NO. _____

Title:

Enjoy the most efficient handwriting experience! Taking notes on the go, whether for inspiration, ideas, knowledge learning, business insights, or even sketches...

NOTE IN

Creative notes

By reading we enrich the mind;
by writing we polish it.

全反应总结

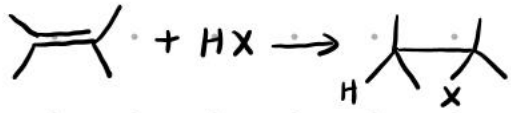
有机化学全反应总结.

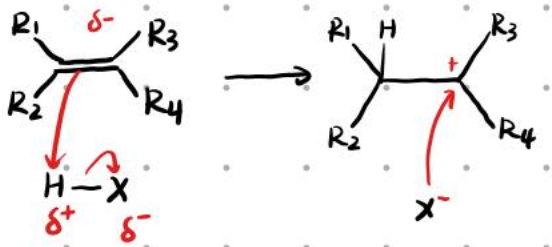
① 烯/炔的亲核反应.

加成反应:

反应机理:

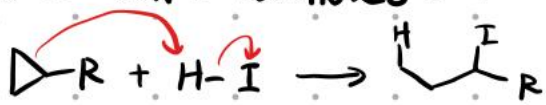
1) 和 HX:





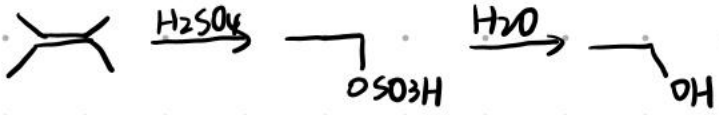
诱导效应影响: 碳正离子稳定性 → 吸电子减弱, 给电子加强(速度同理)

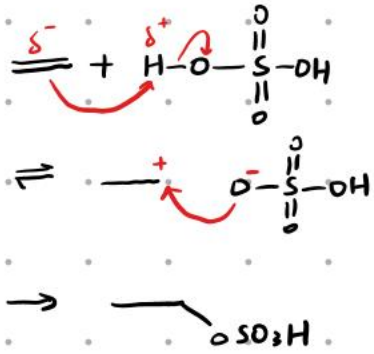
共轭效应影响: 卤素共轭, 稳定3 C^+.

环丙烷 → 

2) 和水 #成醇.

间接水合法.

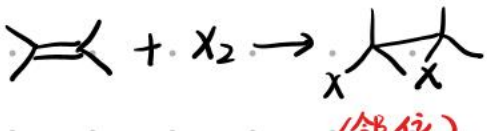




3) 和卤素分子: #反式

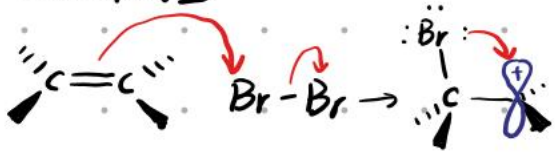
为什么烯能与 X_2 加成 (X_2 亲核)?

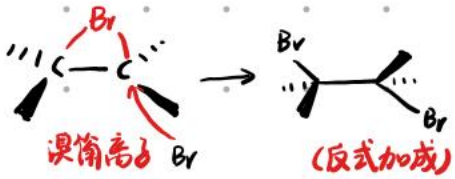
速度一般受诱导效应影响.



(邻位)

反应机理:





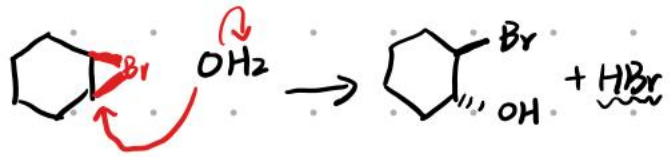
溴慃离子

(反式加成)

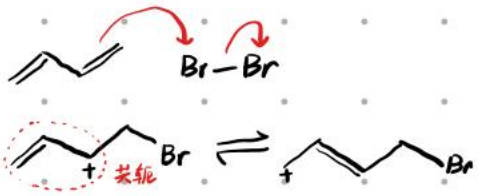
依然受诱导&共轭影响.

Cl半径太小, 无立体选择性.

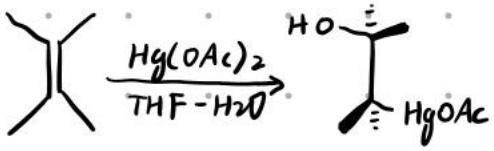
水/醇存在下的加成.



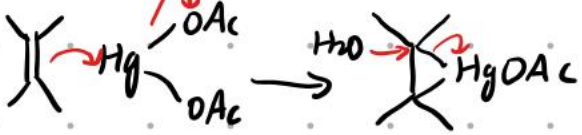
关轭双烯加成



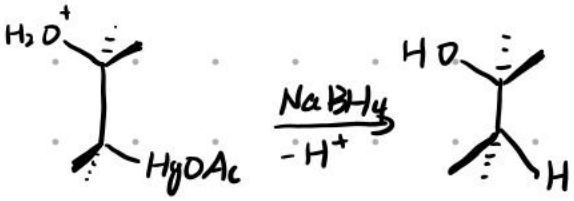
4) 羟汞化-还原反应. #反式 #成醇/醚.



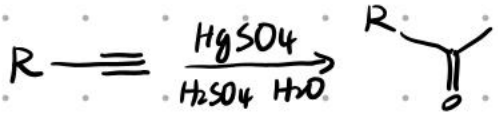
反应机理.



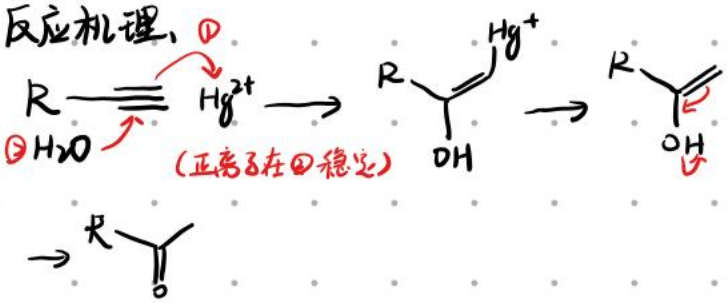
在还原反应一步失去了立体选择性.



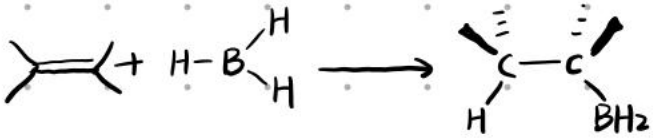
5) 炔烃的羟汞化反应. #成酮.

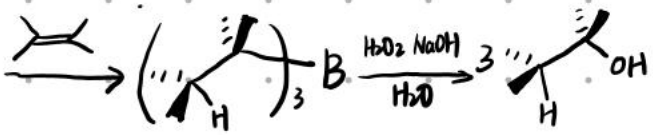


反应机理.

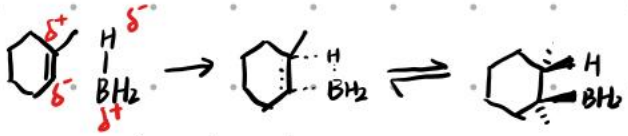


6) 硼氢化-氧化反应. #顺式 #成醇 #反马规则.

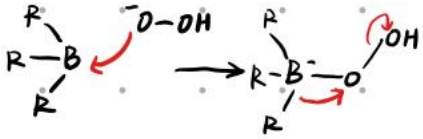




机理:



实践中防止多聚,常用 $(\bigcirc)_2BH$, 9-BBN, $ThBH_2$.

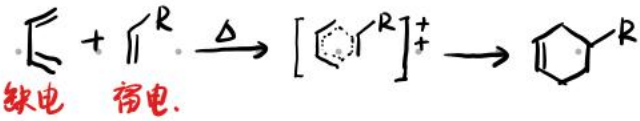


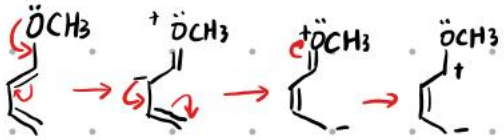
7) Diels - Alder 反应 #顺式

特征：共轭烯烃与含C-C双键的化合物进行环加成反应

双烯体，亲双烯体.

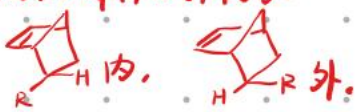
区域选择性：取决于电子效应.





记忆：亲电试剂为路正电.
亲核试剂为路负电.

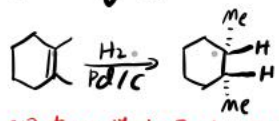
环式双烯体两种构象：



8) 与氢的加成反应

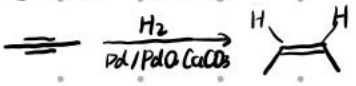
催化氢化，顺式.

① Raney 镍.

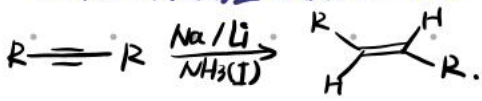


(具有化学选择性，只烯炔)烷烃

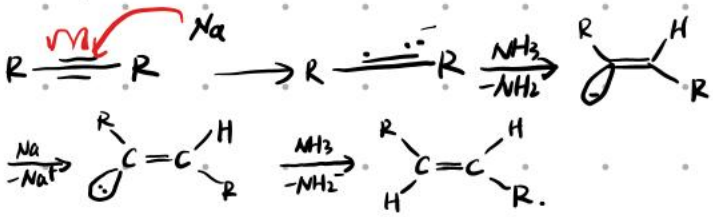
② Lindlar 催化剂



金属还原反应（液氨溶液）



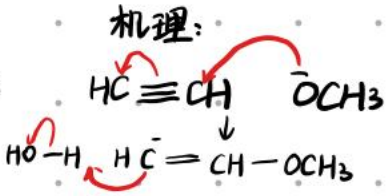
机理：



9) 与亲的亲核加成

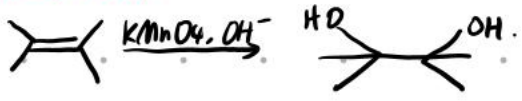
炔比烯更容易发生亲核加成.

机理：

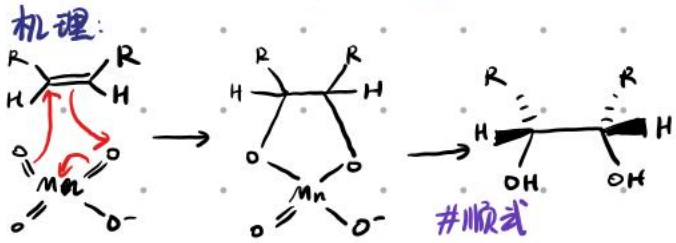


末端炔烃与亲核试剂加成 → 加末端碳上. 空间位阻。双羟化反应.

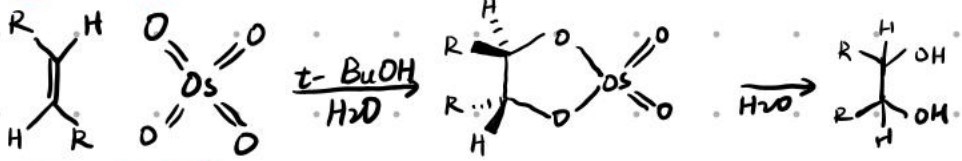
① $KMnO_4$



机理：

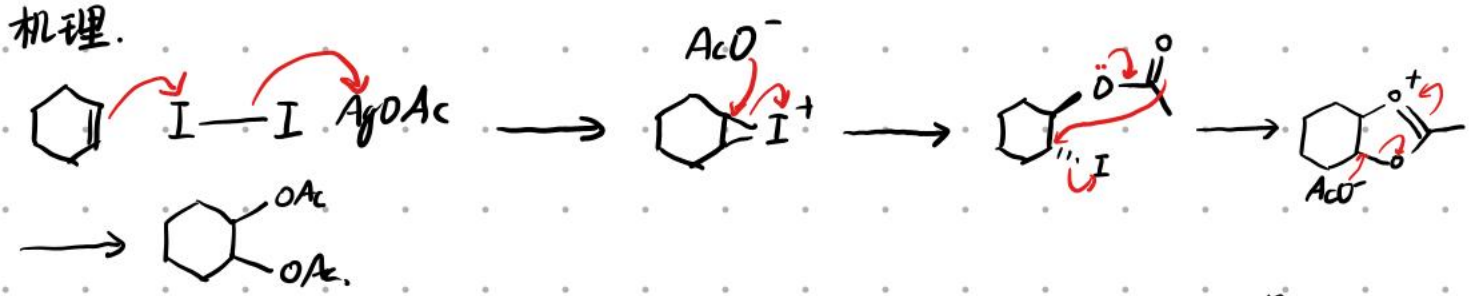


② OsO_4.



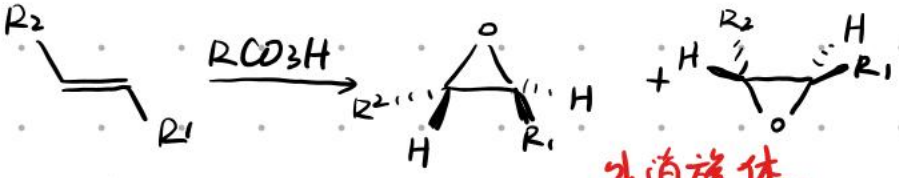
③ I, AgOAc.

机理.



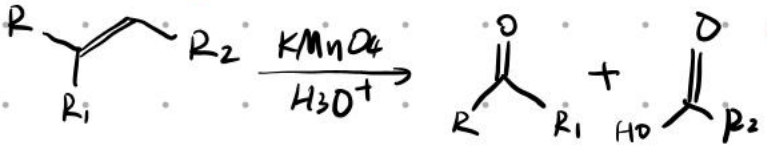
10) 环氧化反应.

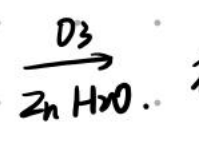
间氯
m-CPBA 过氧苯甲酸



外消旋体.

11) 氧化断裂.

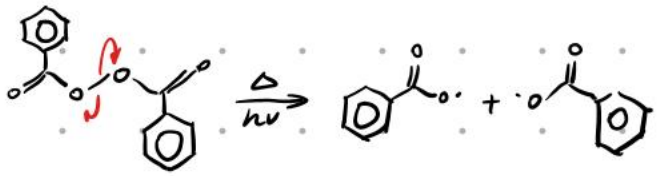




成醛而非酸.

自由基反应.

过氧苯甲酰(BPO)均裂.
偶氮二异丁腈(AIBN)



自由基稳定性: 与碳正离子大致相同. 但受空间位阻影响.

烷基的自由基取代:

1) 甲烷的氯化.

$CH_4 + Cl_2 \xrightarrow[h\nu]{\Delta} CH_3Cl + HCl$. 放热反应 (自催化)
链式反应.

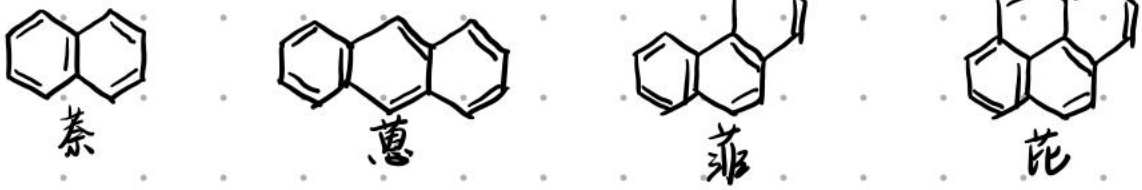
活性 $F_2 > Cl_2 > Br_2 > I_2$.

2) 不饱和烃的 α-H 卤代.

与加成的竞争: ① 用 NBS 做溴提供剂.
② 用 CCl_4 做溶剂防止生成离子.
③ hν, 加入 m-CPBA 引发自由基.

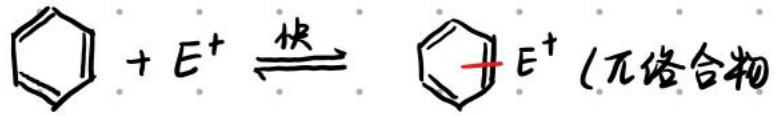
3) 卤代烃脱卤：试剂：丁基 Bu_3SnH

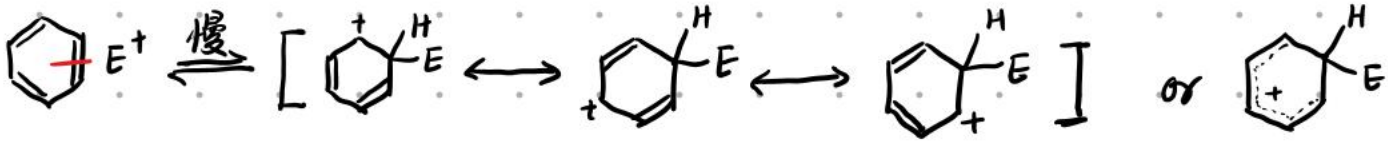
芳香族化合物的亲核反应。

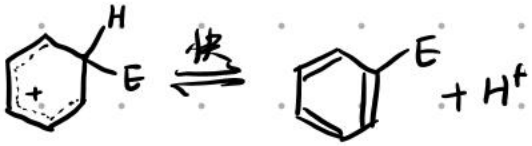


苯环上的亲电取代反应：

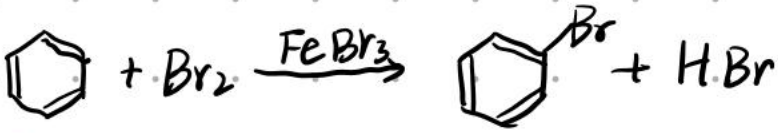
机理：







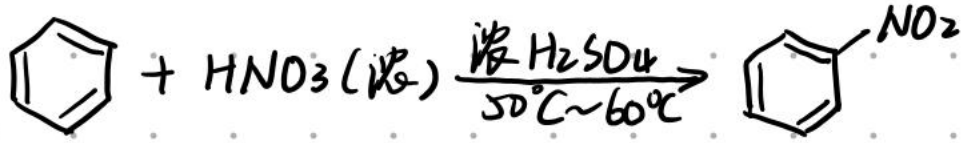
卤化反应：



反应机理：

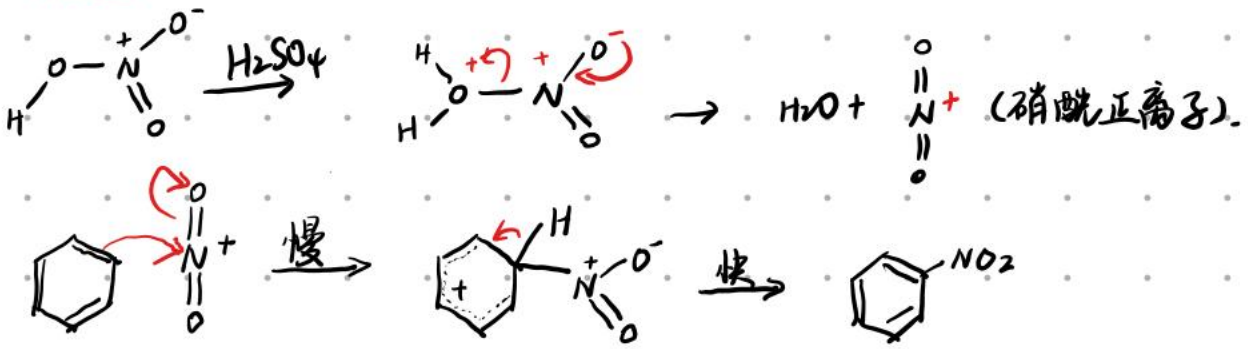
碘化不易发生，需通过 I^+ 或 ICl

硝化反应：

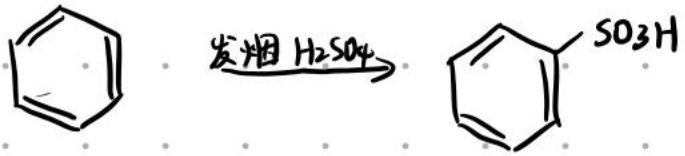


浓H_2SO_4作用：H^+供体，提供质子生成硝酰。

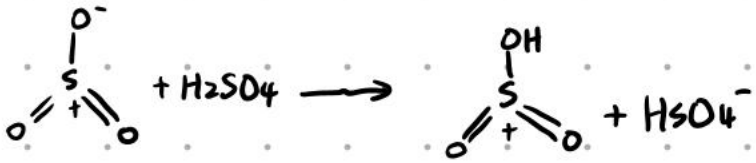
机理：

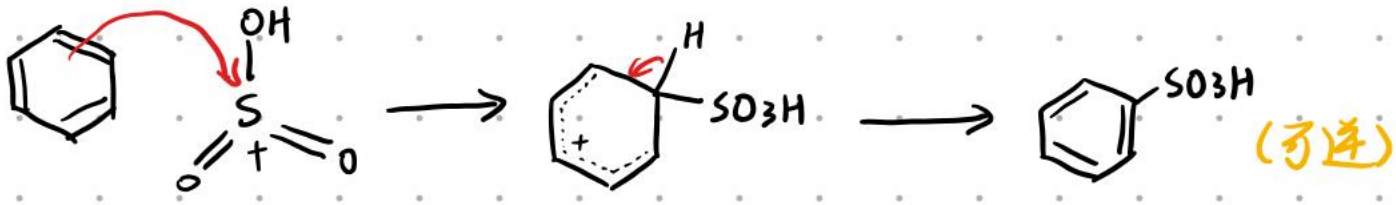


磺化反应：



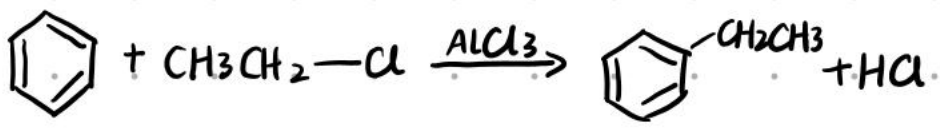
反应机理：



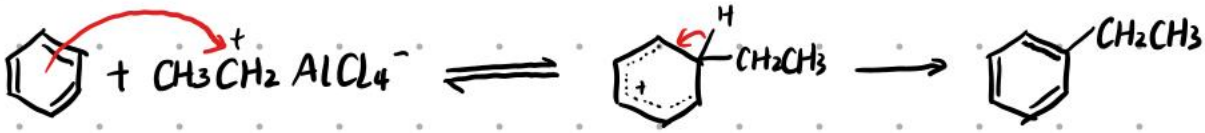


傅克烷基化反应：

催化剂：$AlCl_3$，其他的路易斯酸（BF_3、$SbCl_5$，$FeCl_3$）



反应机理：



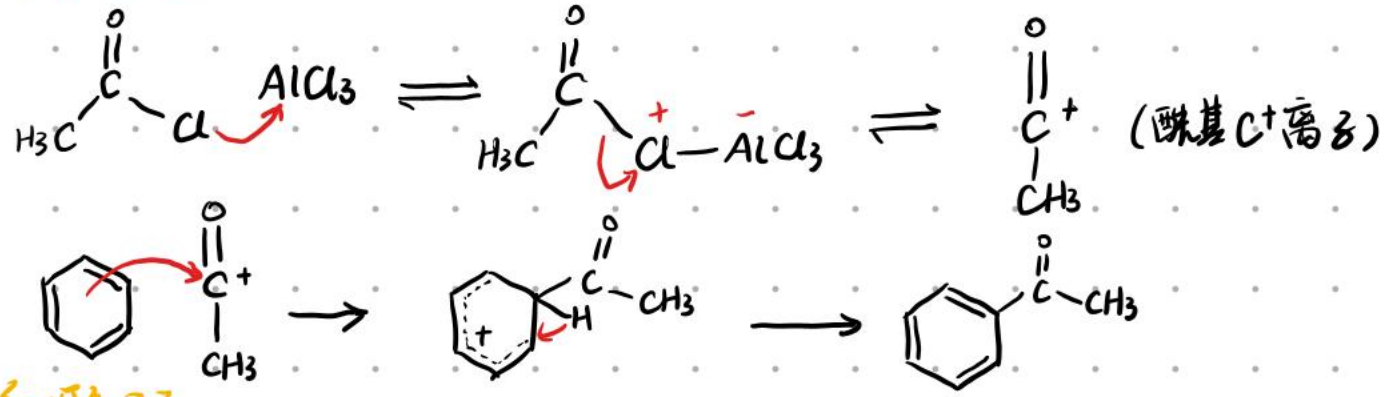
烯烃，醇为在酸催化下也形成 C^+.

副反应 ① C^+ 重排 ② 多烷基化.

傅克酰基化反应：

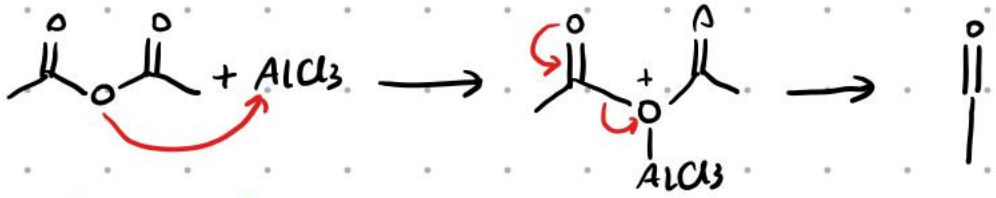
① 和酰氯

反应机理：



② 和酸酐

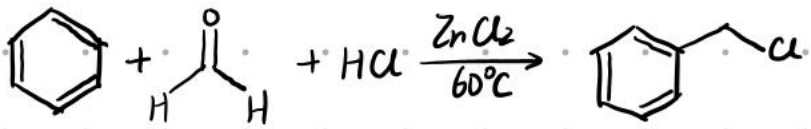
机理：



优点：① 使苯环钝化，避免二次酰基化.

② 不发生重排

氯甲基化反应



反应机理(3步走)

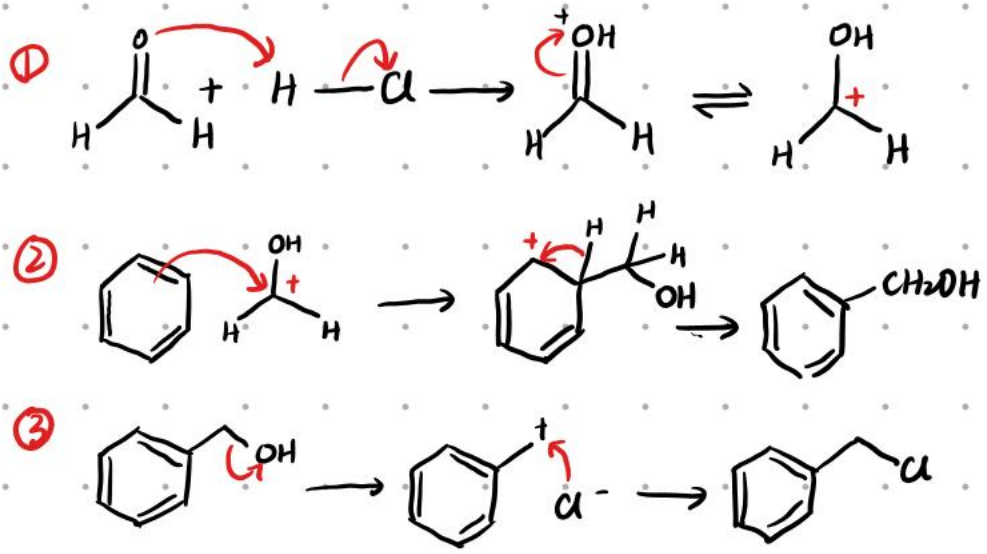


表 6-3 邻、对位和间位定位基

	邻、对位定位基				间位定位基
类别	第一类			第二类	第三类
强度	强	中	弱	弱	强
取代基	$-O^-$ $-NR_2$ $-NHR$ $-NH_2$ $-OH$ $-OR$	$-NHCOR$ $-OCOR$	$-C_6H_5$ $-R$ $-CH_3$	$-F$ $-Cl$ $-Br$ $-I$ $-CH_2Cl$	$-NH_3^+$ $-NO_2$，$-CN$ $-COR$，$-CHO$ $-CO_2R$，$-CONH_2$ $-CO_2H$，$-SO_3H$ $-CF_3$，$-CCl_3$
与苯环相连的原子的键合方式	与苯环直接相连的原子大多数是以单键与其他基团相连，或带负电荷				与苯环直接相连的基团，大多数含有重键，且重键中含有杂原子，或带正电荷
取代基的电子效应	当和苯环直接相连的原子是 N、O 时，基团具有吸电子诱导效应和给电子共轭效应，且给电子共轭效应大于吸电子诱导效应； 当和苯环直接相连的原子是 C 时，基团具有给电子诱导效应和给电子共轭效应			基团的吸电子诱导效应大于给电子共轭效应	$-CF_3$、$-CCl_3$、$-NH_3^+$只有吸电子的诱导效应，其他基团都具有吸电子的诱导效应和吸电子的共轭效应
性质	活化基团			钝化基团	

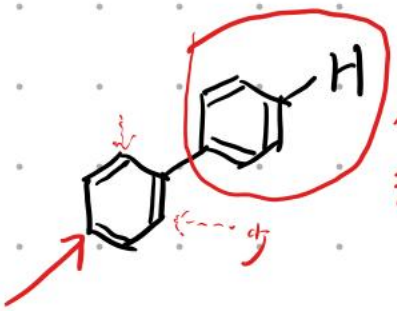
多取代基：

①属于同类取代基：听强的。

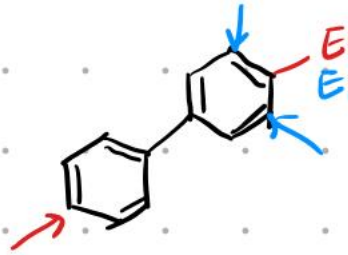
②属于异类取代基：听邻对位的。

多环芳烃.

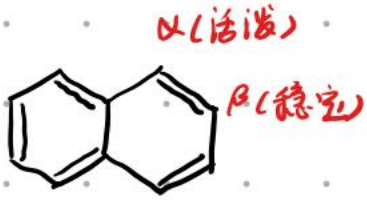
1) 联苯



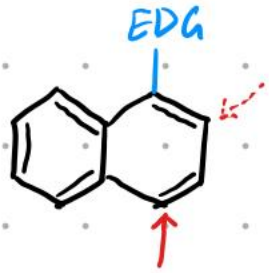
邻对位定位基.
考虑空间位阻.



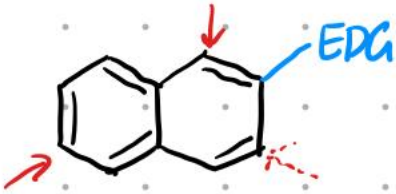
2) 萘:

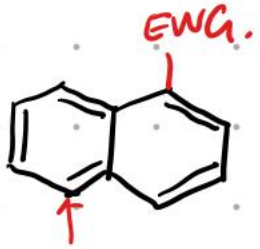


磺化: 80°C 主产物 α
160°C 主产物 β
原因: α与H产生空间位阻. 热力学不利.



活化同环
反应对位.

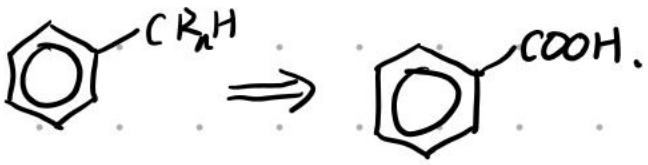




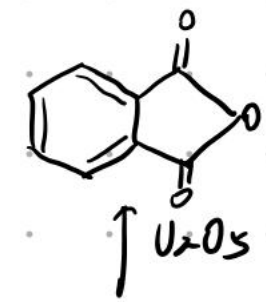
钝化同环
反应α位.

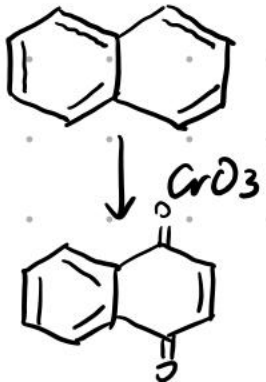
芳烃的氧化还原反应:

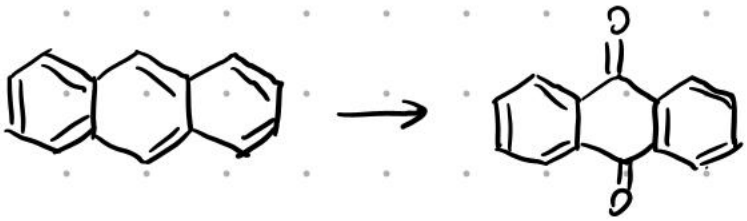
1) 氧化反应.



萘: 活化基同环
钝化基异环



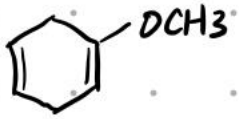




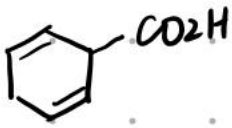
2) 还原反应

苯难还原.

Birch 还原:

给电子基: 

原因: 电子中间体稳定性.

吸电子基 

$CH_3CH_2CH_2C{\equiv}CH \xrightarrow{NaNH_2} CH_3CH_2CH_2C{\equiv}CNa.$

$CH_3CH_2CH_2Br$ ⟶ $CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3$

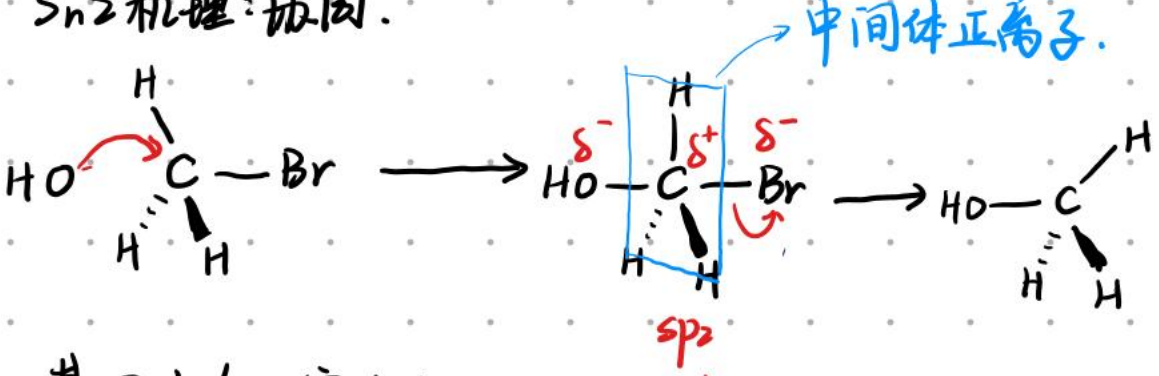
双分子亲核取代 (Sn2)

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

单分子亲核取代 (Sn1)

$(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$ $\quad v = k[(CH_3)_3CBr]$

Sn2机理：协同.



基团太多不宜发生Sn2. 过渡态.

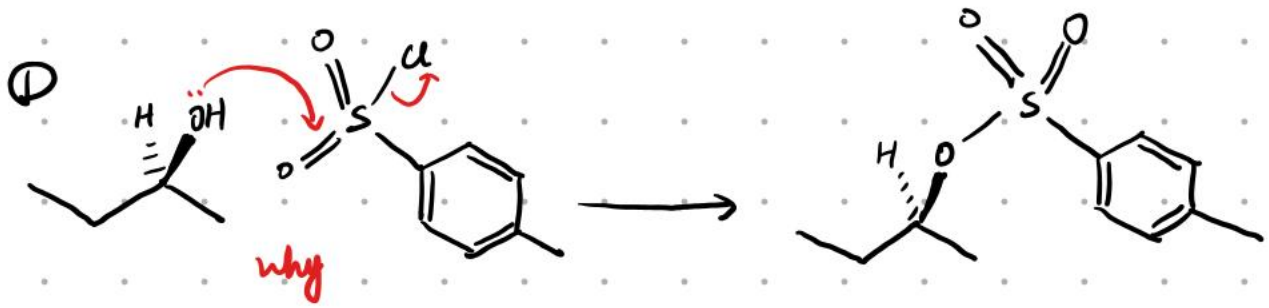
位阻太大不宜.

特征：绝对构型(R,S)翻转.

(看 Clayden 有机).

I 反应：$NaI + RX \Rightarrow NaX\downarrow + RI$ (丙酮)

其它离去基团.

① 

Sn1 机理：分步.

$(CH_3)_3C-Br \underset{\text{慢}}{\rightleftharpoons} (CH_3)_3C^+ + Br^-$

$(CH_3)_3C^+ + H_2O \overset{\text{快}}{\rightleftharpoons} (CH_3)_3C-\overset{+}{O}H_2$

$(CH_3)_3C\overset{+}{O}H_2 + H_2O \overset{\text{快}}{\rightleftharpoons} (CH_3)_3C-OH + H_3O^+$

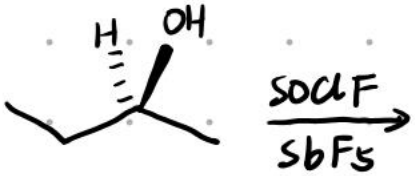
C^+ 稳定 → 反应速率小. 与 Sn2 相反.

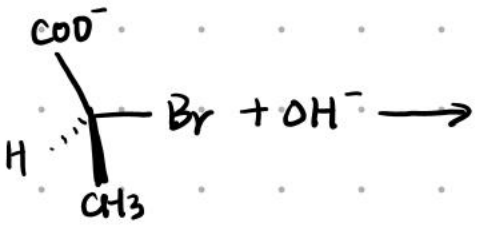
上下概率相当. 多物构型相同. 消旋化.

Sn1 条件：$AgNO_3$.

⇒ 生成 $AgX\downarrow$ ⇒ Sn1 反应发生.

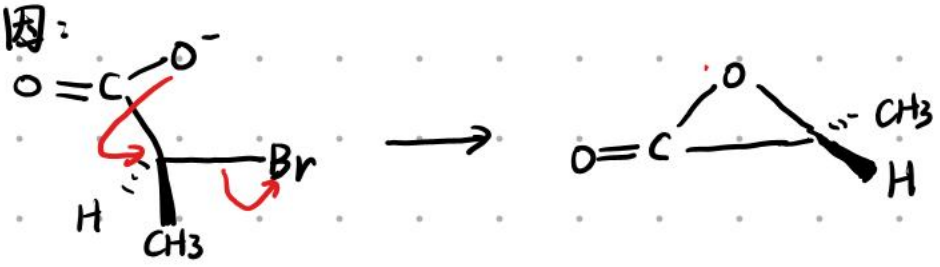
容易发生重排反应.



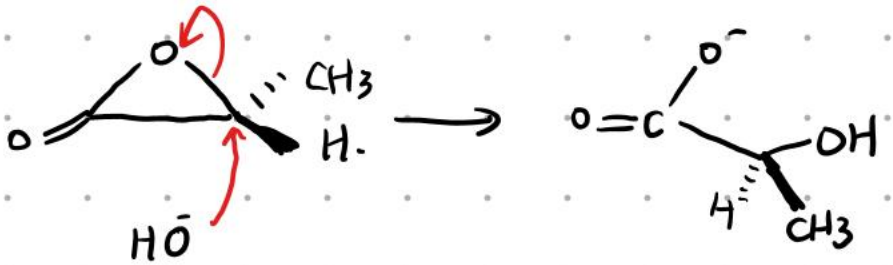


(构型保持).

原因:

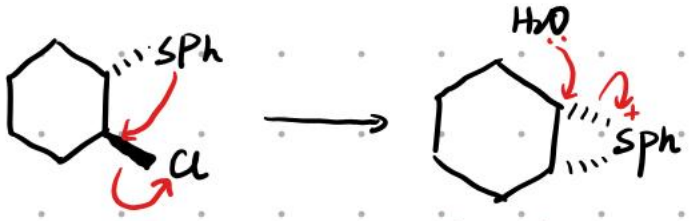


(分子内 Sn2)



(分子间 Sn2)

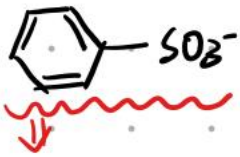
邻基参与反应: (只有反式构型)



硫鎓离子.

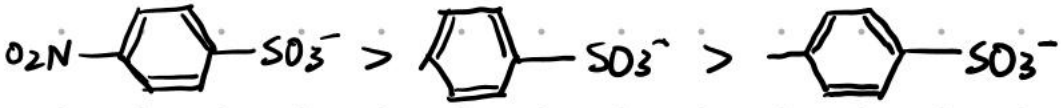
速率：离去基团，底物性质，亲核试剂，反应条件、

离去能力：



> $I > Br > Cl > F$. (NaI 催化剂)

why?



处理条件：(丙酮+亲核)

NaN_3, $NaCN$ > NaI.

桥头碳：既不发生Sn1，也不发生Sn2.

烯丙/苄：都易发生(Sn1, Sn2).

(苄)给电子基→加速Sn1. 吸电子基→加速Sn2. (why?)

α-羰基卤代物.→加快Sn2.（吸电子基，几体系稳定中间体）

杂原子化合物→都加快

Sn1：稳定碳正离子.

Sn2：吸电子诱导.

空间位阻↑，亲核性↓. 叔丁基负离子作碱用

Sn1：极性↑.

SN2：增大非质子溶剂极性，反应↑. 试剂亲核↑.

非质子性：醇，液氨.

消除反应　E2消除

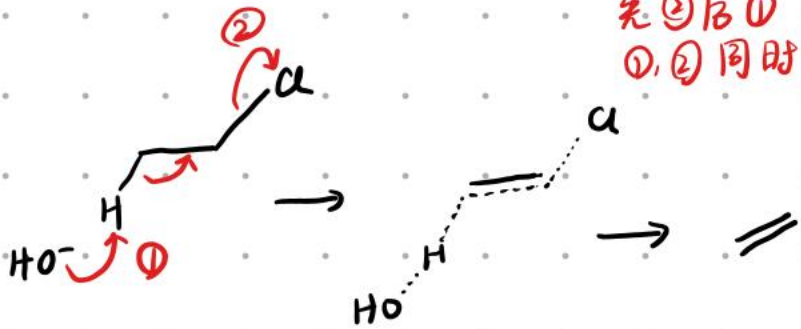
空间选择：

（H去H少　逆反应当民）。

（H去取代基多的）。

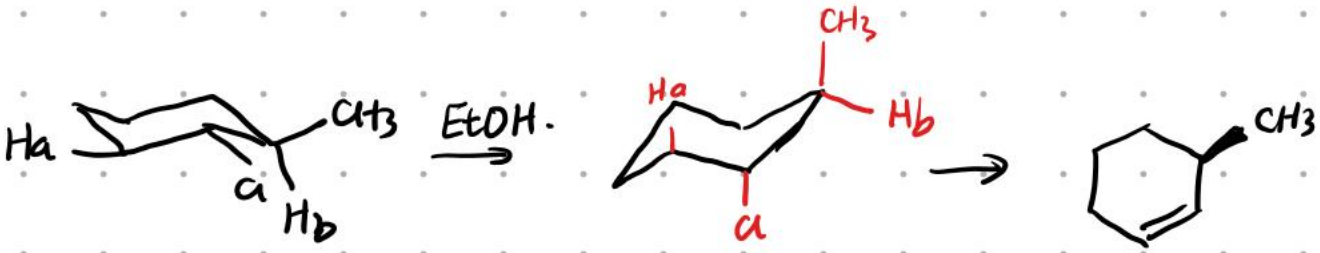
机理：协同机理。

先①后②　E1cb
先②后①　E1
①、②同时　E2



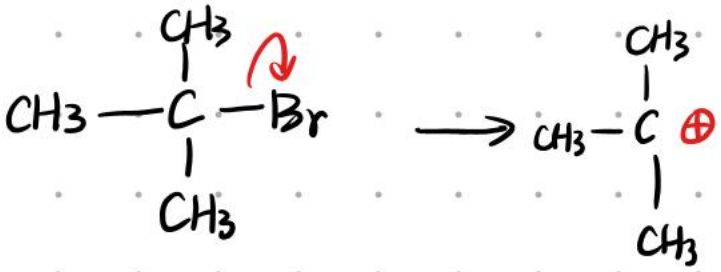
先碱拔质子
再电子对从离去基团背后进攻。SN2取代

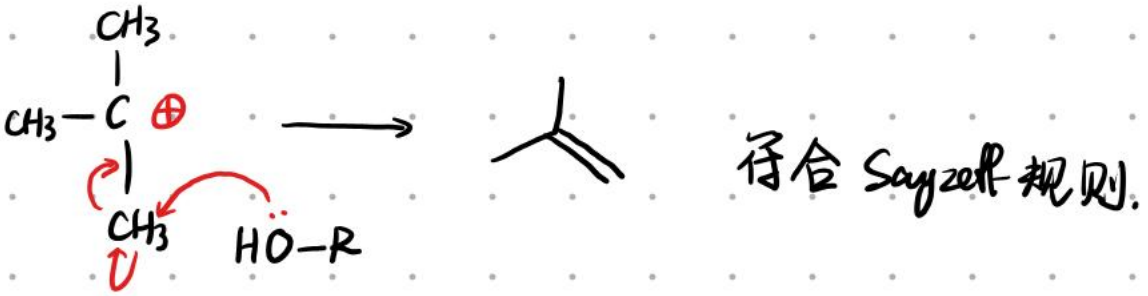
立体构型：反式共平面。



先考虑反式共平面。
再考虑Saytzeff规则。

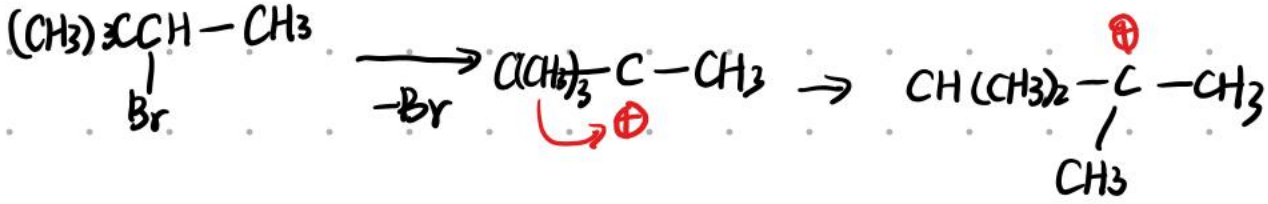
E1消除：



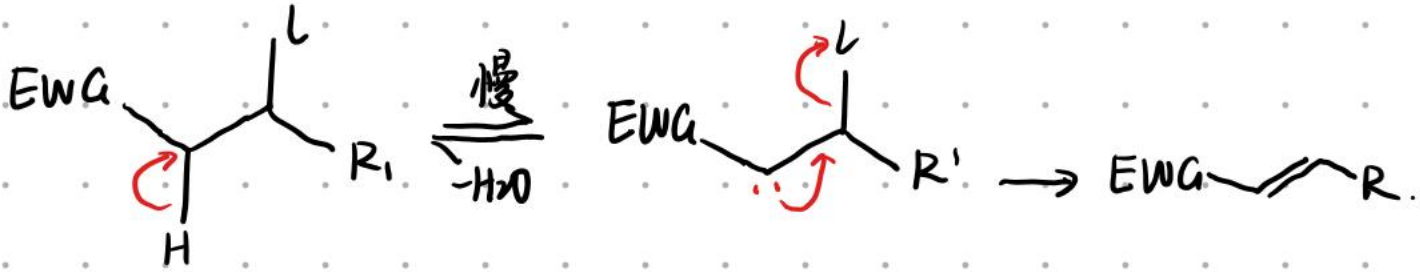


符合 Saytzeff 规则.

特征：①重排后消除.

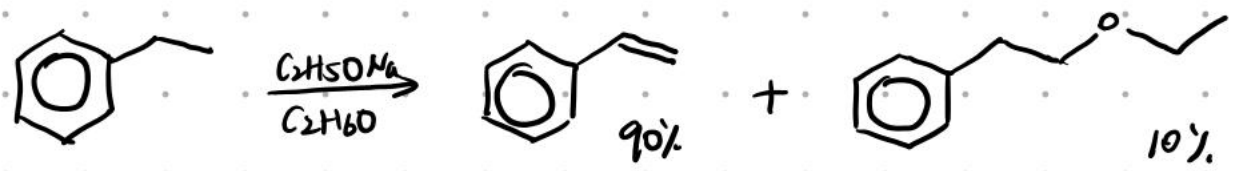


E1cb 消除.



(单分子共轭碱)

大共轭效应增加消除反应比例.

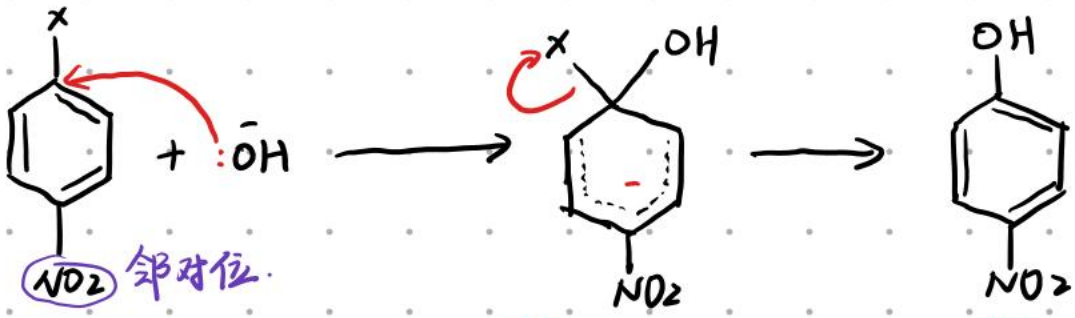


碱性增强. 碱体积增大，加热，有利于消除.

易于拔 H^+　　不利于取代

极性溶剂利于取代.
非极性溶剂利于消除.

芳香亲核取代反应. $SN2Ar$. 芳环.



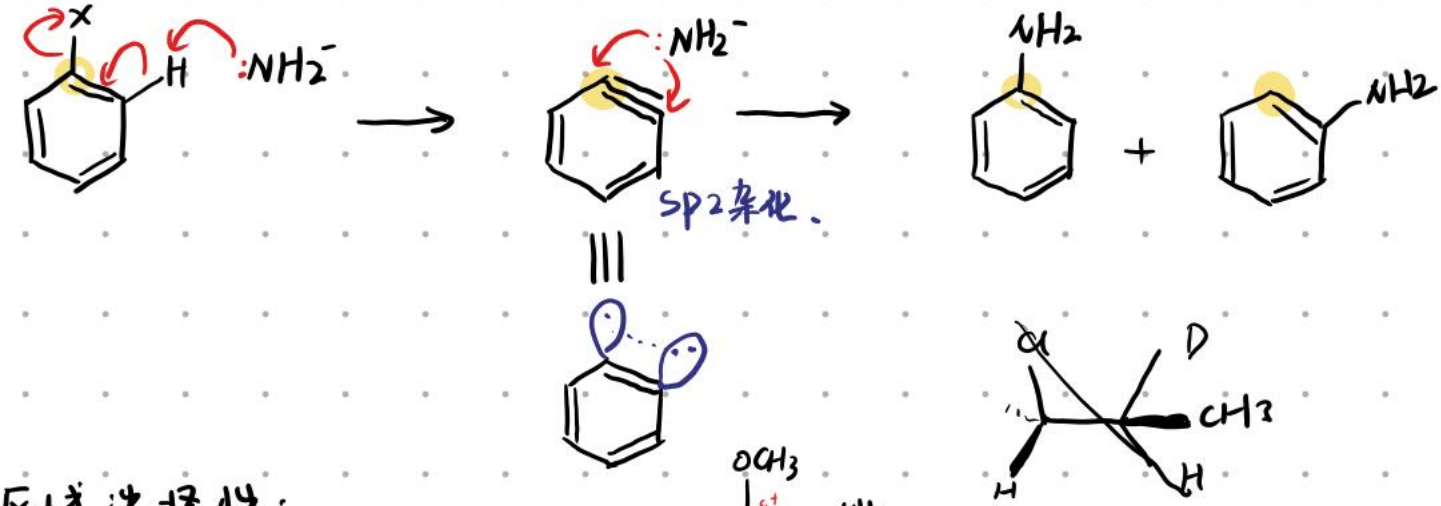
曼森海姆中间体. 吸电子基越多越易反应.

反应机理: 加成后消除.

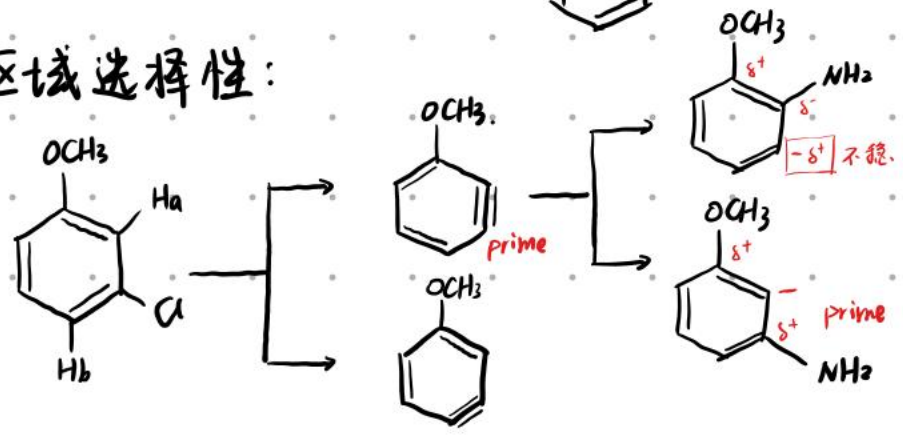
反应速率:
F > Cl > Br > I

F电负性最强, 缺电子利于进攻.
有利于曼森海姆中间体稳定.

苯炔机理: 消除后加成.



区域选择性:



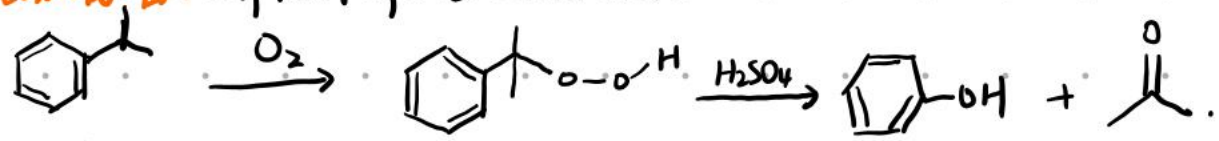
金属有机化合物简介：

$R-\overset{\delta+}{X}\ \overset{\delta-}{} + Mg \xrightarrow{无水乙醚} R-\overset{-}{Mg}\overset{+2}{}X^{-}$ 格氏试剂(提供C^-)

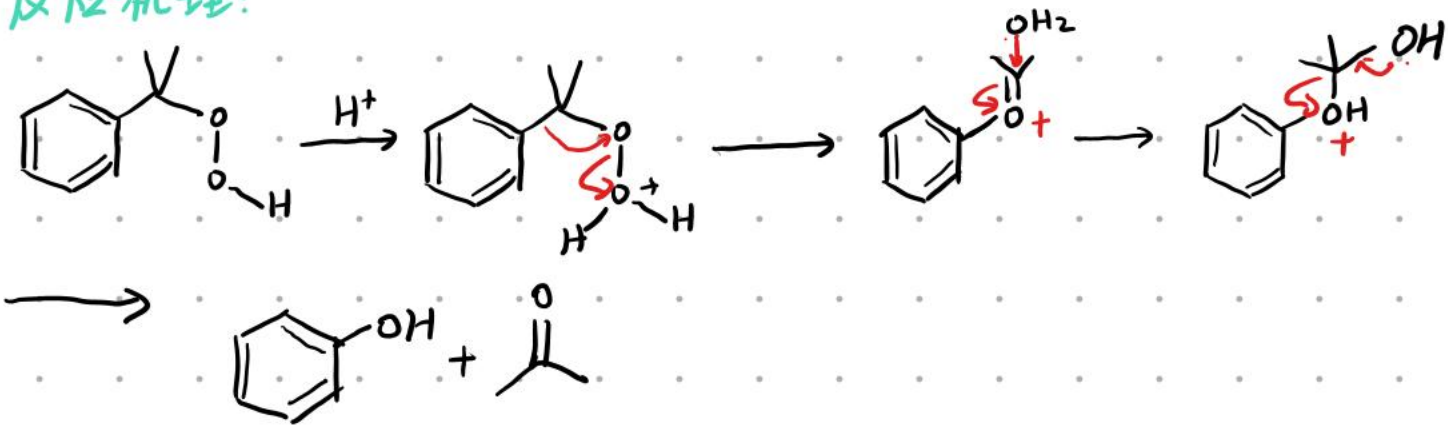
对质子&氧气极其敏感.

醇.酚和醚.

酚制备：异丙苯氧化重排法.



反应机理：



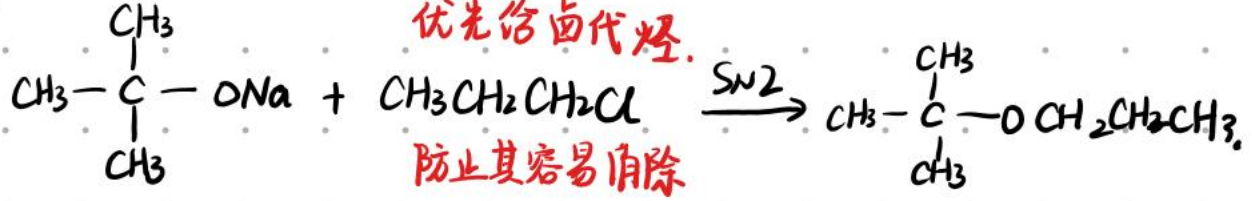
醚制备

Williamson醚合成法.

$CH_3CH_2I + NaOCH$

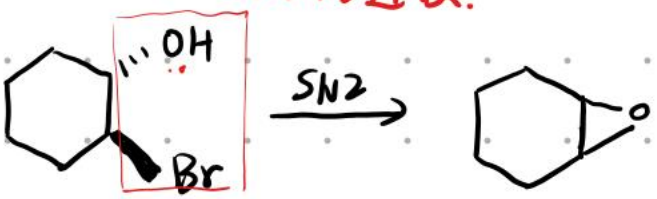
①

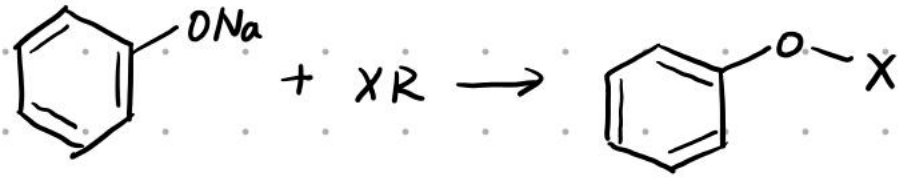
小位阻优先给卤代烃.

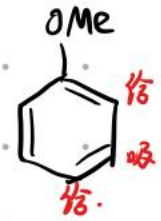


防止其容易消除

反式才能进攻.

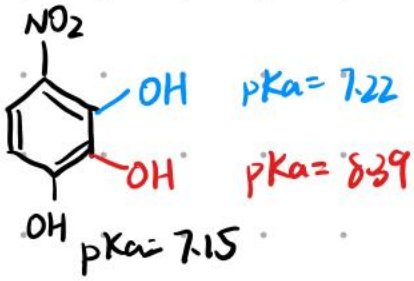






→ 对位电子效应最直接. 邻位由于位阻而减弱. ☆

(共轭效应减弱. 不关闭)

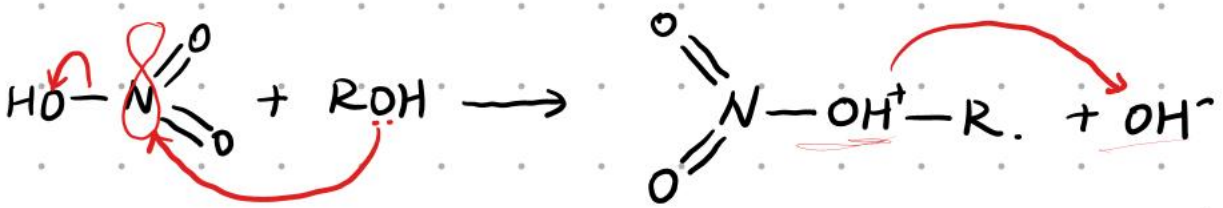


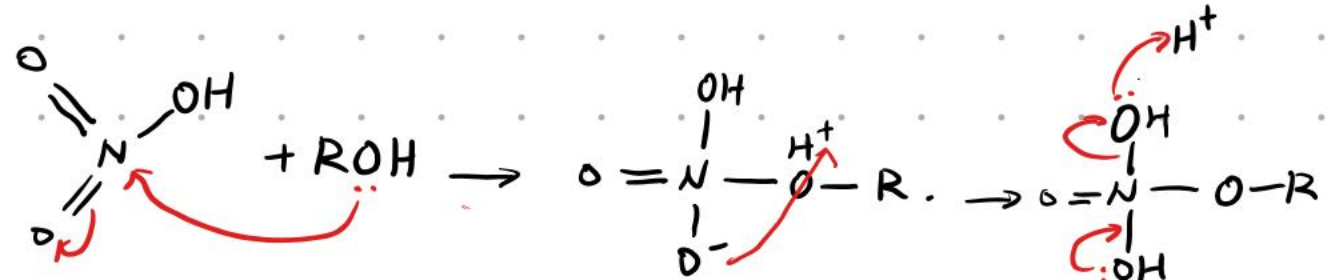
显色反应: 酚类+Fe, 蓝紫色.

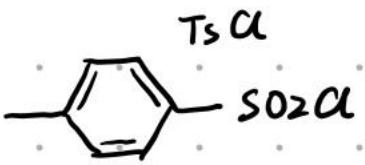
$PhOH + Fe \longrightarrow [Fe(OPh)_6]^{3-} + 3H^+ + 3HCl$

只要含烯酚片段即可.

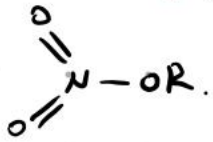
酚: 亲核性强, 作碱与酸反应. (成酯)







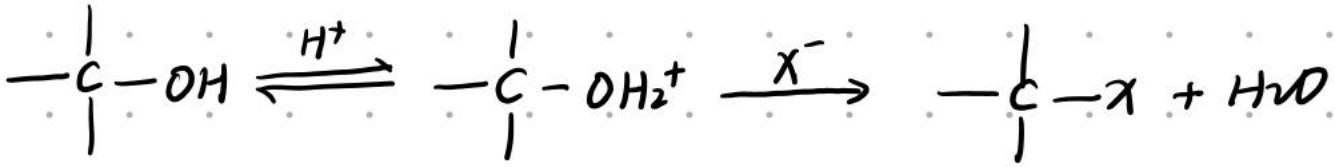
Py = 吡啶.



醇的取代反应：SN1 机理，强酸性.

相对反应活性：与 SN1 接近. 烯丙/苄 > 3 > 2 > 1 > 甲醇.

I > Br > Cl > F.

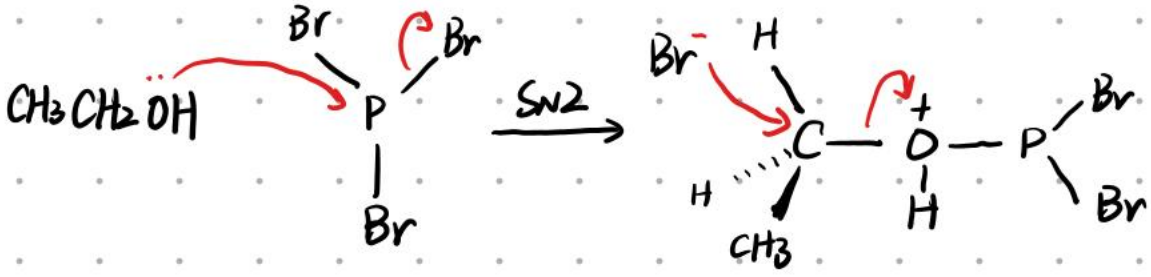


Zn^{2+}, Al^{3+} ⇒ 强路易斯酸.

与卤化磷反应.

$3ROH + PBr_3 \longrightarrow 3RBr + H_3PO_3$

$ROH + PX_5 \longrightarrow RX + HX + POX_3$



5 $SOCl_2$ 反应

1) 无溶剂 / 非亲核试剂. S_Ni 机理, 构型保持.

2) 在亲核溶剂里的反应 S_N2. 构型保持

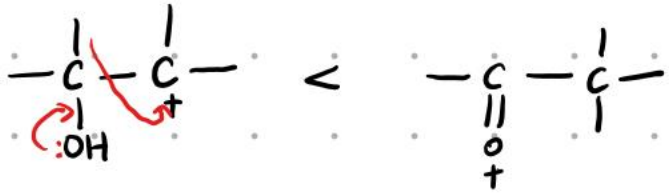
3) 与吡啶做溶剂. S_N2 构型翻转.

消除反应: E_1 消除, 遵守 Saytzeff 规则.

$R_3 > R_2 > R_1$.

除水剂: H_2SO_3, H_3PO_4. 提供质子 & 除水.

邻位 P-P 共轭比 R_3^+ 更稳定.

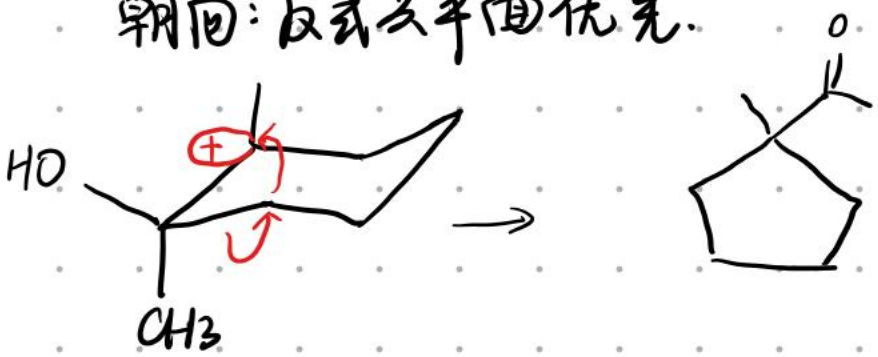


频那酮重排.

朝向: 反式共平面优先.

Ph 优于碳链.

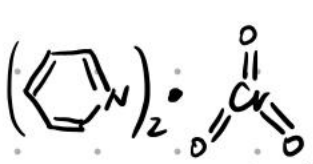
基团大, 富电子者优先.



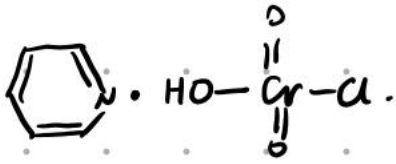
羟基氧化反应

氧化剂: Cr^{6+}.

$CrO_3 \rightarrow H_2CrO_4 \rightarrow H_2Cr_2O_7$. (酸性) Jones 试剂→酸



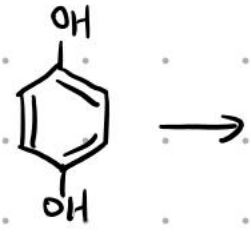
Sarrett. (in Py)
Collins (in CH_2Cl_2)



PCC

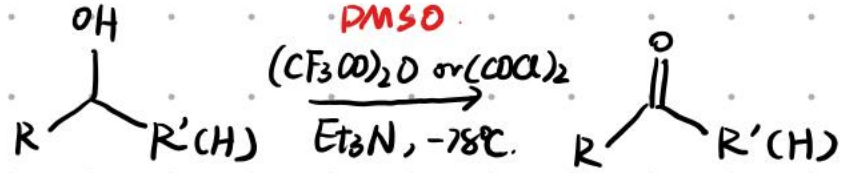
→ 醛/酮.

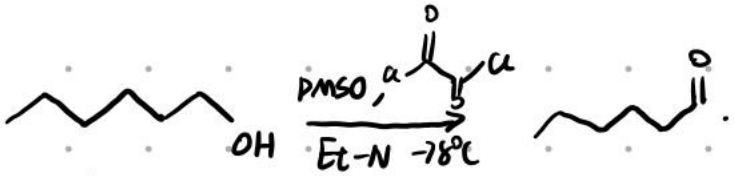
酚的氧化. → 醌, 作有机氧化剂.

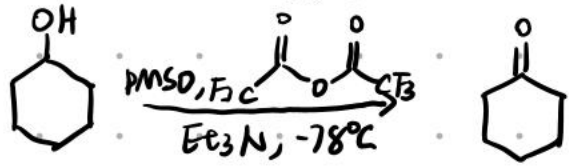


(DDQ)

Swern 氧化



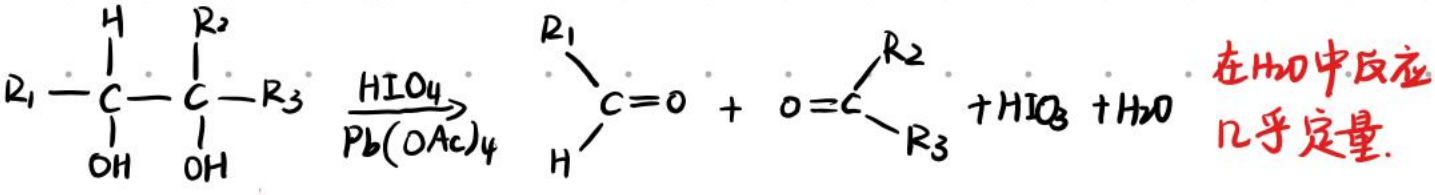




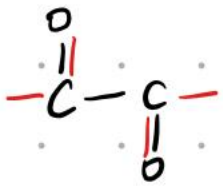
机理.

丙酮氧化. — Oppenauer氧化.

邻二醇氧化断键.

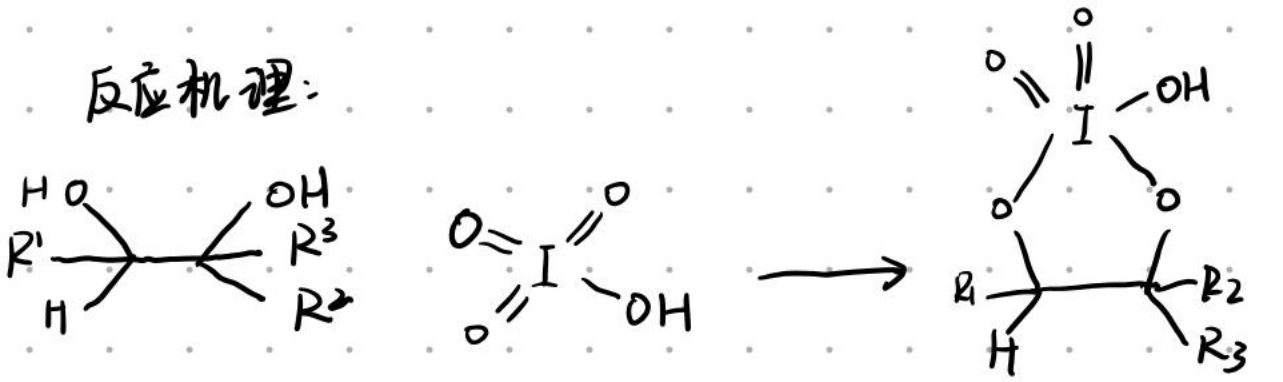


在H_2O中反应
几乎定量.

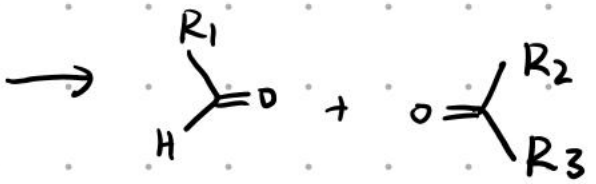


只要邻位 C-O 键
通通能切.

反应机理:

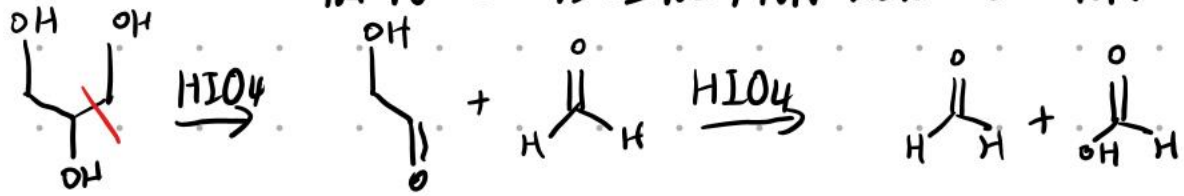


五元环中间体.



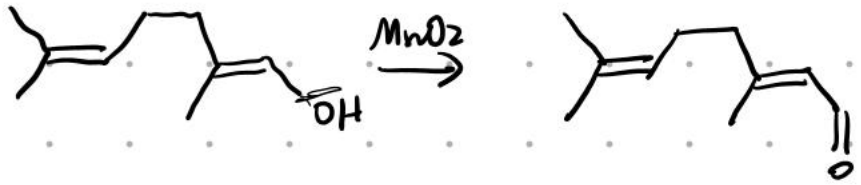
高碘酸断键: 断一次升高一次氧化态.

底物: α-羟基醛/酮/酸, 1,2 二酮.

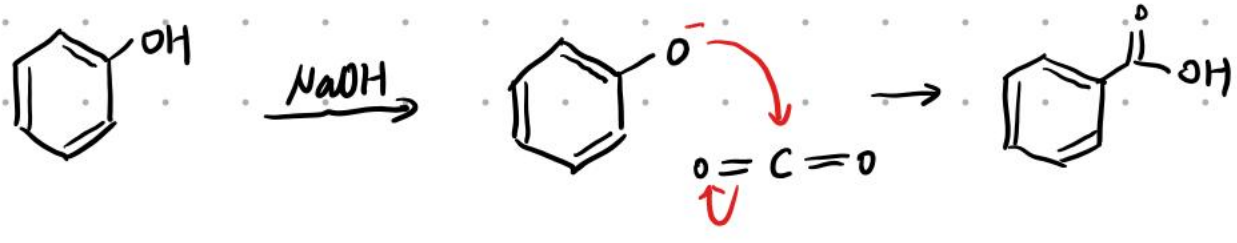


活性高.

MnO_2 氧化: 烯丙醇, 苄醇, 烯丙酮

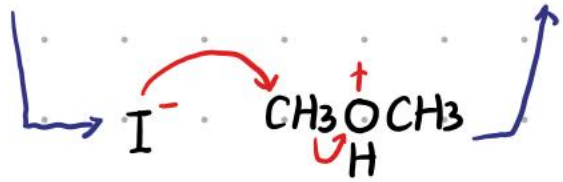


酚: 化学性质趋于苯.

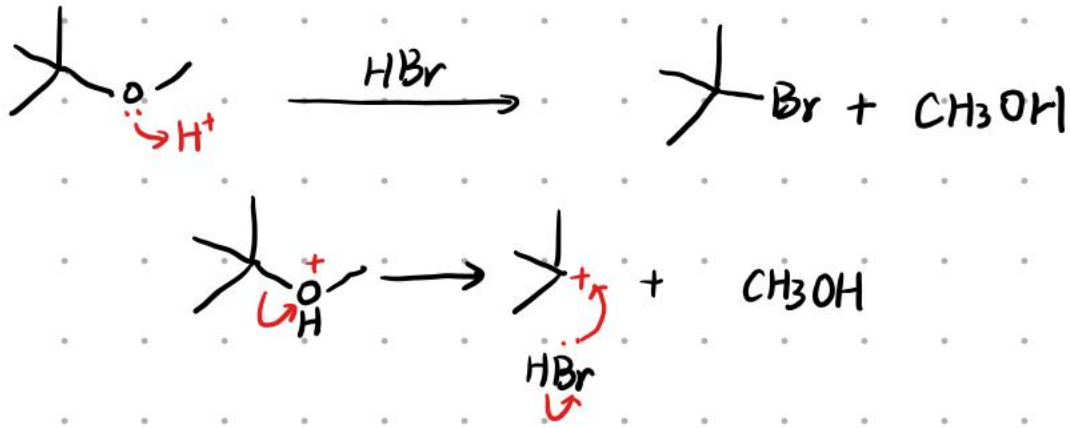


醚：C–O键断裂反应.

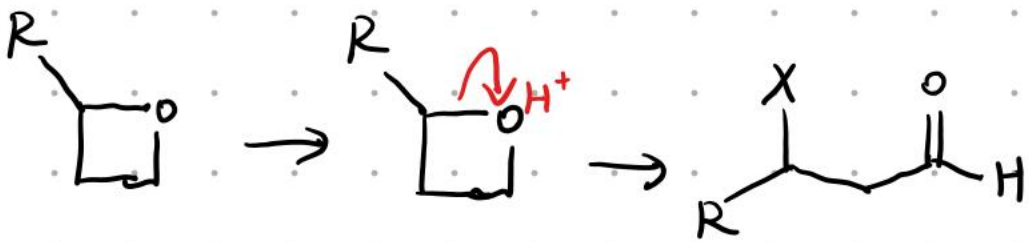
$CH_3OCH_3 + HI \longrightarrow CH_3I + CH_3OH$.



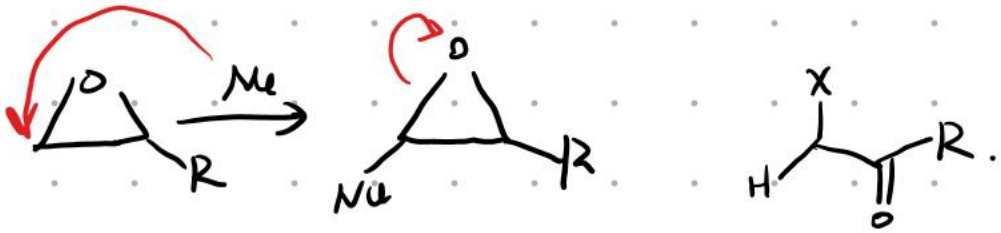
SN1 机理：



环醚的开环反应.



酸性
立体化学：SN2.



碱性.

酸性开环电子效应主导，进攻取代多的C.

碱性开环 SN2.

碱性：直接进攻位阻小的C.

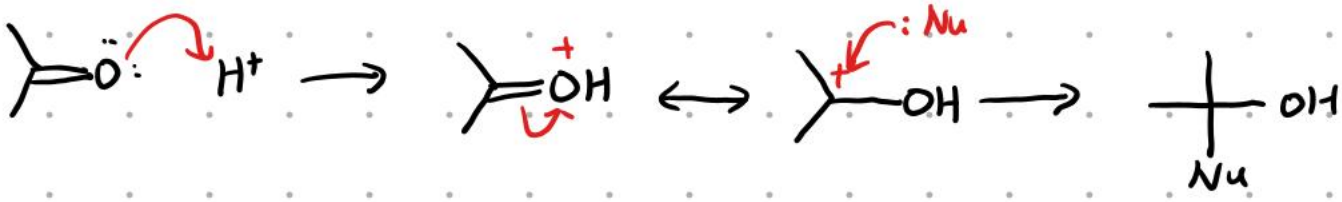
硫醇：亲核性大于O.

重排

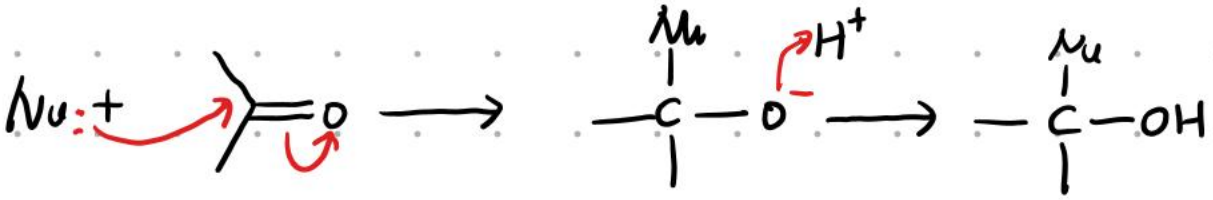
醛与酮.

亲核加成机理：

1）质子化－加成

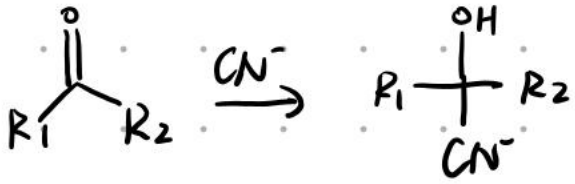


2）加成－质子化（碱性条件）



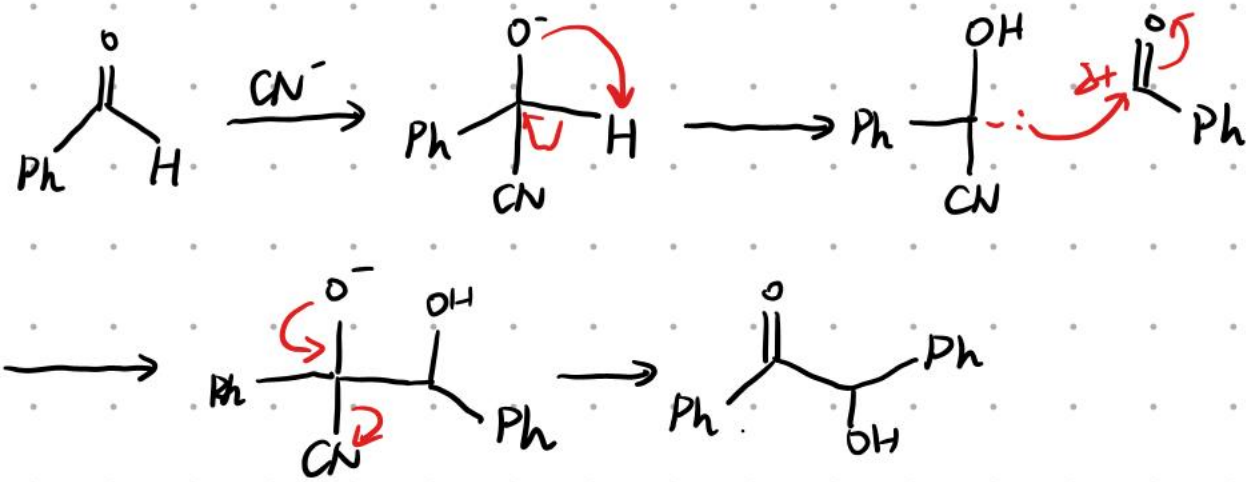
反应类型.

①含C亲核：CN^-

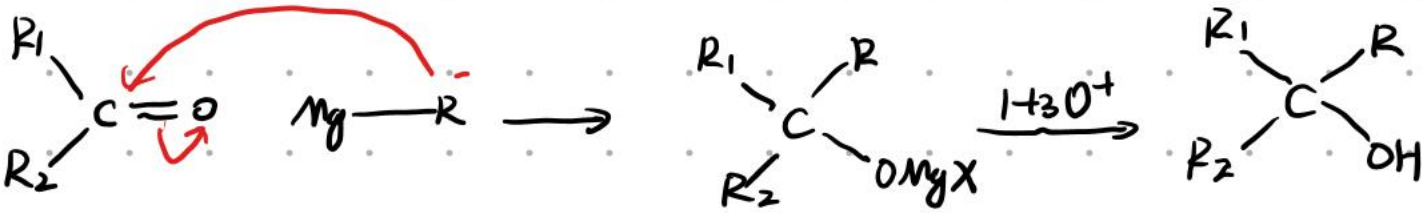


安息香缩合：

机理：



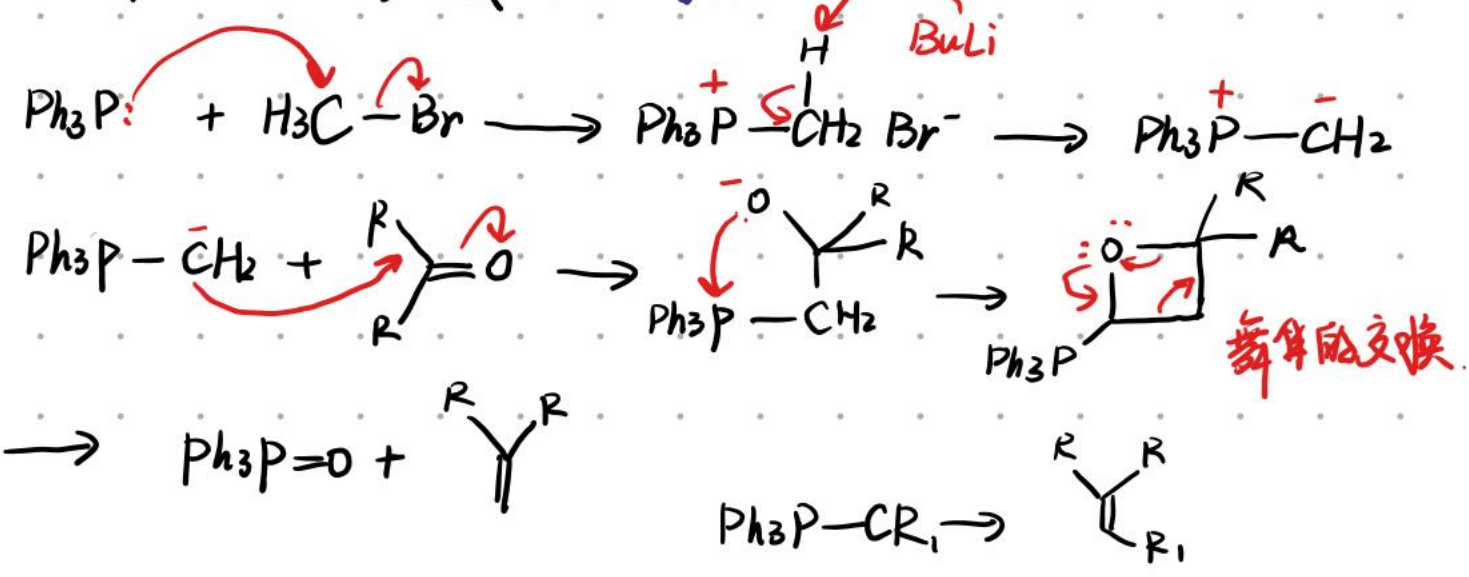
与格氏试剂反应：加成-质子化。



与炔负离子：$\equiv Na^+$

与有机锌试剂（同格氏）

与磷叶立德的加成（Wittig）.



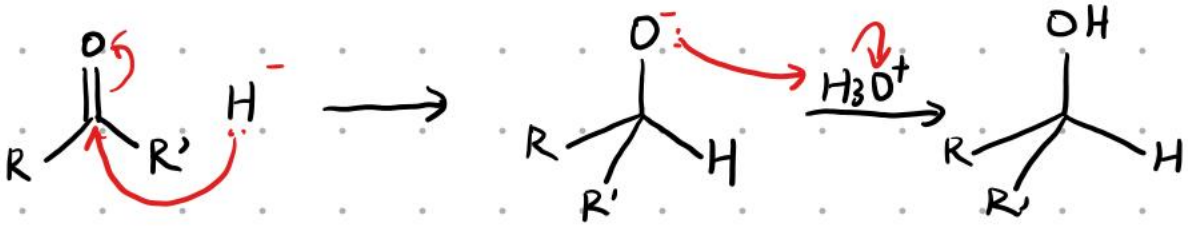
黄鸣龙还原

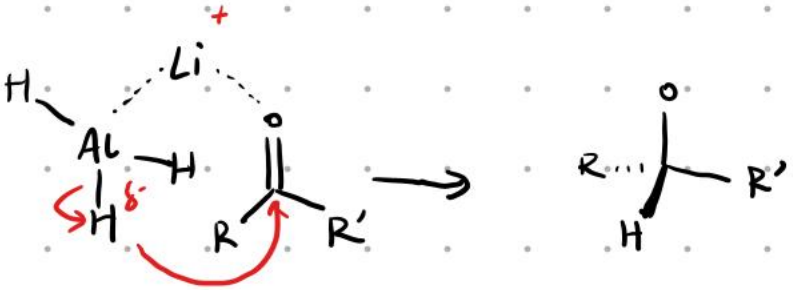
原理：用N取代O，使醛基C带负电荷进攻H.

能消除N_2，热力学有利，所以△.

与负氢试剂加成：还原反应.

$NaBH_4$,　　$LiAlH_4$.

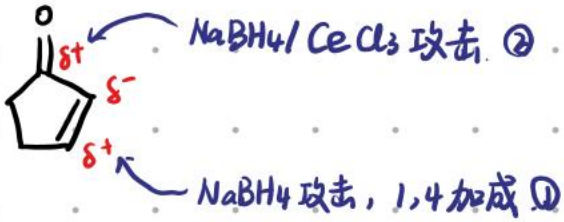




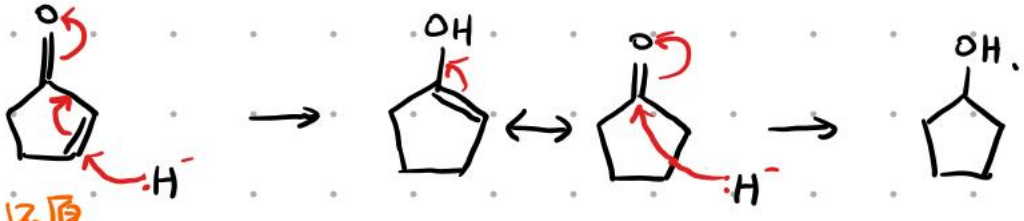
$NaBH_4$ 更温和.

不还原酯基，三键

只还原醛&酮.



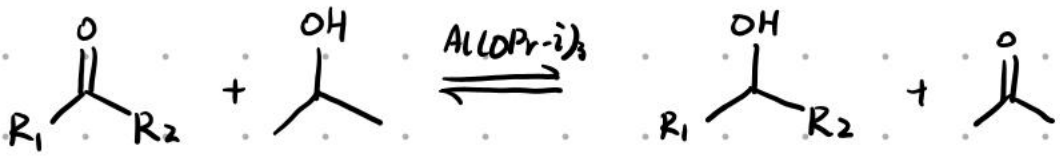
①:



Luche 还原.

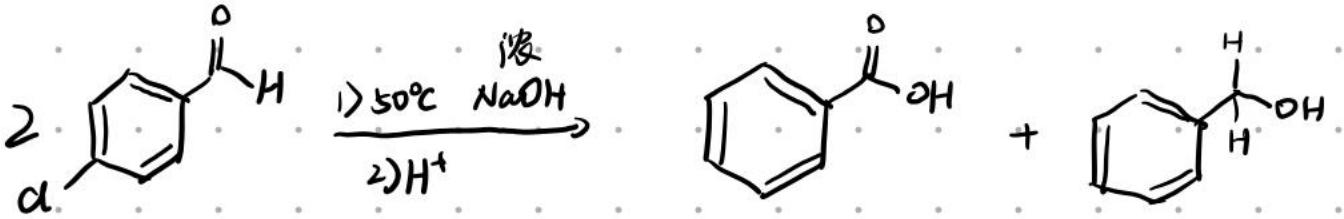
②

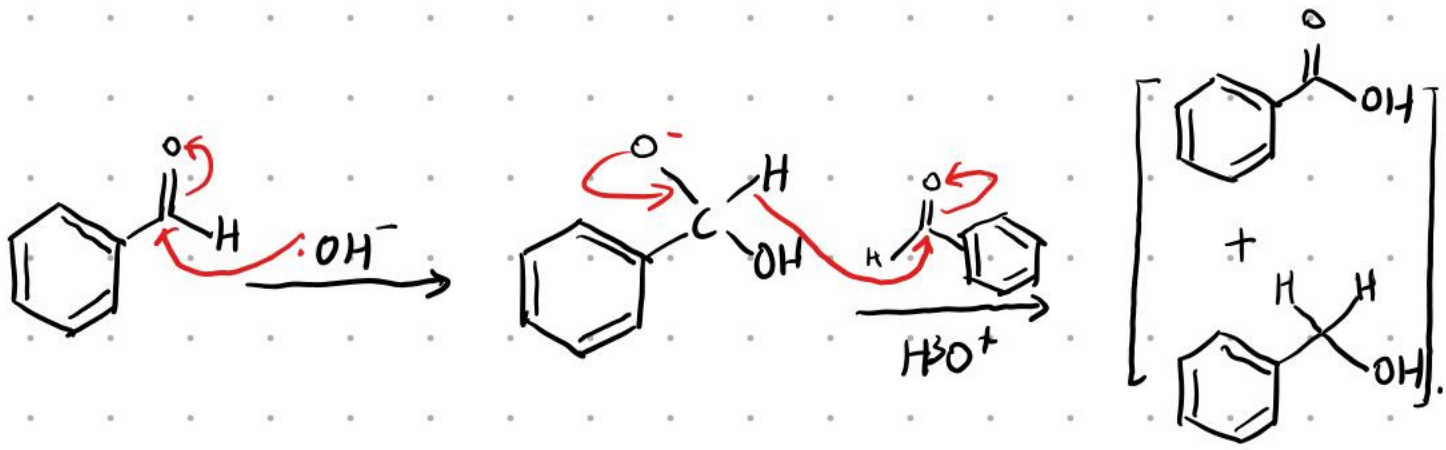
酮：MP还原：



(逆反应：Oppenaure 氧化.)

Cannizzaro 反应（歧化）



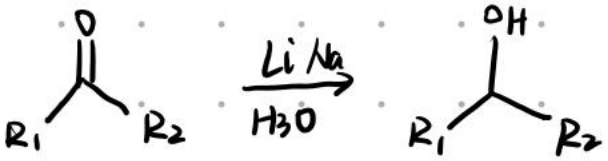


Zn 还原.

镁还原

频那酮.

Li-Na-K 还原

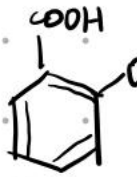


羧酸 & 酰胺.

溶沸点高. 一级酰胺

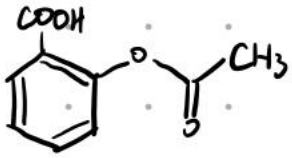
苯甲酸 → 酸性更强.

邻位取代酸性更强(位阻效应).



→生成分子内氢键,稳定共轭碱.

水杨酸.

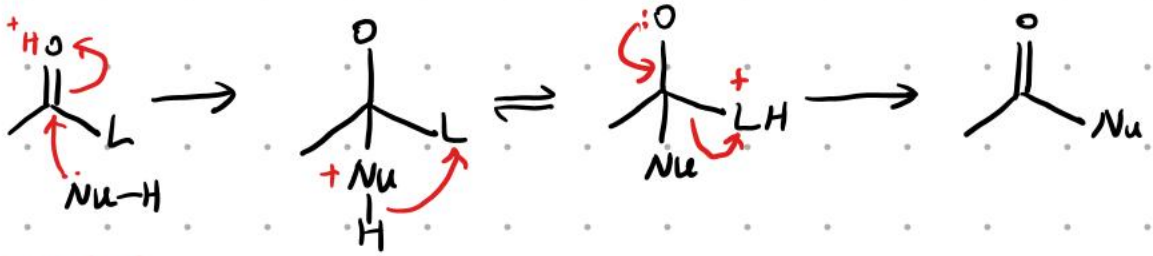


阿司匹林.

加成-消除.

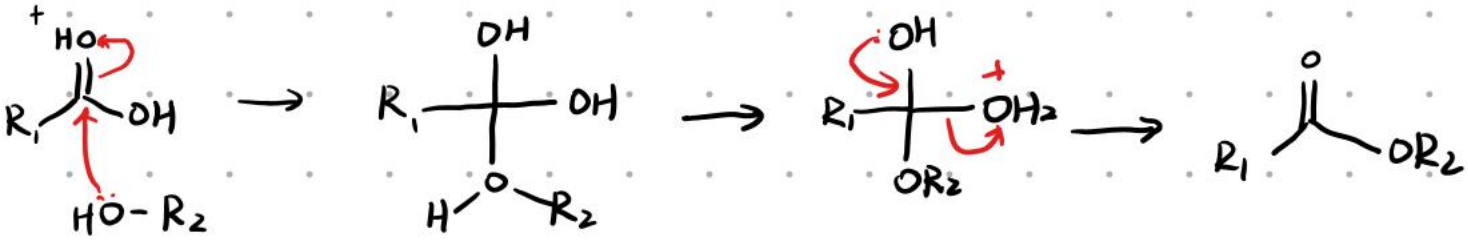
碳氧键易断裂.

酸性条件:



碱性条件

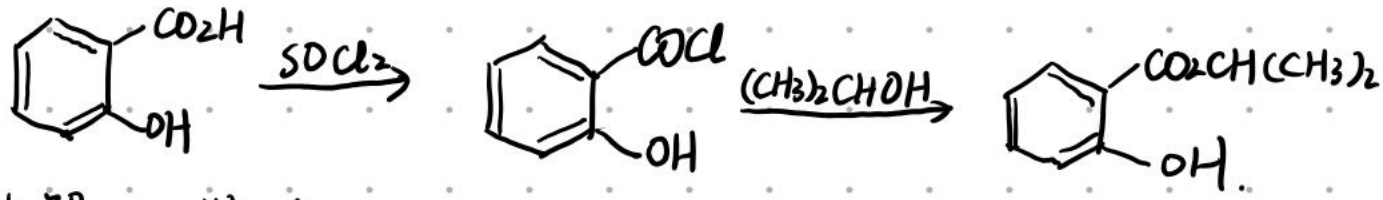
酯化反应机理:



酰氯与醇反应更易成酯

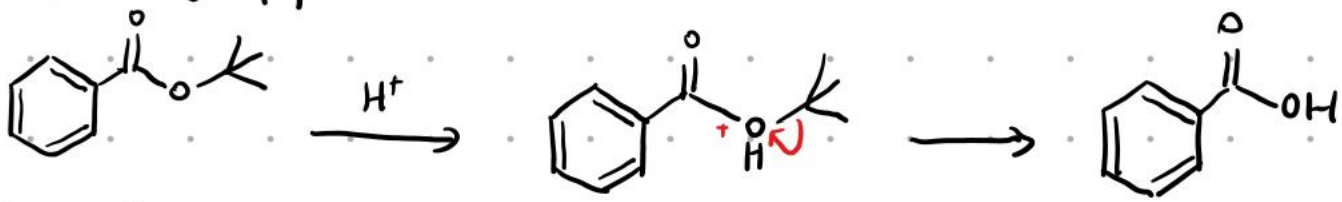
酯的醇解反应(酯交换).

酰酸最稳定. 酰氯最活泼.



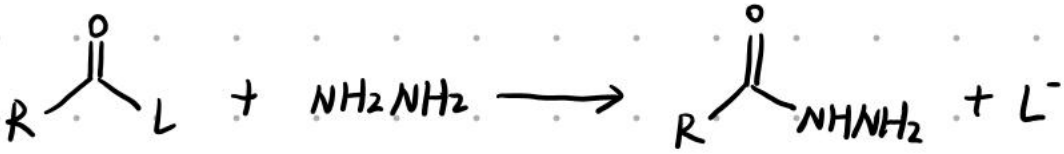
水解 ⇒ 羧酸.

特例:三级酯的水解: SN1.



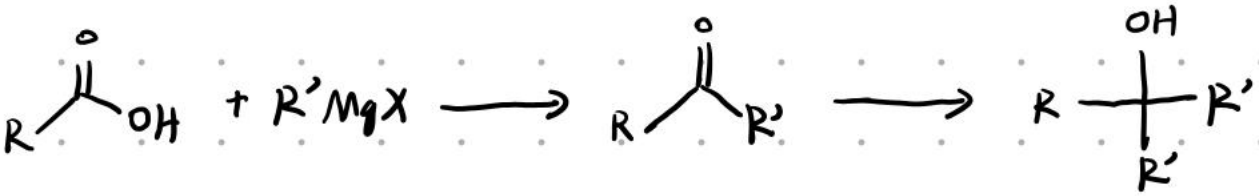
原因. 空间位阻与sp^3超共轭

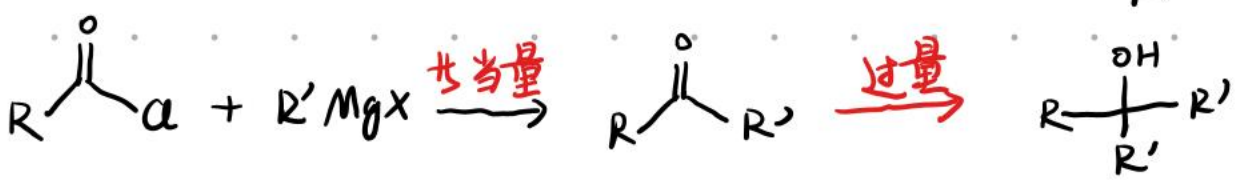
肼解:

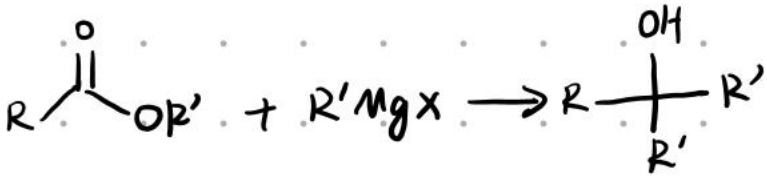


与金属有机试剂的反应:

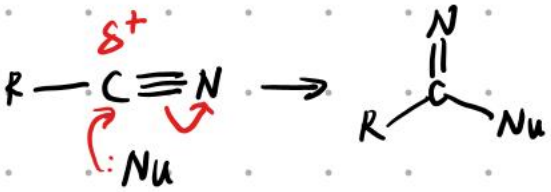
①格氏试剂:





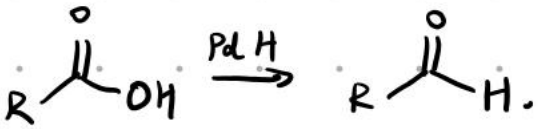


原因：酯活性太低.

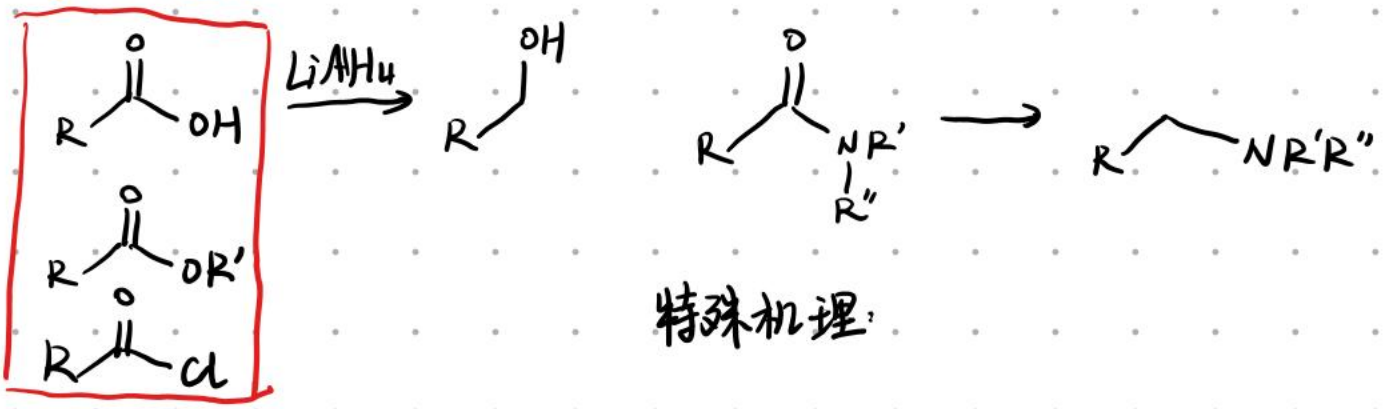


催化氢化：

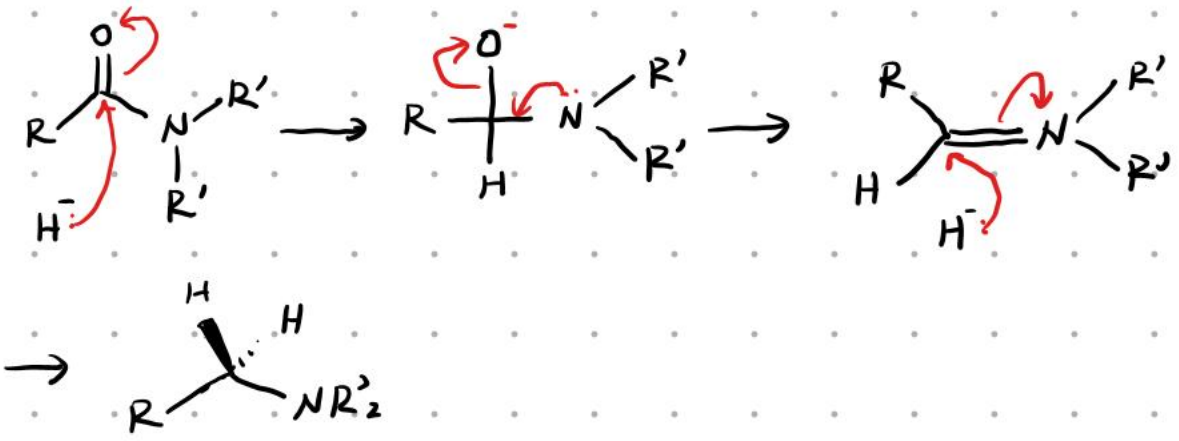
① Lindlar：



② $LiAlH_4$

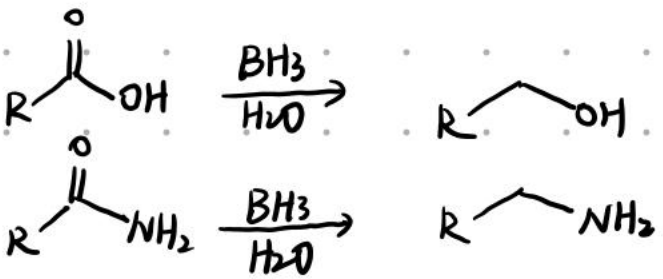


特殊机理：



$NaBH_4$ 还原：能还原酰氯.

硼烷：

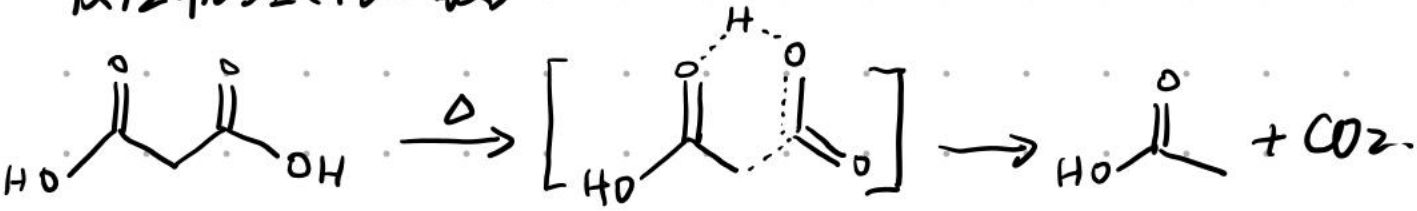


不还原酸衍生物.

亚胺：用 $NaCNBH_4$

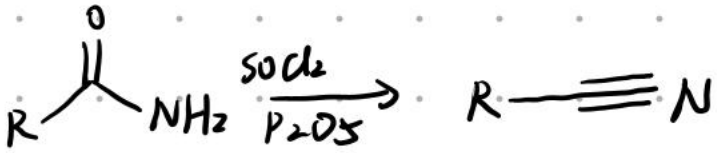
脱羧反应：加热，生成 CO_2.

反应机理（丙二酸）



酰胺脱水反应

酯基水解：逆反应.



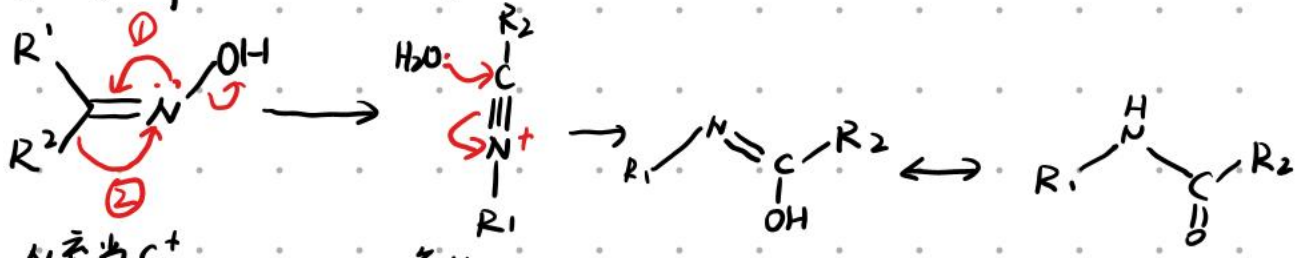
格氏试剂与 CO_2 做羧酸.

碱水解：皂化.

水解时加入除水剂：DCC.

Beckmann 重排 #构型保持.

反式共平面迁移重排.

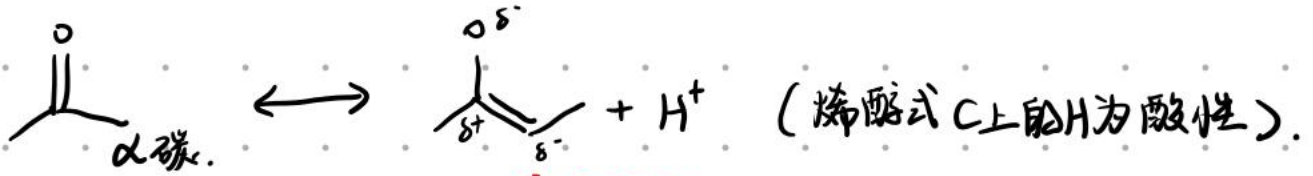


N 充当 C^+

近似于频哪酮.

酯基水解.

羰基化合物α-碳上的反应.



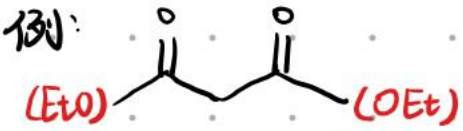
(烯酸式C上的H为酸性).

(亲核试剂)

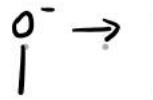
加成&取代.

烯酸式: 与Fe^{3+}显色.

吸电子能力 醛>酮>酯.

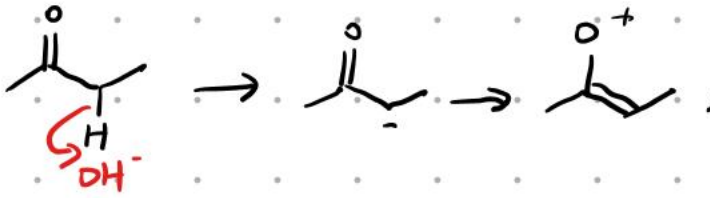
例: 

类化合物.

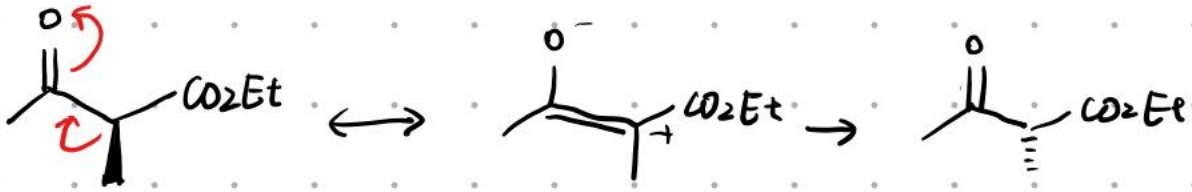
酸性条件下: 

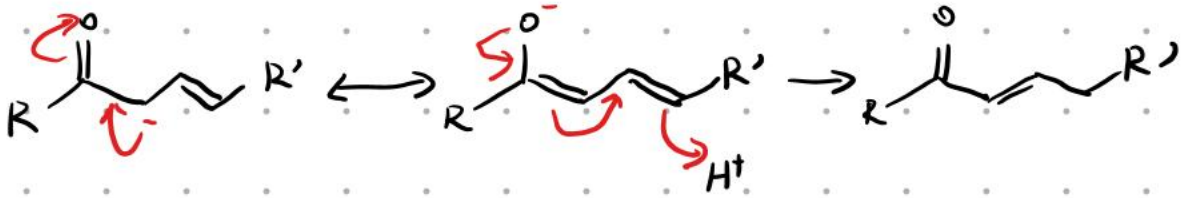
酸不改变平衡常数

碱性条件下:



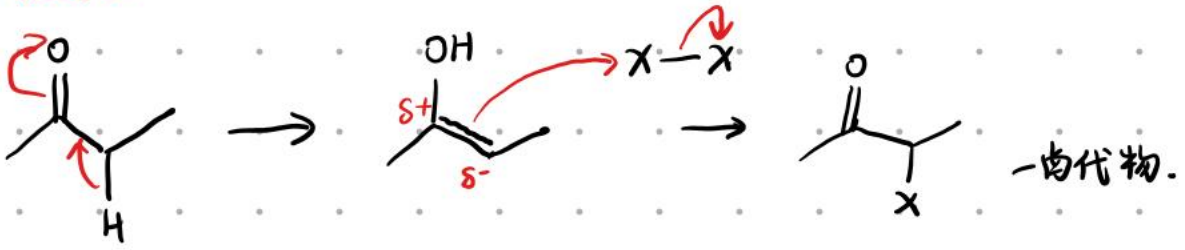
碱改变.





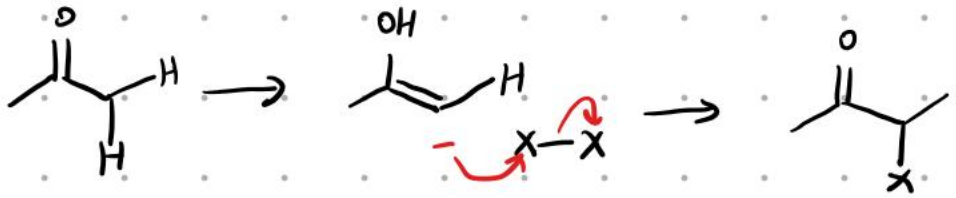
α 卤代反应：

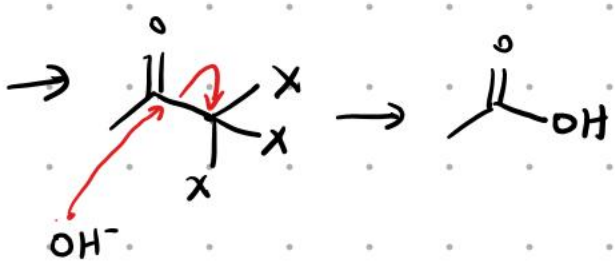
① 酸性：



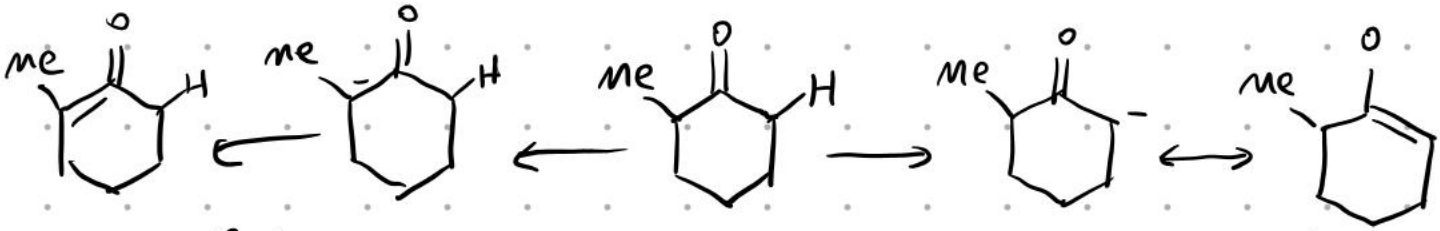
一卤代物.

② 碱性.





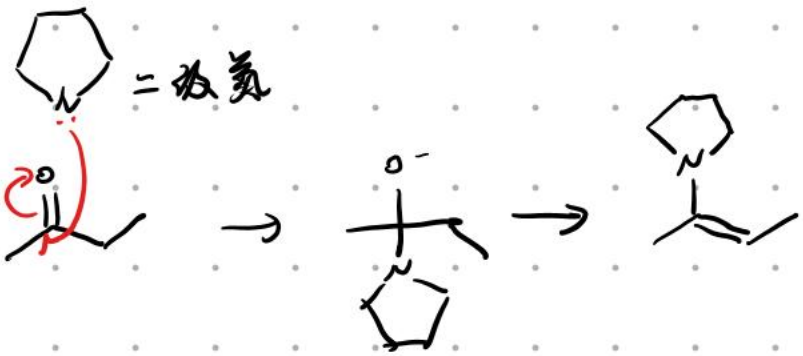
α-烷基化反应.



强碱.
高温
(热力学有利)

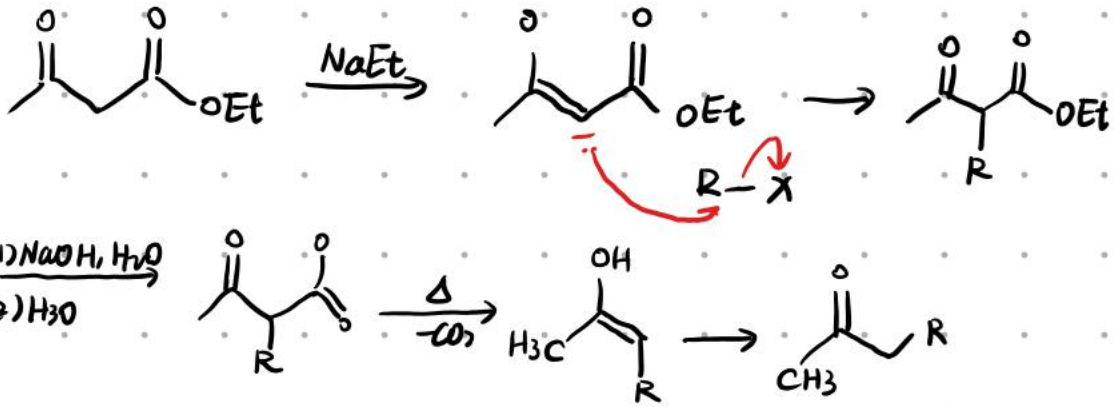
大位阻强碱
低温.
(动力学有利)

烯胺的烷基化.

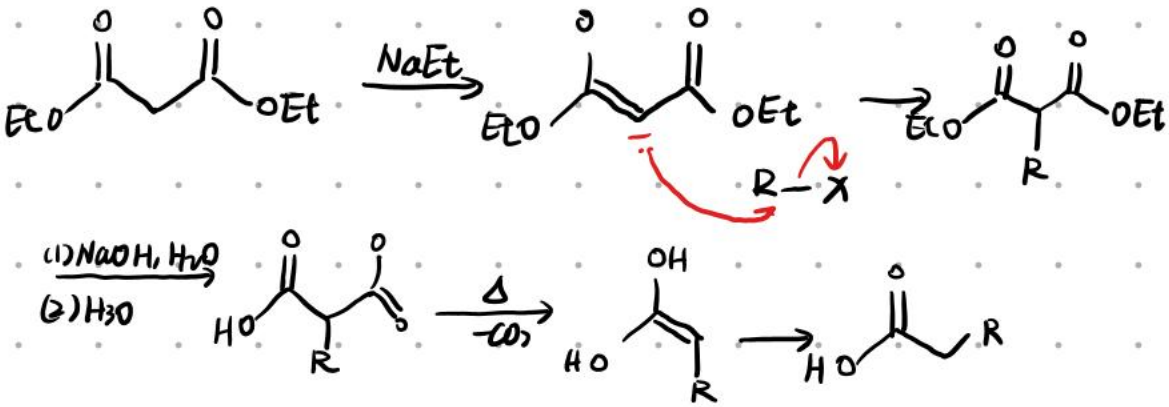


催化反应：位阻小的优先.

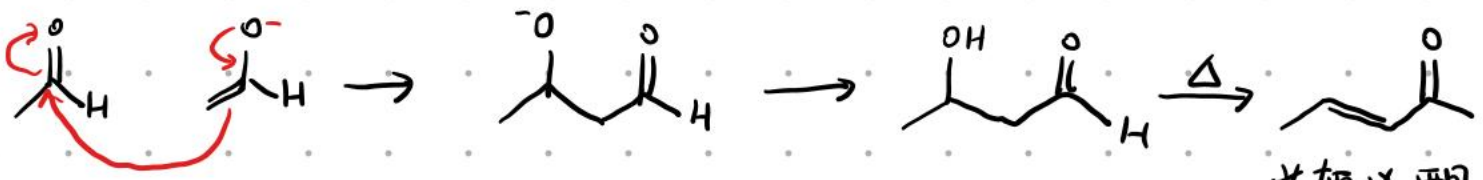
乙酰乙酸乙酯&丙二酸酯. 活性高 负反应少.



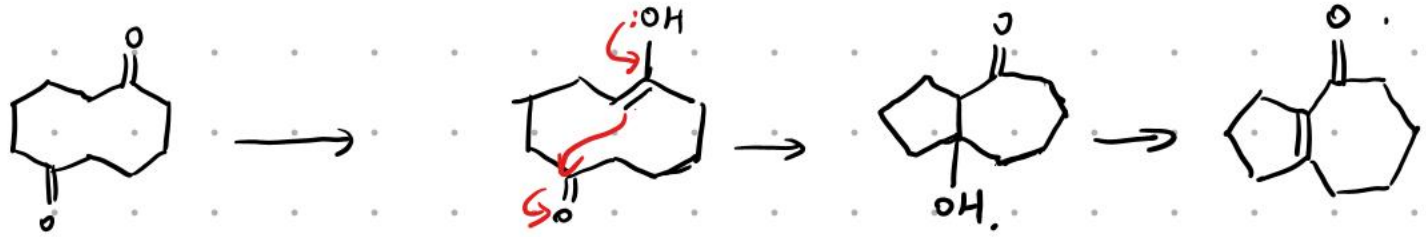
丙二酸二酯.



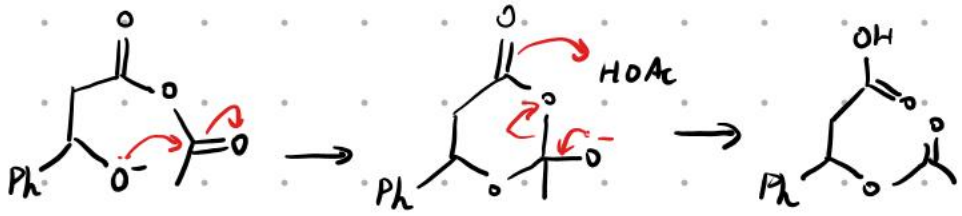
羟醛缩合. Beigan 反应.



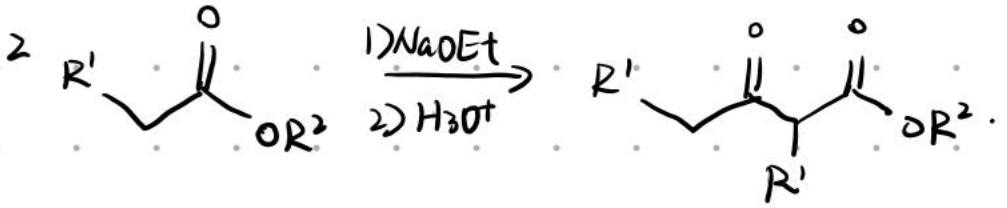
共轭烯酮
热力学稳定.

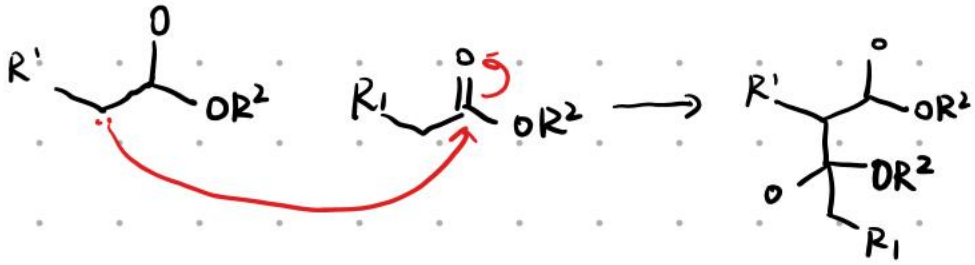


分子内酯化.



酯缩合反应. Claisen

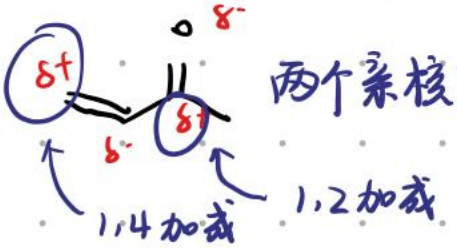




Dieckman: 分子内的 Claisen

保证其中一分子无α氢,只能被缩合.

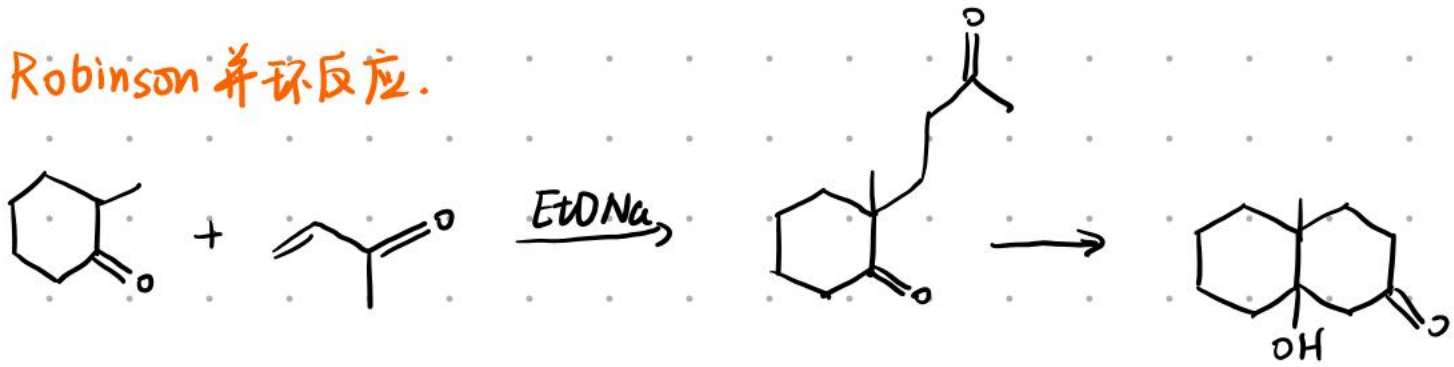
Michale 加成反应:

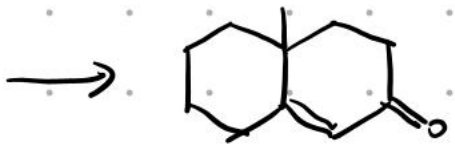


两个亲核进攻位点.

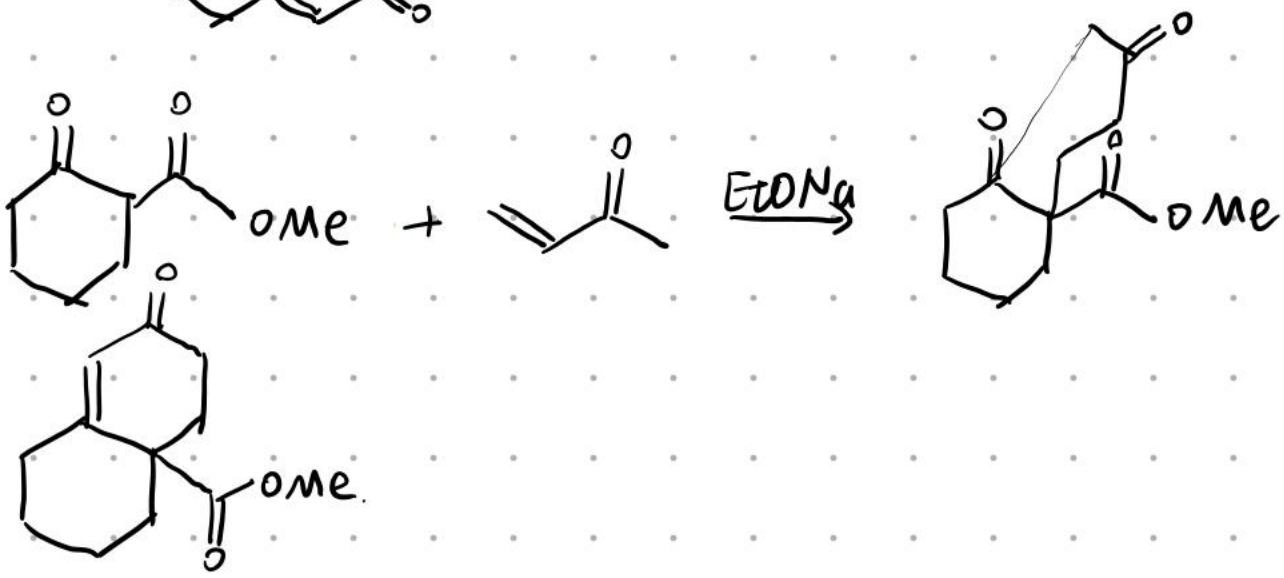
亲核: 硫酚 > 酚.

Robinson 并环反应.

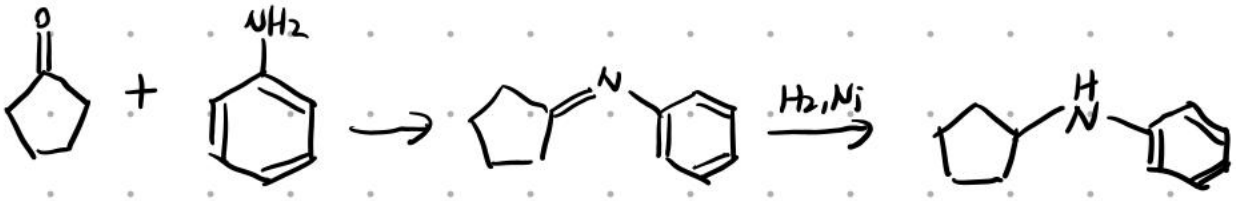




"一锅".

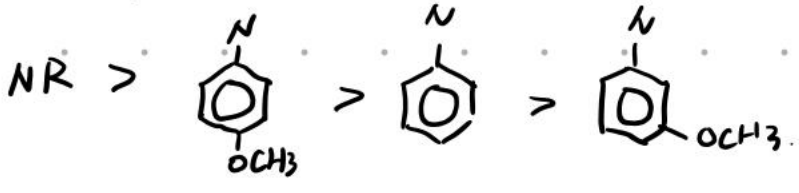


还原氨化.

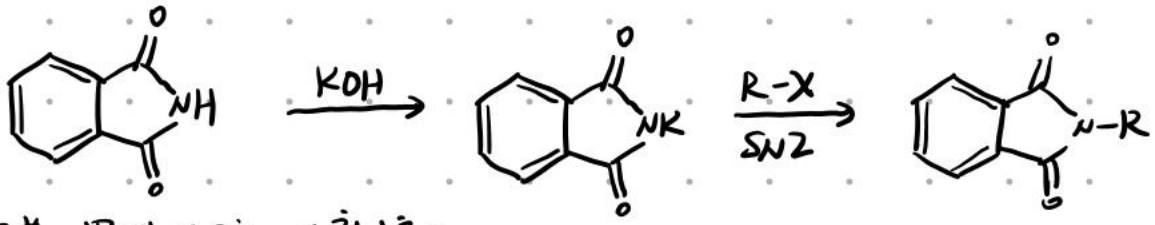


含氮化合物

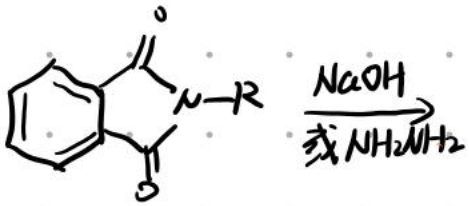
N 的碱性:



制备胺：Gabriel 法：

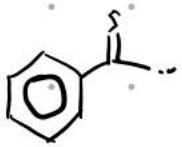


邻苯二甲酰亚胺.（亲核）

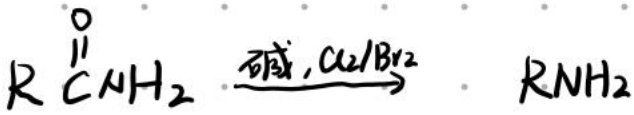


NH_2R.

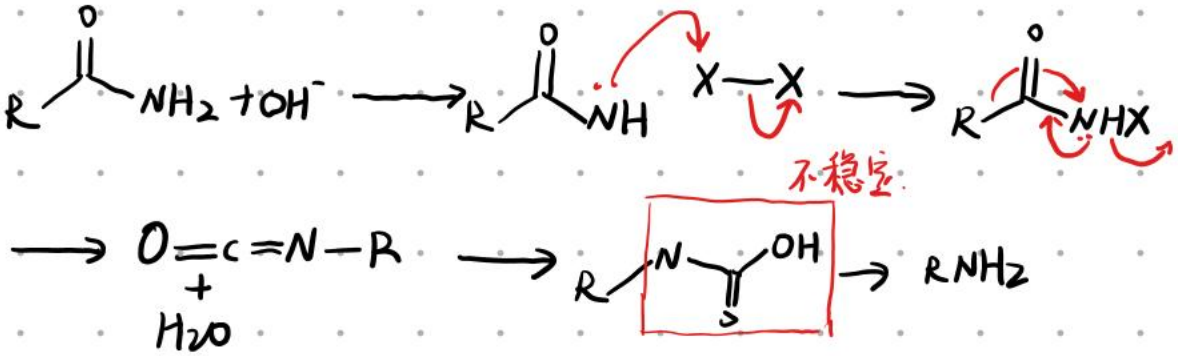
Ts → 苯磺酰.



Hofmann 重排：　#构型保持.



反应机理.



Curtius 重排.

条件：NaN_3　底物：R_1COX，R_2OH / R_2NH_2

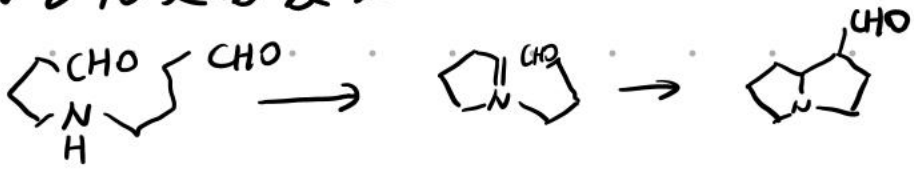
产物：$R_1-NHCONHR_2$ / $R_1-NHCOOR_2$

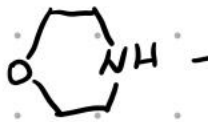
机理：同 Hofmann 重排，倒数第二步不加水而加酸/胺.

Mannich 缩合：

同羟醛缩合，底物为羰基 & 亚胺.

分子内更易发生.　酚也能发生.

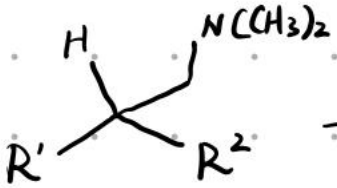


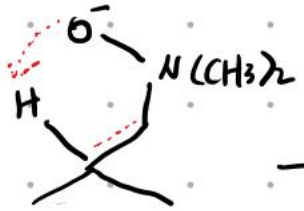
 → N先反应

例：  (michael)

保护 $-NH_2$ → 加 Ac_2O 变酰胺.

Cope 消除反应.

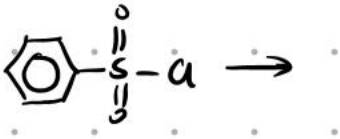


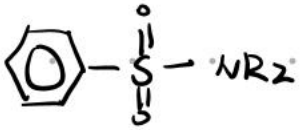


→ 要求有β氢.

顺式消除，具有立体专一性.

Hinsberg 检验：

一级氨：  先沉再溶于碱.

二级氨：  不溶

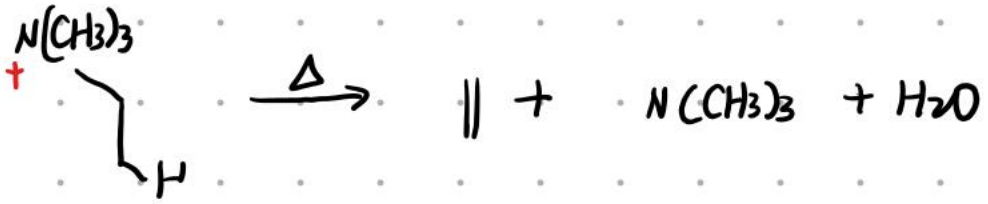
三级氨：不反应.

与 HNO_2 反应：

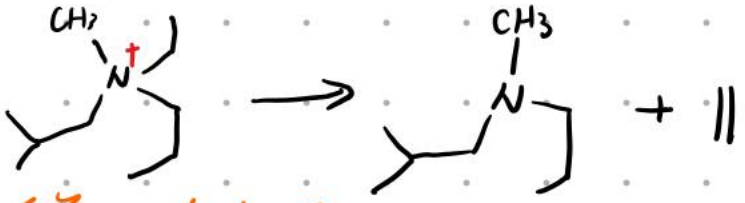
二级胺：亚硝胺. $(CH_3)_2NH \xrightarrow[H_2O_2]{NaNO_2,\ HCl} (CH_3)_2N-NO$

TD 重排

Hofmann 消除.

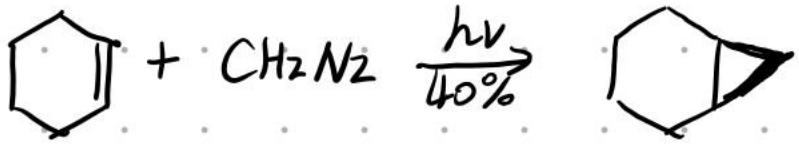


位阻小先消除.

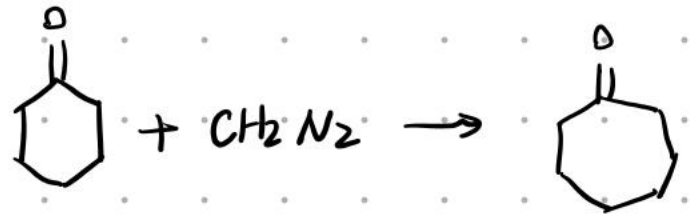


重氮化合物反应:

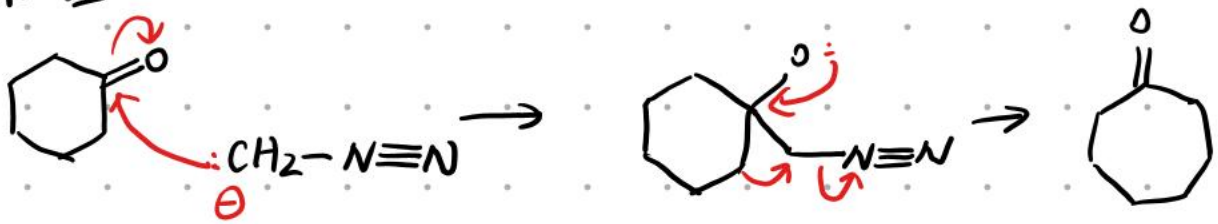
小卒宝. 环丙烷化.



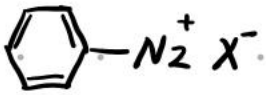
2. 作为亲核试剂: 与酮反应发生扩环.

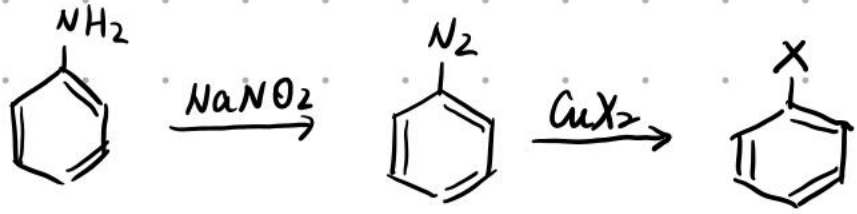


机理:



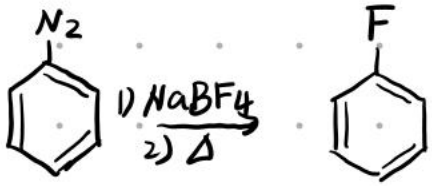
芳基重氮盐的反应. (反应性: 芳基负离子).



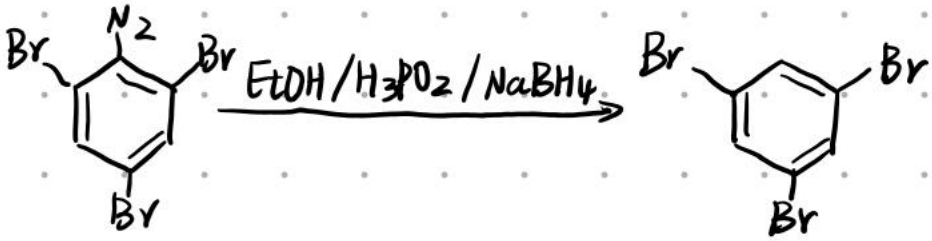


(与卤负).

(唯一方法)

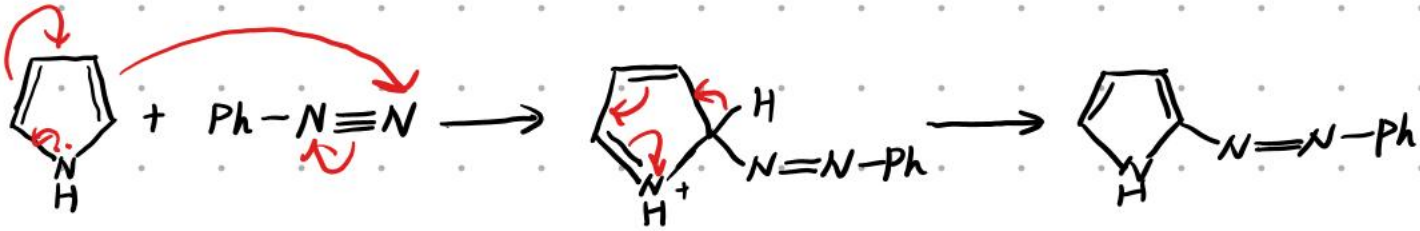


(BS反应).

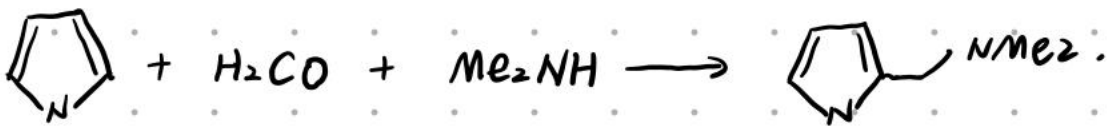


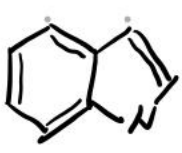
杂环化合物.

① 呋喃, 噻酚, 吡咯.

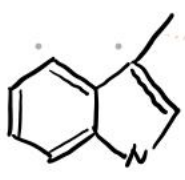


Manish 反应:





吲哚



类臭素..

亲电取代：活性比Ph高，α位优先反应

亲核取代：活性比Ph低.

Michale 加成.

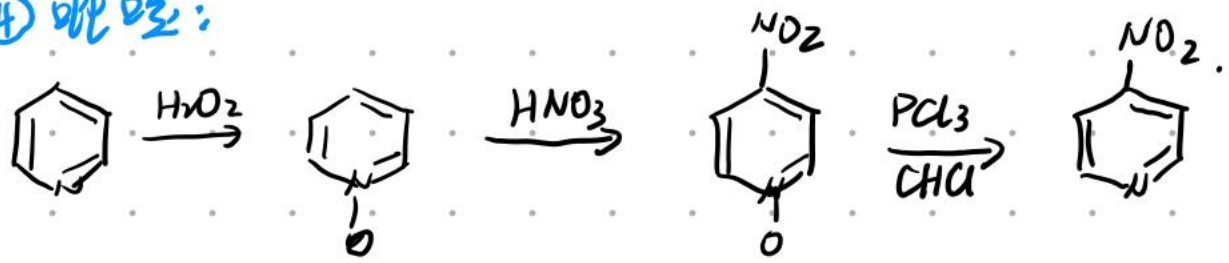
② 苯并(呋喃，噻酚)，吲哚.

① N-烷基化：作为亲核N试剂

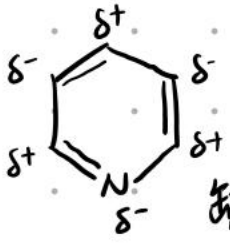
② 亲电取代：β位优先.

③(咪，吡，噻，噁)唑.

④ 吡啶：

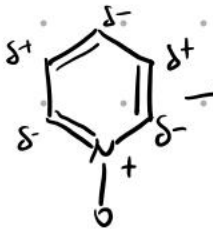


(氧化后活性增强，发生在对位)

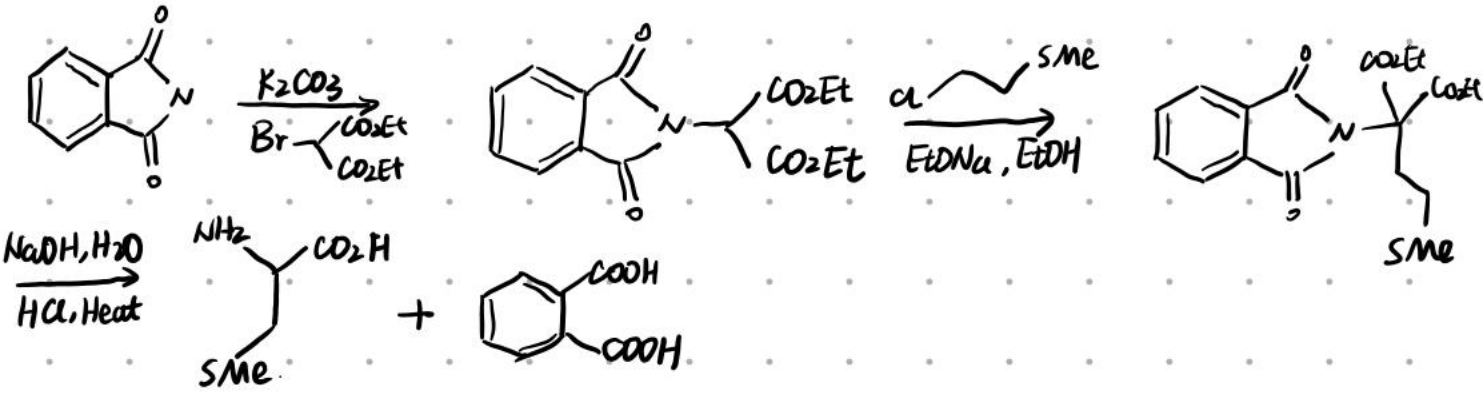


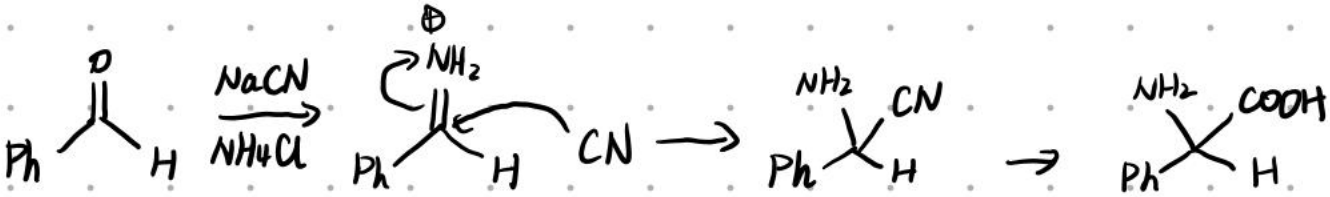
决定了反应位点.　不能做傅克反应.

缺电子杂环



→ 活性升高.

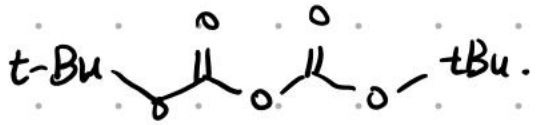




Cbz：苄氧羰基化合物，保护 $-NH_2$.

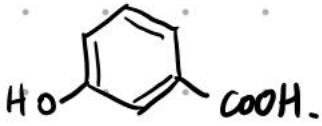
还原去保护：H Pd/C

Boc：二碳酸双叔丁酯. 保护 NH_2.



酸性条件去保护.

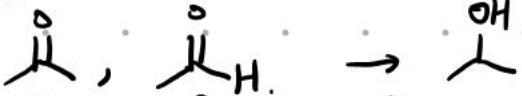
Fmoc：碱性条件去保护.

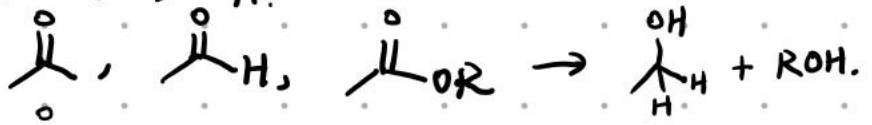


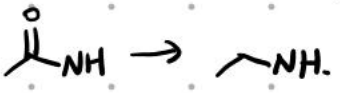
对还原反应的总结：

还原剂种类

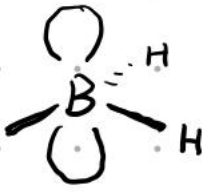
① B，Al类还原剂：

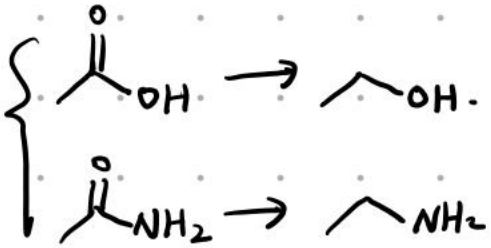
$NaBH_4$ → 还原 

$LiAlH_4$ → 还原 

还原 

硼烷：由于希望得电子而表现出

与富电子基(酸酰胺)反应更活跃 



（不影响酮/酯）.

酯→醛：先还原，再用 Cr^{6+} 氧化.

$NaBH_4(CeCl_3)$ → 只还原醛/酮，不动双键.

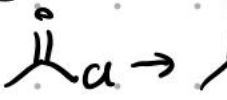
$NaCNBH_4$ → 只还原亚胺.

② 氢化反应(主要看催化剂)：

H_2/PdC → 只还原双键. 硝基→胺基.

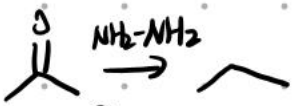
H_2/Ni → 只还原苯环/双键.

H_2/Lindla → 还原三键→双键.

$H_2/Pd.BaSO_4$ → 还原 

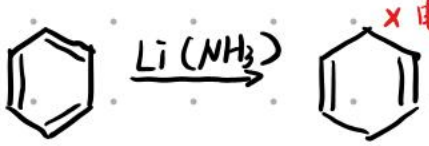
合成中应用：

脱  ：

① 黄鸣龙还原：  （温和）

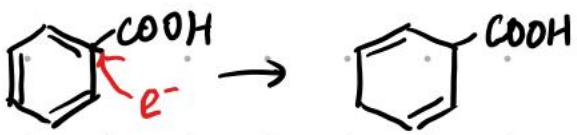
② Clemenson还原：  （暴力）

溶解金属还原：Birch还原.（苯吃还原）.

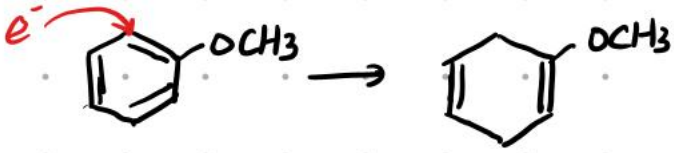


x 电子先攻击的位置.

因而吸电子基：



给电子基：



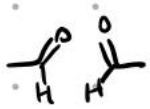
炔烃的Birch还原：E(反)式.

氧化反应总结：

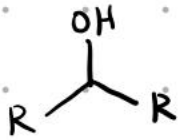
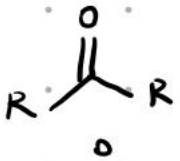
① 关于烯烃：

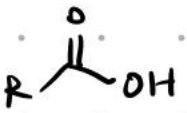
① = $\xrightarrow{m\text{-}CPBA}$ 

② = $\xrightarrow{OsO_4^{2-}}$ 

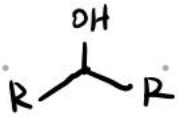
③ = $\xrightarrow{O_3}$ 

② 关于醇：

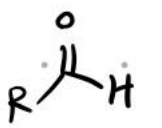
 $\xrightarrow{CrO_3}$ 

 $\xrightarrow{CrO_3}$ 

（Jones试剂）→ 避免水则成醛.

 $\xrightarrow{DMSO.}$  → 斯文氧化. 比较斯文，不会过度.

③ 关于醛：

 $\xrightarrow{K}$ 

④ 邻二醇断键：HIO_4.