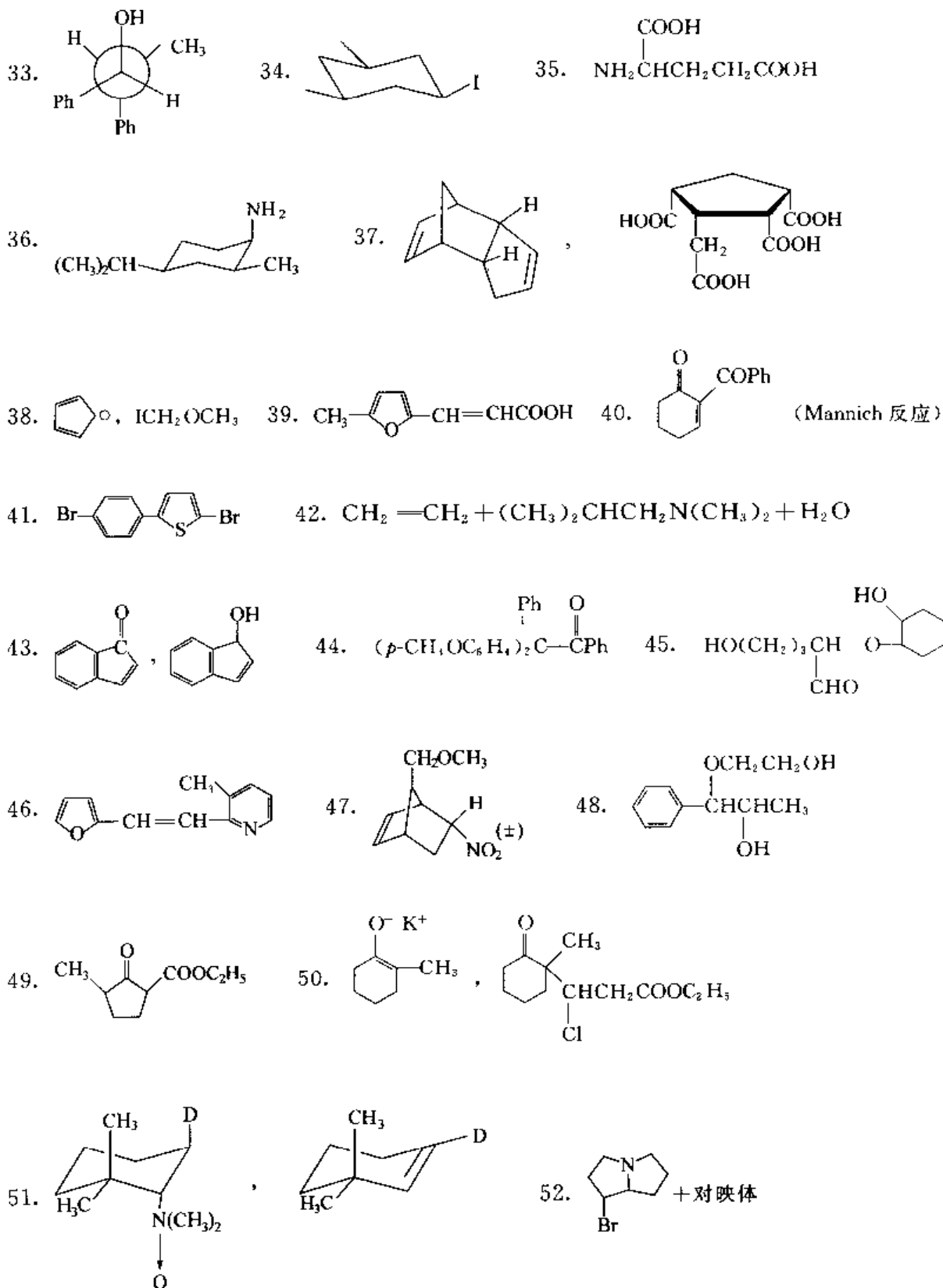


46.  +  $\xrightarrow{\text{NaNH}_2}$?
47.  + $\text{CH}_2=\text{CHNO}_2 \xrightarrow[25^\circ\text{C}]{\text{乙醚}}$?
48.  + $\text{HOCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{H}^-}$?
49. $\text{EtOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{COOEt} \xrightarrow[\text{二甲苯}]{\text{NaOEt}}$?
50.  $\xrightarrow[(\text{CH}_3)_3\text{COH}]{(\text{CH}_3)_3\text{COK}}$?  $\xrightarrow{\text{COOEt}}$?
51.  $\xrightarrow{\text{H}_2\text{O}_2}$? $\xrightarrow{\Delta}$?
52.  + $\text{Br}_2 \rightarrow$?

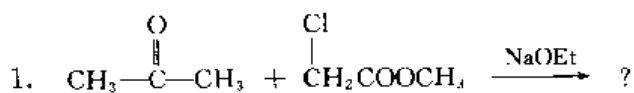
参考答案 (II)

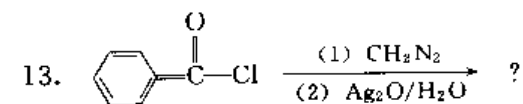
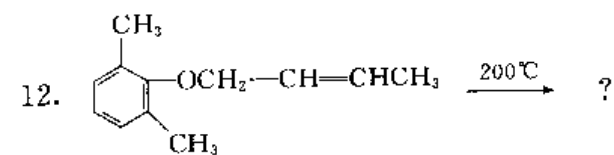
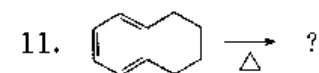
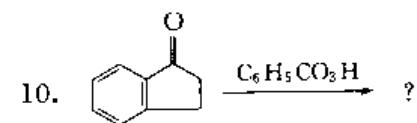
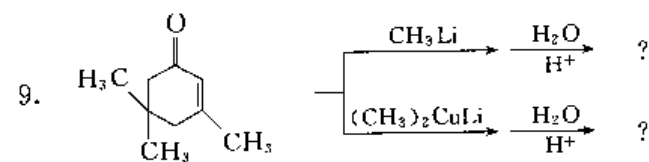
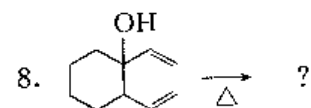
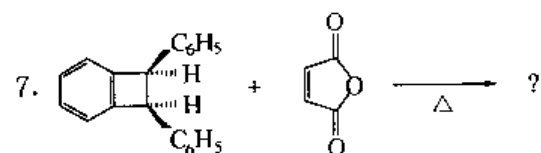
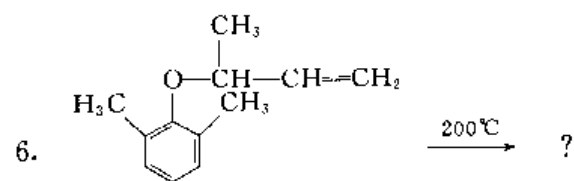
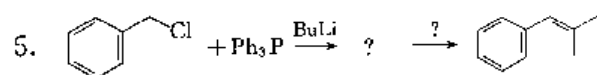
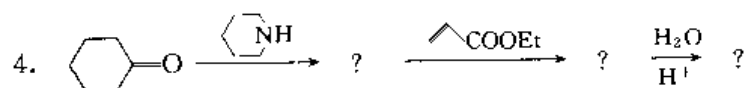
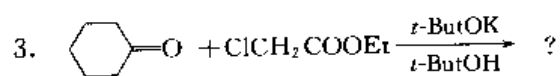
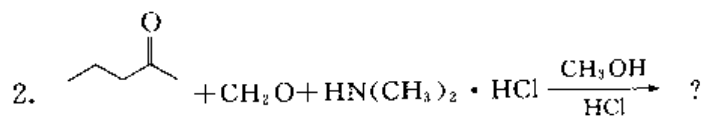
1.  ,  2. 
3.  4.  5. 
6.  7.  8.  9. 
10.  11.  12. 

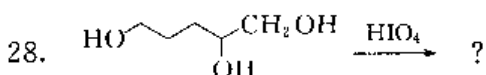
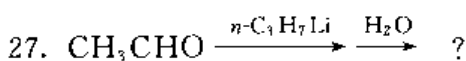
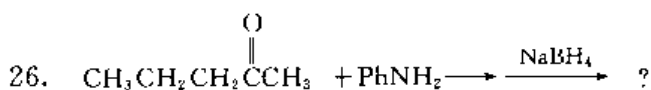
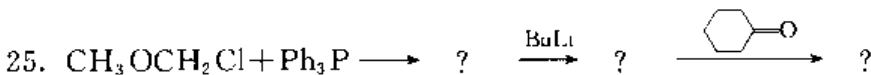
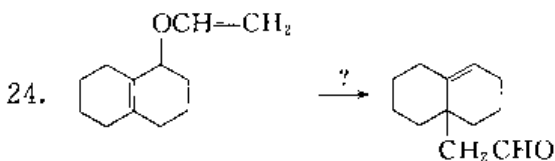
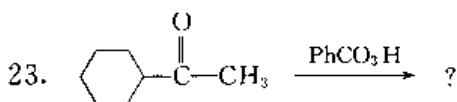
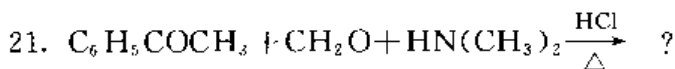
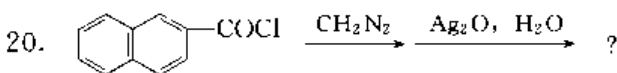
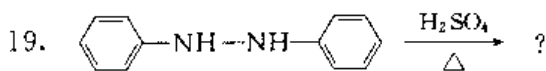
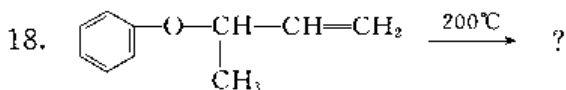
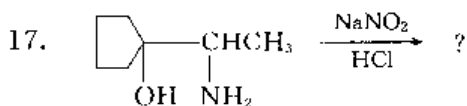
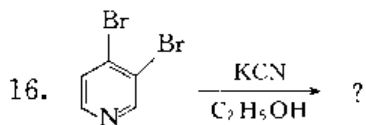
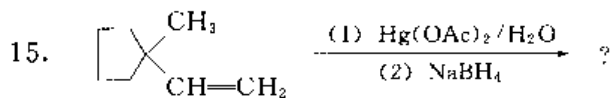
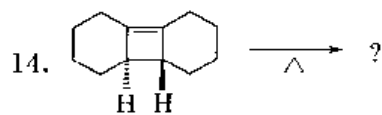


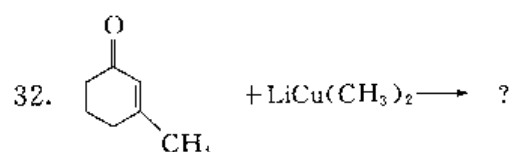
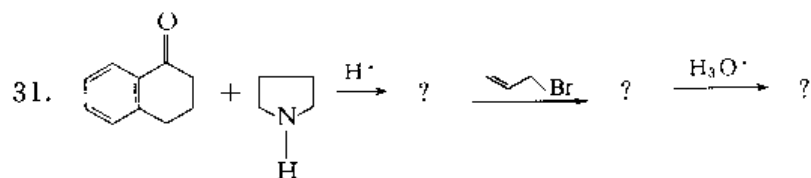
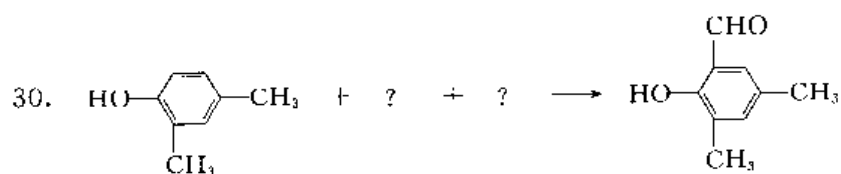
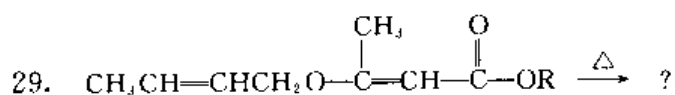


完成反应式练习题 (III)

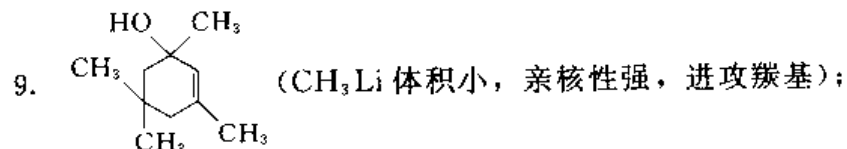
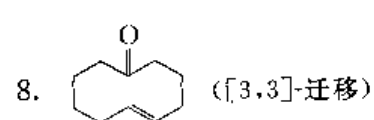
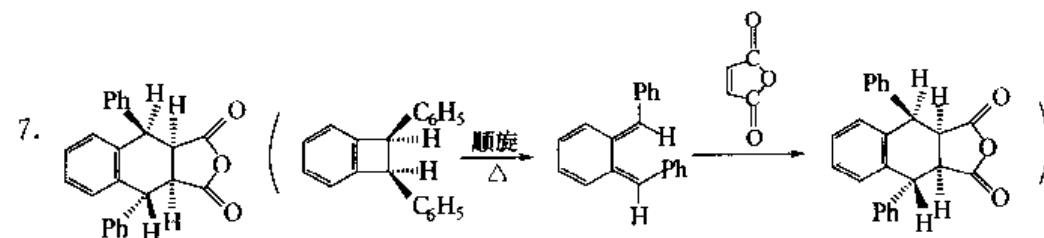
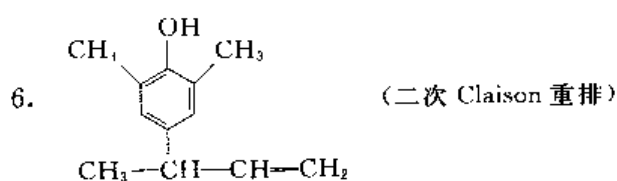
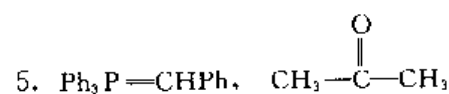
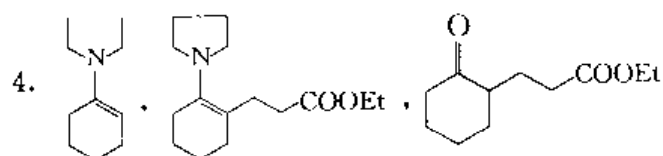
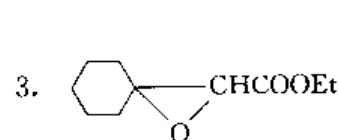
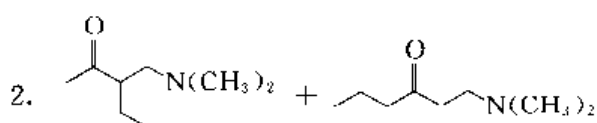
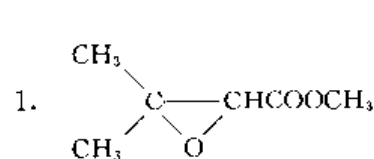


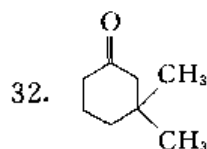
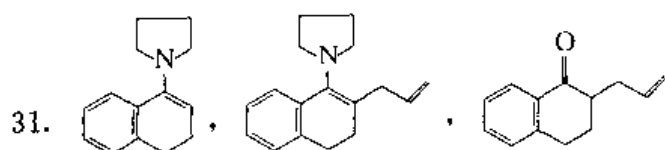
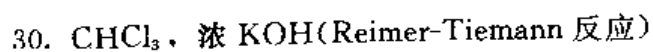
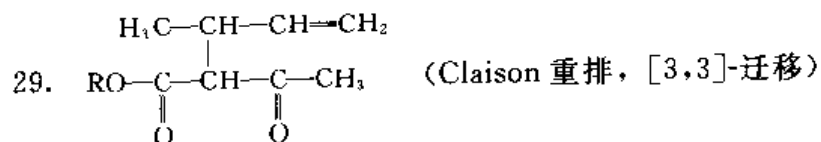
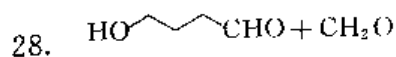
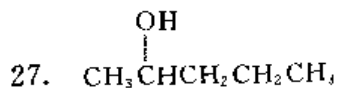
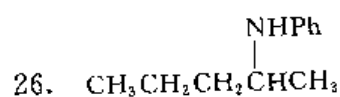
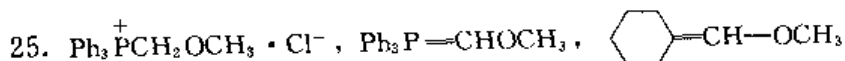
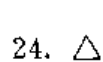
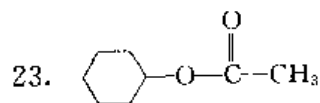
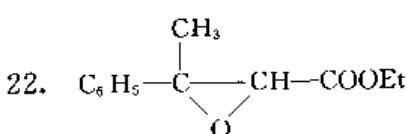
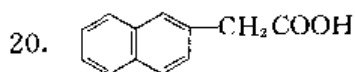
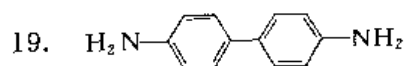
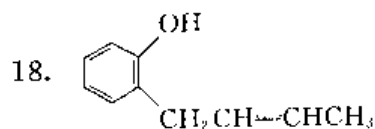
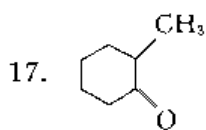
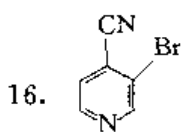
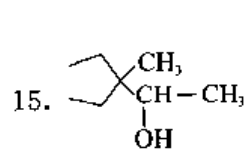
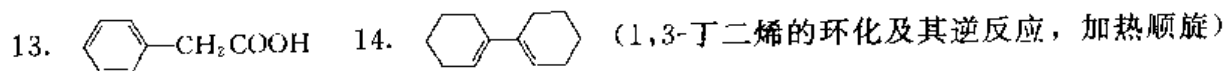
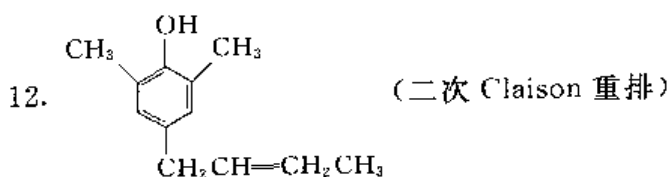
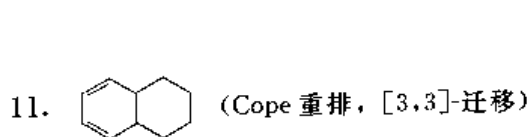
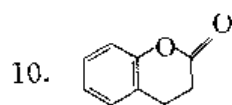
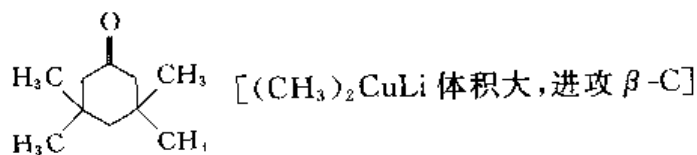






参考答案 (III)





专题总结 III —— 基础有机化学中的合成题

一、引言

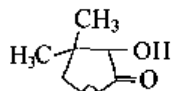
1. 设计合成路线的 3 个指标

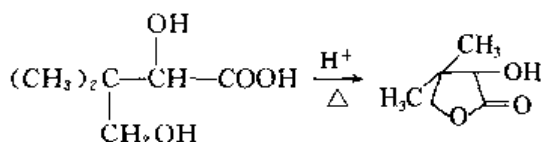
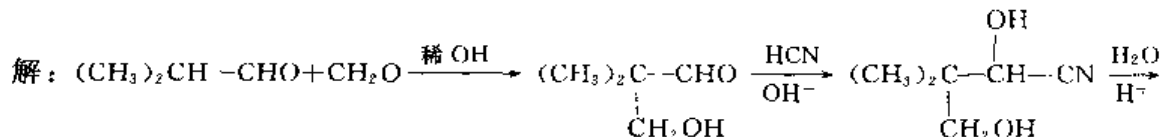
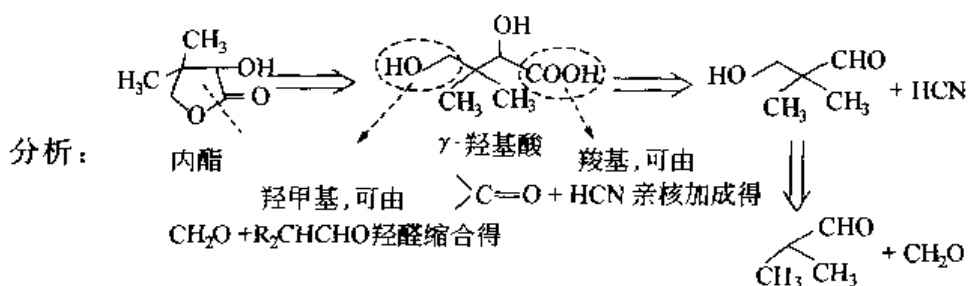
(1) 途径简捷；(2) 原料易得；(3) 总产率高。

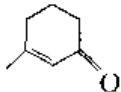
2. 设计合成路线的步骤和方法

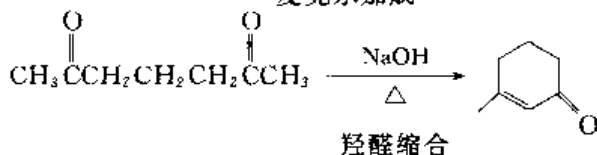
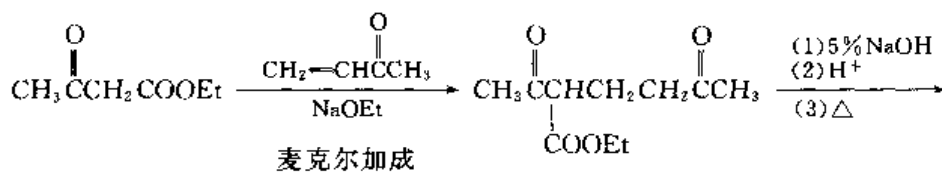
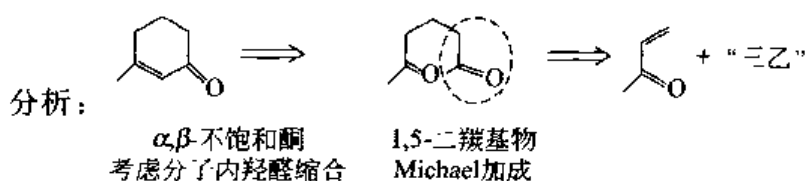
(1) 分析目标分子的结构，进行合理的“切断”

① 化合物的类型 分析目标化合物是哪一类（如酯、醛、酮、醇、醚）。

例 1: 用简单的原料合成 

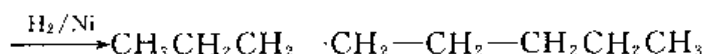
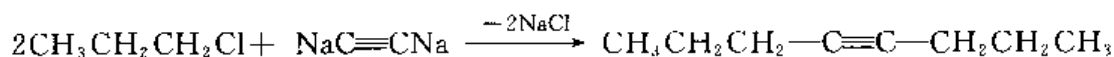
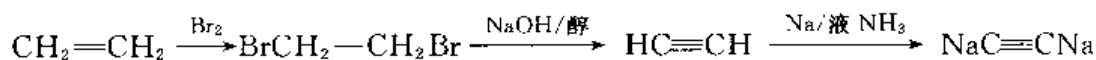
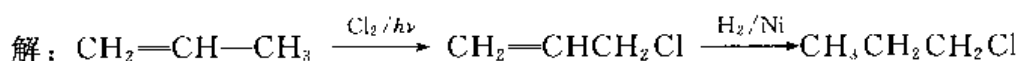
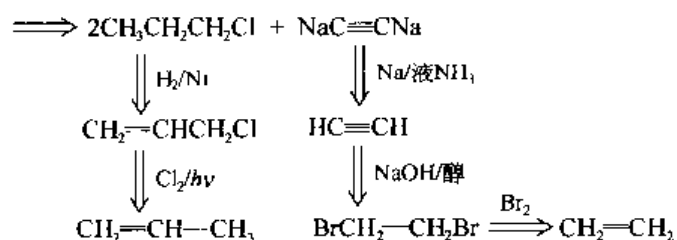
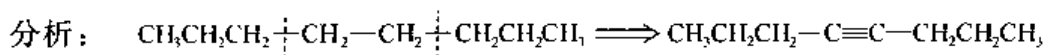


例 2: 由简单化合物合成 



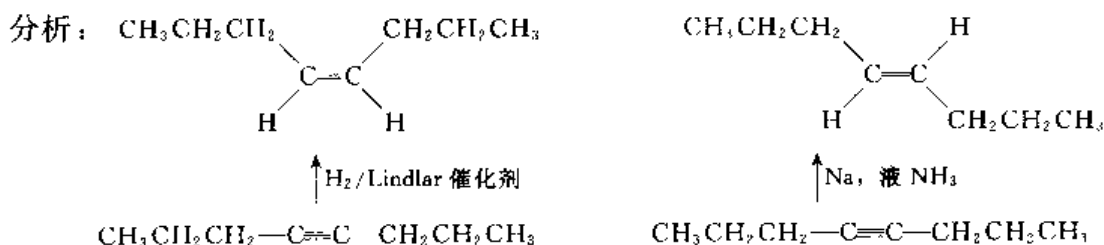
② 碳架 分析碳链是开链还是环状，是增长还是缩短，碳架是脂环、芳环还是杂环。

例：从乙烯、丙烯合成正辛烷

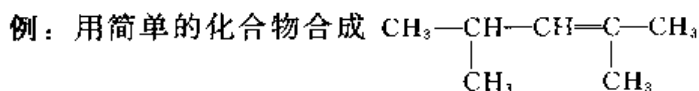


③ 分子的立体构型

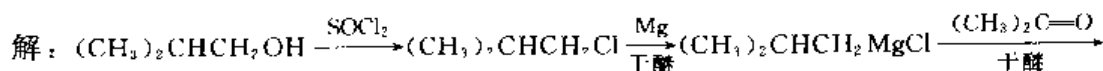
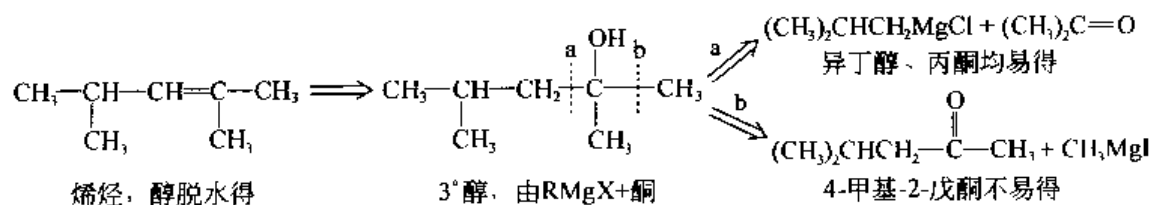
例：从乙烯、丙烯合成顺-4-辛烯、反-4-辛烯

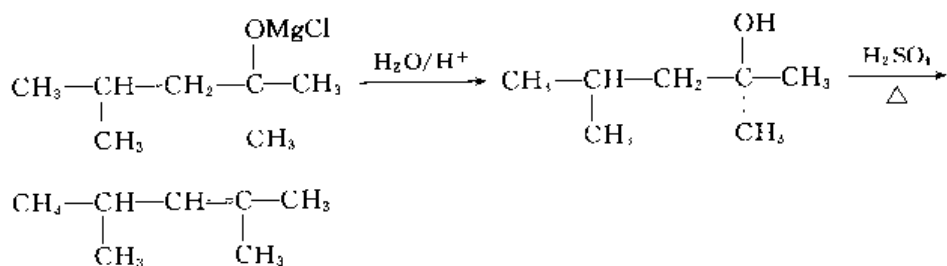


(2) 选择廉价、易得的原料



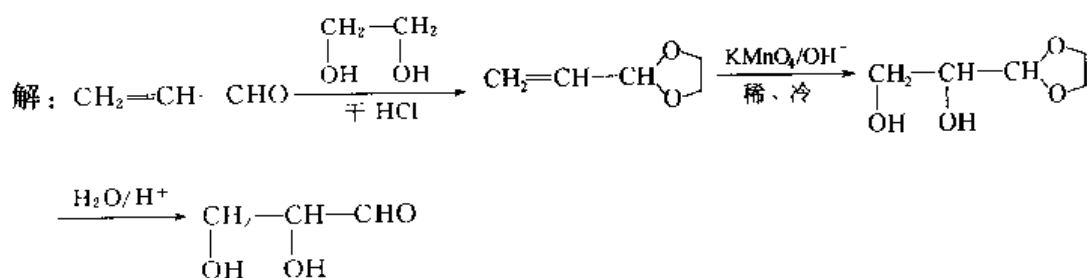
分析：



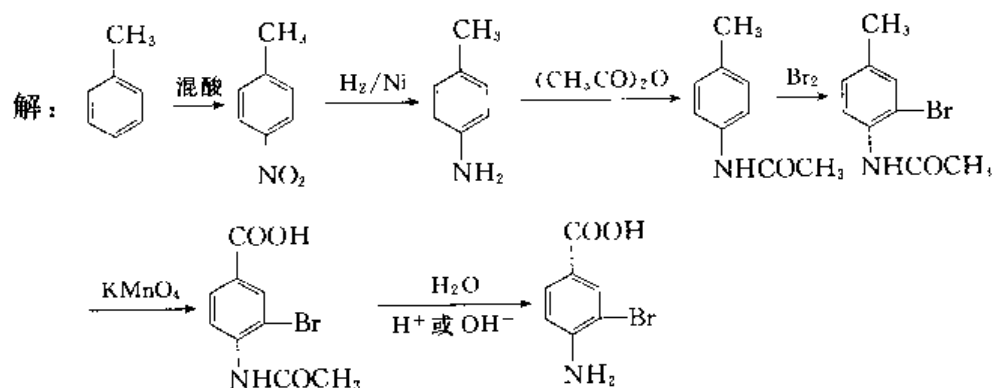


(3) 注意基团保护

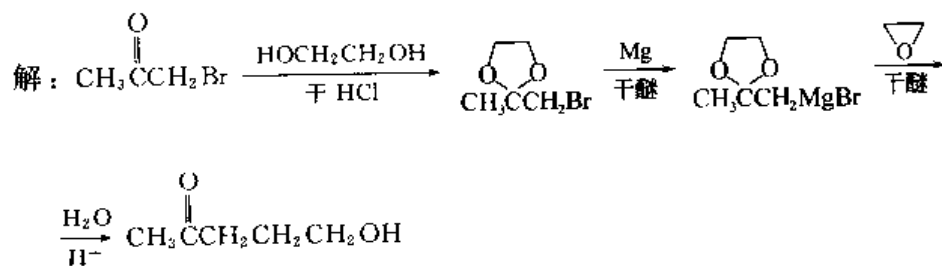
例 1: 由 $\text{CH}_2=\text{CH}-\text{CHO}$ 合成 $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CHO} \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$ (保护醛基)



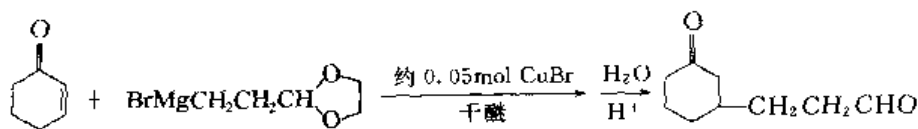
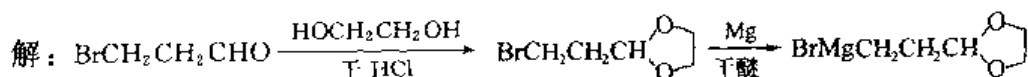
例 2: 由甲苯制备 $\begin{array}{c} \text{HOOC}-\text{C}_6\text{H}_3(\text{Br})-\text{NH}_2 \\ \text{(保护}-\text{NH}_2\text{)} \end{array}$



例 3: 完成转化 $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{Br} \longrightarrow \text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (保护酮羰基)



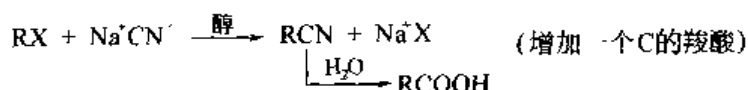
例 4: 完成转化 $\text{BrCH}_2\text{CH}_2\text{CHO} \longrightarrow \begin{array}{c} \text{O} \\ || \\ \text{C}_6\text{H}_{10} \end{array} \text{CH}_2\text{CH}_2\text{CHO}$ (保护醛基)



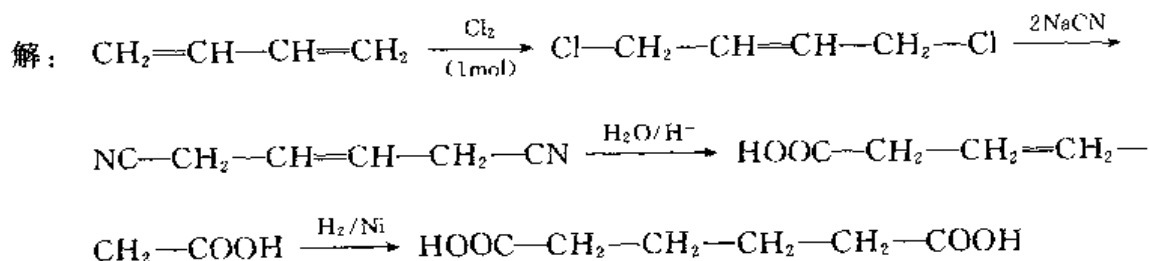
二、增长碳链的方法 (形成碳-碳键的方法)

1. 亲核取代

(1) 卤代烃氰解——制多一个碳的羧酸



例: 由丁二烯合成己二酸。

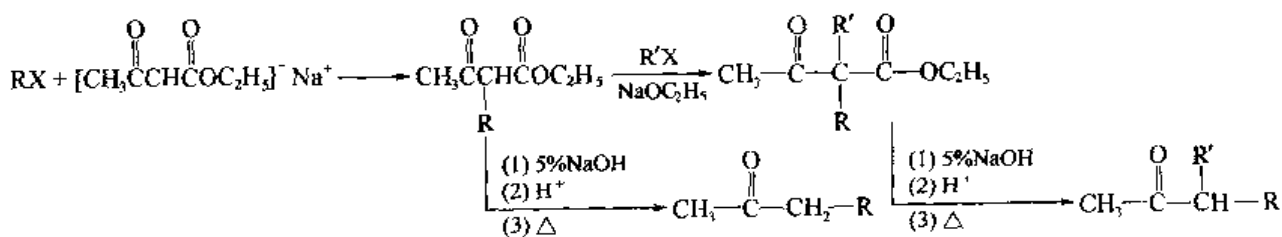


(2) 卤代烃与炔化钠反应

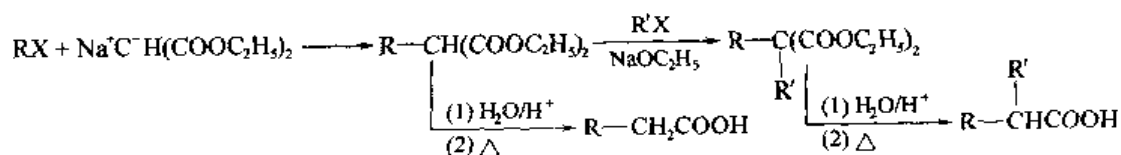


例: 由乙烯、丙烯制正辛烷。

(3) 三乙负离子与卤烃反应——制甲基酮

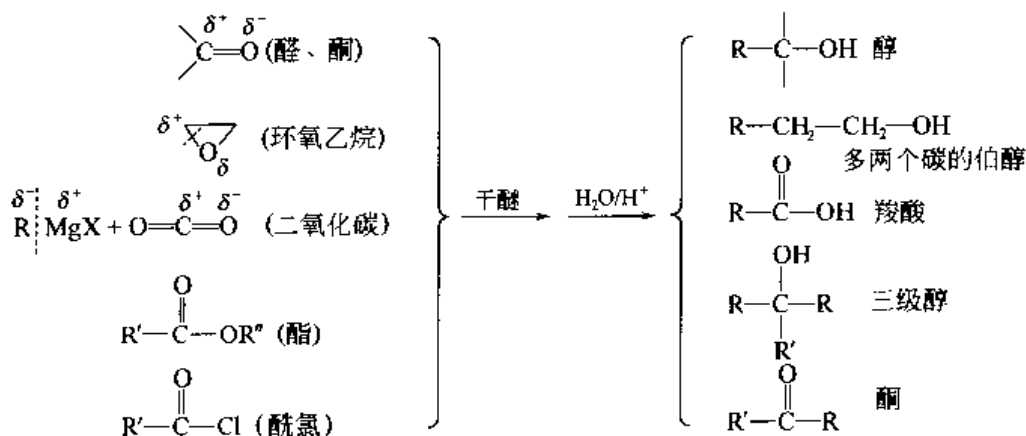


(4) 丙二负离子与卤烃反应——制取代乙酸

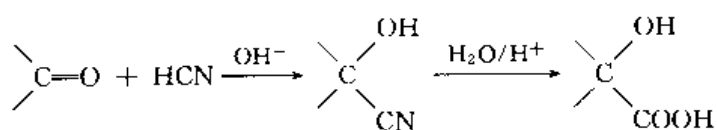


2. 亲核加成

(1) 格氏反应



(2) 醛、酮加氰氢酸



(3) 羟醛缩合

见“专题总结 II”中“4.”。

(4) Perkin 反应

见“专题总结 II”中“5.”。

(5) Knoevenagel 反应

见“专题总结 II”中“6.”。

(6) Reformsky 反应——制 β 羟基酸 (酯)

见“专题总结 II”中“11.”。

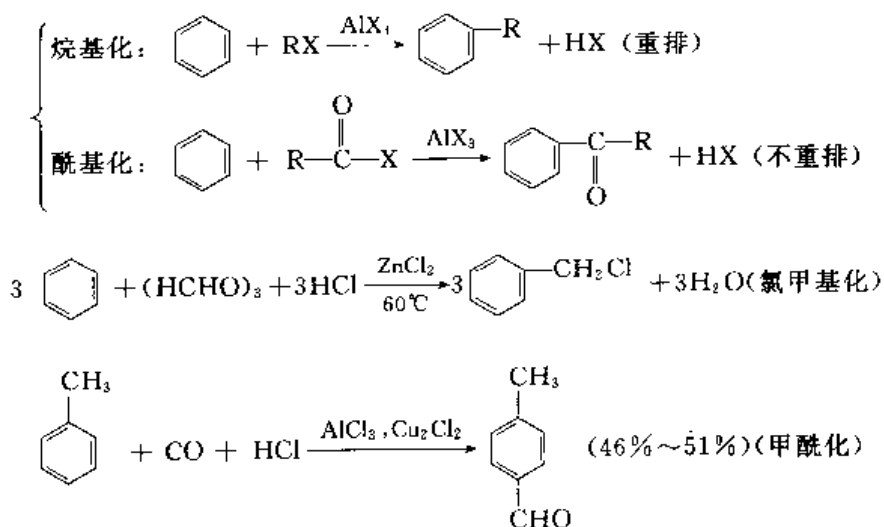
(7) Claisen 酯缩合反应

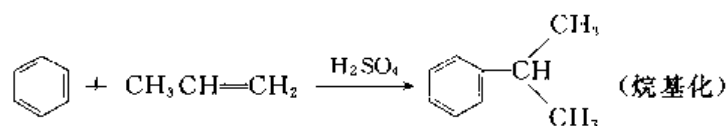
见“专题总结 II”中“7.”。

(8) Michel 加成

见“专题总结 II”中“9.”。

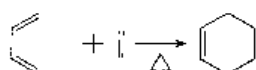
3. 芳环上亲电取代



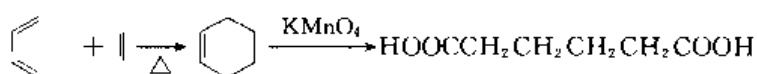


4. 其他方法

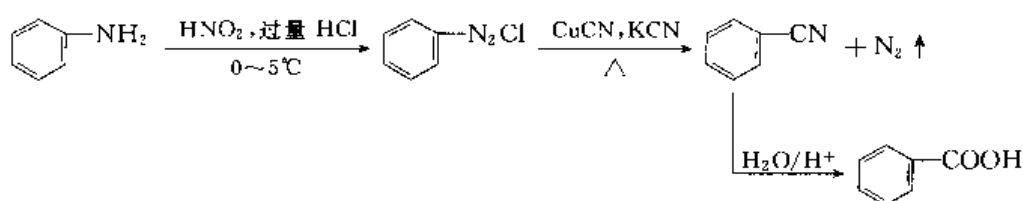
(1) 环化加成



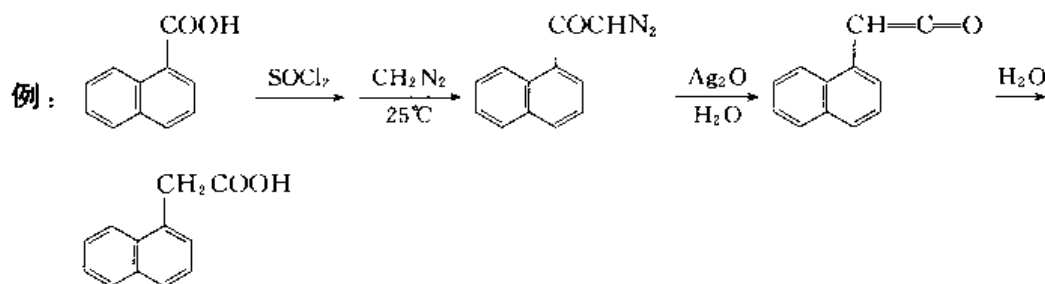
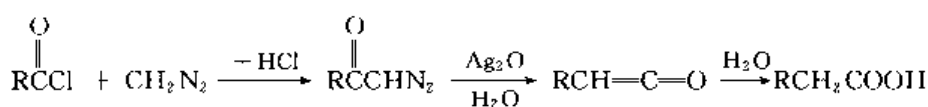
例：由丁二烯合成己二酸。



(2) 重氮盐放氮



(3) 重氮甲烷与酰氯反应——制多一个碳的羧酸

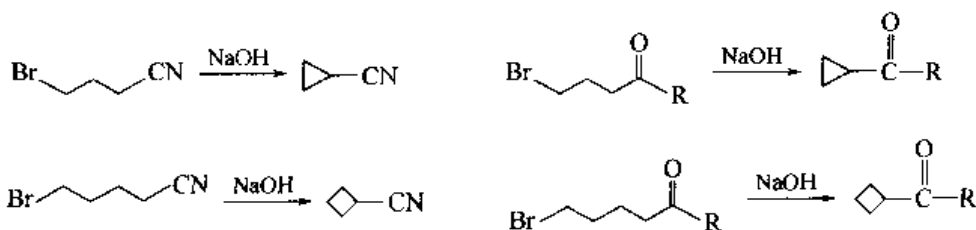


(4) Skraup 合成法——制喹啉类化合物

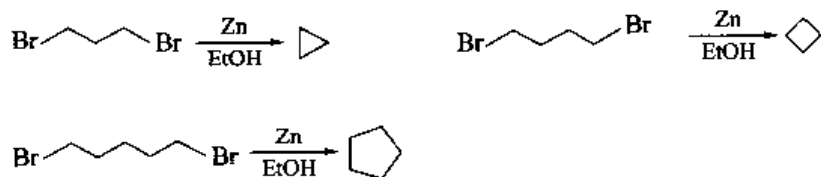
见“专题总结Ⅲ”中“四、重要的有机合成反应”。

三、环的形成和变化

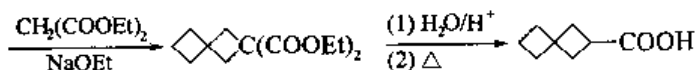
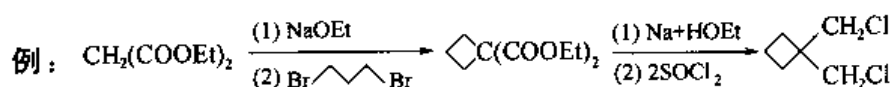
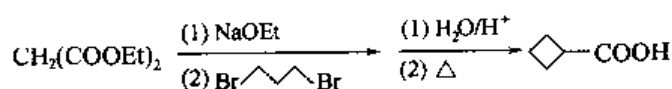
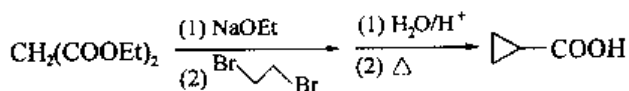
1. 卤代酮、腈、酯的分子内 $\text{S}_{\text{N}}2$ 反应



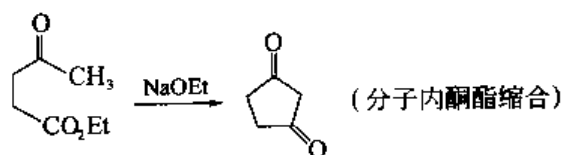
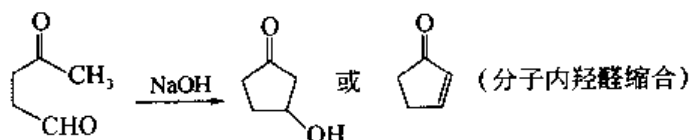
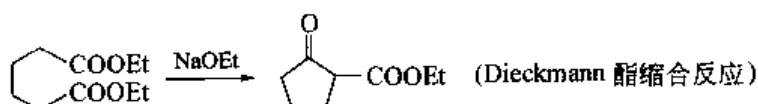
2. 二卤代物脱卤



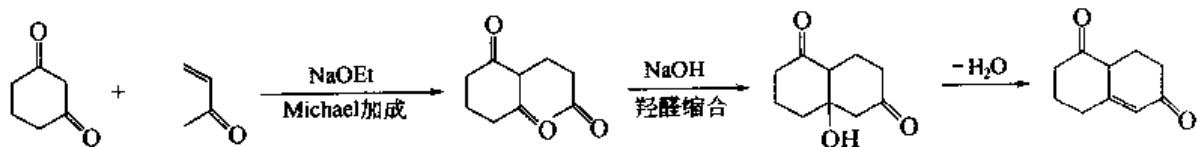
3. 丙二酸酯法



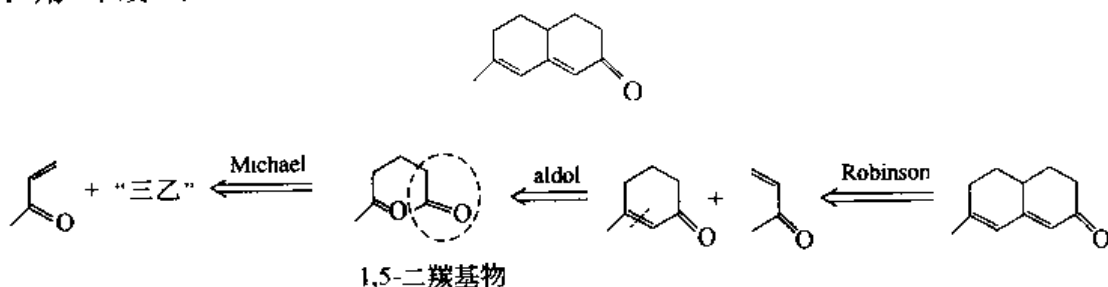
4. 分子内缩合

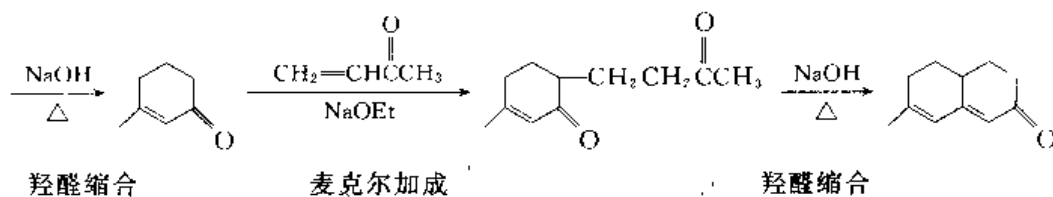
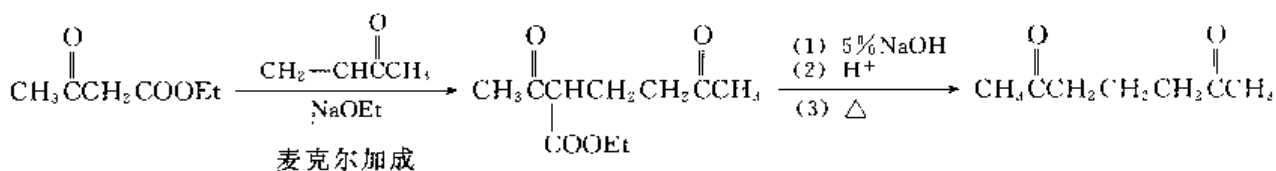


5. Robinson 并环反应

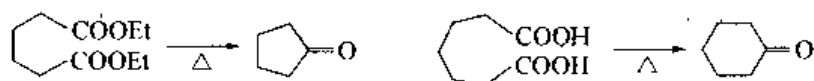


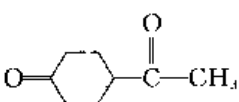
例：用 C_4 或 C_5 以下有机物制备

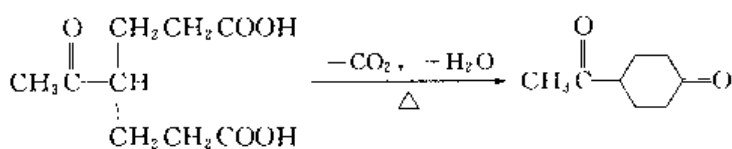
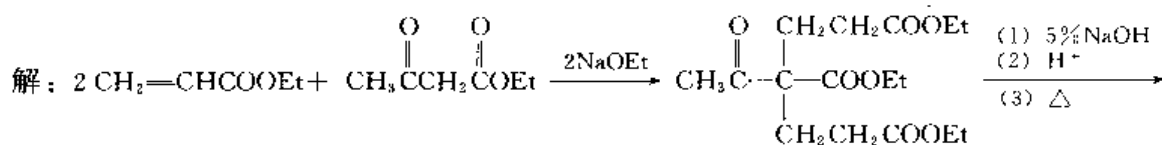
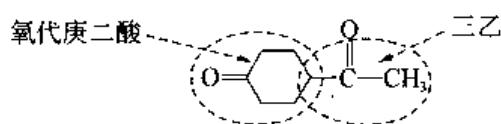




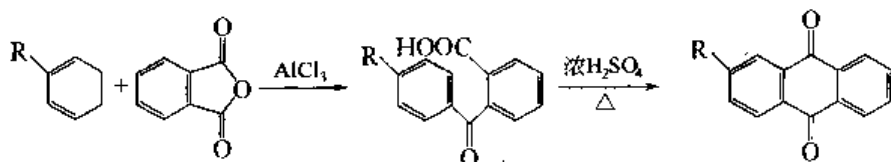
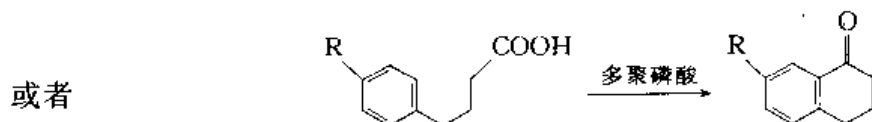
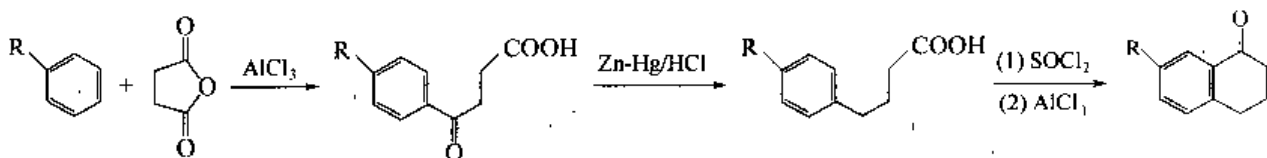
6. 己二酸、庚二酸脱羧脱水



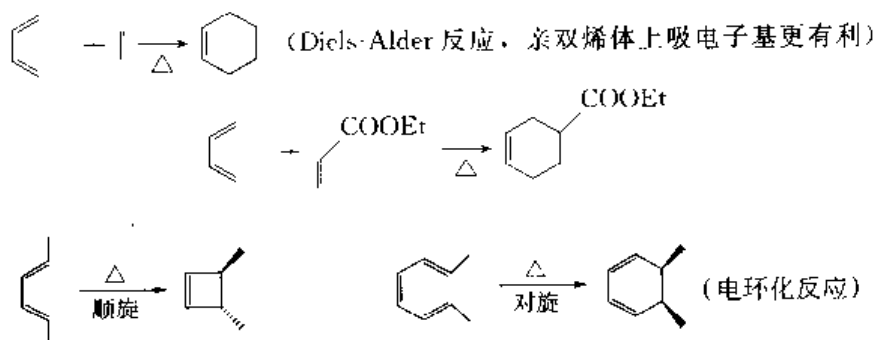
例：用“三乙”、丙烯酸乙酯合成 



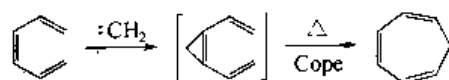
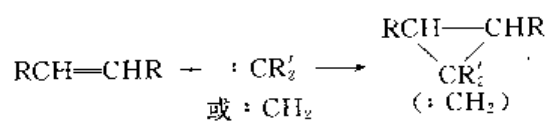
7. 芳烃与环酐的 Friedel-Crafts 反应



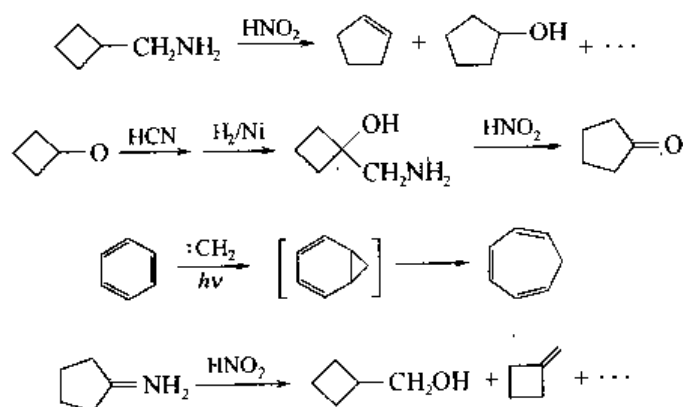
8. 周环反应



9. 卡宾法



10. 环的扩大与缩小



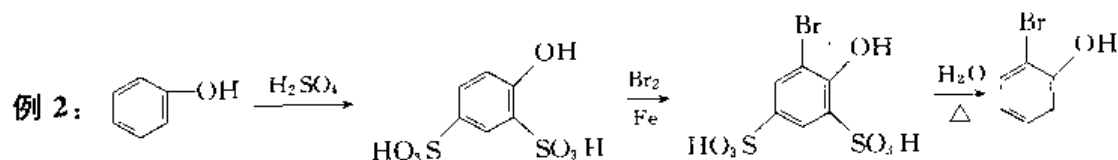
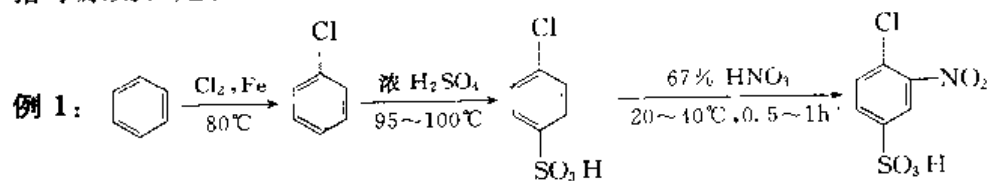
四、重要的有机合成反应

1. 格氏反应——制醇或者多一个碳的羧酸

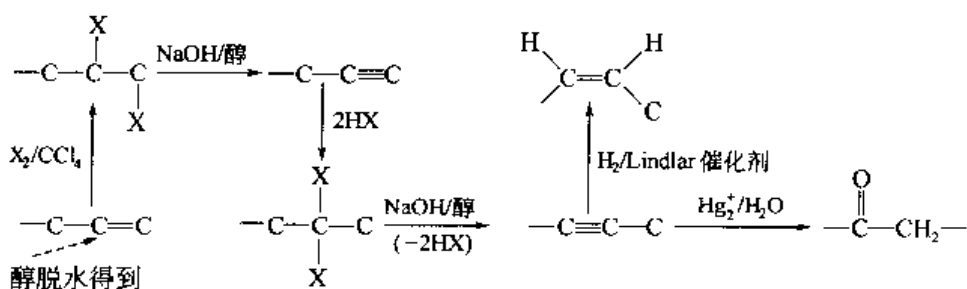
见“专题总结Ⅲ”中“二、2. (1)”。

2. 苯环上亲电取代反应——制一系列芳香族化合物

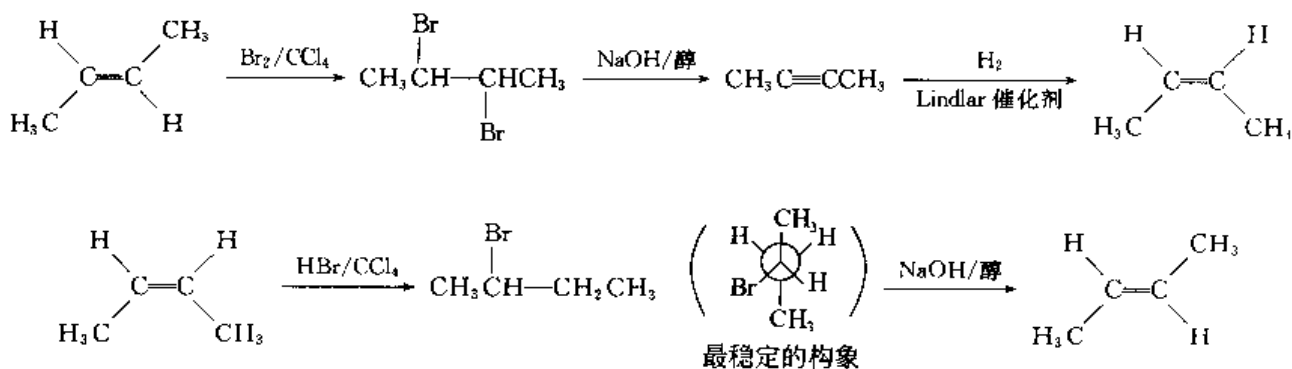
指导原则：定位规律！



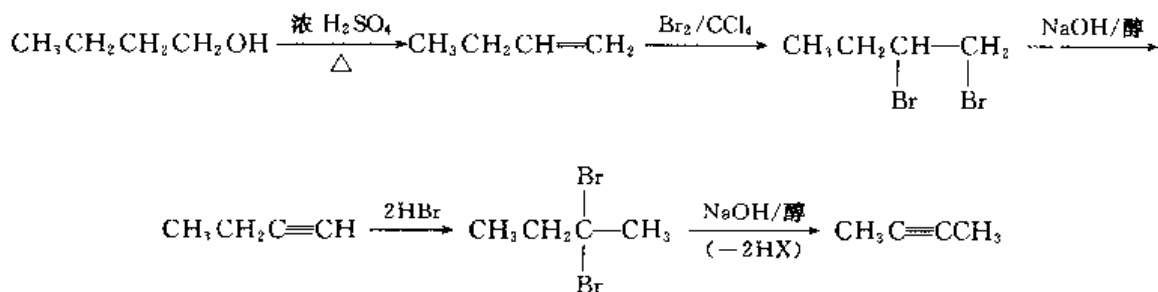
3. C=C 与 C≡C 的转化



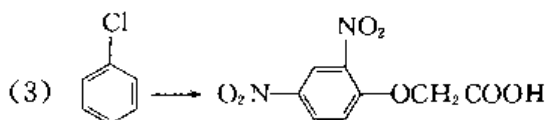
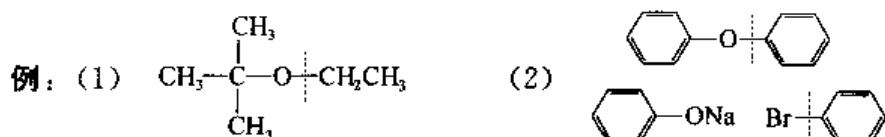
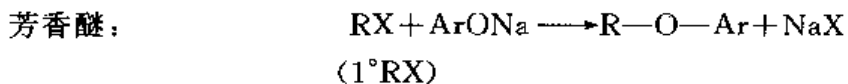
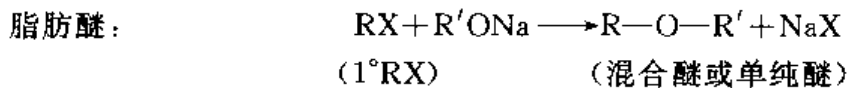
例 1: 顺-2-丁烯与反-2-丁烯的相互转化。



例 2: 由正丁醇制备 2-丁炔。



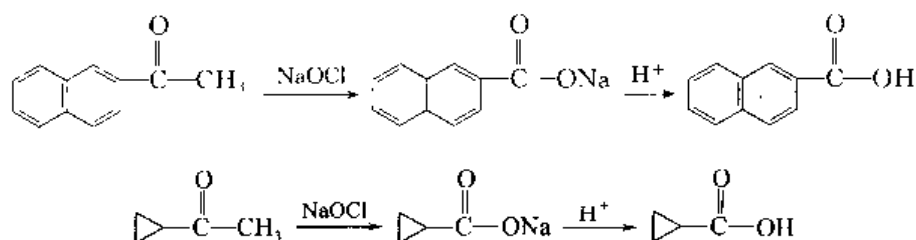
4. Williamson 法制醚



9. 异丙苯氧化法制酚

见“专题总结 I”中“七、1. (2)”。

10. 卤仿反应——制少一个碳的羧酸



11. Rosenmund 还原——由酰氯制醛

见“专题总结 I”中“五、4. (3)”。

12. 由 RX 制酸

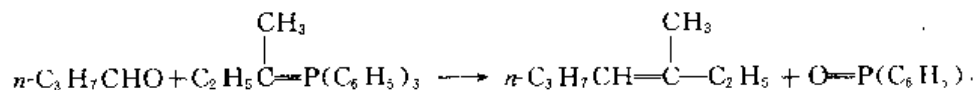
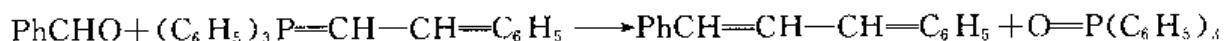
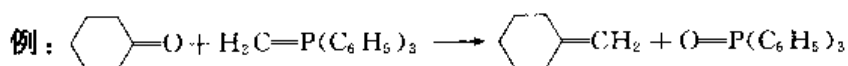
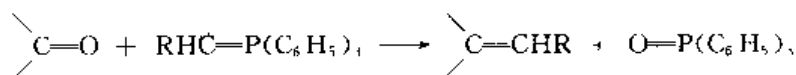
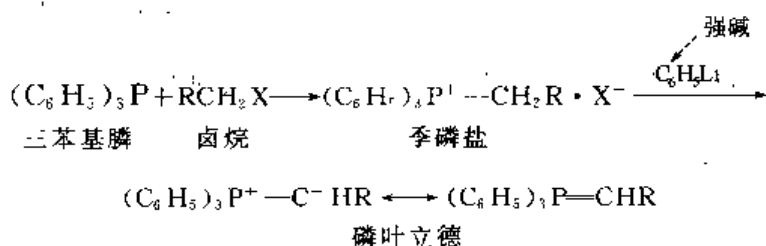
见“专题总结 III”中“二、1. (1)”。

13. Mannich 反应 (胺甲基化反应)——间接制备 α, β -不饱和醛、酮

见“专题总结 II”中“12.”。

14. Wittig 反应——制备烯烃

醛、酮与磷叶立德反应，制备烯烃的反应：



15. Darzen 反应——在羰基碳上引入醛基

见“专题总结 II”中“10. Darzen 反应”。

16. Reimer-Tiemann 反应——在酚羟基的邻位上引入醛基

见“专题总结 II”中“14. Reimer-Tiemann 反应”。

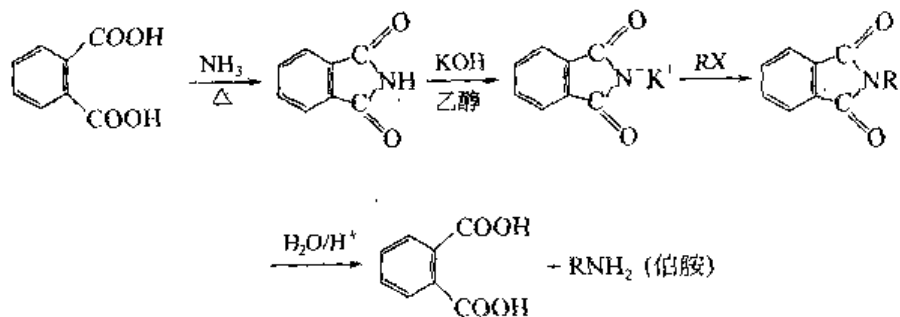
17. Perkin 反应制——由芳醛制 α, β -不饱和酸

见“专题总结 II”中“5. Perkin 反应”。

18. Reformasky 反应——制 β -羟基酸 (酯)

见“专题总结 II”中“11. Reformasky 反应”。

19. Gabriel 法制伯胺



20. Hofmann 降解制伯胺

见“专题总结 I”中“七、2. 碱性条件下发生的重排”。

21. 由三乙制甲基酮

见“专题总结 III”中“二、1. (3)”。

22. 由丙二制取代乙酸

见“专题总结 III”中“二、1. (4)”。

23. Beayer-Villiger 氧化——由酮制备酯

有机过酸与酮反应生成酯。因反应过程中碳架发生变化，又称为 Beayer-Villiger 重排。详见“专题总结 I”中“七、1. 酸性条件下发生的重排”。

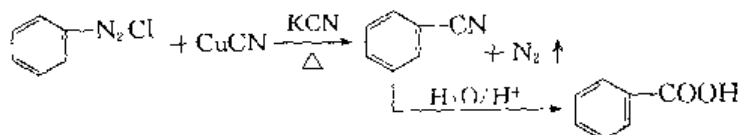
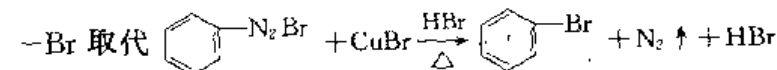
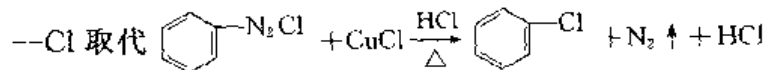
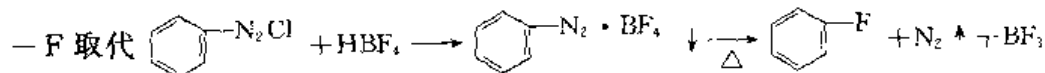
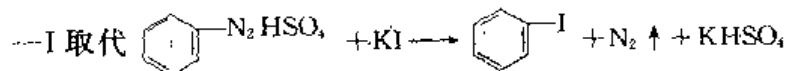
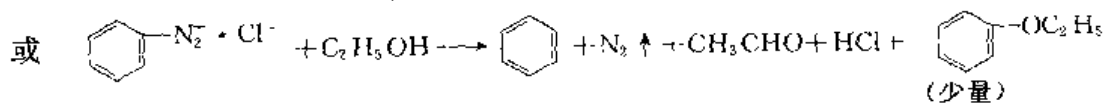
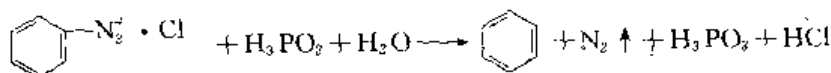
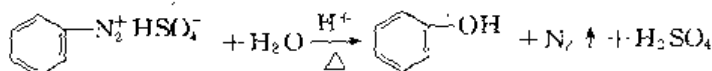
24. 羰基化合物经烯胺的酰基化或烃基化——在羰基的 α -位上引入酰基或烃基

见“专题总结 II”中“13. 羰基化合物经烯胺的酰基化或烃基化”。

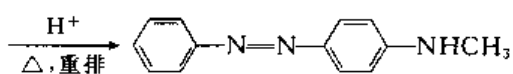
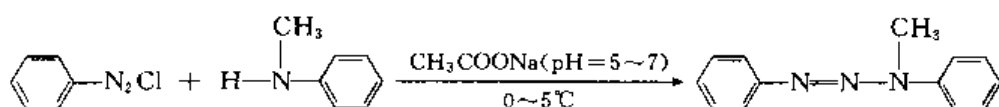
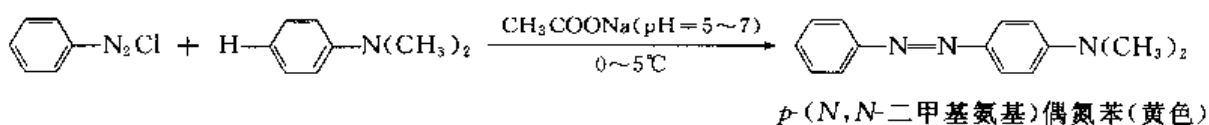
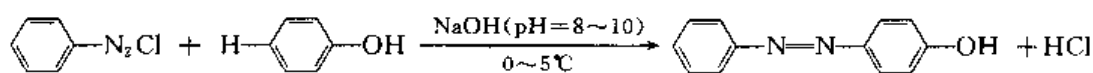
25. Michel 加成——制 1,5-二羰基化合物

见“专题总结 II”中“9. Michel 加成”。

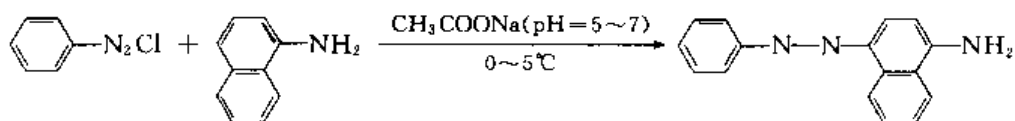
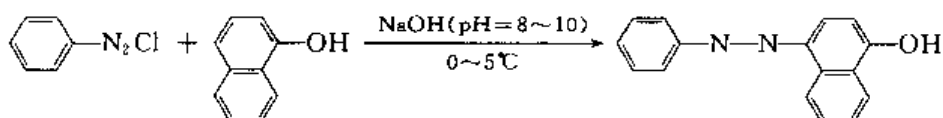
26. 重氮盐的放氮反应——制一系列芳香族化合物



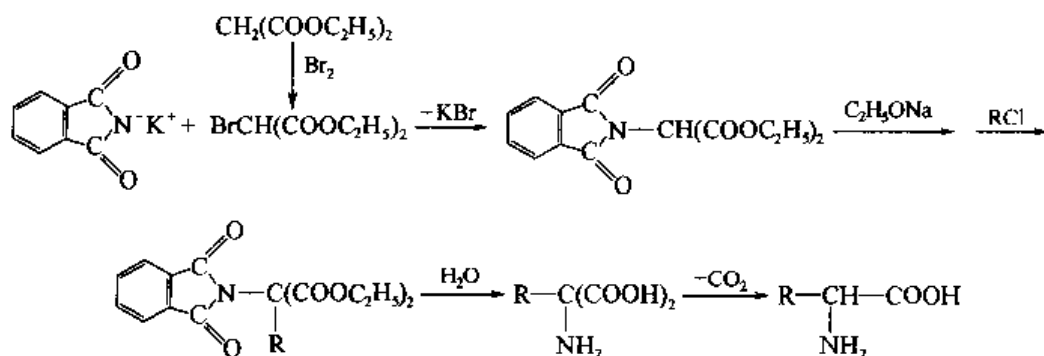
27. 重氮盐的偶联反应——制一系列有颜色的化合物



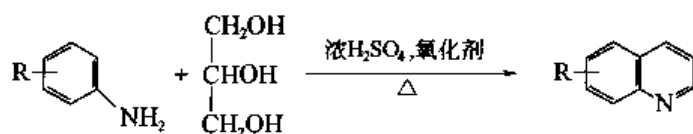
对(N-甲基氨基)偶氮苯



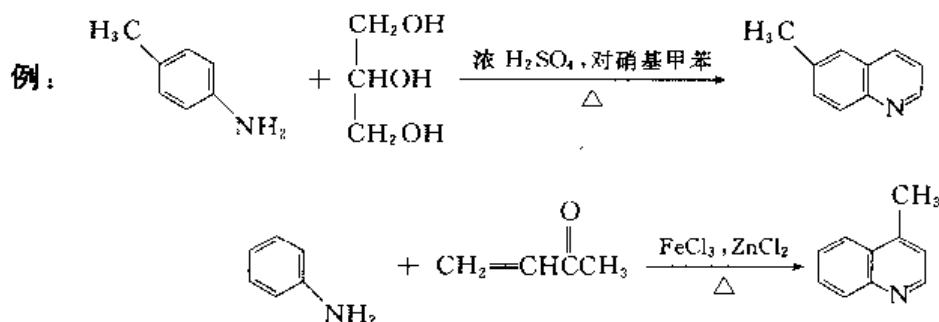
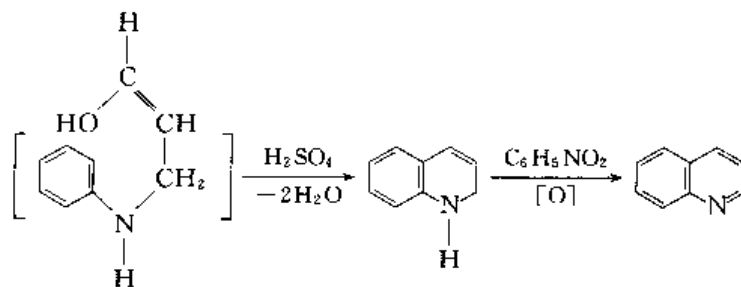
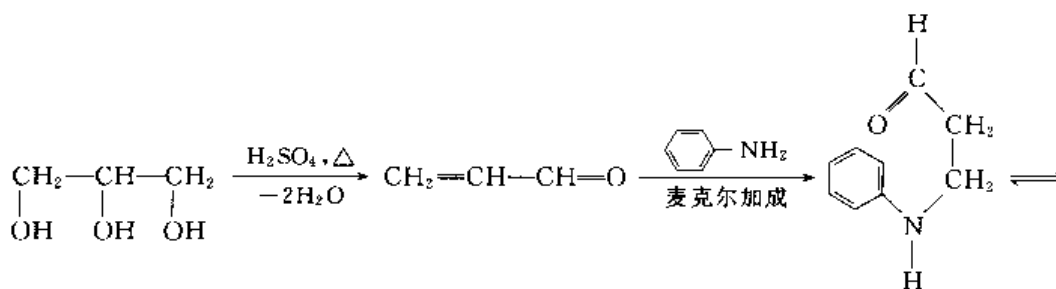
28. 氨基酸的特殊制法——丙二合成法与 Gabriel 合成法联用



29. Skraup 合成法——制喹啉类化合物



反应历程如下所示 (以喹啉的制备为例)。

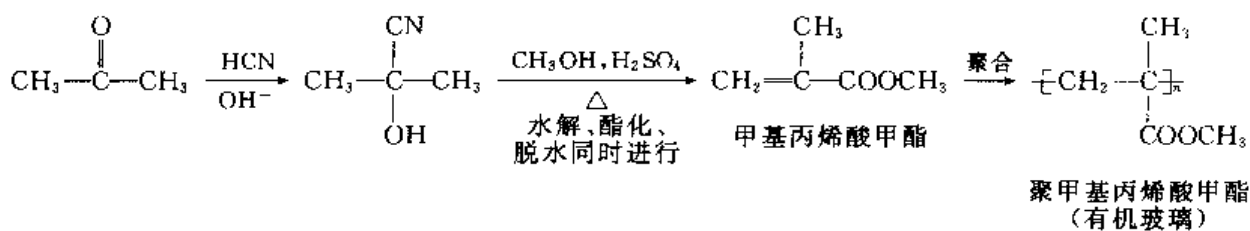


五、重要的工业合成反应

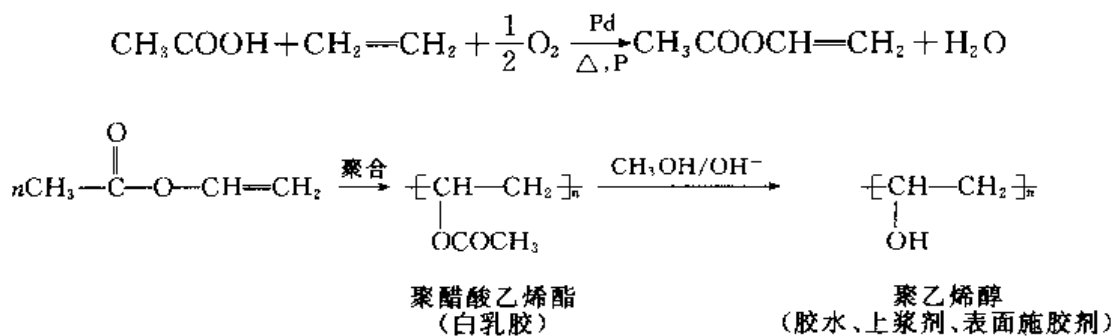
1. 异丙苯氧化法制苯酚

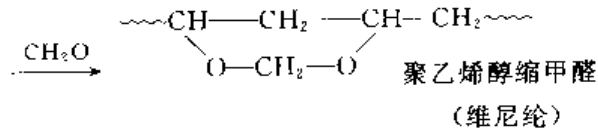
见“专题总结 I”中“七、1. (2)”。

2. 甲基丙烯酸甲酯的制备

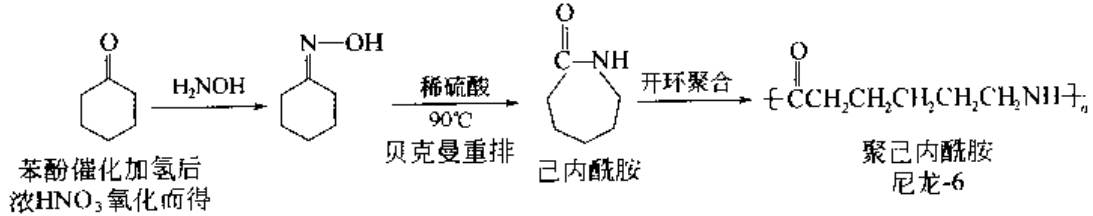


3. 乙酸乙烯酯的制备

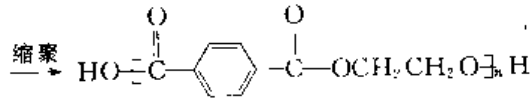
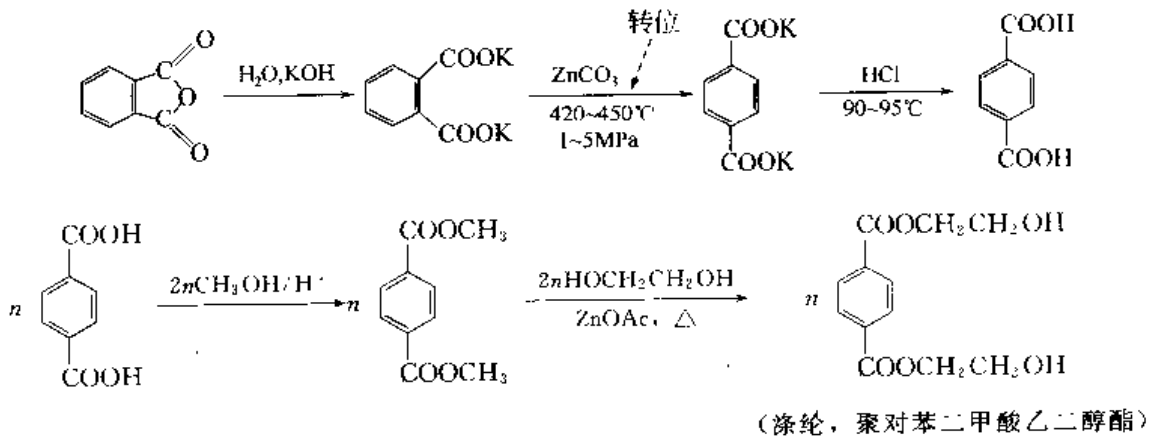




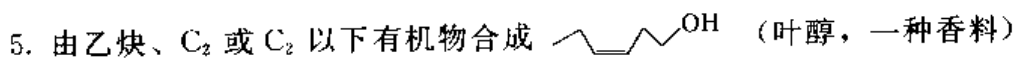
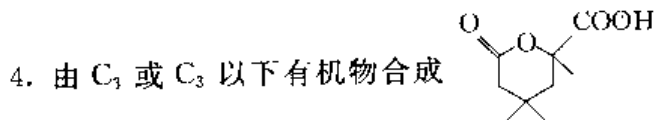
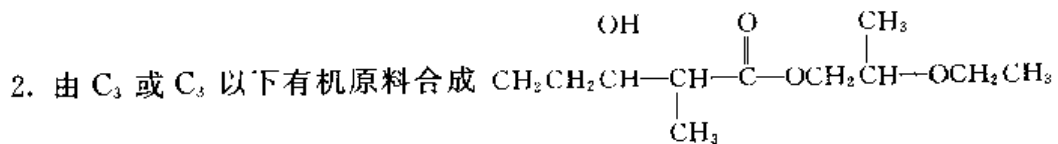
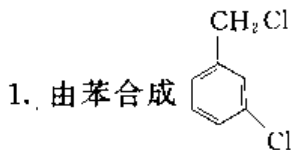
4. 己内酰胺的制备


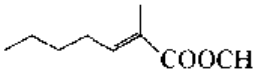


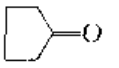
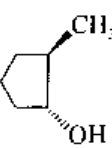
5. 聚对苯二甲酸乙二醇酯的制备

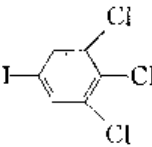


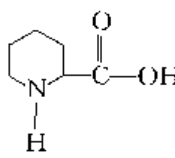
合成练习题 (I)

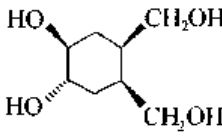


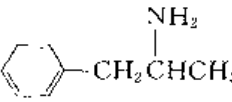
6. 由  Br 为有机原料合成 

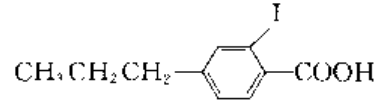
7. 由  合成 

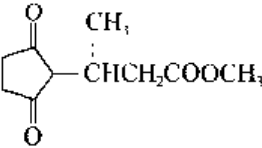
8. 由苯合成 

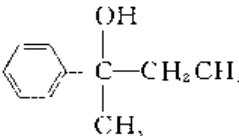
9. 由邻苯二甲酸酐、丙二酸二乙酯合成 

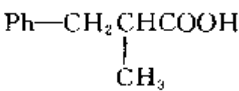
10. 由 C_1 或 C_2 以下有机物合成 

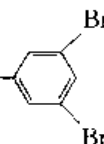
11. 由苯甲醛、 C_2 或 C_3 以下有机物合成 

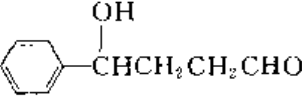
12. 由苯、 C_2 或 C_3 以下有机物合成 

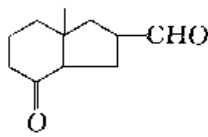
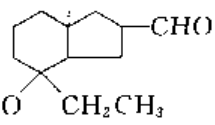
13. 由 C_3 或 C_4 以下有机物合成 

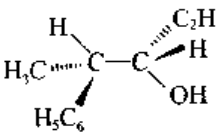
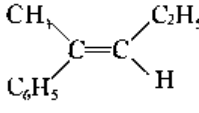
14. 由苯、 C_2 或 C_3 以下有机物合成 

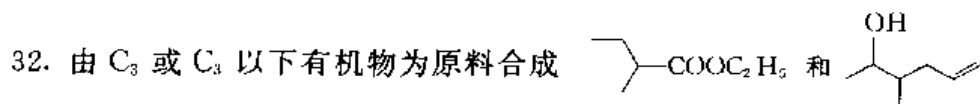
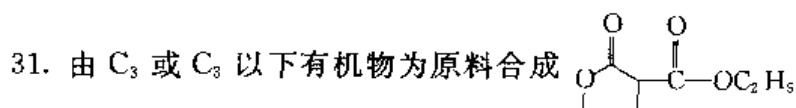
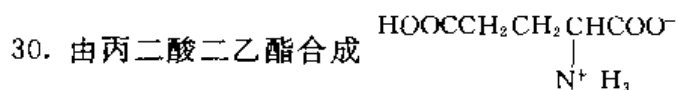
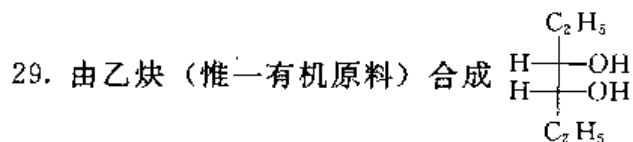
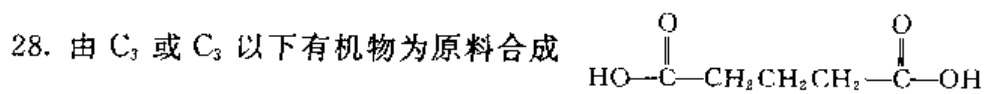
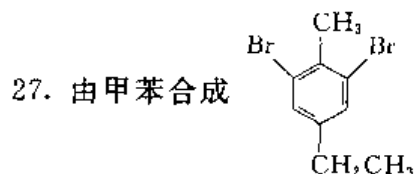
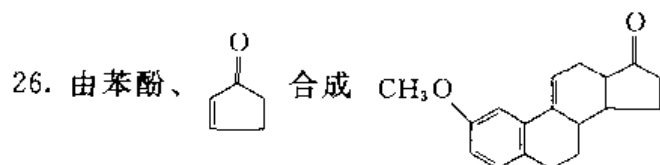
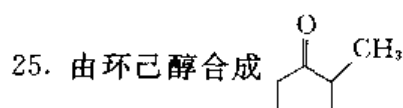
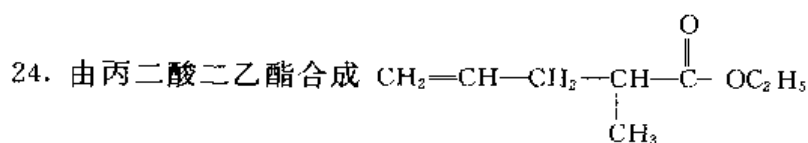
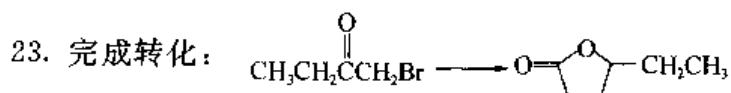
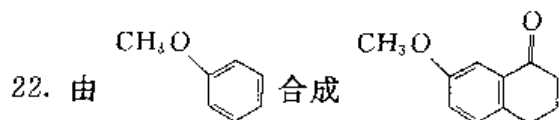
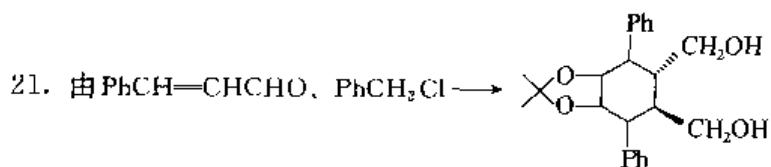
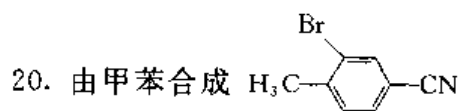
15. 由苯、 C_2 或 C_3 以下有机物合成 

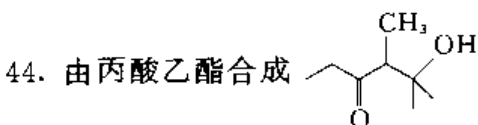
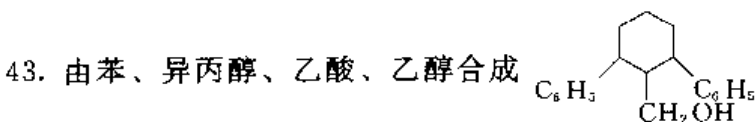
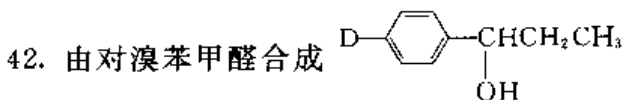
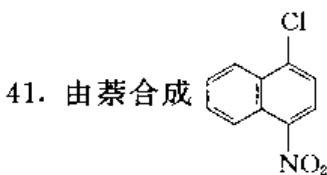
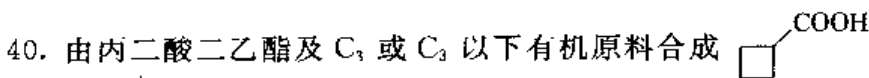
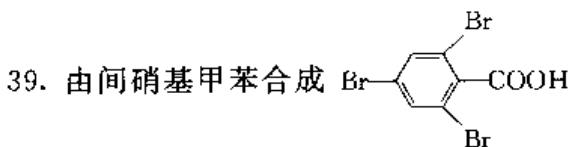
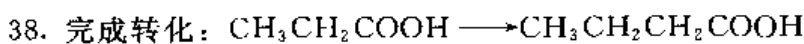
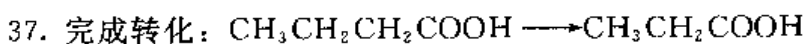
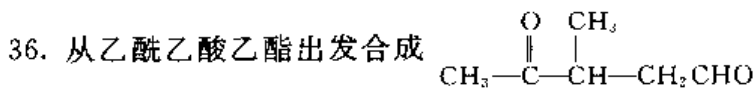
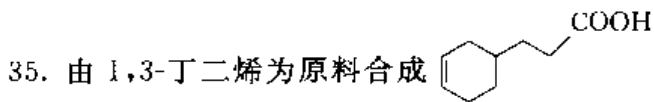
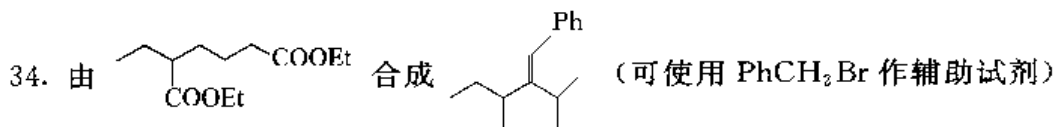
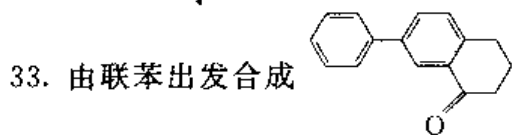
16. 由苯或甲苯、 C_2 或 C_3 以下有机物合成 

17. 完成转化: $\text{ClCH}_2\text{CH}_2\text{CHO} \rightarrow$ 

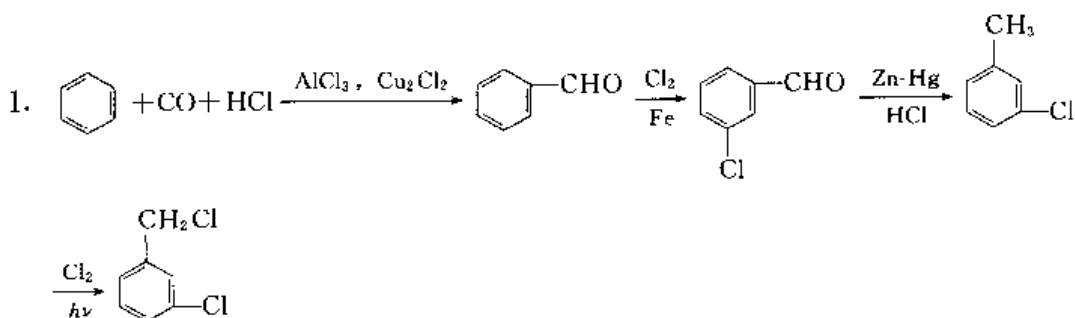
18. 完成转化:  \rightarrow 

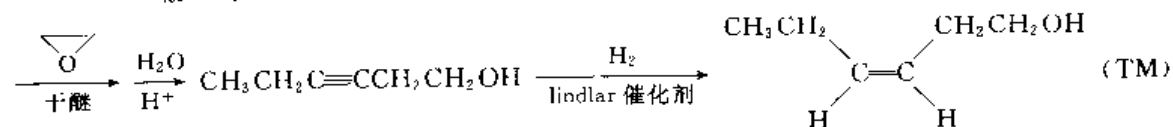
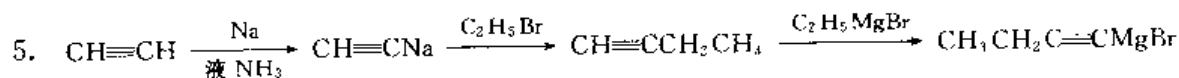
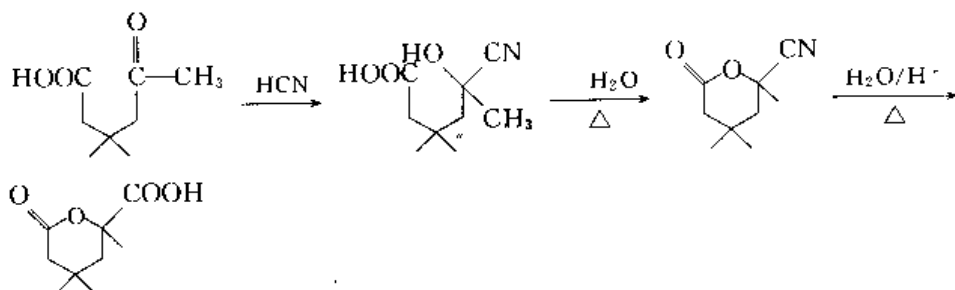
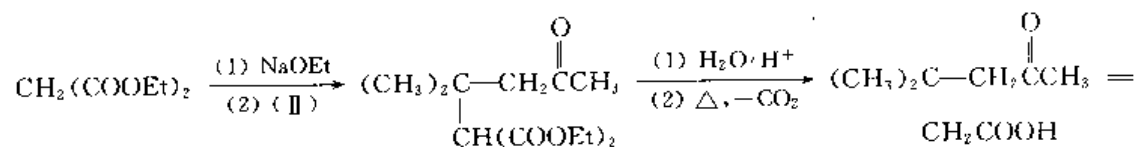
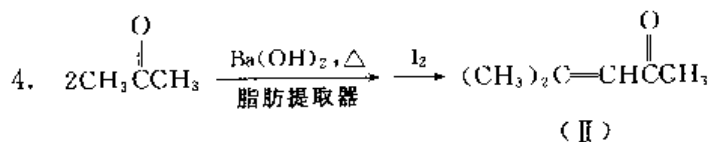
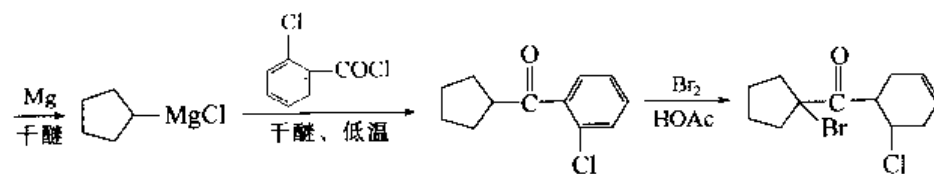
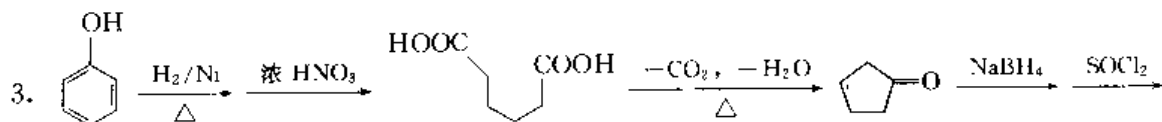
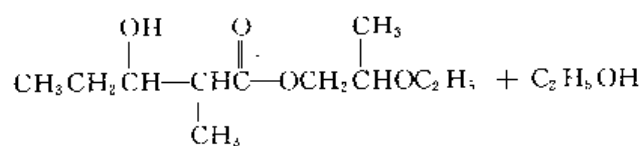
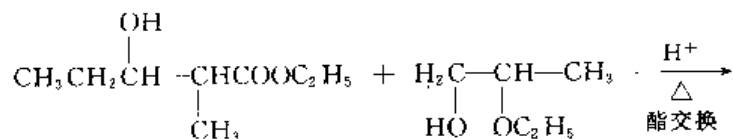
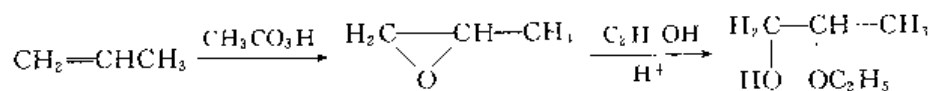
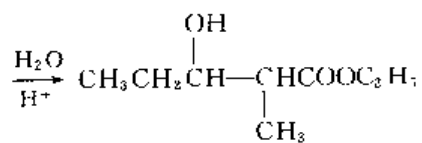
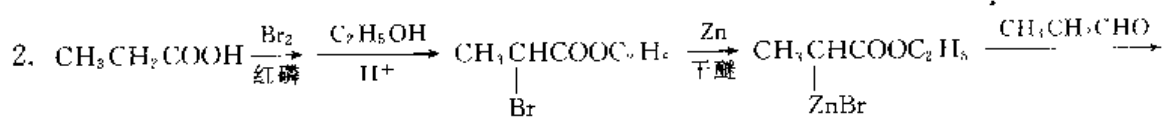
19. 完成转化:  \rightarrow 

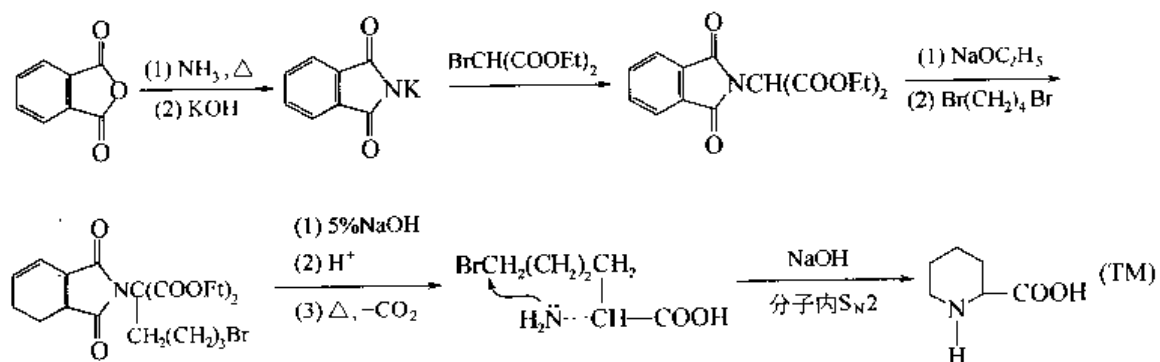
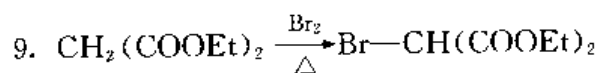
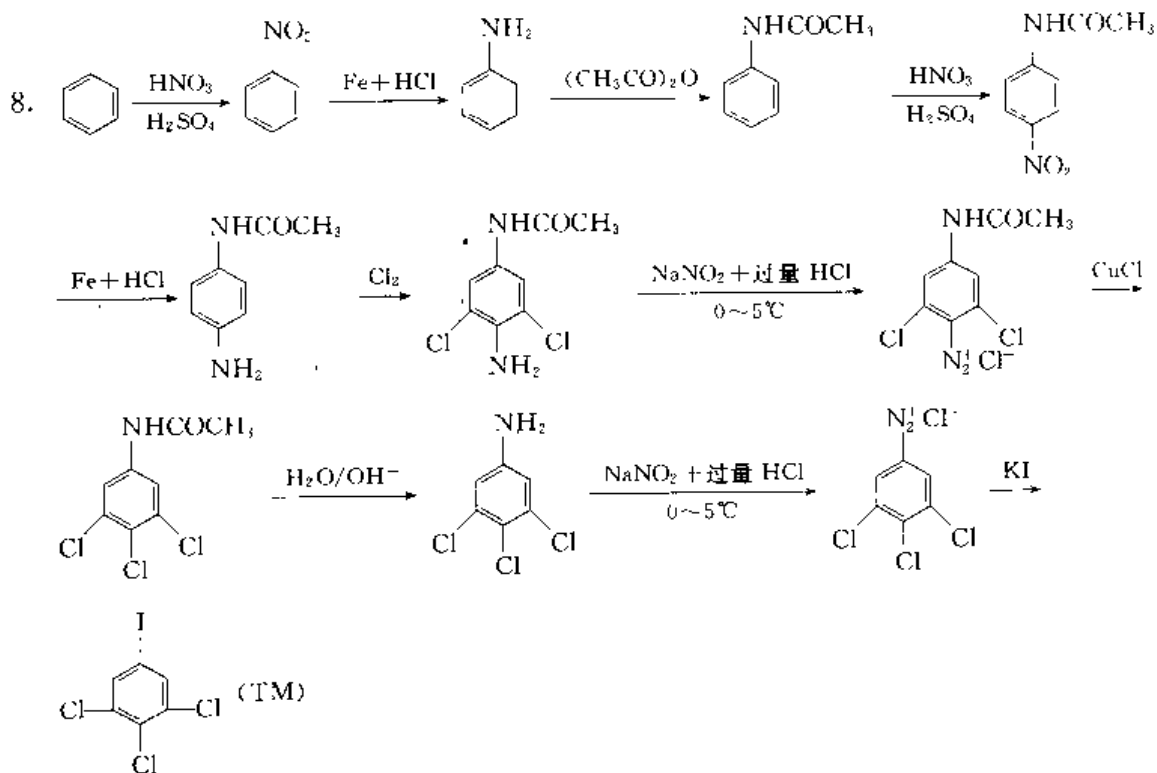
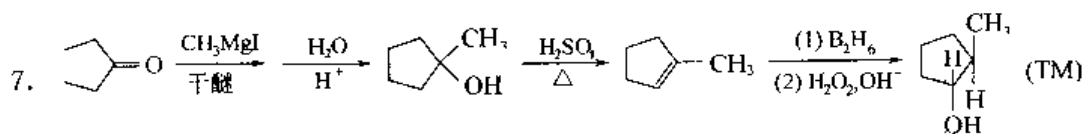
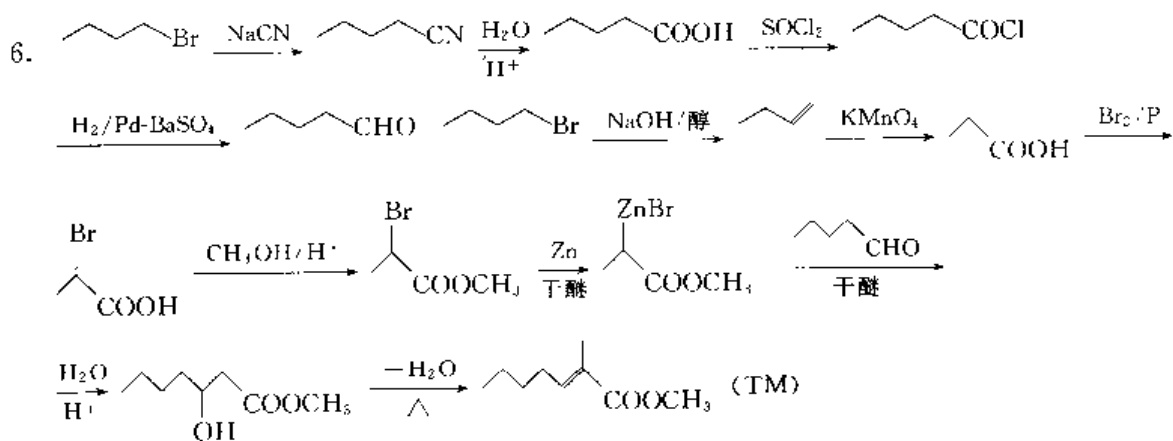


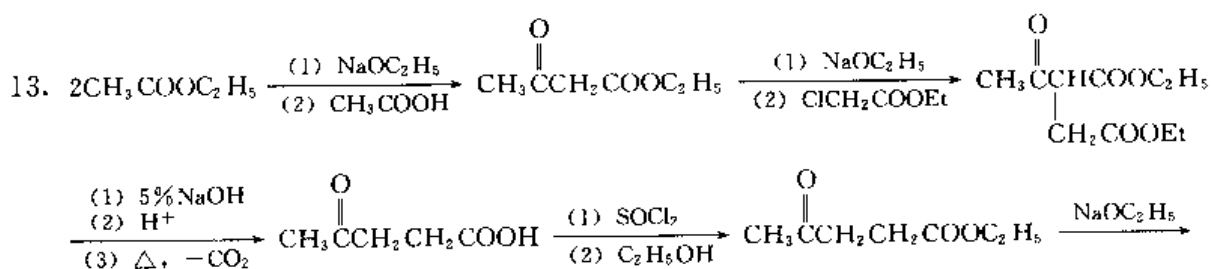
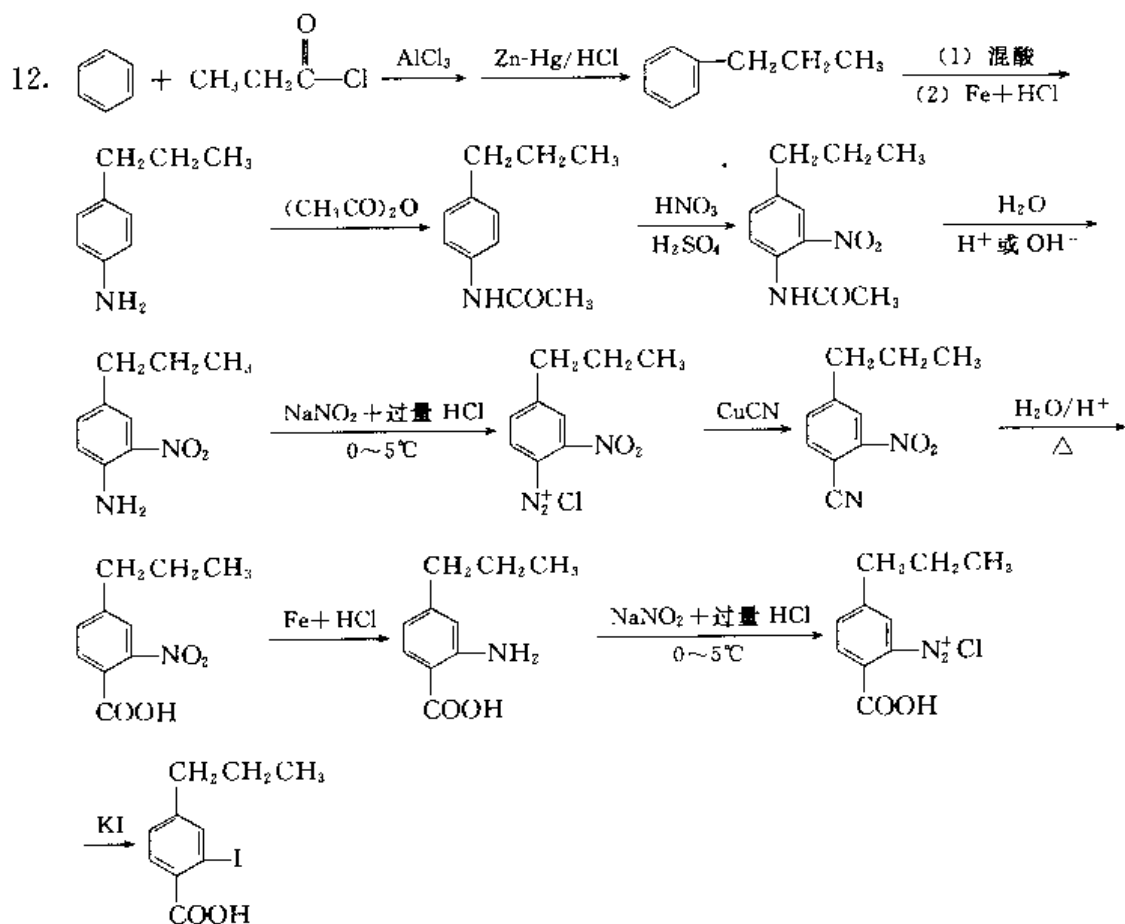
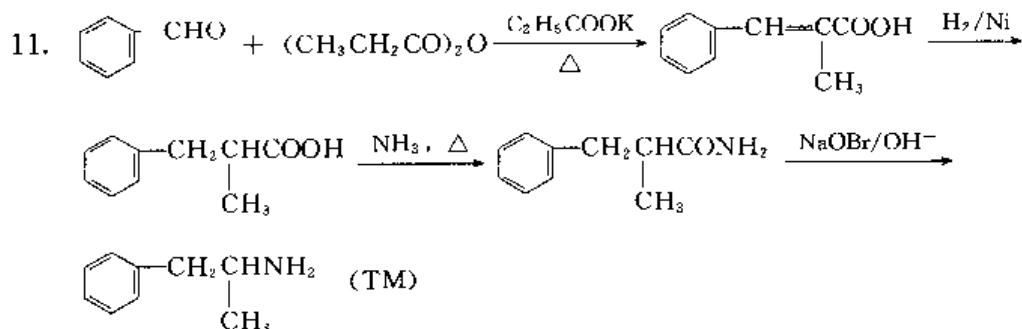
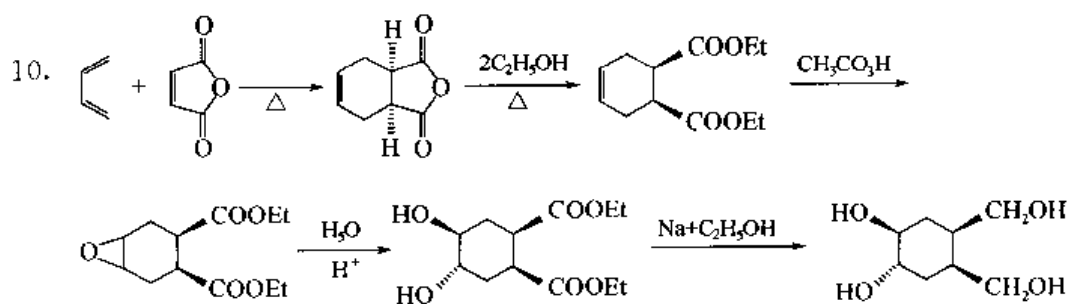


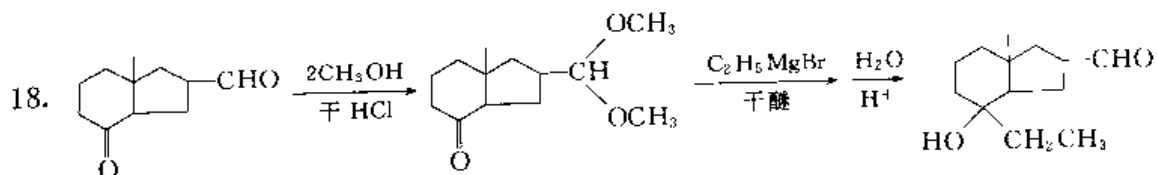
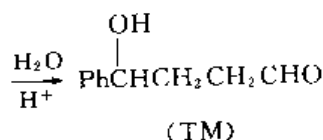
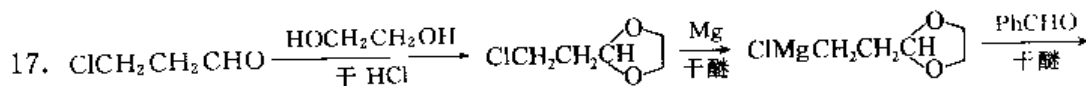
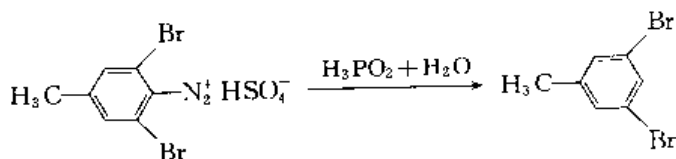
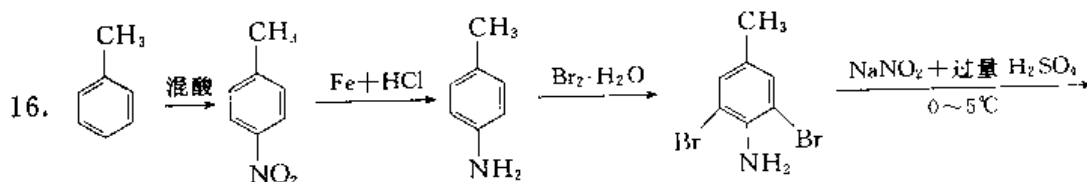
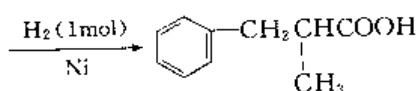
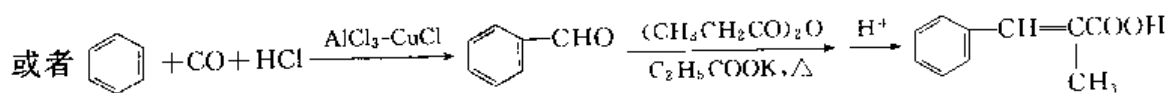
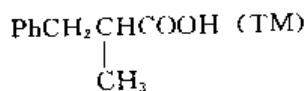
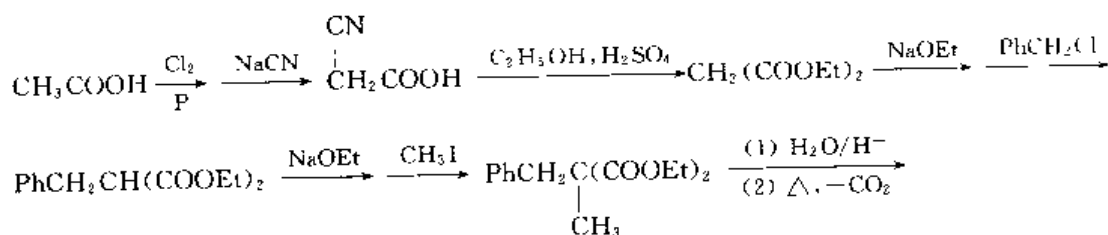
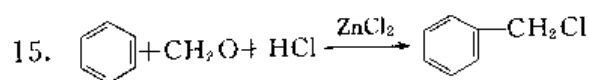
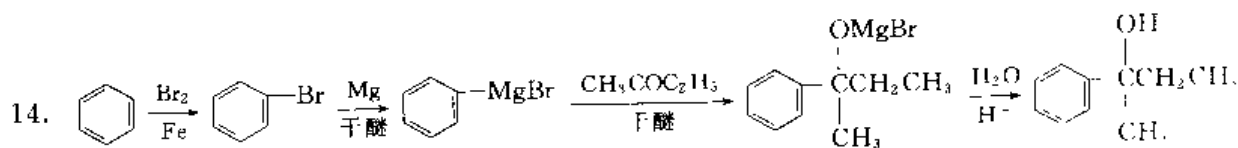
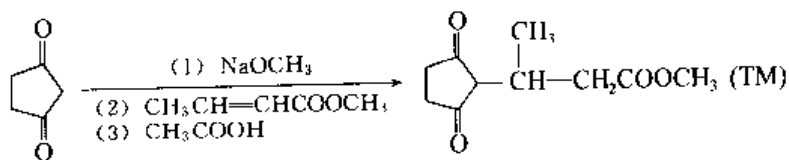
参 考 答 案

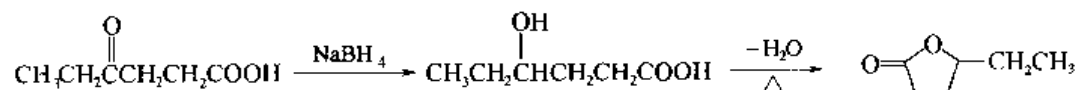
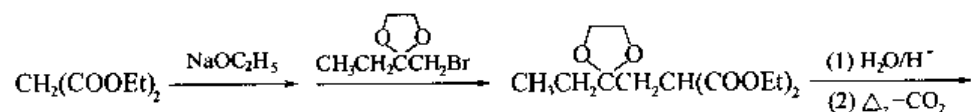
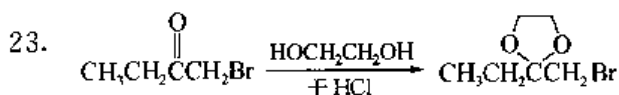
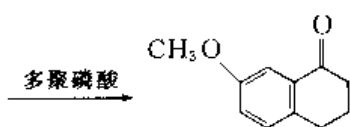
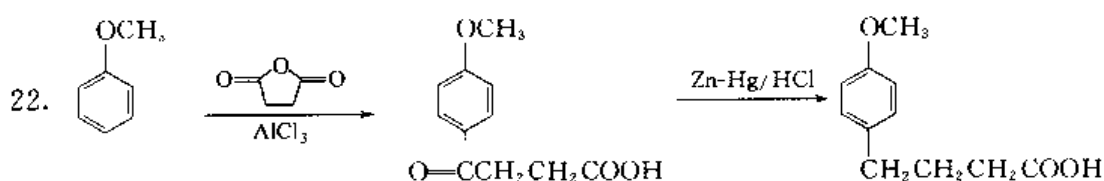
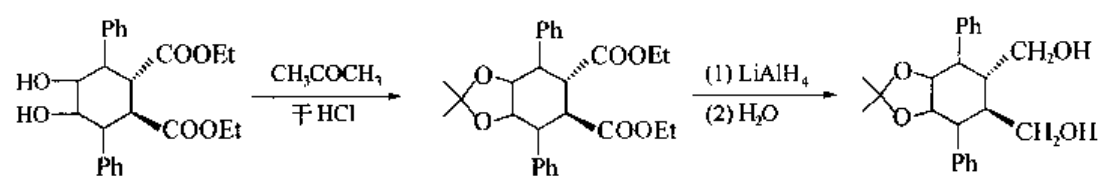
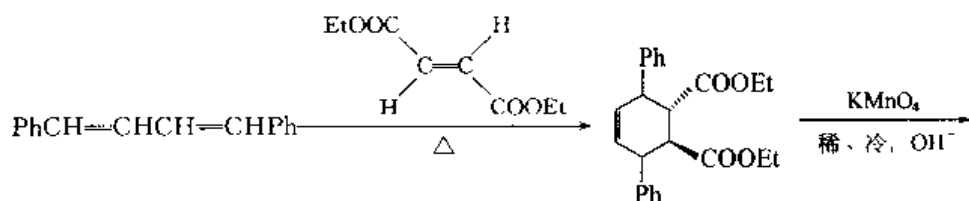
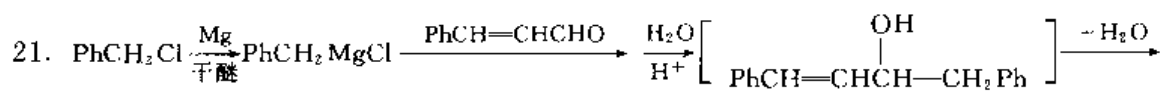
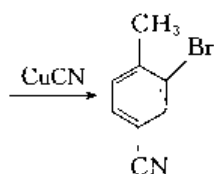
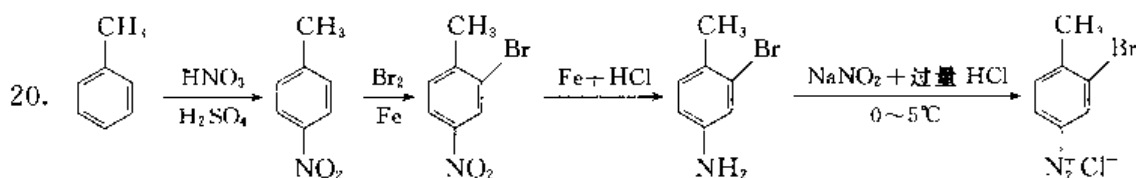
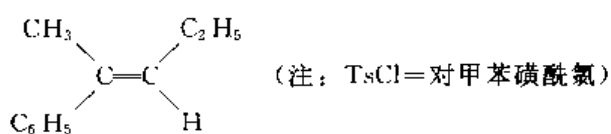
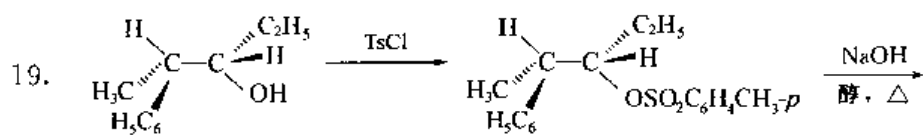


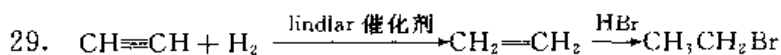
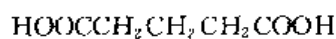
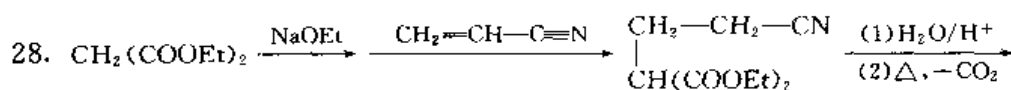
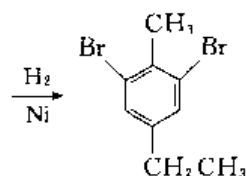
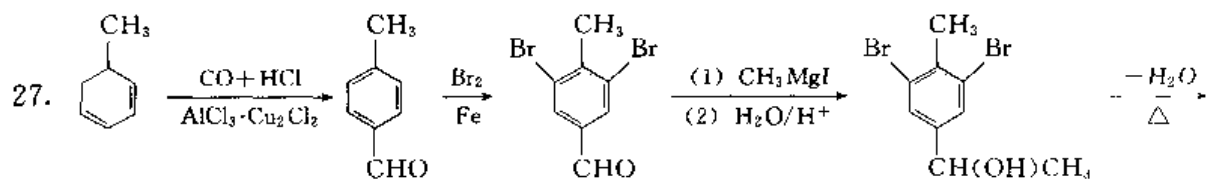
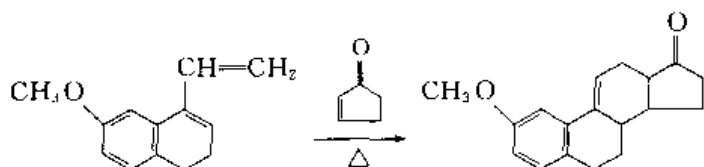
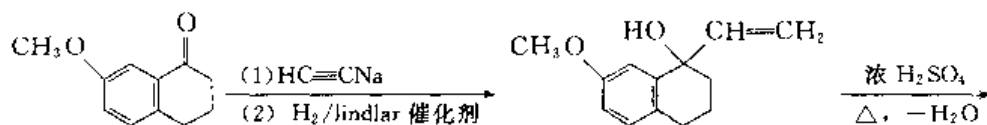
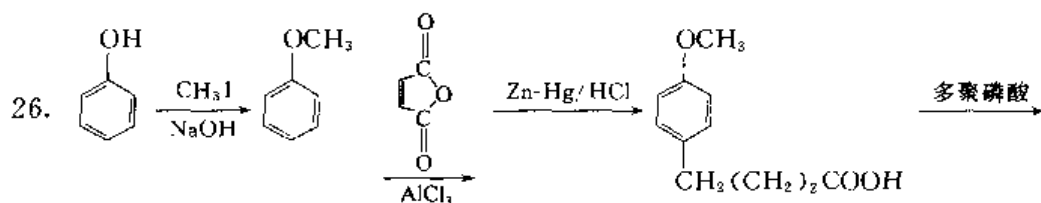
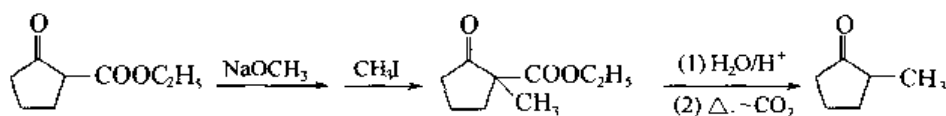
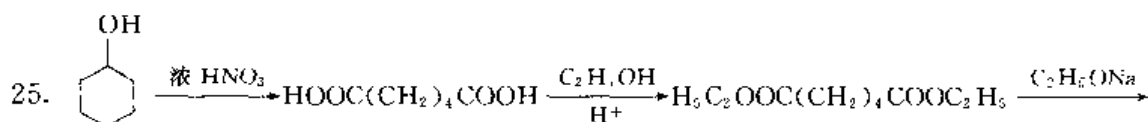
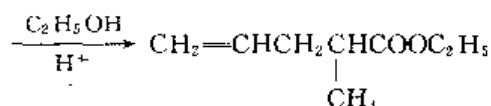
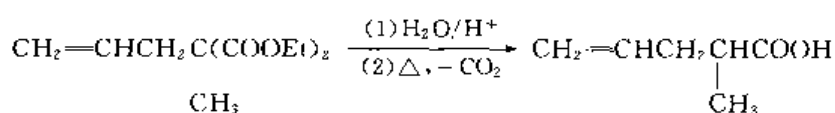
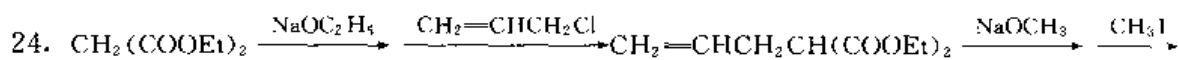


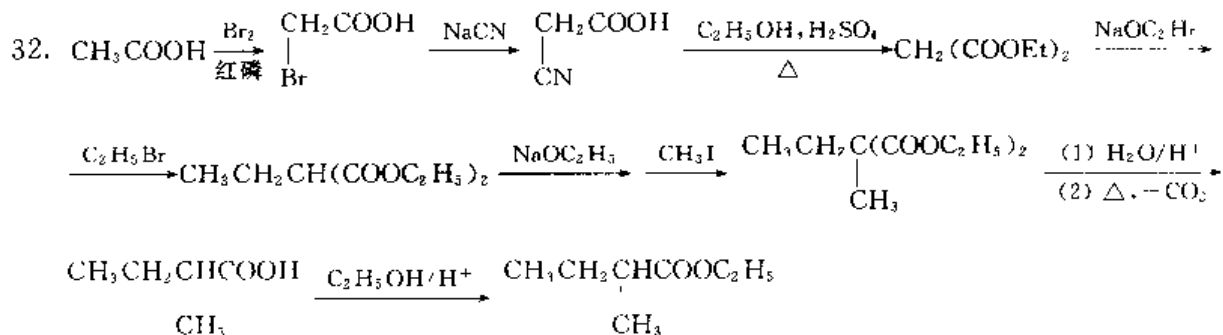
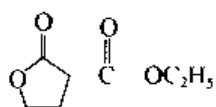
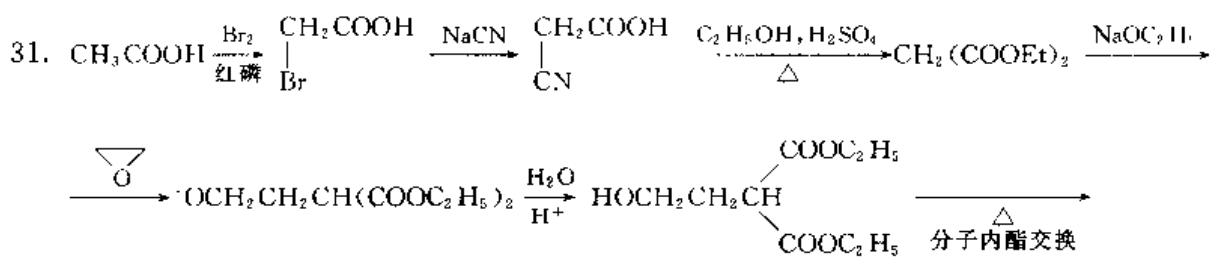
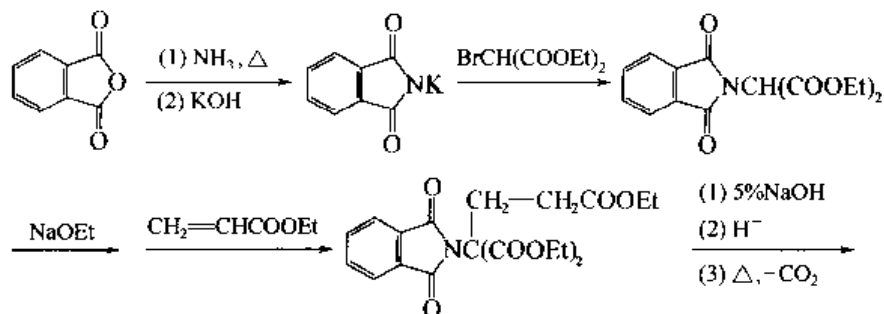
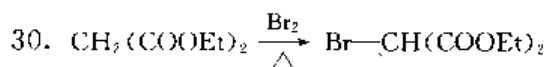
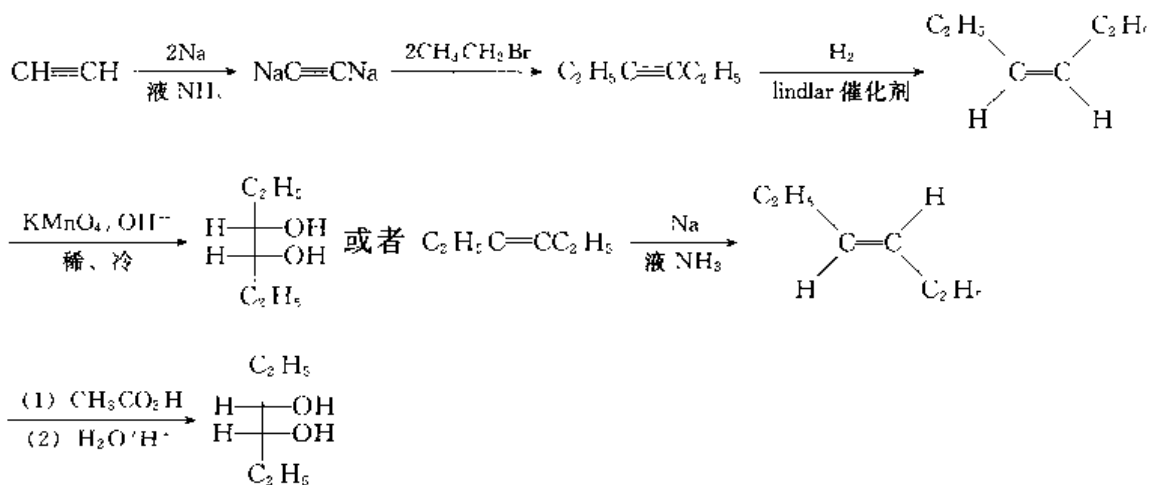


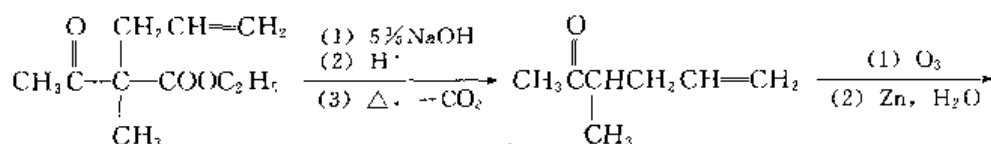
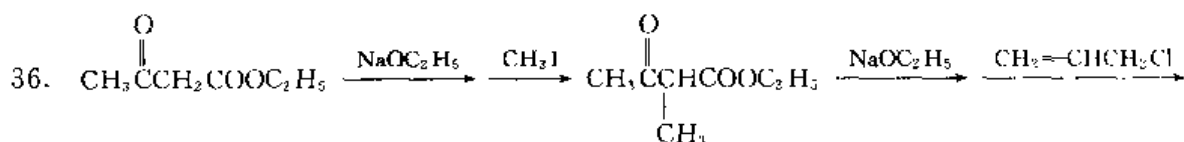
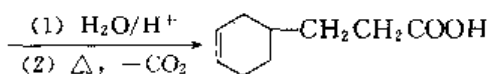
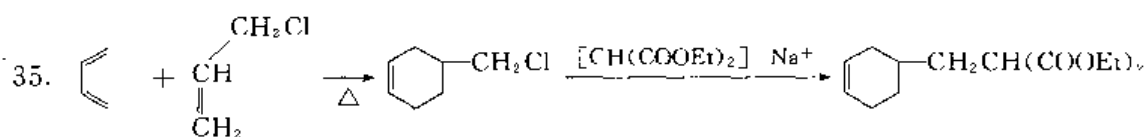
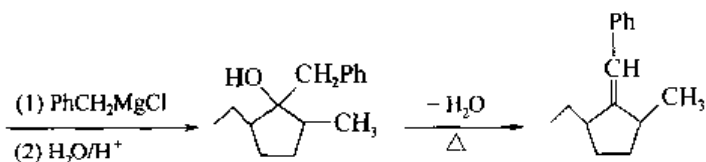
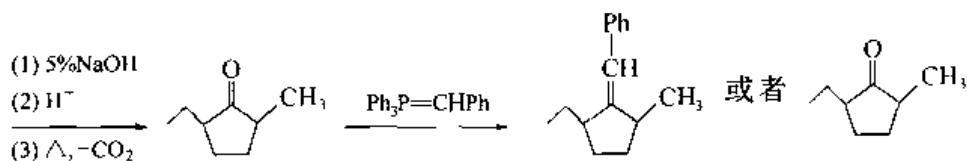
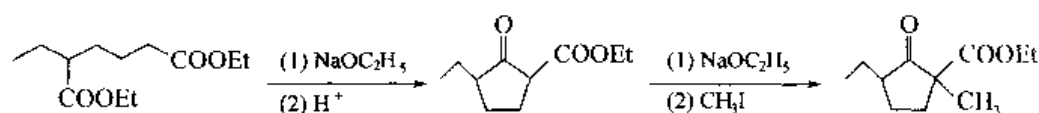
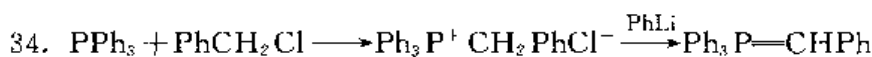
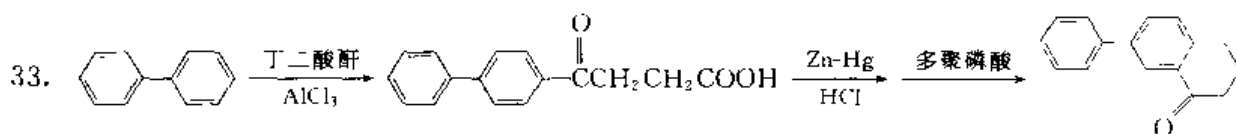
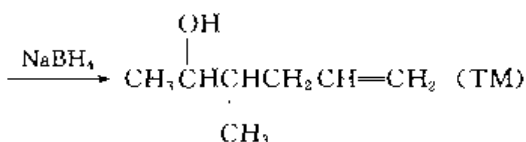
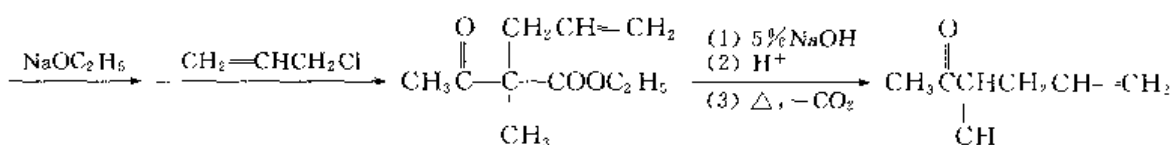
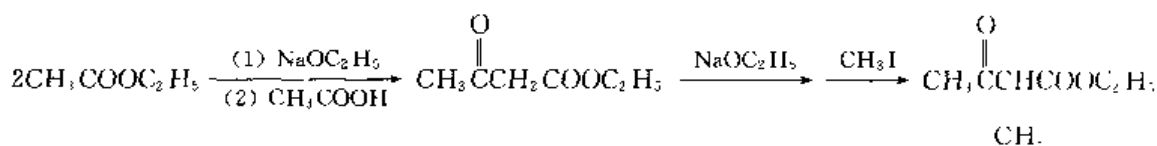


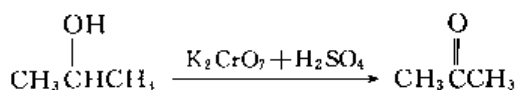
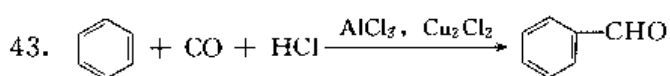
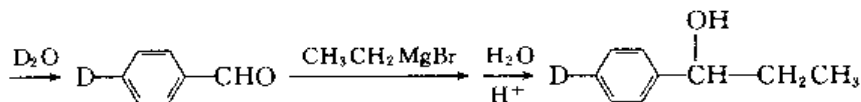
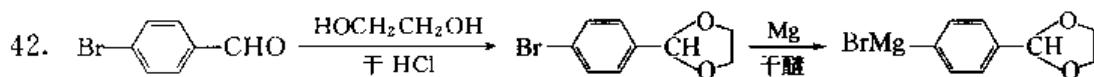
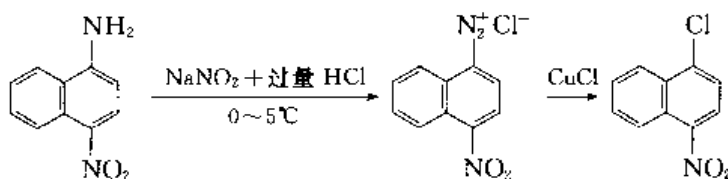
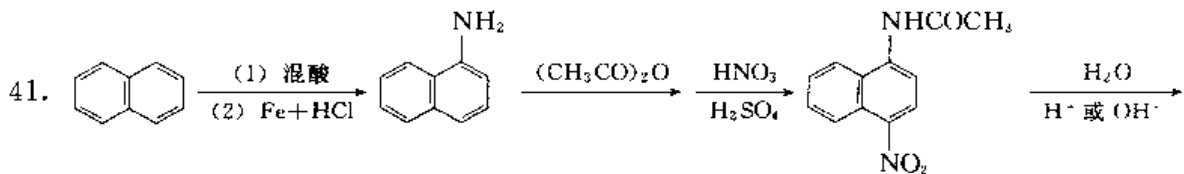
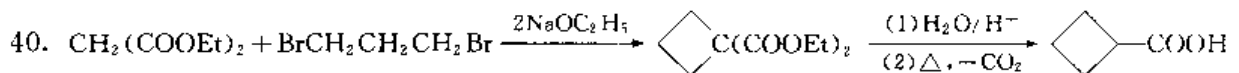
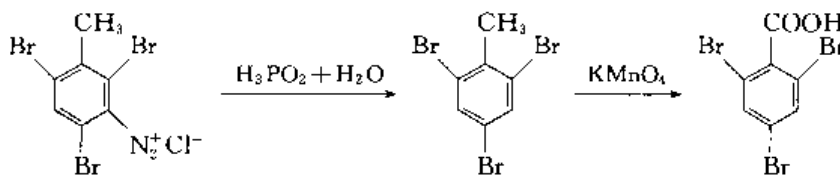
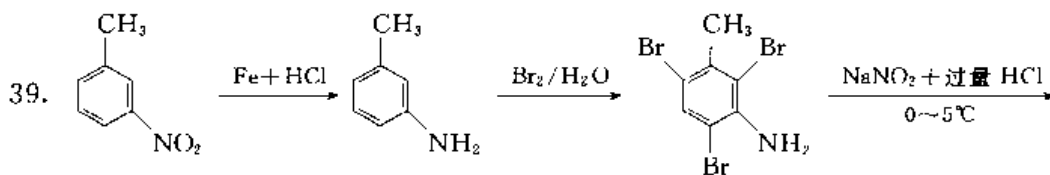
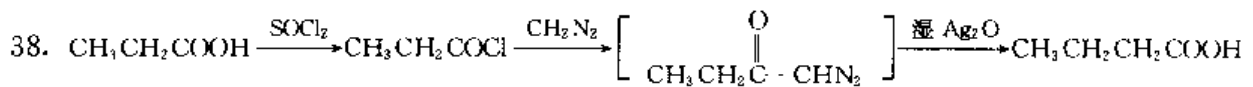
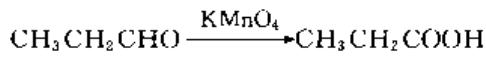
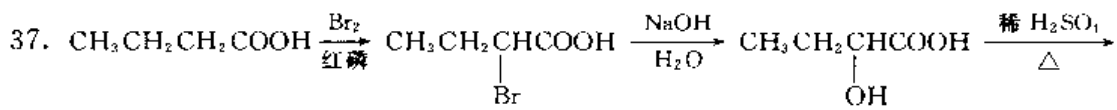
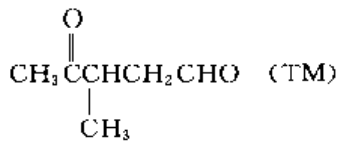


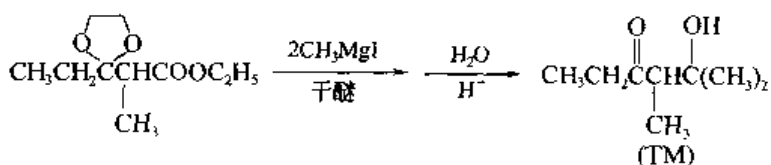
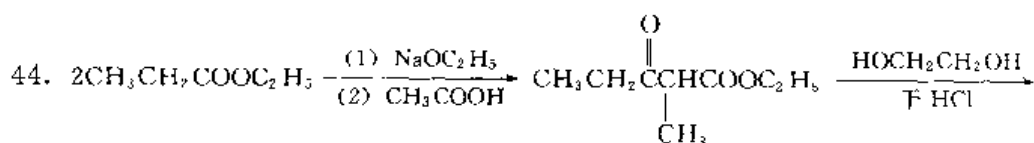
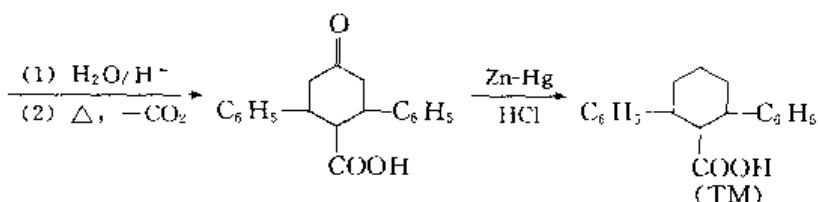
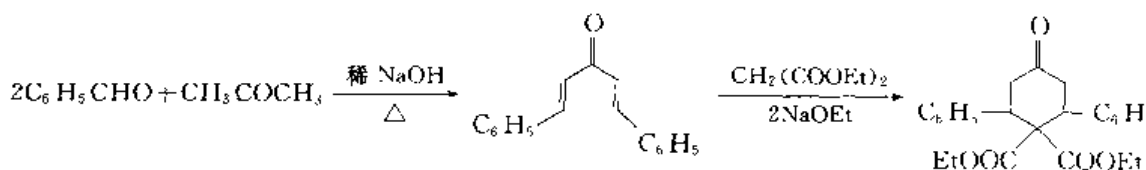
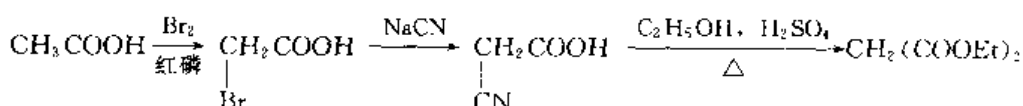




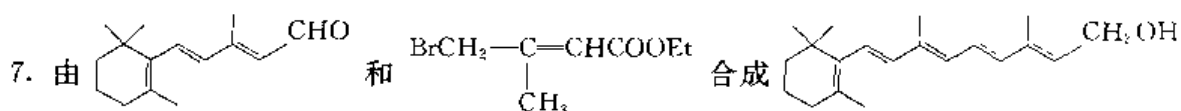
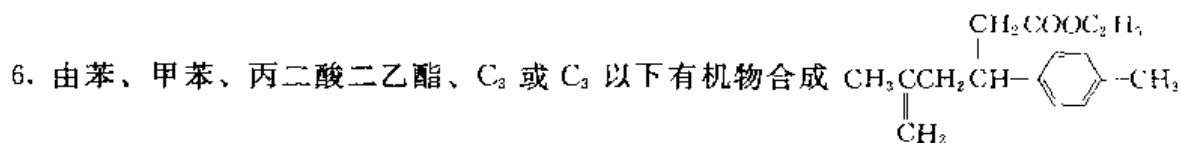
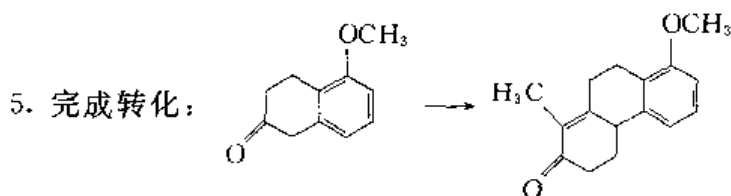
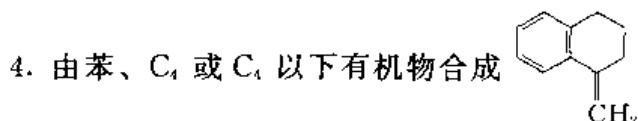
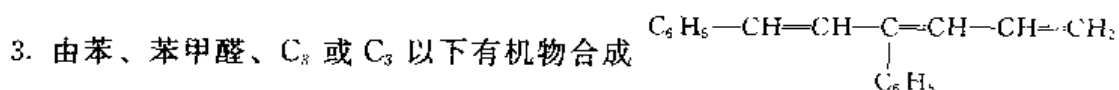
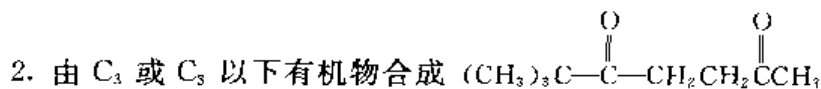
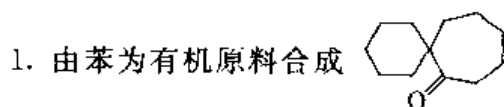


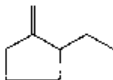
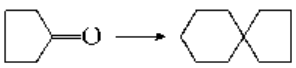
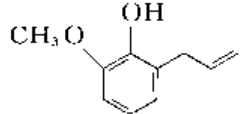
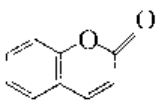
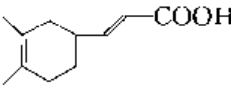




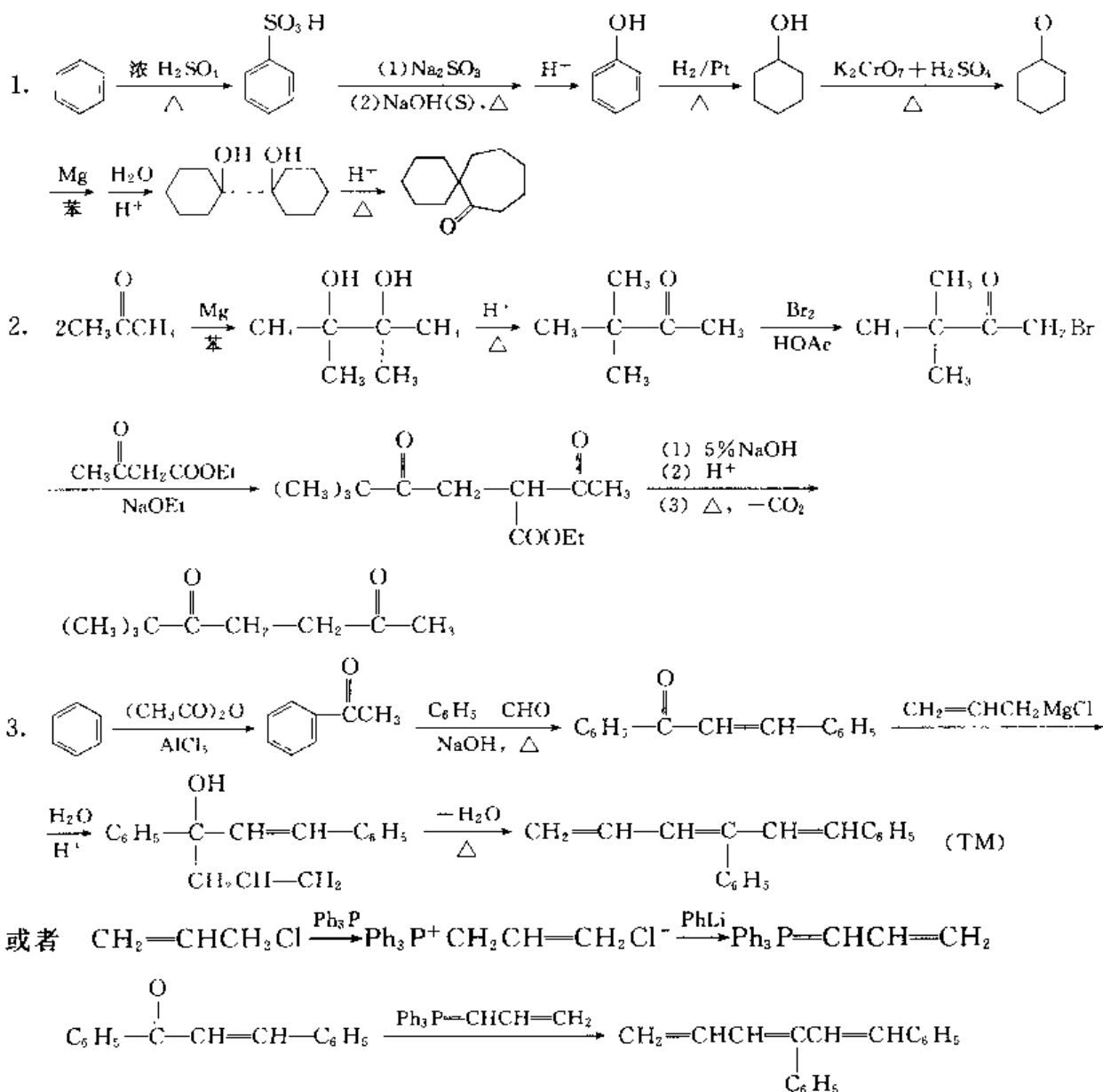


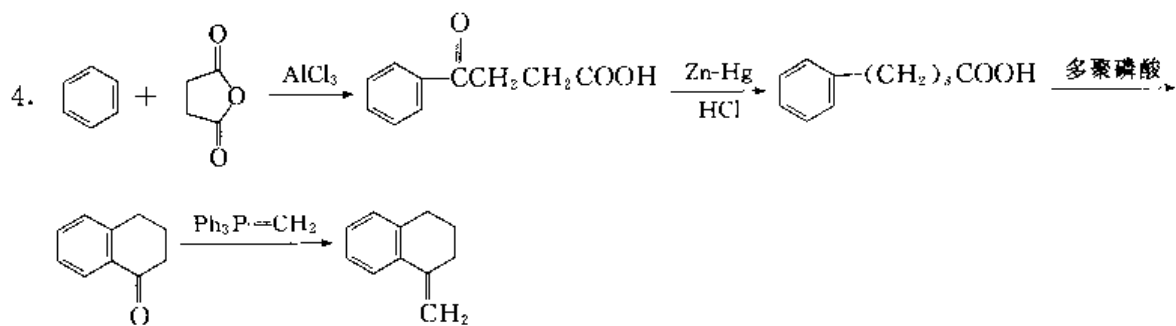
合成练习题 (II)



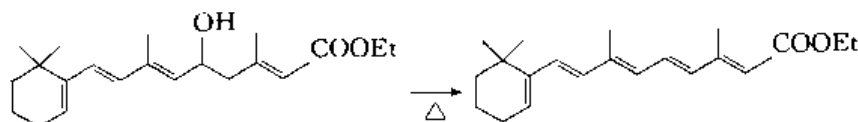
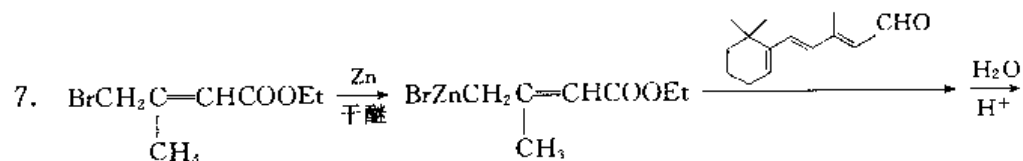
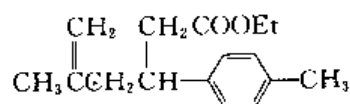
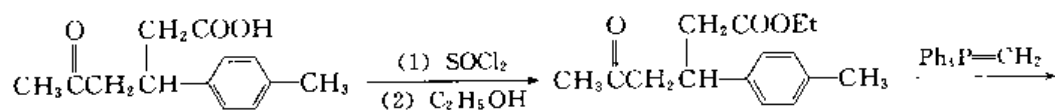
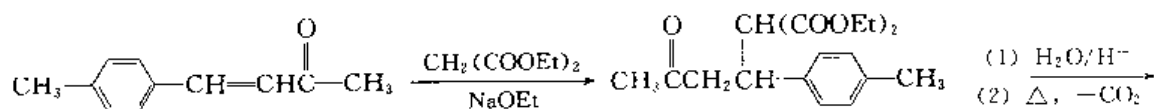
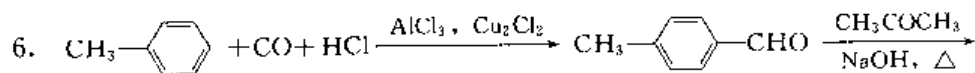
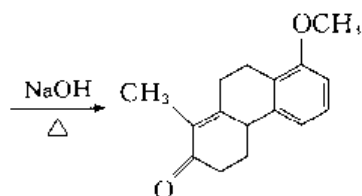
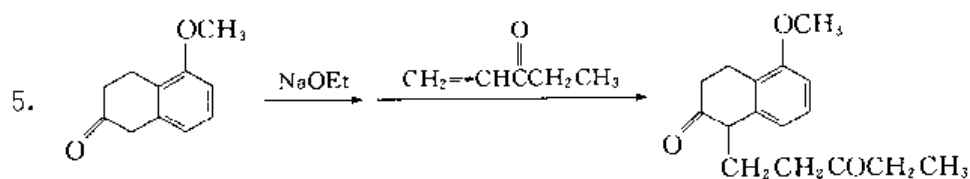
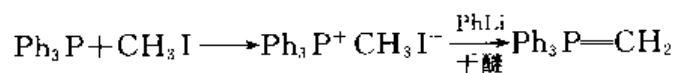
8. 用方便易得的原料合成 
9. 完成转化: 
10. 由邻苯二酚合成 
11. 由苯酚合成 
12. 由 C₃ 或 C₃ 以下化合物为原料合成 

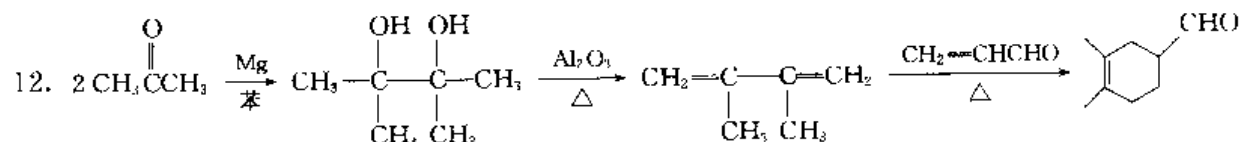
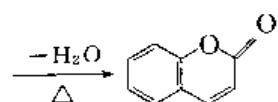
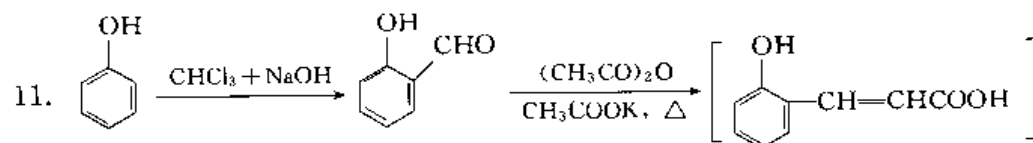
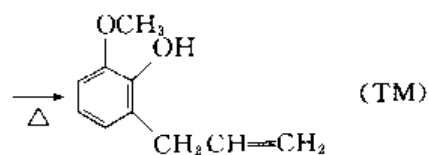
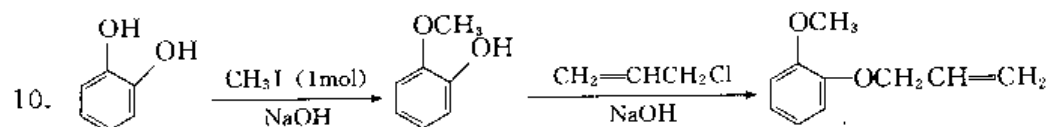
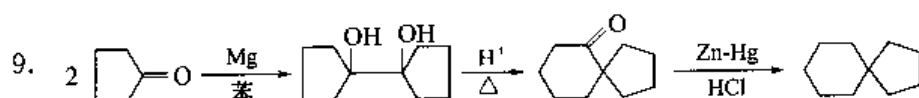
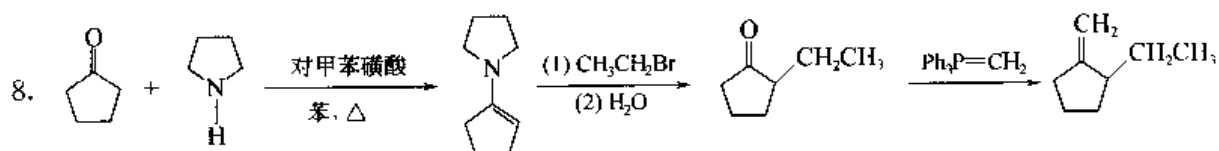
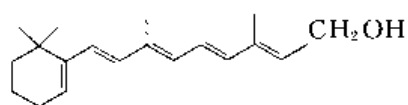
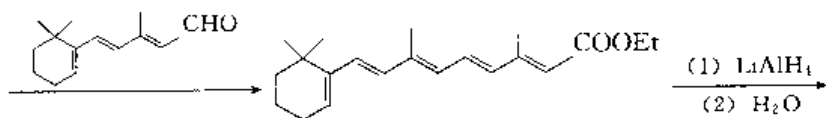
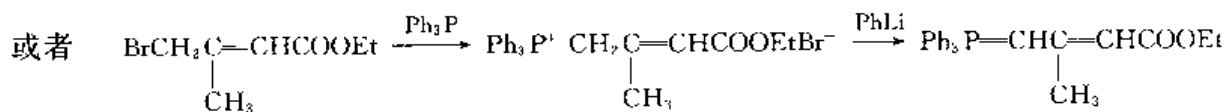
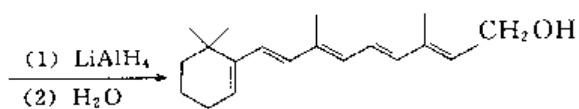
参 考 答 案

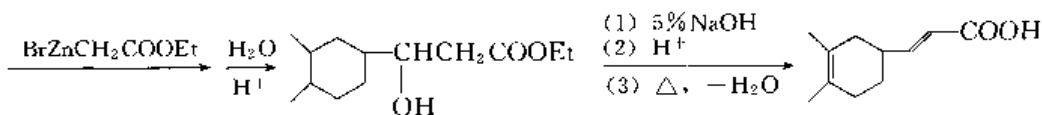




$\text{Ph}_3\text{P}=\text{CH}_2$ 的制法:

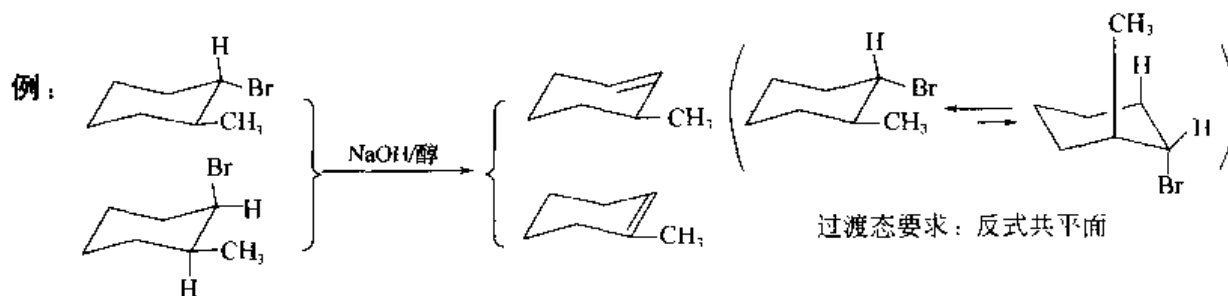




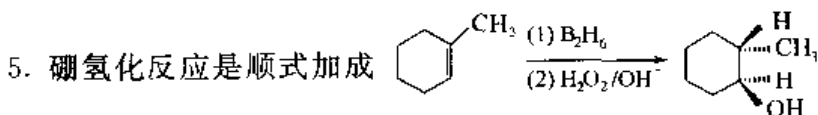
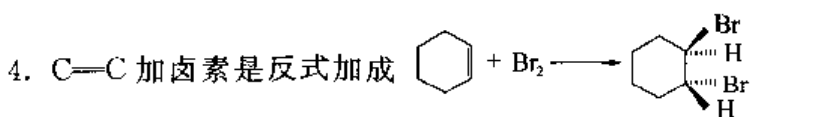
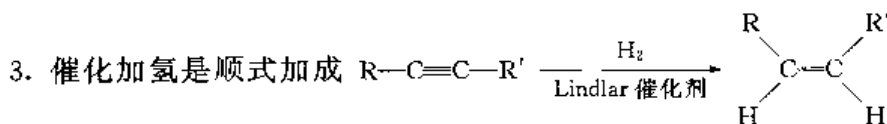


专题总结IV——某些反应的立体化学

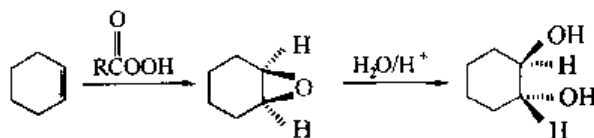
- S_N1 反应中, C^+ 中心碳原子为平面构型, 产物是外消旋化的
 S_N2 反应中, 中心碳原子的构型翻转。Walden 转化是 S_N2 反应的重要标志。
- E2 反应为反式消去



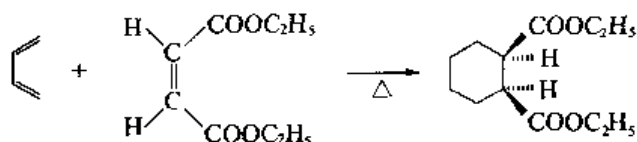
其过渡态的立体化学是“反式共平面”。



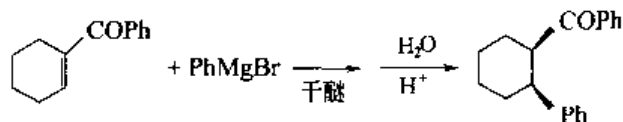
6. $C=C$ 环氧化是顺加, 环氧化物开环为反式开环



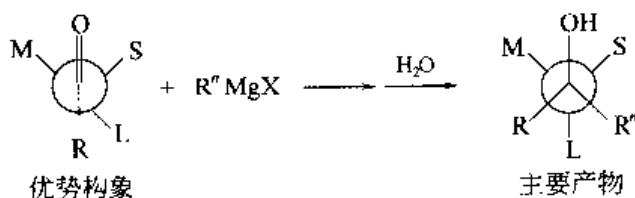
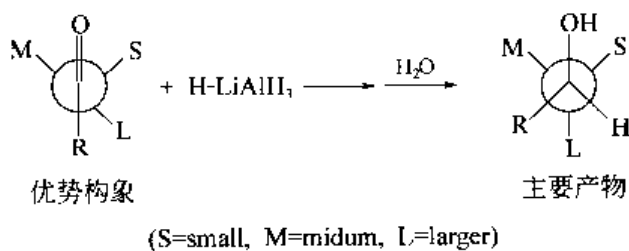
7. 环化加成 (双烯合成) 是顺式加成



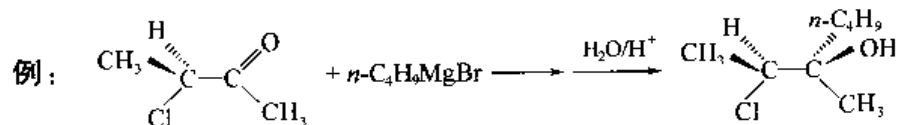
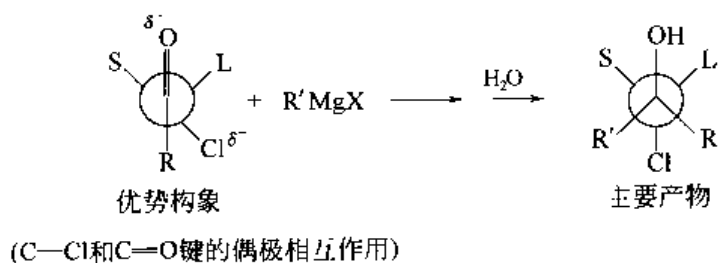
8. α, β -不饱和醛酮的共轭加成是反式加成



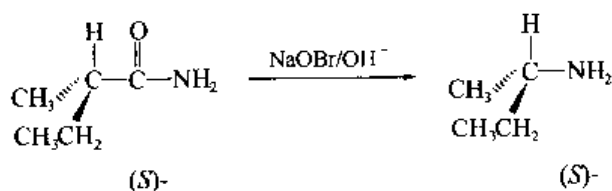
9. 醛酮被 LiAlH_4 还原或与 $\text{R}^{\prime}\text{MgX}$ 加成时的立体化学为



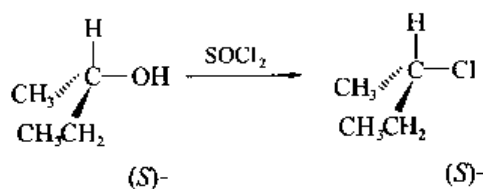
10. α -氯代醛酮与 $\text{R}^{\prime}\text{MgX}$ 加成时的立体化学为



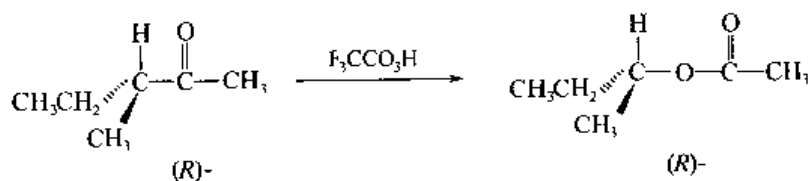
11. Hofmann 降解时, 手性碳的构型保持不变

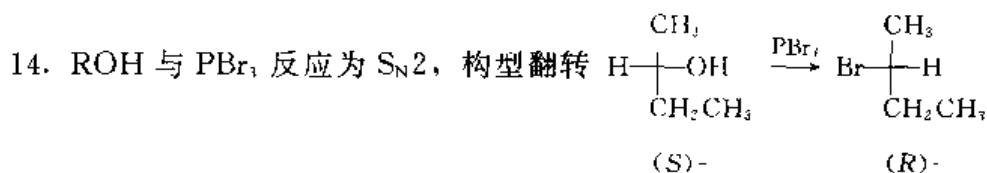


12. SOCl_2 与含有手性碳的醇反应时, 手性碳的构型保持不变

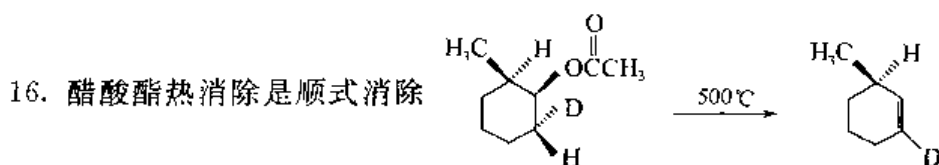
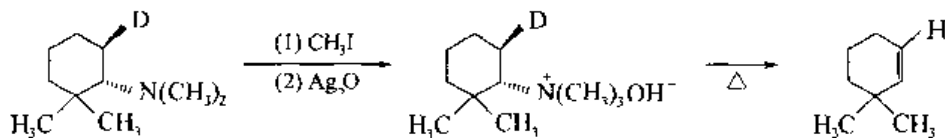


13. Baeyer-Villiger 重排中, 手性碳的构型保持不变

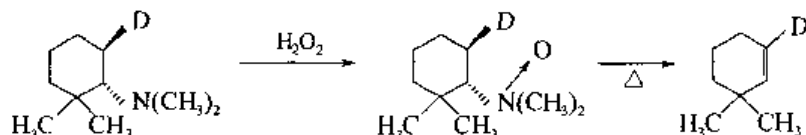




15. Hofmann 热消除的立体化学为反式消除



17. 氧化叔胺的热消除是顺式消除



专题总结 V —— 常用波谱数据

1. 红外光谱

(1) $3700 \sim 3200 \text{cm}^{-1}$ $\nu_{\text{N-H}}$ 、 $\nu_{\text{O-H}}$ ($\nu_{\text{N-H}}$ 波数高于 $\nu_{\text{O-H}}$, 氢键缔合波数低于游离波数)

(2) $3300 \sim 2800 \text{cm}^{-1}$ $\nu_{\text{C-H}}$ [以 3000cm^{-1} 为界, 高于 3000cm^{-1} 为 $\nu_{\text{C-H}}$ (不饱和), 低于 3000cm^{-1} 为 $\nu_{\text{C-H}}$ (饱和)]

2720cm^{-1} $\nu_{\text{C-H}}$ (醛)

(3) 约 2200cm^{-1} $\nu_{\text{C-N}}$ 、 $\nu_{\text{C}\equiv\text{C}}$ (中等强度, 尖峰)

(4) $1900 \sim 1650 \text{cm}^{-1}$ $\nu_{\text{C=O}}$ (干扰少, 吸收强, 酮羰基在约 1715cm^{-1} 出峰)

【讨论】

① 不同羰基的大致吸收位置如下所示。

化合物	酸酐	酰氯	酯	醛	酮	羧酸	酰胺
波数/ cm^{-1}	约 1830、约 1770	约 1790	约 1740	约 1730	约 1715	约 1710	约 1680

② -I 效应、环张力等使 $\nu_{\text{C=O}}$ 波数升高; 共轭效应使 $\nu_{\text{C=O}}$ 波数降低。

化合物	苯乙酮	丙酮	环己酮	环丁酮	环丙酮
波数/ cm^{-1}	1680	1715	1710	1780	1810

(5) $1650 \sim 1600 \text{cm}^{-1}$ $\nu_{\text{C=C}}$ (越不对称, 吸收越强)

(6) 1600、1500、1580、1460 cm^{-1} $\nu_{\text{苯环}}$ (苯环呼吸振动)

(7) 1500 cm^{-1} 以下 单键区。

约 1380 cm^{-1} : $\delta_{\text{C}_6\text{H}_5}$ (诊断价值高); 1450 cm^{-1} : δ_{CH_2} 、 $\delta_{\text{C}_6\text{H}_5}$;

有价值的 $\nu_{\text{C}-\text{O}}$ 如下所示。

$\nu_{\text{C}-\text{O}}/\text{cm}^{-1}$	1050	1100	1150	1230
化合物	1°ROH	1°ROH	1°ROH	ArOH

(8) 1000 cm^{-1} 以下, 苯环及双键上 C—H 面外弯曲振动

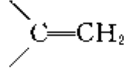
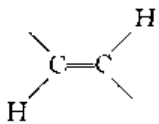
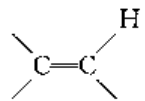
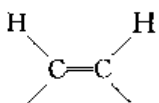
① 苯环上五氢相连 (单取代) 700、750 cm^{-1}

② 四氢相连 (邻二取代) 750 cm^{-1}

③ 三氢相连 (间二取代) 700、780 cm^{-1}

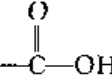
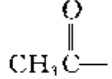
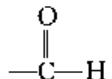
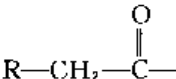
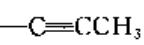
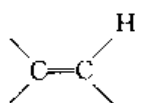
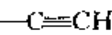
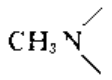
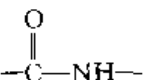
④ 二氢相连 (对二取代) 830 cm^{-1}

⑤ 孤立氢 880 cm^{-1}

⑥ 双键上	$-\text{CH}=\text{CH}_2$	990, 910 cm^{-1}		910 cm^{-1}
		970 cm^{-1}		820 cm^{-1}
		690 cm^{-1}		

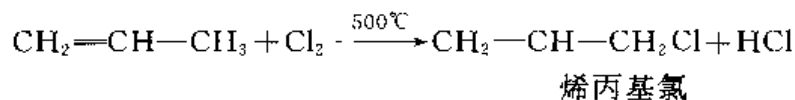
2. 核磁共振谱

常见质子的化学位移值

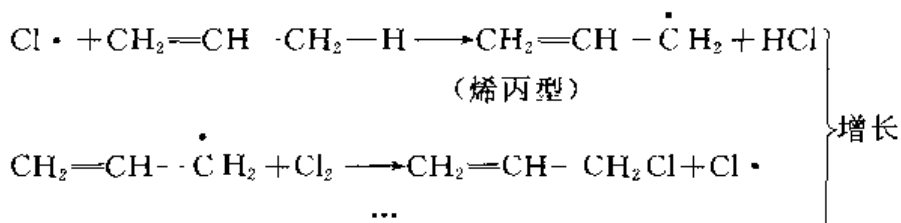
结构	δ/ppm	结构	δ/ppm
	10~11		约 2.1
	8~10		约 2.3
Ar—H	约 7.2		约 1.8
	4.3~6.4		约 2.5
CH3O—	约 3.7	RCH3 (饱和)	约 0.9
—CH2O—	约 4.0	R2CH2 (饱和)	约 1.3
	约 3.0	R3CH (饱和)	约 1.5
	5.5~8.5 (宽峰)	R—SH	1.1~1.5

专题总结 VI —— 反应历程总结

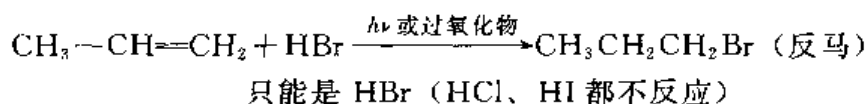
1. 自由基取代



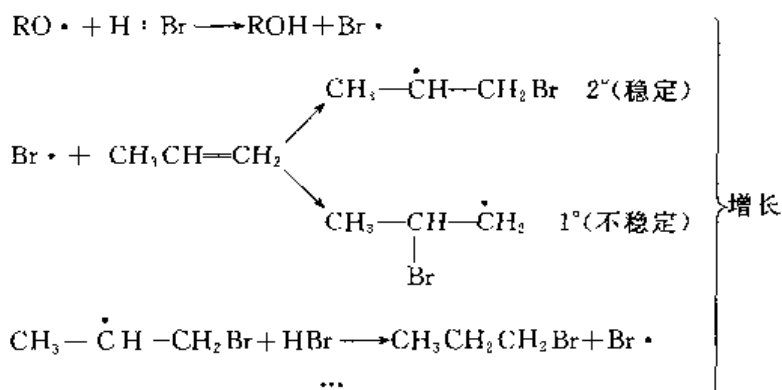
反应历程如下所示（略去引发和终止阶段）。



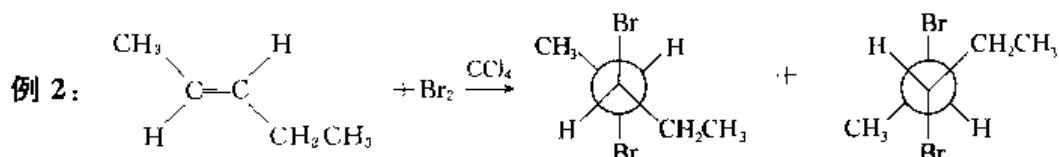
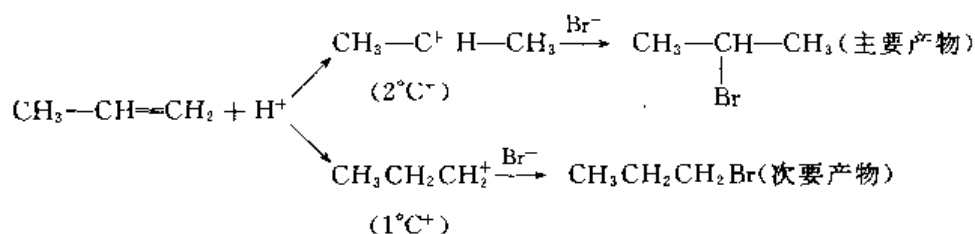
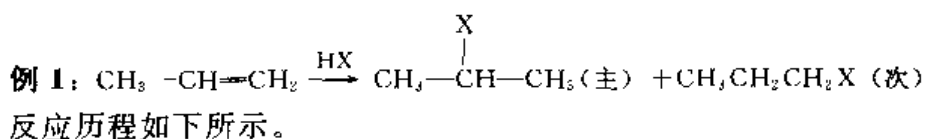
2. 自由基加成



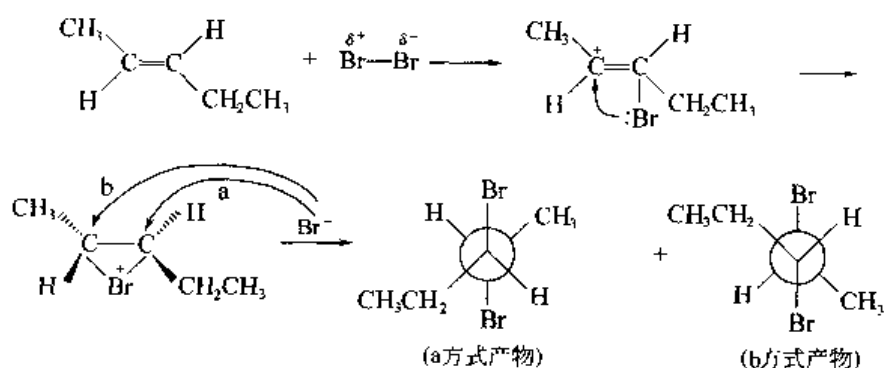
反应历程如下所示（略去引发和终止阶段）。



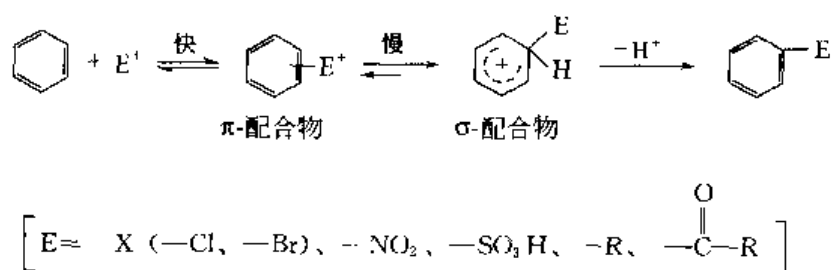
3. 亲电加成



反应历程如下所示。



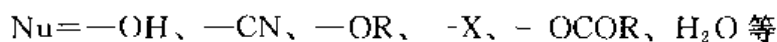
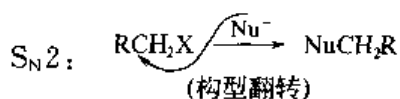
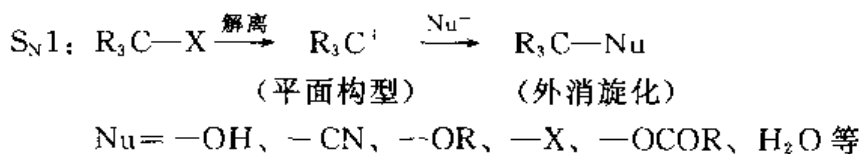
4. 亲电取代 (苯环上“四化”)



由于亲电试剂首先进攻, -OH、-CH₃ 等给电子基使苯环电子云密度增大, 反应速率加快; 而 -NO₂、-COOH 等吸电子基使苯环电子云密度减小, 反应速率缓慢。

由于 -OH、-CH₃ 等的给电子共轭使其邻、对位电子云密度更大, 新引入基上邻位、对位; 而 -NO₂、-COOH 等的吸电子共轭使其间位电子云密度相对较大, 新引入基上间位。

5. 亲核取代



【小结】① 3°RX 易发生 S_N1, 1°RX 易发生 S_N2;

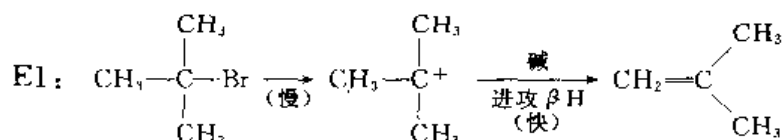
② 离去基易离去者, 有利于 S_N1 和 S_N2;

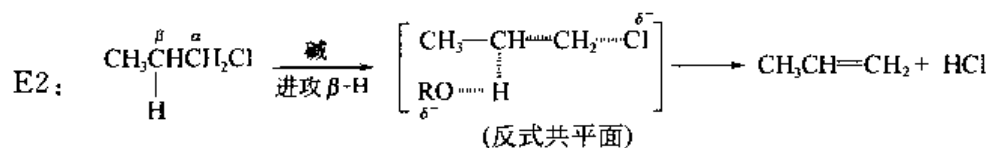
③ 碱的浓度增大, 有利于 S_N2;

④ 亲核性强的试剂有利于 S_N2, 与 S_N1 无关;

⑤ 极性大的介质有利于 S_N1, 极性小的介质有利于 S_N2。

6. 消除反应





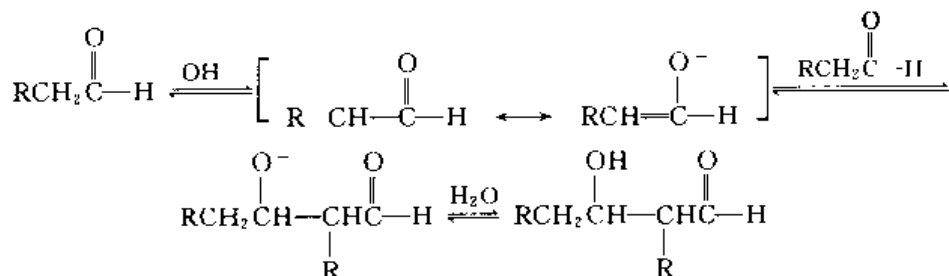
【小结】① 3°RX 易发生消除反应，1°RX 易发生取代反应；

3°RX 易发生 E1，1°RX 易发生 E2；

② 碱性强的试剂有利于消除，亲核性强的试剂有利于取代；

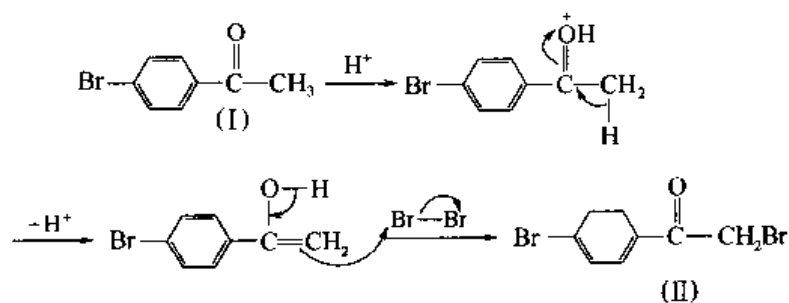
③ 极性弱的试剂有利于消除，极性强的试剂有利于取代。

7. 羟醛缩合反应历程

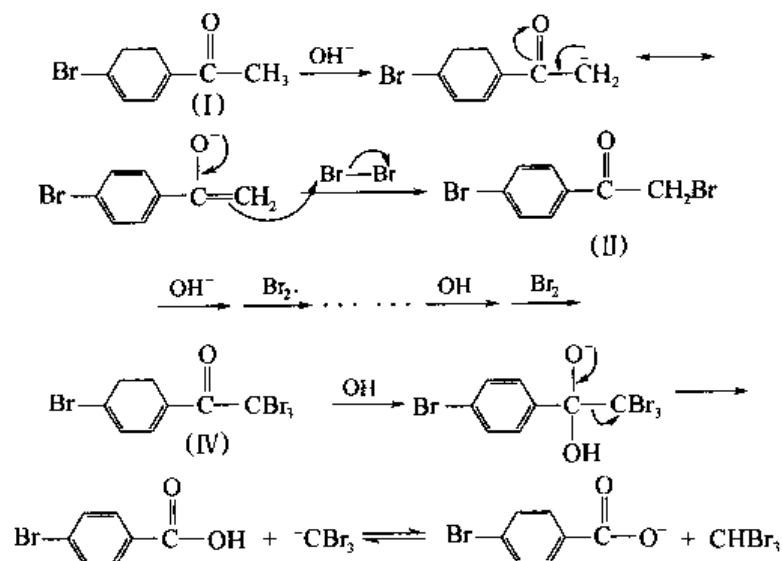


8. 卤代及卤仿反应历程

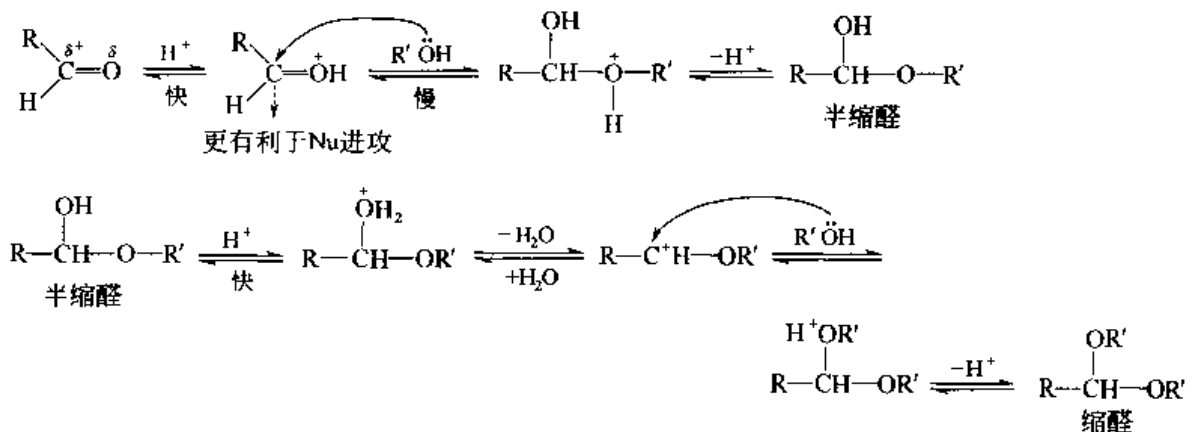
卤代反应在酸性或中性条件下进行，可停留在一元取代阶段，因为 (II) 比 (I) 更难在酸性或中性条件下烯醇化。



卤仿反应在碱性条件下进行，不可停留在一元取代阶段，因为 (II) 比 (I) 更容易在碱性条件下形成烯醇式负离子。

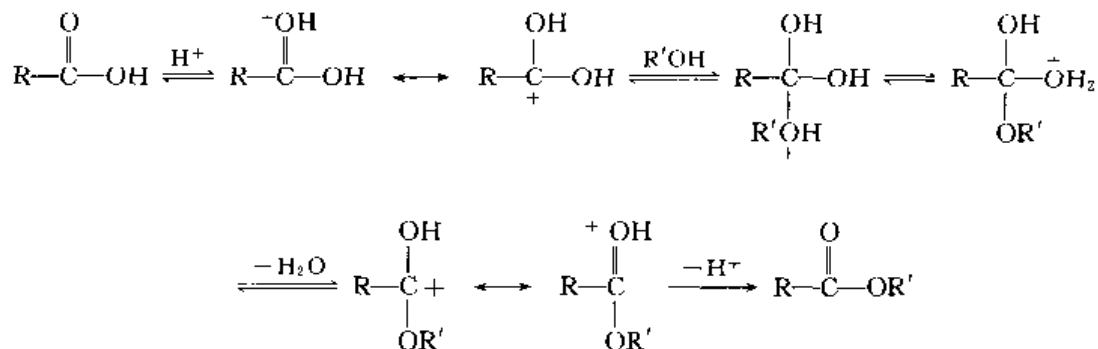


9. 缩醛的形成

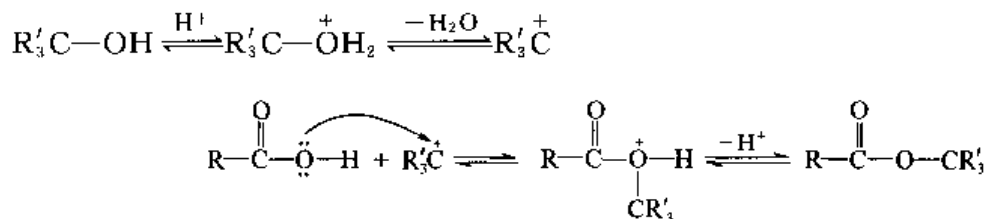


10. 酯化反应历程

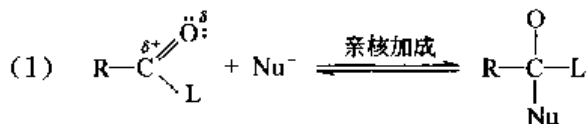
伯醇、仲醇的酯化是按照酰氧断裂的方式进行的。



叔醇的酯化是按照烷氧断裂的方式进行的。



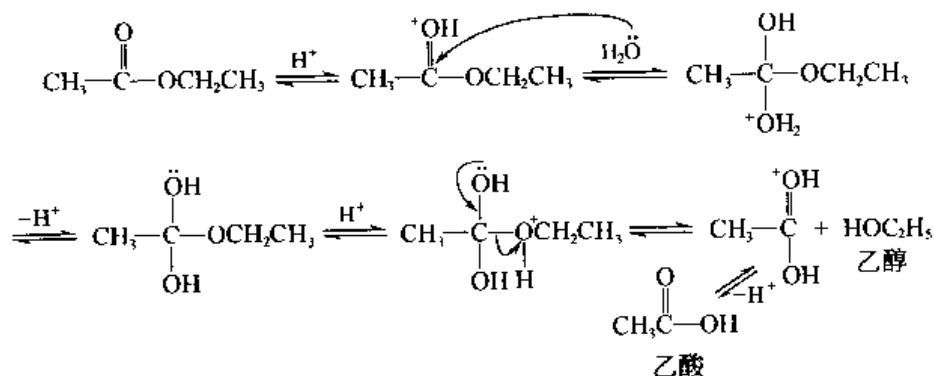
11. 羧酸衍生物的亲核取代（加成-消除）反应历程



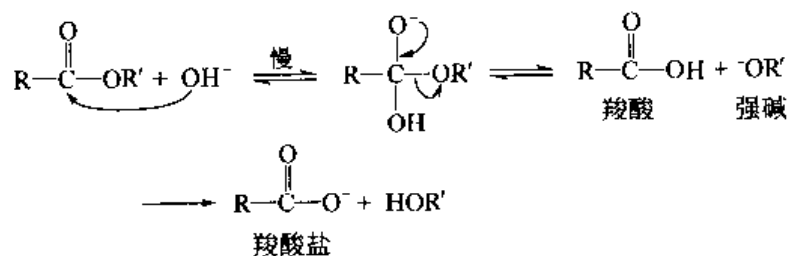
L (离去基团): $-\text{Cl}$ 、 $-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}\text{R}$ 、 $-\text{OR}'$ 、 $-\text{NH}_2$
 酰氧基 烷氧基 氨基

Nu (亲核试剂): H_2O (HO^-)、 $\text{R}'\ddot{\text{O}}\text{H}$ 、 $\ddot{\text{N}}\text{H}_3$

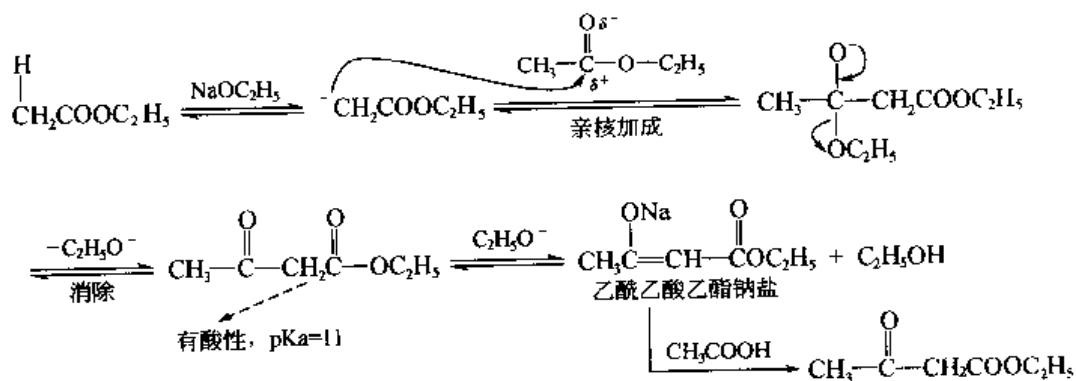
12. 酸催化酯的水解反应历程



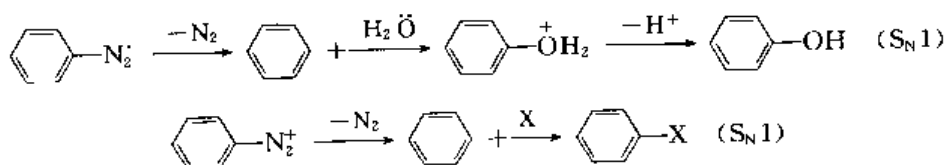
13. 碱催化酯的水解反应历程



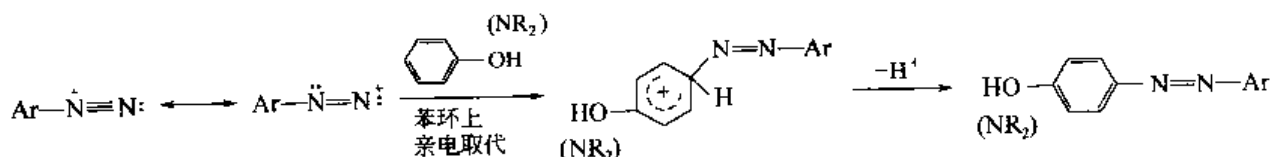
14. 克莱森酯缩合反应历程



15. 重氮盐放氮反应历程



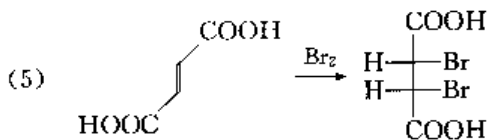
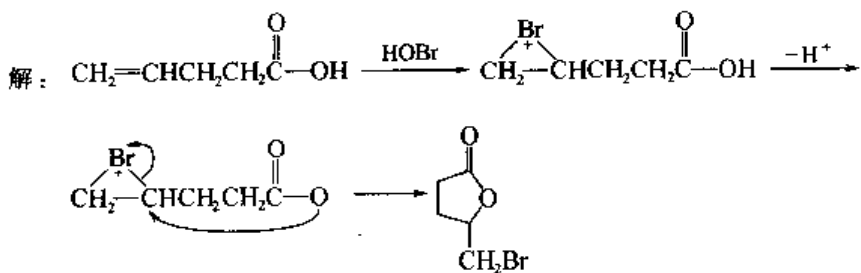
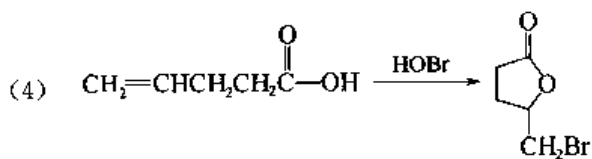
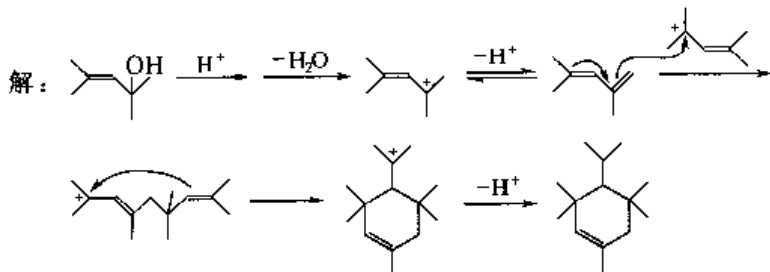
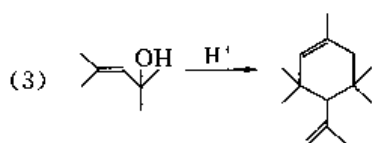
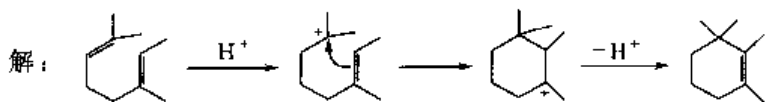
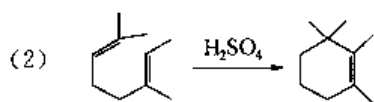
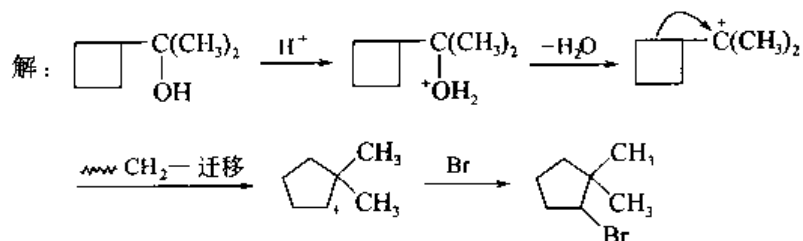
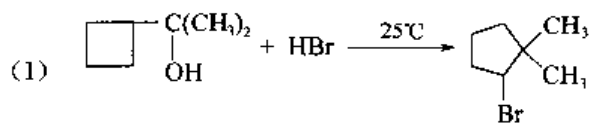
16. 重氮盐偶联反应历程

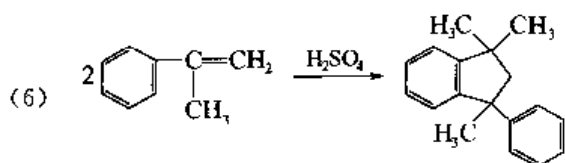
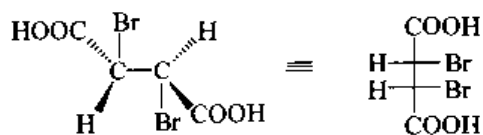
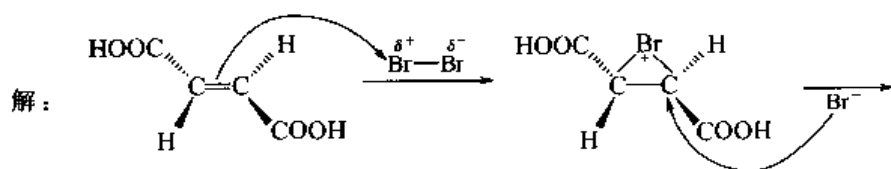




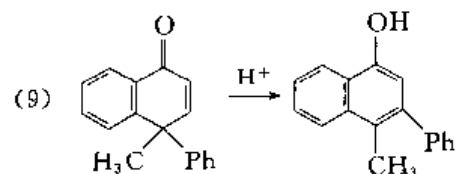
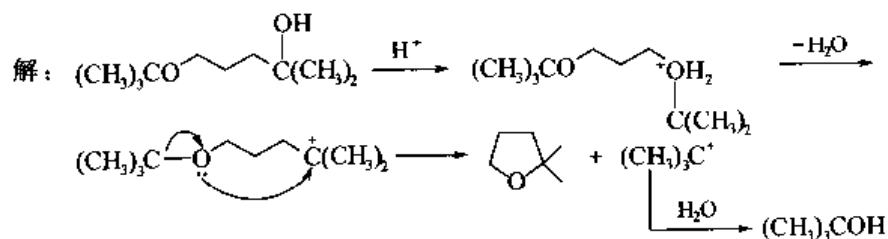
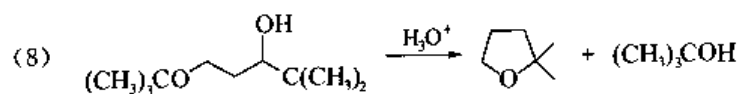
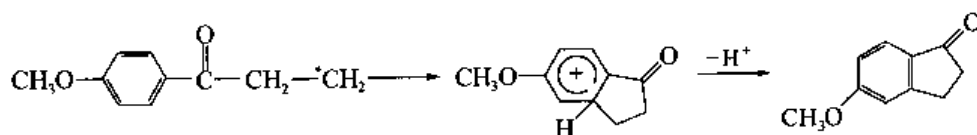
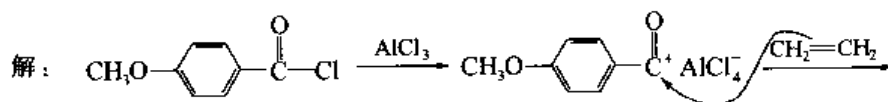
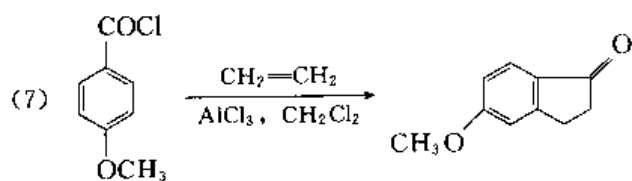
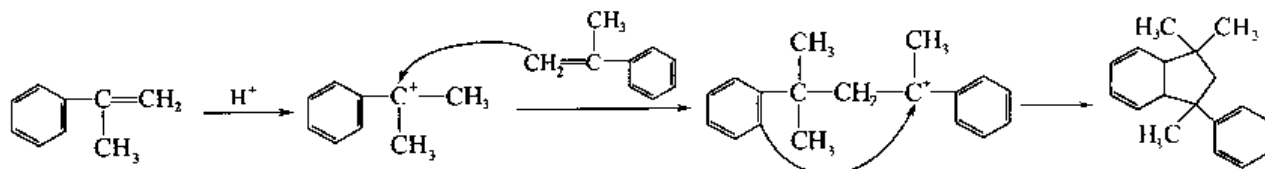
练习题

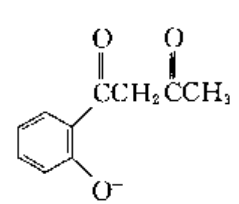
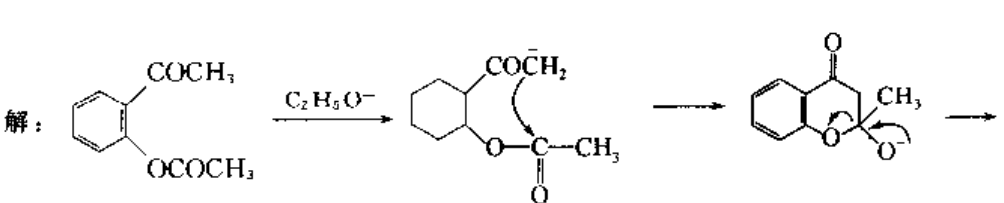
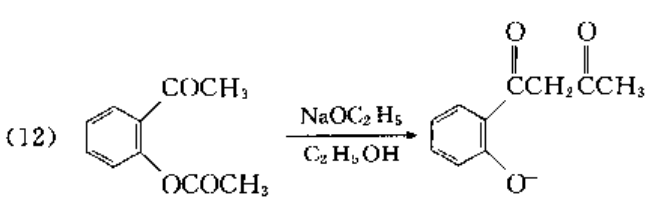
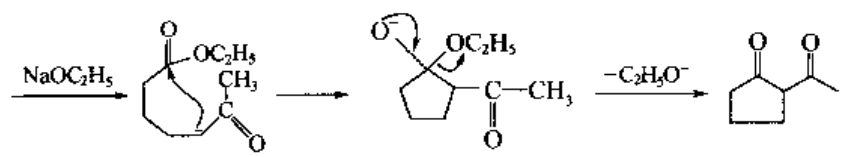
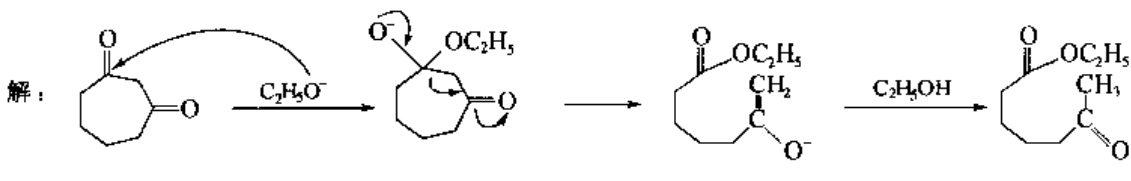
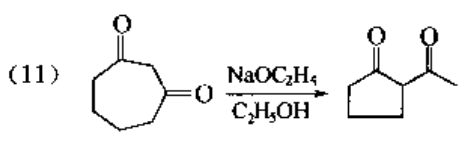
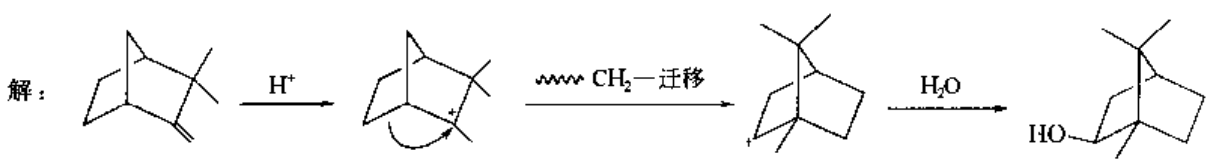
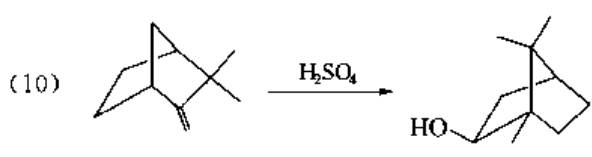
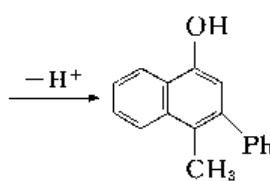
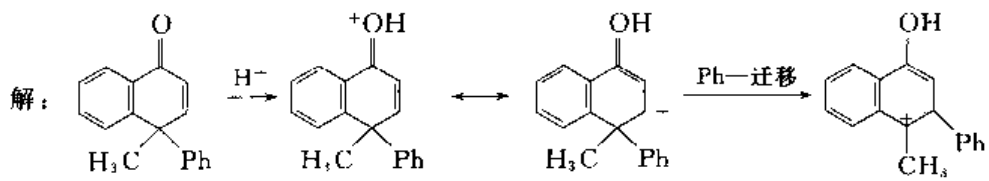
1. 写出下列反应的机理。

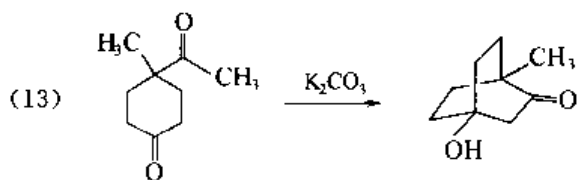




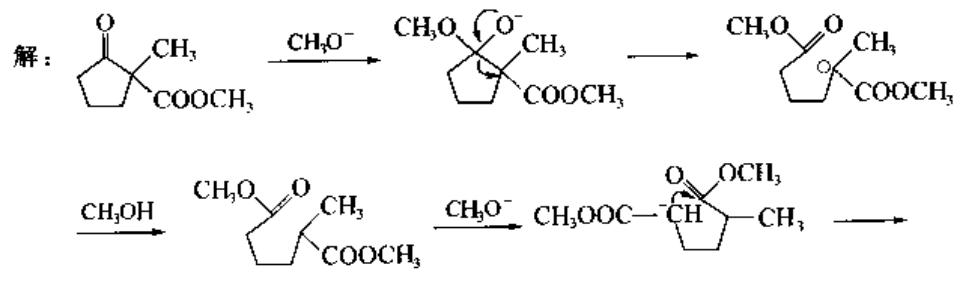
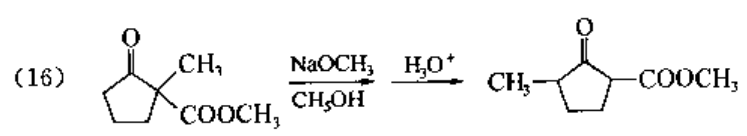
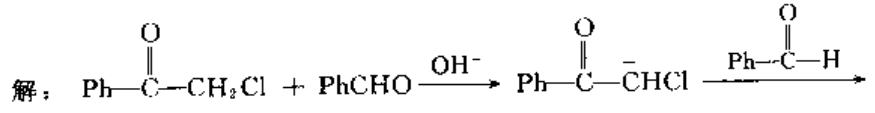
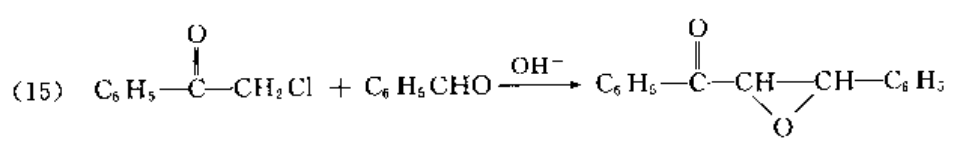
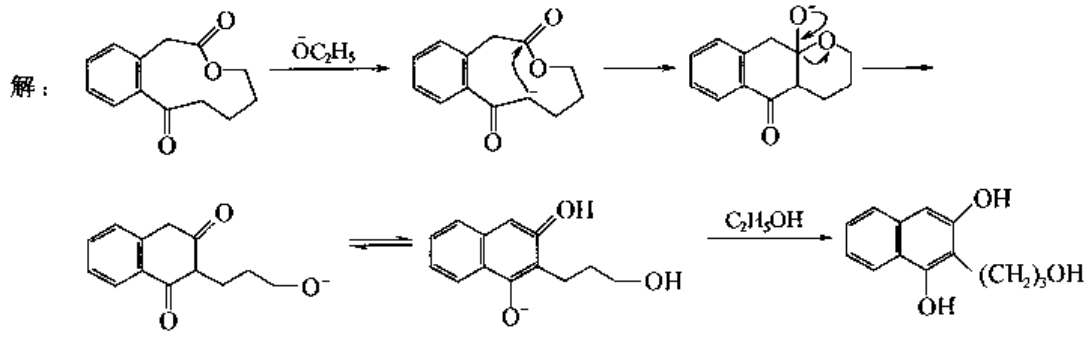
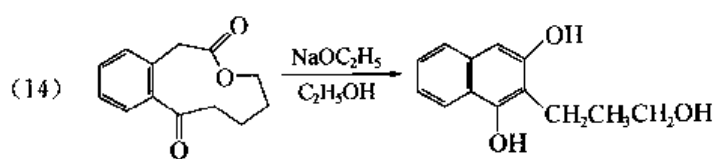
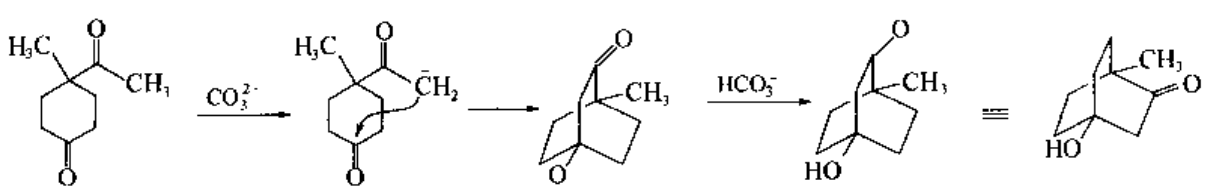
解:

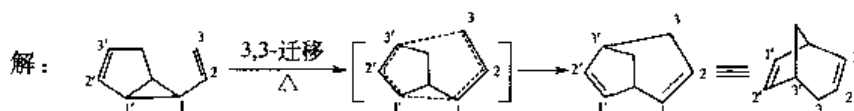
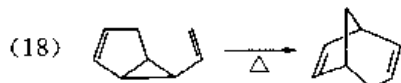
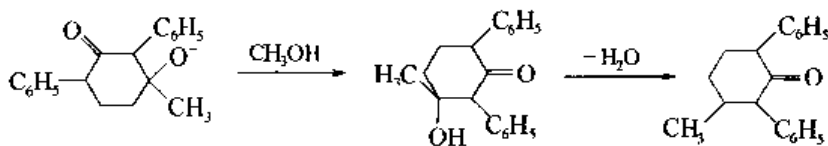
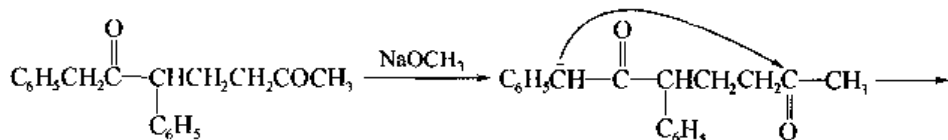
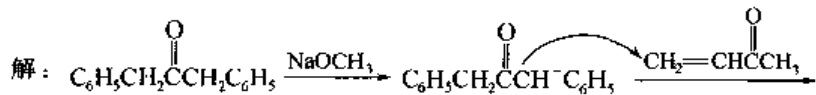
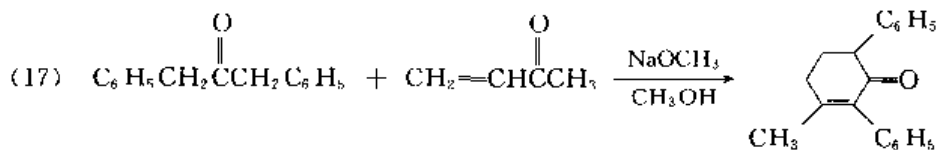
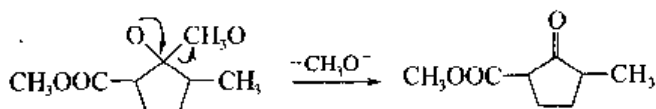






解:

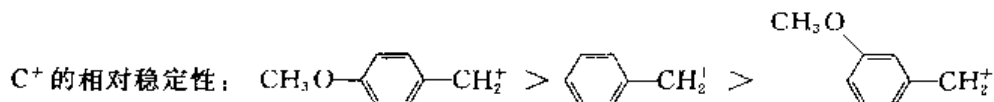




2. 解释下列实验现象

(1) PhCH_2Cl 、 $m\text{-CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$ 、 $p\text{-CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$ 在含水的丙酮中的水解反应相对速率是 $1 : 0.67 : 10^4$ 。

解: 上述反应均为 $\text{S}_{\text{N}}1$ 。

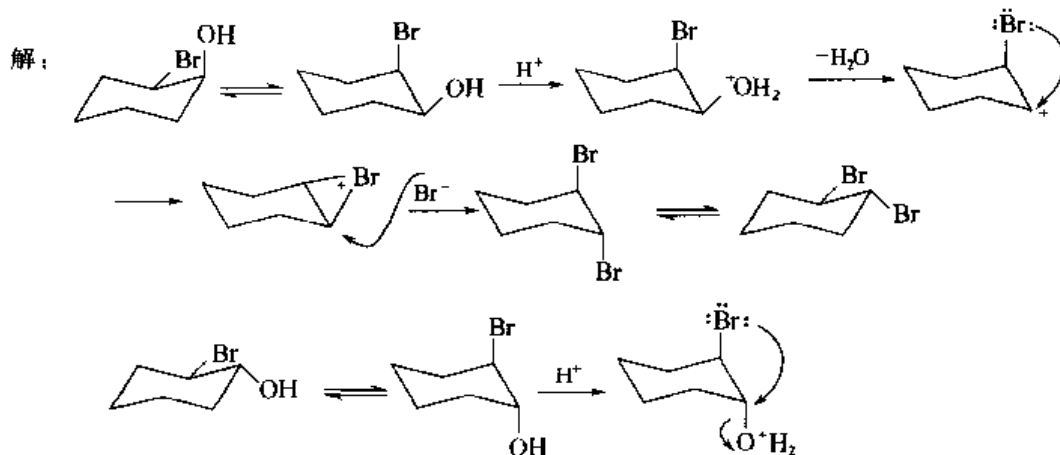


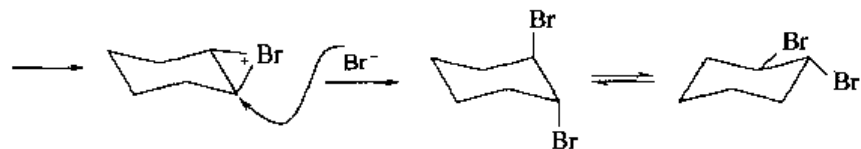
CH_3O —的电子效应: $+C \gg -I$

只有 $-I$

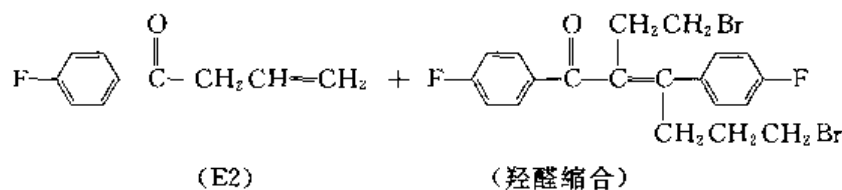
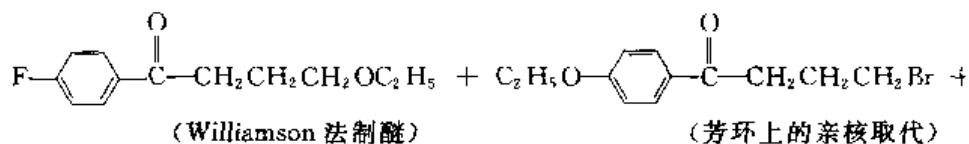
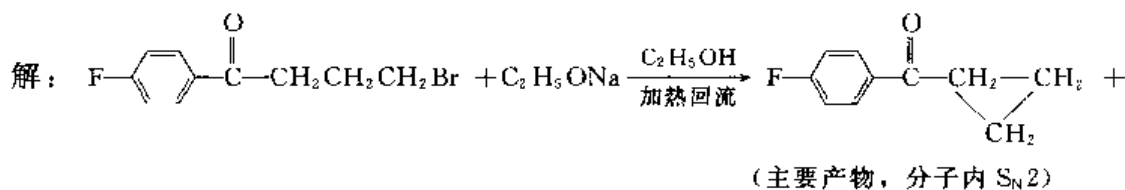
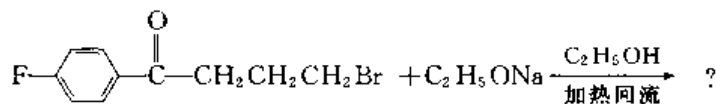
\therefore 水解反应相对速率: $p\text{-CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl} > \text{PhCH}_2\text{Cl} > m\text{-CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}_2\text{Cl}$

(2) 顺-2-溴环己醇和反-2-溴环己醇在 HBr 水溶液中均可转化为反-1,2-二溴环己烷。

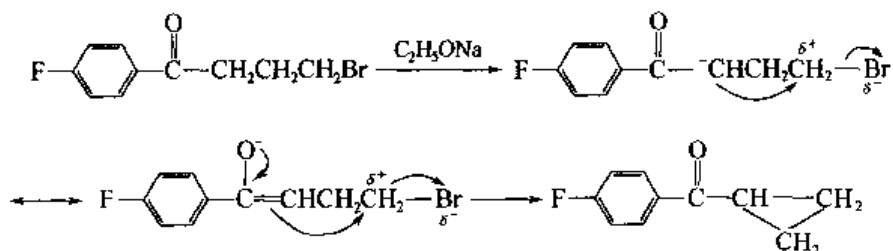




(3) 下列反应的主要产物是什么? 还有哪些可能的副产物? 写出生成主要产物的反应机理。



形成主要产物的反应机理:



专题总结 VII —— 鉴别用试剂

1. Br₂/H₂O 或 Br₂/CCl₄

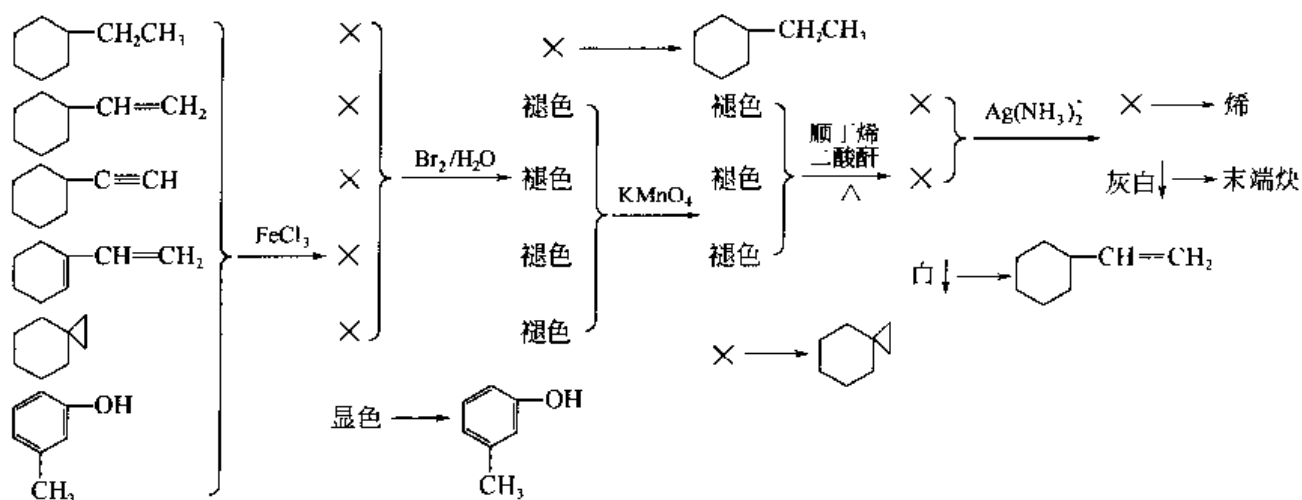
使 C=C、C≡C、小环褪色, 与苯酚生成白色沉淀。

2. KMnO₄

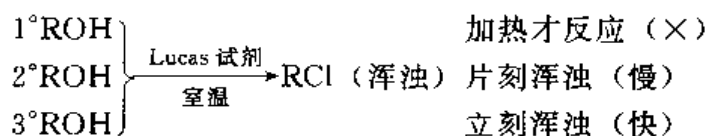
使 C=C、C≡C 褪色, 不使小环褪色。

3. 顺丁烯二酸酐 (顺酐) —— 检验共轭双烯

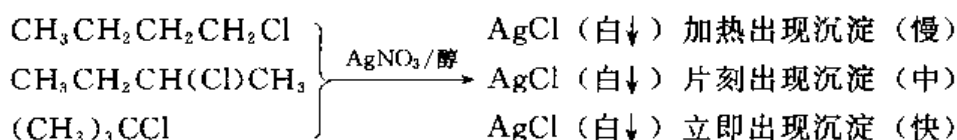
顺酐能与共轭双烯在加热下生成白色沉淀。例:



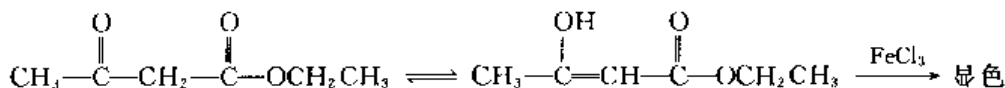
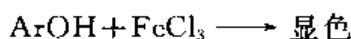
4. Lucas 试剂——区别 1°、2°、3°ROH



5. AgNO₃/醇——检验 1°、2°、3°RX



6. FeCl₃——检验酚羟基、“稳定的”烯醇式结构

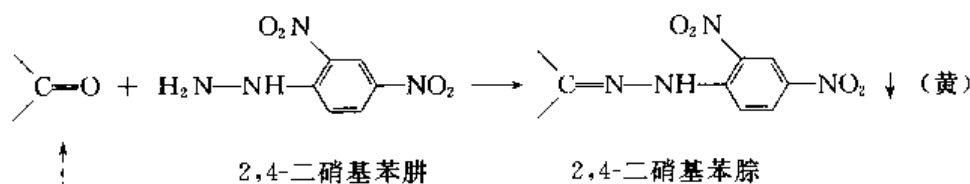
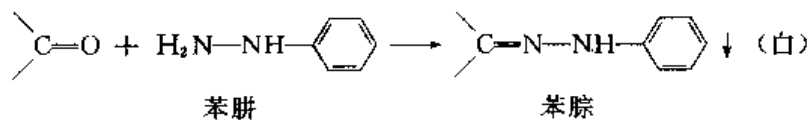


7. 饱和 NaHSO₃ 溶液



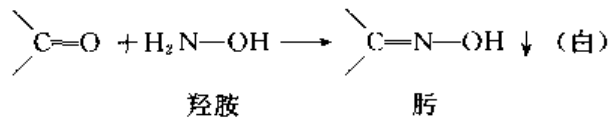
所有的醛、脂肪族甲基酮、低级环酮

8. 苯肼和 2,4-二硝基苯肼——检验羰基

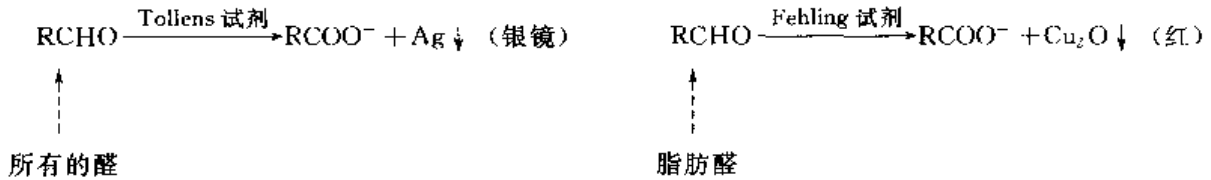


所有的醛、酮

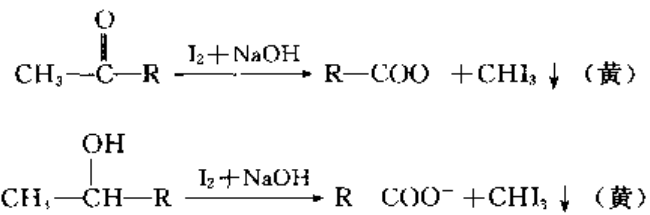
9. NH₂OH——检验羰基



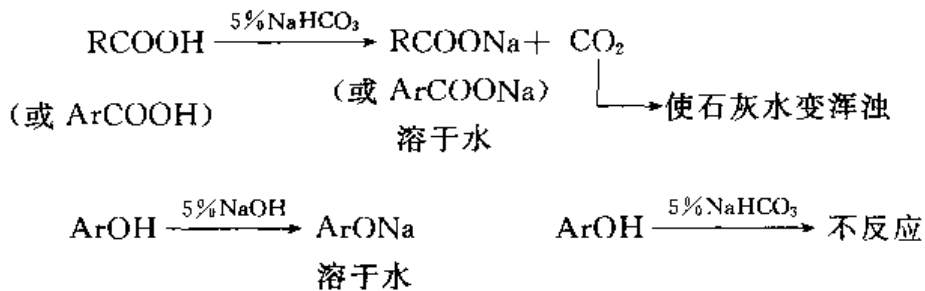
10. Tollens 试剂和 Fehling 试剂——检验醛



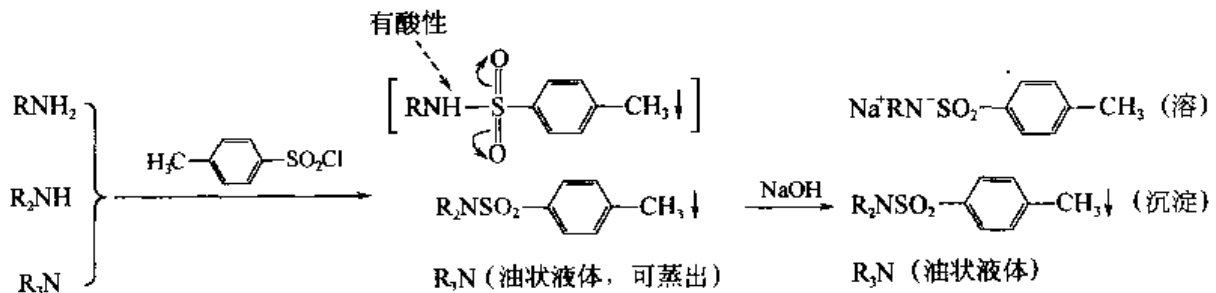
11. I₂ + NaOH——检验甲基酮、乙醛、“甲基醇”



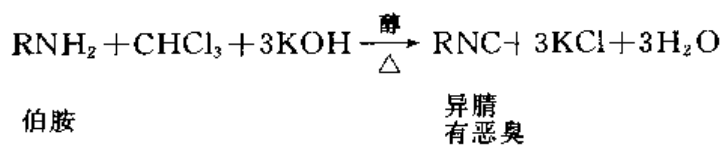
12. 5%NaHCO₃ 和 5%NaOH——检验有酸性的有机化合物



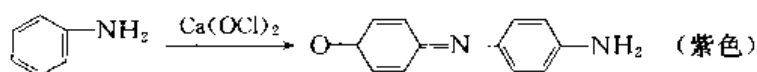
13. 对甲苯磺酰氯、NaOH (Hinsberg 反应, 鉴别胺)



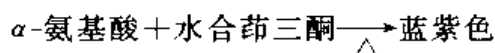
14. CHCl₃/KOH (异腈反应) ——检验伯胺



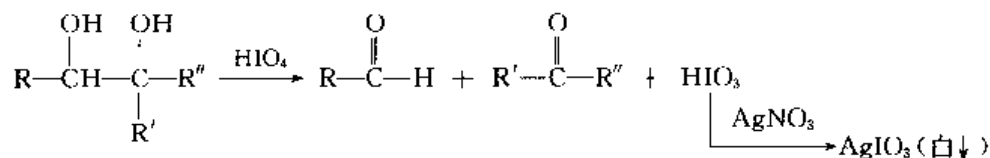
15. 漂白粉——检验苯胺



16. 水合茚三酮——检验 α -氨基酸



17. HIO_4 、 AgNO_3 ——检验邻二醇



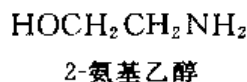
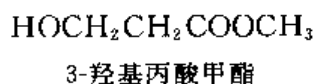
18. HCl -松木片——区别五元杂环化合物



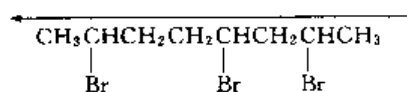
专题总结 VIII——有机化合物的命名

1. 系统命名法

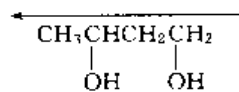
(1) 按官能团优先次序规则选择主要官能团 官能团优先次序规则：羧基、磺酸、酯，酰卤、酰胺、腈、醛基、酮基、醇羟基、酚、硫、氨基、(氢)、烷氧基、烷基、卤素、硝基。将排在前面的官能团作为母体，排在后面的官能团作为取代基。例如：



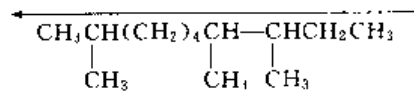
(2) 选择主链并编号 选择含主官能团、取代基最多的最长碳链为主链，从靠近主官能团的一端开始编号。编号时遵守最低系列原则。例如：



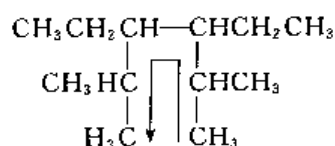
2,4,7-三溴辛烷
(不能叫做 2,5,7-三溴辛烷)



1,3-丁二醇
(不能叫做 2,4-丁二醇)



2,7,8-三甲基癸烷
(不能叫做 3,4,9-三甲基癸烷)



2,5-二甲基-3,4-二乙基己烷
(不能叫做 3,4-二异丙基己烷)

(3) 根据取代基大小次序规则确定取代基列出顺序 先写小的取代基，后写大的取代

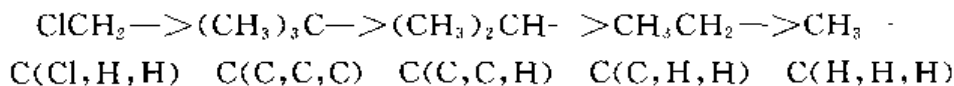
基，最后写母体。

取代基大小次序规则：

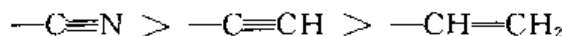
① 按原子序数排列，同位素： $D > H$ 。例如：



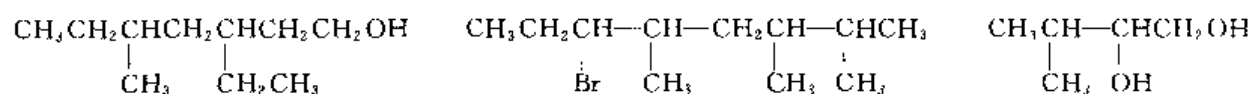
② 第一个都是碳原子时，沿碳链向外延伸。例如：



③ 当取代基不饱和时，把双键碳或叁键碳看成以单键和多个原子相连。例如：



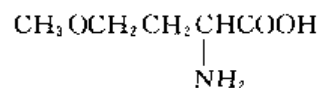
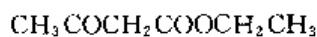
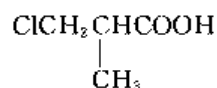
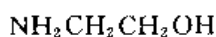
(4) 写出全称 用 1, 2, 3, ... 表示取代基的位次，用一、二、三……表示取代基的个数，用逗号“,” 将阿拉伯数字隔开，用半字线“-” 将阿拉伯数字与汉字隔开。例：



5-甲基-3-乙基(-1)-庚醇

2,3,5-三甲基-6-溴辛烷

3-甲基-1,2-丁二醇

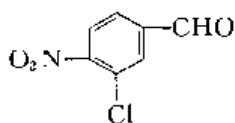


2-氨基乙醇

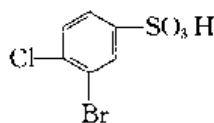
2-甲基-3-氯丙酸

3-丁酮酸乙酯

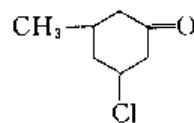
2-氨基-4-甲氧基丁酸



4-硝基-3-氯苯甲醛



4-氨基-3-溴苯磺酸



3-甲基-5-氯环己酮

2. 桥环化合物的命名

双环 [a. b. c] 某烃 ($a \geq b \geq c$)

先找桥头碳 (两环共用的碳原子)，从桥头碳开始编号。沿大环编到另一个桥头碳，再从该桥头碳沿着次大环继续编号。分子中含有双键或取代基时，用阿拉伯数字表示其位次。



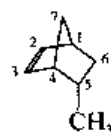
双环 [3,1,1] 庚烷



双环 [2,1,0] 戊烷



双环 [2.2.1]-2-庚烯

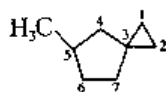


5-甲基双环 [2.2.1]-2-庚烯

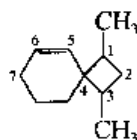
3. 螺环化合物的命名

螺 [a. b] 某烃 ($a \leq b$)

先找螺原子，编号从与螺原子相连的碳开始，沿小环编到大环。例：



5-甲基螺 [2.4] 庚烷



1,3-二甲基螺 [3.5]-5-壬烯

第二部分 模拟试题

模拟试题 1

一、填空或选择填空 (10分)

1. 下列哪种烯烃的氢化热最小? ()

- (A) E-2-丁烯 (B) Z-2-丁烯 (C) 1-丁烯 (D) 异丁烯

2. 下列烃氧基负离子碱性最弱的是 (), 共轭酸酸性最弱的是 ()

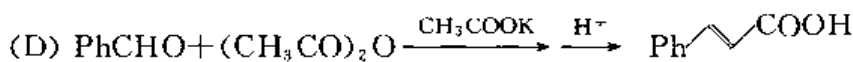
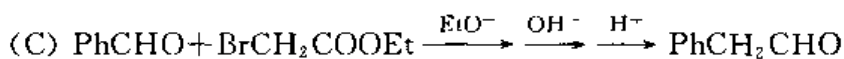
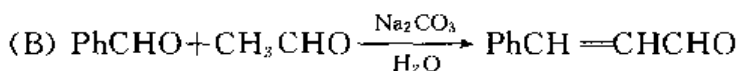
- (A) $C_6H_5O^-$ (B)  O^- (C) $n-C_4H_9O^-$ (D) $(CH_3)_3CO^-$

3. 下列哪种卤代烃发生 E2 过程的反应速率最大 (), 原因是 ()

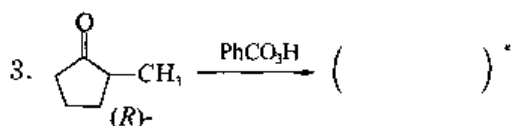
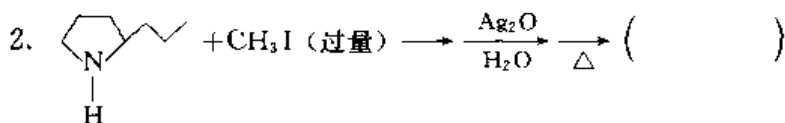
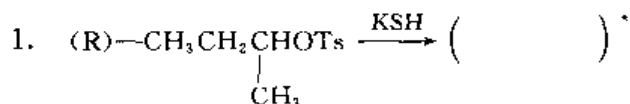
- (A)  CH_2CH_2Br (B) $p-CH_3C_6H_4CH_2CH_2Br$

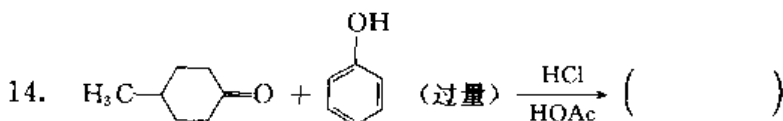
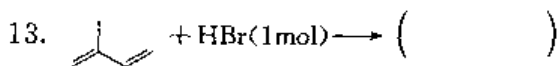
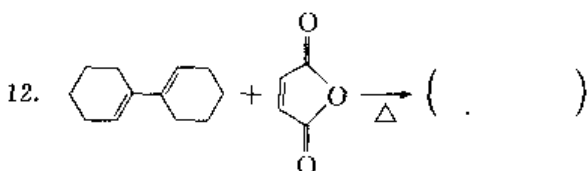
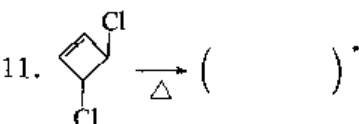
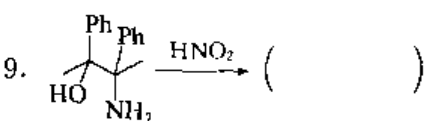
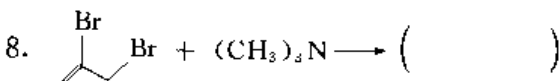
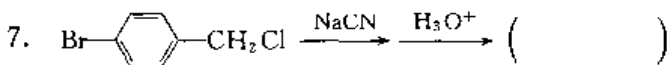
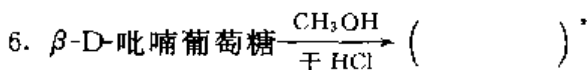
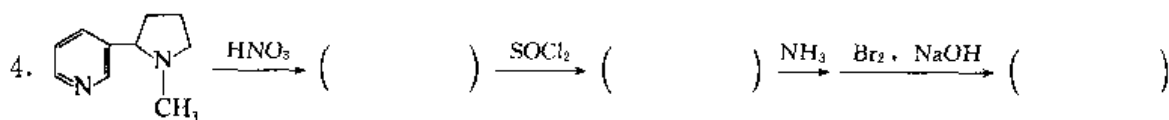
- (C) $p-ClC_6H_4CH_2CH_2Br$ (D) $p-NO_2C_6H_4CH_2CH_2Br$

4. 下列哪个反应叫 aldol 反应 (), 哪个反应为 Darzom 反应 ()



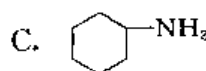
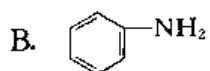
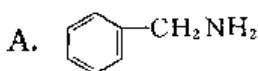
二、完成下列反应, 在括号上标有 x 的结构应标明构型 (20分)





三、按要求完成下列事项 (10分)

1. 排列下列化合物的碱性大小顺序，并作简单解释。



2. 顺-1,2-二溴环戊烷比反-1,2-二溴戊烷的沸点和熔点高，为什么？

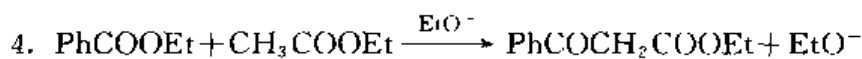
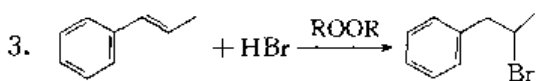
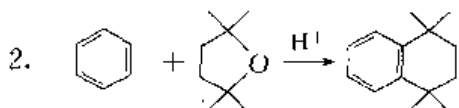
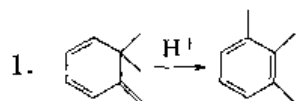
3. 等物质的量的 1,5-环辛二烯和 BH_3 反应生成 9-硼-二环 [3.3.1] 壬烷 (9-BBN)，9-BBN 是比较稳定的液体和很有用的硼氢化试剂，给出它的结构式。

4. 排列下列 3 种化合物与 HBr 发生亲电的活性顺序并作简要解释。

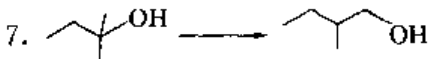
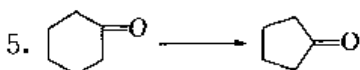
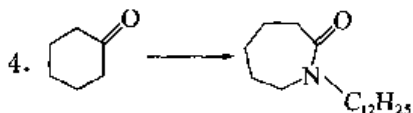
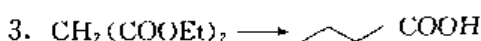
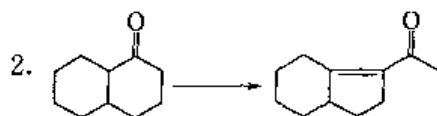
A. $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$ B. $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$ C. $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$

5. 溴代丙酮与 NH_3 反应生成分子式为 $\text{C}_6\text{H}_{10}\text{N}_2$ 的化合物 A, A 的 $^1\text{H NMR}$ 谱上只有两组峰, 写出 A 的结构式。

四、提出下列各反应的机理, 选做 3 个 (15 分)

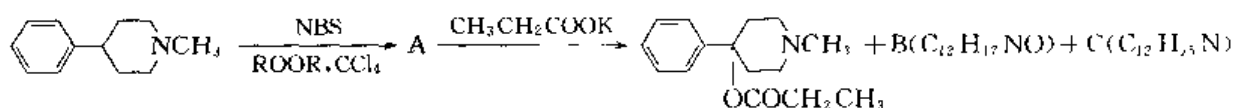


五、由指定原料合成指定产物, 所需无机、有机试剂自选, 选做 5 个 (25 分)

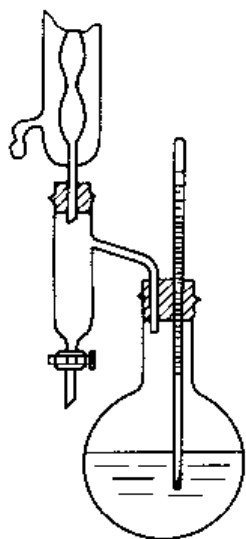


六、推测结构 (10 分)

1. 根据下列反应所给信息, 提出 A、B、C 的结构。



2. 化合物 A ($\text{C}_6\text{H}_{12}\text{O}_3$) 与 I_2/NaOH 作用生成黄色沉淀, 与 Tollen 试剂不作用, A 用稀硫酸处理后所得产物可以与 Tollen 试剂作用, A 的 IR 谱在 1710cm^{-1} 有强吸收峰, A 的

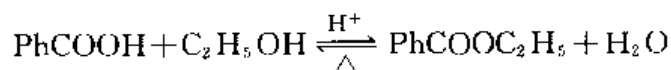


$^1\text{H-NMR}$ 数据为 δ 2.1 (3H, 单峰), δ 2.6 (2H, 二重峰), δ 3.2 (6H, 单峰), δ 4.7 (1H, 三重峰), 试推测出 A 的结构并指认 $^1\text{H-NMR}$ 的归属。

七、实验题 (10 分)

左图是实验室从正丁醇制正丁醚的反应装置图。

1. 写出在烧瓶中发生的反应和副反应。
2. 为什么要采用带油水分离器的回流装置?
3. 如何判断反应是否完成?
4. 如果反应温度超过 135°C 有何害处?
5. 用下述反应制苯甲酸乙酯, 可否采用制正丁醚的这套装置?

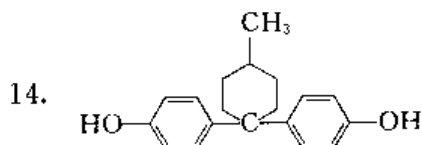
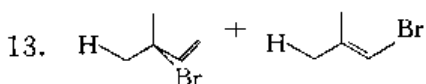
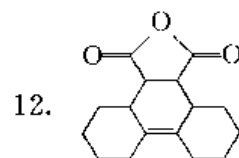
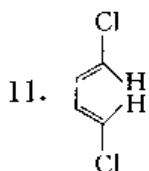
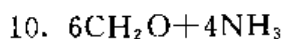
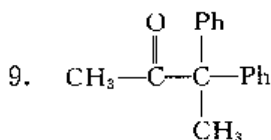
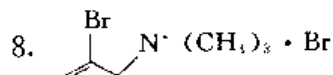
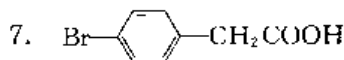
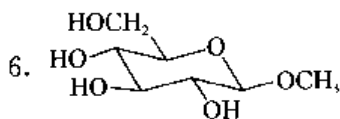
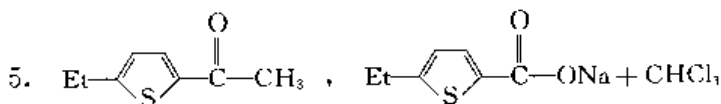
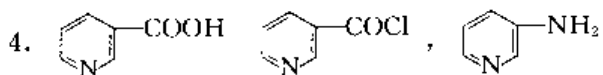
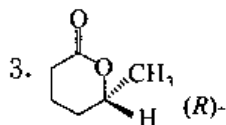
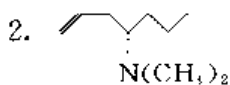
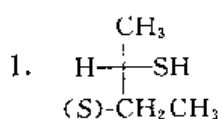


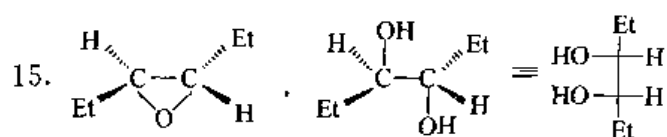
参考答案

一、填空

1. (A); 2. (A), (D); 3. (D), NO_2 使苯环 $\alpha\text{-H}$ 酸性增加; 4. (B), (C)。

二、完成反应式



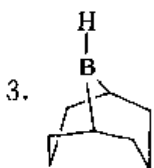


三、按要求完成事项

1. C (脂肪族仲胺) > A (脂肪族伯胺) > B (芳胺);

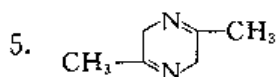
2. 沸点: 顺-1,2-二溴环戊烷 > 反-1,2-二溴戊烷 (顺-1,2-二溴环戊烷的偶极矩比反式的大);

熔点: 顺-1,2-二溴环戊烷 > 反-1,2-二溴戊烷 (顺-1,2-二溴环戊烷的分子对称性比反式的好);

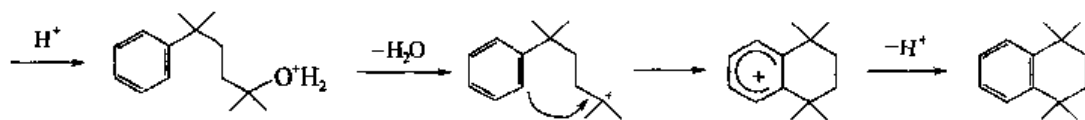
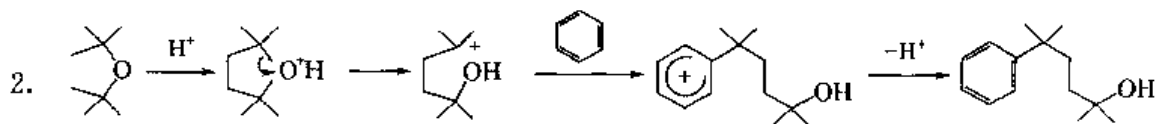
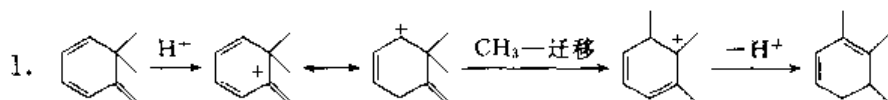


4. 亲电加成反应活性: A > C > B;

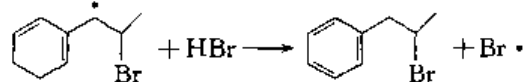
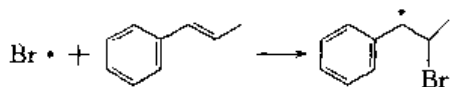
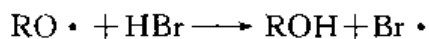
* C⁺ 稳定性: *p*-CH₃C₆H₄CH⁺CH₂ > C₆H₅CH⁺CH₂ > *p*-NO₂C₆H₄CH⁺CH₂



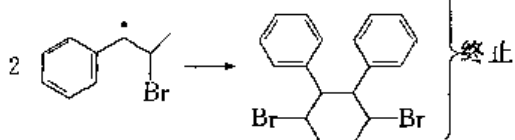
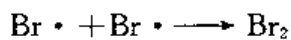
四、机理



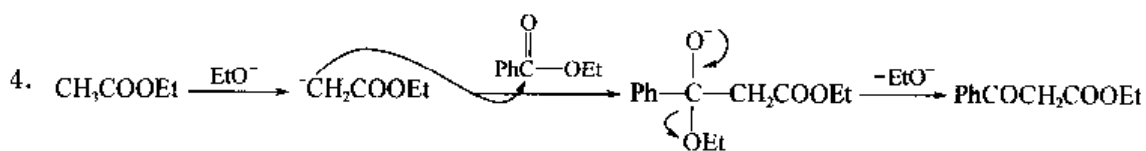
3. ROOR → 2RO· 引发



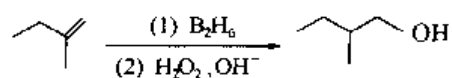
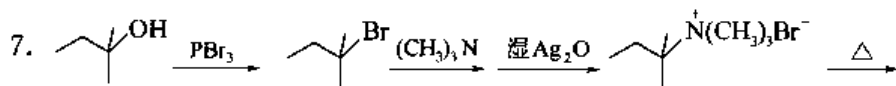
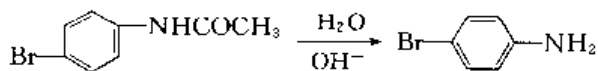
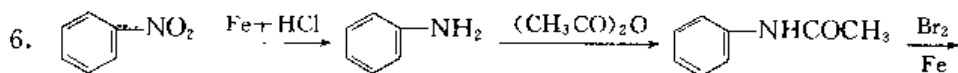
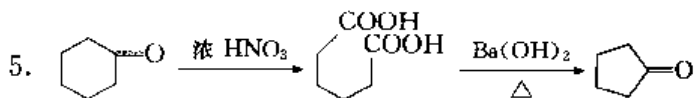
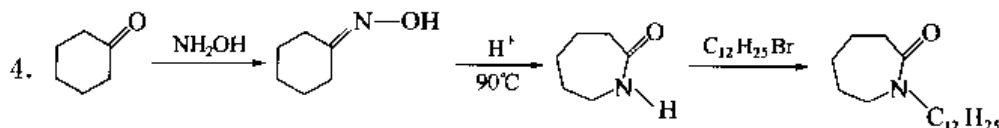
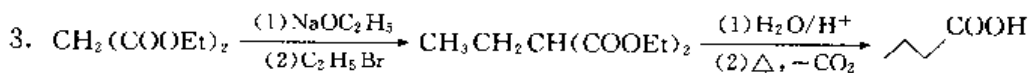
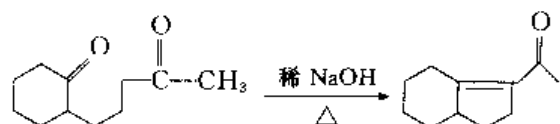
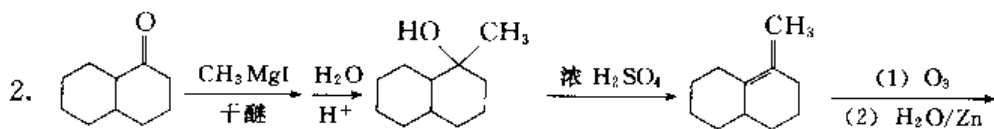
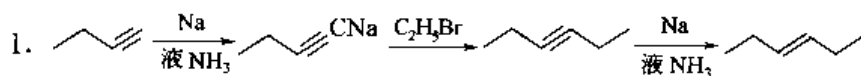
增长



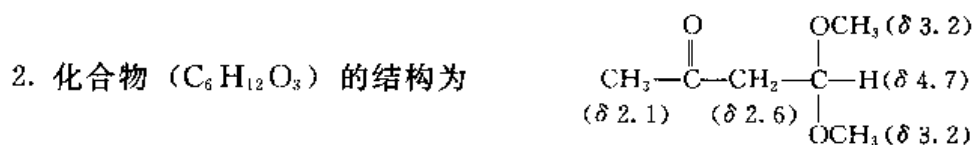
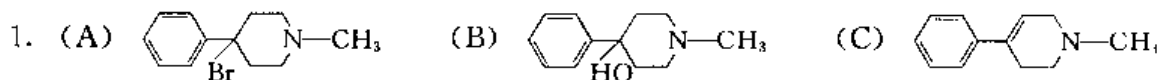
终止



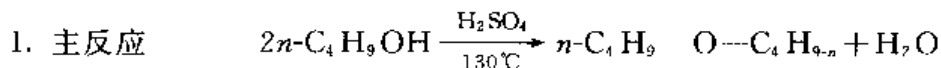
五、合成

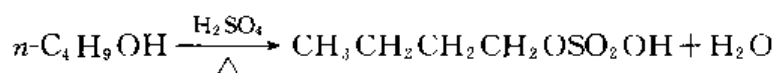
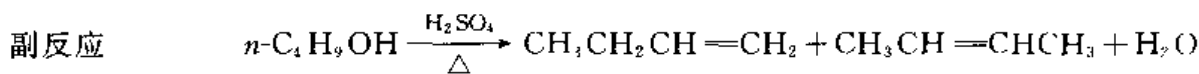


六、推测结构



七、实验题





2. 利用丁醇在水中只有约 8% 的溶解度，且正丁醇的相对密度小于 1，使未反应的正丁醇回到反应瓶中。

3. 球形冷凝管回滴下来的流体中不再有油滴出现时，表明反应已经完成。

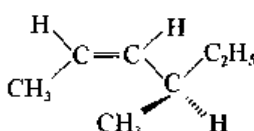
4. 会有较多的副产物烯烃生成。

5. 该装置不能用于制备苯甲酸乙酯。因为反应物之一的乙醇与水无限混溶，油水分离器不能使未反应的乙醇回到反应瓶中。

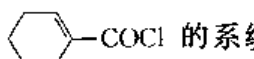
模拟试题 2

一、命名下列各物种或写出结构式 (共 10 分)

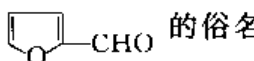
1. 用 Fischer 投影式表示 (R)-3-羟基丁醛。

2. 写出  的系统名称。

3. 写出 $(\text{CH}_3)_3\text{CCHO}$ 的系统名称。

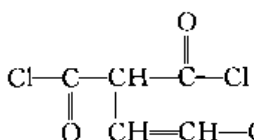
4. 写出  的系统名称。

5. 写出乳酸 $[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]$ 的构型式。

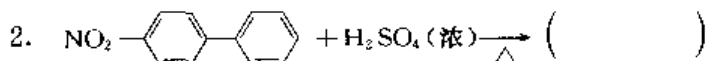
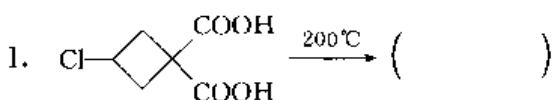
6. 写出  的俗名。

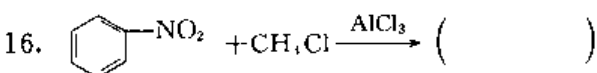
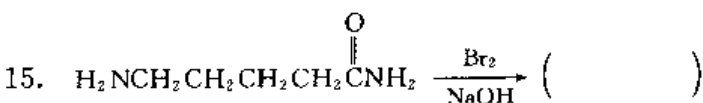
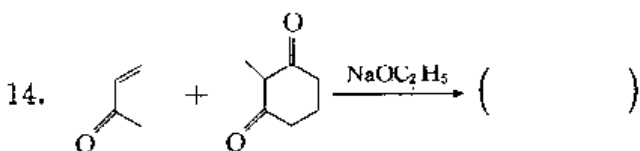
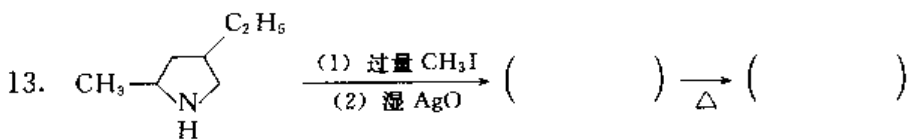
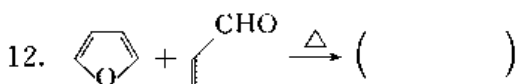
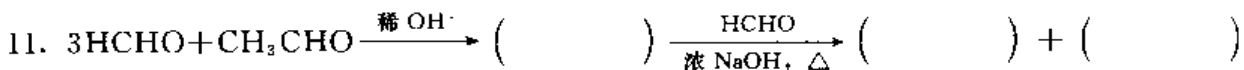
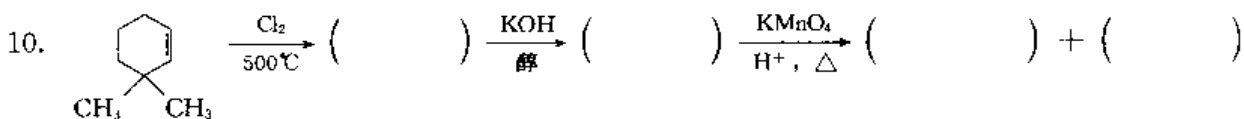
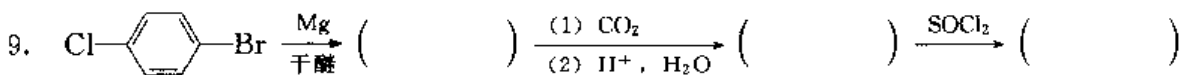
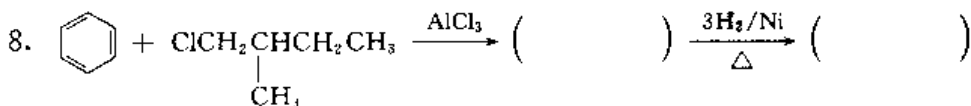
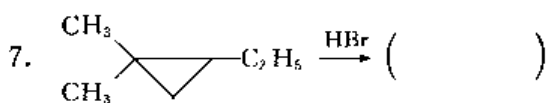
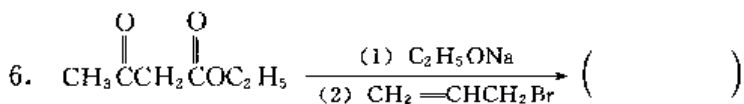
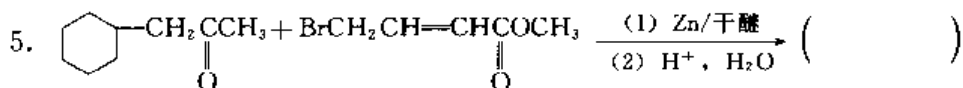
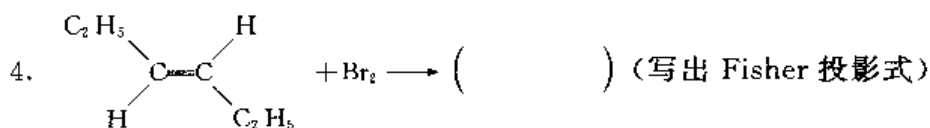
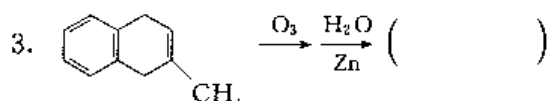
7. 写出氯化三甲基十二烷基铵的构造式。

8. 写出 2-甲基-2-硝基丙烷的构造式。

9. 写出  的系统名称。

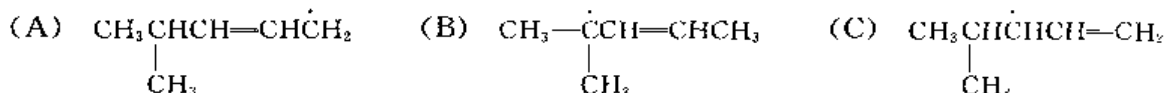
二、完成下列各反应式 (若产物有立体结构，需将立体结构写出，若反应不能进行需用“×”表示。25 分)



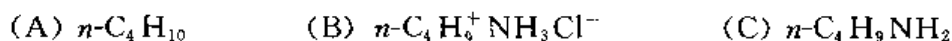


三、基本概念 (12分)

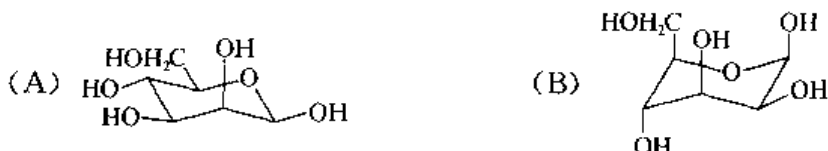
1. 将下列自由基按稳定性大小排列成序。



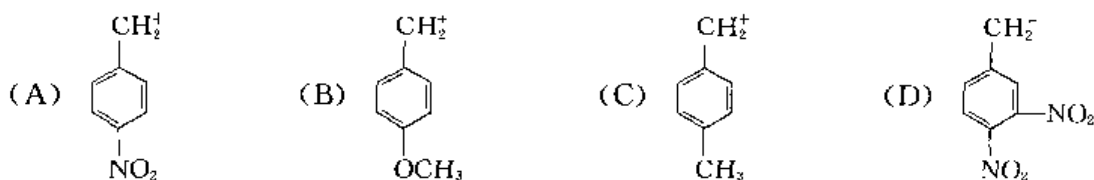
2. 比较下列化合物在水中的溶解度大小。



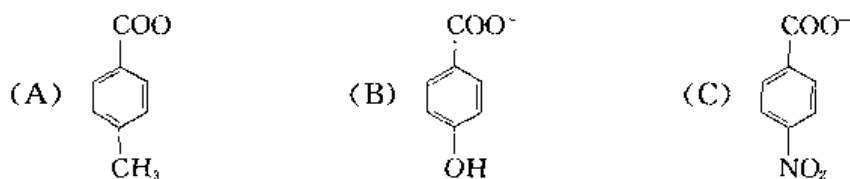
3. 比较吡喃甘露糖结构式的稳定性大小。



4. 将下列碳正离子按稳定性大小排列成序。



5. 将下列负离子按稳定性大小排列成序。



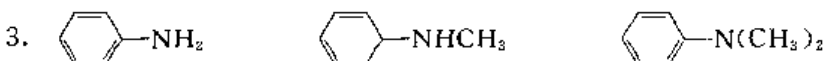
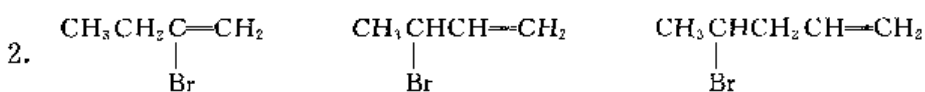
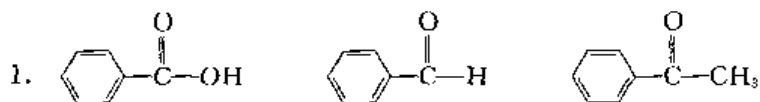
6. 比较下列化合物哪个酸性较强。



7. 比较 (A)、(B) 的碱性大小。



四、用化学方法鉴别下列各组化合物 (8分)



五、请设计分离精制乙酸乙酯粗产物的步骤 (5分)

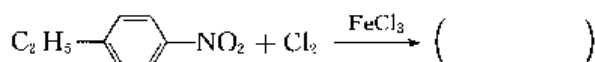
六、推导结构 (9分)

1. 化合物 A (C_7H_8O) 不溶于 $NaHCO_3$ 溶液, 但溶于 $NaOH$ 溶液, 当 A 与溴水作用时, 能迅速生成白色沉淀 B ($C_7H_5OBr_3$)。试写出化合物 A 和 B 的构造式。

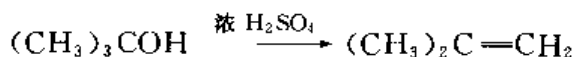
2. 某酯 A ($C_5H_{10}O_2$) 用乙醇钠的乙醇溶液处理后, 生成另一种酯 B ($C_8H_{14}O_3$), B 能使溴水迅速褪色, 依次用乙醇钠、碘乙烷处理 B, 生成 C ($C_{10}H_{18}O_2$)。C 不能使溴水褪色, C 用稀碱水解, 再酸化、加热生成一个酮 D ($C_7H_{14}O$)。D 不起碘仿反应, 进行 Clemmensen 还原反应生成 3-甲基己烷。试推测 A, B, C, D 的构造。

七、反应机理 (6分)

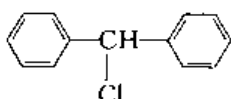
1. 写出下列反应的机理类型和活性中间体及产物结构。

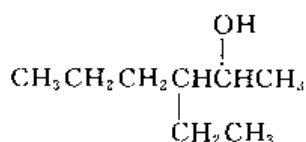


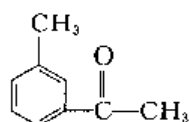
2. 写出下列反应的活性中间体, 并指出其反应机理类型。

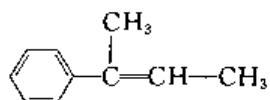


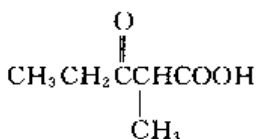
八、有机合成题 (无机试剂任选) (25分, 统考生做)

1. 以苯和甲苯为原料合成 

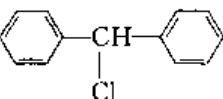
2. 用少于或等于两个碳的有机试剂为原料合成 

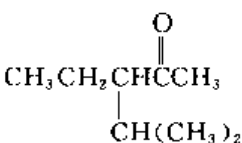
3. 用甲苯和少于或等于两个碳的有机试剂为原料合成 

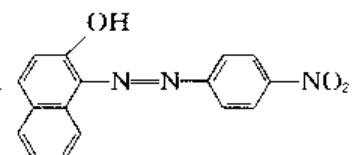
4. 用甲苯和少于或等于两个碳的有机试剂为原料合成 

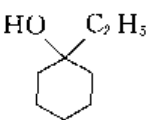
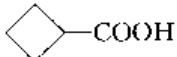
5. 用少于或等于两个碳的有机试剂为原料合成 

九、有机合成题 (无机试剂任选) (25分, 单考生做)

1. 以苯和甲苯为原料合成 

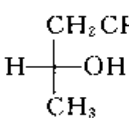
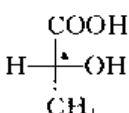
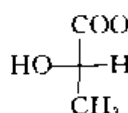
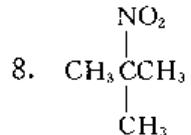
2. 用少于或等于两个碳的有机试剂为原料合成 

3. 以苯和萘为原料 (无机试剂任选) 合成对位红 

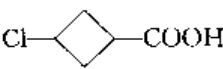
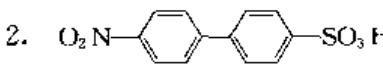
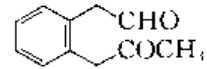
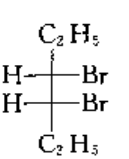
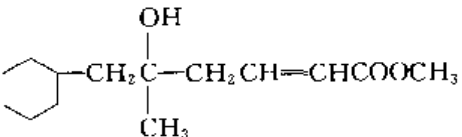
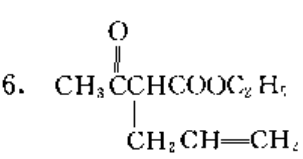
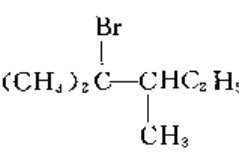
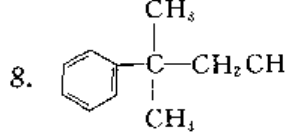
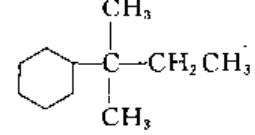
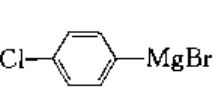
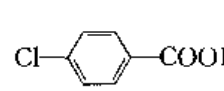
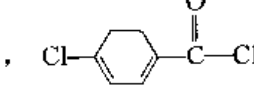
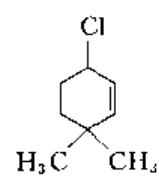
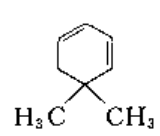
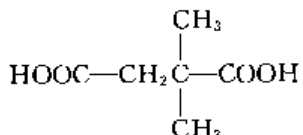
4. 用少于或等于两个碳的有机试剂及环己醇为原料合成 
5. 以丙二酸二乙酯及两个碳以下的有机化合物为原料合成 

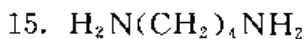
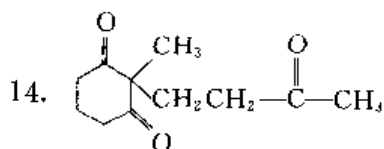
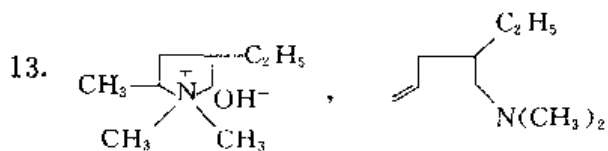
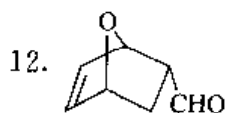
参考答案

一、命名或写结构式

1.  2. (2Z,4R)-4-甲基-2-己烯 3. 2,2-二甲基丙醛
4. 1-氯甲酰基环己烯 5.   6. 糠醛
7. $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$ 8.  9. 2-氯甲酰基-3-戊烯酰氯

二、完成反应式

1.  2.  3. 
4.  5.  6. 
7.  8.  , 
9.  ,  , 
10.  ,  , 
11. $(\text{HOCH}_2)_3\text{C}-\text{CHO}$, $(\text{HOCH}_2)_4\text{C} + \text{HCOONa}$

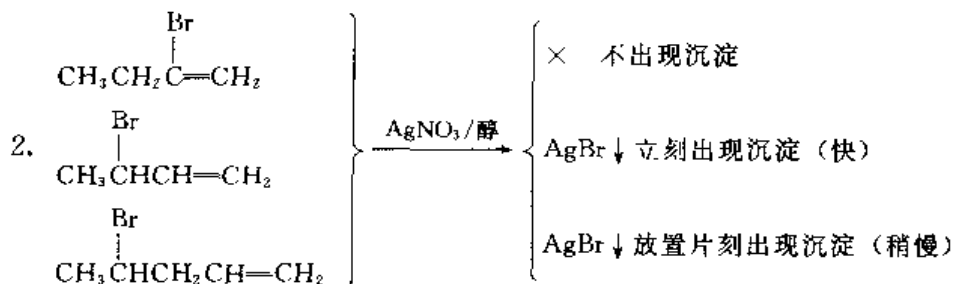
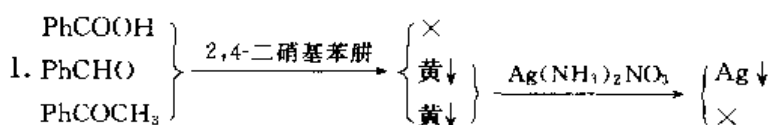


16. 不反应

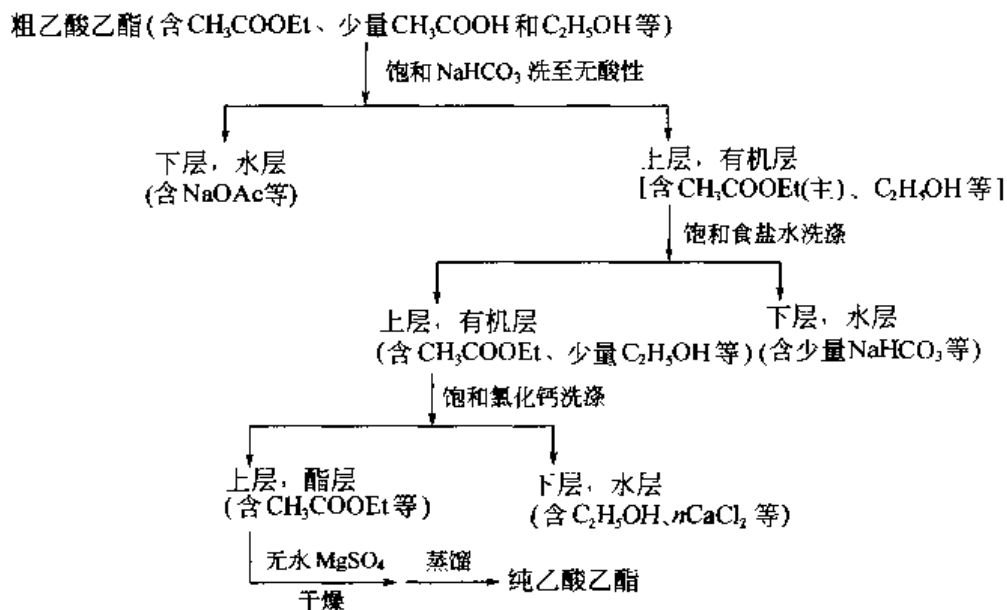
三、基本概念

1. (B) > (C) > (A) 2. (B) > (C) > (A) 3. (A) > (B) 4. (B) > (C) > (A) > (D)
 5. (C) > (A) > (B) 6. 酸性(B) > (A) 7. 碱性(B) > (A)

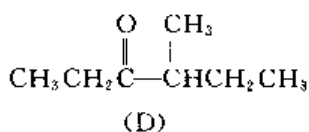
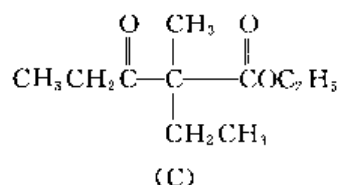
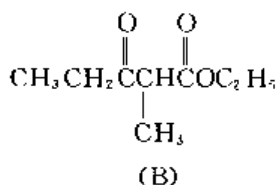
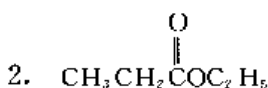
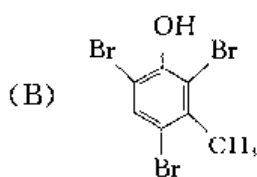
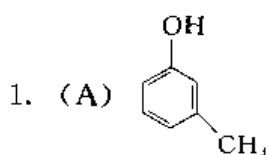
四、用化学方法鉴别下列各组化合物



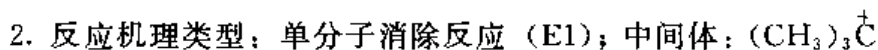
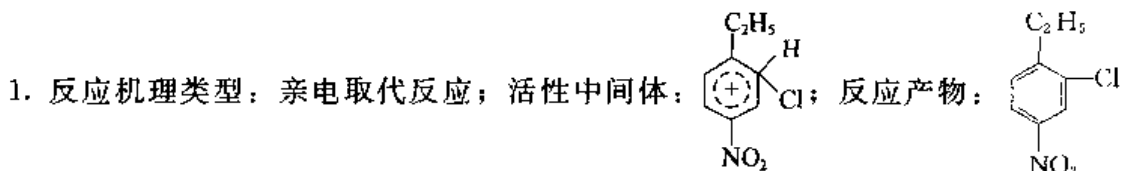
五、分离粗产物



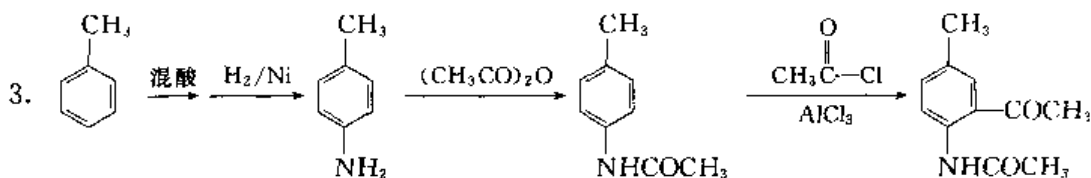
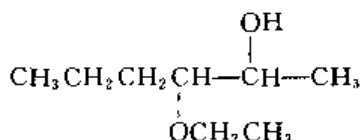
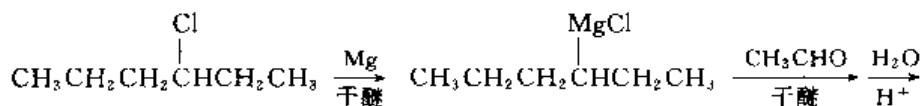
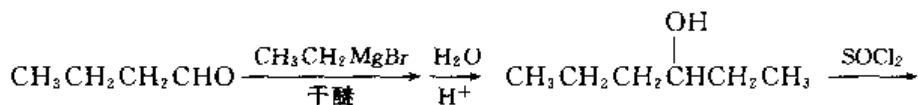
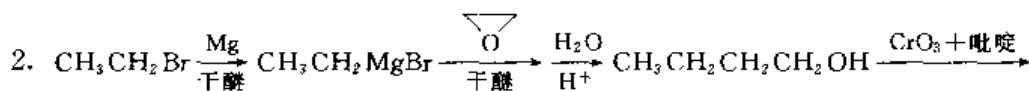
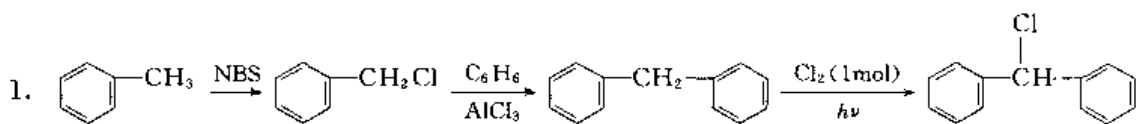
六、推导结构

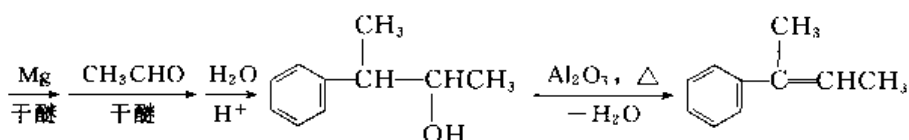
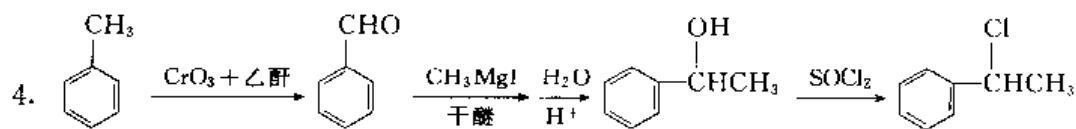
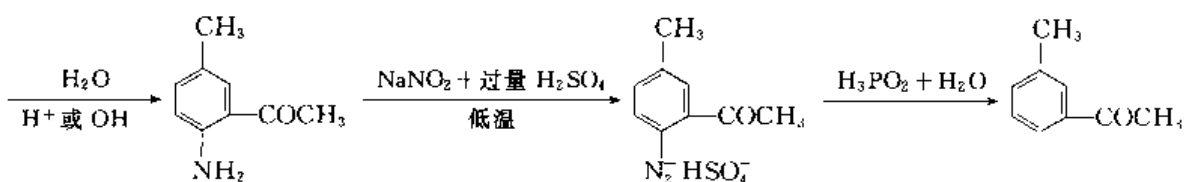


七、反应机理

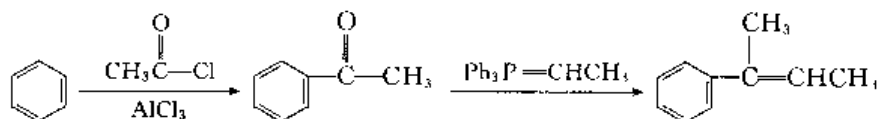


八、有机合成题

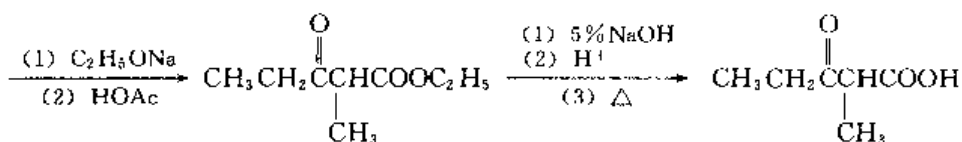
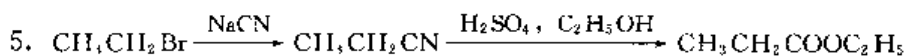
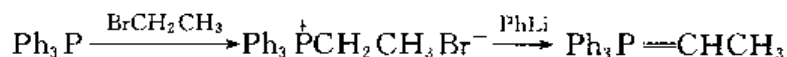




注：题给目标化合物若用苯为起始原料，经 Wittig 反应更易得到。



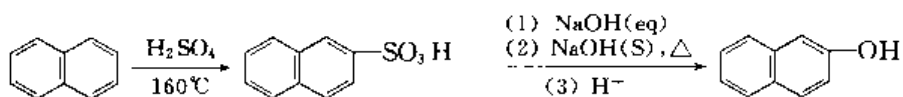
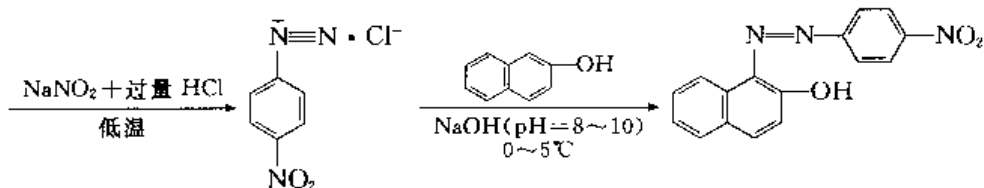
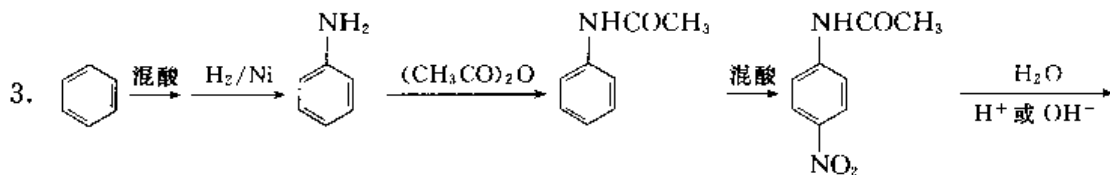
$\text{Ph}_3\text{P}=\text{CHCH}_3$ 的制法：

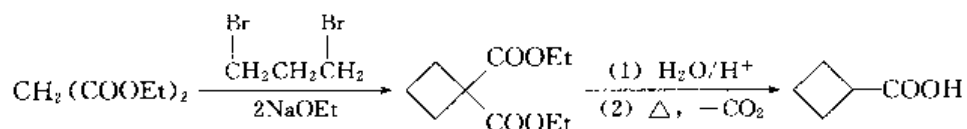
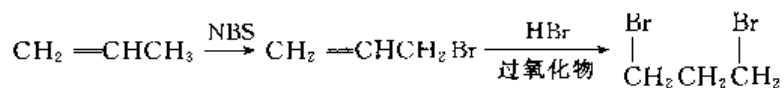
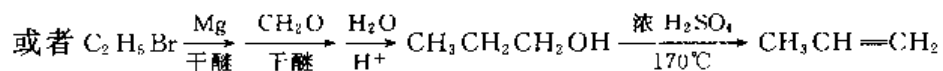
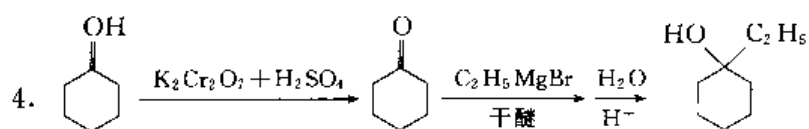


九、有机合成题

1. 略。见本套试题“八、1。”

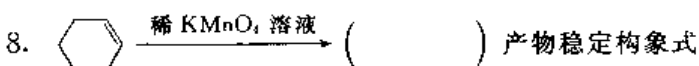
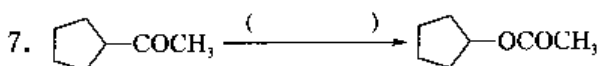
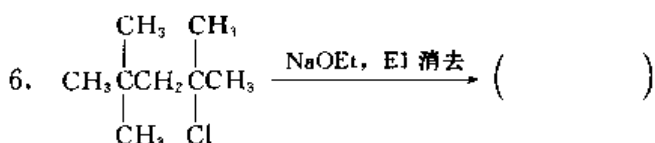
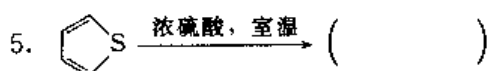
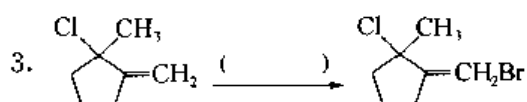
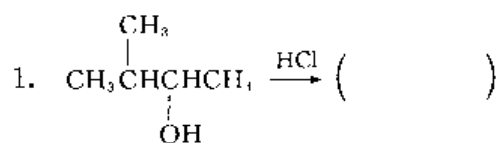
2. 略。见本套试题“八、2。”

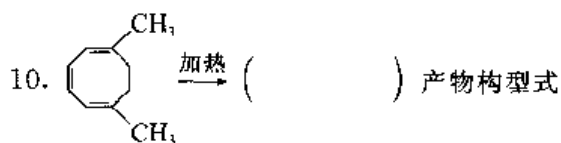
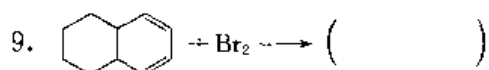




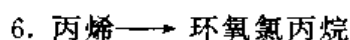
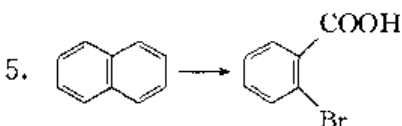
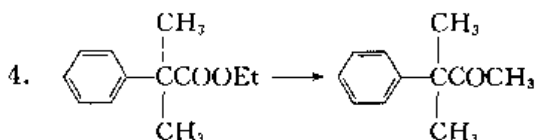
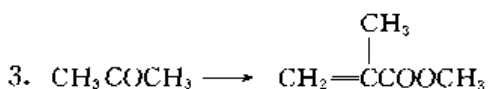
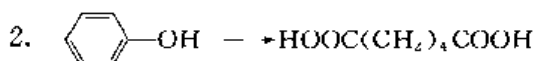
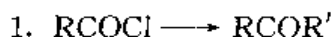
模拟试题 3

一、完成下列反应 (20 分)

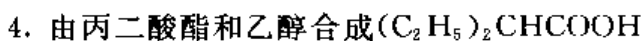
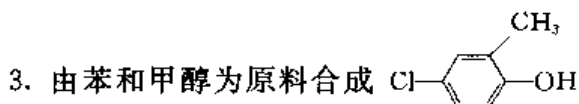
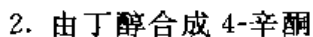
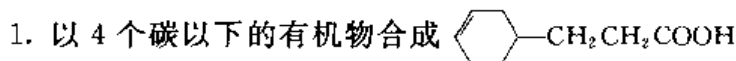




二、完成下列转变 (不超出三步反应式) (18 分)



三、合成题 (无机试剂任选) (1~3 题 5 分, 4 题 4 分, 共 19 分)



四、推测结构 (16 分)

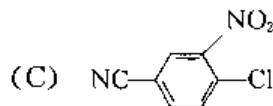
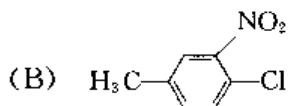
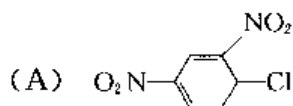
1. 无环化合物 $\text{C}_6\text{H}_{12}\text{O}_2$ 的 IR 谱在 1740 、 1250 和 1060cm^{-1} 出现强的吸收带, 但大于 2950cm^{-1} 无谱带。NMR 谱在 $\delta 3.4$ 和 $\delta 1.0$ 有两个单峰。试推测化合物的结构。(4 分)

2. 化合物 A 与 $\text{Br}_2\text{-CCl}_4$ 溶液作用生成一个三溴化合物 B, A 很容易和 NaOH 水溶液作用, 生成两种同分异构体的醇 C 和 D。A 与 KOH -乙醇溶液作用, 生成一种共轭二烯烃 E, 将 E 臭氧化、锌粉水解后生成乙二醛和 4-氧代戊醛, 试推导 A~E 的构造式。(6 分)

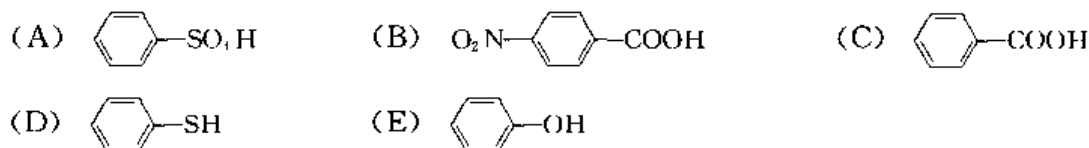
3. 化合物 A, 分子式为 $\text{C}_7\text{H}_8\text{O}_3$, 能溶于氢氧化钠和碳酸钠水溶液, 它与氯化铁有颜色反应, 与乙酸酐作用生成 $\text{C}_8\text{H}_8\text{O}_4$, 在酸催化作用下与甲醇作用生成香味的化合物 $\text{C}_8\text{H}_8\text{O}_3$, $\text{C}_8\text{H}_8\text{O}_3$ 硝化后主要得到一种一元硝基化合物。试写出 A 的构造式及相应的反应式。(6 分)

五、回答问题 (1~4 题 3 分, 5 题 6 分, 6 题 9 分, 共 27 分)

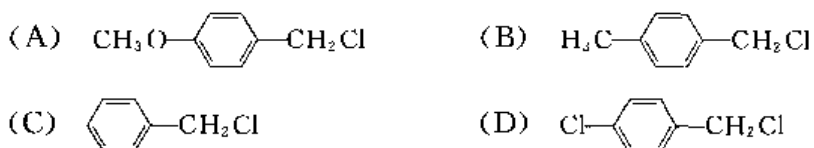
1. 化合物与乙醇钠反应时, 活性最大的是哪一个? 为什么?

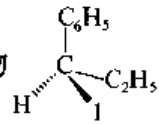


2. 将下列化合物按酸性强弱排序。



3. 比较下列卤代烃在 2% 硝酸银乙醇溶液中反应活性的大小。



4. 化合物  在丙酮水溶液中放置时将会转变成相应的醇，试选择此醇的正确构型。

(A) 构型保持不变 (B) 构型翻转 (C) 外消旋化 (D) 内消旋化

5. 用化学方法鉴别下列各种物质，写出相应的反应式。

(1) 甲醇、乙醇、乙二醇、丙三醇；(3分)

(2) 甲酸乙酯、乙酸乙酯、乙酸乙烯酯；(3分)

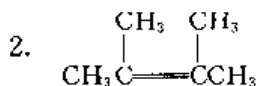
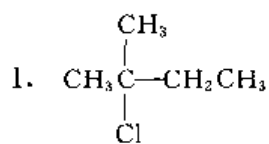
6. 以图解式及简要的叙述回答下列问题。

(1) 用化学方法分离苯甲酸、丁醚、环己酮和苯酚。(6分)

(2) 在由石蜡制备高级脂肪酸时，除产物外尚有未反应的石蜡和副产物醇、醚、酮等含氧衍生物。应如何分离出脂肪酸？(3分)

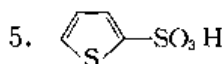
参考答案

一、完成反应式



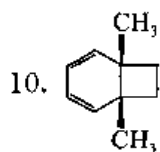
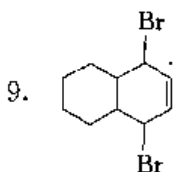
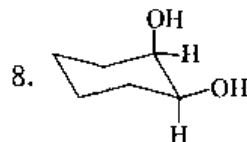
3. HBr, 过氧化物

4. Zn-Hg/HCl

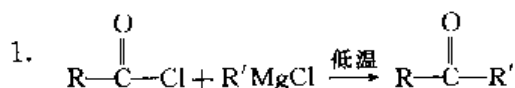


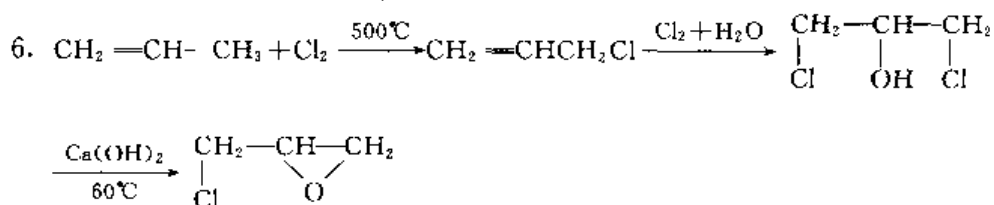
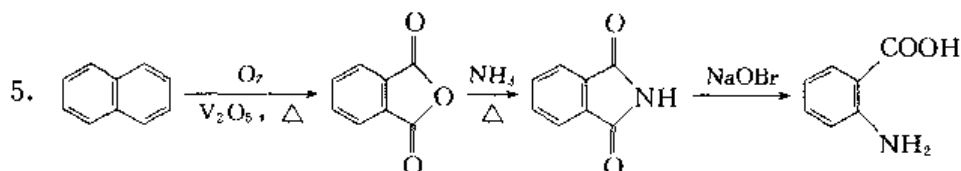
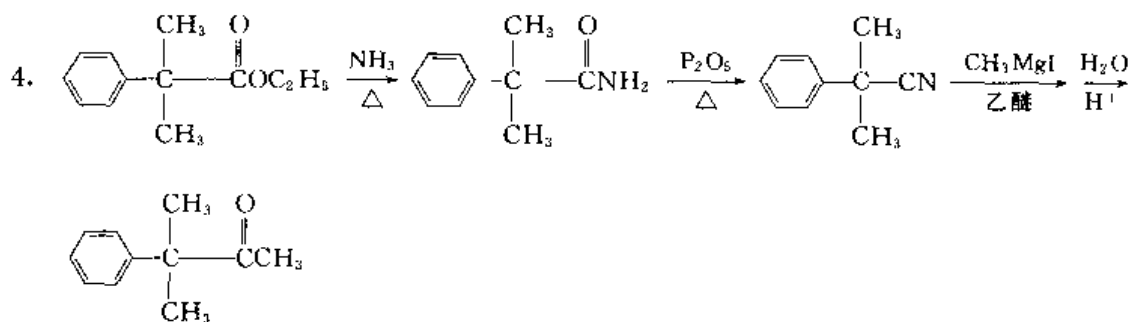
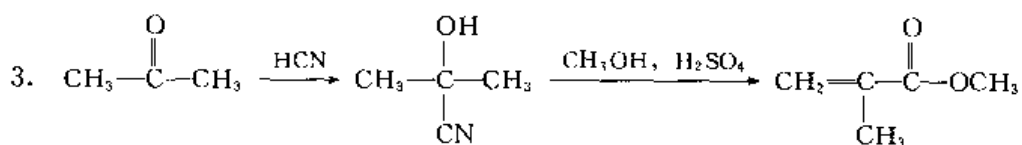
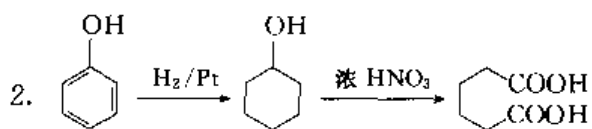
6. $(\text{CH}_3)_3\text{CH}=\text{C}(\text{CH}_3)_2$

7. $\text{CF}_3\text{CO}_3\text{H}$

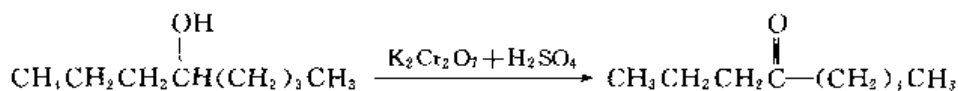
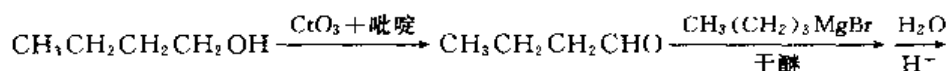
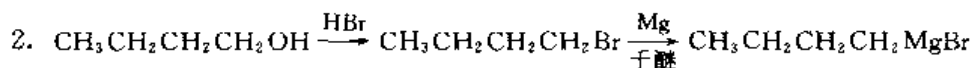
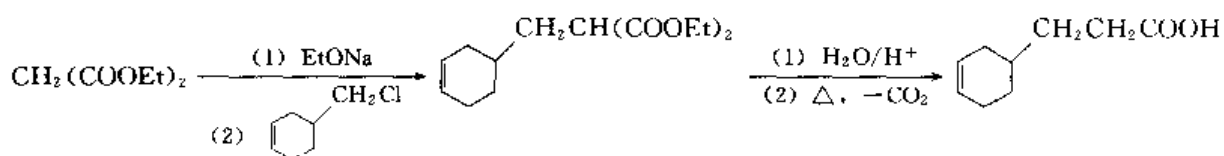
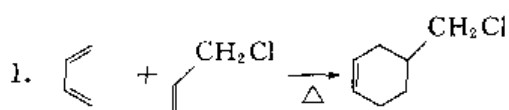


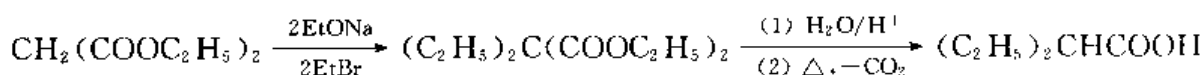
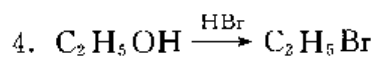
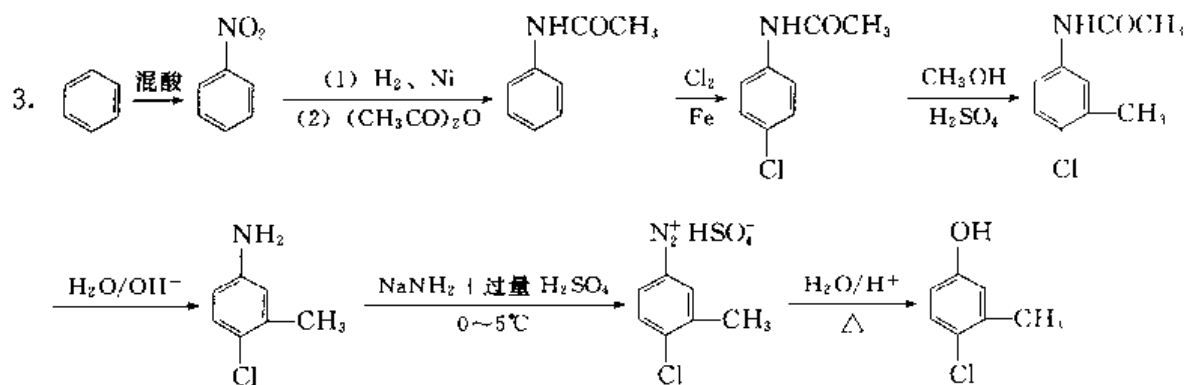
二、完成下列转变



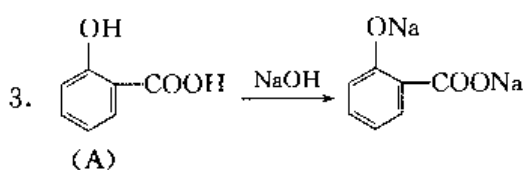
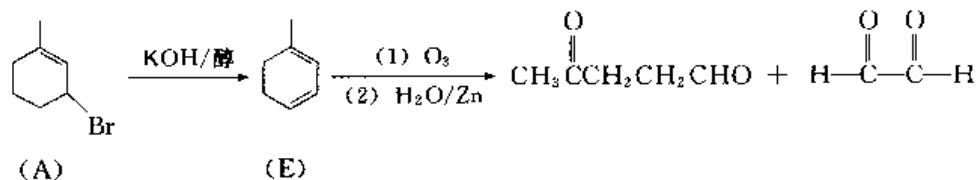
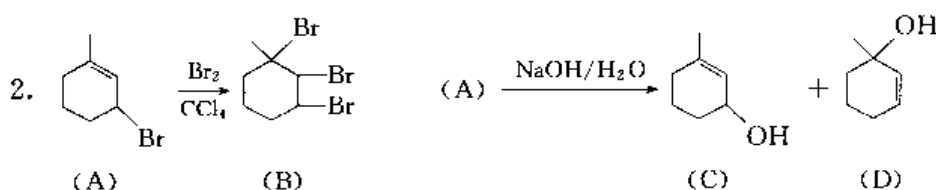
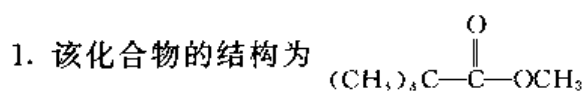


三、合成题





四、推测结构



五、回答问题

1. 反应活性: (A) > (C) > (B)。

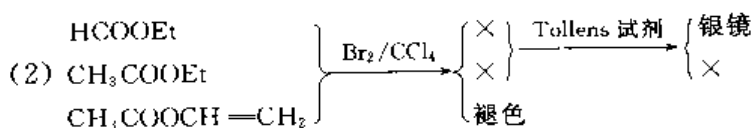
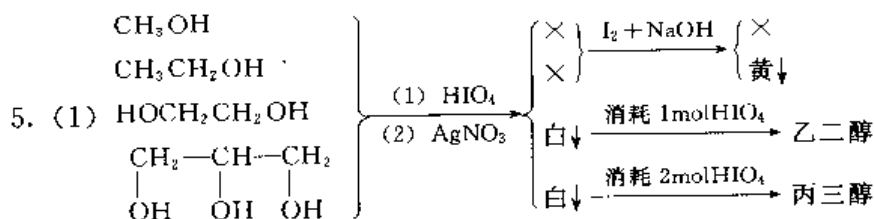
原因: (A) 中 Cl- 的邻、对位有强吸电子基 NO₂-, 使氯原子容易被亲核试剂所取代。

(C) 中 Cl—的对位有 CN—, 吸电子能力不如 NO₂—, 使氯原子亲核取代的反应活性降低。

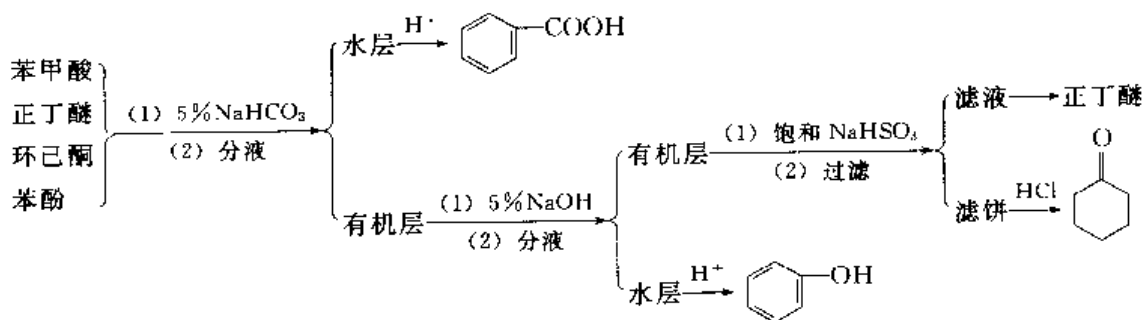
(B) 中 Cl—的对位有给吸电子基 CH₃—, 使氯原子不容易被亲核试剂所取代。

2. 酸性: (A) > (B) > (C) > (D) > (E)。

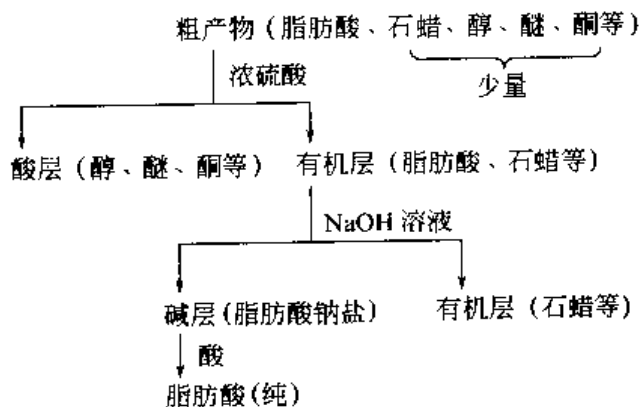
3. 反应活性: (A) > (B) > (C) > (D)。 4. (3)



6. (1)



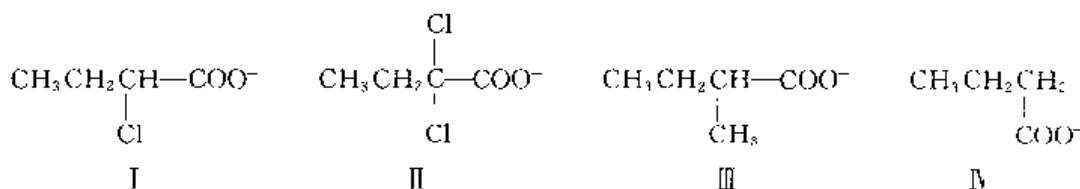
(2)



模拟试题 4

一、选择、填空 (10 分)

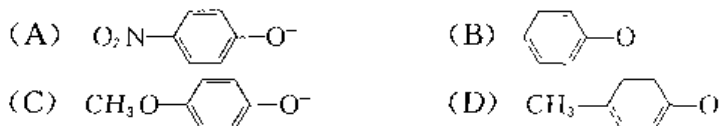
1. 化合物



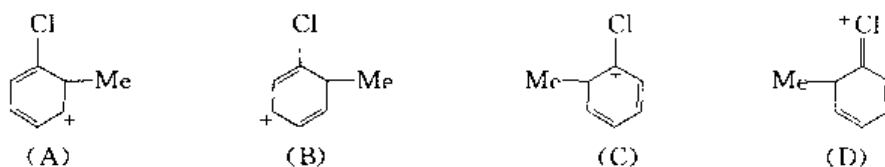
碱性强弱次序是 ()

- (A) I > II > III > IV (B) II > III > I > IV
 (C) III > II > I > IV (D) III > IV > I > II

2. 下列离子中亲核性最强的是 ()



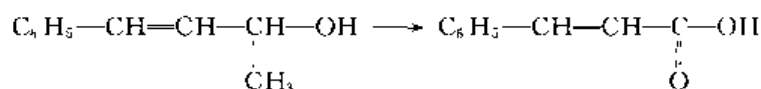
3. 下列共振结构式中 () 共振结构对共振杂化体的贡献最大。



4. 将下列离子按离去基团的难易排序: ()

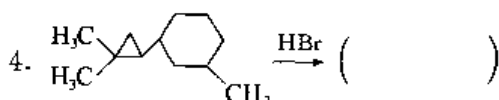
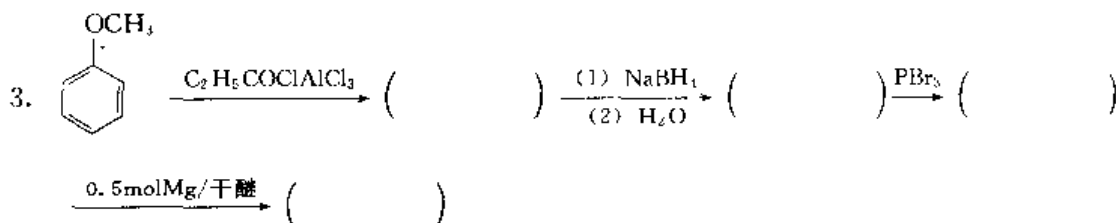
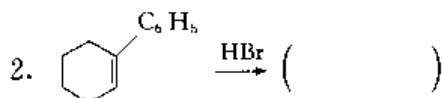
- (A) 对甲苯磺酸酯基 (B) I⁻ (C) RO⁻ (D) HO⁻ (E) NH₂⁻

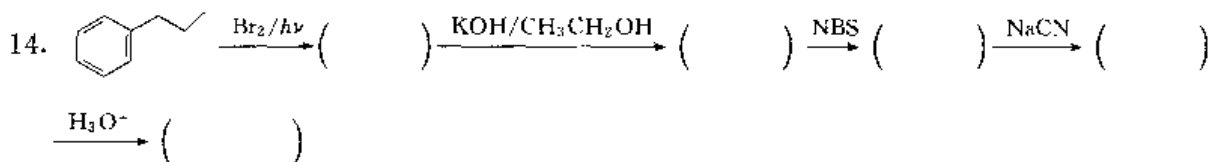
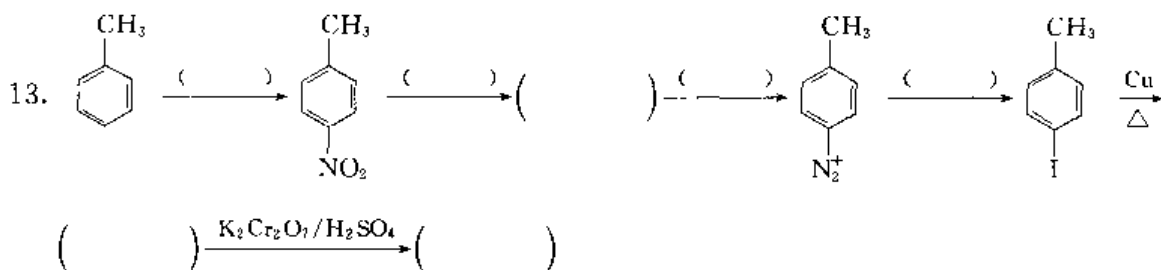
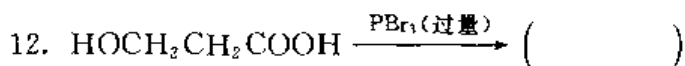
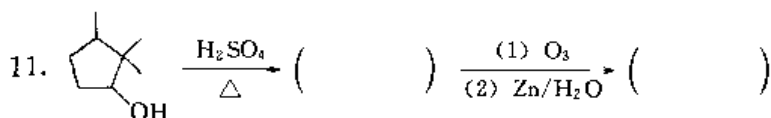
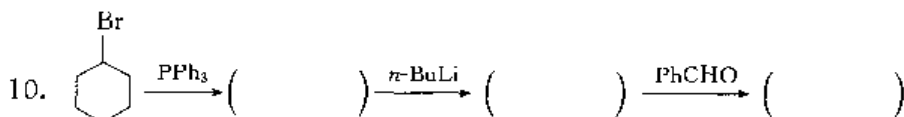
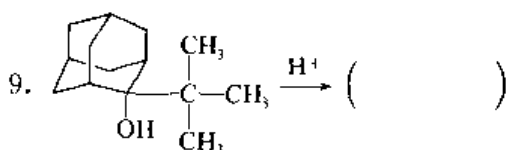
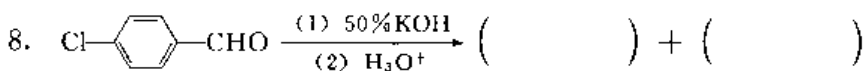
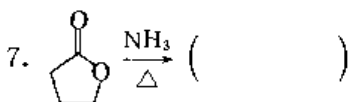
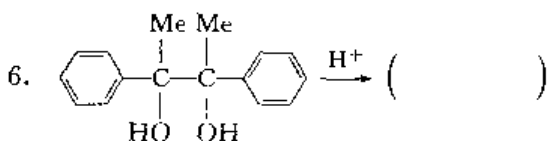
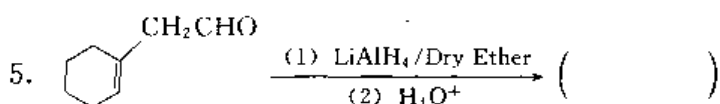
5. 下列反应应该选择 () 作为氧化剂。



- (A) I₂/NaOH (B) O₃ (C) KMnO₄ (D) HNO₃

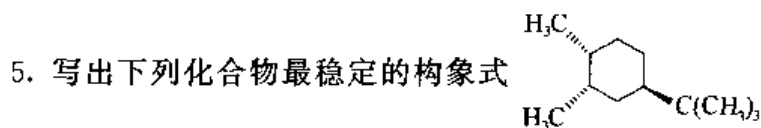
二、完成下列反应 (32分)



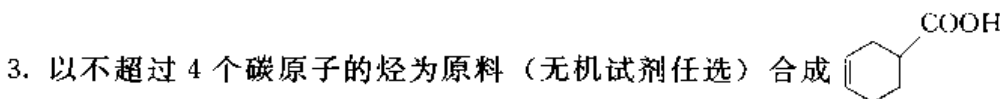
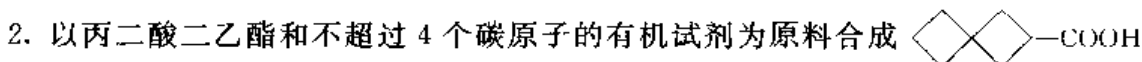
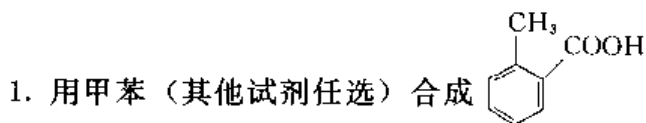


三、简答题 (15分)

1. 写出具有最低相对分子质量且含有一个手性碳原子的一氯代烷的构造式，画出其 S 构型。
2. 在由 1-氯丁烷和 NaOH 溶液合成正丁醇时，往往在体系里加入少量 KI，为什么？
3. 请写出 α -咪喃甲醛和 3-乙基喹啉的结构式。
4. 请画出乙酸乙酯的 $^1\text{H-NMR}$ 草图。



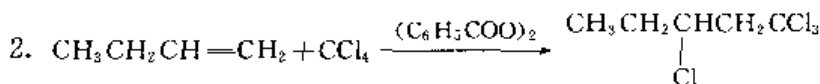
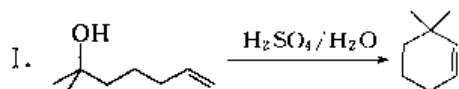
四、合成题 (用指定原料合成所需产物。15 分)



五、用化学方法鉴别下列化合物 (10 分)

1. 异丁烷 2. 环戊二烯 3. 1-丁炔 4. 甲基环丙烷 5. 1-丁烯

六、写出下列反应机理 (8 分)



七、推测结构 (10 分)

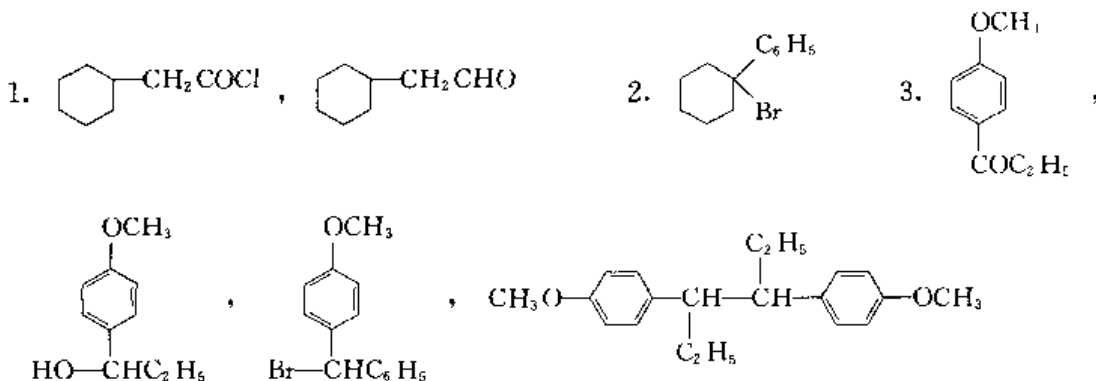
有未知化合物 A、B, 经元素分析, C 含量为 92.31%, H 含量为 7.69%。该化合物不与金属钠反应, 易被 KMnO_4 氧化, 从该两未知物的质谱分析看出, 分子离子峰都在 $m/z = 120$; 从 $^1\text{H-NMR}$ 分析分别可得下述峰值: 对于 A, δ 1.25 (双重峰, 6H); δ 2.95 (七重峰, 1H); δ 7.25 (单峰, 5H)。对于 B, δ 2.25 (单峰, 9H); δ 6.78 (单峰, 3H)。试推测未知化合物 A、B 的结构, 且归属每种氢的化学位移。

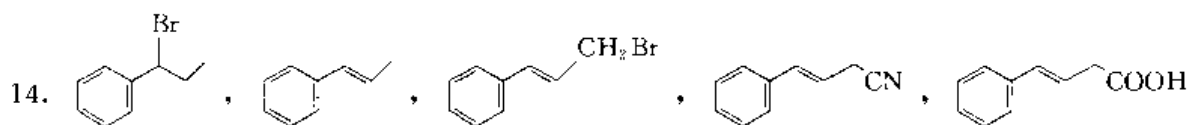
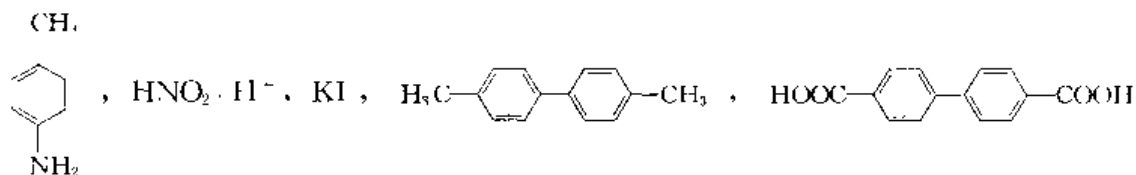
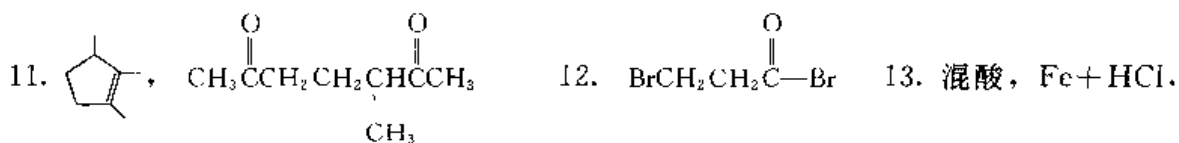
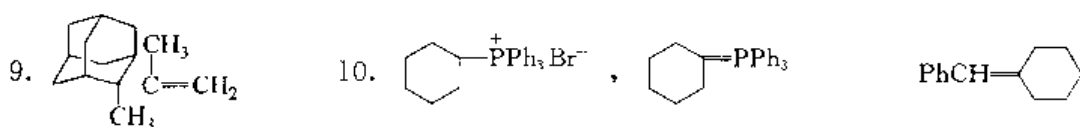
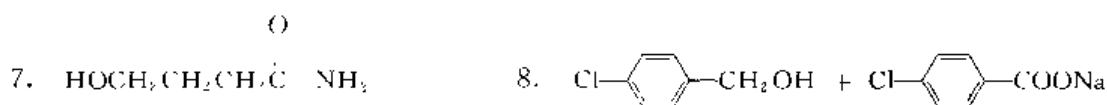
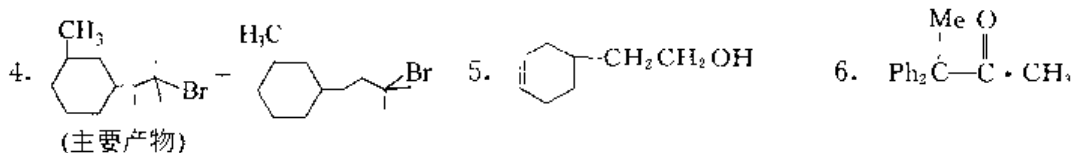
参考答案

一、选择、填空

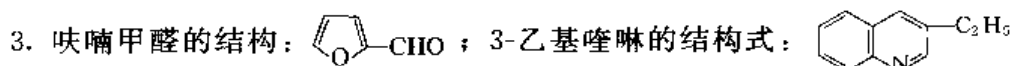
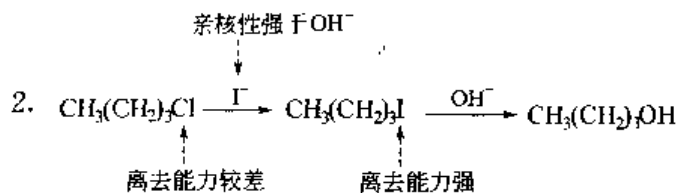
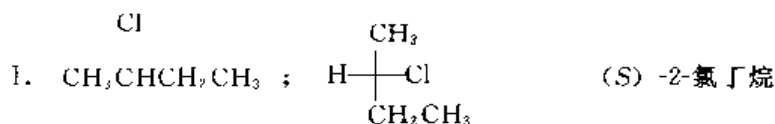
1. (D) 2. (C) 3. (D) 4. (A) > (B) > (D) > (C) > (E) 5. (A)

二、完成反应式

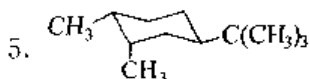




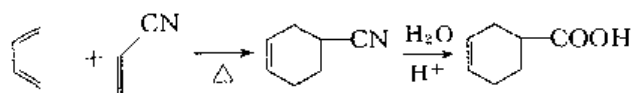
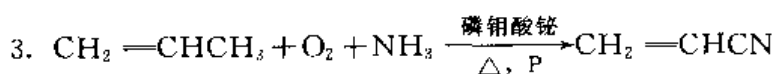
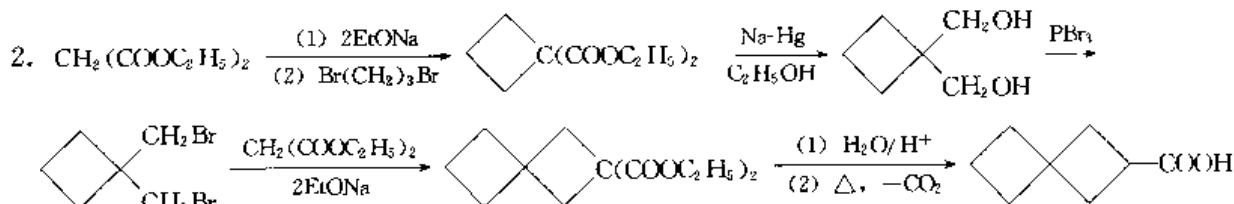
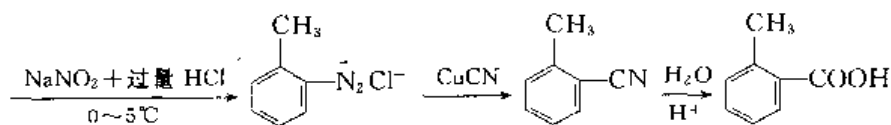
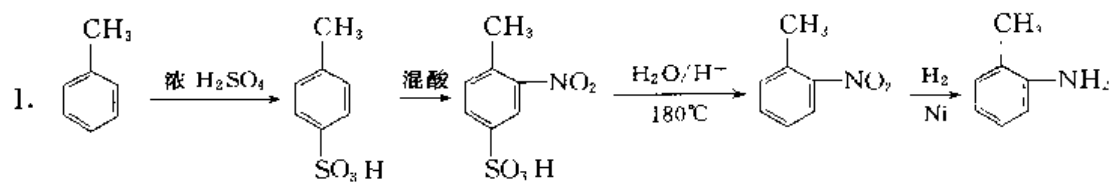
三、简答题



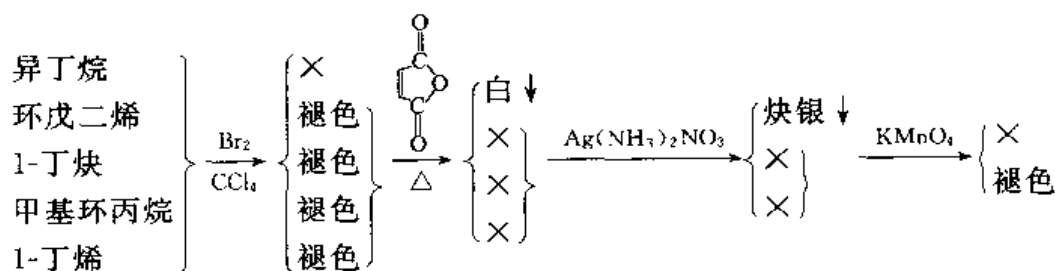
4. 略。



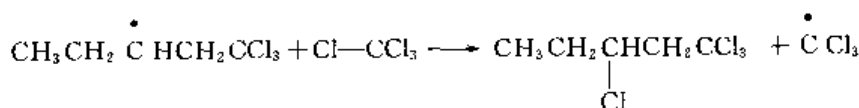
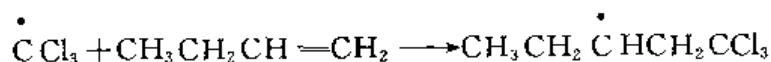
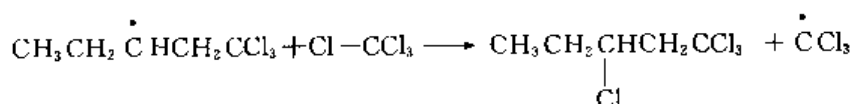
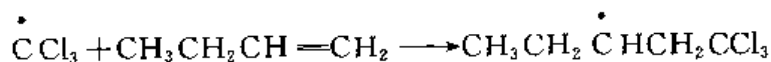
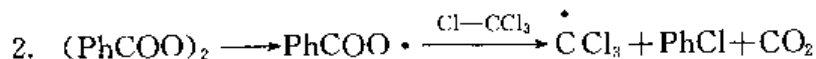
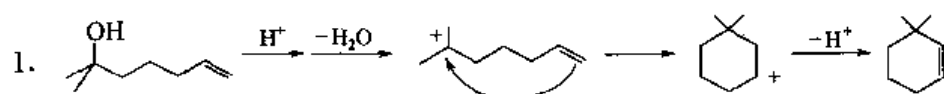
四、合成题



五、用化学方法鉴别下列化合物

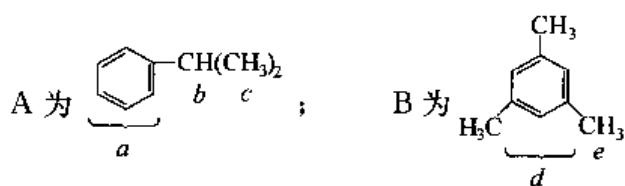


六、反应机理



...

七、推测结构



各种氢的化学位移:

δ_{H_a} 7.25 (单峰, 5H)

δ_{H_b} 2.95 (七重峰, 1H)

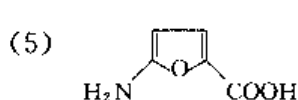
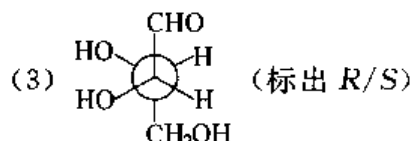
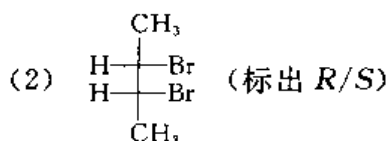
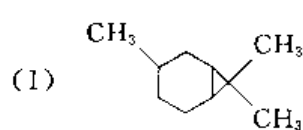
δ_{H_c} 1.25 (二重峰, 6H)

δ_{H_d} 6.78 (单峰, 3H)

δ_{H_e} 2.25 (单峰, 9H)

模拟试题 5

一、命名下列化合物 (5分)



二、写出下列化合物的结构式 (5分)

(1) 顺-3-甲基环己甲酰胺的最稳定构象

(2) 螺[4.5]-6-癸烯

(3) (2S,3R)-2,3-二甲氧基丁烷

(4) 1,3,5-三甲基苯

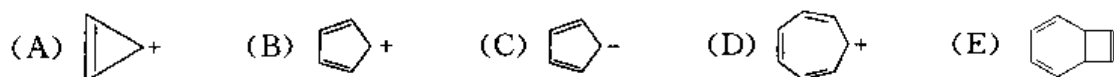
(5) N-甲基-2,4-二氨基苯胺

三、有机化合物性质比较 (10分)

1. 将下列化合物按碱性强弱顺序排列。

(A) 苯胺 (B) 苄胺 (C) 吡咯 (D) 吡啶

2. 下列分子或基团中哪些具有芳香性?



3. 下列分子哪些能进行碘仿反应?

(A) HCHO

(B) CH₃CHO

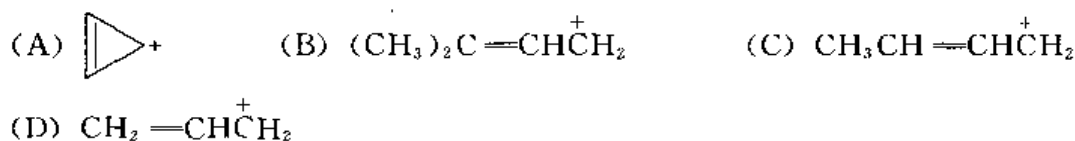
(C) (CH₃)₂CHOH

(D) (CH₃)₃CCHO

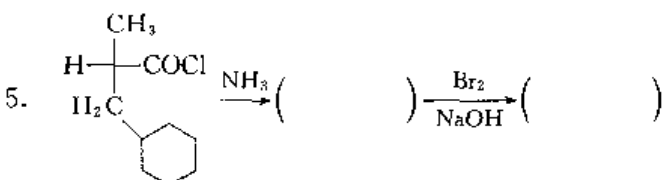
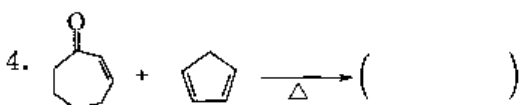
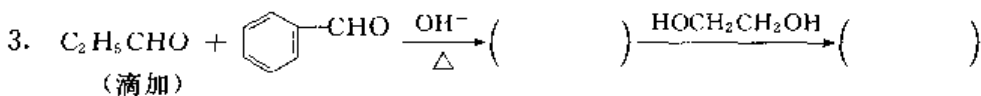
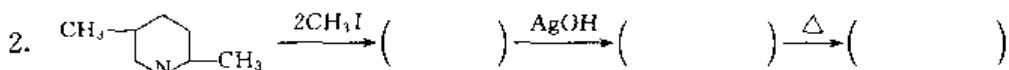
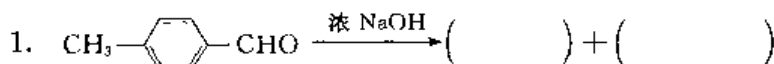
(E) (CH₃CH₂)₂CHOH

(F) (CH₃)₂C=O

4. 将下列离子按稳定性大小排列。



四、完成反应式 (10分)



五、用化学方法鉴别下列化合物 (10分)

1. (1) 苯胺 (2) *N*-甲基苯胺 (3) *N,N*-二甲基苯胺 (4) 苯酚 (5) 苯甲酸
 2. (1) 氯乙烷 (2) 氯乙烯 (3) 3-氯丙烯 (4) 氯苯 (5) 氯苄

六、用化学方法分离下列混合物 (10分)

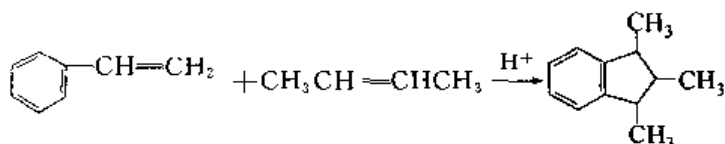
- (1) 苯甲酸 (2) 苯酚 (3) 环己酮 (4) 苯甲醚

七、有机化合物结构推导 (10分)

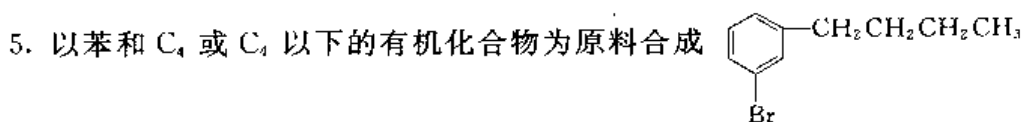
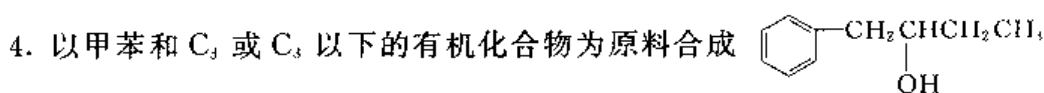
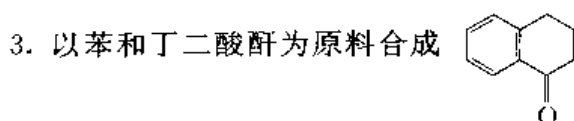
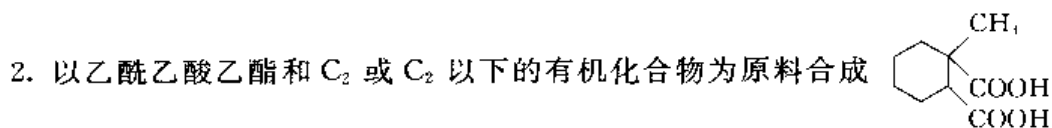
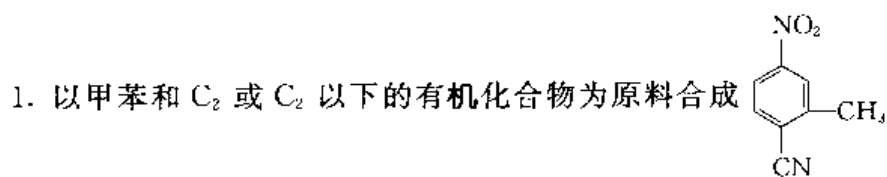
(1) 化合物 A, B 的分子式均为 $\text{C}_9\text{H}_{10}\text{O}_2$ 。化合物 A 的 IR 特征峰如下: 1742cm^{-1} , 1232cm^{-1} , 1028cm^{-1} , 764cm^{-1} , 690cm^{-1} ; $^1\text{H-NMR}$ 谱如下: δ 2.02 (单峰, 3H), δ 5.03 (单峰, 2H), δ 7.26 (单峰, 5H)。化合物 B 的 $^1\text{H-NMR}$ 谱如下: δ 2.7 (三重峰, 2H), δ 3.2 (三重峰, 2H), δ 7.38 (单峰, 5H), δ 10.09 (单峰, 1H)。试推导 A、B 的构造式。

(2) 某化合物的分子式为 $\text{C}_6\text{H}_{12}\text{O}$, 能与羟胺作用生成脎, 但不起银镜反应, 在铂催化下进行加氢得到醇, 此醇经去水、臭氧化、水解等反应后得到两种液体, 其中之一能起银镜反应但不起碘仿反应, 另一种能起碘仿反应, 但不能使费林试剂还原。写出该化合物的构造式。

八、写出下列反应的反应机理 (10分)



九、有机化合物的合成 (无机试剂任选) (30 分)



参考答案

一、命名

(1) 3,7,7-三甲基双环[4.1.0]庚烷

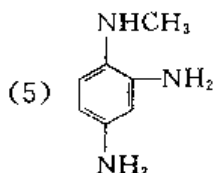
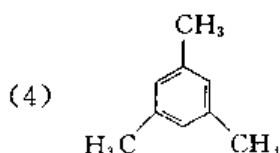
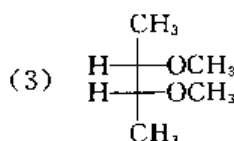
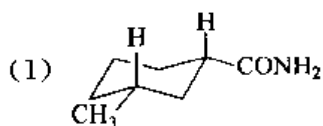
(2) (2*R*,3*S*)-2,3-二溴丁烷

(3) (2*S*,3*R*)-2,3,4-三羟基丁醛

(4) *Z*-5-甲基-4-乙基-2-己烯

(5) 5-氨基-2-咪唑甲酸

二、写结构



三、有机化合物性质比较

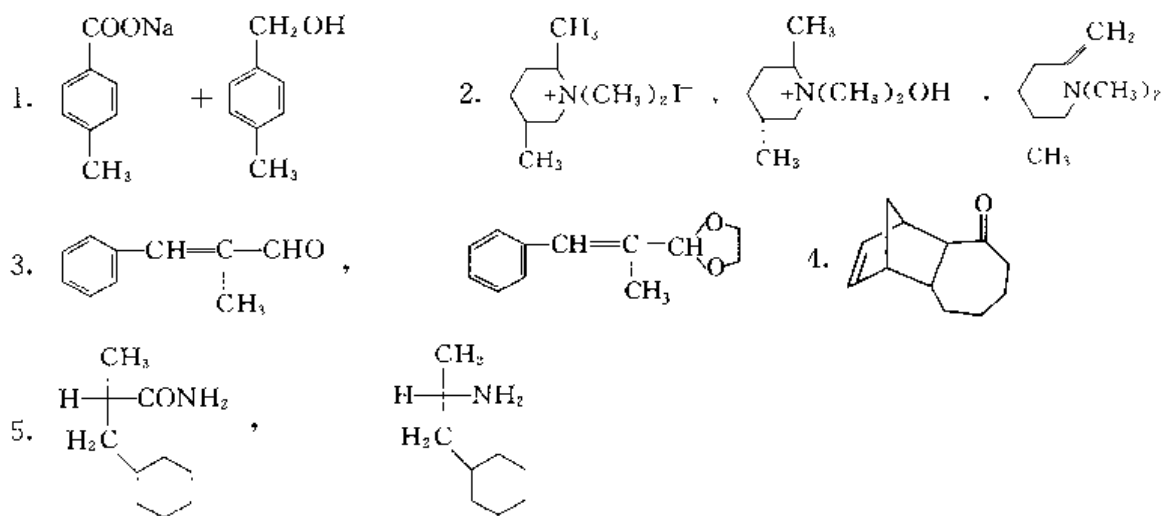
1. 碱性: (B) > (D) > (A) > (C)

2. (A)、(C)、(D)有芳香性

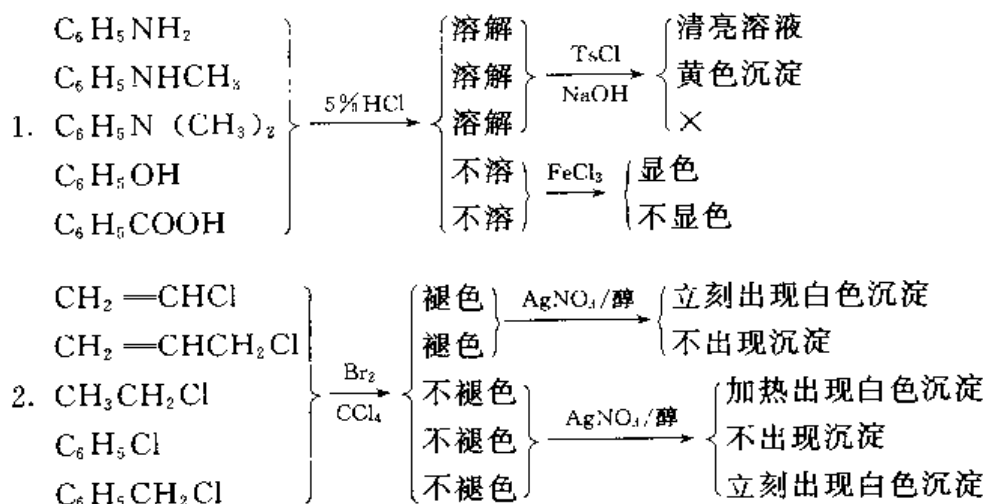
3. (B)、(C)、(F)有碘仿反应

4. 稳定性: (A) > (B) > (C) > (D)

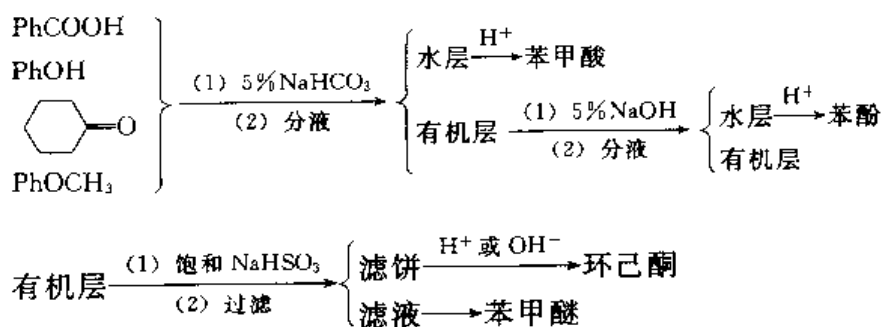
四、完成反应式



五、用化学方法鉴别下列化合物



六、用化学方法分离下列混合物

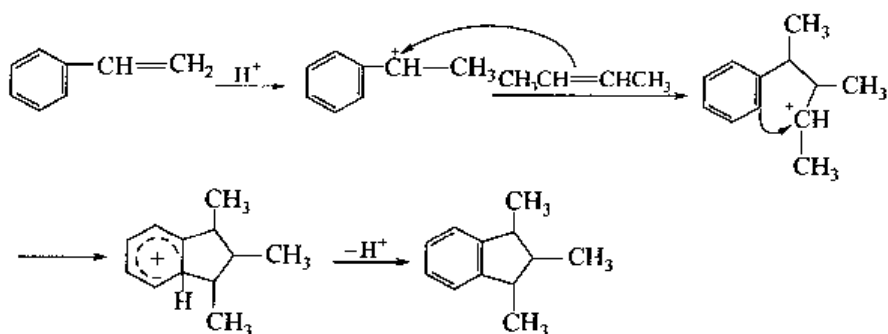


七、有机物结构推导

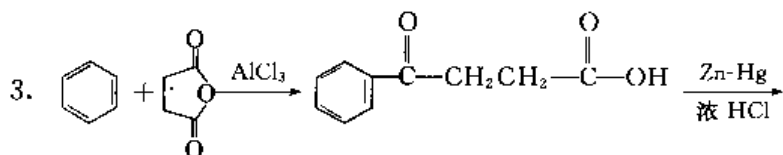
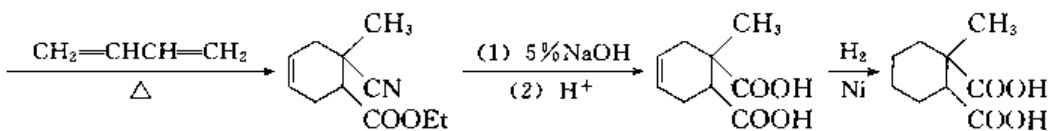
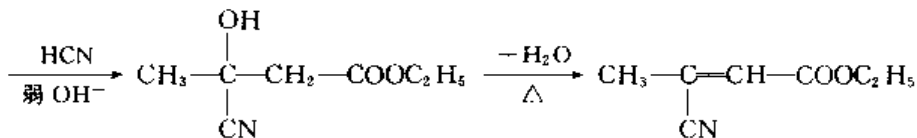
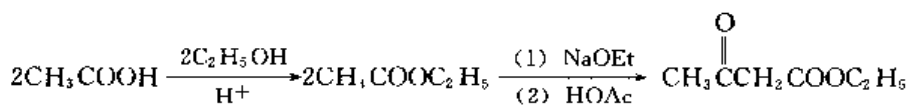
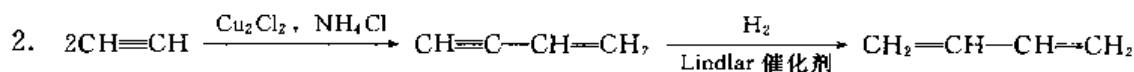
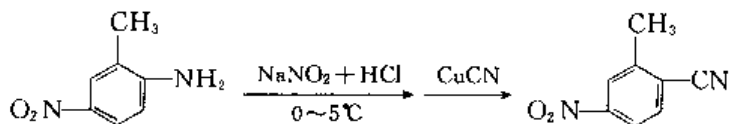
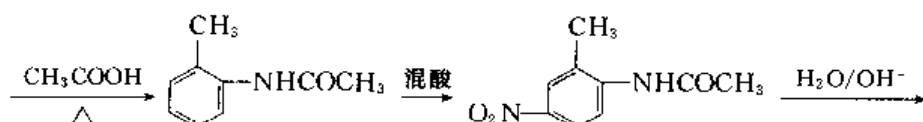
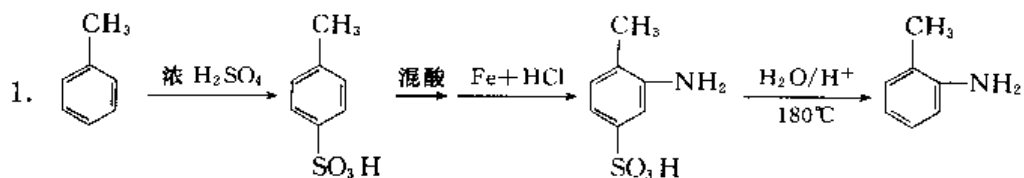


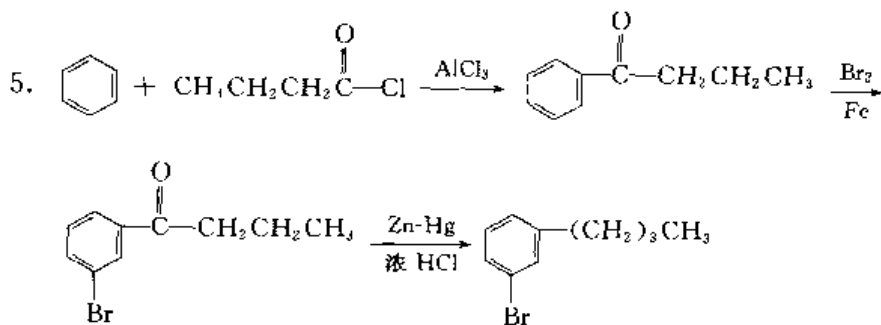
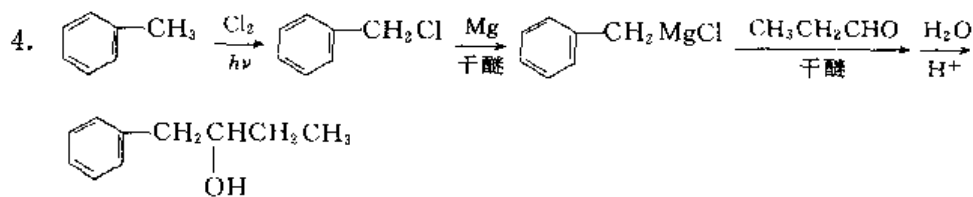
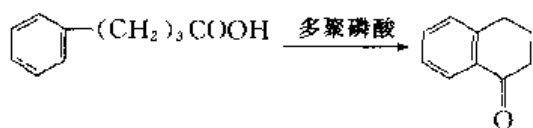
2. 该化合物为： $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{O}}{\text{C}}}-\text{CH}_2\text{CH}_3$

八、反应机理



九、合成



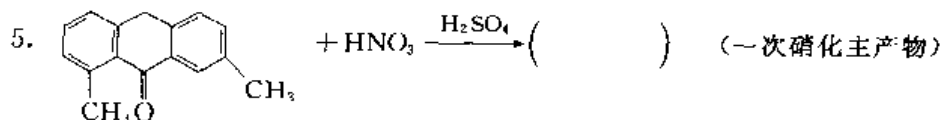
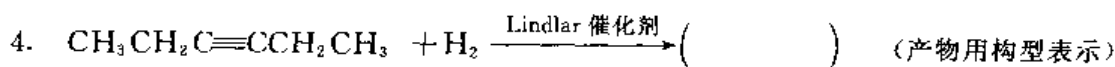
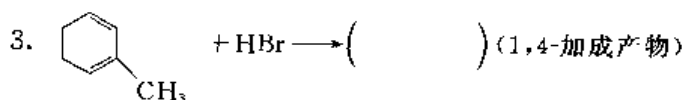
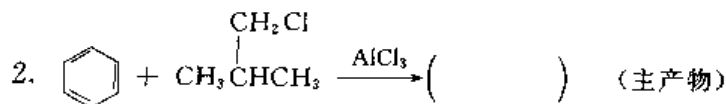
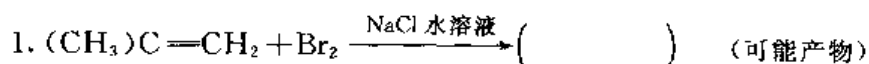


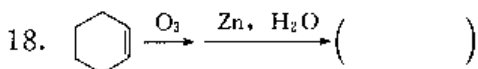
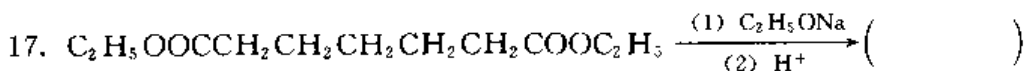
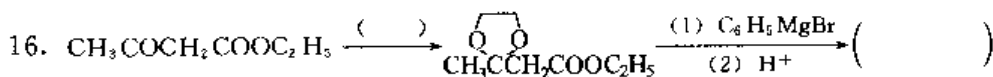
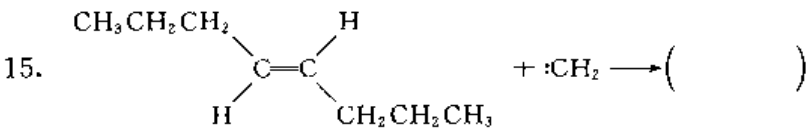
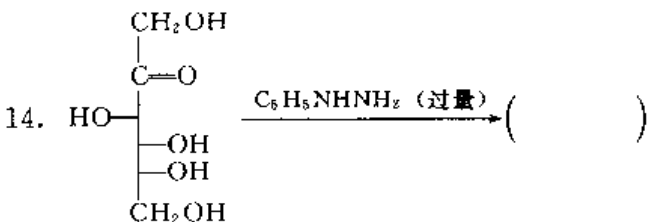
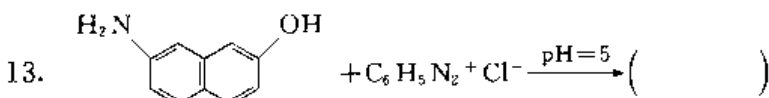
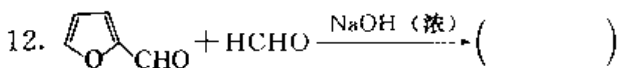
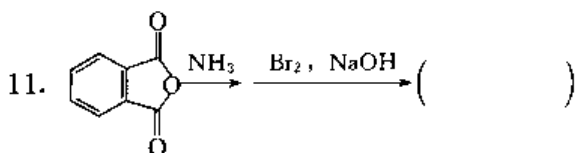
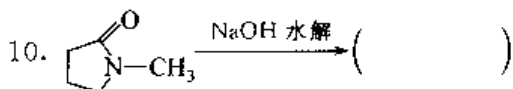
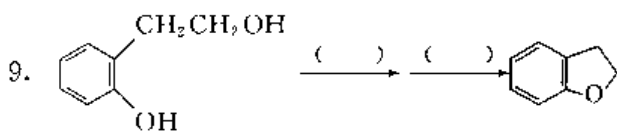
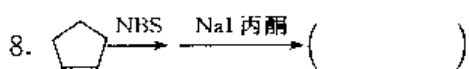
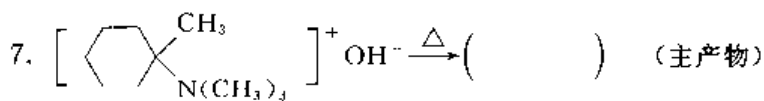
模拟试题 6

一、写出下列化合物的结构式。(15分)

1. Z-1-氯-2-溴-1-碘-1-丁烯
2. 7,7-二氯双环[4.1.0]庚烷
3. 异戊醇
4. D-(+)-甘油醛
5. (2S,3R)-2,3,4-三羟基丁醛
6. 甲醛苯腙
7. 3-(1-甲基-8-氨基-2-萘基)丁酸
8. 对甲苯胺
9. 邻氯甲酰苯甲酸乙酯
10. 碘化N,N-二甲基四氢吡啶

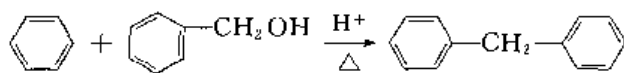
二、按要求完成下列反应式。(30分)



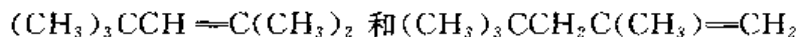


三、回答下列问题。(20分)

1. 写出下列反应的历程。



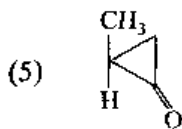
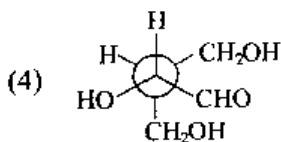
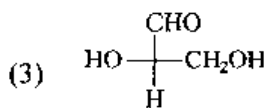
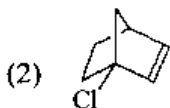
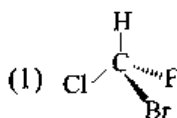
2. 写出异丁烯被 50% H_2SO_4 吸收后在 100°C 时得到下列二聚体的反应过程。



3. 说明直形冷凝管、球形冷凝管、空气冷凝管这 3 种冷凝管分别在什么场合使用?

4. 为什么芳香族重氮正离子 ($\text{Ar}-\text{N}\equiv\text{N}^+$) 比脂肪族重氮正离子 ($\text{R}-\text{N}\equiv\text{N}^+$) 稳定, 请解释之。

5. 将下列化合物中的每个手性碳原子标以 (R) 或 (S)。(任选 4 小题)



6. 用一种具有明显鉴别现象的化学试剂区别下列各组化合物。(任选 5 小题)

(1) 对氯苯甲酸和苯甲酰氯

(2) 苯甲酸甲酯和苯甲酰胺

(3) 2-丁烯-1-醇和 3-丁烯-1-醇

(4) 丙烯和环丙烯

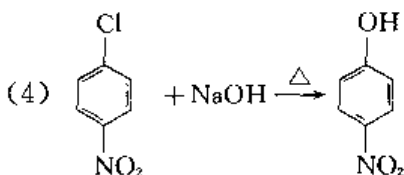
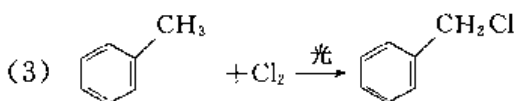
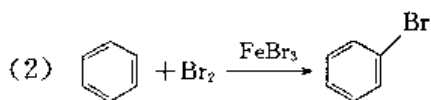
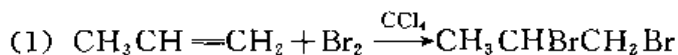
(5) 乙酸乙酯和乙酰乙酸乙酯

(6) 水杨酸和安息香酸

(7) 葡萄糖和 α -甲基葡萄糖苷

(8) 丙酮和丙醛

7. 写出下列反应过程中出现的活性中间体。



四、合成题 (任选 7 小题) (35 分)

有机物只能在下列原料中选用, 无机物任选。

原料: 乙烯、乙炔、苯、甲基环丙烷、甲醇、乙醇。

1. 3-甲基-3-庚烯

2. 3-甲基-1-戊醇

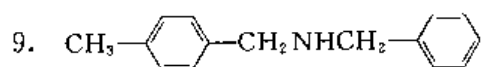
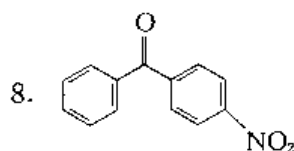
3. 2-己酮

4. 3-甲基-2-戊酮

5. 3,5-二溴甲苯

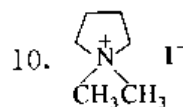
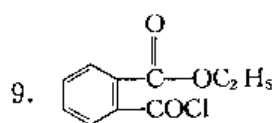
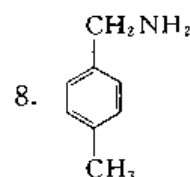
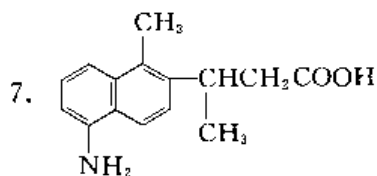
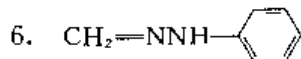
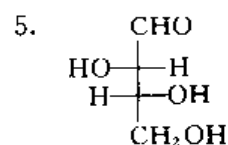
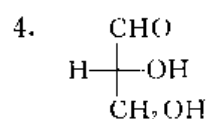
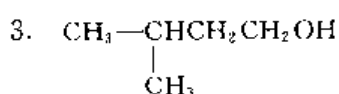
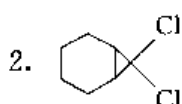
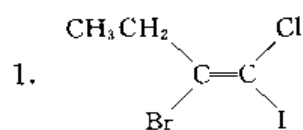
6. 己二酸

7. 顺丁烯二酸二乙酯

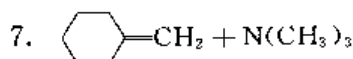
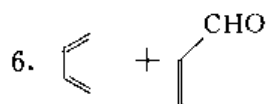
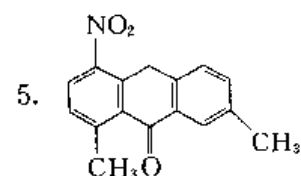
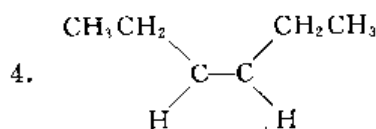
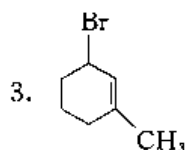
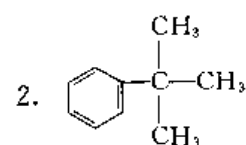
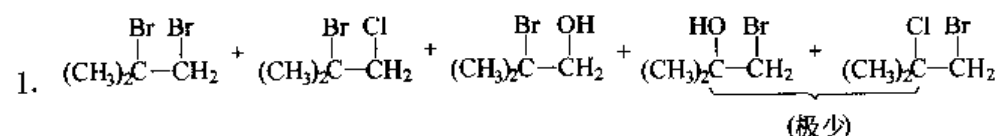


参考答案

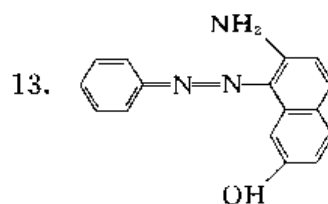
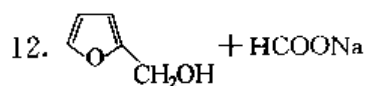
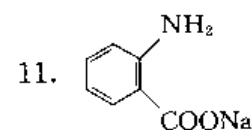
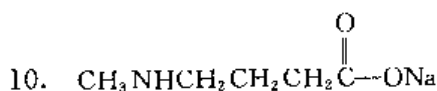
一、写结构式

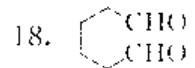
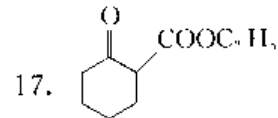
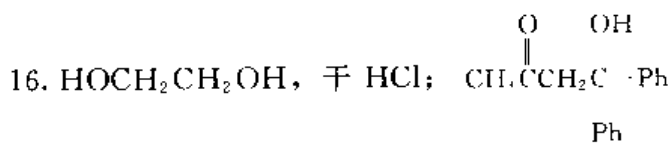
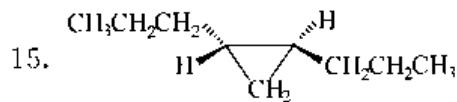
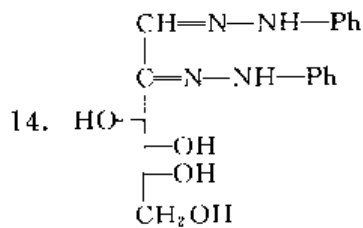


二、完成反应式

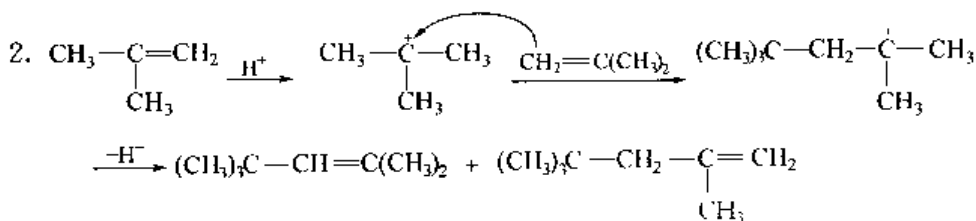
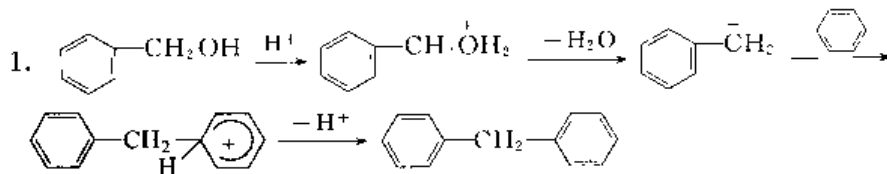


9. (1) PBr_3 或 SOCl_2 , (2) NaOH , Δ





三、回答问题



3. 直形冷凝管用于蒸馏操作；球形冷凝管用于回流操作；空气冷凝管用于蒸馏沸点较高 ($b.p. > 130^\circ\text{C}$) 的液体有机化合物。

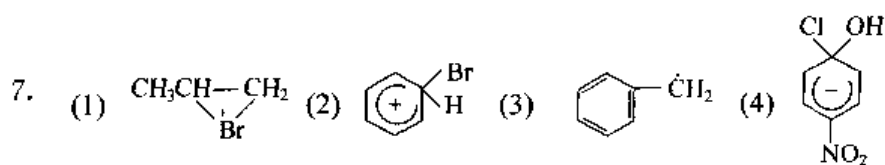
4. $\text{Ar}-\text{N}^+\equiv\text{N}$ 中氮原子上的正电荷可分散到苯环上；

$\text{R}-\text{N}^+\equiv\text{N}$ 中氮原子上的正电荷不能有效地分散。

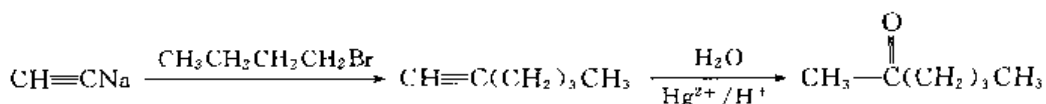
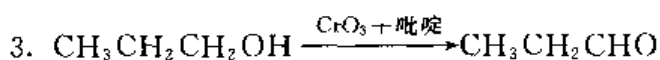
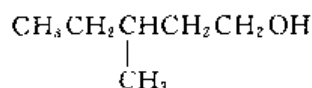
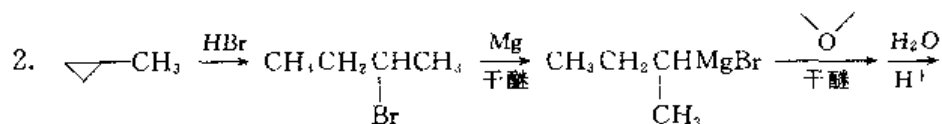
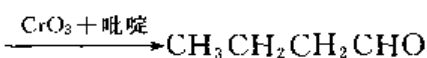
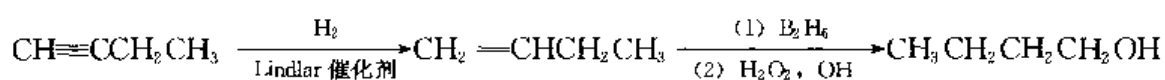
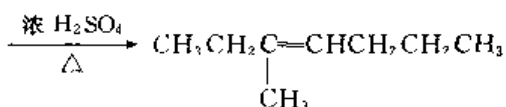
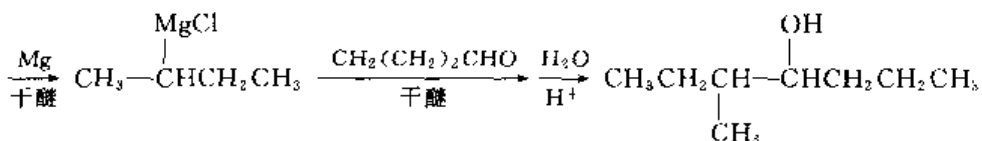
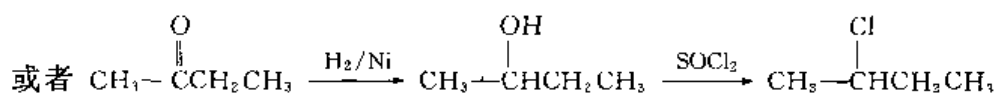
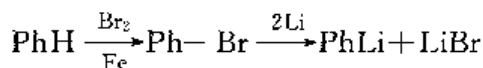
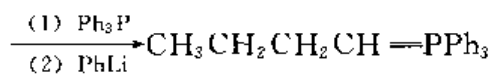
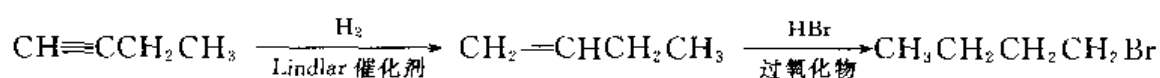
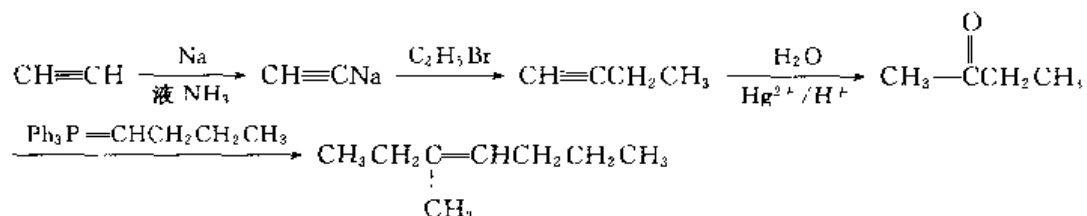
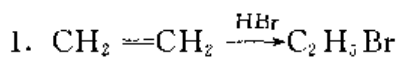
5. (1) (S-) (2) (S-) (3) (R-) (4) (2S-) (5) (S-)

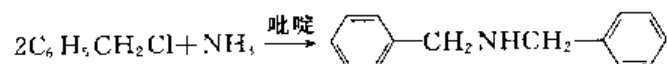
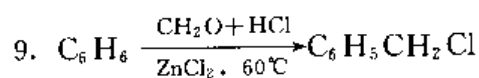
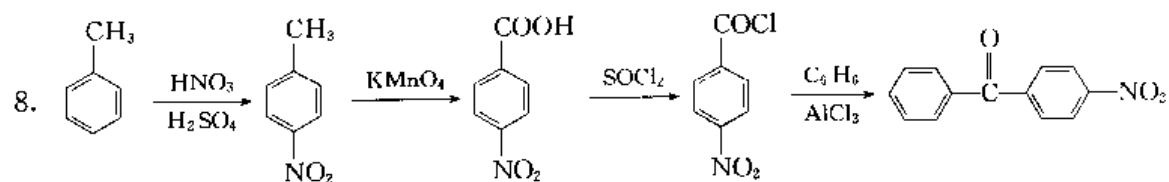
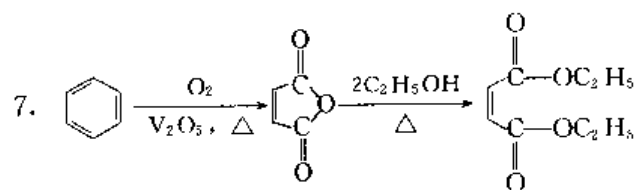
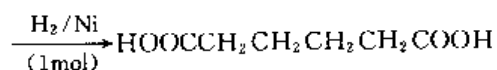
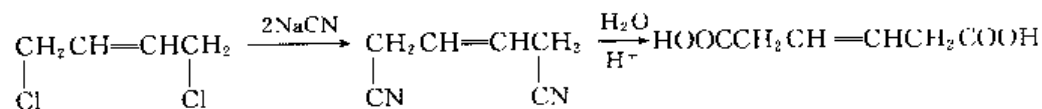
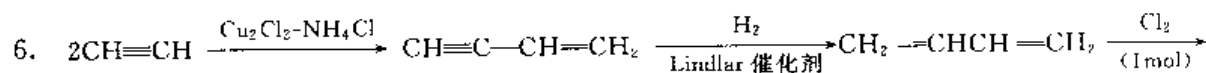
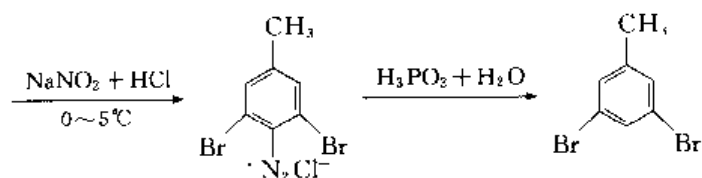
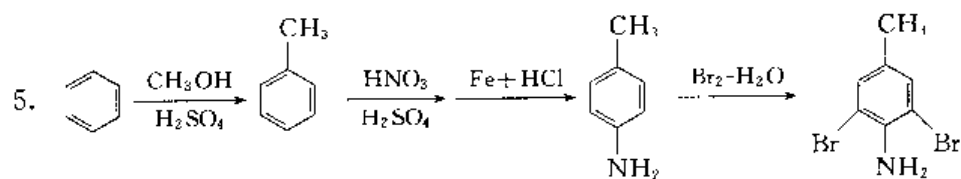
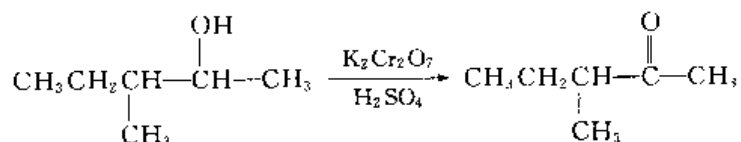
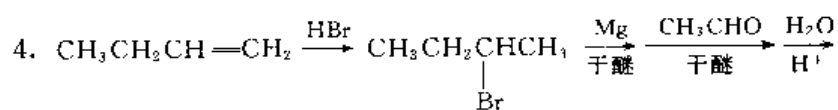
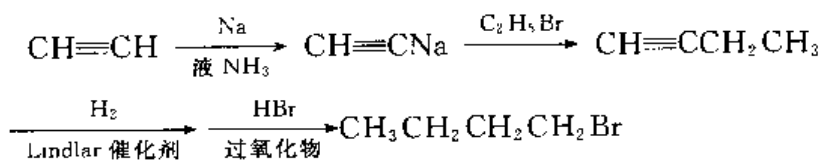
6.

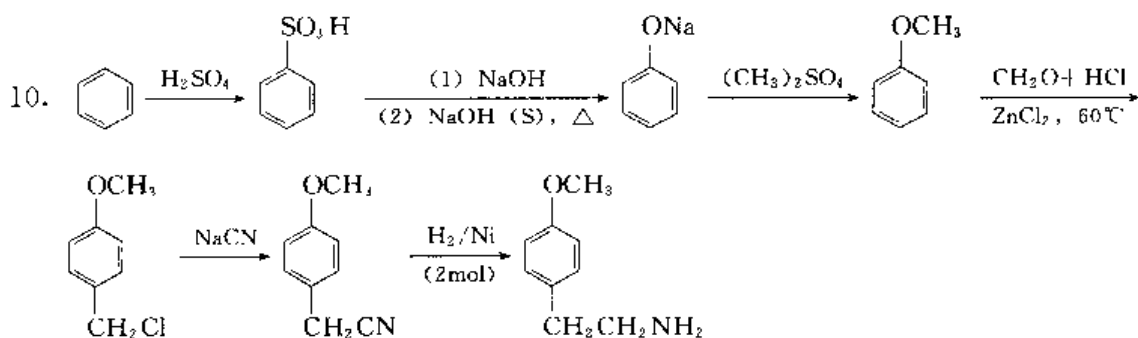
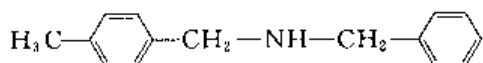
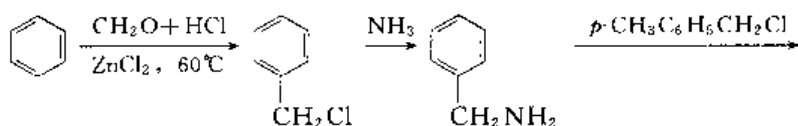
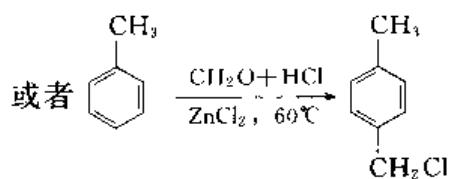
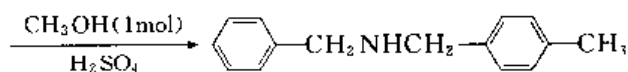
题号	化合物	试剂	现象
(1)	$p\text{-ClC}_6\text{H}_4\text{COOH}$	$\text{AgNO}_3\text{-醇}$	×
	$\text{C}_6\text{H}_5\text{COCl}$		$\text{AgCl}\downarrow$ (白)
(2)	$\text{C}_6\text{H}_5\text{COOCH}_3$	NaOH-水 , 试管口处石蕊试纸	无碱性气体产生, 石蕊试纸不变蓝
	$\text{C}_6\text{H}_5\text{CONH}_2$		产生的 NH_3 可使石蕊试纸变蓝
(3)	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$	Lucas 试剂	立刻出现浑浊
	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$		加热出现浑浊
(4)	$\text{CH}_3\text{CH}=\text{CH}_2$	KMnO_4	褪色
	环氧乙烷		×
(5)	乙酸乙酯	$\text{Br}_2\cdot\text{CCl}_4$	×
	乙酰乙酸乙酯		褪色
(6)	水杨酸	FeCl_3	显色
	安息香酸		×
(7)	葡萄糖	$\text{Ag}(\text{NH}_3)_2\text{NO}_3$	产生银镜
	甲基葡萄糖苷		×
(8)	丙酮	$\text{I}_2 + \text{NaOH}$	$\text{CHI}_3\downarrow$ (黄)
	丙醛		×



四、合成题







模拟试题 7

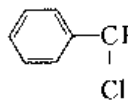
一、命名或写结构 (10 分)

1. 写出 $\text{HOOCCH}(\text{Cl})\text{CH}(\text{Cl})\text{COOH}$ 的系统名称

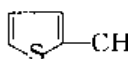


2. 写出 $\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$ 的系统名称

3. 写出 $\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{CH}_3$ 的系统名称



4. 写出 $\text{C}_4\text{H}_7\text{S}\text{CH}_2\text{CH}_2\text{OH}$ 的名称



5. 写出 2-氯-1-溴-5-碘-3-戊酮的构造式

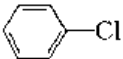
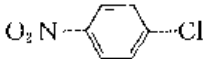
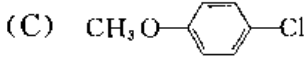
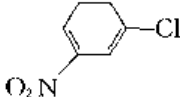
6. 写出 1,8-二羟基萘-3,6-二磺酸的构造式

7. 用 Fischer 投影式表示: (R)-3-甲基-1-戊炔 (2%)

8. 写出 (E)-4-甲基-5-氯-3-戊烯-1-醇的构型式 (2%)

二、理化性质比较题 (由大到小) (10 分)

1. 自由基稳定性: (A) $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$ (B) $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2$ (C) $\text{C}_6\text{H}_{11}\dot{\text{C}}\text{H}_2$

2. 氨解难易: (A)  (B) 
 (C)  (D) 

3. NaHSO₃ 加成活性:

- (A) C₆H₅COCH₂CH₃ (B) C₆H₅CH₂COCH₃ (C) C₆H₅CH₂CH₂CHO

4. 苯甲酸酯化的相对活性:

- (A) 正丙醇 (B) 乙醇 (C) 仲丁醇 (D) 甲醇

5. 酸性:

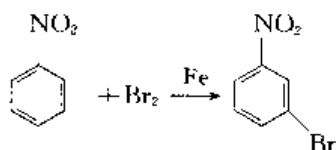
- (A) HOOC-COOH (B) HOOC-CH₂-COOH (C) CH₃-COOH (D) CH₃-CH₂-OH

三、用简便的化学方法鉴别下列各组化合物 (10 分)

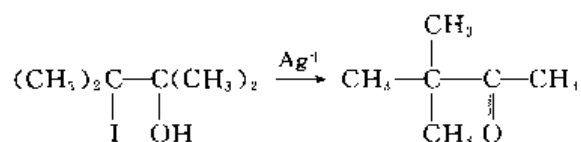
1. (A) 乙醛 (B) 丙醛 (C) 丙酮
 2. (A) 油酸 (B) 油酸甲酯 (C) 石蜡
 3. (A) 苯胺 (B) 苄胺 (C) 苯酚
 4. (A) CH₃(CH₂)₄CH₂NO₂ (B) CH₃(CH₂)₄CH₂NH₂
 (C) CH₃(CH₂)₄CH₃

四、反应机理 (8 分)

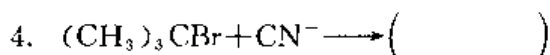
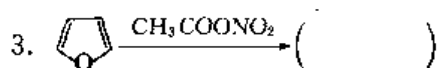
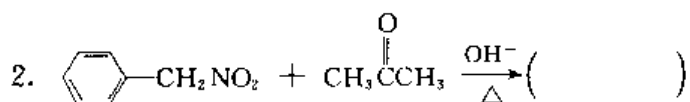
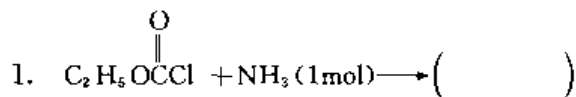
1. 写出下列反应的活性中间体, 并指出反应机理类型:

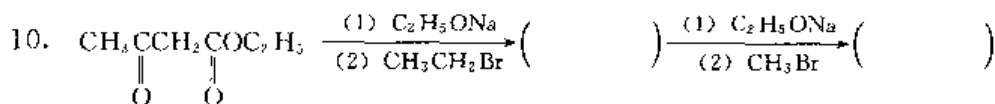
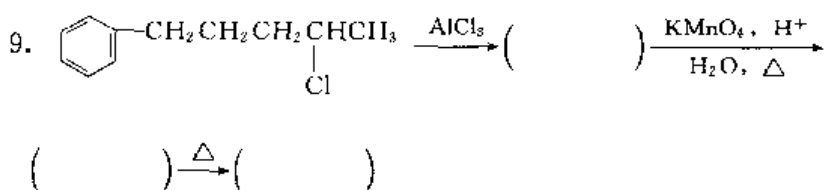
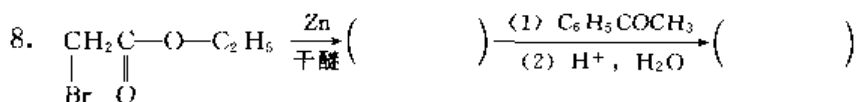
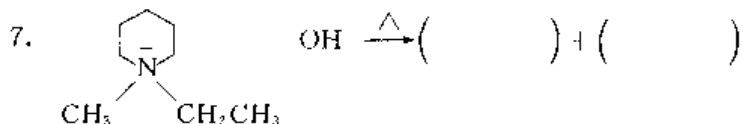
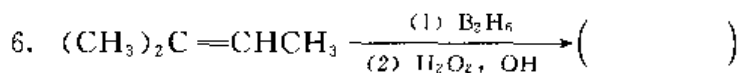
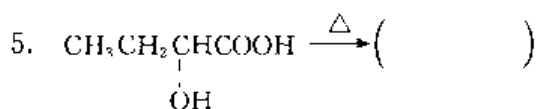


2. 反应机理解释

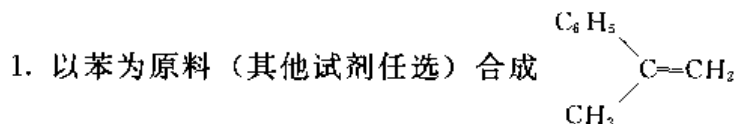


五、完成下列各反应式 (15 分)

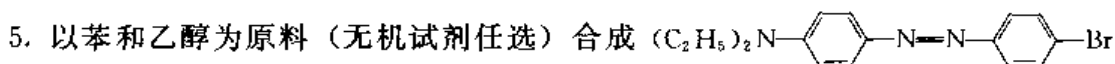
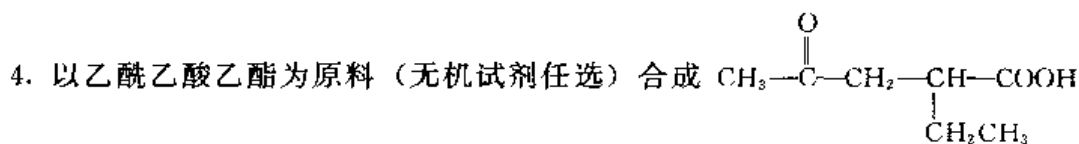
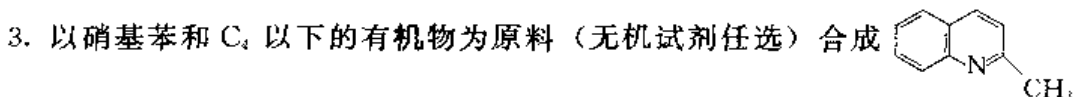




六、有机合成题 (25 分)



2. 用 C_4 以下的烯烃为原料 (无机试剂任选) 合成 3-甲基-3-戊醇。

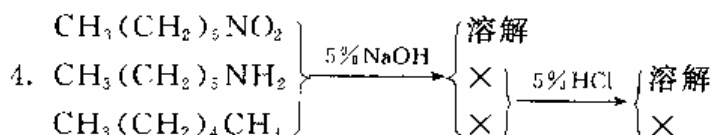
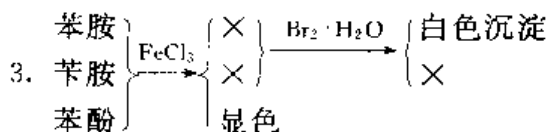
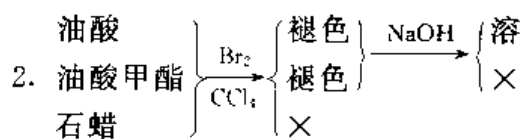


七、推导结构题 (分别按各题要求解答) (22 分)

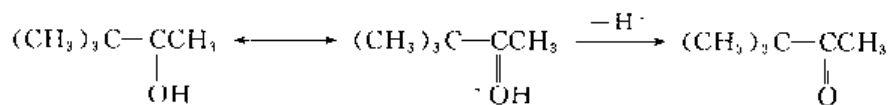
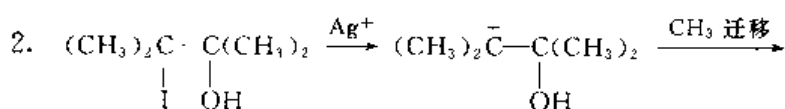
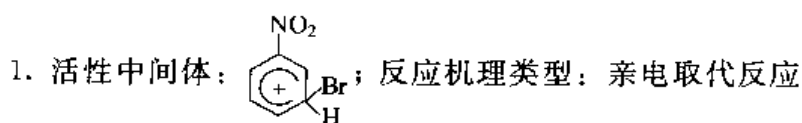
1. 某化合物分子式为 $\text{C}_4\text{H}_8\text{O}$ 。它的红外光谱在 1715cm^{-1} 处有强的吸收峰; 它的核磁共振谱图上有 3 组吸收峰: 单峰 (3H)、四重峰 (2H)、三重峰 (3H)。试写出该化合物的构造式。(4 分)

2. 芳香族化合物 A, 分子式为 $\text{C}_7\text{H}_7\text{N}$, 其苯磺酰基衍生物可溶于氢氧化钠溶液, A 经亚硝化反应可得到一个醇, 并有 N_2 放出。写出 A 的构造式。(4 分)

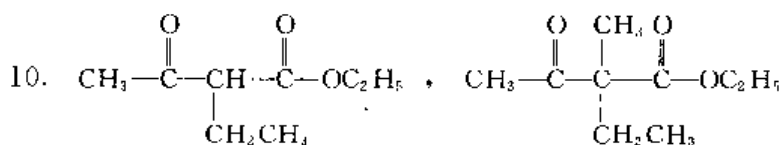
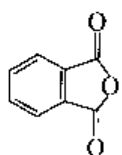
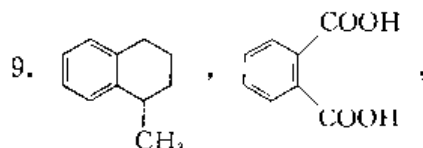
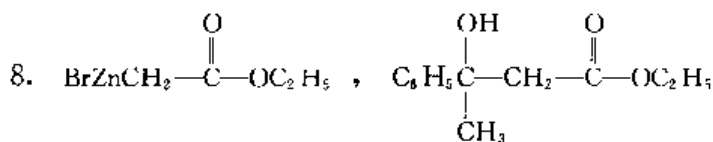
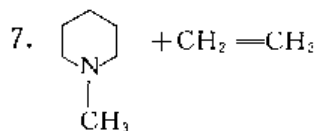
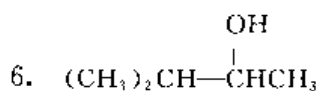
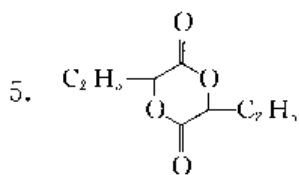
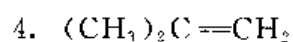
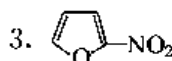
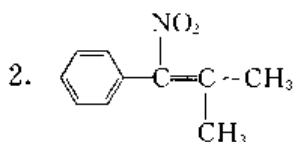
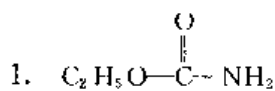
3. 化合物 $\text{C}_{10}\text{H}_{10}\text{O}_2$ 的红外光谱如下图所示。它具有下列性质: 使溴水褪色; 水解得到



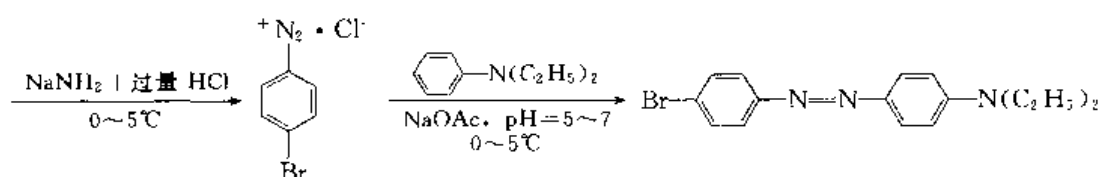
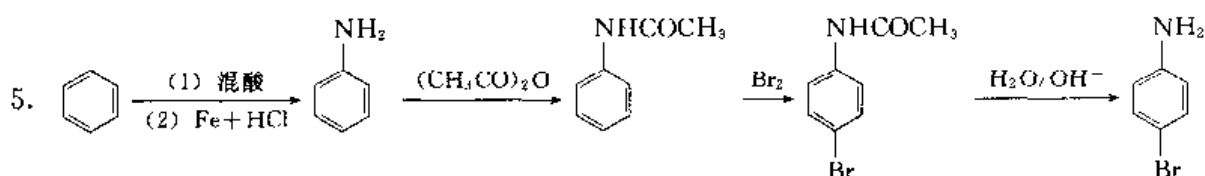
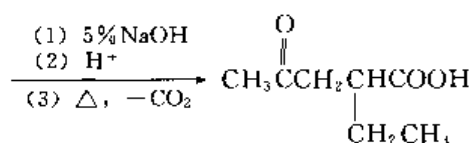
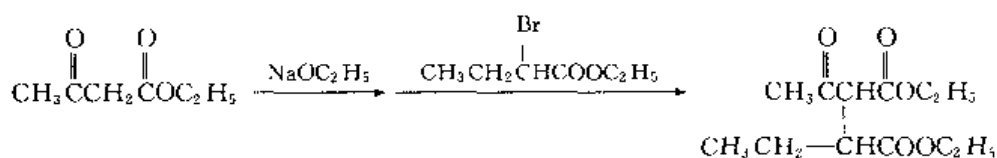
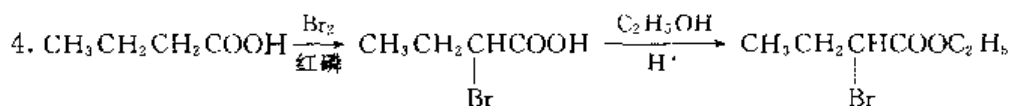
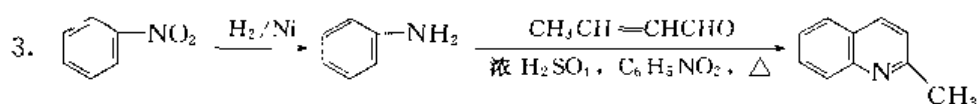
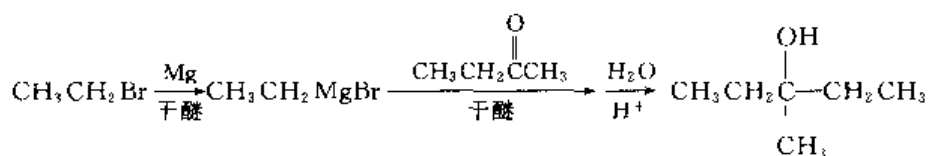
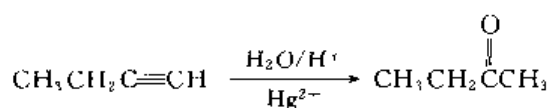
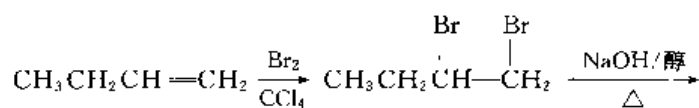
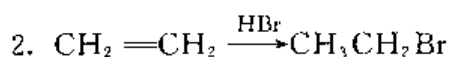
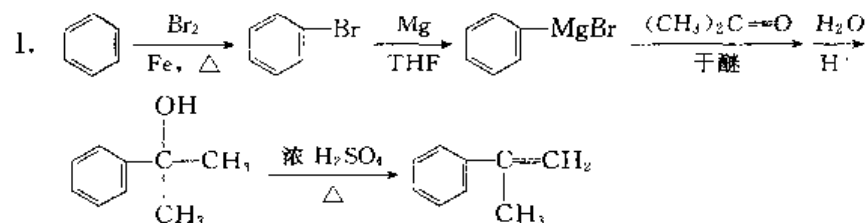
四、反应机理

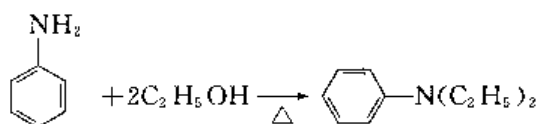


五、完成反应式

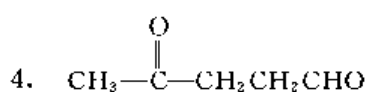
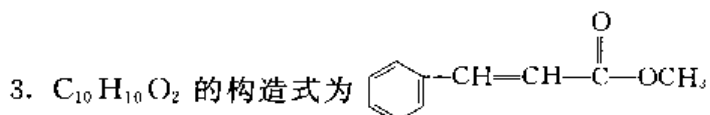
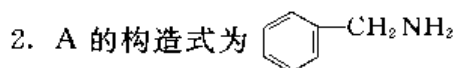
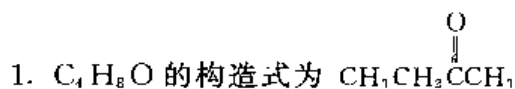


六、合成题

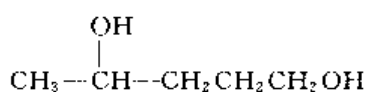




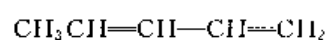
七、推导结构



(A)



(B)



(C)

5. 略。见“模拟试题 2 六、2。”。

模拟试题 8

一、综合题 (20 分)



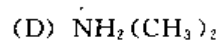
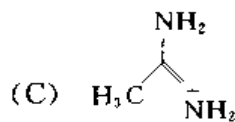
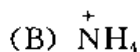
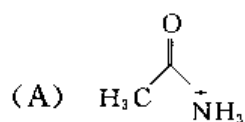
(A) 5,6-二甲基二环[2.2.2]-2-辛烯

(B) 2,3-二甲基二环[2.2.2]-5-辛烯

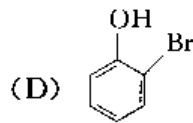
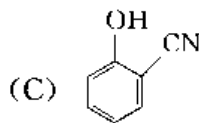
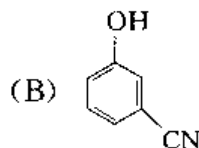
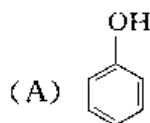
(C) 2,3-二甲基二环[2.2.0]-1-辛烯

(D) 5,6-二甲基二环[2.2.2]-1-辛烯

2. 下列化合物酸性最强的是



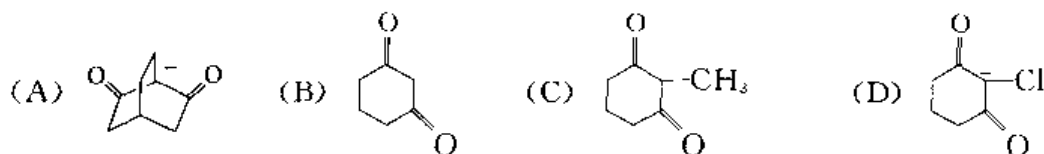
3. 下列化合物碱性最强的是



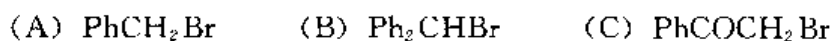
4. 下列碳正离子最稳定的是



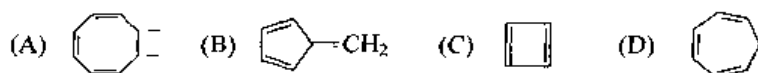
5. 下列碳负离子最稳定的是



6. 下列化合物中 $\text{S}_{\text{N}}1$ 和 $\text{S}_{\text{N}}2$ 都容易的是

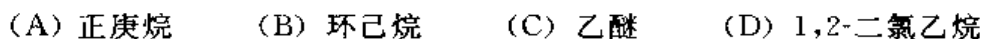


7. 下列化合物中有芳香性的是



8. 写出三羟基戊二酸的 4 种异构体的费歇尔投影式，并标出其不对称碳原子的绝对构型，判断该分子有无手性。

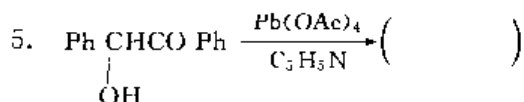
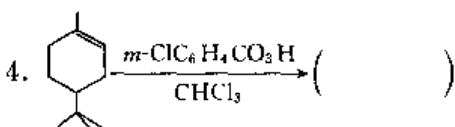
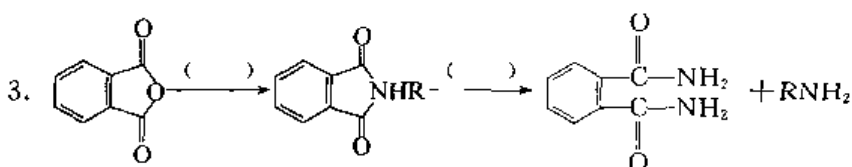
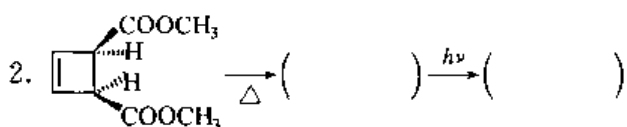
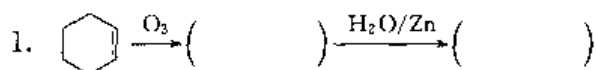
9. 下列 4 种溶剂相对密度大于 1 的是

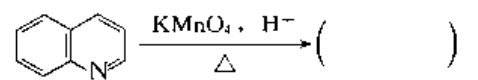
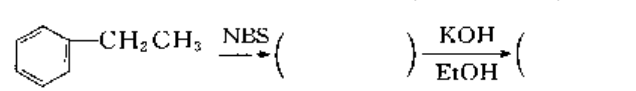
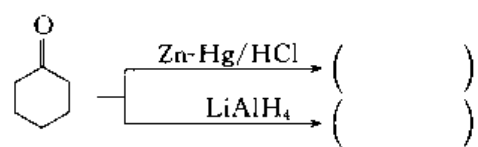
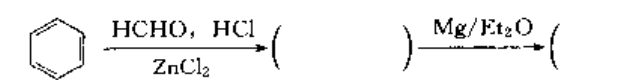


10. 2,3-丁二醇跟 () 反应得到 CH_3CHO

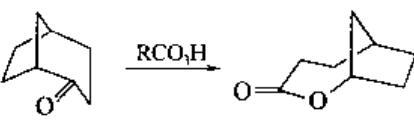
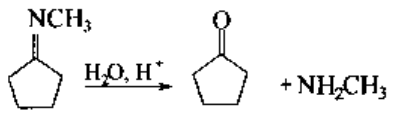
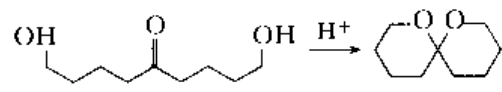
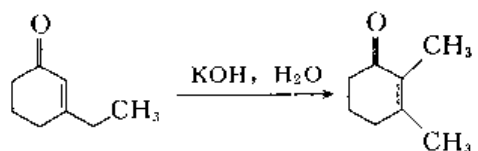


二、填空 (20 分)

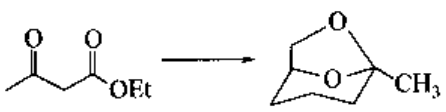
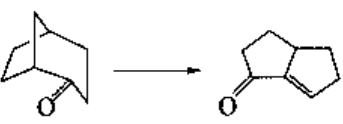
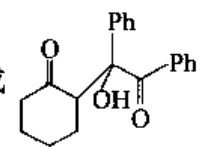
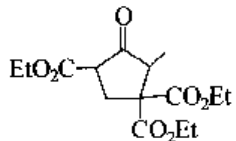


6.  $\xrightarrow[\Delta]{\text{KMnO}_4, \text{H}^+}$ ()
7. $(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}_2 \xrightarrow{\text{H}^+}$ () $\xrightarrow{\text{Br}_2/\text{CCl}_4}$ ()
8.  $\xrightarrow{\text{NBS}}$ () $\xrightarrow[\text{EtOH}]{\text{KOH}}$ ()
9.  $\xrightarrow{\text{Zn-Hg/HCl}}$ ()
 $\xrightarrow{\text{LiAlH}_4}$ ()
10.  $\xrightarrow[\text{ZnCl}_2]{\text{HCHO, HCl}}$ () $\xrightarrow{\text{Mg/Et}_2\text{O}}$ ()

三、写出下列反应机理 (20 分)

1. 
2. 
3. 
4. 

四、合成下列化合物 (20 分)

1. 
2. 
3. 从苯甲醛和环己酮合成 
4. 从 C_2 和 C_3 以下的原料合成 

5. 从 C_3 和 C_3 以下的原料合成 $CH_3CH=CHCH_2OCH_2\overset{OH}{\underset{|}{CH}}-CH_3$

五、推测下列化合物结构并写出反应过程

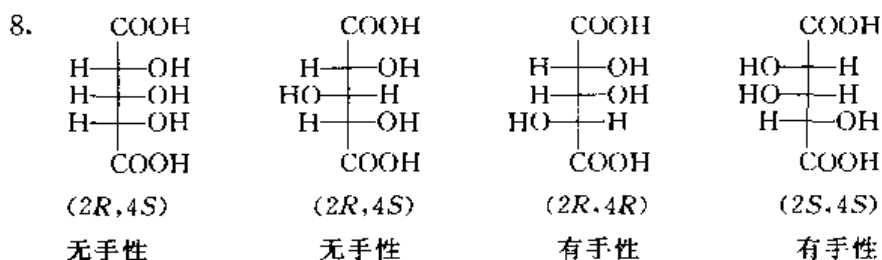
1. 碱性化合物 A ($C_5H_{11}N$) 臭氧化可产生醛及其他化合物。A 催化加氢生成化合物 B ($C_5H_{13}N$)，B 亦可从己酰胺用 Br_2 在水合 NaOH 溶液中得到。在过量的碘甲烷作用下，A 转变成盐 C ($C_8H_{18}IN$)，C 在 AgOH 作用下伴随产物热分解生成二烯 D (C_4H_8)，D 和 $MeO_2C-C\equiv C-CO_2Me$ 反应生成酯 E ($C_9H_{14}O_4$)，E 在铂上脱氢生成 3-甲基邻苯二甲酸甲酯。写出用字母表示的化合物和化学反应过程。

2. 一光学活性化合物 A ($C_5H_{13}N$) 溶解于过量的稀 HCl 中，加入 $NaNO_2$ 溶液变成无色的液体 B ($C_5H_{12}O$)，B 也是光学活性异构体。用 $KMnO_4$ 氧化 B 生成 C ($C_5H_{10}O$)，C 不再有光学活性。B 或 C 更激烈地氧化(如 $K_2Cr_2O_7 + H_2SO_4$) 主要生成酮和酸。推测 A、B、C 的结构并写出反应过程。

参考答案

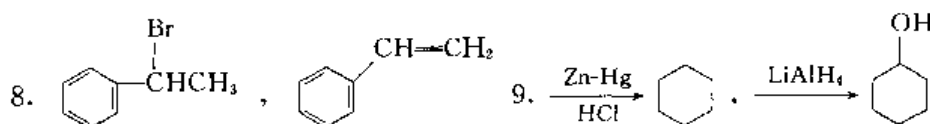
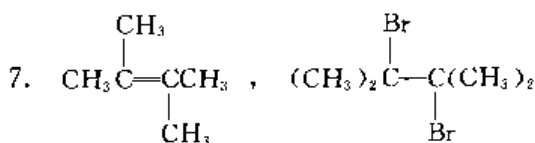
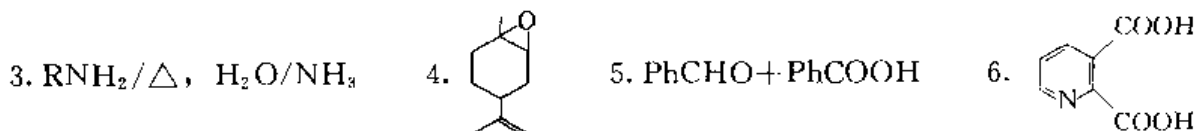
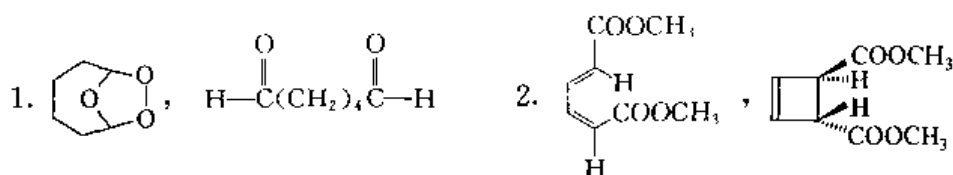
一、综合题

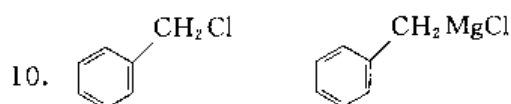
1. (A) 2. (A) 3. (C) 4. (B) 5. (D) 6. (A) 7. (A)



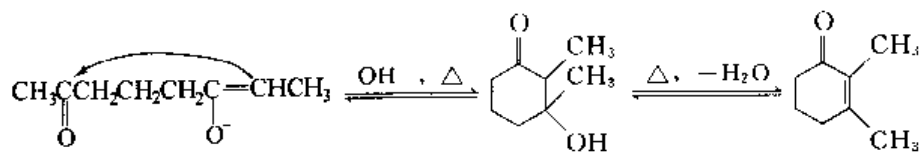
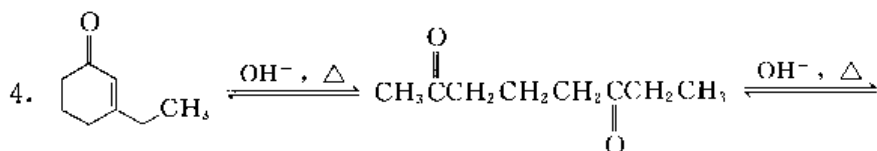
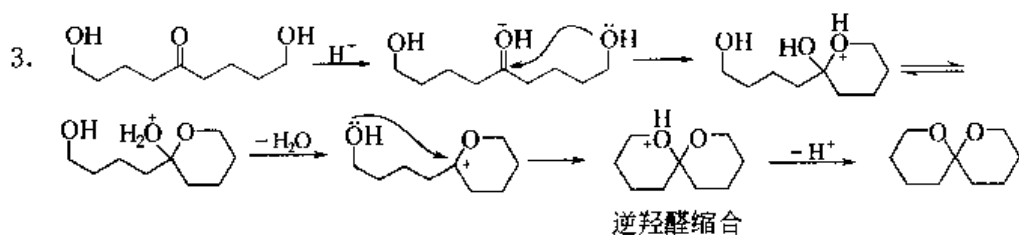
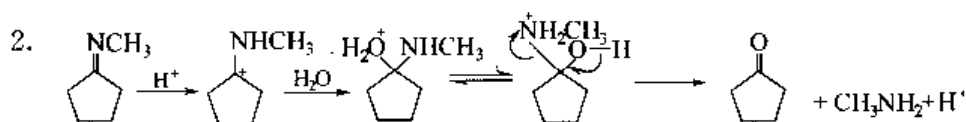
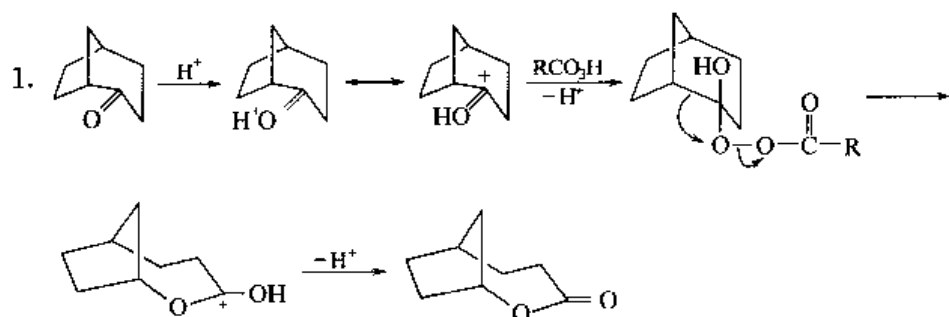
9. (D) 10. (D)

二、填空

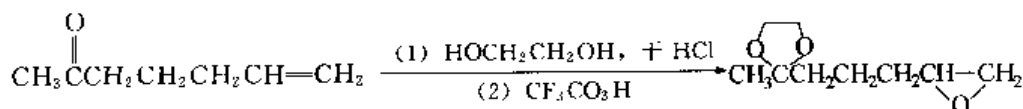
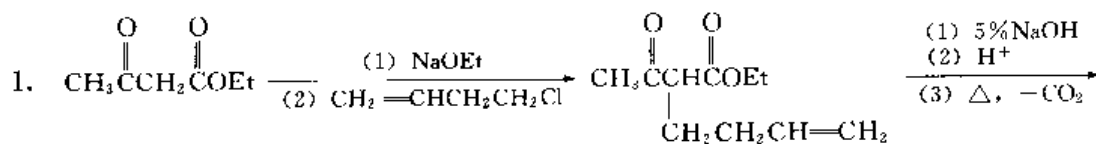


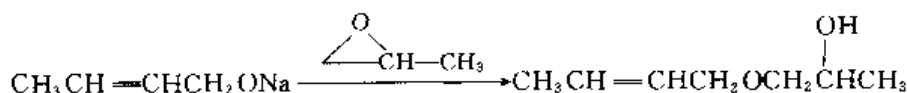
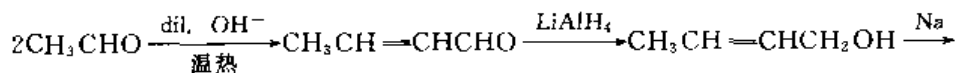
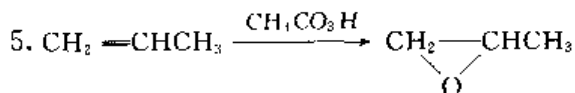
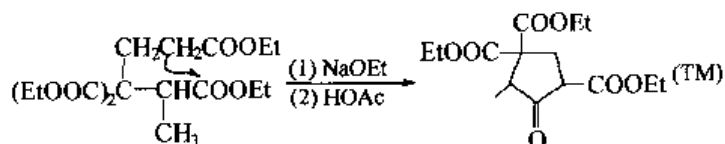
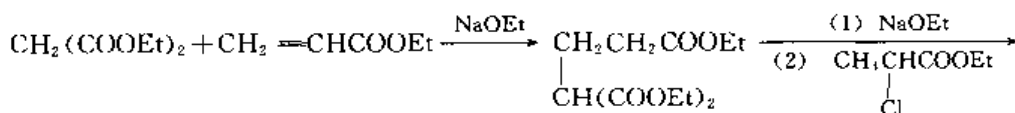
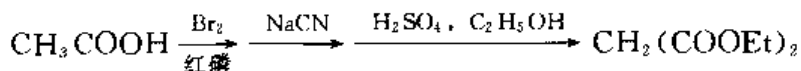
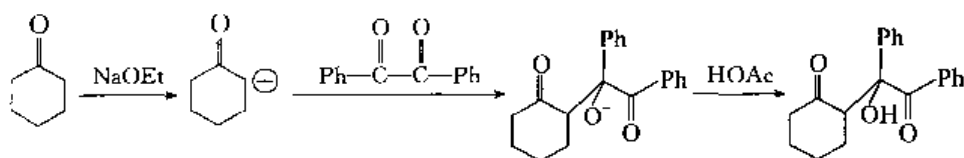
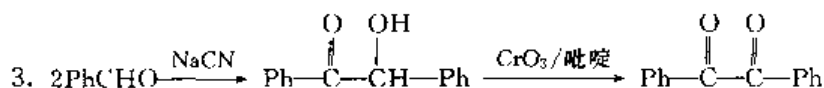
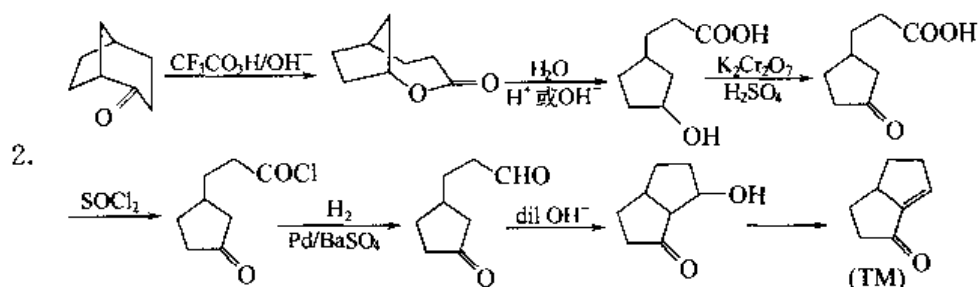
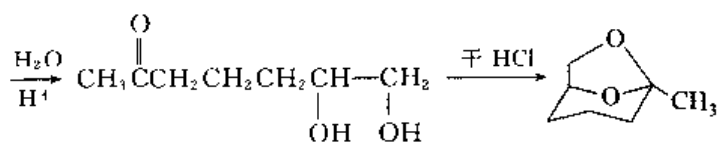


三、反应机理



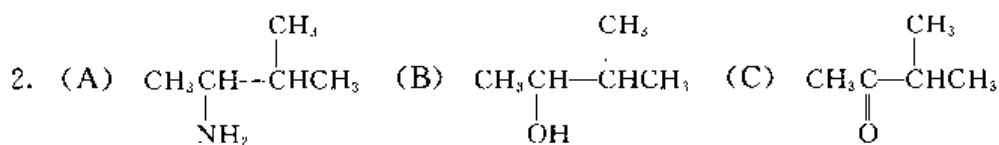
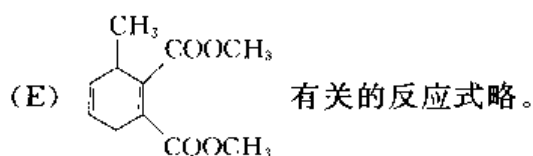
四、合成题





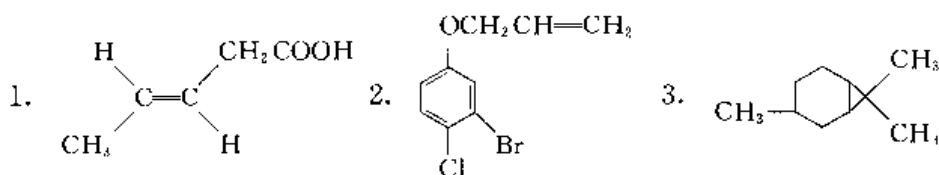
五、推测结构

1. (A) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{NH}_2$ (B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
 (C) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{I}^-$ (D) $\text{CH}_3\text{CH}=\text{CHCH}=\text{CH}_2$

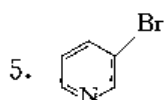


模拟试题 9

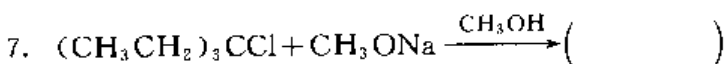
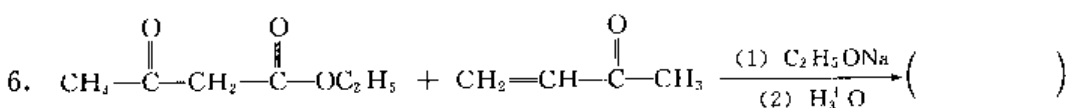
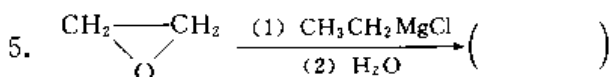
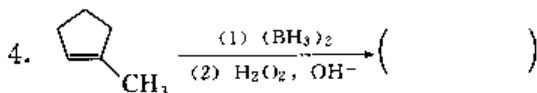
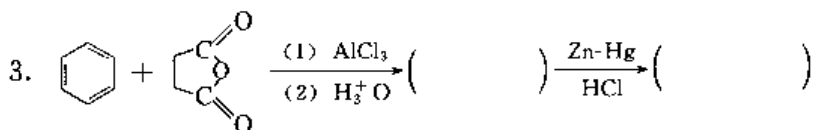
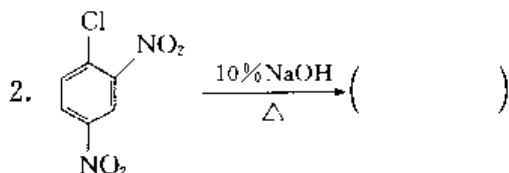
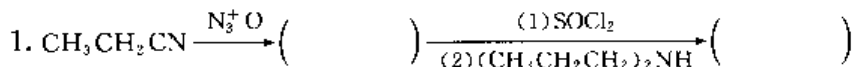
一、用系统命名法命名下列各化合物或根据名称写出结构式 (10 分)

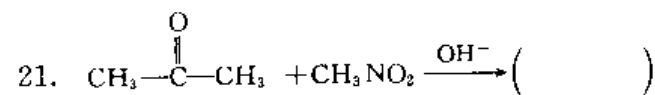
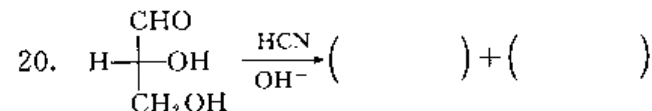
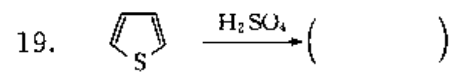
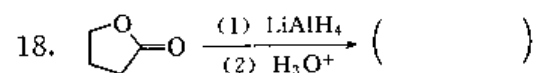
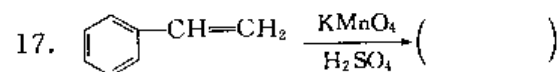
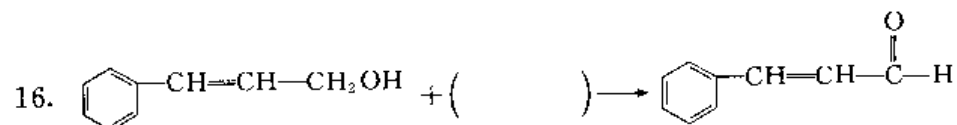
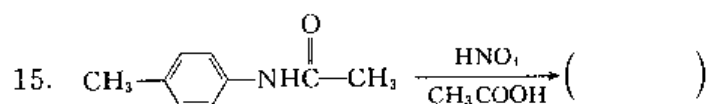
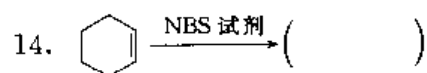
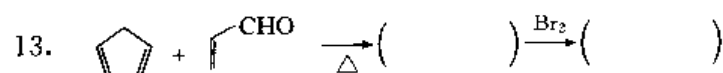
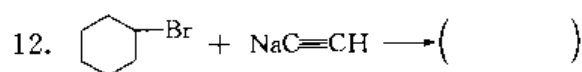
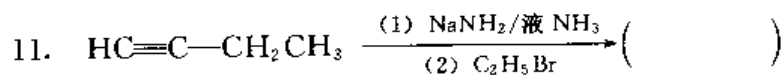
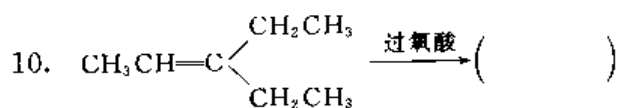
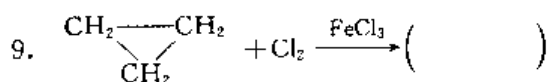
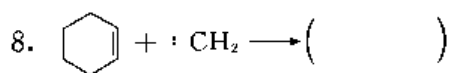


4. 甲基-β-D-吡喃葡萄糖苷



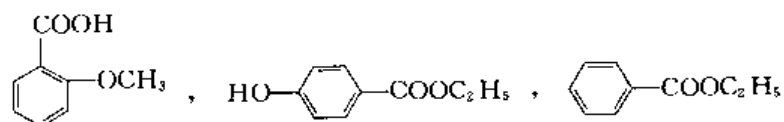
二、完成下列反应式 (25 分)





三、实验题 (10分)

有一混合物，含有

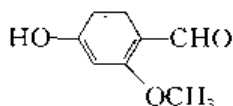


请设计实验方案，分离回收各组分（用简单的流程表示）。

四、推导结构式（10分）

1. 化合物 A 的分子式为 $C_6H_{12}O_2$ ，有旋光性，催化加氢时生成醇 B，B 无旋光性，请写出 A 和 B 的结构式。

2. 化合物 A 的分子式为 $C_{10}H_{12}O_3$ ，能溶于 NaOH 溶液，但不溶于 $NaHCO_3$ 水溶液，当用苯甲酰氯和吡啶处理 A 时，生成分子式为 $C_{24}H_{20}O_5$ 的化合物 B，用热的 HI 处理 A，得到一种挥发性得化合物，经鉴定为 CH_3I 。如用 CH_3I 的碱性溶液处理 A，得分子式为 $C_{11}H_{14}O_3$ 的化合物 C。C 不溶于 NaOH 溶液，但可与金属钠反应，也能与 $KMnO_4$ 反应，并使 Br_2/Cl_2 褪色。A 经臭氧分解能生成香草醛



及其他化合物。试写出 A、

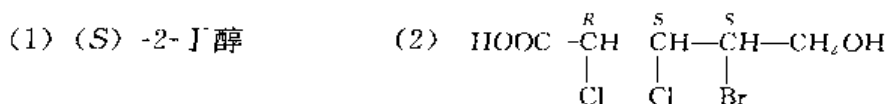
B、C 的结构。

五、反应机理题（9分）

新戊基溴在 50% $C_2H_5OH-H_2O$ 溶液中与银盐作用，反应产物中有醇，醚，烯烃。请写出反应过程，并说明理由。

六、立体化学（10分）

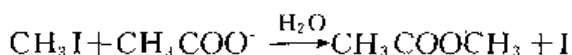
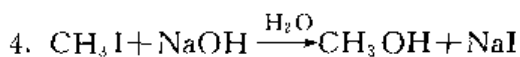
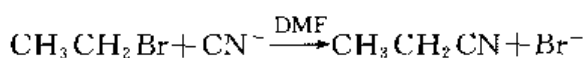
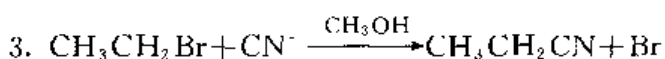
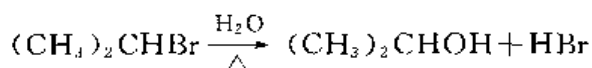
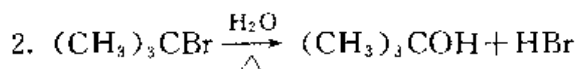
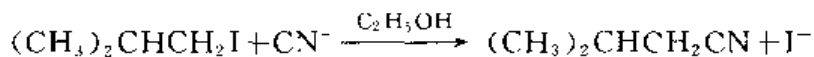
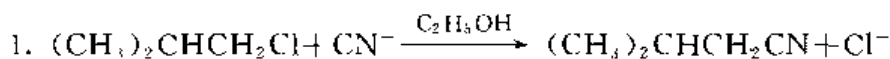
1. 写出下列分子的费歇尔投影式。



2. 你认为下列阐述哪些是正确的？哪些是错误的？（只需回答对或错）

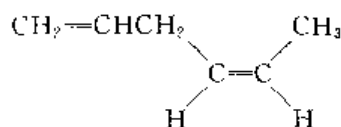
- (1) 具有 R-构型的手性化合物必定有右旋的旋光方向。
- (2) 对映异构体可通过单键旋转相互重合。
- (3) 所有具有手性碳的化合物都是手性分子。
- (4) 构象异构体都没有光学活性。
- (5) 所有手性分子都有非对映异构体。
- (6) 一对对映体总有实物和镜像的关系。

七、预测以下各对反应按什么机理进行？哪个较快？并说明理由。（10分）



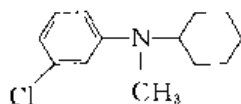
八、合成题 (26 分, 统考生做)

1. 以丙烯为原料 (无机试剂任选), 合成

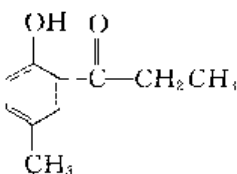


2. 以乙烯为原料 (无机试剂任选), 合成 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OH}$

3. 以苯, 甲苯和小于或等于 C_2 的有机物为原料合成



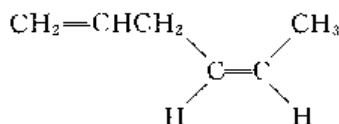
4. 以甲苯及丙酰氯为原料, 合成



5. 以苯为原料, 合成 $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{NO}_2$

九、合成题 (26 分, 单独考生做)

1. 以丙烯为原料 (无机试剂任选), 合成



2. 以乙烯为原料 (无机试剂任选), 合成 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OH}$

3. 以苯和萘为原料, 合成 1-苯偶氮基-2-萘酚。

4. 以乙烯为原料合成 1,4-丁二胺。

5. 以苯及小于或等于 C_2 以下的有机物为原料, 合成 $\text{C}_6\text{H}_5-\text{CH}_2-\underset{\text{CH}_2\text{CH}_3}{\text{CH}}-\text{COOH}$

参考答案

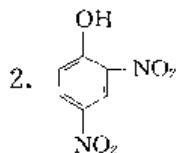
一、命名或写结构式

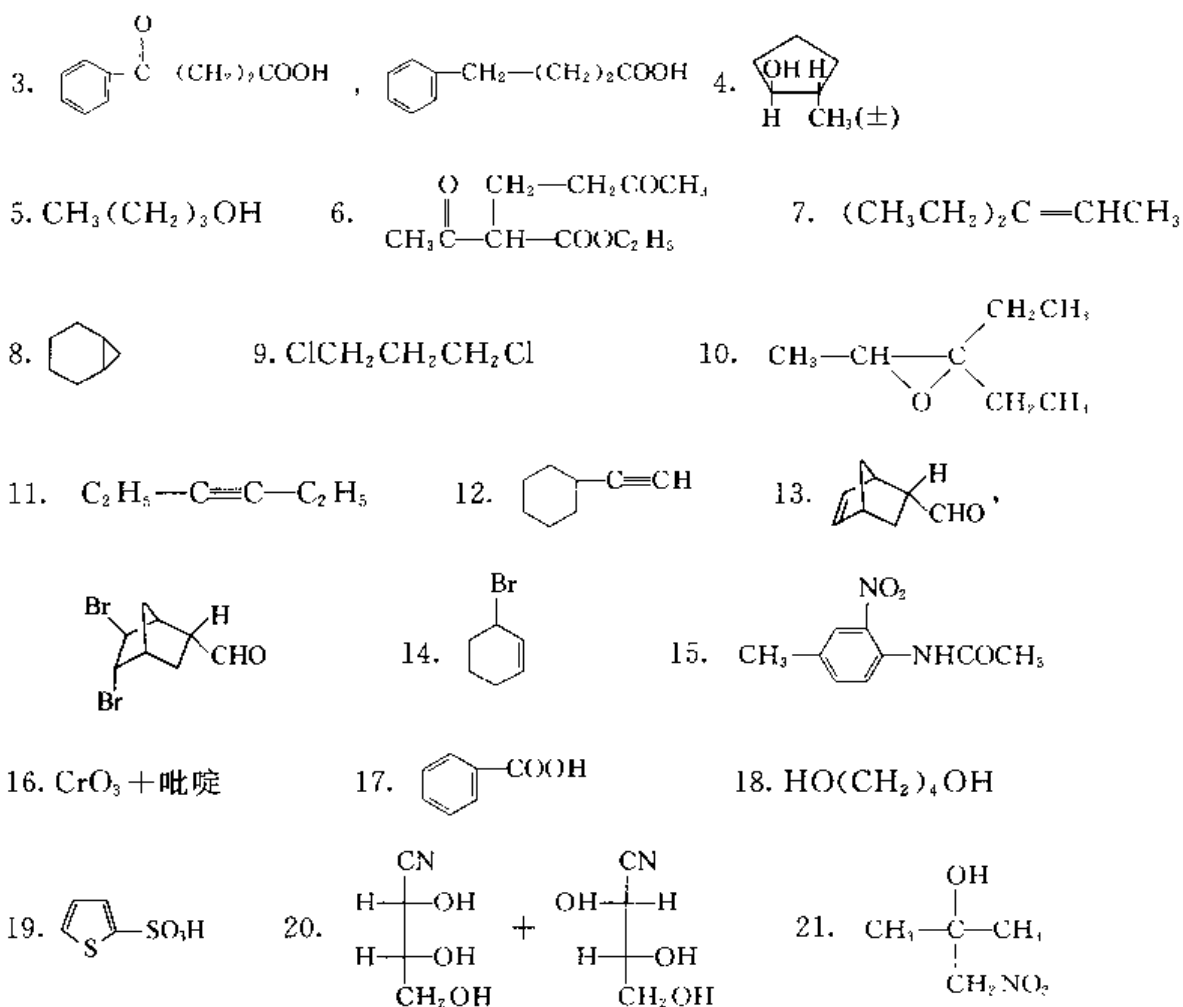
1. (E)-3-戊烯酸 2. 4-氯-3-溴苯烯丙醚 3. 3,7,7-三甲基双环[4.1.0]庚烷

4. 5. 3-溴吡啶

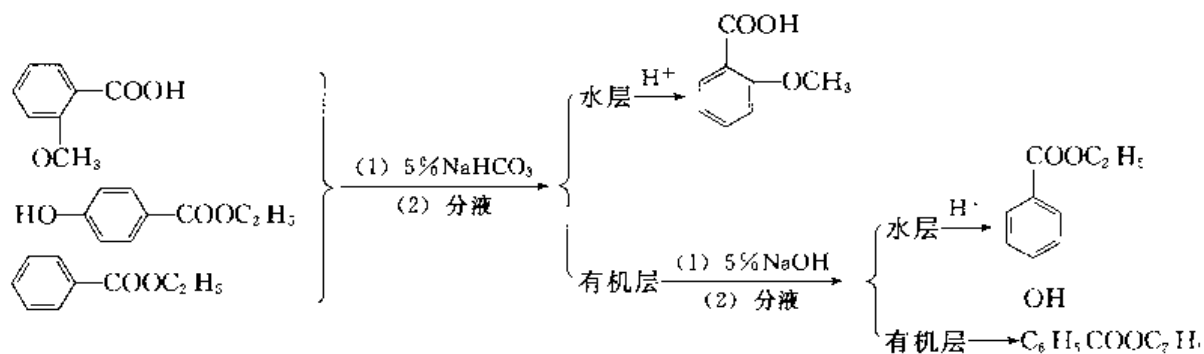
二、完成下列反应式

1. $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{CON}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$

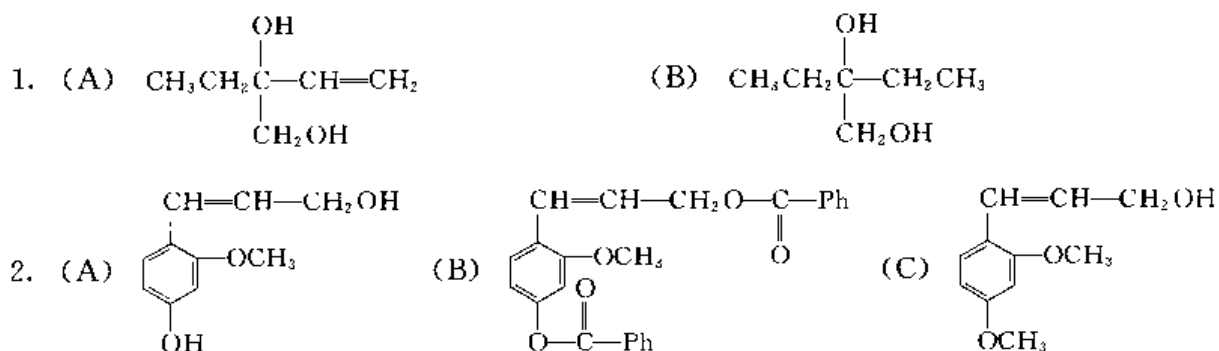




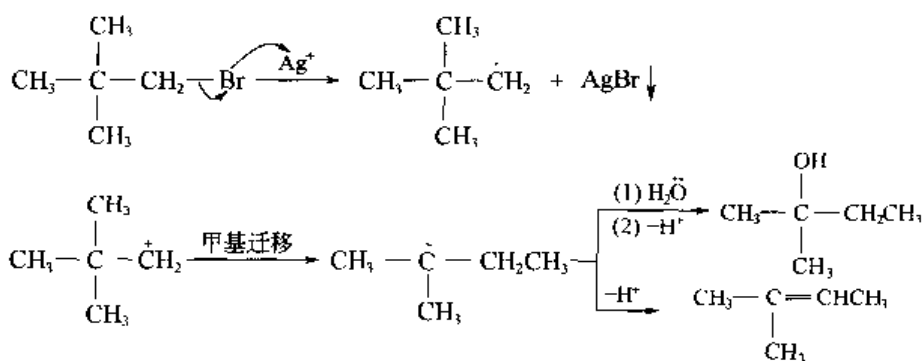
三、实验题



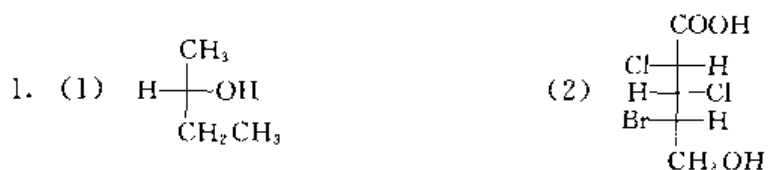
四、推导结构式



五、反应机理题



六、立体化学

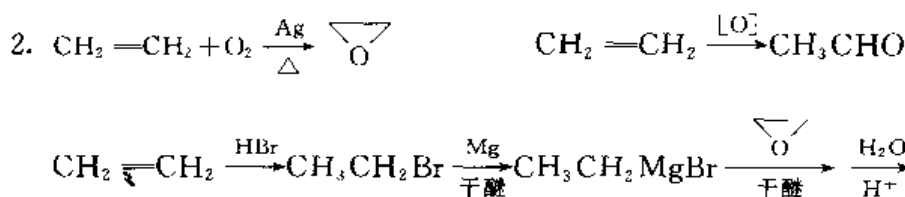
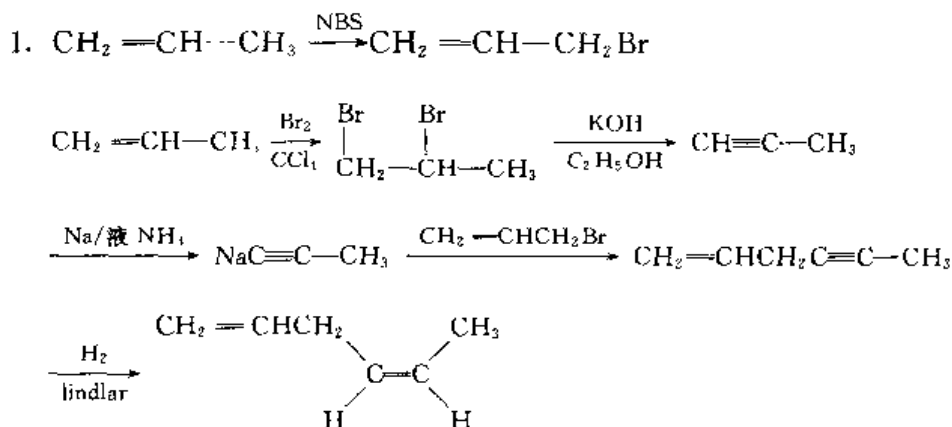


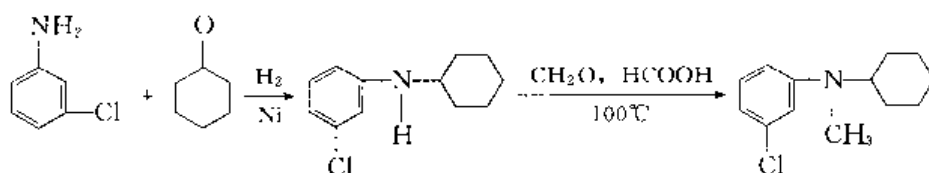
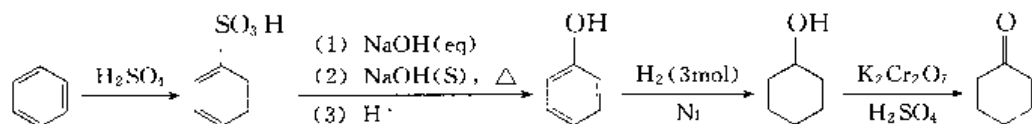
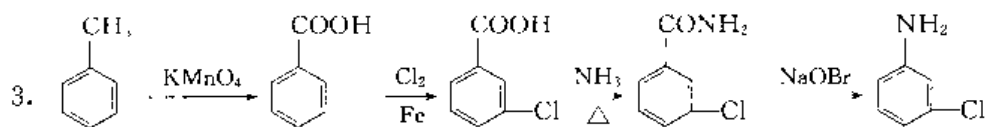
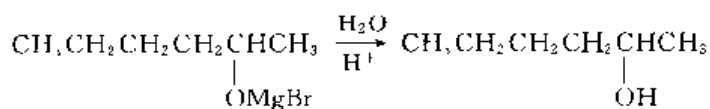
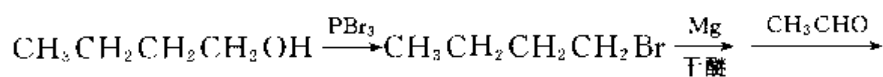
2. (1) 错 (2) 错 (3) 错 (4) 错 (5) 错 (6) 对

七、反应机理

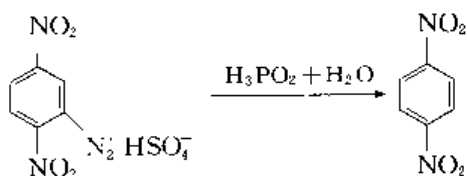
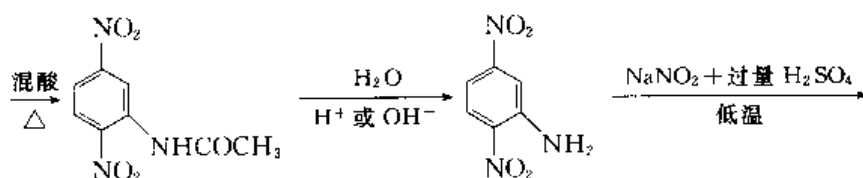
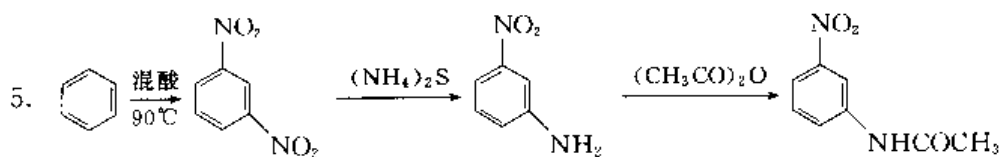
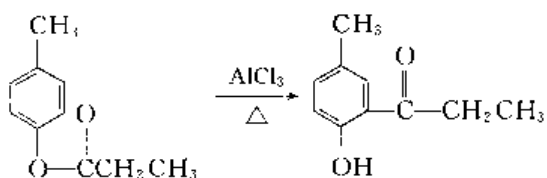
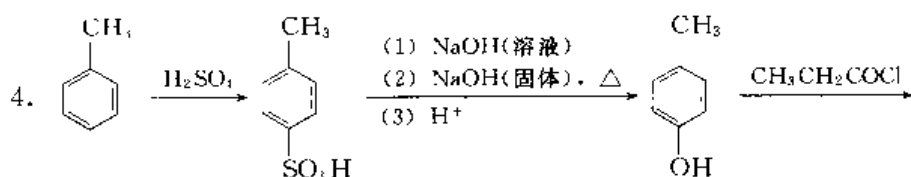
- 两者均为一级卤代烷，在乙醇中发生 $\text{S}_{\text{N}}2$ 反应。
后者快。理由： $\text{C}-\text{I}$ 键能 $<$ $\text{C}-\text{Cl}$ 键能， $\text{C}-\text{I}$ 更易断开，有利于 $\text{S}_{\text{N}}2$ 。
- 在水中，两者均为 $\text{S}_{\text{N}}1$ 反应。
前者快。理由： C^+ 稳定性： $(\text{CH}_3)_3\text{C}^+ > (\text{CH}_3)_2\text{C}^+\text{H}$
- 两者均为一级卤代烷，均发生 $\text{S}_{\text{N}}2$ 反应。
后者快。因为后者溶剂极性较低，更有利于 $\text{S}_{\text{N}}2$ 。
- 两者均为 $\text{S}_{\text{N}}2$ 反应。
前者快。因为亲核性： $\text{OH}^- > \text{CH}_3\text{COO}^-$

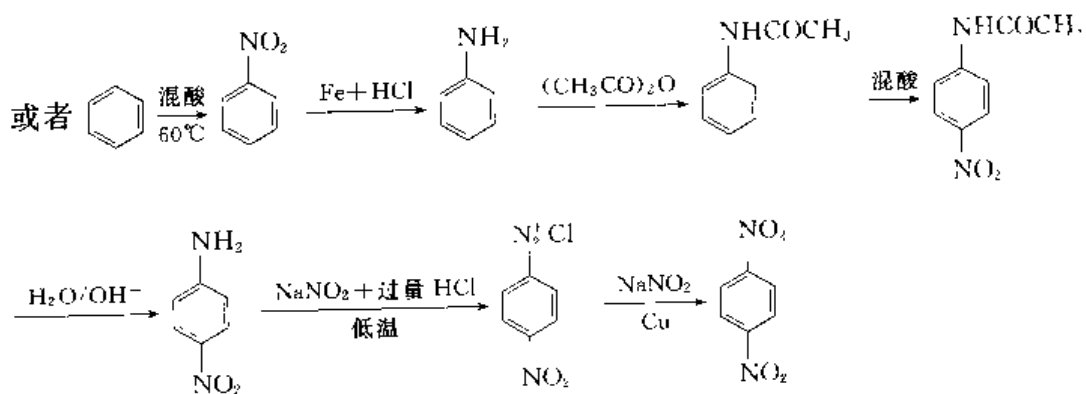
八、合成题





(Eschweiler W-Clarke H T 反应)

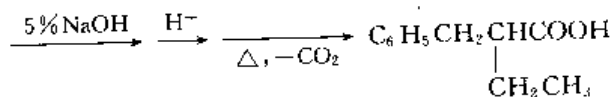
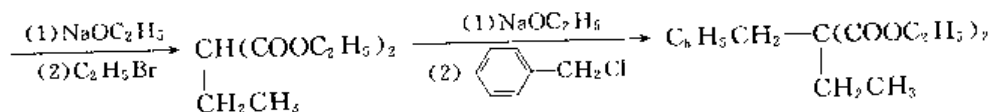
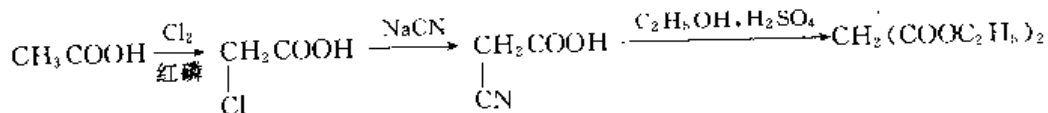
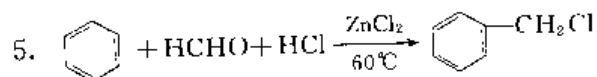
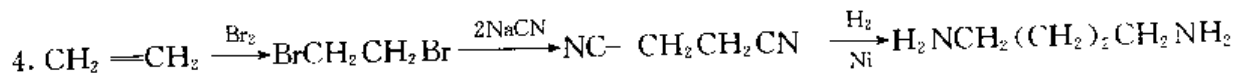
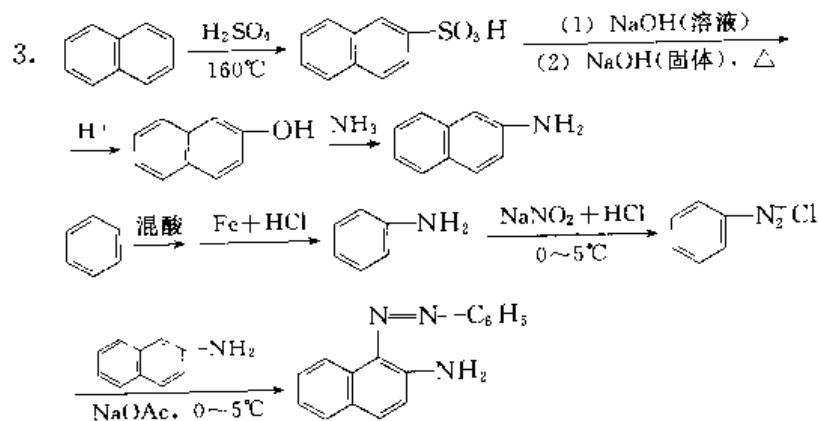




九、合成题

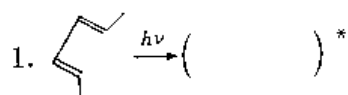
1. 略。

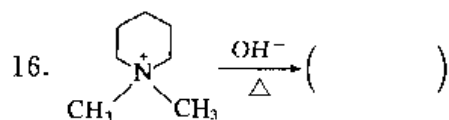
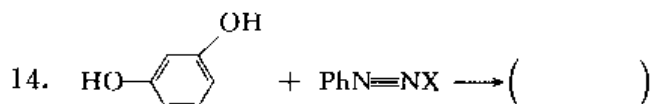
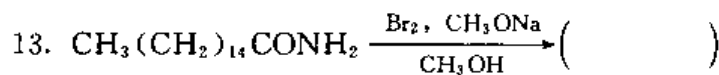
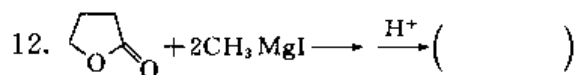
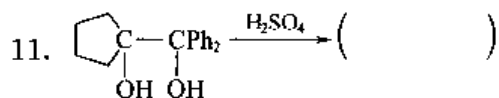
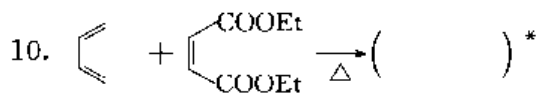
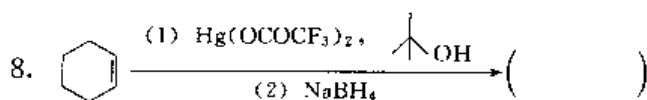
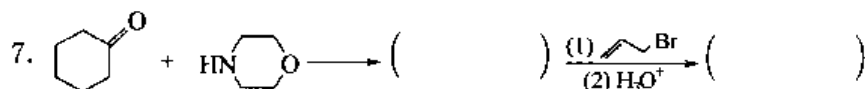
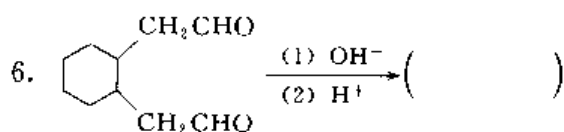
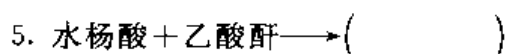
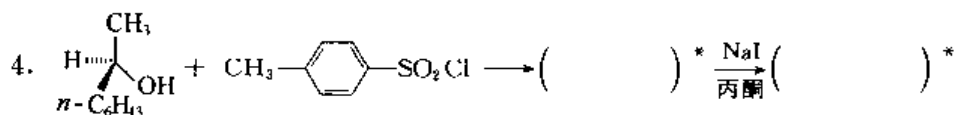
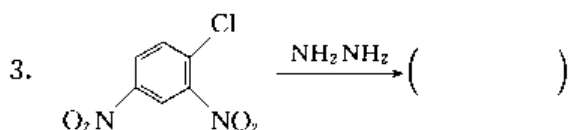
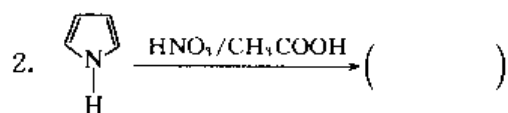
2. 略。

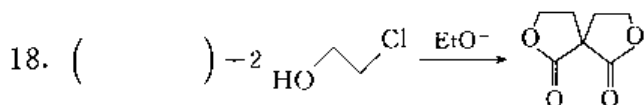
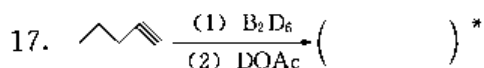


模拟试题 10

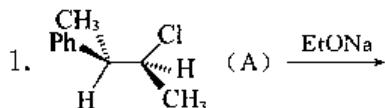
一、完成下列反应，在标有 * 的括号内应标明产物的构型 (20 分)



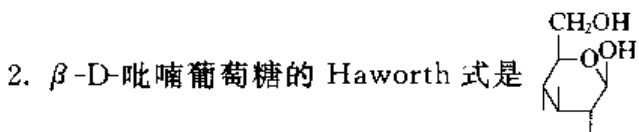




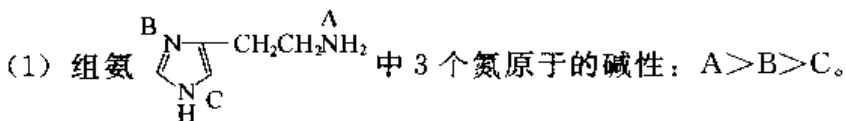
二、完成下列事项 (15 分)



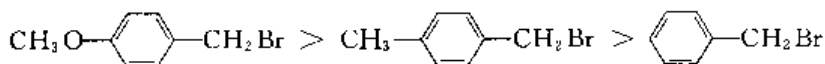
- (1) 用系统命名法命名化合物 A (2) 写出上述反应的主要产物
(3) 写出化合物 A 的对映体 (4) 写出上述反应产物的系统名



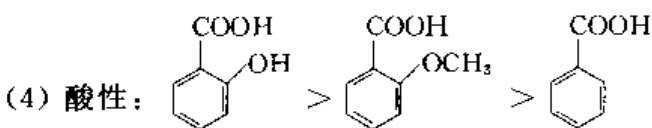
- (1) 将上述 Haworth 式改写成构象式。
(2) β -D-吡喃葡萄糖溶于水后，其旋光度会发生改变，这个现象叫 ()。
(3) 写出 β -D-吡喃葡萄糖与 1mol CH3OH 在干 HCl 存在下的反应式。
(4) 写出上述反应产物之一的名称。
3. 下列化合物的各性质比较中，哪些排列次序是正确的？



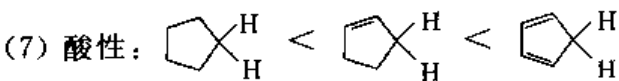
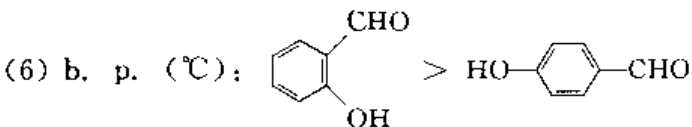
(2) 与 CH3OH 溶剂解速率：



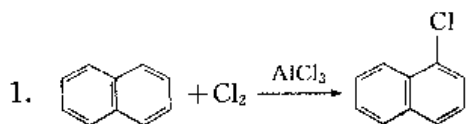
(3) 亲核性： CCO^- > CCS^- > CCSH

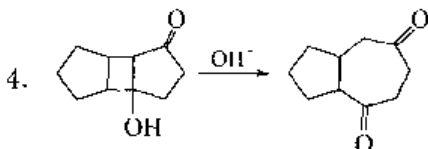
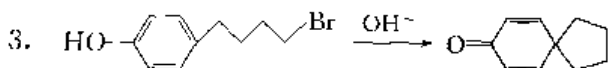
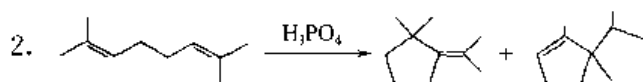


(5) 稳定性： CC(C)C=C > CC(C)=C

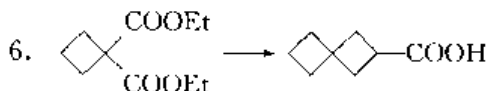
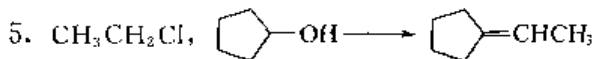
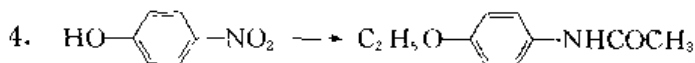
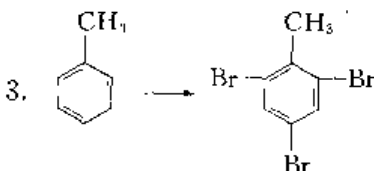
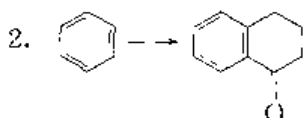


三、写出下列反应机理 (15 分)





四、按要求完成下列转变 (25 分)



五、推测结构 (15 分)

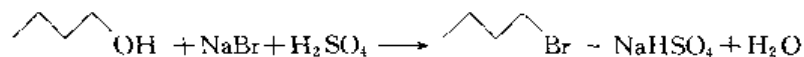
1. 化合物 A (C_5H_{10}), 用浓 H_2SO_4 的热溶液处理, 生成产物 B, B 的 IR 谱上 3600cm^{-1} 处有吸收, 其 NMR 谱为: δ 0.9 (三重峰), δ 1.2 (单峰), δ 1.4 (四重峰), δ 3.0 (单峰), 峰的强度比为 3:6:2:1, B 用浓 H_2SO_4 处理后得化合物 C (C 是 A 的异构体)。写出 A、B、C 的结构。

2. 化合物 D ($\text{C}_7\text{H}_{14}\text{O}$), IR 显示 1710cm^{-1} 有强吸收峰, $^1\text{H-NMR}$ 由 3 个单峰构成, 其峰面积比为 9:3:2, δ 1.0、 δ 2.1 和 δ 2.3, 推出化合物 D 的结构, 并指出 ^1H 的 NMR 谱的归宿。

3. 化合物 E ($\text{C}_{10}\text{H}_{12}\text{O}_3$) 具有旋光性, 能溶于 NaHCO_3 水溶液, 并可起碘仿反应。将 E 强烈加热得化合物 F, F 无旋光性, 也能溶于 NaHCO_3 水溶液, F 经臭氧化, 在 Zn 粉存在下分解得化合物 G 和 H, G 可进行碘仿反应, H 加热放出 CO_2 得化合物 J ($\text{C}_7\text{H}_6\text{O}$), J 可进行坎尼扎罗 (Cannizzaro) 反应。写出化合物 E、F、G、H、J 的结构式和有关反应。

六、实验题 (10 分)

在实验室用正丁醇制正溴丁烷是按式进行的。

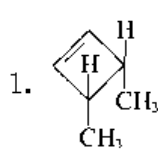
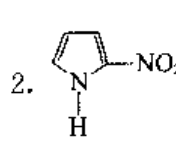
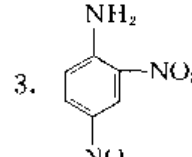
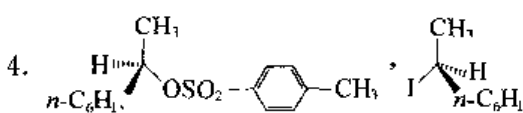
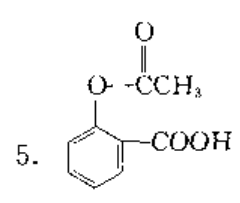
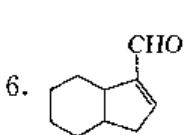
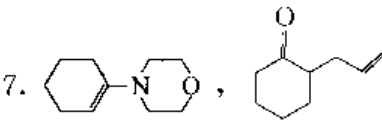
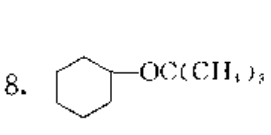
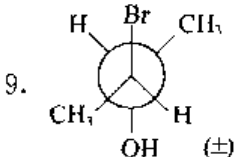
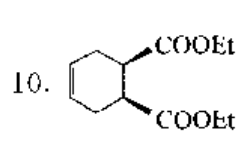
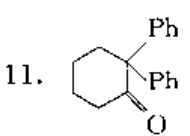
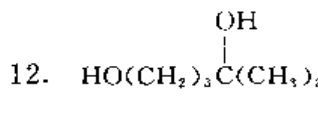
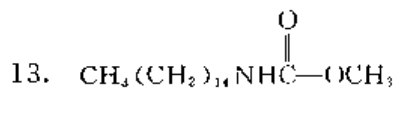
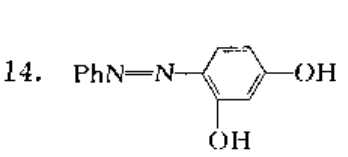
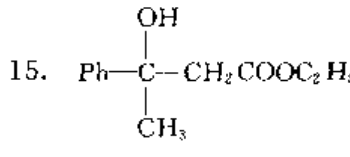
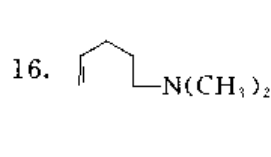
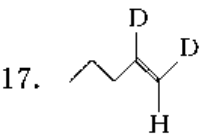
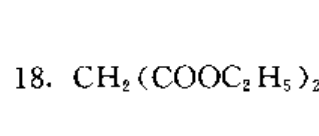


据此请回答下列问题：

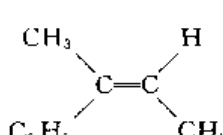
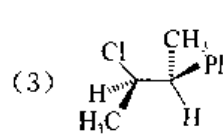
1. 可能发生哪些副反应？
2. 反应完成后，如何将反应混合物中的正溴丁烷分离出来？
3. 分离出来的粗产物中含有少量正丁醇和正丁醚，如何除去？
4. 如果反应的副产物中还有少量的 2-溴丁烷，请写出其形成机理。
5. 画出制备 1-溴丁烷的装置简图。

参考答案

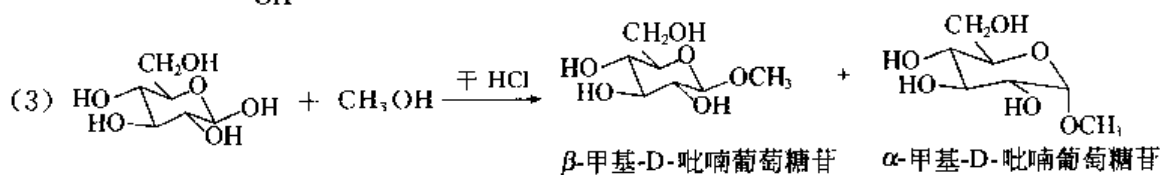
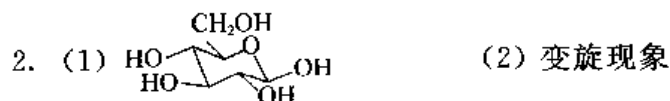
一、完成反应式

1. 
2. 
3. 
4. 
5. 
6. 
7. 
8. 
9. 
10. 
11. 
12. 
13. 
14. 
15. 
16. 
17. 
18. 

二、完成下列事项

1. (1) (2R, 3S) 2-苯基-3-氯丁烷
- (2) 
- (3) 

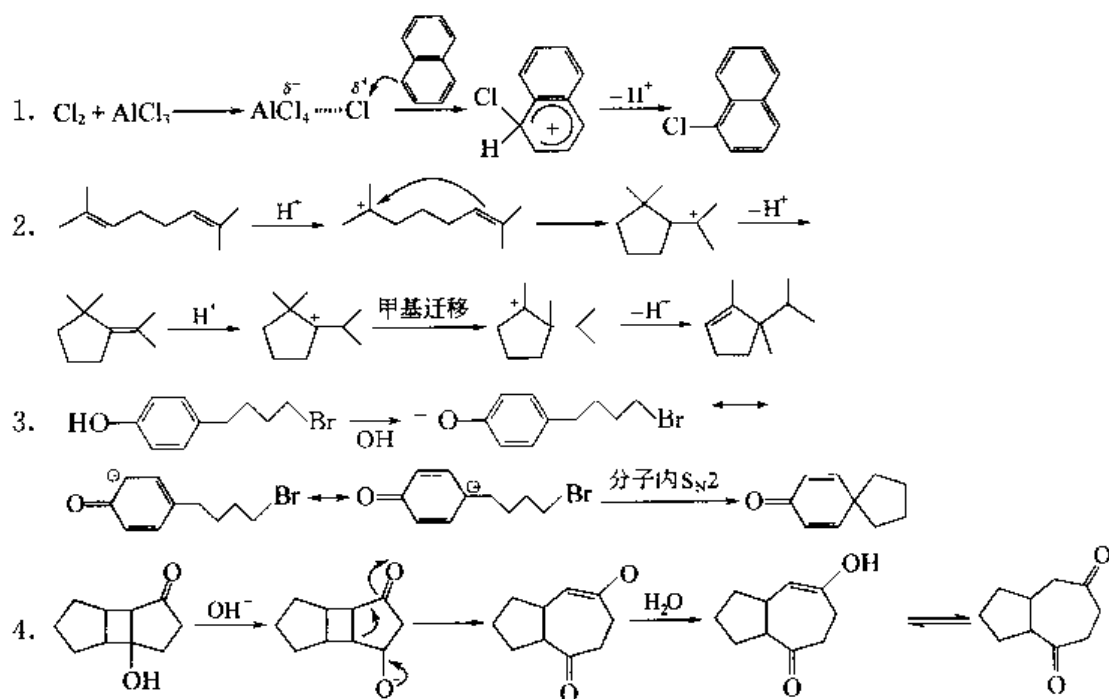
(4) Z-2-苯基-2-丁烯



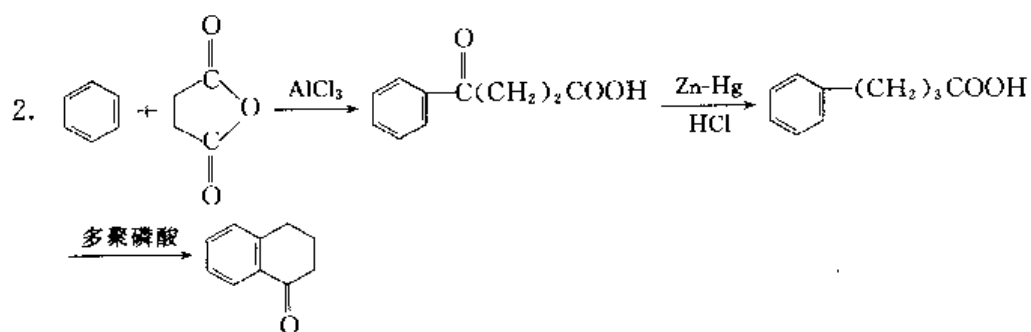
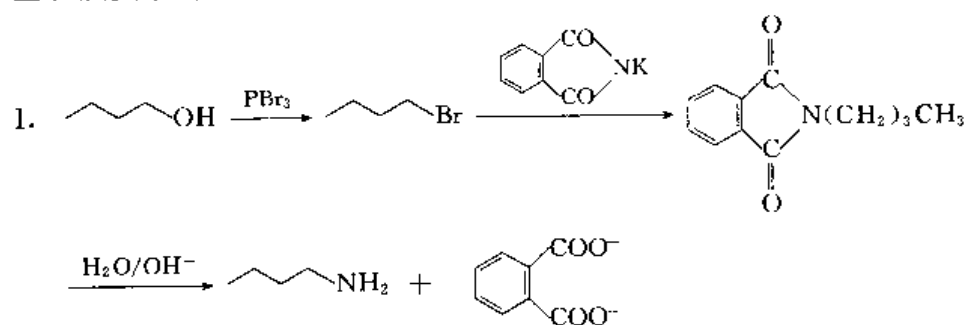
(4) β -甲基-1-吡喃葡萄糖苷

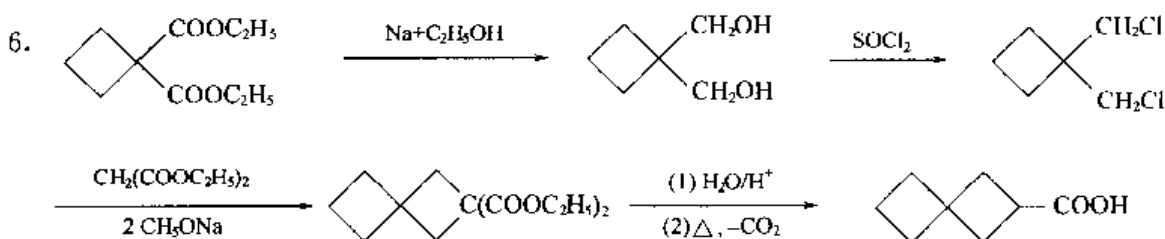
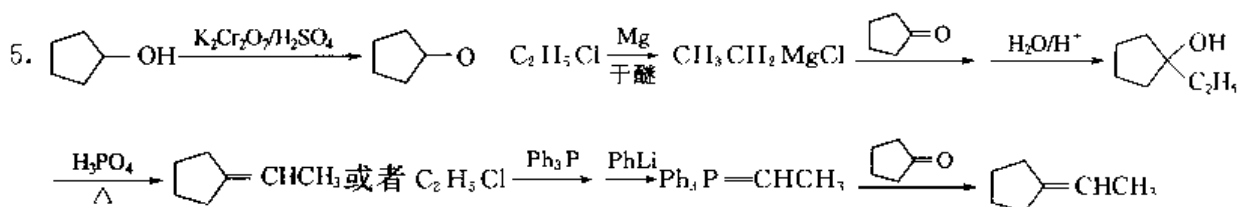
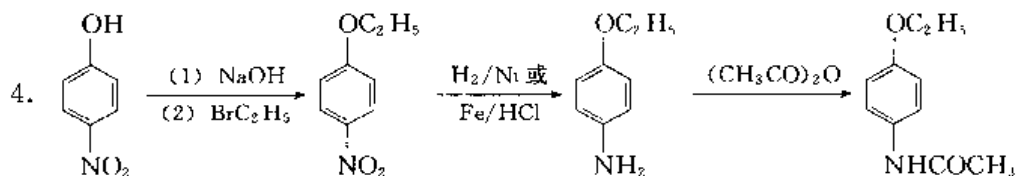
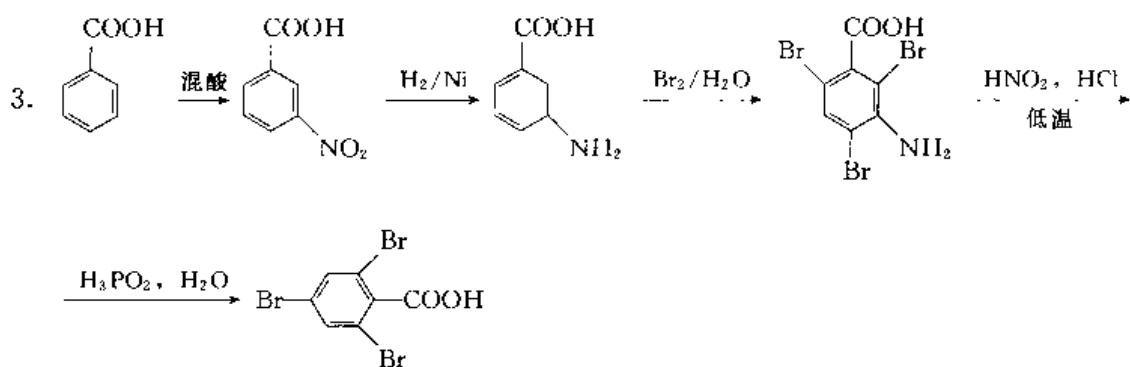
3. (1) 对 (2) 错 (3) 错 (4) 错 (5) 错 (6) 错 (7) 对

三、反应机理

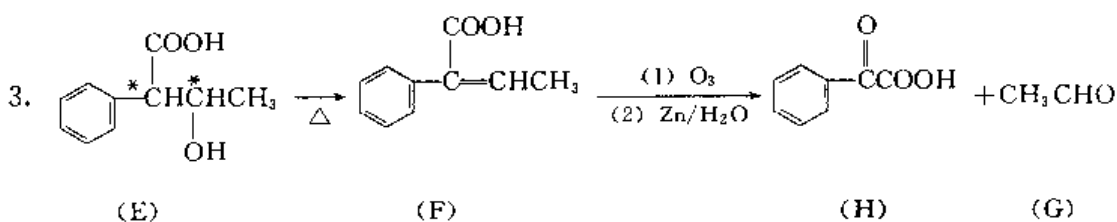
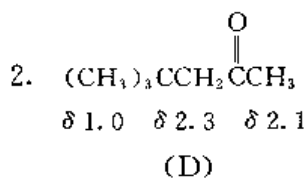
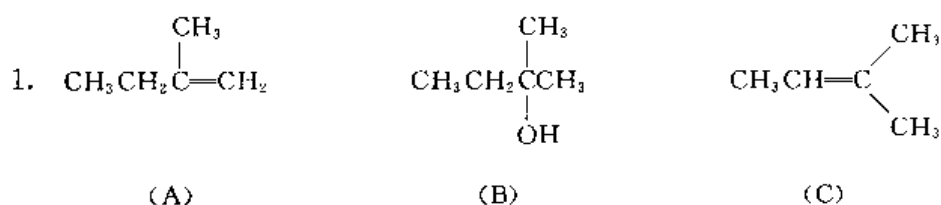


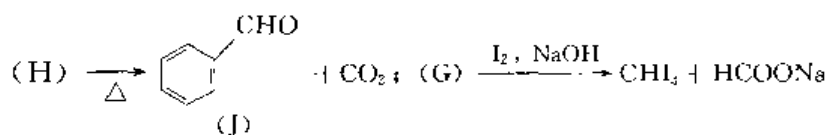
四、按要求完成下列转变



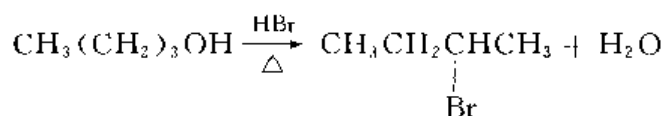
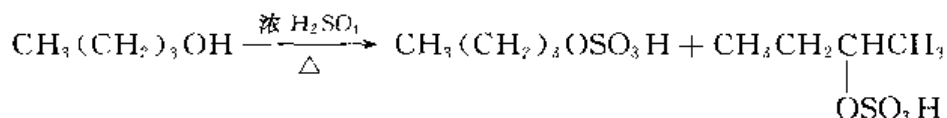
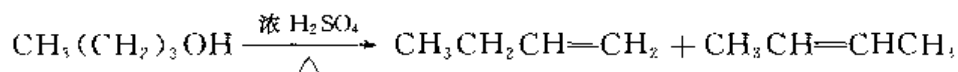
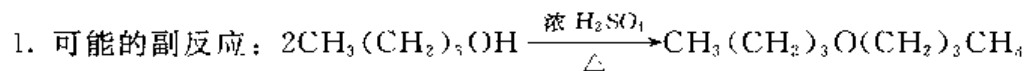


五、推测结构



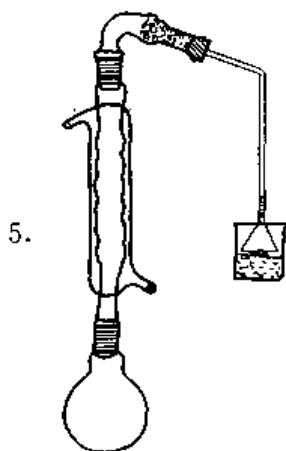
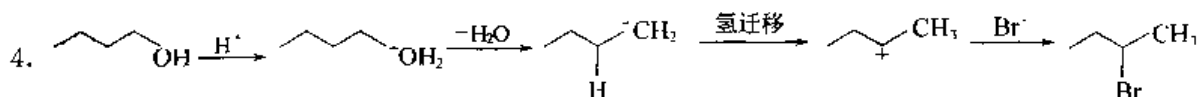


六、实验题



2. 通过蒸馏将 1-溴丁烷蒸出。因为沸点: $n\text{-C}_4\text{H}_9\text{Br} < n\text{-C}_4\text{H}_9\text{OH}$ 。

3. 先加入浓 H_2SO_4 使正丁醚和正丁醇质子化而溶解于酸层, 分液后, 可除去正丁醚和大部分正丁醇。再加入饱和 CaCl_2 使之与残余的正丁醇形成分子复合物而被除去。



模拟试题 11

一、命名及写结构式 (6 分)

1. 用 Fischer 式表示 2-羟基-3-戊烯醛的所有构型异构体, 并命名每个异构体。
2. 用 Newman 式表示 2-氯-3-溴戊烷的所有构型异构体的优势构象, 并指出其中哪些是对映体, 哪些是非对映体。

二、选择正确答案填充下列各题 (15 分)

1. 2,2,3-三甲基戊烷在光照下与溴反应, _____ 是主产物。

- (1) 2,2,3-三甲基-1-溴戊烷 (2) 2,2,3-三甲基-3-溴戊烷
 (3) 2,2,3-三甲基-4-溴戊烷 (4) 3,4,4-三甲基-1-溴戊烷

2. (S)-2-溴戊烷在¹H-NMR谱上有_____组峰。

- (1) 4组 (2) 5组 (3) 3组 (4) 6组

3. 下列化合物沸点最高的是_____。

- (1) 3-甲基-1-己醇 (2) 正己醇 (3) 正己烷 (4) 正氟代己烷

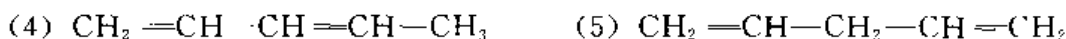
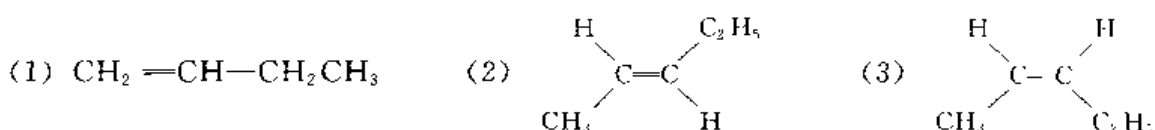
4. 下列物种中_____最稳定。

- (1) 三苯甲基自由基 (2) 苯基自由基 (3) 甲基自由基 (4) 叔丁基自由基

5. 下列C-H键在IR谱图上_____的波数最大。

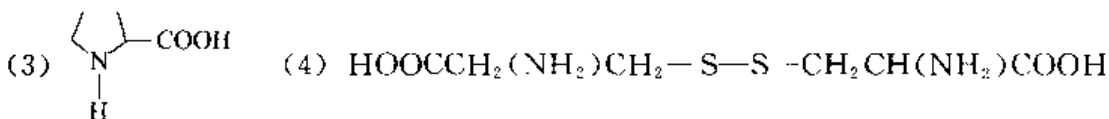
- (1) $\equiv\text{C}-\text{H}$ (2) $-\text{CH}_2-\text{H}$ (3) $=\text{CH}-\text{H}$

6. 下列化合物中, 热力学最稳定者是_____。



7. 下列氨基酸中, 等电点最小的是_____。

- (1) $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ (2) $\text{HOOCCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$

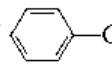


8. 下列化合物中, _____不能与2,4-二硝基苯肼反应; _____不能发生碘仿反应; _____不能发生银镜反应; _____不能发生自身羟醛反应。

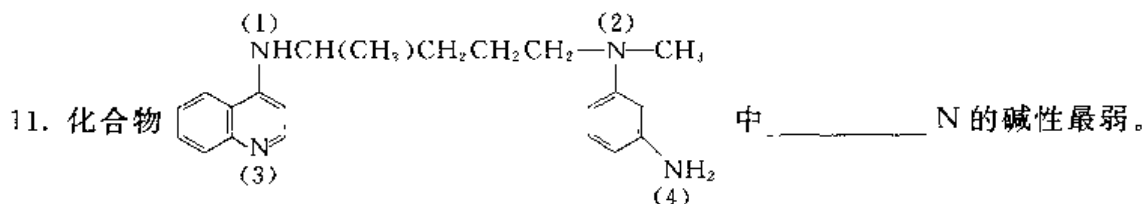
- (1) HCHO (2) CH_3CHO (3) $\text{CH}_3\text{CHOHCH}_3$ (4) CH_3COCH_3

9. 下列化合物在液态时, _____酸性最弱。

- (1) $\text{CH}_3\text{COCH}_2\text{COCH}_3$ (2) $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$
 (3) $\text{CH}_3\text{COCH}(\text{COCH}_3)_2$ (4) $\text{CH}_3\text{COCH}(\text{COOC}_2\text{H}_5)_2$

10. 化合物 - $\text{CH}=\text{CH}-\text{CH}_3$ 在过氧化物存在下与HBr反应, 主要产物是_____。

- (1) 1-苯基-2-溴丙烷 (2) 1-苯基-1-溴丙烷 (3) 1-苯基-3-溴丙烷
 (4) 邻溴苯基丙烷 (5) 对溴苯基丙烷



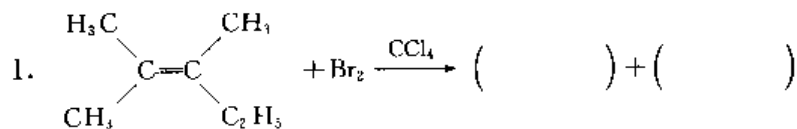
12. 下列化合物中, _____的磺化反应最易进行。

- (1) 呋喃 (2) 噻吩 (3) 吡啶 (4) 苯 (5) 联苯 (6) 萘

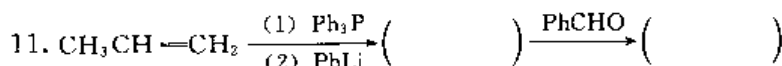
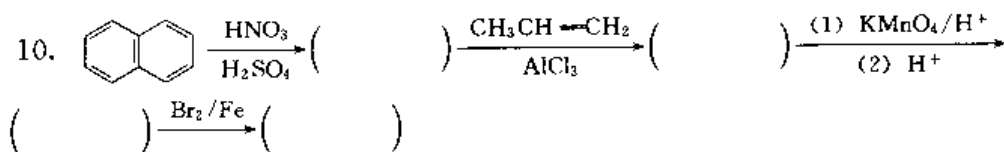
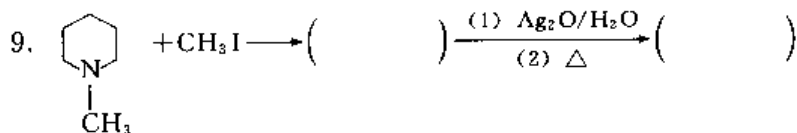
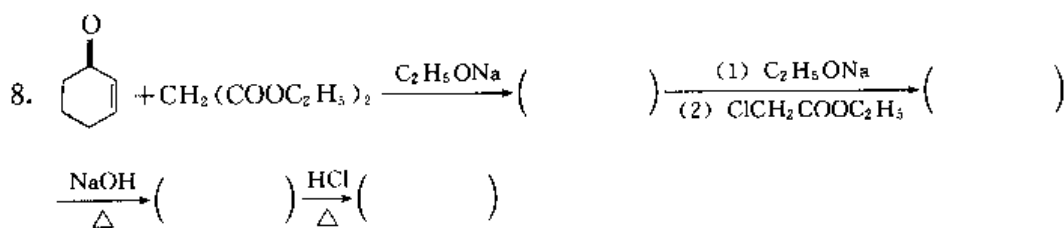
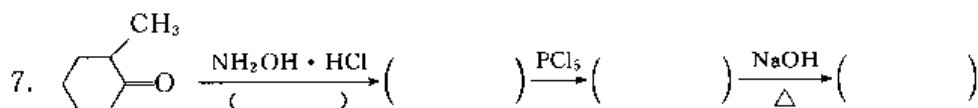
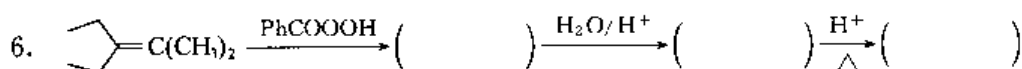
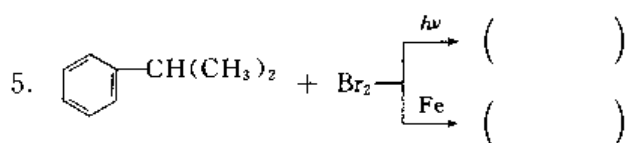
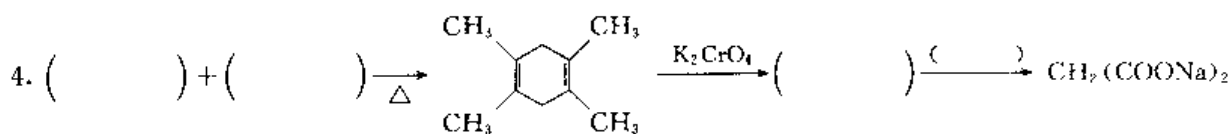
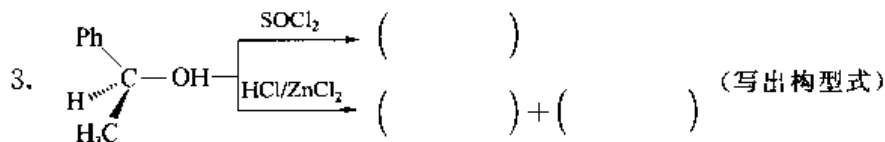
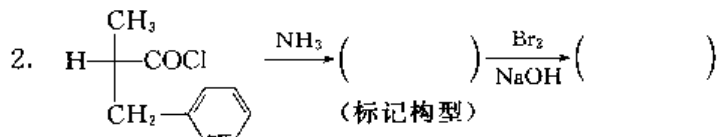
13. 下列化合物中, _____能被溴水氧化。

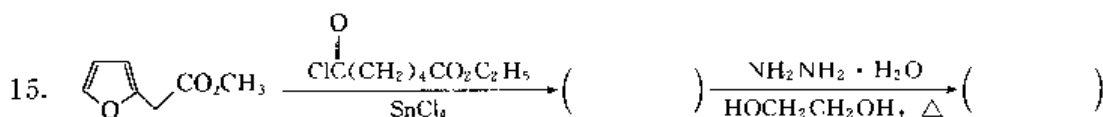
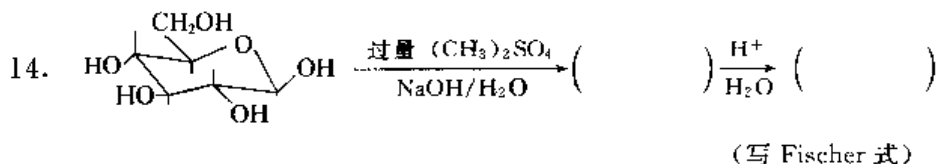
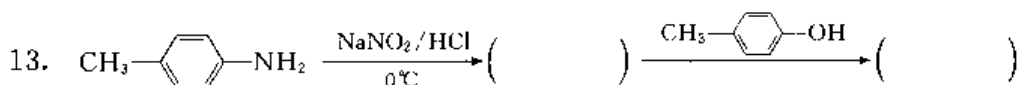
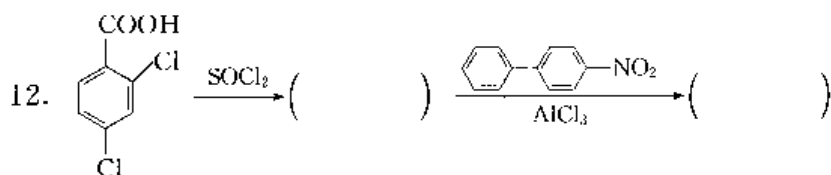
- (1) D-葡萄糖 (2) D-甲基葡萄糖苷 (3) D-果糖 (4) 蔗糖

三、完成下列反应，写出主要产物 (22分)



(写出 Newman 投影式)





四、推导结构 (单考生可选作两题, 但 1, 2 题中至少选作 1 题) (16 分)

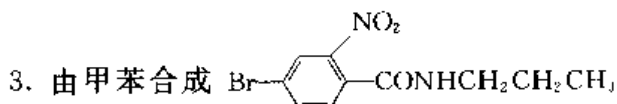
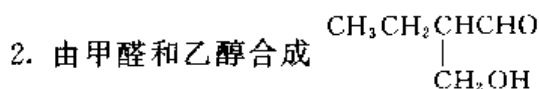
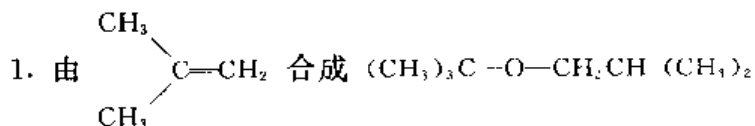
1. A、B、C 3 个化合物的分子式都为 $\text{C}_3\text{H}_6\text{O}$, 在 $^1\text{H-NMR}$ 谱上 A 只有 1 组峰, B 有 3 组峰, C 有 4 组峰。A、B、C 都能与 HCN 反应。A 与 HCN 反应产物经酸性水解得 D, D 没有旋光活性, D 的 $^1\text{H-NMR}$ 谱有 3 组峰。B 与 HCN 反应的产物经水解得 E, E 是一种外消旋体。C 与 HCN 反应产物经水解得 F, F 有一个 (R)-构型的手性碳, 其 $^1\text{H-NMR}$ 谱图上有 6 组峰。写出 A、B、C、D、E、F 的结构式。(5 分)

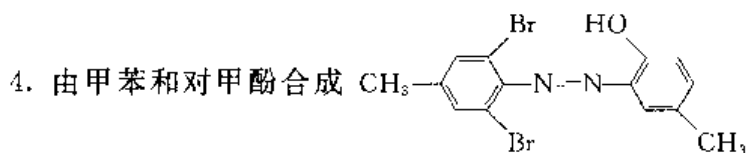
2. 分子式为 $\text{C}_{10}\text{H}_{12}\text{O}_2$ 的化合物, 其 IR 谱为: 3010cm^{-1} , 2900cm^{-1} , 1735cm^{-1} , 1600cm^{-1} , 1500cm^{-1} 等吸收峰; 其 $^1\text{H-NMR}$ 化学位移为: δ 1.3 (三重峰 3H), δ 2.4 (四重峰 2H), δ 5.1 (单峰 2H), δ 7.3 (单峰 5H)。写出该化合物的构造式, 并归属 IR 和 $^1\text{H-NMR}$ 峰。(5 分)

3. 烃 A 的分子式为 C_4H_8 , 在低温下与 Cl_2 反应生成分子式为 $\text{C}_4\text{H}_8\text{Cl}_2$ 的 B; 在光照下生成分子式为 $\text{C}_4\text{H}_7\text{Cl}$ 的 C。C 与 NaOH 的水溶液加热作用生成 D ($\text{C}_4\text{H}_7\text{OH}$); 与 NaOH 的醇溶液加热作用生成 E (C_4H_6)。E 能与顺丁烯二酸酐反应生成 F ($\text{C}_8\text{H}_8\text{O}_3$), 写出 A~F 的构造式。(3 分)

4. 化合物 A 的分子式为 $\text{C}_6\text{H}_7\text{N}$, A 与 NaNO_2 和稀 H_2SO_4 作用生成分子式为 $\text{C}_6\text{H}_8\text{O}$ 的 B, B 的钠盐与 $\text{Br-CH}_2\text{CH=CH}_2$ 作用生成 $\text{C}_9\text{H}_{10}\text{O}$ (C), C 与稀硫酸在 230°C 反应异构成 D, D 异构化变成 E, E 臭氧化还原水解生成乙醛和 F。试推导 A~F 的构造。

五、由指定原料 (其他试剂任选) 合成化合物 (单考生可从 1, 2 和 3, 4 中各选做 1 题) (16 分)





六、实验题 (25 分):

仔细阅读“肉桂酸的制备”操作步骤，然后回答问题。

(已知: 乙酐 b. p. = 140°C, 苯甲醛 b. p. = 178°C, 肉桂酸 (反) m. p. = 136°C)

在干燥的小梨形单口烧瓶中放入 3g 新熔融并研细的无水醋酸钾粉末, 3ml 新蒸馏的苯甲醛和 5.5ml 乙酐, 混合后在烧瓶口装一个两口连接管, 正口插入一支温度计, 侧口接空气冷凝管, 加热使反应液微微沸腾 1h。

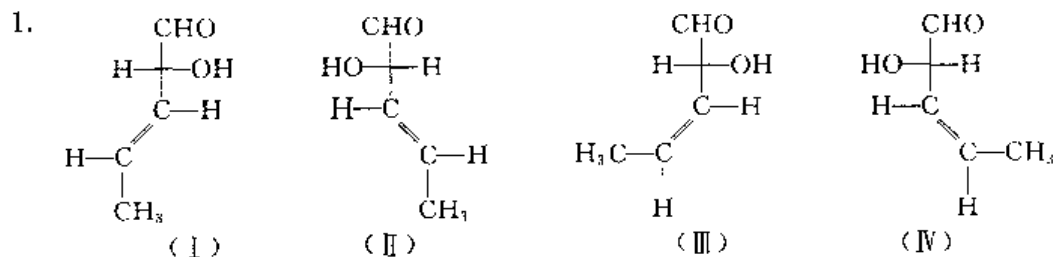
将反应混合物趁热倒入盛有 25ml 水的 250ml 圆底烧瓶中, 边振荡边慢慢加入饱和碳酸钠溶液, 使反应呈弱碱性。然后进行水蒸气蒸馏, 直至馏出液中无油珠为止。

往剩余液体中加入少许活性炭, 加热煮沸 10min, 趁热过滤。用浓盐酸酸化滤液, 使呈明显酸性, 冷却后滤出晶体肉桂酸。粗产物用 30% 的乙醇溶液重结晶。

1. 写出合成肉桂酸反应的反应机理。
2. 为什么采用梨形烧瓶? 应选用多少 ml 容积的梨形烧瓶?
3. 合成反应的温度计应选用多大量程的温度计才合适?
4. 反应仪器为什么必须是干燥的?
5. 使用的乙酐和苯甲醛为什么需要新蒸馏过的?
6. 为什么要用新熔融的并研细的无水醋酸钾?
7. 反应液中焦油状物质是什么? 它是如何被除去的?
8. 混合物分离过程中, 为什么用到中和及酸化两步化学反应?
9. 中和一步用饱和碳酸钠溶液, 为什么不用 NaOH 溶液?
10. 为什么用水蒸气蒸馏? 水蒸气蒸馏分出什么物质?
11. 用有机溶剂重结晶, 热饱和溶液应如何制备?
12. 画出合成反应和用 30% 乙醇制备肉桂酸热饱和溶液的仪器装置图, 并标明仪器名称。

参考答案

一、命名及写结构式

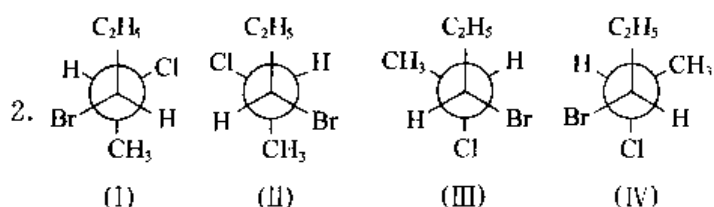


(I) (2R, 3E) - 2-羟基-3-戊烯醛

(II) (2S, 3E) - 2-羟基-3-戊烯醛

(III) (2R, 3Z) - 2-羟基-3-戊烯醛

(IV) (2S, 3Z) - 2-羟基-3-戊烯醛



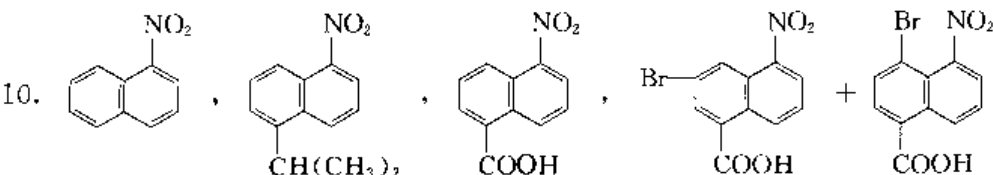
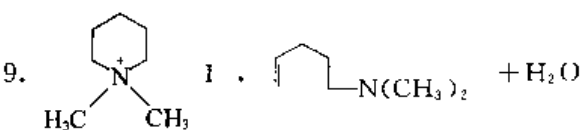
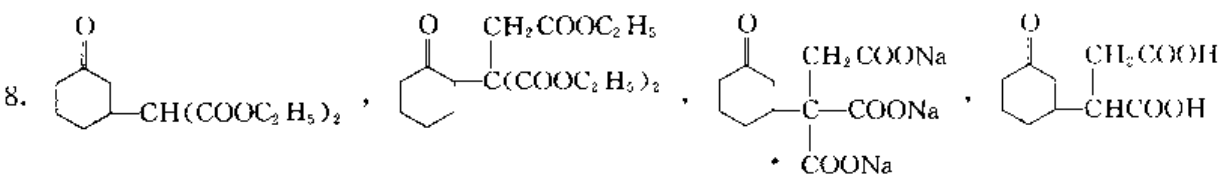
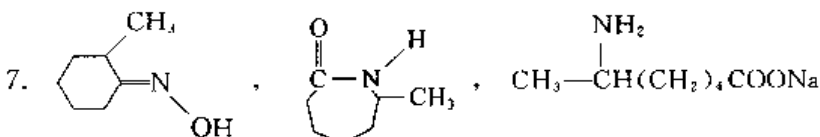
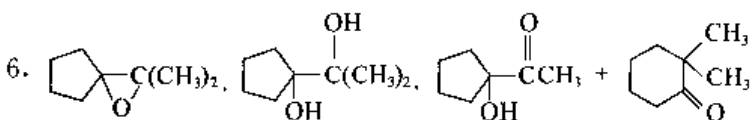
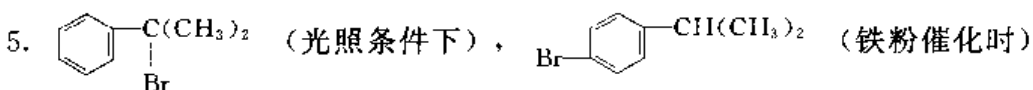
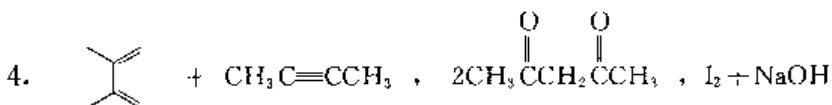
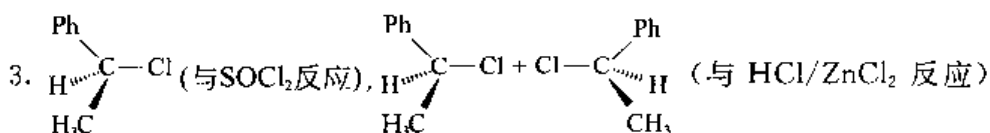
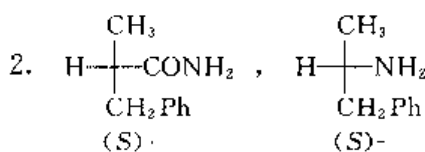
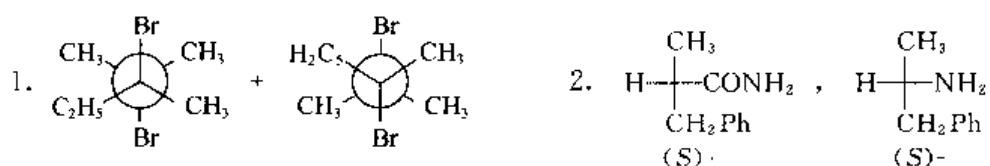
(I) 和 (II)、(III) 和 (IV) 是对映体；

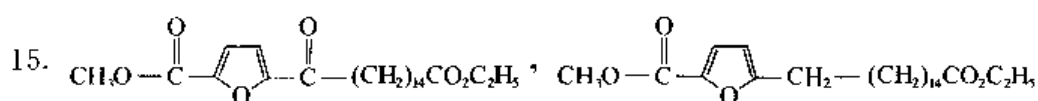
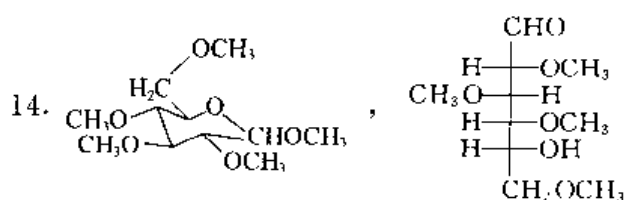
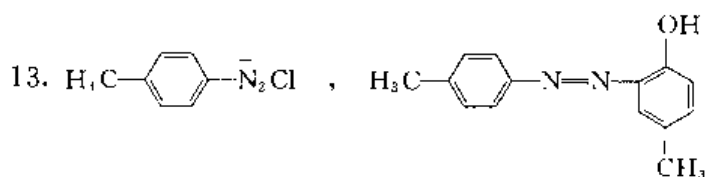
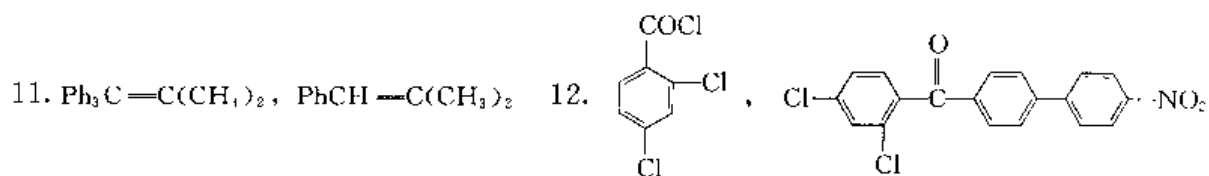
(I) 和 (III)、(I) 和 (IV)、(II) 和 (III)、(II) 和 (IV) 是非对映体。

二、填空

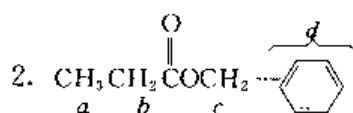
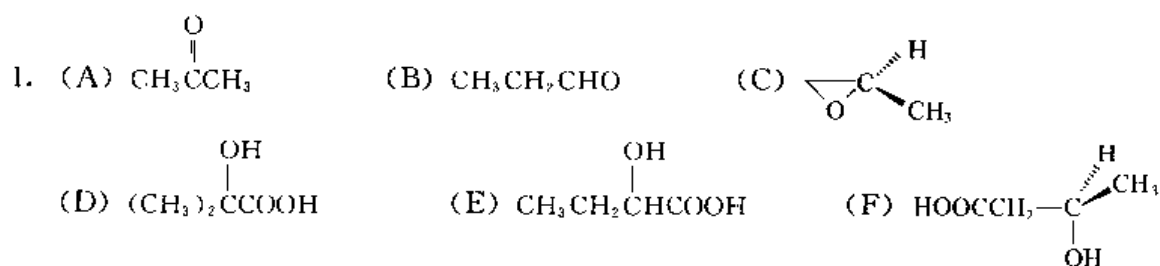
1. (2) 2. (2) 3. (2) 4. (1) 5. (1) 6. (2) 7. (2) 8. (3) 不与 2,4-二硝基苯肼反应, (1) 不能发生碘仿反应, (3) 和 (4) 不发生银镜反应, (1) 和 (3) 不发生自身羟醛缩合反应; 9. (2) 10. (1) 11. (2) 12. (2) 13. (1)

三、完成反应式





四、推导结构



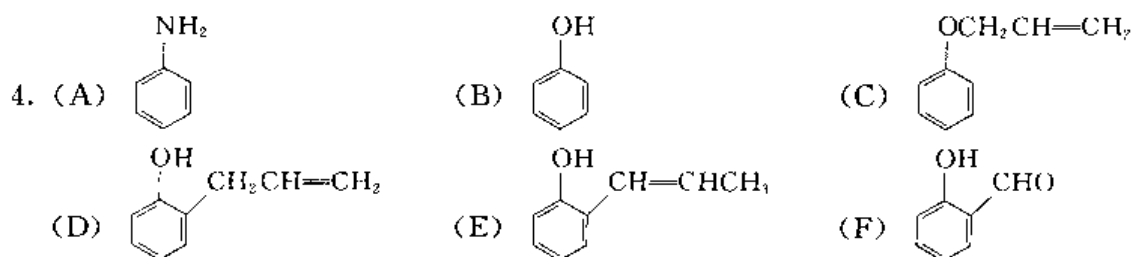
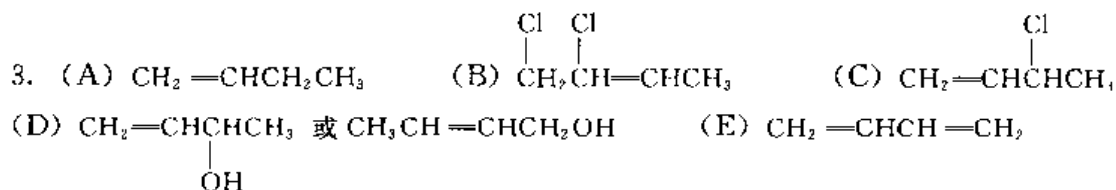
$^1\text{H NMR}$ δ_{H} = 1.3 (三重峰, 3H) δ_{H} = 2.4 (四重峰, 2H)
 δ_{H} = 5.1 (单峰, 2H) δ_{H} = 7.3 (单峰, 5H)

IR 3010cm^{-1} : C—H (不饱和) 伸缩振动吸收;

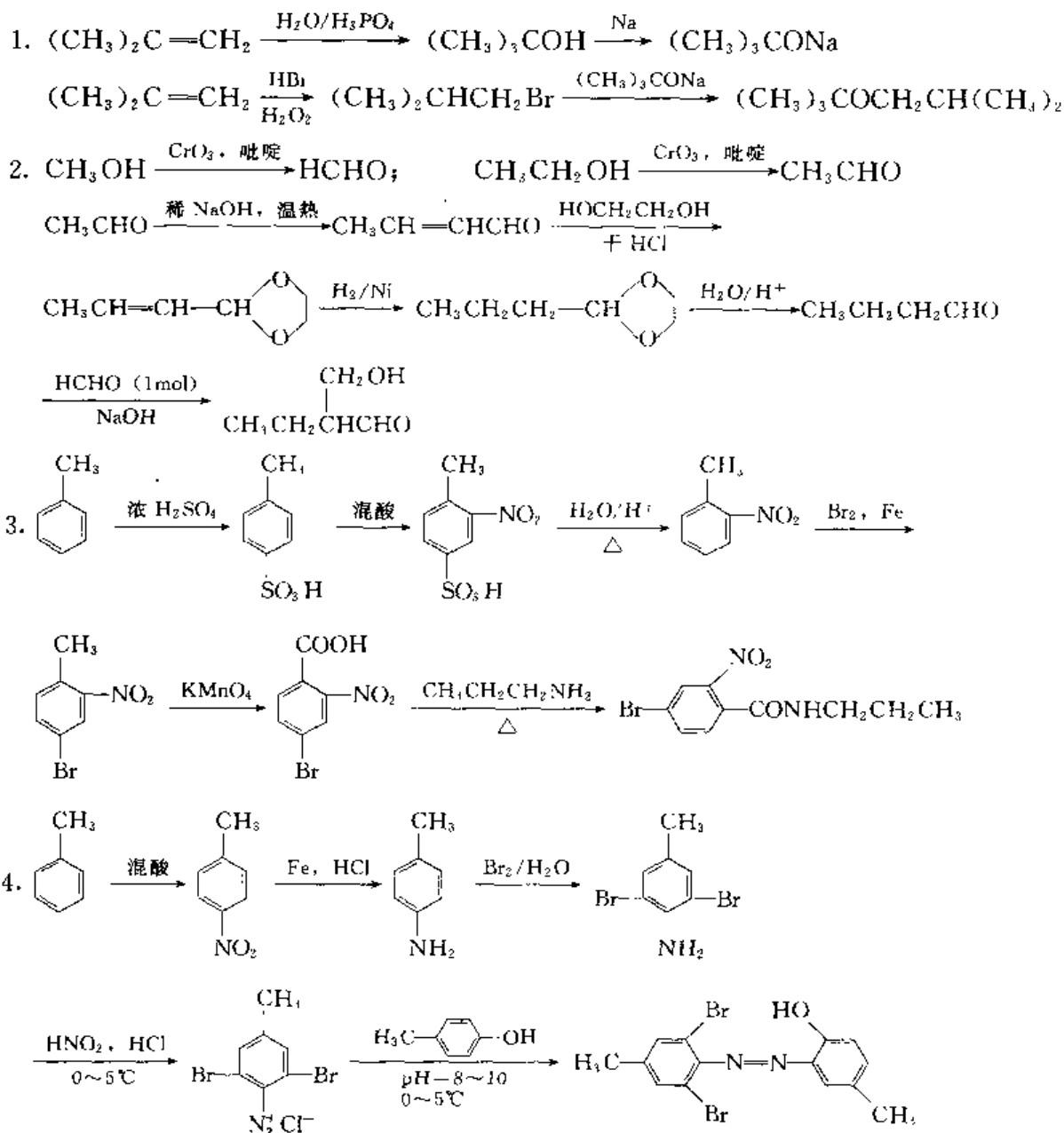
2900cm^{-1} : C—H (饱和) 伸缩振动吸收;

1735cm^{-1} : C=O (酯) 伸缩振动吸收;

1600 、 1500cm^{-1} : 苯环呼吸振动吸收。

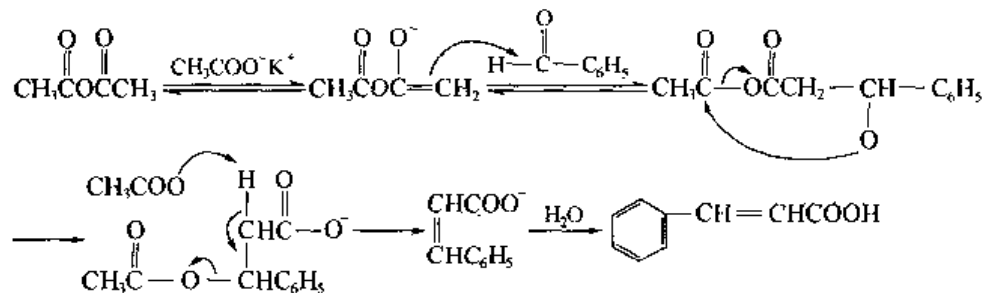


五、合成



六、实验题

1. 合成肉桂酸反应的机理:

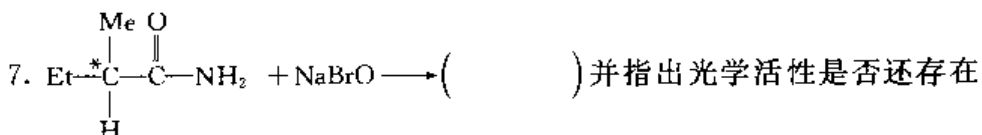
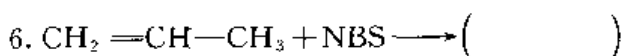
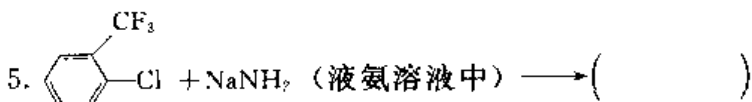
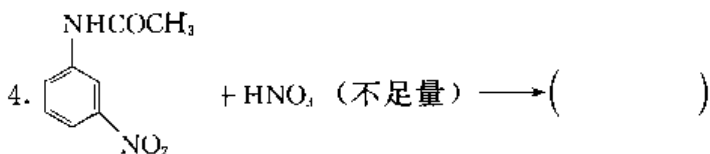
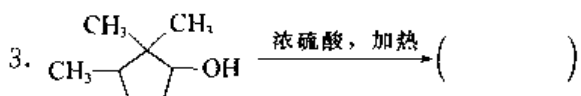
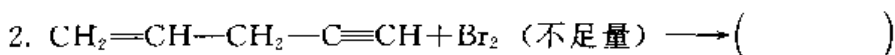
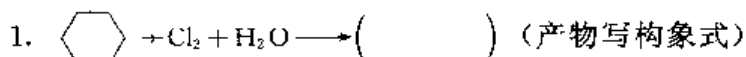


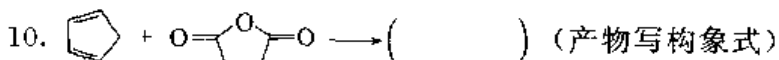
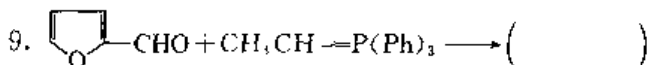
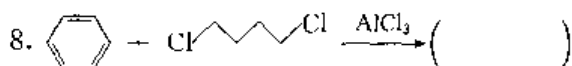
2. 选用梨形烧瓶的原因是本实验反应物料的量太少。为了方便而准确地测定反应温度，选用底部较尖的梨形烧瓶，使液面较高，便于测量反应温度。本实验应选用 50ml 的梨形烧瓶。

3. 合成时应选用量程为 250℃ 的温度计。
4. 反应仪器必须干燥，否则乙酸酐遇水而水解，不利于缩合反应的进行。
5. 乙酸酐久置可能水解生成乙酸；苯甲醛久置可能氧化生成苯甲酸。而 Perkin 是在碱性介质中进行的，所以两种酸都不利于缩合反应的进行。反应前重新蒸馏，可将乙酸或苯甲酸除去。
6. 无水醋酸钾易吸水，使用前必须熔融，除去水分。研细的目的是使无水醋酸钾与反应物料充分接触，加快反应速率。
7. 反应液中焦油状物质可能是高分子物质，可在热过滤时除去。
8. 前面的中和是为了使肉桂酸以钠盐形式存在，防止在水蒸气蒸馏时被蒸出。后面的酸化是在除去了未反应的苯甲醛及其他水不溶性杂质后使肉桂酸晶体析出。
9. 用饱和碳酸氢钠溶液中和反应可生成 CO₂，带走大量的中和热；同时，根据有无气泡冒出很容易判断是否需要继续加碱中和。
10. 用水蒸气蒸馏可分离出水不溶的易挥发性物质。本实验采用水蒸气蒸馏是为了除去没有参加反应的苯甲醛。
11. 首先应该选好溶剂，比如不与被重结晶物质反应，在高温和低温时的溶解度差别较大等（5 条）；操作时应采用回流装置，防止溶剂的挥发；溶剂的用量应适当，一般为制成完全饱和溶液时用量的 110%~120%。具体操作时，应逐步添加溶剂并记录溶剂的加入量，至被重结晶物质在高温时完全溶解后，再加入 10%~20% 的溶剂，经活性炭脱色后热过滤。
12. 略。

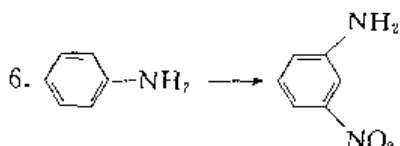
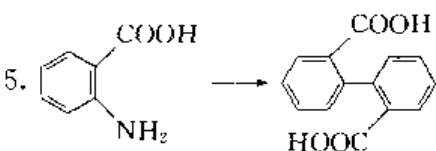
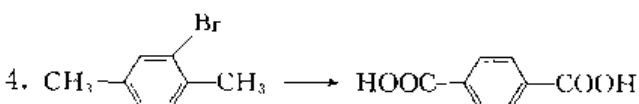
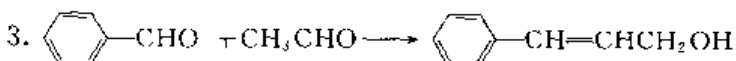
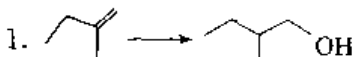
模拟试题 12

一、写出下列反应主要产物的结构简式（20 分）

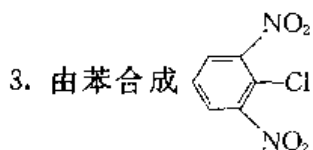
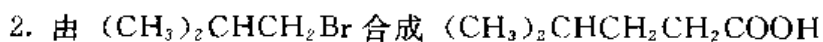
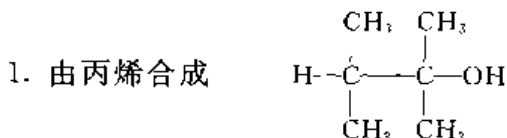




二、完成下列转变 (只允许使用无机试剂和有机溶剂) (18分)



三、合成题 (15分)



四、推测结构 (17分)

1. 化合物 A 和 B 互为异构体, 分子式均为 C₉H₁₀O。A 的 IR 谱中 1690cm⁻¹ 处显一强吸收峰; NMR 谱数据为: δ 1.2 (3H, 三重峰); δ 3.0 (2H, 四重峰); δ 7.7 (5H, 多重峰); A 不发生碘仿反应。B 的 IR 谱中 1705cm⁻¹ 处显强的吸收峰; NMR 谱数据为: δ 2.0 (3H, 单峰); δ 3.5 (2H, 单峰), δ 7.1 (5H, 多重峰); B 可发生碘仿反应。试推测 A 和 B 的构造。(5分)

2. 有 A、B 两种化合物, 其分子式分别为 C₇H₁₀N₂ 和 C₇H₉N, 两者都能溶于盐酸, 与苯磺酰氯作用都得到水溶性的碱式盐。A 和 B 都可氧化为 2-甲基-1,4-苯醌, 试写出 A 和 B 的构造式。(4分)

3. A 分子式为 C₆H₁₂O, 氧化得 B, B 溶于 NaOH 溶液, B 酯化后发生分子内缩合关环反应, 生成环状化合物。这个化合物皂化、酸化及脱羧后生成 C, C 可以和盐酸羟胺生成

肪, C用 Zn-Hg/HCl 还原生成 D, D 的分子式为 C_5H_{10} 。试写出 A、B、C 和 D 的构造式。(8分)

五、回答题 (30分)

1. 写出下列化合物的构造式, 立体异构体写构型式或构象式。(5分)

(1) 7,7-二甲基二环 [2.2.1] -2,5-庚二烯

(2) (S)-2-碘辛烷

(3) 顺-1,3-环己二醇的最稳定构象

(4) 1,3-丙二醇甲乙醚

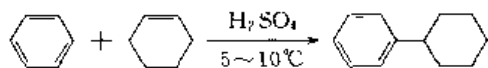
(5) (E)-2,3-二甲基-2-丁烯-1,4-二醇

2. 比较下列化合物消去 HBr 的速度快慢, 并简述理由。(3分)

(A) -CHBrCH₃ (B) O₂N--CHBrCH₃

(C) CH₃O--CHBrCH₃ (D) CH₃--CHBrCH₃

3. 推测形成下列反应产物的机理。(3分)






4. 比较下列化合物的酸性强弱。(3分)

(A) $\text{CH}_3-\underset{\text{OH}}{\text{C}}-\text{CH}-\underset{\text{O}}{\text{C}}-\text{CH}_3$ (B) CH₃OH (C) CH₃SH (D) CH≡CH

5. 用化学方法鉴别下列各组化合物, 并写出相关反应式。(8分)

(1) (A) 己烷 (B) 1-丁醇 (C) 丁醚 (D) 1-溴丁烷 (E) 苯酚

(2) (A) HO--CH₂CHO (B) HO--CHO (C) -COCH₂OH

(D) -OCOCH₃ (E) -OCH₂COOH

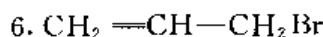
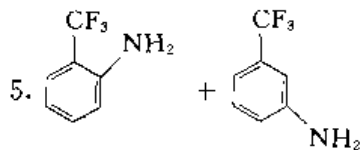
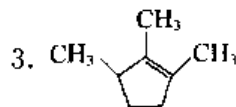
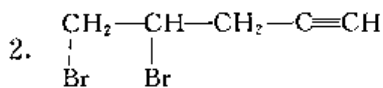
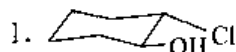
6. 分离或提纯下列各组化合物。

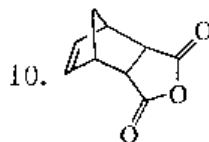
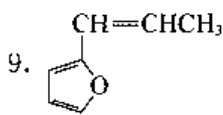
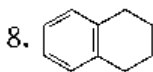
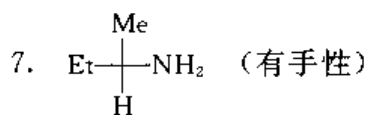
(1) 如何除去混入苯甲醇中的少量苯甲醛和苯甲酸? (3分)

(2) 在浓硫酸催化下苯甲酸与乙醇发生酯化反应, 为了提高直接酯化的平衡转化率, 可采取什么措施? 试设计一个从反应混合物中获得纯的苯甲酸乙酯的方法, 以图解式表示。(5分)

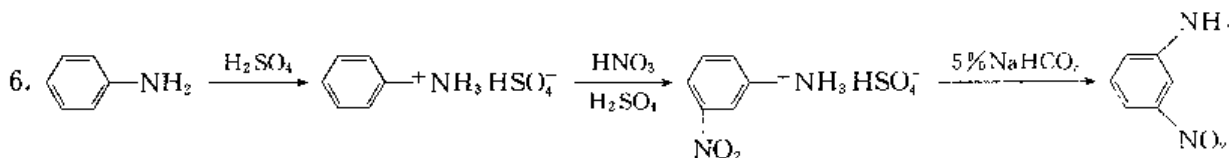
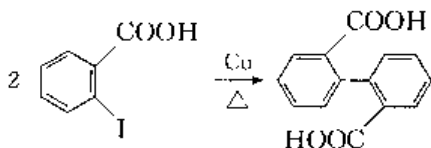
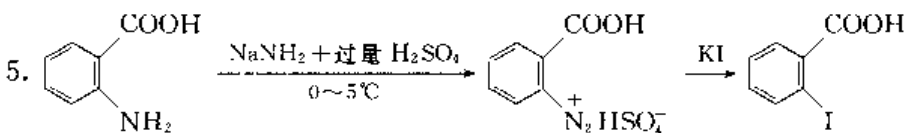
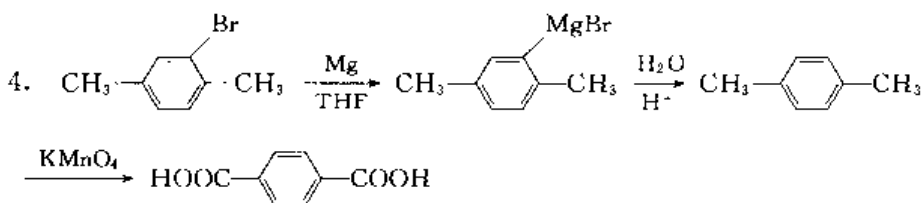
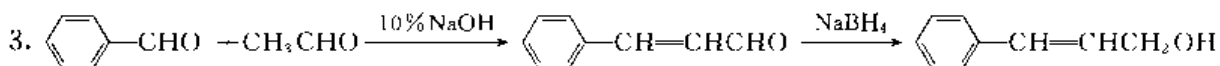
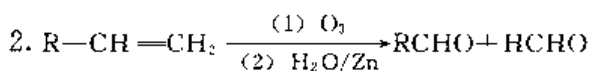
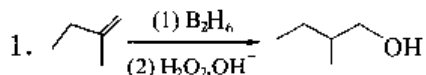
参考答案

一、完成反应式

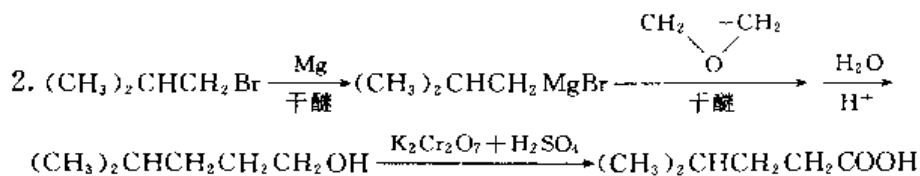
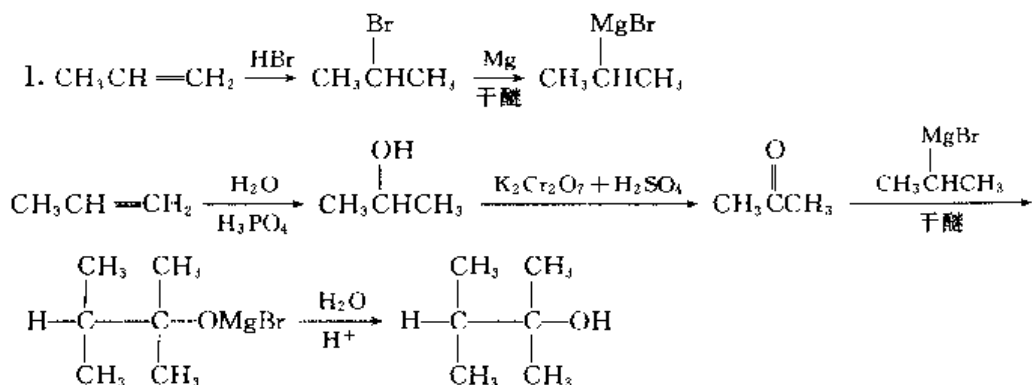


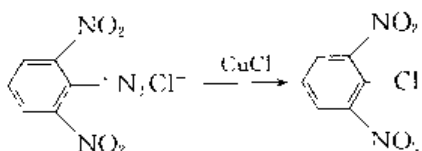
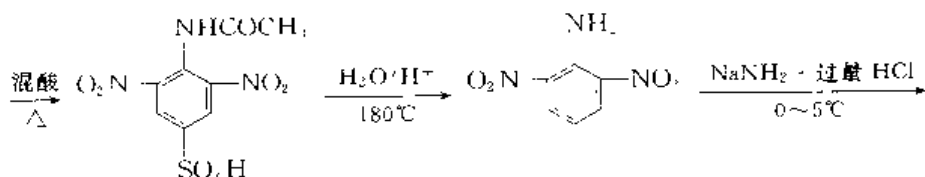
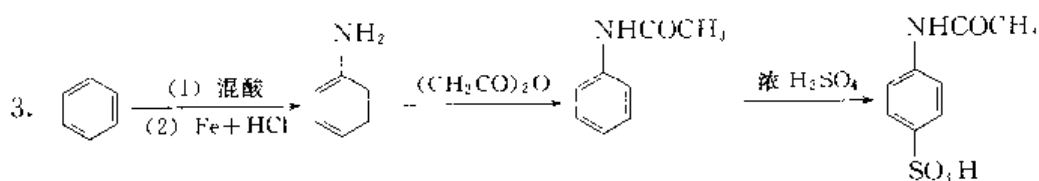


二、完成下列转变

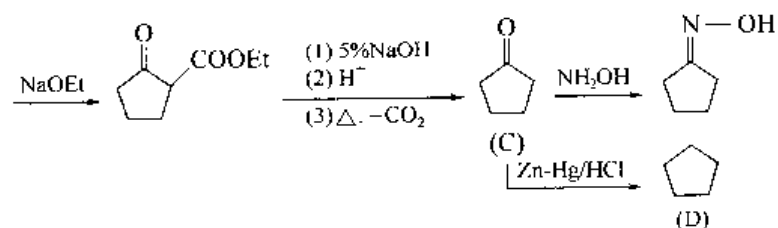
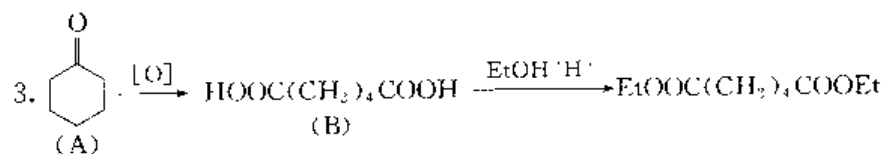
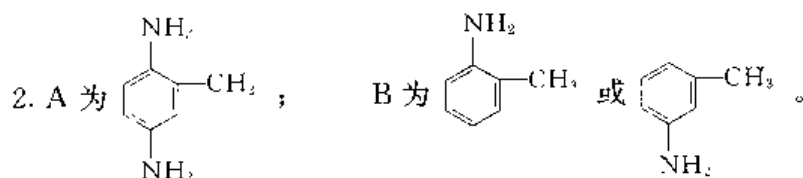
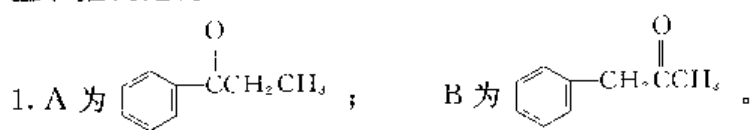


三、合成题

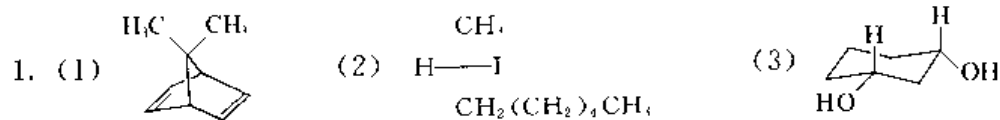




四、推测结构

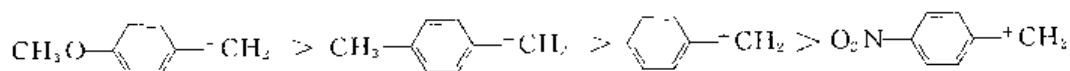


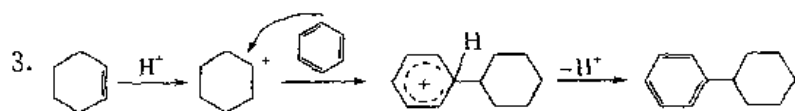
五、回答案



2. 消去反应速率: C > D > A > B.

原因: 题中 4 种化合物消去 HBr 的反应均为 E1, C⁺ 稳定性:





4. 酸性: A > C > B > D

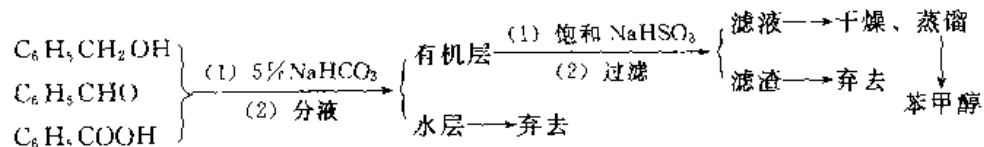
5. (1)

项 目	FeCl ₃	AgNO ₃ 醇, Δ	浓 H ₂ SO ₄	CH ₃ COCl
己烷				
1-丁醇			溶解	酯香味
丁醚			溶解	
1-溴丁烷		AgBr ↓ (淡黄)		
苯酚	显色			

(2)

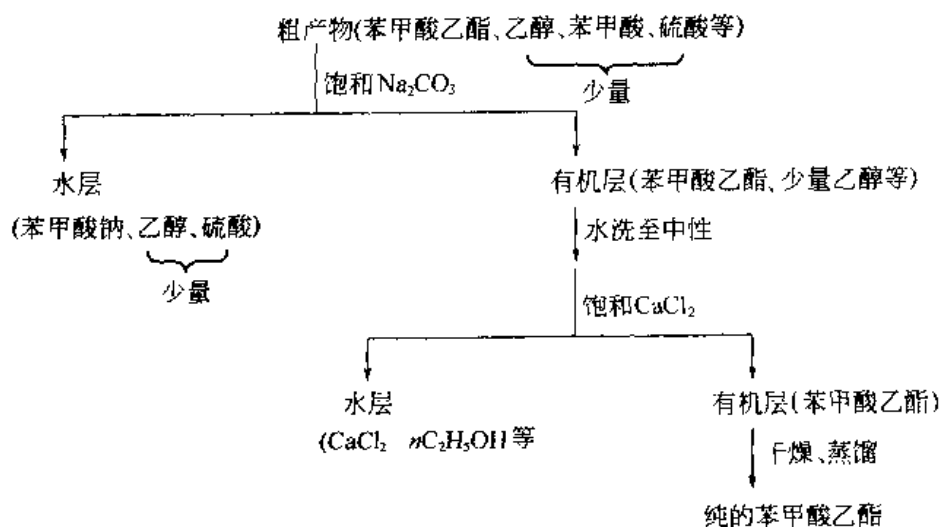
项 目	FeCl ₃	Fehling's	5% NaOH	2,4-二硝基苯腈
<i>p</i> -HO-C ₆ H ₄ -CH ₂ CHO	显色	砖红色 ↓	溶解	黄色 ↓
<i>p</i> -HO-C ₆ H ₄ -CHO	显色		溶解	黄色 ↓
C ₆ H ₅ COCH ₂ OH				黄色 ↓
C ₆ H ₅ OCOCH ₃				
C ₆ H ₅ OCH ₂ COOH			溶解	

6. (1)



(2) 可利用化学平衡移动的原理提高酯的产率。可采取如下的措施: a. 增大乙醇的用量; b. 采用干燥的仪器等。

粗产物的提纯方法如下。



模拟试题 13

一、选择题 (20 分)

1. 下列化合物在水中溶解度最大的是 ()。

- (A) 正丁醇 (B) 丙醇 (C) 1-氯丁烷 (D) 2-氯丙烷

2. Lindler 催化可用于哪种反应 ()。

- (A) 二元醇脱水 (B) 末端炔烃水合成醛
(C) 芳烃的硝化 (D) 炔烃部分还原成顺式烯烃

3. Williamson 合成法是合成什么的重要方法? ()

- (A) 卤代烃 (B) 高级炔 (C) 混合醚 (D) 伯胺

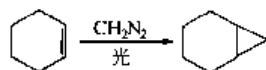
4. 分子式为 C_5H_{10} , 分子内含有三元环, 这样的异构体 (包括构造异构和构型异构) 应该有几个? ()

- (A) 2 个 (B) 3 个 (C) 4 个 (D) 5 个

5. 上题中, 这些异构体中有几个是旋光的? ()

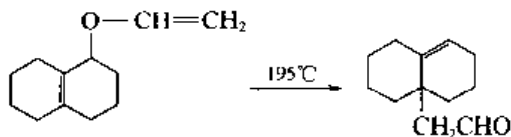
- (A) 2 个 (B) 3 个 (C) 4 个 (D) 5 个

6. 下列反应经过的主要活性中间体是 ()。



- (A) 碳正离子 (B) 碳负离子 (C) 碳烯 (D) 氮烯

7. 下列反应属于什么类型的反应 ()。

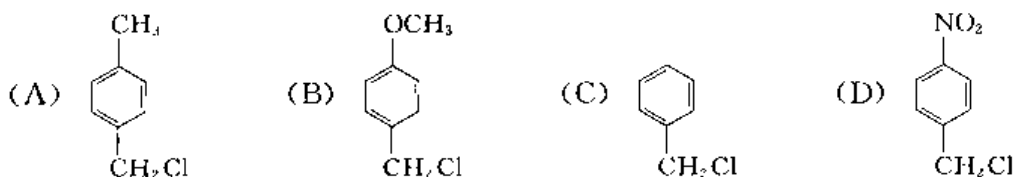


- (A) $[1,3]\sigma$ 迁移 (B) $[3,3]\sigma$ 迁移 (C) $[1,5]\sigma$ 迁移 (D) $[2,3]\sigma$ 迁移

8. 在核磁共振氢谱图中, $\delta=1.3\text{ppm}$ 处具有双峰, 在 $\delta=3.8\text{ppm}$ 处具有七重峰的化合物是 ()。

- (A) $\text{CH}_3\text{CHOCH}_3$ (B) $\text{CH}_3\text{CH}_2\text{CH}_3$ (C) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ (D) $\text{CH}_3\text{CHOC(CH}_3)_2$

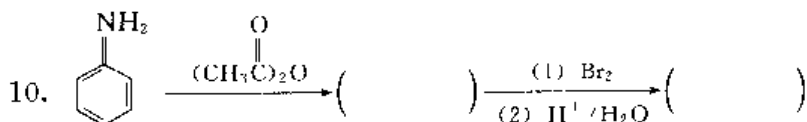
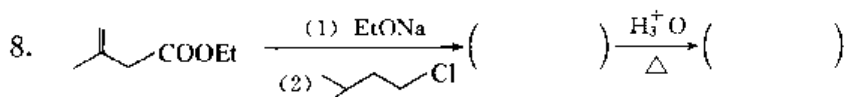
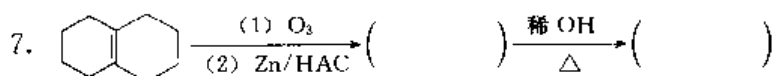
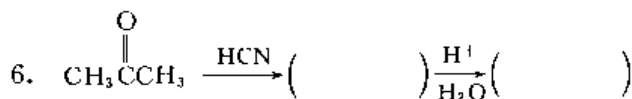
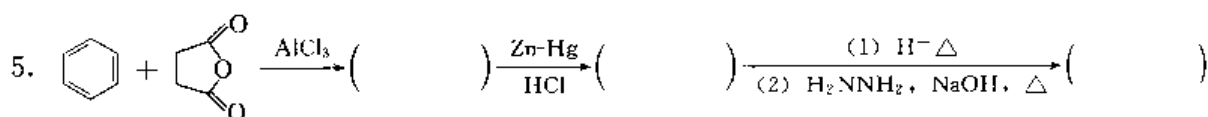
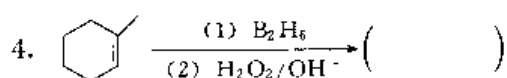
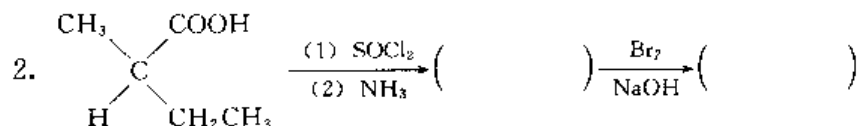
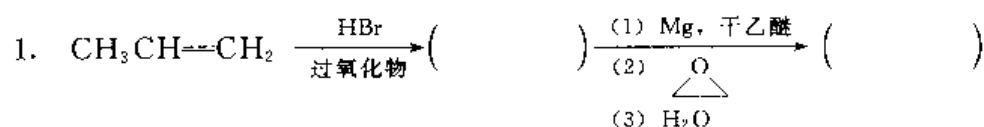
9. 下列化合物与 NaOH 乙醇溶液发生 S_N1 反应速率最快的是 ()。



10. 用 α -溴代酯和金属锌与醛或酮反应生成 ()。

- (A) β -羟基酯 (B) γ -酮酸 (C) δ -内酯 (D) α -羟基酸

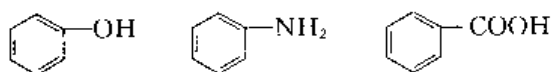
二、填空题 (20 分)



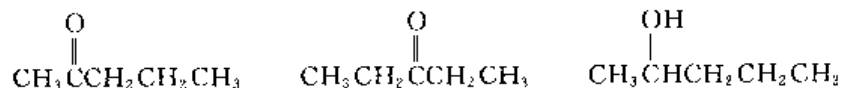
三、分离与鉴定题 (12 分)

1. 1-溴丁烷中含有少量的 1-丁醇和正丁醚，如何获得纯的 1-溴丁烷？(4 分)

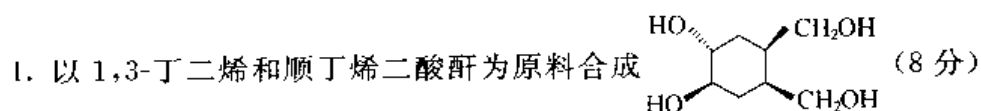
2. 试用化学方法分离下列化合物。(4 分)



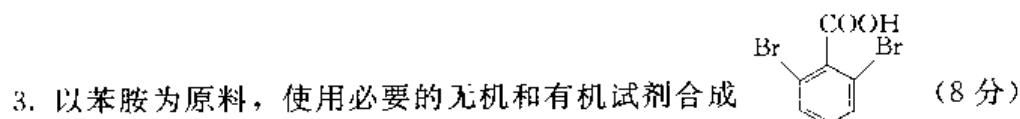
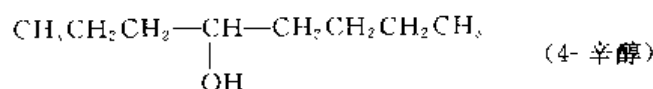
3. 用化学方法鉴别下列化合物。(4 分)



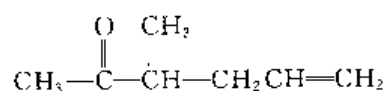
四、由指定的原料及必要的有机、无机试剂制备下列化合物 (32 分)



2. 由 1-丁醇为原料, 使用必要的无机和有机试剂合成 (8 分)



4. 由乙酰乙酸乙酯与其他 3 个碳或 3 个碳以下的原料和无机试剂合成 (8 分)



五、推断题 (16 分)

1. 不饱和化合物 A ($\text{C}_{16}\text{H}_{16}$), 与 OsO_4 反应, 再用亚硫酸钠处理得 B ($\text{C}_{16}\text{H}_{18}\text{O}_2$), B 与四乙酸铅反应生成 C ($\text{C}_8\text{H}_8\text{O}$), C 经黄鸣龙还原法得 D (C_8H_{10}), D 只能生成一种单硝基化合物。B 用无机酸处理能重排为 E ($\text{C}_{16}\text{H}_{16}\text{O}$), E 用托伦试剂 (硝酸银的氨溶液) 氧化得酸 F ($\text{C}_{16}\text{H}_{16}\text{O}_2$)。试写出化合物 A、B、C、D、E、F 的结构式。(8 分)

2. 有一化合物, 其分子式为 $\text{C}_4\text{H}_8\text{O}_2$, 能起下面一系列反应:

- (1) 其水溶液呈酸性;
- (2) 其与重铬酸钾 (在硫酸存在的条件下) 一起加热, 溶液变为蓝绿色;
- (3) 当该化合物受强热时将转化为另一化合物 $\text{C}_4\text{H}_6\text{O}_2$;
- (4) 化合物 $\text{C}_4\text{H}_8\text{O}_2$ 可使稀高锰酸钾溶液褪色;
- (5) 与碘在氢氧化钠水溶液中作用, 有黄色结晶固体产生;
- (6) 有旋光性, 能旋转平面偏振光。

试问该化合物是什么? 并用反应方程式表示 (1)→(5) 的化学反应。并标出该化合物中的手性碳原子。(8 分)

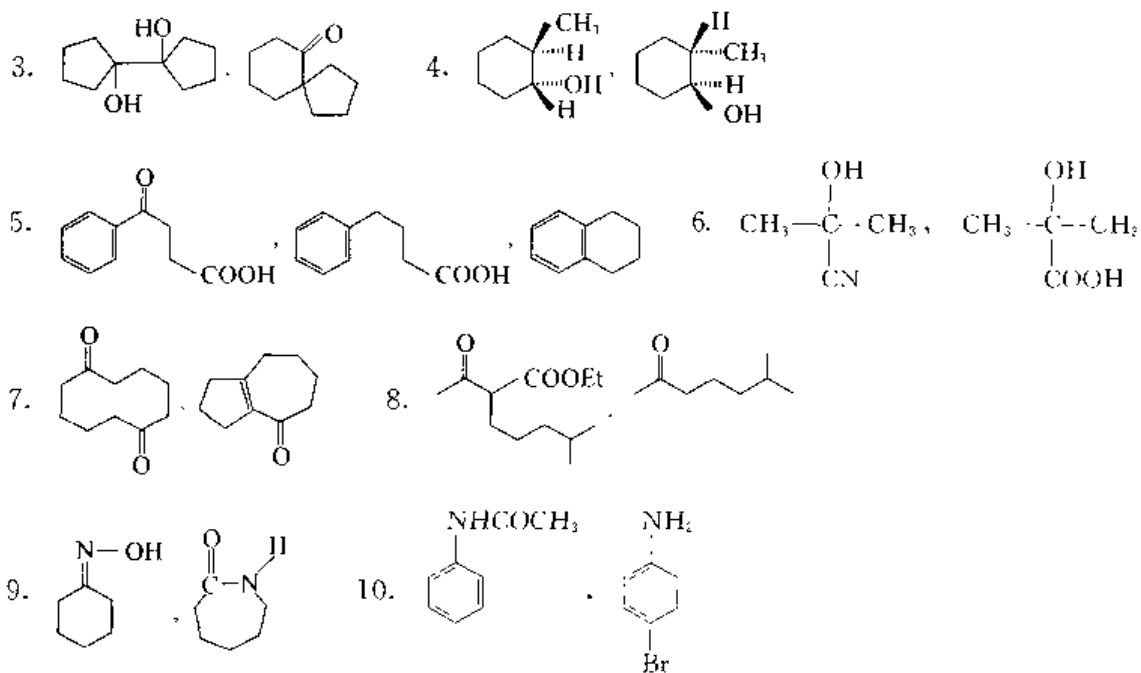
参考答案

一、选择题

1. (B) 2. (D) 3. (C) 4. (D) 5. (A) 6. (C) 7. (B) 8. (D)
9. (B) 10. (A)

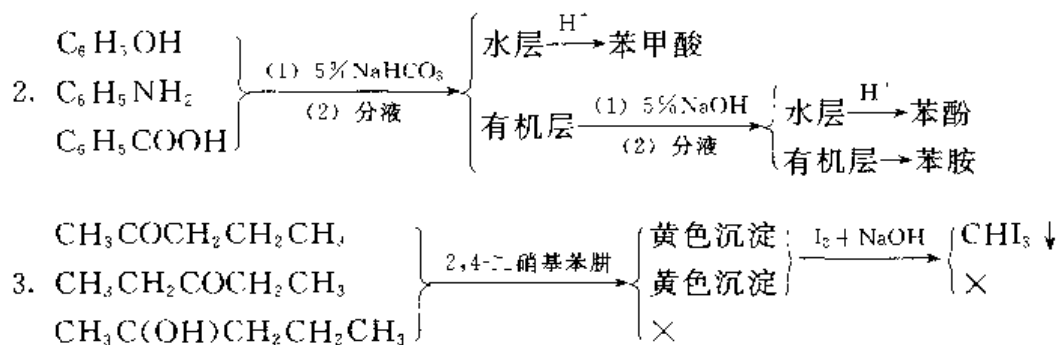
二、填空题

1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, $\text{CH}_3(\text{CH}_2)_4\text{OH}$ 2. $\text{CH}_3\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{CONH}_2$, $\text{CH}_3\text{CH}_2\underset{\text{CH}_3}{\text{CH}}-\text{NH}_2$

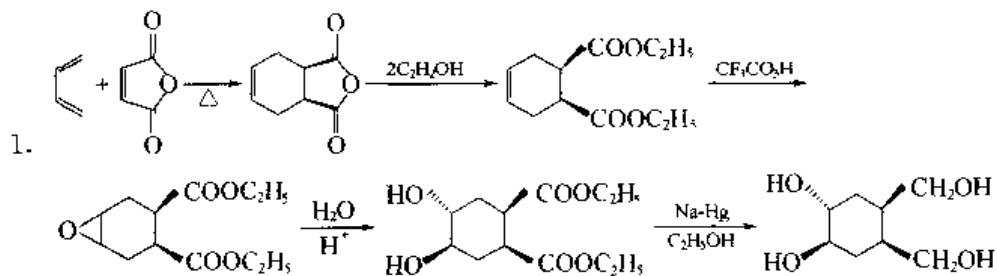


三、分离与鉴定

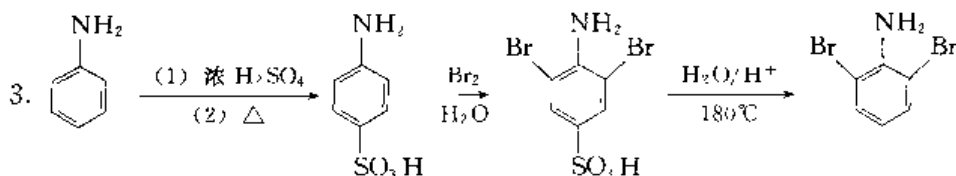
1. 将混合物用浓硫酸洗涤后，分去酸层。将有机层用无水硫酸镁干燥，然后蒸馏可得纯的 1-溴丁烷。

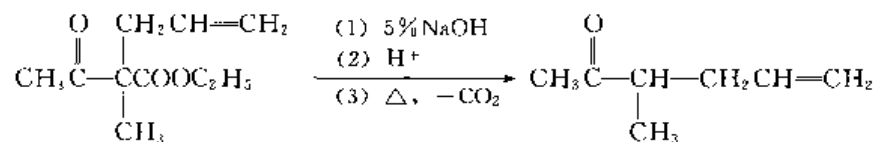
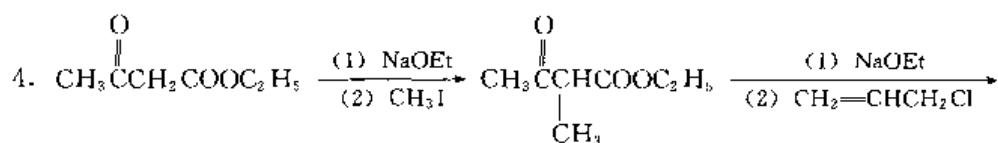
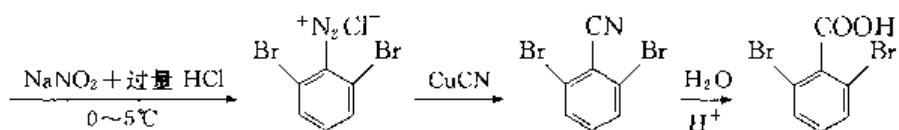


四、合成

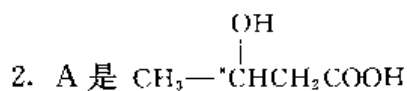
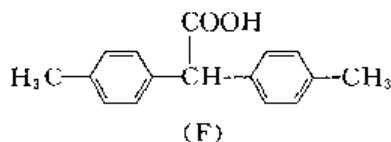
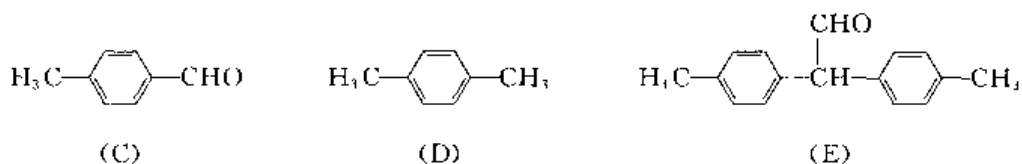
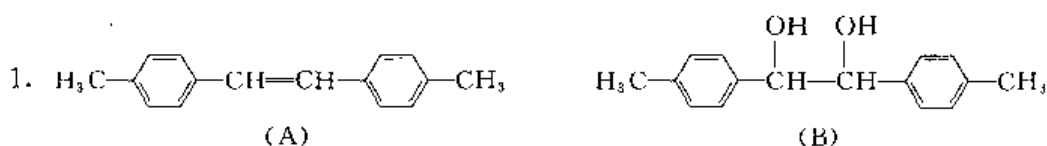


2. 略。见“模拟试题 3”。

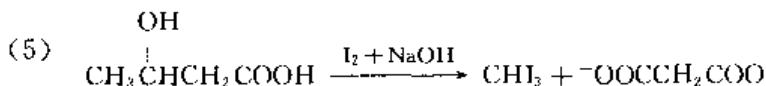
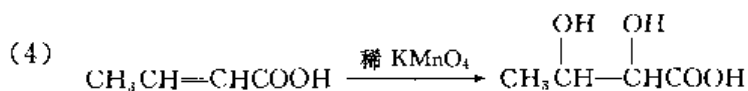
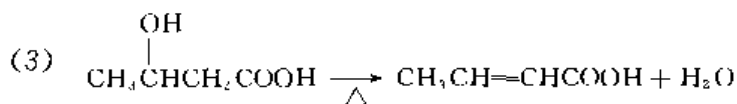
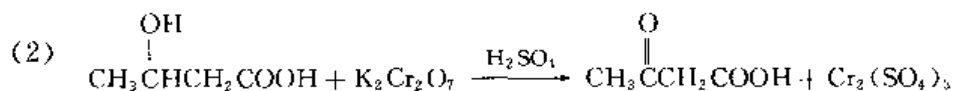
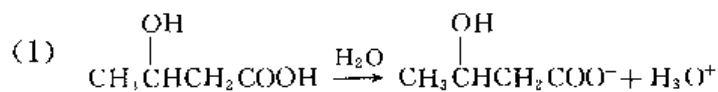




五、推断题



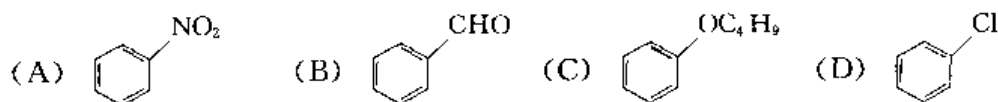
(1)→(5) 的反应方程式为



模拟试题 14

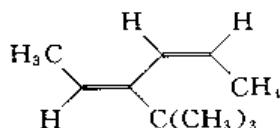
一、选择题 (24 分)

1. 下面化合物进行硝化反应的速率顺序是



- (A) (3) > (4) > (2) > (1) (B) (3) > (2) > (4) > (1)
 (C) (4) > (2) > (3) > (1) (D) (4) > (3) > (1) > (2)

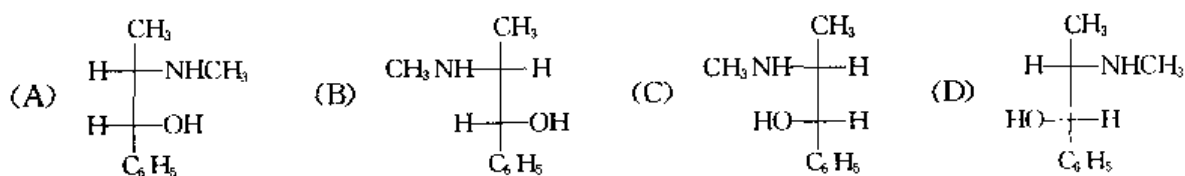
2. 下面化合物的中国化学会命名是



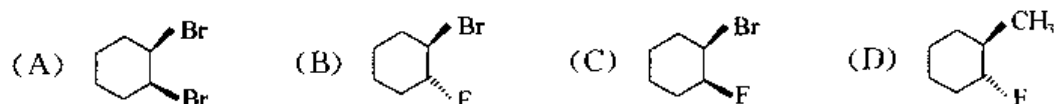
- (A) (2Z,4E)-4-叔丁基-2,4-己二烯 (B) (2E,4Z)-3-叔丁基-2,4-己二烯
 (C) (2Z,4E)-3-叔丁基-2,4-己二烯 (D) (2E,4Z)-4-叔丁基-2,4-己二烯
3. 可以进行分子内酯缩合的二酯是

- (A) 丙二酸二乙酯 (B) 丁二酸二乙酯
 (C) 对苯二甲酸二乙酯 (D) 己二酸二乙酯

4. (1R,2S)-2-甲氨基-1-苯基-1-丙醇的费舍尔 (Fischer) 投影式是



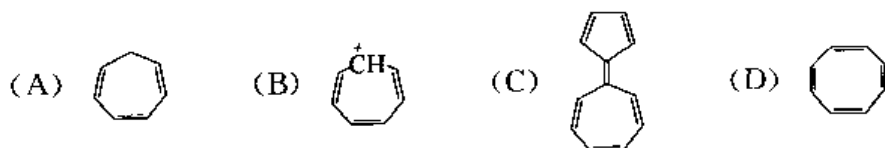
5. 环己烯 + Br₂ + AgF → 主要产物为



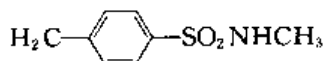
6. 1848 年首次研究酒石酸盐晶体, 从而分离出旋光异构体的是谁?

- (A) 巴斯德 (Paster. L) (B) 比奥 (Biot)
 (C) 勒贝尔 (Label. J. A) (D) 拜尔 (Baeyer)

7. 下列化合物有芳香性的是



8. 下面化合物的正确名称是

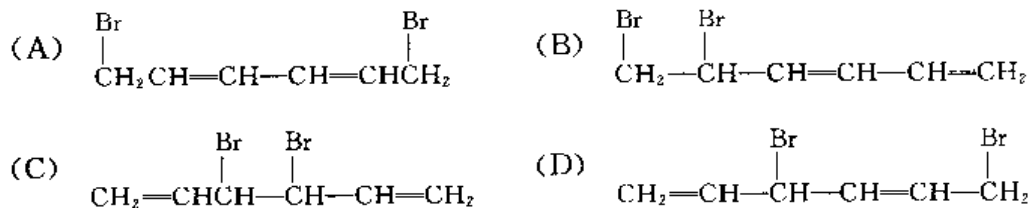


- (A) 对甲基苯磺酰胺 (B) N-甲基对甲苯磺酰胺
(C) 对甲苯甲基磺酰胺 (D) 甲氨基对甲苯磺酰胺

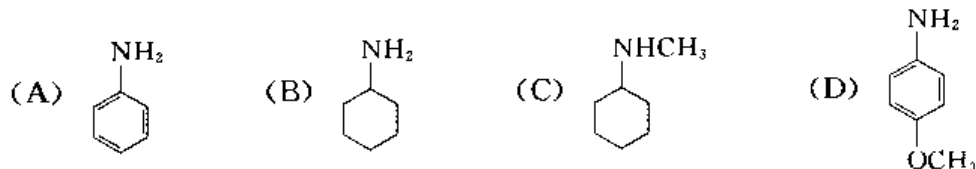
9. 己酮糖理论上具有的立体异构体的数目是

- (A) 4 种 (B) 8 种 (C) 16 种 (D) 32 种

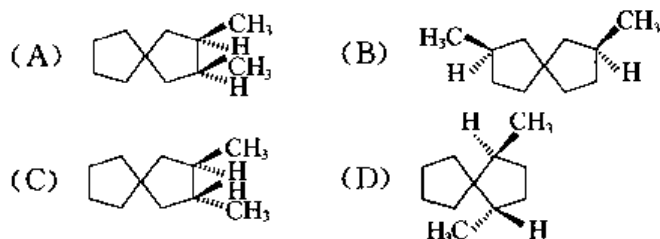
10. 己三烯与 1mol 溴加成, 最不易形成的产物是



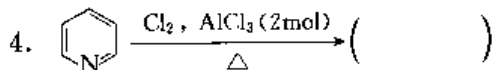
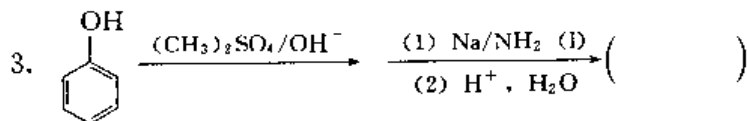
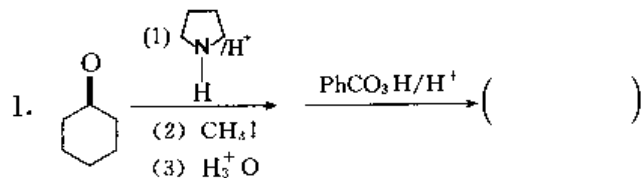
11. 下列化合物碱性最强的是

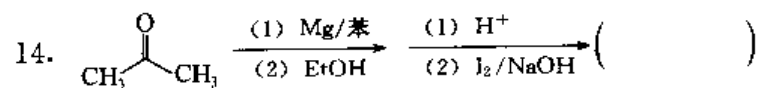
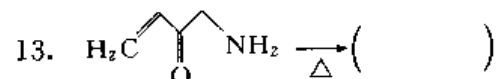
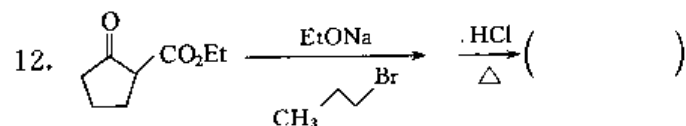
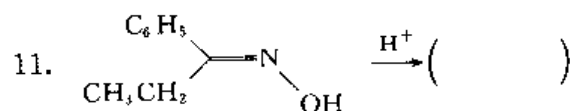
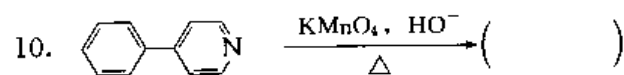
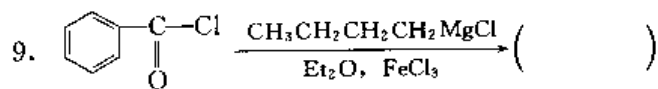
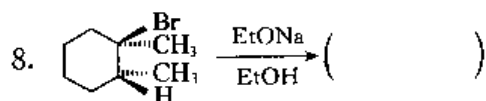
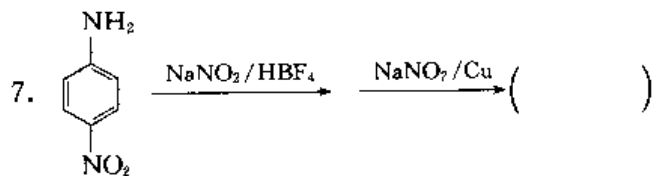
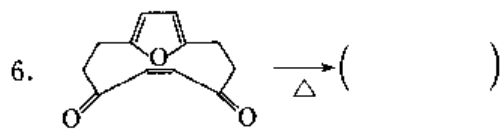
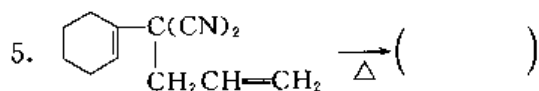


12. 下列化合物没有旋光性的是



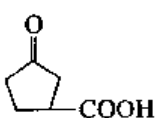
二、写出下列反应的主要产物, 若有立体异构体请标明 (30 分)

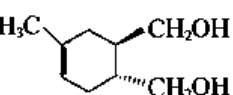


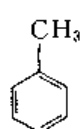
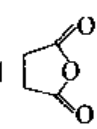
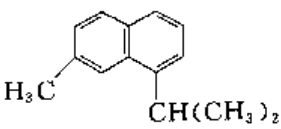


三、合成题 (20 分)

1. 乙炔 \rightarrow 苏式-2,3-二溴丁烷

2. 由丁二烯和丙烯酸乙酯合成 

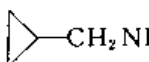
3. 由 C_5 及 C_3 以下的原料合成 

4. 由  和  合成 

四、写出下列反应的主要产物，并提出合理的分步反应机理（16分）

1. 4-甲基-4-羟基-2-戊酮在碱性水溶液中部分地转变为丙酮（6分）

2. 硝基苯 + $\text{H}_2\text{SO}_4 + \text{HNO}_3 \longrightarrow$ （5分）

3. - CH_2NH_2 与亚硝酸反应得到 3 种产物，一个三元环，两个四元环。（5分）

五、结构题（10分）

1. 有一化合物 A，分子式为 $\text{C}_5\text{H}_{11}\text{Br}$ ，和氢氧化钠水溶液共热后生成 $\text{C}_5\text{H}_{12}\text{O}$ (B)，B 能和钠作用放出氢气，能被重铬酸钾氧化，能和浓硫酸共热生成 C_5H_{10} (C)，C 经臭氧化和水解则生成丙酮和乙醛，试推测 A、B、C 的结构，并写出各步反应式。（5分）

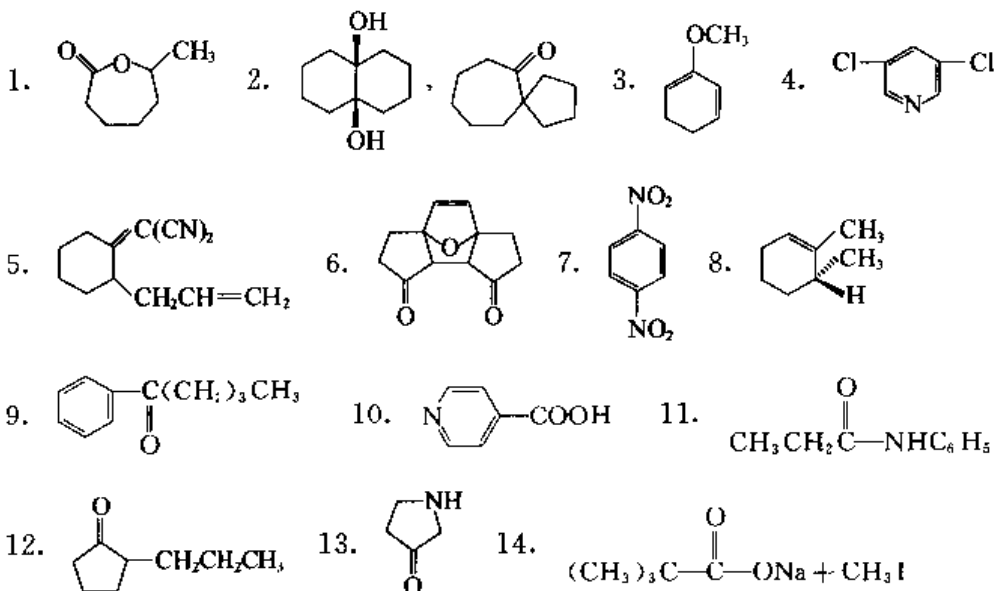
2. 化合物 A ($\text{C}_9\text{H}_{12}\text{O}$) 的 IR 在 $3600 \sim 3200\text{cm}^{-1}$ 、 760cm^{-1} 、 700cm^{-1} 有特征吸收， ^1H NMR 谱数据如下： δ 0.9（三重峰，3H）； δ 1.6（多重峰，2H）； δ 2.6（宽单峰，1H）； δ 4.4（三重峰，1H）； δ 7.20（单峰，5H）。试推测 A 的结构式。（5分）

参考答案

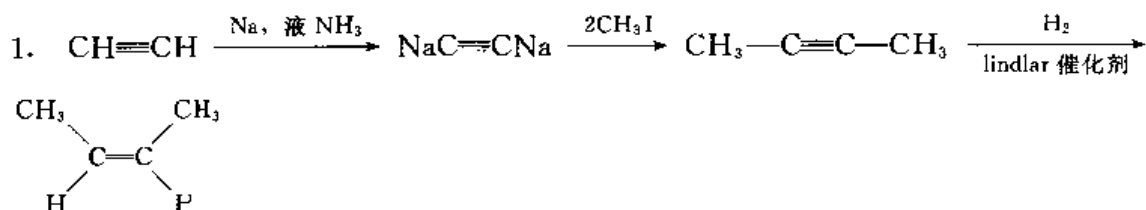
一、选择题

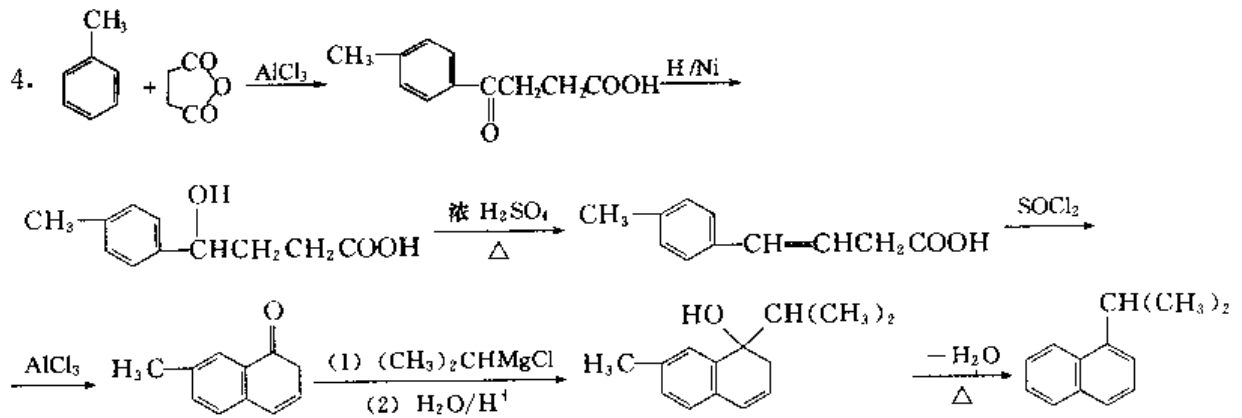
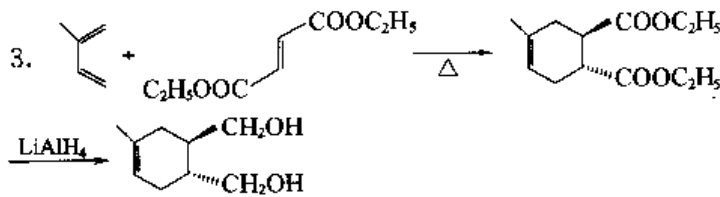
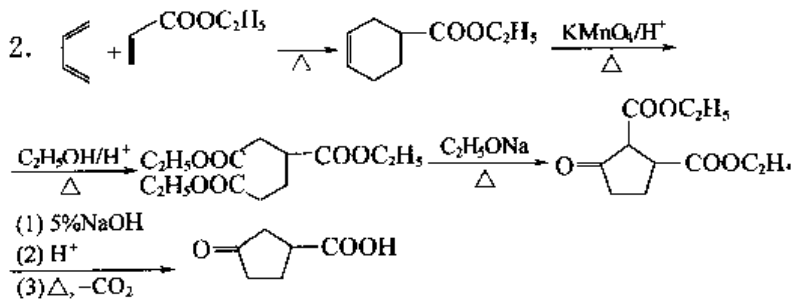
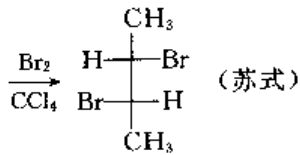
1. (A) 2. (B) 3. (D) 4. (A) 5. (B) 6. (A) 7. (B) 和 (C) 8. (B)
9. (B) 10. (C) 11. (C) 12. (A)

二、完成反应式

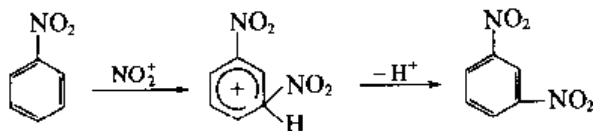
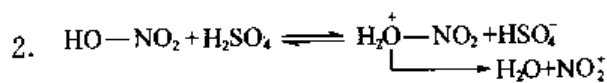
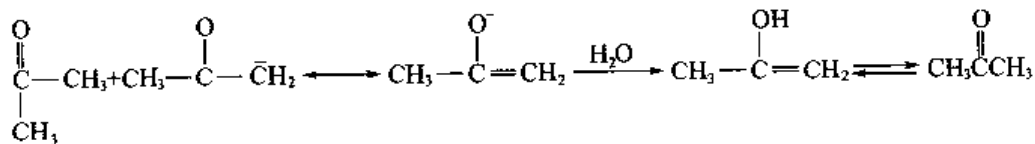
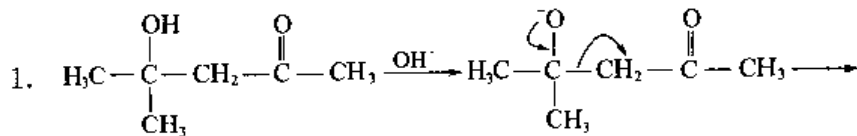


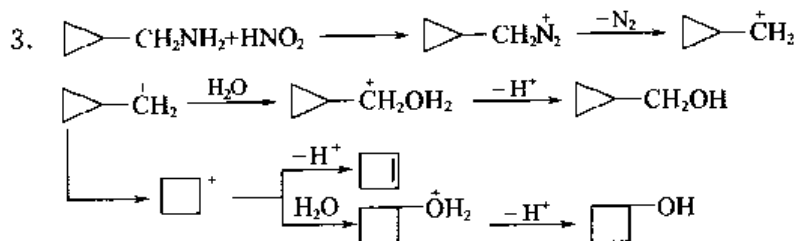
三、合成题



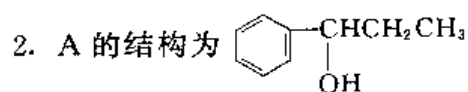
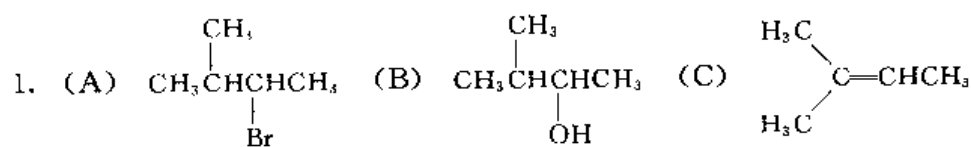


四、机理题



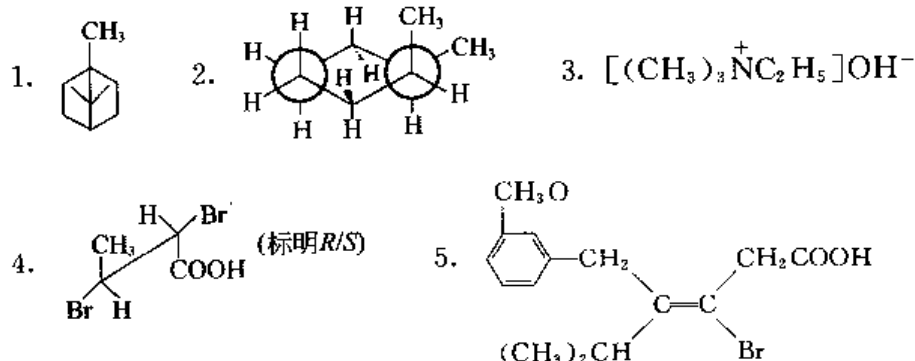


五、结构题



模拟试题 15

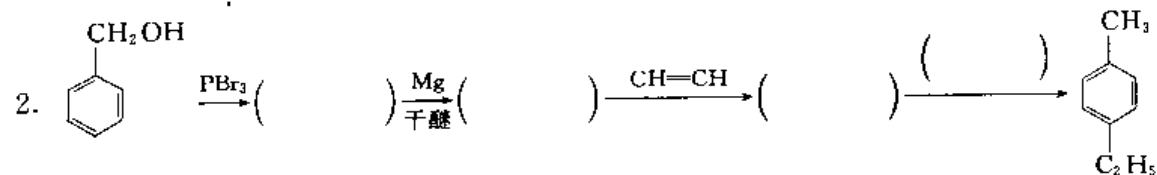
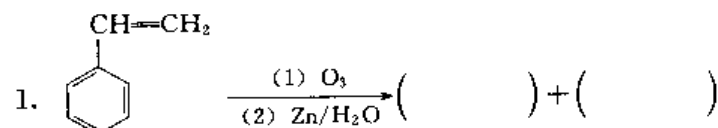
一、命名下列化合物 (5分)

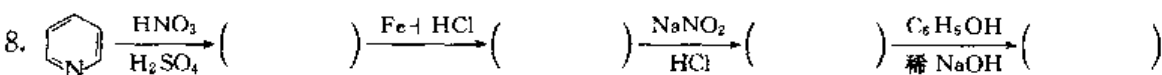
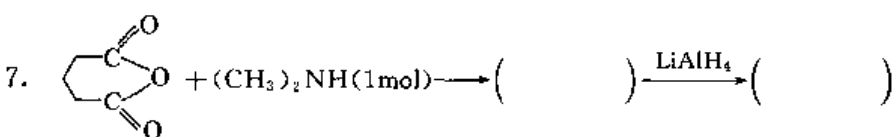
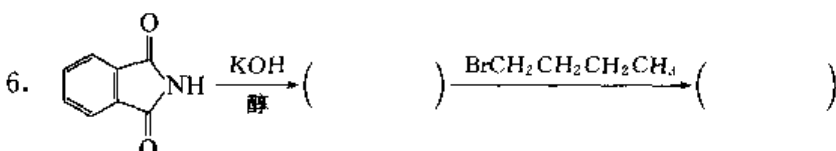
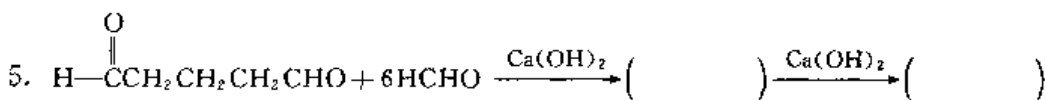
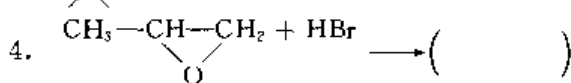
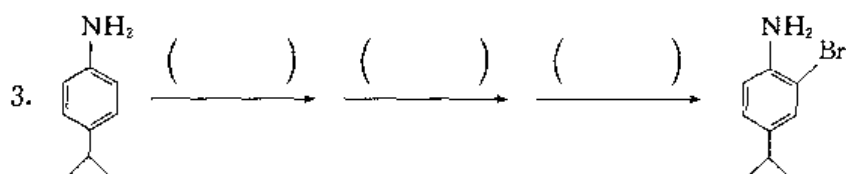


二、写出下列化合物的结构式 (5分)

1. 螺[2.5]-6-辛酮 2. 5-硝基噻唑 3. (2R,3S)-2-羟基-3-氟丁二酸
 4. 顺环己烷-1,3-二醇的最稳定构象 5. (E)-1-苯基-3-戊烯-1-醇

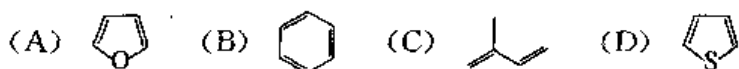
三、完成反应式 (10分)



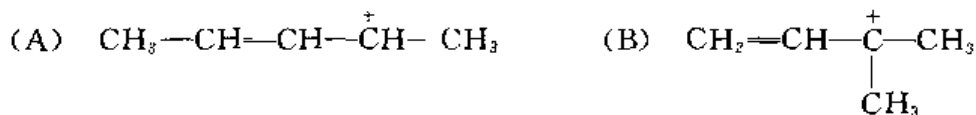


四、比较下列化合物性质 (12分)

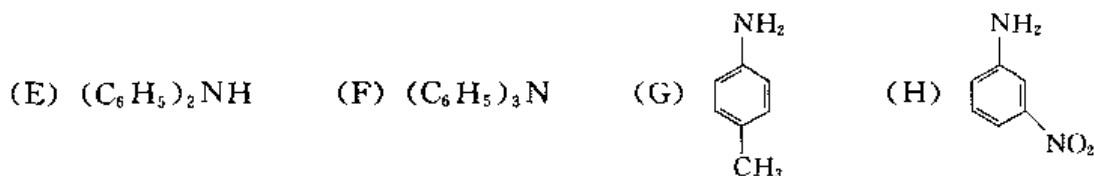
1. 将下列化合物与 $\text{C}_2\text{H}_5\text{Cl}/\text{FeCl}_3$ 的反应活性按由大到小的顺序排列。



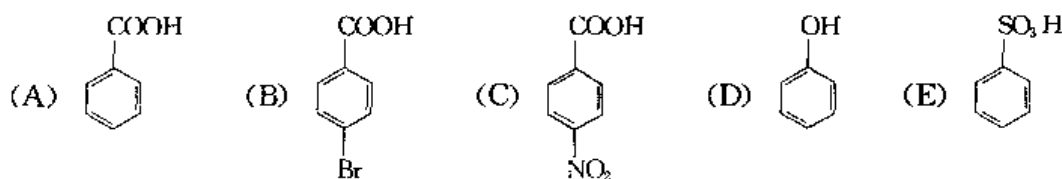
2. 比较下列碳正离子的稳定性。



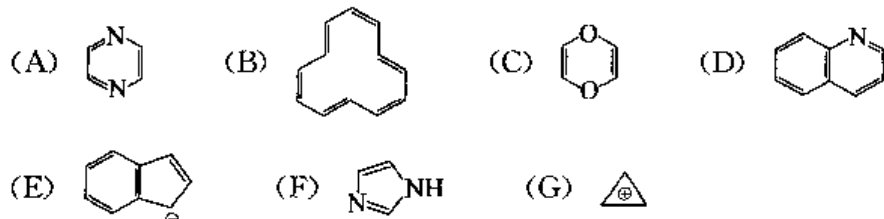
3. 将下列化合物按碱性由大到小的顺序排列。



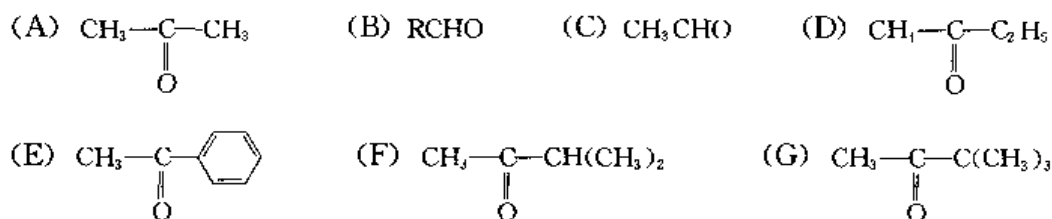
4. 将下列化合物按酸性由大到小的顺序排列。



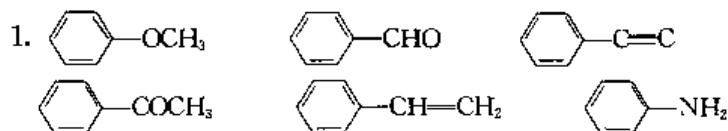
5. 下列化合物中哪个具有芳香性?



6. 将下列化合物与饱和 NaHSO_3 溶液加成的活性由大到小的顺序排列。

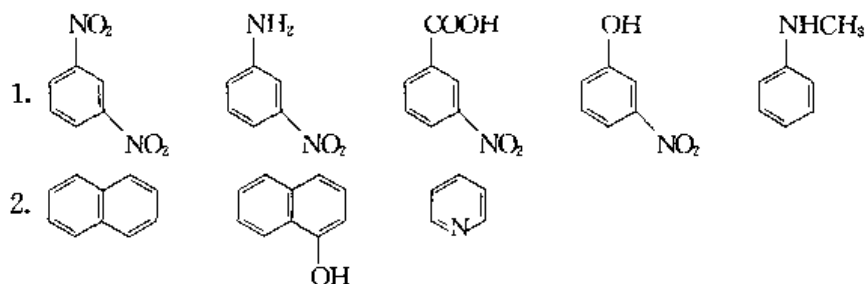


五、鉴别下列各组化合物 (10分)



2. 对苯甲酚, 苯甲醚, 对甲苯甲酸, 苯甲醛, 苯乙酮, 对甲苯胺

六、分离下列各组化合物 (10分)

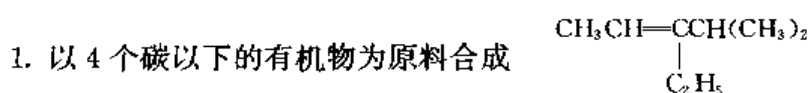


七、有机化合物结构推导 (10分)

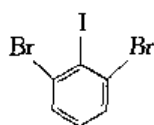
1. 化合物 A 和 B 互为异构体, 分子式均为 $\text{C}_9\text{H}_{10}\text{O}$ 。A 的 IR 谱中在 1690cm^{-1} 处显一强吸收峰; NMR 谱数据为 δ 1.2 (3H, 三重峰), δ 3.0 (2H, 四重峰), δ 7.7 (5H, 多重峰); A 不发生碘仿反应。B 的 IR 谱中 1705cm^{-1} 显强吸收峰; NMR 谱数据为 δ 2.0 (3H, 单峰); δ 3.5 (2H, 单峰); δ 7.1 (5H, 多重峰); B 可发生碘仿反应。试推测 A 和 B 的构造。

2. 化合物的分子式为 $\text{C}_8\text{H}_{12}\text{O}_3$, 红外光谱在 1710cm^{-1} 有强吸收峰。用 I_2/NaOH 溶液处理产生黄色沉淀, 用 Tollens 试剂处理时无反应, 但如先用一滴 H_2SO_4 溶液处理后再和 Tollens 试剂作用, 则有银镜生成。该化合物的核磁共振谱数据如下: δ 2.1 (3H, 单峰); δ 2.6 (2H, 双峰); δ 3.2 (6H, 单峰); δ 4.7 (1H, 双峰)。

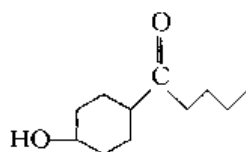
八、有机化合物的合成 (无机试剂任选) (30分)



2. 苯为原料合成

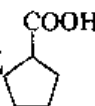


3. 5个碳以下的有机物合成

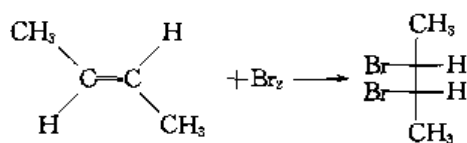


4. 以丙烯为原料合成 γ -溴代丁酸

5. 以4个碳以下(含 C_4)的醇为原料, 经丙二酸酯法合成



九、试用反应机理解释下列实验结果 (8分)

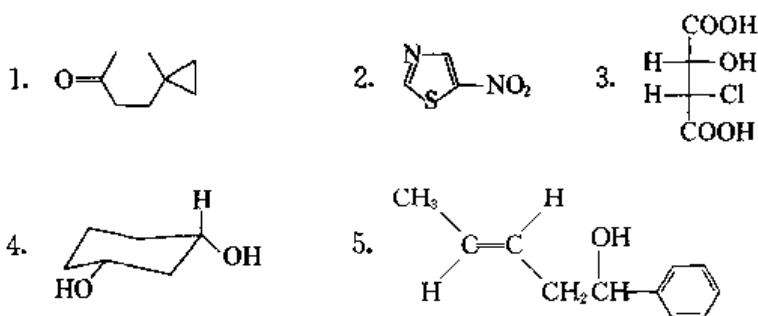


参考答案

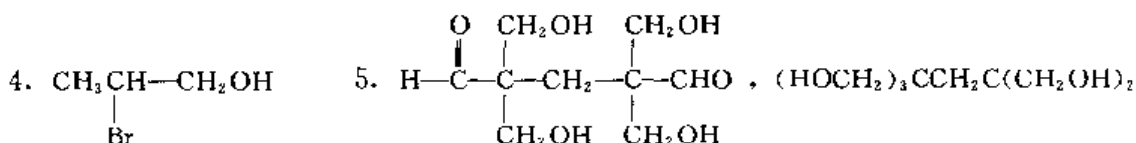
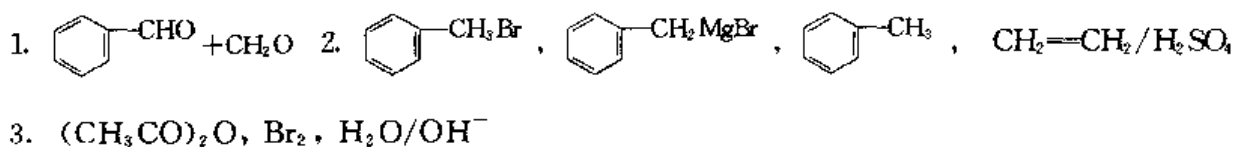
一、命名

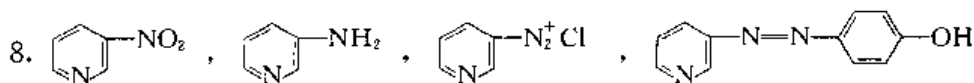
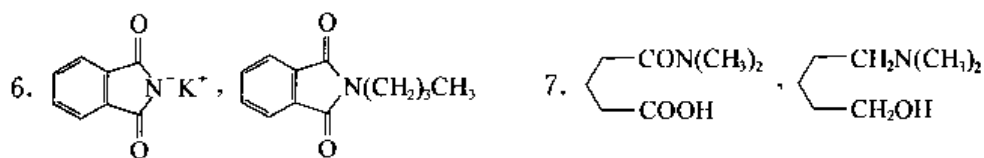
- 1,7,7-三甲基双环 [2.2.1] 庚烷
- 顺-1,2-二甲基环己烷
- 氢氧化三甲基乙基铵
- (2R,3R)-2,3-二溴丁酸
- (Z)-5-甲基-4-间甲氧基苄基-3-溴-3-己烯酸

二、写结构式



三、完成反应式

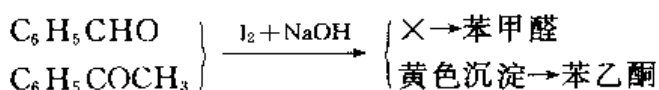
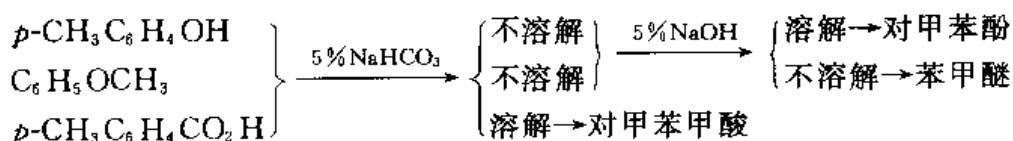
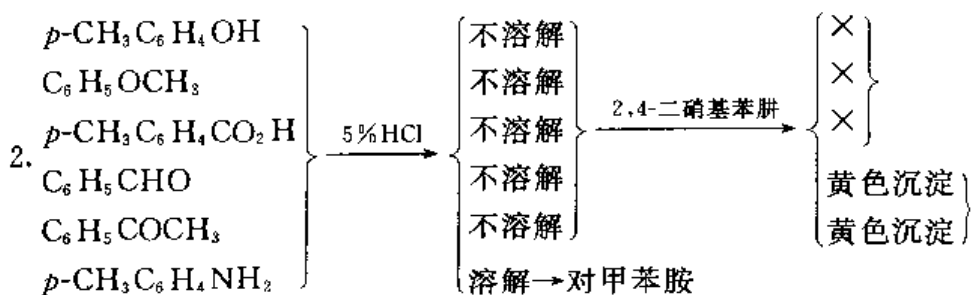
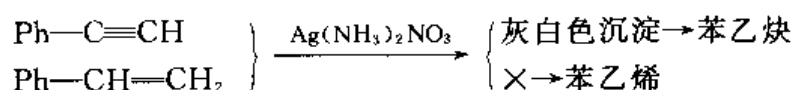
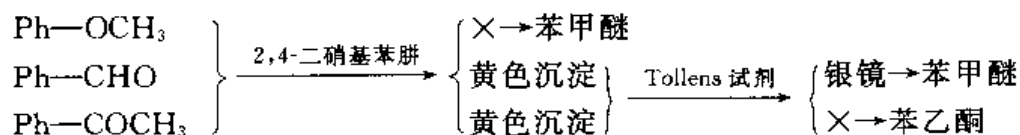
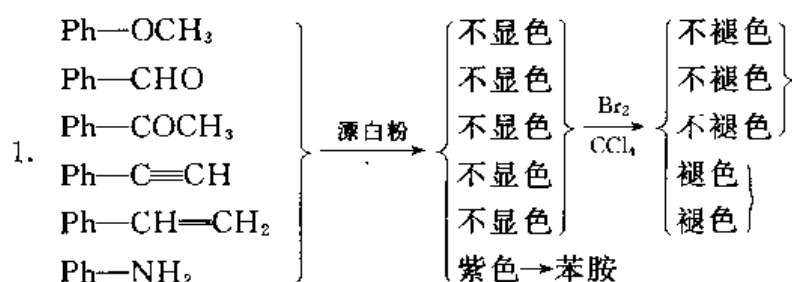




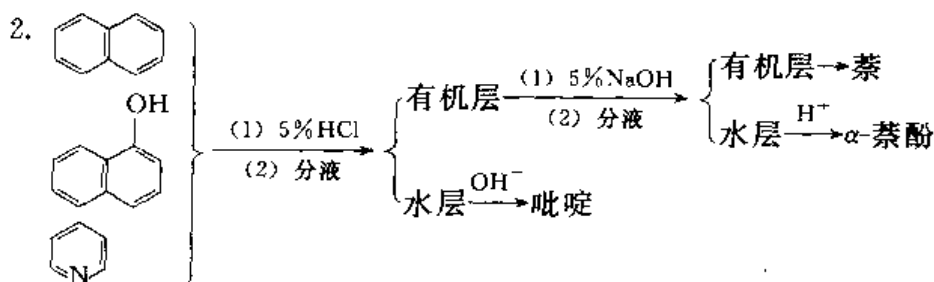
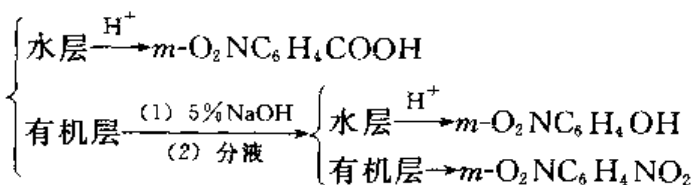
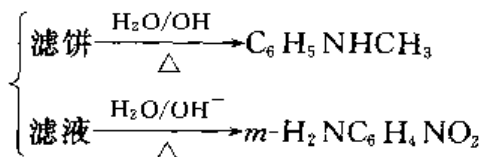
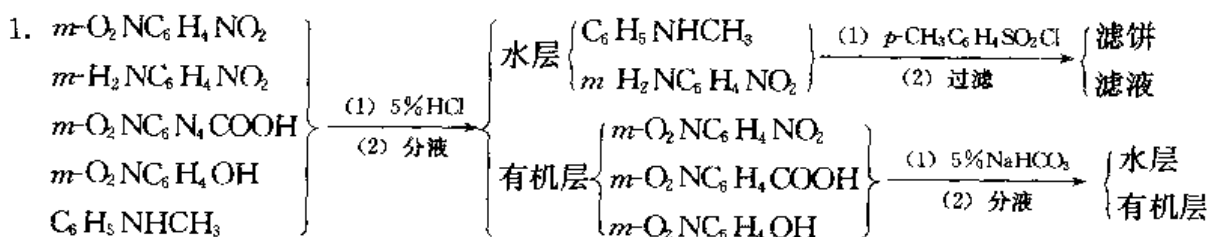
四、理化性质比较

1. 反应活性: (D) > (C) > (A) > (B)
2. 稳定性: (B) > (A) > (D) > (C)
3. 碱性: (B) > (C) > (A) > (G) > (D) > (H) > (E) > (F)
4. 酸性: (E) > (C) > (B) > (A) > (D)
5. (A)、(D)、(E)、(G)、(F)有芳香性
6. 加成活性: (C) > (B) > (A) > (D) > (F) > (G) > (E)

五、鉴别



六、分离

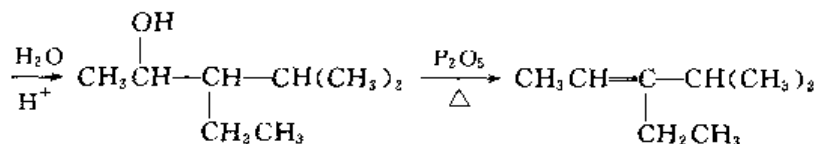
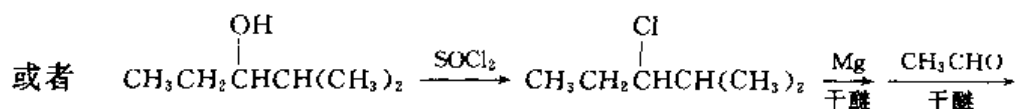
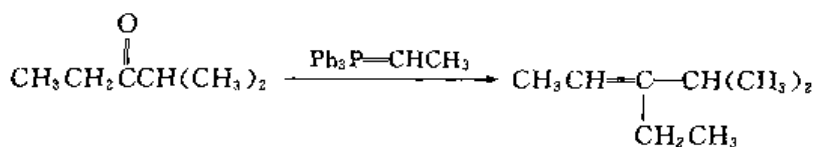
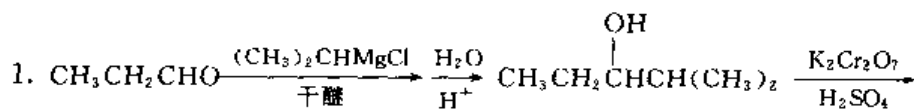


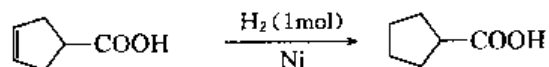
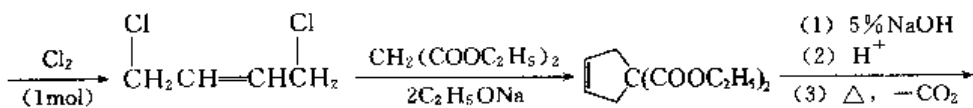
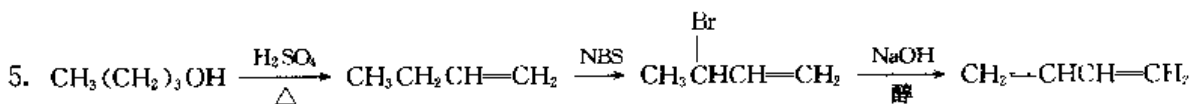
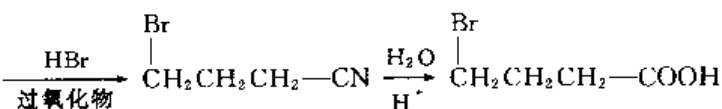
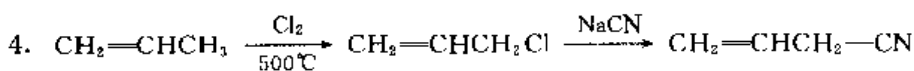
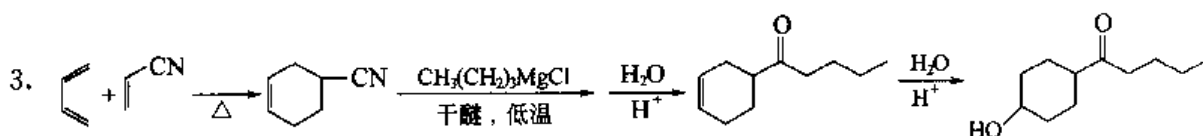
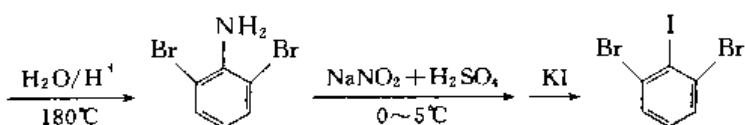
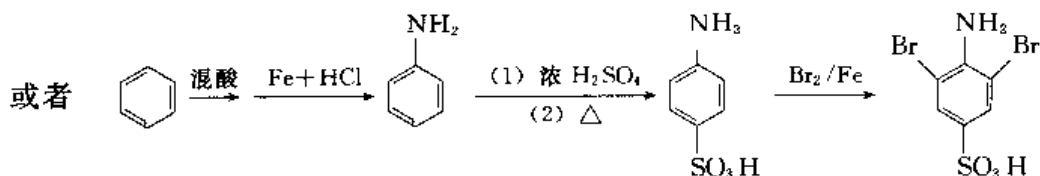
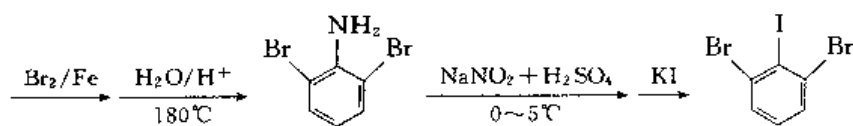
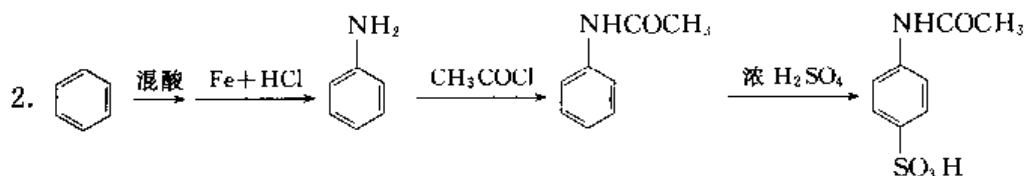
七、结构推导

1. 略。见“模拟试题12”中“四、1。”。

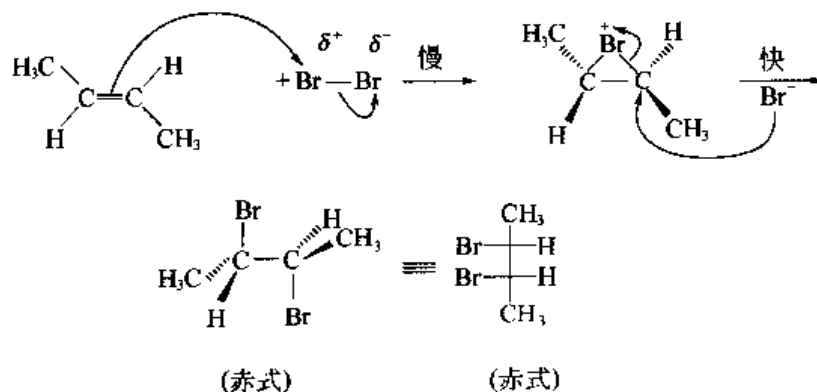
2. 略。见“模拟试题1”中“六、2。”。

八、合成



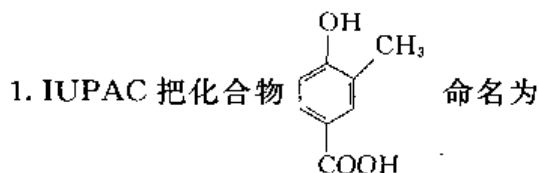


九、反应机理



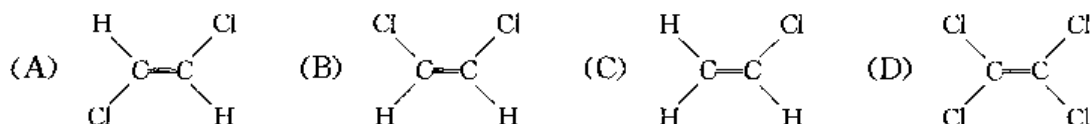
模拟试题 16

一、选择题 (30 分)



- (A) 4-羟基-3-甲基苯甲酸 (B) 2-甲基-4-羧基苯酚
(C) 2-羟基-5-羧基甲苯 (D) 对羟基间甲苯甲酸

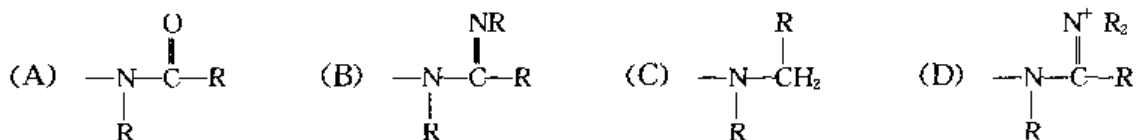
2. 1,1,2-三氯乙烯的偶极矩应和下列化合物中的哪一个相似?



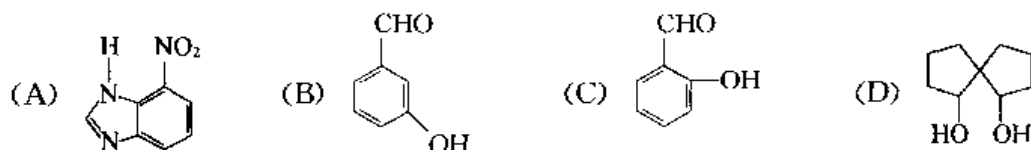
3. 下列平衡中, 哪一个反应的 K_{eq} 值小于 1?

- (A) $\text{HBr} + \text{F}^- \rightleftharpoons \text{HF} + \text{Br}^-$
(B) $\text{CH}_3\text{OH} + \text{CH}_3^- \rightleftharpoons \text{CH}_4 + \text{CH}_3\text{O}^-$
(C) $\text{CH}_3\text{OH} + \text{CH}_3\text{S}^- \rightleftharpoons \text{CH}_3\text{SH} + \text{CH}_3\text{O}^-$
(D) $\text{CH}_3\text{MgCl} + \text{HCl} \rightleftharpoons \text{CH}_4 + \text{MgCl}_2$

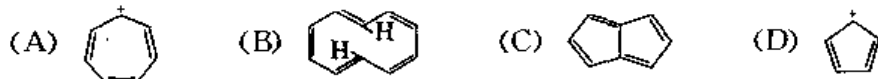
4. 判断下列哪一个基团具有最大的推电子共轭效应 (+C)



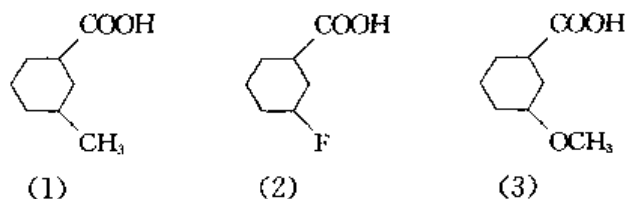
5. 下列化合物哪一个不能形成分子内氢键?



6. 判断下列物种哪一个具有芳香性?



7. 比较下列化合物酸性的强弱。

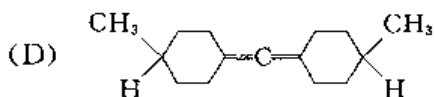
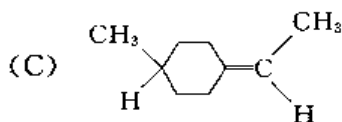
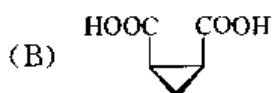
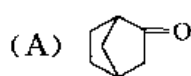


- (A) (1) > (2) > (3) (B) (3) > (2) > (1) (C) (1) > (3) > (2) (D) (2) > (3) > (1)

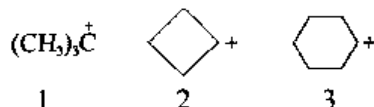
8. 把氨 (a)、苯胺 (b)、苯甲酰胺 (c) 和苯磺酰胺 (d) 按碱性增大顺序排列。

- (A) $a < b < c < d$ (B) $d < c < b < a$ (C) $b < a < d < c$ (D) $d < a < c < b$

9. 下列化合物哪一个没有光学活性?

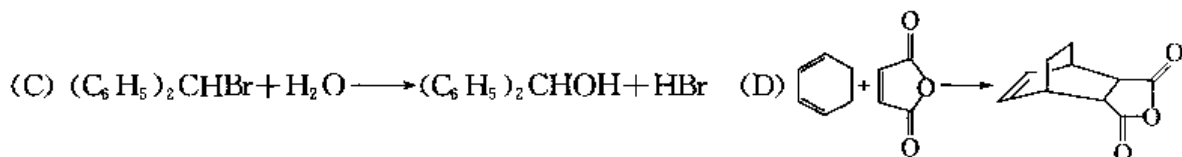
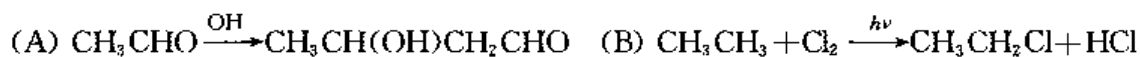


10. 下列正碳离子的稳定性次序为

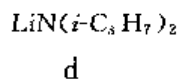
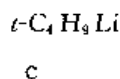
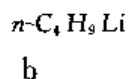
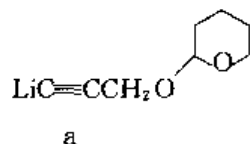


- (A) $1 > 2 > 3$ (B) $1 > 3 > 2$ (C) $1 \approx 3 > 2$ (D) $1 > 2 \approx 3$

11. 下列反应中, 哪一个涉及到碳正离子中间体?

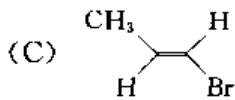
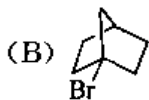
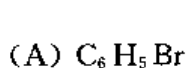


12. 按亲核性从强到弱的次序排列, 哪一个是对的?



- (A) $a > b > c > d$ (B) $c > b > a > d$ (C) $d > c > a > b$ (D) $c > a > b > d$

13. 下列化合物中, 哪一个最易起 S_N2 反应?



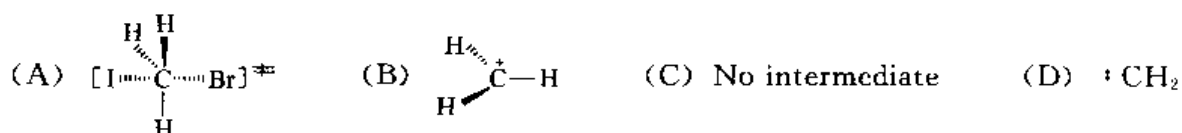
14. 用氧化铝柱色谱法来分离对硝基甲苯 (1) 和对硝基苯胺 (2), 下面答案中哪一个正确的?

- (A) 不行, 因为它们分子大小相近。
 (B) (1) 先被洗脱下来, 因为固定相对极性物质吸附力强。
 (C) (1) 先被洗脱下来, 因为 (1) 的沸点低。
 (D) (2) 先被洗脱下来, 因为 (2) 是极性的物质。

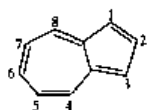
15. 在制备格氏试剂时, 一般溴代烃的加入采用

- (A) 一次性加入, 促使反应进行。 (B) 缓缓滴入, 保持反应溶液微沸。
 (C) 在短时间内很快滴入, 促使反应溶液回流。 (D) 分批加入, 维持室温反应。

16. 溴代甲烷在丙酮中与 KI 反应中间体 (intermediate) 为



17. 下列化合物的亲核取代反应容易发生在哪些位置?

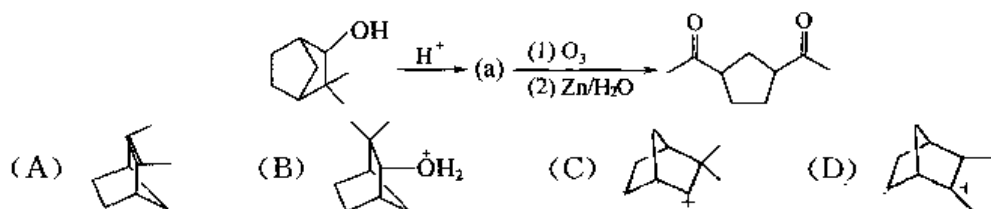


(A) 1,2 和 3 位 (B) 1 和 3 位 (C) 5 和 7 位 (D) 4,6 和 8 位

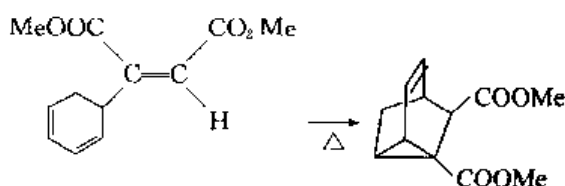
18. 如果该化合物进行亲电取代反应, 那么它容易发生在哪些位置?

(A) 1,2 和 3 位 (B) 1 和 3 位 (C) 5 和 7 位 (D) 4,6 和 8 位

19. 下列反应中, 中间产物 (a) 的结构为



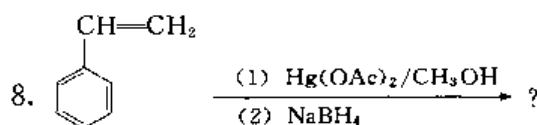
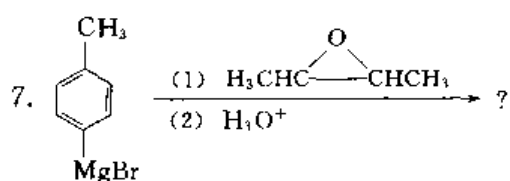
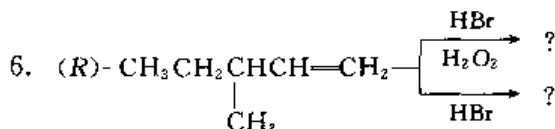
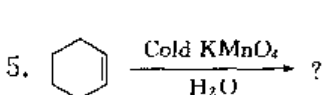
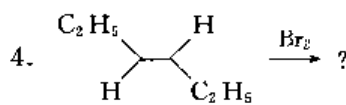
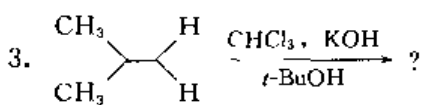
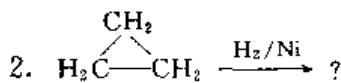
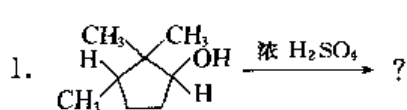
20. 下列周环反应类型为

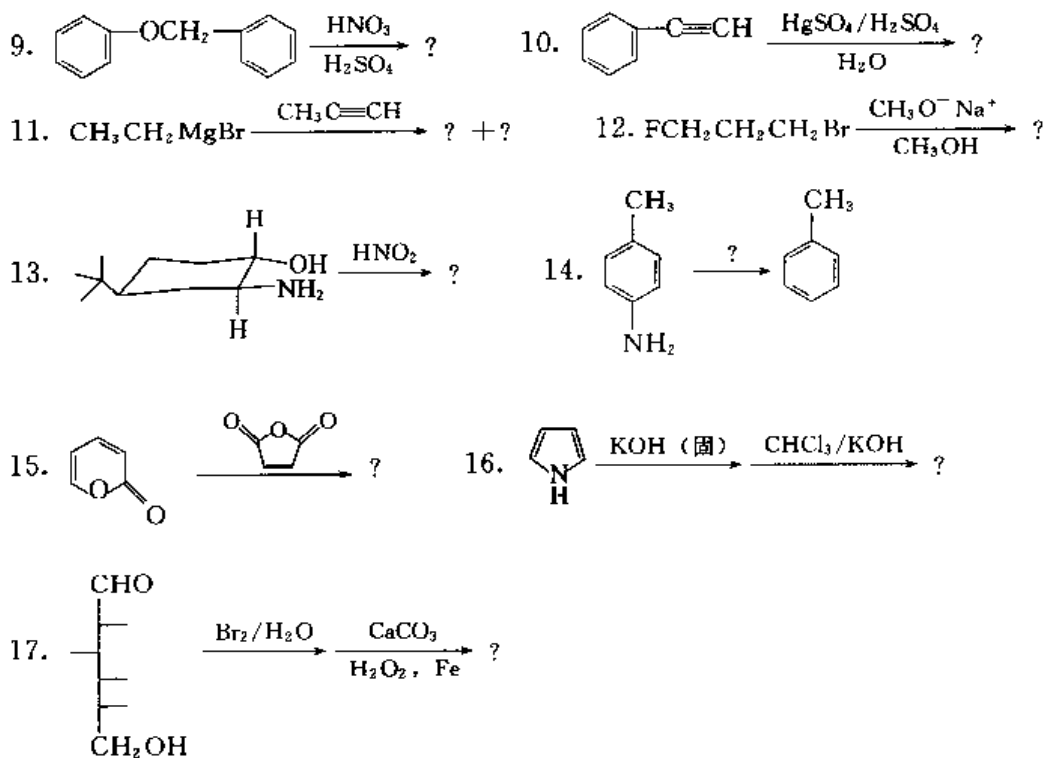


(A) 电环化反应 (B) 分子内 D-A 反应 (C) [1,3]- σ 迁移反应 (D) 螯环反应

二、完成下列反应 (30 分)

(在“?”处填上合适的产物和试剂以及反应条件)



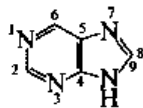


三、根据下列题意在括号内填入正确内容 (15分)

1. 卤代烷与氢氧化钠在含水乙醇溶液中进行反应。在括号内填上那些属于 $\text{S}_{\text{N}}2$ 机理？那些属于 $\text{S}_{\text{N}}1$ 机理？

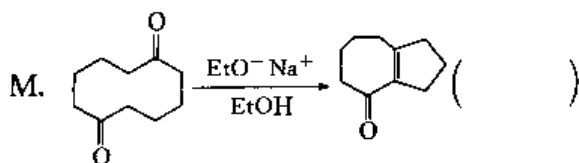
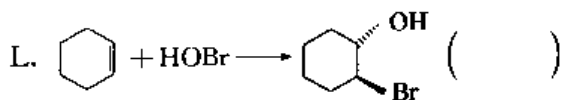
- A. 产物的绝对构型完全转化； ()
- B. 有重排产物； ()
- C. 碱的浓度增加，反应速率加快； ()
- D. 三级卤代烷反应速率大于二级卤代烷； ()
- E. 增加溶剂的含水量，反应速率明显增加； ()
- F. 反应历程只有一步； ()
- G. 进攻试剂亲核性愈强，反应速率愈快。 ()

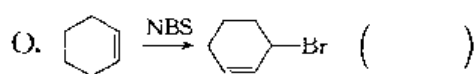
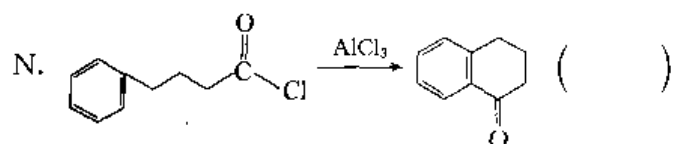
2. 指出嘌呤分子中每个氮原子的类型 (吡啶型或吡咯型)。



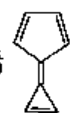
- H. N_1 () I. N_3 () J. N_7 () K. N_9 ()

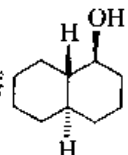
3. 在下列反应后的括号内填上其反应中间体

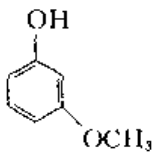
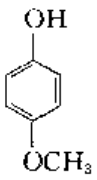




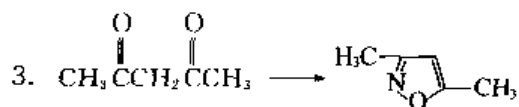
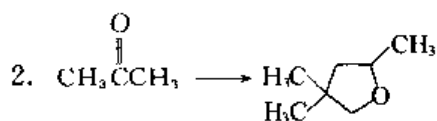
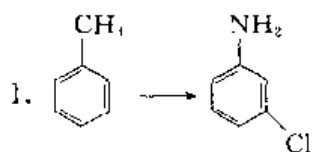
四、解释说明题 (6分)

1. 杯烯  具有较大的偶极矩, 为什么?

2. 画出 (1*S*, 9*S*, 10*R*)-1-羟基十氢萘  的优势构象。

3.  的酸性比  强。为什么?

五、由指定的原料和必要的无机试剂进行合成 (9分)



六、推断结构题 (10分)

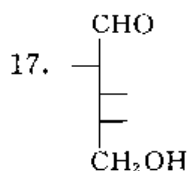
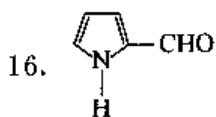
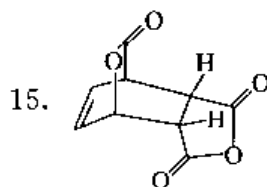
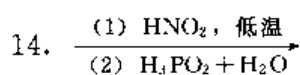
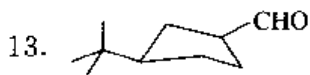
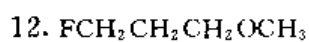
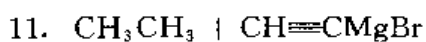
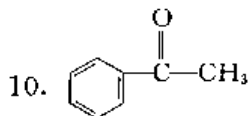
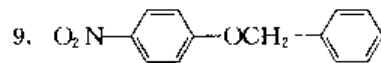
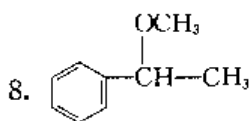
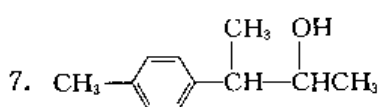
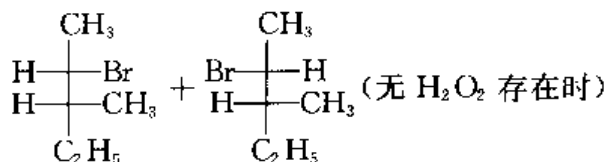
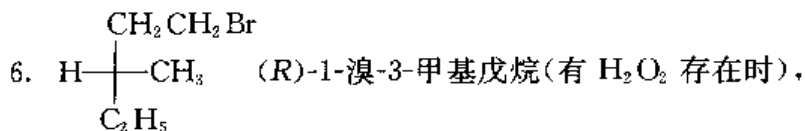
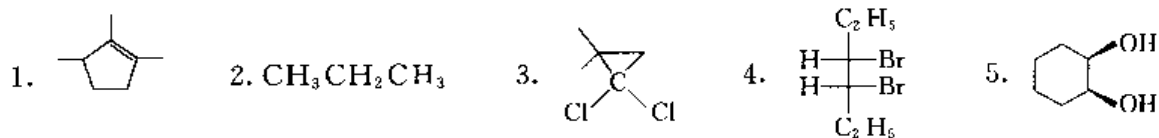
一有机化合物 A 含 C、H、O 3 种元素, 测得其蒸气密度在标准状况下是 4.47g/L。分析其百分含量可知其含 C 72.1%、含 H 11.9%。该化合物经催化氧化脱一分子氢得 B。B 能与羟胺反应得 C。C 在发烟硫酸作用下发生 Beckmann 重排得到一种硫酸酯 D。D 用氨水中和得到一种能够用水引发聚合的内酰胺单体 E。推导 A~E 的结构并写出分子式的计算过程和每一步反应式。

参考答案

一、选择题

1. (A) 2. (C) 3. (C) 4. (C) 5. (B) 6. (A) 7. (D) 8. (B)
 9. (B) 10. (B) 11. (C) 12. (B) 13. (D) 14. (B) 15. (B) 16. (A)
 17. (D) 18. (B) 19. (D) 20. (B)

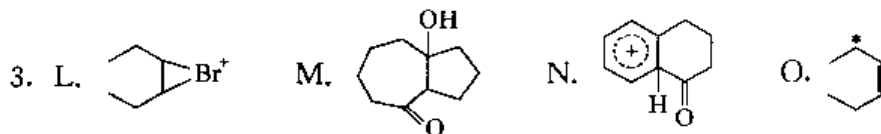
二、完成反应式



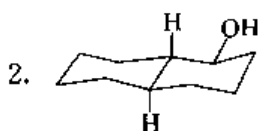
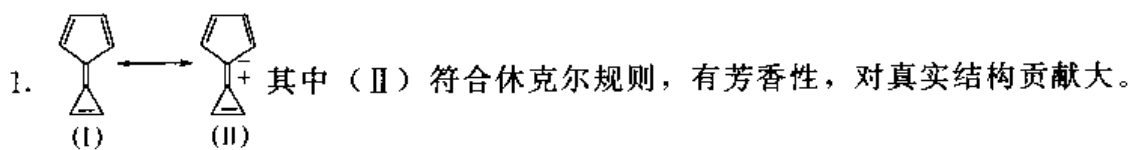
三、填空

1. A. $\text{S}_{\text{N}}2$ B. $\text{S}_{\text{N}}1$ C. $\text{S}_{\text{N}}2$ D. $\text{S}_{\text{N}}1$ E. $\text{S}_{\text{N}}1$ F. $\text{S}_{\text{N}}2$ G. $\text{S}_{\text{N}}2$

2. H. 吡啶型 I. 吡啶型 J. 吡啶型 K. 吡咯型



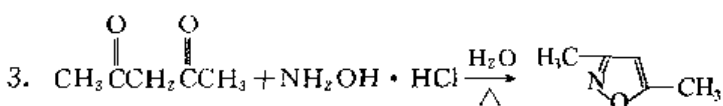
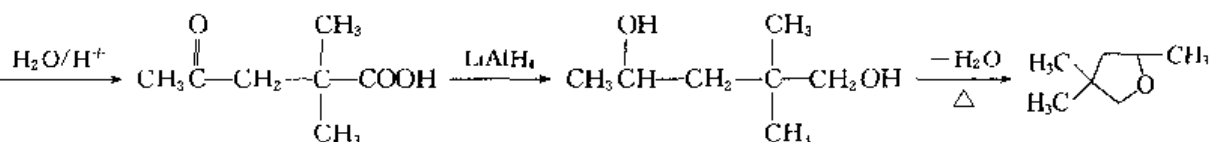
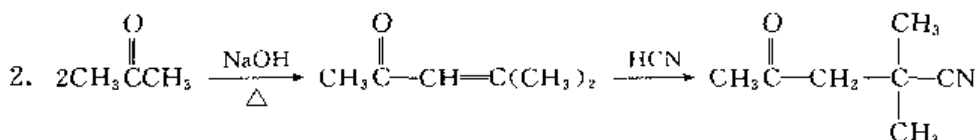
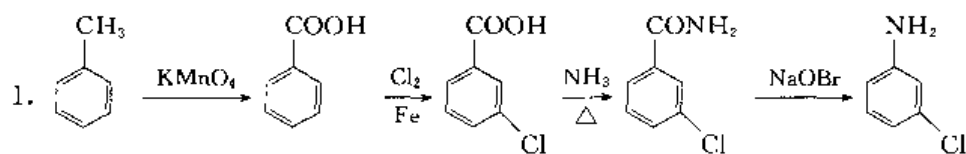
四、解释说明



3. 间甲氧基苯酚：甲氧基对羟基只有吸电子的诱导效应（-I），使酚羟基上电子云密度降低，酸性增强；

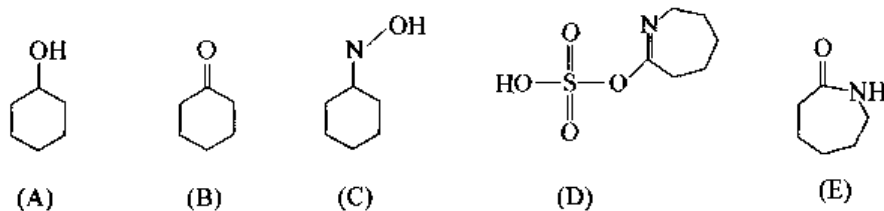
对甲氧基苯酚：甲氧基对羟基有吸电子的诱导效应（-I）和给电子的共轭效应（+C），而且 +C ≫ -I。总的结果是酚羟基上电子云密度增大，酸性减弱。

五、合成



六、推测结构

1. A~E 的结构



2. 分子式的计算

① 计算实验式

项目	元素分析结果	相对原子质量	各种原子的相对个数	实验式
C	72.15%	12	6	C ₆ H ₁₂ O
H	11.9%	1	12	
O	15.95%	16	1	

② 计算相对分子质量

∴ 在标准状况下，每升理想气体的物质的量为 1/22.4 mol；

化合物 A 的蒸气在标准状况下是 4.47 g/L

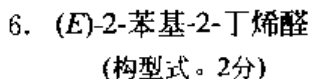
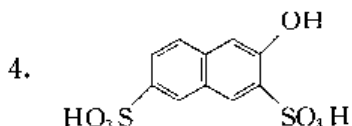
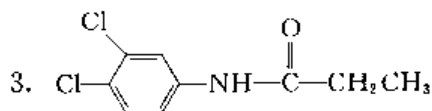
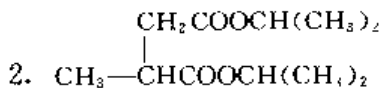
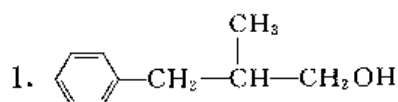
$$\therefore \frac{1}{22.4} = \frac{4.47}{M_A} \quad M_A = 22.4 \times 4.47 = 100.2$$

③ A 的分子式为 C₆H₁₂O

3. 有关的反应式（略）

模拟试题 17

一、命名或写结构 (10 分)

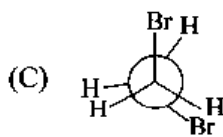
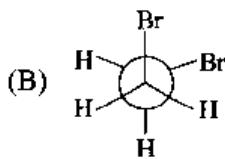
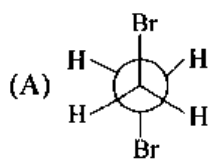


7. 乙烯基乙醚

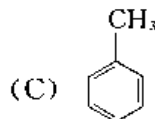
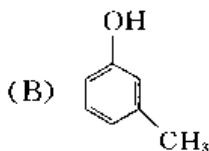
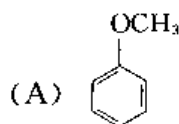
8. 2,4-甲基-6-乙氧基嘞啉

二、选择题 (10 分)

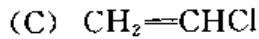
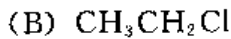
1. 二溴乙烷不同构象中, 最稳定的是



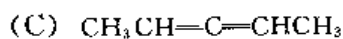
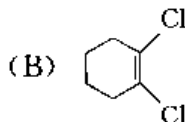
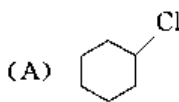
2. 下列化合物沸点最高的是



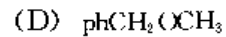
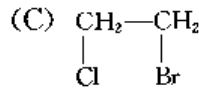
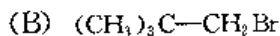
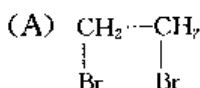
3. 下列化合物偶极矩最小的是



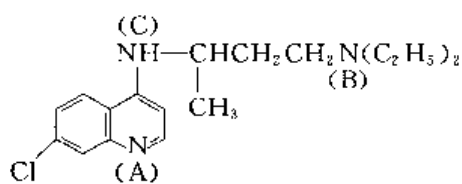
4. 下列化合物具有光学异构体的是



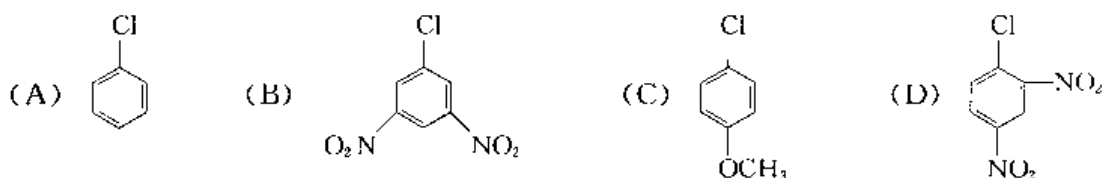
5. 下列化合物的¹H NMR 谱中, 亚甲基 (CH_2) 发生裂分的是



6. 下列化合物中的不同氮原子碱性最大的是



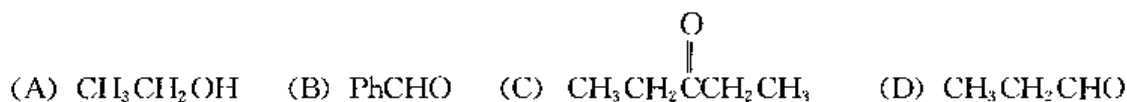
7. 下列化合物中, 哪个与 NaOH 反应最易转变为相应的酚



8. 芳香族伯胺的重氮化反应是在什么溶液中进行的

(A) 强酸性 (B) 中性 (C) 碱性 (D) 弱酸性

9. 下列化合物能发生碘仿反应的是

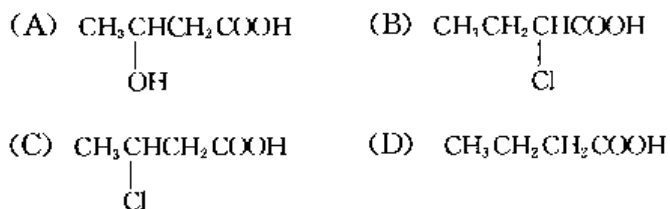


10. 下列化合物芳香性最小的是

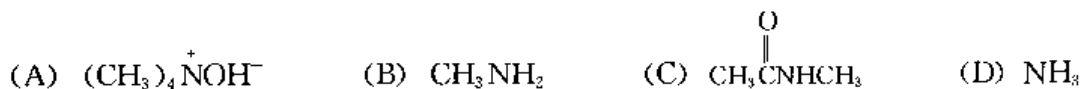
(A) 呋喃 (B) 噻吩 (C) 萘 (D) 苯

三、按指定要求, 由大到小顺序排列下列化合物 (10 分)

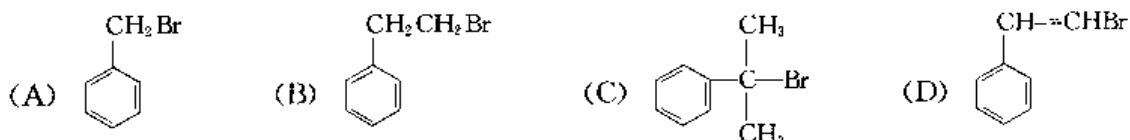
1. 酸性



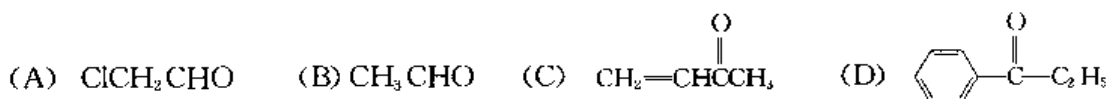
2. 碱性



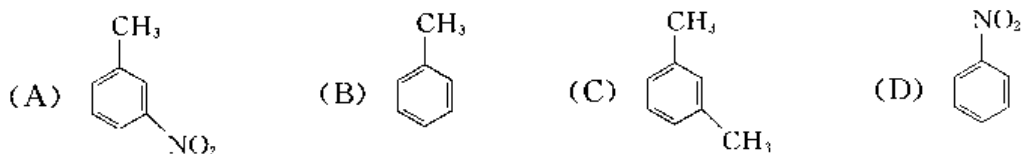
3. 与硝酸银醇溶液反应活性



4. 与 HCN 加成反应活性

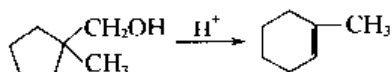


5. 硝化反应活性

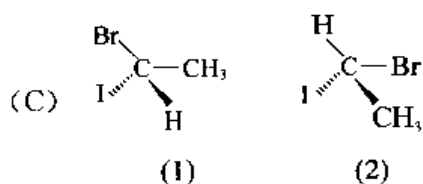
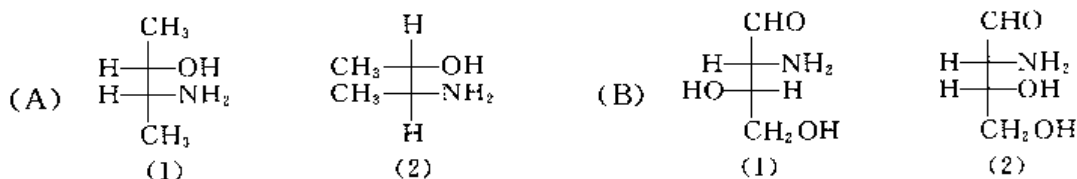


四、扼要回答下列问题 (15分)

1. 用反应机理解释下列反应结果 (4分)



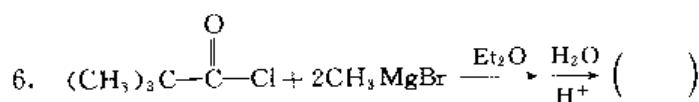
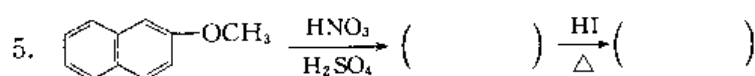
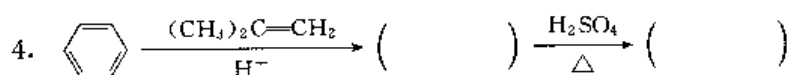
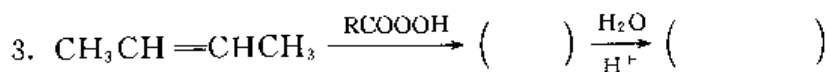
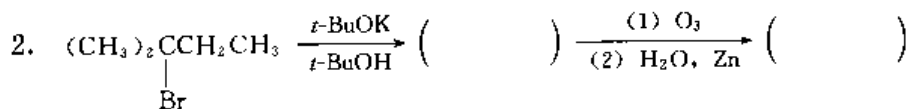
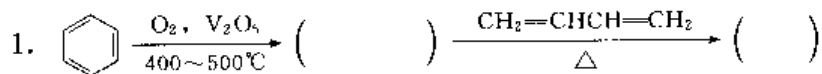
2. 下列化合物中, (1) 和 (2) 是对映体、非对映体还是同一化合物? (3分)

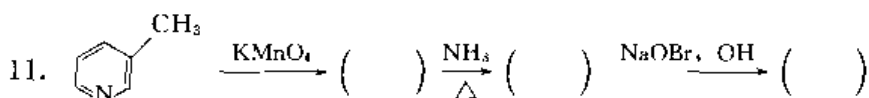
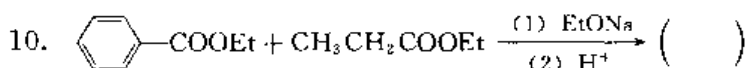
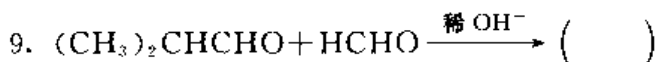
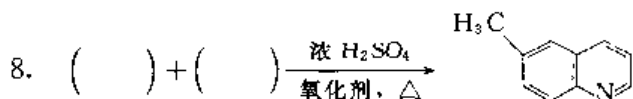
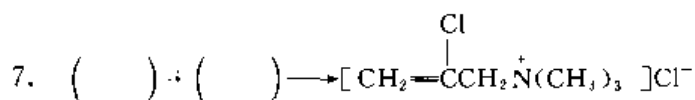


3. 用简便的化学方法鉴别下列各组化合物 (8分)

- (1) (A) 3-甲基己烷 (B) 1-甲基-2-乙基环丙烷
(C) 3-甲基-1-溴-2-丁烯 (D) 2-甲基-3-溴-2-丁烯
(2) (A) $\text{CH}_3\text{CH}_2\text{NO}_2$ (B) $\text{CH}_3\text{CH}_2\text{NH}_2$ (C) $(\text{CH}_3\text{CH}_2)_2\text{NH}$ (D) $(\text{CH}_3\text{CH}_2)_3\text{N}$

五、完成下列反应 (20分)





六、测定结构 (15 分)

1. 化合物 A ($\text{C}_5\text{H}_{11}\text{Br}$), A 和 NaOH 水溶液共热后生成 B ($\text{C}_5\text{H}_{12}\text{O}$)。B 能和钠作用放出氢气, B 具有旋光性, 能和浓硫酸共热生成 C (C_5H_{10}), C 经臭氧化和还原水解生成丙酮和乙醛。试推测 A、B、C 的结构。

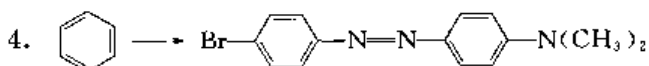
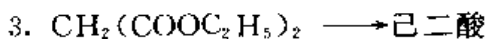
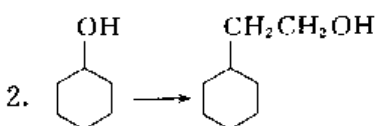
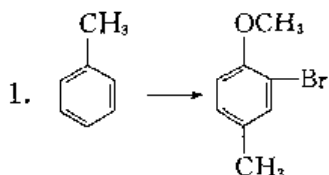
2. 化合物 A ($\text{C}_5\text{H}_{13}\text{N}$) 与对甲苯磺酰氯作用生成一种不溶于 NaOH 溶液的磺酰胺。A 与过量的 CH_3I 反应, 然后与适量的氧化银共热后得 $(\text{CH}_3)_3\text{N}$ 和另一化合物 B, B 吸收 1mol 氢后生成正丁烷。试推测 A、B 的结构式。

3. 某化合物, 分子式为 $\text{C}_6\text{H}_{12}\text{O}_2$, 其 $^1\text{H NMR}$ 谱为

δ/ppm	峰面积比	信号类型
1.2	6	单峰
2.2	3	单峰
2.6	2	单峰
4.0	1	单峰

此化合物与金属钠放出氢气, 也可与 2,4-二硝基苯肼反应生成黄色沉淀, 但不易氧化, 用 IR 谱测定, 在 1700cm^{-1} 及 3400cm^{-1} 有吸收峰, 试推出其结构。

七、合成 (可选用等于或少于两个碳的有机原料和任何无机试剂。20 分)



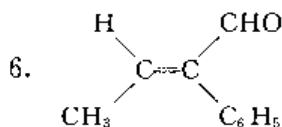
参考答案

一、命名或写结构

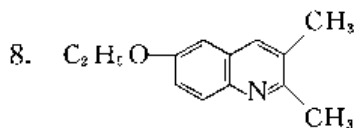
1. 2-甲基-3-苯基-1-丙醇 2. 2-甲基丁二酸二异丙酯
3. *N*-丙酰基-3,4-二氯苯胺 4. 2-羟基-3,6-萘二磺酸

[或者 *N*-(3,4-二氯苯基)丙酰胺]

5. (*S*)-3-溴-1-戊烯



7. $\text{CH}_2=\text{CH}-\text{OC}_2\text{H}_5$



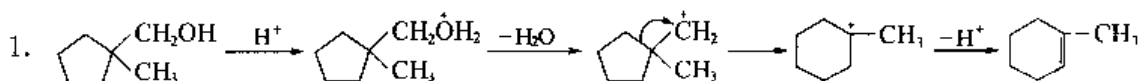
二、选择题

1. (A) 2. (B) 3. (C) 4. (C) 5. (C) 6. (B) 7. (D) 8. (A) 9. (A) 10. (A)

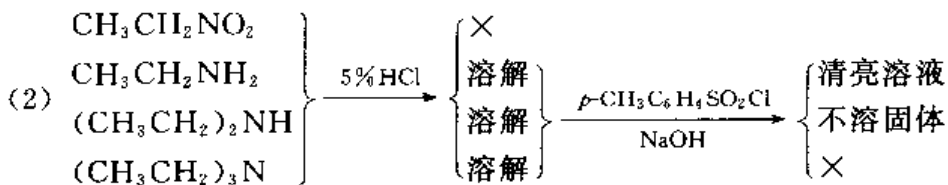
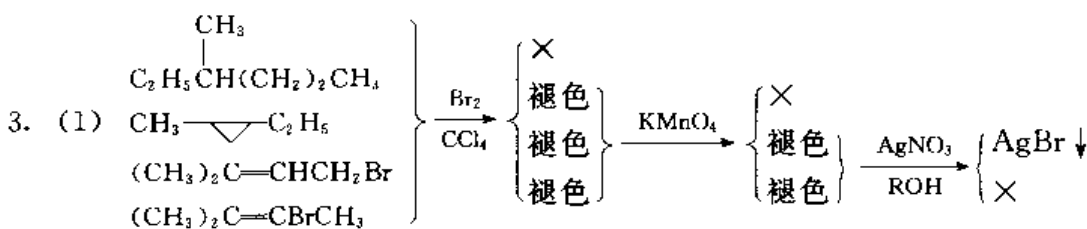
三、排序

1. $B > C > A > D$ 2. $A > B > D > C$ 3. $C > A > B > D$ 4. $A > B > C > D$
5. $C > B > A > D$

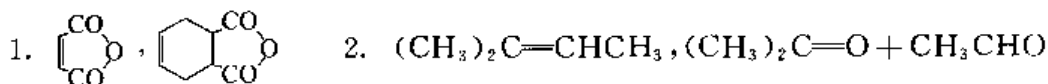
四、扼要回答

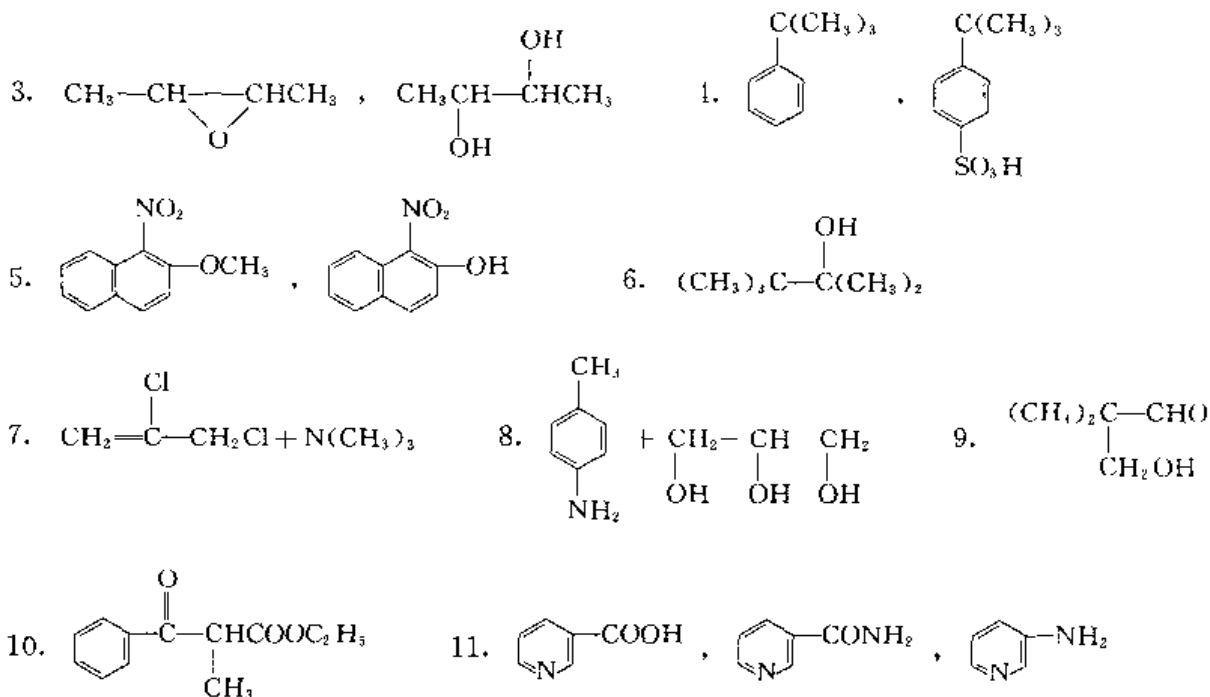


2. (A) 对映体 (B) 非对映体 (C) 同一化合物

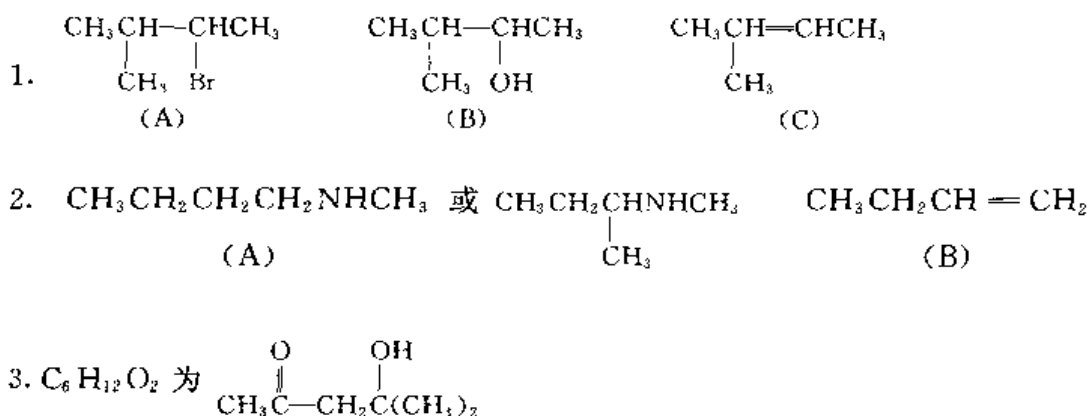


五、完成下列反应

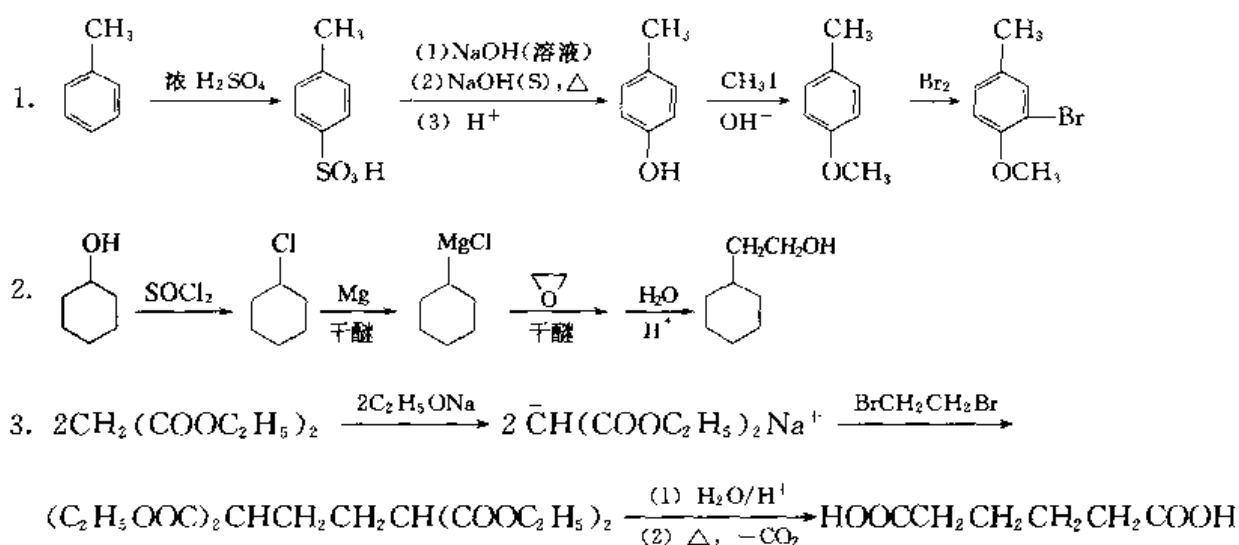




六、测定结构



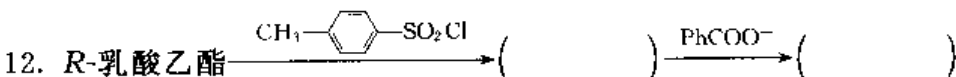
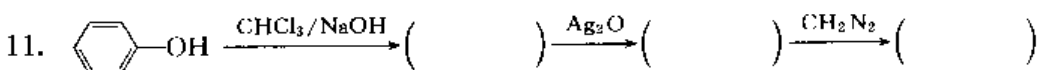
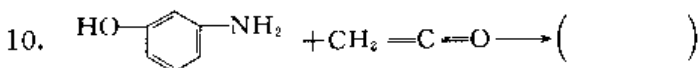
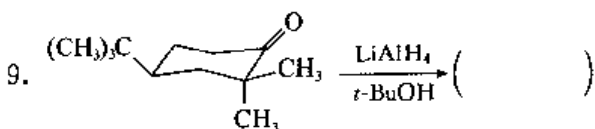
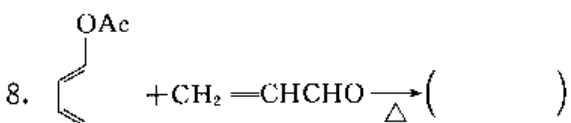
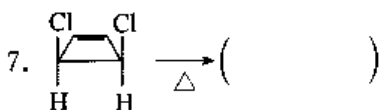
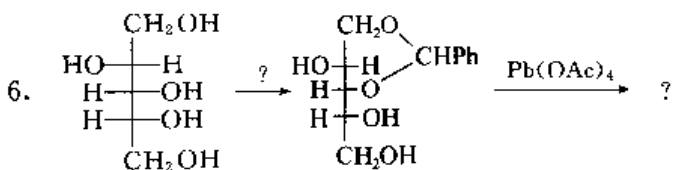
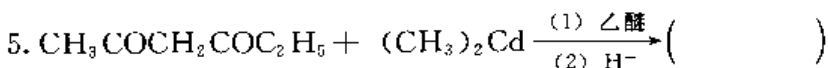
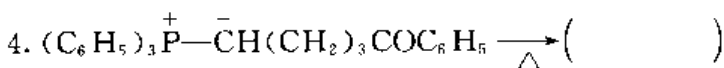
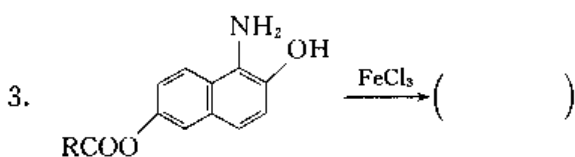
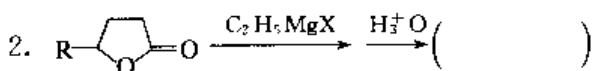
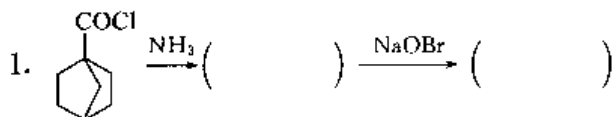
七、合成

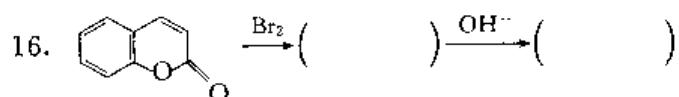
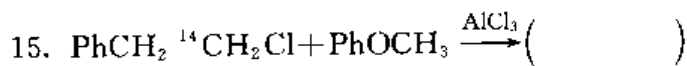
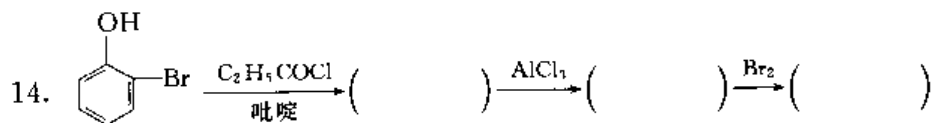
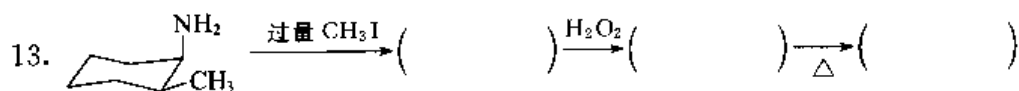


4. 略。见“模拟试题7”中“六、5。”。

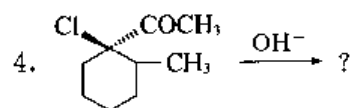
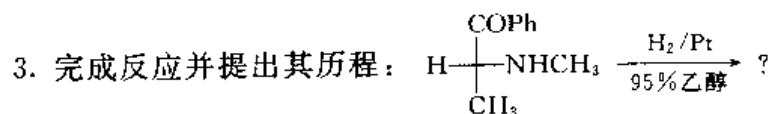
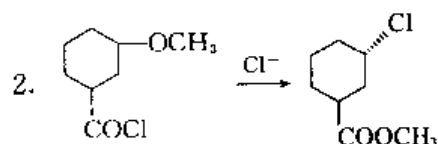
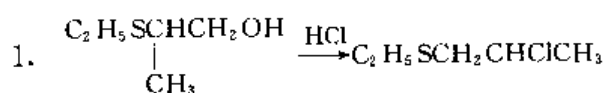
模拟试题 18

一、完成反应并注明立体化学问题 (31分)

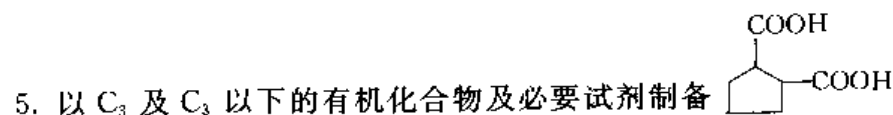
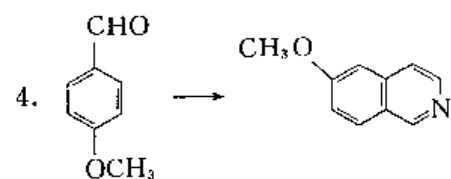
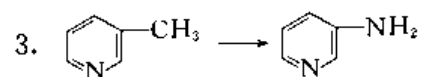
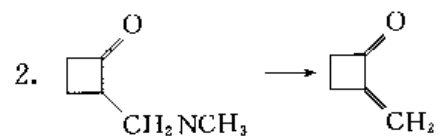
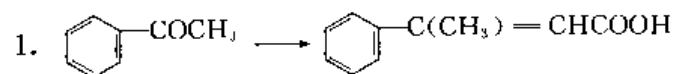




二、试为下列各反应提出合理的反应历程 (20 分)



三、合成题 (25 分)



四、推测结构 (24分)

1. 2,4-戊二酮与等物质的量的 NaH 反应, 有气体放出, 产物用碘甲烷处理, 得分子式为 $C_6H_{10}O_2$ 的两化合物 A 和 B, A 用酸水解, 又得到 2,4-戊二酮, 化合物 B 对稀酸稳定。试推测 A、B 结构式。

2. 化合物 A ($C_7H_{12}O_4$) 与亚硝酸反应得 B ($C_7H_{11}O_3N$), B 和 C 是互变异构体, C 经乙酸酐反应, 得 D ($C_9H_{15}O_5N$); D 在碱作用下与苯氯反应, 得 E ($C_{16}H_{21}O_5N$), E 用稀碱水解, 再酸化加热, 得 F ($C_9H_{11}O_2N$), F 同时具有氨基和羧基, 一般以内盐形式存在。试推测 A、B、C、D、E、F 的结构式。

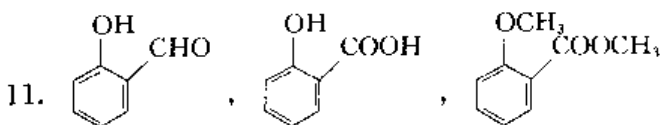
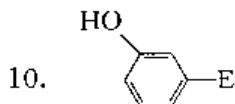
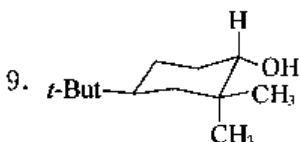
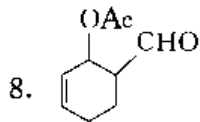
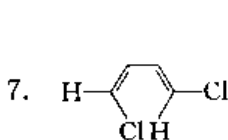
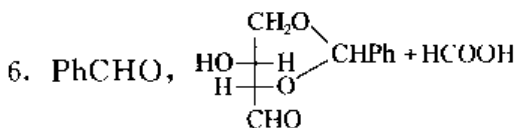
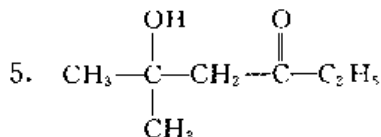
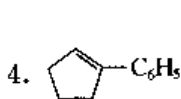
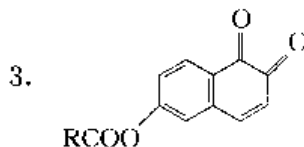
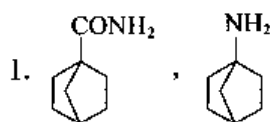
3. 化合物 A ($C_9H_{18}O_2$) 对碱稳定, 经酸性水解得 B ($C_7H_{14}O_2$) 和 C (C_2H_6O), B 与硝酸银氨溶液反应, 再酸化得 D, D 经碘仿反应酸化得 E, 将 E 加热得化合物 F ($C_6H_8O_3$); F 的 NMR 数据: δ 1 (3H, 二重峰); δ 2.1 (1H, 多重峰); δ 2.8 (4H, 二重峰)。推测 A、B、C、D、E、F 结构式。

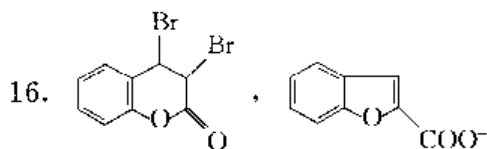
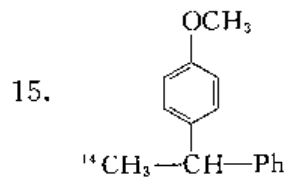
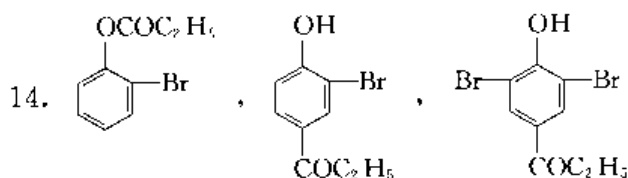
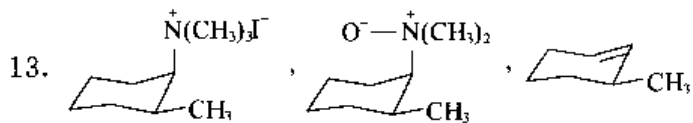
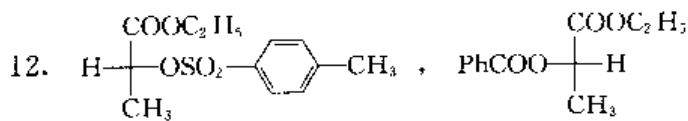
4. 化合物 A 的 IR 为 $3200\sim 3600\text{cm}^{-1}$; NMR: δ 0.9 三重峰, δ 1.1 单峰, δ 1.6 四重峰。3 个峰面积比为 3 : 7 : 2 质谱: 弱的分子离子峰的 $m/z=88$, 基峰为 $m/z=59$, 其他各主要峰分别为 $m/z=73, 70, 59, 55$ 。

推测 A 的结构, 并解释各峰的归属。

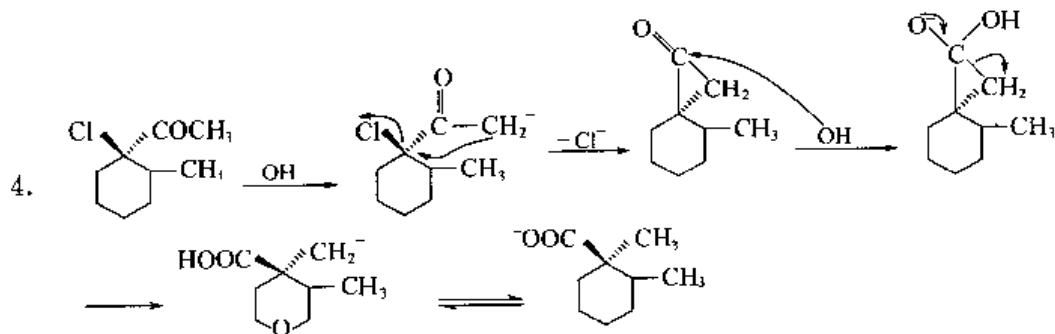
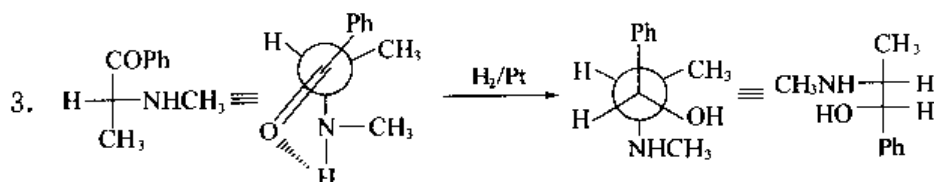
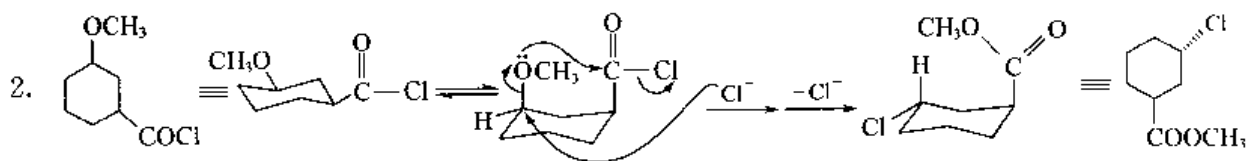
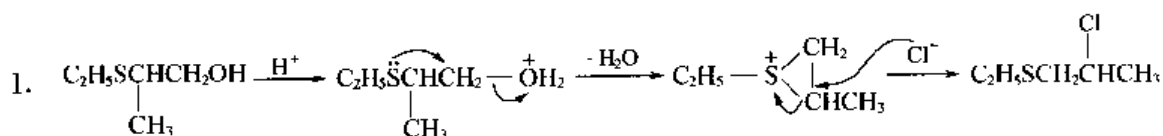
参考答案

一、完成反应式

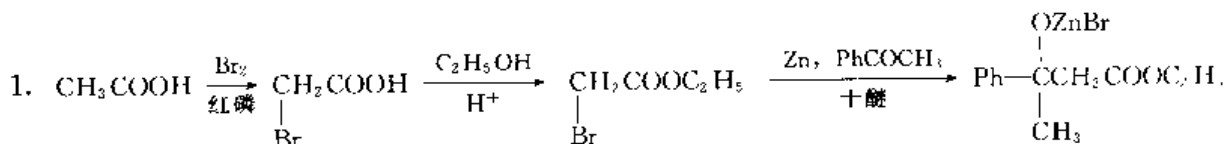


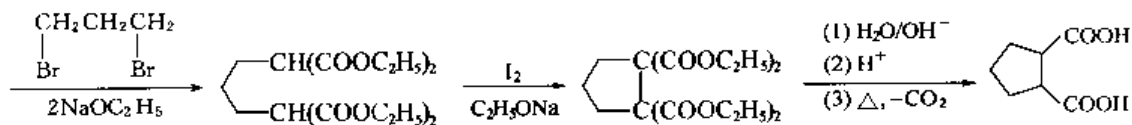
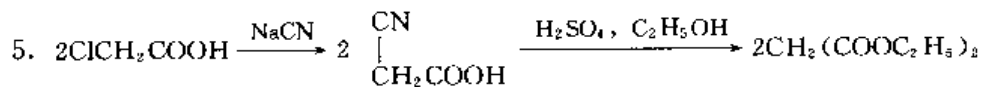
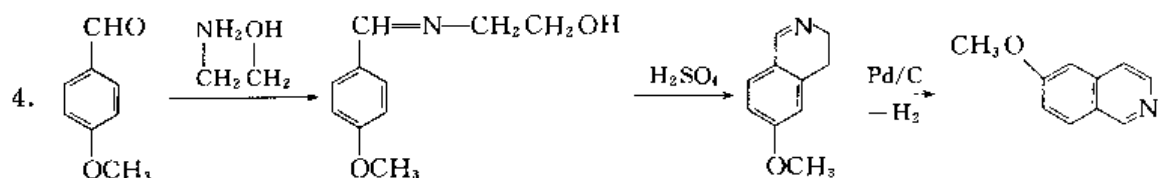
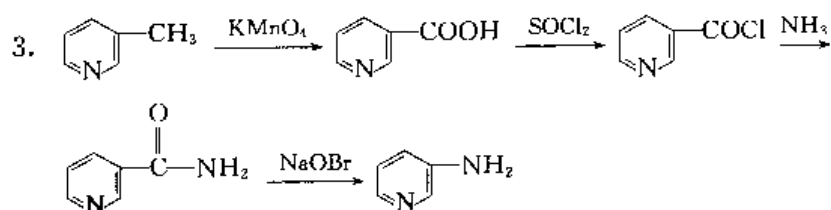
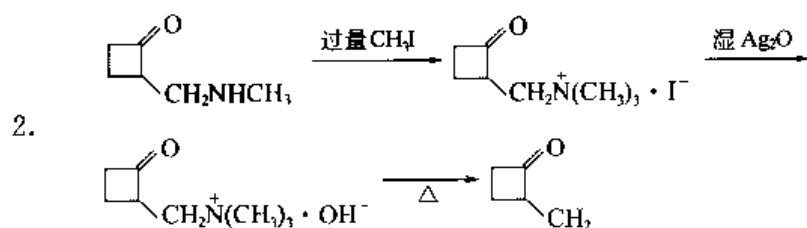
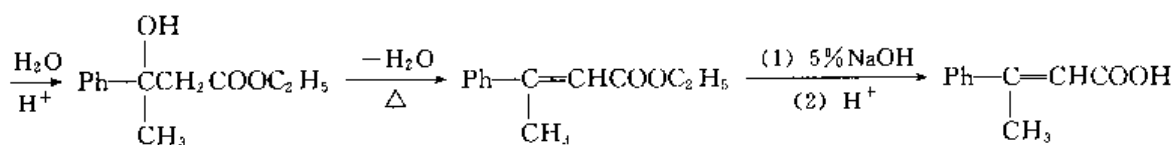


二、反应机理

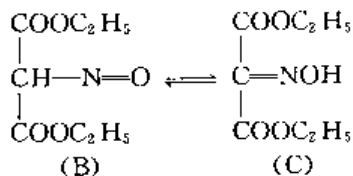
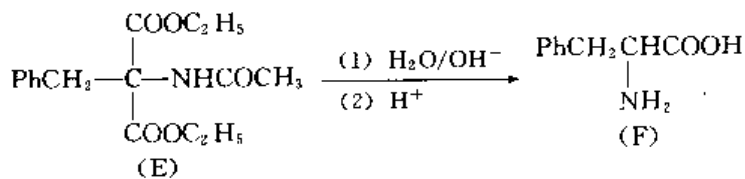
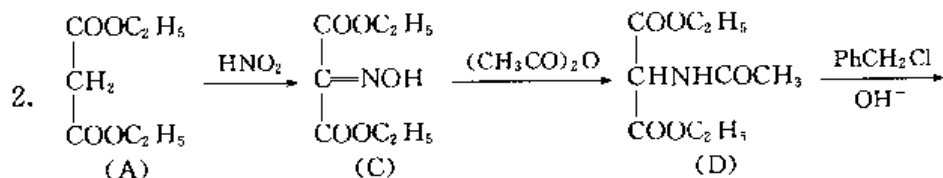
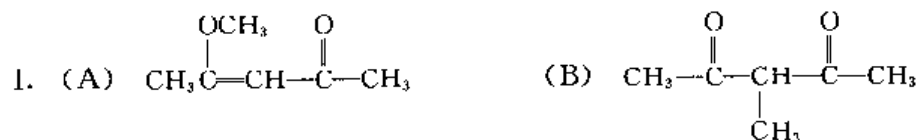


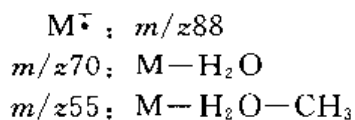
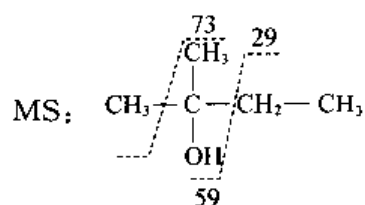
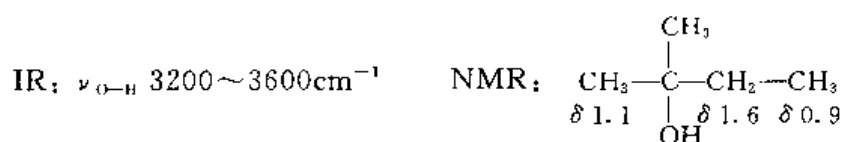
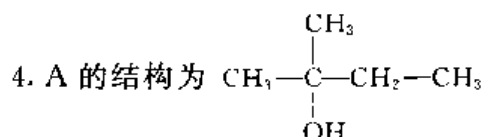
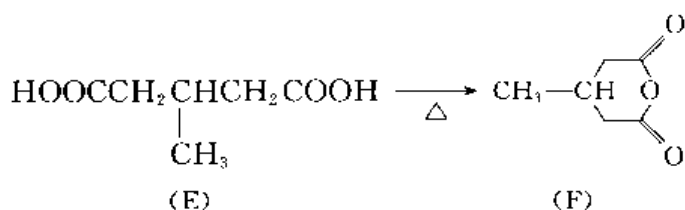
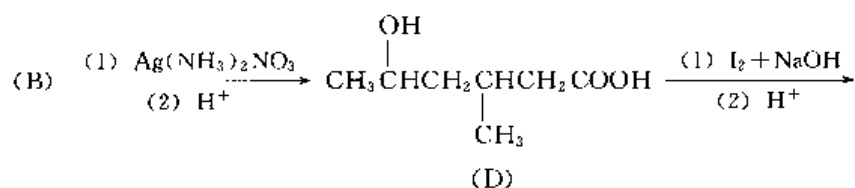
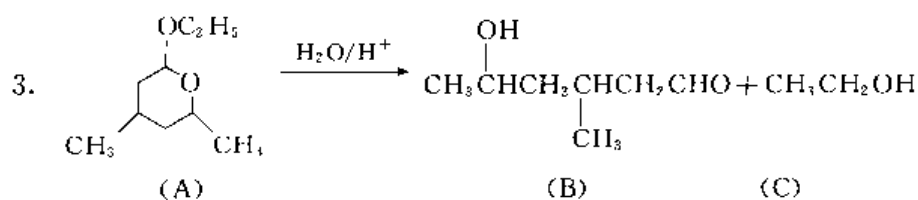
三、合成题





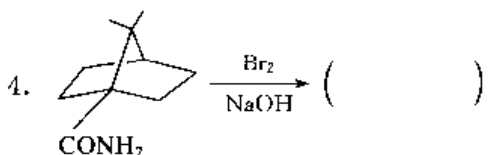
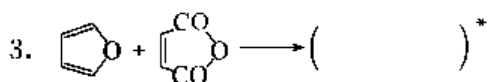
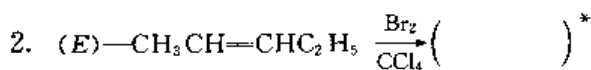
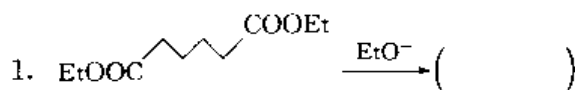
四、推导结构

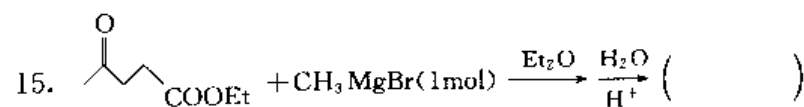
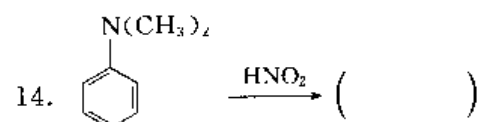
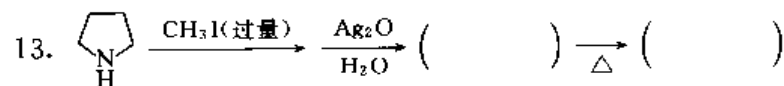
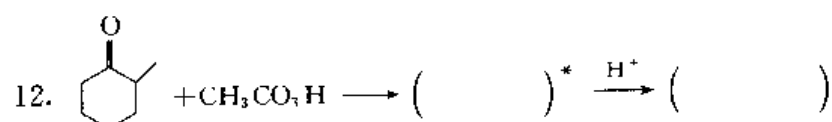
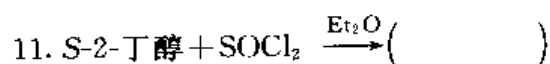
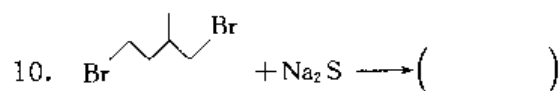
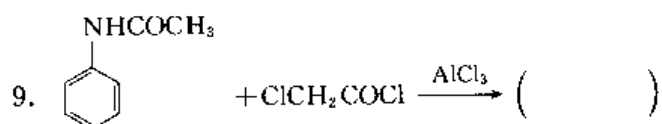
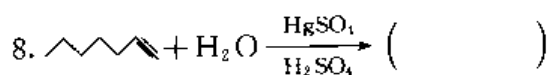
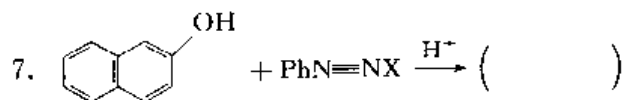
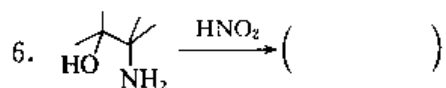
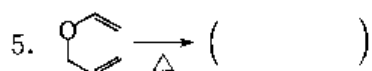




模拟试题 19

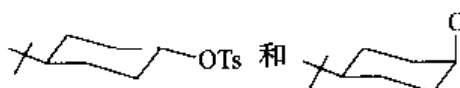

一、完成下列反应，在标有*的括号内写构型式或标明构型 (20分)





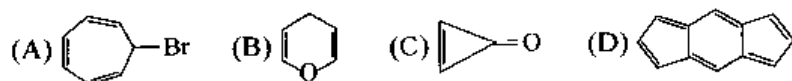
二、回答下列问题 (18分)

1. 为什么 $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{COOH}$ 不能形成偶极分子, 而 $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$ 则可?

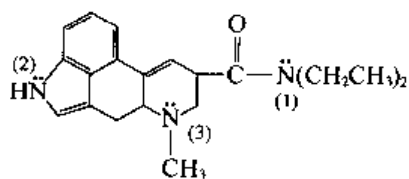
2. 化合物  和  如按 E2 历程消去, 哪个的反应速率快?

为什么?

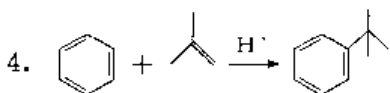
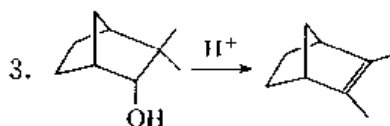
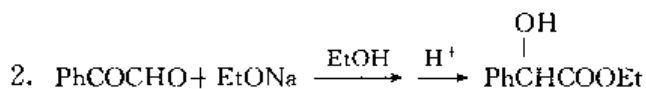
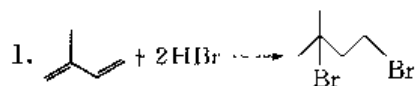
3. 下列化合物哪些具有芳香性? 为什么?



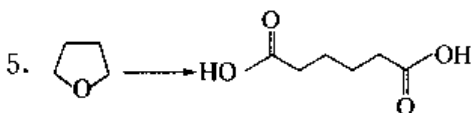
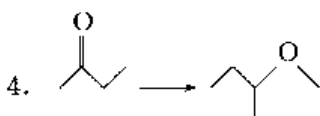
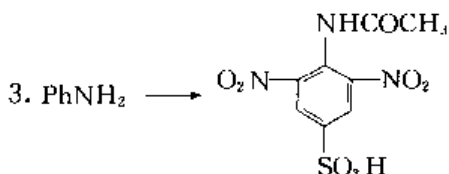
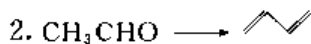
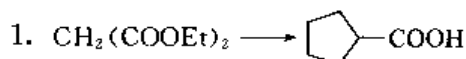
4. 化合物 LSD 中, 碱性最大的氮原子是哪个? 为什么?



三、写出下列反应机理 (18 分)



四、合成 (24 分)



五、推测结构题 (16%)

1. 化合物 A (C_7H_{12}) 在 20°C 与干 HCl 反应得化合物 B ($\text{C}_7\text{H}_{13}\text{Cl}$), B 在叔丁醇中与叔丁醇钾反应生成化合物 C, C 与 A 是同分异构体, C 与臭氧反应后再还原水解生成环己酮和甲醛。试写出化合物 A、B、C 的结构。

2. 化合物 A ($\text{C}_3\text{H}_6\text{Br}_2$) 与 NaCN 反应生成化合物 B ($\text{C}_5\text{H}_8\text{N}_2$); B 酸性水解生成 C, C 与乙酸酐共热生成 D 和乙酸; D 的 IR 在 1820 、 1755cm^{-1} 处有强吸收; NMR, $\delta_{\text{H}} 2.0$ (五重

峰, 2H), δ_H 2.8 (三重峰, 4H) 处有吸收。请写出 A、B、C、D 的结构式, 并标明各吸收峰的归属。

3. 某具有光活性的化合物 A (C_8H_{12}), 当 A 在 Pt 存在下加氢得化合物 B (C_8H_{18}), B 无光活性; 当 A 用 Lindlar 催化剂加氢得化合物 C (C_8H_{14}), C 有光活性。当 A 在液氨中与金属钠还原时得化合物 D (C_8H_{14}), D 不具光活性。根据这些反应, 推测出化合物 A、B、C、D 的结构式。

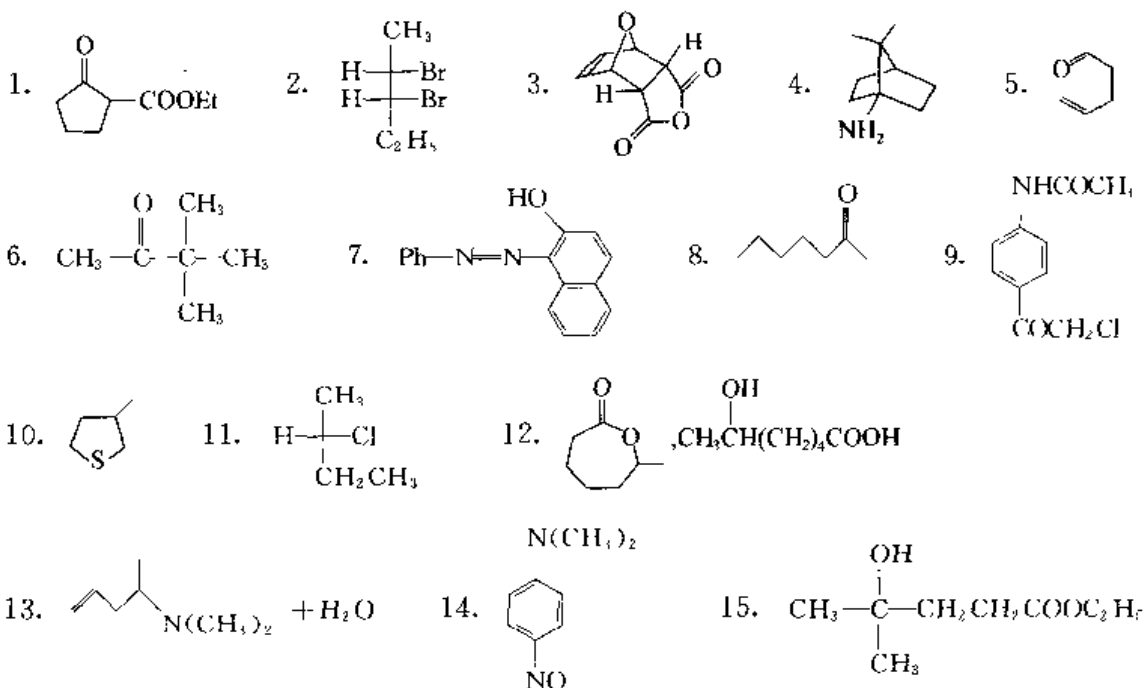
六. 实验题 (10 分)

要经克莱森酯缩合反应制备乙酰乙酸乙酯, 请回答下列问题:



1. 制备乙酰乙酸乙酯所用原料是什么?
2. 缩合剂是什么?
3. 缩合剂与反应物的物质的量之比是怎样的?
4. 以哪些物质为基础计算产率?
5. 反应完成时为何要用 50 份 HAc 处理?
6. $FeCl_3$ 与乙酰乙酸乙酯产生红色现象, 如何解释?


参考答案

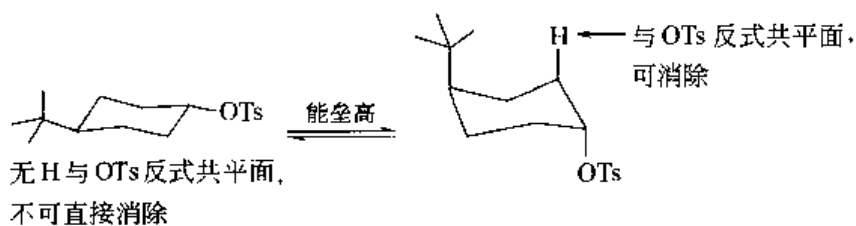
一、完成反应式



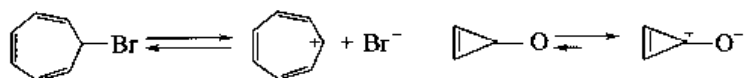
二、回答问题

1. 因为酸性  $>$ , $-SO_3H$ 更趋于电离形成 $-SO_3^- + H^+$ 。

2. 后者快。因为  H 与 OTs 反式共平面, 可直接消除



3. (A)、(C) 有芳香性。(B) 不是环状离域体系, (D) 不符合 $(4n+2)$ 规则。



符合 Huckel 规则

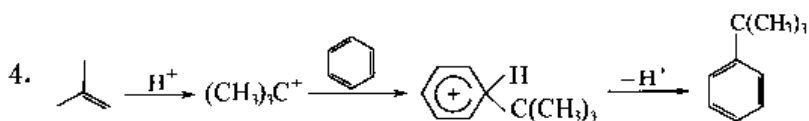
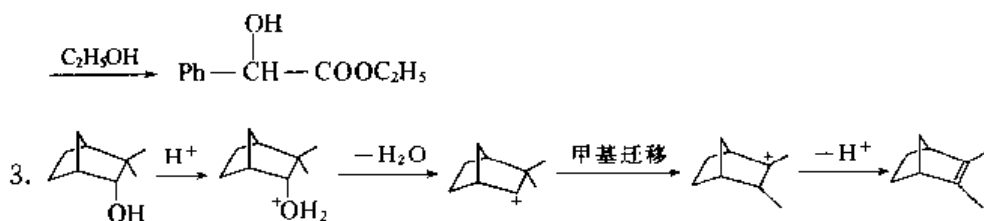
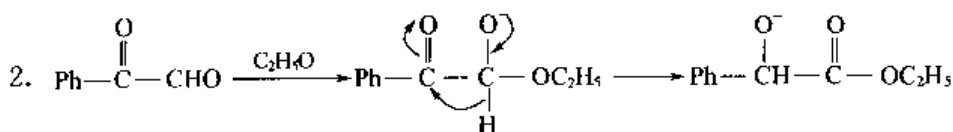
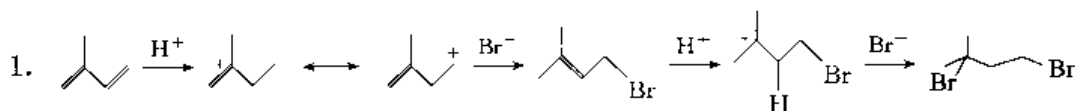
符合 Huckel 规则

4. 碱性最强者为编号 (3) 的氮原子。

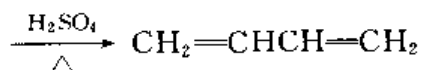
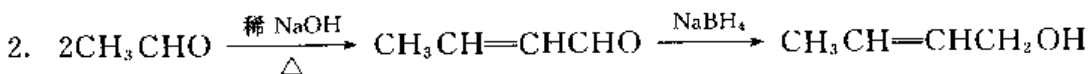
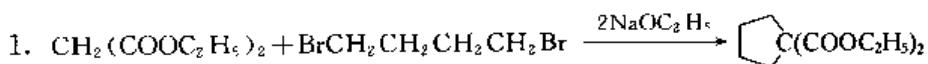
因为 (1) 号氮有 —C(=O)—N< 给电子 $p-\pi$ 共轭, 使 N 上电子云密度下降;

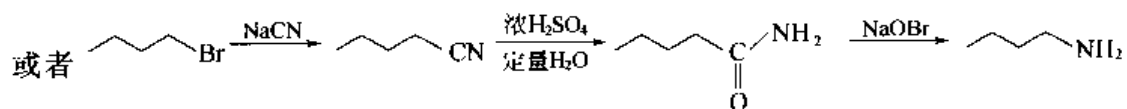
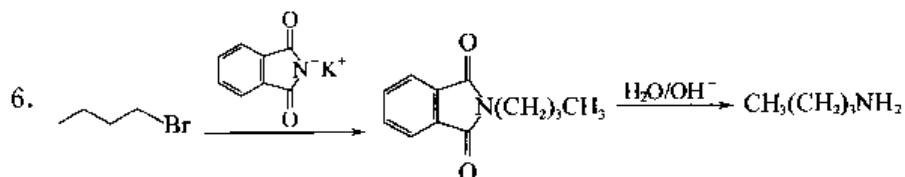
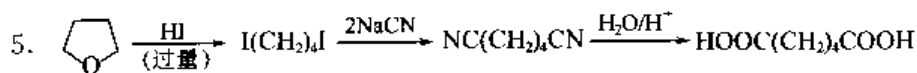
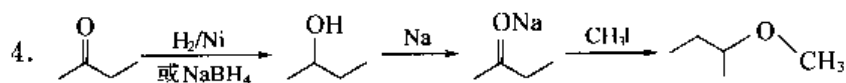
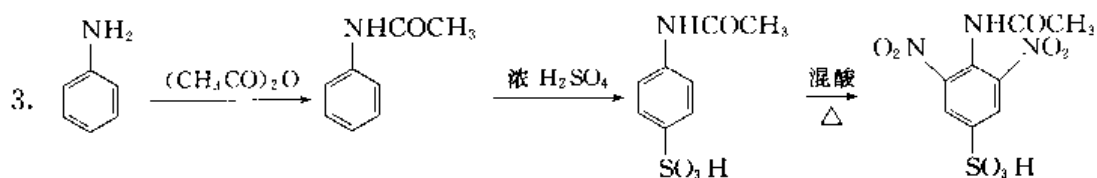
(2) 号氮也有 $p-\pi$ 共轭, HN< 同样使 N 上电子云密度下降。

三、反应机理

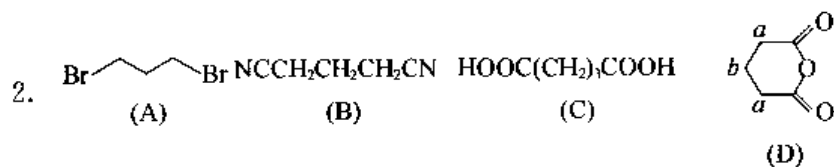
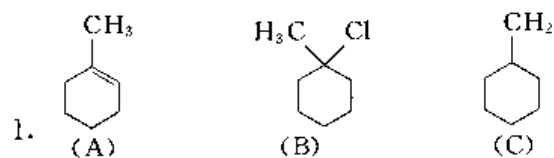


四、合成

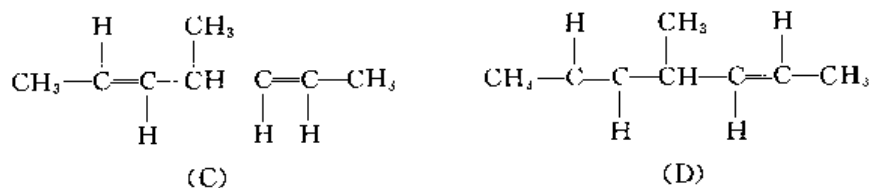
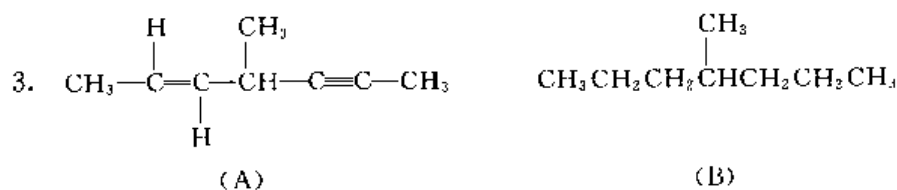




五、推测结构



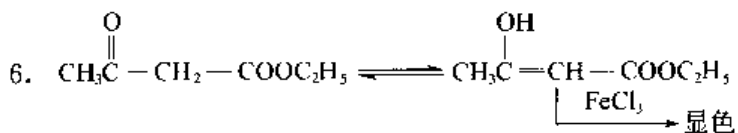
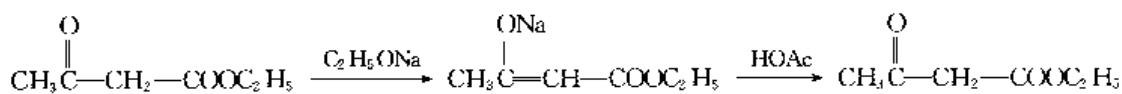
1820 cm^{-1} : C=O 的反对称伸缩振动吸收
 1755 cm^{-1} : C=O 的对称伸缩振动吸收 } 波数差约为 60 cm^{-1}
 H_a : δ 2.8 (三重峰, 4H) H_b : δ 2.0 (五重峰, 2H)



六、实验题

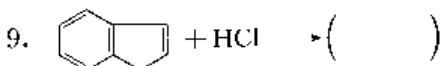
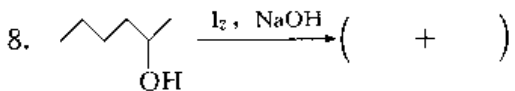
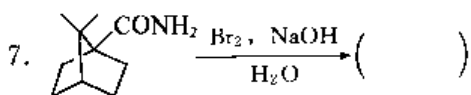
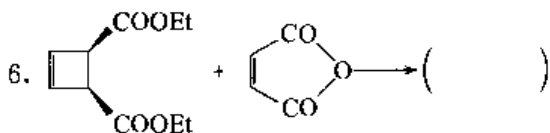
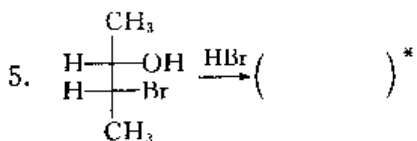
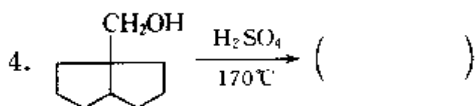
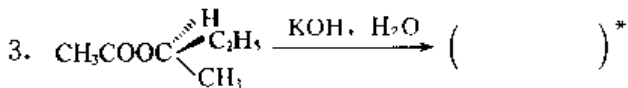
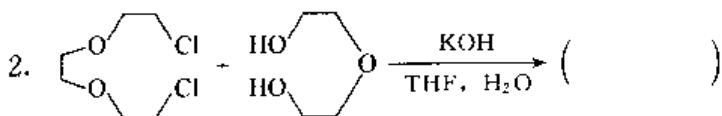
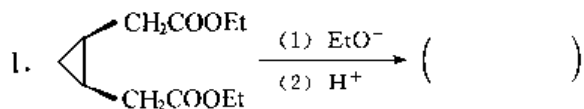
1. 制备乙酰乙酸乙酯所用的原料是 $\text{CH}_3\text{COOC}_2\text{H}_5$ (乙酸乙酯)。
2. 缩合剂是 NaOC_2H_5 (由于商品乙酸乙酯中含有少量乙醇)。

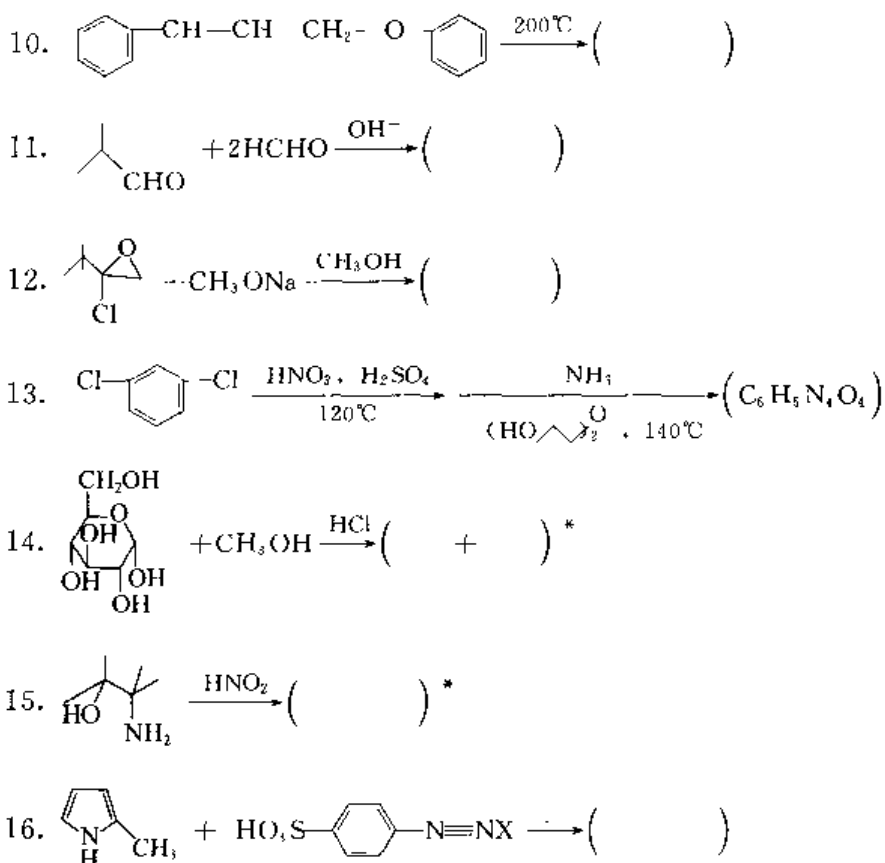
3. $\text{NaOC}_2\text{H}_5 : \text{CH}_3\text{COOC}_2\text{H}_5 = 1 : 2$ ，实际操作时，乙酸乙酯的用量要略大于理论值。
4. 计算产率时，以钠的用量为基础。
5. 在碱性条件下，乙酰乙酸乙酯以烯醇式负离子形式存在。



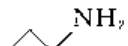
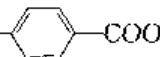
模拟试题 20


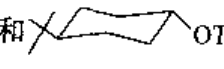
一、完成下列反应，在标有 * 的括号内写构型式或标明构型



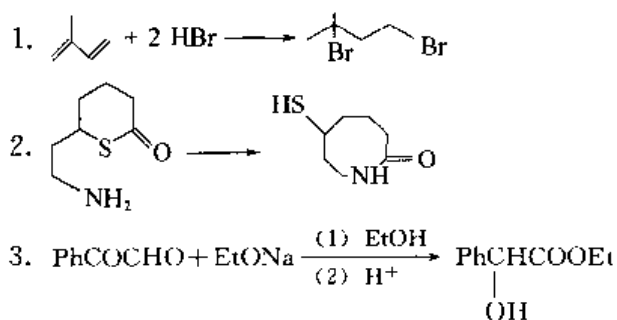


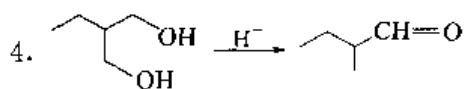
二、回答下列问题 (14 分)

1. 1 mol $(\text{CH}_3\text{CO})_2\text{O}$ 与  在 K_2CO_3 存在下, 是 HO 被酰化还是 NH_2 被酰化? 在 HCl 存在下, 是 OH 被酰化还是 NH_2 被酰化? 为什么?
2. 水杨酸的酸性比苯甲酸的酸性强 15 倍, 为什么?
3. 为什么  不能以偶极离子的形式存在? 而甘氨酸却能以偶极离子形式存在 ($\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$)?
4. 化合物 A ($\text{C}_7\text{H}_{14}\text{O}$) 的 IR 图谱上有一强吸收峰在 1710cm^{-1} 处, 在 $^1\text{H NMR}$ 图谱上有 3 个单峰, (δ -1.0, δ -2.1 和 δ -2.3), 其峰面积比为 9:3:2, 化合物 A 的结构是什么?

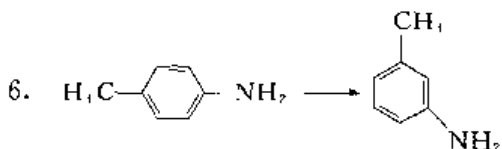
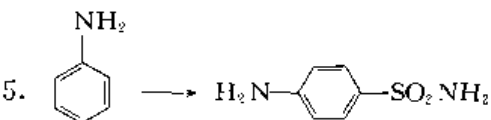
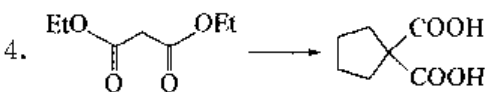
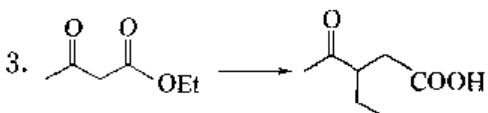
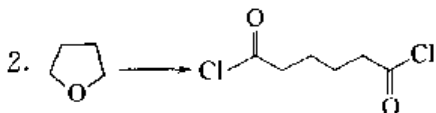
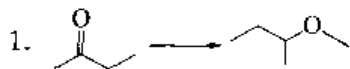
5. 化合物  和  如按 E2 历程消去, 哪个反应速率快? 为什么?

三、写出下列反应机理 (12 分)





四、合成题, 选作 5 题 (25 分)



五、推结构题 (15 分)

1. 碳氢化合物 A (C_8H_{12}) 具有光活性, 在铂存在下催化氢化成 B (C_8H_{18}), B 无光活性; A 用 Lindlar 催化剂小心催化氢化成 C (C_8H_{14}), C 有光活性。A 在液氨中与金属钠作用得 D (C_8H_{14}), D 与 C 互为同分异构体, 但 D 无光活性。写出 A、B、C、D 的结构式。

2. 化合物 A (C_7H_{12}) 用 $KMnO_4$ 氧化得 B, B 能与苯肼反应, B 也能与 Br_2-NaOH 反应生成 C, C 的核磁共振谱 (ppm): δ 1.3 (三重峰, 4H), δ 2.4 (三重峰, 4H), δ 13 (单峰, 2H), 将 C 与碱石灰一道加热生成环戊酮。写出 A、B、C 的结构式。

3. 某二元酸 A ($C_8H_{14}O_4$) 经加热转化为一个非酸性的化合物 B ($C_7H_{12}O$), B 用浓 HNO_3 氧化得一二元酸 C ($C_7H_{12}O_4$), 经加热, C 形成一个酸酐 D ($C_7H_{10}O_3$), A 经 $LiAlH_4$ 还原转化为 E ($C_8H_{18}O_2$), E 能脱水形成 3,4-二甲基-1,5-己二烯。写出 A、B、C、D、E 的结构式。

六、实验题 (10 分)

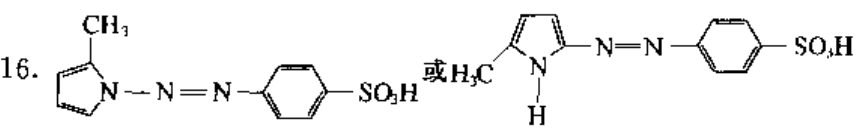
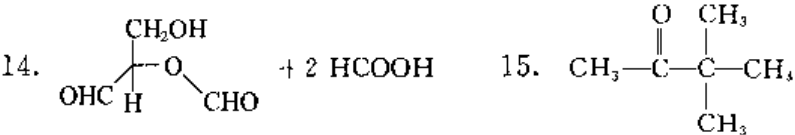
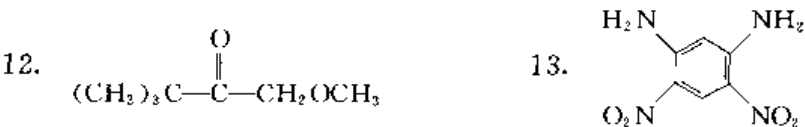
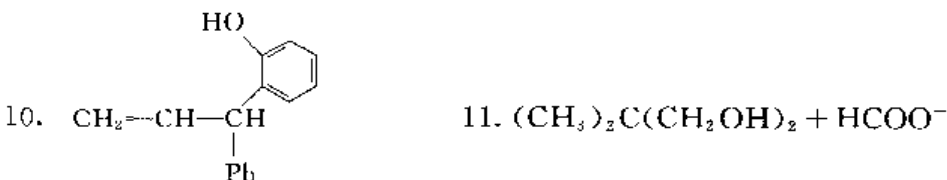
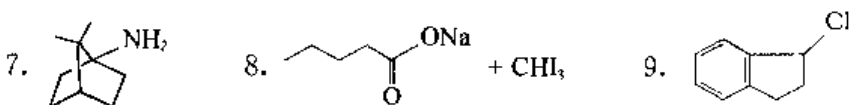
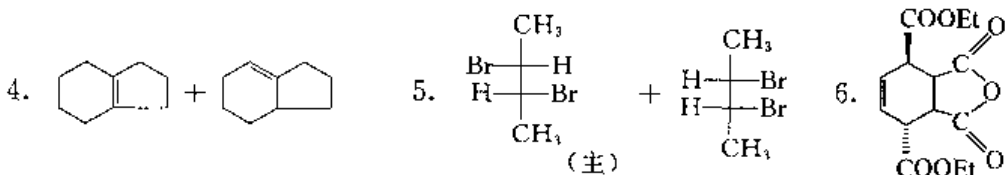
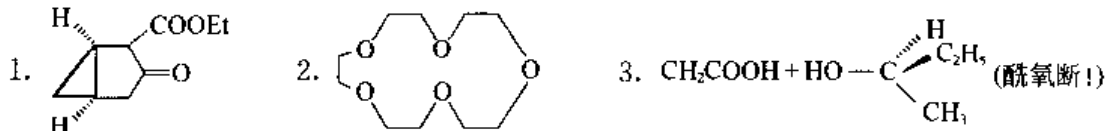
克莱森酯缩合反应是制备 β -酮酸酯的重要途径, 请回答制备乙酰乙酸乙酯时:

- ① 所用的原料是什么?
- ② 该反应真正的缩合剂是什么?
- ③ 缩合剂与反应物的物质的量之比如何?
- ④ 本实验以哪些物质为基础计算产率?
- ⑤ 反应完成时为何要用 50 份醋酸处理?

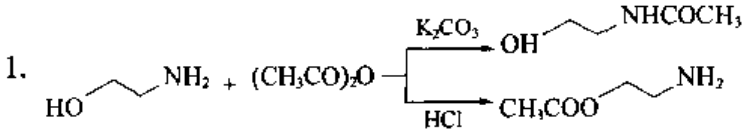
⑥ 解释乙酰乙酸乙酯与 FeCl_3 水溶液振摇出现红色的原因。

参考答案

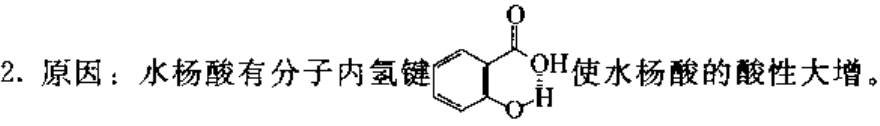
一、完成下列反应式



二、回答下列问题



原因：在碱性条件下， $-\text{OH}$ 与 $-\text{NH}_2$ 都是以游离形式存在，但由电负性 $\text{O} > \text{N}$ ，亲核性 $-\text{OH} < -\text{NH}_2$ ，所以 $-\text{NH}_2$ 被酰化。在酸性条件下， $-\text{NH}_2$ 可被质子化，形成 $-\text{NH}_3^+$ ，而 $-\text{OH}$ 无亲核性，所以 $-\text{OH}$ 被酸化。



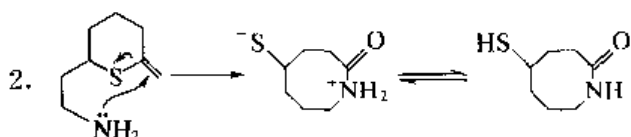
3. 在 $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{COOH}$ 中, $-\text{NH}_2$ 与苯环相连, N 上孤对电子可与苯环共轭, 碱性大减, 接受 H^+ 的能力大大减弱。而甘氨酸中, 氨基中 N 上电子云密度不减, 碱性不减, 接受 H^+ 的能力不减, 因而顺利与 $-\text{COOH}$ 形成内盐。

4. 化合物 A 是: $(\text{CH}_3)_3\text{CCH}_2\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_3$

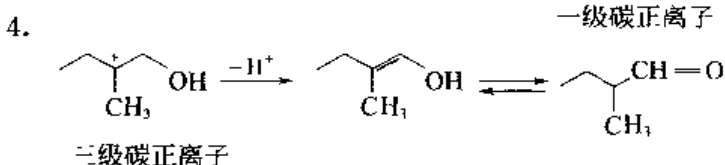
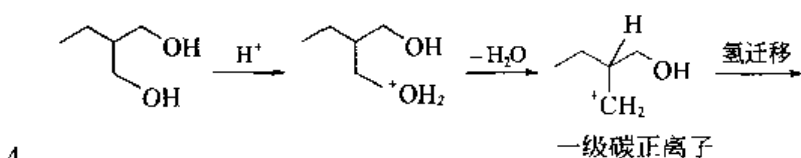
5. 略。见“模拟试题 19”。

三、写出下列反应机理

1. 略。见“模拟试题 19”。



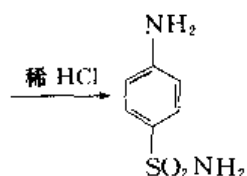
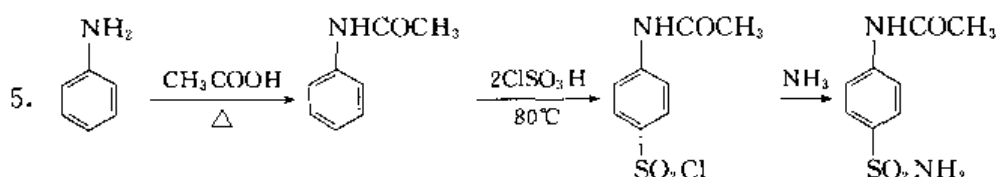
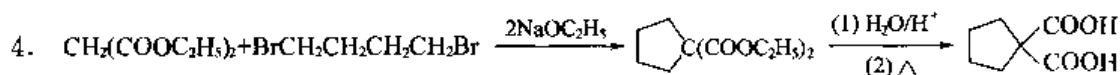
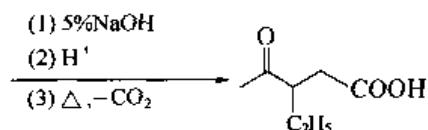
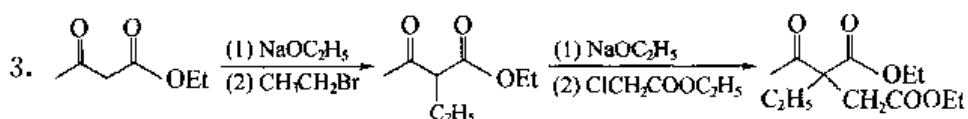
3. 略。见“模拟试题 19”。

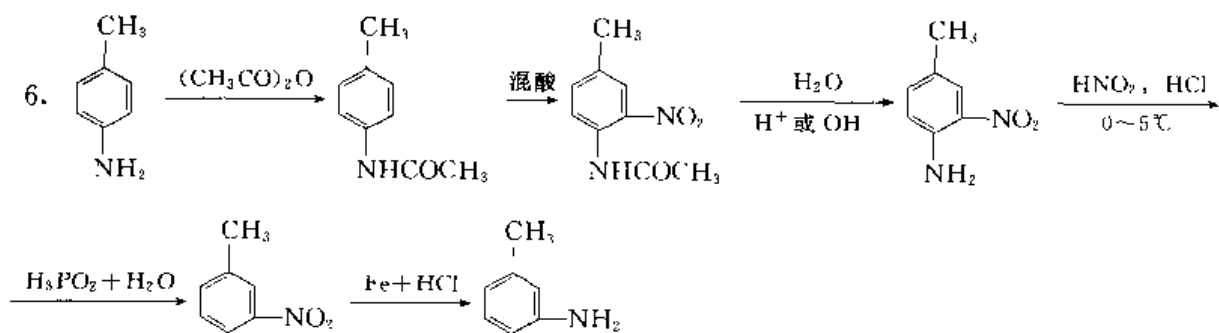


四、合成题, 选作 5 题

1. 略。见“模拟试题 19”。

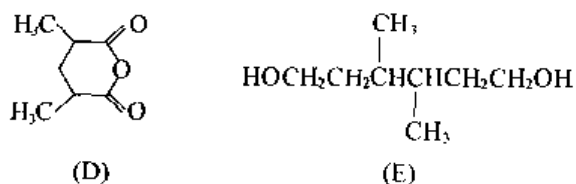
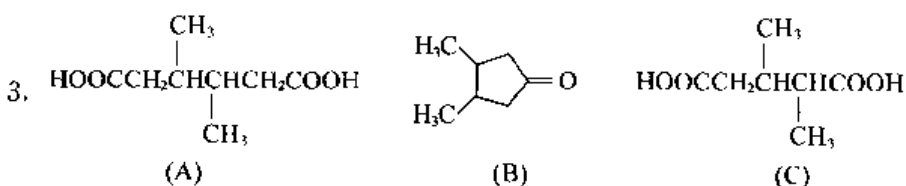
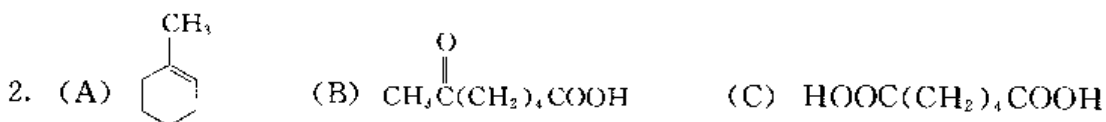
2. 略。见“模拟试题 19”。





五、推结构题

1. 略。见“模拟试题 19 五、3。”

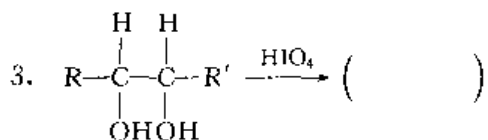
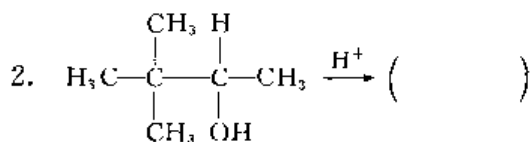
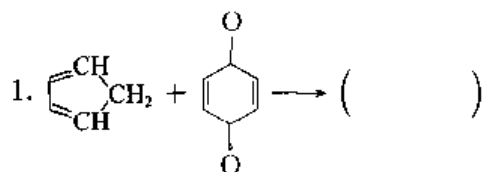


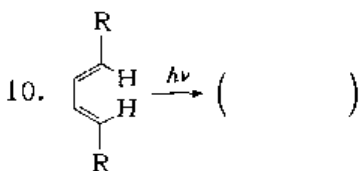
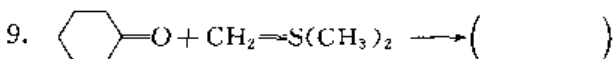
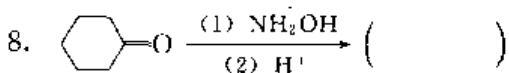
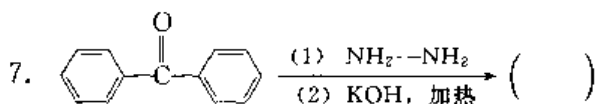
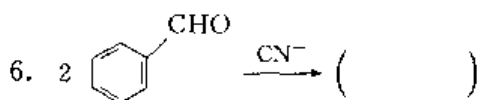
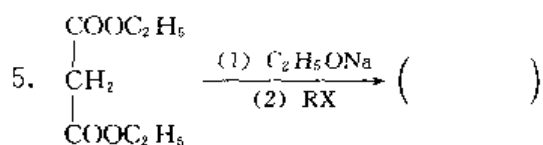
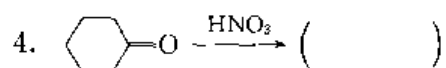
六、实验题

略。见“模拟试题 19 六、”。

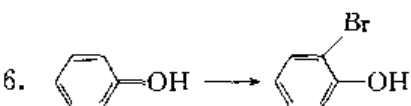
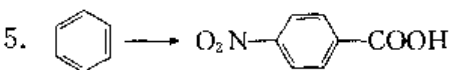
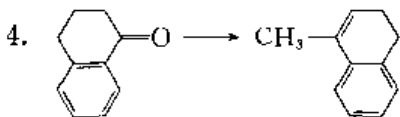
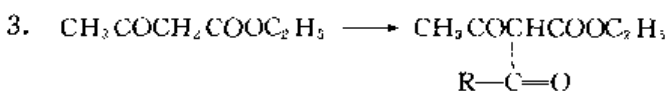
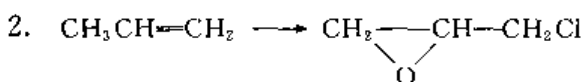
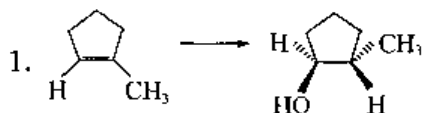
模拟试题 21

一、写出下列反应的主要产物 (20 分)

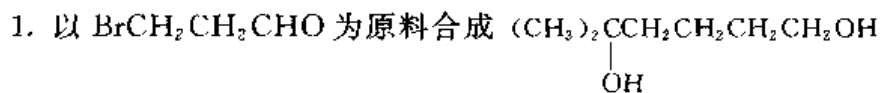




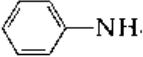
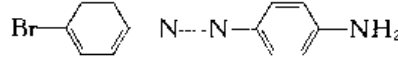
二、完成下列转变 (18分)



三、合成 (可選用任何有机溶剂和无机试剂, 18分)



2. 以正丁醇为原料合成正己胺

3. 以  为原料合成 

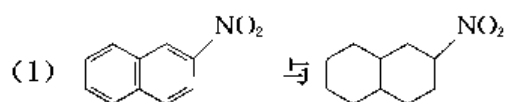
四、推测结构 (12分)

1. 有一中性化合物 $C_7H_{13}O_2Br$, 与羟胺和苯肼均没有反应。红外光谱在 $2850 \sim 2950\text{cm}^{-1}$ 区域有吸收峰, 而在 3000cm^{-1} 以外区域没有吸收峰, 另一个较强的吸收峰在 1740cm^{-1} 。核磁共振谱有 δ 1.0(3H, 三重峰); δ 2.1(2H, 多重峰); δ 4.2(1H, 三重峰); δ 4.6(1H, 多重峰) 等吸收峰。试推测它们的结构并标明它们的吸收峰。

2. 于 1g 化合物 A 中加入 1.9g 溴, 恰好使溴完全褪色。A 与高锰酸钾溶液一起回流后, 在反应液中的产物只有甲丙酮, 试写出化合物 A 的结构式。

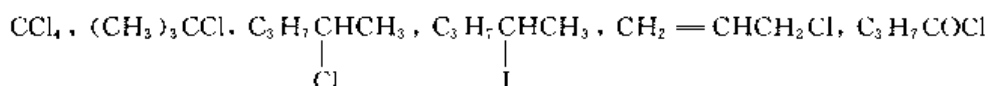
五、回答下列问题 (24分)

1. 用简便的方法区别下列各组化合物。

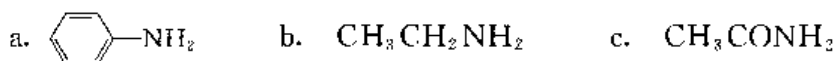


(2) 丁醛和正丁醇

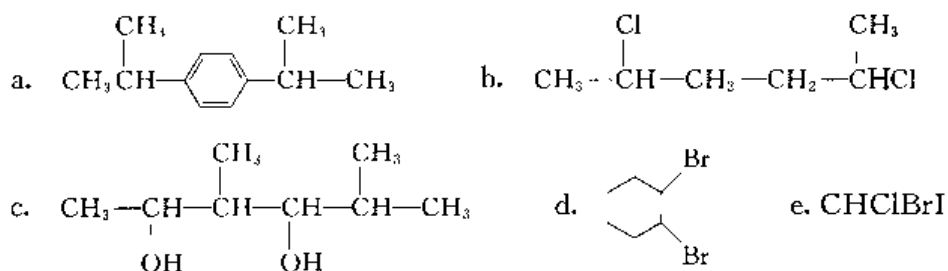
2. (1) 按与 AgNO_3 醇溶液反应的活性从大到小顺序排列下列化合物。



(2) 按碱性递增次序排列下列化合物, 并说明理由。



3. 下列化合物哪些能以内消旋体存在? 是 (1) a, b, c (2) a, c, e (3) b, d, e (4) a, d 还是 (5) b, d?



4. 乙醛在少量浓硫酸催化下可生成不具醛特性而像缩醛的三聚乙醛, 后者加稀硫酸蒸馏即可解聚成乙醛。写出其可能的反应历程。

5. 怎样用构象分析来说明 2-氯丁烷脱氯化氢后生成的反式和顺式 2-丁烯的比率为 6:1。

6. 解释以下实验现象:

当 Ph_3COH (三苯基甲醇) 用浓硫酸处理或当 Ph_3CCl 用 AlCl_3 处理时产生黄色沉淀, 当加入 H_2O 时, 此黄色褪去并产生白色固体。

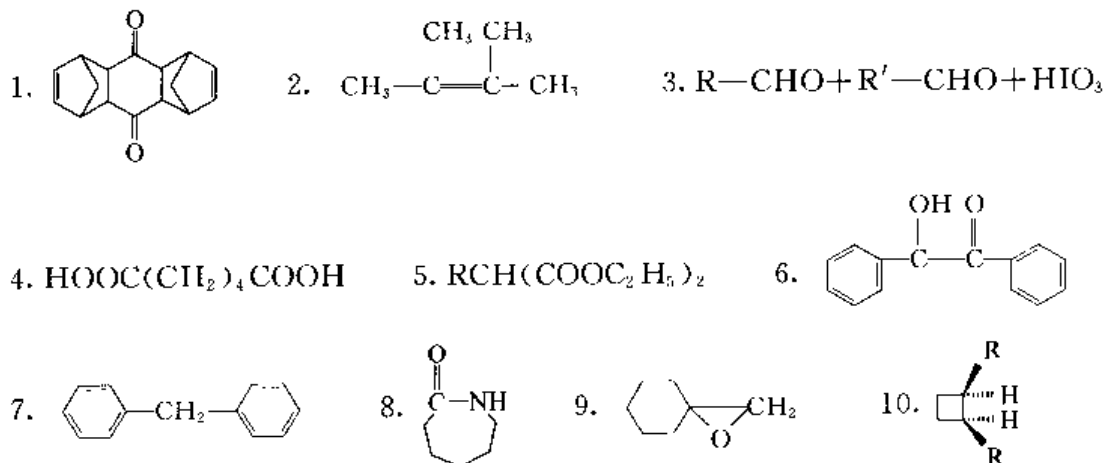
六、分离题

分离并几乎定量的回收由下列水不溶型化合物所组成的混合物: 苯甲醛(A)、N,N-二甲

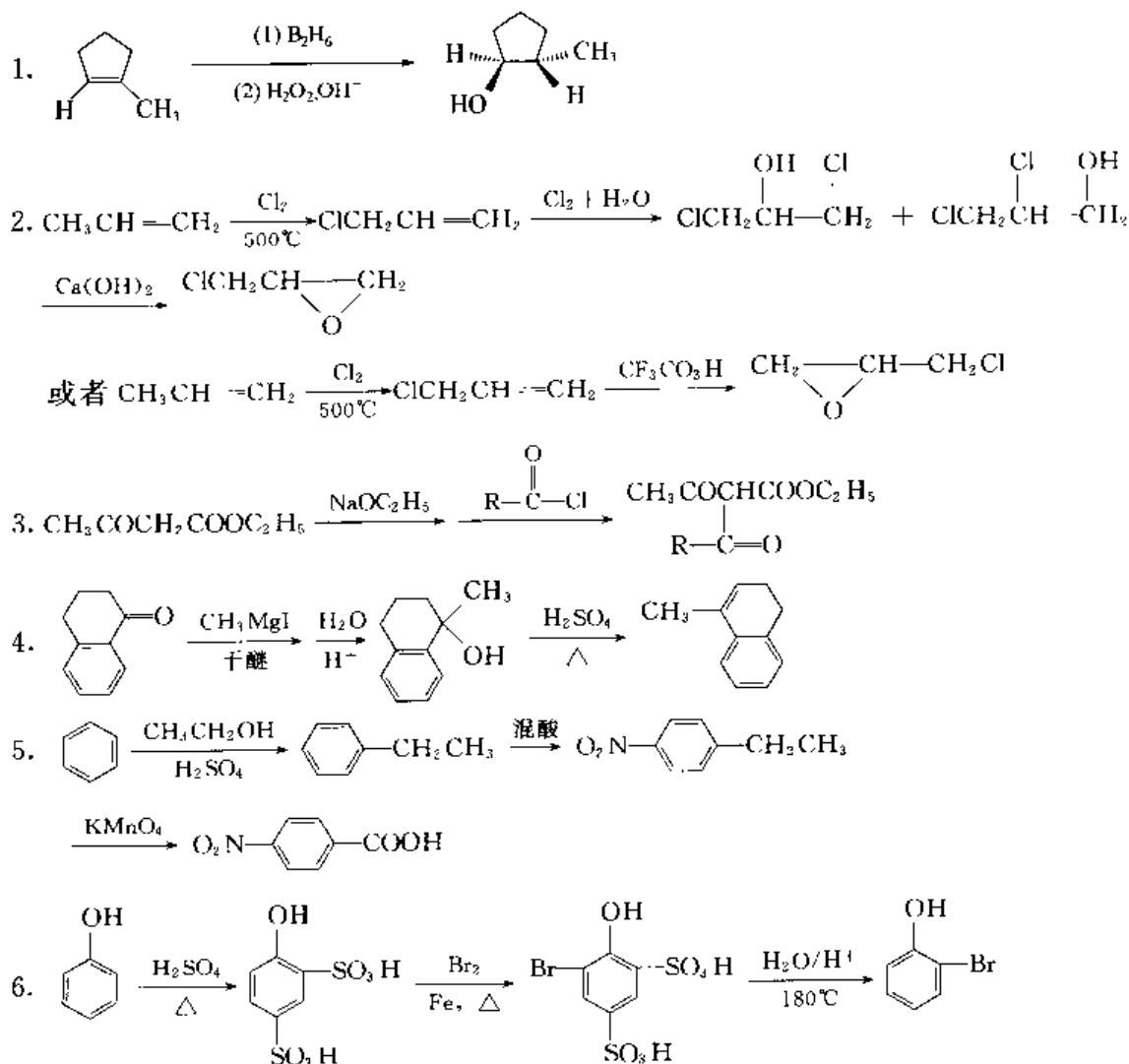
基苯胺 (B)、氯苯 (C)、对甲苯酚 (D)、苯甲酸 (E)。用流程图表示分离步骤。(8分)

参考答案

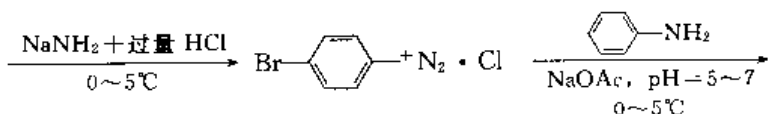
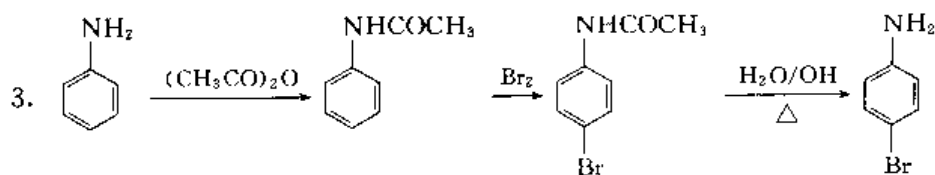
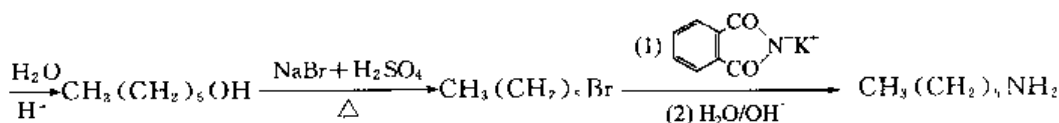
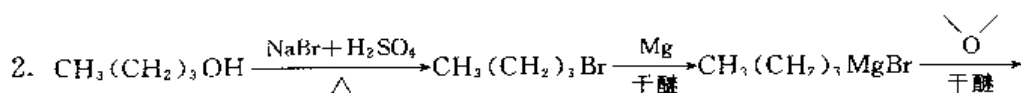
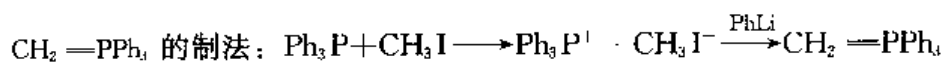
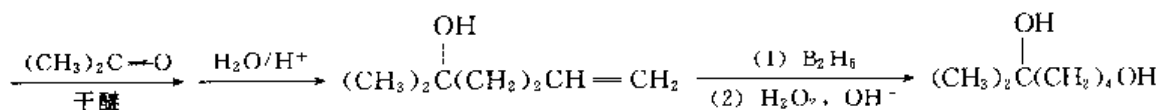
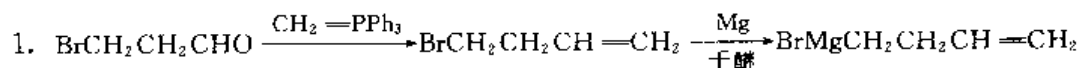
一、写出下列反应的主要产物



二、完成下列转变

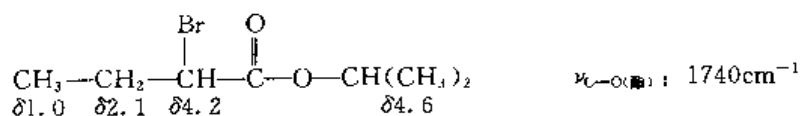


三、合成

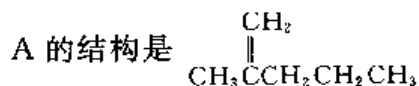


四、推测结构

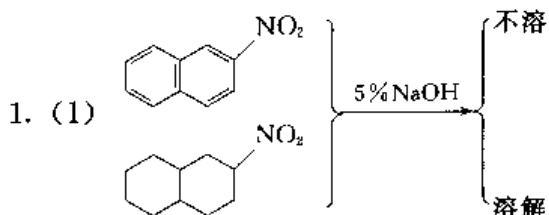
1. $\text{C}_7\text{H}_{13}\text{O}_2\text{Br}$ 的结构为

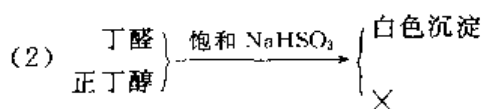


$$2. \text{A 的相对分子质量} \frac{1.9}{160} = M_A \quad \frac{1}{M_A} = \frac{160 \times 1}{1.9} = 84.2$$

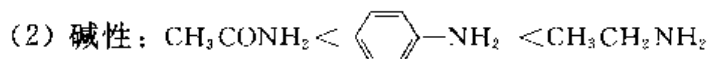
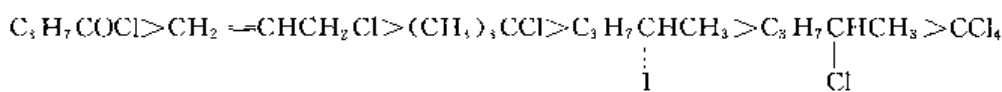


五、回答问题





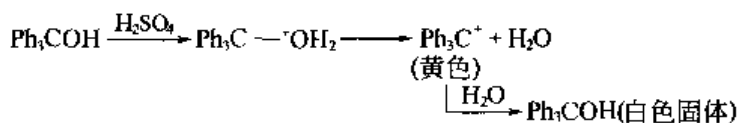
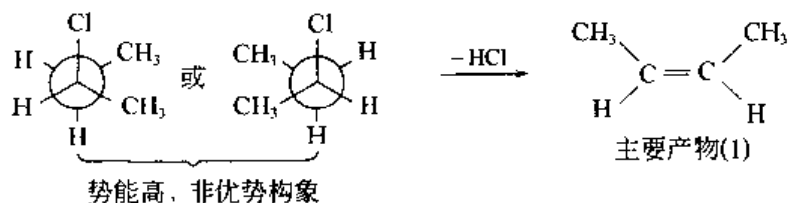
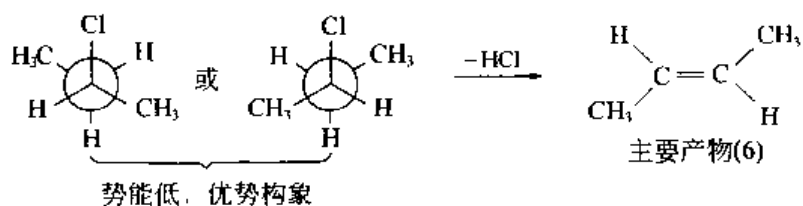
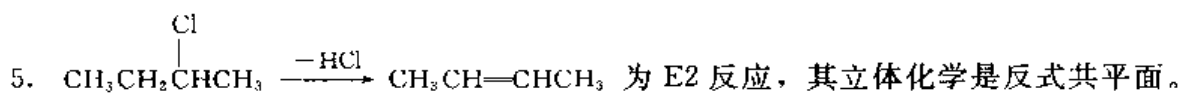
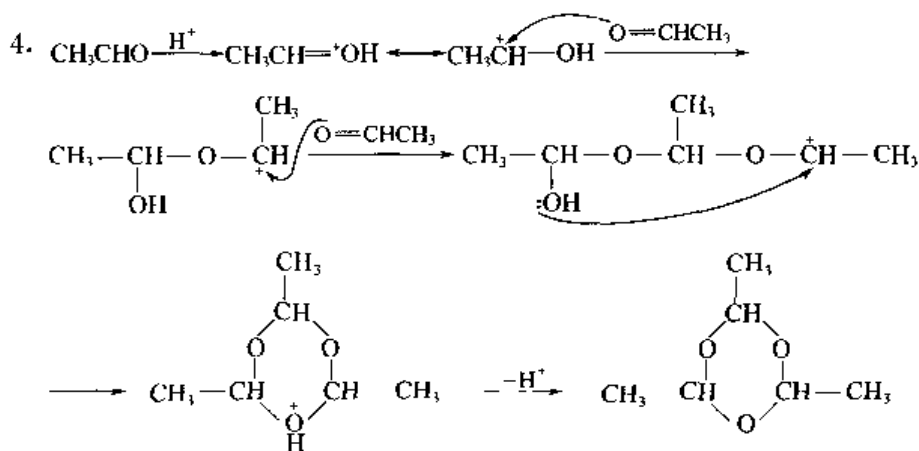
2. (1) 反应活性:



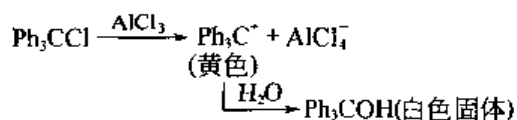
原因: ① 由于氧的电负性大于碳, 导致乙酰胺分子中的 p-π 共轭效应使电子云更多地流向氧原子, 结果使氮原子上电子云密度更低, 碱性最弱。

② 苯胺分子中也有 p-π 共轭, 使氮上电子云密度降低, 分子的碱性降低, 所以乙胺的碱性最强;

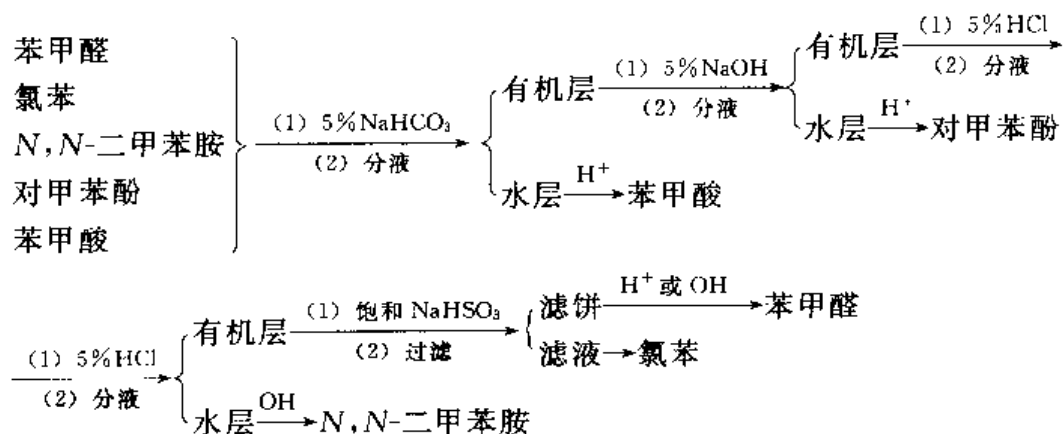
3. b、d 能以内消旋体存在。



6.



六、分离题



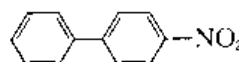
模拟试题 22

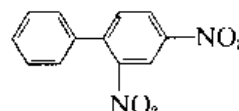
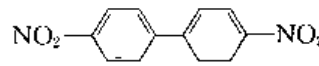
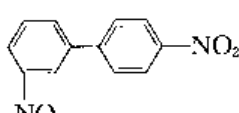
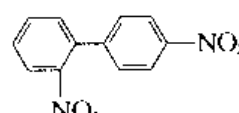
一、选择题 (30 分)

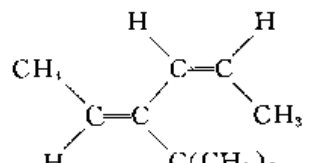
- $\text{CH}_3\text{CH}=\text{CHCH}_3$ 与 $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ 是什么异构体?
 (A) 碳架异构 (B) 位置异构 (C) 官能团异构 (D) 互变异构
- IR 谱中醛酮 C=O 的伸缩振动应在的波数范围是
 (A) $1400\sim 1600\text{cm}^{-1}$ (B) $1300\sim 1500\text{cm}^{-1}$
 (C) $1800\sim 1900\text{cm}^{-1}$ (D) $1600\sim 1750\text{cm}^{-1}$

3. 为合成 $\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$, 应采用乙酸乙酰乙酯和下列哪种试剂反应

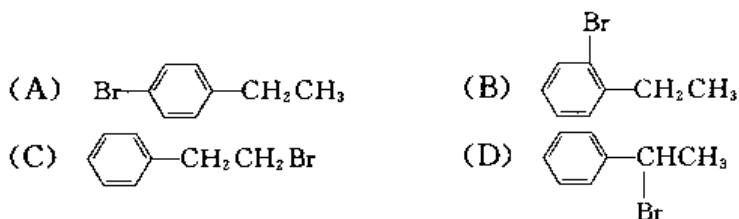
- (A) 碘甲烷和溴丙烷 (B) 2-氯戊烯 (C) 溴乙烷及溴丙烷 (D) 乙酰溴

4.  与 $\text{HNO}_3 + \text{H}_2\text{SO}_4$ 反应的主要产物是

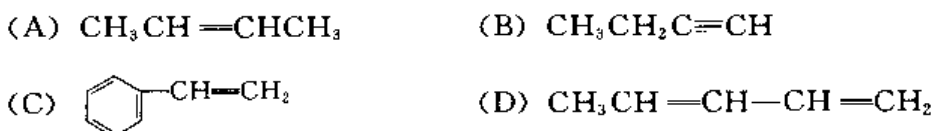
- (A)  (B) 
- (C)  (D) 

5.  的 CCS 名称为

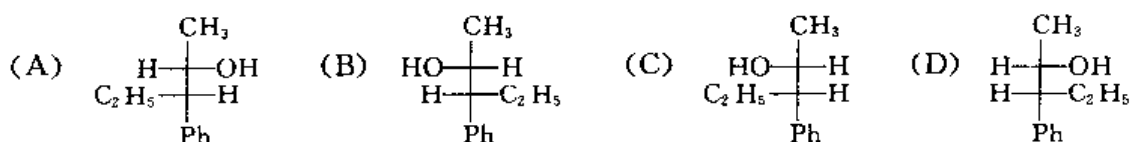
- (A) (2*Z*, 4*E*)-4-叔丁基-2,4-己二烯 (B) (2*E*, 4*Z*)-3-叔丁基-2,4-己二烯
 (C) (2*Z*, 4*E*)-3-叔丁基-2,4-己二烯 (D) (2*E*, 4*Z*)-4-叔丁基-2,4-己二烯
6. 写出乙苯在光照下一元溴化的主要产物



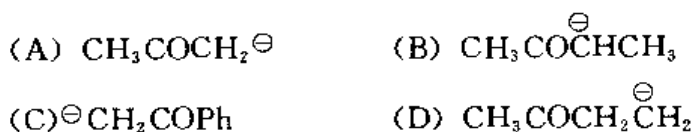
7. 下列哪一种化合物能与氯化亚铜氨溶液作用产生红色沉淀?

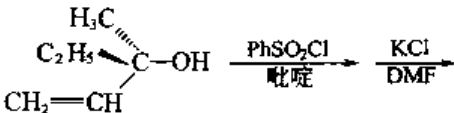


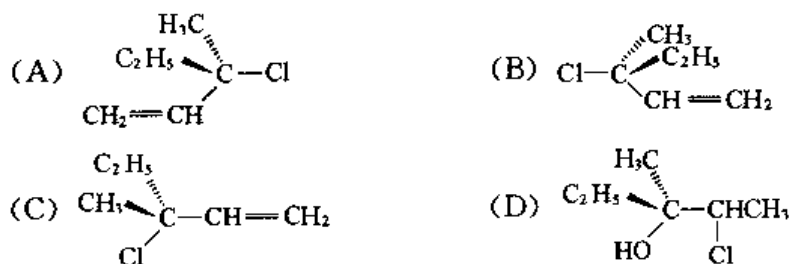
8. (S) α -苯基丁醛 $\text{C}_2\text{H}_5-\overset{\text{CHO}}{\underset{\text{Ph}}{\text{C}}}-\text{H}$ 与 CH_3MgI 反应后水解所获得的主要产物是



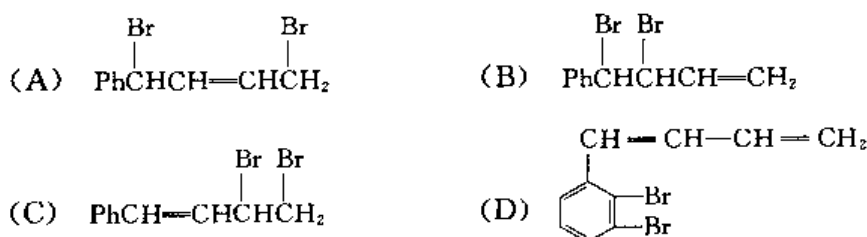
9. 下列碳负离子最稳定的是



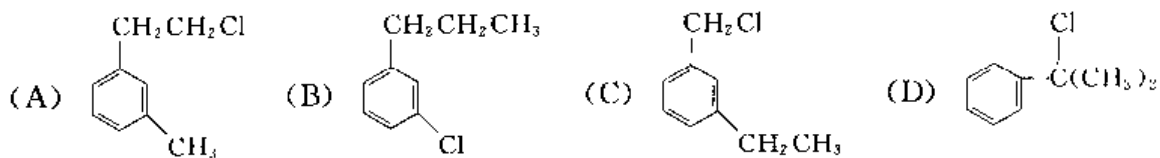
10. 下列反应的主要产物是 



11. 1-苯基-1,3-丁二烯与 1mol Br_2 加成, 主要产物是



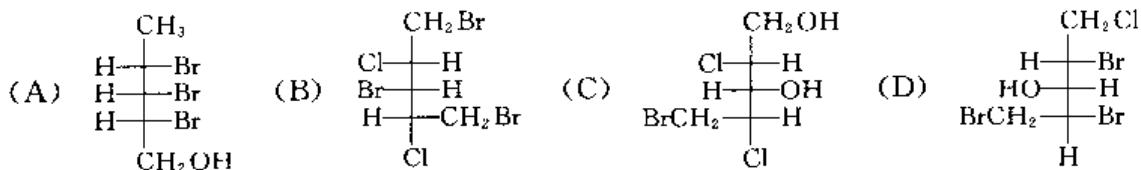
12. 下列各异构体中, 不与硝酸银醇溶液反应的是



13. 可以进行分子内酯缩合的是

- (A) 丙二酸二乙酯 (B) 丁二酸二乙酯
(C) 对苯二甲酸二乙酯 (D) 己二酸二乙酯

14. 下列化合物没有光学活性的是



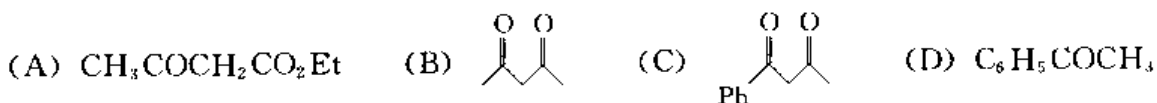
15. Fe+NaOH 还原硝基苯可以得到

- (A) 苯胺 (B) 氧化偶氮苯 (C) N-羟基苯胺 (D) 偶氮苯

16. 下列反应能用来制备伯醇的是

- (A) 甲醛与格式试剂加成, 然后水解 (B) 乙醛与格式试剂加成, 然后水解
(C) 丙酮与格式试剂加成, 然后水解 (D) 苯甲腈与格式试剂加成, 然后水解

17. 下列化合物中, 哪个烯醇式含量最高?



18. 通过 Michael 加成, 可以合成下列哪类化合物?

- (A) 1,5-二羰基化合物 (B) 1,3-二羰基 (C) 1,6-二羰基 (D) 1,4-二羰基

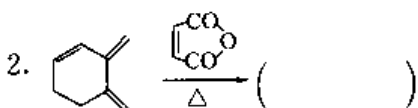
19. 下列化合物, 无芳香性的是

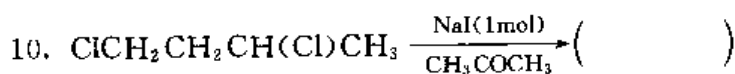
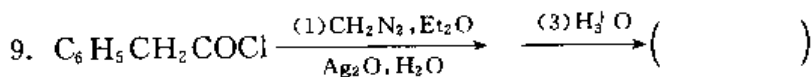
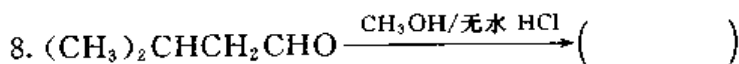
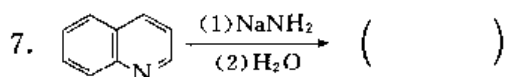
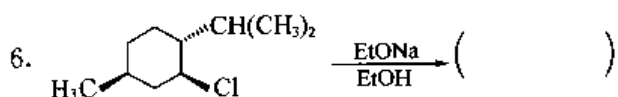
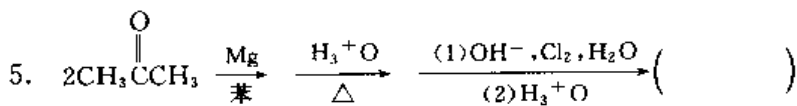
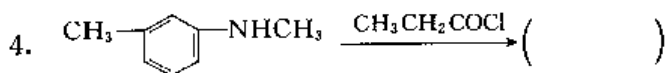
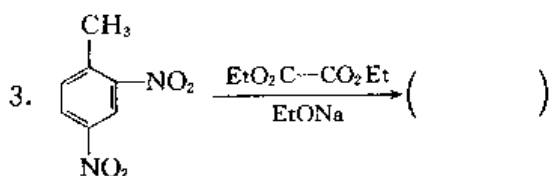


20. 下面哪个化合物在硝化时主要得到间位产物?

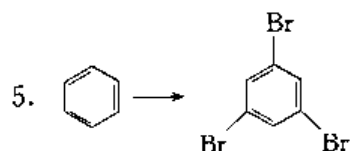
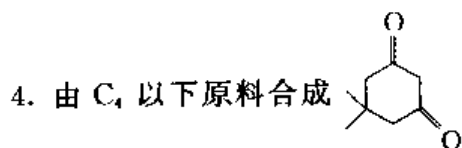
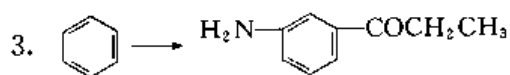
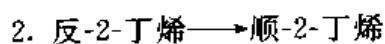
- (A) $\text{PhN}^+(\text{CH}_3)_3$ (B) $\text{PhCH}_2\text{N}^+(\text{CH}_3)_3$
(C) $\text{PhCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3$ (D) $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3$

二、填空题 (20 分, 写主要产物, 若有立体异构体请标明)

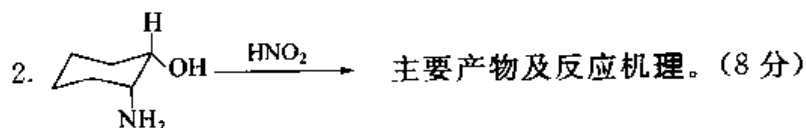
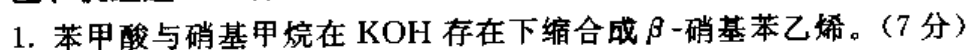




三、合成题 (25 分)



四、机理题 (15 分, 写出合理的, 分步的反应机理)



五、结构题 (10分)

1. 化合物 A (C_8H_{12}) 有光学活性, 在 Pt 催化下加氢得 B (C_8H_{18}) 无光学活性。将 A 在 Lindler 催化剂下小心氢化得到 C (C_8H_{14}) 有光学活性。如果将 A 和 Na 在液氨中反应得到 D, 分子式也是 (C_8H_{14}), 但无光学活性。试推出 A、B、C、D 的结构 (写出必要推理过程)。

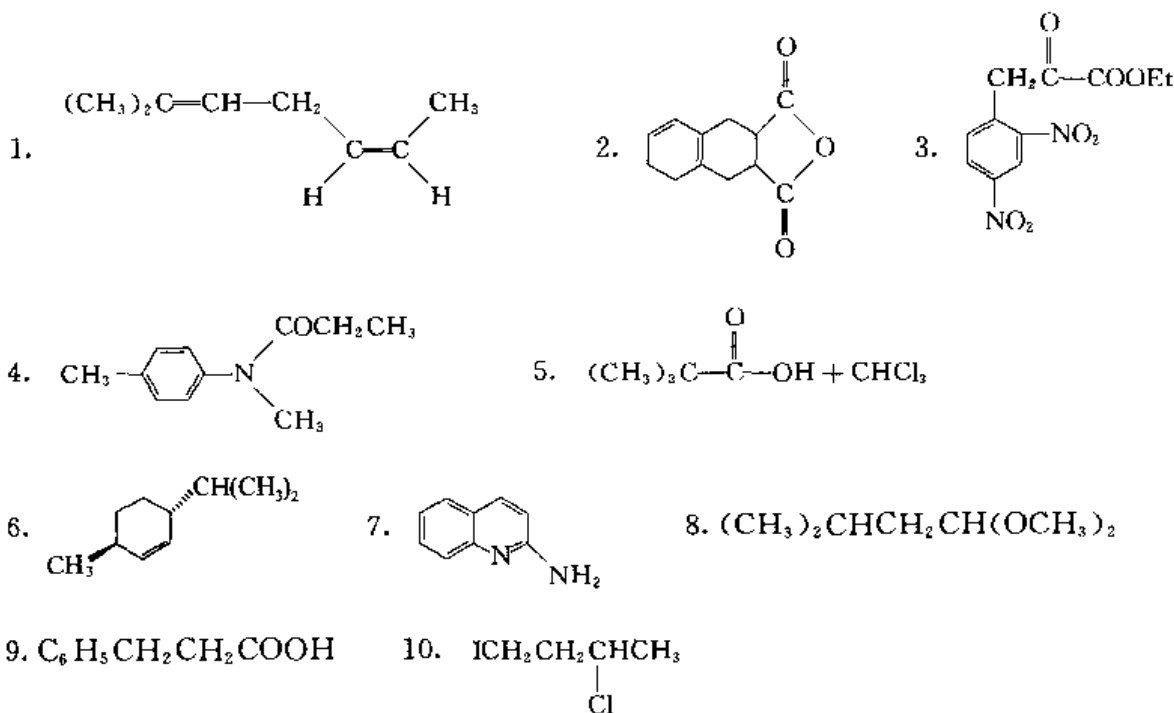
2. 在 3-溴-3-甲基-2-丁酮的乙醚溶液中加入甲氧基钠时得到沸点为 101°C , $n_D^{20} = 1.3890$ 的无色油状液体, 收率为 40%, 它不溶于水, 可是与氢氧化钠水溶液一起加热时被分解而溶解, 它的红外光谱在 1730cm^{-1} , 1190cm^{-1} , 1153cm^{-1} 显示强吸收, 又在 NMR 谱中于 $\delta 1.15$ 、 $\delta 3.58$ 分别显示很尖的单峰, 其强度比为 3:1, 在质谱中, 除了 $m/z 15, 28, 31, 57, 85$ 之处, 于 116 看到分子离子峰, 元素分析值为 C 62.07%, H 10.34%, O 27.59%。写出这一化合物的结构式, 并说明推定其结构的理由。

参考答案

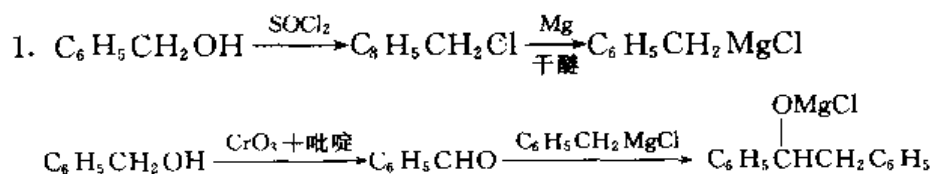
一、选择题

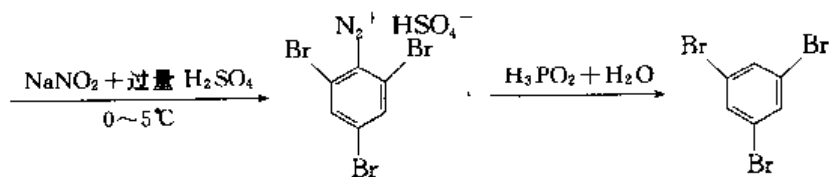
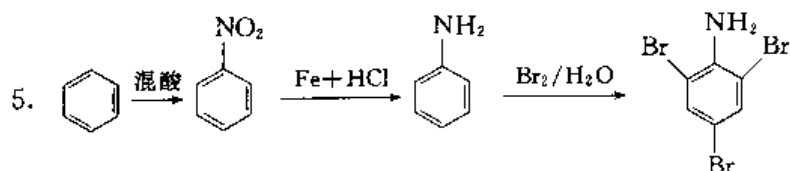
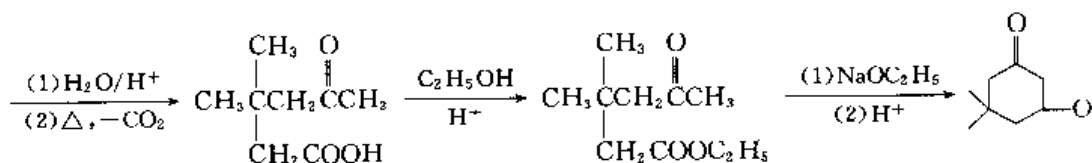
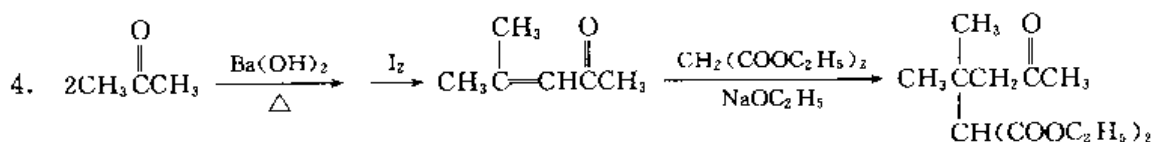
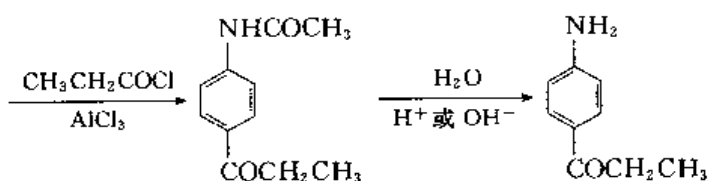
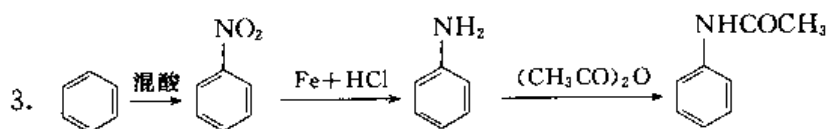
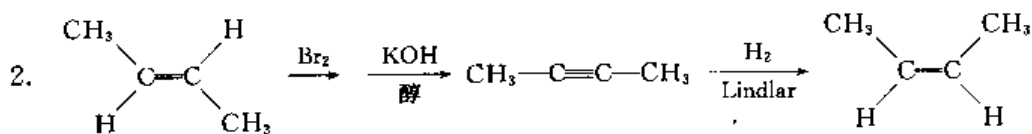
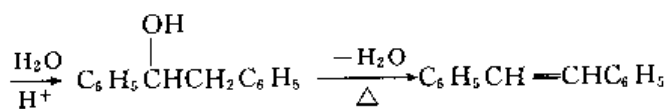
1. (B) 2. (D) 3. (A) 4. (B) 5. (B) 6. (D) 7. (B) 8. (A)
 9. (C) 10. (B) 11. (C) 12. (B) 13. (D) 14. (B) 15. (D)
 16. (A) 17. (C) 18. (A) 19. (C) 20. (A)

二、填空题

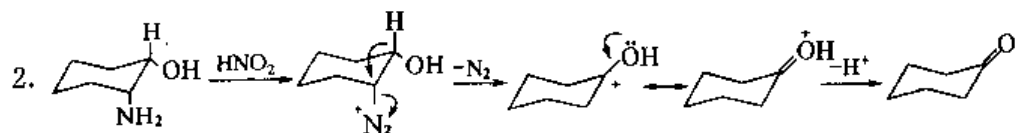
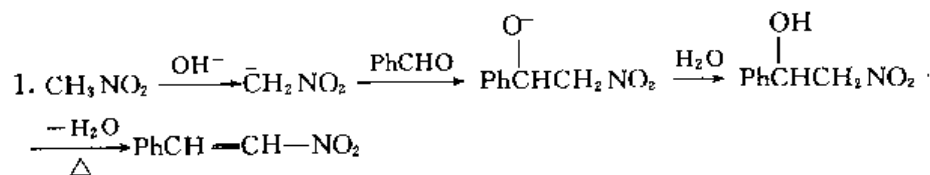


三、合成题





四、机理题



五、结构题

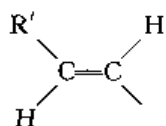
1. 推理过程

① 由分子式知，A 的不饱和度为 3，在铂催化下可加 3 分子氢，说明 A 可能含有 3 个双键或者一个双键和一个叁键；

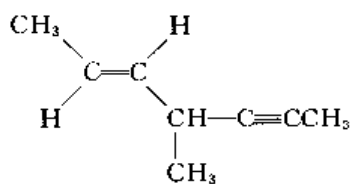
② A 有光学活性，说明 A 有手性，含有一个双键和一个叁键更为合理；

③ 考虑到 A 在 Lindler 催化下加氢与在液氨中与金属钠反应得到不同结果，A 应该为下列结构片断： $-\text{C}\equiv\text{C}-\text{R}$ ；

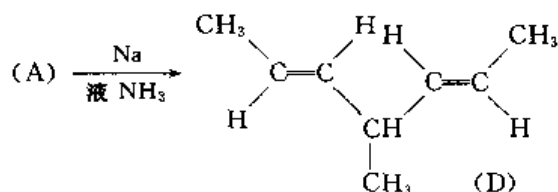
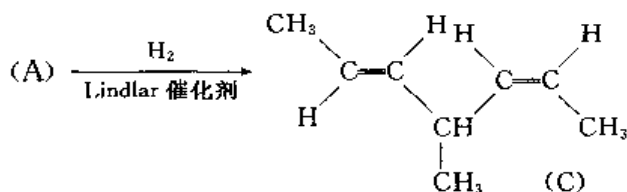
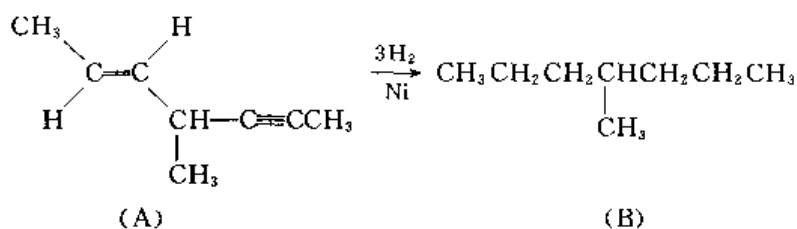
④ A 在液氨中与金属钠反应得到无光学活性的产物，表明 A 中含有如下的结构片断



⑤ 结合分子式 C_8H_{12} ，A 的结构应为



相关反应方程式



2. 该化合物为 $(\text{CH}_3)_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$

理由：

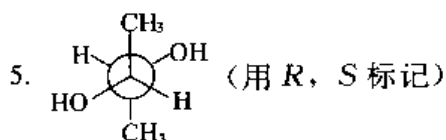
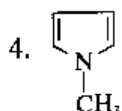
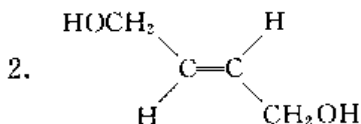
由质谱数据及元素分析数据，得到样品的分子式为 $\text{C}_6\text{H}_{12}\text{O}_2$ ；

红外光谱在 1730cm^{-1} ， 1190cm^{-1} ， 1153cm^{-1} 显示强吸收，表明该化合物是酯；

由 NMR 知，样品分子中含有两种化学环境不同的氢。 δ 3.58 单峰是连在氧原子上的甲基； δ 1.15 单峰则是叔丁基上质子的吸收。所以，样品的结构如上。

模拟试题 23

一、用系统命名法命名下列化合物 (5分)



二、写出下列化合物的结构式 (5分)

1. 甲基异丙基乙炔

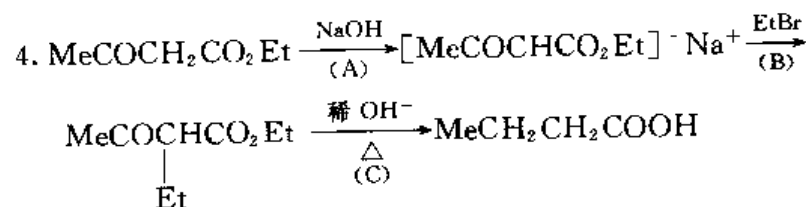
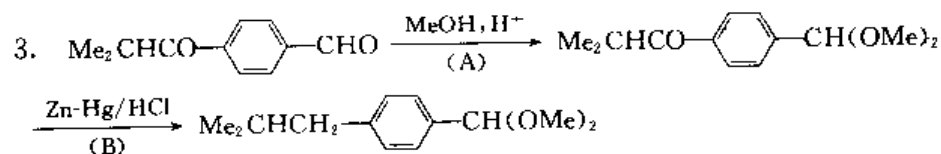
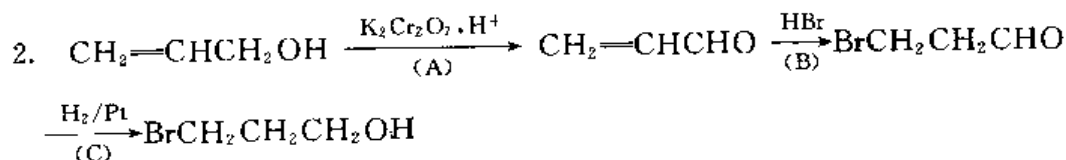
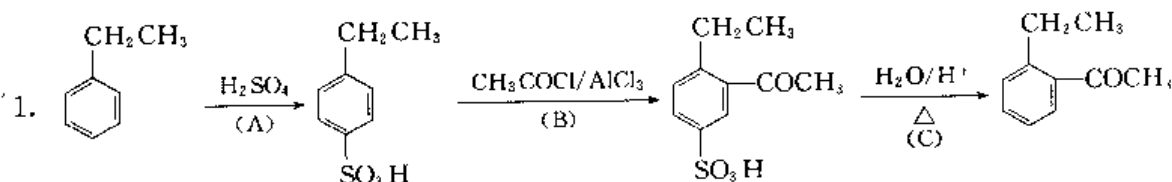
2. 四氢呋喃 (THF)

3. 1,7,7-三甲基二环[2.2.1]庚烷

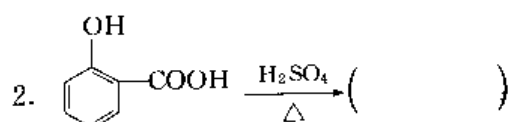
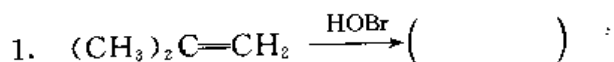
4. (R)-1-苯基乙胺

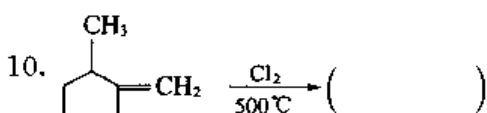
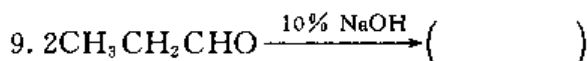
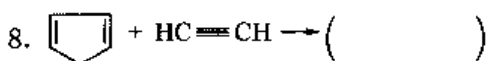
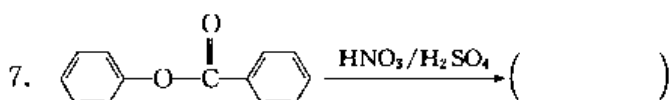
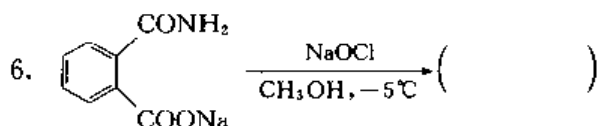
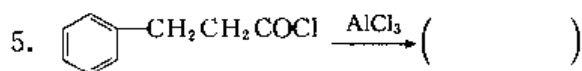
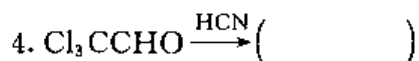
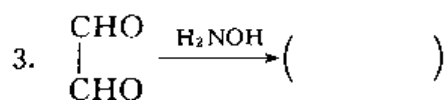
5. 顺-3-甲基环己甲酸的优势构象式

三、指出下列反应中的错误, 说明原因, 并予以更正 (5分)



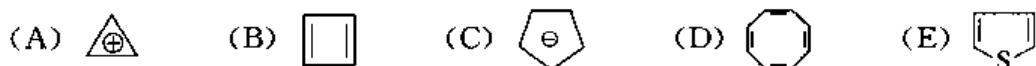
四、完成下列反应式 (5分)



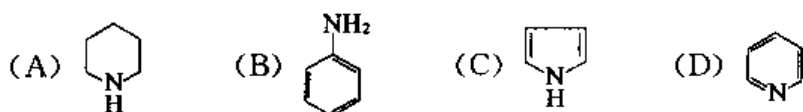


五、有机化合物性质比较 (10分)

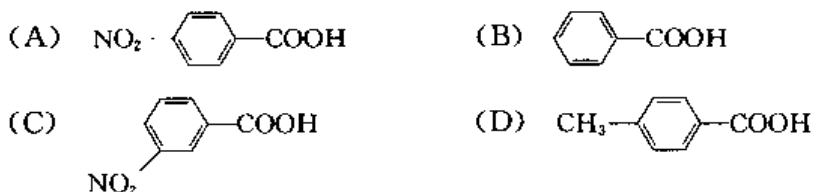
1. 下列的分子式或基团中哪些具有芳香性?



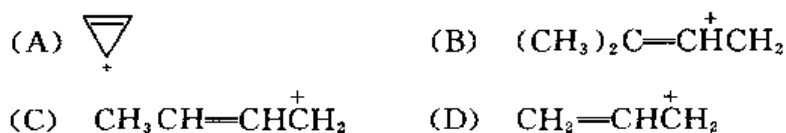
2. 将下列化合物按碱性强弱排列顺序。



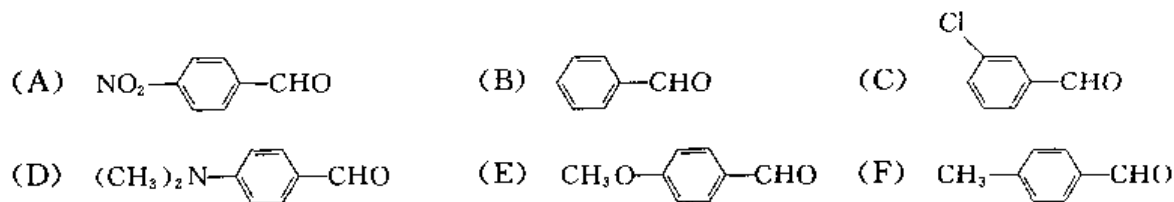
3. 将下列化合物按酸性强弱排列顺序。



4. 下列离子哪一个较稳定 (由大到小排列顺序)?



5. 下列化合物与 HCN 反应，哪个活性最大？哪个活性最小？

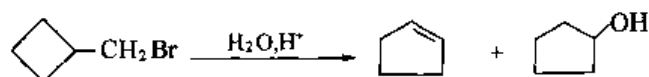


六、试分离苯甲酸、对甲苯酚、苯胺与苯 (10 分)

七、有机化合物结构的推导 (5 分)

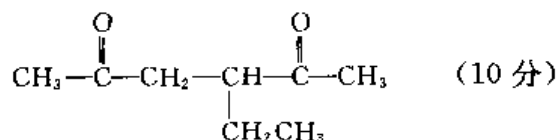
某化合物 (A) 分子式为 $C_6H_{12}O_3$ ，在 1710cm^{-1} 有一强的吸收峰，当用 I_2 的 NaOH 溶液处理时，得到一黄色沉淀，A 与氢氧化银的氨溶液不反应。若 (A) 先用一滴 H_2SO_4 处理，然后再用氢氧化银的氨溶液处理，则发生反应并有银镜生成。(A) 的 ^1H-NMR 数据如下： δ 2.1 (单峰，3H)； δ 3.2 (单峰，6H)； δ 2.6 (双重峰，2H)； δ 4.7 (三重峰，1H)。写出 (A) 的结构式。

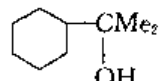
八、试用反应机理解释下面过程 (10 分)

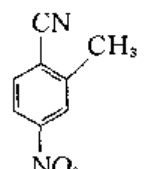


九、有机化合物的合成 (无机试剂任选) (40 分)

1. 以乙炔为原料合成 α -羟基丙酸 (5 分)
2. 以 $(CH_3)_3CBr$ 为原料合成 $(CH_3)_3CNH_2$ (5 分)
3. 以 4 个碳原子以下的醇为原料，经乙酰乙酸乙酯法合成



4. 用 4 个碳原子以下 (含 4 个碳原子) 的有机物为原料合成  (10 分)

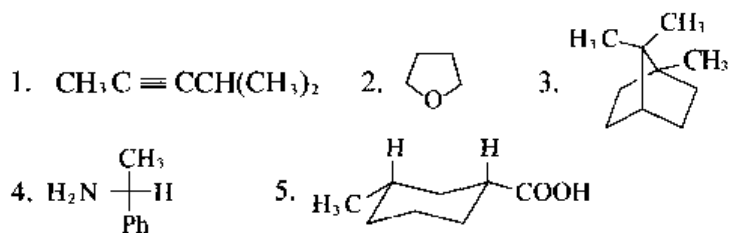
5. 甲苯为原料，其他有机试剂任选，合成  (10 分)

参考答案

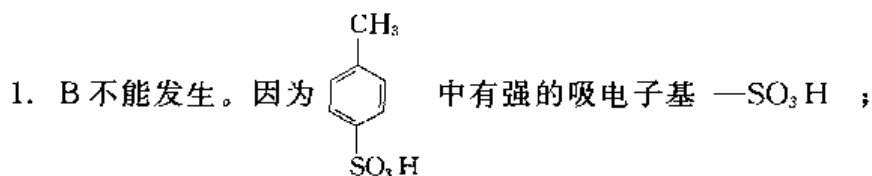
一、命名

1. 2,4-戊二酮
2. (E)-2-丁烯-1,4-二醇
3. 螺[3.4]-5,7-辛二烯
4. N-甲基吡咯
5. (2R,3S)-2,3-丁二醇

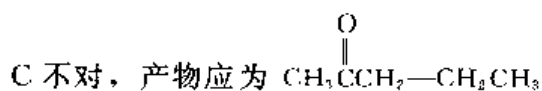
二、写结构式



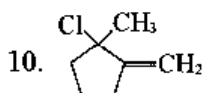
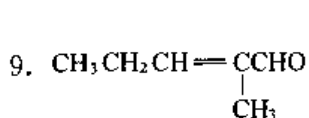
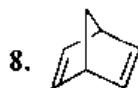
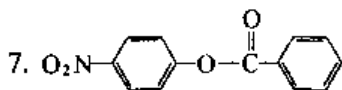
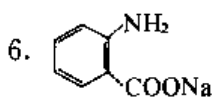
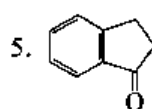
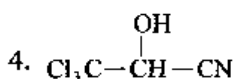
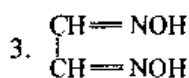
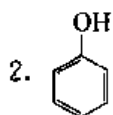
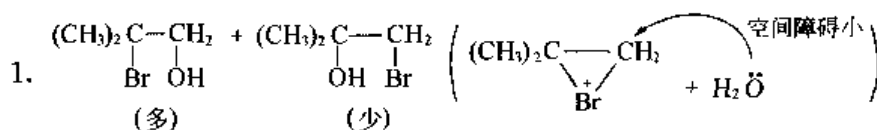
三、指出下列反应中的错误



2. A 不对，因为 $\text{CH}_2=\text{CHCHO}$ 中的 $\text{C}=\text{C}$ 双键可以被 $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ 氧化；
 C 不对，如果不限制 H_2 的用量，会使产物成为 $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ 。
3. A 不对，反应条件应该为 CH_3OH ，干 HCl ，并使用 2mol MeOH 反应；
 B 不对，因为缩酮基对酸敏感，应该在碱性条件下还原，如黄鸣龙还原。
4. A 不对，应该使用碱性更强的乙醇钠；



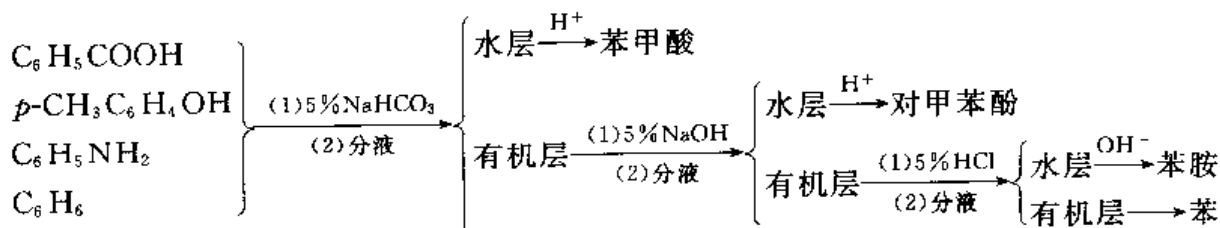
四、完成反应式



五、有机化合物性质比较

1. (A)、(C)、(E)有芳香性； 2. 碱性：(A) > (D) > (B) > (C)；
 3. 酸性：(A) > (C) > (B) > (D)； 4. 稳定性：(A) > (B) > (C) > (D)；
 5. (A)活性最大，(D)活性最小。

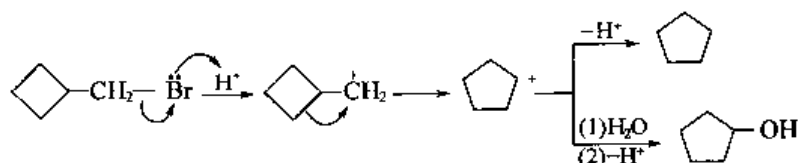
六、分离



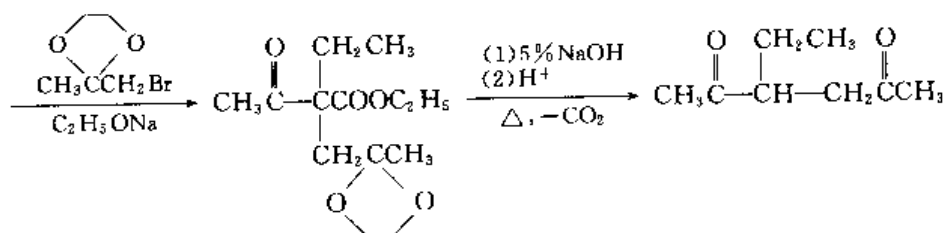
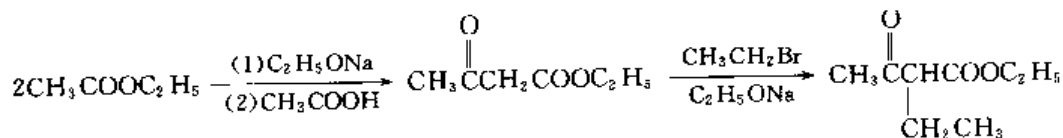
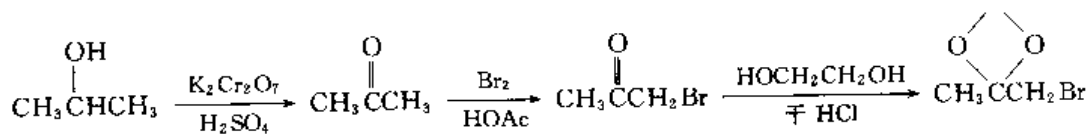
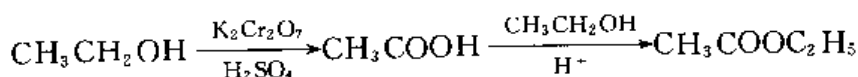
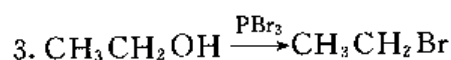
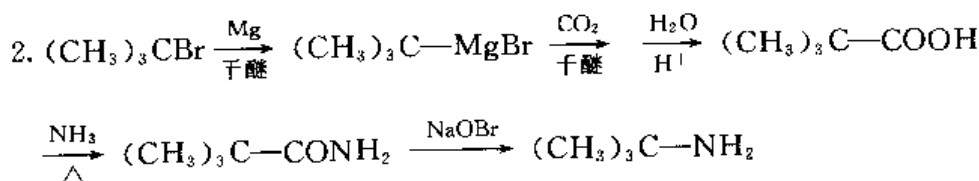
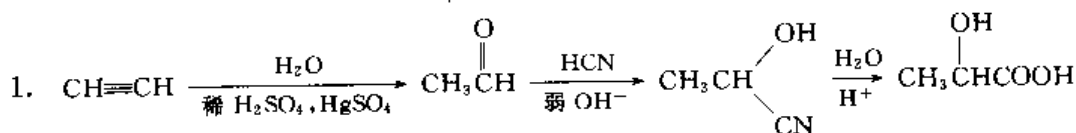
七、结构推导

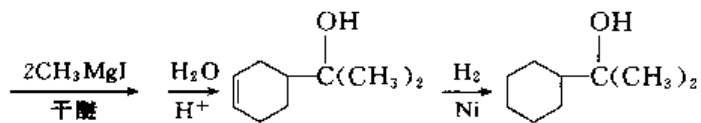
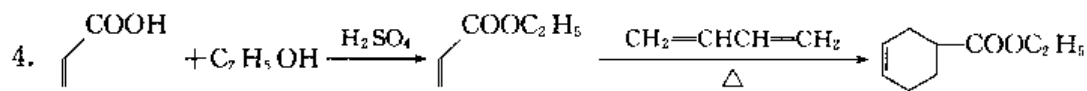
略。见“模拟试题1”中“六、2。”

八、反应机理



九、合成



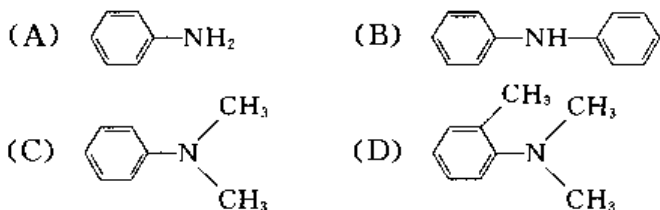


5. 略。见“模拟试题 5 九、1。”。

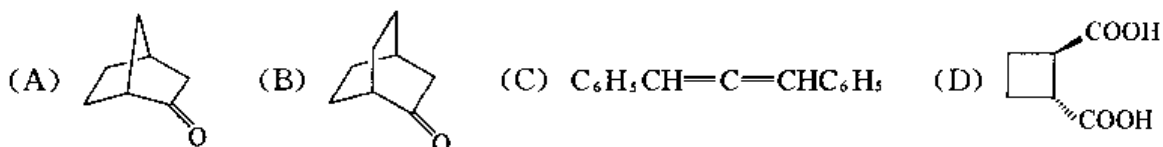
模拟试题 24

一、选择题 (30 分)

- 烷基多取代烯烃的稳定性是由于
(A) σ -p 超共轭效应 (B) σ - π 超共轭效应
(C) p- π 共轭效应 (D) 烷基推电子效应
- 有机化合物的熔点取决于其分子量和分子对称性，在下列化合物中哪一个熔点最高
(A) 甲苯 (B) 邻硝基甲苯 (C) 对硝基甲苯 (D) 间硝基甲苯
- 下述哪一个化合物的酸性最强
(A) 苯甲酸 (B) 邻甲氧基苯甲酸 (C) 邻羟基苯甲酸 (D) 苯酚
- 下述哪一个化合物的碱性最强?



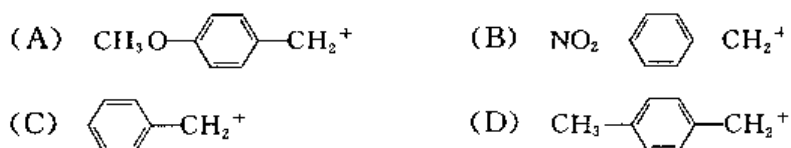
5. 下述哪一个化合物没有光学活性?



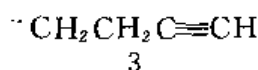
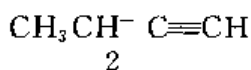
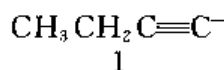
6. 下述哪一个化合物具有“芳香性”?



7. 下述正碳离子中哪一个最稳定?

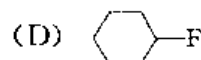
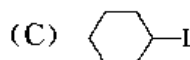
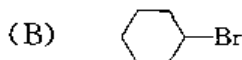


8. 下述负离子的稳定性次序是



- (A) 1>2>3 (B) 3>2>1 (C) 2>3>1 (D) 2>1>3

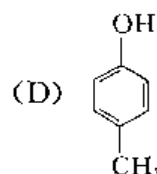
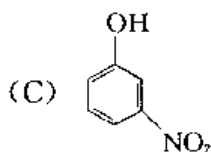
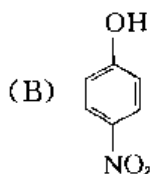
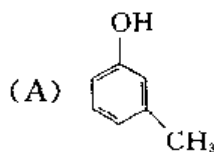
9. 下述哪一个化合物在进行 S_N1 反应时最快?



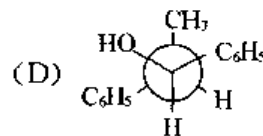
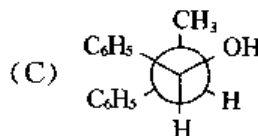
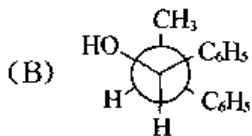
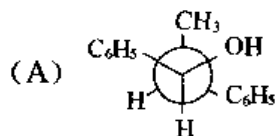
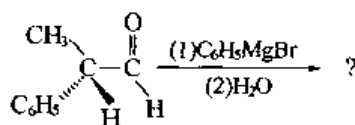
10. 进行 S_N2 反应时最慢的是

- (A) CH₃CH₂Br (B) (CH₃)₂CHBr (C) (CH₃)₃CBr (D) (CH₃)₃CCH₂Br

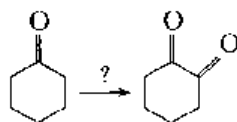
11. 下述芳香烃卤化反应速率最快的是



12. 下述反应的主产物是



13. 下述氧化反应的氧化剂 ([O]) 是



- (A) KMnO₄ (B) Pb(OAc)₄ (C) O₃ (D) SeO₂

14. Ruff-Fenton 降解法能使哪些化合物的碳链减短?

- (A) 醛糖 (B) 酮糖 (C) 醇 (D) 直链烷烃

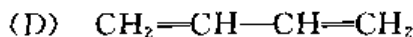
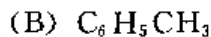
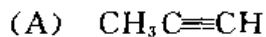
15. 2-甲基-3-戊醇脱水后的主要产物是

- (A) 2-甲基-1-戊烯 (B) 2-甲基-2-戊烯 (C) 2-甲基-3-戊烯 (D) 异丁烯

16. Claisen 酯缩合经常用来制备

- (A) β-羟基酯 (B) γ-羟基酯 (C) δ-羟基酯 (D) β-酮酯

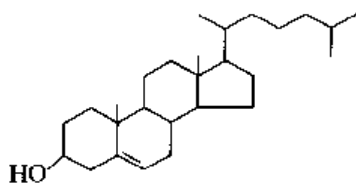
17. 下列化合物中哪一个有 σ_{sp-sp³} 键?



18. 下列化合物中哪一个不是 Lewis 酸

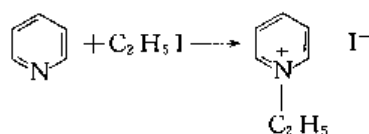
(A) SnCl_4 (B) BF_3 (C) AlCl_3 (D) SiF_4

19. 下述结构式代表了哪类化合物



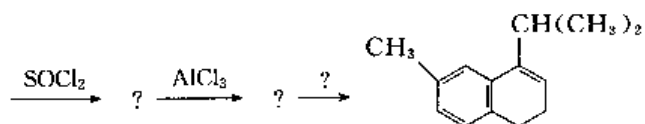
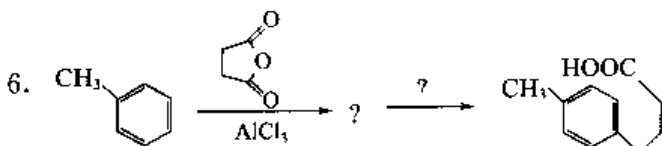
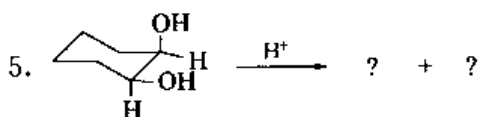
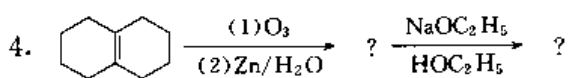
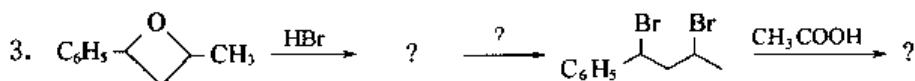
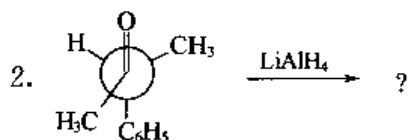
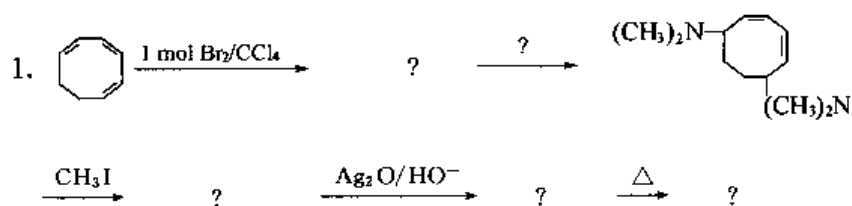
(A) 萜类 (B) 甾类 (C) 碳水化合物 (D) 生物碱

20. 下述反应显示了吡啶具有



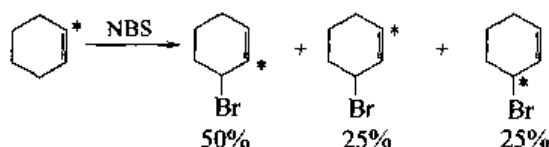
(A) 亲核性 (B) 亲电性 (C) 碱性 (D) 芳香性

二、完成下列反应 (30 分)



三、根据下列各题意，完成题目（16分）

1. 解释下列反应的结果。



* 为 C^{14} 同位素标记

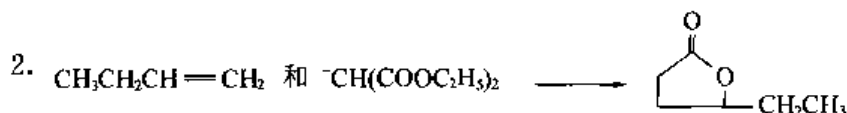
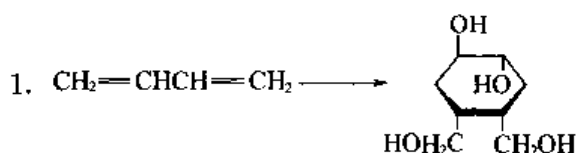
2. 填空

萘低温磺化上（ ）位，高温磺化上（ ）位，这是由于上（ ）位所形成的 σ -络合物比上（ ）位的稳定，因此相应的过渡态位能较低，反应活化能较低，所以上（ ）位，这种现象称为（ ）控制。但在高温时（ ）位产物成为主要产物，是由于（ ）萘磺酸比（ ）萘磺酸稳定，因此反应平衡趋于（ ）萘磺酸，这种现象叫作（ ）控制。

3. 用简单的化学反应区别蔗糖和麦芽糖。并画出蔗糖的构象式。

4. 写出核酸中碱基部分的结构式。

四、由指定的原料和必要的无机试剂进行合成（10分）



五、推测 A~G 的结构（每个 2 分，共 14 分）

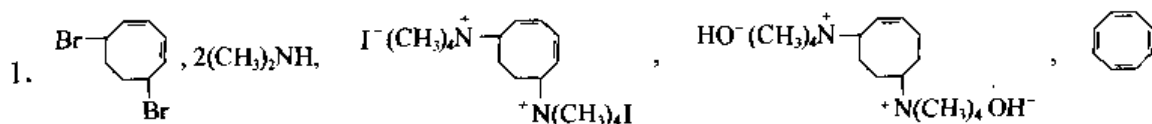
A (C_8H_9Cl) 为芳卤烃，与 KCN 反应，随后水解得 B ($C_9H_{10}O_2$)。B 的氨盐加热得到 C。C 与 Br_2 的碱溶液反应得到 D ($C_8H_{11}N$)。将 D 与 HNO_2 作用水解或由 A 与 KOH 作用均可得到 E ($C_8H_{10}O$)，且 E 可氧化为 F ($C_8H_6O_4$)，F 分子内脱水成酸酐 G ($C_8H_4O_3$)。

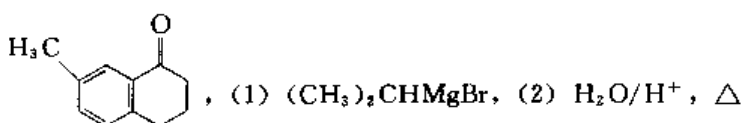
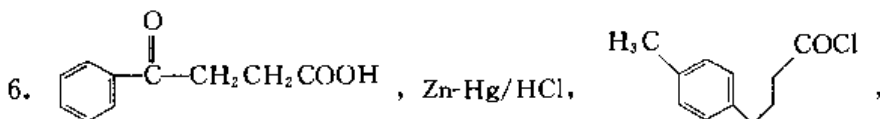
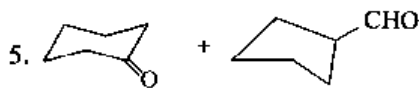
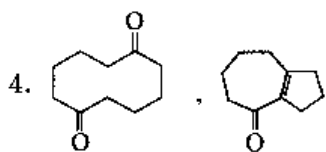
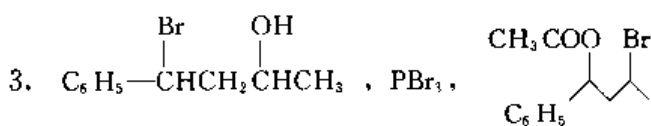
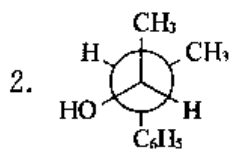
参考答案

一、选择题

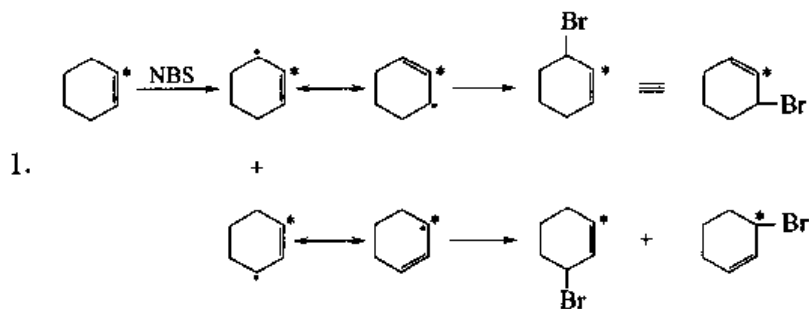
1. (B) 2. (C) 3. (C) 4. (A) 5. (B) 6. (C) 7. (A)
 8. (A) 9. (C) 10. (C) 11. (A) 12. (A) 13. (D) 14. (A)
 15. (B) 16. (D) 17. (A) 18. (D) 19. (B) 20. (A)

二、完成反应式

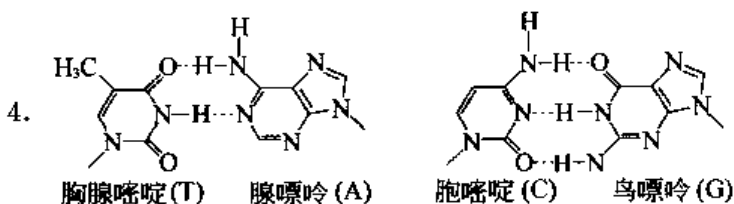
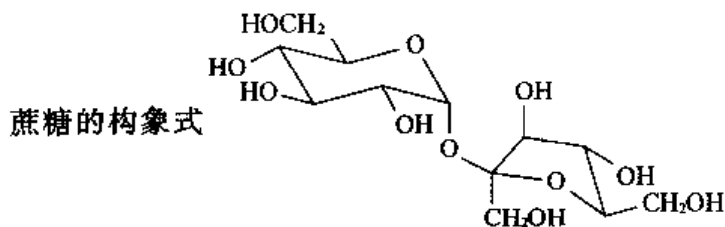
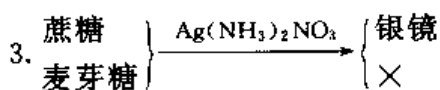




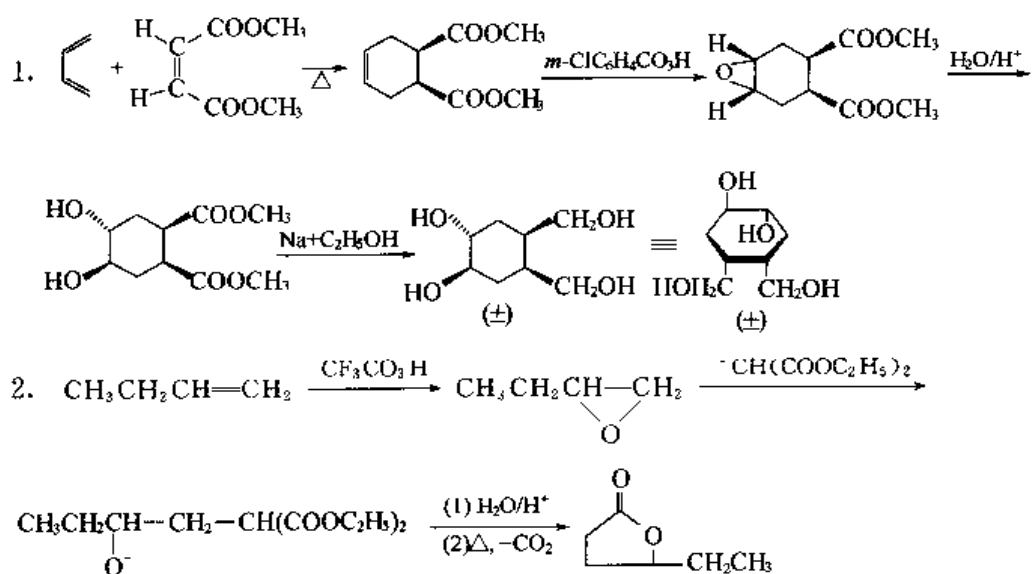
三、根据下列各题意，完成题目



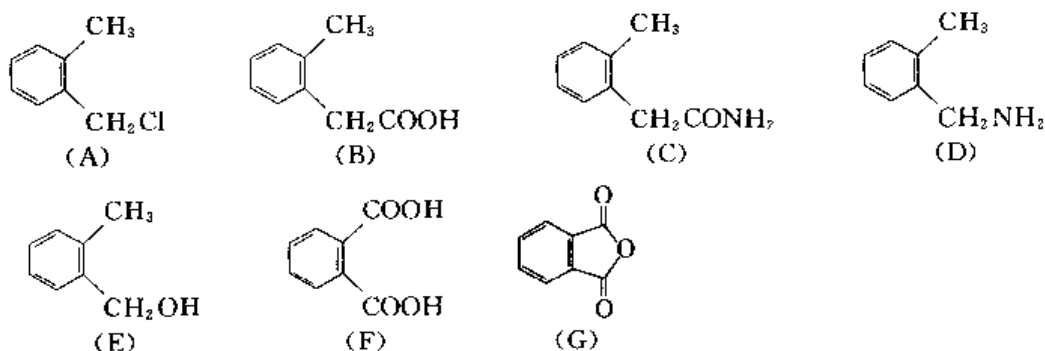
2. 萘低温磺化上 (α) 位，高温磺化上 (β) 位，这是由于上 (α) 位所形成的 σ -配合物比上 (β) 位的稳定，因此相应的过渡态位能较低，反应活化能较低，所以上 (α) 位，这种现象称为 (动力学) 控制；但在高温时 (β) 位成为主要产物，是由于 β -萘磺酸比 α -萘磺酸稳定，因此反应平衡趋于 β -萘磺酸，这种现象叫作 (热力学) 控制。



四、合成

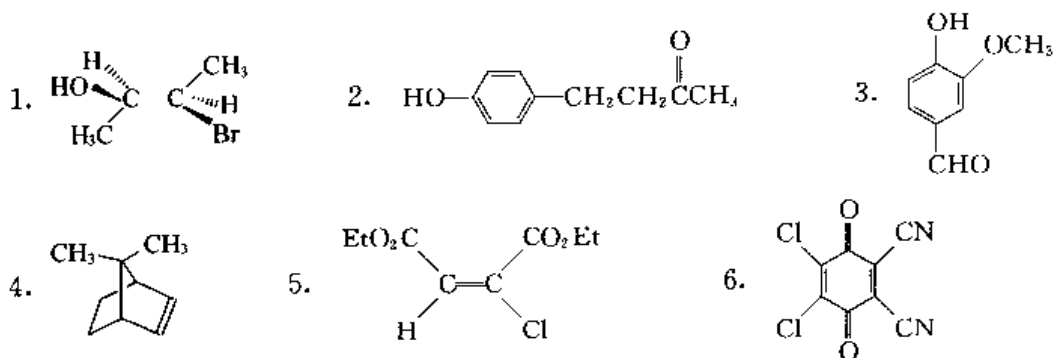


五、推测结构



模拟试题 25

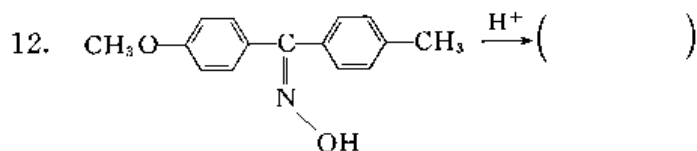
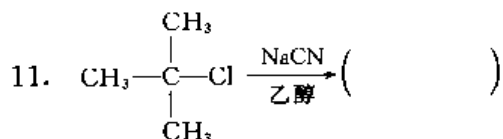
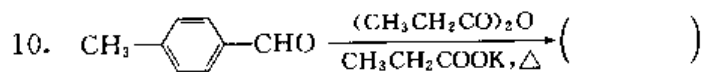
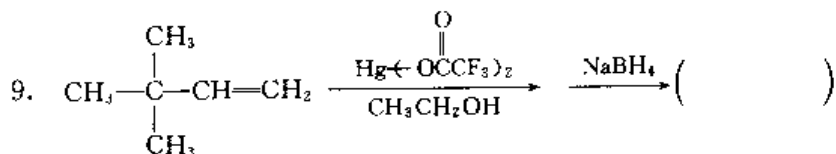
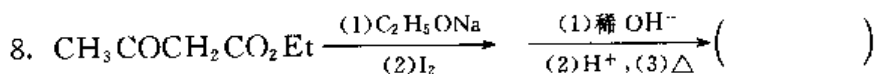
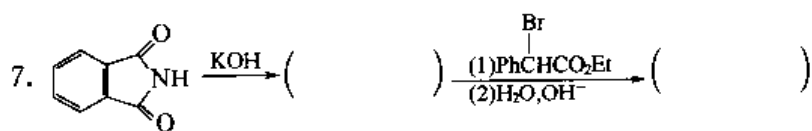
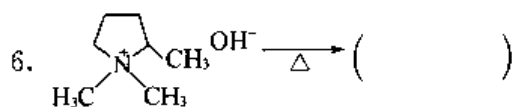
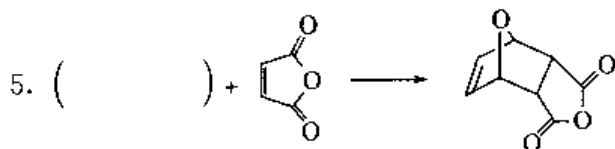
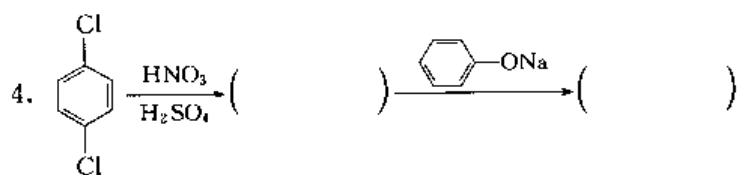
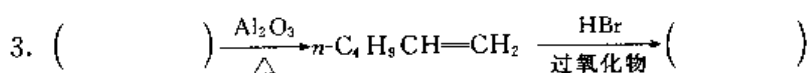
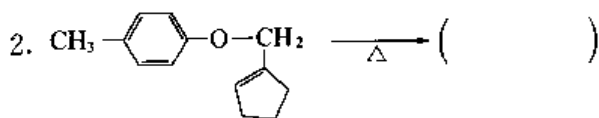
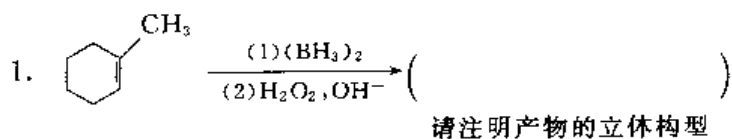
一、命名下列化合物或写出它们的结构式 (8分)

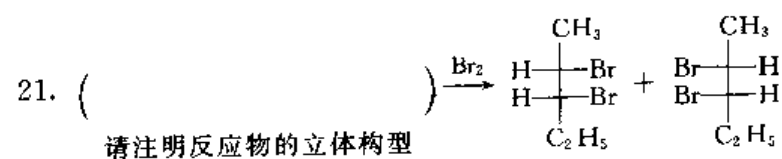
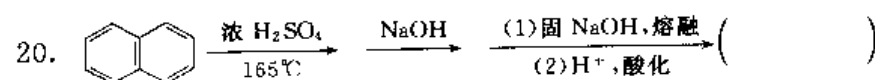
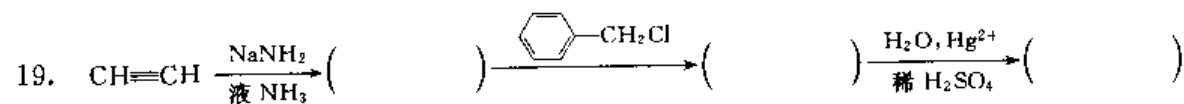
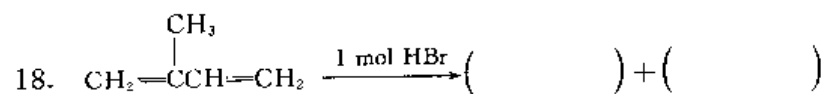
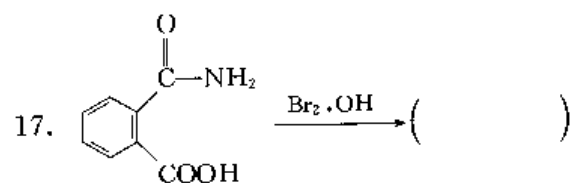
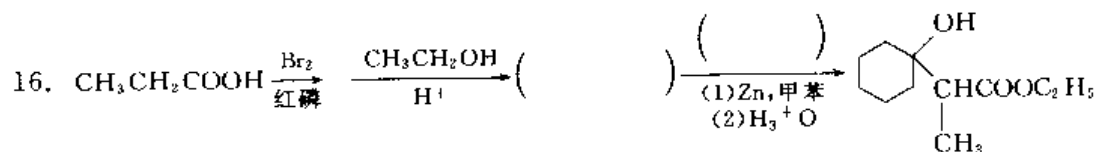
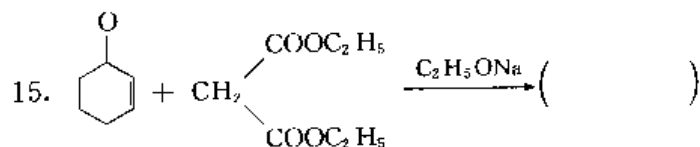
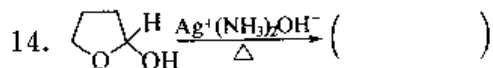
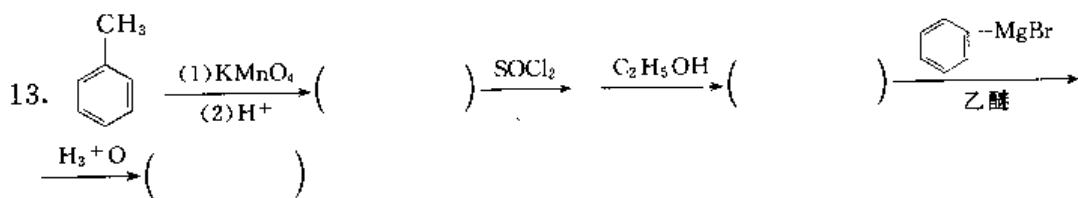


7. D-葡萄糖 (Haworth 式)

8. 1-氨基-2-萘磺酸

二、完成下列反应 (30分)



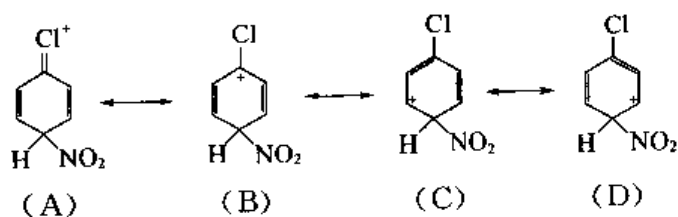


三、选择题 (14分)

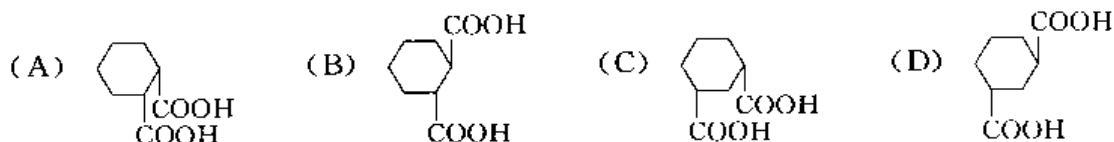
1. 下列化合物具有芳香性的是 ()



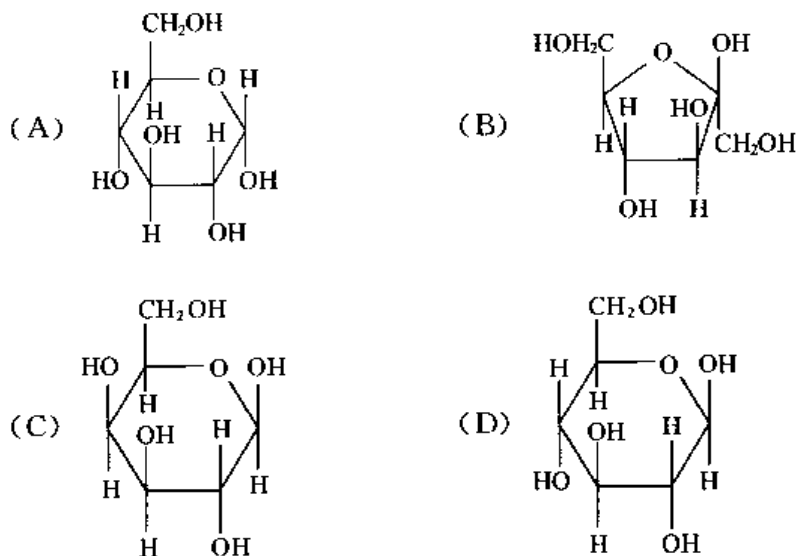
2. 氯苯硝化形成硝基氯苯时, 其中间体—— σ 配合物的极限结构式中贡献最大的是 ()



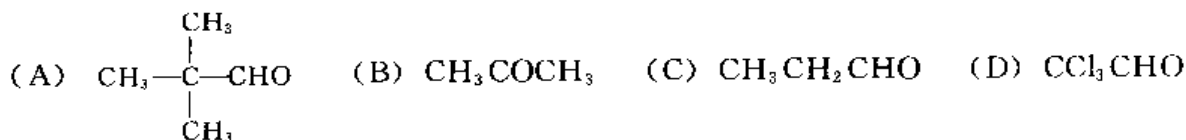
3. 下列化合物中具有手性的是 ()



4. 下列化合物与苯肼反应生成脎, 惟一不同的是 ()

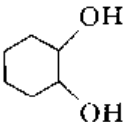


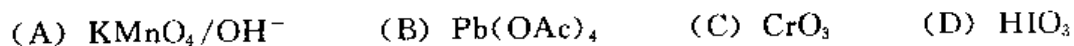
5. 下列羰基化合物能形成稳定水合物的是 ()



6. 将下列化合物按碱性由强到弱排列成序 ()



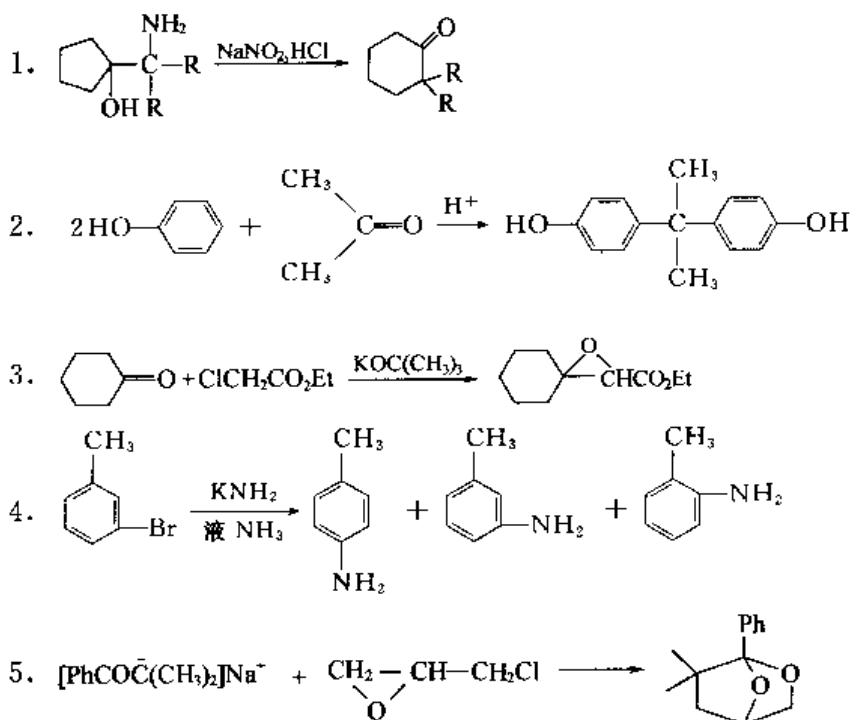
7. 能将  氧化为己二醛的试剂是 ()



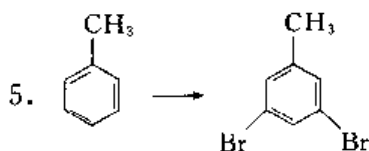
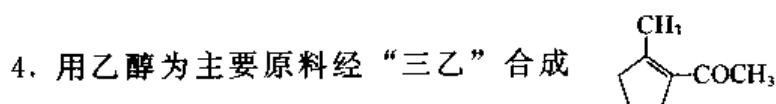
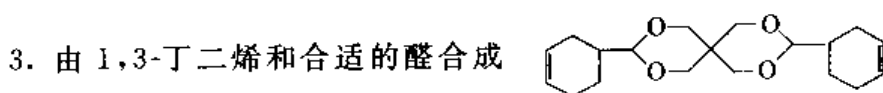
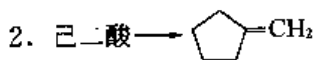
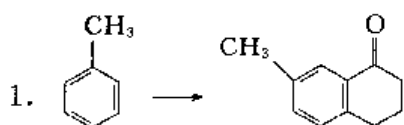
8. 下列化合物中芳香性最强的是 ()



四、写出下列反应的历程 (从中任选 3 题, 共 12 分, 每小题 4 分)

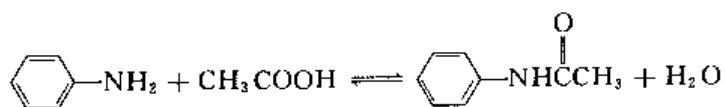


五、由指定原料合成下列化合物 (其他试剂任选, 从中任选 3 题, 15 分)



六、实验题 (8 分)

乙酰苯胺的制备反应如下



1. 反应使用的苯胺一般有颜色, 其原因是 ()

(A) 苯胺是淡黄色液体

(B) 苯胺长期放置, 自身缩合形成偶氮苯

- (C) 苯胺氧化形成醌 (D) 苯胺中含有少量硝基苯
2. 反应中通常要加少许锌粉, 其目的是 ()
- (A) 作为催化剂 (B) 避免苯胺在反应中被氧化
(C) 避免苯胺在反应中聚合 (D) 避免苯胺生成联苯胺
3. 为使反应中生成的水能及时脱出, 使用的方法是 ()
- (A) 使用分馏柱蒸出反应中生成的水
(B) 使用分水器分出反应中生成的水
(C) 使用无水 CuSO_4 吸附反应生成的水
(D) 使用无水 CaCl_2 吸收反应生成的水
4. 粗乙酰苯胺用水作溶剂重结晶, 制备饱和溶液时, 烧瓶中出现油滴的原因是 ()
- (A) 水不适宜作溶剂 (B) 乙酰苯胺在水中严重水解
(C) 乙酰苯胺几乎不溶于热水 (D) 溶剂量不够

七、推测结构 (13分)

1. 化合物 A ($\text{C}_{10}\text{H}_{10}$), 经 O_3 氧化、还原水解得到 B ($\text{C}_{10}\text{H}_{10}\text{O}_2$)。B 既可与斐林试剂反应, 也可发生碘仿反应。A 经 KMnO_4 氧化、酸化后得到邻苯二甲酸。试写出 A 的构造式及各步反应。(5分)

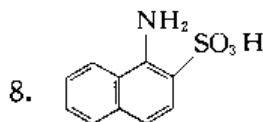
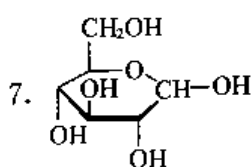
2. 化合物 C ($\text{C}_8\text{H}_{11}\text{N}$) 与对甲基苯磺酰氯在 KOH 溶液中作用, 生成清亮的溶液, 酸化后得到白色沉淀。当 C 用 $\text{NaNO}_2\text{-HCl}$ 在 $0\sim 5^\circ\text{C}$ 时处理后, 再与 2-萘酚作用, 生成一种红色的化合物 D, C 的 IR 谱图表明在 $810\sim 840\text{cm}^{-1}$ 处有一强吸收峰。试写出 C 及 D 的构造式。(4分)

3. 化合物 E ($\text{C}_4\text{H}_8\text{Br}_2$) 有 4 组质子峰, 其 $^1\text{H-NMR}$ 数据如下: δ 1.7 (3H, 双重峰); δ 2.2 (2H, 四重峰); δ 3.5 (2H, 三重峰); δ 4.2 (1H, 四重峰); 试写出 E 的构造式并指出各峰的归属。(4分)

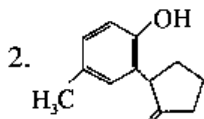
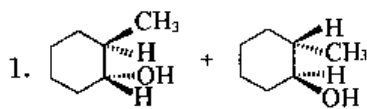
参考答案

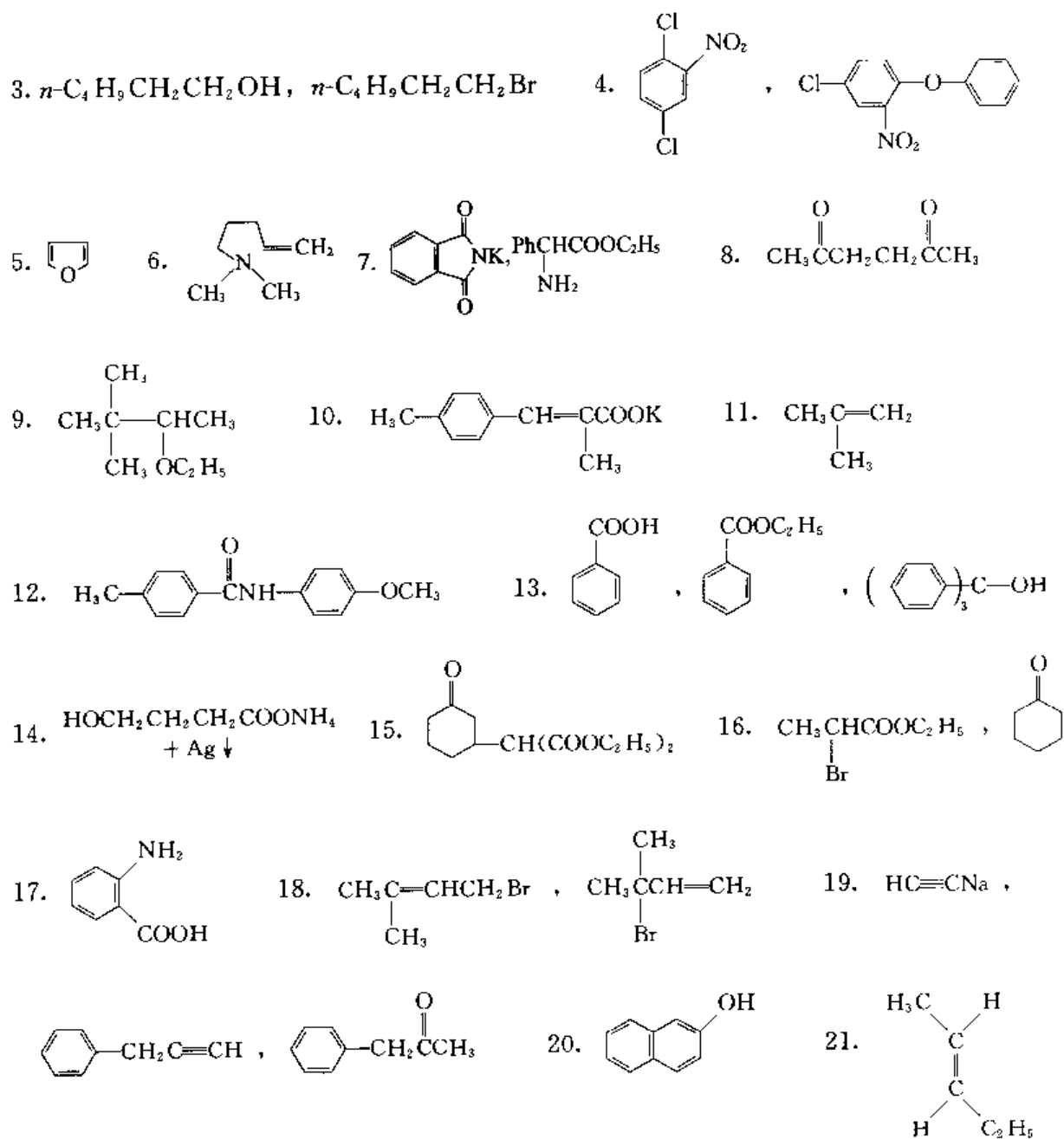
一、命名或写出下列化合物的构造式

1. (2R,3R)-3-溴-2-丁醇 2. 4-对羟基苯基-2-丁酮
3. 4-羟基-3-甲氧基苯甲醛 4. 7,7-二甲基双环[2.2.1]-2-庚烯
5. 2-氯-2-丁烯二酸二乙酯 6. 2,3-二氰基-5,6-二氯对苯醌



二、完成下列反应

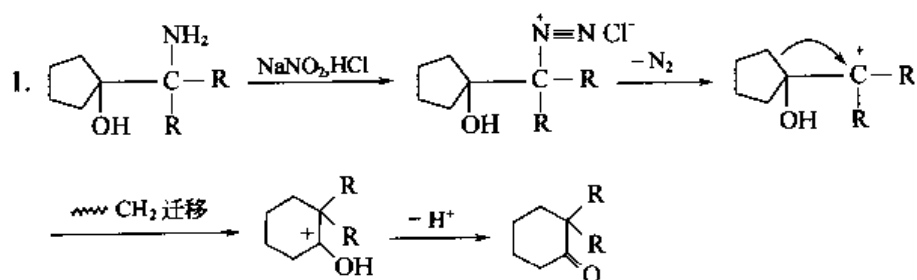


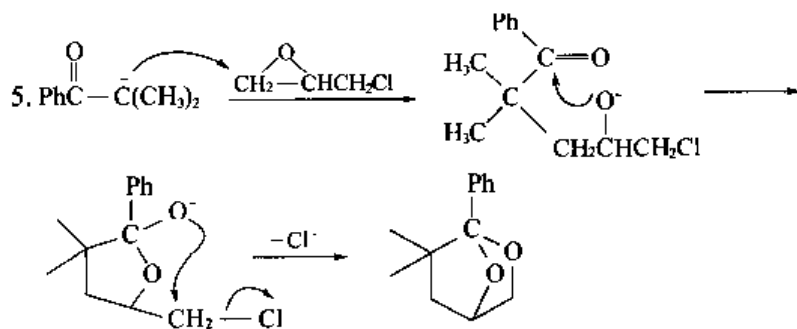
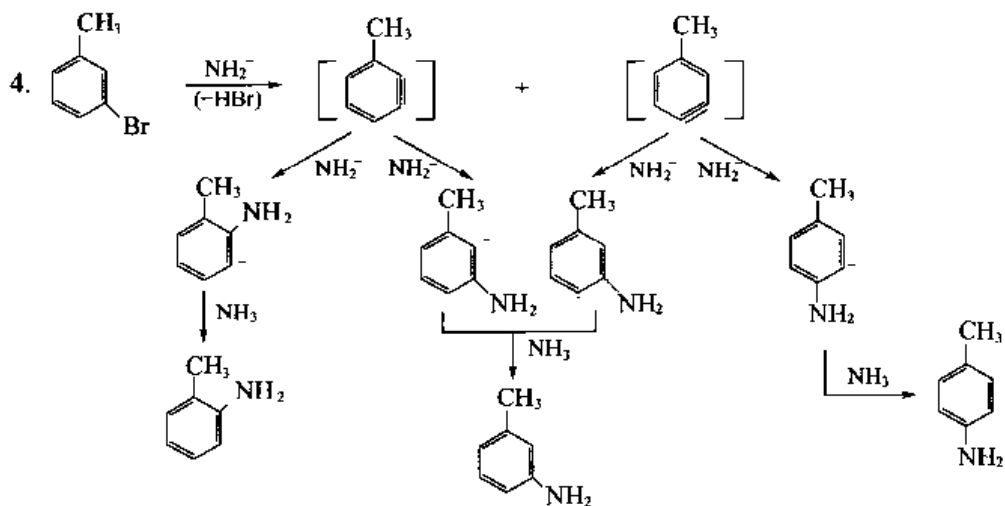
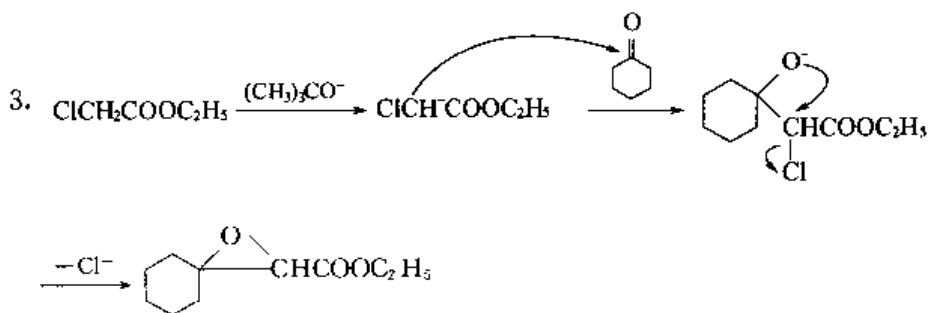
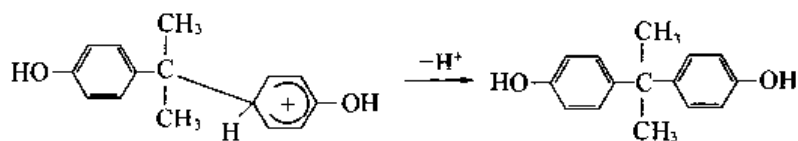
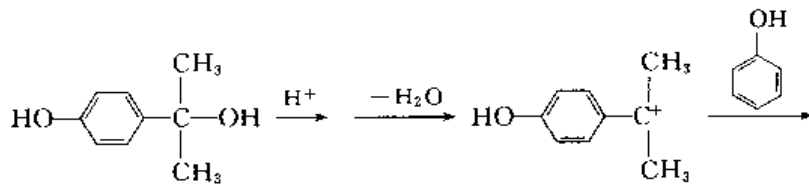
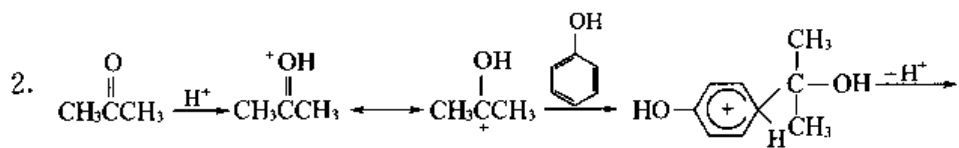


三、选择题

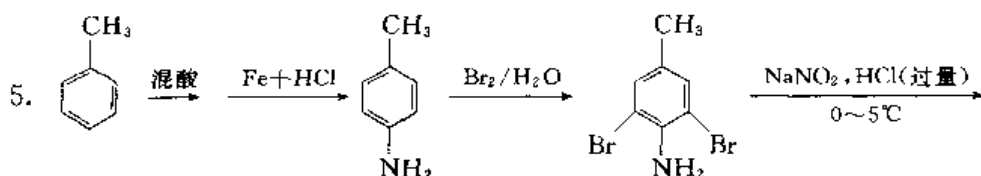
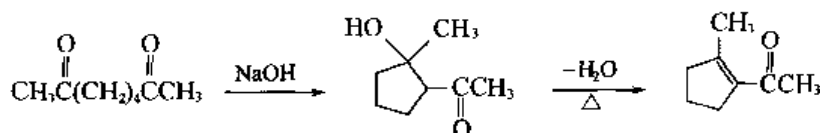
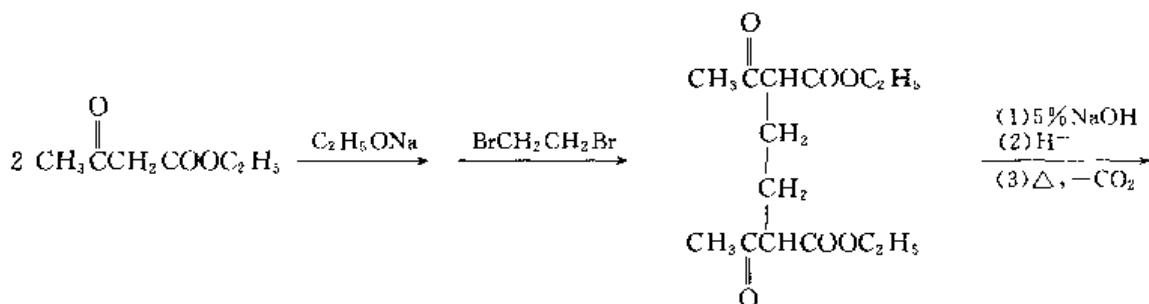
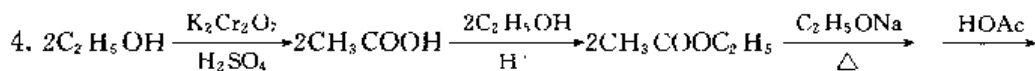
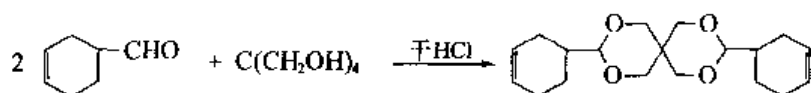
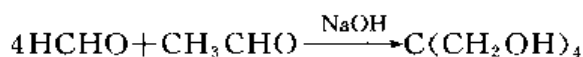
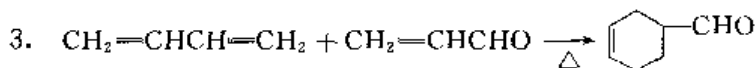
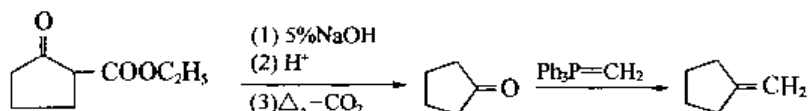
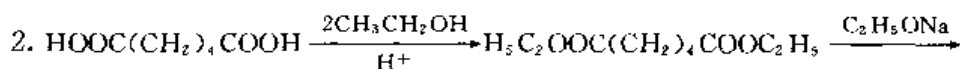
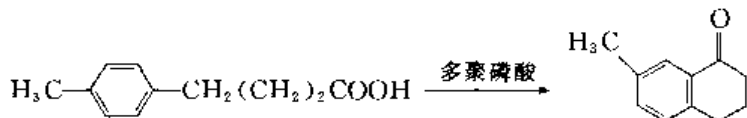
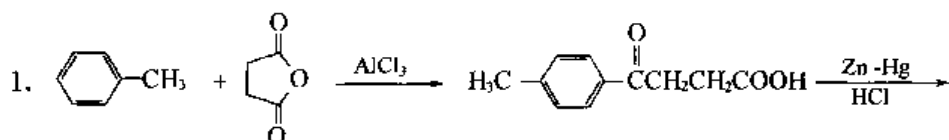
1. (B, C) 2. (A) 3. (B, D) 4. (C) 5. (D) 6. $D > B > A > C$
7. (B) 8. (A)

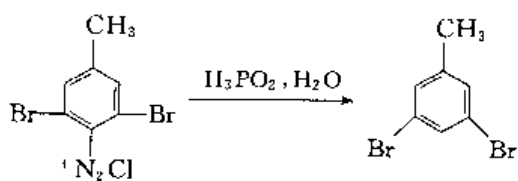
四、写出下列反应的历程





五、合成题

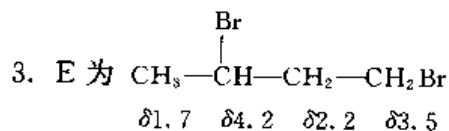
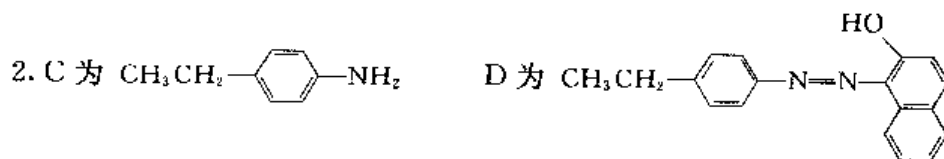
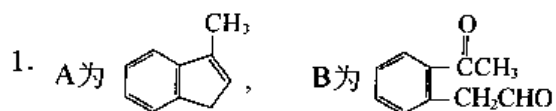




六、实验题

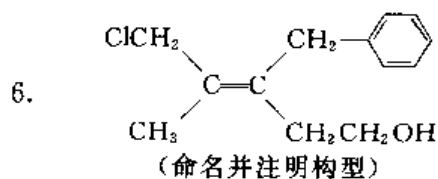
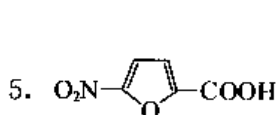
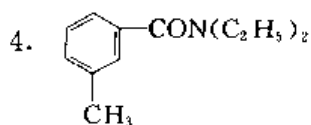
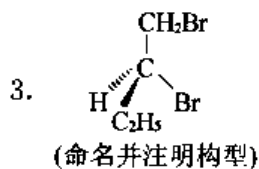
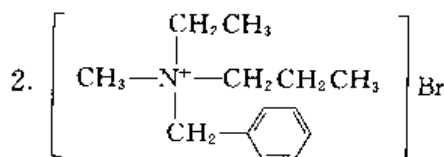
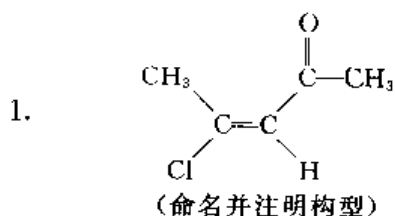
1. (C) 2. (B) 3. (A) 4. (D)

七、推断结构



模拟试题 26

一、命名或写出结构式 (10分)



7. 反-4-甲基环己醇
 (最稳定的构象)

8. (R)- α -溴代乙苯
 (Fischer 投影式)

9. 对氨基苯磺酰胺

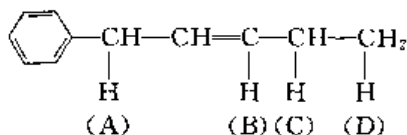
10. 碘化-N, N-二甲基四氢吡啶

二、选择题 (10分)

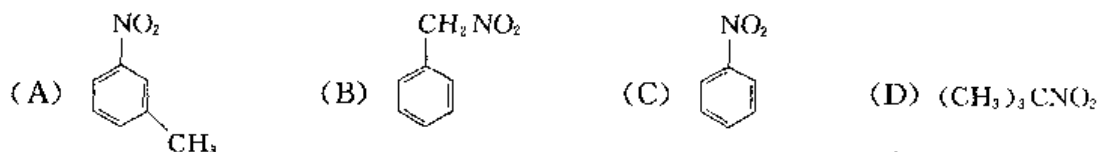
1. 1,2-二溴环戊烷的立体异构体数为 ()

- (A) 两个 (B) 3个 (C) 4个

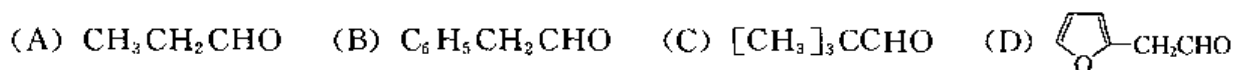
2. 下列化合物中的 H 原子, 在光照下氯代反应活性最大的是 ()



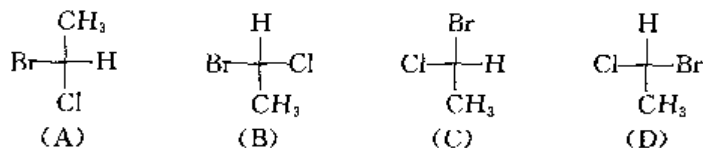
3. 下列化合物能溶于氢氧化钠溶液的是 ()



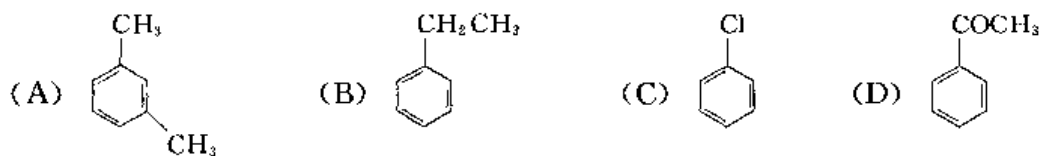
4. 下列化合物能发生歧化反应的是 ()



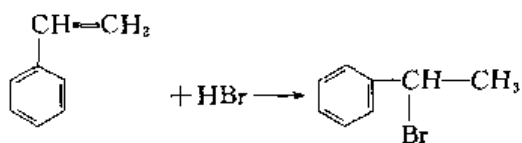
5. 下列 1-氯-1-溴乙烷中与 $\text{CH}_3-\overset{\text{Br}}{\underset{\text{Cl}}{\text{C}}}-\text{H}$ 同一构型的是 ()



6. 下列化合物中最易发生苯环上硝化反应的是 ()

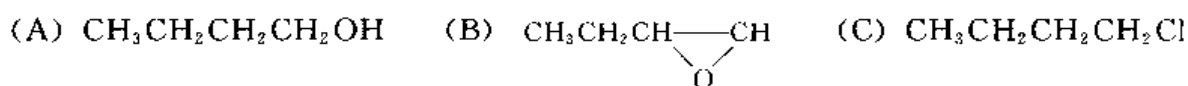


7. 下列反应是按什么机理发生的? ()

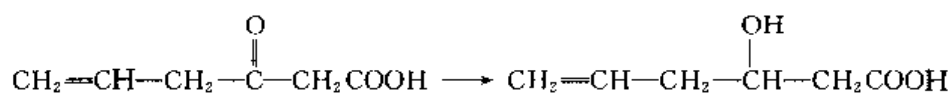


- (A) 亲电加成 (B) 自由基加成 (C) 亲核加成 (D) 取代反应

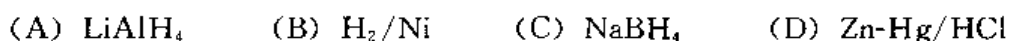
8. 不查表, 你认为下列化合物沸点最高的是 ()



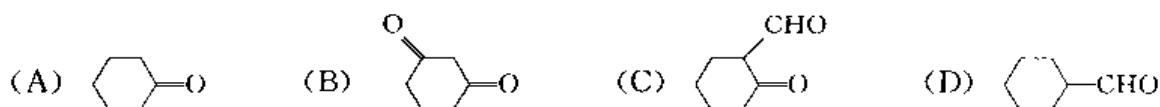
9. 要完成反应



适当的试剂是 ()

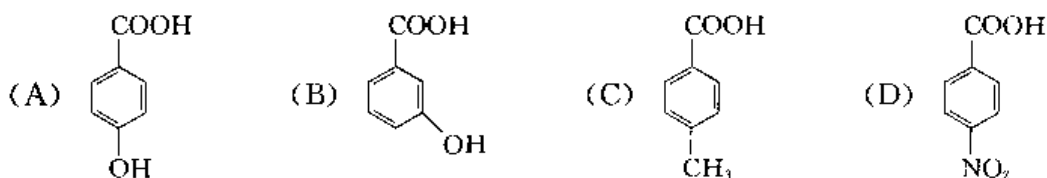


10. 下列化合物互变异构体中烯醇式含量最多的是 ()

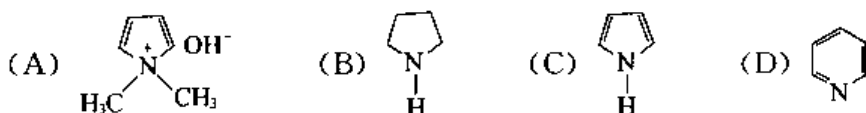


三、按指定要求自大到小排列顺序 (10分)

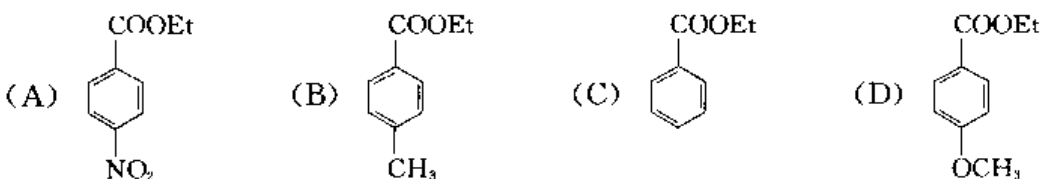
1. 酸性 ()



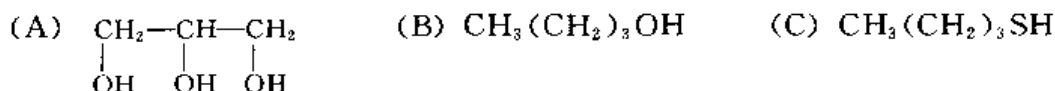
2. 碱性 ()



3. 碱催化下水解速率 ()



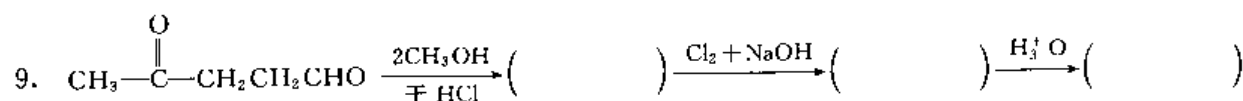
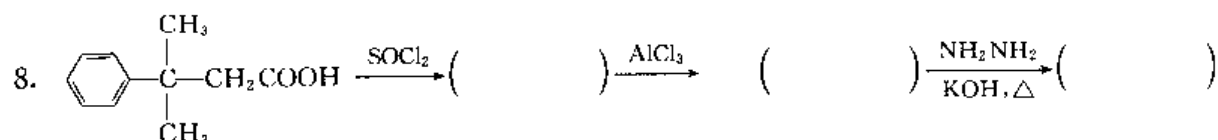
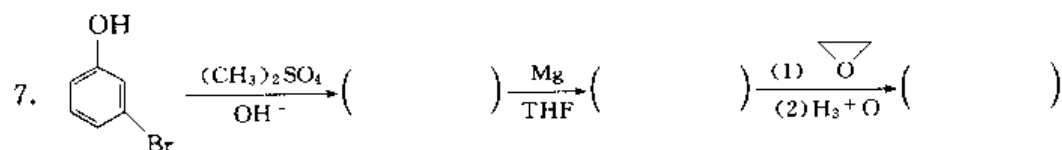
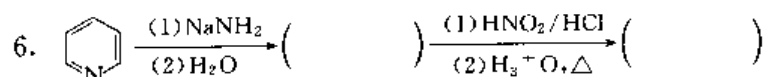
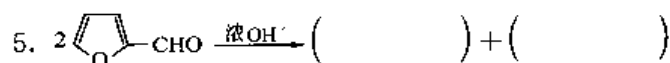
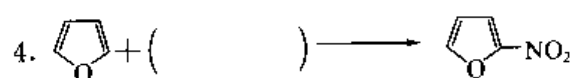
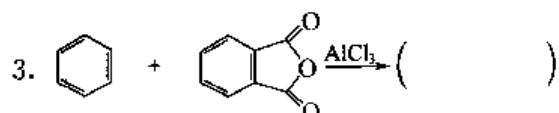
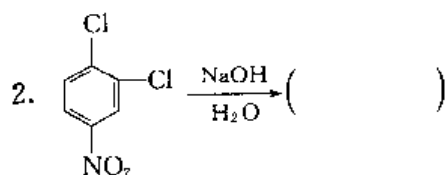
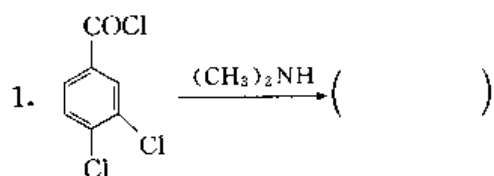
4. 水溶性 ()



5. 进行 $\text{S}_\text{N}2$ 反应的活性 ()



四、完成反应 (20分)

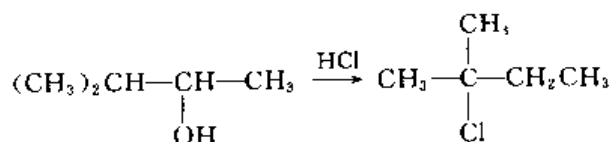


五、简要回答下列问题 (12 分)

1. 用简便的化学方法鉴别下化合物

- (1) 2-戊酮 3-戊酮 2,4-戊二酮 戊醛
(2) 环己醇 苯酚 环己烷 苯甲醚

2. 写出下列反应的历程



六、测定结构 (14 分)

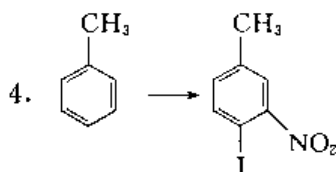
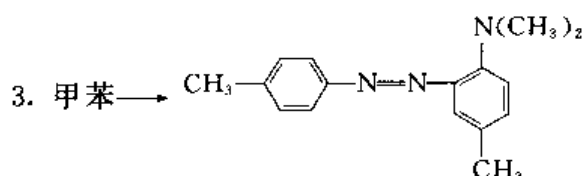
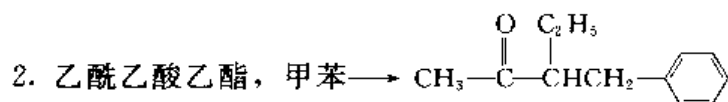
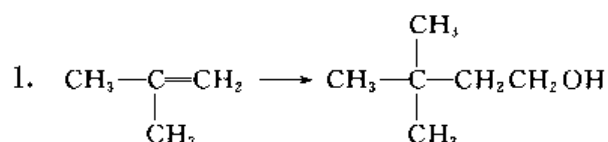
1. 化合物 A 分子式为 $C_6H_{12}O$, 能与羟胺作用生成肟, 但不起银镜反应。将 A 催化加氢得到醇 B, B 经脱水、臭氧化、还原水解等反应后得到两种液体 C 和 D, C 能起银镜反应但不能起碘仿反应, D 能起碘仿反应但不能起银镜反应。试推测出 A、B、C、D 的结构, 并写出各步反应式。(6 分)

2. 某化合物 ($C_9H_{10}O$) 能起碘仿反应, 其红外光谱表明在 1705cm^{-1} 处有一强吸收峰。核磁共振谱如下: δ 2.0(3H) 单峰; δ 3.5(2H) 单峰; δ 7.1(5H) 多重峰。试推出该化合物的结构。(4 分)

3. 两个芳香族化合物 A 和 B, A 能溶于 10 份 NaOH 水溶液, B 则溶于稀盐酸中。当 B 与甘油在浓硫酸存在下于硝基苯中加热时, 主要生成 7-甲基喹啉, 另外尚有副产物异构体 C。将 B 溶于硫酸中, 加 NaNO_2 溶液低温反应, 然后加热水解得 A。试推测 A、B、C 的结构, 并写出各步反应式。(4 分)

七、合成题 (24 分)

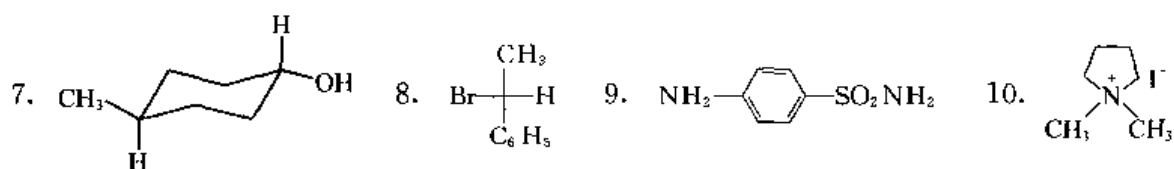
(以下合成可选用小于或等于两个碳的有机原料和任何无机试剂)



参考答案

一、命名或写出结构式

1. (E)-4-氯-3-戊烯-2-酮 2. 溴化甲基乙基丙基苄基铵 3. (S)-1,2-二溴丁烷
4. N,N-二乙基间甲基苯甲酰胺 5. 5-硝基-2-咪喃甲酸 6. (E)-4-甲基-3-苄基-5-氯-3-戊烯-1-醇



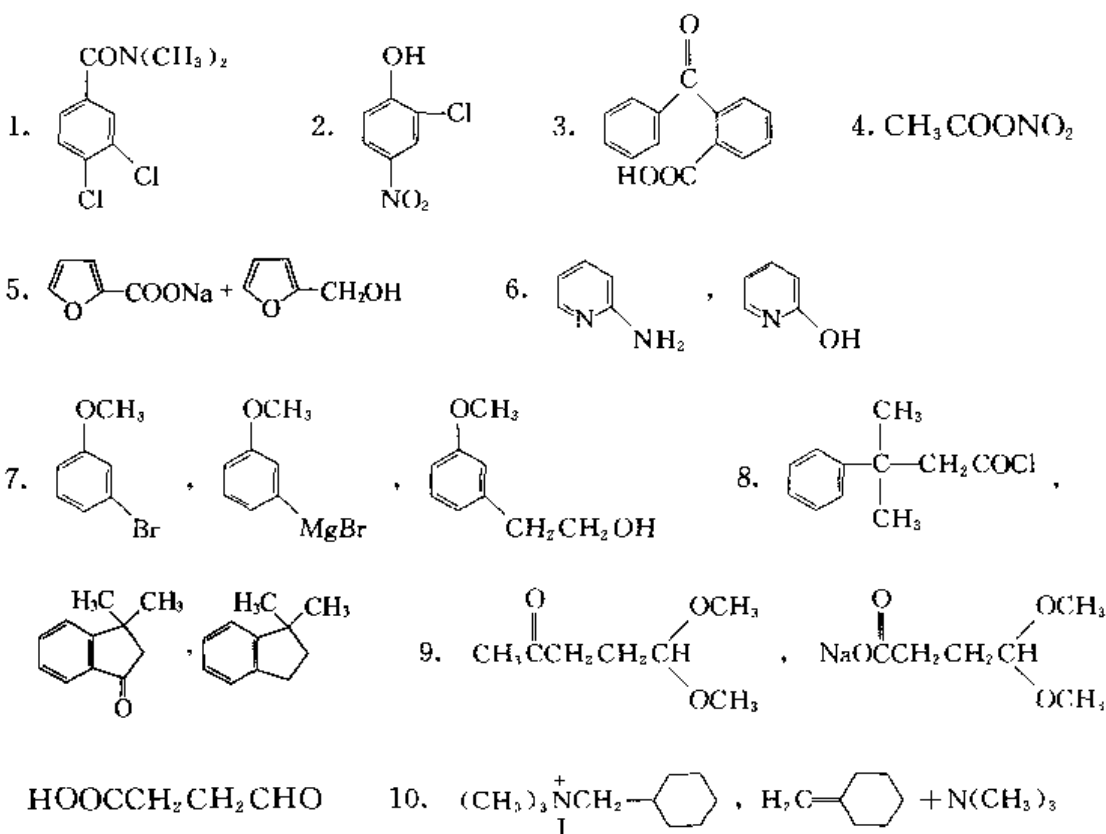
二、选择题

1. (B) 2. (A) 3. (B) 4. (C) 5. (D) 6. (A) 7. (A) 8. (A)
9. (C) 10. (C)

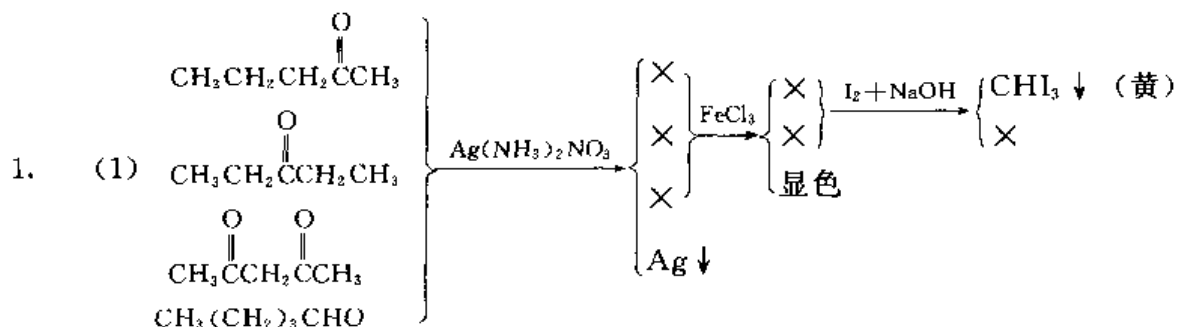
三、按指定要求自大到小排列顺序

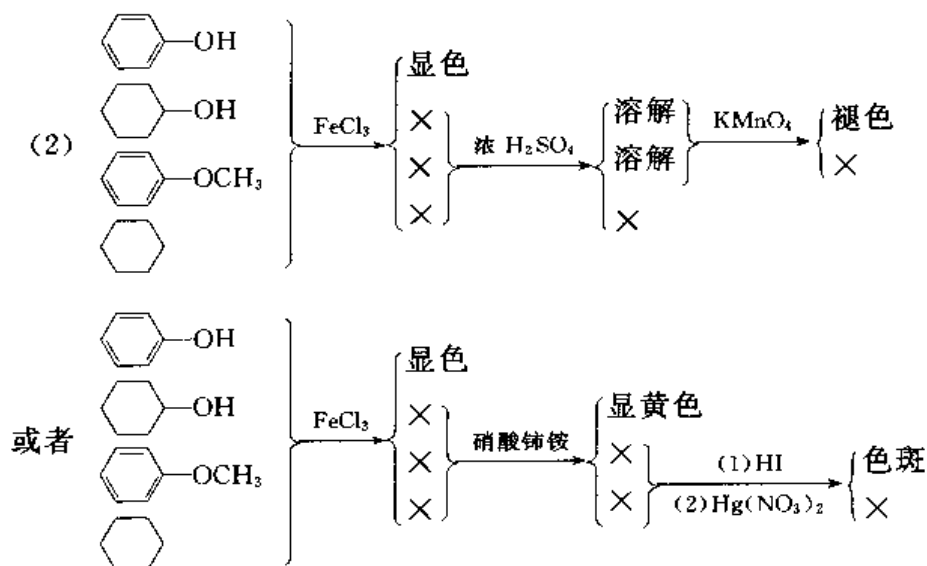
1. (D) > (B) > (C) > (A) 2. (A) > (B) > (D) > (C) 3. (A) > (C) > (B) > (D)
4. (A) > (B) > (C) 5. (A) > (C) > (B)

四、完成反应

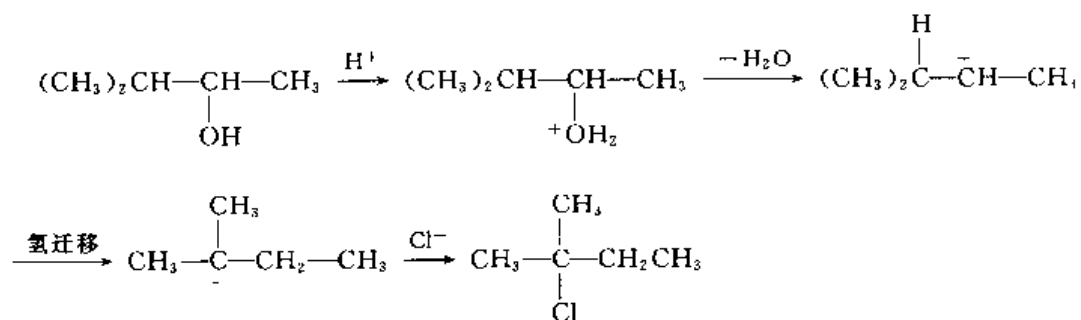


五、简要回答下列问题

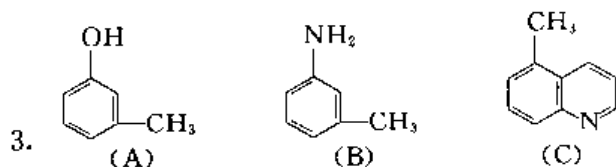
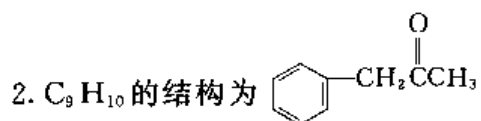
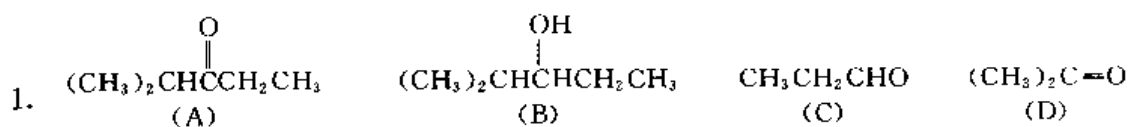




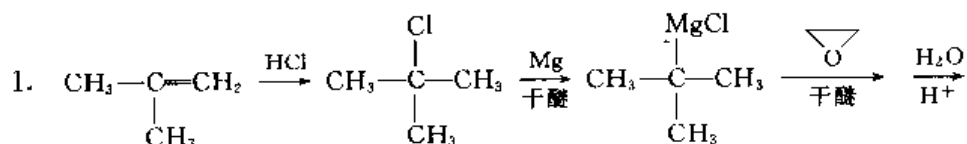
2. 反应历程

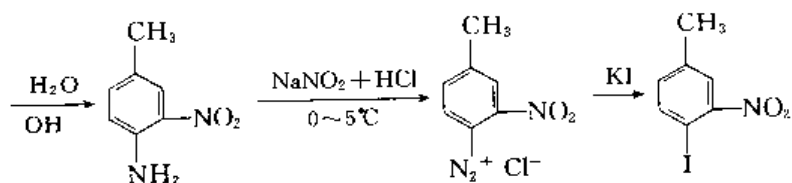
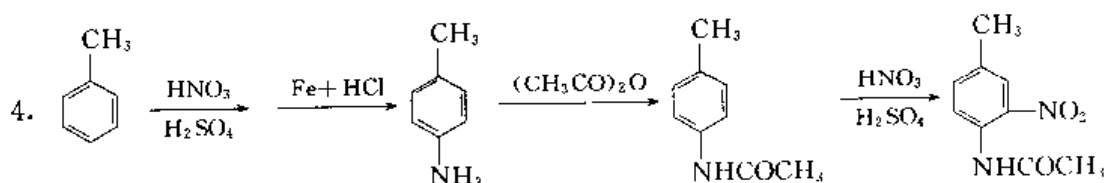
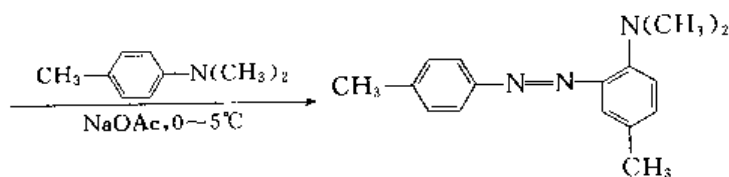
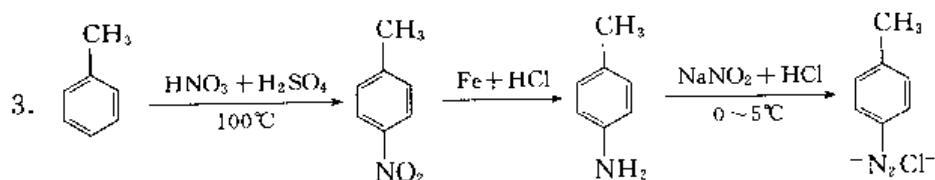
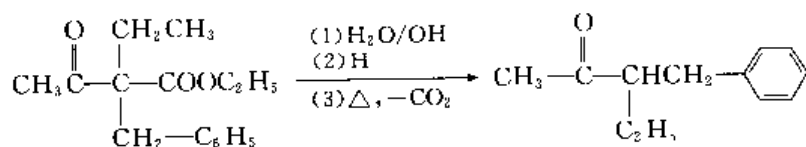
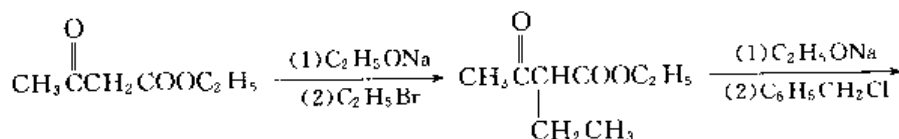
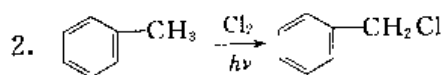
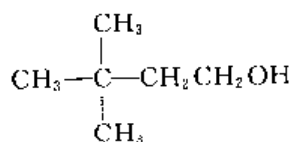


六、测定结构



七、合成题





模拟试题 27

一、分别用 Fischer 投影式及 Newman 投影式表示下列化合物的所有的光学异构体，并用 R/S 加以标记 (6 分)

1. 2-羟基-3-氯丁二酸 2. 2,2,3,4,5,5-六甲基己烷

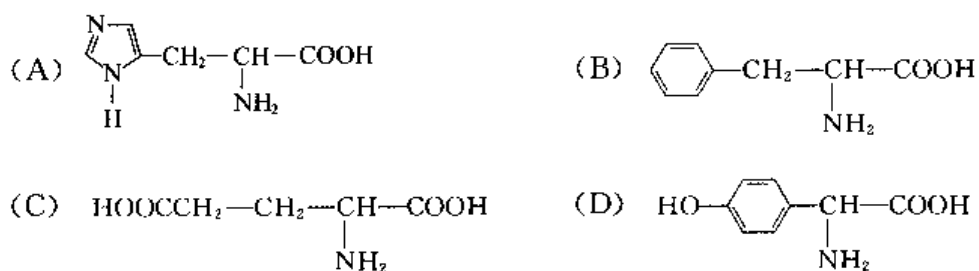
二、选择正确答案，填充下列各题。(15 分)

1. 下列化合物中，可以发生 Cannizzaro 反应的是_____。
(A) 乙醛 (B) 苯甲醛 (C) 丙醛 (D) 苯甲醚

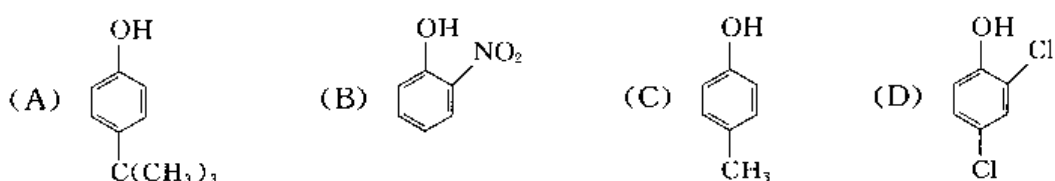
2. 芳香族伯胺的重氮化反应是在_____溶液中进行的。

- (A) 强酸性 (B) 中性 (C) 碱性 (D) 弱酸性

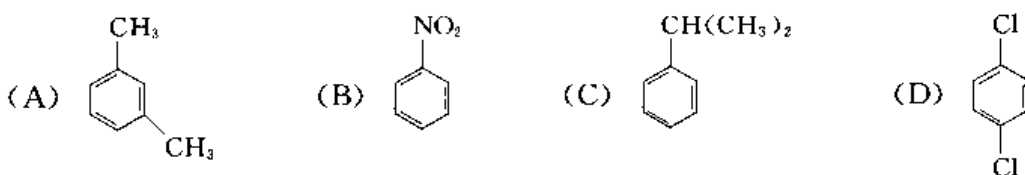
3. 下列氨基酸中，_____的等电点 (IP) 最小。



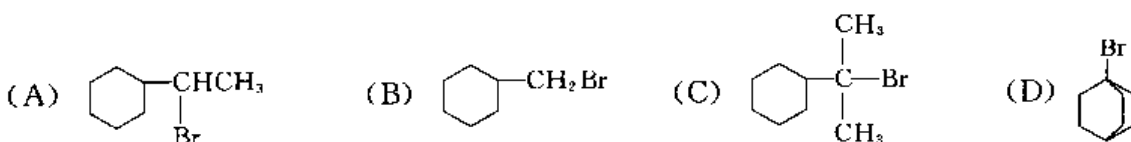
4. 下列化合物中，_____的酸性最强。



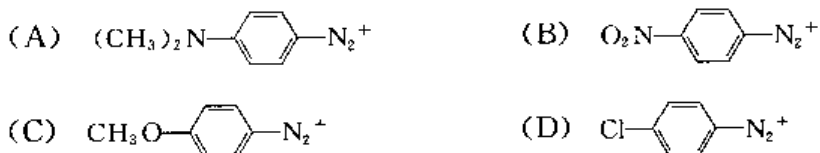
5. 下列各化合物中，_____最容易与浓 H_2SO_4 发生磺化反应。



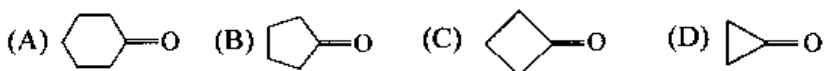
6. 下列各溴代反应中，_____在无水丙酮中与 NaI 的反应最快。



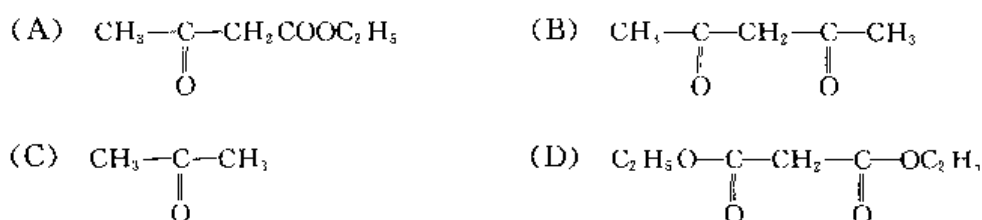
7. 下列重氮盐，_____在偶合反应中活性最大。



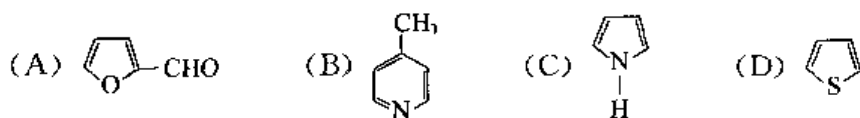
8. 下列各环酮中，_____与 HCN 的加成反应最容易。



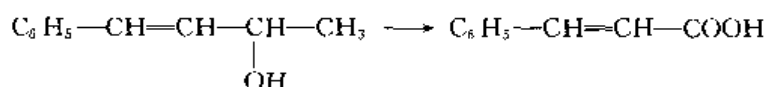
9. 下列各化合物中，在互变异构的动态平衡中，_____的烯醇化程度最大。



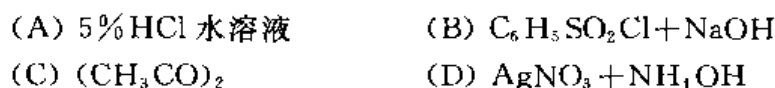
10. 下列各杂环化合物中，_____的环上硝化反应最容易。



11. 下列氧化反应，应该选择_____氧化剂。



12. 下列试剂中，_____可以把苯胺与 *N*-甲基苯胺定性地区别开来。



13. 化合物 $\text{C}_6\text{H}_5-\underset{\text{I}}{\text{CH}}-\text{C}_2\text{H}_5$ 在 $\text{CH}_3\text{COCH}_3/\text{H}_2\text{O}$ 中放置久时会转变为相应的醇。产物

的构型是_____。



14. 某化合物的分子式为 $\text{C}_3\text{H}_6\text{O}$ ，IR 谱在 3600cm^{-1} 和 1021cm^{-1} 处有明显的吸收峰，其结构是_____。

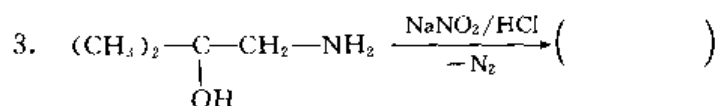
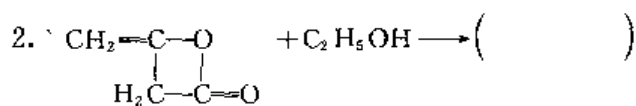
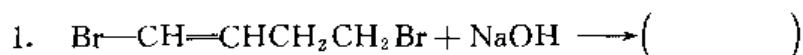


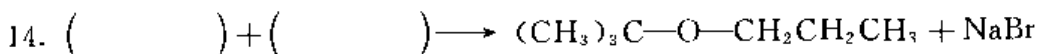
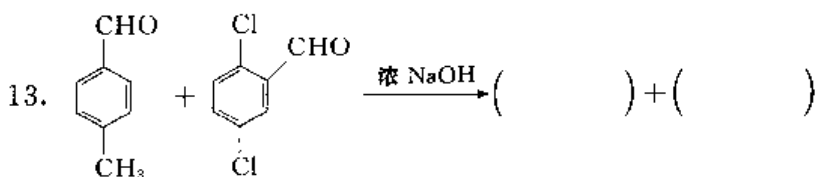
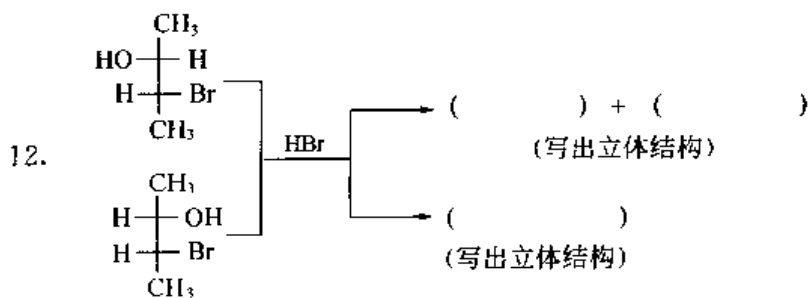
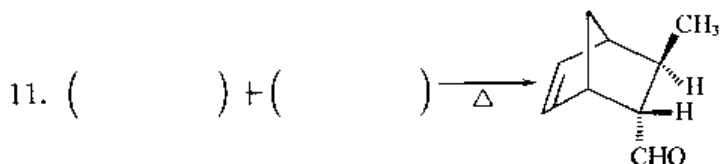
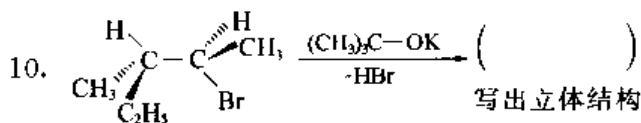
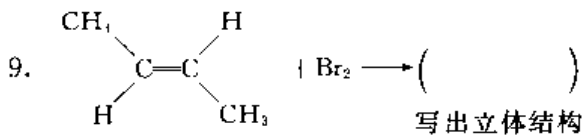
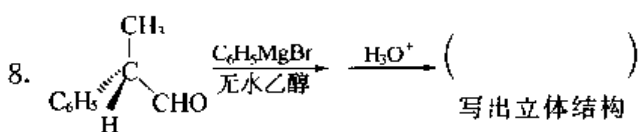
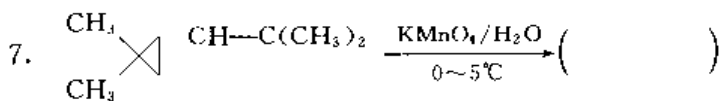
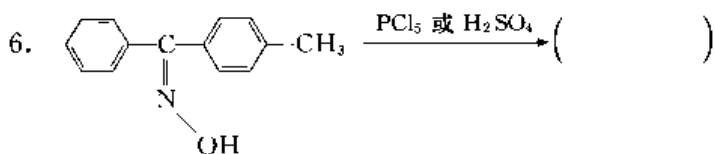
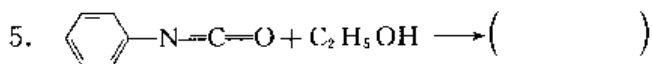
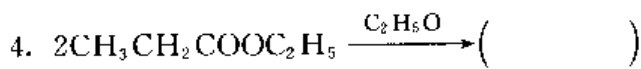
15. 某化合物的分子式为 $\text{C}_5\text{H}_{10}\text{O}$ ， $^1\text{H-NMR}$ 谱数据如下，其结构是_____。

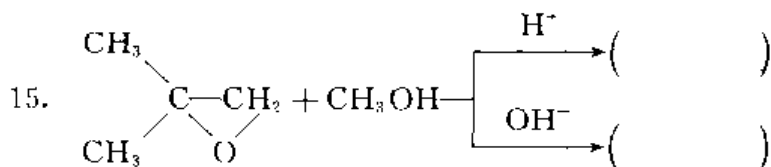
δ 1.02(6H)双峰， δ 2.13(3H)单峰， δ 2.22(1H)七重峰。



三、完成下列反应式（把主产物或底物写在括号内）（21分）

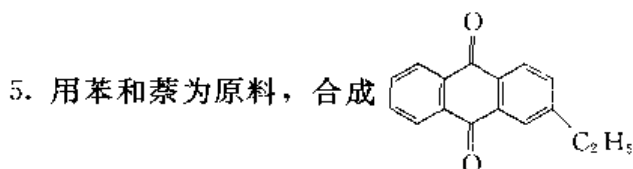
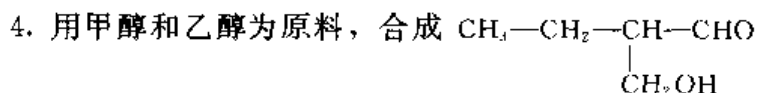
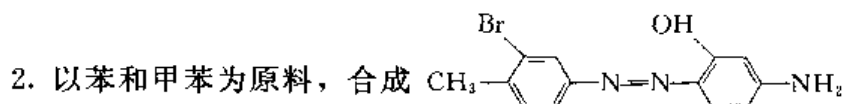
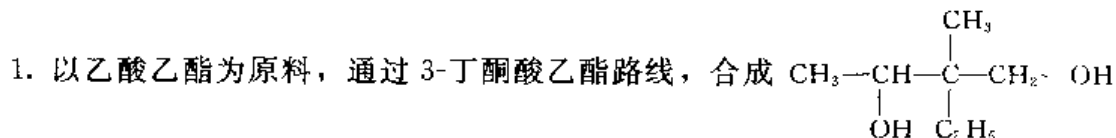






四、合成题 (除指定原料外, 其他试剂任选) (20 分)

(单考生任选两题)



五、推断结构题 (12 分) (单考生任选两题)

1. 某化合物分子式为 C_5H_{12} , 有同分异构体 A、B, 它们在室温下均能使 Br_2/CCl_4 溶液褪色, 而不被 KMnO_4 氧化, 加氢后均生成 3-甲基戊烷。但 A 与 HBr 反应主要生成 3-甲基-3-溴戊烷, 而 B 则得 3-甲基-2-溴戊烷。试推测 A、B 的构造式。

2. 某二元羧酸 A, 分子式 $\text{C}_5\text{H}_6\text{O}_4$, 能使溴水褪色, 加热时容易脱羧生成 B。B 的相对分子质量 86, A 和 B 均无几何异构体。推测 A 和 B 的构造式。

3. 化合物 A, 分子式为 $\text{C}_6\text{H}_{12}\text{O}$, 氧化得 B, B 能溶于 NaOH 水溶液, B 酯化后发生分子内缩合关环反应, 生成一环状化合物。这个环状化合物经皂化、酸化及脱羧后生成 C。C 可以和羟胺作用生成脎; C 用 $\text{Zn-Hg}/\text{HCl}$ 还原生成 $\text{D}(\text{C}_5\text{H}_{10})$ 。试推测 A、B、C、D 的构造式。

4. 某芳烃 A, 分子式 C_9H_{12} , 在光照下与不足量的 Br_2 作用, 生成同分异构体 B 和 $\text{C}(\text{C}_9\text{H}_{11}\text{Br})$ 。B 无旋光性, 不能拆分。C 也无旋光性, 但能被拆分成一对对映体。写出 A、B、C 的构造式, 并用 Fischer 投影式表示 C 的一对对映体, 分别用 R-S 标记其构型。

六、实验题 (26 分)

阅读“7,7-二氯双环[4.1.0]庚烷的制备”实验操作后, 简要回答问题。

依次放入 10ml 新蒸馏的环己烯, 24ml 无乙醇的氯仿, 0.3g 溴化四乙基铵于反应烧瓶中。在强烈搅拌下, 在 5min 内从回流冷凝管上口分 3~4 次加入新配制的 16ml 50% 的氢氧化钠溶液。在 25min 后, 反应温度可自行上升至 $50\sim 55^\circ\text{C}$, 保持此温度 1h。室温下继续搅拌 1h, 然后加 60ml 冰水, 分出氯仿层, 用 30ml 氯仿萃取碱水层, 合并氯仿层, 用饱和食盐水洗涤, 硫酸镁干燥后, 先常压蒸馏, 再减压蒸馏, 收集 $79\sim 80^\circ\text{C}/2\text{kPa}$ 的馏分约 10ml。

本试验如不加溴化四乙基铵，产率仅 0.5%。

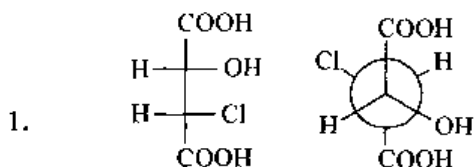
(已知沸点：氯仿 61℃，环己烯 83℃，7,7-二氯双环[4.1.0]庚烷 197℃)

问题：

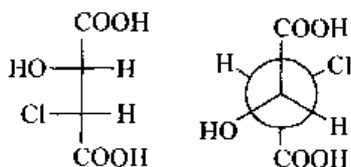
1. 为什么用无乙醇的氯仿？如何除去氯仿中的少量乙醇？
2. 写出溴化四乙基铵催化反应过程。
3. 此试验中，氯仿都起什么作用？
4. 为什么用回流反应装置？
5. 为什么要强烈搅拌？实验室中常用哪些搅拌方式？
6. 溴化四乙基铵加入量对实验有何影响？举出 3 个可作本实验催化剂的化合物名称。
7. 用饱和食盐水溶液比用水洗涤具有什么优点？
8. 常压蒸馏分离出什么？减压蒸馏的作用是什么？
9. 本试验如不加溴化四乙基铵等催化剂，产率很低，试分析其原因。
10. 画出反应装置图和减压蒸馏装置（包括真空系统）的简图。

参考答案

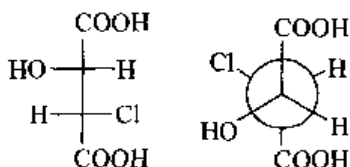
一、旋光异构



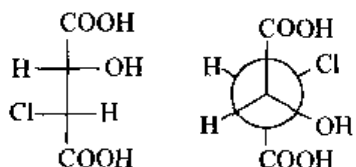
(2S,3S)-2-羟基-3-氯丁二酸



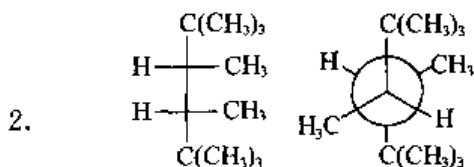
(2R,3R)-2-羟基-3-氯丁二酸



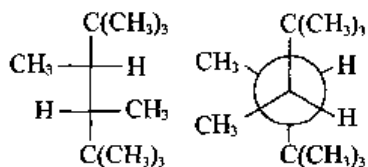
(2R,3S)-2-羟基-3-氯丁二酸



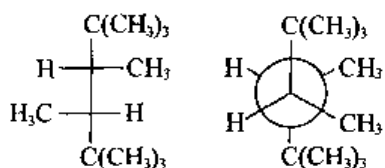
(2S,3R)-2-羟基-3-氯丁二酸



(4R,5S)-2,2,3,4,5,5-六甲基己烷



(4S,5S)-2,2,3,4,5,5-六甲基己烷

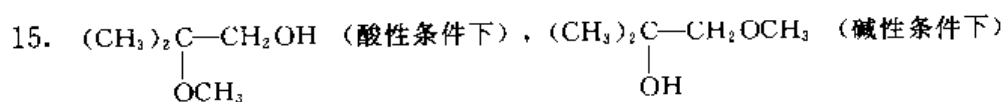
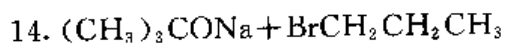
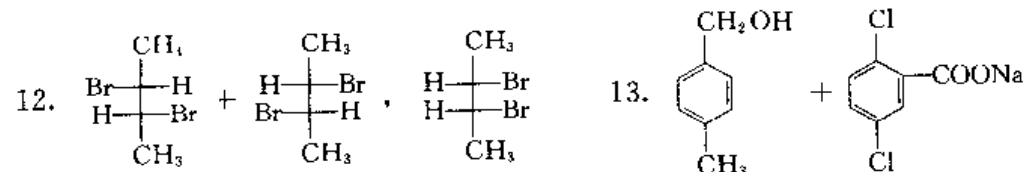
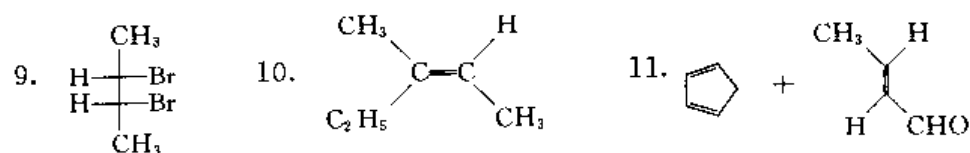
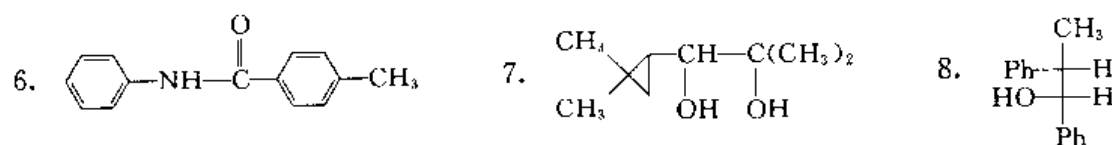
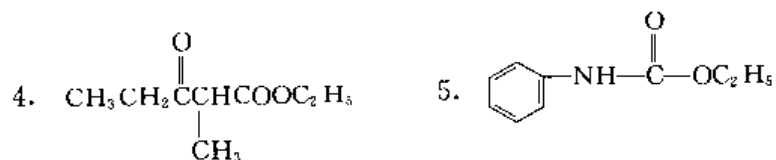
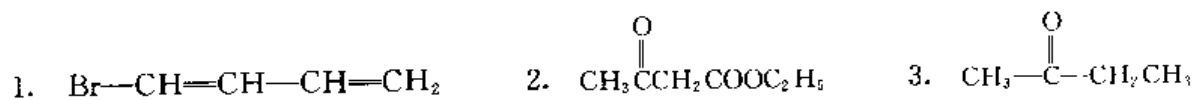


(4R,5R)-2,2,3,4,5,5-六甲基己烷

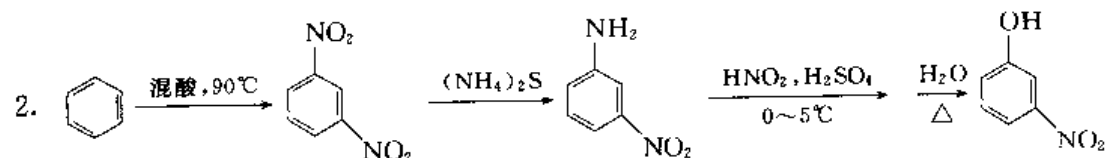
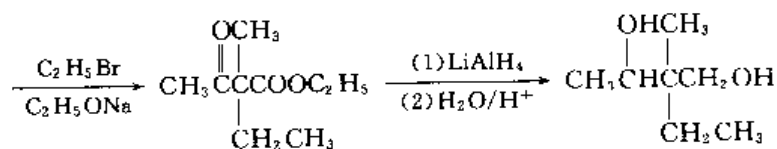
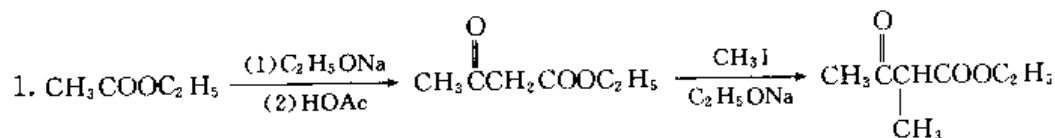
二、选择正确答案

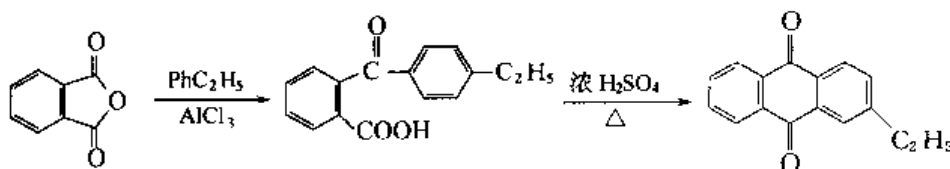
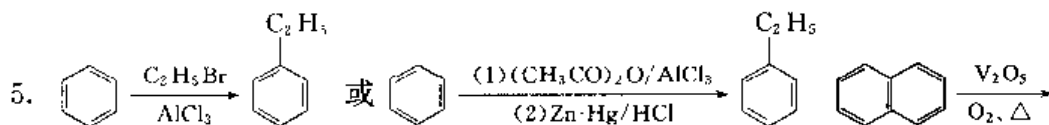
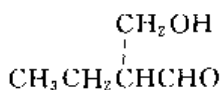
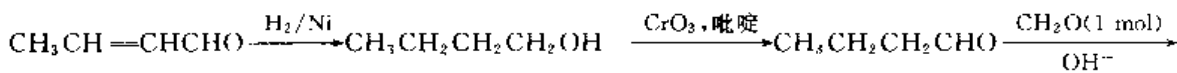
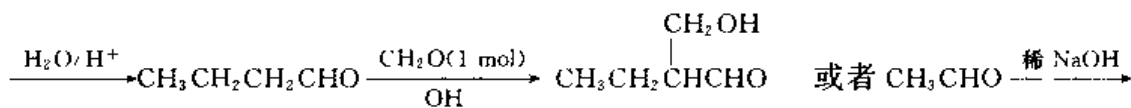
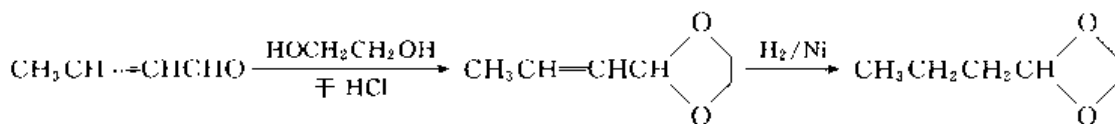
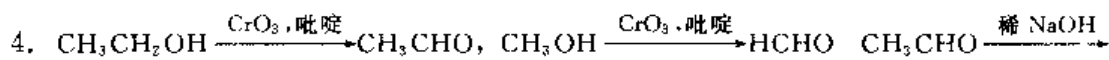
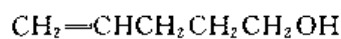
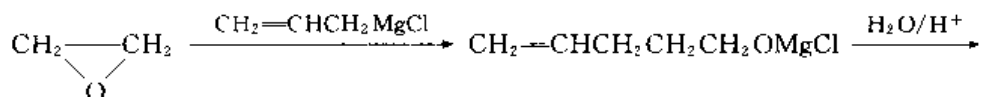
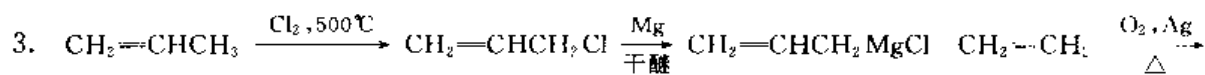
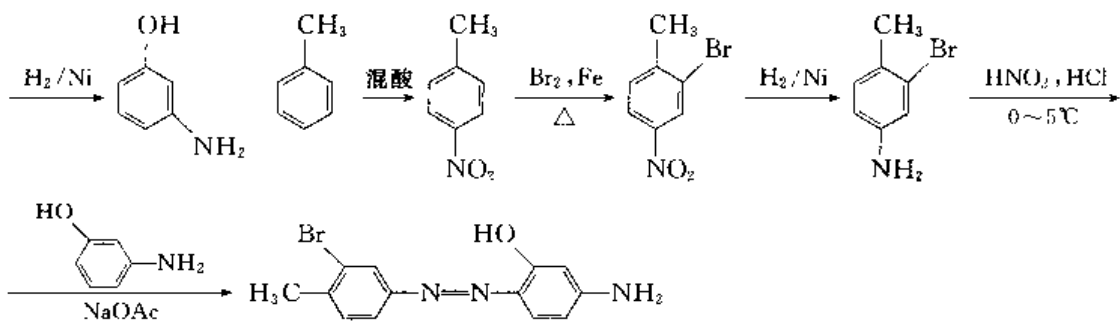
1. (B) 2. (A) 3. (C) 4. (D) 5. (A) 6. (B) 7. (B) 8. (D)
 9. (B) 10. (D) 11. (A) 12. (B) 13. (C) 14. (A) 15. (B)

三、完成下列反应式



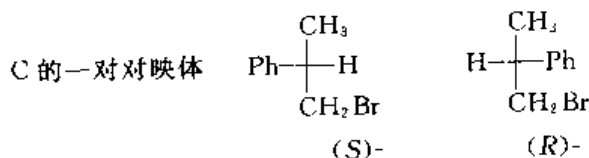
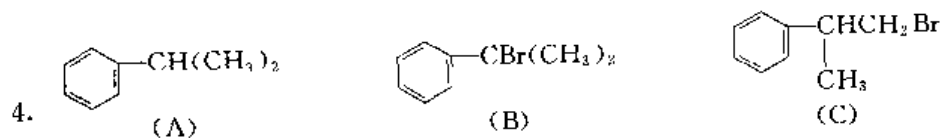
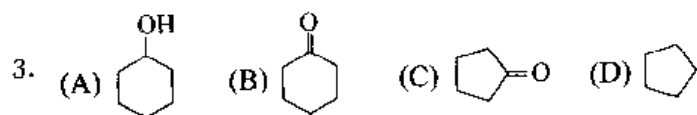
四、合成题





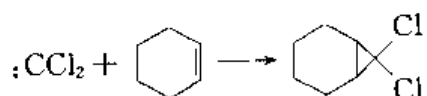
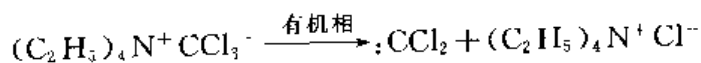
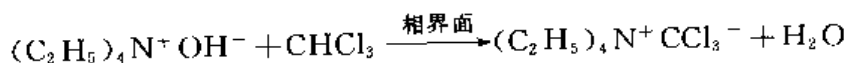
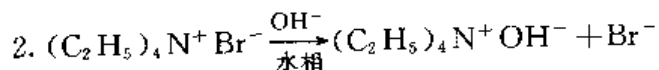
五、推测结构





六、实验题

1. 普通氯仿中，为了防止氯仿分解产生光气，一般加入少量的乙醇作为稳定剂，在使用时必须除去。可用水多次洗涤氯仿后，用无水氯化钙干燥，除去乙醇。



3. 氯仿的作用是：

- ① 作为反应物之一，与浓的氢氧化钠水溶液反应，产生二氯卡宾；
- ② 作为有机相的溶剂，使环己烯溶解于其中。

4. 回流反应装置可以在保持一定的反应温度的同时防止反应物料挥发，有利于提高反应的速率和收率。

5. 为使相转移催化反应顺利进行，必须使水相和有机相充分接触，反应必须在强烈搅拌下进行。实验室中最常用的搅拌方式是机械搅拌。其次，还可采用振摇反应瓶及采用电磁搅拌的方式达到搅拌的目的。

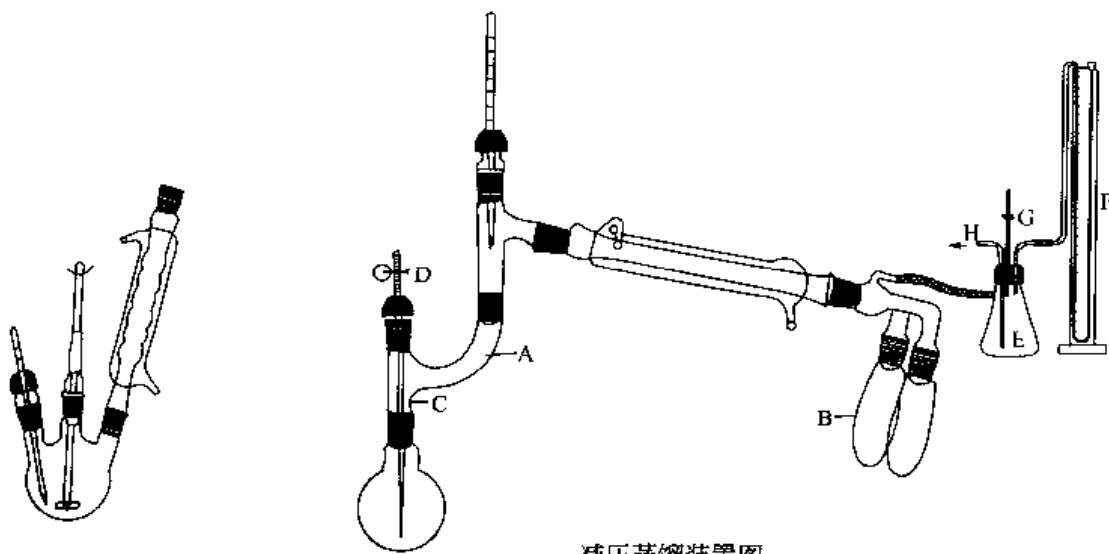
6. 溴化四乙基铵是相转移催化剂，加入量太小时反应速率达不到要求，加入量太大时可能会造成乳化现象，影响后面的分离提纯。除了溴化四乙基铵以外，溴化十六烷基三甲基铵、氯化三乙基苄基铵、氯化十二烷基二甲基苄基铵等都可作为本实验的催化剂。

7. 饱和食盐水相对密度大，极性大，对有机物的溶解度更小，更有利于有机相与无机相的分层。

8. 常压蒸馏分离出过量的未反应的氯仿和环己烯；减压蒸馏可在相对较低温度下使产物 7,7-二氯双环[4.1.0]庚烷被蒸出，防止其受热分解。

9. 本实验为相分离反应。若不加相转移催化剂，环己烯和氯仿在水中溶解度很低，而氢氧化钠又不溶于有机溶剂，不能与氯仿及环己烯充分接触，反应不能顺利进行。

10. 反应装置图及减压蒸馏装置图如下。



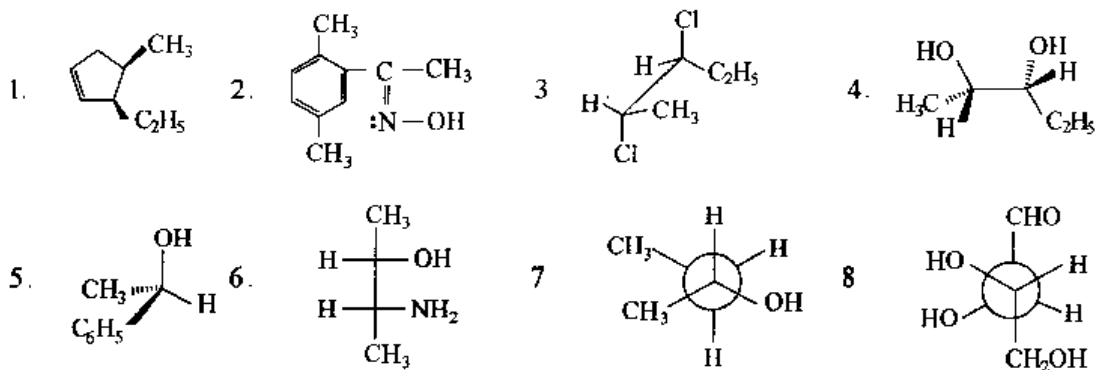
反应装置图

减压蒸馏装置图

A 二口连接管；B 接受器；C—毛细管；D—螺旋夹；E—安全瓶；
F 水银压力计；G—三通活塞；H—连接真空泵的导管

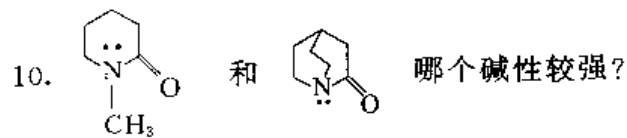
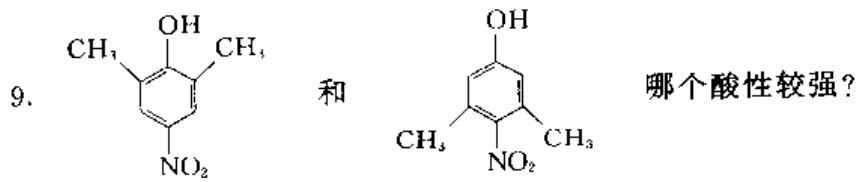
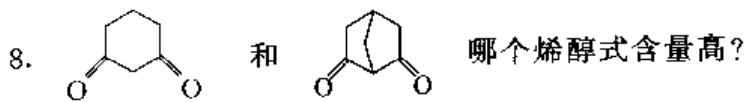
模拟试题 28

一、命名下列化合物，并标明其构型（12分）

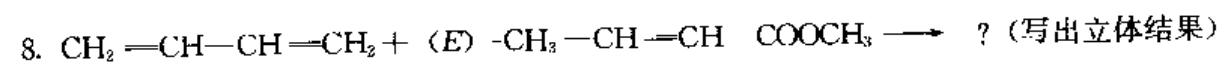
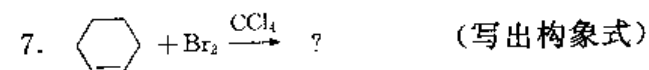
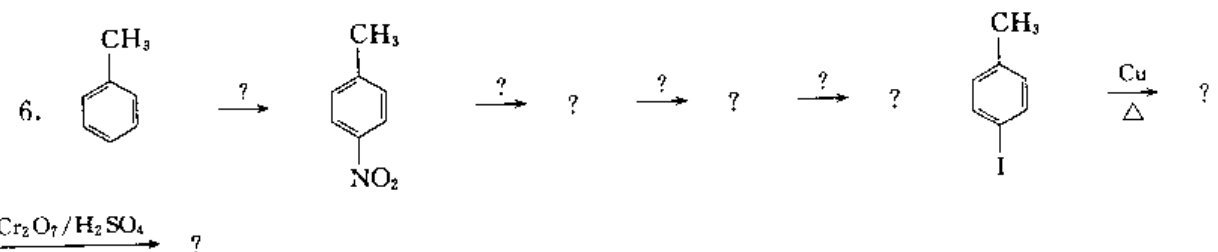
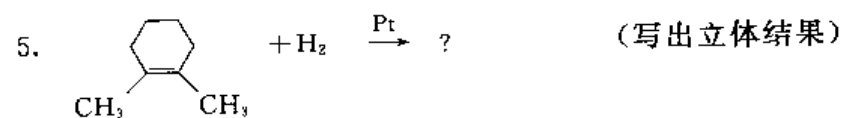
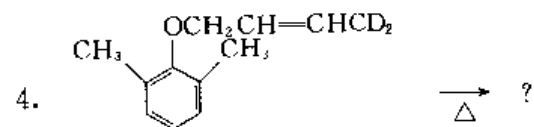
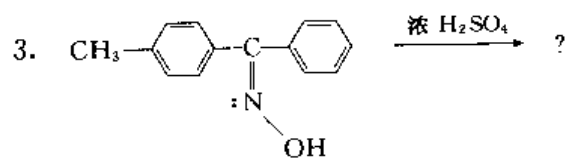
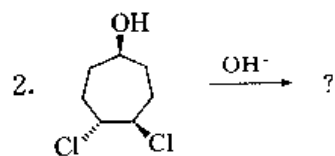
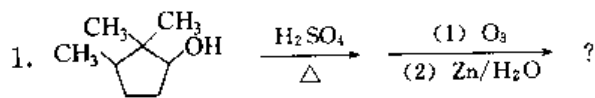


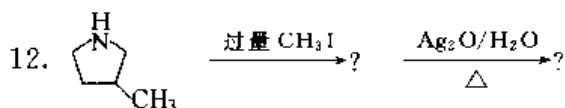
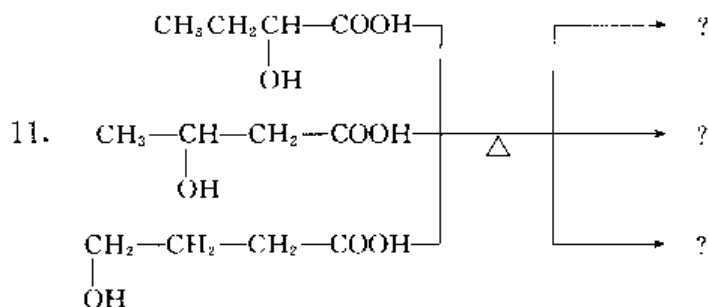
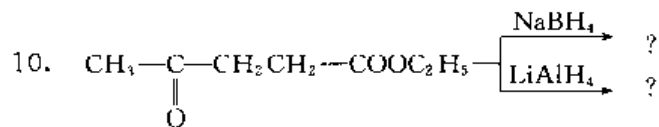
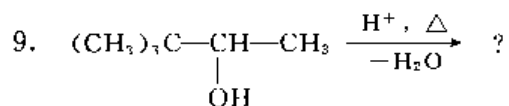
二、回答下列问题（10分）

- 丙酮和丙腈哪个沸点较高？
- 乙酰乙酸乙酯的酮式和烯醇式哪个沸点较高？
- 辛烷和 2,2,3,3-四甲基丁烷哪个沸点较高？
- 正丁醇和叔丁醇哪个水溶性较大？
- 乙醚和四氢呋喃哪个水溶性较大？
- $\text{CH}_3\text{CH}_2-\ddot{\text{O}}-\text{CH}_2^+$ 和 $\text{CH}_3\text{CH}_2-\text{O}^+=\text{CH}_2$ 哪个较稳定？
- $^-\text{CF}_3$ 和 $^-\text{C}(\text{NO}_2)_3$ 哪个较稳定？



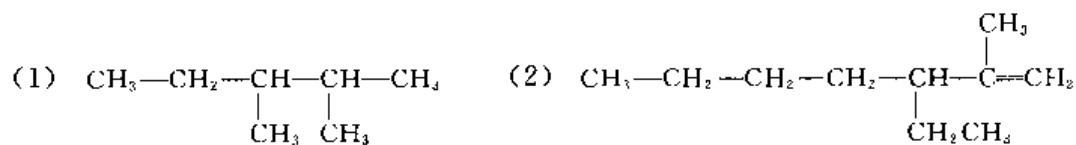
三、完成下列反应式 (23分)



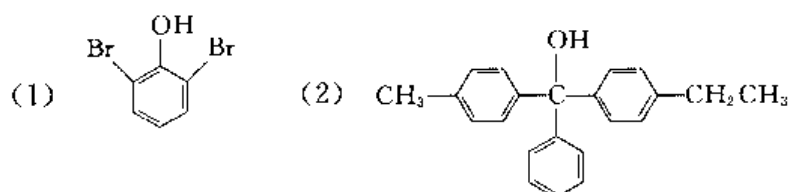


四、合成下列化合物 (16 分)

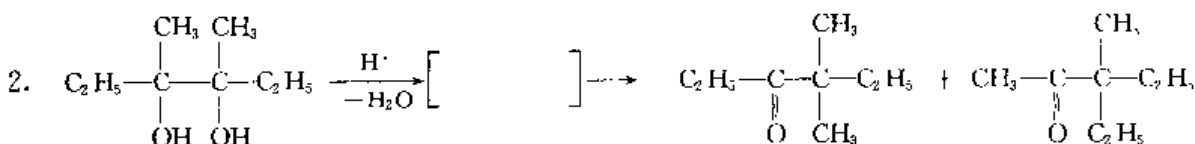
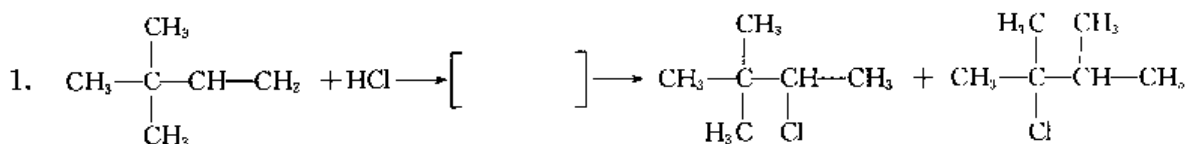
1. 以不多于 4 个碳原子的脂肪族化合物为原料 (其他试剂任选) 合成 (单考生任选其一)

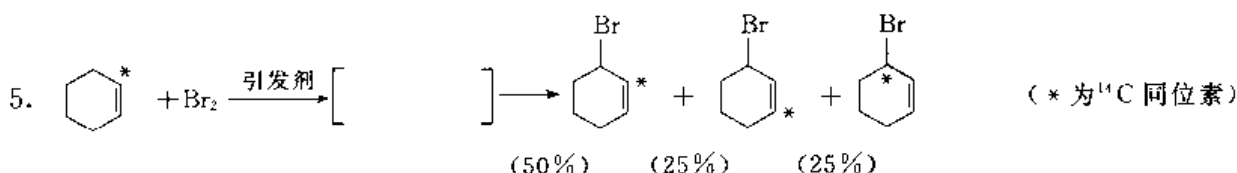
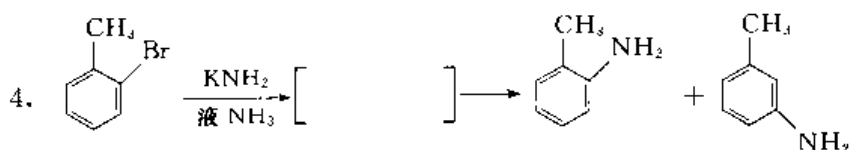


2. 苯、甲苯为原料 (其他试剂任选) 合成 (单考生任选其一)



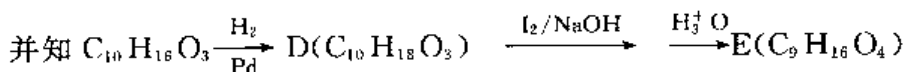
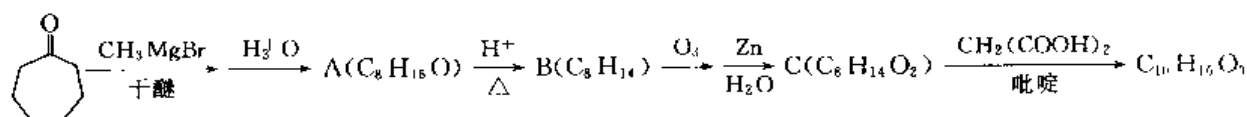
五、根据下列反应结果, 将反应中间物填入方括号内 (10 分) (单考生任选 4 题)





六、推导结构式 (单考生任选一题) (10 分)

1. 某化合物的分子式为 $\text{C}_{10}\text{H}_{16}\text{O}_3$ (其中有一羰基), 可由如下步骤合成



写出此化合物 ($\text{C}_{10}\text{H}_{16}\text{O}_3$) 及中间物 A~E 的各结构式。

2. 某化合物 $\text{C}_6\text{H}_{12}\text{O}_2$ 的红外光谱在 1700cm^{-1} 和 3400cm^{-1} 处有吸收峰, 核磁共振谱数据是

$$\delta 1.2 \times 10^{-6} \text{ (单峰, 6H)} \quad \delta 2.2 \times 10^{-6} \text{ (单峰, 3H)}$$

$$\delta 2.6 \times 10^{-6} \text{ (单峰, 2H)} \quad \delta 4.0 \times 10^{-6} \text{ (单峰, 1H)}$$

试推断此化合物的结构。

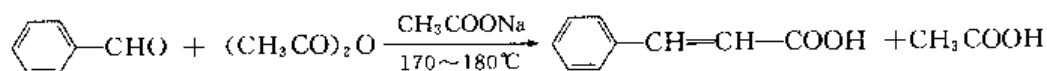
七、实验题 (19 分)

1. 画出水蒸气蒸馏的装置图, 注明所用仪器的名称, 简述操作步骤以及进行水蒸气蒸馏时应注意的问题。

2. 各选择一种合适的干燥剂, 干燥下列物质。

(1) 乙醚 (2) 乙酸乙酯 (3) 苯 (4) 苯胺 (5) 溴 (6) 苯甲醛

3. 根据下述反应制备肉桂酸 (Perkin 反应)



原料、产物的主要物理常数如下。

项 目	d_4^{25}	m. P. / $^{\circ}\text{C}$	溶解度/ $\text{g} \cdot (100\text{g})^{-1}, 20^{\circ}\text{C}$		
			H_2O	$\text{C}_2\text{H}_5\text{OH}$	$(\text{C}_2\text{H}_5)_2\text{O}$
苯甲醛	1.0504	—	0.33	∞	∞
醋酸酐	1.0871	—	13.6	∞	∞
肉桂酸	—	133	0.1	23	易溶

试设计如何从反应物中（还会有树脂状物）分离得到肉桂酸。

注：苯甲醛可以随水蒸气蒸出。

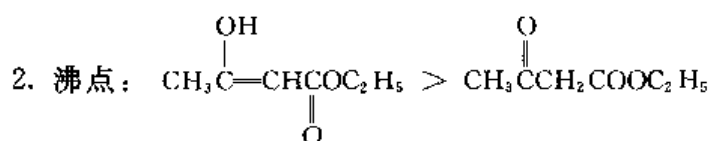
参考答案

一、命名并标明其构型

1. 顺-4-甲基-3-乙基环戊烯
2. (*E*)-2,5-二甲基苯乙酮肟
3. (2*S*,3*S*)-2,3-二氯戊烷
4. (2*S*,3*R*)-2,3-戊二醇
5. (*R*)-1-苯乙醇
6. (2*S*,3*R*)-3-氨基-2-丁醇
7. (*R*)-2-丁醇
8. (2*R*,3*S*)-2,3,4-三羟基丁醛

二、回答下列问题

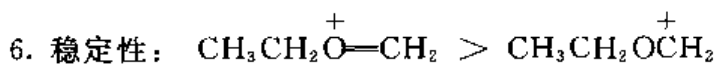
1. 沸点：丙腈 > 丙酮



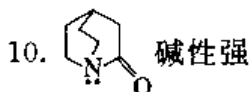
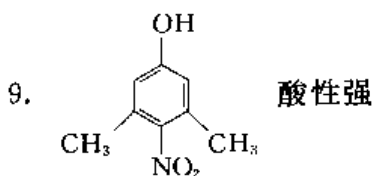
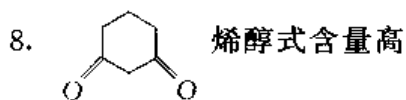
3. 沸点：正辛烷 > 2,2,3,3-四甲基丁烷

4. 叔丁醇水溶性较大

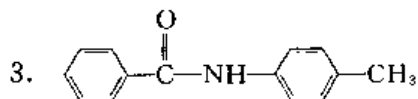
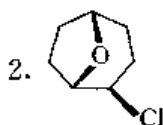
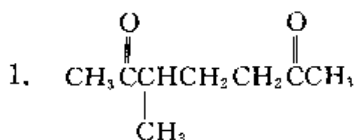
5. 四氢呋喃水溶性较大

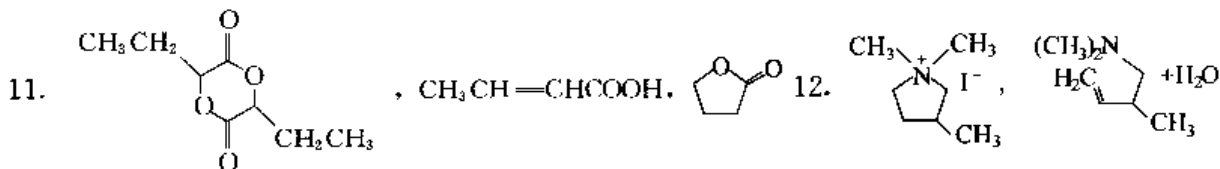
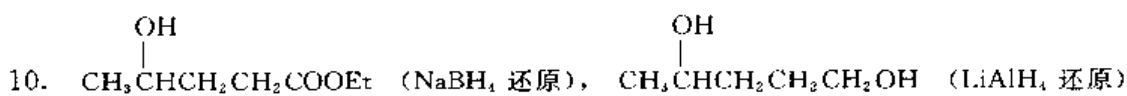
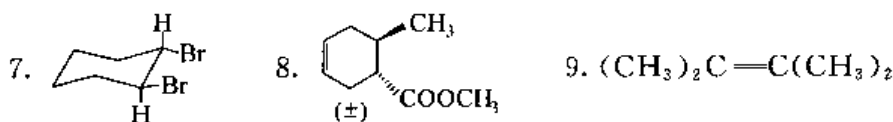
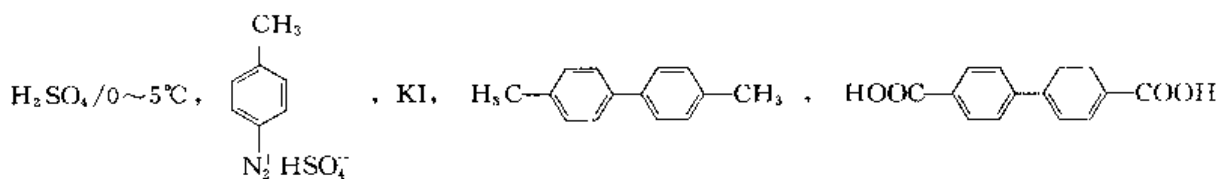
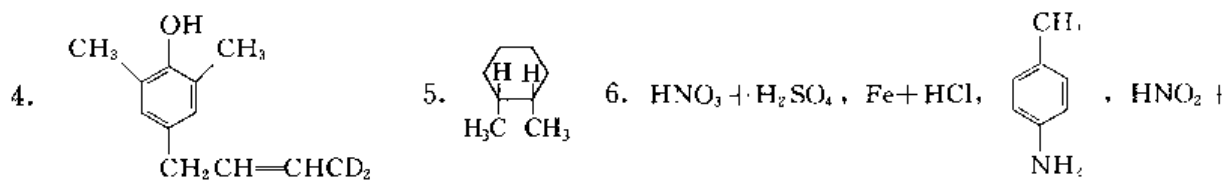


7. 稳定性： $^-\text{C}(\text{NO}_2)_3 > ^-\text{CF}_3$

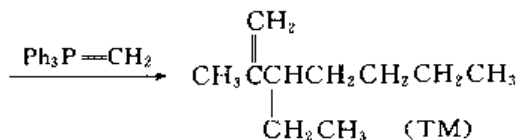
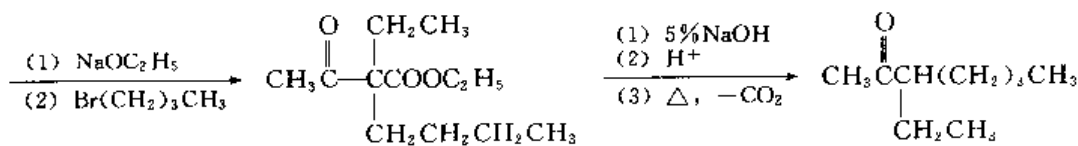
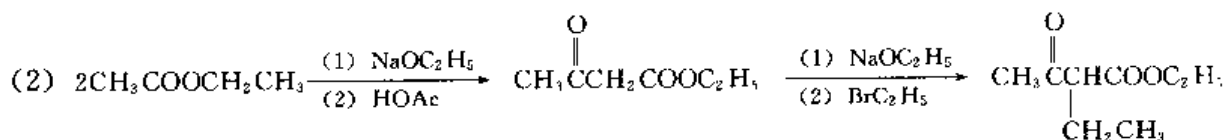
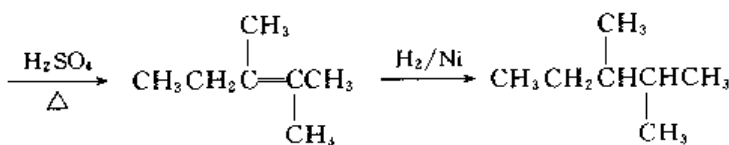
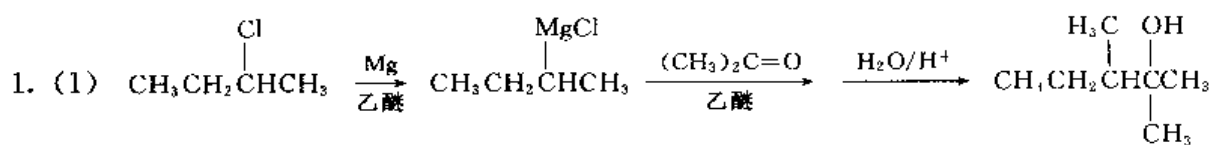


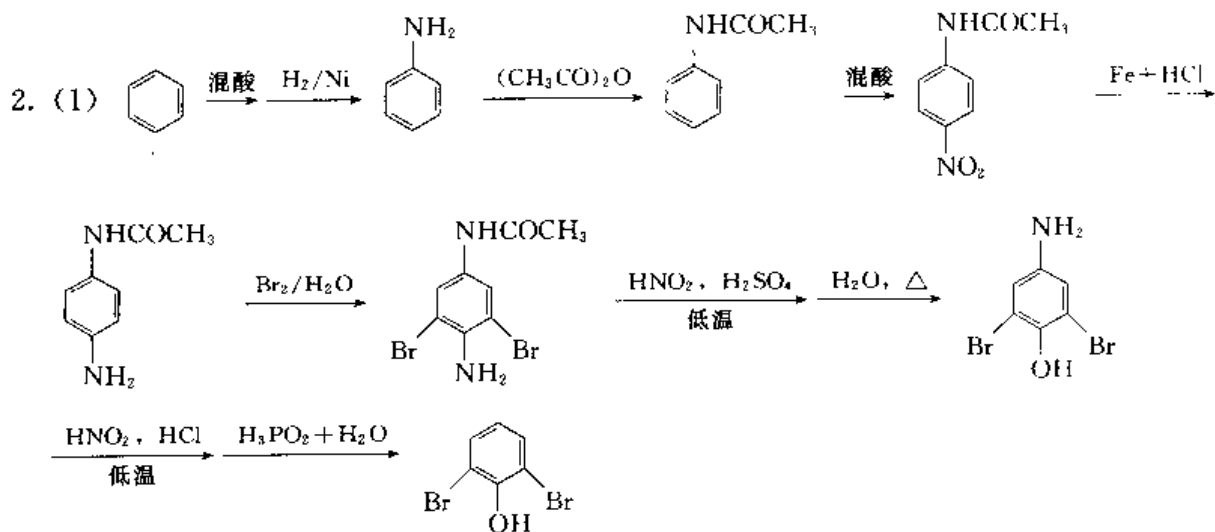
三、完成下列反应式



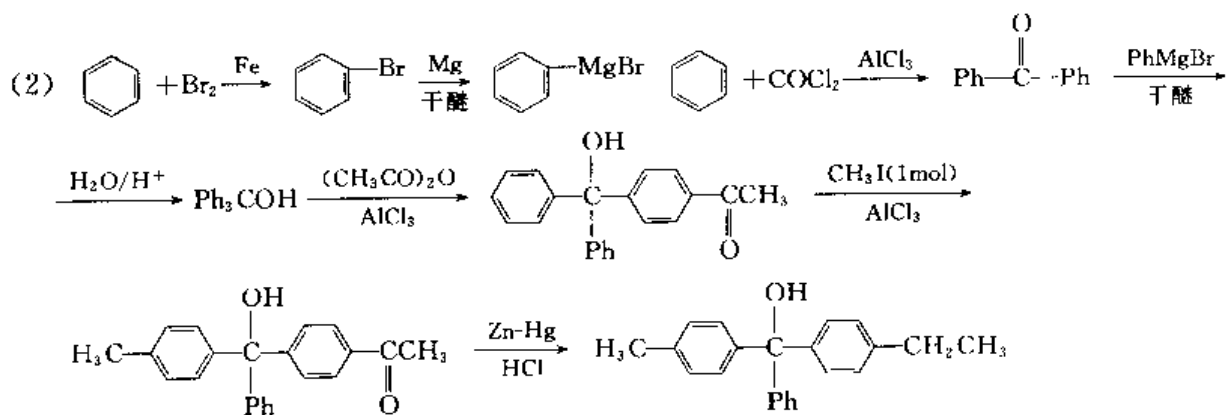
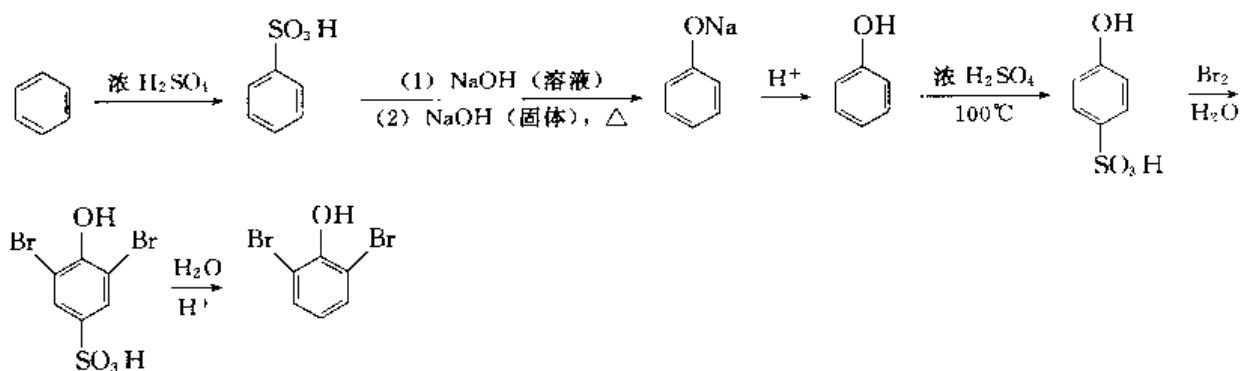


四、合成

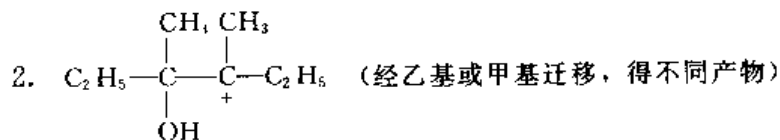
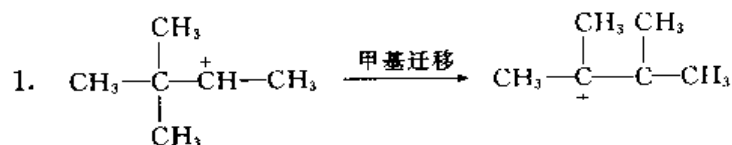


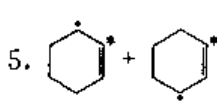
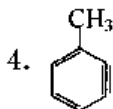
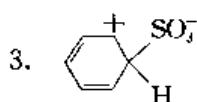


或者



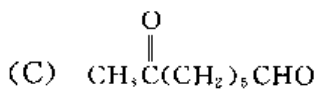
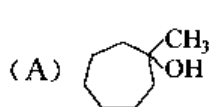
五、将反应中间物填入方括号内





六、推导结构式

1. 化合物 $C_{10}H_{16}O_3$ 是 $CH_3C(=O)(CH_2)_5CH=CHCOOH$



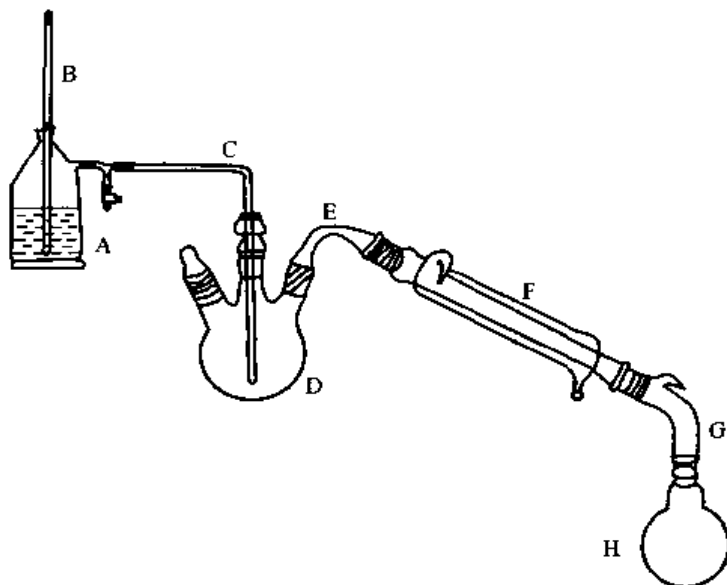
(D) $CH_3C(=O)(CH_2)_7COOH$ (E) $HOOC(CH_2)_7COOH$

2. 化合物 ($C_6H_{12}O_2$) 的结构为 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-\overset{\overset{OH}{|}}{C}-CH_3$

δ_{H_a} 2.2 (单峰, 3H)
 δ_{H_b} 2.6 (单峰, 2H)
 δ_{H_c} 1.2 (单峰, 6H)
 δ_{H_d} 4.0 (单峰, 1H)

七、实验题

1. 水蒸气蒸馏装置图如下。



水蒸气蒸馏装置图

A 水蒸气发生器；B—安全管；C—水蒸气导气管；D—三口瓶；E—蒸馏弯管；
F 直形冷凝管；G—尾接管；H—接受瓶

操作步骤：

- ① 将要蒸馏的物质加入三口瓶 D 中，其体积一般不超过烧瓶容积的 1/3；
- ② 如图装好仪器并检查不漏气后，打开 T 形管处的夹子，用直接火加热水蒸气发生器；

③ 待水蒸气从 T 形管的支管中冲出时，旋紧夹子，将水蒸气通入三中瓶底部，使瓶中液体上下翻滚。然后，会有浑浊的水蒸气与有机物的混合物馏出；

④ 当馏出液清澈透明时，表明不再有有机物馏出，打开夹子，移去火焰，停止蒸馏。

注意事项：

① 注意观察安全管 B 中液面高低，调节火焰大小，防止安全管中液体因压力太大而溢出。

② 注意观察导气管是否有倒吸现象。一旦发现倒吸，立刻打开 T 形管处的夹子，移去火焰。经检查排除故障后，可继续蒸馏。

2. 选择干燥剂

序号	需干燥的物质	干燥剂	序号	需干燥的物质	干燥剂
(1)	乙醚	金属钠	(4)	苯胺	无水碳酸钾
(2)	乙酸乙酯	无水硫酸镁	(5)	溴	无水硫酸钠
(3)	苯	无水氯化钙	(6)	苯甲醛	无水硫酸镁

3. 从反应物中分离得到肉桂酸可采用如下方法。

① 待缩合反应完成后，向反应混合物中加入一定量的饱和碳酸钠溶液，直到不再冒出气泡为止。

② 如上图装置，进行水蒸气蒸馏，除去未反应的苯甲醛。

③ 加入活性炭脱色后，趁热过滤，除去焦油状树脂物质及其他不溶性杂质。

④ 将滤液用盐酸酸化，使肉桂酸晶体析出。

⑤ 待晶体完全析出后，减压抽滤，得到肉桂酸晶体。

⑥ 可进一步用水或乙醇重结晶。


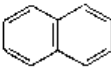
模拟试题 29

一、选择题 (30 分)

1. 与 HNO_2 反应能生成 N-亚硝基化合物的是

- (A) 伯胺 (B) 仲胺 (C) 叔胺 (D) 所有胺

2. 下面哪个化合物的氢原子处于磁屏蔽区。

- (A) $\text{CH}\equiv\text{CH}$ (B) $\text{CH}_2=\text{CH}_2$ (C)  (D) 

3. 含有两个相同手性碳原子的 A-A 型化合物有几种立体异构体？

- (A) 2 种 (B) 3 种 (C) 4 种 (D) 5 种

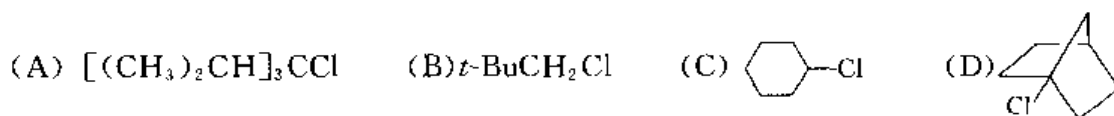
4. 用下列哪种方法可由 1-烯烃制得伯醇？

- (A) H_2O (B) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$
 (C) ① B_2H_6 /② $\text{H}_2\text{O}_2, \text{OH}^-$ (D) 稀、冷 KMnO_4

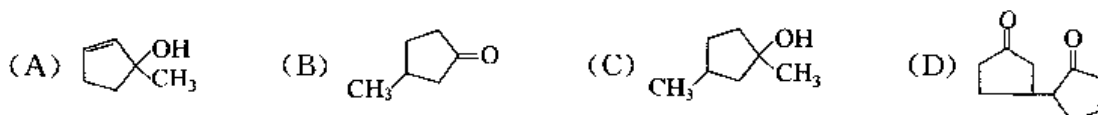
5. 2-戊烯与 NBS 反应的主要产物是

- (A) $\text{BrCH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$ (B) $\text{CH}_3\text{CHBrCH}=\text{CHCH}_3$
 (C) $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{Br}$ (D) $\text{BrCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{Br}$

6. 对氨基苯磺酸的熔点高达 228°C, 是由于该分子
 (A) 对称性好 (B) 形成氢键 (C) 分子量大 (D) 生成内盐
7. 下面哪种化合物与 AgNO₃-醇溶液反应最慢?



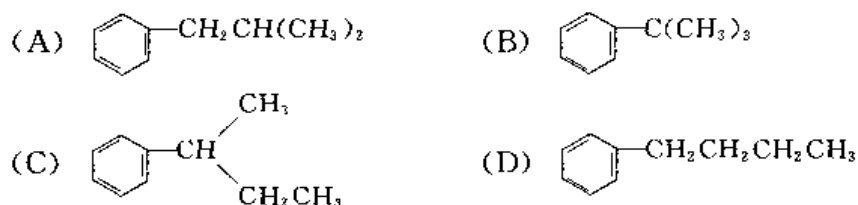
8. α,β-环戊烯酮与二甲基酮锂反应的产物是



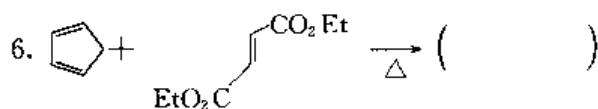
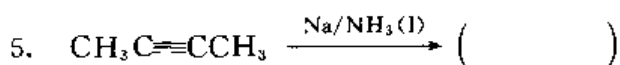
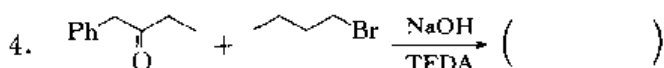
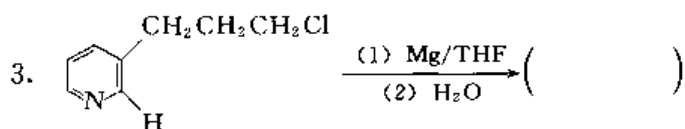
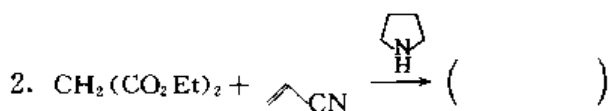
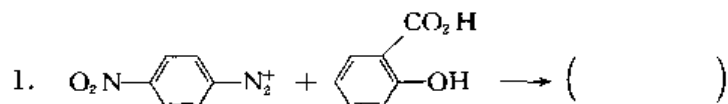
9. 化合物 Ph₃P 的名称为

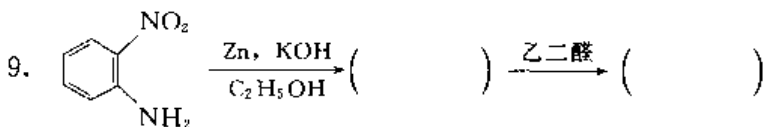
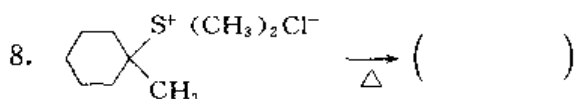
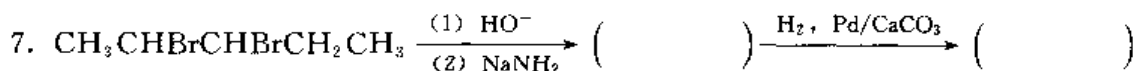


10. 苯与(CH₃)₂CHCH₂Cl 在无水 AlCl₃ 作用下主要生成什么产物?



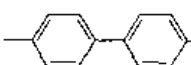
二、填空题 (每小题 3 分, 共 30 分, 写主要产物; 若有立体结构, 请标明)

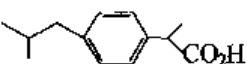




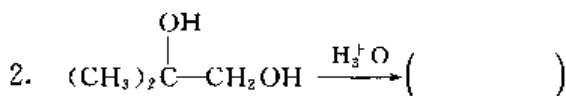
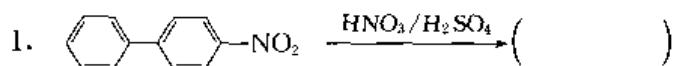
三、合成题 (每题 6 分, 共 18 分)

1. 由丙酮合成新戊酸 $(\text{CH}_3)_3\text{CCO}_2\text{H}$

2. 由苯及 C_4 以下原料合成  COCH_3

3. 由苯及 C_4 以下原料合成  CO_2H

四、机理题 (每题 5 分, 共 10 分, 需写出主要产物及形成过程)



五、推测结构 (每题 6 分, 共 12 分, 写出分析过程)

1. 乙酰基环己烷的 CHCl_3 溶液用过氧苯甲酸处理 (16h, 25°C) 后生成 A。A 的 $^1\text{H-NMR}$ 数据如下: δ 2.0 (单峰, 3H); δ 4.8 (多峰, 1H), 此外尚有其他质子。IR: 1740cm^{-1} , 1250cm^{-1} ; MS(m/z): 142, 43 (base)。写出 A 的结构及其形成过程。

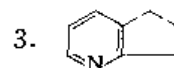
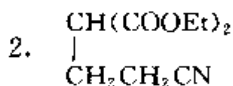
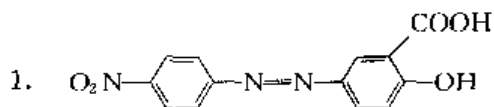
2. 化合物 A ($\text{C}_{10}\text{H}_{11}\text{Br}$) 能使 KMnO_4 溶液褪色, 与 Br_2/CCl_4 作用生成 $\text{C}_{10}\text{H}_{11}\text{Br}_3$ 。A 与 $\text{KMnO}_4/\text{H}_2\text{SO}_4$ 作用得 B 和 C, B 是一个酮, 测知 C 的分子式为 $\text{C}_7\text{H}_5\text{O}_2\text{Br}$, C 进行硝化反应得到两个一硝基化合物。试推出 A、B、C 的结构。

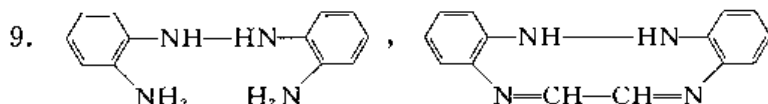
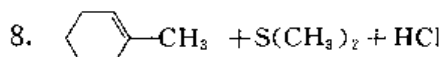
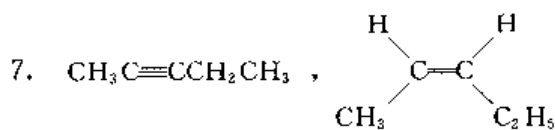
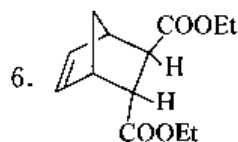
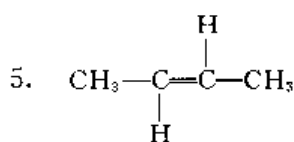
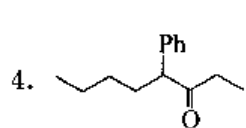
参考答案

一、选择题

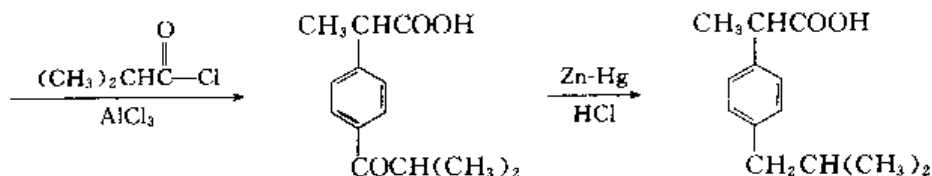
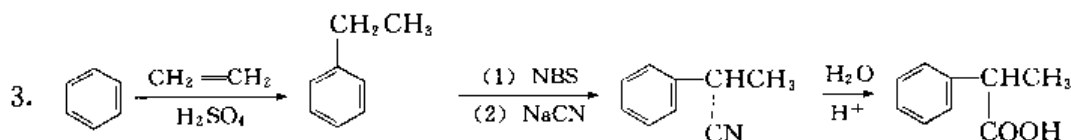
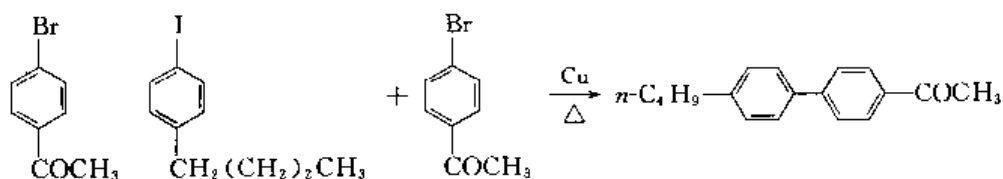
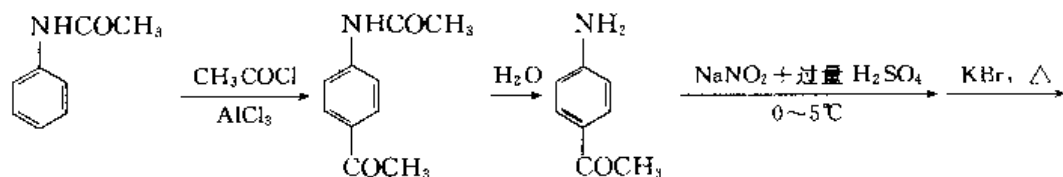
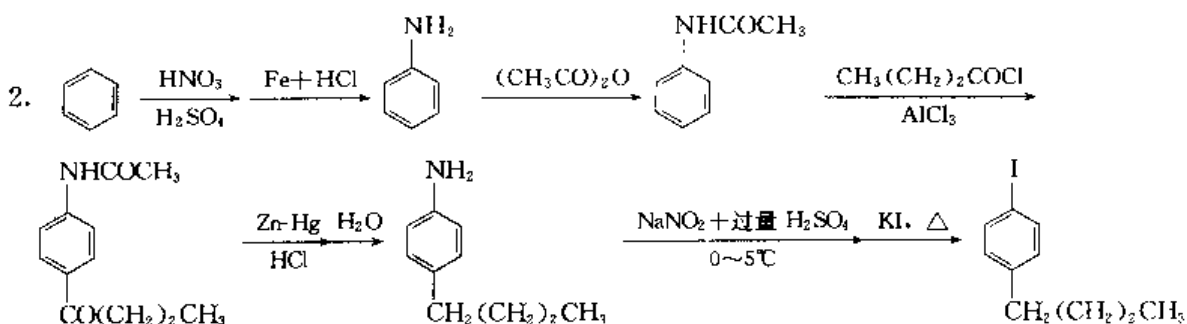
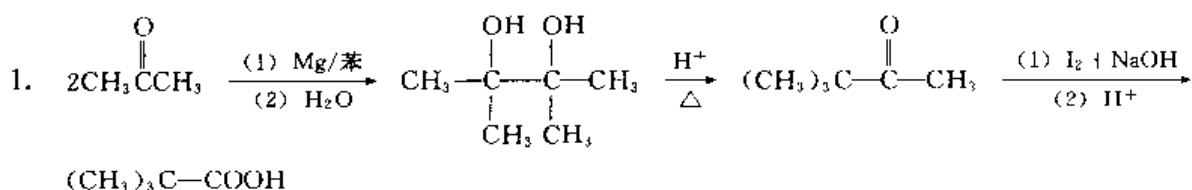
1. (B) 2. (A) 3. (B) 4. (C) 5. (B) 6. (D) 7. (D) 8. (B)
9. (C) 10. (B)

二、填空题

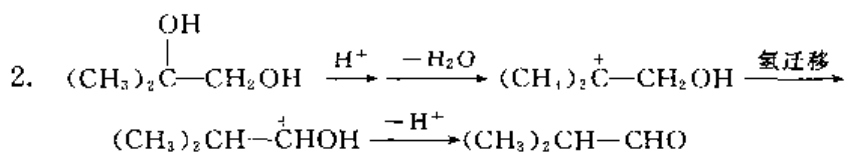
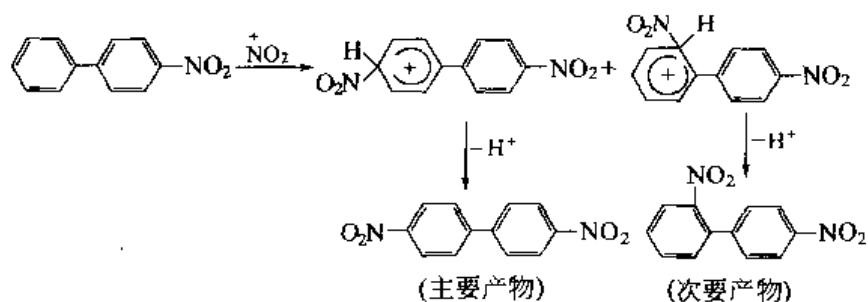
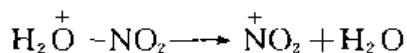
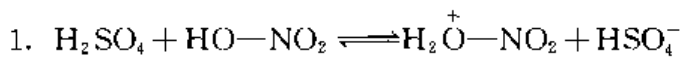




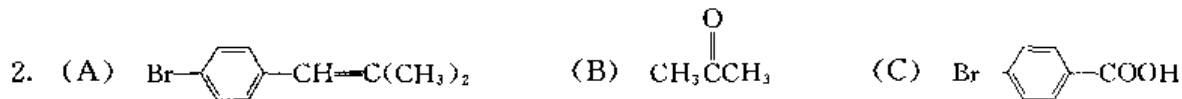
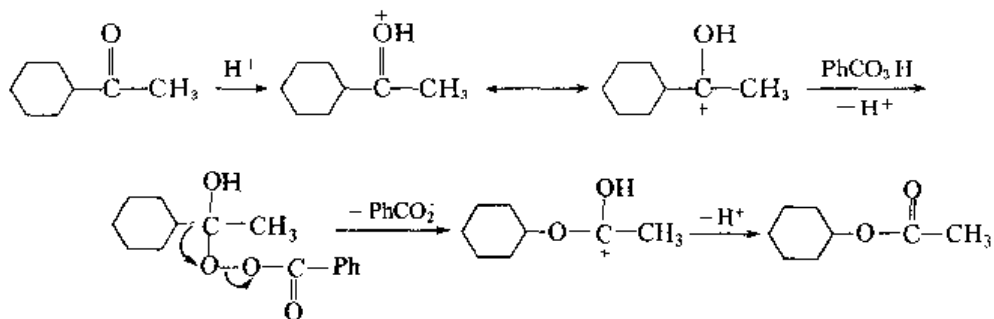
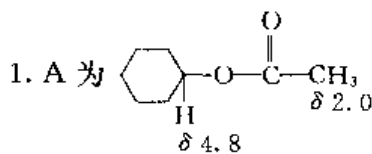
三、合成题



四、机理题

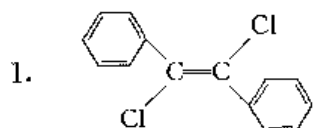


五、推测结构

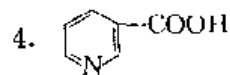
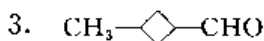
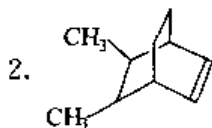


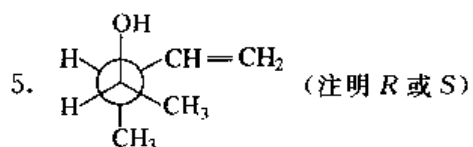
模拟试题 30

一、命名下列化合物 (5分)



(写出顺/反或E/Z各称)

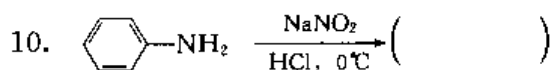
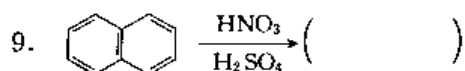
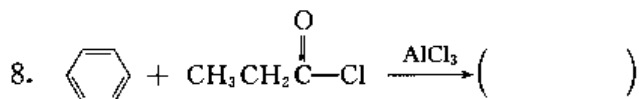
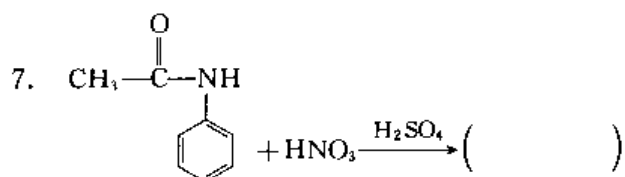
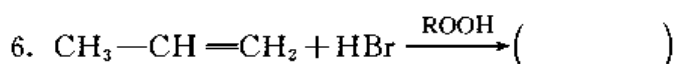
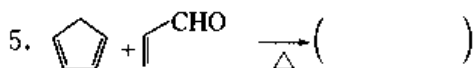
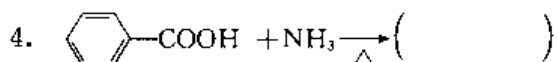
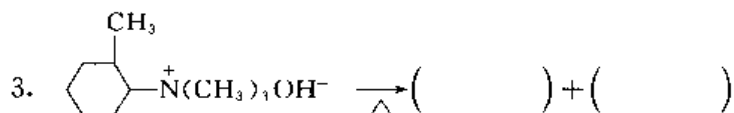
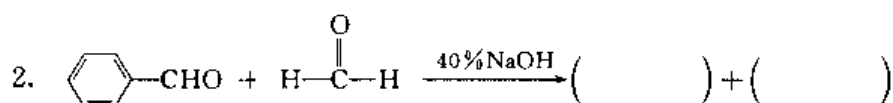
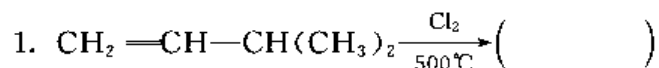




二、写出下列化合物的构造式 (5 分)

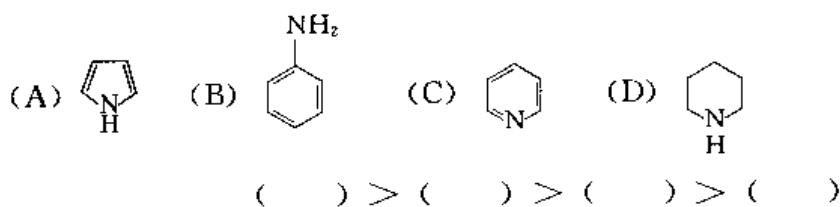
1. 对-仲丁基氯化苧 2. β -氯蒽醌 3. 对-(N,N-二甲氨基)偶氮苯
4. α -噻吩磺酸 5. 3-甲基-3-戊烯-1-炔

三、填空完成反应式 (10 分)

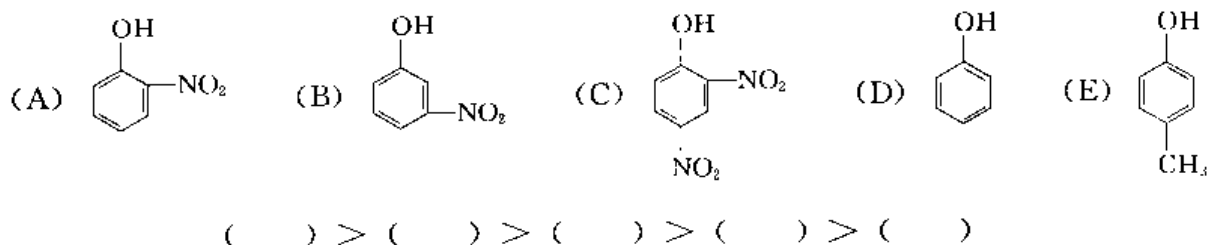


四、理化性质比较 (10 分)

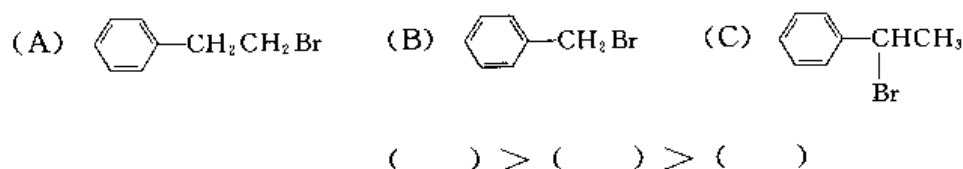
1. 比较下列化合物的碱性



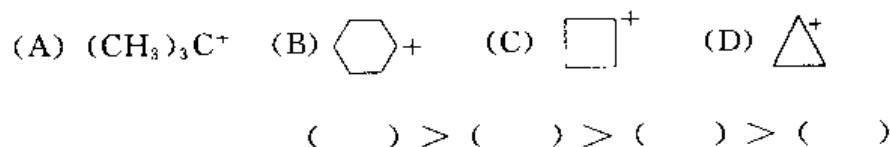
2. 比较下列化合物的酸性



3. 将下列化合物按 S_N1 反应的速率大小排列

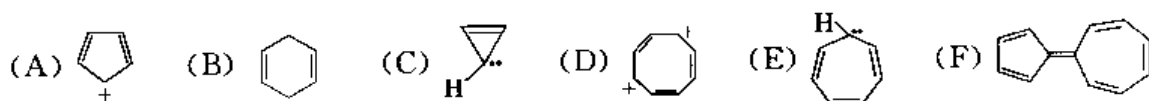


4. 比较下列碳正离子的稳定性

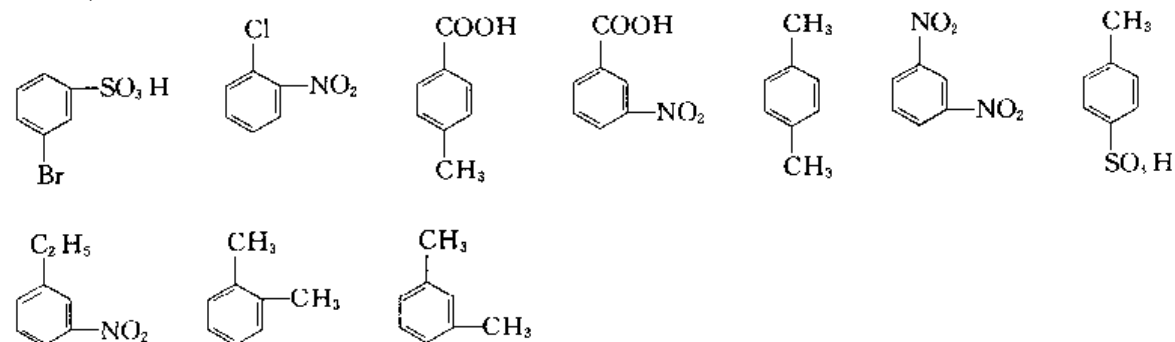


五、基本概念 (15分)

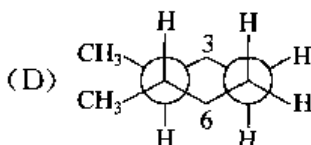
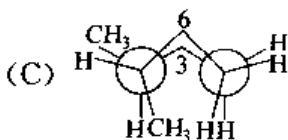
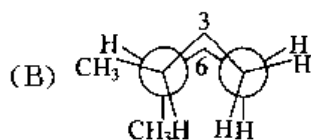
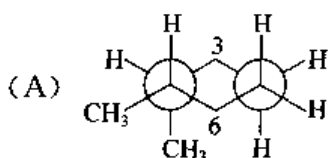
1. 指出下列化合物哪些有芳香性



2. 用箭头表示第三个取代基进入苯环的位置



3. 下述 4 个 1,2-二甲基环己烷的 Newman 投影式中, 哪个是最稳定的构象?



六、推断下列反应的机理 (5分)

当乙烯气体通入含有氯化钠和溴的水溶液时, 产生 $\text{BrCH}_2\text{CH}_2\text{Br}$ 、 $\text{BrCH}_2\text{CH}_2\text{OH}$ 和 $\text{BrCH}_2\text{CH}_2\text{Cl}$, 写出其机理。

七、用化学方法分别鉴别下列各组化合物 (10分)

1. 对甲基苯胺 N-甲基苯胺 N,N-二甲基苯胺
2. 戊醛 2-戊酮 3-戊酮

八、混合物分离 (10分)

1. 用化学方法分离苯甲酸, 丁醚, 环己酮和苯酚。
2. 除去苯甲醇中的少量苯甲醛和苯甲酸。

九、推导下列各组未知化合物的构造式 (10分)

1. 化合物 A (C_9H_{16}) 催化加氢时得到化合物 B (C_9H_{20}), 将 A 进行臭氧化反应, 然后还原水解, 得到等物质的量的 CH_3CHO 、 $(\text{CH}_3)_2\text{CHCHO}$ 和丙酮醛 CH_3COCHO , 试推导化合物 A 的可能构造式。

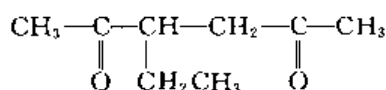
2. 有 A、B、C 和 D 4 种化合物, 分子式均为 $\text{C}_7\text{H}_{14}\text{O}_2$, 其中 A 易与 Lucas 试剂 ($\text{ZnCl}_2 + \text{HCl}$) 作用, 也与 Tollens 试剂反应 (银镜反应)。A 脱水后经臭氧化水解所得的产物都发生碘仿反应。B 也易和 Lucas 试剂反应, 并发生碘仿反应, 当 B 脱水后, 臭氧化水解产物不与 Tollens 试剂作用。C 和 D 的红外光谱显示都有酯的羰基, 核磁共振表明 C 有 3 种不同的质子, D 有 4 种不同的质子, C 的水解产物之一可以发生碘仿反应, D 的水解产物之一与 Tollens 试剂作用。试写出 A、B、C 和 D 的构造式。

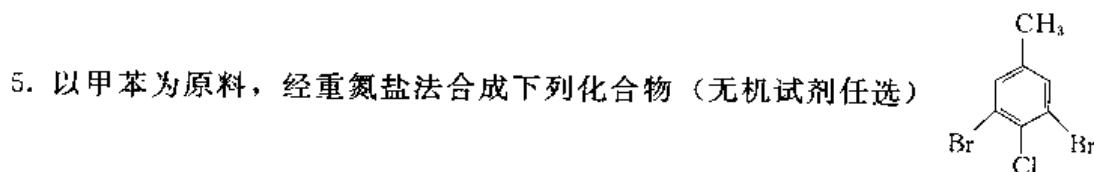
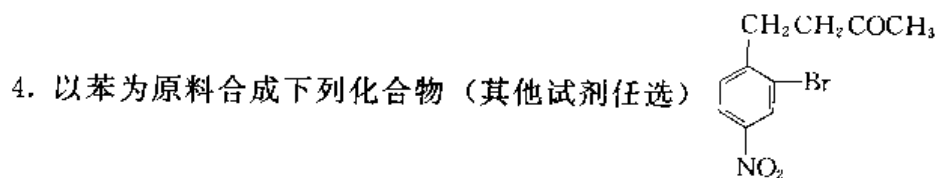
十、有机化合物的合成 (20分)

1. 以丙烯为原料合成以下化合物 (无机试剂任选) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{CH}_3)_2$

2. 由乙醛和丙烯醛合成 (无机试剂任选)

3. 以 C_4 以下的醇为原料, 经乙酰乙酸乙酯法合成下列化合物 (无机试剂任选)



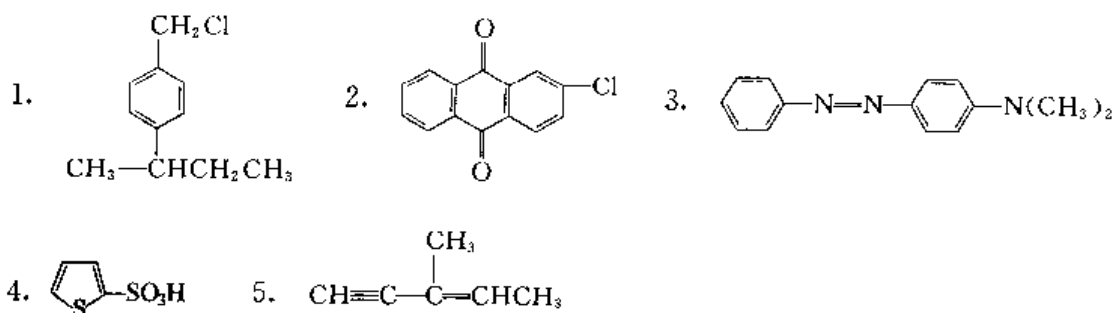


参考答案

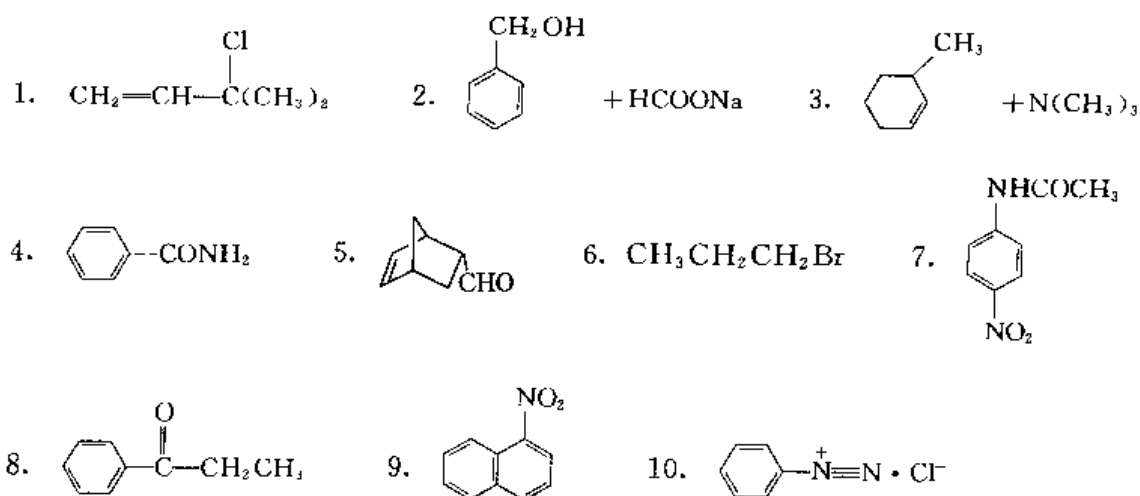
一、命名

- 反-1,2-二苯-1,2-二氯乙烯
- 5,6-二甲基双环 [2.2.2]-2-辛烯
- 3-甲基环丁基甲醛
- 3-吡啶甲酸
- (2R, 3R)-3-甲基-4-戊烯-2-醇

二、写出下列化合物的构造式



三、填空完成反应式

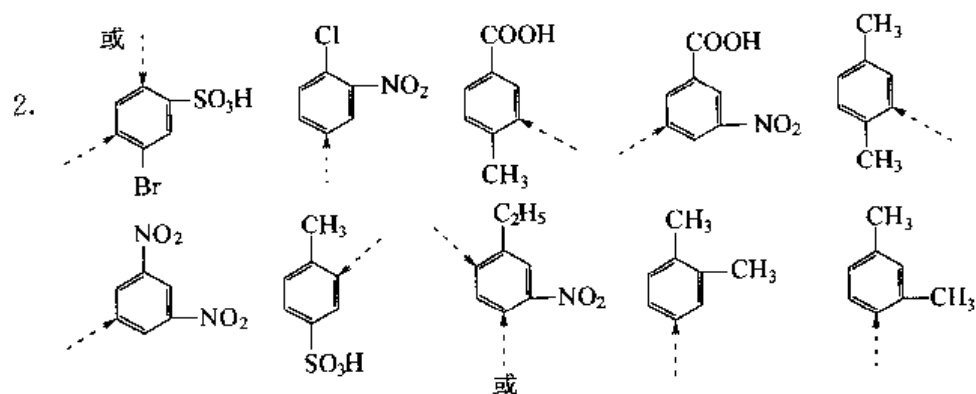


四、理化性质比较

- (D) > (C) > (B) > (A)
- (C) > (B) > (A) > (D) > (E)
- (C) > (B) > (A)
- (A) > (B) > (C) > (D)

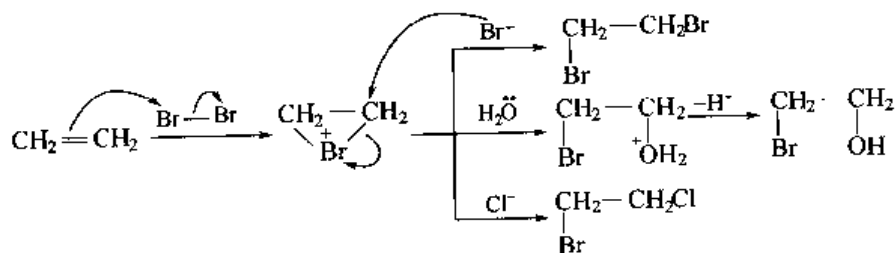
五、基本概念

1. (D)、(F) 有芳香性

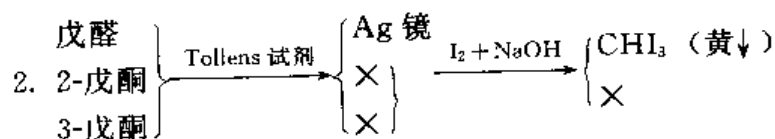
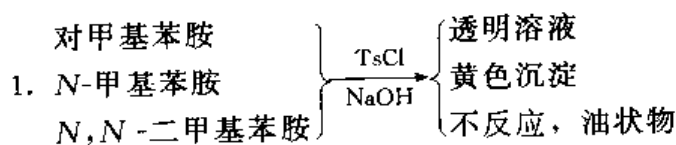


3. (D) 最稳定。

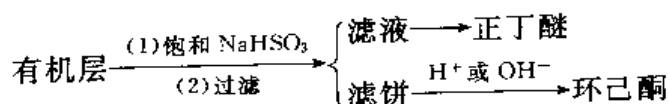
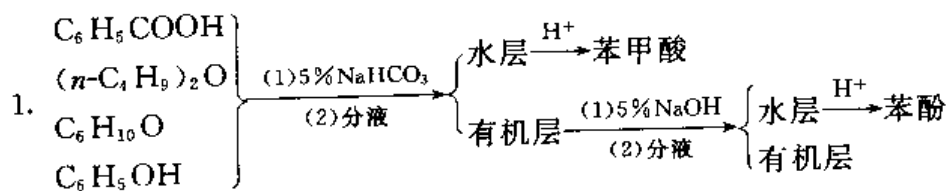
六、推断下列反应的机理

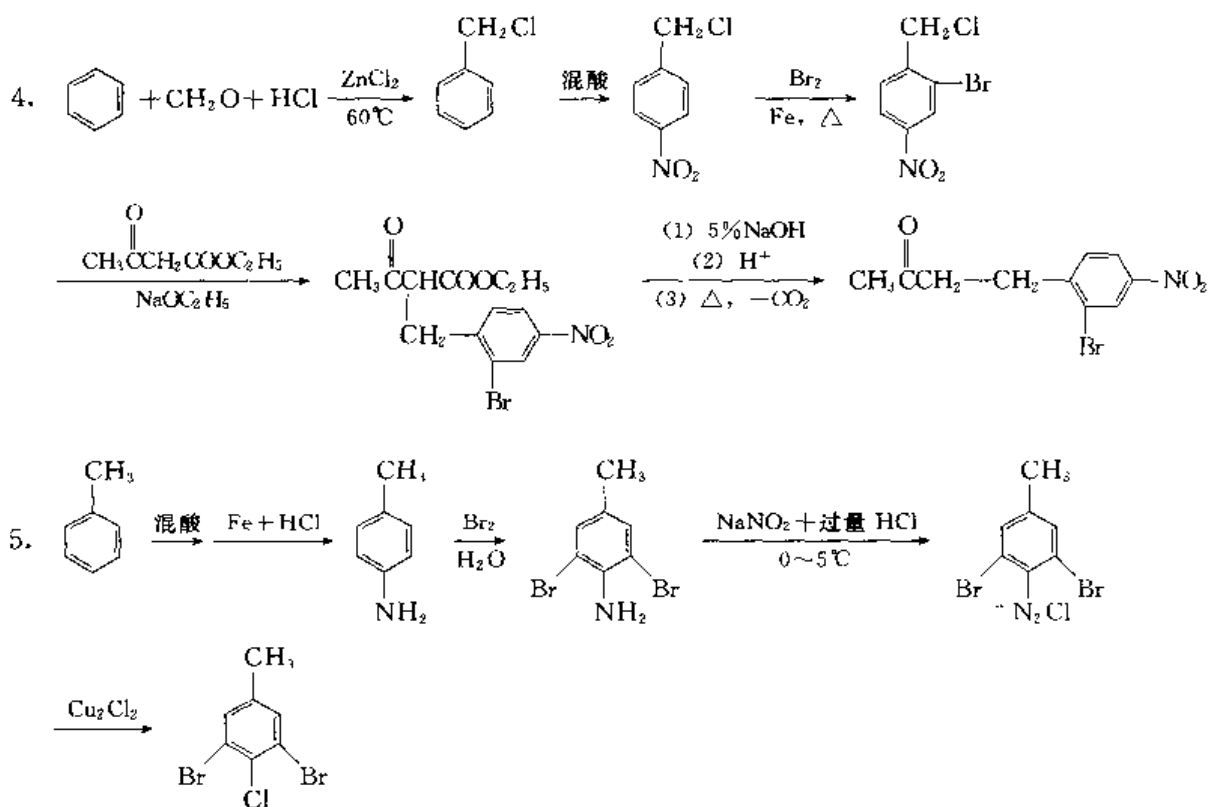


七、鉴别



八、混合物分离





模拟试题 31

一、选择题 (按题意选择正确的答案) (12 分)




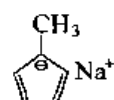
1. 二氯溴苯有几个异构体?

- (A) 3 个 (B) 2 个 (C) 5 个 (D) 6 个

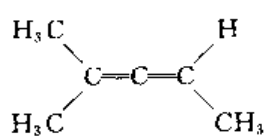
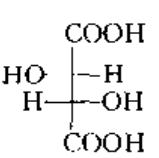
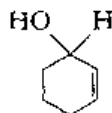
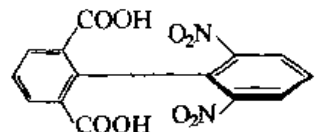
2. 在 CH_3I 的亲核取代反应中, 哪种离子的亲核性最强?

- (A) CH_3COO^- (B) $\text{CH}_3\text{CH}_2\text{O}^-$ (C) OH^- (D) $\text{C}_6\text{H}_5\text{O}^-$

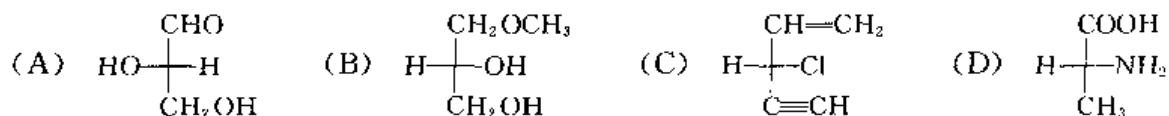
3. 下列各化合物中哪些具有芳香性?

- (A)  (B)  (C)  (D) 

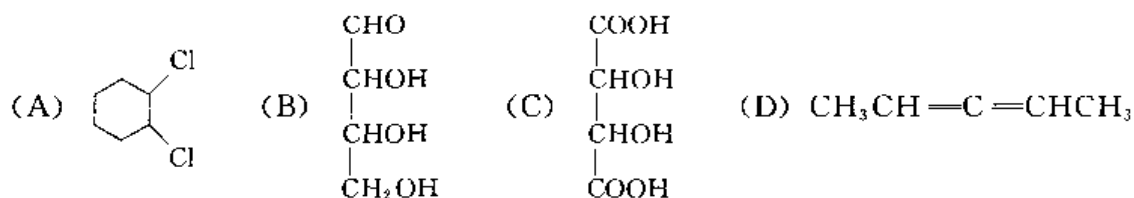
4. 下列化合物中具有手性的是

- (A)  (B)  (C) 
- (D) 

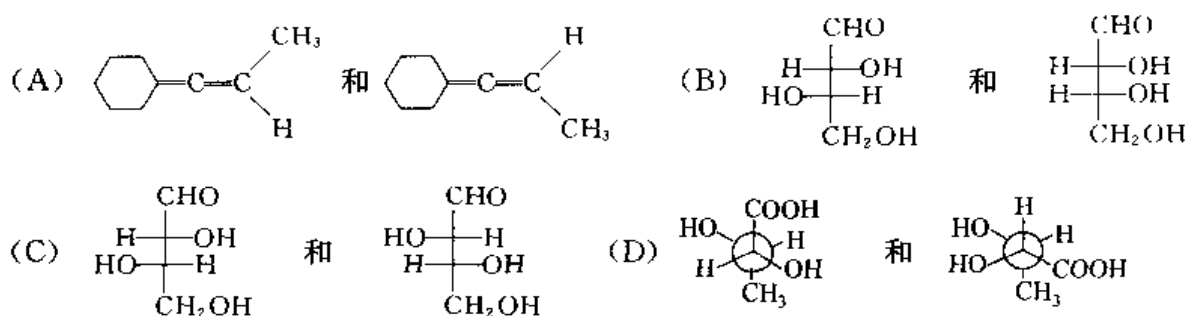
5. 下列 Fischer 投影式中, 用 R 命名的化合物是



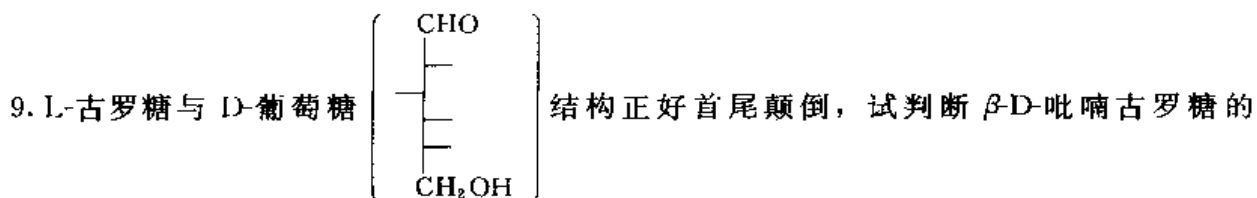
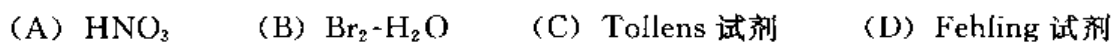
6. 下列化合物中, 具有 3 个立体异构体的化合物是



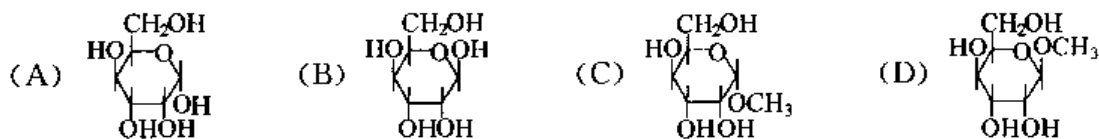
7. 下列各组化合物中, 属于对映异构体的化合物是



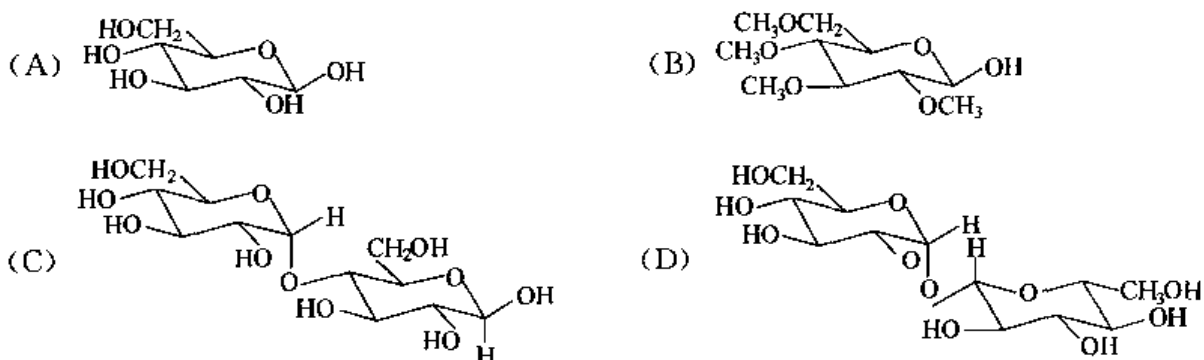
8. 区别己醛糖和己酮糖, 可用下列哪种试剂?

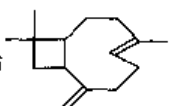


Haworth 式是

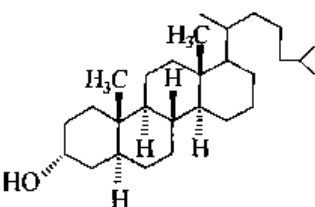


10. 不能与 Tollens 试剂反应的非还原糖是



11. 划出石竹烯  中的异戊二烯单位，它属于哪一类萜？

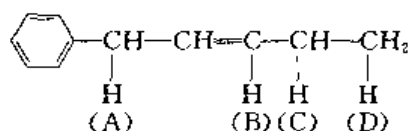
- (A) 单萜 (B) 倍半萜 (C) 双萜 (D) 三萜

12. 甾族化合物  的命名是

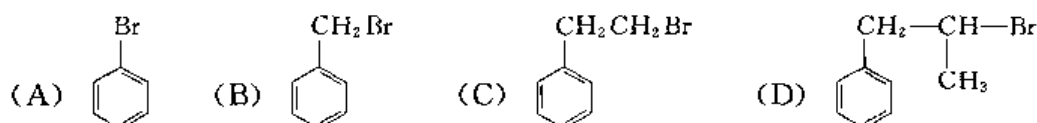
- (A) 5 α -胆甾烷-3 α -醇 (B) 5 β -胆甾烷-3 α -醇
(C) 5 α -胆甾烷-3 β -醇 (D) 5 β -胆甾烷-3 β -醇

二、比较题 (按题意填写正确答案) (8分)

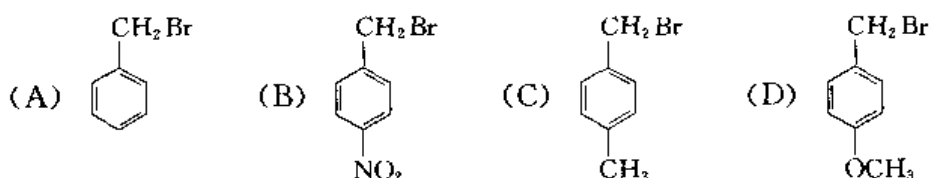
1. 下列化合物中的氢原子，在光照溴代反应中被溴取代的速率由快到慢为



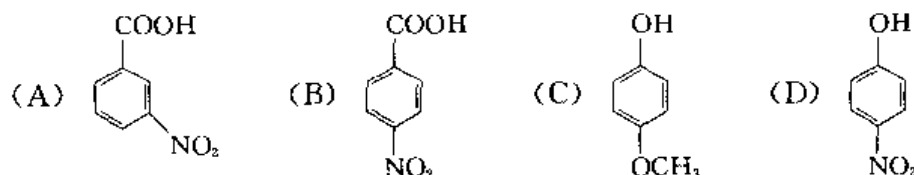
2. 在无水丙酮中，下列各化合物与 NaI 进行 S_N2 反应时，反应速率由快到慢为



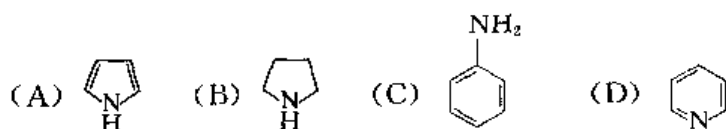
3. 下列各化合物与甲酸进行反应时，反应速率由快到慢为



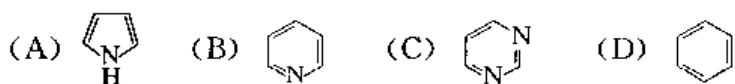
4. 下列化合物中，酸性由强到弱为



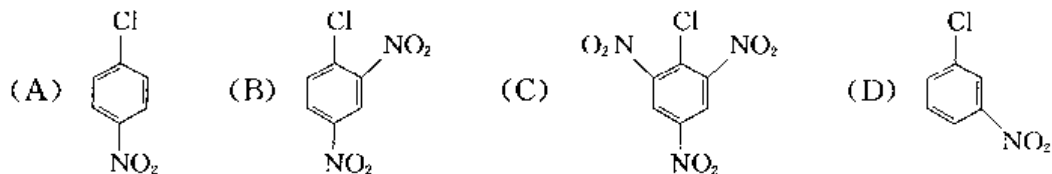
5. 下列化合物中，碱性由强到弱为



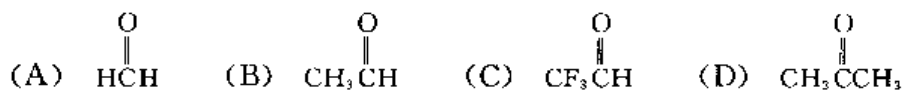
6. 下列化合物进行亲电取代反应由易到难为



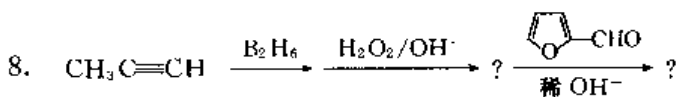
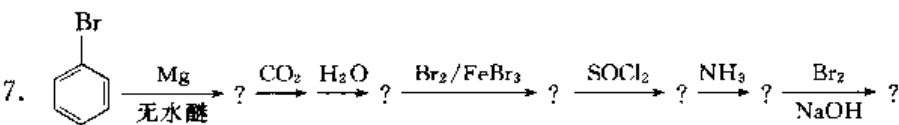
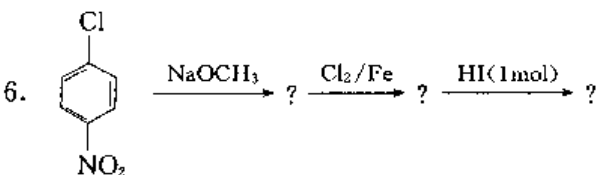
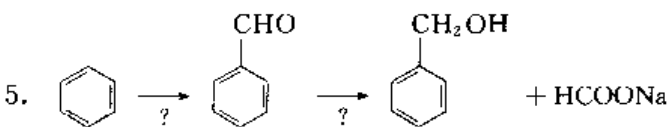
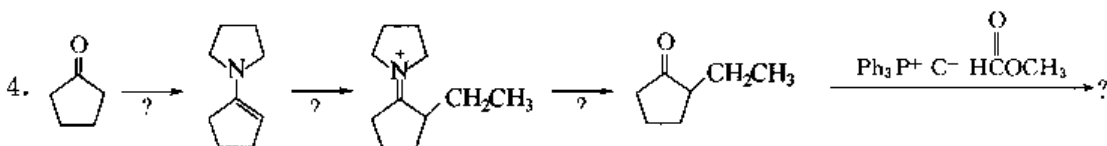
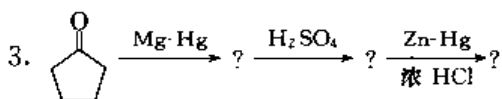
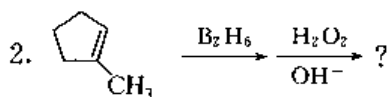
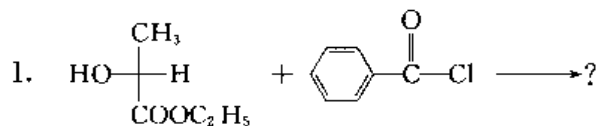
7. 下列化合物与碱反应生成酚时, 反应速率由快到慢为

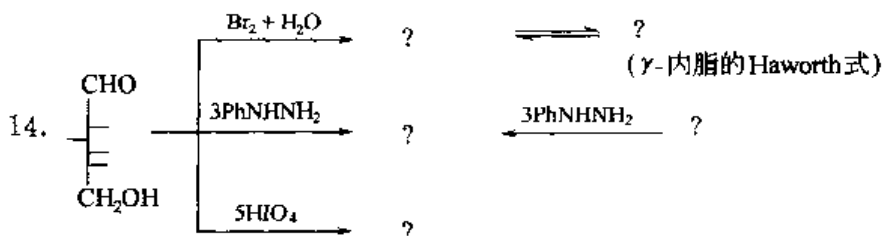
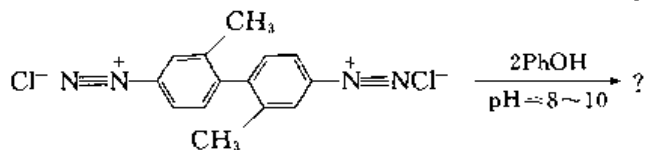
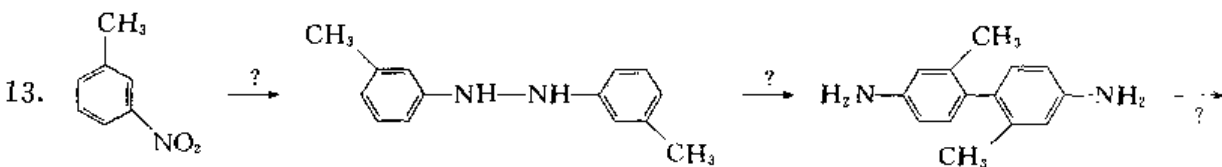
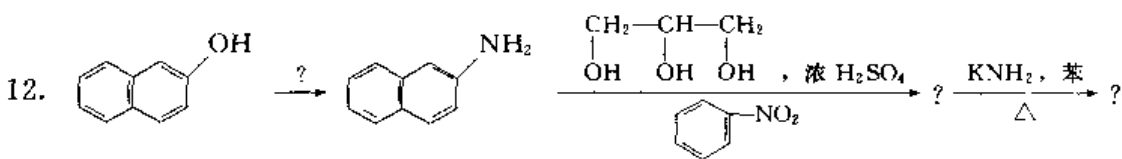
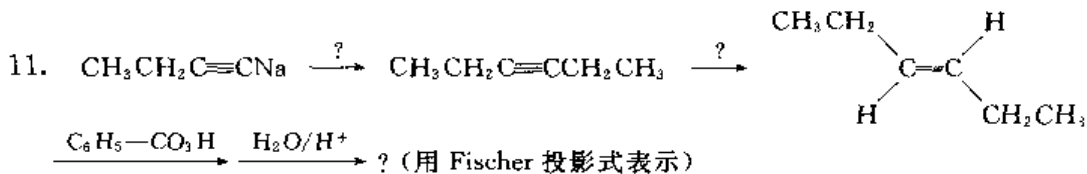
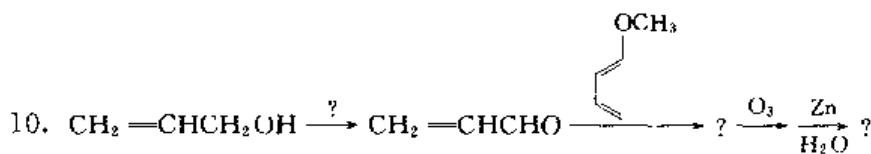
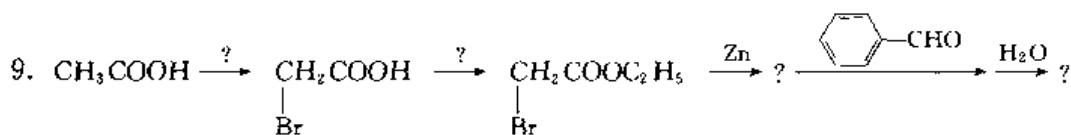


8. 下列化合物进行亲核加成反应时, 反应速率由快到慢为



三、完成下列反应 (写出试剂条件或主要产物) (44 分)

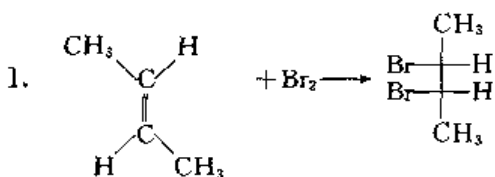


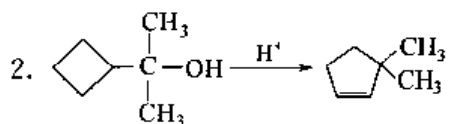


四、用简单的化学方法区别下列各组化合物 (6分)

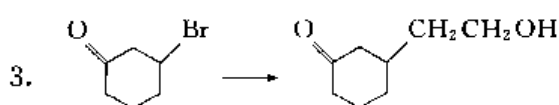
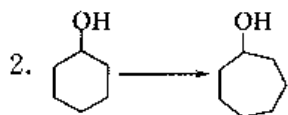
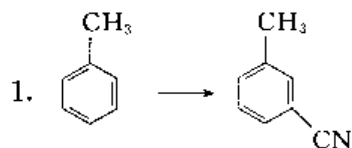
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

五、试用反应机理 (反应各步反应过程) 说明下列实验结果 (6分)

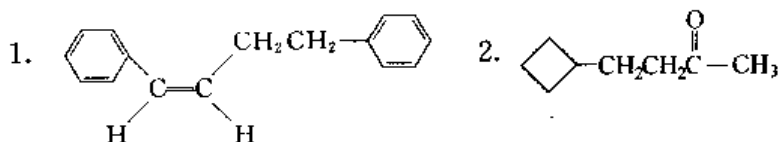




六、完成下列转换 (可用所需的有机和无机试剂) (9 分)



七、以苯和乙醇为有机原料, 合成下列化合物 (12 分)



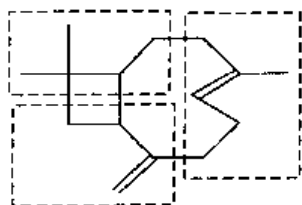
八、推测结构题 (3 分)

用 HNO_3 氧化己醛糖 A, 得到一光学活性的糖二酸 B, A 经递降得到一个戊醛糖 C, 它经 HNO_3 氧化得到一个无光学活性的糖二酸 D。当 A 经过一系列反应, 使 C_1 变成 $-\text{CH}_2\text{OH}$, C_6 变成 $-\text{CHO}$, 仍然得到 A。假定这个糖是 D-构型的糖。试写出 A、B、C、D 的结构式。

参考答案

一、选择题

1. (D) 2. (B) 3. (A) 和 (D) 4. (B) 和 (C) 5. (B) 和 (D) 6. (A) 和 (C) 7. (C) 8. (B) 9. (B) 10. (D) 11. (B) 划分异戊二烯单位



12. (A)

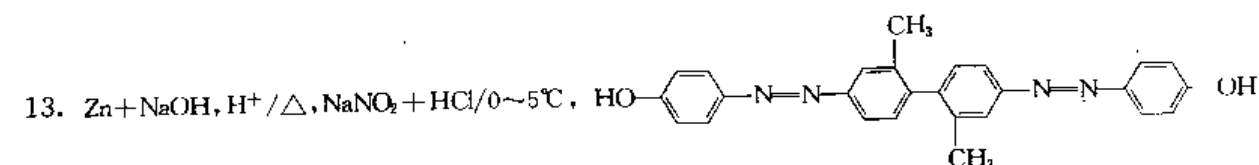
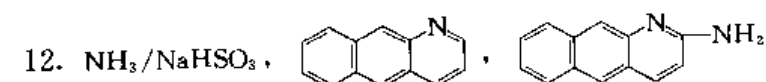
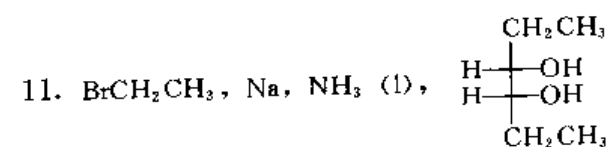
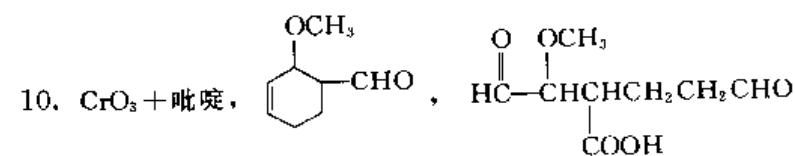
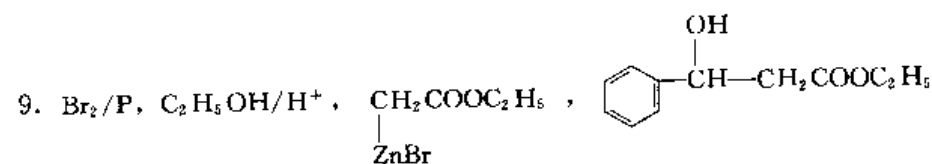
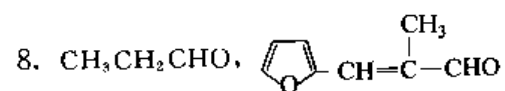
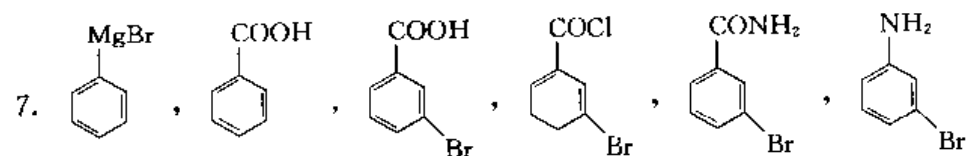
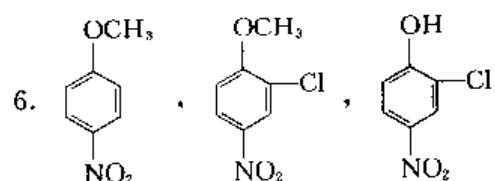
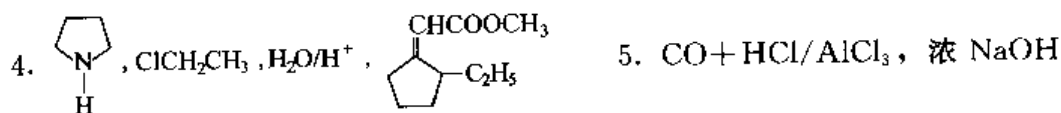
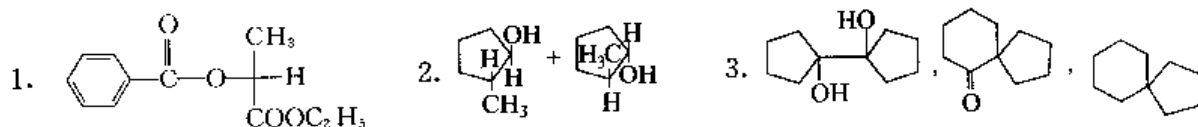
二、比较题

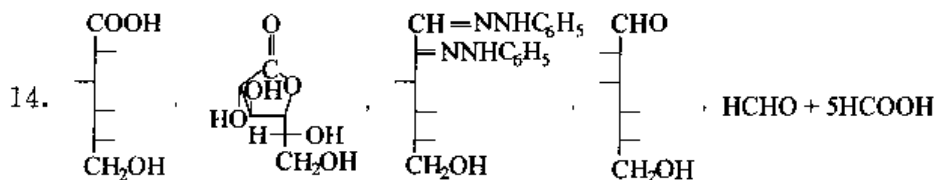
1. (A) > (C) > (D) > (B) 2. (B) > (C) > (D) > (A)
 3. (D) > (C) > (A) > (B) 4. (B) > (A) > (D) > (C)
 5. (B) > (D) > (C) > (A) 6. (A) > (D) > (B) > (C)

7. (C) > (B) > (A) > (D)

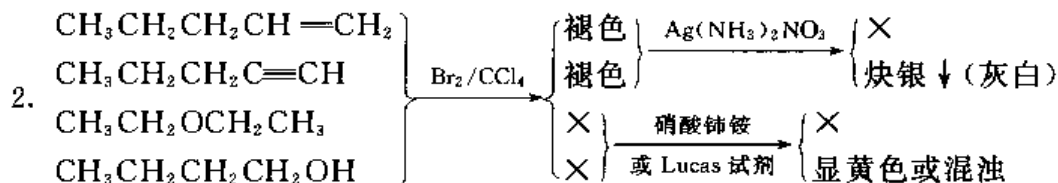
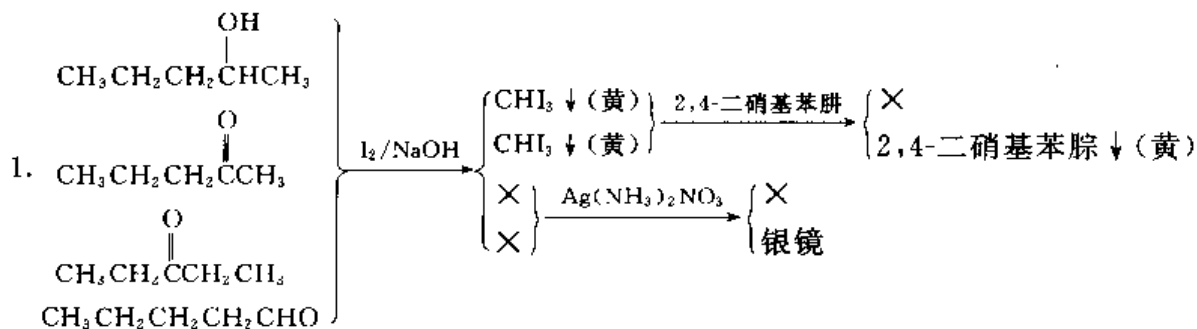
8. (C) > (A) > (B) > (D)

三、完成下列反应



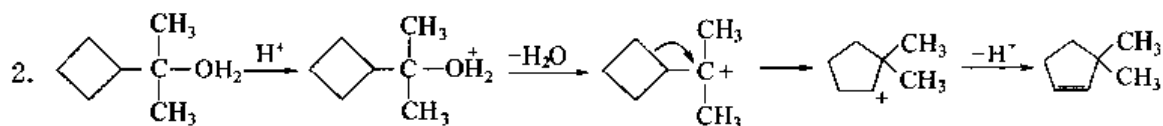
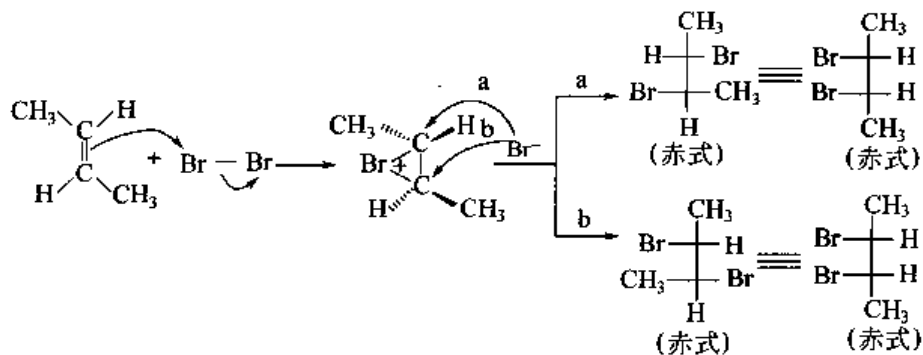


四、区别化合物

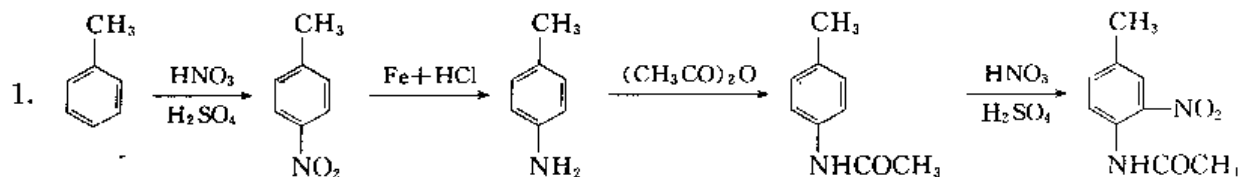


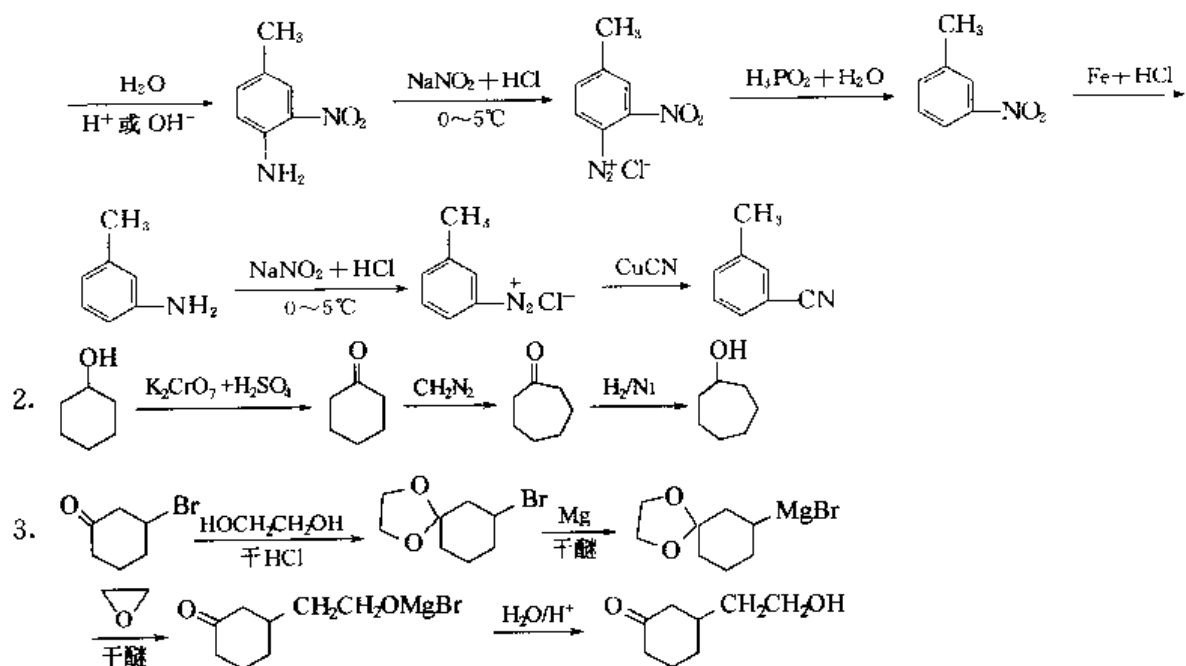
五、反应机理

1.

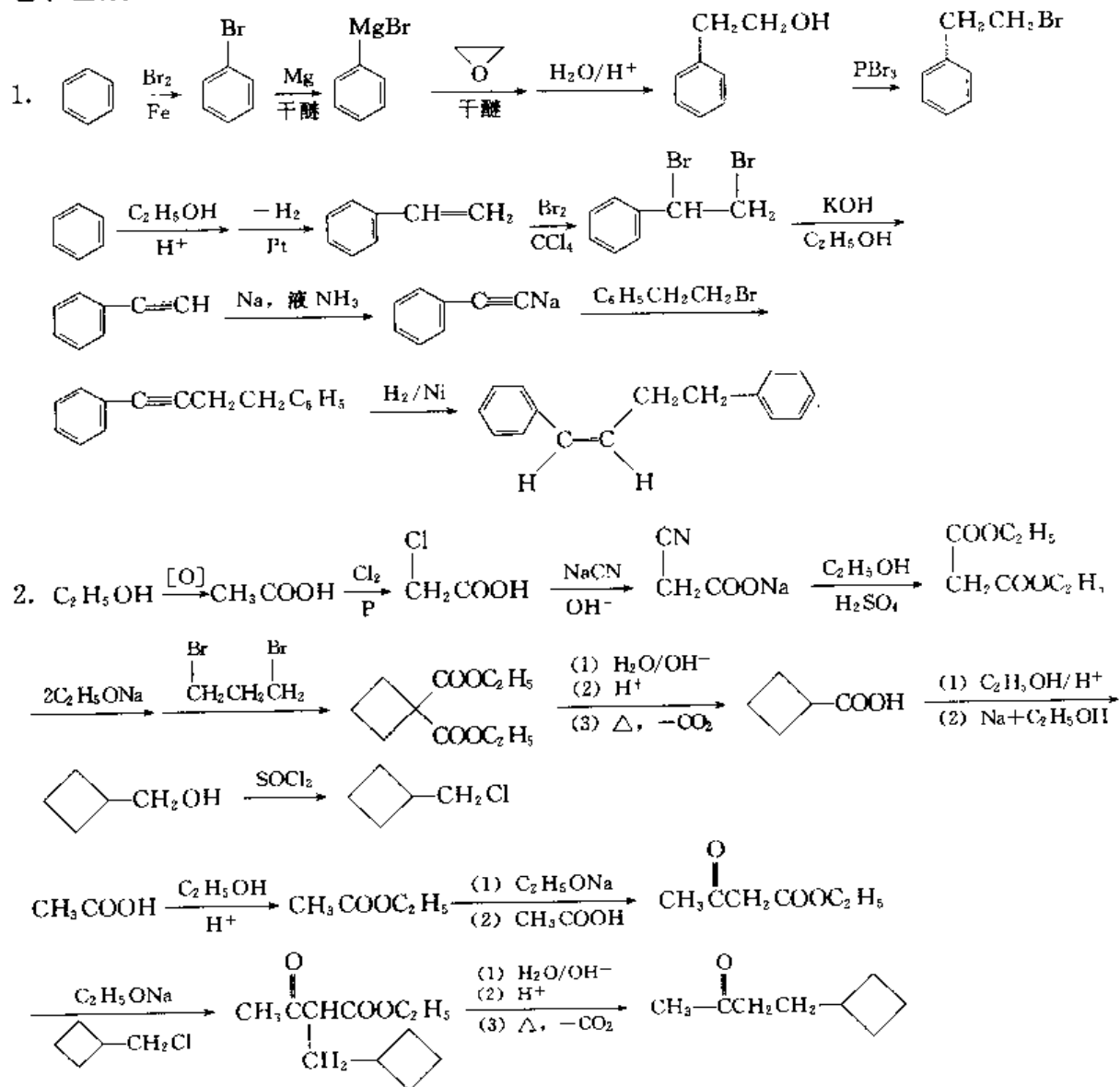


六、完成转换

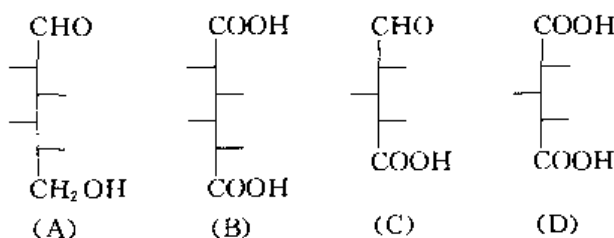




七、合成



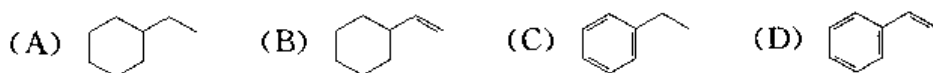
八、推测结构



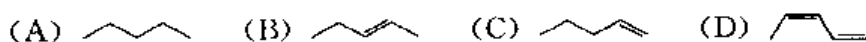
模拟试题 32

一、选择题 (20 分)

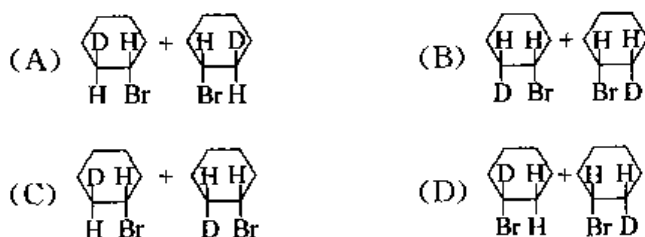
1. 下列 4 种化合物的 IR 谱在 3000cm^{-1} 以上没有吸收的是 ()



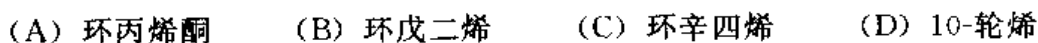
2. $\text{CH}_3\text{C}\equiv\text{CH}-\text{CH}=\text{CH}_2$ Lindlar 催化 (Pd/BaSO_4) 加氢的产物是 ()



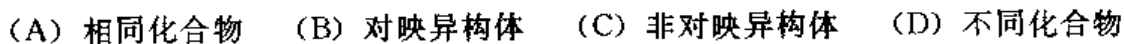
3. 环己烯 + DBr \rightarrow 主要产物是 ()

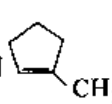
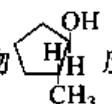


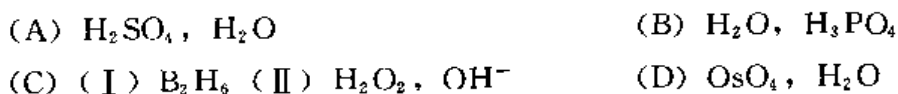
4. 下列哪种化合物具有芳香性? ()



5. $\begin{matrix} \text{CH}_3 \\ | \\ \text{H}-\text{C}-\text{Br} \\ | \\ \text{C}_2\text{H}_5 \end{matrix}$ 与 $\begin{matrix} \text{H} \\ | \\ \text{H}_5\text{C}_2-\text{C}-\text{CH}_3 \\ | \\ \text{Br} \end{matrix}$ 这对化合物的相互关系是 ()



6. 由  转化为产物  应采取的试剂为 ()

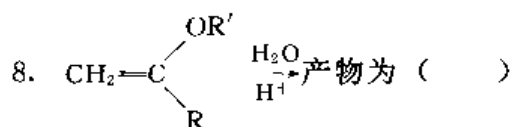


7. $\text{CH}_3(\text{CH}_2)_5\text{CHO} \rightarrow \text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH}$ 应选择的试剂是 ()



(C) (I)Mg(Hg)(II)H₂O

(D) Na+C₂H₅OH



(A) CH₃COR+R'OH

(B) CH₃COR'+ROH

(C) $\text{CH}_3-\underset{\text{R}}{\text{CH}}-\text{OR}'$

(D) $\text{CH}_2-\underset{\text{R}}{\text{CH}}-\text{OR}'$
 | |
 OH R

9. PhCH₂COCl 经 (1) CH₂N₂/Et₂O 处理, (2) Ag₂O/H₂O 处理, 再酸化水解, 主要产物是 ()

(A) PhCOOH+CH₄

(B) PhCOOH+CH₃OH

(C) PhCH₂COOH

(D) PhCH₂CH₂COOH

10. 吡啶与 NaNH₂ 液氨反应生成 2-氨基吡啶, 反应历程属于 ()

(A) 吡啶负离子历程

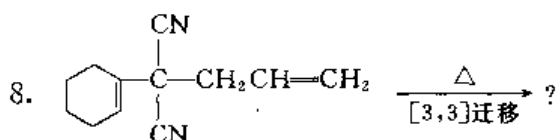
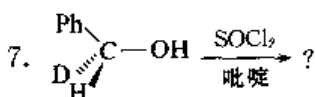
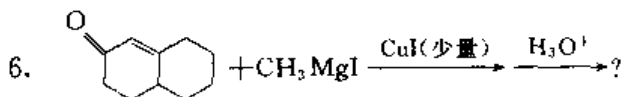
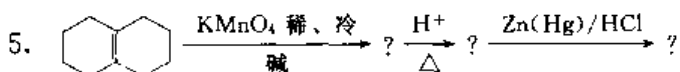
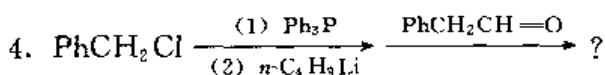
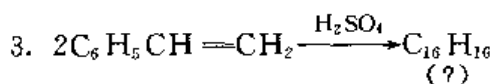
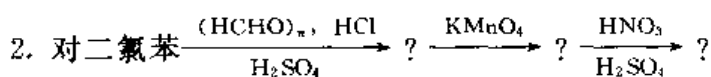
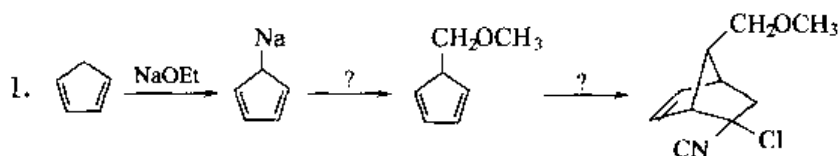
(B) 吡啶炔历程

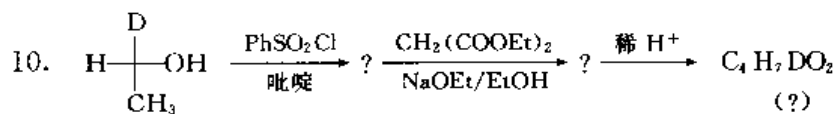
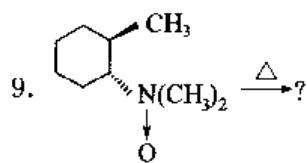
(C) 吡啶正离子历程

(D) 自由基历程

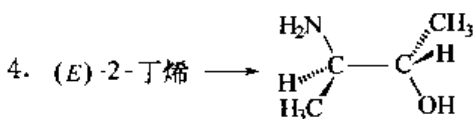
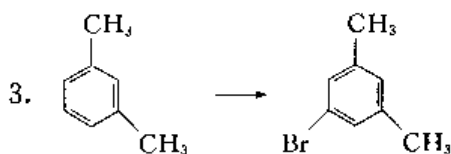
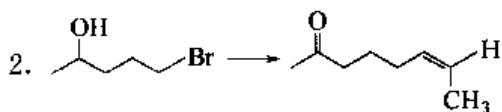
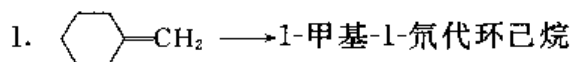
由基历程

二、填空题 (20 分)



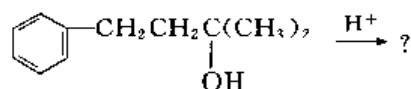


三、合成题 (20 分)

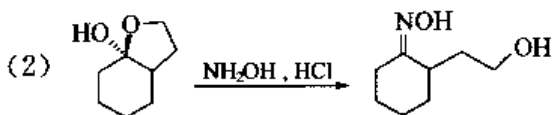
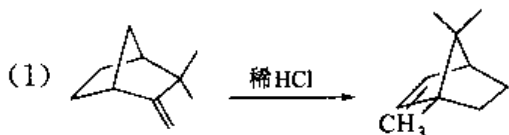


四、机理题 (20 分)

1. 预料下述反应的主要产物，并提出合理的反应机理。



2. 试为下述反应建议合理、可能的分步反应机理。



3. (*Z*)-2-丁烯与(*E*)-2-丁烯分别用过氧酸氧化后进行酸性水解，两者的产物都不旋光，但前者的产物可拆分，而后者却不可拆分。

4. 丙酰胺在 NaOH 中用溴处理，获得乙胺，而用 *N*-甲基丙酰胺进行同样反应却得不到甲乙胺。

五、推结构题 (20分)

1. 测得某烃 A 含 C 88.9%, H 11.1%, 此烃能使 Br_2/CCl_4 褪色, 能吸收 2molH_2 , 与银氨溶液无反应, 与 $\text{KMnO}_4/\text{H}_2\text{SO}_4$ 作用得一种一元酸。将 A 与钠在液氨中还原得 B, B 能与 Cl_2 作用得 C, 将 C 与 KOH/EtOH 作用得 (E)-2-氯-2-丁烯。试推出 A、B 的结构 (注明 Z/E 构型)、C 的 Newman 投影式 (最优势构象)。

2. 用硝酸氧化己醛糖 A, 得到一光活性的糖二酸 B, A 经递降得到一个戊醛糖 C, 它经 HNO_3 氧化得到一个无光活性的糖二酸 D。当 A 经过一系列反应, 使 C_1 变成 $-\text{CH}_2\text{OH}$, C_6 变成醛基, 仍然得到 A。假定这个糖是 D-构型的糖, 试推测从 A 到 D 的结构。

3. 一中性化合物 $\text{C}_7\text{H}_{13}\text{O}_2\text{Br}$ 不产生脎或苯腙衍生物, IR 谱显示在 $2850\sim 2950\text{cm}^{-1}$ 有一些吸收峰, 但在 3000cm^{-1} 以上没有, 另一强吸收峰在 1740cm^{-1} 。 $^1\text{H-NMR}$ 谱显示如下的信号: $\delta 1.0$ (三重峰, 3H), $\delta 1.3$ (二重峰, 6H), $\delta 2.1$ (多重峰, 2H), $\delta 4.2$ (三重峰, 1H), $\delta 4.6$ (多重峰, 1H)。试推断其结构并指认各谱峰的归属。

4. 某未知化合物的 IR、 $^1\text{H-NMR}$ 和 MS 的数据如下所示。

IR: 3300cm^{-1} (弱峰), $2850\sim 2950\text{cm}^{-1}$ (强峰), 1460cm^{-1} (强峰), $1380\sim 1370\text{cm}^{-1}$ (强峰, 双峰), $1175\sim 1140\text{cm}^{-1}$ (中等偏强, 双峰), 700cm^{-1} (强峰);

$^1\text{H-NMR}$: $\delta 1.0$ (双重峰, 12H), $\delta 2.9$ (七重峰, 2H), $\delta 0.6$ (单峰, 1H);

MS: $m/z 101(\text{M}^+)$ (7%), $m/z 86$ (80%), $m/z 44$ (100%)。

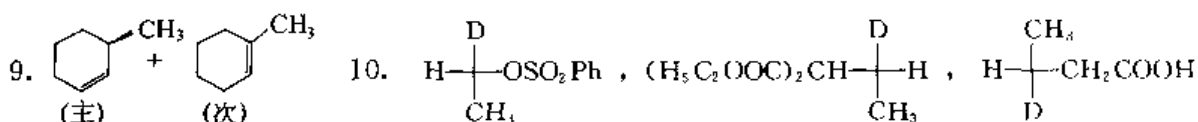
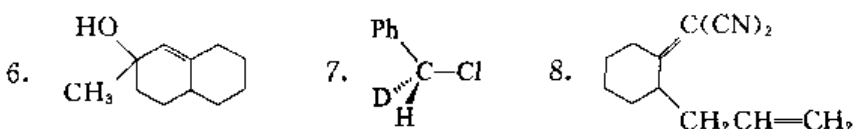
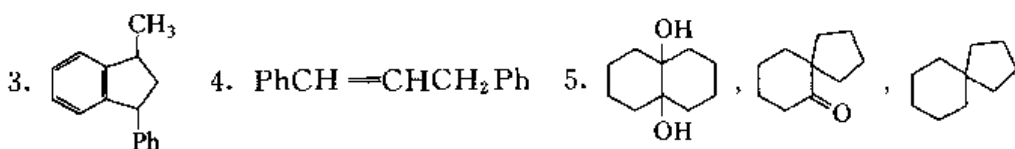
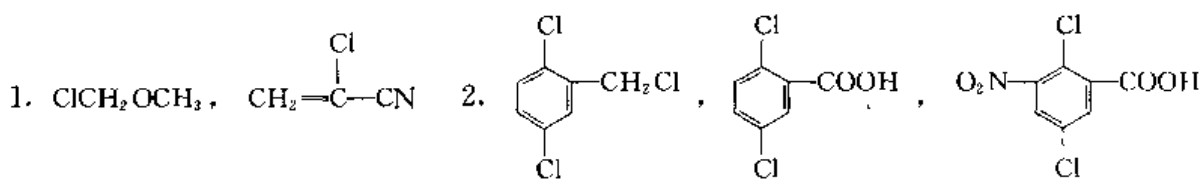
提出该化合物的结构, 并作简要的说明。

参考答案

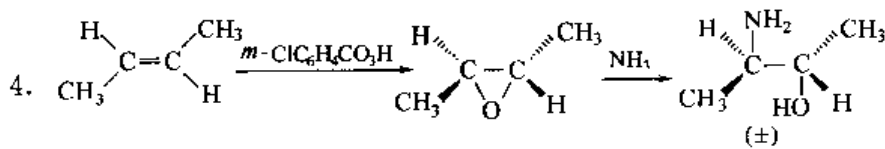
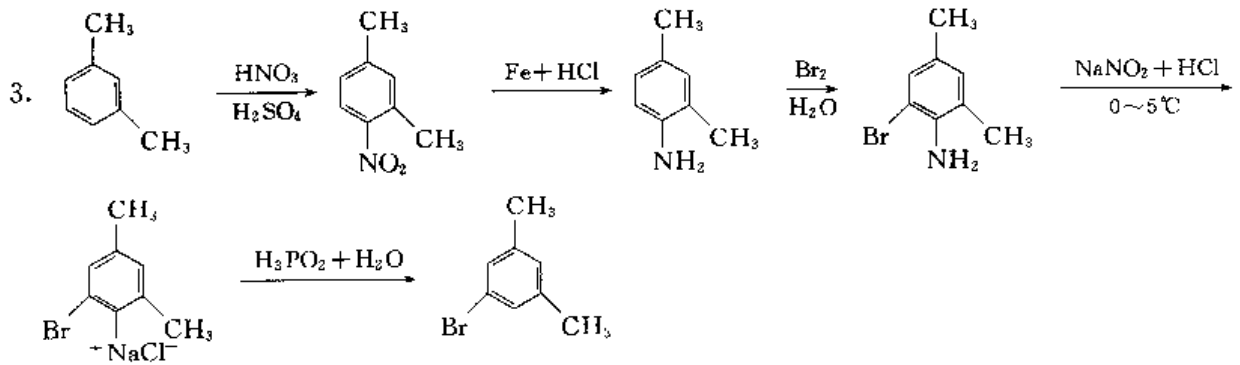
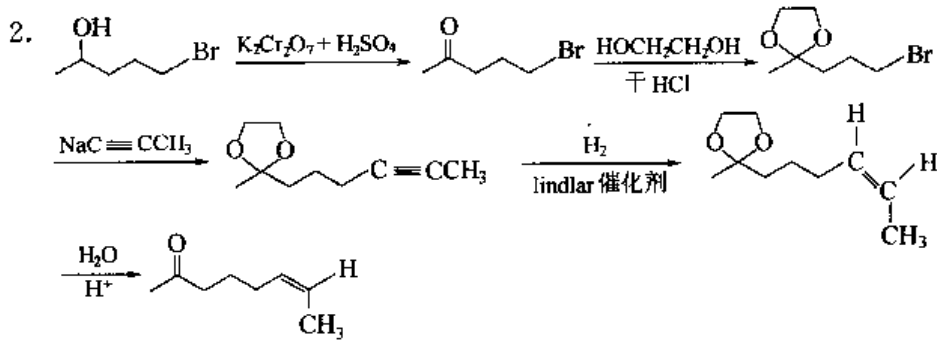
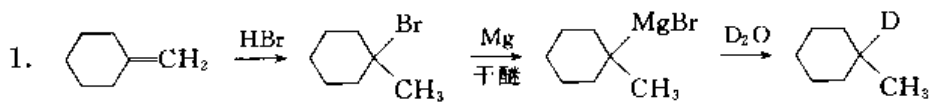
一、选择题

1. (A) 2. (D) 3. (A) 4. (A) 5. (B) 6. (C) 7. (D) 8. (A)
9. (D) 10. (B)

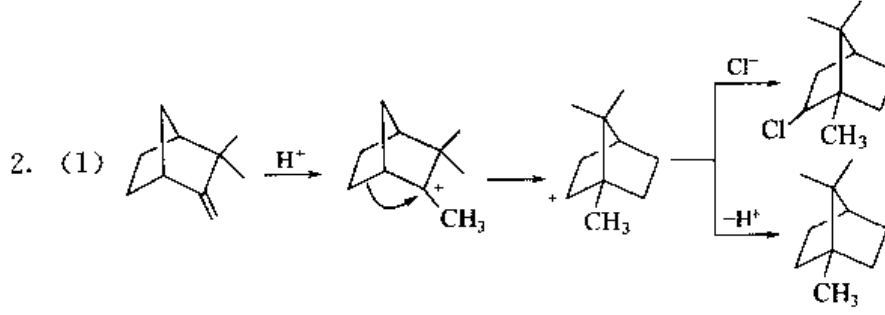
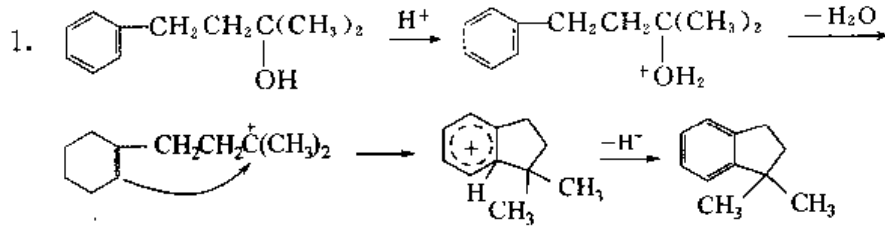
二、填空题

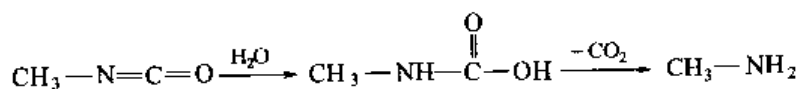
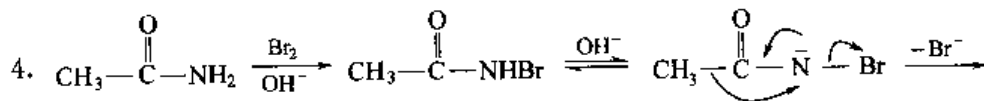
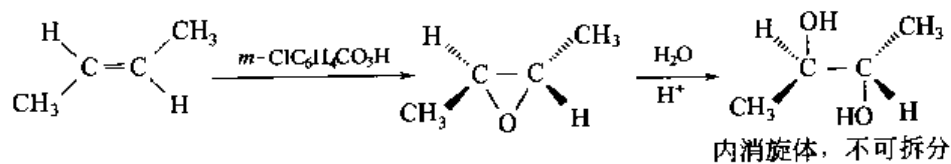
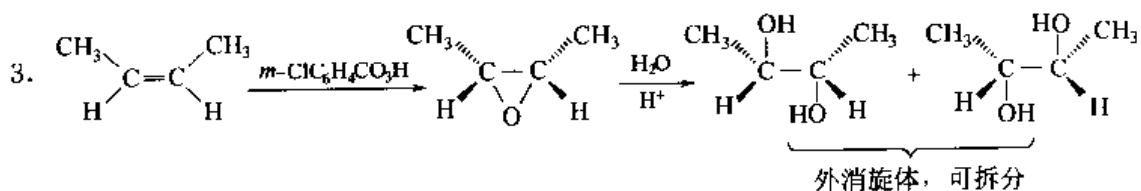
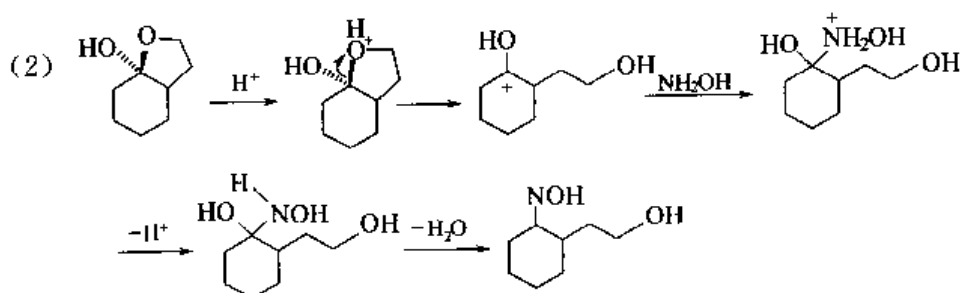


三、合成题



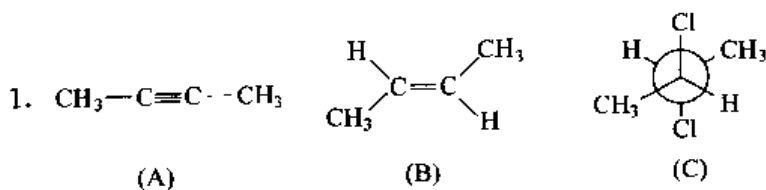
四、机理题



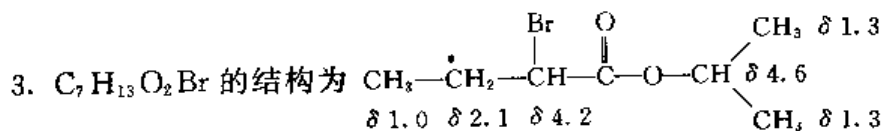


而 $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHCH}_3$ 中氮原子上只有一个氢, 不能经上述历程重排生成异氰酸酯后水解得到相应的胺。

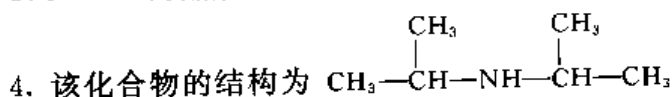
五、推结构题



2. 略。见“模拟试题 31 八。”。

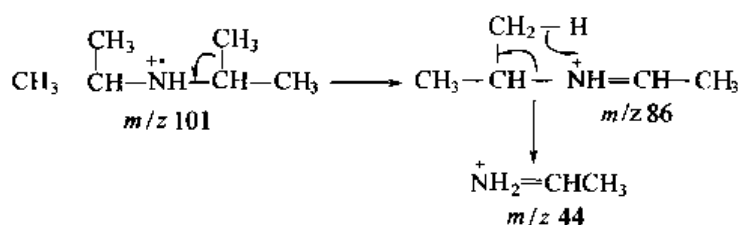
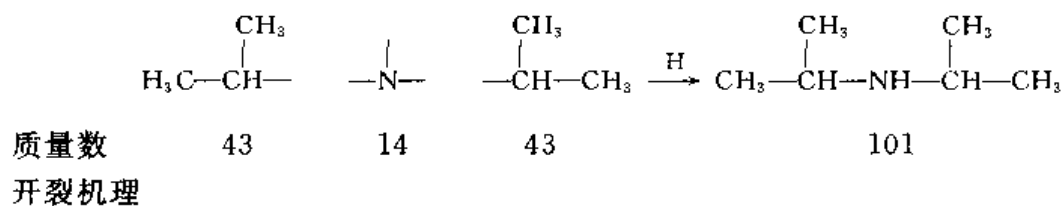


1740cm^{-1} 为酯羰基伸缩振动特征吸收峰。



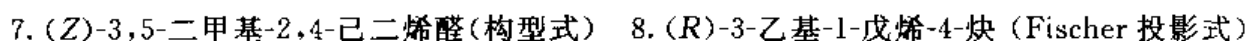
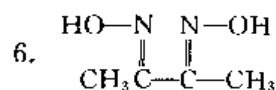
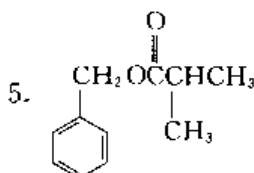
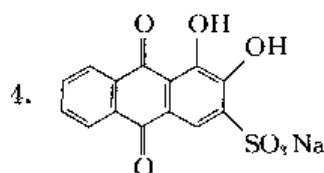
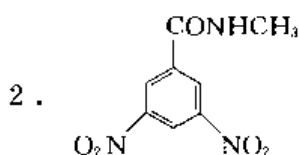
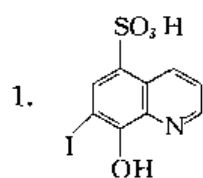
由 IR $1380\sim 1370\text{cm}^{-1}$ (s, 双峰) 和 $^1\text{H-NMR}$ δ 1.0 (双重峰, 12H), δ 2.9 (七重峰, 2H) 知, 样品中含有两个 $-\text{CH}(\text{CH}_3)_2$; 由 MS 知, 样品的相对分子质量为 101, 可能含 1 个氮。由碎片离子拼凑结构。

结构片断



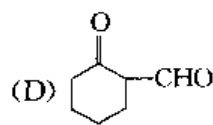
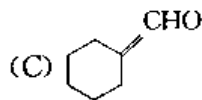
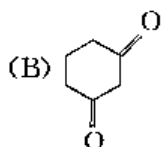
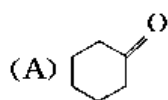
模拟试题 33

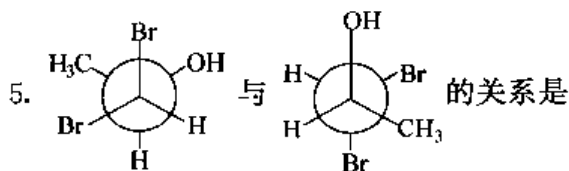
一、命名或写结构式 (10 分)



二、选择题 (18 分)

- 下列化合物中哪个偶极矩最小
(A) $\text{CH}_3\text{CH}_2\text{F}$ (B) $\text{CH}_3\text{CH}_2\text{Cl}$ (C) $\text{CH}_2=\text{CHCl}$ (D) CH_3Cl
- 下列化合物或离子哪个具有芳香性
(A) 环辛四烯 (B) [16]轮烯 (C) 环戊二烯正离子 (D) 环戊二烯钾
- 1,2-二溴环戊烷立体异构体的数目是
(A) 2个 (B) 3个 (C) 4个 (D) 无
- 下列化合物的互变异构体中烯醇式含量最多的是



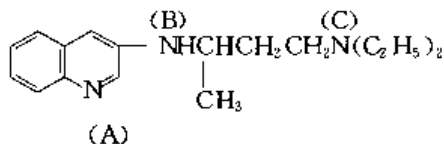


- (A) 对映体 (B) 非对映体 (C) 相同 (D) 没有关系

6. 下列化合物中不与 CH_3MgBr 反应的是

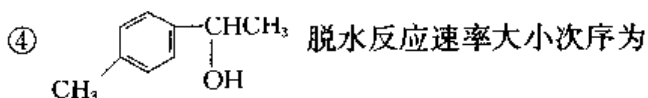
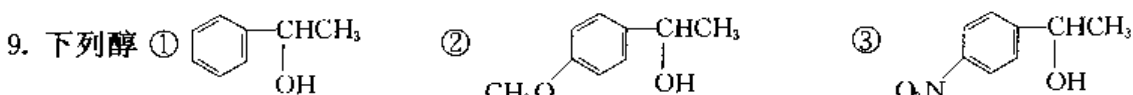
- (A) 乙醇 (B) 乙胺 (C) 环氧乙烷 (D) 四氢呋喃

7. 下列化合物不同氮原子碱性最大的是



8. 下列化合物酸性最大的是

- (A) 草酸 (B) 丙酸 (C) 碳酸 (D) 苯酚

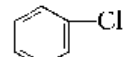


- (A) ①>②>③>④ (B) ③>①>④>② (C) ②>④>①>③ (D) ④>②>③>①

10. 下列化合物 ① $\text{CH}_3\text{CH}_2\text{COOEt}$ ② $\text{CH}_3\text{CH}_2\text{COCl}$ ③ $\text{CH}_3\text{CH}_2\text{CONH}_2$

④ $(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$ 水解反应活性大小次序为

- (A) ①>②>③>④ (B) ②>④>①>③
(C) ②>①>④>③ (D) ④>②>③>①

11. 下列化合物 ① $\text{CH}_3\text{CH}_2\text{Cl}$ ② $\text{CH}_3\text{CH}_2\text{Br}$ ③ $\text{CH}_3\text{CH}_2\text{I}$ ④  在

$\text{NaOH}/\text{H}_2\text{O}$ 中进行水解反应速率大小次序为

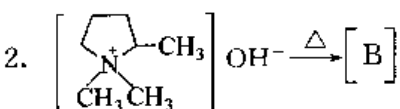
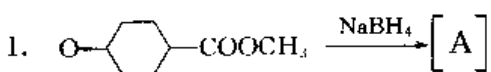
- (A) ③>②>①>④ (B) ①>②>③>④ (C) ④>①>②>③ (D) ③>④>①>②

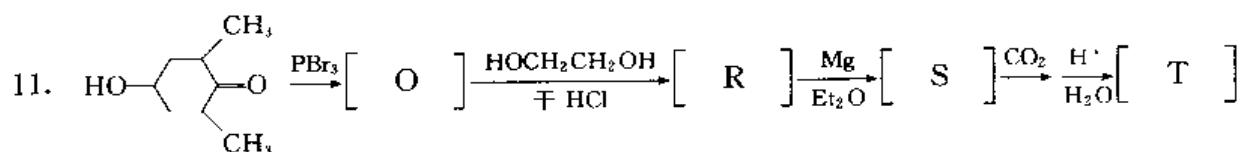
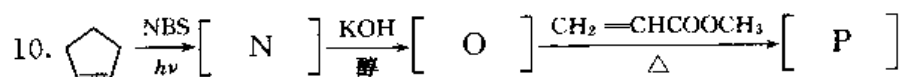
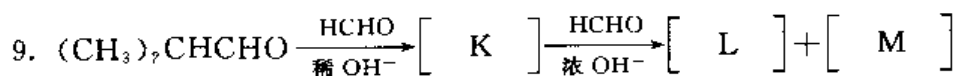
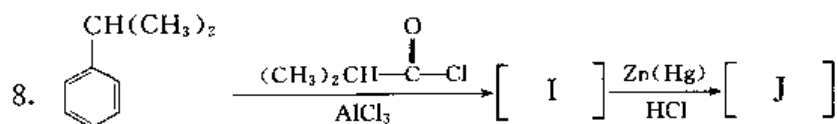
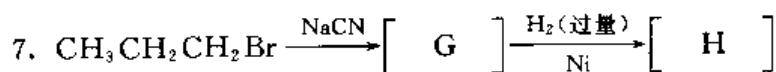
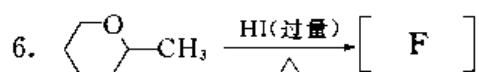
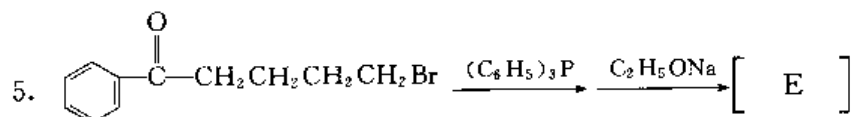
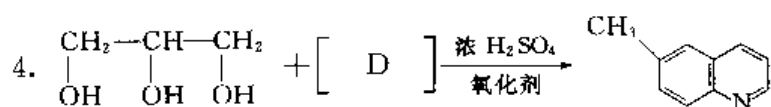
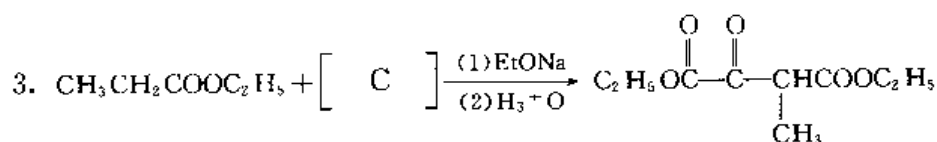
12. 实验室用熔点测定管测定熔点时, 使熔点偏高的因素是

- (A) 试样有杂质 (B) 试样不干燥 (C) 熔点管太厚 (D) 温度上升太慢

三、完成下列反应 (20分)

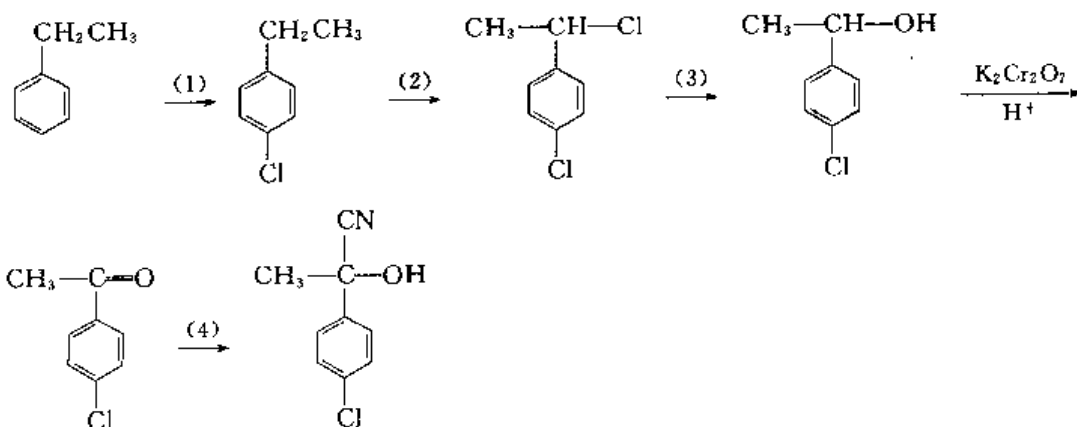
(写出主要产物或相应的试剂和重要反应条件)





四、扼要回答下列问题 (18分)

1. 按表格要求填充 (8分)



反应编号	反应试剂和必要条件	反应历程名称	活性中间体结构
(1)			
(2)			
(3)		S _N 1(单分子亲核取代)	
(4)			

2. 用简便的化学方法鉴别下列化合物 (6分)

- A. 对甲苯酚 B. 对甲基苄醇 C. 对甲苯甲醚
D. 1-苯基乙醇 E. 对甲苯甲醛 F. 苯乙酮

3. 解释下列现象 (4分)

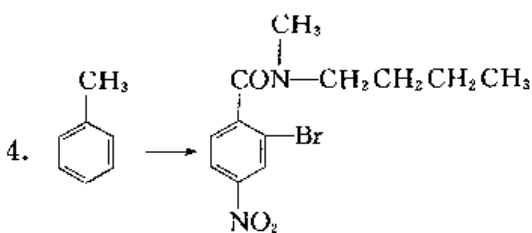
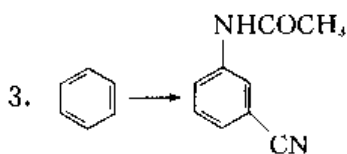
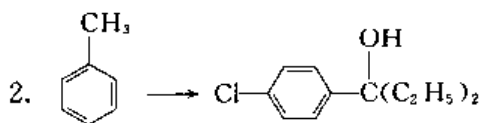
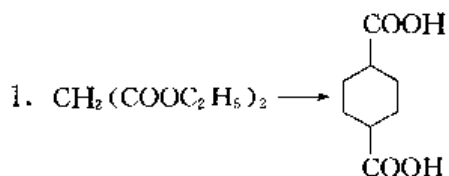
- (1) 邻硝基苯酚的沸点比对硝基苯酚低。
(2) 烯丙基溴进行 S_N1、S_N2 反应的活性都很强。

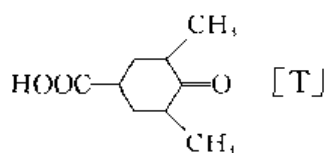
五、推测结构 (14分)

1. 化合物 A(C₆H₁₄O), ¹H-NMR 如下: δ 0.9 (9H, 单峰), δ 1.10 (3H, 双峰), δ 3.40 (1H, 四重峰), δ 4.40 (1H, 单峰)。A 与酸共热生成 B(C₆H₁₂), B 经臭氧化和还原水解生成 C(C₃H₆O), C 的 ¹H-NMR 只有一个信号: δ 2.1, 单峰。请写出 A、B、C 的构造式。(6分)

2. 化合物 A(C₉H₁₀O₂)能溶于 NaOH 水溶液, 可以和羟胺加成, 但不和 Tollens 试剂反应。A 经 NaBH₄ 还原生成 B(C₉H₁₂O₂)。A 和 B 均能发生碘仿反应。A 用 Zn-Hg/HCl 还原生成 C(C₉H₁₂O), C 与 NaOH 溶液反应, 再和碘甲烷反应得 D(C₁₀H₁₄O), 用高锰酸钾氧化 D 生成对甲氧基苯甲酸。写出 A、B、C、D 的构造式及反应方程式。(8分)

六、合成下列化合物 (20分)



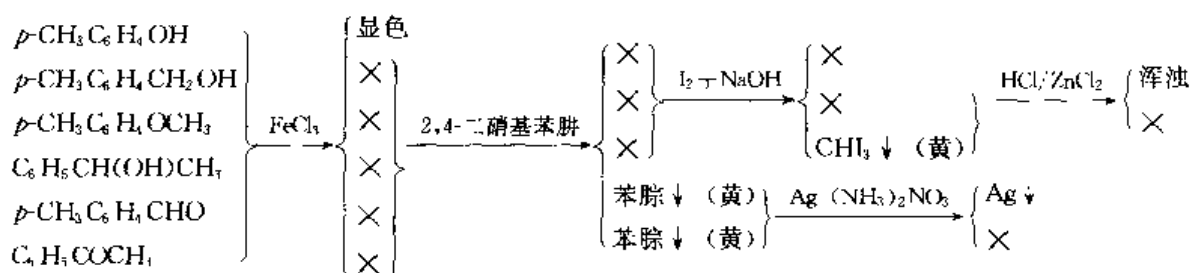


四、扼要回答下列问题

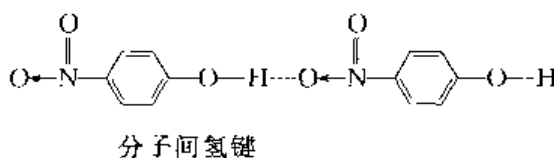
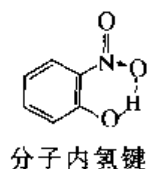
1. 按表格要求填充 (8分)

反应编号	反应试剂和必要条件	反应历程名称	活性中间体结构
(1)	$\text{Cl}_2 \cdot \text{Fe}$	亲电取代	
(2)	$\text{Cl}_2, h\nu$	自由基取代	
(3)	$\text{NaOH}/\text{H}_2\text{O}$	$\text{S}_{\text{N}}1$ (单分子亲核取代)	
(4)	HCN	亲核加成	

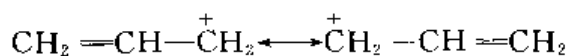
2.



3. (1) 邻硝基苯酚有分子内氢键, 分子间作用小, 沸点低;
对硝基苯酚有分子间氢键, 分子间作用大, 沸点高。

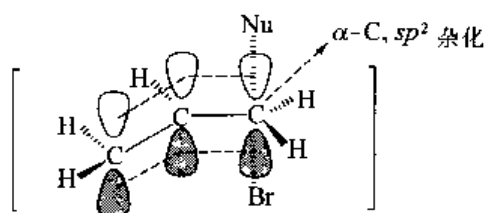


(2) $\text{CH}_2=\text{CHCH}_2\text{Br}$ 进行 $\text{S}_{\text{N}}1$ 时, 形成的中间体有缺电子 p- π 共轭, 具有特殊稳定性,

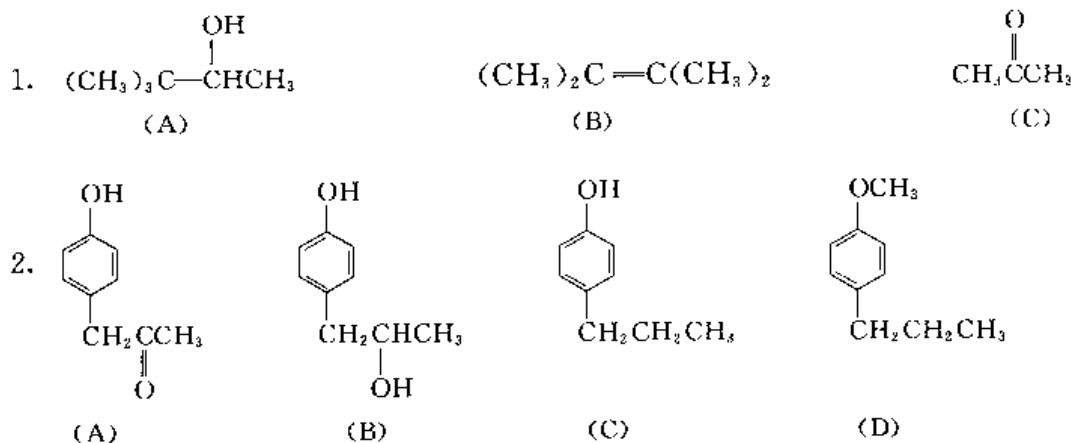


因而反应活化能低, 反应速度快。

$\text{CH}_2=\text{CHCH}_2\text{Br}$ 进行 $\text{S}_{\text{N}}2$ 时, 形成的过渡态有 p- π 共轭, 能量较低。

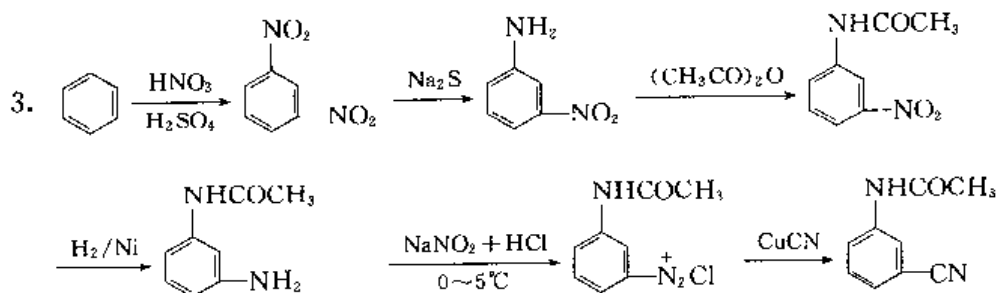
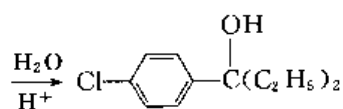
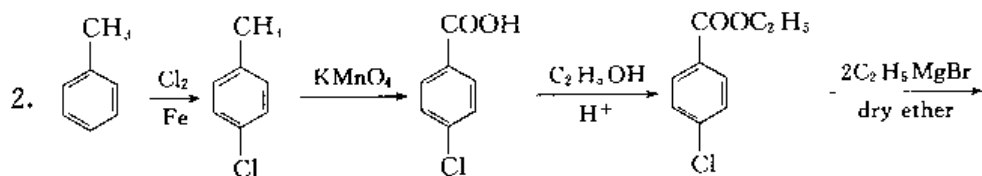
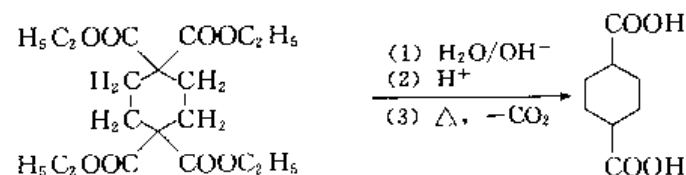
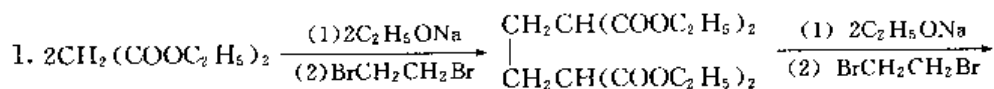


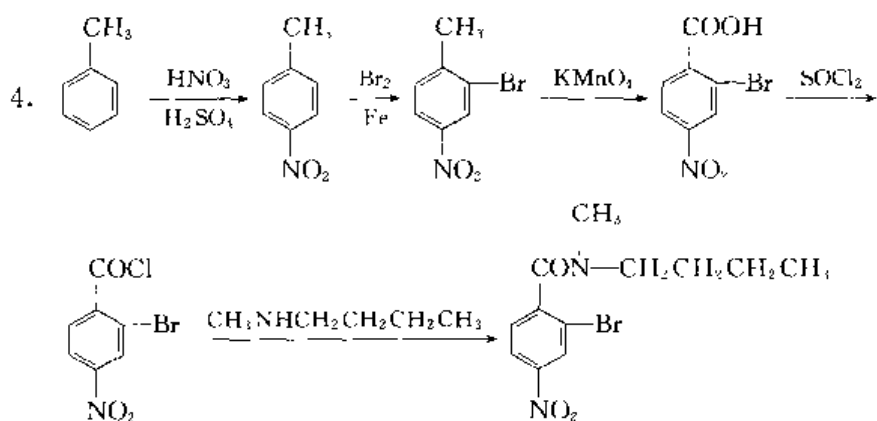
五、推测结构



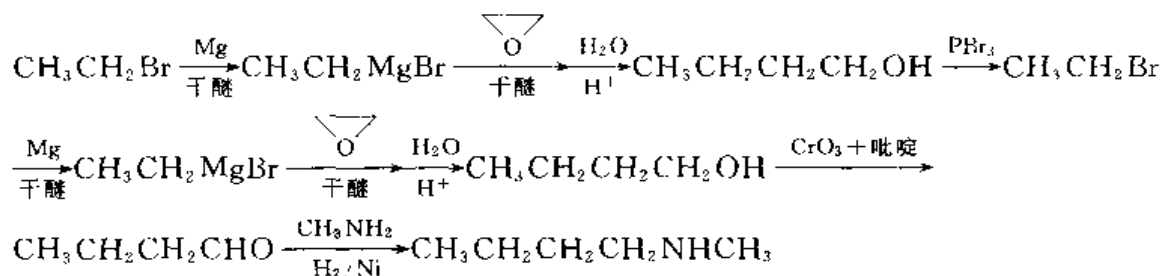
有关反应式略。

六、合成下列化合物



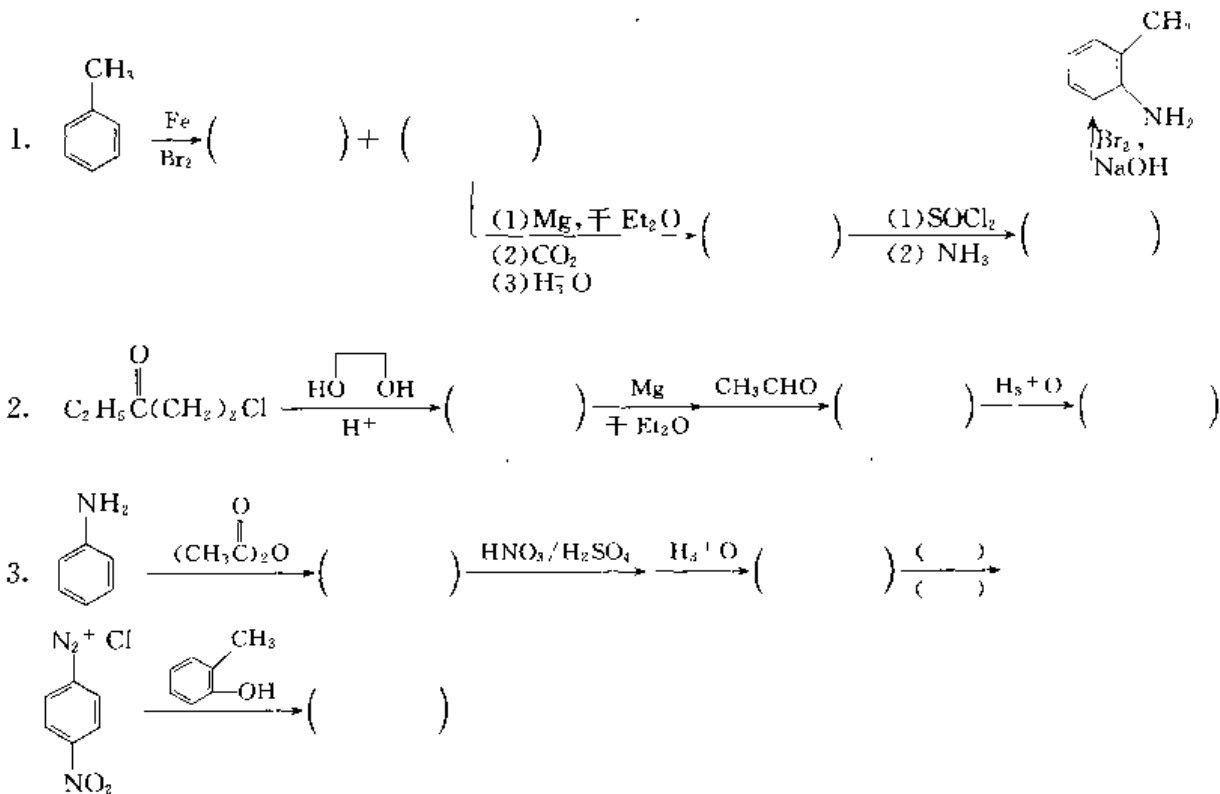


CH₃NHCH₂CH₂CH₂CH₃ 的制法



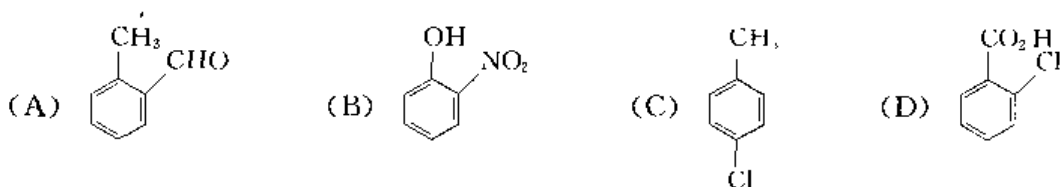
模拟试题 34

一、完成下列反应（必要时，请注明产物的立体构型）（21 分）



(A) 亲电取代 (B) 苯炔机理 (C) 亲核加成-消去 (D) 亲核取代

7. 分子内氢键最易形成的分子为 ()



8. 下列化合物中哪一个最合乎下列红外光谱数据 ()

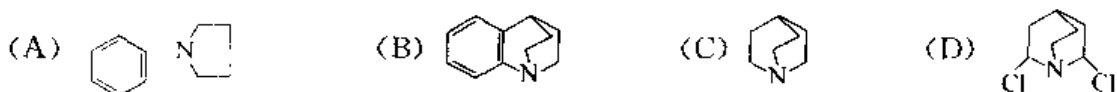
IR/cm⁻¹: 3400, 2980, 2860, 1050



9. 下列化合物中哪一个无论按 S_N1 或 S_N2 机理反应时, 其相对活性均为最小 ()

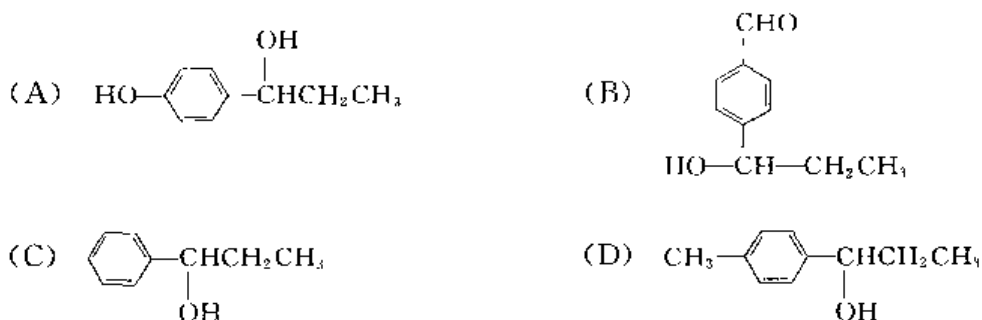


10. 下面化合物中碱性最强的是 ()

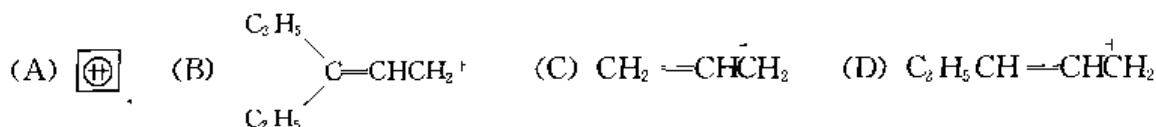


三、按题意排顺序 (20分)

1. 在酸性条件下脱水的快慢顺序为 ()

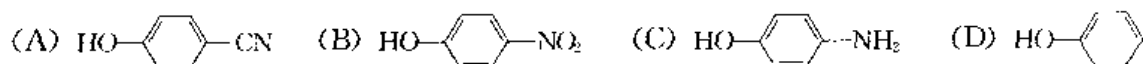


2. 比较下列各物种的稳定性 ()

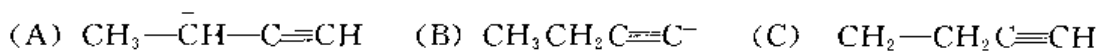


环丁二烯二价正离子

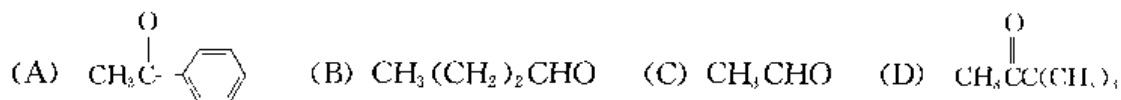
3. 按酸性强弱排列 ()



4. 按碳负离子的稳定性 ()



5. 比较下列化合物与饱和 NaHSO_3 溶液加成的活性 ()



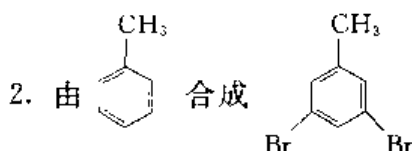
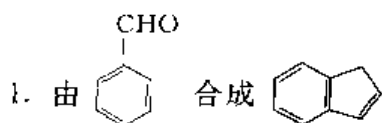
四、推导结构 (20分)

1. 一中性化合物 A ($\text{C}_{10}\text{H}_{16}\text{O}$) 可使 Br_2/CCl_4 试剂迅速褪色, 也能被托伦 (Tollens) 试剂氧化。A 经催化氢化得 B ($\text{C}_{10}\text{H}_{20}\text{O}$), B 可用 NaBH_4 还原得 C ($\text{C}_{10}\text{H}_{22}\text{O}$)。A 经臭氧氧化再还原水解得乙二醛、丙酮及 D。D 在温和条件下氧化得 E ($\text{C}_5\text{H}_8\text{O}_4$), E 与 I_2/NaOH 试剂作用生成碘仿及另一化合物, 该化合物经酸化后为 F。F 受热可生成酸酐, 试推测 A~F 的所有结构式, 并写出有关反应式。

2. 化合物 A (C_9H_{12}) 的 IR 谱证明其为苯的一元取代物, A 经光照溴代反应得到两种苯的一元取代物 B 及 C。其分子式均为 $\text{C}_9\text{H}_{11}\text{Br}$, B 不具有光学活性, 也不可拆分; 而 C 虽无光学活性, 但可拆分为一对对映体。试推测 A、B、C 的结构。

五、合成下列化合物 (24分)

(请使用指定原料, 并自选适当的有机及无机试剂)



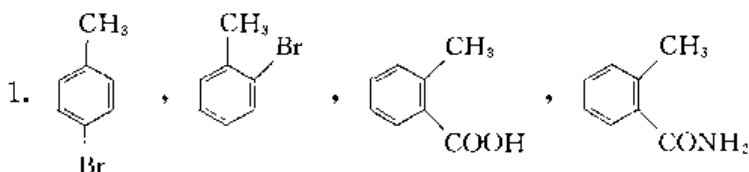
3. 由乙烯合成顺丁烯二酸酐

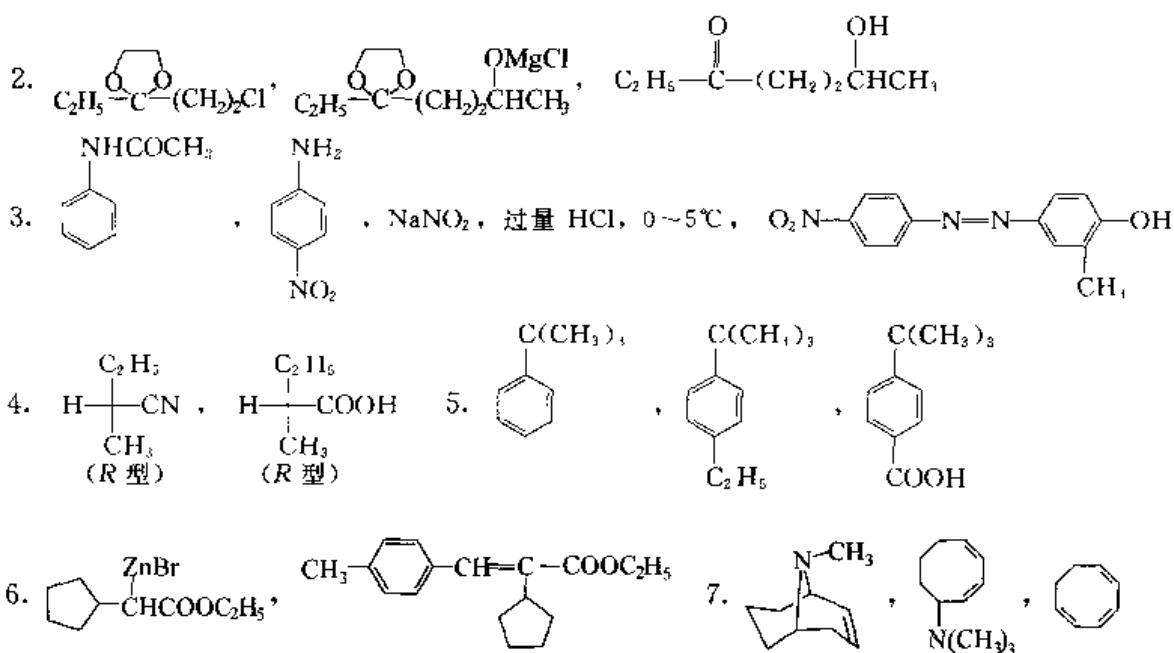
六、实验 (5分)

由苯甲酸和过量乙醇在酸催化下合成苯甲酸乙酯, 试设计一实验步骤, 将产物分离提纯。

参考答案

一、完成下列反应





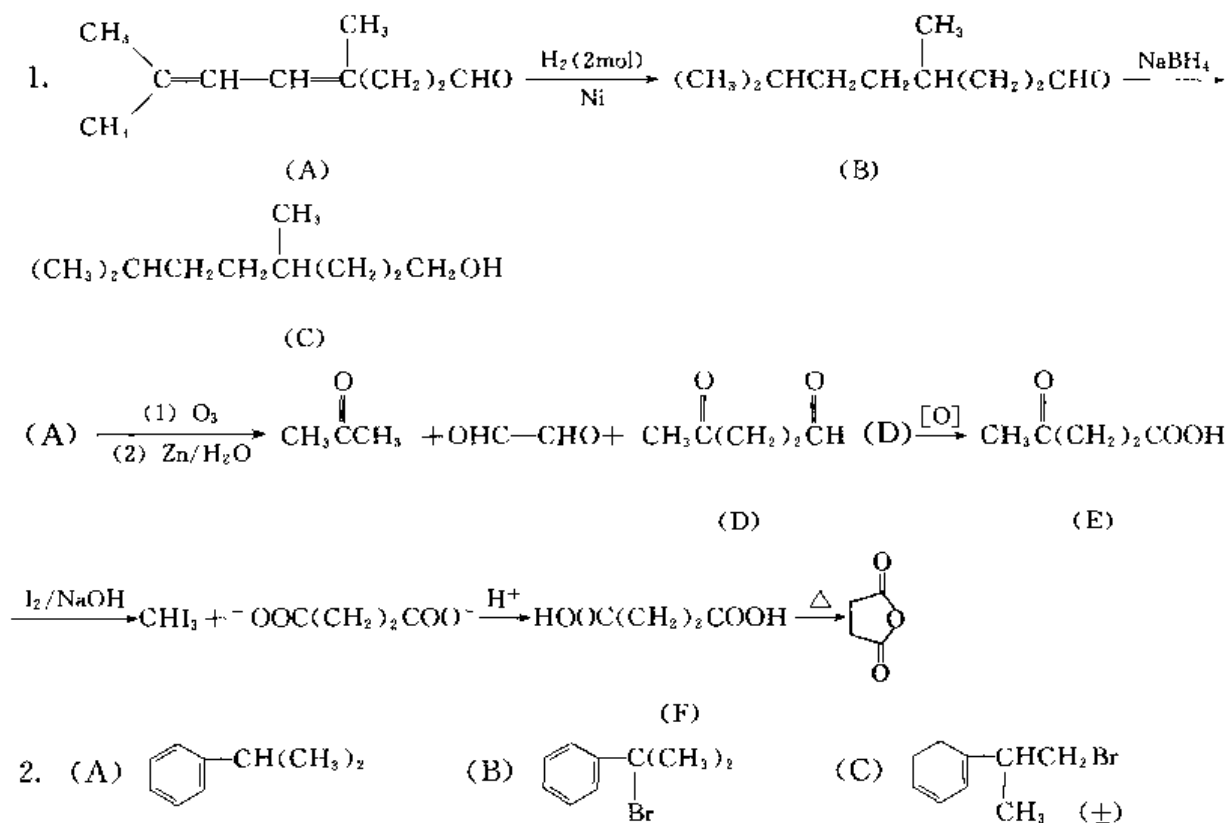
二、选择填空

1. (B) 2. (D) 3. (A) 4. (C) 5. (C) 6. (B) 7. (B) 8. (C)
9. (D) 10. (C)

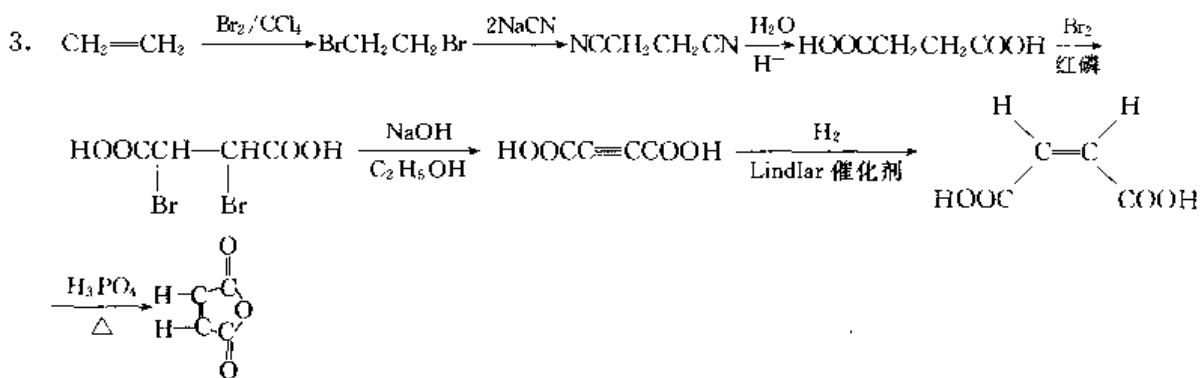
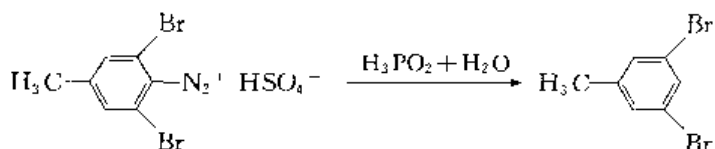
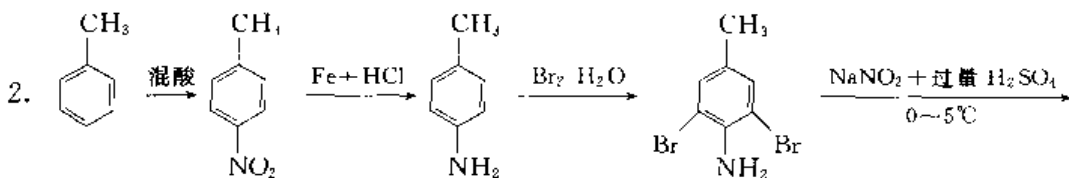
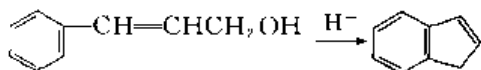
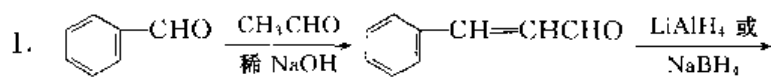
三、按题意排顺序

1. (A) > (D) > (C) > (B) 2. (A) > (B) > (D) > (C) 3. (B) > (A) > (D) > (C)
4. (B) > (A) > (C) 5. (C) > (B) > (D) > (A)

四、推导结构



五、合成下列化合物



六、实验

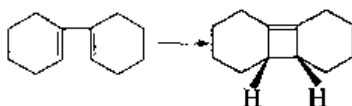
将粗产物依次用等体积的饱和 Na_2CO_3 、 H_2O 、饱和 CaCl_2 、 H_2O 洗涤后，用无水碳酸钾或无水硫酸镁干燥。30min 或更长长时间后，过滤除去干燥剂，蒸馏，收集苯甲酸乙酯馏分。

模拟试题 35

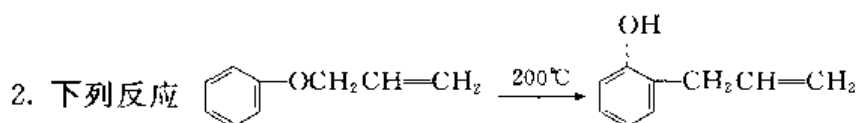
一、选择题 (30 分)

1. 下面反应在哪种条件下进行?

- (A) 加热自旋 (B) 光照对旋 (C) 加热对旋 (D) 光照顺旋



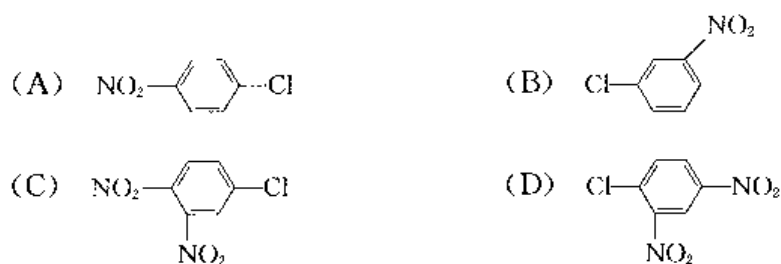
()



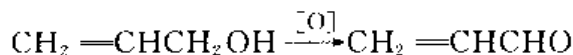
叫克莱森重排，它是 ()

- (A) 碳正离子重排 (B) 自由基重排 (C) 周环反应 (D) 亲电取代反应

9. 下列化合物，与 NaOH 水溶液反应时，哪一个速率最快？



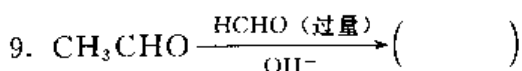
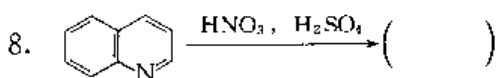
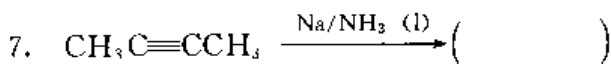
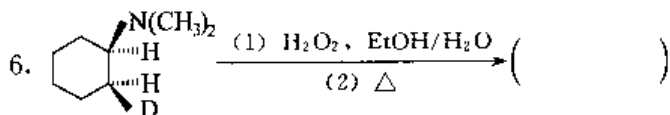
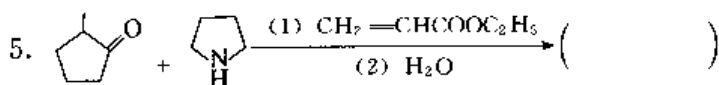
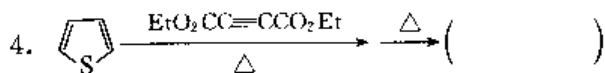
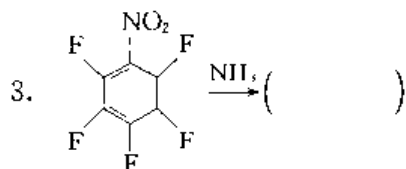
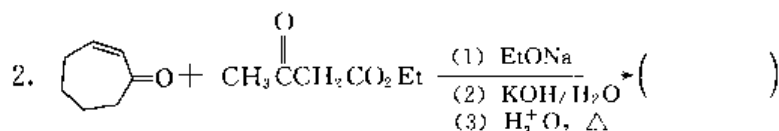
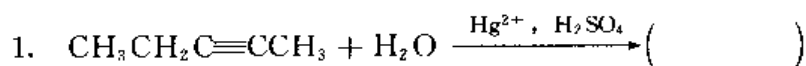
10. 选择一个合适的氧化体系，完成下述转变



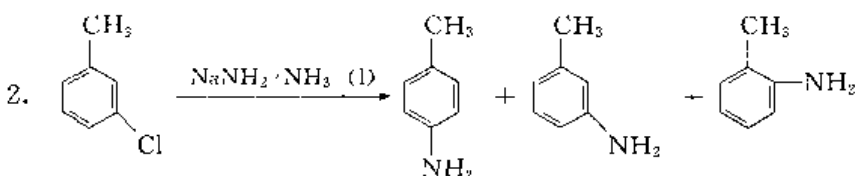
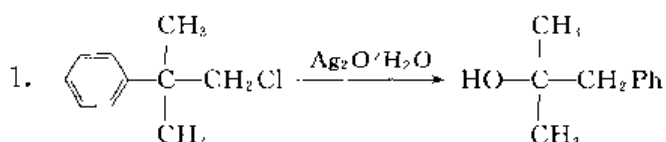
(A) $\text{KMnO}_4/\text{H}_2\text{O}$ (B) $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ (C) H_2O_2 (D) $\text{CrO}_3 \cdot (\text{Py})_2$ (Py: 吡啶)

二、填空题 (30 分)

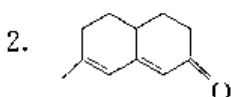
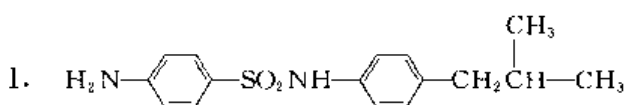
(写出下列反应的主要有机产物，如有立体化学问题请注明，每题 3 分)



三、写出下列反应的机理 (12 分)



四、以苯及含有 C₄ 以下的有机原料合成下述化合物 (16 分)

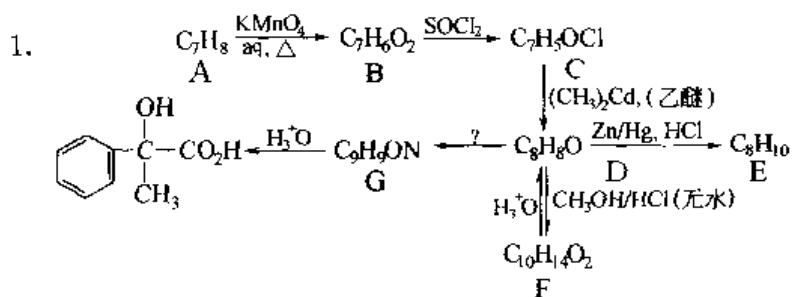


五、推结构题 (12 分)

1. 某有机化合物经元素分析，确知分子式为 C_8H_8O ，IR 图谱发现在 1680cm^{-1} 、 1430cm^{-1} 和 1360cm^{-1} 处有强吸收峰，质谱分析：分子离子峰在 120，最强峰在 105，另外在 m/z 43，和 m/z 77 处有较强的峰。依据这些数据，确定该化合物的结构，并确定各个峰的可能来源。

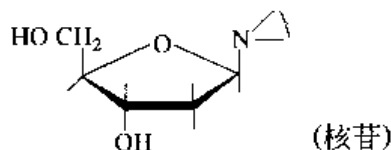
2. 分子式为 $C_7H_7NO_2$ 的化合物 A、B、C、D，它们都含有芳环。A 能溶于酸和碱中，B 能溶于酸，而不能溶于碱，C 能溶于碱而不能溶于酸，D 不能溶于酸和碱中。它们的一硝化产物只有两种（主要产物为一种）。试推测 A、B、C、D 的结构式。

六、完成下列反应 (第 1 小题 8 分，第 2 小题 7 分，共 15 分)



七、DNA 和 RNA 水解所得的核苷在稀碱溶液中稳定，然而它们在稀酸中却迅速水解为糖（脱氧核糖或核糖）和杂环碱（10 分）

1. 核苷的什么结构特征能说明这种行为？（5 分）
2. 写出核苷水解反应的历程。（5 分）



八、如何用化学方法区别下列各组化合物（15 分）

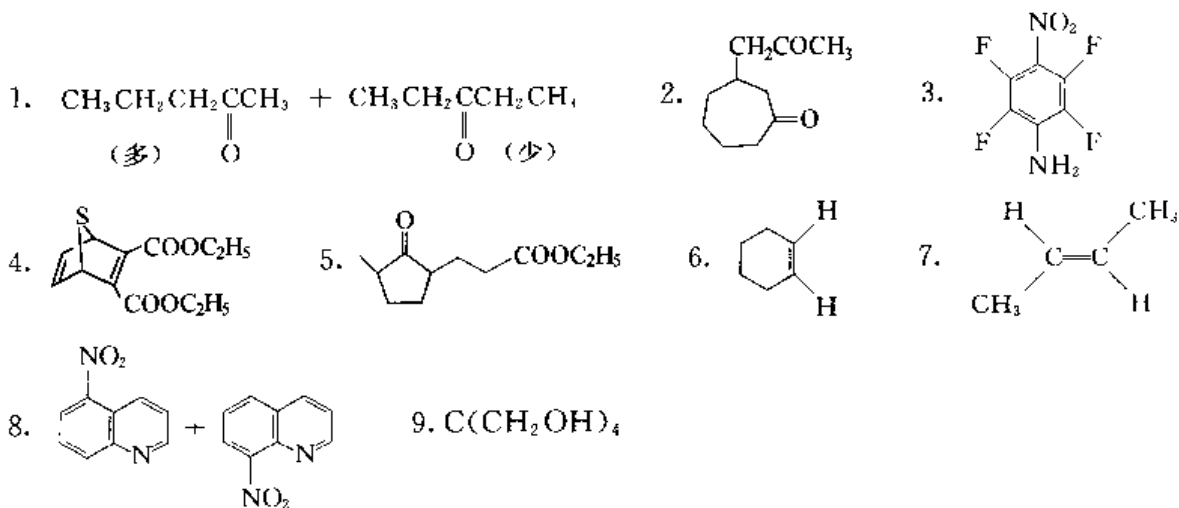
1. 麦芽糖和蔗糖；
2. 蔗糖和淀粉；
3. 半乳糖和葡萄糖；
4. 淀粉和纤维素；
5. 甲基葡萄糖苷，2-甲基葡萄糖及 3-甲基葡萄糖。

参考答案

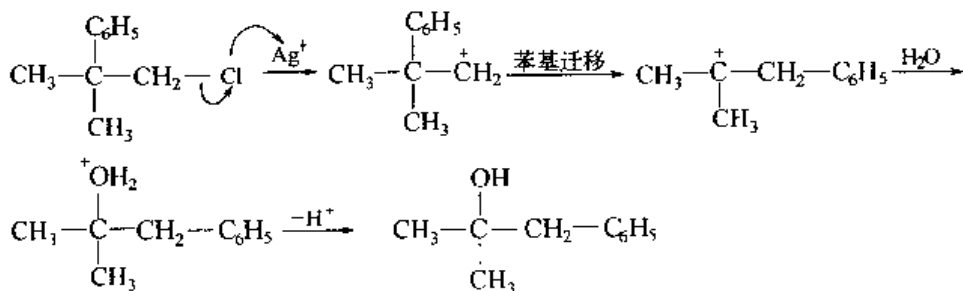
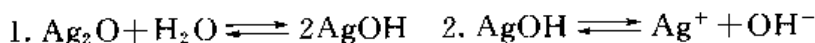
一、选择题

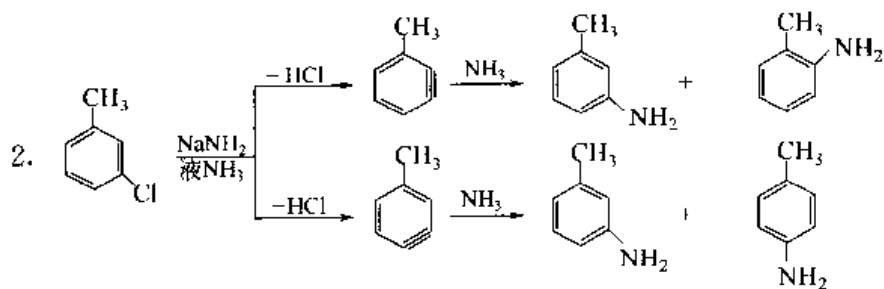
1. (B) 2. (C) 3. (B) 4. (B) 5. C 6. (C) 7. (A) 8. (A) 9. (D) 10. (D)

二、填空题

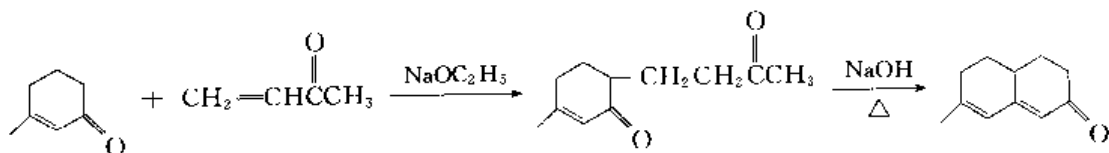
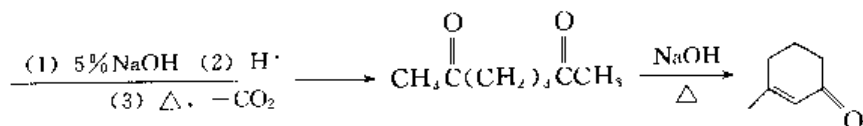
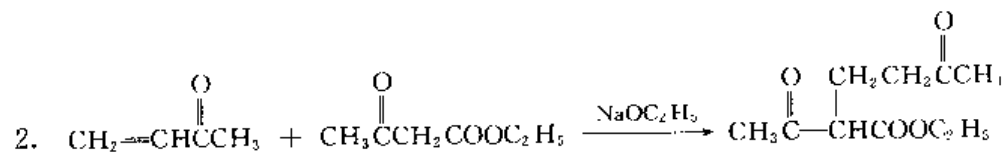
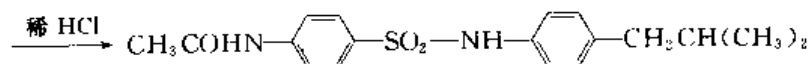
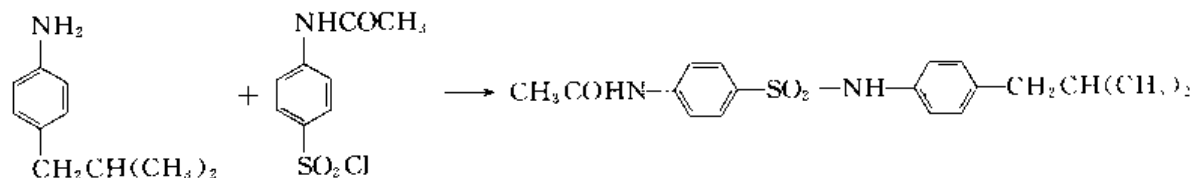
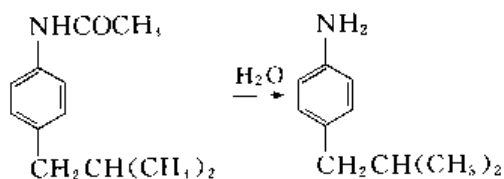
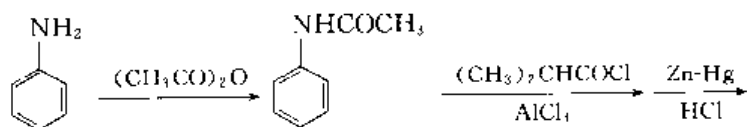
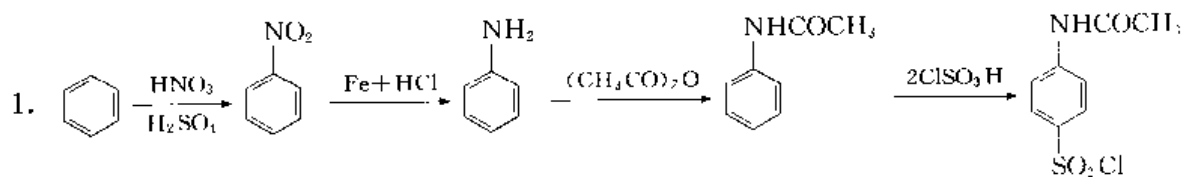


三、写出下列反应的机理



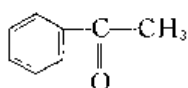


四、以苯及含有 C₄ 以下的有机原料合成下述化合物



五、推结构题

1. 该化合物的结构为

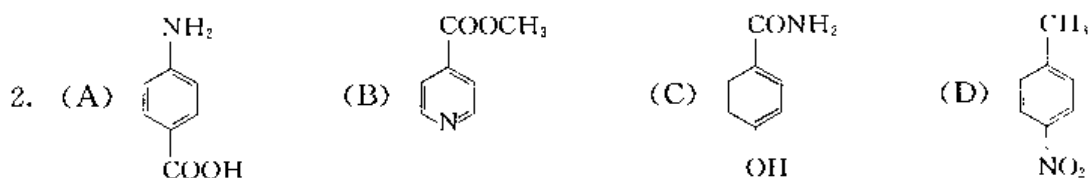
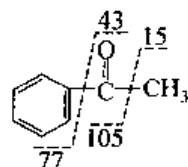


各峰来源如下所示。

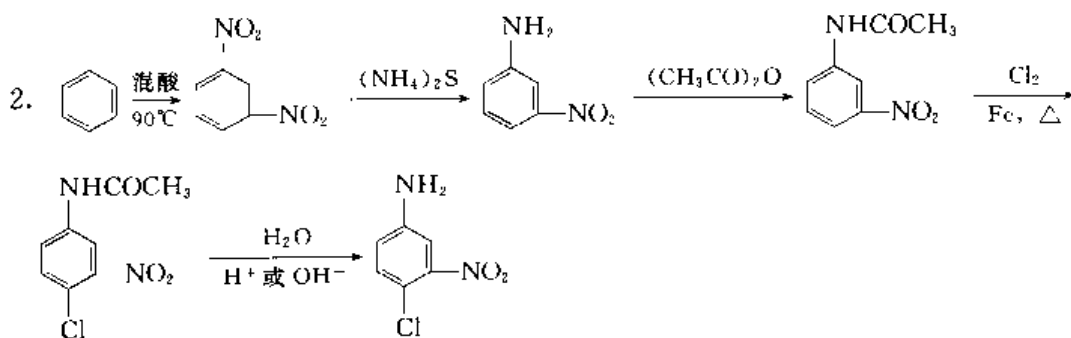
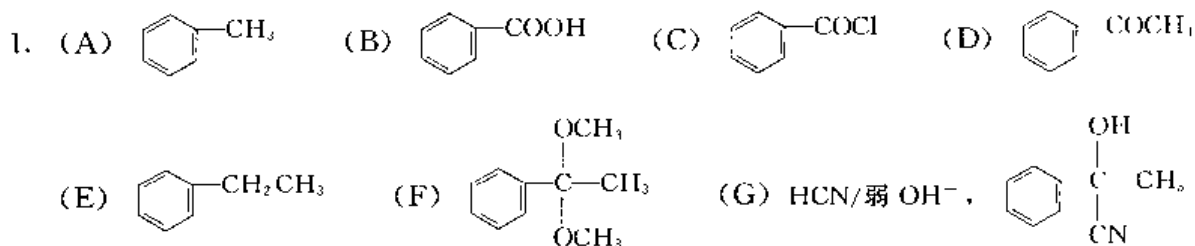
(1) 红外光谱

吸收峰/cm ⁻¹	来源或归属
1680	共轭羰基的伸缩振动吸收
1430	甲基面内弯曲振动(不对称)
1360	甲基面内弯曲振动(对称)

(2) 质谱

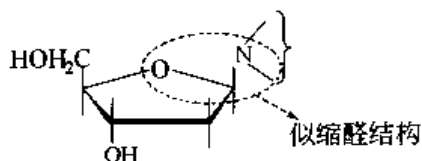


六、完成下列反应

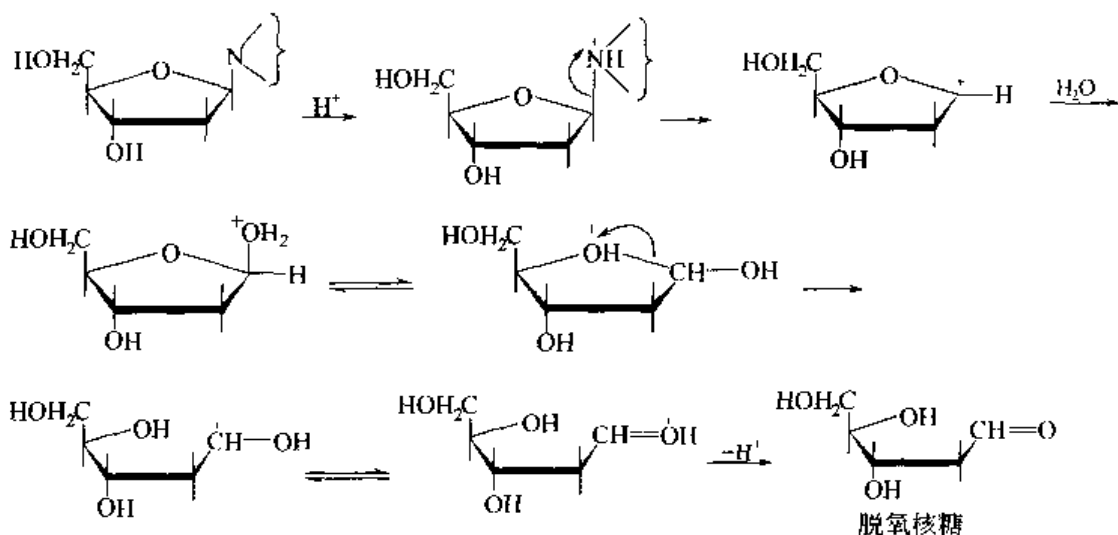


七、DNA 和 RNA 水解所得的核苷在稀碱溶液中稳定，然而它们在稀酸中却迅速水解为糖（脱氧核糖或核糖）和杂环碱。

1. 核苷分子中类似于缩醛的结构特征可说明其题中所示的行为

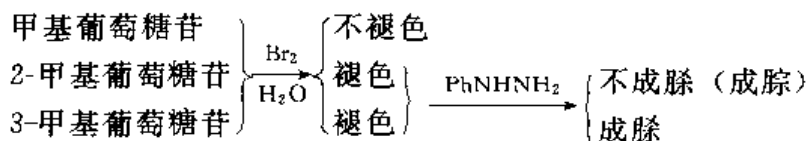
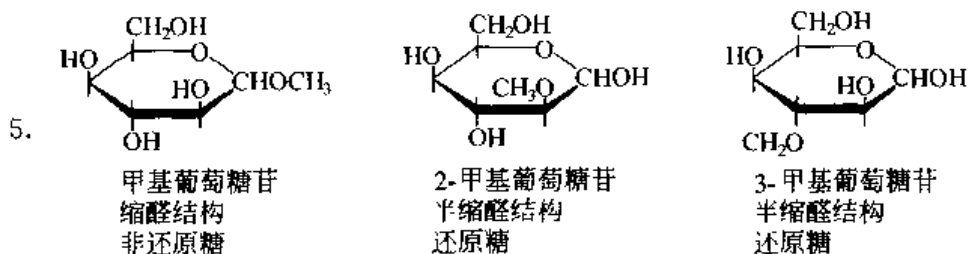


2. 核苷水解反应的历程



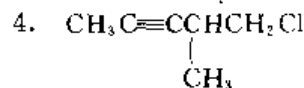
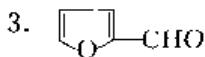
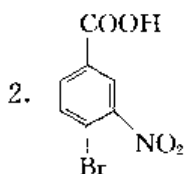
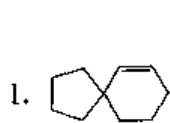
八、如何用化学方法区别下列各组化合物

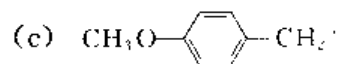
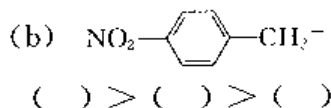
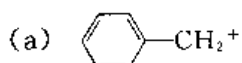
- | | | |
|-----|---------------------------------------|-------|
| 麦芽糖 | } $\xrightarrow{\text{Fehling 试剂}}$ { | 砖红色 ↓ |
| 蔗糖 | | × |
- | | | |
|----|--------------------------------|-----|
| 蔗糖 | } $\xrightarrow{\text{I}_2}$ { | × |
| 淀粉 | | 显蓝色 |
- | | | |
|-----|-------------------------------------|---------------------|
| 半乳糖 | } $\xrightarrow{\text{PhNHNH}_2}$ { | 与葡萄糖标准溶液成脎速率及脎的晶形不同 |
| 葡萄糖 | | (与葡萄糖标准溶液对照) |
- | | | |
|-----|--------------------------------|-----|
| 淀粉 | } $\xrightarrow{\text{I}_2}$ { | 显蓝色 |
| 纤维素 | | × |



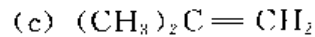
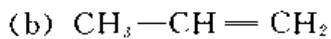
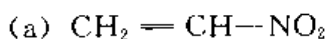
模拟试题 36

一、命名下列化合物 (5分)





3. 下列烯烃的亲电加成反应速度的大小次序为



() > () > ()

五、用化学方法鉴别下列多组化合物 (10 分)

1. 1-丁烯 1-戊炔 环丙烷

2. 1-溴丁烷 1-丁醇 丁醛 丁酮

3. 苯甲酸 苯酚 苯胺 苯甲醛 苯乙酮

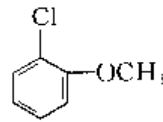
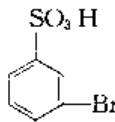
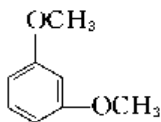
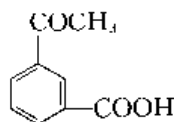
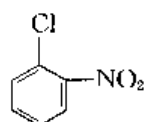
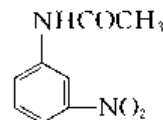
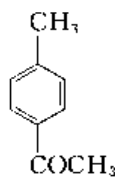
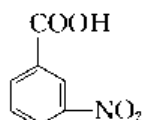
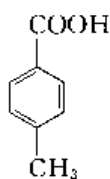
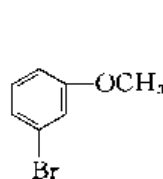
六、用化学方法分离混合物 (10 分)

1. 苯酚 苯甲醛 丁醚 环己酮

2. 1-硝基己烷 正己烷 正己腈 正己酸

七、基本概念 (10 分)

1. 用箭头标出下列化合物进行硝化反应时硝基进入的位置



2. 哪些化合物有芳香性



(A)

(B)

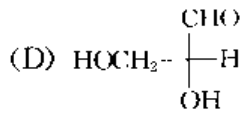
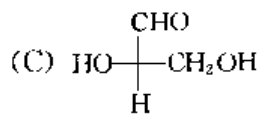
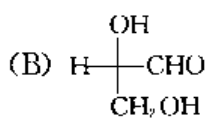
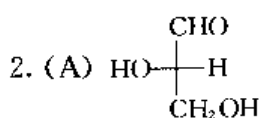
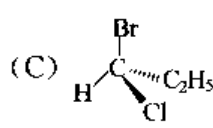
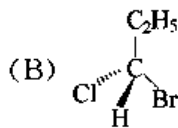
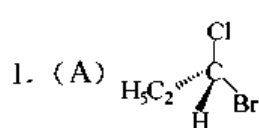
(C)

(D)

(E)

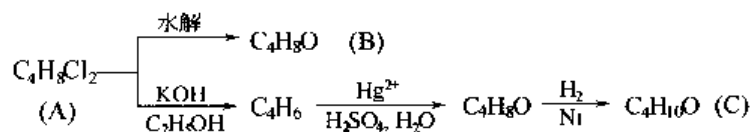
八、立体化学概念 (10 分)

指出哪些是相同的, 哪些是对映体。



九、推断有机化合物的分子式 (10 分)

1. 试推测有机化合物 A、B 和 C 的结构式



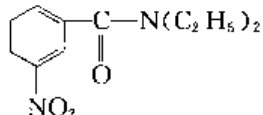
(B) 有碘仿反应, 红外光谱图在 1715cm^{-1} 有强吸收峰。A 的 NMR 数据为 3H (单峰), 2H (四重峰), 3H (三重峰)。

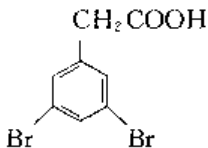
2. 两个芳香族含氧化合物 A 和 B, 分子式均为 $\text{C}_7\text{H}_8\text{O}$ 。A 可与金属钠作用, 而 B 不能, 用浓氢碘酸处理 A 容易转变成 C ($\text{C}_7\text{H}_7\text{I}$), B 则转变成 D ($\text{C}_6\text{H}_6\text{O}$), D 遇溴水迅速生成白色沉淀。写出 A、B、C 和 D 的构造式及各步反应式。

十、有机合成题 (限定用下列有机物为原料, 无机试剂可任用。20 分)

1. 以乙炔为原料, 合成 $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$

2. 用丙二酸二乙酯及 3 个碳原子以下的饱和烃合成 $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_2\text{CH}_3)\text{COOH}$

3. 以甲苯与两个碳原子以下的有机化合物合成 

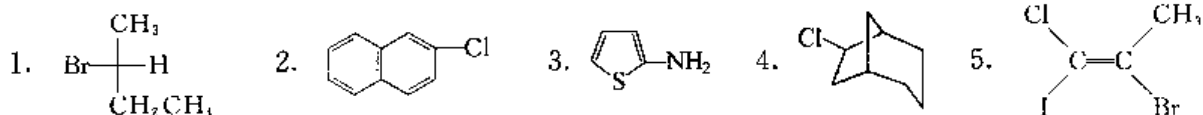
4. 由苯与一个碳原子的有机化合物合成 

参考答案

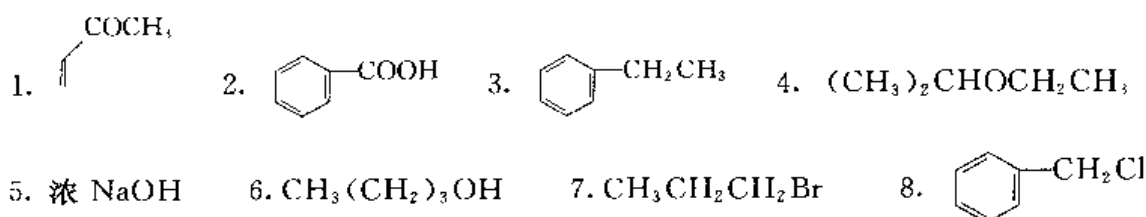
一、命名下列化合物

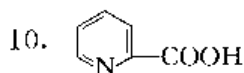
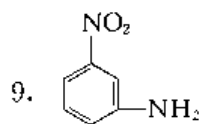
1. 螺[4.5]-6-癸烯 2. 3-硝基-4-溴苯甲酸 3. 2-咪喃甲醛
4. 4-甲基-5-氯-2-戊炔 5. 2,3,6-三甲基庚烷

二、写出下列化合物的结构式



三、完成下列反应式

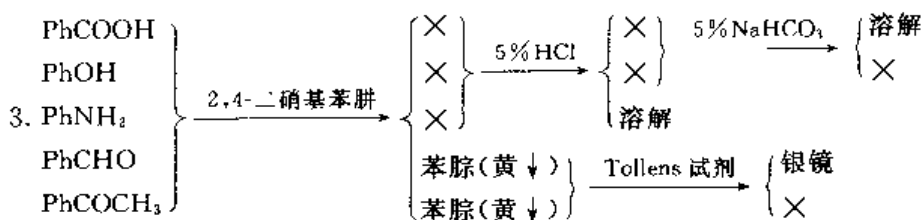
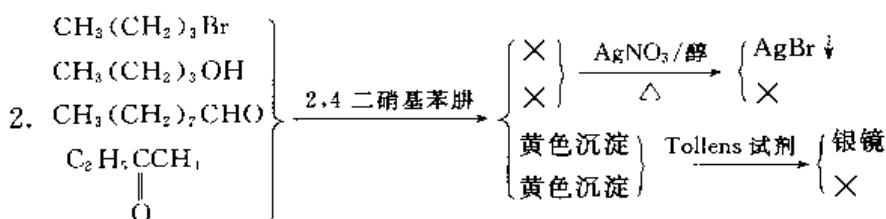
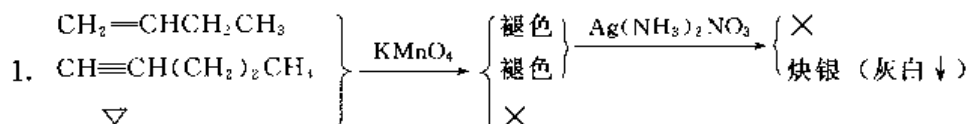




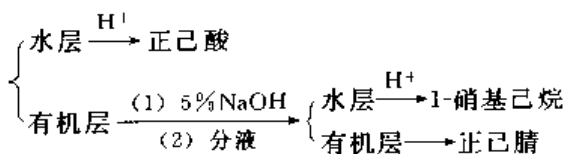
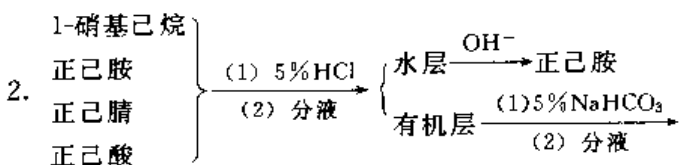
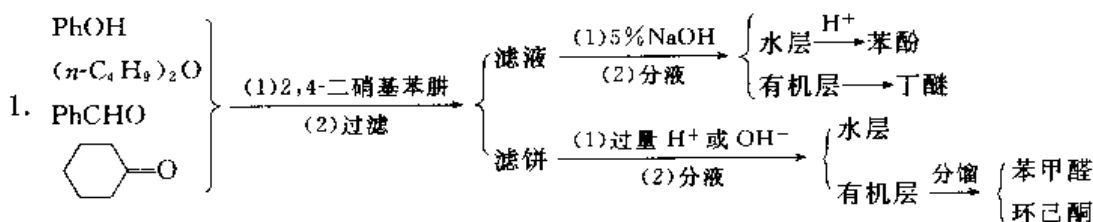
四、有机化合物性质比较

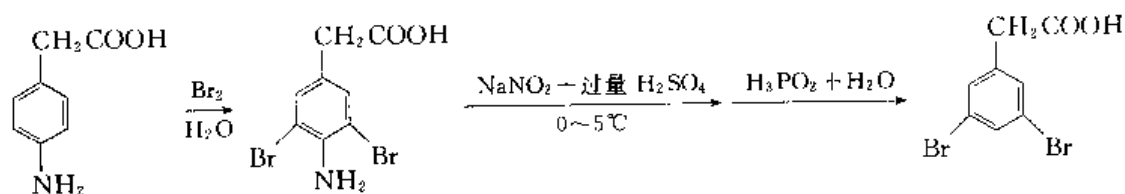
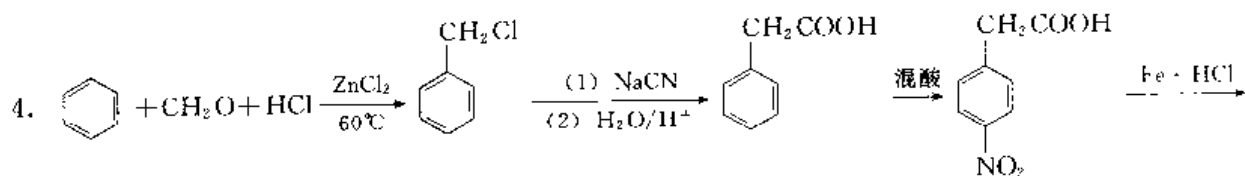
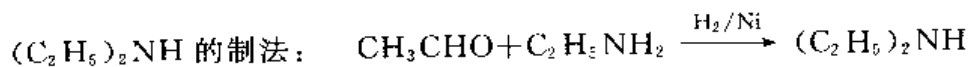
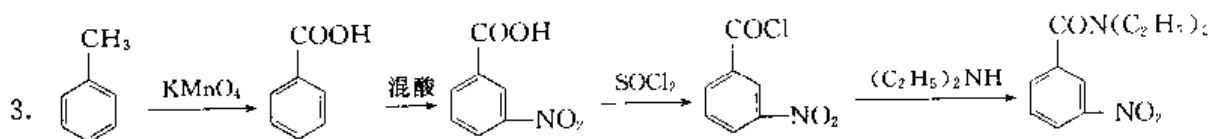
1. $b > d > c > a$ 2. $c > a > b$ 3. $c > b > a$

五、用化学方法鉴别下列多组化合物



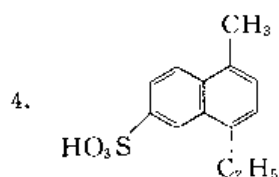
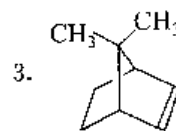
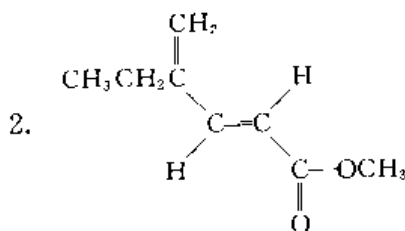
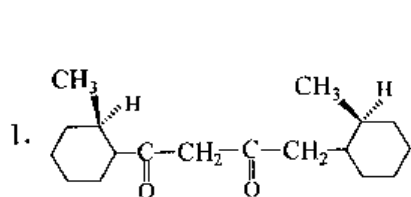
六、用化学方法分离混合物





模拟试题 37

一、命名下列化合物或写出它们的结构式 (6分)

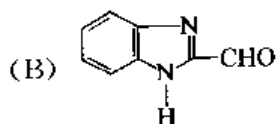
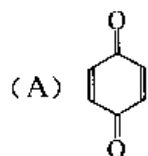


5. 10-苯亚甲基-9-蒽酮

6. *R*-3-乙基-1-戊烯-4-炔

二、填空 (9分)

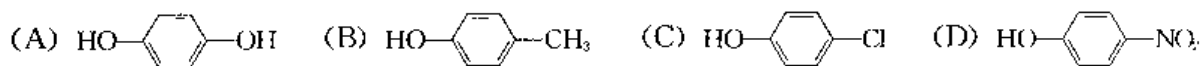
1. 下列化合物具有芳香性的是 ()



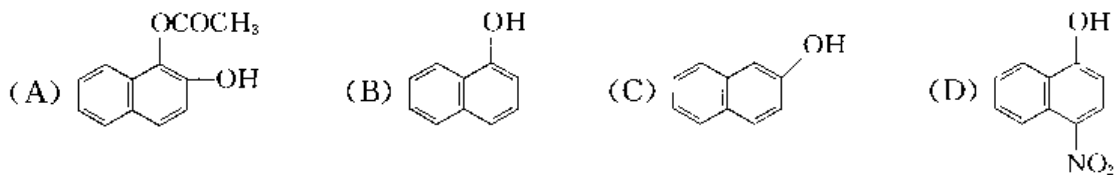
2. 下列糖中哪一个不与 Filling 试剂反应 ()

(A) D-核糖 (B) D-果糖 (C) 纤维二糖 (D) 蔗糖

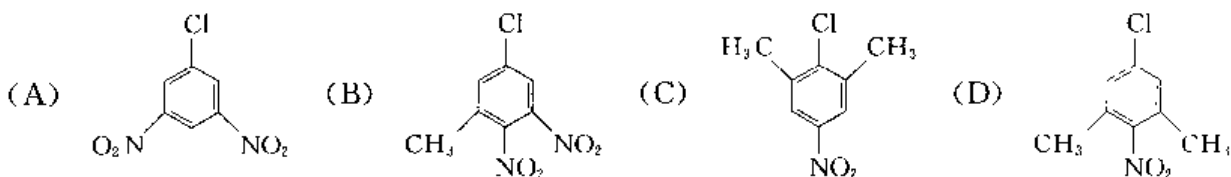
3. 下列化合物哪一个最易与对苯醌形成电荷转移络合物 ()



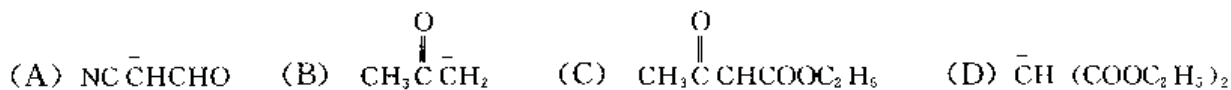
4. 把下列化合物按酸性由强到弱排列成序 ()



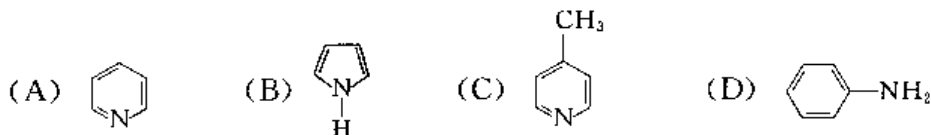
5. 下列化合物哪一个最易发生芳环上的亲核取代反应 ()



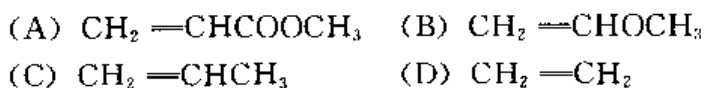
6. 下列负离子哪一个亲核性最强 ()



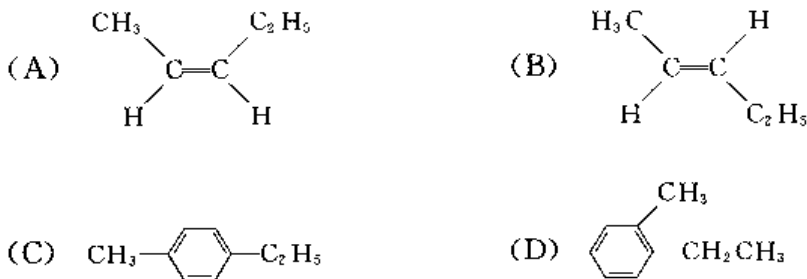
7. 将下列化合物按碱性由强到弱排列成序 ()



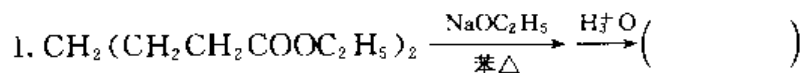
8. 下列化合物哪一个最易与环戊二烯发生反应 ()

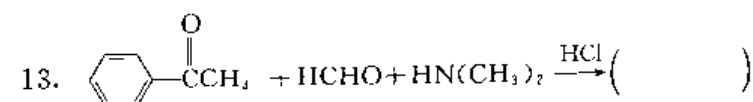
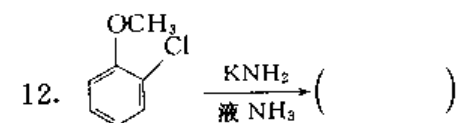
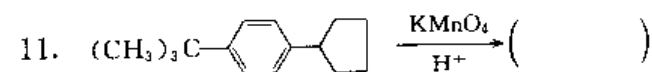
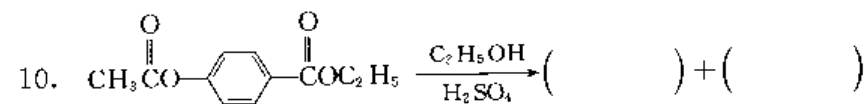
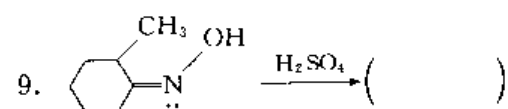
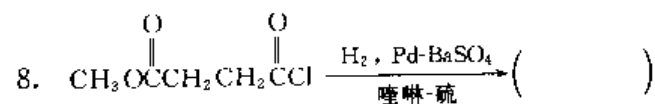
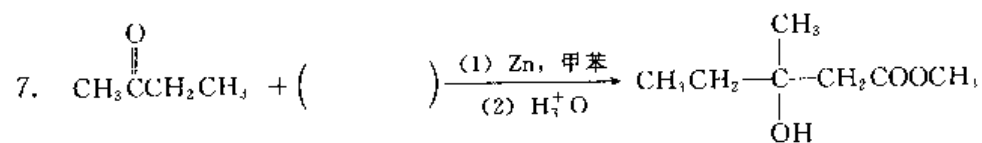
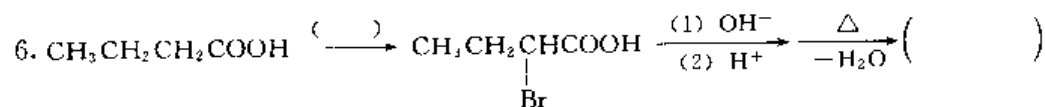
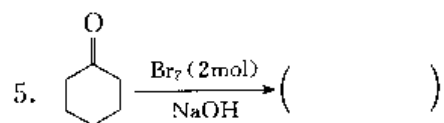
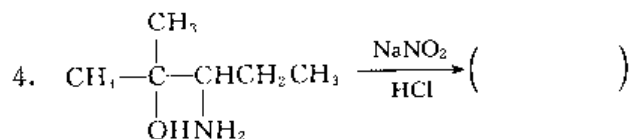
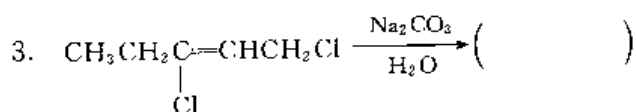
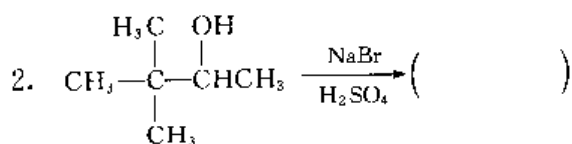


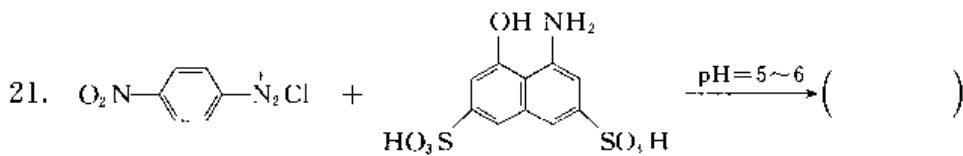
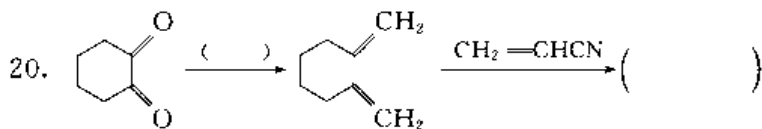
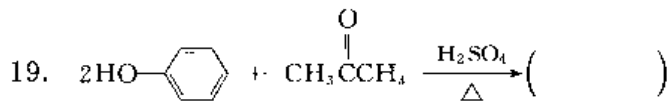
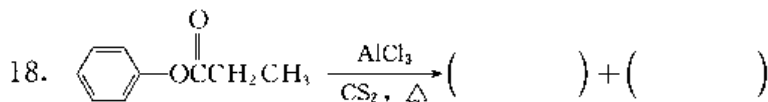
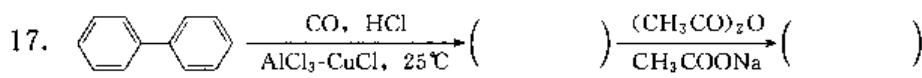
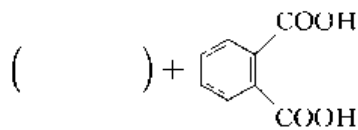
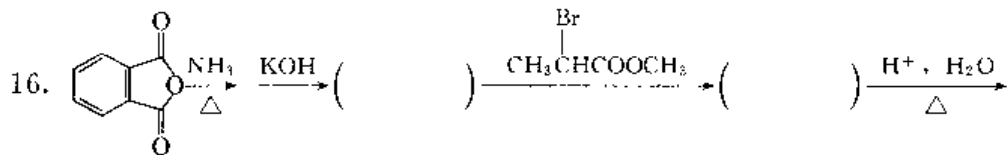
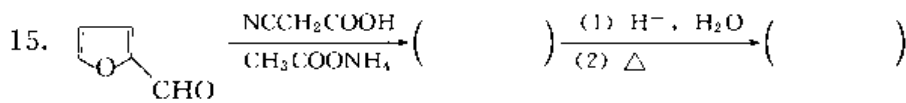
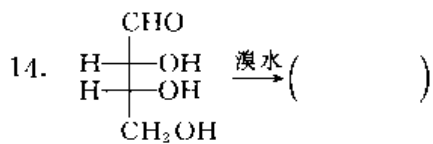
9. 下列化合物的红外光谱中, 何者在 970cm^{-1} 处有强的吸收峰 ()



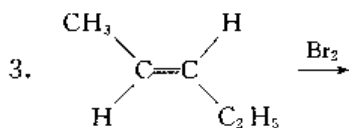
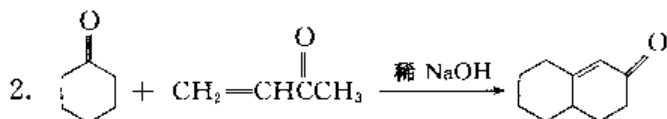
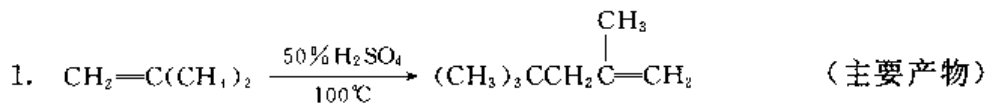
三、完成下列反应 (29 分)





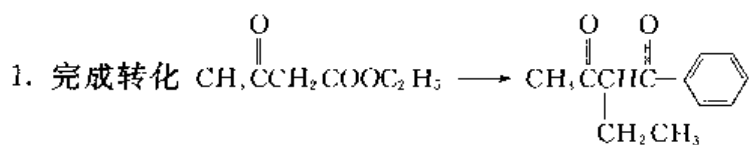


四、写出下列反应的机理 (15分)

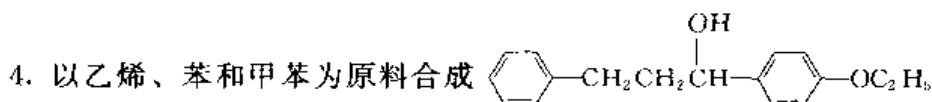
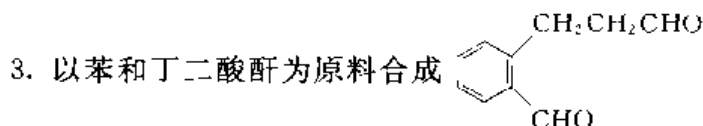


(写出反应产物的 Fischer 投影式及机理)

五、合成题 (无机试剂任选) (20 分)



2. 以甲苯为主要原料合成间硝基苯甲酸。

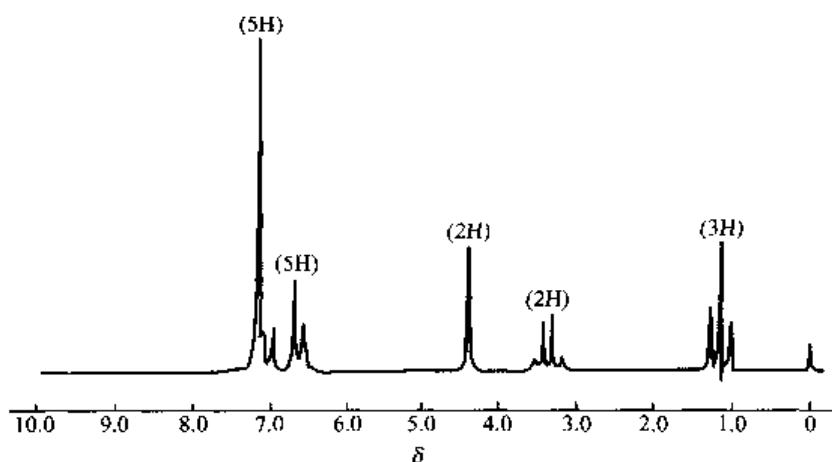


六、推断结构 (11 分)

1. 化合物 A ($\text{C}_6\text{H}_{12}\text{O}_3$) 其红外光谱在 1710cm^{-1} 处有强的吸收峰, A 与碘的 NaOH 溶液作用立即生成黄色沉淀。与 Tollens 试剂无银镜生成, 但用稀 H_2SO_4 处理 A 后所得化合物可以有银镜反应。A 的 $^1\text{H-NMR}$ 数据如下: δ 2.1 (单峰, 3H), δ 2.6 (双峰, 2H), δ 3.2 (单峰, 6H), δ 4.7 (三重峰, 1H) 试写出 A 的结构及各步反应。(4 分)

2. 化合物 B 和 C 的分子式都是 C_6H_8 , 它们都能使 $\text{Br}_2\text{-CCl}_4$ 溶液迅速褪色。用酸性高锰酸钾氧化后都能得到产物 $\text{CH}_3\text{COCH}_2\text{COOH}$, 但 B 能与 $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ 溶液生成白色沉淀, C 却不能; C 能与丙烯醛进行 Diels-Alder 反应, B 却不能。试推测 B 和 C 的结构式。

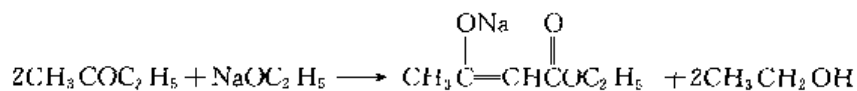
3. 有一化合物 D, 分子式为 $\text{C}_{15}\text{H}_{17}\text{N}$, 用对甲苯磺酰氯和氢氧化钾处理后无明显变化。这个混合物酸化后得一澄清溶液, D 的核磁共振谱如下图所示。试写出 D 的构造式。(3 分)



七、实验题 (10 分)

1. 有一混合物 (50g), 其中含甲苯 (30g)、苯胺 (25g) 和苯甲酸 (5g)。请根据它们的化学物理性质选择合适的试剂, 设计一个合理方法, 从混合物中分离出纯净的甲苯、苯胺和苯甲酸 (用操作流程图表示)。(4 分)

2. 合成 3-丁酮酸乙酯的反应如下。



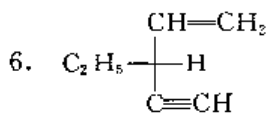
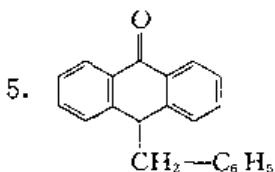
加入乙酸乙酯 22g (0.25mol), 金属钠 2.5 克 (0.11mol), 请问:

- (a) 在实验室中用 50% 醋酸酸化反应混合物至弱酸性, 如何估计所用 50% 醋酸的量?
 (b) 酸化后为何加饱和 NaCl 水溶液?
 (c) 为什么最后一步要用减压蒸馏? 请画出减压蒸馏装置图。(6 分)

参考答案

一、命名或写结构式

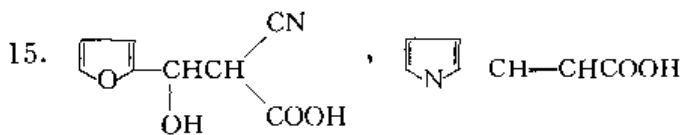
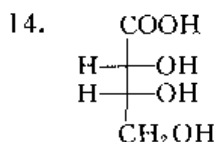
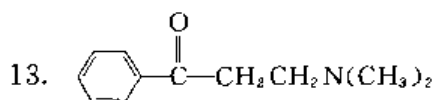
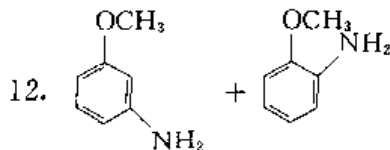
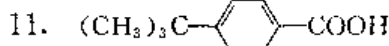
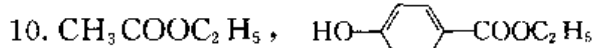
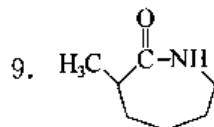
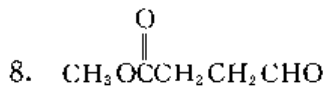
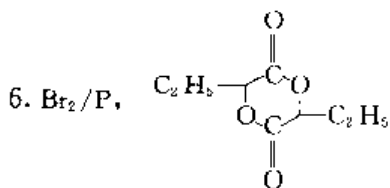
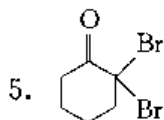
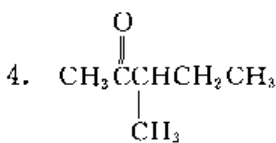
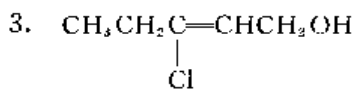
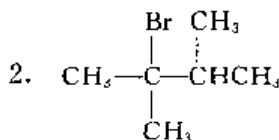
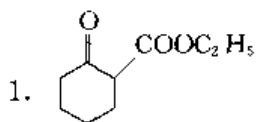
- 1-(2*R*-甲基环己基)-4-(2'*S*-甲基环己基)-1,3-丁二酮
- (2*E*)-4-乙基-2,4-戊二烯酸甲酯
- 7,7-二甲基双环[2,2,1]-2-庚烯
- 5-甲基-8-乙基-2-萘磺酸

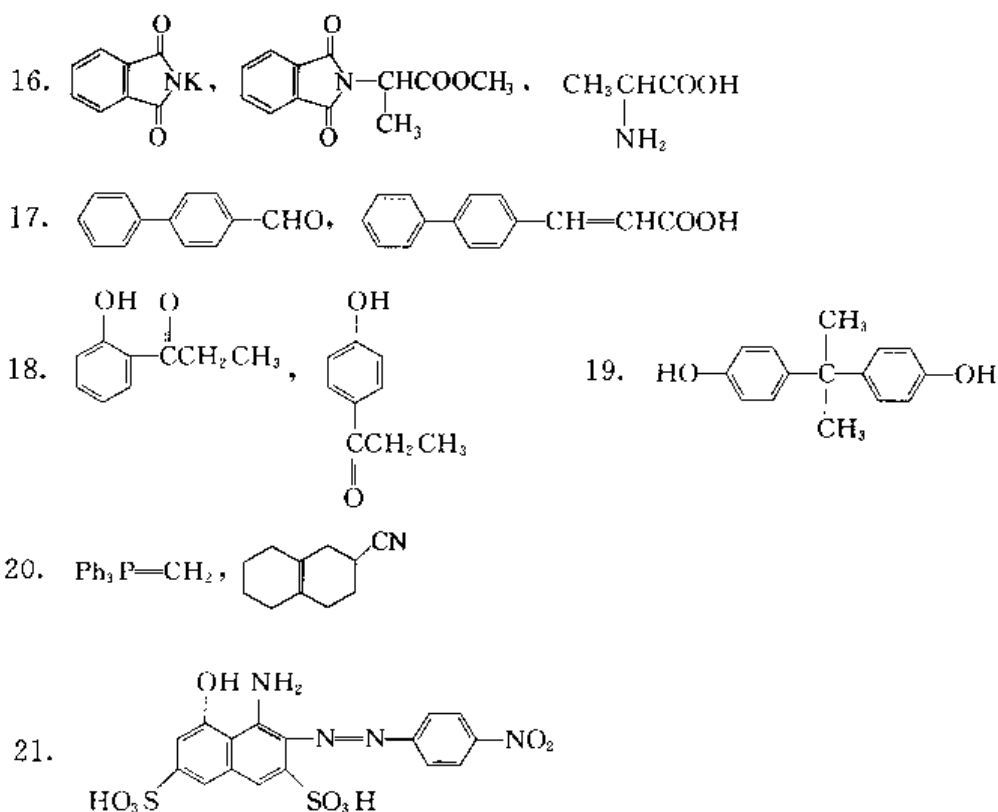


二、填空

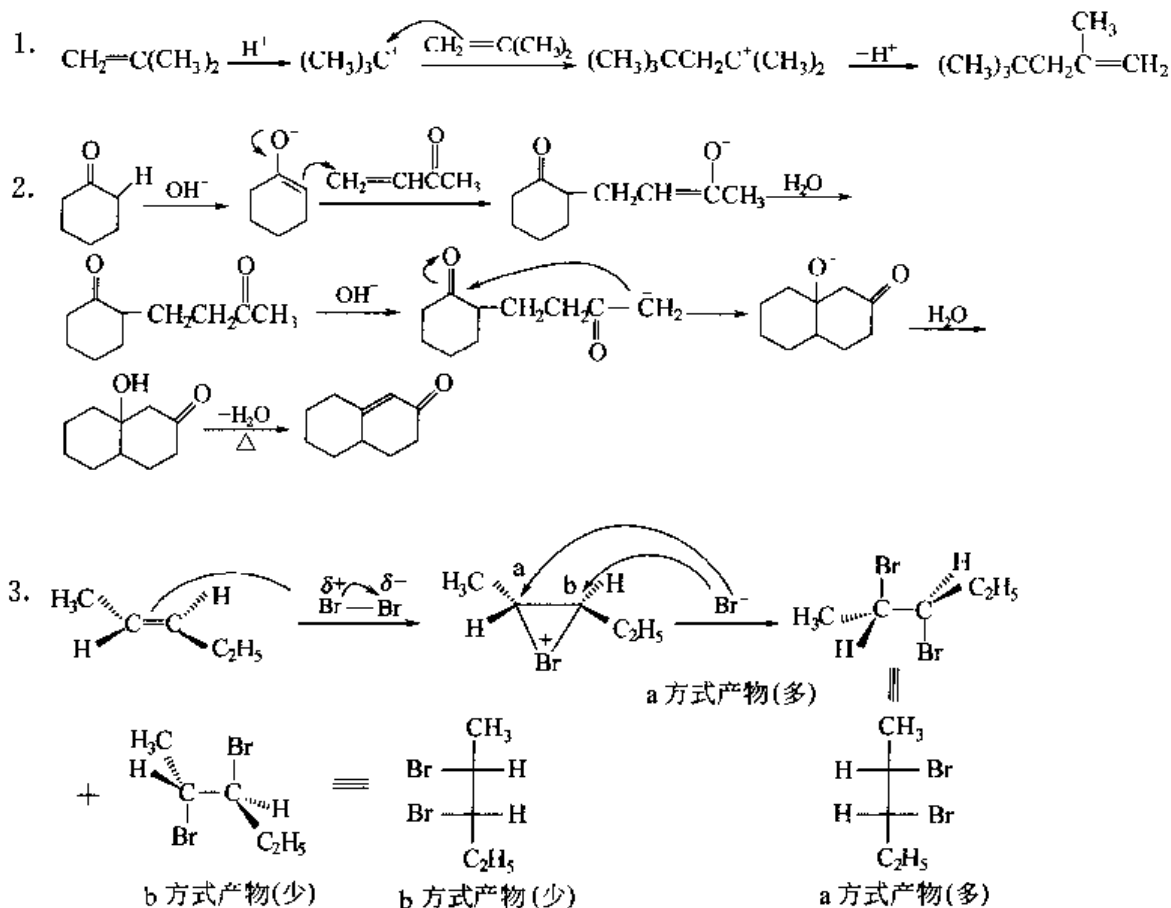
1. (B), (C) 2. (D) 3. (A) 4. (D) > (C) > (B) > (A) 5. (B)
 6. (B) 7. (C) > (A) > (D) > (B) 8. (A) 9. (B)

三、完成反应

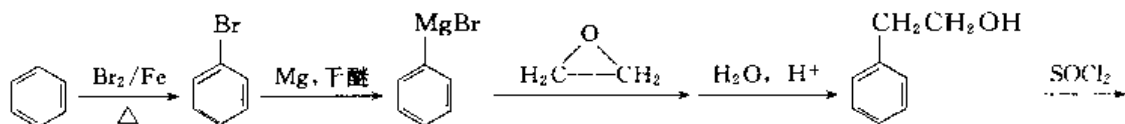
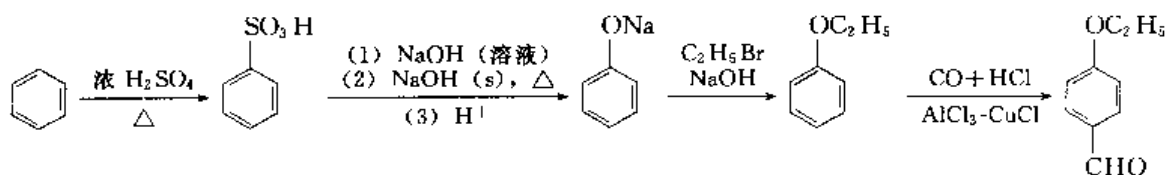
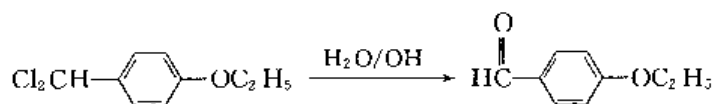
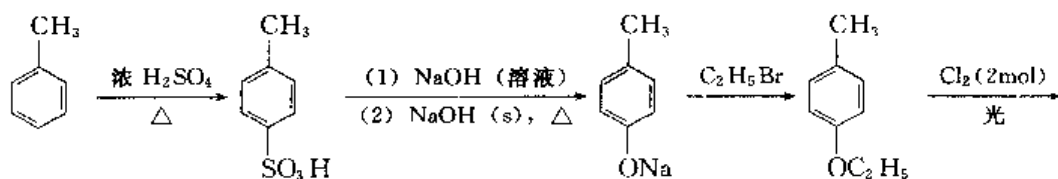
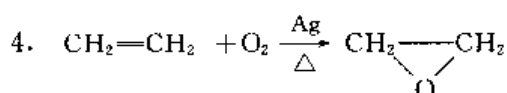
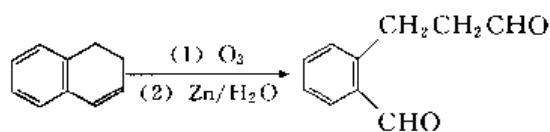
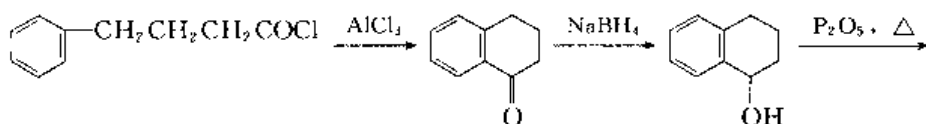
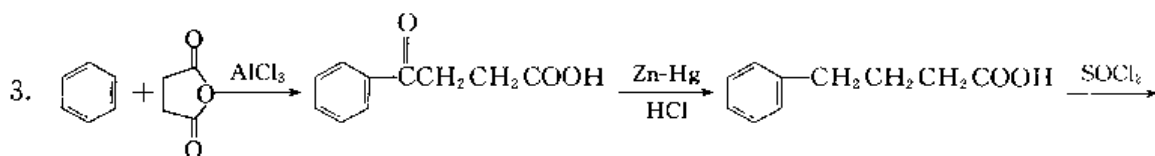
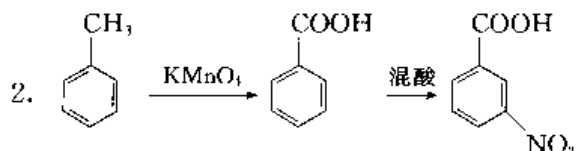
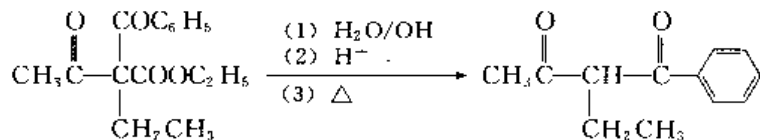
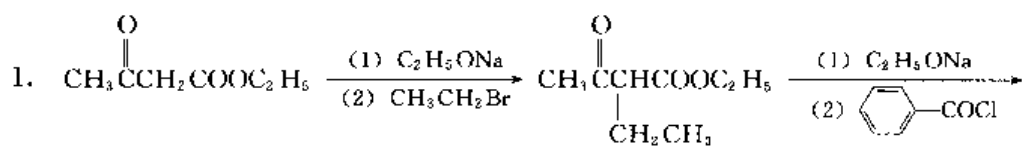


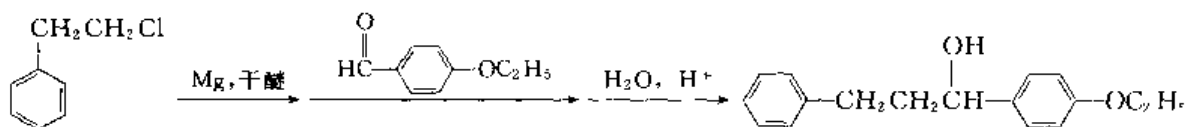


四、写出下列反应的机理



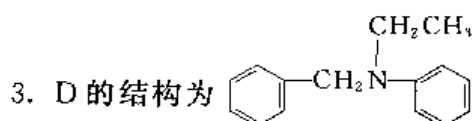
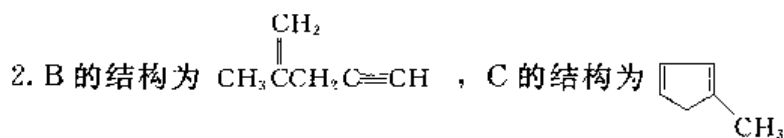
五、合成题



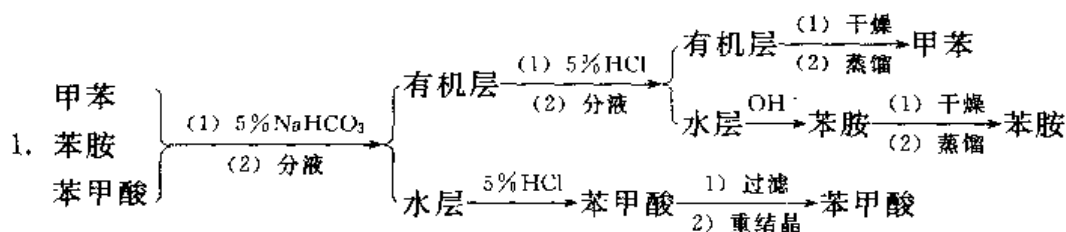


六、推断结构

1. 略。见“模拟试题 1 六、2。”



七、实验题



2. (a) 中和三乙钠盐的醋酸用量大约为 0.11mol, 需要约 120ml 5% HOAc。

(b) 促进分层, 减少三乙在水中的溶解度。

(c) 降低蒸馏温度, 防止三乙分解。

装置图略。

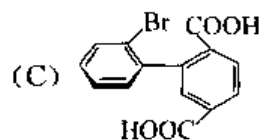
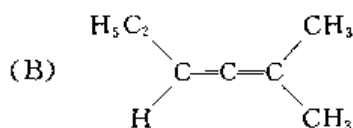
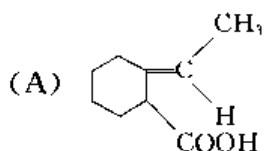
模拟试题 38

一、回答问题 (15 分)

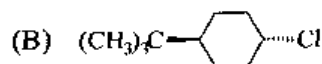
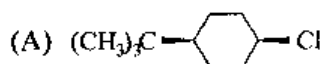
1. 分子式为 C₅H₁₀ 且具有三元环的所有异构体 (包括顺反、对映异构体) 共有多少个?

(A) 7 个 (B) 6 个 (C) 5 个 (D) 4 个

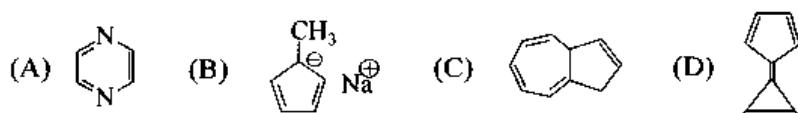
2. 下列化合物哪一个能拆分为对映体?



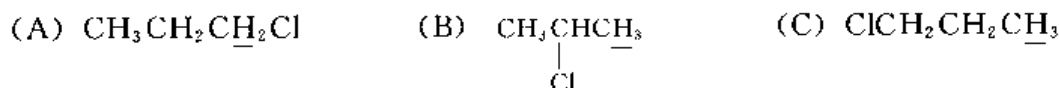
3. 下列化合物中哪一个在用乙醇钠的乙醇溶液处理时易发生 E2 反应?



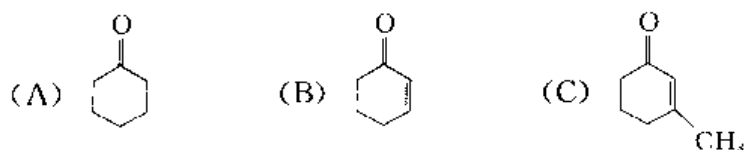
4. 下列化合物哪几个具有芳香性?



5. 下列化合物中用黑线标记的氢原子, 哪个在 NMR 的较低场出峰?



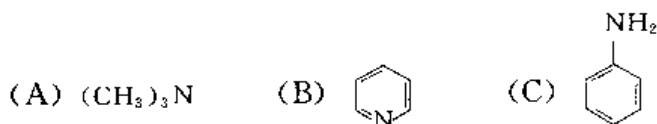
6. 排列下列化合物紫外光谱吸收波长的长短顺序:



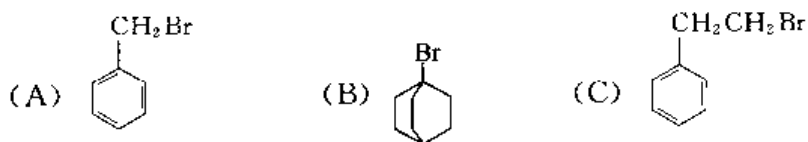
7. 比较下列化合物的酸性大小



8. 比较下列化合物的碱性大小



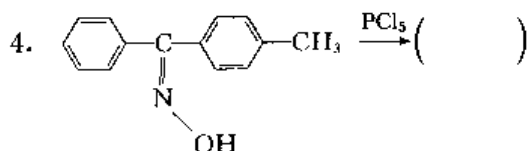
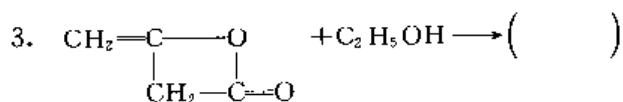
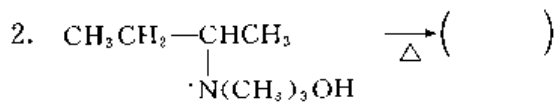
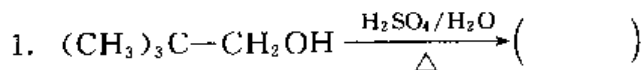
9. 比较下列化合物与 $\text{AgNO}_3/\text{C}_2\text{H}_5\text{OH}$ 溶液反应活性 (由大到小)

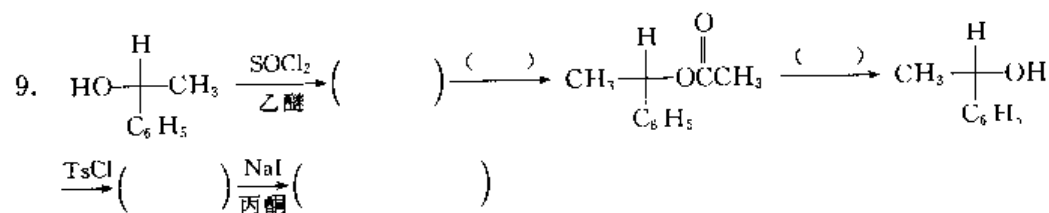
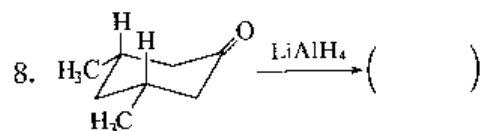
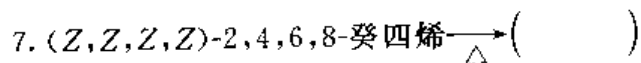
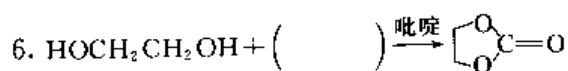
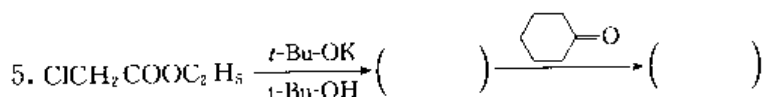


10. 画出下列化合物最稳定的构象 (优势构象):



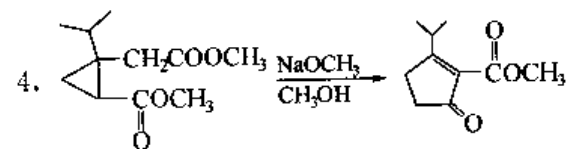
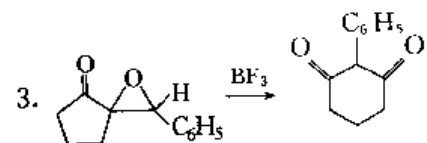
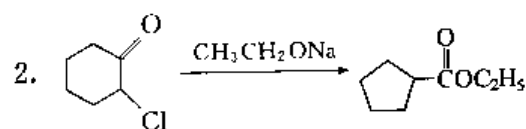
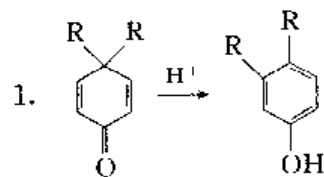
二、完成反应式 (20 分)





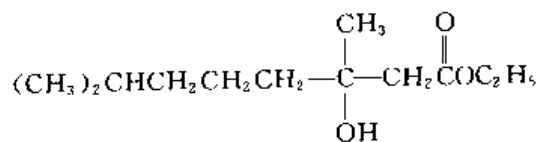
表示出最终产
物的立体结构

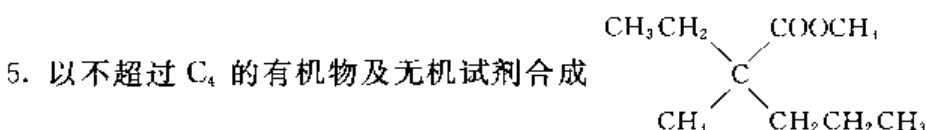
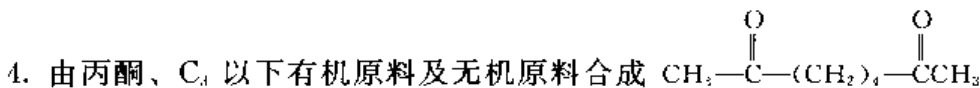
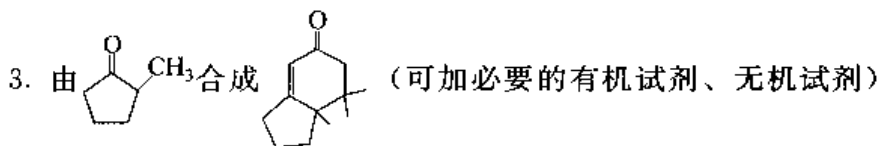
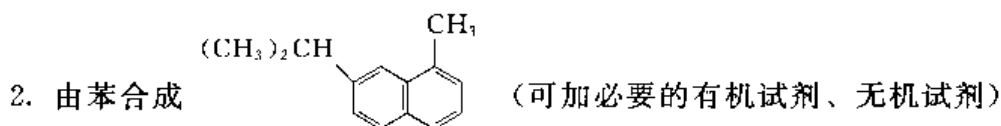
三、试为下列各反应提出其合理的反应机理 (20 分)



四、合成题 (20 分)

1. 以乙酰乙酸乙酯、 C_6 以下有机物及必要的无机试剂合成





五、测定结构 (20 分)

1. 某化合物 A (含一个溴原子) 与溴作用生成含有 3 个溴原子的化合物 B。A 能使 $KMnO_4$ 水溶液褪色, 生成含有一个溴的 1,2-二醇。A 易和 NaOH 作用生成 C 和 D, C 和 D 氢化后分别产生两种互为异构体的饱和一元醇 E 和 F。E 比 F 易脱水, E 脱水后产生两种异构化合物, F 脱水后只生成一种化合物, 这些脱水化合物都还原成正丁烷。写出 A、B、C、D、E、F 的结构式和各步反应, 并标明化合物 A~F 中哪个有立体异构体, 各有几个?

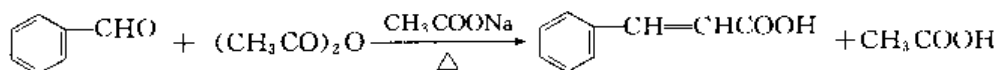
2. 由元素分析知某化合物分子式为 C_8H_8O 。IR 谱在 $1680cm^{-1}$ 、 $1430cm^{-1}$ 、 $1360cm^{-1}$ 处有强吸收峰。质谱分子离子峰在 120, 最强峰 m/z 105, 另外 m/z 43、 m/z 77 处有较强峰, 试确定该化合物结构。

3. 某饱和酮 A ($C_7H_{12}O$) 与甲基碘化镁反应再经酸化水解后得到醇 B ($C_8H_{16}O$), B 用硫酸氢钾处理脱水得两个异构烯烃 C 和 D (C_8H_{14}) 的混合物, C 还能通过 A 和亚甲基三苯基膦 ($CH_2=PPh_3$) 反应得到。D 经臭氧化分解生成酮醛 E ($C_8H_{14}O_2$), E 用湿的氧化银氧化变为酮酸 F ($C_8H_{14}O_3$), F 用溴在氢氧化钠中处理得到 3-甲基-1,6-己二酸。试写出 A、B、C、D、E、F 的结构式和反应式。

4. 某化合物 A, $C_{10}H_{16}O$ 能吸收 Br_2 , 也能使 $KMnO_4$ 溶液褪色。A 的 IR 谱: $1700cm^{-1}$ (强)、 $1640cm^{-1}$ (弱); NMR 谱: δ 1.05 (6H) 单峰; δ 1.70 (3H) 宽单峰; δ 2.0~2.4 (4H) 多重峰; δ 2.6~2.8 (2H) 多重峰; δ 5.1~5.4 (1H) 多重峰。A 与水合肼反应, 再在二甘醇中与 KOH 加热得 B ($C_{10}H_{18}$)。B 与臭氧反应, 再用 Zn/H_2O 处理得 C ($C_{10}H_{18}O_2$)。C 对 Tollen 试剂呈阳性反应, 且能生成双苯胺, 在稀碱中加热得 D ($C_{10}H_{16}O$)。D 用 Pd/C 催化氢化, 可吸收 1mol H_2 生成 E ($C_{10}H_{18}O$)。E 与 $I_2/NaOH$ 反应生成 CHI_3 和 1,4-二甲基-1-环己烷甲酸。写出 A~E 的结构式。

六、实验题 (5 分)

用苯甲醛和醋酸酐在醋酸钠存在下于 $170\sim 180^\circ C$ 加热回流, 制取肉桂酸, 反应如下:



原料和产物的主要物理常数如下。

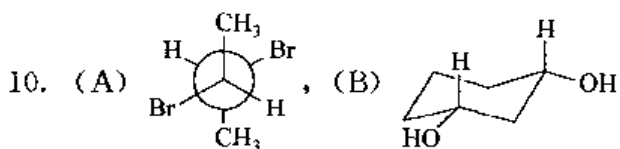
原料、产物	相对密度 (d_4^{25})	m. p. / $^{\circ}\text{C}$	b. p. / $^{\circ}\text{C}$	溶解度, (20 $^{\circ}\text{C}$)/g · (100g) $^{-1}$		
				H ₂ O	C ₂ H ₅ OH	(C ₂ H ₅) ₂ O
苯甲醛	1.054	—	180	0.33	∞	∞
醋酐	1.087	—	140	13.6	∞	∞
肉桂酸		133	300	300	23	易溶

试设计如何从反应混合物中分离得到肉桂酸。

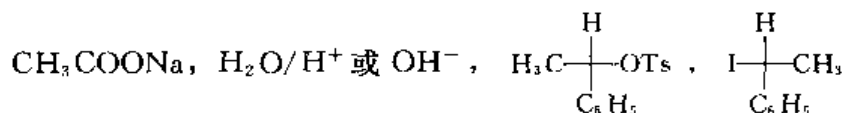
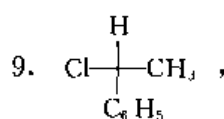
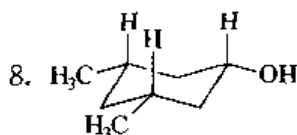
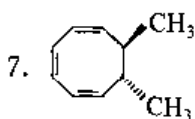
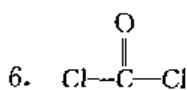
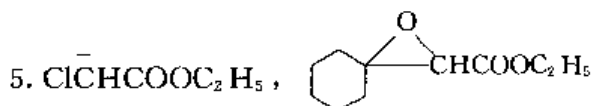
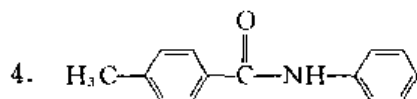
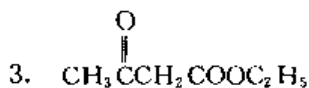
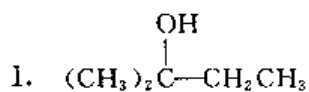
参考答案

一、回答问题

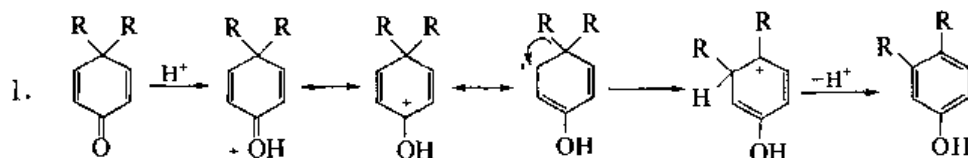
1. (C) 2. (A) 3. (A) 4. 都有芳香性 5. (A) 6. λ_{\max} : C>B>A
7. 酸性: D>A>C>B 8. 碱性: A>B>C 9. 活性: A>C>B

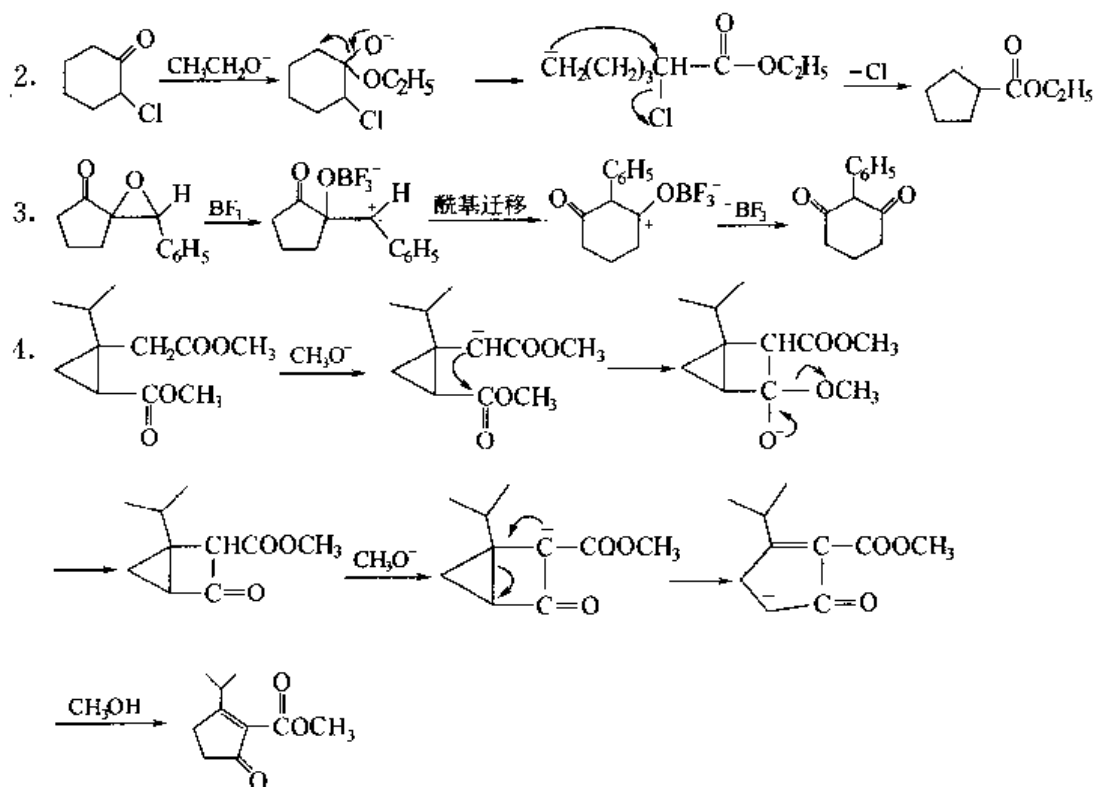


二、完成反应式

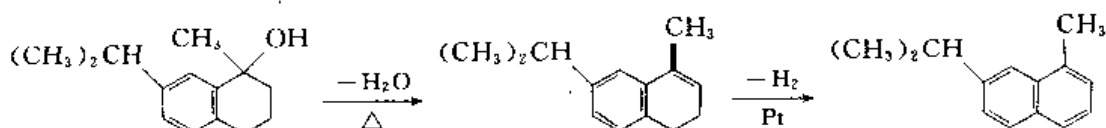
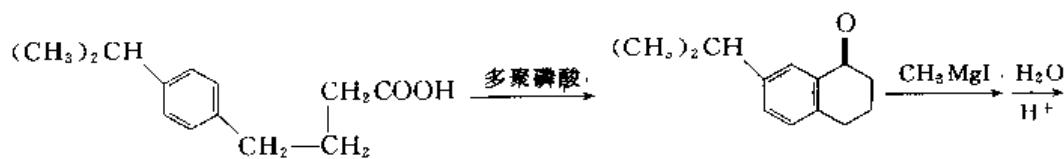
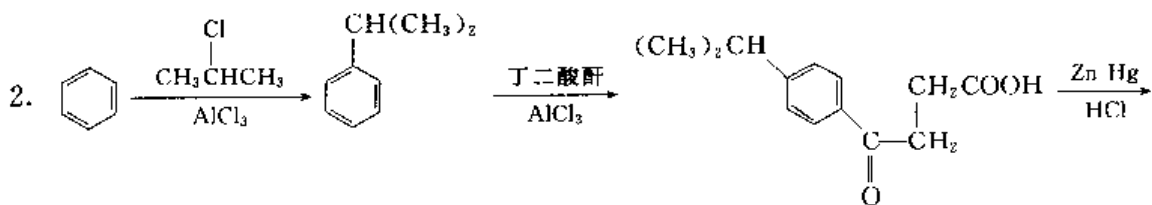
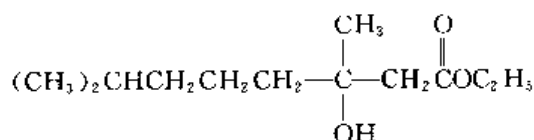
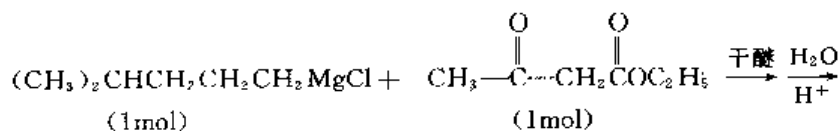
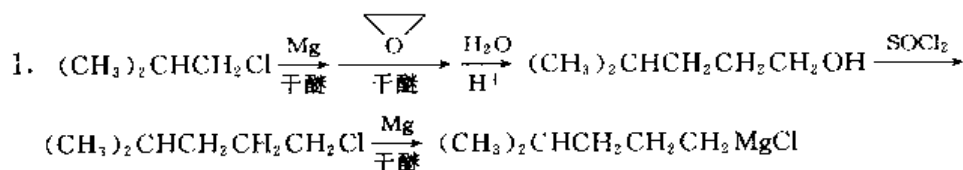


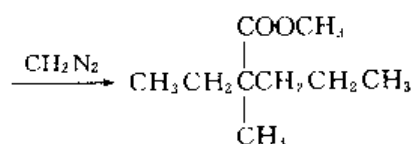
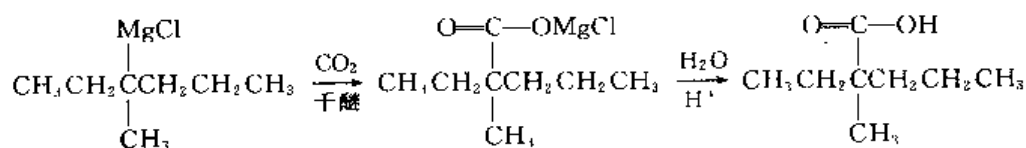
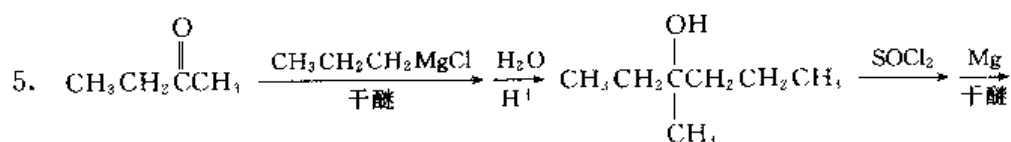
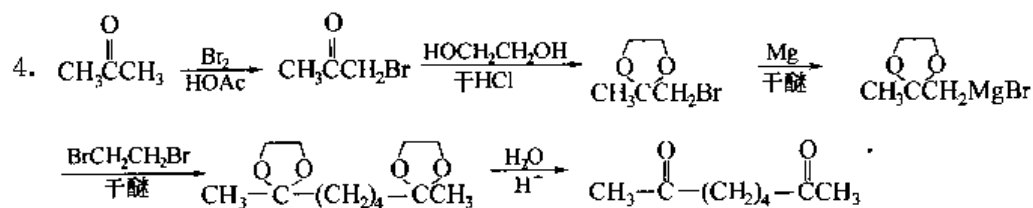
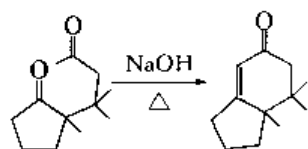
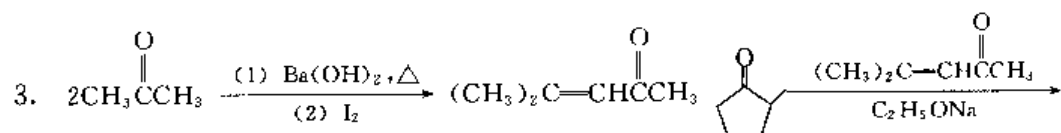
三、试为下列各反应提出其合理的反应机理





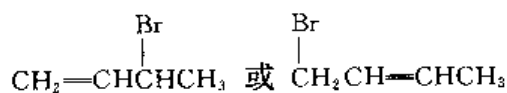
四、合成题





五、测定结构

1. 各步反应式略。

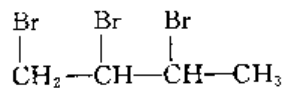


(A)

2 个旋光异构体

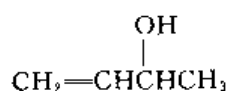
(A)

2 个顺反异构体



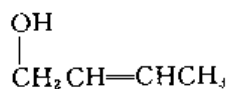
(B)

4 个旋光异构体



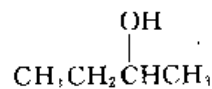
(C)

两个旋光异构体



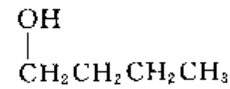
(D)

两个顺反异构体



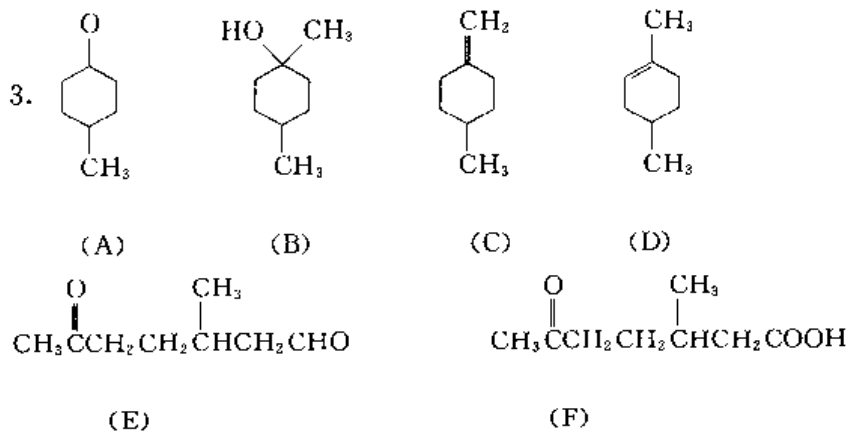
(E)

两个旋光异构体

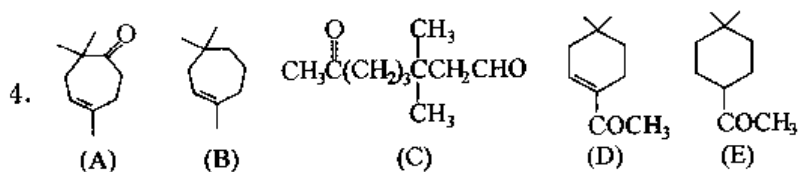
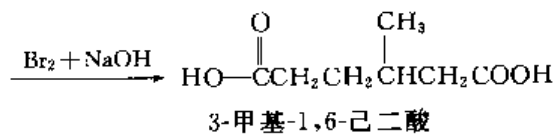
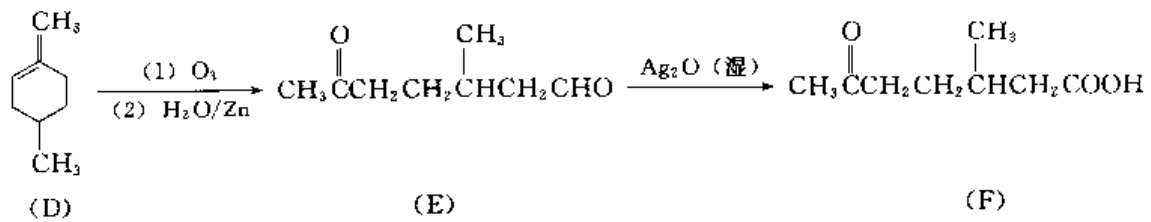
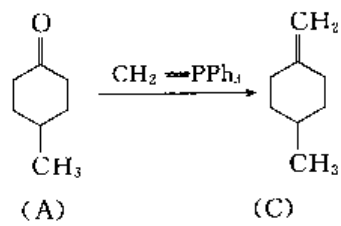
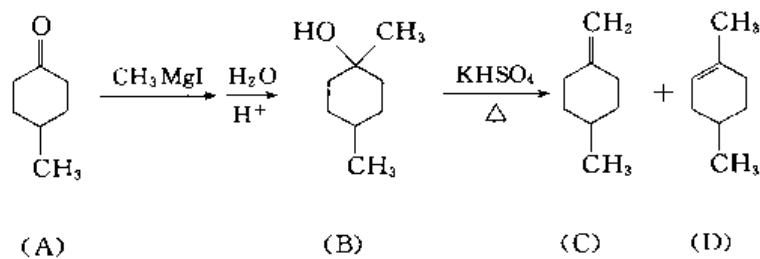


(F)

2. 略。见“模拟试题 35 五、1。”



反应式

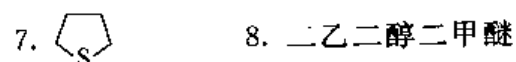
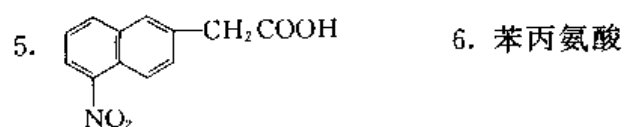
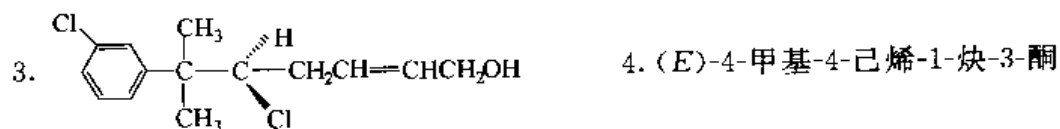
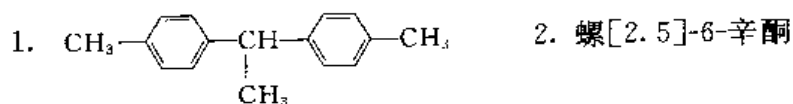


六、实验题

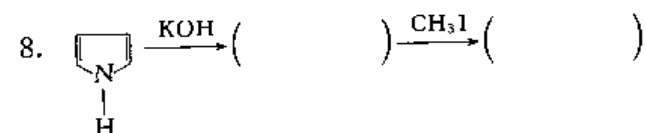
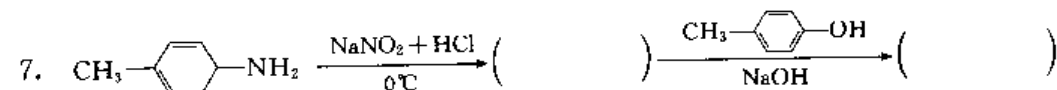
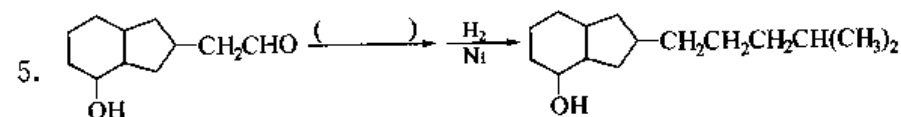
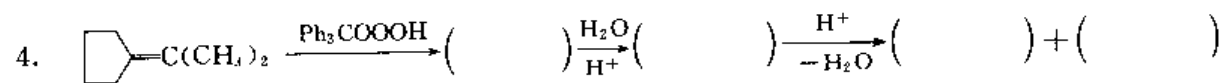
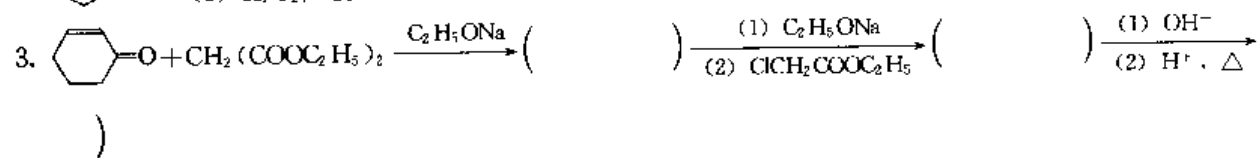
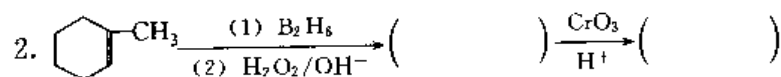
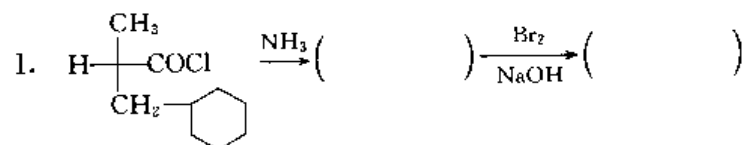
略。见“模拟试题 28”。

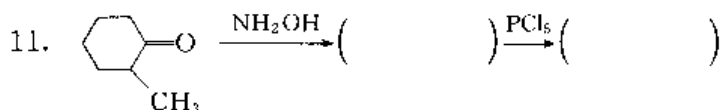
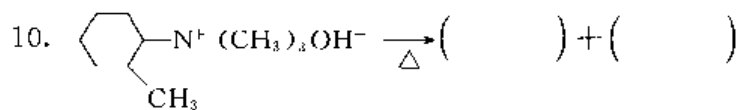
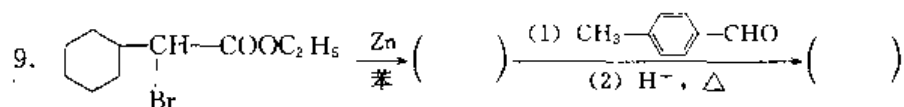
模拟试题 39

一、命名下列化合物或写出它们的结构式 (8分)





二、完成下列反应 (25分)





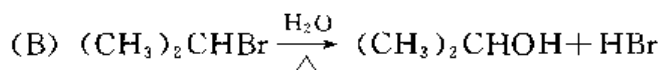
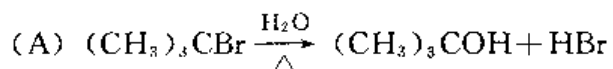
三、选择填空 (18分)

1. Br_2 分别与 (A)  $=\text{CH}_2$ 和 (B)  $=\text{CH}_2$ 在醋酸溶液进行加成反应, 请问哪一个反应速率快? ()

2. 下列化合物中哪一个没有芳香性? ()



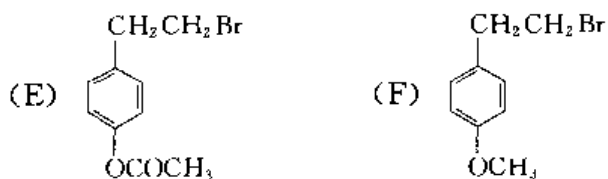
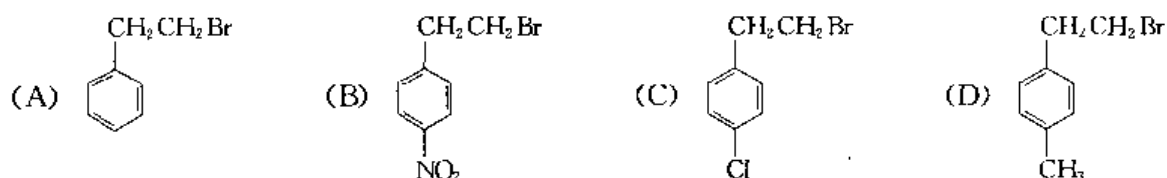
3. 下列两个反应中哪一个反应速率较快? ()



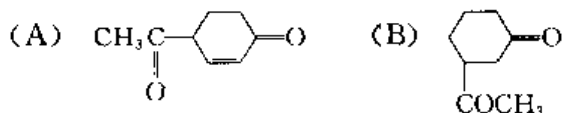
4. A 与 B 是: (A) 相同的; (B) 对映异构体; (C) 非对映异构体? ()



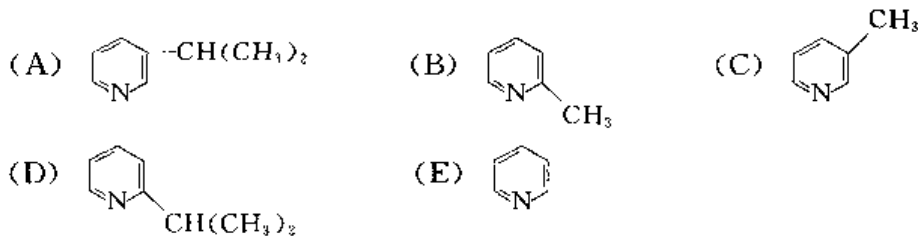
5. 下列化合物进行 E2 反应时, 反应速率最大者为 () 反应速率最小者为 ()

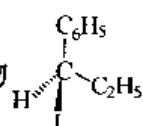


6. 以下一对化合物中, 哪一个更易形成烯醇式结构? ()



7. 判断下列化合物与碘甲烷反应的活性, 哪个最大 (), 哪个最小 ()

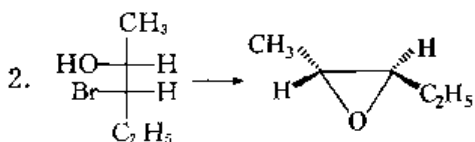
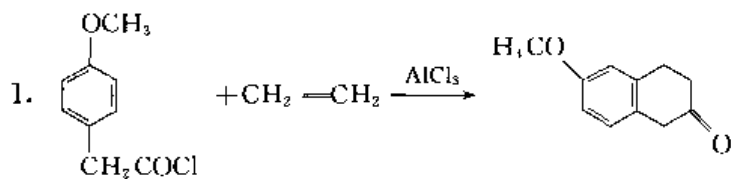


8. 化合物  在丙酮-水溶液中放置时会转变为相应的醇, 试从下列答案中选择此

醇的正确构型。

(A) 构型保持不变 (B) 构型翻转 (C) 外消旋化

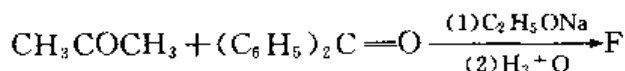
四、请写出下列反应的机理 (8分)



五、推断以下化合物的结构 (8分)

1. 化合物 A ($C_{10}H_{16}O$) 能吸收溴, 也能使高锰酸钾溶液褪色。其红外吸收如下: 在 1700cm^{-1} (强)、 1640cm^{-1} (弱) 有吸收峰; 其 NMR 数据如下: δ 1.05 (单峰, 6H), δ 1.70 (单峰, 宽, 3H), δ 2.0~2.4 (多重峰, 4H), δ 2.6~2.8 (多重峰, 2H), δ 5.1~5.4 (多重峰, 1H)。A 与水合肼作用, 再在二乙二醇中与 KOH 加热得 B ($C_{10}H_{18}$); B 与臭氧作用再用锌和水得 C ($C_{10}H_{18}O_2$), C 对 Tollens 试剂呈阳性反应, 且能生成双苯腙; 化合物 C 在稀碱中加热得 D ($C_{10}H_{16}O$), D 用 Pd-C 催化氢化吸收 1mol 氢生成 E ($C_{10}H_{18}O$), E 与碘/NaOH 反应生成碘仿和 4,4-二甲基-1-环己烷甲酸。试写出 A、B、C、D、E 的构造式。

2. 化合物 F 是下列反应之产物:



F 的 NMR 谱如下: δ 7.2 (单峰, 10H), δ 5.3 (单峰, 1H), δ 2.3 (单峰, 3H)

请写出 F 的构造式。

六、分离与鉴别 (6分)

1. 用简便的化学方法鉴别正丁酰氯与正丁基氯。

2. 说明如何用化学的方法分离苯甲酸和苯甲酸乙酯，并相当纯地回收每一组分。

七、合成下列化合物，无机试剂任选（20分）

1. 用 C_3 以下（含 3 个碳）的有机物合成 $OHC-CH_2CH_2CH_2COOH$

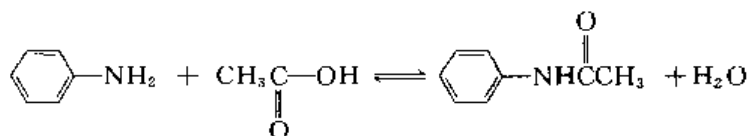
2. 由氯苯为起始原料合成 $CH_3CH_2O-C_6H_4-NHC(=O)CH_3$ ，其他有机原料可任选。

3. 用苯、甲苯及适当的有机物为主要原料合成 $m-C_6H_4-COOH-N=N-C_6H_4-N(CH_3)_2$

4. 由不超过 3 个碳原子的烃合成 $CH_3CH(CH_3)CH_2CH(CH_3)CHO$

八、实验题（7分）

乙酰苯胺的制备是按以下反应进行的：

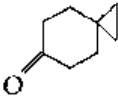


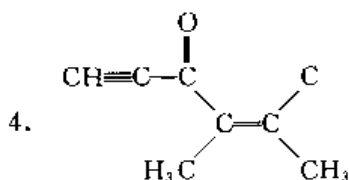
请回答以下问题：

1. 试叙述该实验的操作过程。
2. 该实验中加入锌粉的作用是什么？如锌粉过量会产生什么影响？
3. 精制产品时，为什么采用热过滤的方法？
4. 请预测该产品在红外光谱图中将会出现哪些主要特征吸收峰？

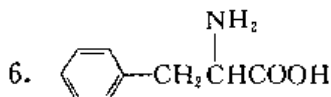
参考答案

一、命名或写结构式

1. 1,1-二对甲苯基乙烷 2.  3. (5R)-6-甲基-6-间氯苯基-5-氯-2-庚烯-1-醇



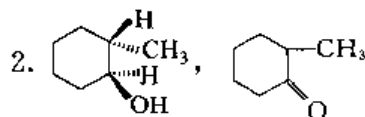
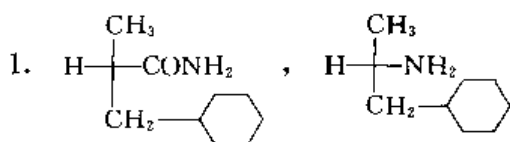
5. 5-硝基-2-萘乙酸

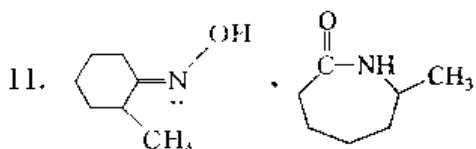
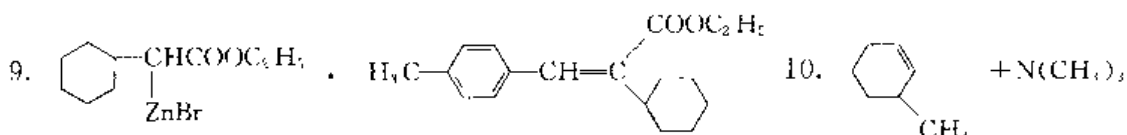
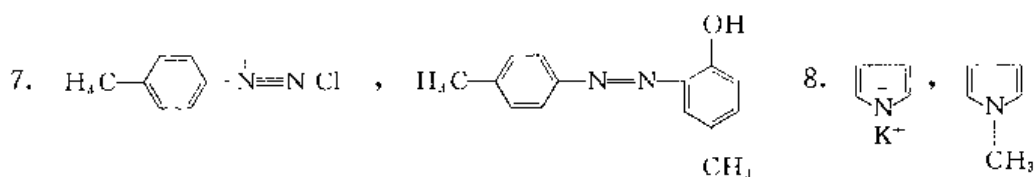
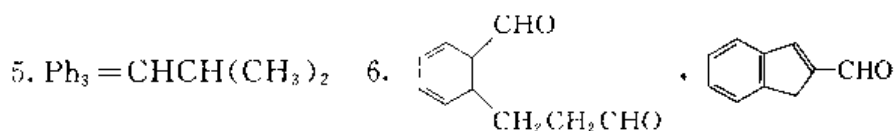
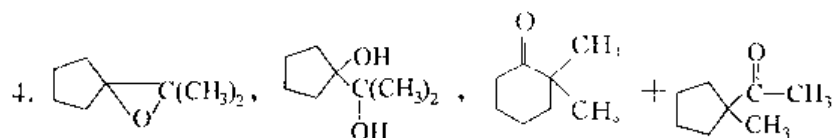
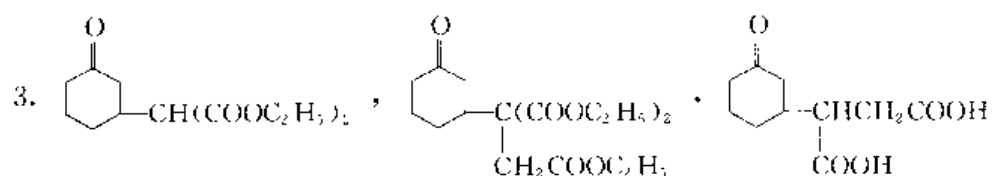


7. 四氢噻吩

8. $CH_3OCH_2CH_2OCH_2CH_2OCH_3$

二、完成下列反应



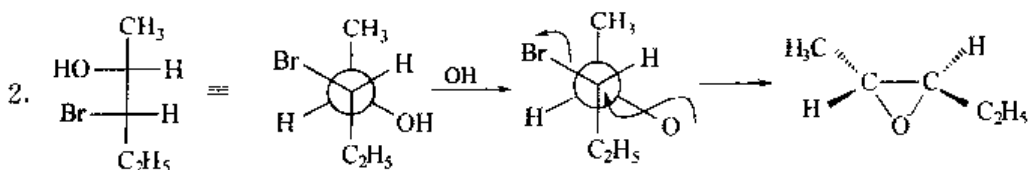
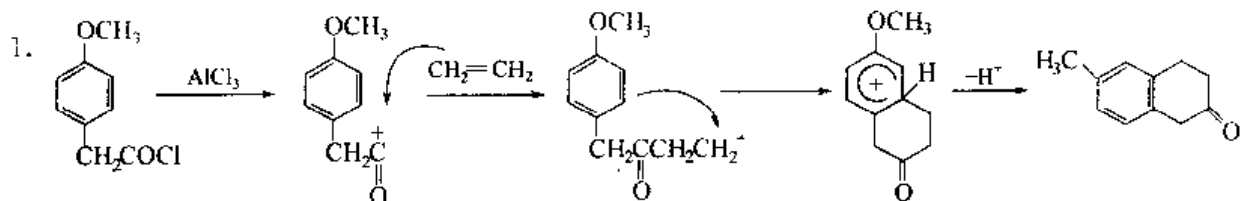


三、选择填空

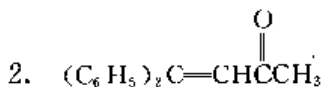
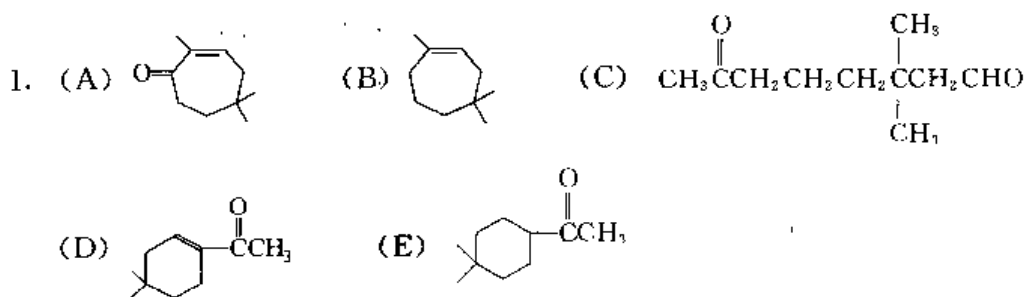
1. (B) 2. (D) 3. (A) 4. (C) 5. (B), (F) 6. (A) 7. (B), (E)

8. (C)

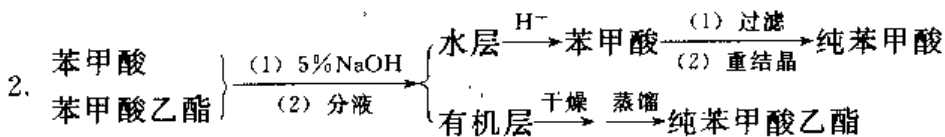
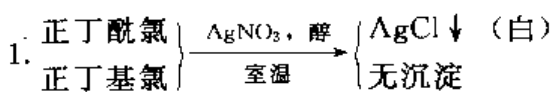
四、写出下列反应的机理



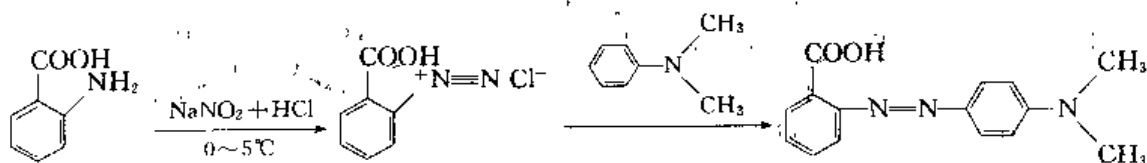
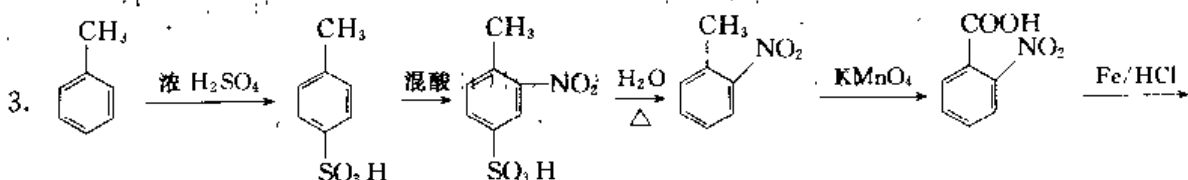
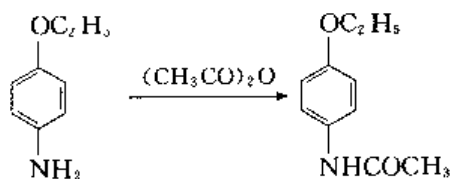
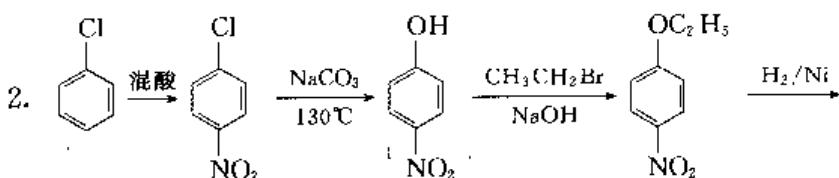
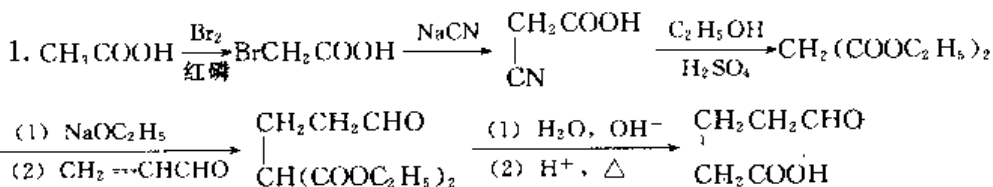
五、推断下列化合物的结构

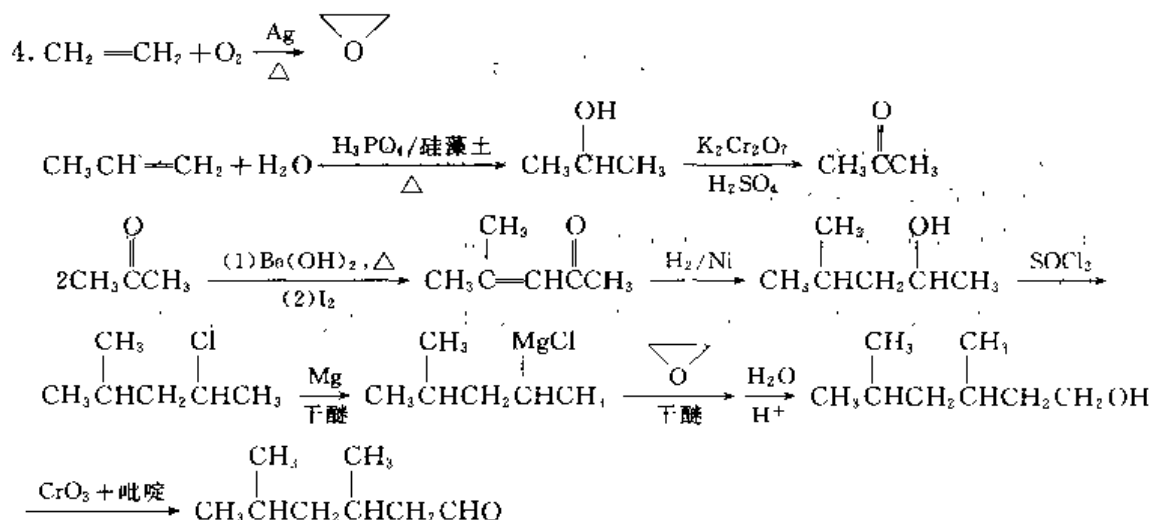


六、分离与鉴别



七、合成题





八 实验题

1. 该实验的操作过程如下:

① 由 50ml 锥形瓶、分馏柱、蒸馏头、温度计、小量筒等组装成一分馏装置。

② 在锥形瓶中加入新蒸过的苯胺、冰醋酸(稍过量)及少量锌粉。在石棉网上用小火加热,保持温度计读数为 105℃ 左右,使反应生成的水不断蒸出。

③ 待反应完成时,温度计读数会出现波动,反应瓶中也出现白雾,此时,停止加热。

④ 剧烈搅拌下,将反应混合物趁热以细流慢慢倒入 100ml 冷水中,使粗产物析出。充分冷却后抽滤,得到粗乙酰苯胺。

⑤ 将粗乙酰苯胺用水重结晶。

2. 该实验中加入锌粉的作用是防止苯胺在反应过程中氧化。如锌粉过量会在后处理时出现不溶于水的氢氧化锌。

3. 精制产品时,采用热过滤的方法可除去不溶性杂质。热过滤操作一定要“趁热过滤”,否则,乙酰苯胺将不会顺利通过滤纸,而在滤纸上面析出,达不到使不溶性杂质与乙酰苯胺分离的目的。

4. 该产品在红外光谱图中将会出现的主要特征吸收峰有以下几种。

① 苯环呼吸振动: 1600cm^{-1} 、 1500cm^{-1} 、 1580cm^{-1} 、 1460cm^{-1} ;

② 氮氢键伸缩振动: 约 3300cm^{-1} ;

③ 羰基伸缩振动: 约 1680cm^{-1} ;

④ 氮氢键弯曲振动: 约 1560cm^{-1} ;

⑤ 甲基弯曲振动: 约 1380cm^{-1} 。