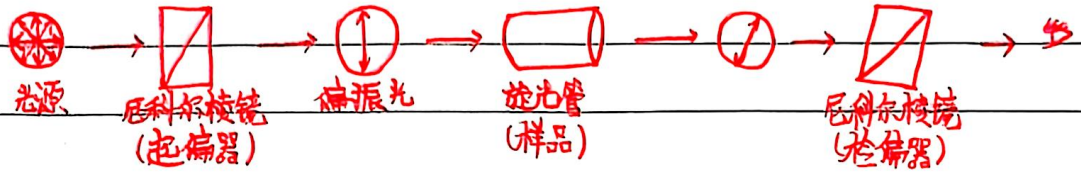
对映异构

Date Page

立体异构体：构造相同，但原子在空间的排列不同。

↳ 包括：对映异构 & 非对映异构

· 旋光性：测定：旋光仪



旋转的角度 α 为旋光度（右旋 +，左旋 −）。符号 α_λ^t，t 温度，λ 波长

· 比旋光度：α 不仅与物质本身结构有关，且与浓度 & 旋光管长度有关

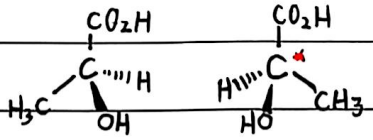
↳ 某物质在单位物质浓度、单位旋光管长度下测得的旋光度

用 $[\alpha]_\lambda^t$ 表示（λ 为测定时的波长，一般用钠光，波长 589.3nm，D 表示）。

$$[\alpha]_\lambda^t = \frac{\alpha}{l \cdot c}$$

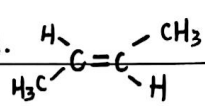
l 为旋光管长度，dm；c 为浓度：g/mL。

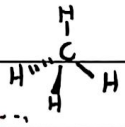
· 手性：实体与镜相不能重合 ⇒ 对映异构体 eg. 乳酸



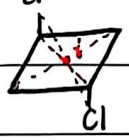
手性碳 ⇒ 连有4个不同基团的 C 原子

判断：(1). 对称轴（C_n）：n 重对称轴，以此直线为轴旋转 360°/n 后与原来相同。

eg.  为 C_2

 为 C_3。

(2). 对称面（σ）：eg. 有对称面一定能与镜像重合

(3). 对称中心（i）：eg. 

⇒ 若一个分子存在对称面或对称中心，则一定无手性。但对称轴不能作为判断依据。

↳ 含有一个手性 C 原子的分子一定是手性分子

对一对对映体而言，每个对映体都有旋光性，一个对映体使右旋，另一个左旋

但当等量左旋体与右旋体混合时，混合物无旋光性，称为外消旋体。

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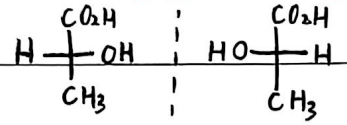
构型表示方法：Fischer 投影式

eg. 乳酸： 

P.S. 规定横键基团朝前，竖键基团朝后

注意：①. Fischer投影式不能离开纸面翻转

②. Fischer投影式不能在纸面上转 90°或270°，但可转180°

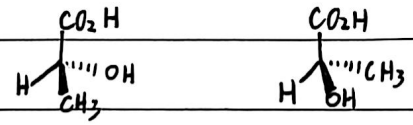
③. Fischer 投影式不能将两个基团互换奇数次，但可以互换偶数次.

画 Fischer 投影式时习惯把含碳原子的基团放在竖键的方向且编号最小在上端

· 构型的标记

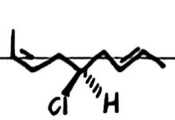
(1). R/S 标记法

与手性C相连的四个原子或基团按次序规则排序：a>b>c>d，使d远离观察者再沿a→b→c观察，若为顺时针：R构型；逆时针：S构型

eg.  若最小的d在横键上，要反一次.

(S)-乳酸　　(R)-乳酸.

当手性中心上带有2个除构型外相同的烯烃取代基时，按(Z)>(E)，顺>反进行排序 eg.



(2Z,5R,7E)-5-氯壬-2,7-二烯

(R)-3,3-二甲基螺[4.4]壬-1,6-二烯

注意：R/S标记对旋光性方向("+"或"-"无关!)

(2). D/L 标记法.

以(+)-甘油醛的构型为标准来标记其它与甘油醛相关联手性化合物的相对构型.

eg.

D-(+)-甘油醛　D-(-)-甘油酸　L-(-)-甘油醛　L-(+)-甘油酸.

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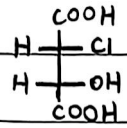
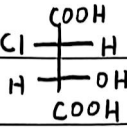
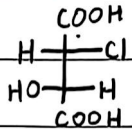
9. 含两个手性C原子的化合物

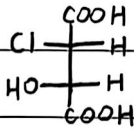
ps. 含一个C* 2个立体异构. 两个C* 4个立体异构, n个不同C* 2^n个立体异构.

eg.


(I)


(II)


(III)

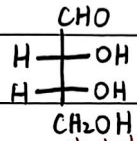

(IV).

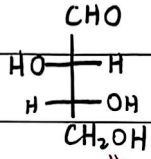
(2R,3R)-2-氯-3-羟基丁二酸.

I、II同III、IV为对映异构; 其他两两为非对映异构.

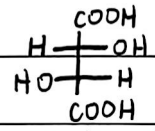
若分子内含有两个手性C且两个手性C至少含有一个相同的基团时, 常用赤式&苏式表示两个非对映异构体的相对构型

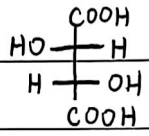
在同侧为赤式, 在异侧为苏式. eg.

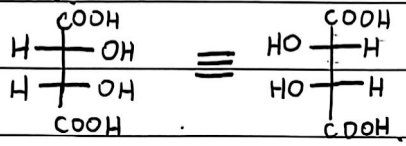

D-(-)-赤藓糖.


D-(-)-苏阿糖

含有2个相同手性C原子的化合物: eg. 酒石酸


(2R,3R)-酒石酸.
(I)


(2S,3S)-酒石酸.
(II)

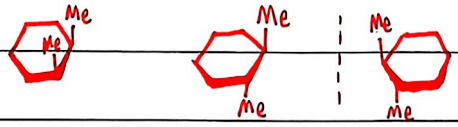

(2R,3S)-酒石酸
(III) (IV).

(III). (IV)为同一个化合物, 非手性分子, 为内消旋体.

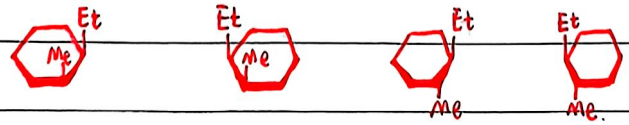
因此含两个相同C*的分子只有3个立体异构体: 一对对映体和一个内消旋体.

9. 环状化合物的立体异构

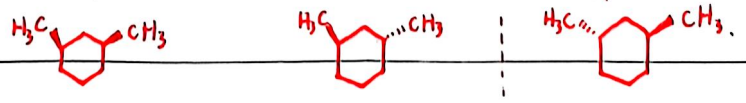
• 二取代环己烷: (1). 1,2-二取代环己烷: 1,2-二甲基环己烷立体异构体数目为3.



1-乙基-2-甲基环己烷有4个立体异构体



(2). 1,3-二取代环己烷. 1,3-二甲基环己烷有3个立体异构体.



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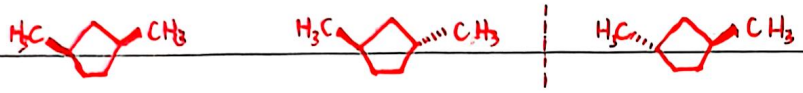
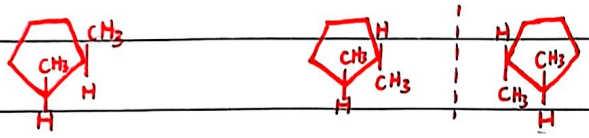
(3)、1,4-二取代环己烷：反式和顺式无论取代基都有对称面或对称中心，非手性分子

• 二取代环戊烷.

(1)、1,3-二甲基环戊烷. 3个立体异构体.



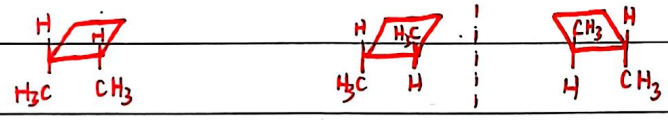
(2)、1,2-二甲基环戊烷 3个立体异构体



• 二取代环丁烷

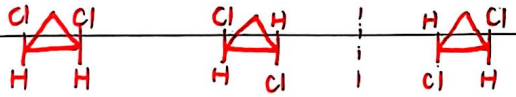
(1)、1,3-二取代环丁烷无论顺、反式，无论取代基，都有一对称面，均无手性.

(2)、1,2-二甲基环丁烷 3种立体异构体



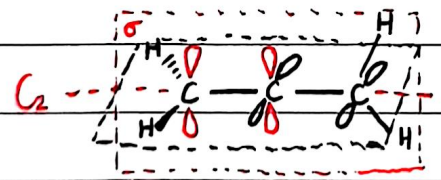
当两个取代基不同时，则有4种立体异构体.

• 二取代环丙烷：1,2-二氯环丙烷 3种立体异构体.



9. 含手性轴化合物的对映异构.

• 丙二烯型：$H_2C=C=CH_2$

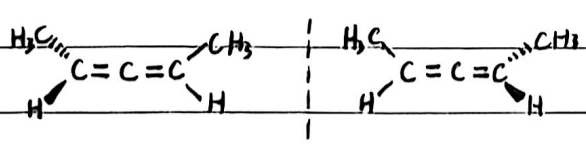


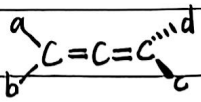
有两个沿H-C-H平面的对称面

故不具有手性.

若两端C原子分别连有两个不同的基团，则这个分子没有对称面与对称中心

从而有手性. C_2对称轴变为 C_2 手性轴

eg. 

具有手性仅需 

$a \neq b$ 且 $c \neq d$

即使 $a=c$，$b=d$ 时也有手性.

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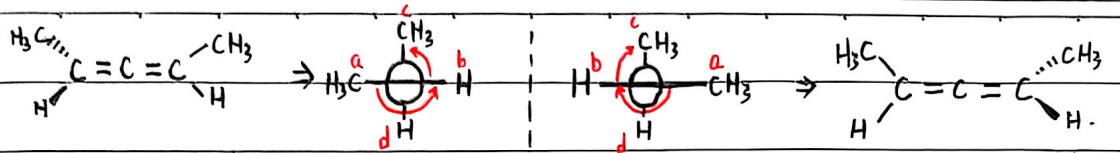
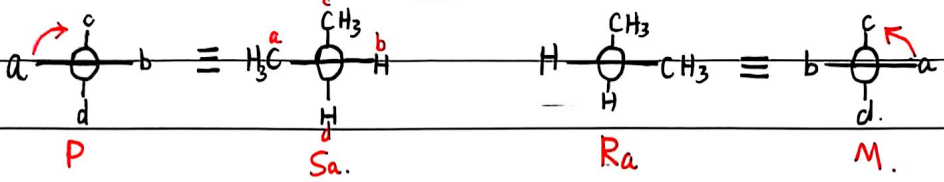


(Sa)-戊-2,3-二烯　　Sa　　Ra　　(Ra)-戊-2,3-二烯

同样也可用螺旋规则来标记，P、M. 近端有a>b，远端为c>d.

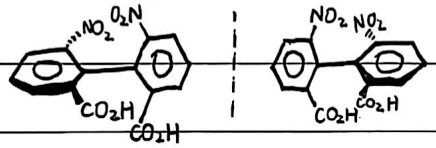
则只判断 a→c 方向　顺时针 P，逆时针 M.



P　　Sa.　　Ra　　M.

·联苯型化合物对映异构.

当苯环两个邻位连有体积较大的取代基时，两个苯环之间单键旋转受阻，不再共平面. eg. 两个对映体.



(P)-6,6'-二硝基联苯-2,2'-二甲酸

9.外消旋体的拆分

(1). 用手性试剂拆分法：将对映体转变为非对映体 ⇒ 分步结晶或其它方法分开 ⇒ 两种衍生物变回原来的旋光化合物　eg. 拆分外消旋酸可用旋光性的碱.

(2). 动力学拆分：在手性催化剂或手性试剂存在下，一对对映体能发生选择性，转变为非对映异构体。由于二者反应速率不同，可利用催化剂或不足量的手性试剂与外消旋体作用，反应快的对映体优先完成反应

(3). 诱导结晶法：在外消旋体的过饱和溶液中加入一定量的某一种旋光体的纯晶种，与晶种相同的旋光体先结晶出来

All：判断手性分子 ①. 是否为丙二烯型、联苯型、螺型化合物；若是，可能为手性分子

②. 是否含手性碳，只有一个一定为手性分子；含多个则观察是否对称分子.

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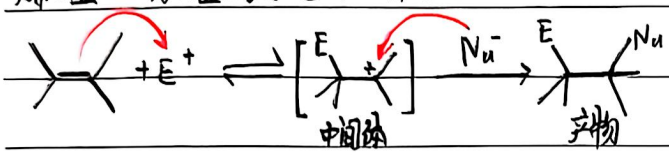
烯烃及炔烃的亲电加成反应

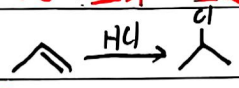


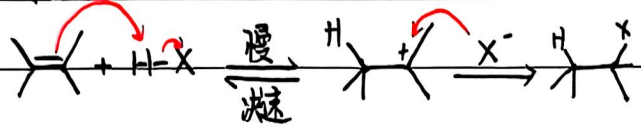
C^+中间体

1、烯烃与HX加成

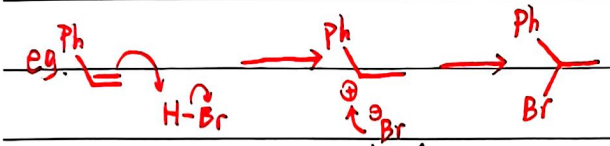
* 速率：HI > HBr > HCl.　　* 双键C上取代基越多，双键电子云密度高，反应越快.

区域选择性：Markovnikov规则：

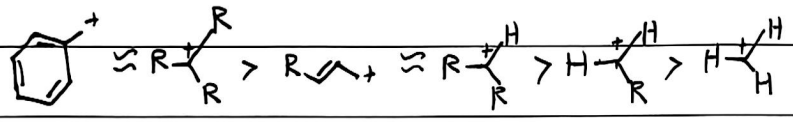




C^+越稳定，反应越快.

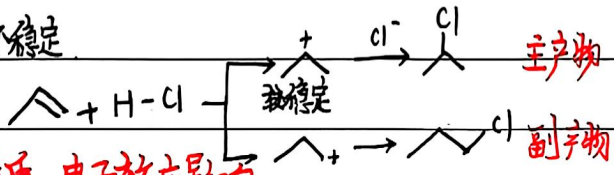


更稳定的C^+中间体.

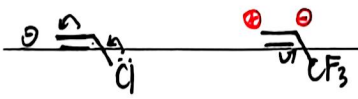


没共轭，很不稳定

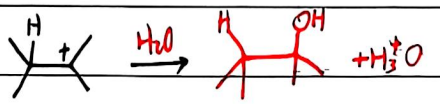
区域选择性解释：



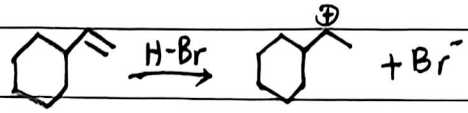
Markovnikov规则本质：电子效应影响.



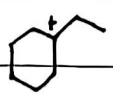
15、在水或醇中竞争反应.



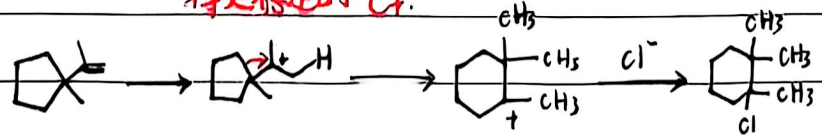
多种亲核试剂



重排



得更稳定的C^+.



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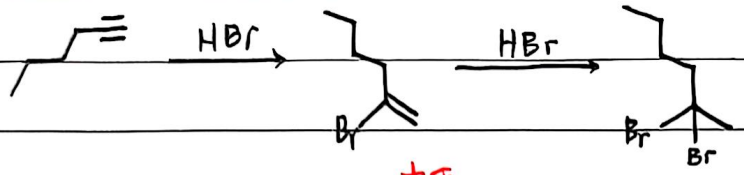
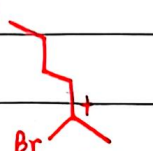
区域选择性：符合马氏规则.

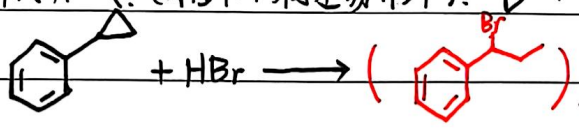


由于  比

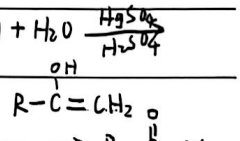
P-P共轭 稳定.

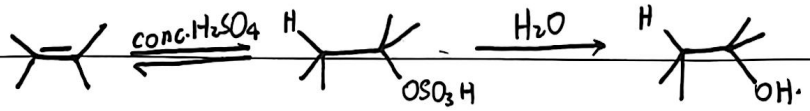
过氧化物效应：HBr 反马式加成. (自由基稳定)

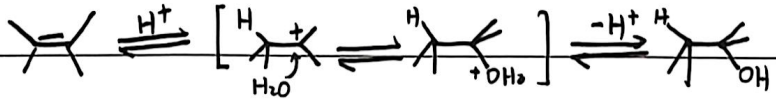
环丙烷与HX加成. (小环不稳定易开环).



2. 烯&炔的水合反应.

炔烃与 H_2O 加成 $R-C\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4}$ 

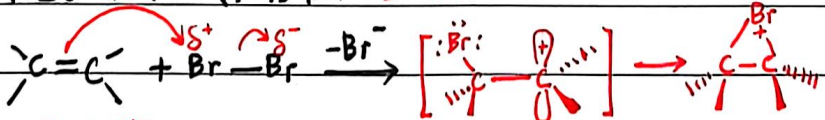
i) 间接水合 

ii) 直接水合 

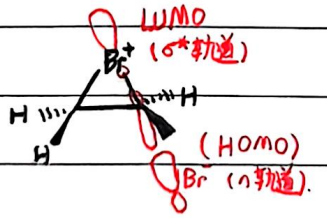
H_3PO_4 催化

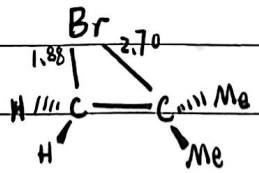
3. 与卤素加成.

立体化学：反式加成. 活性 $F_2 > Cl_2 > Br_2 > I_2$



环正离子.

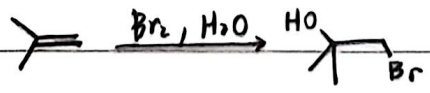




进攻右边取代基多的C.

Ps. 加 Cl_2 的立体选择性比较差，会有顺式产物生成.

Ps. 在水/醇存在下烯烃与卤素反应，(HO-X). 区域选择，马氏规则.



CS 扫描全能王
3亿人都在用的扫描App

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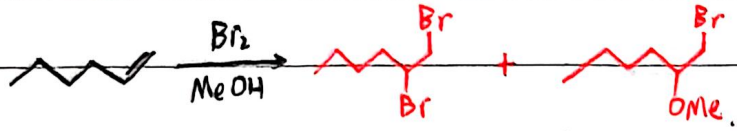
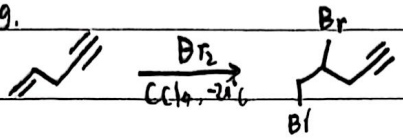
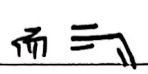
亲电试剂加在 C多H的 C上，亲核试剂加在含H少的C上.



eg.

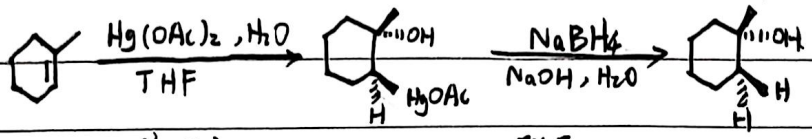




先与三键加成

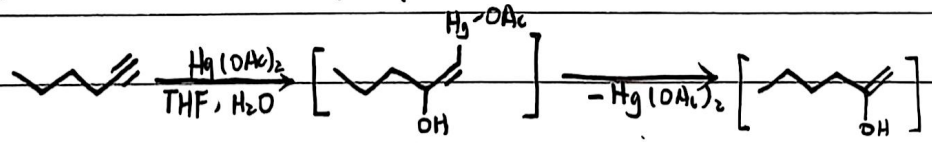
因为生成共轭二烯更稳定

• 羟汞化-脱汞反应.



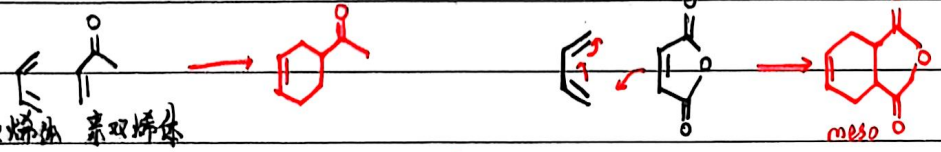
羟汞化　　脱汞.

炔烃生成酮.



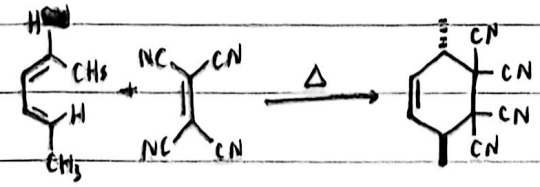
常用末端炔制备甲基酮.

• Diels-Alder 反应.

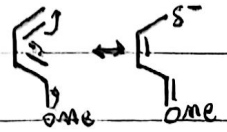


亲双烯体：缺电子　　双烯体：富电子

• 不改变几何构型.（同面加成）　通常为内型产物



Warning!:



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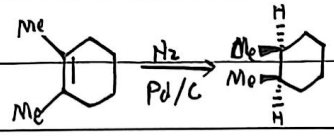
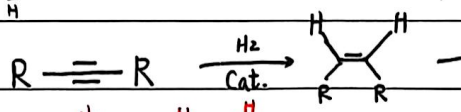
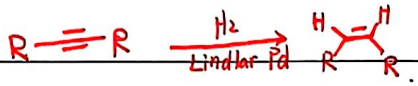
· 烯烃的催化加氢



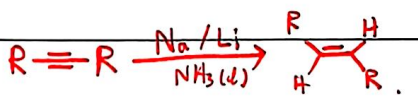
一定是顺式加成.

· 炔烃催化加氢：

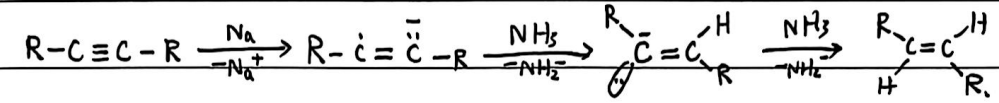


顺 

Lindlar Pd：Pd/CaCO3/PbO/Pb(OAc)2/喹啉.

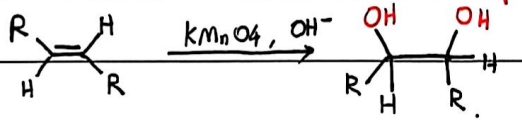
反 

(Na/Li 提供电子)



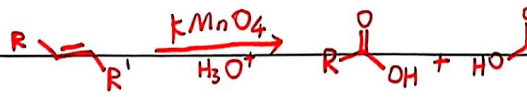
· KMnO4 氧化反应.

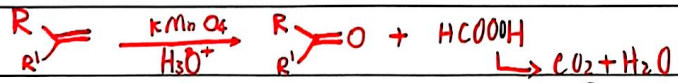
(1)、碱性或稀的 KMnO4 氧化. 顺式加氧 也可以用 OsO4.



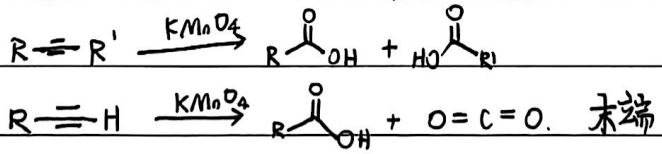
邻二醇.

(2)、酸性或中性的 KMnO4 氧化. (酮或羧酸或放出 CO2).



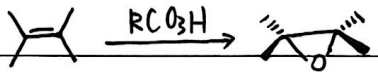


(3)、炔烃：



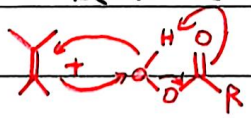
末端

· 环氧化反应. (m-CPBA).

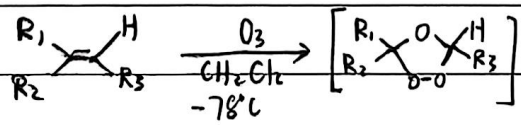


顺式加氧

电子云密度高的双键优先



· O3 化反应.



有Zn粉水时，酸→醛

无Zn粉水时被弄成酸

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炔烃聚合☆：

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9. 自由基反应

中心原子电负性越大 能量越高，自由基稳定性越差

$R_3C\cdot > R_2N\cdot > RO\cdot$ $I\cdot > Br\cdot > Cl\cdot > F\cdot$

自由基越稳定，离解能越小.

苯基自由基

稳定.

稳定性因素：(1). 空间位阻 (2). 电子效应稳定化作用

1. 甲烷的氯化反应

$CH_4 + Cl_2 \xrightarrow[或h\nu]{\triangle} CH_3Cl + HCl$

机理：链引发：$Cl-Cl \xrightarrow[或h\nu]{\triangle} 2Cl\cdot$

链增长：$H_3C-H + \cdot Cl \longrightarrow \cdot CH_3 + HCl$

$CH_3\cdot + Cl-Cl \longrightarrow CH_3Cl + \cdot Cl$

链终止：$Cl\cdot + \cdot CH_3 \rightarrow CH_3Cl + HCl$

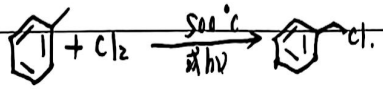
$Cl\cdot + Cl\cdot \rightarrow Cl_2$ $\cdot CH_3 + \cdot CH_3 \rightarrow CH_3CH_3$

2. 与其它卤素的卤化：$F_2 > Cl_2 > Br_2 > I_2$

3. 其它烷烃的卤代：$3^\circ > 2^\circ > 1^\circ$. Br代选择性比Cl代选择性更强.

· α-H卤代.

$CH_2=CH-CH_3 + Cl_2 \xrightarrow{高温} CH_2=CH-\underset{Cl}{CH_2}$



9 芳香烃

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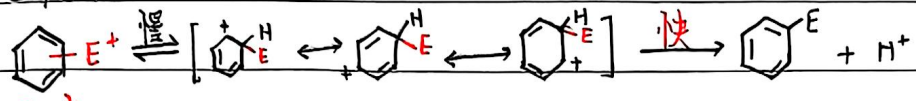
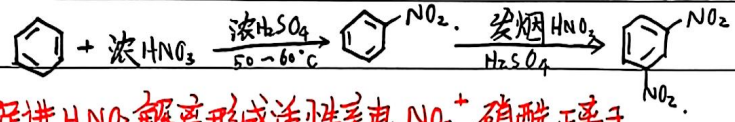
· 亲电取代:



π络合物　　σ络合物

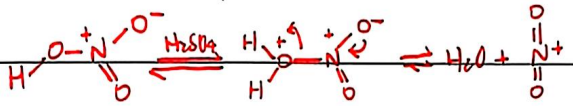
⇒ 加成一消除过程（σ络合物形成是决速步）.

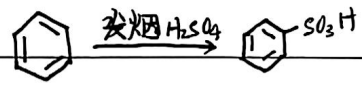
→ 较高温度.

1. 硝化: 

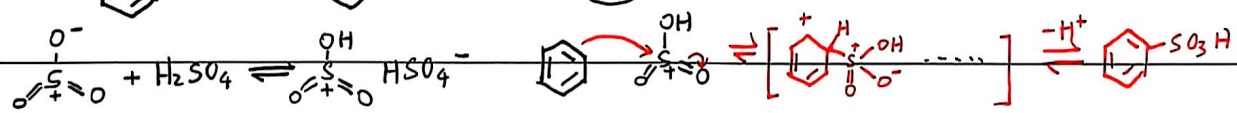
上加硝基

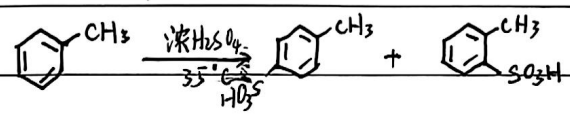
浓H_2SO_4: 促进HNO_3解离形成活性亲电NO_2^+硝酰正离子.　　很稳定

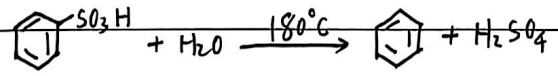


2. 磺化: 

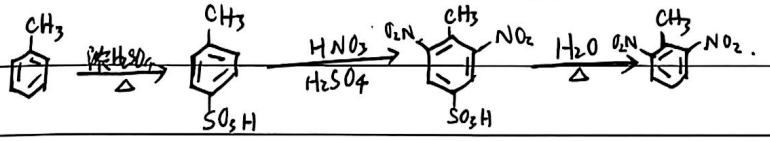
可逆!



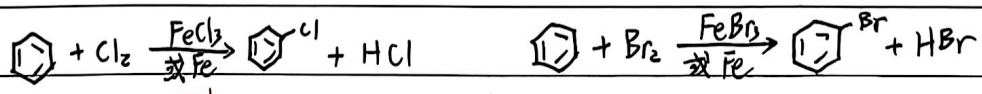




用途: "保护基团" 先磺化占据对位, 再去除 eg.



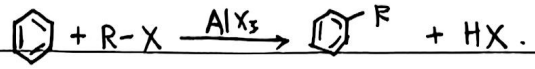
3. 卤化:

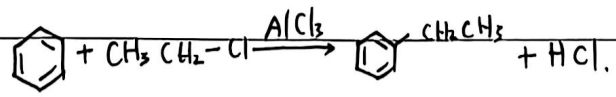


$Br-Br + FeBr_3 \longrightarrow Br-\overset{+}{Br}-\overset{-}{FeBr_3}$

F_2太强难控制, I_2太差（但可用I^+, ICl等）.

4. Friedel-Crafts 烷基化



eg. 

CS 扫描全能王
3亿人都在用的扫描App

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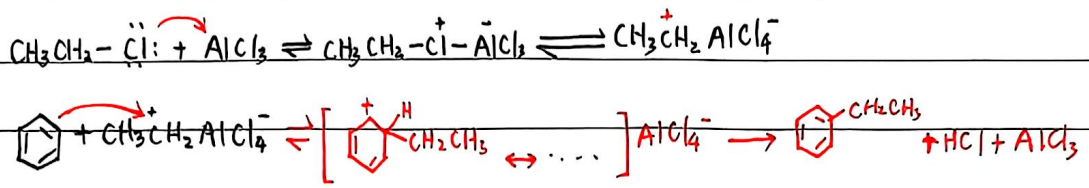
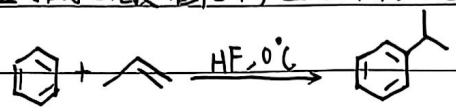
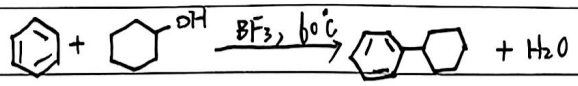


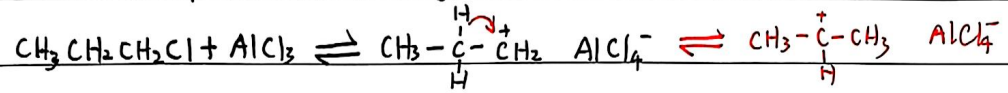
② 烯烃与醇在酸催化下产生 C+ 离子，也可用作傅克烷基化反应的亲电试剂

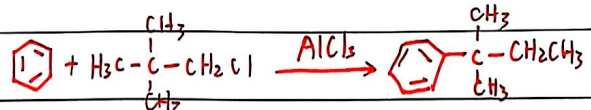
eg.





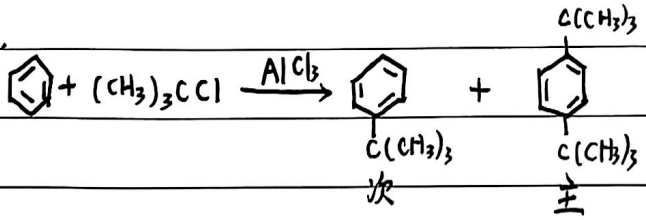
若生成 C+ 稳定性差会重排 eg.





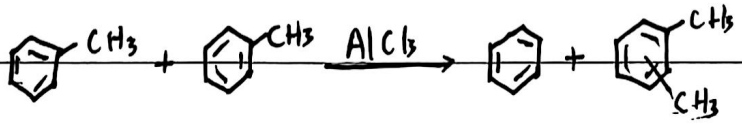
由于烷基苯比苯有较高反应活性，因此烷基化产物可发生二次烷基化

eg.



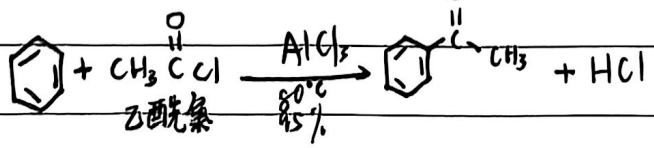
当苯环上有强吸电子基 (eg. $^+NR_2$, NO_2, CO_2H, CO_2R, COR, CF_3, SO_3H 时) Friedel-Crafts 烷基化反应一般较难发生

ps. Friedel-Crafts 烷基化反应可逆，常伴随歧化反应发生.

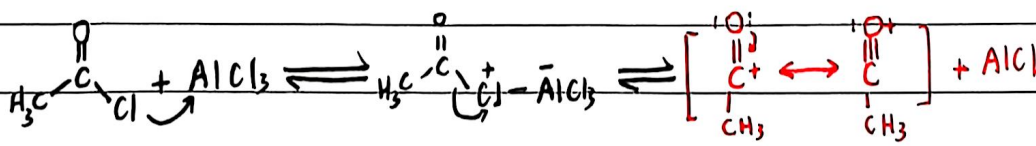


5. Friedel-Crafts 酰基化反应

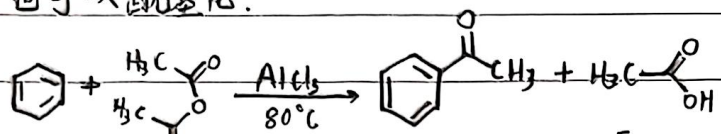
Lewis 酸下，苯与酰基作用，引入酰基

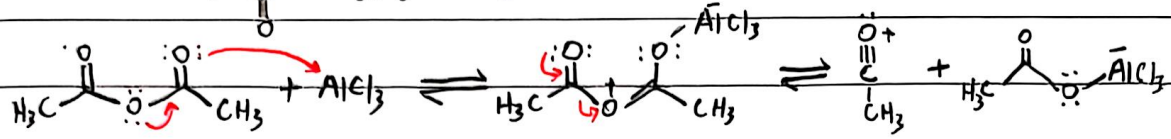


乙酰氯



酸酐也可以酰基化.

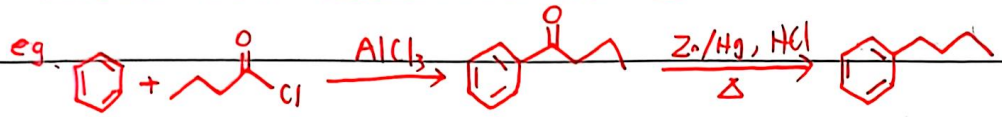




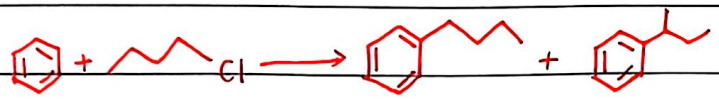
ps. 酰基化反应由于生成的酰基化产物分子中羰基为吸电子基，使苯环钝化

Friedel-Crafts 酰基化反应不会发生重排 !!!

eg.

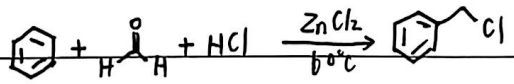


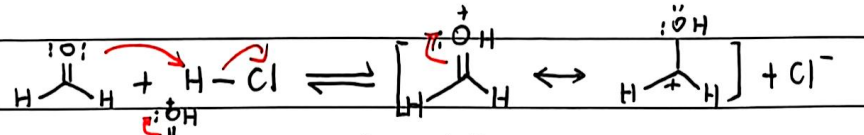
而

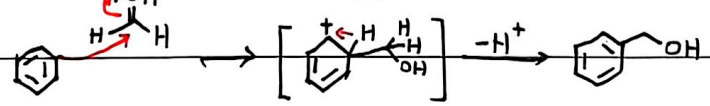


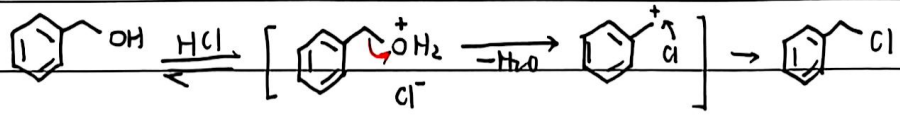
6. 氯甲基化反应

苯在甲醛、HCl、Lewis酸作用下发生反应生成苄氯.







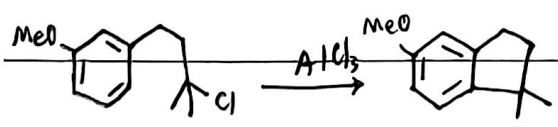


定位：(1). 邻对位活化基团：$-R$、$-OR$ $-NH_2$ $-Ph$ $-OH$ ……

(2). 邻对位钝化基团：卤素

(3). 间位定位钝化基团：$-CO_2R$，$-CONH_2$，$-COR$，$-CN$，$-\overset{+}{N}R_3$

ps. 分子内烷基化



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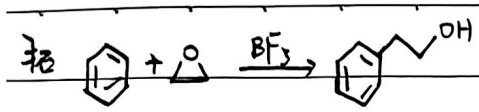
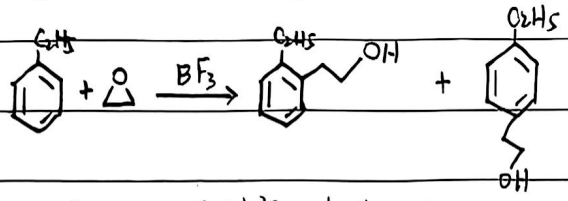
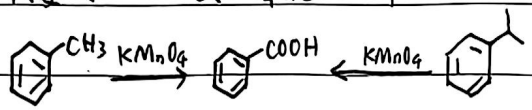


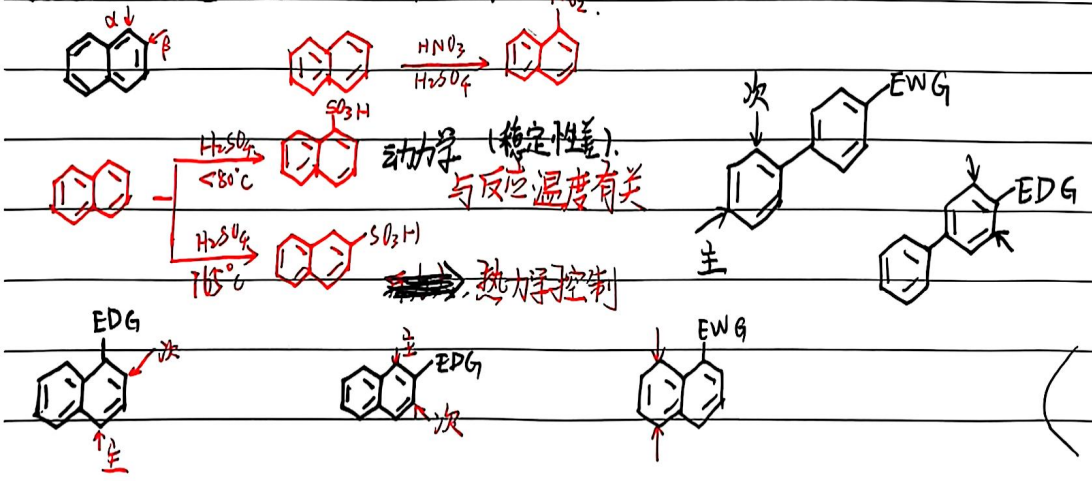


ps. 只要有α-H，会被氧化为苯甲酸

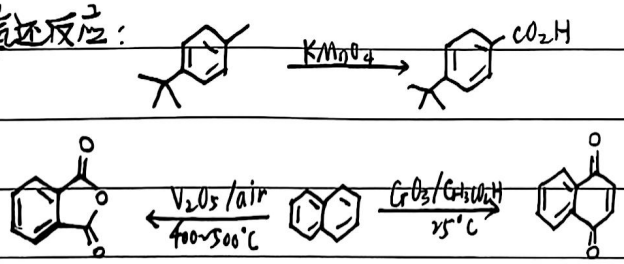


·二取代苯定位：1. 最强致活基团控制定位权 2. 空间位阻大难取代。

对于萘：优先发生在α-位取代



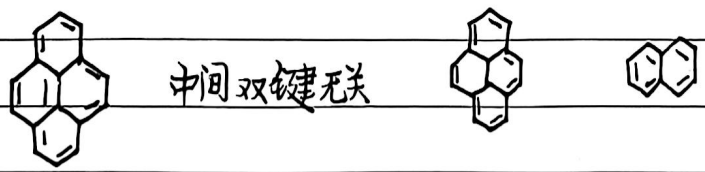
·氧还反应：



·芳香性：稳定，亲电取代而非加成。

·休克尔规则：①、环状体系 ②、平面共轭体系 ③、$4n+2$ P电子

对多环体系的芳香烃不能简单用 Hückel 规则。稠环体系有芳香性：eg.



中间双键无关

花

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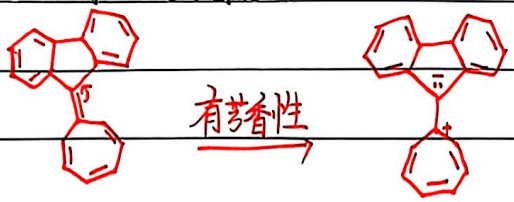
非苯芳香烃：(1)轮烯 [14]-轮烯，[18]-轮烯有芳香性.

[10]-轮烯不共面 无芳香性. ⇒ 有芳香性

(2)、芳香离子：eg.

P5. 当电子为4n时为反芳香性.



9. 卤代烃：

卤代烷，卤代烯，卤代芳烃

卤代烃的卤素交换反应：$R-\underset{Br}{Cl} + NaI \xrightarrow{丙酮} R-I + \underset{+\,NaBr\downarrow}{NaCl\downarrow}$

- 亲核取代反应

$Nu^- + R-X \longrightarrow R-Nu + X^-$ 活性 R-I > R-Br > R-Cl > R-F.

(1)、水解反应

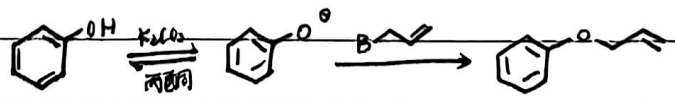
$R-X + NaOH \xrightarrow{H_2O} ROH + NaX$.

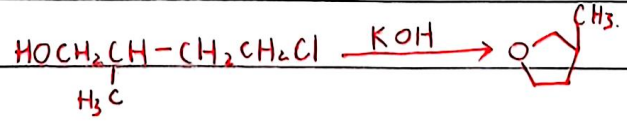
通常不用来制醇等.（成本问题）.

(2). 与烷氧基/苯氧基负离子反应.

醇钠或酚钠作用成醚，不对称醚合成（Williamson 合成法）

$RX + R'ONa \longrightarrow R-O-R' + NaX$

eg. 

分子内： 

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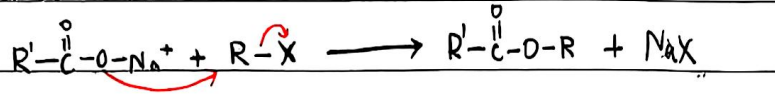
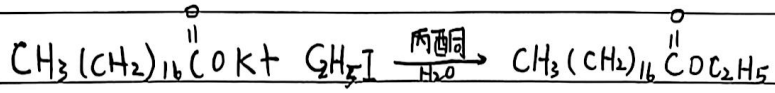
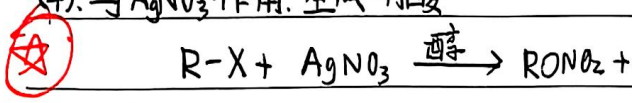
(3)、与羧酸根负离子成酯

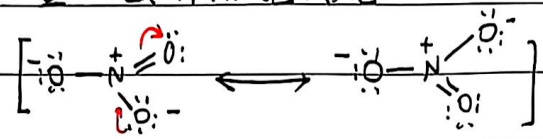




(4)、与 $AgNO_3$ 作用，生成硝酸



用于鉴别伯、仲、叔卤代烷



• 饱和C上亲核取代反应的机理与立体化学.

(1)、双分子亲核取代反应 (S_N2).

反应速率既与碱浓度正比，又与底物浓度正比.

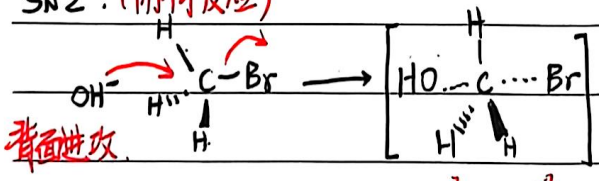
eg. $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$ $\quad v = k[CH_3Br][OH^-]$

(2)、单分子亲核取代反应

反应速率仅与底物有关. $(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$

$v = k[(CH_3)_3CBr]$

S_N2：(协同反应)



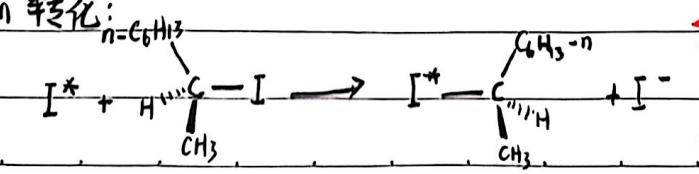
空间位阻越小，形成过渡态越有利，反应越容易进行

$RC-I > RC-Br > RC-Cl > RC-F$. 因为离去后 I^- 更稳定.

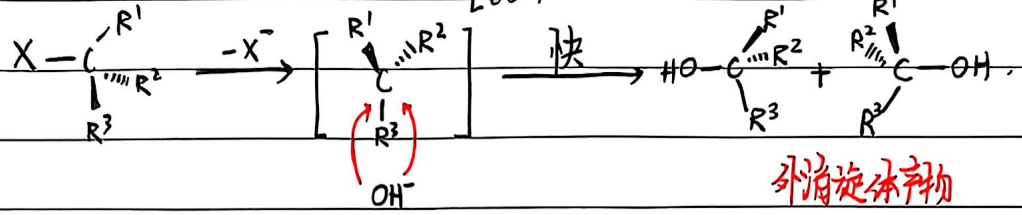
$CH_3X > CH_2RX > CHR_2X > CR_3X$.

ps. $RBr + NaI \xrightarrow{丙酮} RI + NaBr$ 典型 S_N2 反应.

Walden 转化：



S_N1机理：经C+ 典型：$R-X \xrightarrow[EtOH]{AgNO_3} RONO_2 + AgX\downarrow$.



外消旋体产物

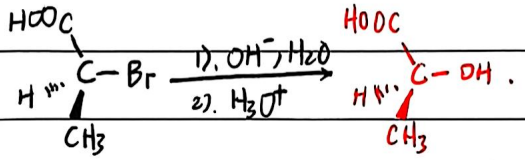
C+越稳定越易发生.

由于C+生成易发生重排

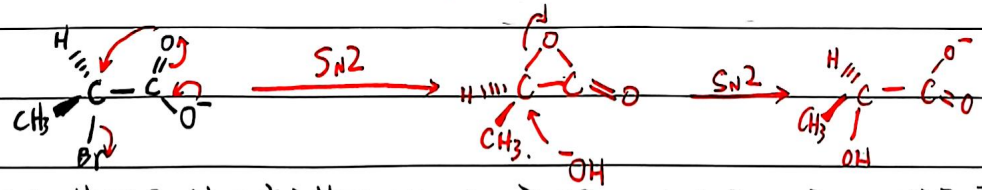
邻近基团参与机理：(NGP). ☆.

β位有亲核基团存在时，在反应过程中通过环状中间体参与亲核取代反应，导致反应速率加快，使产物有立体化学专一性.

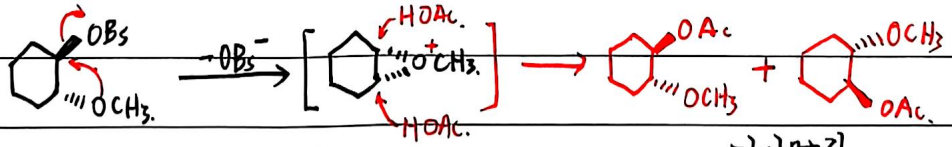
eg.



构型保持!

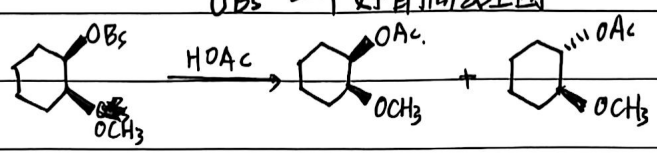


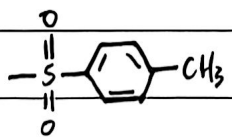
ps. 邻近基团应处于离去基团反位时，才可背面进攻中心碳从而发生邻基参与.



OBs 一个好的离去基团

一对对映体



Ts： 

良好的离去基团

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6 卤代烷烃消除反应

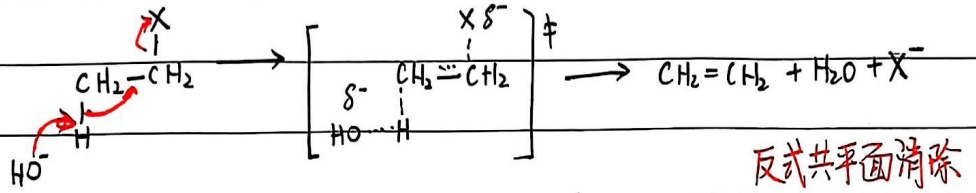
卤代烃的 β-H 有弱酸性，强碱可进攻 β-H. β-消除制烯烃.

$$R-\underset{H}{CH}-\underset{Cl}{CH}-R + NaOH \xrightarrow[\triangle]{C_2H_5OH} RCH=CHR + H_2O + NaCl$$

亲核试剂 → 进攻 α-C，取代
→ β-H ⇒ 消除反应. } 竞争

双分子消除 (E2) 单分子消除 (E1). 单分子共轭碱消除 (E1cb).

(1). E2反应 (碱作用于 β-H).



反式共平面消除

β-C-H 和 α-C-X 越易断裂，E2反应越易进行.

(a). 烃基结构不同的卤代烃反应活性为 $R_3CX > R_2CHX > RCH_2X$.

(b). 试剂碱性越强，β-C-H越易断裂，反应越易进行

(c). 离去基团越易离去，反应越有利：RI > RBr > RCl

区域选择性 Saytzeff 规则

$$CH_3-\underset{H}{CH}-\underset{Br}{CH}-\underset{H}{CH_2} \xrightarrow[\triangle]{KOH/C_2H_5OH} CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2$$

81% 19%

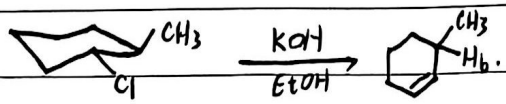
- β碳体积大小也会影响 E2 反应的区域选择性. 卤代烃 β-位空间位阻和碱体积都比较大时，不利于 Saytzeff 烯生成，而有利于 Hofmann 烯生成.

$$CH_3-\underset{Br}{\overset{CH_3}{C}}-\overset{H}{C}-CH_3 \xrightarrow[(CH_3)_3CONa]{RONa,\ ROH} H_2C=\underset{CH(CH_3)_2}{\overset{CH_3}{C}}$$

主.

- ps. 对卤代环烷烃，C-C旋转受约束，只有X与反式β-H消除 (且消除两个处于α键)

eg.



ps.

消除 B > A.

比较在优势构象下是否易消除.

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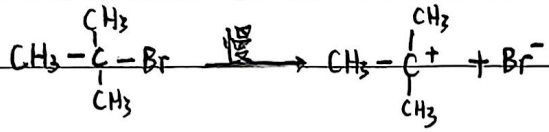
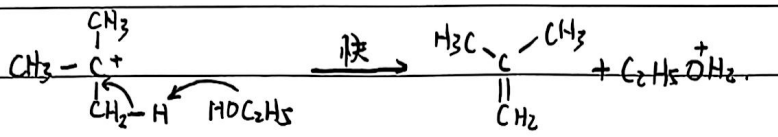
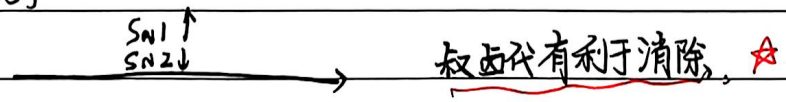
E1：无碱或弱碱条件下进行





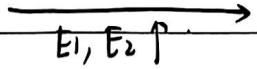
由于C+生成，E1反应中常有重排产物生成.

•消除与取代竞争



叔卤代有利于消除。★

CH_3X RCH_2X R_2CHX R_3CX



碱性↑ V↑，浓度↑ 消除↑ Ps：若消除后可共轭，则会增加消除产物

亲核性↑ V↓ 越有利S_N2反应

溶剂对反应影响：极性越大，有利于电荷集中的过渡态，不利于电荷分散的过渡态。增加极性有利于取代，不利于消除。S_N2电荷集中，E2分散 ★

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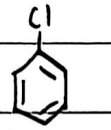
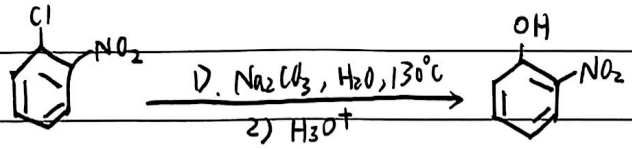
• 邻二卤代烷消除反应：

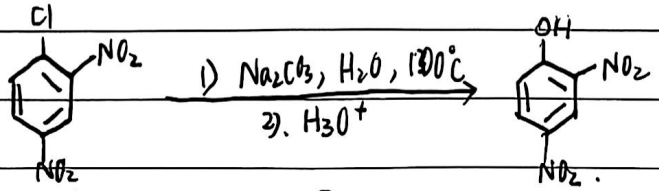
$$CH_3CH(Br)-CHClH_3 \xrightarrow[\Delta]{KOH,\ C_2H_5OH} H_2C=CH=CH_2$$

• 卤代芳烃的亲核取代：



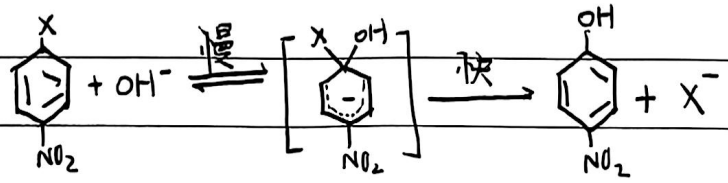
C-X有部分双键性质，难断裂，但当邻对位含强吸电子基时可发生亲核取代。（芳香亲核取代反应 S_NAr）。 越多越易反应



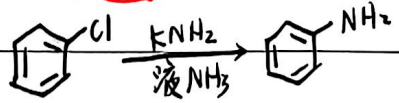


也可以为 F^-、Cl^-、Br^-、I^-。

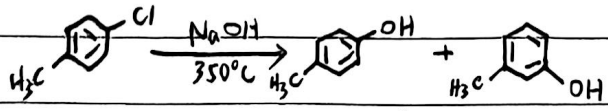
• 机理：加成—消除

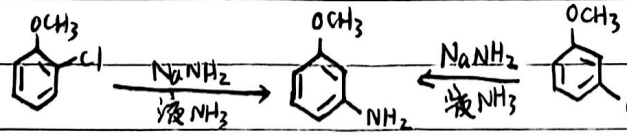


• 苯炔机理：当苯环上无强吸电子基时难以发生 S_N-Ar 反应，但强碱作亲核试剂时可发生亲核取代反应 eg.



卤代苯在 $NaNH_2$/液 NH_3 下取代相对反应速率：Ph-Br > PhI > PhCl > PhF





PhBr > PhI > PhCl > PhF

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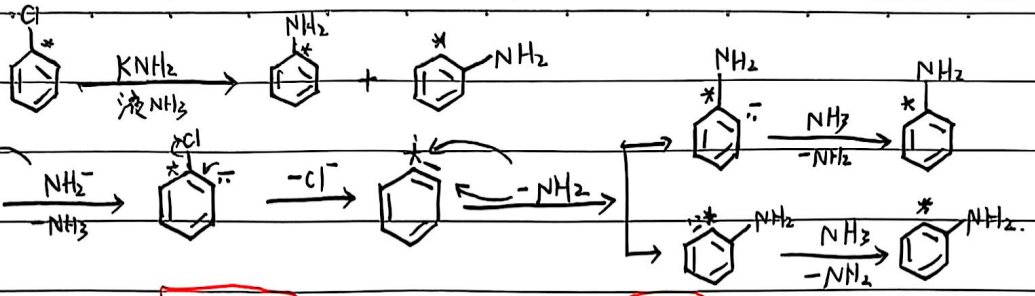
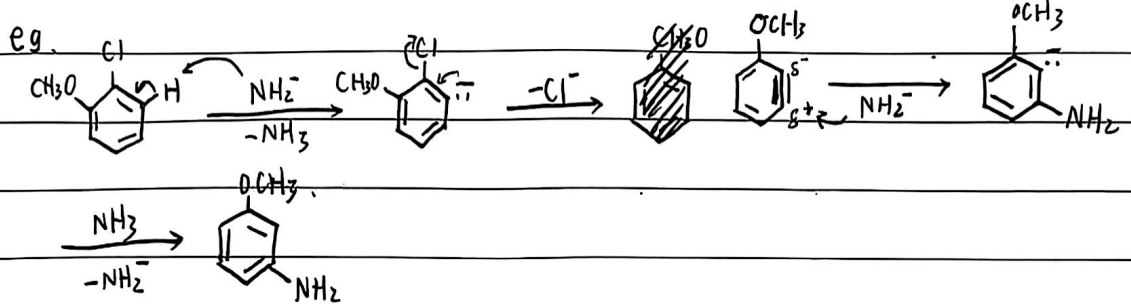
机理：



氨基负离子优先进攻位阻较小且电子云密度相对较低的碳原子。

eg.



·卤代烃与金属：有机镁化合物又称 Grignard 试剂，格式试剂

$$R-X + Mg \xrightarrow[THF]{\text{无水乙醚(或四氢呋喃)}} R-MgX.$$

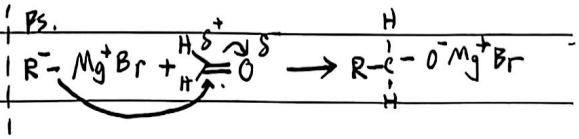
制备反应活性：RI > RBr > RCl > RF.

格氏试剂 C-Mg 高度极化，C 带部分负电荷，显著 C⁻ 性质，强碱&强亲核

eg

$$R-MgBr \xrightarrow{H_2O} R-H + Mg(OH)Br$$

$$R-MgBr \xrightarrow{AcOH} R-H + AcOMgBr.$$



有机锂化合物（无水溶剂中）R-X 与 Li 反应生成。

$$n-C_4H_9Br + 2Li \xrightarrow{\text{正己烷}} n-C_4H_9Li + LiBr$$

与格氏试剂相似，更活泼，碱性更强

·烷基钠的形成：RX 在 Na 作用下亲核取代产生 R-R

$$2RX + 2Na \longrightarrow R-R + 2NaX \quad \text{偶联反应}$$

1. $RX + 2Na \longrightarrow R^-Na^+ + NaX$

2. $R^-Na^+ + RX \longrightarrow R-R + NaX$

·R-X 与有机金属化合物偶联：$R-M + R'-X \longrightarrow R-R' + MX$

学懂：$RC\equiv C^{\ominus}$ $RC\equiv C$.

S_N2 机理！不重排。

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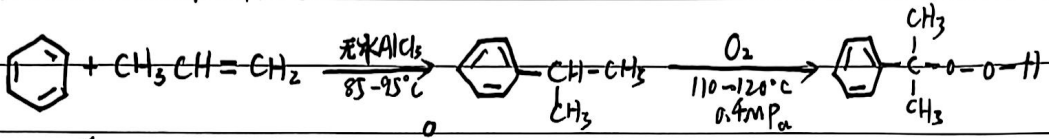
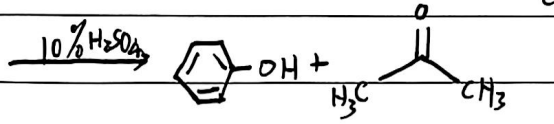
9. 醇酚醚

制醇：烯烃水合、羟汞化-还原反应，硼氢化-氧化反应

羰基化合物制备：格氏试剂、有机锂试剂等与醛、酮反应

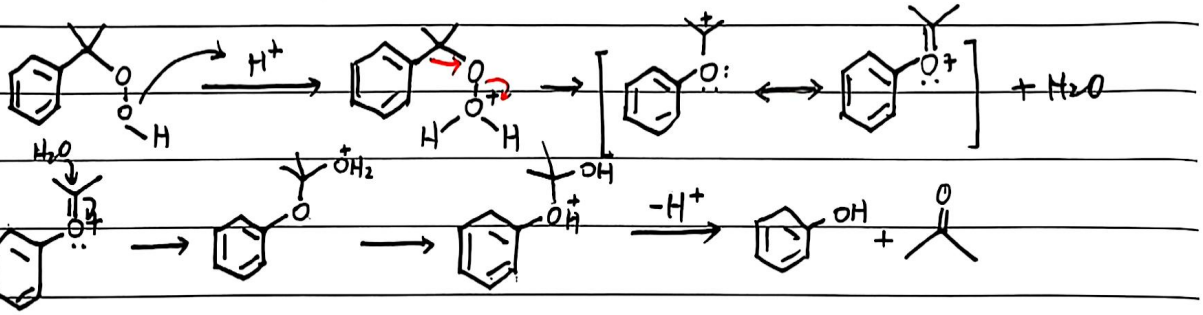
制酚：(1). 异丙苯氧化重排.



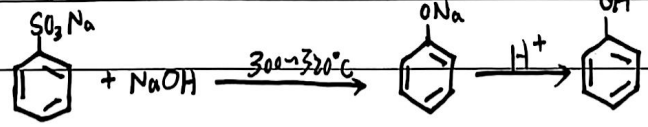


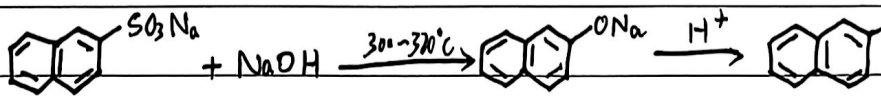
Hock重排

*：

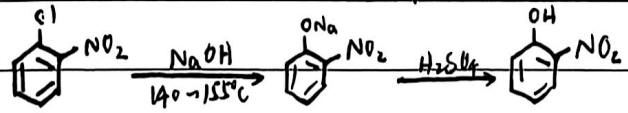


(2). 碱熔法：





(3). 卤代芳烃水解（卤原子邻对位连有强吸电子基）



制醚：(1). 醇脱水.

$$2ROH \xrightarrow[\triangle]{\text{浓}H_2SO_4} R-O-R + H_2O$$

伯醇分子间脱水 S_N2 反应机理，仲醇脱水一般 SN1.

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该反应不适用通过叔醇制备醚迷（因为叔C+易失去一个质子成烯烃）

工业制乙醚一般用 Lewis 酸.（eg. Al_2O_3）.

$$2CH_3CH_2OH \xrightarrow[240°C]{Al_2O_3} C_2H_5OC_2H_5 + H_2O.$$ （不适用于制混合醚，得混合物不易溶

(2). Williamson 反应：R-X与醇钠发生 S_N2 亲核取代反应生成醚迷. 制混合醚迷.

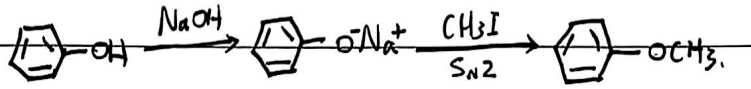
$$C_2H_5I + n\text{-}C_4H_9ONa \longrightarrow n\text{-}C_4H_9OC_2H_5 + NaI.$$

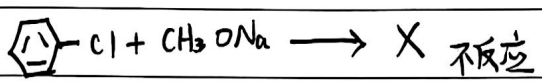
醇钠既是亲核，又是强碱. 因此最好选用伯卤代烷，可避免消除反应

eg. 制 $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_2CH_2CH_3$ 选取 $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-ONa + CH_3CH_2CH_2-Cl$.

不用 $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl + CH_3CH_2CH_2ONa$

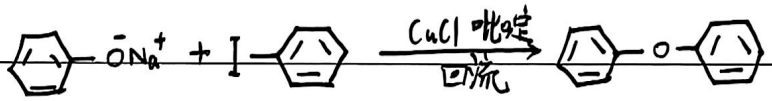
PS. 制备芳醚迷时用酚钠与伯卤代烷反应（仅之不行）.

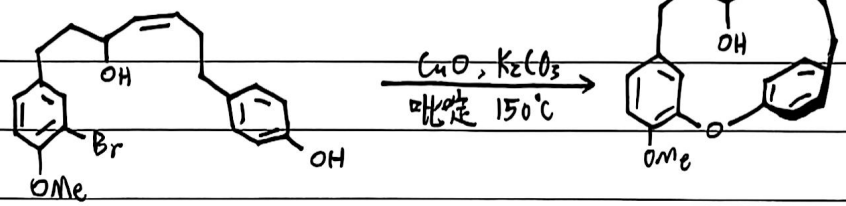
eg. 



(3) Ullmann 缩合. Cu、Pd 等过渡金属催化剂制芳基醚迷.

卤代芳烃发生偶联生成联苯类化合物.





$$CH_3OH > RCH_2OH > R_2CHOH > R_3COH.$$

7. 酸性：i). 醇. 弱酸性 烷基给电子效应越强，酸性越弱.

溶剂化作用影响共轭碱稳定性：体积↑溶剂化作用↓稳定性↓（共轭碱）

eg. $ROH + NaNH_2 \longrightarrow RONa + NH_3$.

$$\begin{matrix}CH_2-OH\\ |\\ CH_2-OH\end{matrix} + Cu(OH)_2 \longrightarrow \begin{matrix}CH_2-O\\ |\\ CH_2-O\end{matrix}\!\!>Cu + 2H_2O$$

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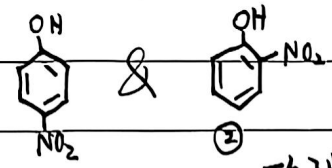
iii. 酚：O-H键极化程度更大，利于质子离去，酸性↑.

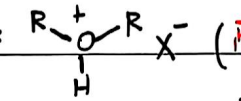
P5.  邻位取代基由于位阻不能共平面而共轭效应降低.

① ②

酸性：① > ②

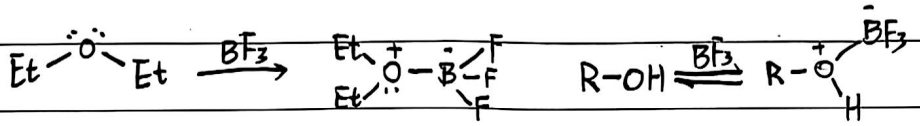
碱性：醇、酚、醚.

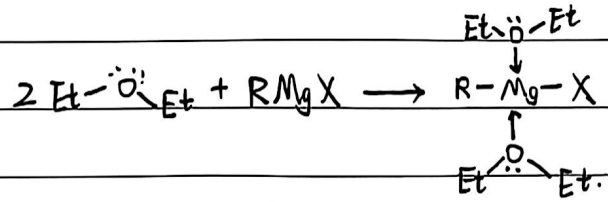
$R-OH + HX \rightleftharpoons R-\overset{+}{O}H_2X^-$ (鎓盐).

$R-O-R + HX \rightleftharpoons$  (只有在浓酸中稳定，遇水分解出醚.)

从烷烃混合物中分离醚.

醚与 Lewis 酸形成配合物，稳定性增强.（有机镁化合物也能与醚形成络合物，制备 Grignard 试剂用无水乙醚 /THF）.



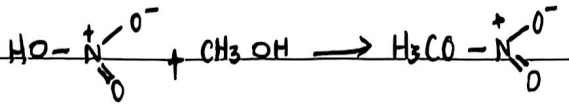


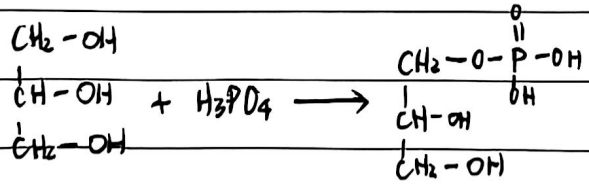
酚与 $FeCl_3$ 发生酸碱反应生成配合物并显色现象.

$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(OC_6H_5)_6]^{3-} + 3H^+ + 3HCl$.

· 反应：

· 酯化反应





$CH_3OH + H_2SO_4 \longrightarrow CH_3O-\overset{O}{\overset{\|}{S}}-OH$.

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与磺酰氯反应 $R-OH \xrightarrow[Py]{TsCl} R-OTs \xrightarrow{Nu^{\ominus}} R-Nu$.

使C-O易于断裂，转化为好的离去基团，易于亲核

·亲核取代 (1)、与HX卤代反应，接受质子成鎓盐. 活性：HI > HBr > HCl.

$-\overset{|}{\underset{|}{C}}-OH \overset{H^+}{\rightleftharpoons} -\overset{|}{\underset{|}{C}}-\overset{+}{O}H_2 \xrightarrow{X^-} -\overset{|}{\underset{|}{C}}-X + H_2O$. 苄醇/烯丙醇 > R_3COH > R_2CHOH > RCH_2OH.

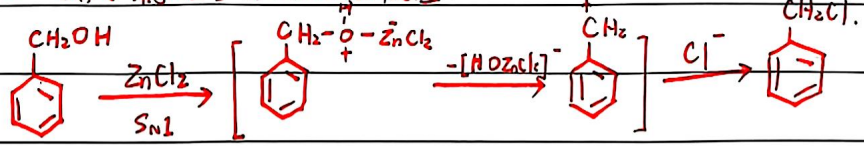
大多1°ROH按S_N2机理 3°ROH、大多2°ROH与带支链的1°ROH按S_N1机理.

eg: $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-OH \overset{H^+}{\rightleftharpoons} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{+}{O}H_2 \xrightarrow[-H_2O]{} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}H_2 \longrightarrow CH_3-\overset{CH_3}{\overset{+}{C}}-CH_2CH_3$ (Br^-)

·Lucas试剂：浓HCl、无水$ZnCl_2$混合液 (C_6以下的醇可溶于Lucas试剂，而反应生成的卤代烃不溶于Lucas试剂，浑浊或分层.

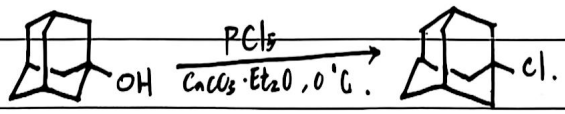
苄醇、烯丙醇、叔醇 > 仲醇 > 伯醇. ⇒鉴别醇的类型 (C_6以上不行)

C+离子稳定，利于S_N1反应.

eg. 

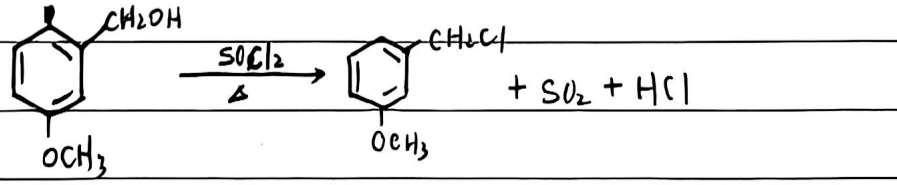
(2)、醇与PX_3或PX_5生成卤代烷.

$3(CH_3)_2CHCH_2OH + PBr_3 \xrightarrow[4h]{10\sim0^\circ C} 3(CH_3)_2CHCH_2Br + H_3PO_3$



第一步为醇与PBr_3的S_N2反应，伯醇第二步S_N2，叔醇第二步S_N1.

(3)、醇与氯化亚砜的氯化



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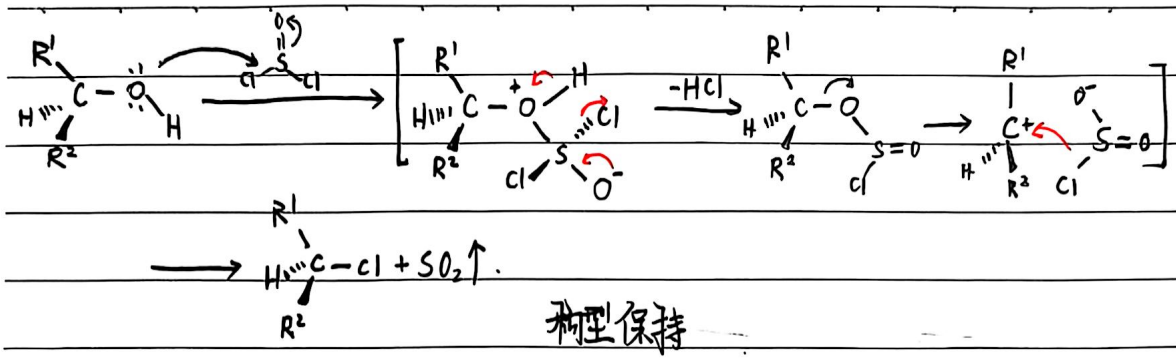
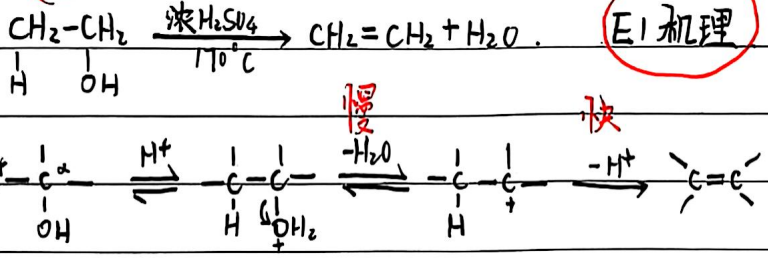


构型保持

Ps. 上述反应在亲核试剂中进行，可能促进并调控立体选择性。

溶剂为二氧六环时，两次 S_N2 构型不变，吡啶中构型翻转。

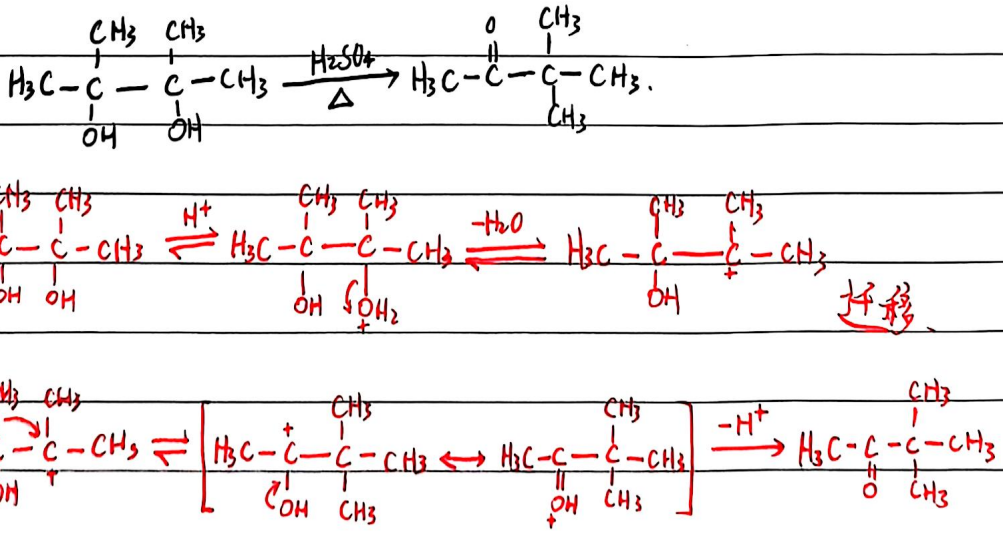
消除：分子内脱水



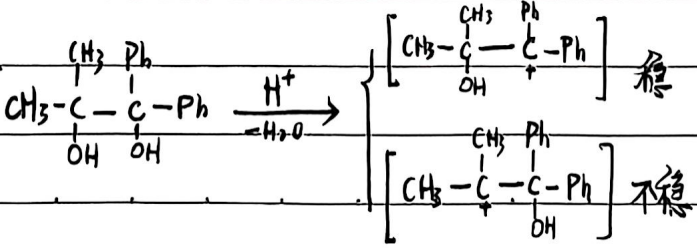
E1 机理 ☆

叔醇 > 仲醇 > 伯醇。

• 邻二醇的重排反应（频哪醇重排）



八隅体结构，形成较稳定的 C+ 上的羟基先提质子



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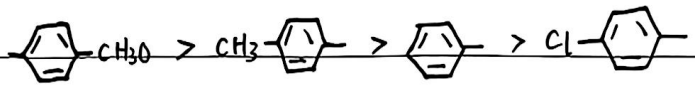
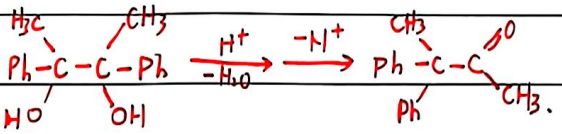
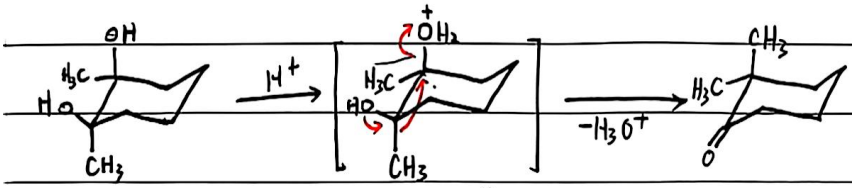
迁移基团越富电子反应越容易，电子云密度较大的基团优先迁移.

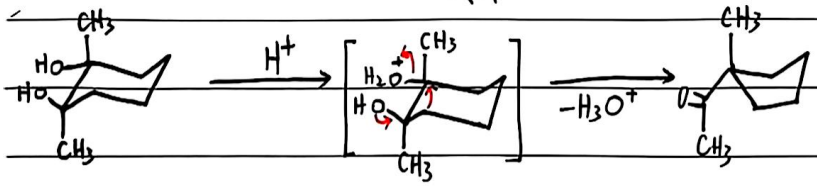
eg. 

苯基比烷基优先迁移： 

苯基 > H > $-C(CH_3)_3$ > $-CH(CH_3)_2$ > $-CH_2CH_3$ > $-CH_3$.

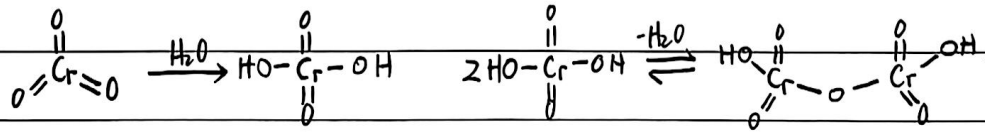


反式



• 醇、酚的氧化.

(1). 铬氧化剂氧化：铬酸不稳定，用 CrO_3 或 $Na_2Cr_2O_7$ 溶于水或稀 H_2SO_4 制备.



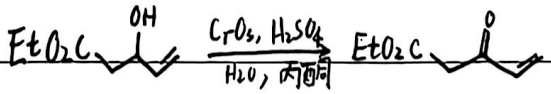
铬氧化剂氧化性较强，可将伯醇→羧酸；仲醇→酮.

eg. $CH_3CH(CH_2)_5CH_3$ (OH) $\xrightarrow[\triangle]{K_2Cr_2O_7\text{-稀}H_2SO_4}$ $CH_3C(CH_2)_5CH_3$ ($=O$)

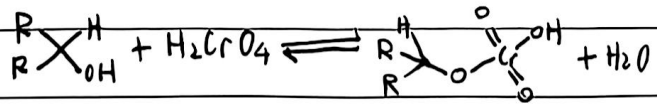
• Jones试剂：CrO_3 溶于稀 H_2SO_4.

常把醇溶于丙酮中，滴加 Jones 试剂进行氧化反应.

丙酮：i) 溶剂 ii) 过量氧化剂作用，阻止过氧化.



过程：形成铬酸酯中间体，E2 消除生成醛或酮.（醛在 H^+ 下进一步为羧酸）



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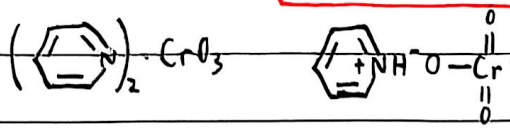
CrO_3 吡啶络合物和**氯铬酸吡啶盐（PCC）**：氧化醇在无水有机溶剂 (eg. CH_2Cl_2) 进行，(伯醇的氧化可停在醛阶段)



Sarrett 试剂：CrO_3 溶于吡啶所形成的络合物（在吡啶溶剂中进行），对伯醇氧化效率低，产物的分离纯化难。

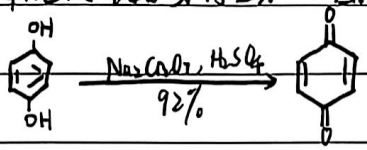
Collins 试剂：吡啶溶于 CH_2Cl_2 中再加入 CrO_3。伯醇→醛　仲醇→酮

反应条件温和，选择性好，产率高。

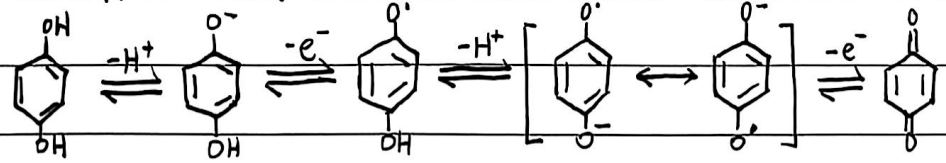
eg. $CH_3(CH_2)_4C\equiv CCH_2OH \xrightarrow[CH_2Cl_2,\ rt]{CrO_3\cdot Py} CH_3(CH_2)_4C\equiv CCHO$

$n\text{-}C_4H_9OH \xrightarrow[CH_2Cl_2,\ rt]{PCC} n\text{-}C_3H_7CHO$

·铬酸类氧化剂很容易将酚→醌。 eg.



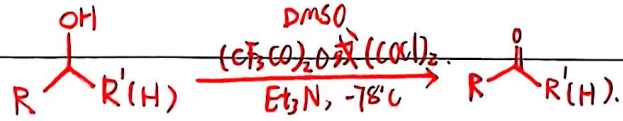
Ag_2O 等氧化剂也可将酚→醌（过程涉及自由基中间体，且可逆）。



⇒ 酚类易与自由基反应，常用作自由基抑制剂/清除剂

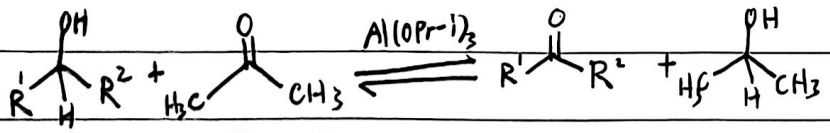
★★。

(2). 用二甲基亚砜氧化：二甲基亚砜 (DMSO) 与草酰氯（或三氟乙酸酐）以及三乙胺组成的"复合"氧化剂。伯醇→醛　仲醇→酮　Swern 氧化。



(3). 用丙酮氧化（脱氢）—— Oppenauer 氧化　　可逆

仲醇与丙酮的氢交换反应，在异丙醇铝 [$Al(OPr\text{-}i)_3$] 存在下。



PS！ 没有催化剂，醇与丙酮不反应！

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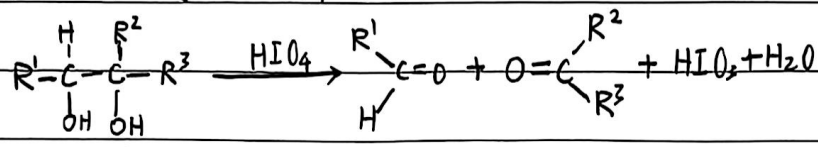
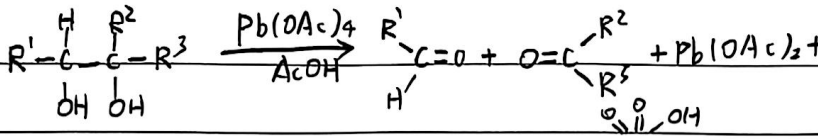
(4). 用高碘酸和四醋酸铅氧化. (邻二醇)特殊氧化.

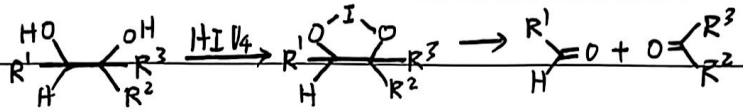
HIO_4 或偏高碘酸(H_5IO_6)的水溶液将邻二醇生成醛/酮.

$[Pb(OAc)_4]$ 也有类似的氧化活性.



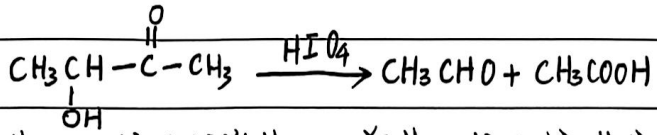


经历五元环状中间体:



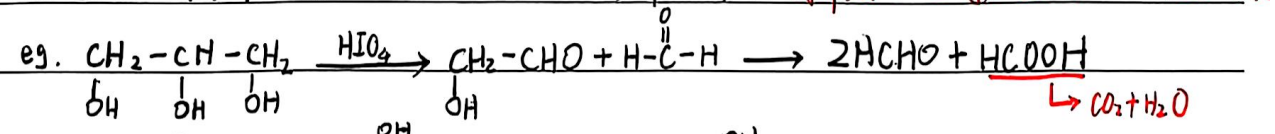
P5: 氧化后生成 IO_3^- 遇 $AgNO_3$ 有白色沉淀生成 ⇒ 判断反应是否发生.(定量测定)

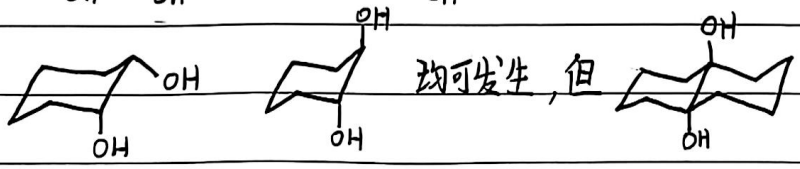
还有:



含羰基的一端生成羧基,含羟基一端生成醛或酮

对羟基连在相邻C原子上的多羟基化合物氧化,可简单看作连有羟基的C-C键断裂

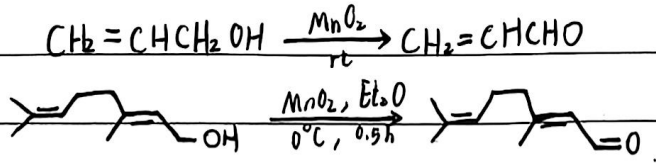




均可发生,但 X (限制环状中间体生成).

(5). $KMnO_4$ 很强氧化剂(不仅氧化醇,还可氧化醛、双键、三键)

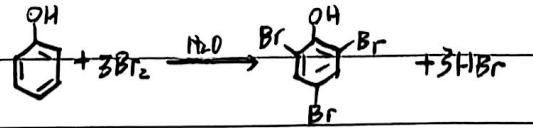
但 MnO_2 氧化活性弱,选择性较好(选择性把烯丙型→醛/酮).



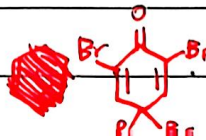
· 酚的亲电取代:

由于羟基强的邻对位活化基团,使很容易发生亲电取代,不用催化剂

(1). 卤化:



定性、定量

(白色沉淀) → 过量溴水 →  (黄色↓).

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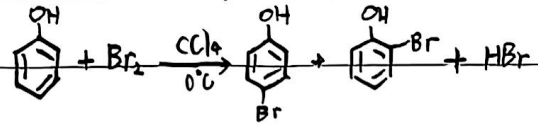
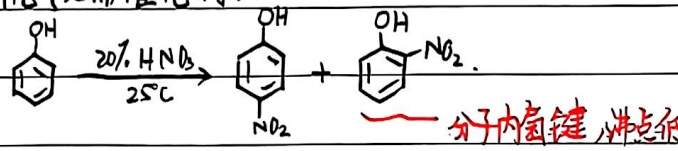
低温&弱极性溶剂中，可生成一取代产物。



(2). 硝化（无需催化剂）。

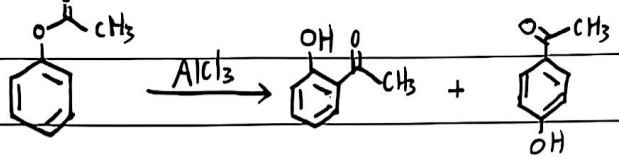


分子内氢键，沸点低，蒸出分离。

(3). 磺化 (4). Friedel-Crafts 反应

(5). Fries 重排反应

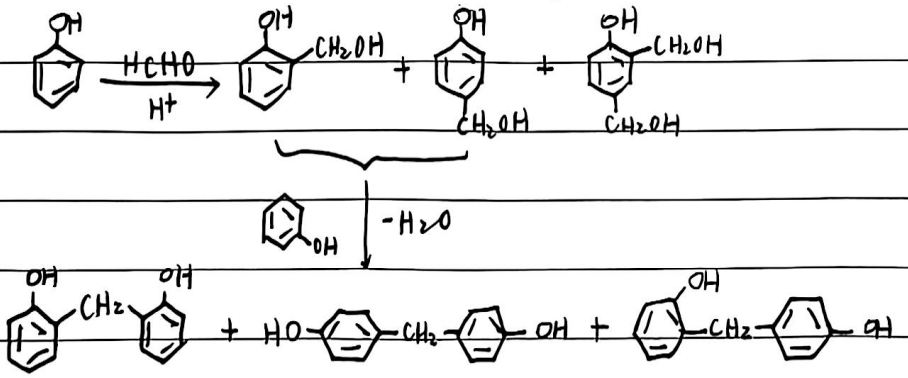
酚的羧酸酯在 Lewis 酸或质子酸催化下可重排，生成邻/对位酰基酚



Lewis 酸促进酯的 C-O 键断裂

(6). 与醛酮的缩合反应

苯酚与甲醛在酸催化下发生亲电取代反应，先在邻对位引入羟甲基，所得产物醇进一步与酚发生烷基化反应，得一系列脱水产物。



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·醚键断裂的反应 S_N1 或 S_N2 机理 锌盐

醚稳定性仅次于烷烃、常温下常用作溶剂.

$CH_3OCH_3 + HI \longrightarrow CH_3I + CH_3OH$

$I^- + CH_3-\overset{+}{O}(H)-CH_3 \xrightarrow{S_N2}$

$CH_3-C(CH_3)_2-O-CH_3 \xrightarrow{H^+} CH_3-C(CH_3)(H)-\overset{+}{O}(CH_3)-CH_3 \xrightarrow{S_N1} CH_3-C^+(CH_3)_2 + CH_3OH$

对于芳醚迷，在浓HX作用下将发生烷基 C-O 键断裂，生成相对的酚与卤代烃. eg.

$Ph-O-CH_2CH_3 \xrightarrow{浓HI} Ph-OH + CH_3CH_2I$. $HI > HBr > HCl$ (浓).

混合醚迷C-O断裂顺序：3°烷基 > 2°烷基 > 1°烷基 > 芳基.

$R-OH \xrightarrow[2)\ PhCH_2Br]{1)\ OH^-} R-O-CH_2Ph \xrightarrow{H_2, Pd/C} ROH + PhCH_3$

$\xrightarrow{H_3O^+} ROH + PhCH_2OH$.

环醚迷反应：$\triangle O + HI \longrightarrow ICH_2CH_2CH_2CH_2OH \xrightarrow{HI} ICH_2CH_2CH_2CH_2I$

·环氧化合物开环反应.

1). H^+条件. 质子化-亲核取代机理.

$-\overset{|}{C}-\overset{|}{C}- \overset{H^+}{\rightleftharpoons} -\overset{|}{C}-\overset{|}{C}=\overset{+}{O}(H) \xrightarrow{Nu^-} -\overset{|}{C}(Nu)-\overset{|}{C}(OH)-$

$\triangle O \overset{H^+}{\rightleftharpoons} [\triangle \overset{+}{O}(H)] \xrightarrow{CH_3OH} HO-CH-CH_2-OCH_3$

碱性开环(亲核试剂亲核能力较强).

2). OH^-条件下：亲核取代-质子化机理

$-\overset{|}{C}-\overset{|}{C}- \xrightarrow[S_N2]{Nu^-} -\overset{|}{C}(Nu)-\overset{|}{C}(O^-)- \xrightarrow{H^+} -\overset{|}{C}(Nu)-\overset{|}{C}(OH)-$

eg. $R'NH_2$, HO

$R-CH(H)-\overset{O}{\backslash\!/}CH_2 \rightarrow R-CH(H)-CH_2-NHR'$

$R'MgX$; $LiAlH_4$, H_2O 等试剂!!!

区域选择性&立体选择性：

1). H^+条件下：区域选择性 S_N1 特征. $H_3C-\triangle O \overset{H^+}{\rightleftharpoons}$ 三级C+(较稳定)

立体：S_N2 特征 反式开环，构型翻转.

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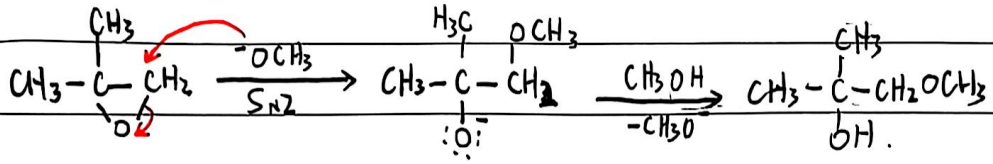
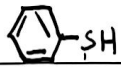
2)、OH^-下：亲核试剂亲核能力强 S_N2机理（进攻位阻较小的C原子）.

取代基少的一侧开环，反式开环

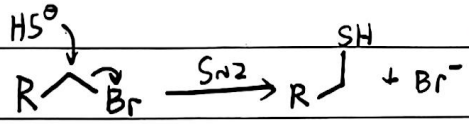
eg.



·硫醇 $R-S-H$ 硫酚  硫醚 $R-S-R'$

亚砜 $R-\overset{\overset{O}{\|}}{S}-R'$ 砜 $R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R'$ RS⁻亲核性比RO^-强.（易S_N2成硫醚）

而碱性比RO^-弱



$R'-Br \xrightarrow{R-SNa} R-S-R'$

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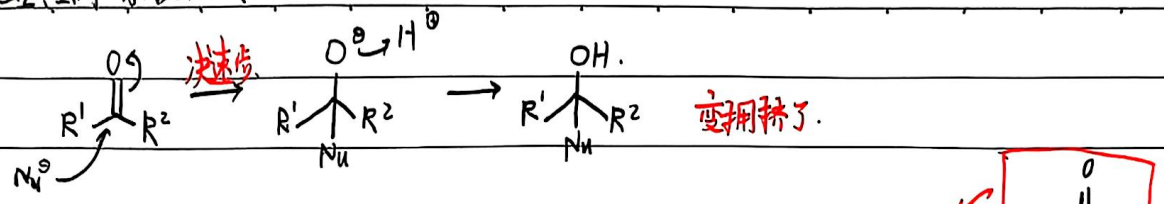
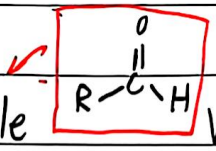
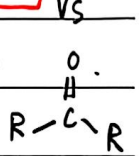
·醛、酮 亲核加成.



羰基相连基团越小越有利；基团越大，位阻越大.



less stable but more reactive Vs



C^+越强，越有利.

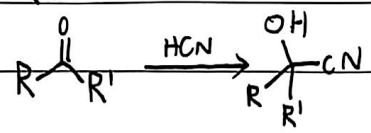
反应活性：脂肪醛 > 芳香醛 > 脂肪酮 > 芳香酮.

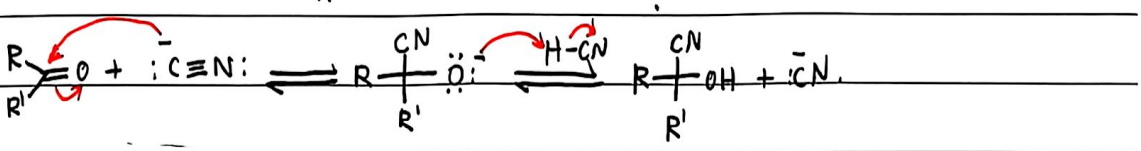
有时空间因素决定性作用：$CH_3COAr > (CH_3)_3CCOC(CH_3)_3$

含C亲核加成.

(1). HCN加成.

机理：保持在偏碱(微量碱)下进行

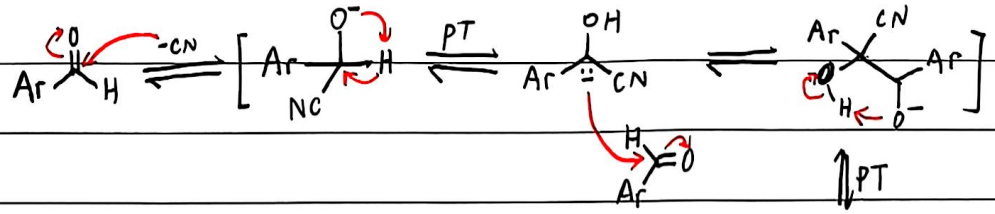


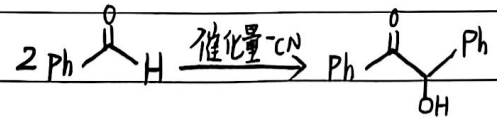


常用 NaCN (KCN)水溶液，再缓慢滴加浓HCl或H_2SO_4

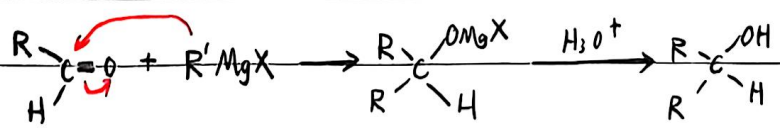
(2). 安息香缩合反应.

对于芳香醛，在没有酸存在下，^-CN对羰基亲核加成.





(3). 与格氏试剂加成.



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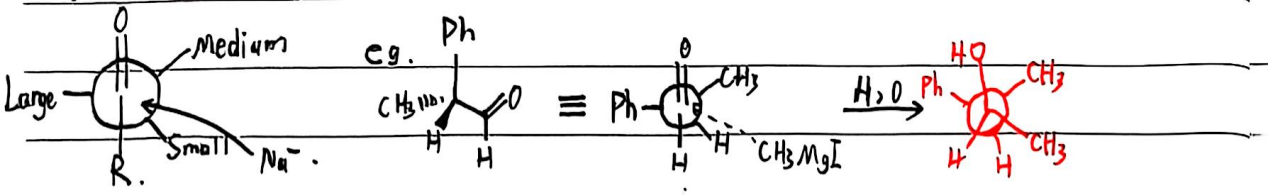
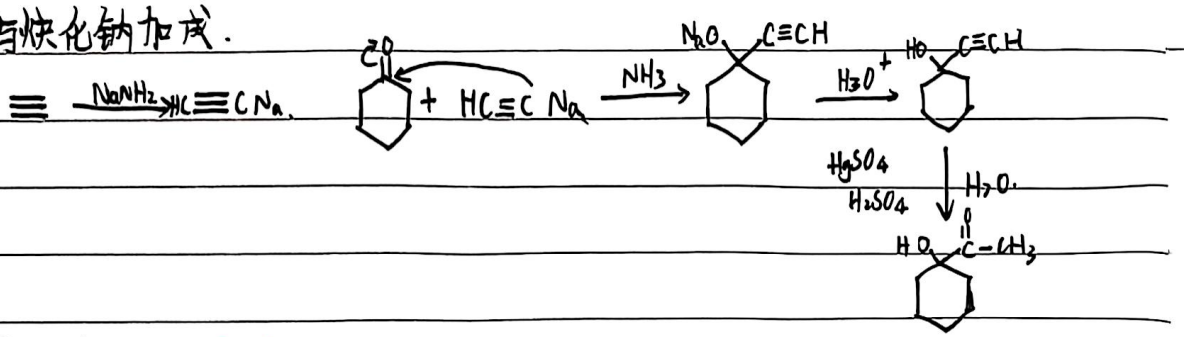
从位阻最小一侧进攻.

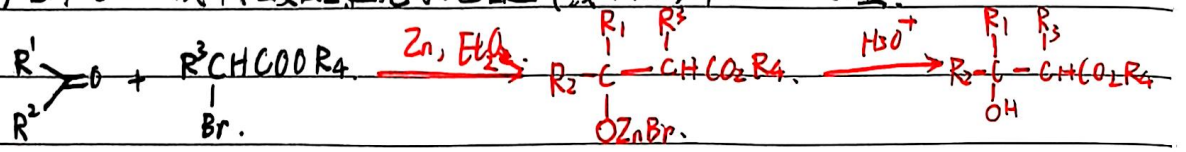


(4). 与炔化钠加成.



(5). 有机锌试剂. Reformatsky.

醛/酮与α-溴代酸酯在无水乙醚(或THF)中用Zn处理.

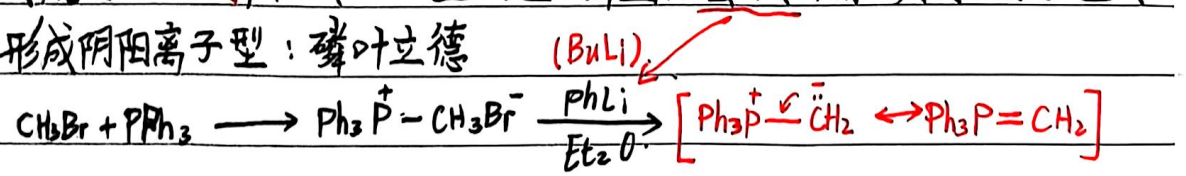


ps. 保留了酯基(不能用格氏试剂,会反应酯基).

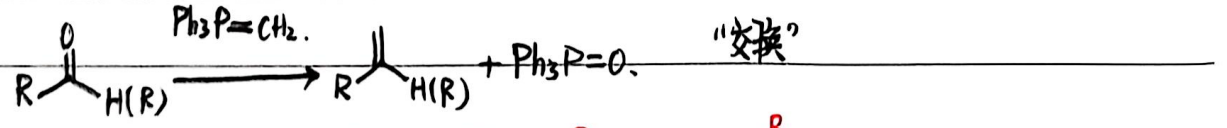
wittig试剂.

(6). 磷叶立德试剂加成, Wittig反应.

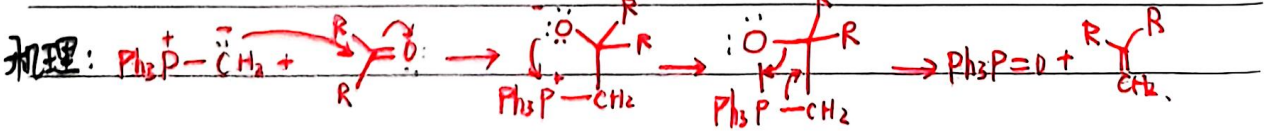
卤代烷与三苯基膦形成的烷基三苯基鏻盐在强碱作用下失去一分子卤代氢,形成阴阳离子型:磷叶立德



与醛/酮亲核加成⇒烯烃.且产生 $Ph_3P=O$.



机理:



不会产生双键位置异构体! (O喜欢P).

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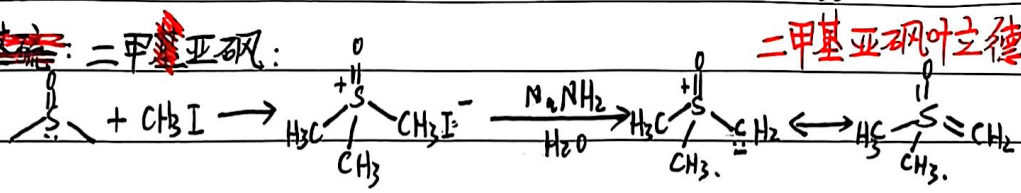
$(CH_3)_2S=CH_2$ 、

(7). 硫叶立德试剂加成.

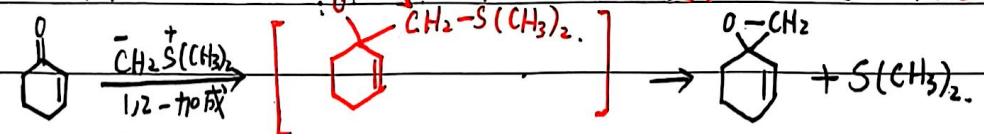
二甲基硫醚 $CH_3-\ddot{S}-CH_3 + CH_3I \xrightarrow{THF} CH_3-\overset{CH_3}{\overset{|}{\overset{+}{S}}}-CH_3I^- \xrightarrow[H_2O]{NaOH} (CH_3)_2\overset{+}{S}-\bar{C}H_2$ 二甲基硫叶立德.

~~二甲基硫~~ 二甲基亚砜:



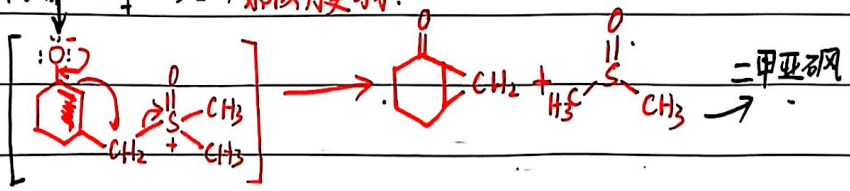
二甲基亚砜叶立德.

生成环氧化合物



O更喜欢 C.(与S相比).

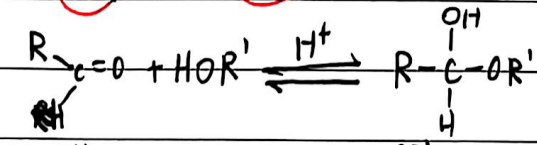
1,4-加成 $\bar{C}H_2\overset{+}{S}(CH_3)_2$ ⇒亲核力更弱.



9 与含氧亲核试剂加成.

(1). 与醇加成. ROH ☆

醛在干燥 HCl 或无水强酸催化下. 生成(半)缩醛



半缩醛. 连在同一个C原子上.

缩醛. → 对碱&氧化剂相当稳定. 但生成可逆. 在稀酸水中可变为原来的醛、醇.

类似 S_N1.

-OH与H^+成 $-\overset{+}{O}H_2$ 易离去.

分子内同时含 -OH & -CHO. 符合成环规律. 可自动生成环状半缩醛

(保护羰基).

PS. 酮在酸下也可生成(半)缩酮. (酮反应活性较低. 反应一般较困难, 常用原甲酸酯在酸催化下与酮反应制缩酮.)

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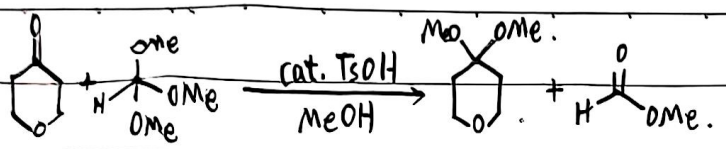
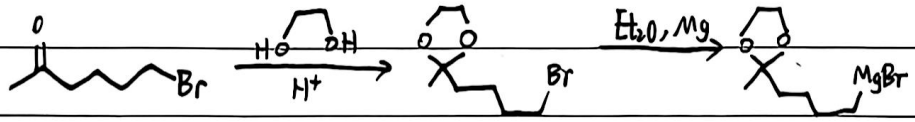
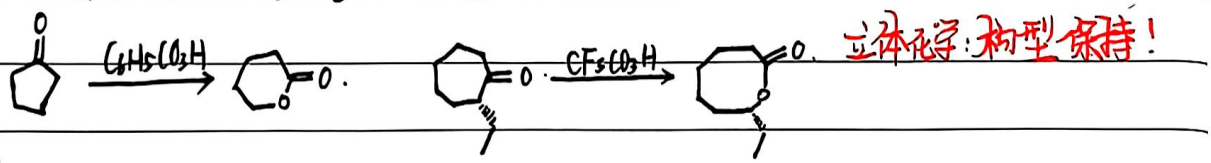


ps. 硫醇也可以生成硫代缩醛/酮

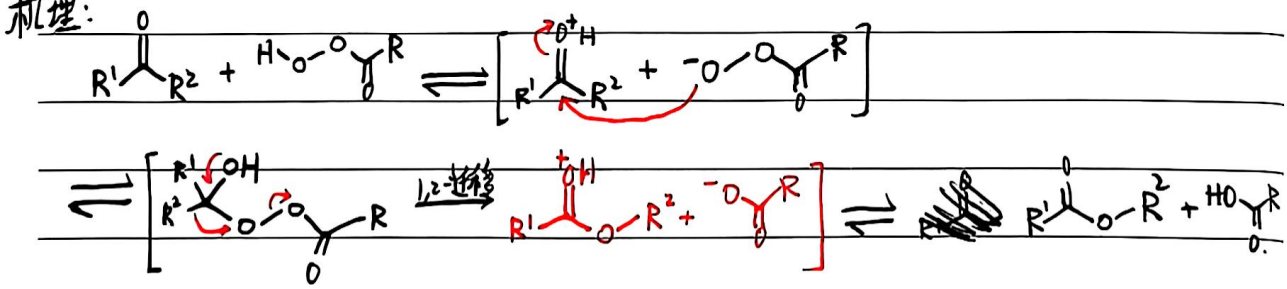
缩醛保护羰基：



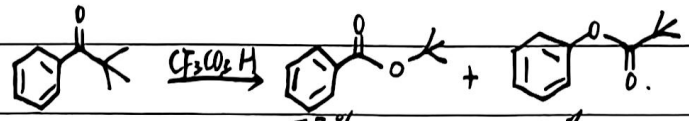
(2). 与过氧酸加成. (Baeyer-Villiger 反应). 迁移很"酒迷".



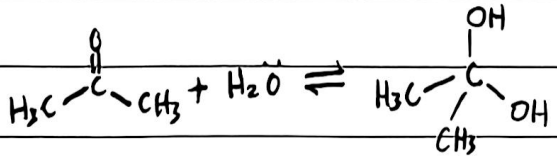
机理：



迁移：$R_3C > c\text{-}C_6H_{11} \approx R_2CH \approx C_6H_5CH_2 \approx C_6H_5 > CH_2=CH > RCH_2 > c\text{-}C_3H_5 > CH_3$



(3). 与水加成一形成水合物.



偕二醇. 一般不稳定.

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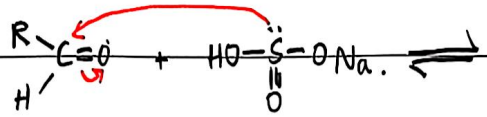
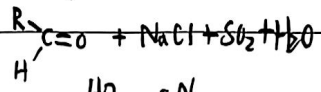
6、与含硫亲核试剂加成.

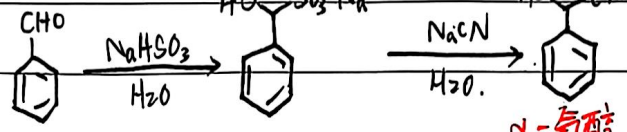
(1)、亚硫酸氢钠反应 较弱亲核试剂,与HCN相当



在稀酸或碱中分解为原来的醛或酮. | HCl. H2O. 分离提纯.



交换反应

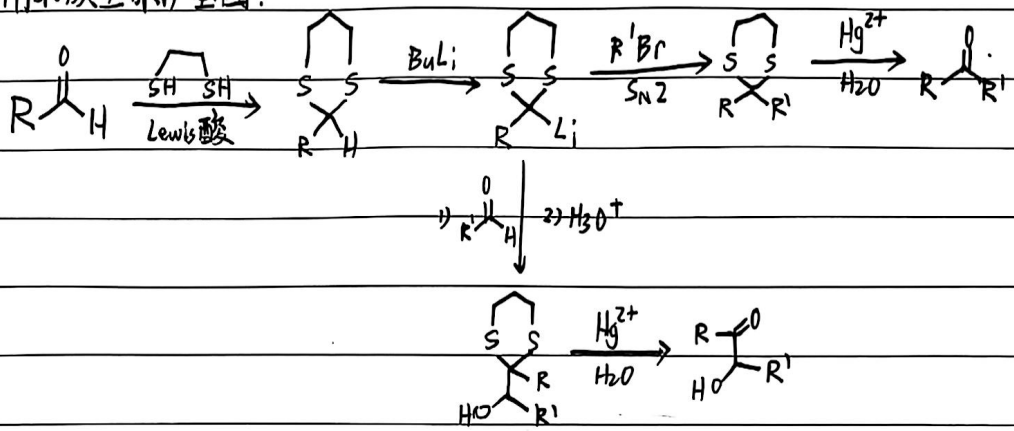


避免低沸点 HCN 使用.

α-氰醇.

(2)、硫醇(同硫代缩醛/酮).

也是常用的羰基保护基团.

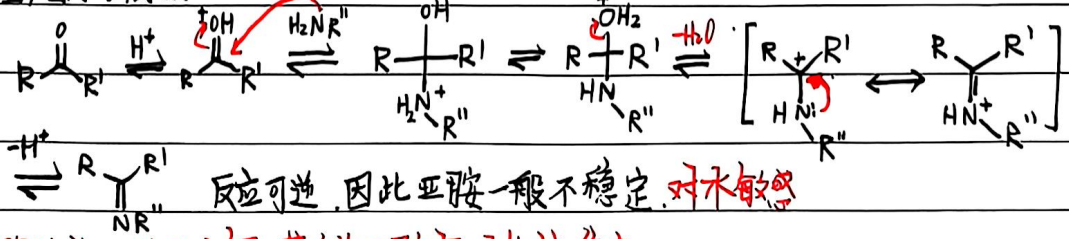


9、含氮亲核试剂加成.

RNH_2 伯胺 R_2NH 仲胺 NH_2NH_2 肼 NH_2OH 羟胺

(1)、与胺:

1) 醛/酮与伯胺反应: ⇒ 亚胺



反应可逆,因此亚胺一般不稳定,对水敏感

脂肪族亚胺易水解,芳香族亚胺相对比较稳定.

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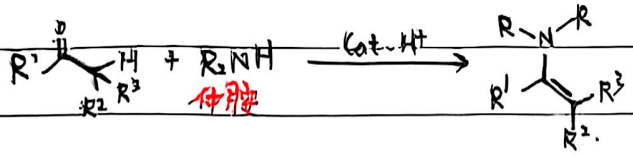
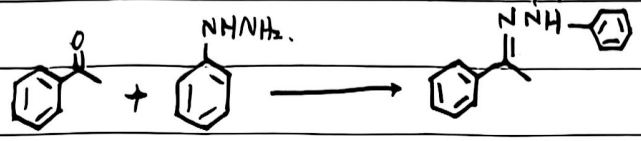
拟与补胺(R_2NH)反应生成烯胺

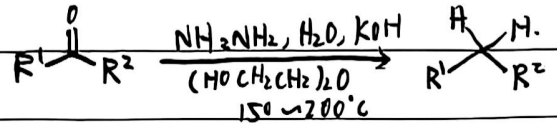


形成的烯胺可能是顺、反异构体的混合物

(2)、与肼加成 ~~[illegible]~~ $RNHNH_2$ 与伯胺相似 加成-脱水 生成腙、



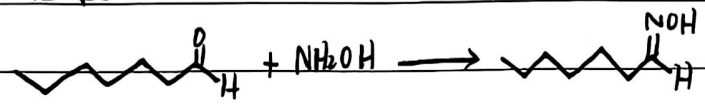
Wolff-Kishner-黄鸣龙还原.



强碱,高沸点溶剂.
C=O 还原为亚甲基.

适用于对酸敏感对碱稳定的底物,与克莱门森 Zn-Hg/HCl 互补.

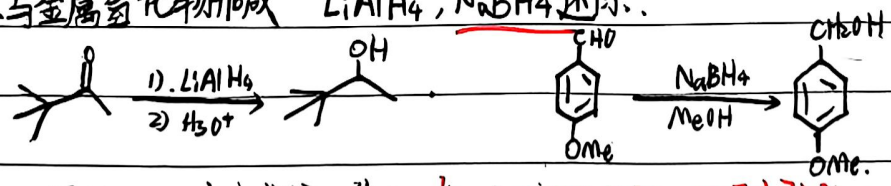
(3)、与羟胺加成 NH_2OH 与其反应生成肟.



有顺反异构!

9.与负氢试剂加成.

(1)、与金属氢化物加成 $LiAlH_4$, $NaBH_4$ 还原. 醛,酮,亚胺(烯夫碱).

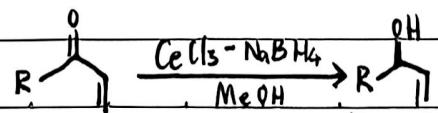


NaH 提供 H^- 但负电荷过于集中,常只表现强碱性,不具亲核性!

$LiAlH_4$ 还原力最强, $NaBH_4$ 不如 $LiAlH_4$ 但 $NaBH_4$ 较高选择性!

eg. $NaBH_4$ 可使 $-CO_2R$, $-CO_2H$, $-CN$, $-NO_2$ 不受影响.

而 $LiAlH_4$ 还原所有.



共轭时联用 $CeCl_3$ 才能特异选择 , 否则 C=C 也还原

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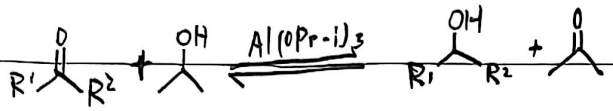
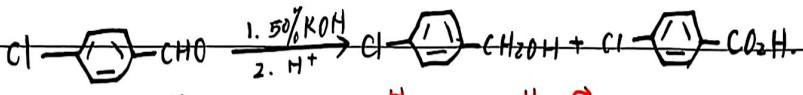
2、与金属转移试剂加成 (Meerwein-Ponndorf)还原

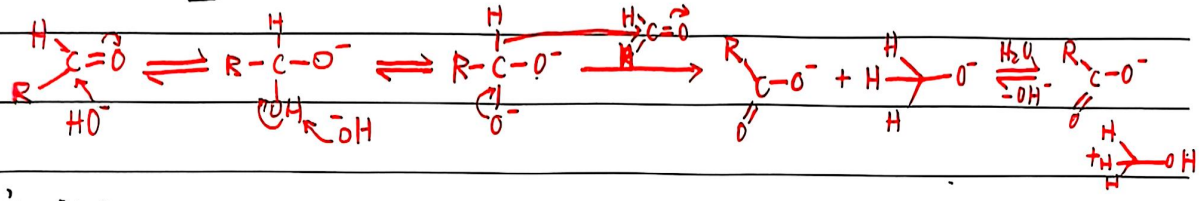


逆反应：Oppenauer氧化.

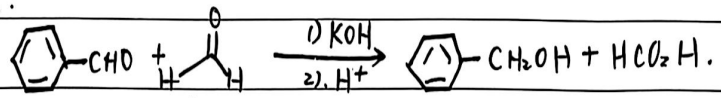
机理☆☆☆

(3)、康尼查罗(Cannizzaro)歧化反应：碱性条件下，无α-氢的醛可歧化生成等物质的量的醇和酸 ☆.





交叉歧化：



甲醛羰基比苯甲醛活泼，首先被OH^-进攻.

其他反应：1.金属还原 K > Na > Li > Mg > Al > Zn > Fe.

克莱门森(被Zn还原) Zn-Hg/HCl.

2.催化氧化 Pt/H_2 → 醇.

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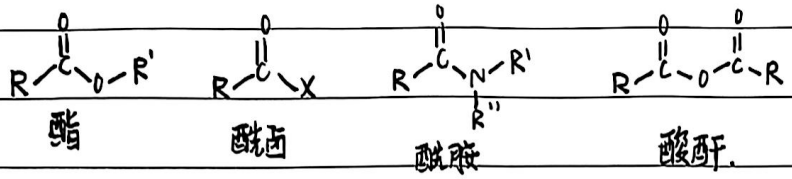
• 羧酸及衍生物.

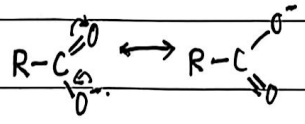


酯　酰卤　酰胺　酸酐.

Ps. 命名时最优先的是-COOH

羧酸溶、沸点比相应分子量的醇高.

• 酸性：$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$

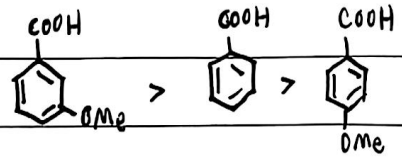


比较酸性：分散电荷，共轭.

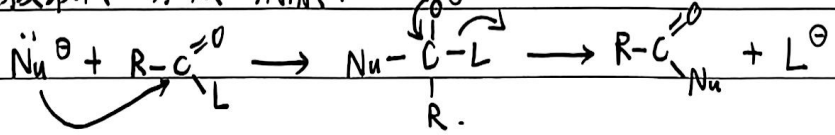
eg. $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$. 吸电子.

$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

$O_2NCH_2COOH > NCCH_2COOH > CH_3OCH_2COOH$.

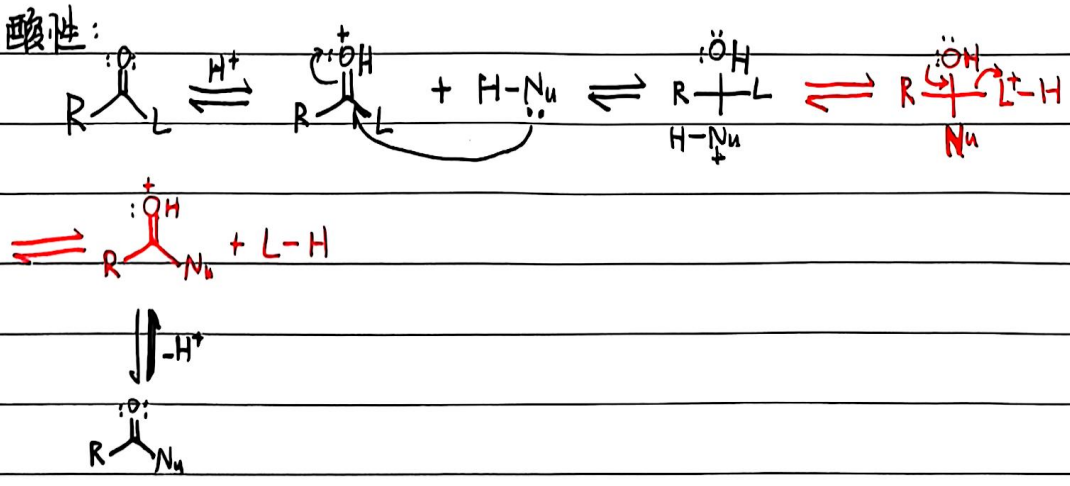


亲核取代：加成-消除.

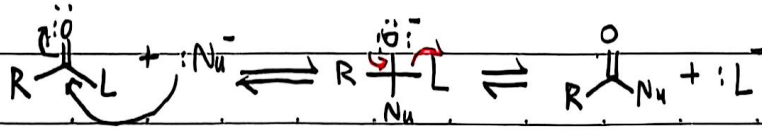


L：$Cl > O_2CR > OR > NH_2$

(1). 酸性：



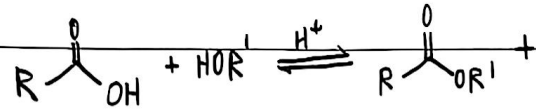
(2). 碱性：



扫描全能王
3亿人都在用的扫描App

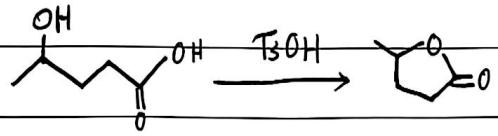
Date. Page.

1. 酯解反应（酯化反应）

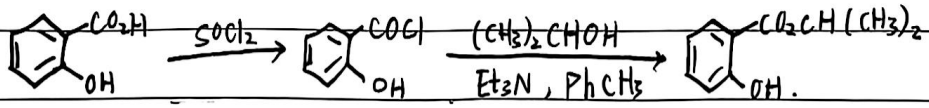


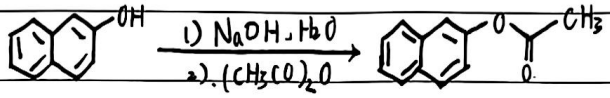
常用浓 H_2SO_4 催化，苯/甲苯溶剂。
共沸带水方法将产生的水除去。

分子内：一般五、六元环内酯稳定。

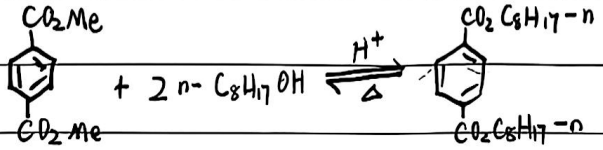


酰氯和酸酐反应活性高，易与醇发生酯解反应成酯。常在碱（eg. 三乙胺、吡啶等）存在下进行（难以直接羧酸&醇直接发生酯化制备的酯可用此方法）eg.



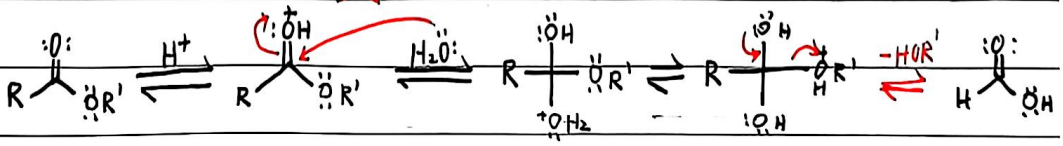


在酸/醇钠存在下，酯的醇解可得另一种酯和另一种醇（酯交换反应）。可逆。



2. 水解反应

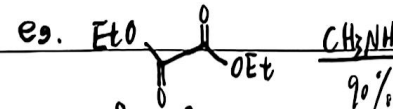
酸催化：

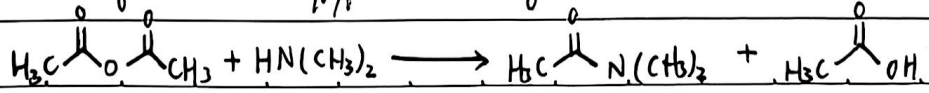


碱催化：加成消除机理。

3. 氨解反应

酰氯，酸酐，酯易与氨/胺发生亲核取代生成酰胺（制备酰胺）

eg. 



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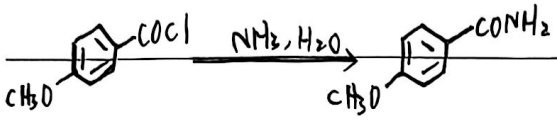
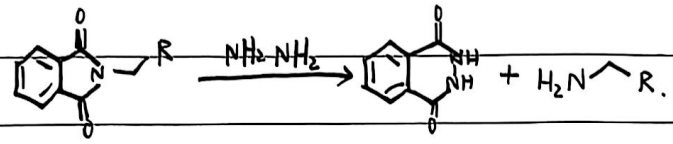


羟胺和肼也可作亲核试剂发生类似反应，与肼反应为肼解.

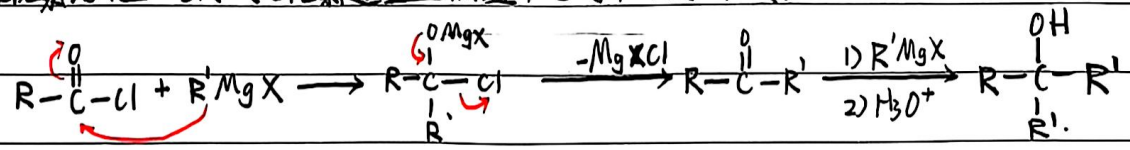


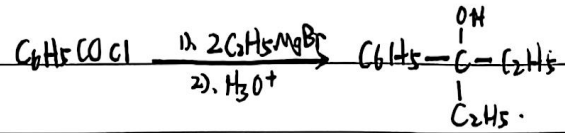
5.与金属有机试剂反应、☆☆.

eg. 格式试剂，有机锂试剂 RLi，有机铜锂试剂 (R_2CuLi).

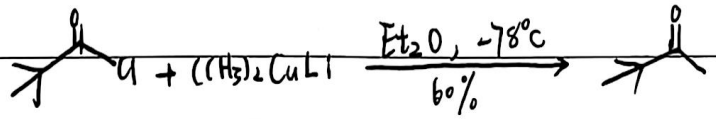
酰氯活性很大 ⇒ 加成-消除生成酮 → 再与过量试剂生成叔醇.

ps. 但酰氯活性 > 酮.（酰氯过量且低温下可停在酮阶段）.

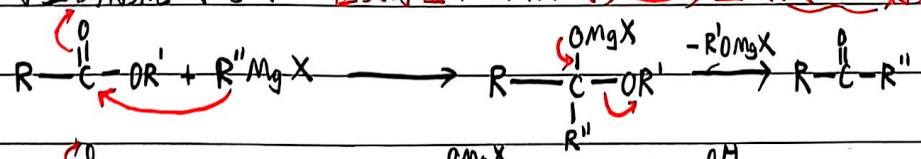


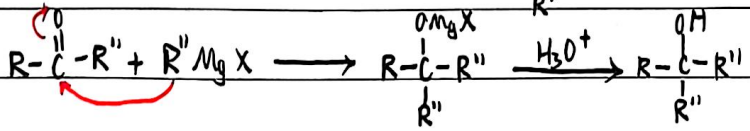


有机铜锂试剂反应活性不如格氏试剂，与酰氯反应一般为酮.



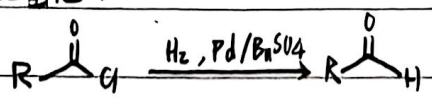
酯与金属有机试剂反应难以停留在酮阶段，进一步生成叔醇. ☆☆☆



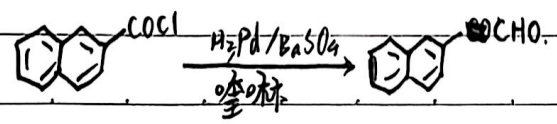


羧酸及其衍生物的还原

· 催化氢化.



Rosenmund 还原.



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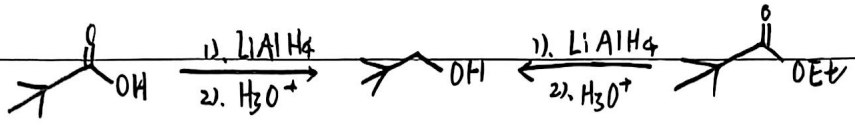
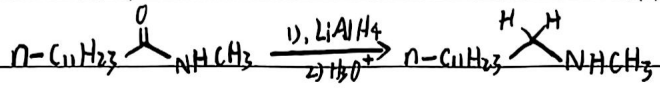
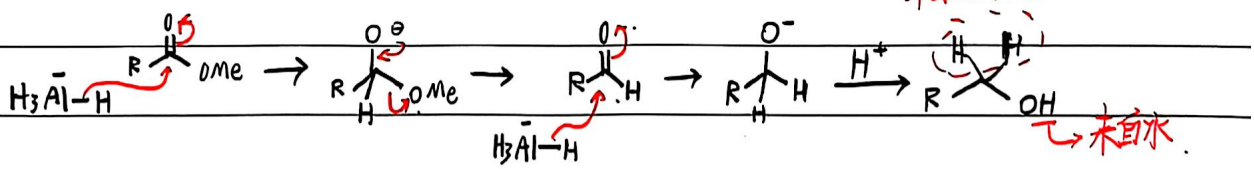
金属氢化物还原

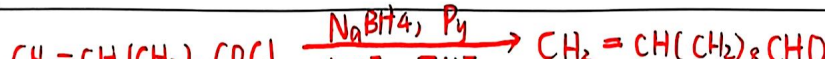


氢化锂铝还原能力很强：醛/酮 → 醇　酰氯，酯，羧酸 → 伯醇，酰胺 → 胺

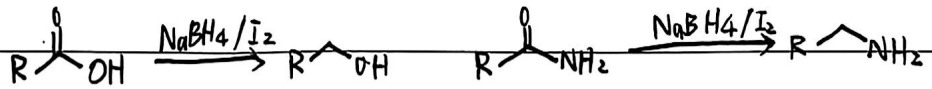




$NaBH_4$ 还原：一般还原醛，酮为醇，不能直接还原羧酸及其衍生物，但在吡啶或三氯化铝存在下，在 N,N-二甲基甲酰胺中反应，可将酰氯选择性还原成醛

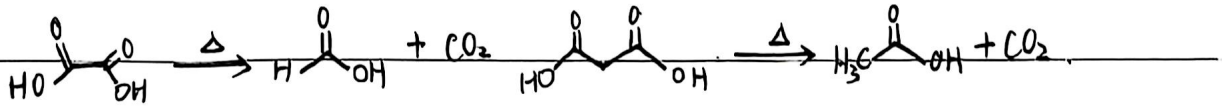


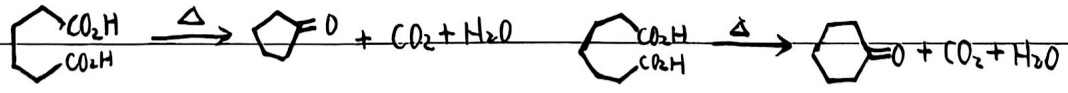
ps. 在亲电试剂（I_2, H_2SO_4, $AlCl_3$）下，$NaBH_4$ 可将羧酸还原为醇，酰胺 → 胺



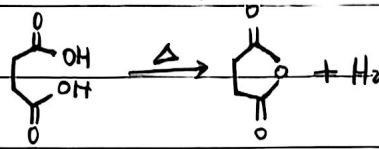
其它反应：

1. 脱羧反应：加热时失去 CO_2 的反应

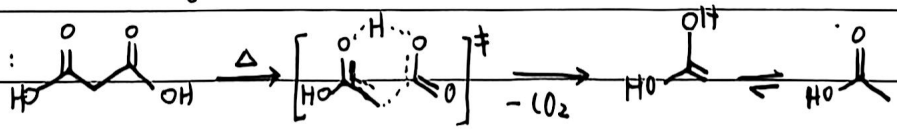




丁二酸和戊二酸只失水成酸酐：



六元环过渡态：



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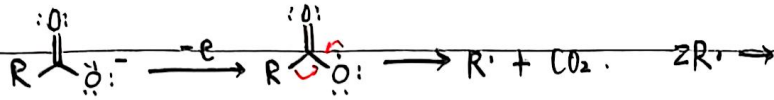
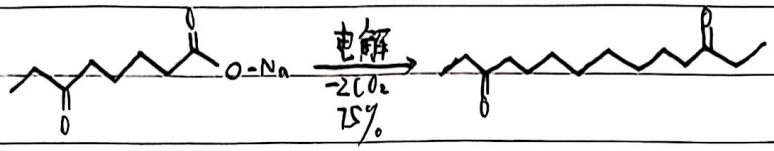
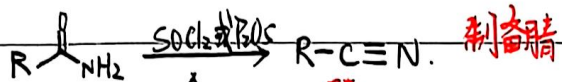
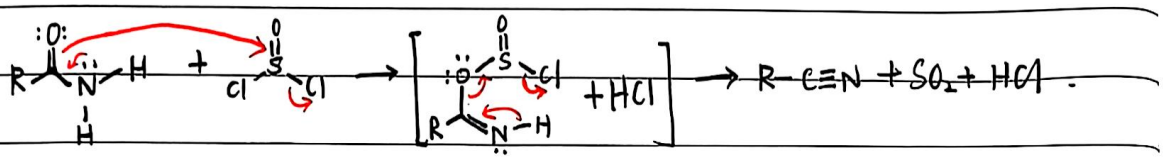
kolbe反应：



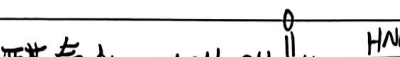


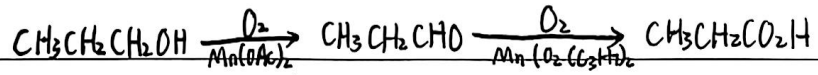
3.脱水反应



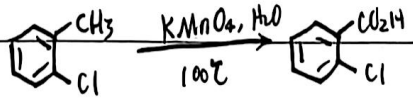


制备.

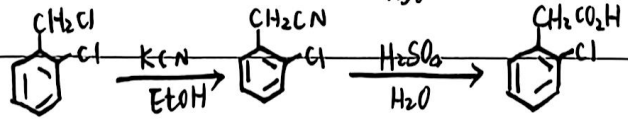
i羧酸.(1).醇,醛氧化： 

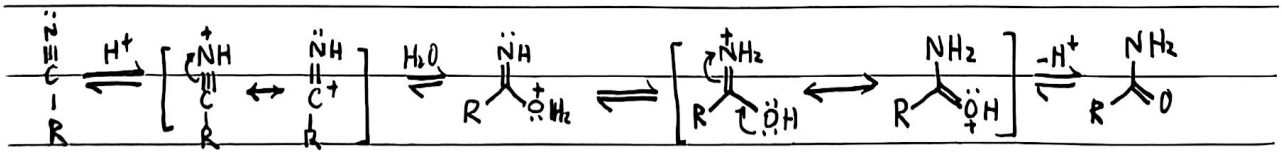


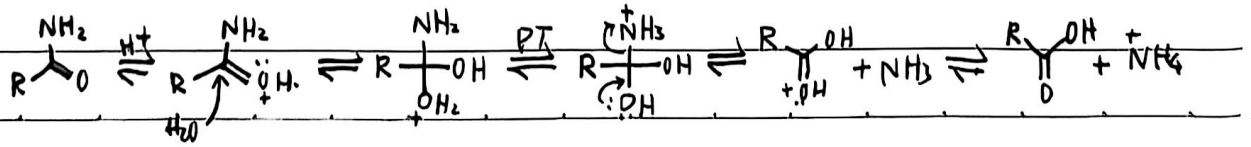
(2).烃的氧化：

烷基苯氧化： 

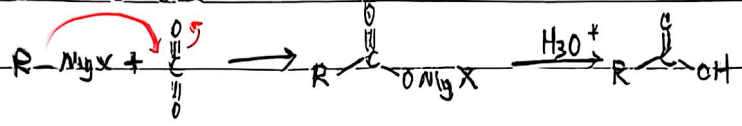
(3).腈的水解：

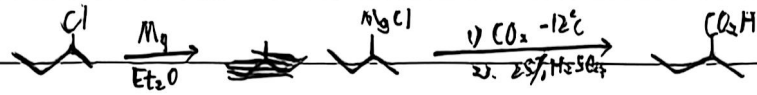




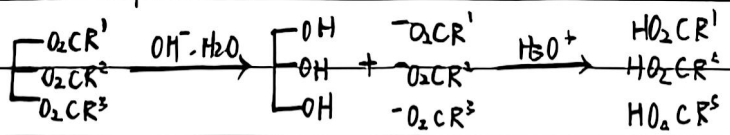


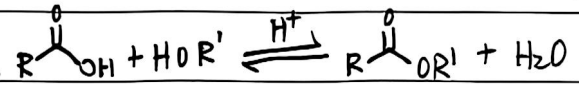
(4)、格氏试剂制备：



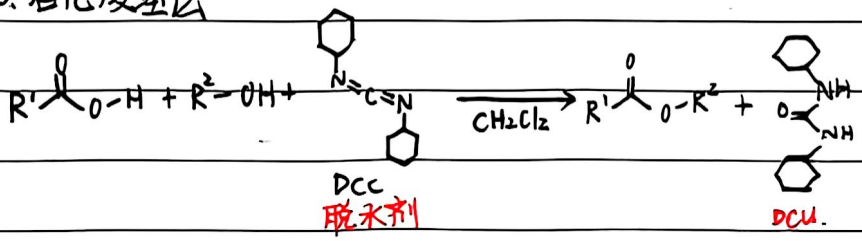


(5)、油脂水解



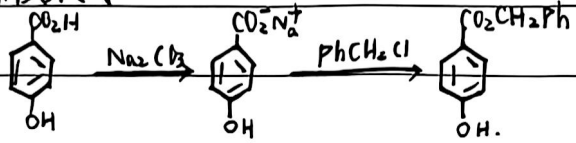
iii 酯：(1)酯化反应 

(2)、活化羧基法

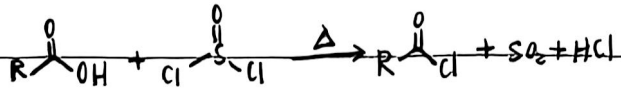


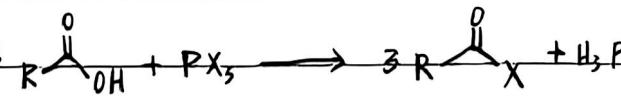
DCC 脱水剂　　DCU.

(3)、亲核取代

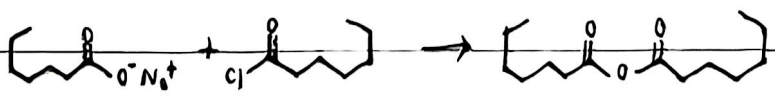


iv 酰卤　酰化试剂 PBr_3、PCl_3、PBr_5、PCl_5.

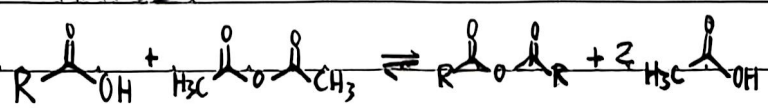




v 酸酐：(1)、酰氯与羧酸钠盐反应.



(2)、酸酐交换反应.



扫描全能王 3亿人都在用的扫描App

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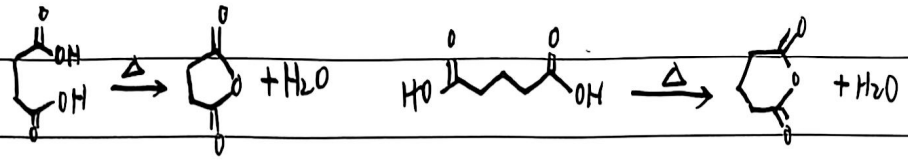
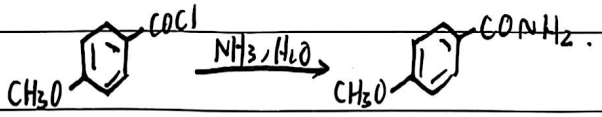
(3). 二元酸脱水. (仅适用于生成五、六元环酸酐).



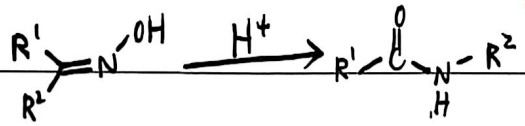
V. 酰胺

(1). 羧酸衍生物氨解

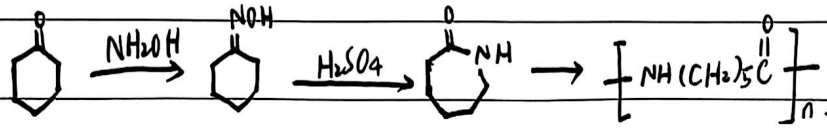


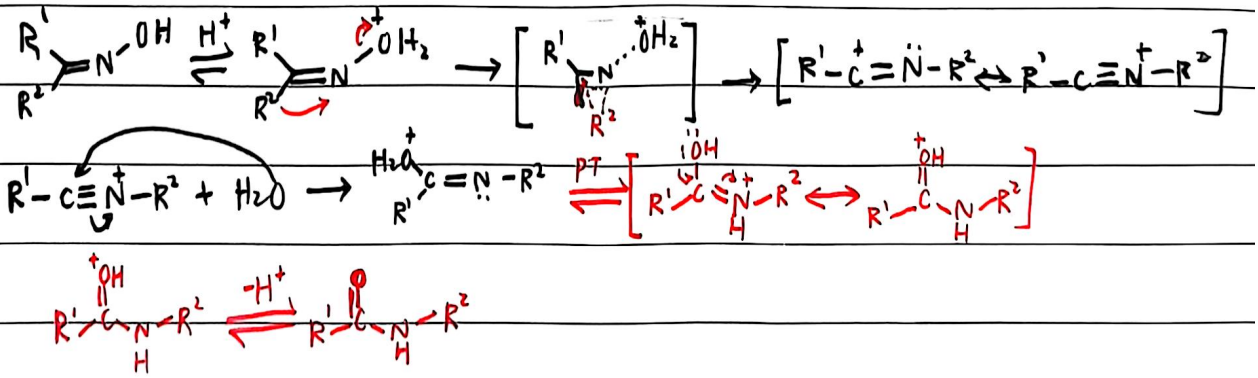
(2). 活化羧基法: $RCO_2H + H_2NR' + DCC \xrightarrow{DMAP} RCONHR' + DCU$.

(3). Beckmann 重排

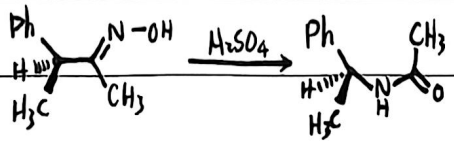


反式基团迁移.





迁移基团构型保持:



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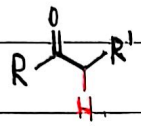
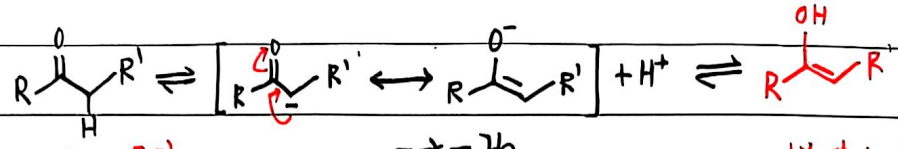
一、羰基化合物α-C上的反应

羰基吸电子效应，α-氢表现一定的酸性。





酮式 弱酸 互变异构 烯醇式 强酸

酸催化能加速互变异构，但不改变平衡常数。强碱催化平衡向烯醇负离子方向移动。

影响α-H酸性因素：电子效应。

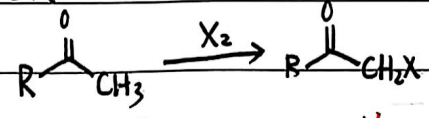
吸电子：$-NO_2 > -CHO > -COR > -CN > -COX > -CO_2R > -CONR_2 > -CO_2H$

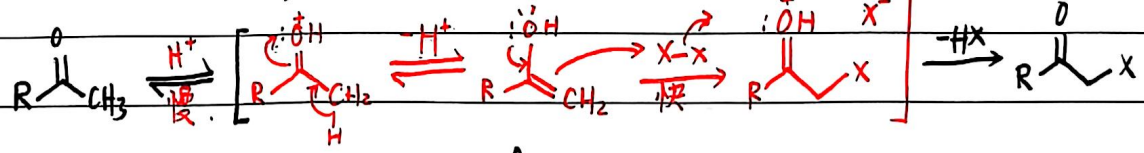
烯醇特征：与Br_2加反应，与$FeCl_3$在乙醇中发生紫红色反应 ☆

1. α-卤化反应

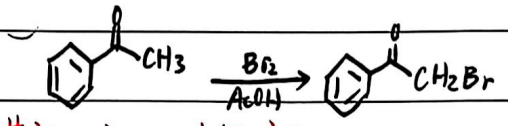
1). 酮的α-卤化反应

·酸催化。



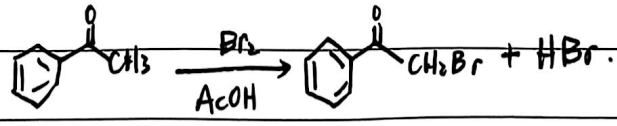


可停在单取代阶段。



卤原子吸电子效应使羰基氧上电子云密度降低

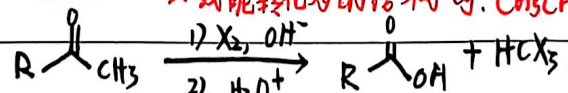
eg.

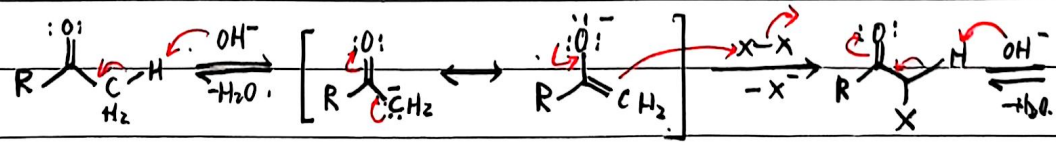


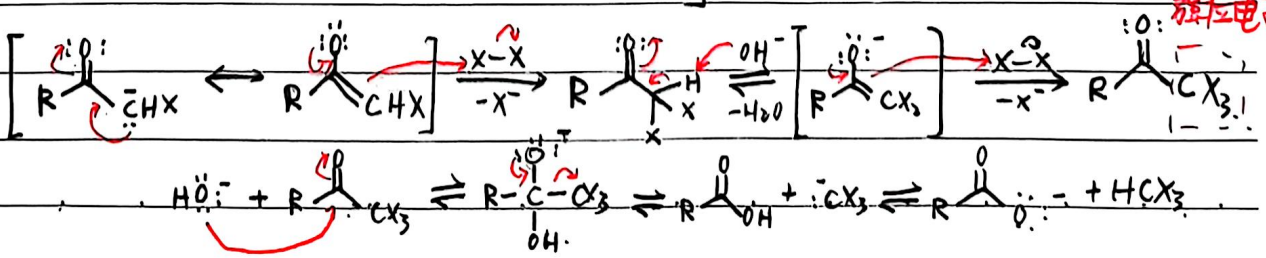
Ps. 对不对称酮，区域选择性取决于所形成的烯醇中间体稳定性。

·碱性条件：甲基酮与卤素反应生成羧酸和卤仿。⇒卤仿反应。

☆或能转化为的结构 eg. CH_3CH_2OH也能反应







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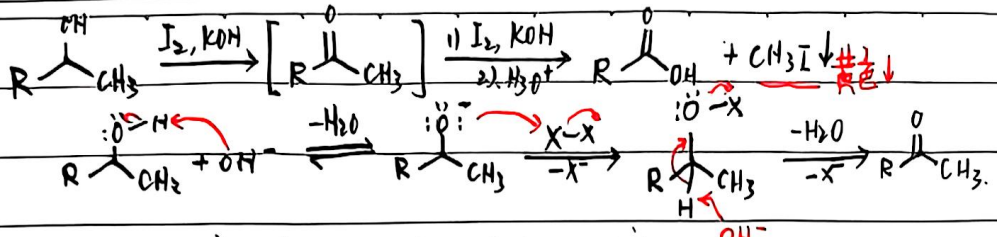
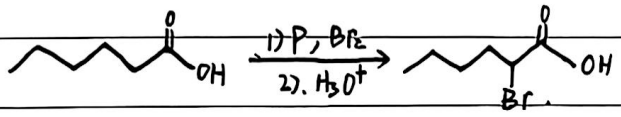


PS. α-C上只有一个H原子时，碱催化生成单卤代物

(2) 羧酸及其衍生物的α-卤化反应. ☆

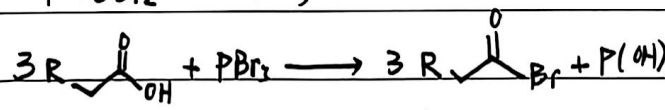
羧酸α-H酸性比酮弱　酰卤&酸酐的α-H酸性一般较强，易于卤化

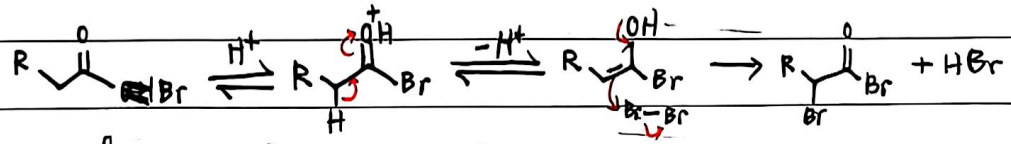
P催化.

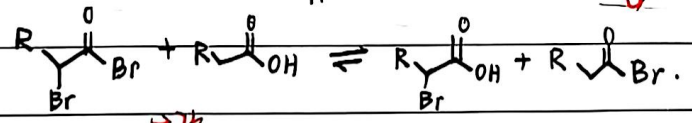


实际底物为酰卤.

$2P + 3Br_2 \longrightarrow 2PBr_3$



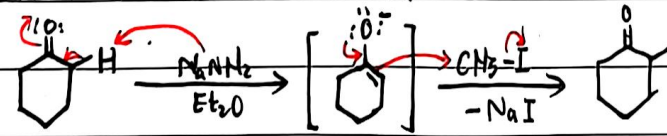


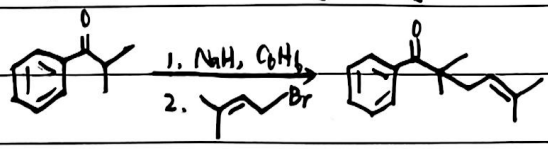


交换

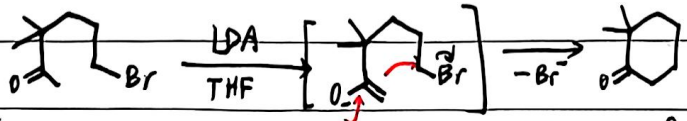
• α-烷基化反应.

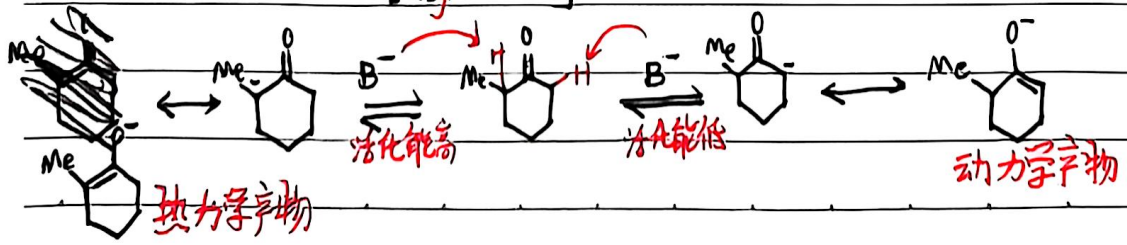
1. 经由烯醇负离子的烷基化反应





LDA：大位阻强碱.





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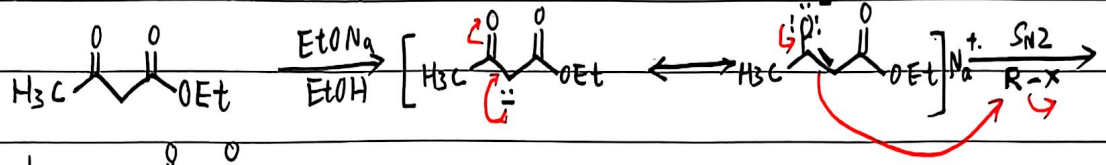
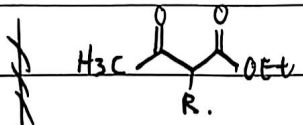
小体积碱 eg. NaH, $NaNH_2$. 热力学稳定；

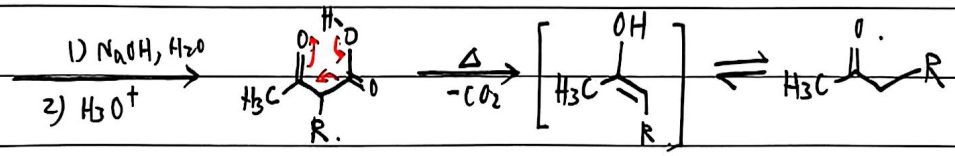
大体积碱 eg LDA 动力学稳定

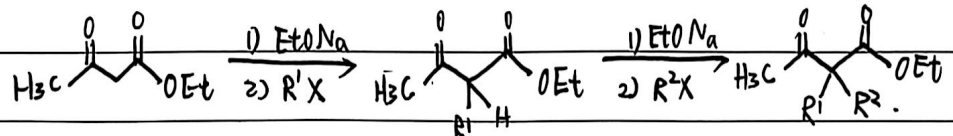
乙酰乙酸酯和丙二酸酯

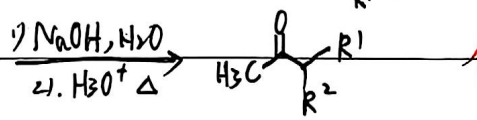
①





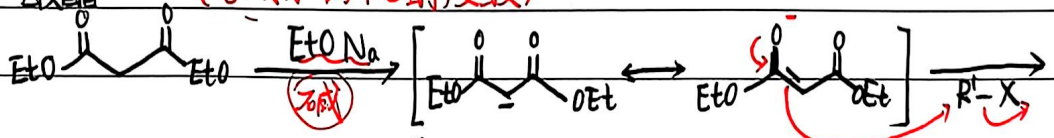


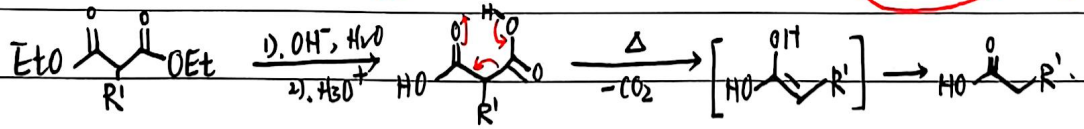


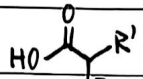
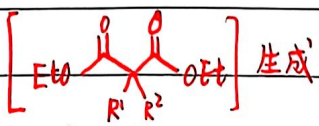


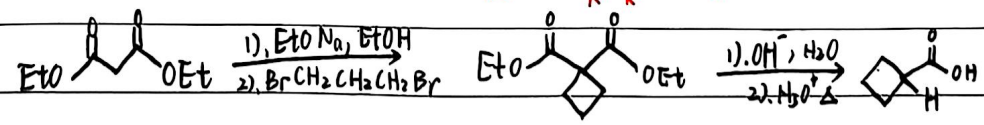
合成增C的甲基酮

②. 丙二酸酯 (合成加两个C的羧酸)

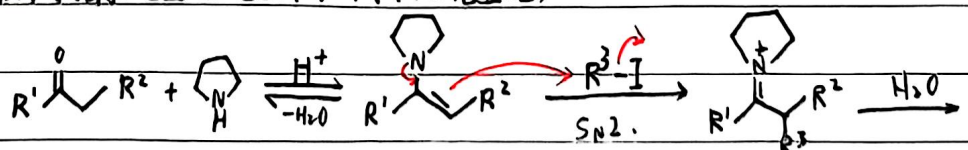


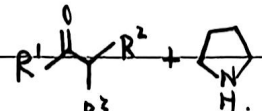


可再加一个形成   生成

eg. 

• 经由烯胺的烷基化反应. (烯胺的烷基化)





条件温和，副反应少，对醛也适用

CS 扫描全能王
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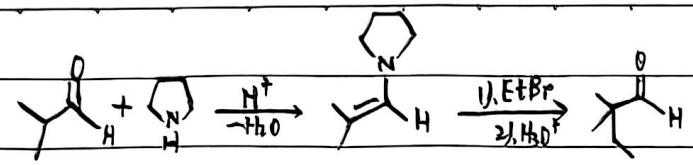
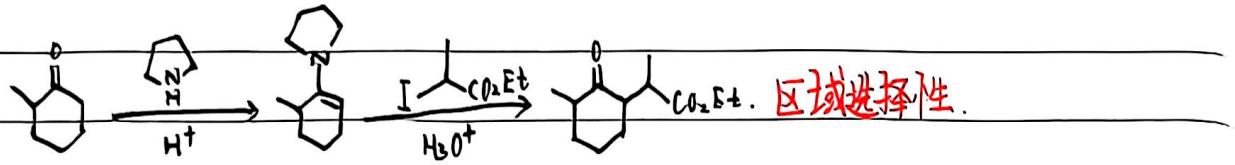
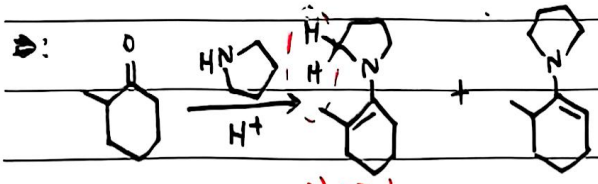
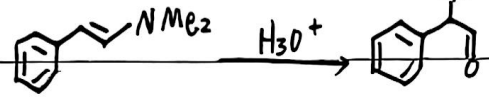
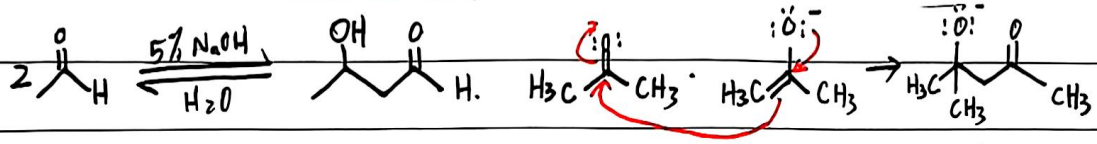


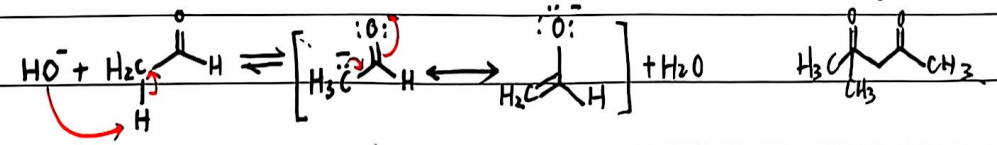




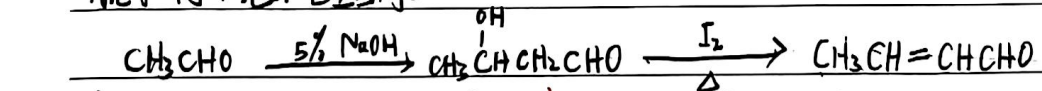
同理类似： 

• 羟醛缩合. 有α-氢的醛或酮.

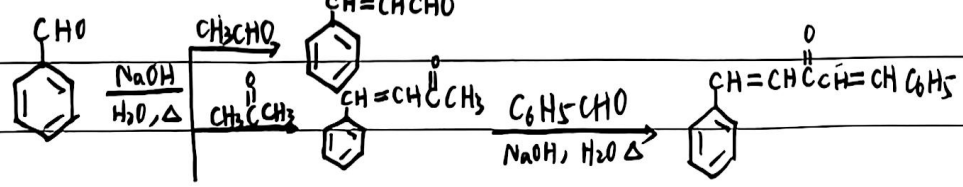


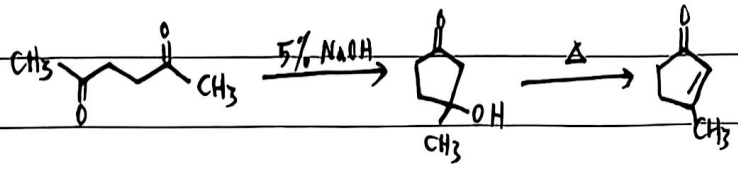
机理： 

脱水制不饱和醛酮.

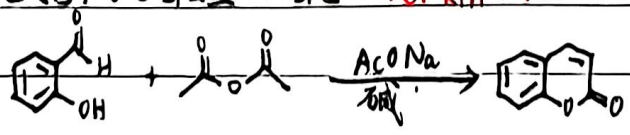


有α-H的醛与无α-H发生交叉羟醛缩合反应



eg. 

• 醋酸酐与芳香醛的缩合 Perkin 反应



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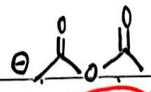

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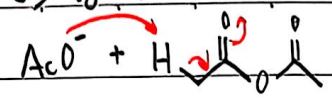
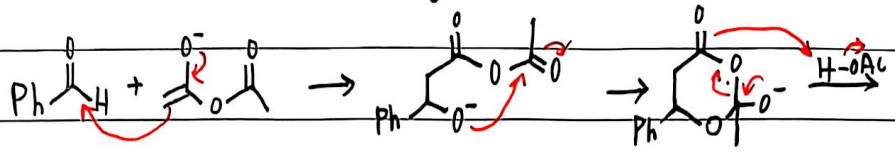
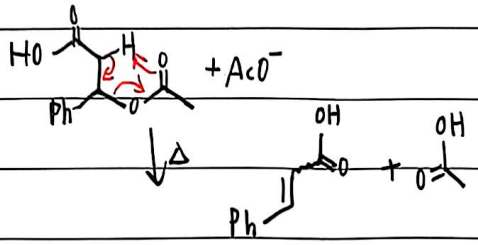
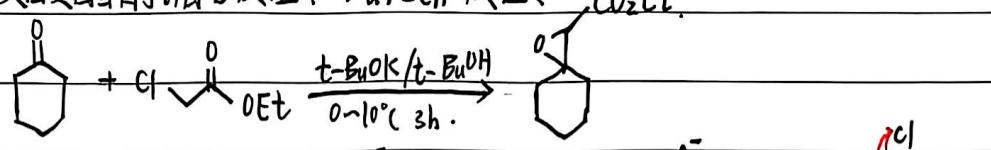
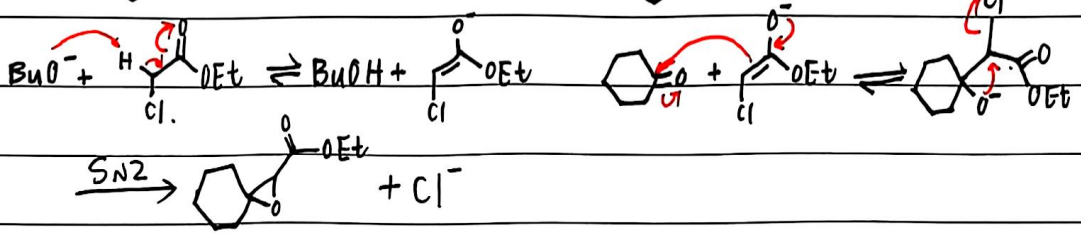






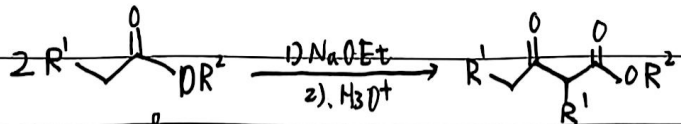
α-卤代羧酸酯的缩合反应. Darzen 反应.

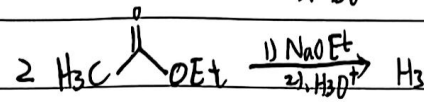


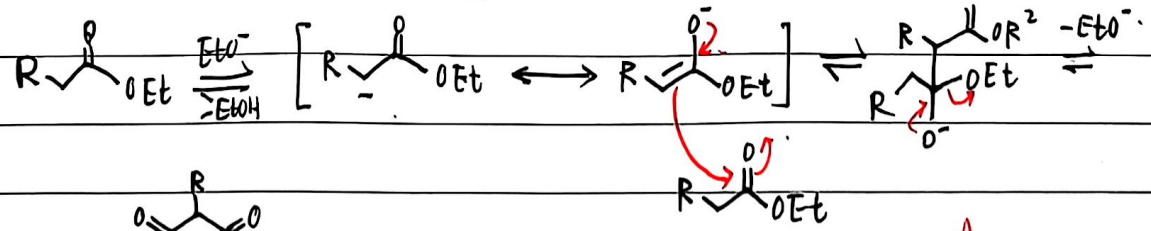


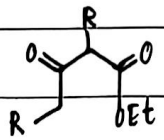
酯缩合反应. 机理 ☆☆☆.

1. Claisen 缩合反应. 碱条件下. α-H 羧酸酯双分子缩合. 生成 β-酮酸酯

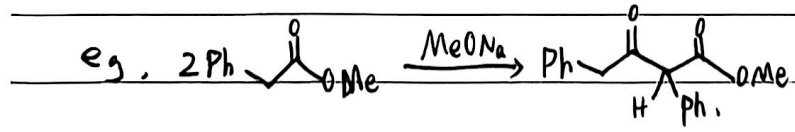








ps. 必须 2 分以上活泼 H 才可以发生 Claisen 缩合反应



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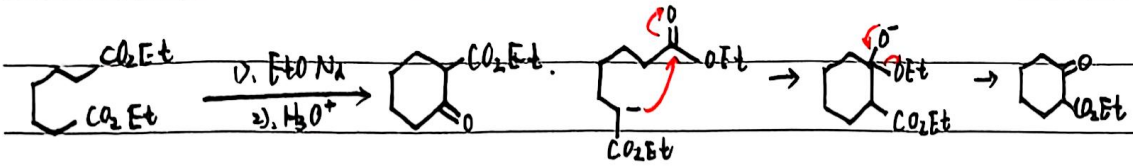
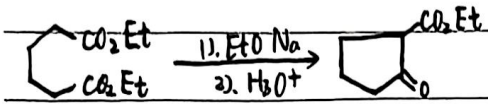
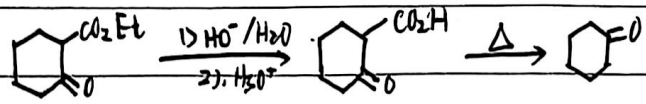
分子内 Claisen 缩合 — Dieckmann 缩合反应

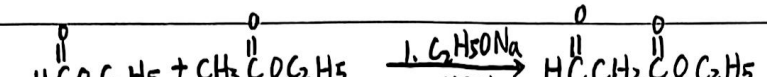


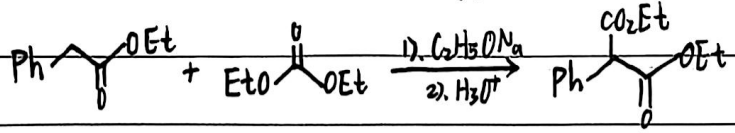


适合于5~6元环酮酸酯的合成

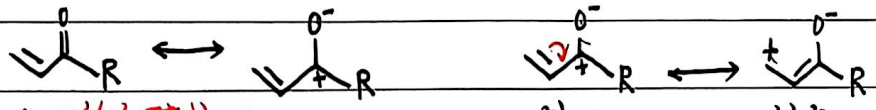


易脱羧

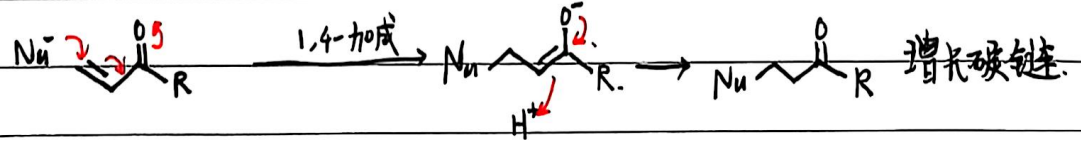
交叉： 



- Michael 加成. 共轭加成；1,4-加成

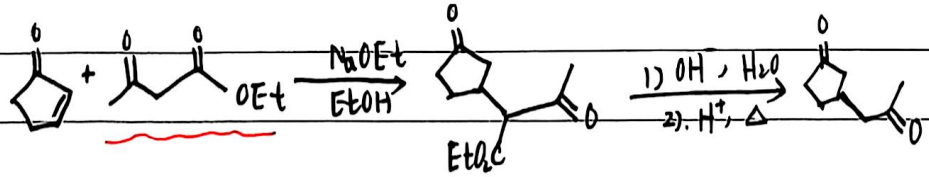


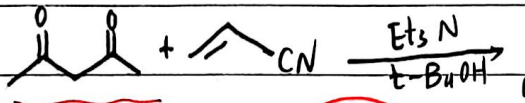
α,β-不饱和醛或酮　　较硬　　较软.

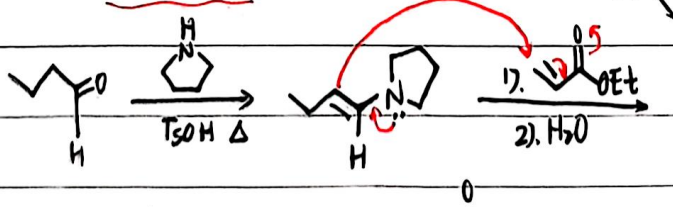


增长碳链.

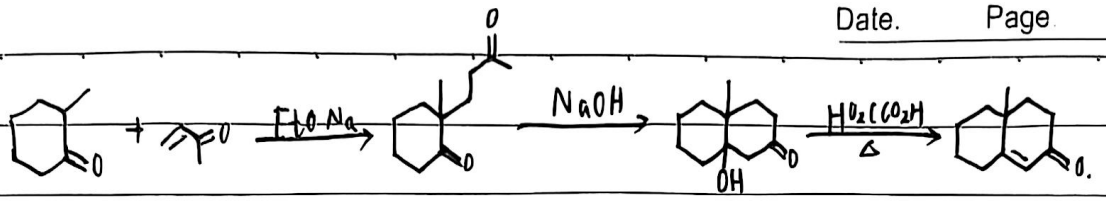
eg.







- Robinson 增环反应



• 胺及其衍生物

1. 胺的碱性 （胺的水溶液呈碱性）

$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$　　$RNH_2 + HCl \rightleftharpoons R\overset{+}{N}H_3\,Cl^-$

N原子周围电子云密度↑ 接受 H^+ 越强，碱性越强　脂肪胺 > 氨 > 芳香胺

有机溶剂，气相：碱性：叔胺 > 仲胺 > 伯胺.

水中：$(C_4H_9)_2NH > C_4H_9NH_2 > (C_4H_9)_3N$　仲胺大. 溶剂化作用

共轭 给电子与溶剂化

脂环仲胺 > 脂肪仲胺 > 脂肪伯、叔胺 > 芳伯胺 > 芳仲胺 > 芳叔胺

2. 胺的酸性：

$R\text{-}NH_2 + B^- \rightleftharpoons R\text{-}\bar{N}H + HB$

胺的制备：烷基化：$NH_3 + CH_3Br \rightarrow CH_3\overset{+}{N}H_3Br^-$

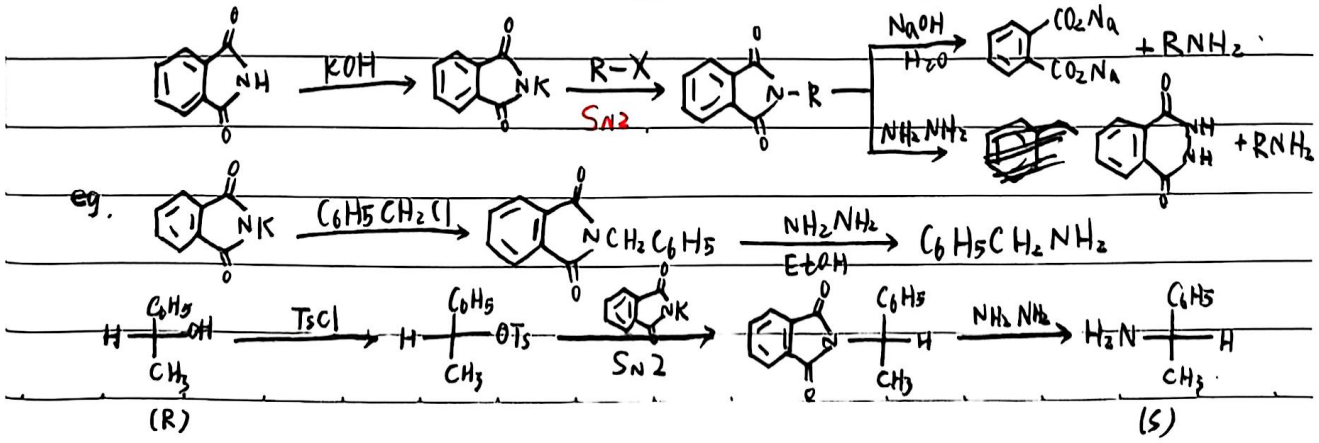
$CH_3\overset{+}{N}H_3Br^- + NH_3 \rightleftharpoons CH_3NH_2 + \overset{+}{N}H_4Br^-$

$CH_3NH_2 + CH_3Br + NH_3 \rightleftharpoons (CH_3)_2NH + \overset{+}{N}H_4Br^-$

过量 NH_3：$CH_3(CH_2)_6CH_2Br \xrightarrow{\text{过量}NH_3} CH_3(CH_2)_6CH_2NH_2 + [CH_3(CH_2)_6CH_2]_2NH$.

$(C_2H_5)_2NH + \triangle O \rightarrow (C_2H_5)_2NCH_2CH_2OH$

• Gabriel合成法：以邻苯二甲酰亚胺的钾盐为亲核试剂，与卤代烷进行烷基化反应，得 N-烷基邻苯二甲酰亚胺，经水解或肼解得伯胺.



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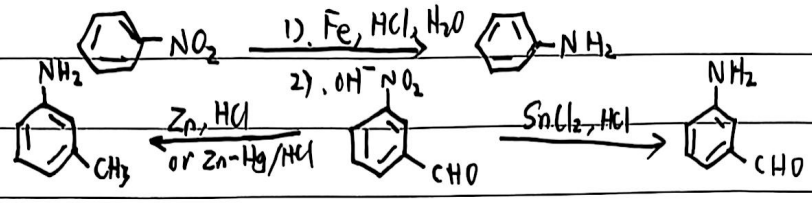
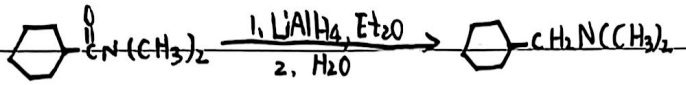
含N化合物还原.

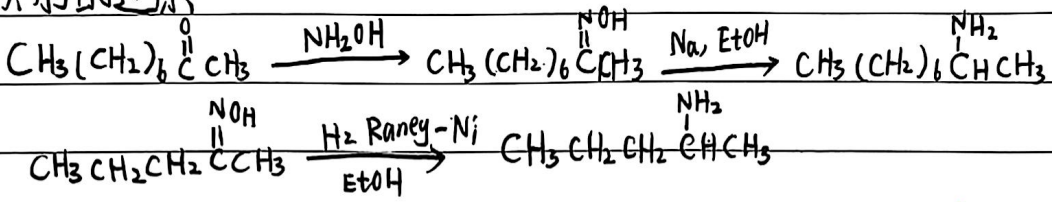
(1). 硝基化合物还原：常用还原剂）：锡、铁、锌、$SnCl_2$、$NaSH$、$LiAlH_4$、Na/ROH 等



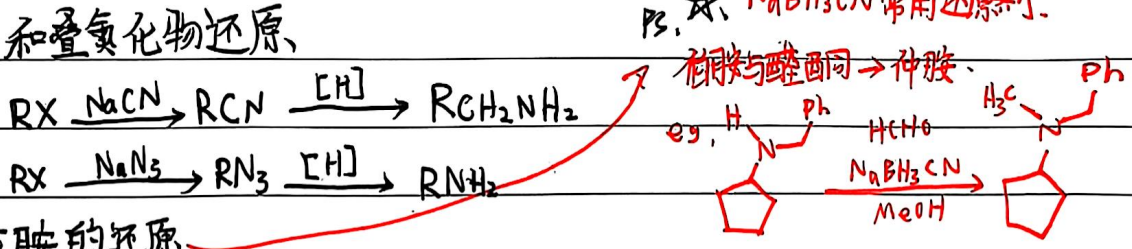
(2). 酰胺的还原.



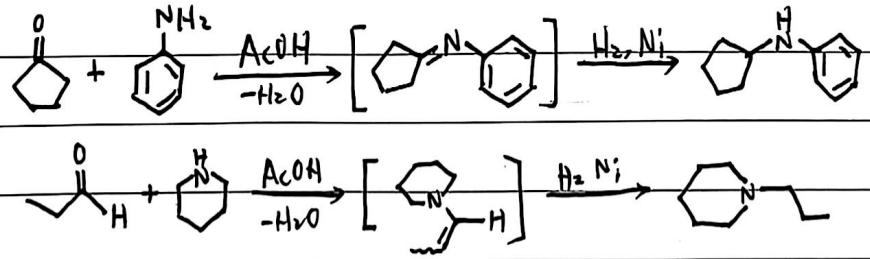
(3). 肟的还原.



(4). 腈和叠氮化物还原.

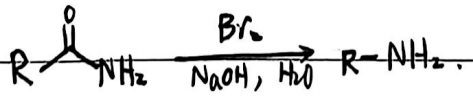


(5). 亚胺的还原.



• Hofmann 重排 & Curtius 反应.

(1). Hofmann 重排：酰胺与 Cl_2 或 Br_2 在碱溶液中反应. 少一个C原子的伯胺.



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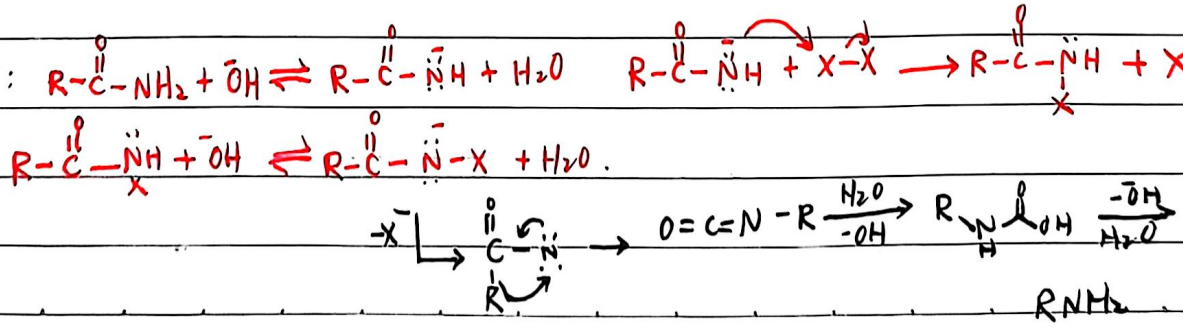

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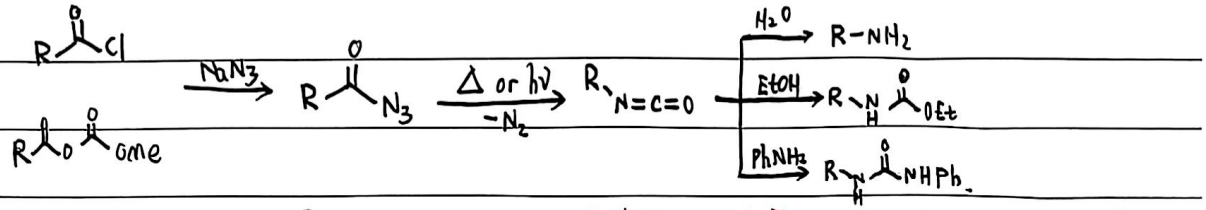
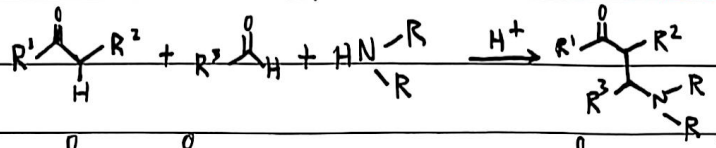
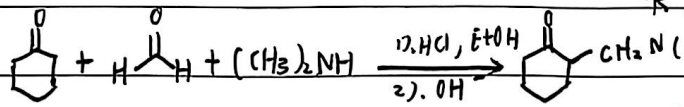
若发生迁移的烃基C原子为手性C，迁移时构型保持！

(2). Curtius 重排：酰基叠氮在惰性溶剂中加热分解，失去氮气，也生成 氮烯中间体，重排水吽得伯胺. eg.



· Mannich 三组分反应：含活泼H的化合物（常为羰基化合物）与甲醛和二级胺或氨缩合.





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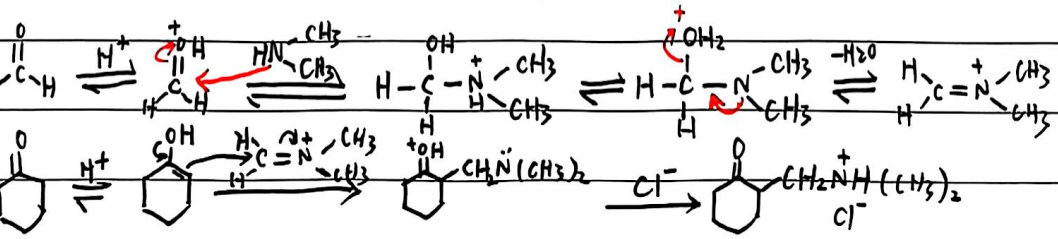
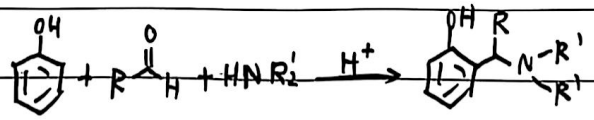
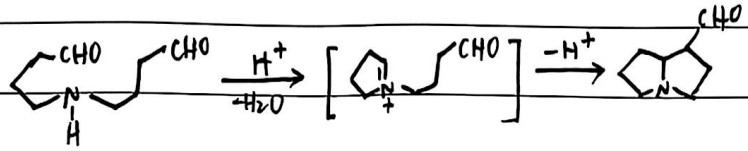


酚可替代烯醇.

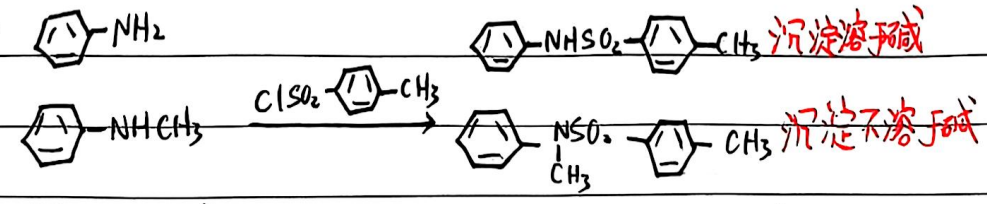


分子内更易发生：



· 胺的酰化：氮上有H的胺发生. eg. $CH_3CH_2CH_2NH_2 + \bigcirc\!\!-COCl \rightarrow CH_3CH_2CH_2NHCOC_6H_5$

石磺酰化：



· 胺的氧化与 Cope 消除反应（热消除）

含β-H的氧化叔胺可发生热分解反应，生成烯烃和羟胺.

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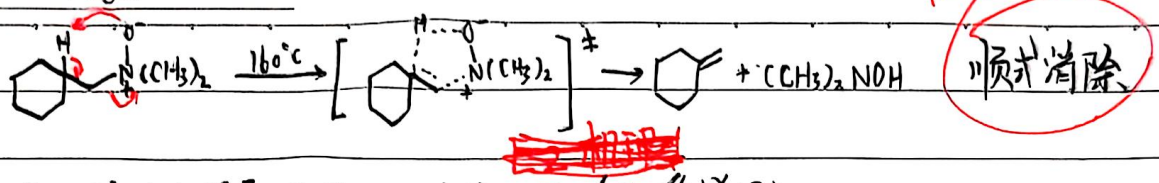
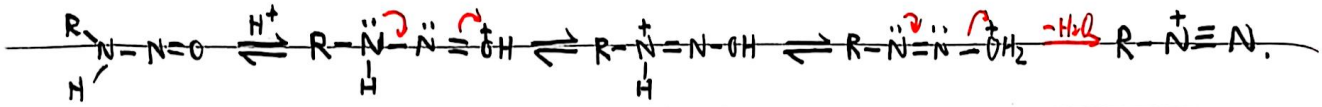


ps. Cope消除主要是 Hoffmann消除（取代少的烯烃）

优先消除含H多的β-C.

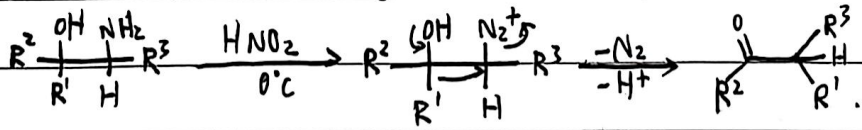
·胺与亚硝酸反应：(1)、仲胺：生成N-亚硝基胺. $(CH_3)_2NH \xrightarrow[H_2O]{NaNO_2,\ HCl} (CH_3)_2N-NO$ N-亚硝基胺

(2)、伯胺：也生成N-亚硝基胺，但不稳定 → 进一步转化为重氮阳离子.

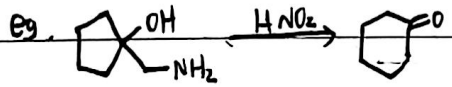


邻氨基醇与亚硝酸反应的重氮盐可发生类频哪醇重排反应.

(TDR). Tiffeneau-Demjanov重排.

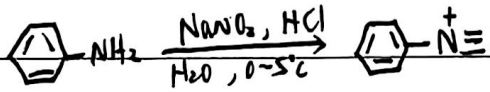


Eg.

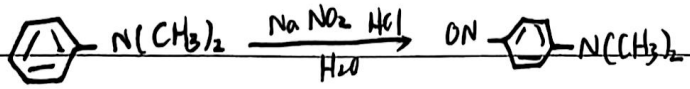


芳香族伯胺与亚硝酸反应生成芳香重氮盐比烷基重氮盐稳定很多.可在水溶液中.

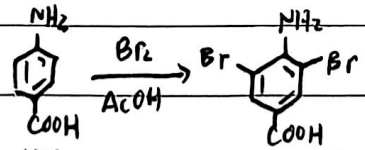
0~10°C下保存一段时间.



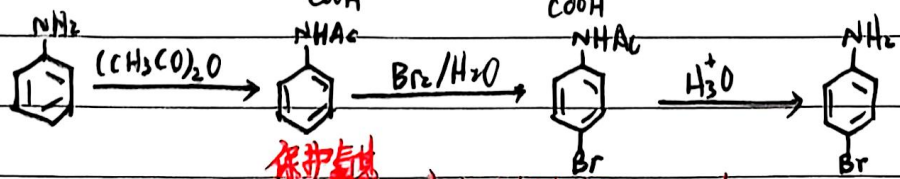
叔胺上氮无H，不能与亚硝酰正离子反应. 可发生亲电取代.



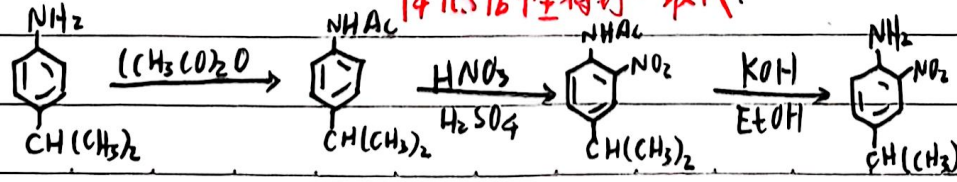
·芳胺的亲电取代：

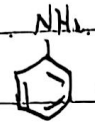


一般情况下都要保护!



降低活性得到一取代.





不能直接硝化&磺化反应.

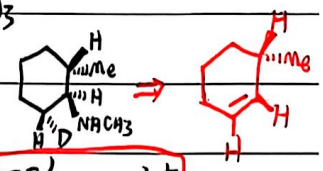
· 季铵盐 : $PhCH_2Br + Et_3N \xrightarrow{\Delta} PhCH_2\overset{+}{N}Et_3Br^-$ 相转移催化剂

季铵碱的生成其热消除反应 Hofmann消除

$R_4\overset{+}{N}X^- + KOH \rightleftharpoons R_4\overset{+}{N}OH^- + KX$. 制备季铵碱.

$CH_3CH_2-\overset{+}{N}(CH_3)_3OH^-\ CH-CH_3 \xrightarrow{\Delta} CH_3CH_2CH=CH_2 + CH_3CH=CHCH_3$

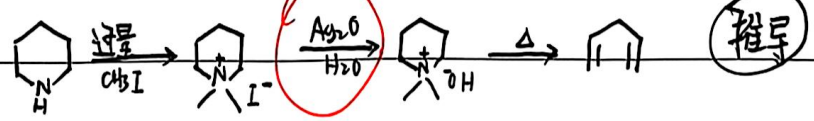
主要

eg: 

Hofmann规则: 生成含烷基少的烯烃. E2机理.

切除C-N键

$-\overset{\cdot\cdot}{O}H \rightarrow H-\overset{H_2}{C}-\overset{+}{N}(CH_3)_3 \xrightarrow{E_2} H_2C=CH_2 + N(CH_3)_3 + H_2O$.

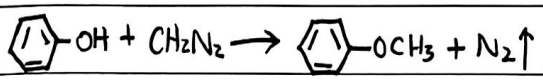
eg. 

推导

· 重氮化合物. $H-\overset{N_2}{\overset{\|}{C}}-H$ 重氮甲烷 $H-\overset{N_2}{\overset{\|}{C}}-CO_2Et$ 2-重氮乙酸乙酯.

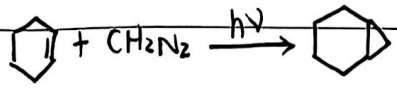
$CH_2=\overset{+}{N}=\overset{-}{N}:$

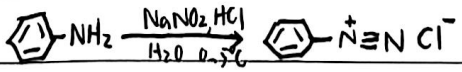
$R-\overset{O}{\overset{\|}{C}}-O-H + CH_2-\overset{+}{N}\equiv N \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^- + CH_3-\overset{+}{N}\equiv N \xrightarrow{S_{N2}} R-\overset{O}{\overset{\|}{C}}-OCH_3 + N_2$.



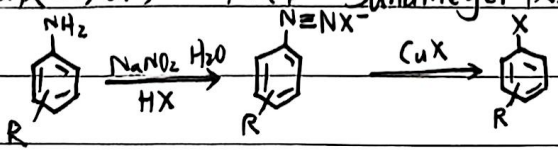
重氮化合物在光照/加热时生成卡宾(碳烯). $R_2C:$

$H_2C=\overset{+}{N}=\overset{-}{N}: \xrightarrow[\text{or } h\nu]{heat} H_2C: + N_2$.



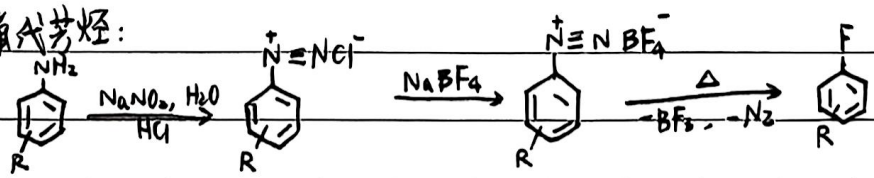
· 芳基重氮盐. 

1. 重氮盐基被Cl, Br, CN取代. Sandmeyer反应.



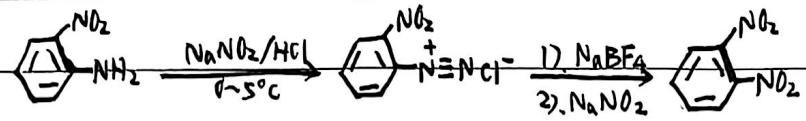
(X=Cl, Br).

制氟代芳烃:



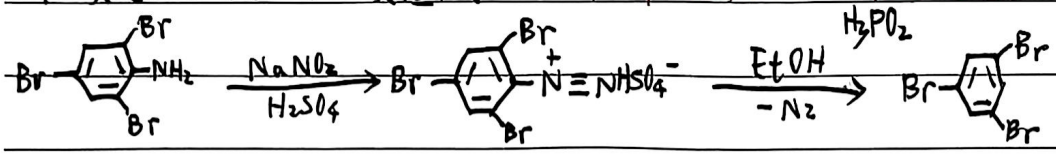
Date. Page.

2、重氮基被硝基和亚磺酸基取代



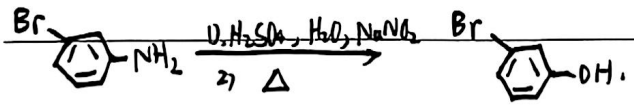
$$C_6H_5\overset{+}{N_2}Cl^- + Na_2SO_3 \xrightarrow{Cu} C_6H_5SO_3^-Na^+ + N_2 + NaCl$$

3、重氮盐还原（重氮基被H取代）常用还原剂次磷酸、乙醇，$NaBH_4$

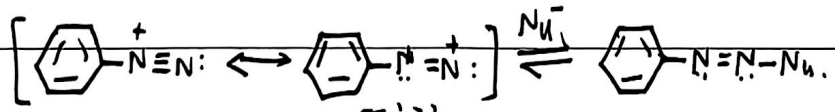


（合成不合定律规律

4、水吽

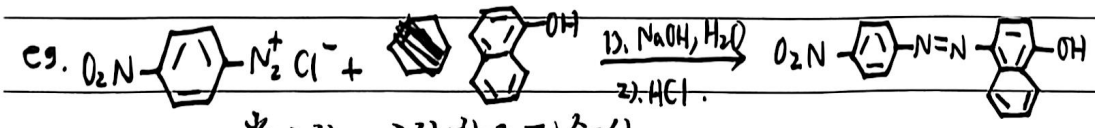


5、重氮盐的亲电取代.



弱亲核

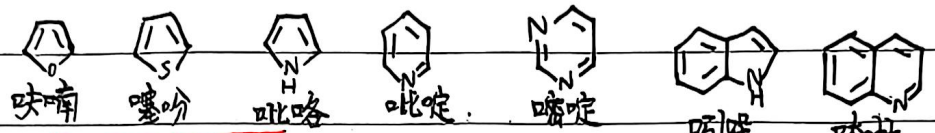
eg.



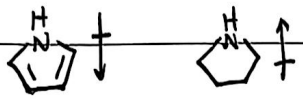
常对位，对位被占则邻位

Date. Page.

· 杂环化合物：

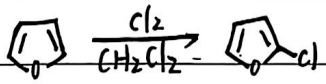


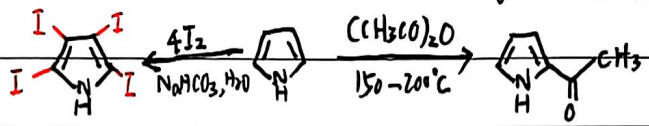
均为 sp^2 杂化。富电子芳杂环、比苯易发生亲电取代，一般易在 α 位



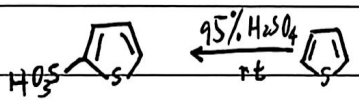
⇒ ps. 吡啶碱性比脂肪胺弱，比芳香胺强

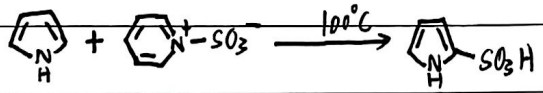
· 亲电取代反应（比苯活泼）不用催化：



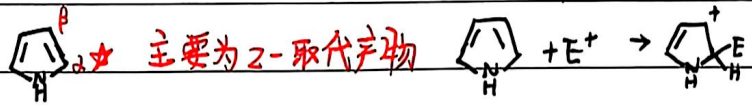


活性：



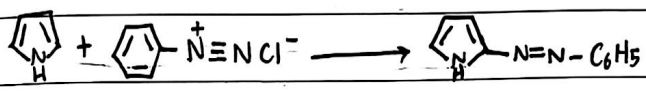


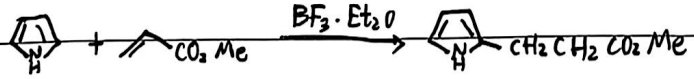
区域选择性：



★ 主要为 2-取代产物

eg.



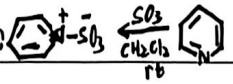


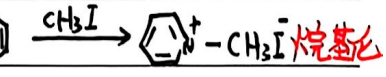
· 共轭加成反应（芳香性不如苯）

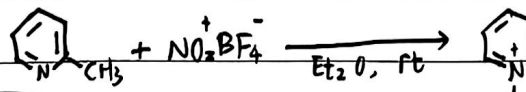
· 吡啶

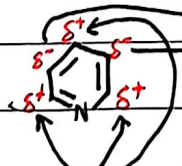
↓ 相当于硝基苯中的硝基。

亲核性：



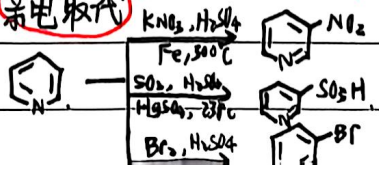






亲电取代。

eg. 亲电取代 → 比苯难。



类比硝基苯

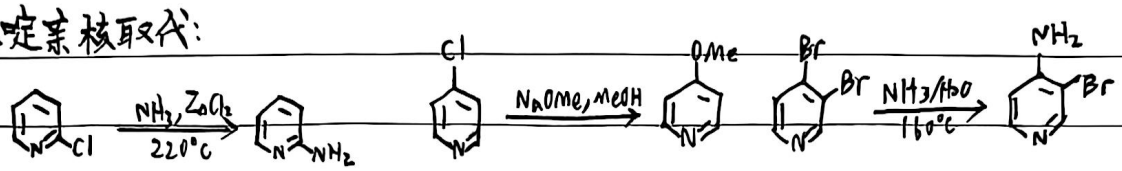
无傅克反应！

Nu^- 亲核取代。

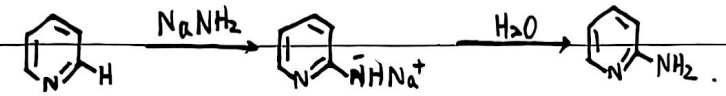
扫描全能王
3亿人都在用的扫描App

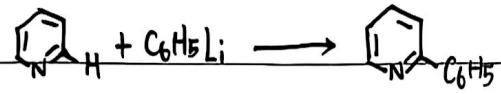
Date. Page.

吡啶杂核取代：

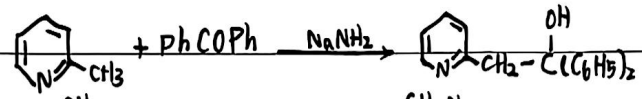


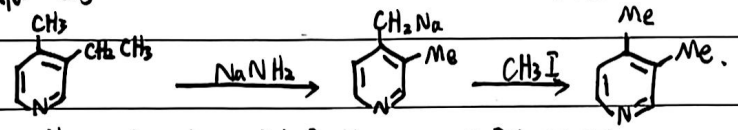
Chichibabin 反应：齐齐巴宾反应——氨化。



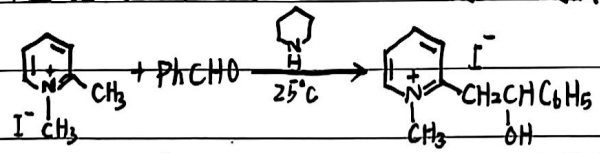


由于吡啶基的强吸电子，侧链 α-H 的酸性相当于甲基酮的 α-H。



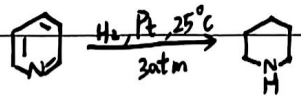


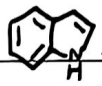
N-甲基吡啶正离子侧链的 α-H 酸性更强。



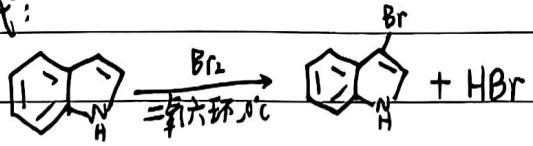
氧化反应：吡啶环本身不易被氧化，侧链易被氧化

还原反应：



• 吲哚  碱性（极弱）酸性（弱）。

亲电取代：



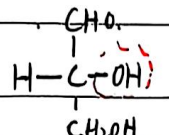
比吡咯活泼。3-位取代。

CS 扫描全能王
3亿人都在用的扫描App

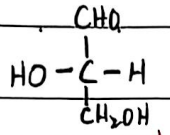
Date. Page.

碳水化合物

相对构型 (D.L)

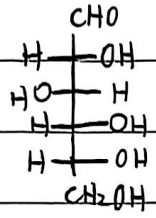


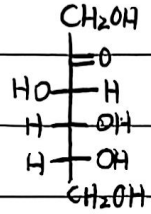
D-(+)甘油醛

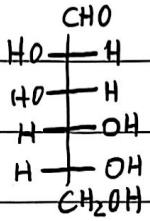


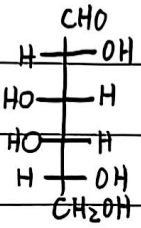
L-(-)-甘油醛

D-葡萄糖 D-果糖 D-甘露糖 D-半乳糖



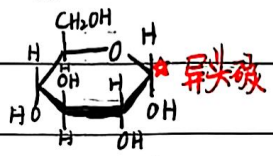






环状结构 & 变旋现象:

Haworth式:



异头碳

α-D-吡喃葡萄糖 β-D-吡喃葡萄糖

差向异构体.

一、化学性质: 氧化反应: 1. 与 Tollens, Benedict 与 Fehling 试剂反应.

Tollens: 与醛糖和酮糖反应产生银镜.

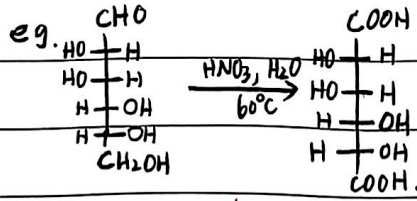
Fehling: $CuSO_4$ 溶液与酒石酸钾及 NaOH 的溶液在使用时混合而成.

Benedict: $CuSO_4$, 柠檬酸 & Na_2CO_3 配成蓝色溶液, 与醛/酮糖 Δ → 砖红色 Cu_2O

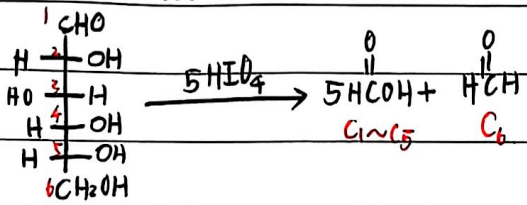
2. Br2水氧化: 溴水 (pH 5~6) 使醛糖氧化成糖酸.

3. 稀 HNO_3 氧化: HNO_3 强氧化剂, 与醛糖作用时, 把醛糖氧化成糖二酸.

eg.

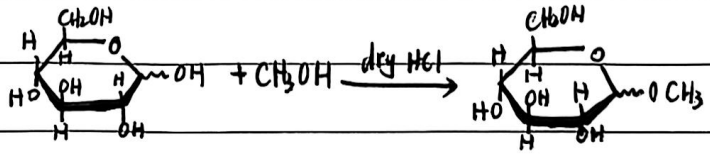


4. 高碘酸氧化:

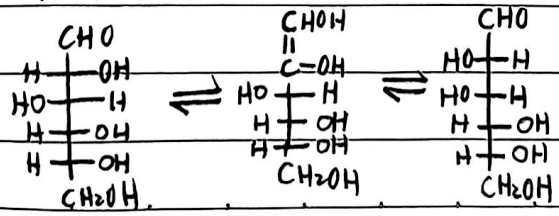


C_1~C_5 C_6

- 糖苷 — 糖的缩醛.



- 差向异构化



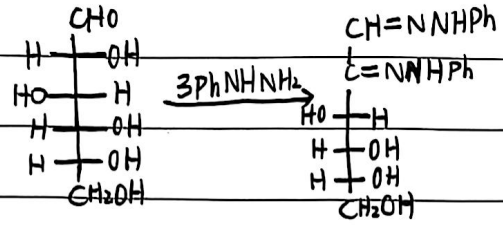
是否变旋?

⇒ 有无半缩醛羟基

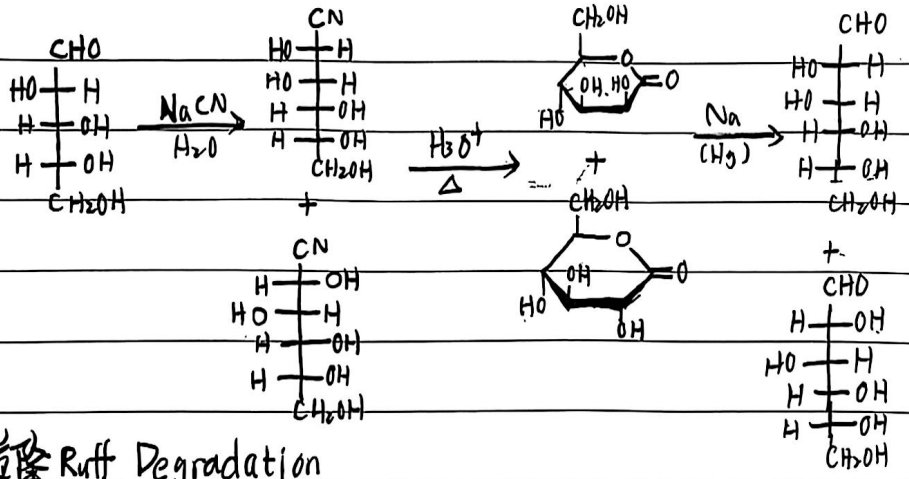
CS 扫描全能王
3亿人都在用的扫描App

Date. Page.

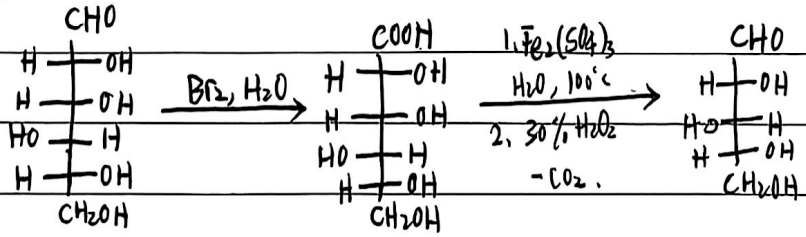
· 成脎反应.



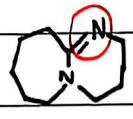
· 醛糖的递升 & 递降 Kiliani-Fischer合成法.

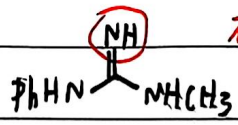


递降 Ruff Degradation

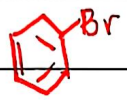


氰基水解成羧酸

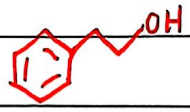




碱性最强、双键给、

ps. 

不好直接反应可以作成格氏试剂

eg. 

(由

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Date. Page.

续：补充：

比较酸性：比较其共轭碱稳定性.

常见缩写：CH_3- Me 乙基 Et 正丙基 n-Pr 异丙基 i-Pr

丁基 - Bu

命名：①、C数最多 ②、重键最多 ③双键最多 ④、重键位次最低

⑤双键位次组最低 ⑥、取代基最多 ……

强吸电子

$-N^+(CH_3)_3$, $-NO_2$, $-CN$, $-SO_3H$, $-CHO$, $-COOH$, $-COOCH_3$, $-CONH_2$, $-CF_3$, CCl_3

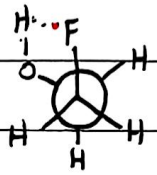
烯烃的稳定性：氢化热：1mol不饱和化合物加氢时放出的热量

中间烯烃比末端稳定，反式比顺式稳定.

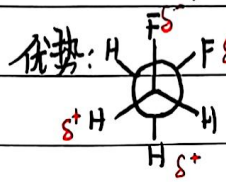
$\sigma-\pi^*$ 超共轭解释. $\pi-\pi$共轭 > $P-\pi$共轭 > $\sigma-\pi^*$超共轭

Newman投影式两种例.

① eg. 分子内形成氢键利于分子稳定.



② 1,2-二氟乙烷



Brønsted 酸碱理论：能给出质子：酸 接受质子：碱

$R-C\equiv C-H \xrightarrow{Ag(NH_3)_2^+} R-C\equiv CAg$ 白色沉淀

$R-C\equiv C-H \xrightarrow{Cu(NH_3)_2^+} R-C\equiv CCu$ 红棕色沉淀

烷烃，环烷烃，烯烃，芳香烃，氨，末炔烃，醇，水，硫醇，酚，H_2CO_3，羧酸，H^+

HCl，HBr，HI ——→ 酸性↑.

碱性↑亲核能力↑ NaI溶于丙酮，NaCl，NaBr则不溶.

·比较亲核性：①、带电 > 无电 $OH^- > H_2O$ $NH_2^- > NH_3$

②、电负性 $CH_3^- > NH_2^- > OH^- > F^-$，同族 $I^- > Br^- > Cl^- > F^-$

③、位阻：大位阻亲核↓ $CH_3O^- > (CH_3)_3CO^-$.

碱性强，亲核弱

扫描全能王
3亿人都在用的扫描App