高中有机化学知识拓展

从非竞赛高中生的视角

带你拓展大学里常出现在高考中的有机知识

本套教程说明

高考有机大题充斥着复杂的信息，对于中学生来说，在考场上时间紧、任务重的背景下，想要充分理解运用题目信息对物质进行推断并不容易。有机化学大题需要长期大量练习才能推断得又快又好，但是在平时的训练与考试中，很多同学往往卡在“不知道这是啥信息”“理解错了题目信息”的第一步，导致推不出来，浪费时间，甚至畏惧这道有机推断。实际上，由于高考出题人大部分为大学教授，他们对于大学本科化学专业《有机化学》课程里面的有机反应烂熟于心，因此在出题时往往会加入一些在化学竞赛、大学课程里面稀松平常但是高考生没怎么见过的条件。如果我们高中生能够在平时学有余力的基础上，站在中学生视角去看待、了解一点大学知识的话，对于我们又快又好的解题是大有裨益的。

不适用人群（必看！）

1、对于高中教材基础知识掌握不熟的同学，请你们赶紧归去补基础，切记先学会走，再学会跑，最后再学飞！

2、应付大学期末考试甚至是考研的学生，因为这个教程针对的是非竞赛高中生，几乎不会涉及复杂命名、反应机理、产率判断、产物判断、立体异构、复杂路线合成等大学《有机化学》期末考试的重点内容，所以临阵磨枪的大学生请去专业的应对大学期末考试的up主那里或者做做自己学校往年期末题，祝大家期末都能顺利通过。至于考研党的话，勤学苦练，祝你上岸。

3、高中化学竞赛生，竞赛有机化学建议系统学习大学《有机化学》课程，个人推荐使用邢大本或者巨本，不推荐南开有机化学教材（我们当时本科都不用自己学校的书，改用邢大本），课程的话清华大学李艳梅老师个人感觉不错，当然也可以参考有机考研up主。

适用人群（必看！）

1、对于教材中的有机反应烂熟于心，熟练掌握教材基础知识点，但是没学过化学竞赛也并不打算学化学竞赛的高中生。

2、虽然选考化学学科，但是未来对化学学科兴趣不大，大学里面不打算学习化学、化学工程、药学等需要用到大量有机化学知识的专业的同学。

3、有较为充足的时间，没有严重的偏科的同学。

本套教程说明

本套课程内容全部为课外知识，对于我们的高中生来说，课外知识就是了解用的，不要背诵！不要背诵！不要背诵！重在理解、学会“怎样看待反应前后的变化”和“对这个条件眼熟，明白它是氧化还是还原”这种程度即可。

本套教程仅仅列出大学本科阶段《基础有机化学》常见的、容易出现在高考题目里面的反应并且带领大家从高中生视角去分析，以提高学生对陌生信息的处理能力。本教程不能涵盖也不可能涵盖出题可能用到的全部反应，这个系列只是一个知识拓展，不是什么题库。

在有机合成路线设计里面，只能使用本道题目给出的信息和高中教材里面的有机反应，在书写时要注意条件。其他的课外知识、反应都不准用，谁用谁没分。

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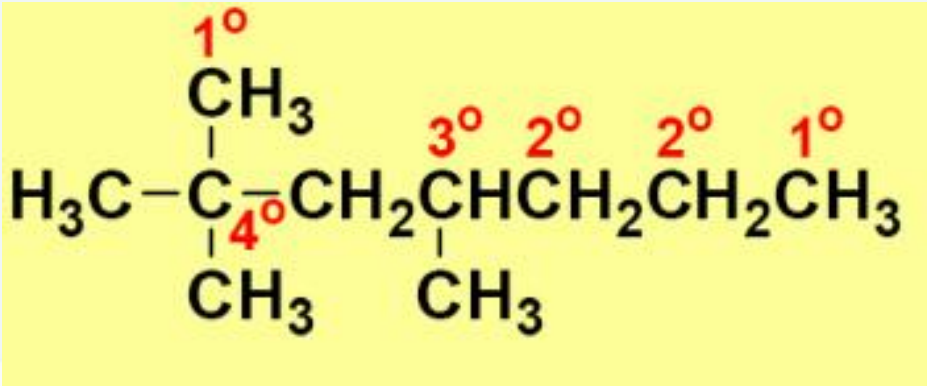
01 烷烃 环烷烃

1.烷烃中碳种类

1、直接与一个碳原子相连的称为“伯碳”或一级碳原子，用1°表示；上面的氢为1°H。
2、直接与二个碳原子相连的称为“仲碳”或二级碳原子，用2°表示；上面的氢为2°H。
3、直接与三个碳原子相连的称为“叔碳”或三级碳原子，用3°表示；上面的氢为3°H。
4、直接与四个碳原子相连的称为"季碳"或四级碳原子，上面没有氢。
5、手性碳问题找叔碳或者季碳原子。



2.烷烃合成的反应

$$2\,RX + 2\,Na \xrightarrow[\text{ether}]{\text{diethyl}} R-R + 2\,NaX$$

$$R-X + 2\,Li \xrightarrow[\text{ether}]{\text{diethyl}} \underset{\text{Alkyllithium}}{RLi} + LiX$$

$$2\,RLi + CuI \longrightarrow \underset{\substack{\text{Lithium}\\ \text{dialkylcuprate}}}{R_2CuLi} + LiI$$

$$R_2CuLi + R'-X \longrightarrow R-R' + RCu + LiX$$

$$R-X \xrightarrow[HX]{Zn} R-H + ZnX_2$$

$$R-\overset{\overset{O}{\|}}{C}-R'(H) \xrightarrow[\substack{\text{conc. HCl}\\ \triangle}]{\text{Zn-Hg}} RCH_2R'(H)$$

Clemmensen Reduction

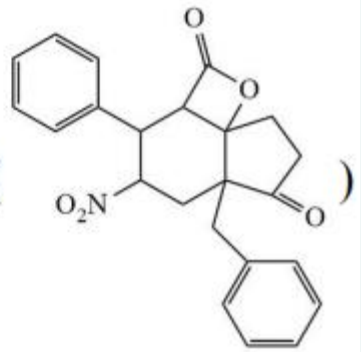
$$R-\overset{\overset{O}{\|}}{C}-R'(H) + H_2N-NH_2 \xrightarrow[\triangle]{\text{base}} RCH_2R'(H) + N_2 + H_2O$$

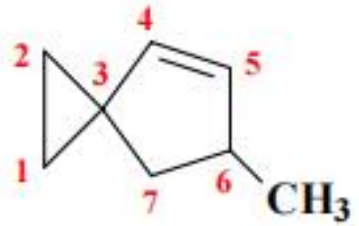
Wolff-Kishner Reduction

3.环烷烃

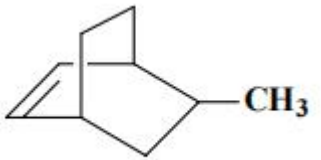
1、环烷烃不等于烷烃，是两种不同的有机化合物

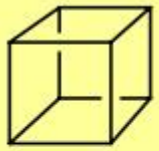
2、对于稠环、螺环、桥环化合物环上面不饱和度的计数问题：

(2022·全国甲卷)H()



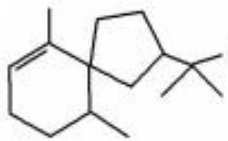
6-甲基螺[2.4]-4-庚烯





立方烷

金刚烷

(2019·天津卷)茅苍术醇(

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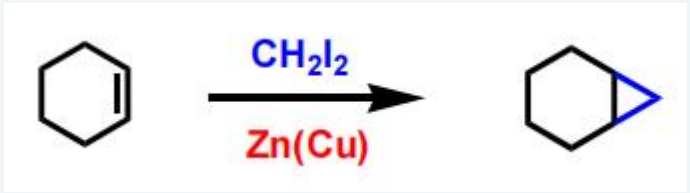
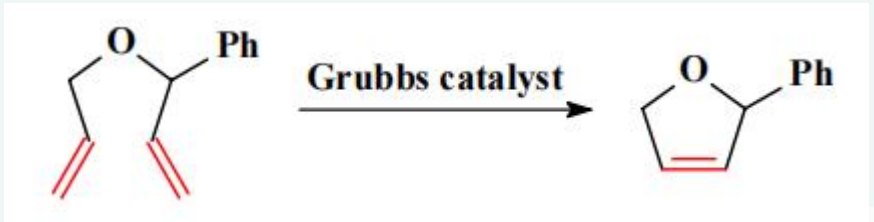
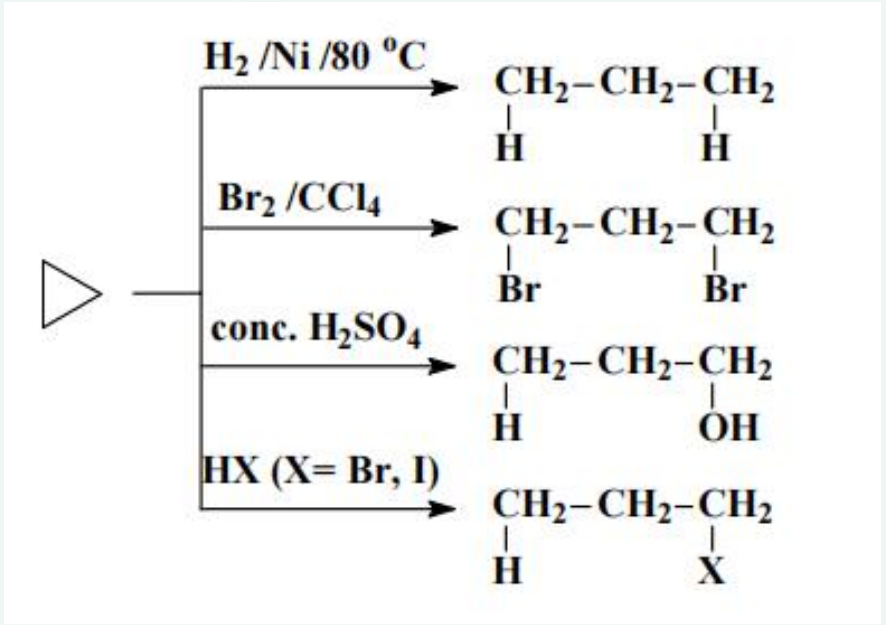
3.环烷烃的合成与开环分解

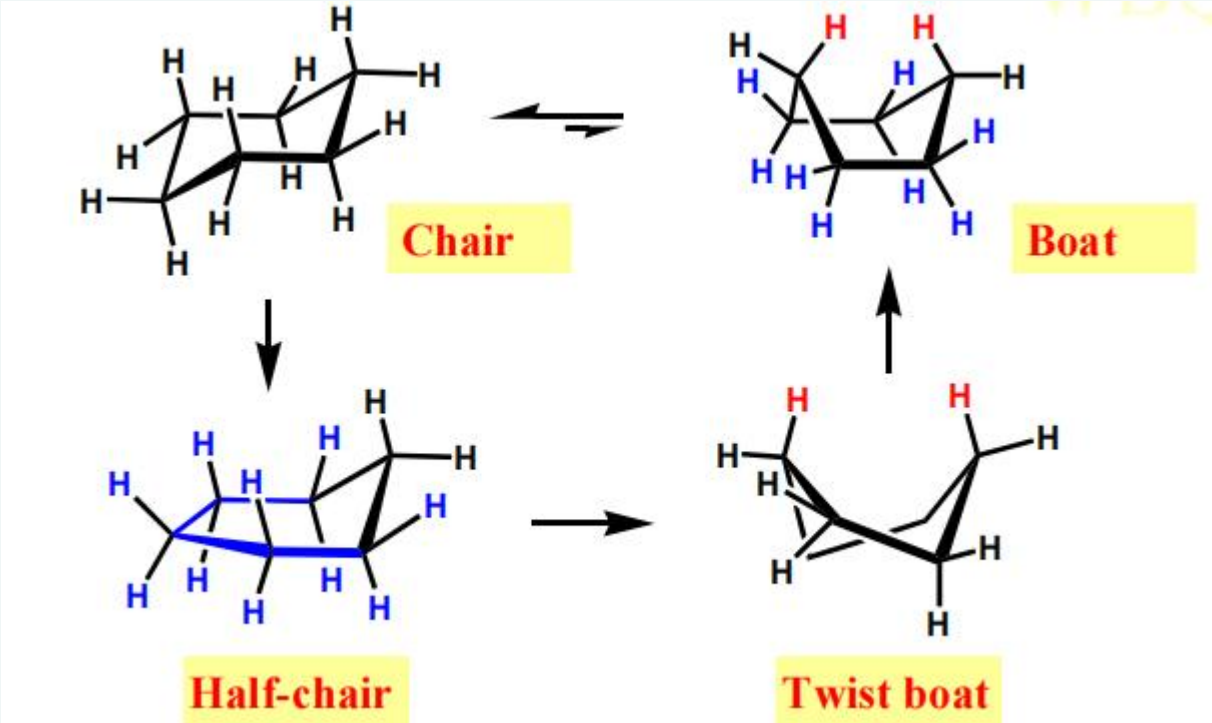






环丙烷易开环、环丁烷反应活性下降；环戊烷、环己烷很稳定不易开环

4.环己烷的构象



$\triangle E=E_{椅式}-E_{船式}\approx 29.7kJ/mol$，室温下可以相互转化

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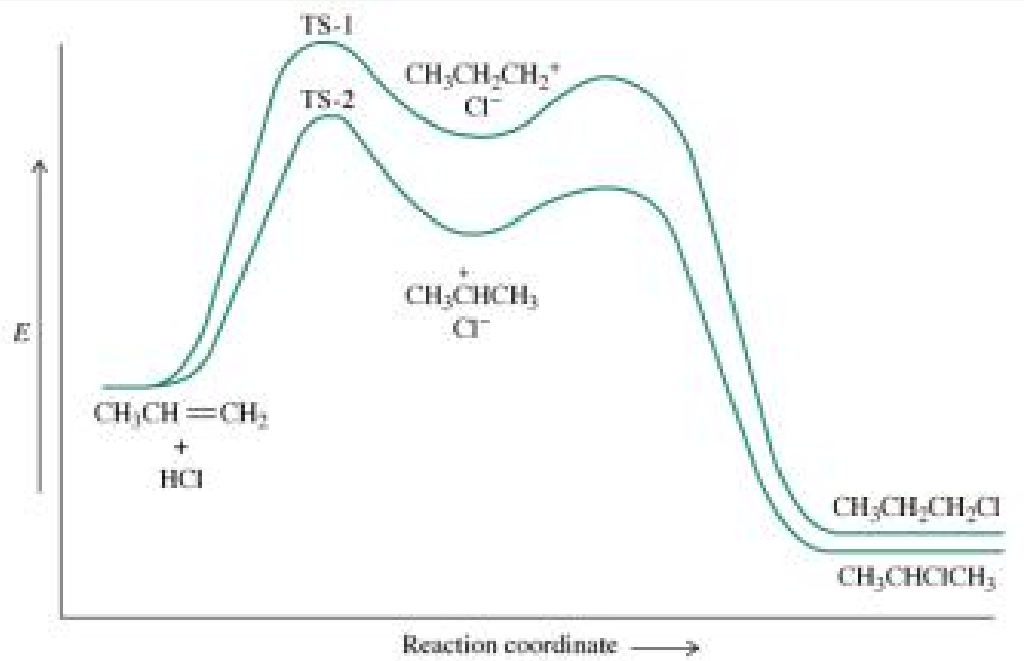
02 烯烃

1.不对称烯烃与不对称小分子的加成——马氏加成

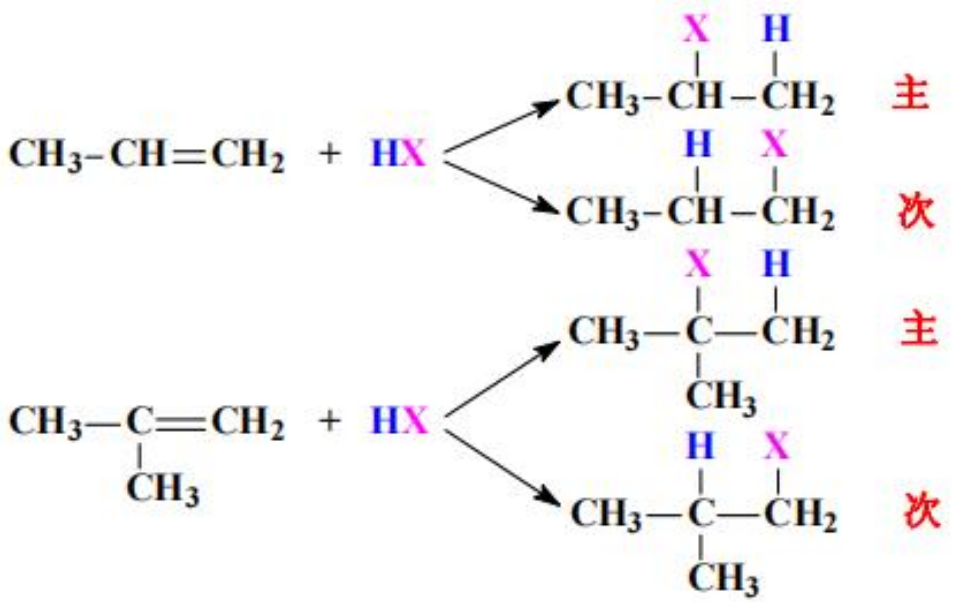
马氏规则：（经验规则）在HX与不对称烯烃的加成中，H总是加在含H较多的C那一侧。

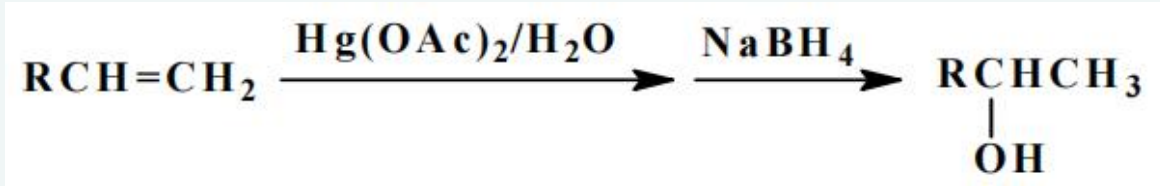
本质：不对称烯烃发生亲电加成时，总是倾向生成更稳定的碳正离子中间体。

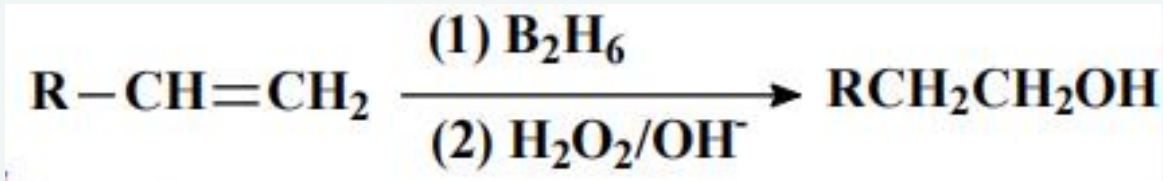


马氏规则是经验规则，存在特例（例如一侧连有吸电子基团或者改变条件），具体加在哪边情况根据题干来决定！

1.不对称烯烃与不对称小分子的加成——马氏加成

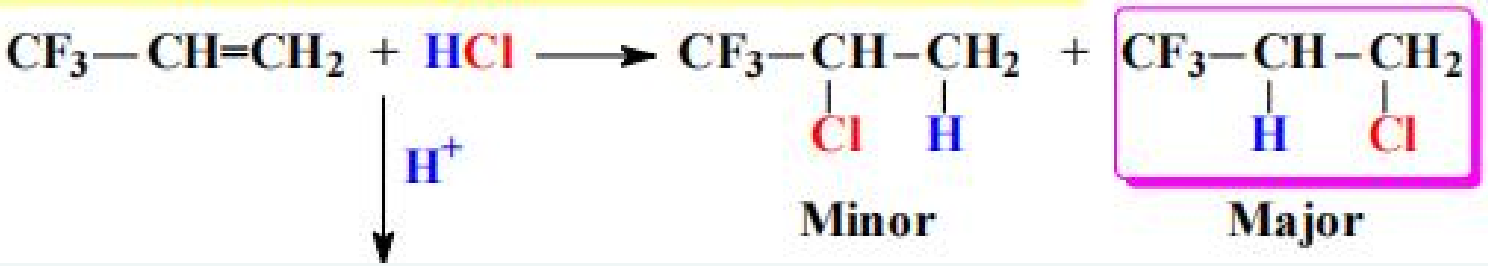


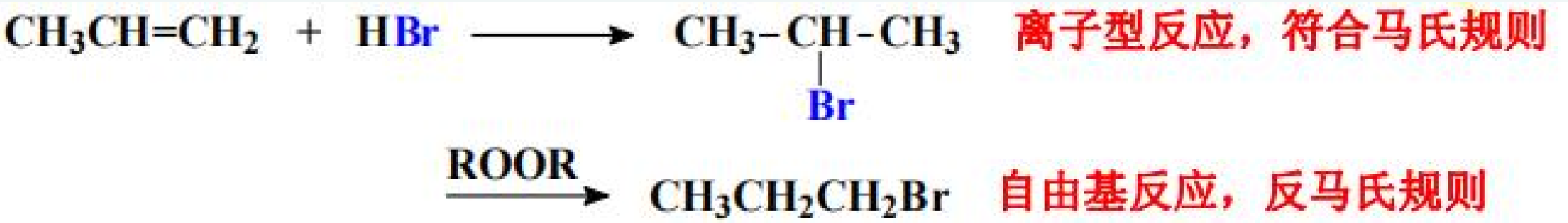




2.不对称烯烃与不对称小分子的加成——反马氏加成

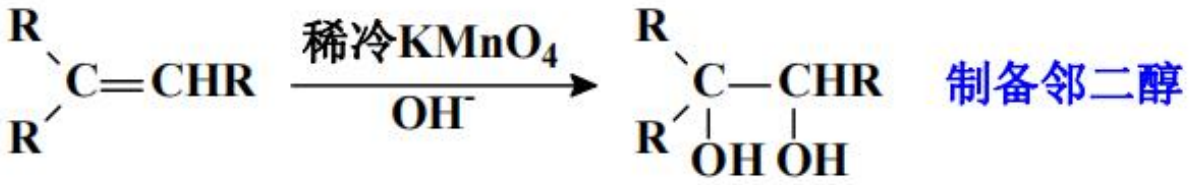
烯碳上有拉电子基团时，反马氏规则





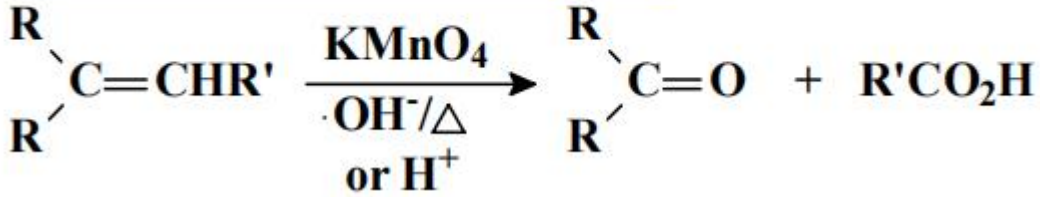
3.烯烃与高锰酸钾、四氧化锇的反应

(a) 稀冷的$KMnO_4$碱性溶液氧化



制备邻二醇

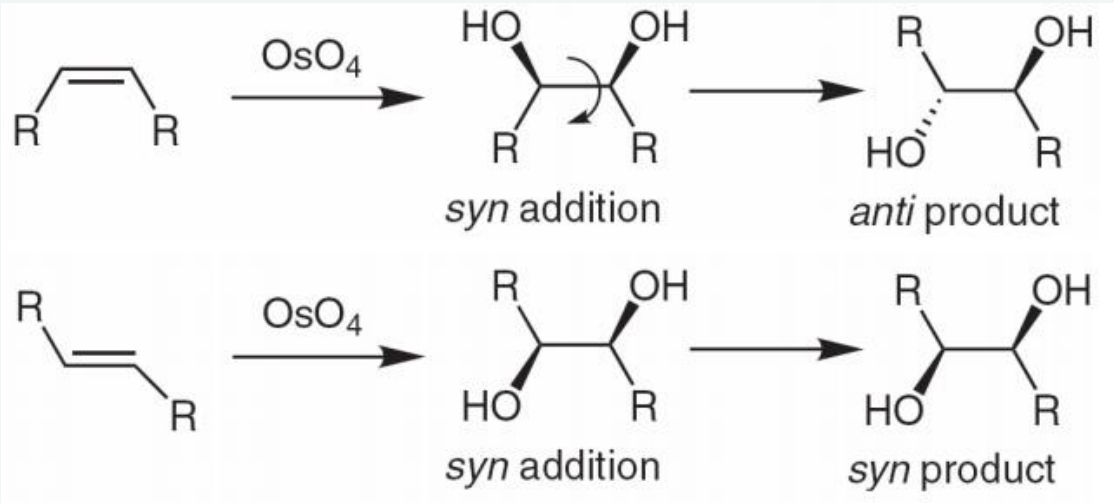
(b) 加热或酸性条件下$KMnO_4$氧化



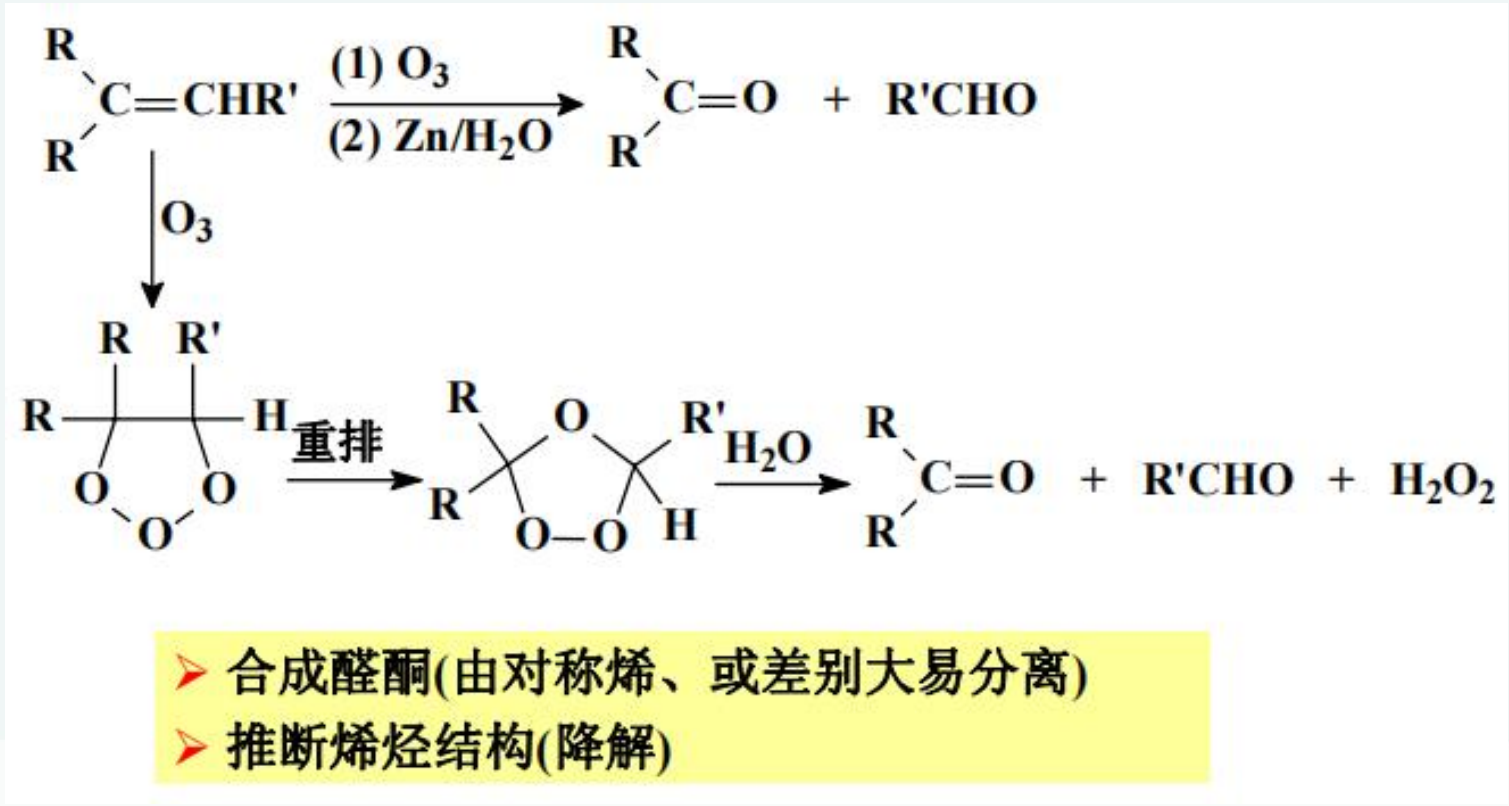
$R_2C= \longrightarrow R_2C=O$

$RCH= \longrightarrow [RCH=O] \longrightarrow RCO_2H$

$CH_2= \longrightarrow [CH_2=O] \longrightarrow [H_2CO_3] \longrightarrow CO_2 + H_2O$

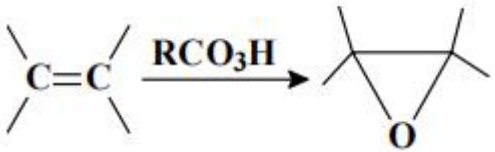


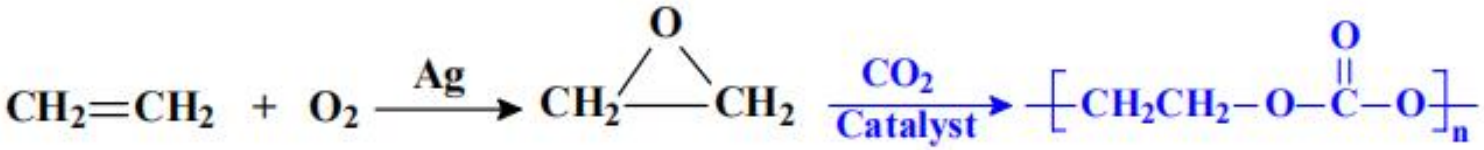
4.烯烃的臭氧氧化，还原水解

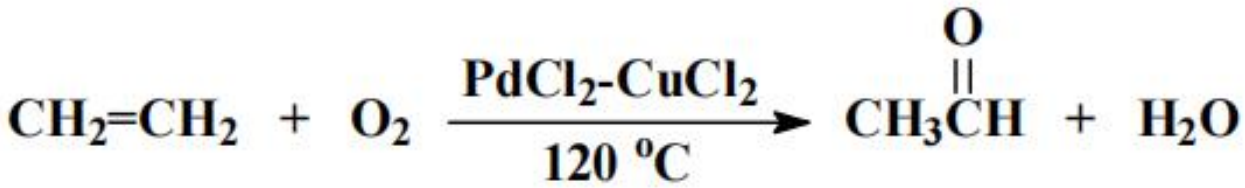


- 合成醛酮(由对称烯、或差别大易分离)
- 推断烯烃结构(降解)

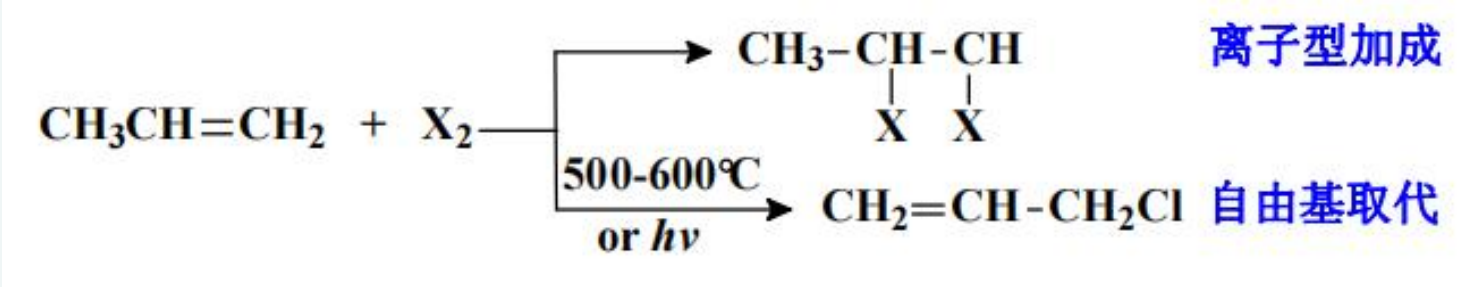
5.烯烃的过氧酸氧化或者催化氧化

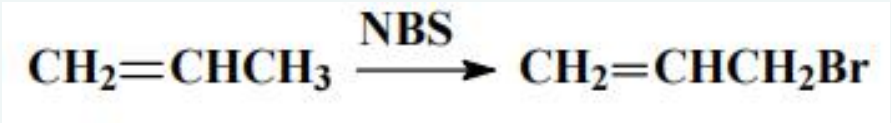




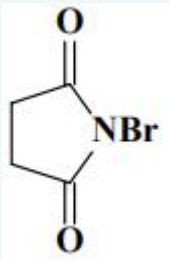


6.烯烃的取代反应





NBS：N-溴代丁二（琥珀）酰亚胺



7.二烯烃

二烯烃分为累积二烯烃、共轭二烯烃、孤立二烯烃

（1）累积二烯烃不稳定，中间碳原子sp杂化，两个双键所在平面互相垂直

（2）孤立二烯烃按照两个普通的烯烃处理即可

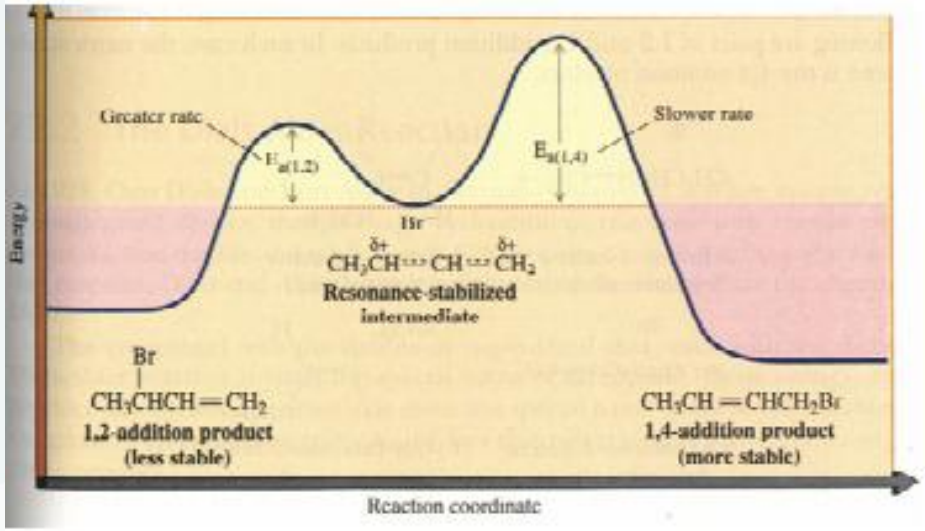
（3）共轭二烯烃具有1,4加成的特殊性质，着重讨论共轭二烯烃。

7.共轭二烯烃的1,2加成与1,4加成讨论

二烯烃实际上也不应该算作纯正的烯烃

1,4加成产物双键在中间，产物稳定，热力学控制产物

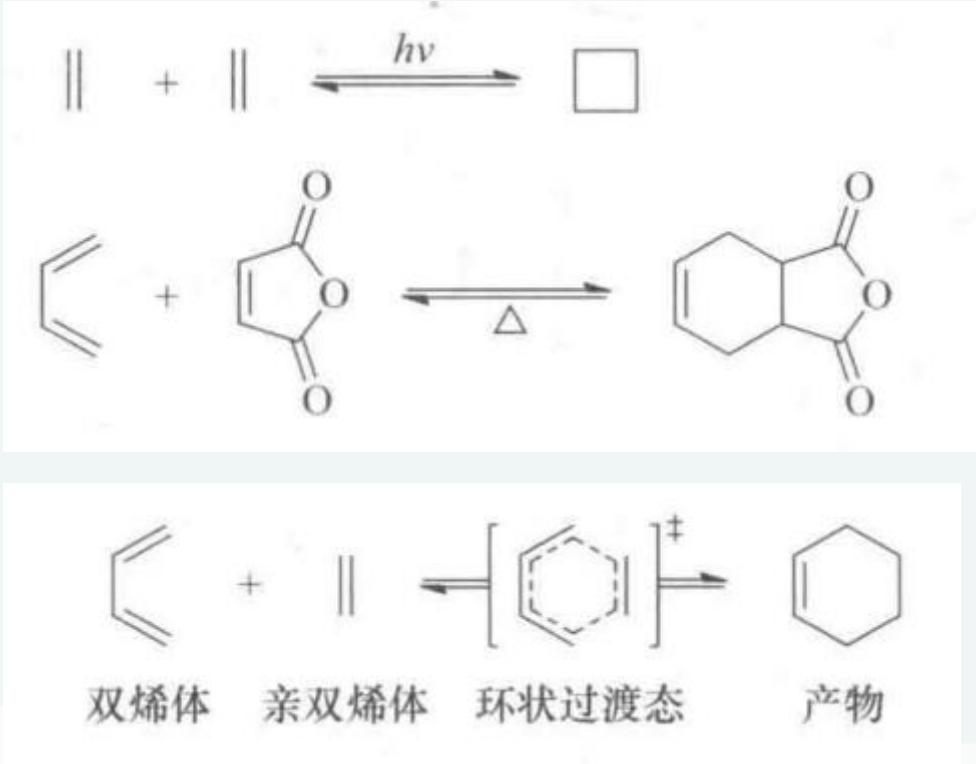
1,2加成中间体稳定，速度快，动力学控制产物



$CH_2=CH\overset{\oplus}{C}H-CH_3 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH-CH_3$

- 较低温度下，经历低能量通道形成1,2-加成产物，动力学控制；较高温度下，经历高能量通道形成1,4-加成产物，热力学控制；
- 1,2-加成产物可以在高温下分解退回到中间体，再经历高能量通道形成1,4-加成产物即热力学稳定产物.

8.D-A反应



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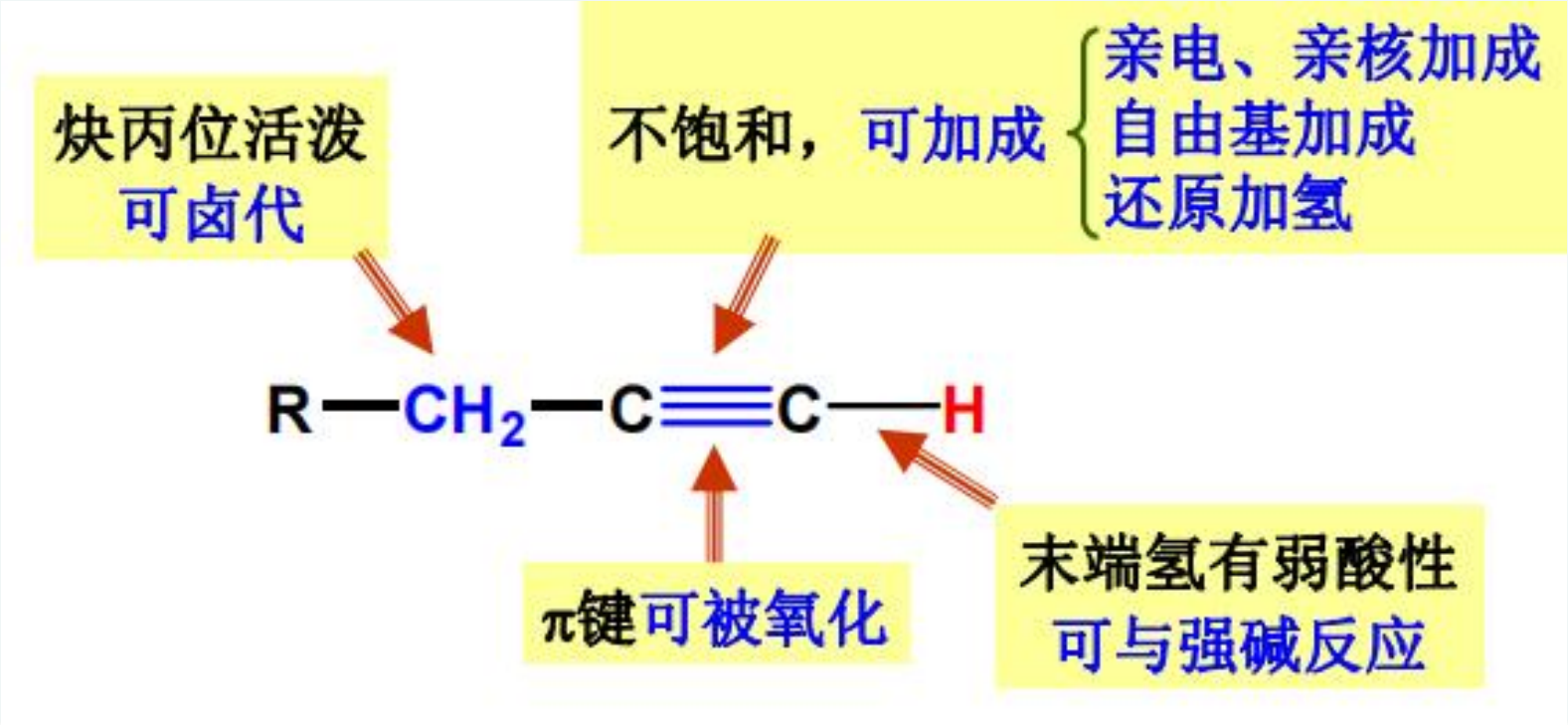
03 炔烃

1.炔烃性质概述


炔丙位活泼
可卤代
不饱和，可加成
亲电、亲核加成
自由基加成
还原加氢
R—CH2—C≡C—H
π键可被氧化
末端氢有弱酸性
可与强碱反应

2.端位炔烃H的“弱酸性”

$RC{\equiv}CH + Na \longrightarrow RC{\equiv}CNa + 1/2\ H_2\uparrow$

$RC{\equiv}CH + NaOH \rightleftharpoons RC{\equiv}CNa + H_2O$

$pKa = 25$ $\qquad$ $pKa = 15.7$

$RC{\equiv}CH + NaNH_2 \longrightarrow RC{\equiv}CNa + NH_3$

$pKa = 34$

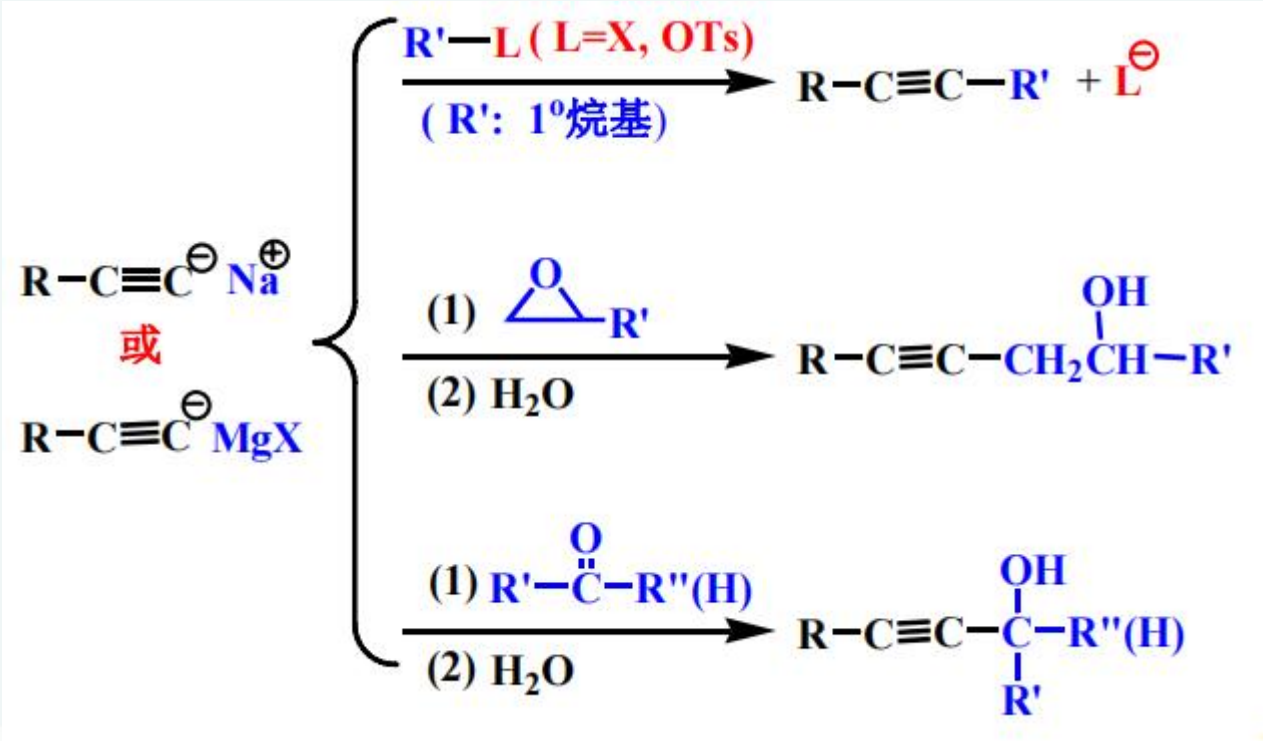
$RC{\equiv}CH + R'MgX \longrightarrow RC{\equiv}CMgX + R'H$

or R'Li $\qquad$ $RC{\equiv}CLi$ $\qquad$ $pKa = 50$

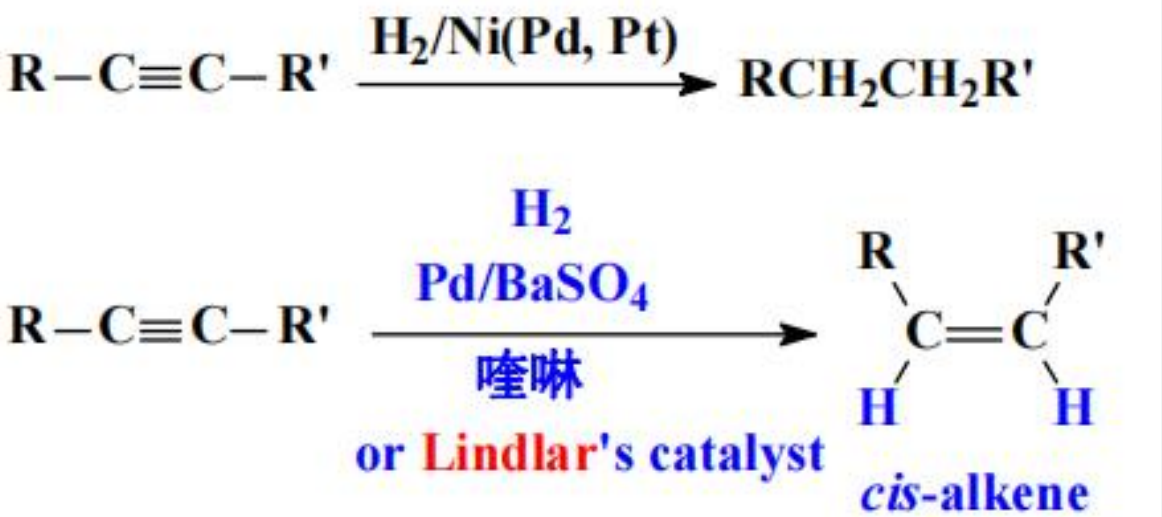
$HC{\equiv}CH \xrightarrow{Na} \xrightarrow{RX} HC{\equiv}CR$

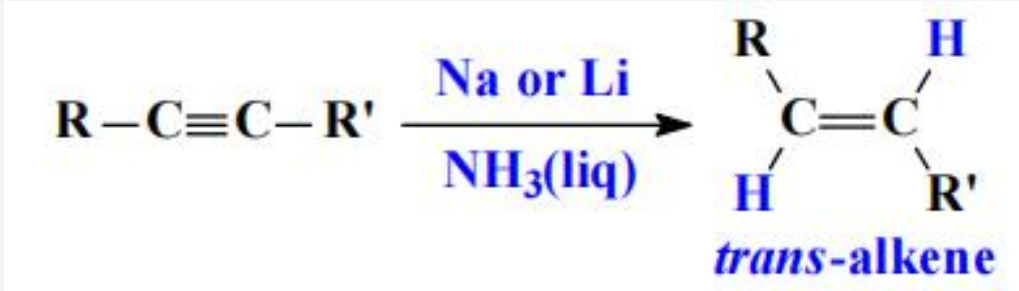
酸性:	CH_3CO_2H	> H_2O	> ROH	> $CH_3C{\equiv}CH$	> NH_3	> $CH_2{=}CH_2$	> CH_3CH_3
p*K*a	4.8	15.7	16~19	25	34	44	50

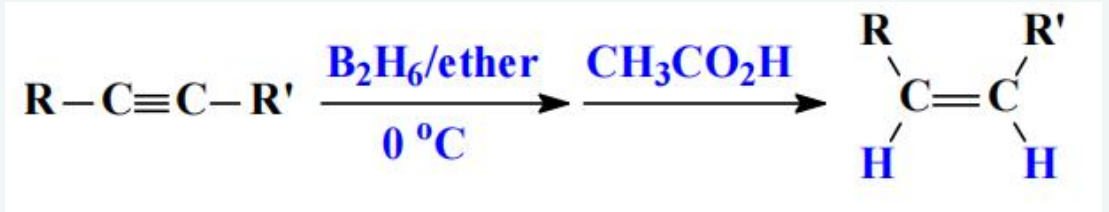
3.炔基负离子的合成应用



4.炔烃加氢


R–C≡C–R'
H2/Ni(Pd, Pt)
RCH2CH2R'
R–C≡C–R'
H2
Pd/BaSO4
喹啉
or Lindlar's catalyst
R
R'
C=C
H
H
cis-alkene


R–C≡C–R'
Na or Li
NH3(liq)
R
H
C=C
H
R'
trans-alkene


R–C≡C–R'
B2H6/ether
0 °C
CH3CO2H
R
R'
C=C
H
H

5.炔烃加成

$$HC{\equiv}CH + HCN \xrightarrow{NH_4Cl,\ Cu_2Cl_2} H_2C{=}CHCN$$

丙烯腈

$$2\,HC{\equiv}CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2{=}CH{-}C{\equiv}CH$$

乙烯基乙炔

$$HC{\equiv}CH + HO\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[210\text{-}250\ ^{o}C]{Zn(OAc)_2} H_2C{=}CHO\overset{\overset{O}{\|}}{C}CH_3$$

醋酸乙烯酯

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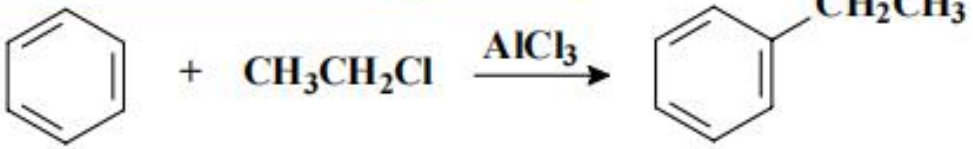
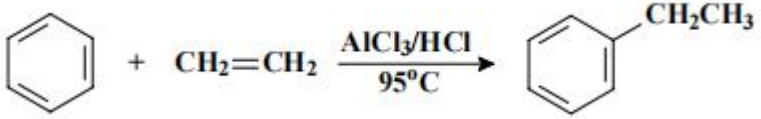
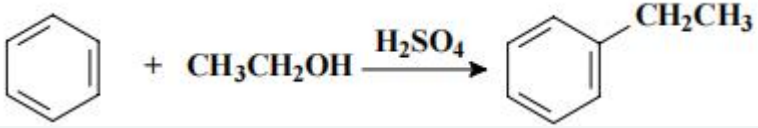
04 芳香烃

1.芳香烃的取代反应

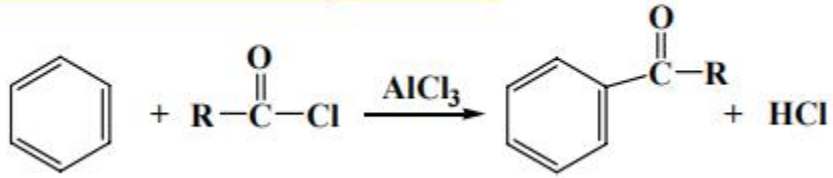
(1) Friedel-Crafts Alkylation:

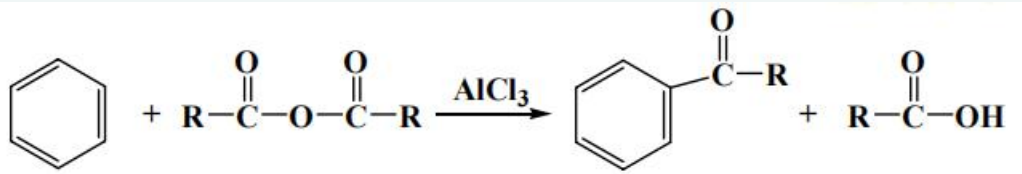






(2) Friedel-Crafts Acylation:

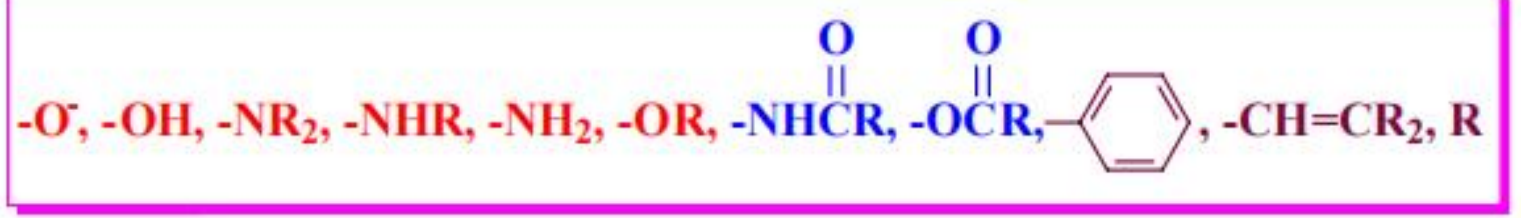


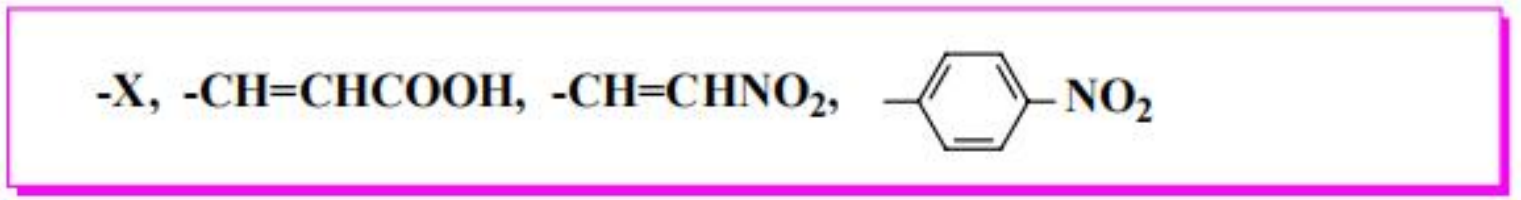


2.一取代芳香烃上面再发生取代反应

邻对位定位基可能是致活也可能是致钝，间位定位基只能是致钝

第一类：邻对位定位基





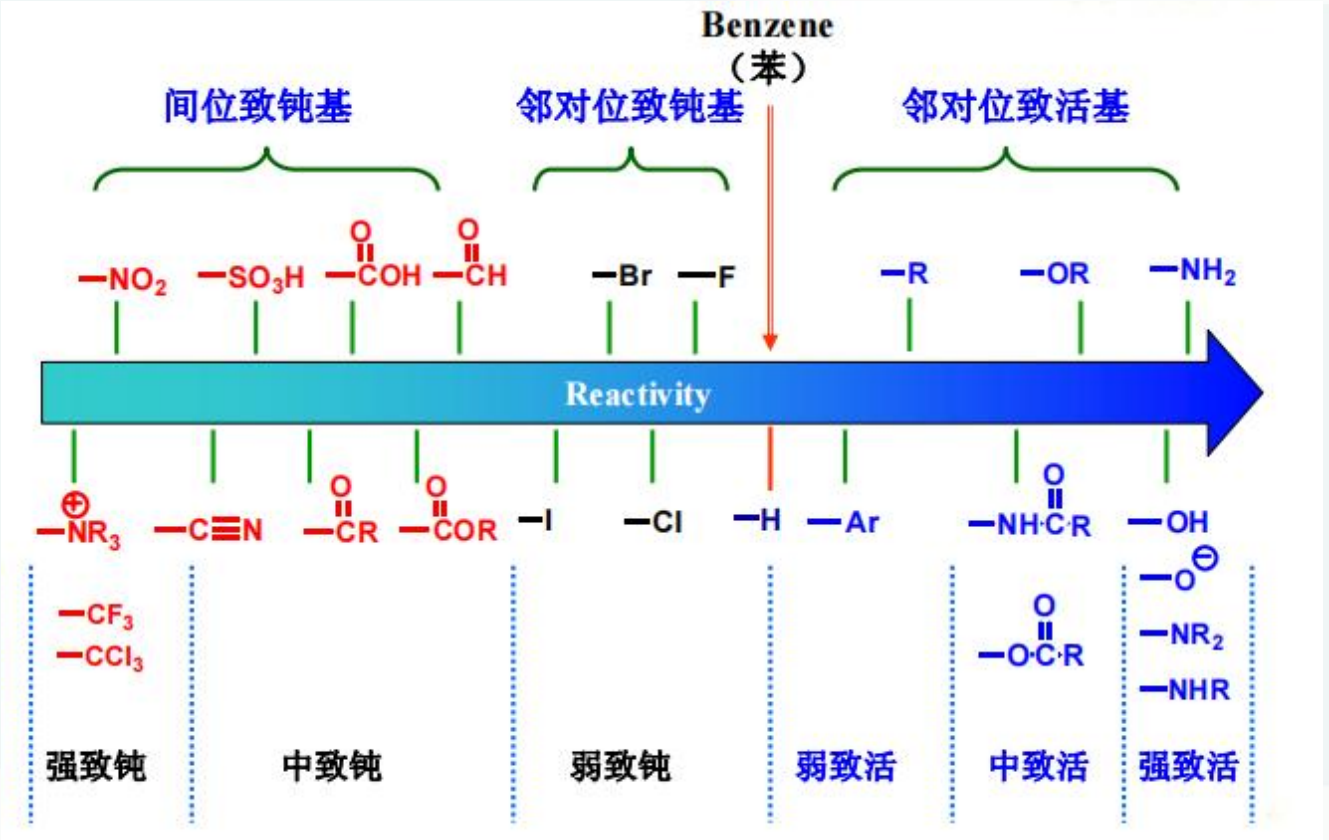
2.一取代芳香烃上面再发生取代反应

邻对位定位基可能是致活也可能是致钝，间位定位基只能是致钝

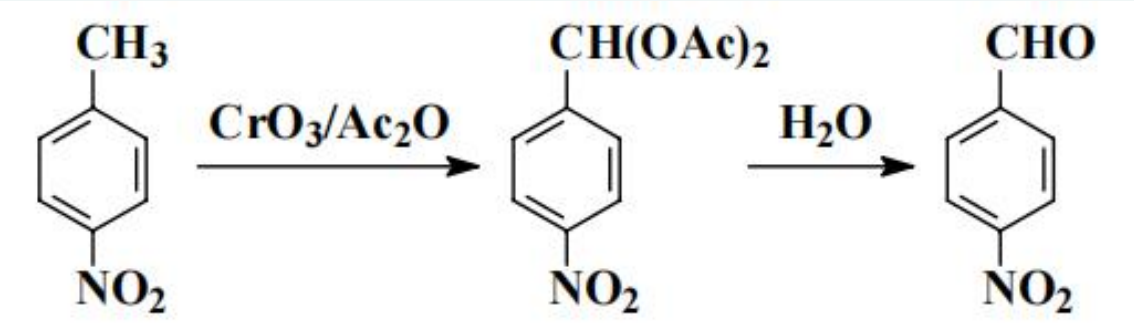
第二类：间位定位基

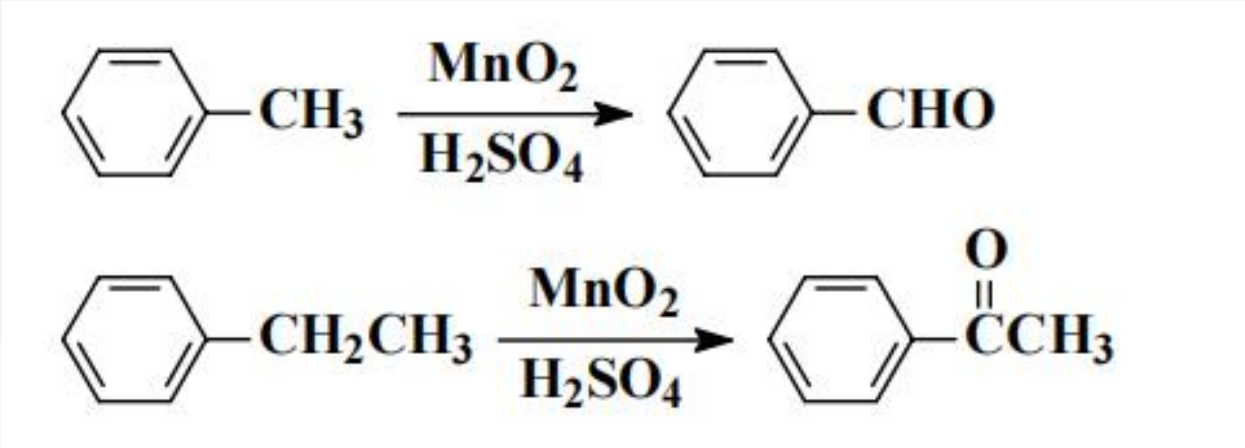
$-NR_3^+$, $-NO_2$, $-CF_3$, $-CCl_3$, $-CN$, $-SO_3H$, $-\overset{\overset{O}{\|}}{C}R(H)$, $-\overset{\overset{O}{\|}}{C}OR(H, NR_2)$

2.一取代芳香烃上面再发生取代反应



3.芳香烃脂肪链氧化反应





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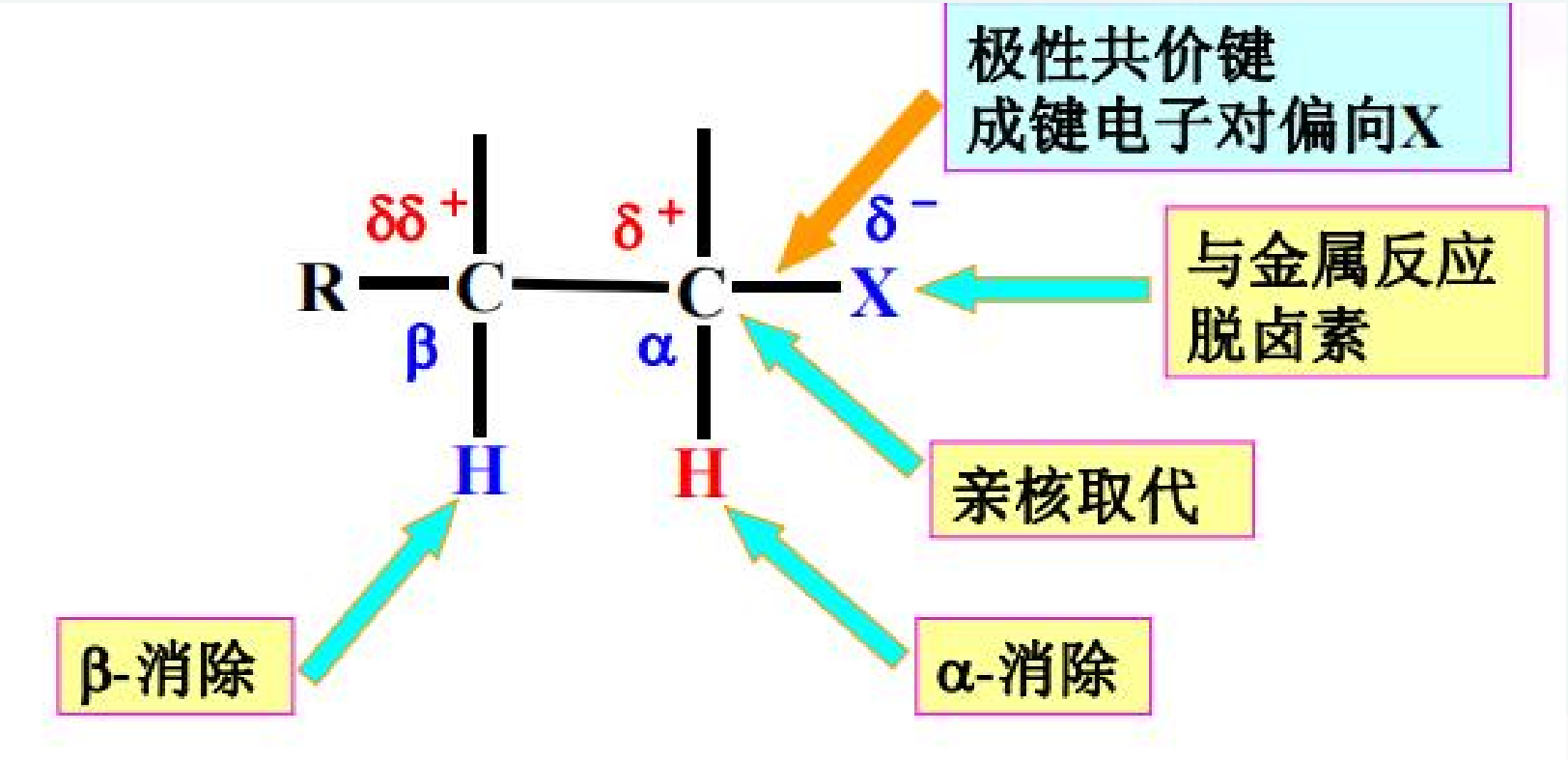
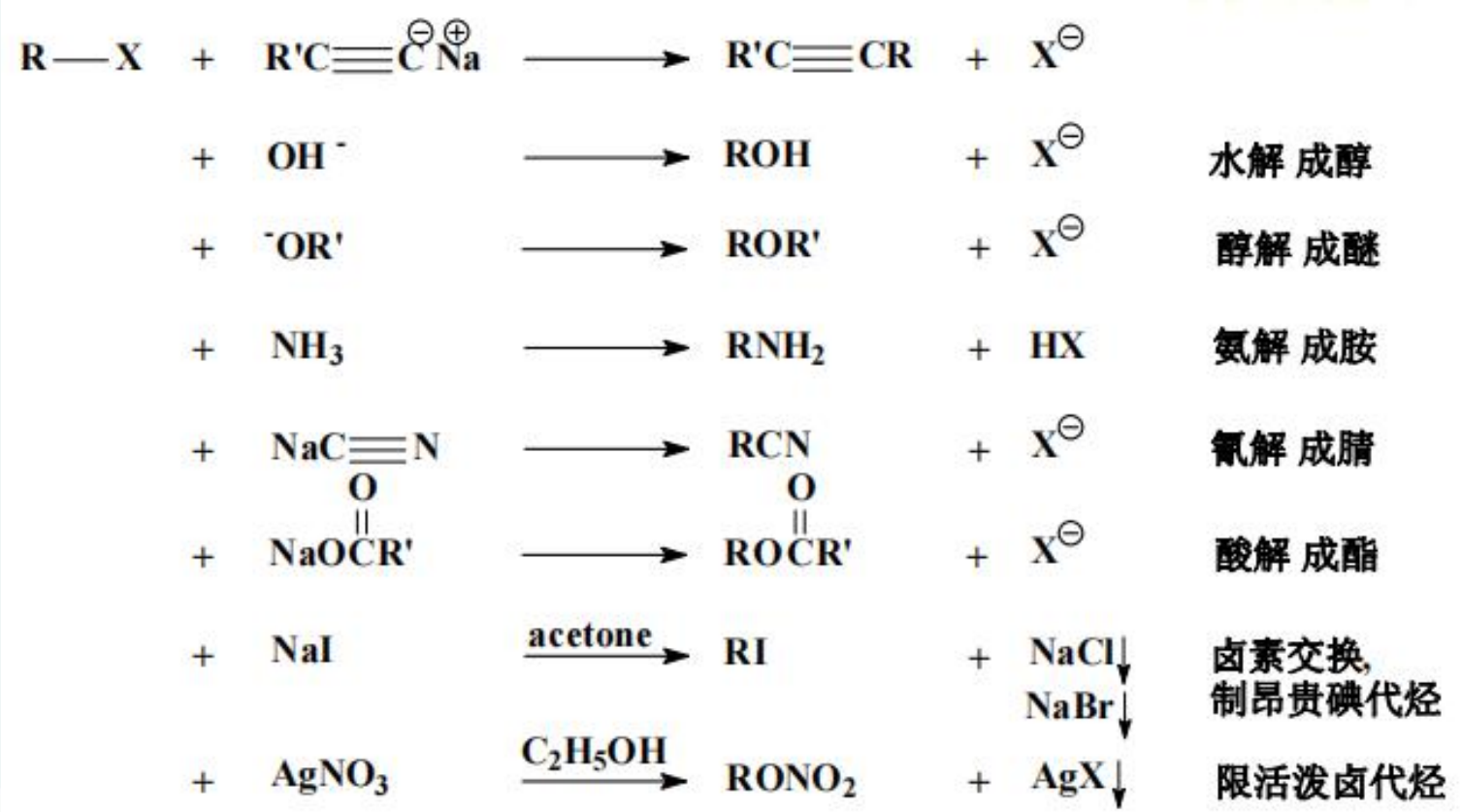
05 卤代烃

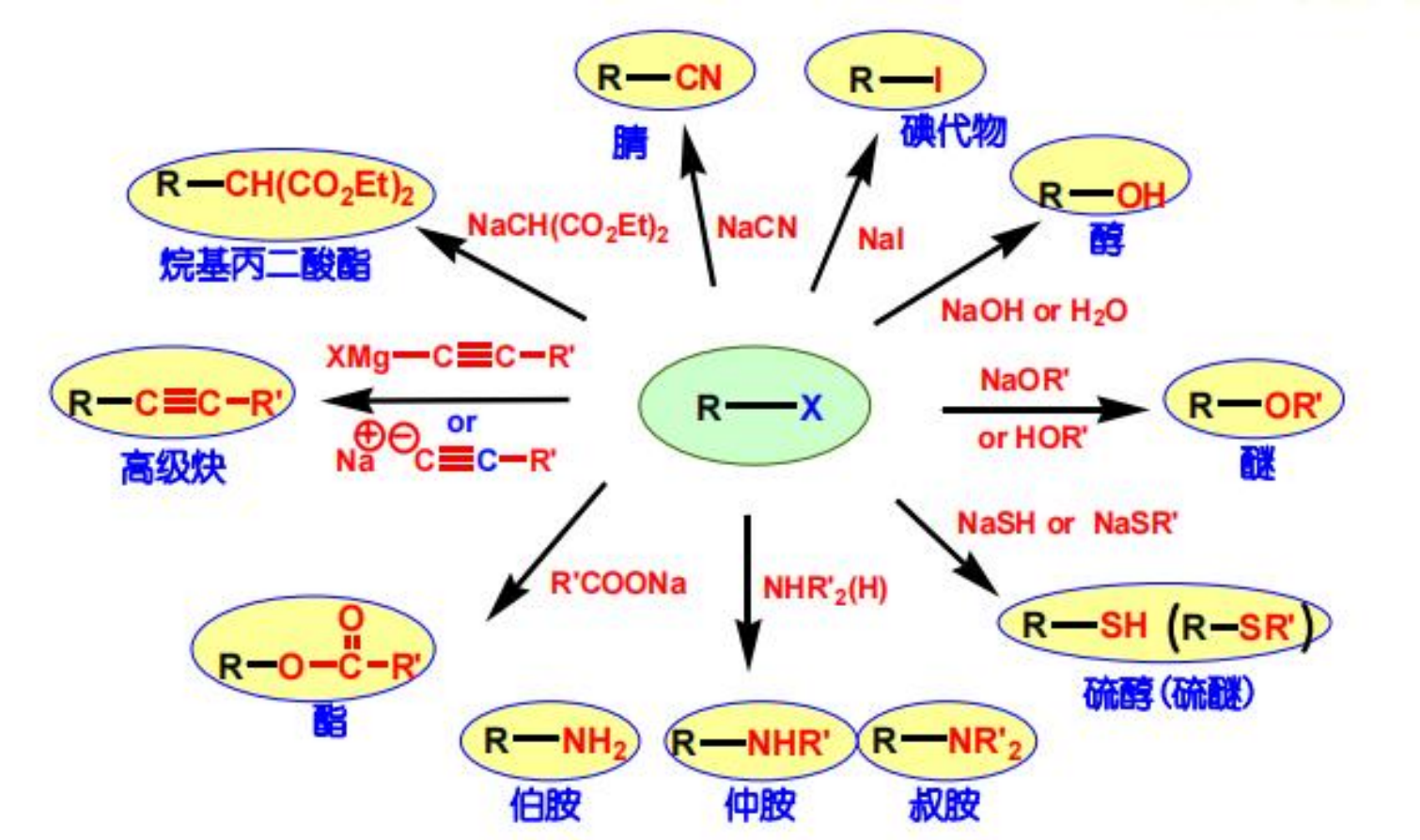
1.卤代烃性质概述



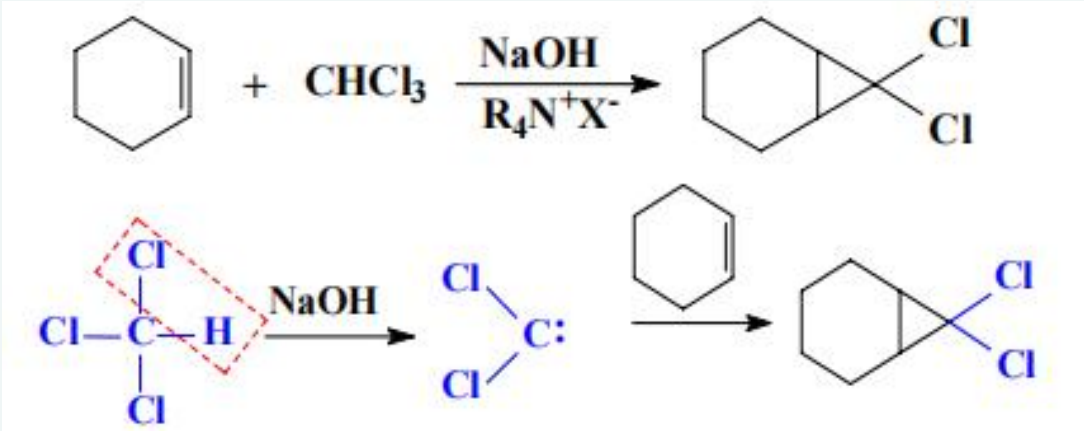
1.卤代烃性质概述


R—X + R'C≡C⊖ Na⊕ → R'C≡CR + X⊖
+ OH⁻ → ROH + X⊖ 水解 成醇
+ ⁻OR' → ROR' + X⊖ 醇解 成醚
+ NH3 → RNH2 + HX 氨解 成胺
+ NaC≡N → RCN + X⊖ 氰解 成腈
+ NaOCR' → ROCR' + X⊖ 酸解 成酯
+ NaI acetone → RI + NaCl↓ NaBr↓ 卤素交换, 制昂贵碘代烃
+ AgNO3 C2H5OH → RONO2 + AgX↓ 限活泼卤代烃

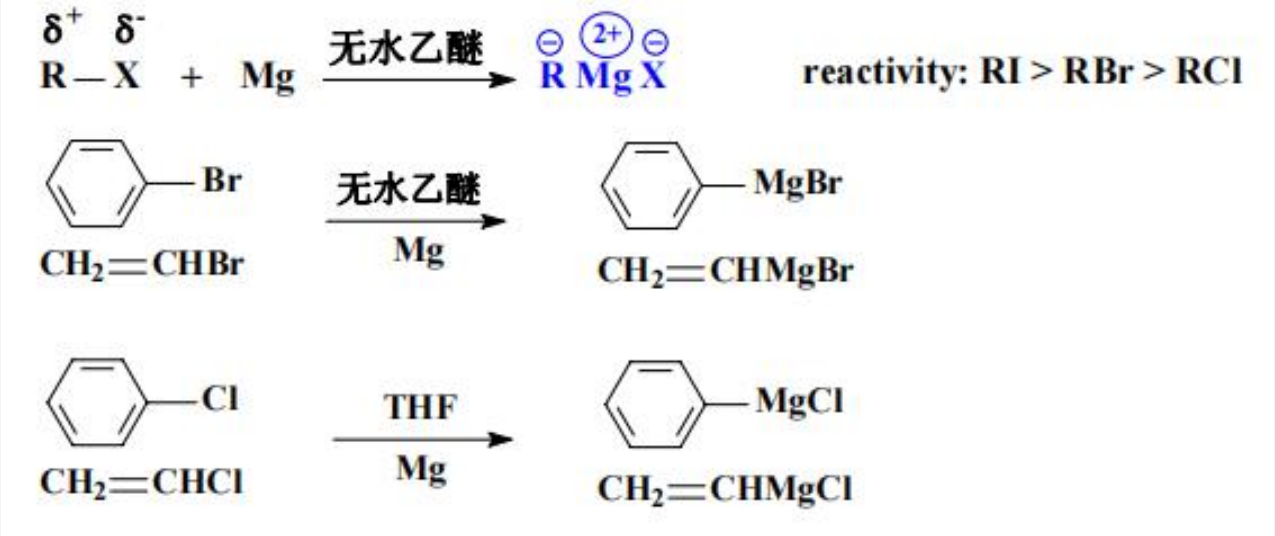
1.卤代烃性质概述


R—CN
腈
R—I
碘代物
R—CH(CO2Et)2
烷基丙二酸酯
NaCH(CO2Et)2
NaCN
NaI
R—OH
醇
NaOH or H2O
XMg—C≡C—R'
R—C≡C—R'
高级炔
or
Na⊕ ⊖C≡C—R'
R—X
NaOR'
or HOR'
R—OR'
醚
NaSH or NaSR'
R'COONa
NHR'2(H)
R—SH (R—SR')
硫醇(硫醚)
R—O—C(=O)—R'
酯
R—NH2
伯胺
R—NHR'
仲胺
R—NR'2
叔胺

2.α-消去——生成卡宾的反应



3.格氏试剂的制备


δ+ δ-
R—X + Mg
无水乙醚
2+
R Mg X
reactivity: RI > RBr > RCl
Br
CH2=CHBr
无水乙醚
Mg
MgBr
CH2=CHMgBr
Cl
CH2=CHCl
THF
Mg
MgCl
CH2=CHMgCl

4.格氏试剂的反应

(a) 与活泼氢反应

$RMgX + H-OH \longrightarrow RH + Mg(OH)X$ （还原卤代烃）

$+ D-OD \longrightarrow RD + Mg(OD)X$ （分子中引入同位素）

$+ H-OR \longrightarrow RH + Mg(OR)X$

$+ H-NHR \longrightarrow RH + Mg(NHR)X$

$+ H-C\equiv CR' \longrightarrow RH + R'C\equiv CMgX$ （制备炔格氏试剂）

$+ H-OOCR \longrightarrow RH + RCOOMgX$

$+ H-Y \longrightarrow RH + MgY_2$

制格氏试剂需严格无水或其它活泼氢存在

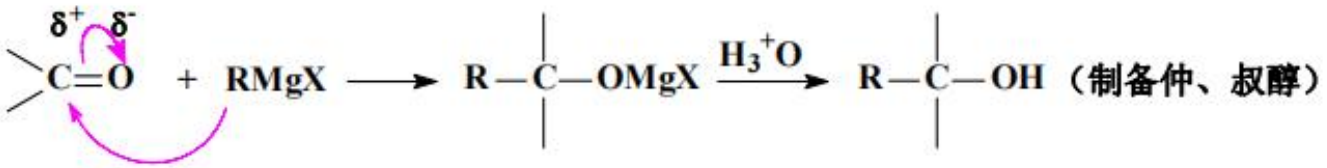
(b) 与O_2反应

$$RMgX + O_2 \longrightarrow ROMgX \xrightarrow{H_2O} ROH + Mg(OH)X$$

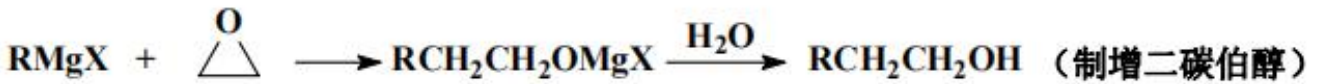
制格氏试剂需严格无氧

4.格氏试剂的反应

(c) 与极性不饱和官能团反应

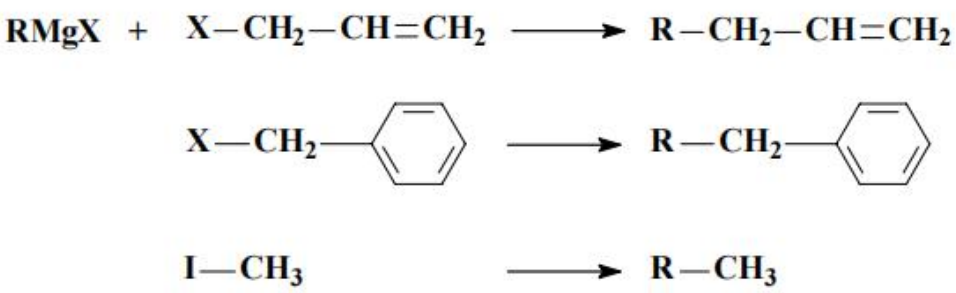


$RMgX + HCHO \longrightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH$ （制增一碳伯醇）

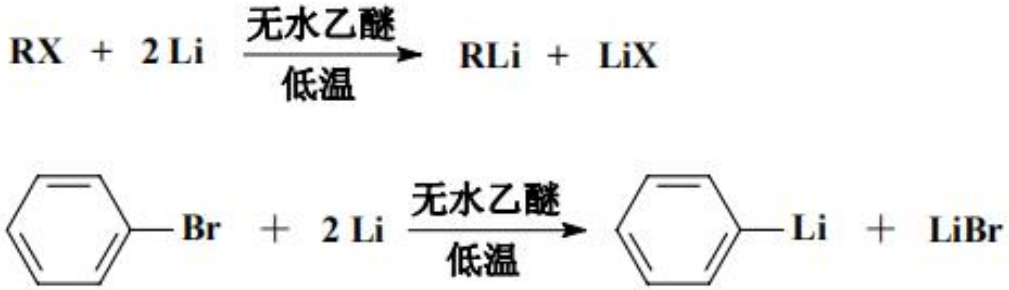


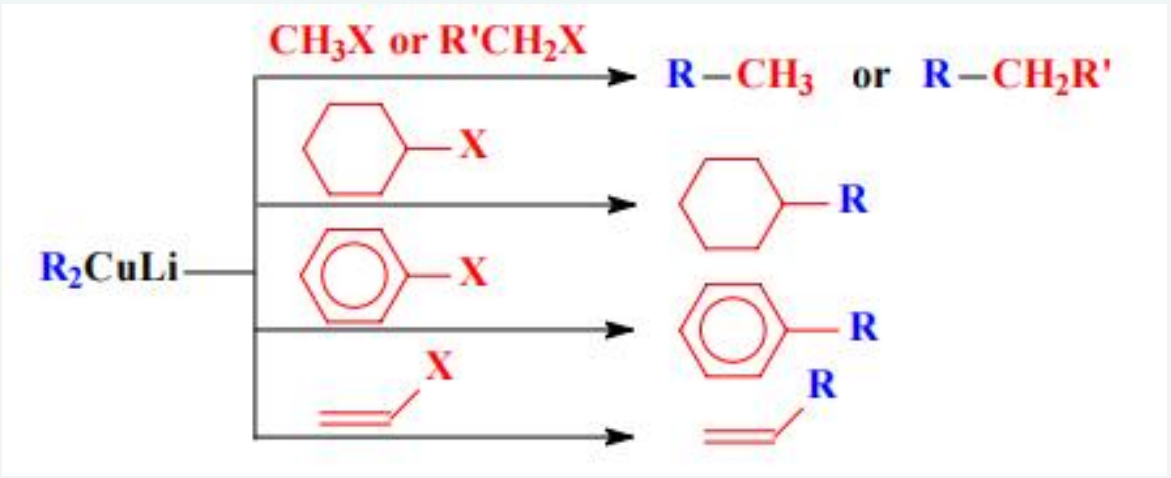
$RMgX + CO_2 \longrightarrow RCOOMgX \xrightarrow{H_2O} RCOOH$ （制增一碳酸）

(d) 偶联反应

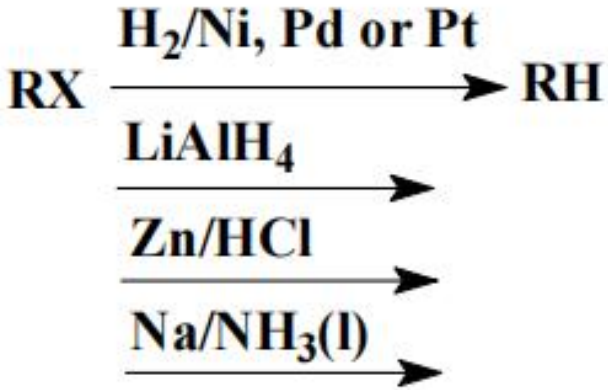


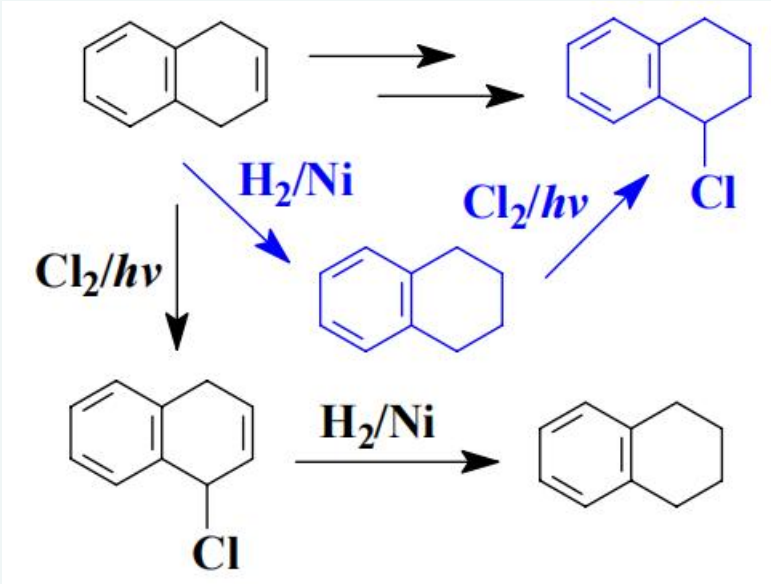
5.锂试剂与二烷基铜锂试剂

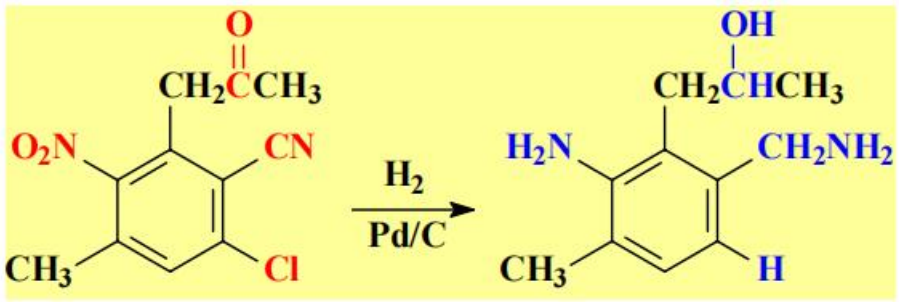




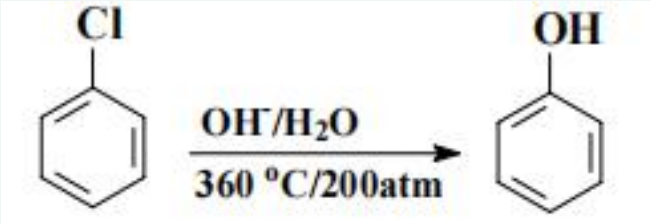
6.卤代烃的还原

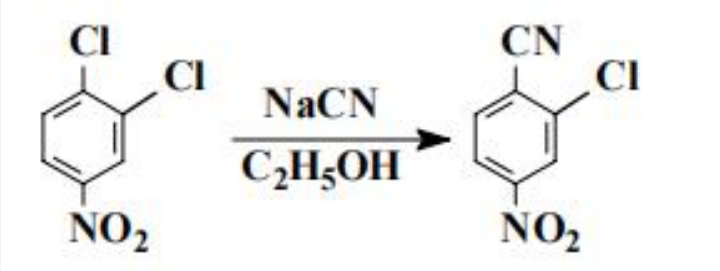

RX
H_2/Ni, Pd or Pt
RH
$LiAlH_4$
Zn/HCl
$Na/NH_3(l)$

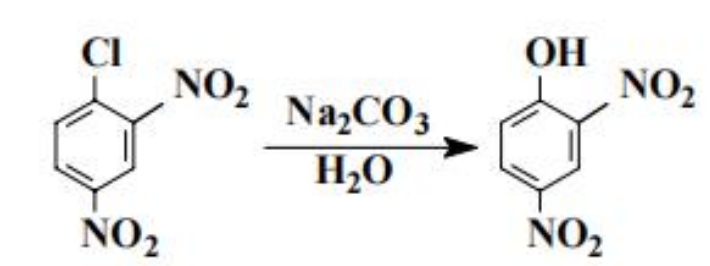

H_2/Ni
Cl_2/hv
Cl
Cl_2/hv
H_2/Ni
Cl


O
CH_2CCH_3
O_2N
CN
CH_3
Cl
H_2
Pd/C
OH
CH_2CHCH_3
H_2N
CH_2NH_2
CH_3
H

7.芳香卤代烃的取代


Cl
OH
OH⁻/H₂O
360 °C/200atm

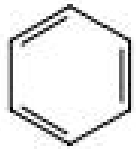

Cl
Cl
NO₂
NaCN
C₂H₅OH
CN
Cl
NO₂


Cl
NO₂
NO₂
Na₂CO₃
H₂O
OH
NO₂
NO₂

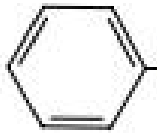
8.卤代烃的其他制备方法

$$ROH + \begin{matrix} HX \\ PX_3 \\ PX_5 \end{matrix} \longrightarrow R—X + H_2O$$

$$ROH + SOCl_2 \longrightarrow R—X + HCl + SO_2$$



$$+ HCHO + HCl \xrightarrow{ZnCl_2}$$



$$—CH_2Cl$$

（相当于付氏烷基化）

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06 醇

1.取代反应（制备卤代烃）

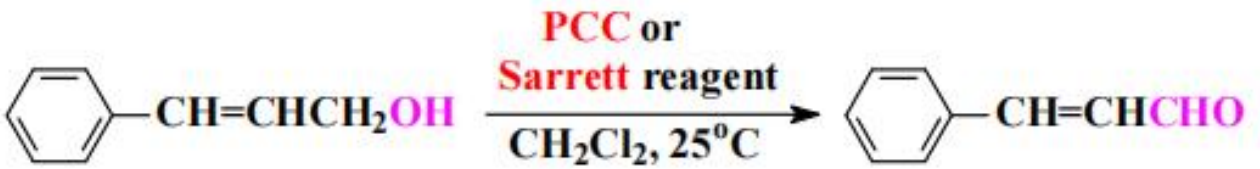
$$CH_3CH_2CH_2OH + HCl \xrightarrow[\triangle]{ZnCl_2} CH_3CH_2CH_2Cl + H_2O$$

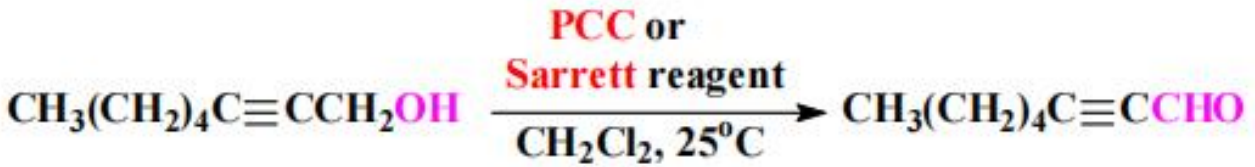
$$3\,ROH + PX_3 \longrightarrow 3\,RX + P(OH)_3$$

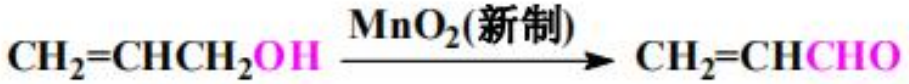
(X = Br, I)

$$ROH + SOCl_2 \xrightarrow{\triangle} RCl + SO_2 + HCl$$

2.氧化反应





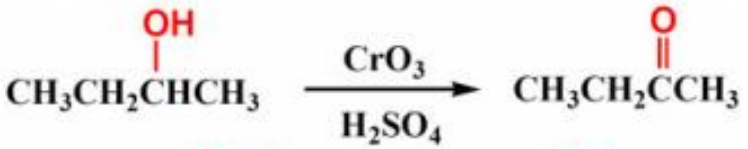


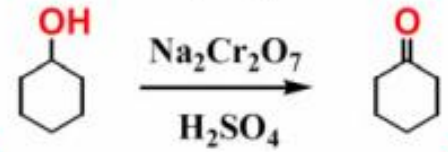
都可以温和地将伯醇氧化成醛，同时对不饱和键无影响

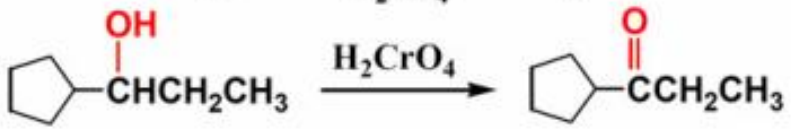
2.氧化反应

$R_2CHOH \longrightarrow R_2C{=}O$

铬氧化剂都可将仲醇氧化成酮, 其中Jones试剂对双键无影响







Jones reagent:

CrO_3-H_2SO_4-Me_2CO aq.

2.氧化反应

$$RCH_2OH \longrightarrow RCOOH$$

$$CH_3CH_2CH_2OH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} CH_3CH_3COOH$$

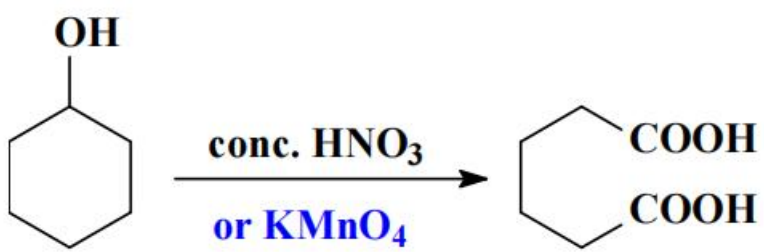
HNO_3

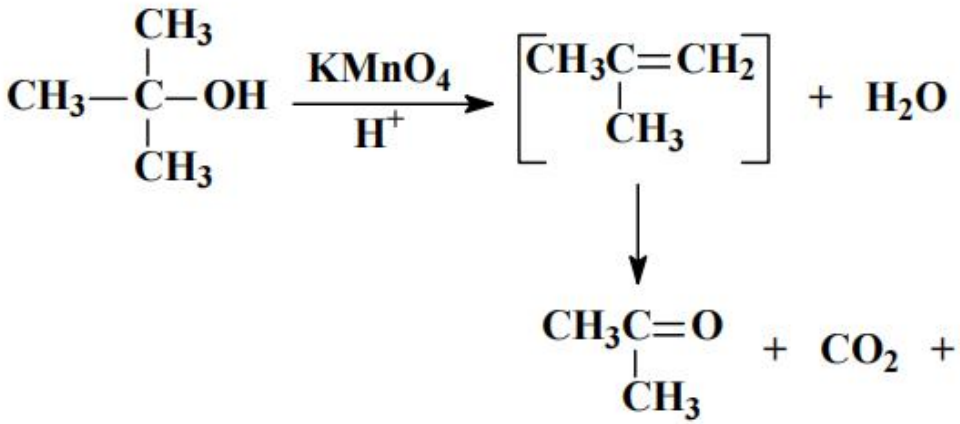
$KMnO_4/OH^-$ or H^+

- 冷、稀、中性高锰酸钾不能氧化醇，但在较强烈的条件下(如酸、碱、加热)醇可被氧化
- $KMnO_4$在不同条件下的活性：酸性> 碱性> 中性
- 加热有利于反应

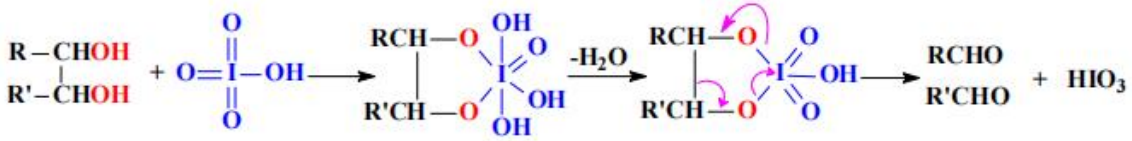
2.氧化反应

$R_2CHOH \longrightarrow RCOOH$



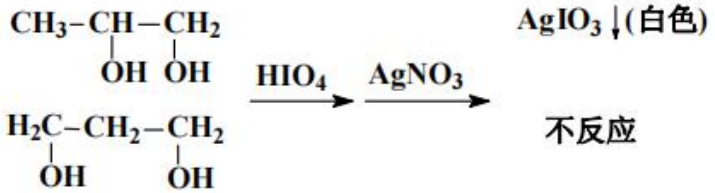


3.多元醇氧化反应

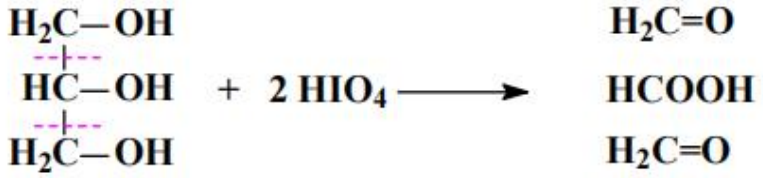


$$HIO_3 + AgNO_3 \longrightarrow AgIO_3\downarrow\text{(白色)}$$

只有邻二醇反应，可用于鉴别邻二醇



- 反应是定量的，可根据HIO_4的用量推知有多少组邻二醇



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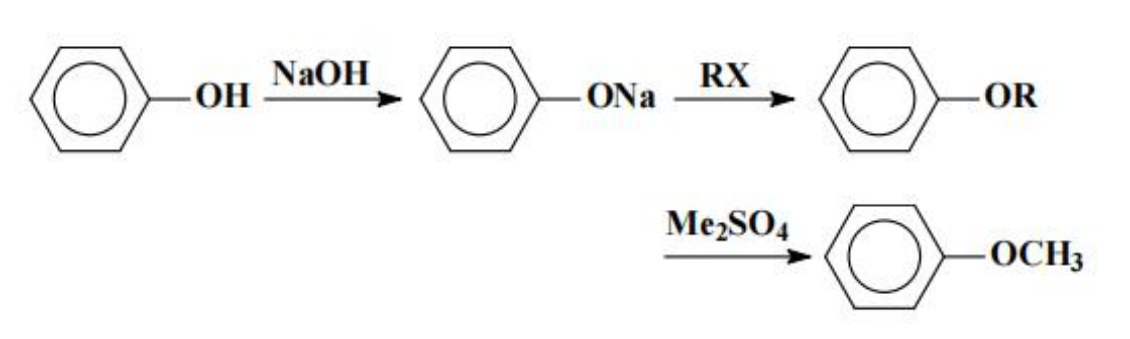
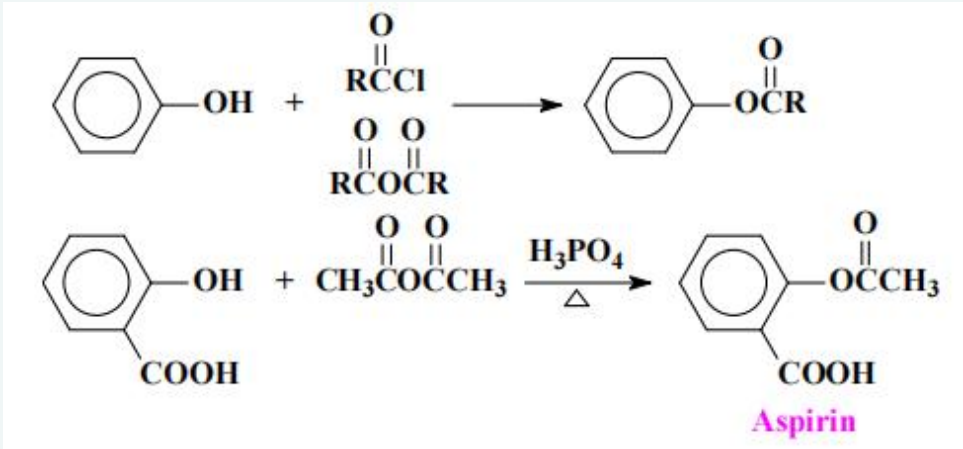
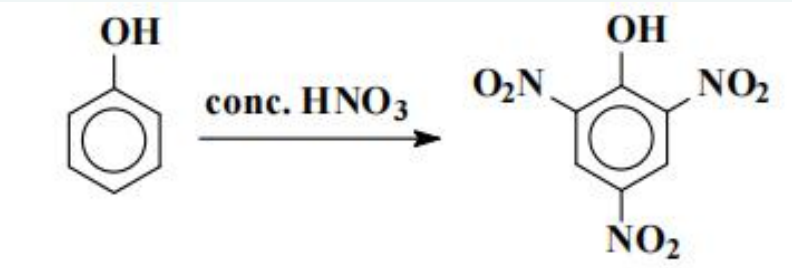
高中有机化学知识拓展

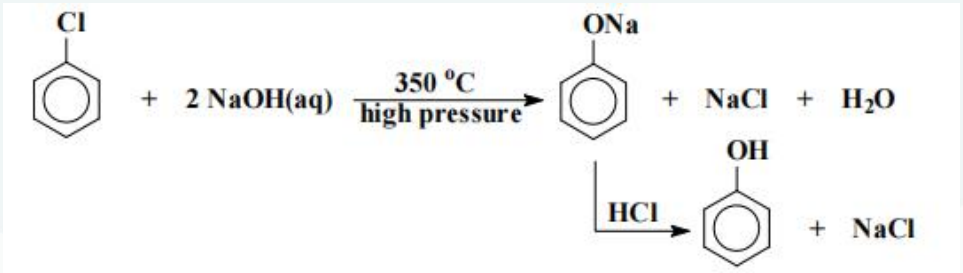
07 酚

1.酚羟基取代


OH
NaOH
ONa
RX
OR
Me_2SO_4
OCH_3


OH
RCCl
O
RCOCR
OCR
CH_3COCCH_3
H_3PO_4
$OCCH_3$
COOH
Aspirin


OH
conc. HNO_3
O_2N
NO_2
NO_2

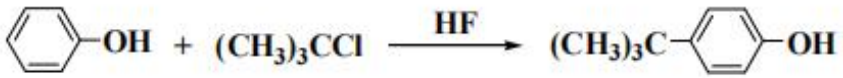

Cl
2 NaOH(aq)
350 °C
high pressure
ONa
NaCl
H_2O
HCl
OH
NaCl

2.傅克反应

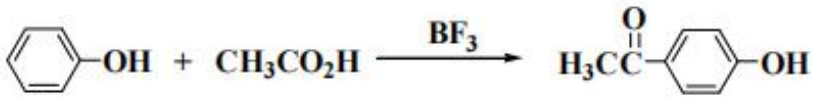
酚的傅-克反应一般不用$AlCl_3$，因为$AlCl_3$与酚羟基反应使其失活

$$ArOH + AlCl_3 \longrightarrow ArOAlCl_2 + HCl$$

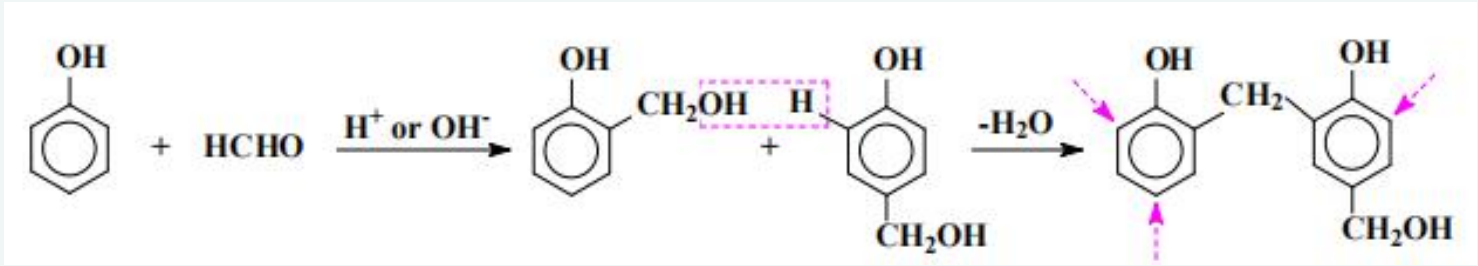
酚的傅-克反应常用H_3PO_4、HF、BF_3、PPA、$ZnCl_2$等作催化剂

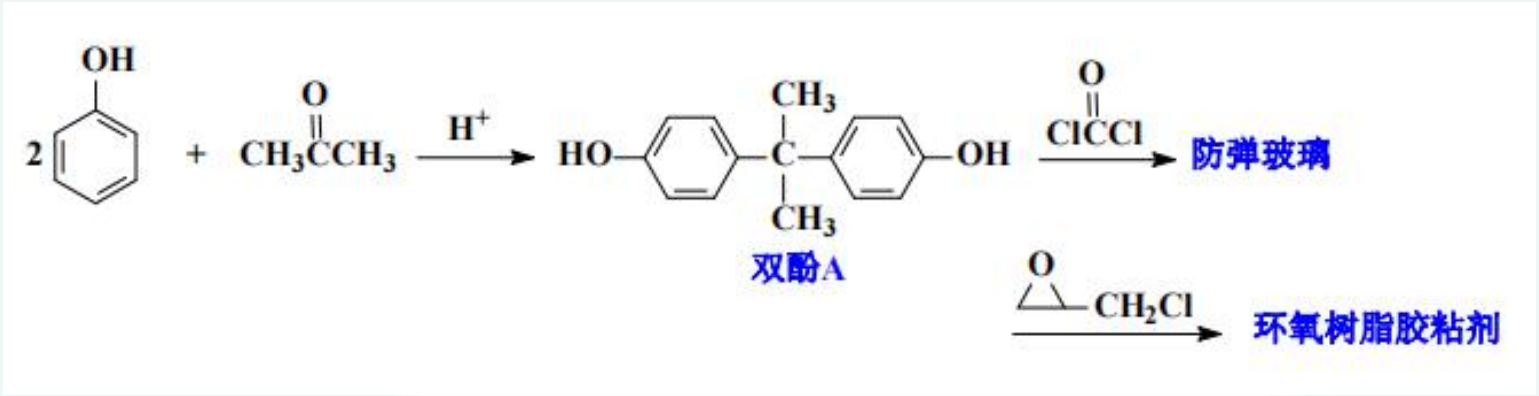


在酰基化反应中，用BF_3, $ZnCl_2$作催化剂时，可直接用羧酸作酰基化试剂

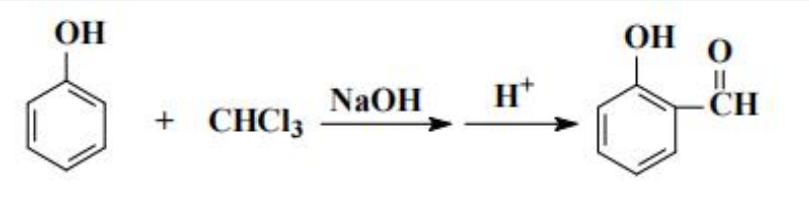


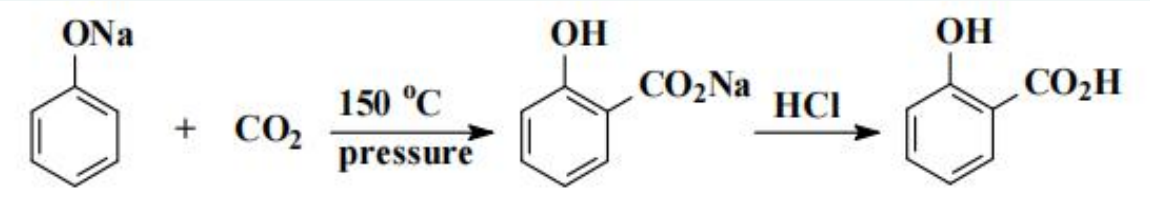
3.酚和醛的反应


OH
+ HCHO
H+ or OH-
CH2OH
H
+
CH2OH
-H2O
CH2


OH
2
+
O
CH3CCH3
H+
HO
CH3
C
OH
CH3
双酚A
O
ClCCl
防弹玻璃
O
CH2Cl
环氧树脂胶粘剂

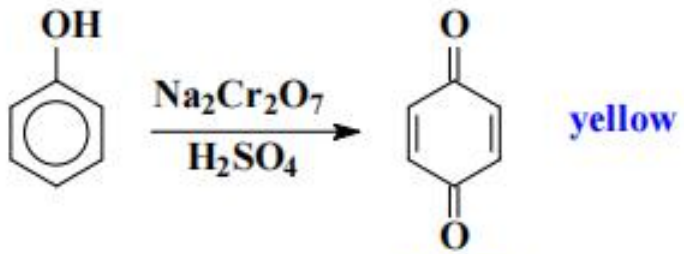
4.其他苯环邻对位反应


OH
+ CHCl3
NaOH
H+
OH
O
CH


ONa
+ CO2
150 °C
pressure
OH
CO2Na
HCl
OH
CO2H

5.酚与醌

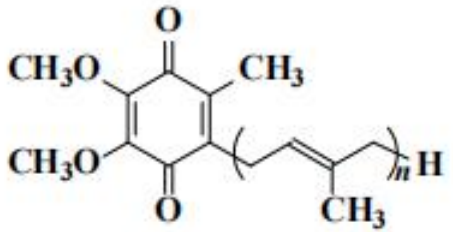
酚比醇更容易被氧化, 酚被氧化后颜色变红变深



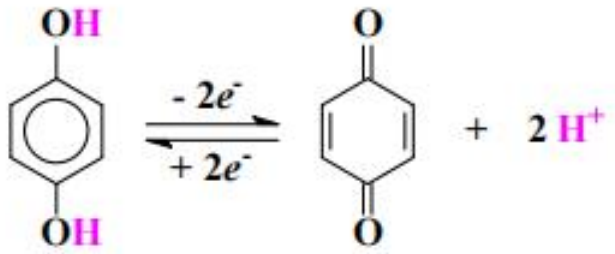
yellow

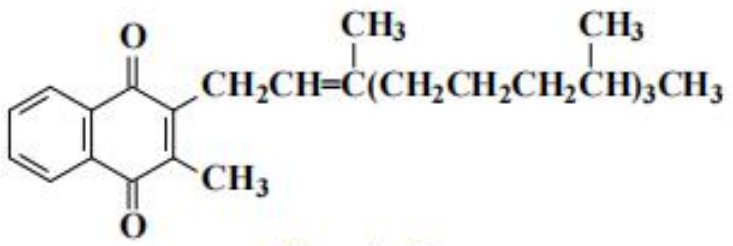
对苯醌

p-Benzoquinone



Ubiquinones (n = 6-10)
(coenzumes Q)





Vitamin K_1

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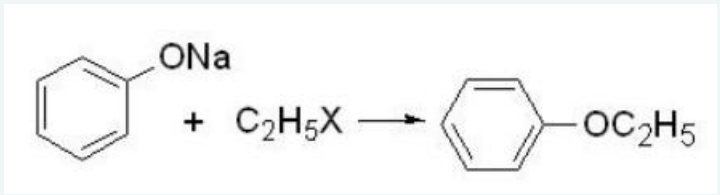
08 醚和环氧化合物

1.醚的制备

$$ROH + R'OH \xrightarrow[\triangle]{H^+} ROR + R'OR' + ROR'$$



$$(CH_3)_3CO^- + C_2H_5X \longrightarrow (CH_3)_3COC_2H_5$$

$$RCH{=}CH_2 \xrightarrow[(2)\ NaBH_4]{(1)\ Hg(OAc)_2/H_2O} RCHCH_3 \quad (OH)$$

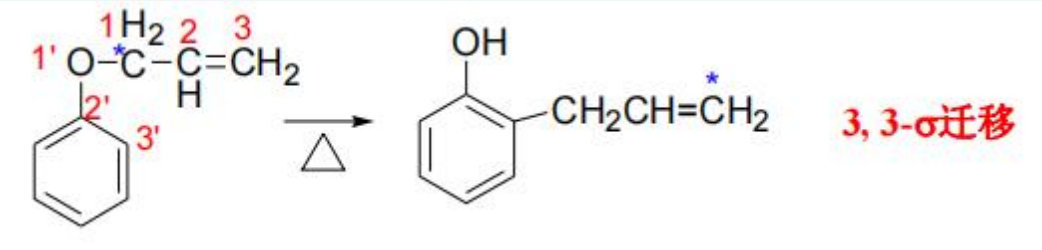
羟汞化－脱汞制醇

$$RCH{=}CH_2 \xrightarrow[(2)\ NaBH_4]{(1)\ Hg(OAc)_2/R'OH} RCHCH_3 \quad (OR')$$

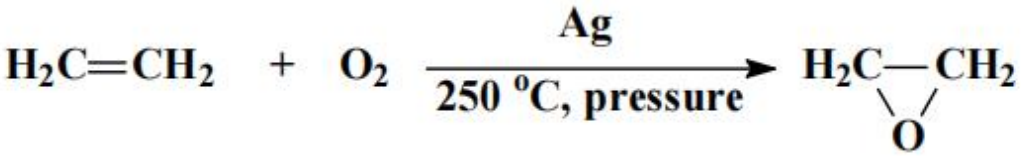
烷汞化－脱汞制醚

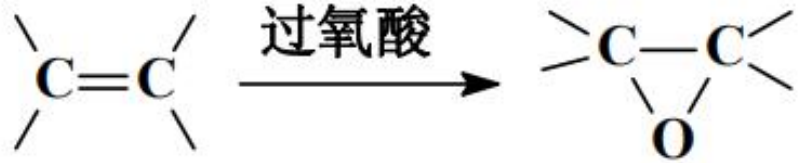
$$RC{\equiv}CH + R'OH \xrightarrow{Hg^{2+}/H^+} RC(OR')=CH_2$$

2.醚的烯丙重排



3.环氧的制备





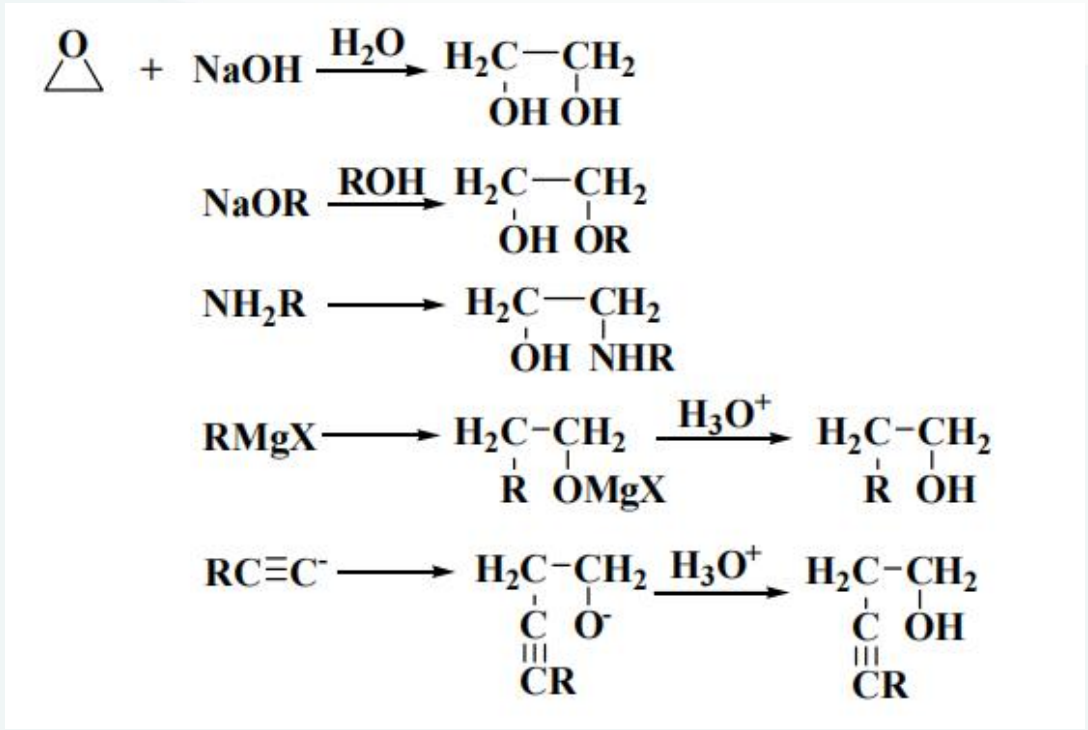
$PhCO_3H$

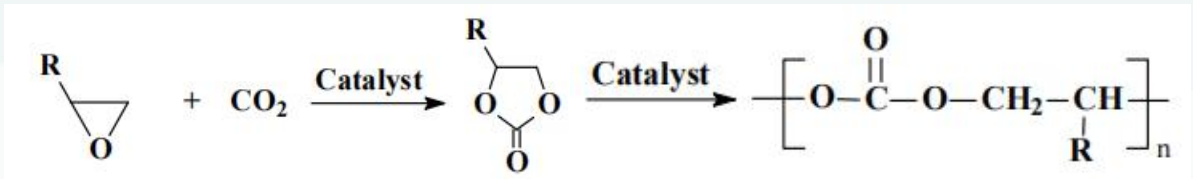
CH_3CO_3H

Cl_3CCO_3H

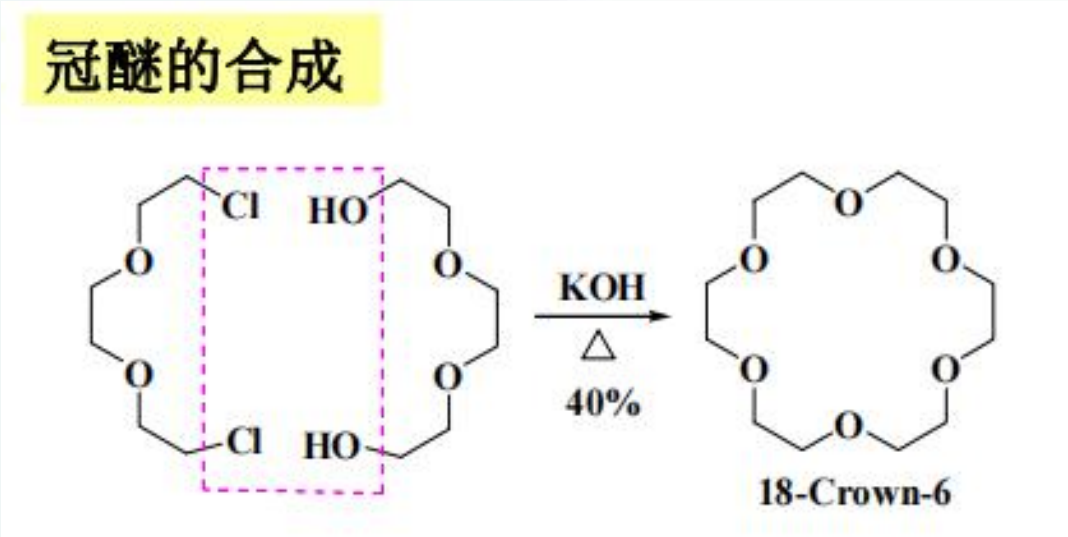
H_2O_2/HCO_2H

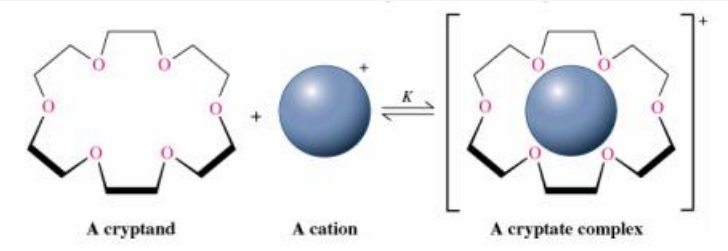
4.环氧的开环


+ NaOH
H2O
OH OH
NaOR
ROH
OH OR
NH2R
OH NHR
RMgX
H3O+
R OMgX
R OH
RC≡C-
C O-
CR
C OH
CR


R
+ CO2
Catalyst
Catalyst
n

5.冠醚


冠醚的合成
Cl
HO
O
O
O
O
Cl
HO
KOH
△
40%
O
O
O
O
O
O
18-Crown-6


A cryptand
A cation
A cryptate complex

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人总会上岸的

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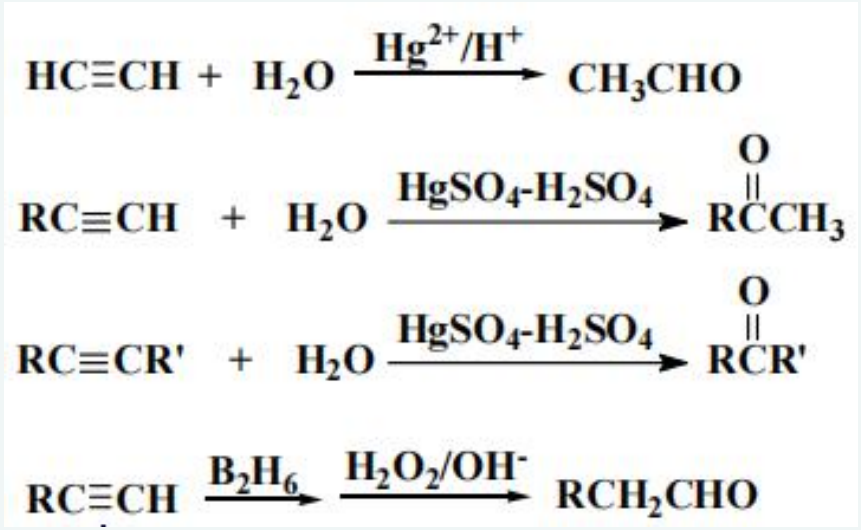
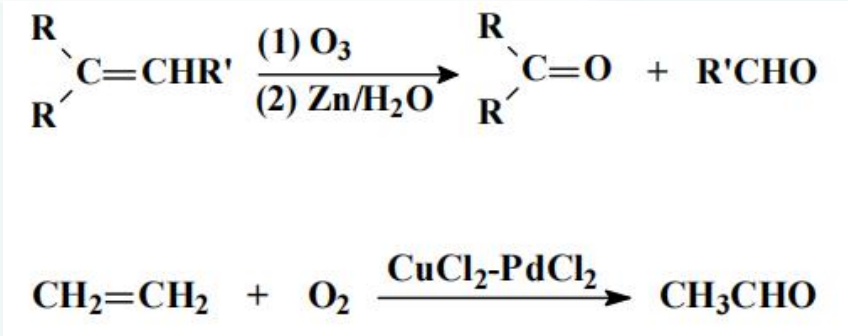
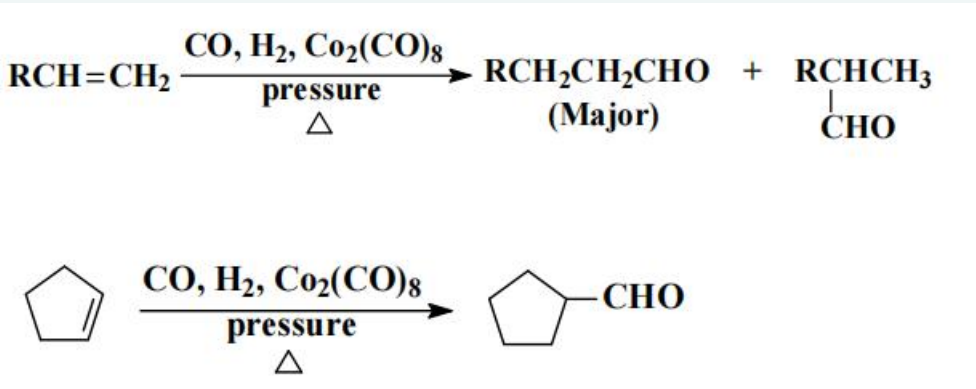
09 醛和酮

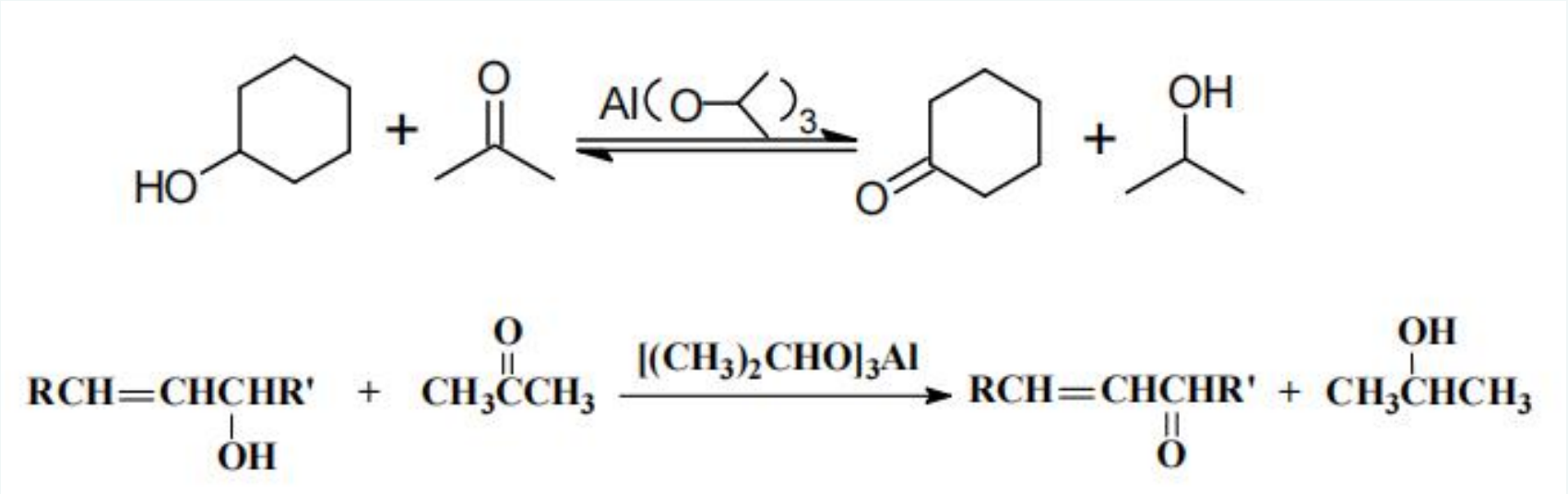
1.制备


HC≡CH + H2O Hg2+/H+ CH3CHO
RC≡CH + H2O HgSO4-H2SO4 RCCH3 O
RC≡CR' + H2O HgSO4-H2SO4 RCR' O
RC≡CH B2H6 H2O2/OH- RCH2CHO

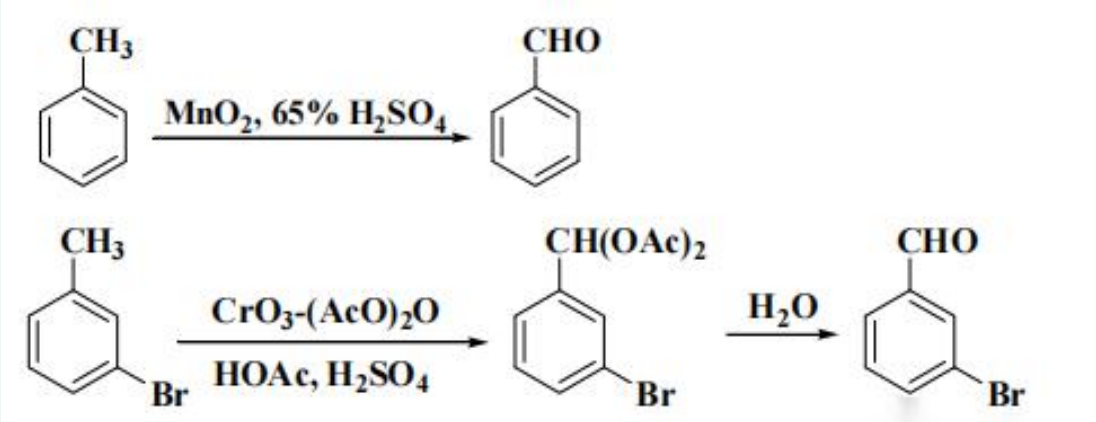

R C=CHR' R (1) O3 (2) Zn/H2O R C=O R + R'CHO
CH2=CH2 + O2 CuCl2-PdCl2 CH3CHO

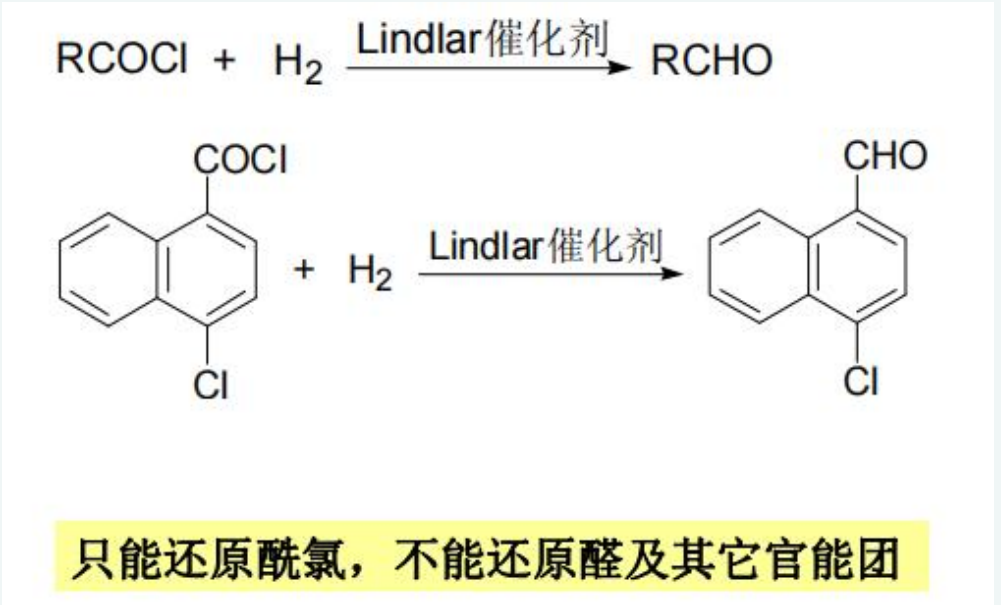

RCH=CH2 CO, H2, Co2(CO)8 pressure △ RCH2CH2CHO (Major) + RCHCH3 CHO
CO, H2, Co2(CO)8 pressure △ CHO

1.制备

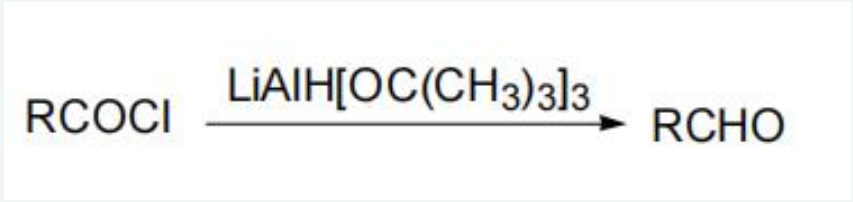

HO
O
Al(O)3
O
OH
RCH=CHCHR'
OH
O
CH3CCH3
[(CH3)2CHO]3Al
RCH=CHCHR'
O
OH
CH3CHCH3

1.制备

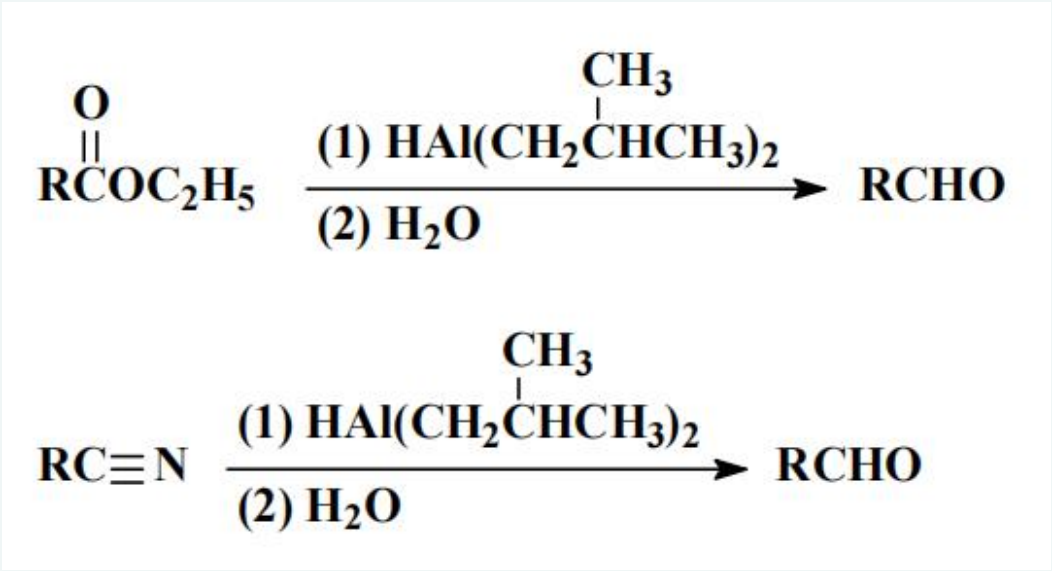

CH3
MnO2, 65% H2SO4
CHO
CH3
Br
CrO3-(AcO)2O
HOAc, H2SO4
CH(OAc)2
Br
H2O
CHO
Br


RCOCl + H2
Lindlar催化剂
RCHO
COCl
Cl
+ H2
Lindlar催化剂
CHO
Cl
只能还原酰氯，不能还原醛及其它官能团

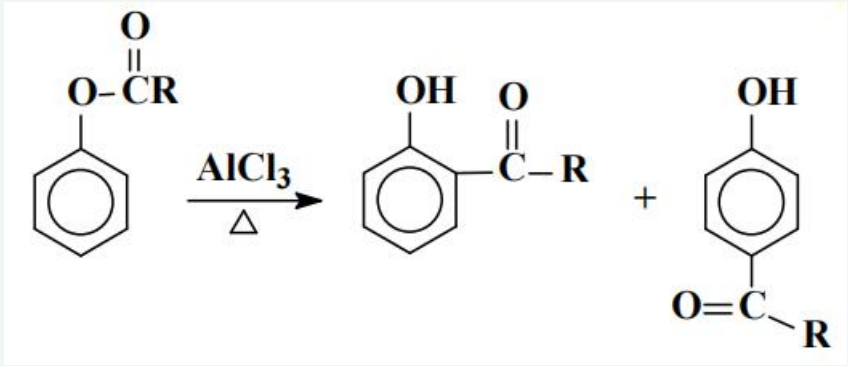
1.制备

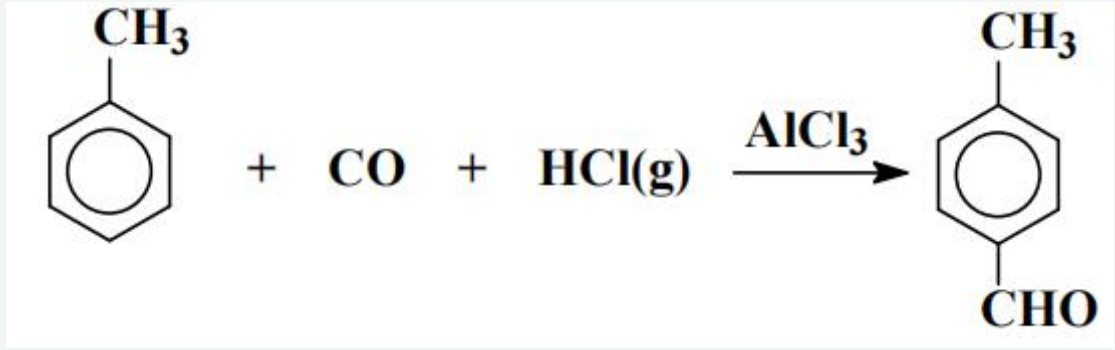

RCOCl
LiAlH[OC(CH3)3]3
RCHO

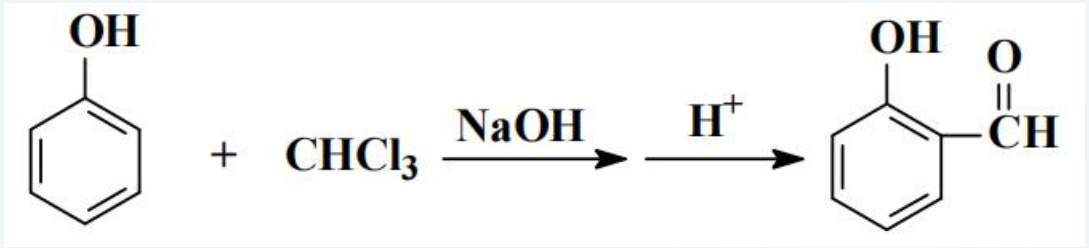

RCOCl + R'2CuLi
RCOR'


O
RCOC2H5
CH3
(1) HAl(CH2CHCH3)2
(2) H2O
RCHO
RC≡N
CH3
(1) HAl(CH2CHCH3)2
(2) H2O
RCHO

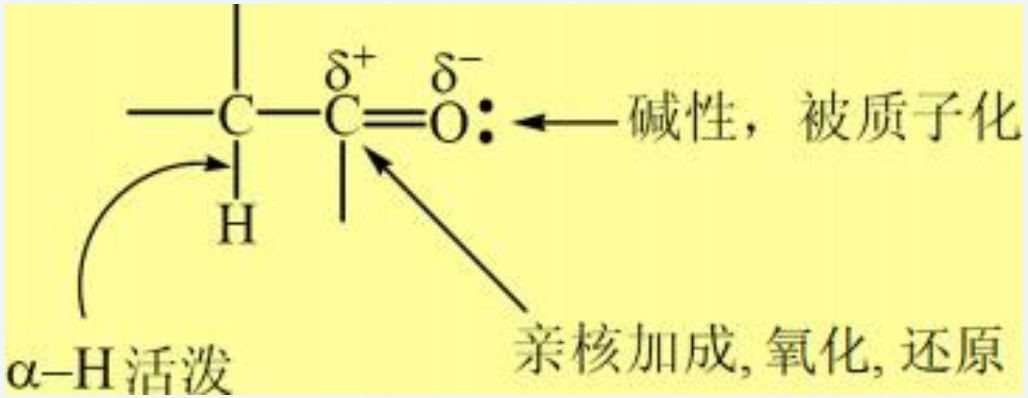
1.制备


O
O–CR
AlCl3
△
OH
O
C–R
+
OH
O=C
R

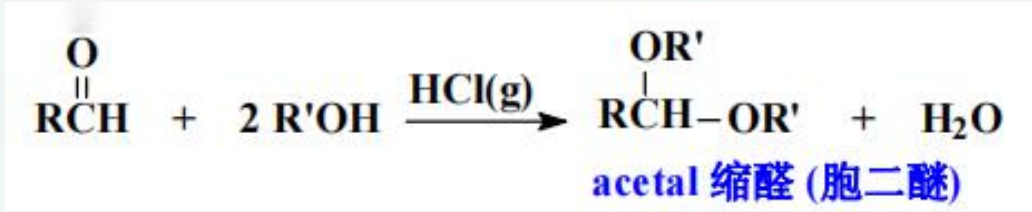

CH3
+ CO + HCl(g)
AlCl3
CH3
CHO


OH
+ CHCl3
NaOH
H+
OH
O
CH

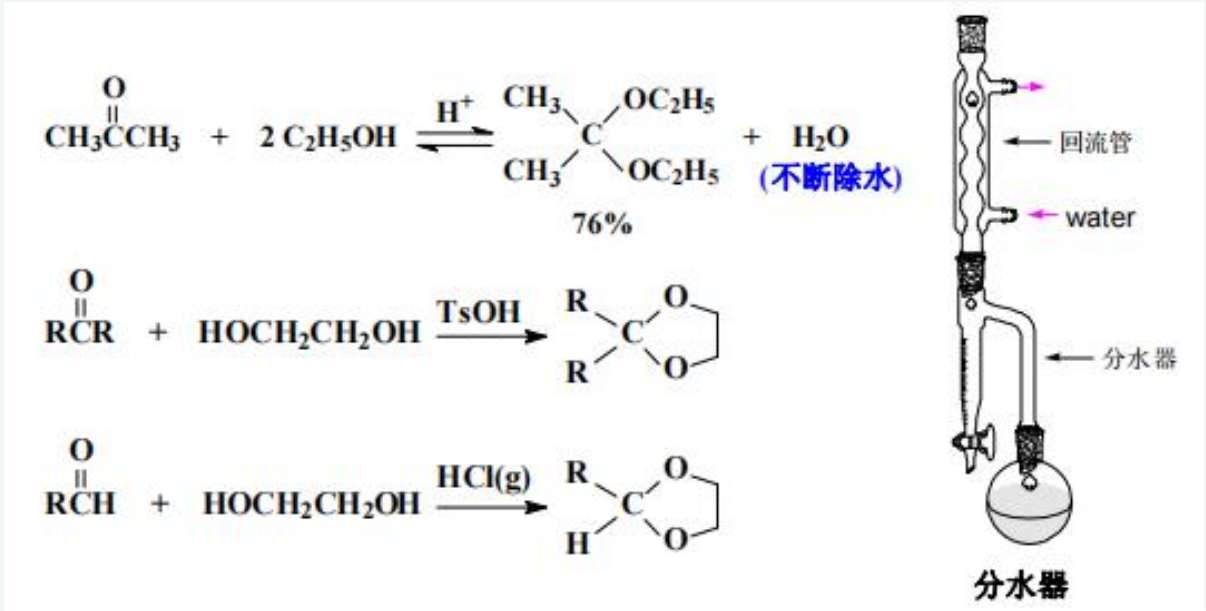
2.性质概述



3.醛基、酮羰基和羟基互相保护



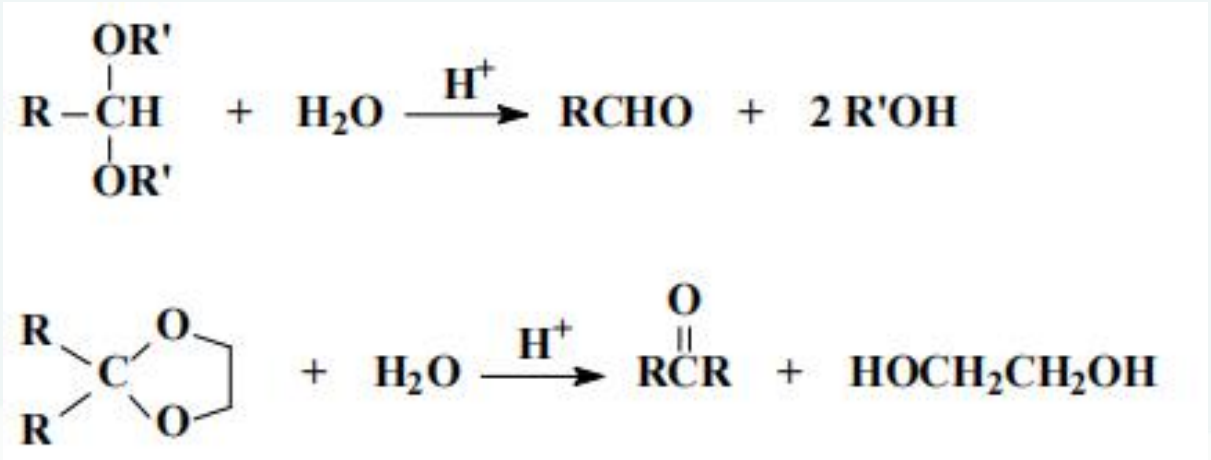
缩酮一般难以生成，但通过分水器不断除去生成的水，可以得到缩酮；酮和乙二醇容易得到五元环的环状缩酮（六元环也容易生成）。



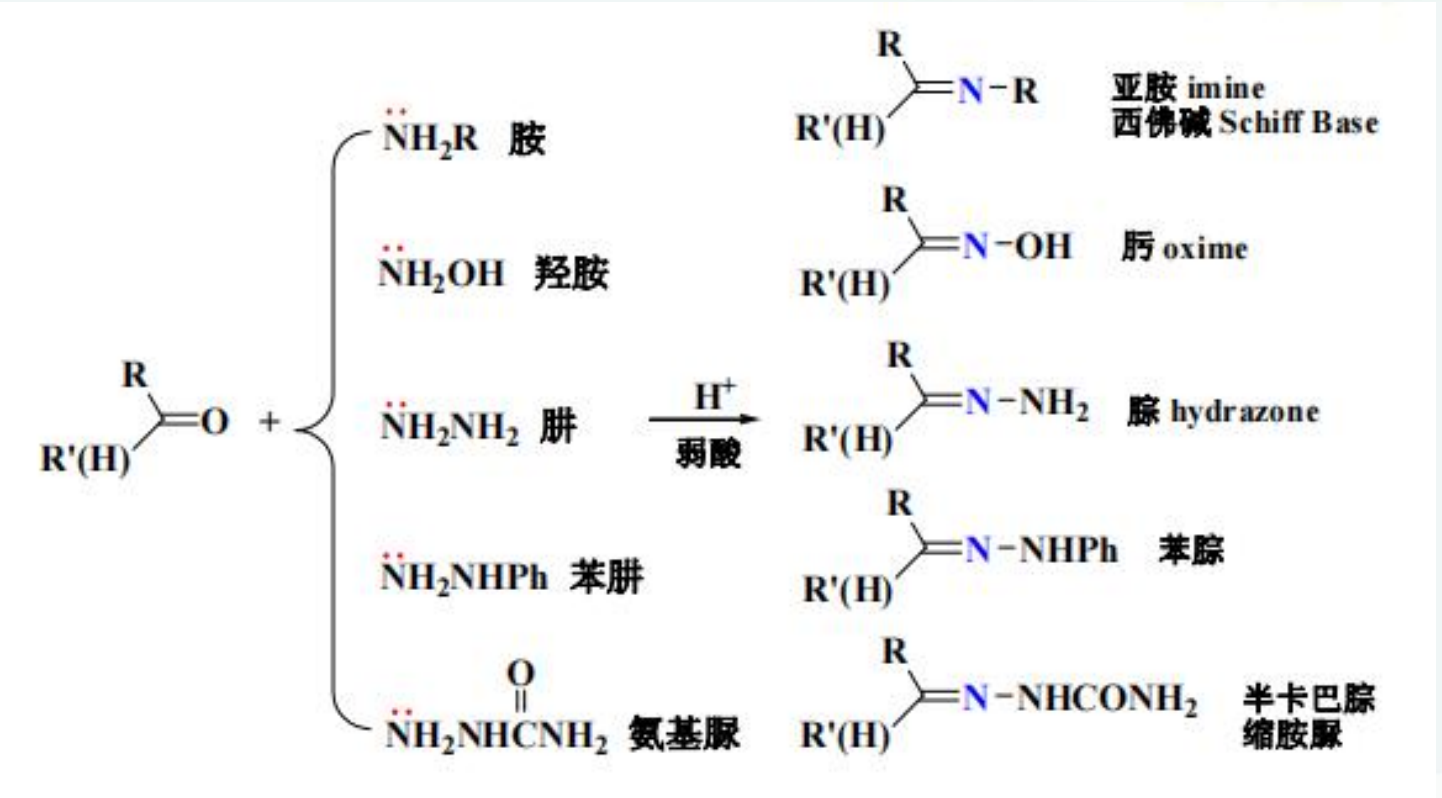
3.醛基、酮羰基和羟基互相保护

缩醛、缩酮对碱、氧化剂稳定，但是在室温下稀酸水溶液中可以水解得到原来的醛或者酮。

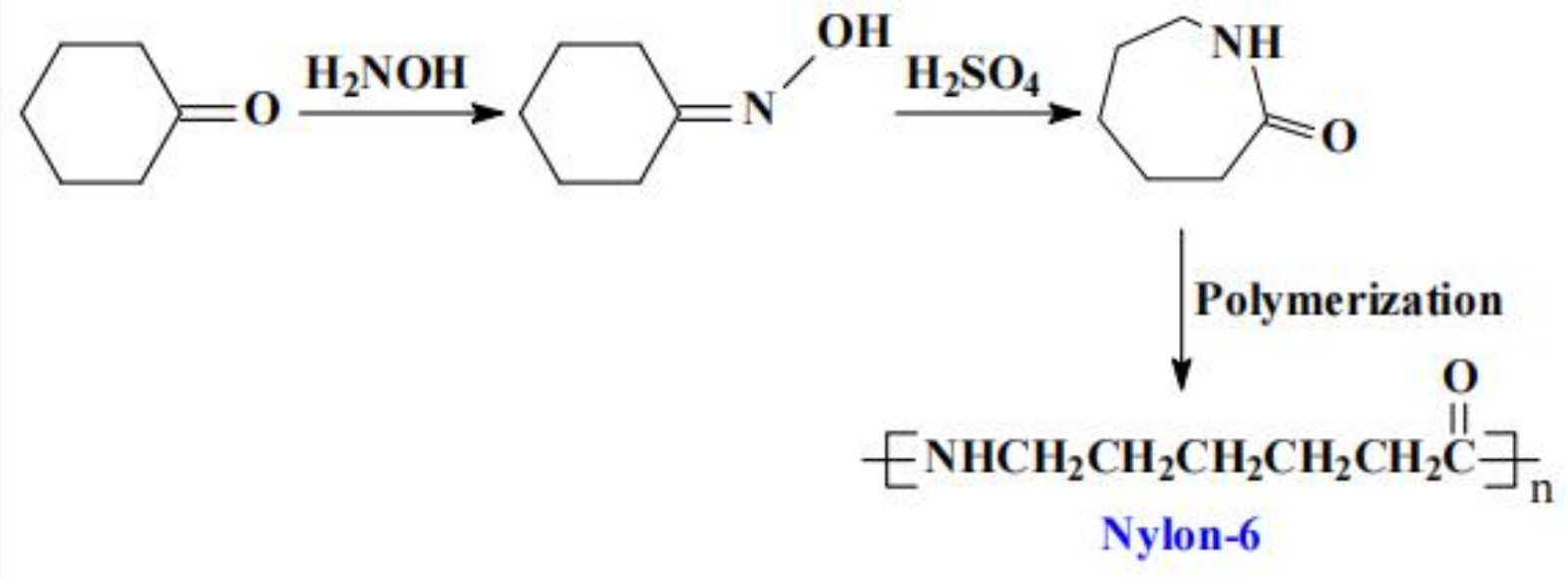
缩醛、缩酮常用做醛基、酮羰基的保护。



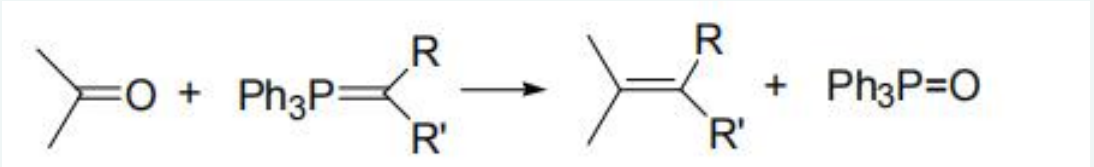
4.醛基、酮羰基与胺类的反应



5.Beckmann 重排

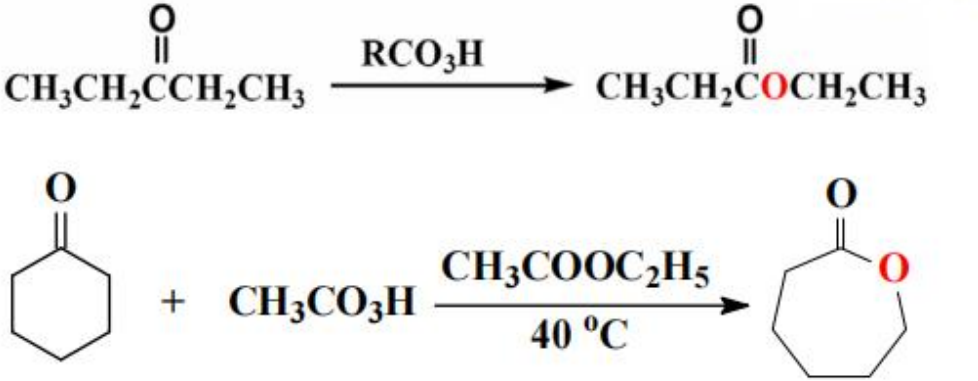


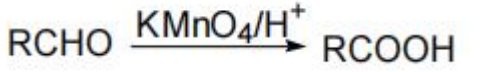
6.Wittig反应

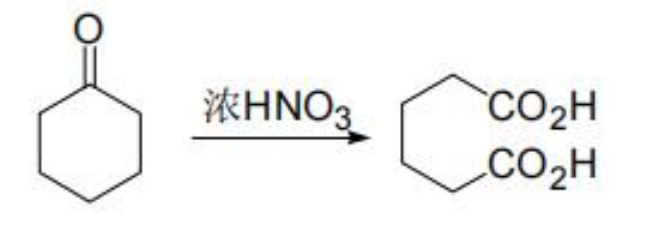


通过延长碳链制备烯烃

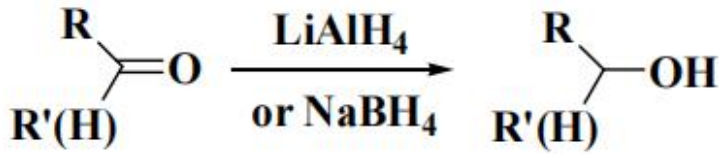
7.其他的氧化


CH3CH2CCH2CH3
RCO3H
CH3CH2COCH2CH3
O
CH3CO3H
CH3COOC2H5
40 °C

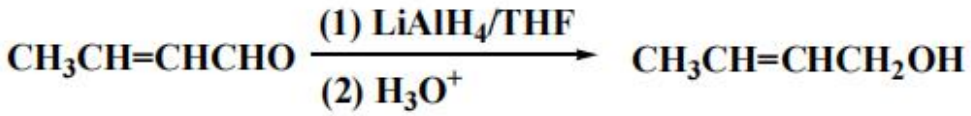

RCHO
KMnO4/H+
RCOOH

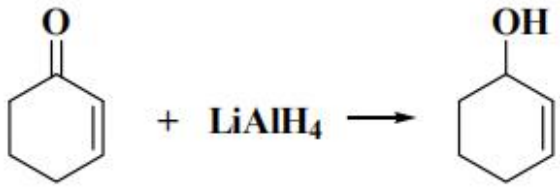

O
浓HNO3
CO2H
CO2H

8.还原

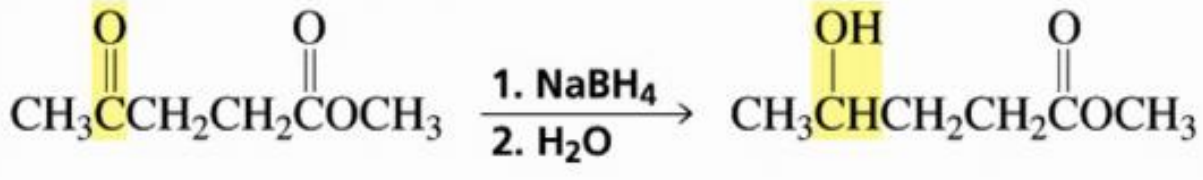


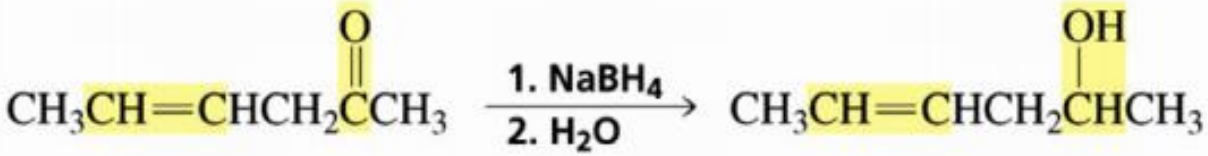
选择性较好，孤立碳碳双键和叁键都不干扰



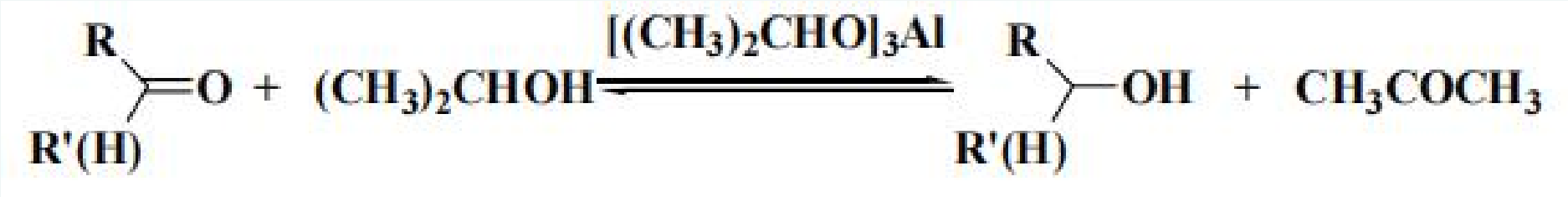


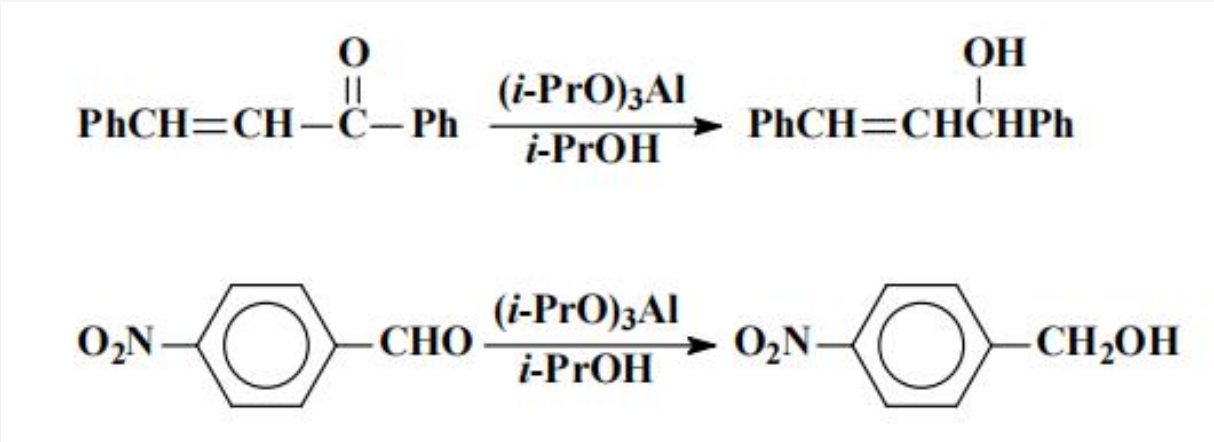
$NaBH_4$只还原醛酮，部分还原α, β不饱和醛酮的C=C双键，不能还原其它所有不饱和键，包括孤立的碳碳双键和叁键





8.还原



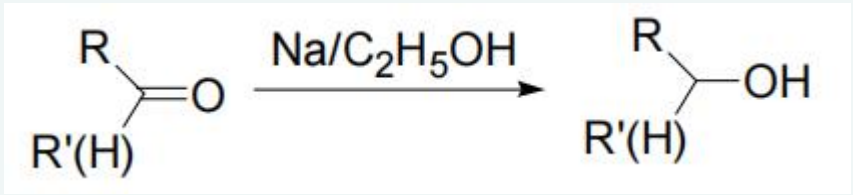


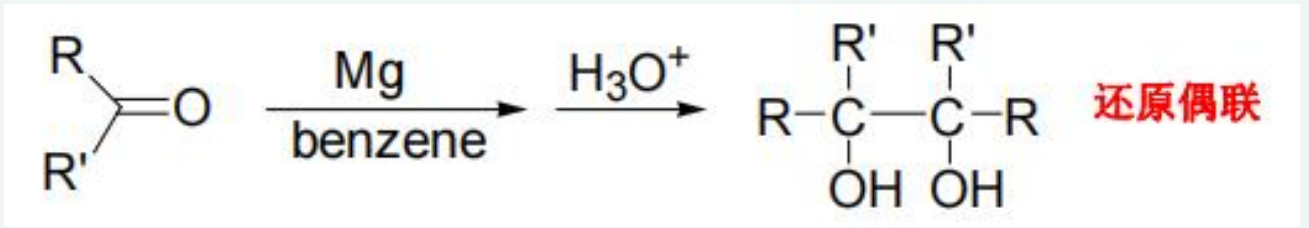
特点：

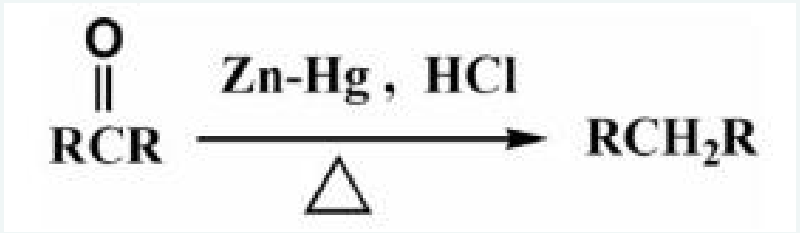
高度选择性

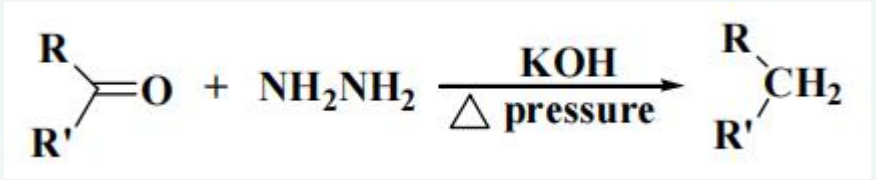
双键、叁键和其他官能团都不受干扰

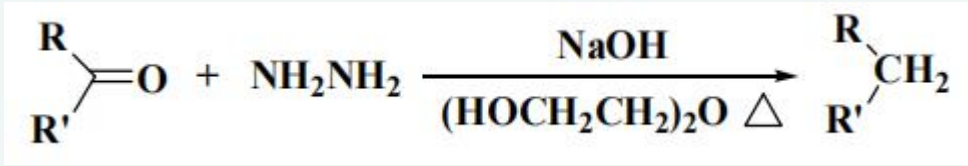
8.还原


R
O
R'(H)
Na/C2H5OH
R
OH
R'(H)


R
O
R'
Mg
benzene
H3O+
R'
R'
R
C
C
R
OH
OH
还原偶联

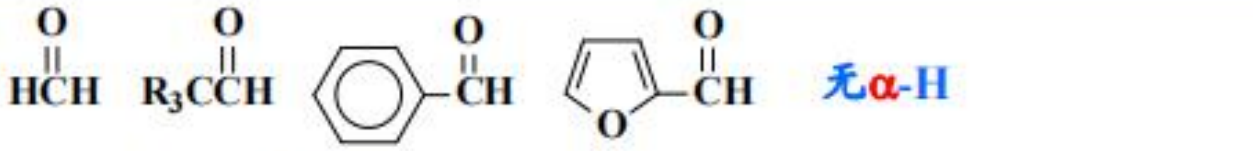

O
RCR
Zn-Hg , HCl
△
RCH2R

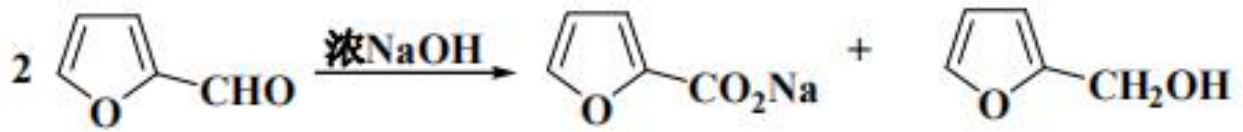

R
O
R'
+ NH2NH2
KOH
△ pressure
R
CH2
R'


R
O
R'
+ NH2NH2
NaOH
(HOCH2CH2)2O △
R
CH2
R'

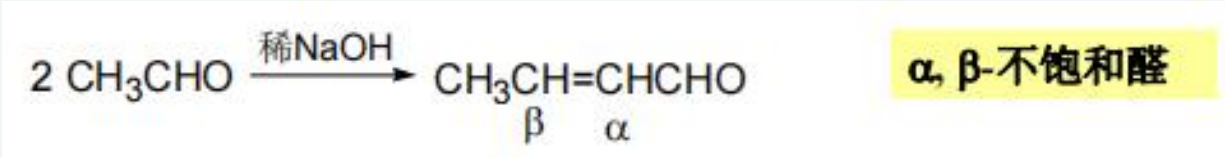
9.康尼扎罗反应

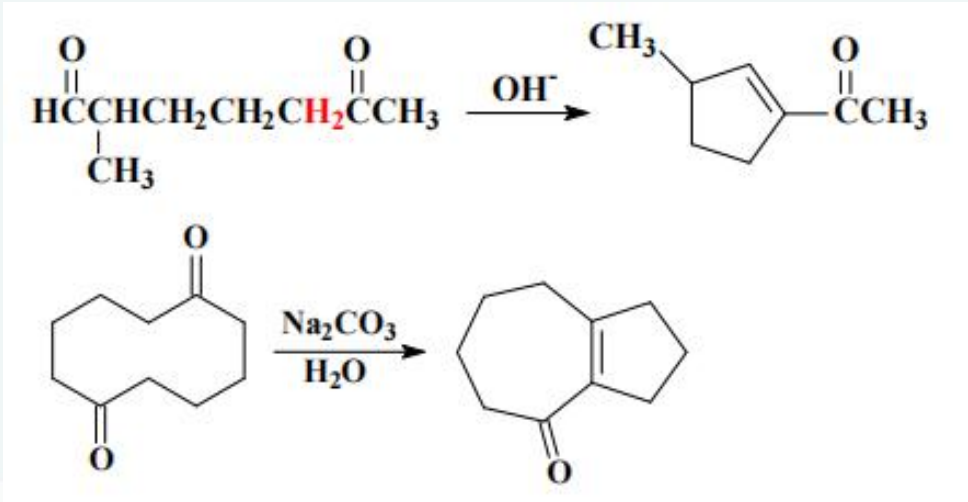
不含α-H的醛在浓碱作用下发生的自身氧化还原或歧化反应, 其中一分子醛被氧化成羧酸，另一分子醛被还原成醇





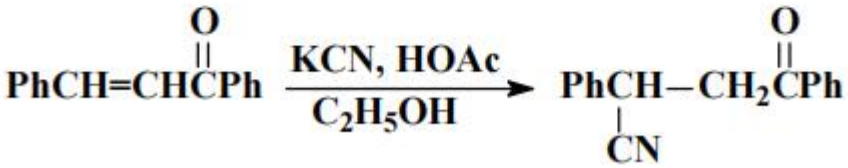
10.羟醛缩合反应


2 CH3CHO
稀NaOH
CH3CH=CHCHO
β α
α, β-不饱和醛

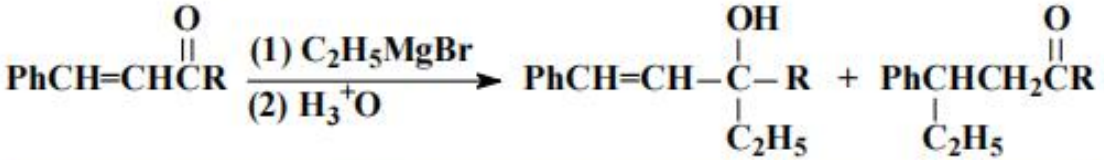

O
O
HCCHCH2CH2CH2CCH3
CH3
OH-
CH3
O
CCH3
O
O
Na2CO3
H2O
O

11.α,β不饱和醛酮的反应

α, β不饱和醛主要1, 2加成，酮主要1, 4加成



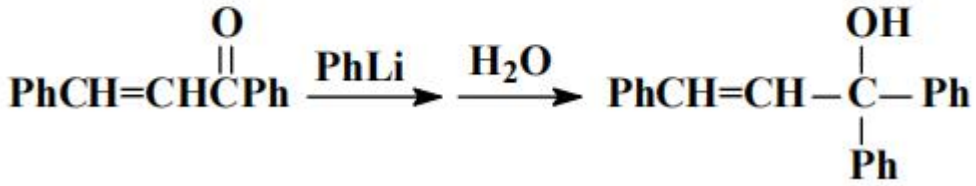
底物与格氏试剂的体积效应决定产物比例，醛1, 2加成



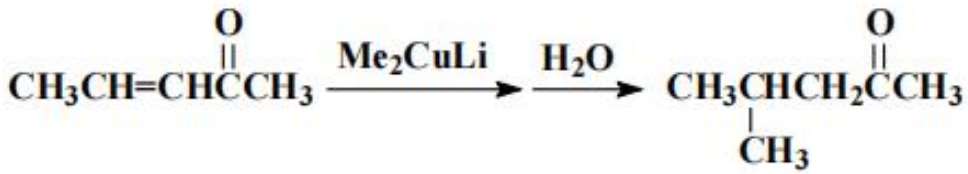
R:	H	CH_3	C_2H_5	$CH(CH_3)_2$	$C(CH_3)_3$	Ph
1,4加成产物(%):	0	60	71	100	100	99

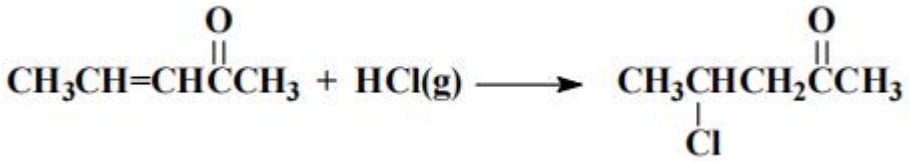
11.α,β不饱和醛酮的反应

RLi活性高，亲核性强，主要发生1, 2加成



R_2CuLi活性较低，主要发生1, 4加成





11.α,β不饱和醛酮的反应

还原反应：

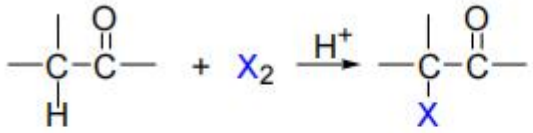
（1）选择性还原羰基（还原到醇）：三异丙醇铝、氢化铝锂等

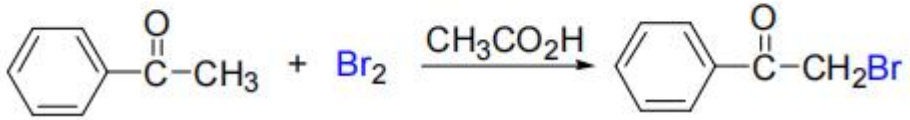
（2）选择性还原碳碳双键：催化氢化、液氨锂

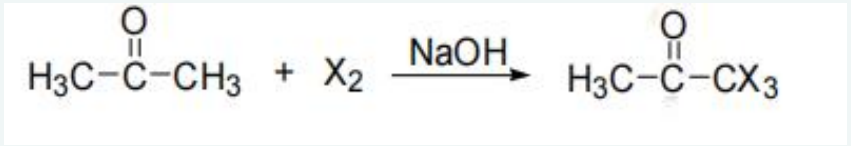
（3）同时还原羰基和双键：彻底催化氢化、高浓度硼氢化钠

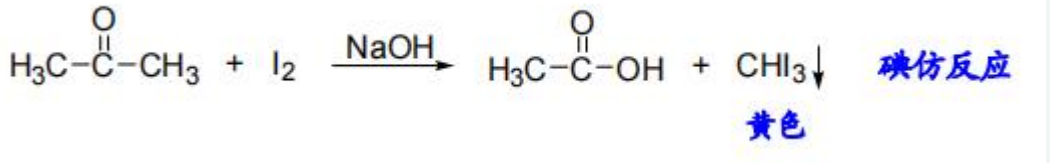
（4）选择性还原羰基（还原到亚甲基）：硫代缩酮、硫代缩醛还原法

12.α-卤代反应



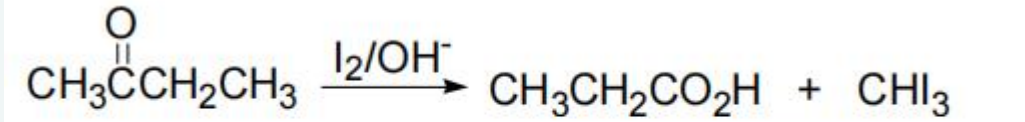






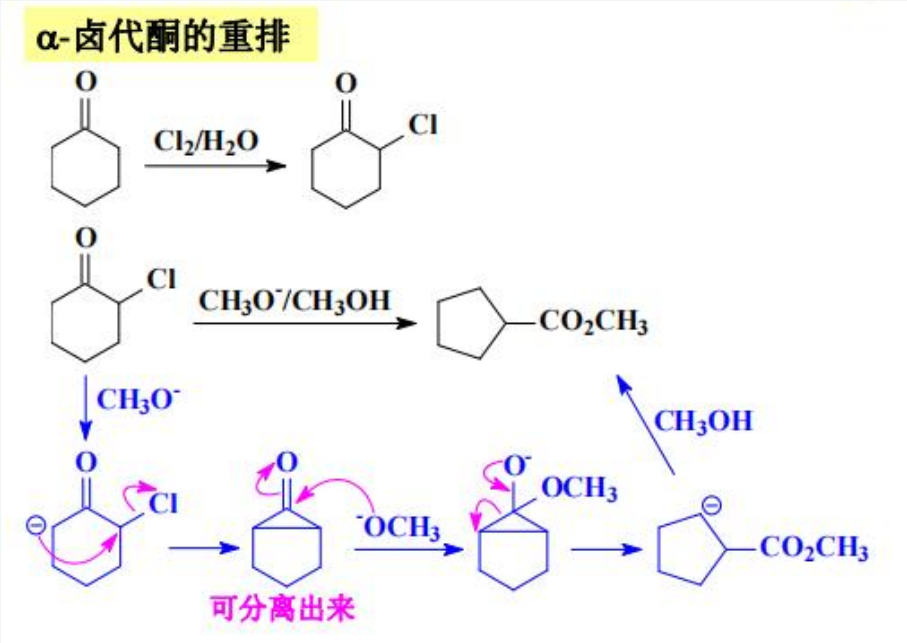
碘仿反应

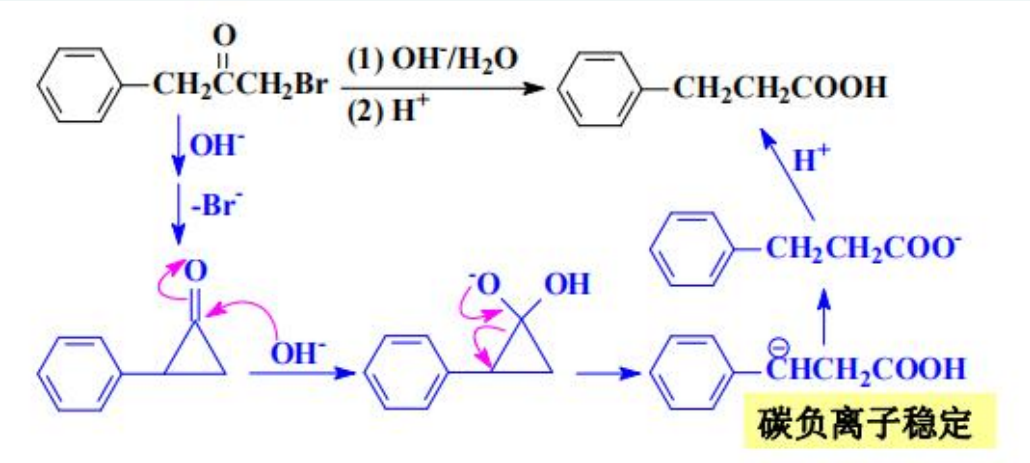
黄色



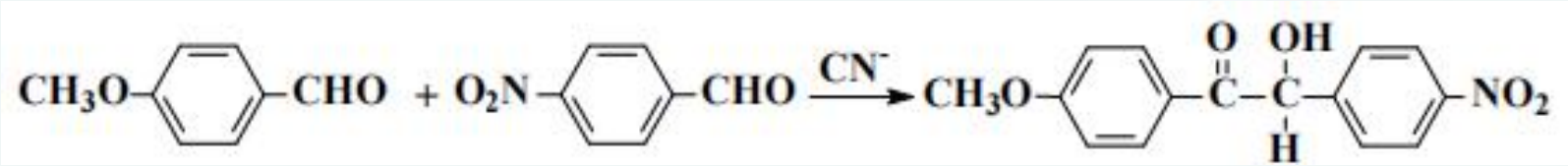
碱性条件：
卤代反应发生在取代基少的α碳上

13.α-卤代酮的重排

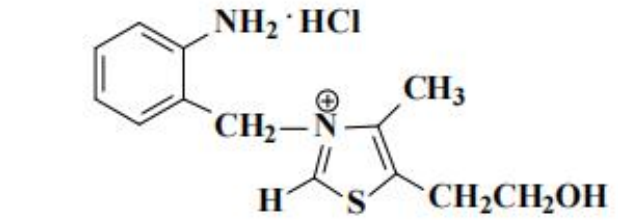

α-卤代酮的重排
O
Cl
Cl_2/H_2O
CH_3O^-/CH_3OH
CO_2CH_3
CH_3O^-
CH_3OH
$^-OCH_3$
OCH_3
可分离出来


CH_2CCH_2Br
(1) OH^-/H_2O
(2) H^+
CH_2CH_2COOH
OH^-
$-Br^-$
^-O
OH
H^+
$CH_2CH_2COO^-$
$CHCH_2COOH$
碳负离子稳定

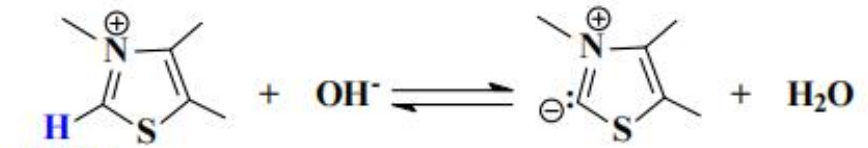
14.安息香缩合



由于氰化物剧毒，常用VB_1代替氰化物催化安息香缩合



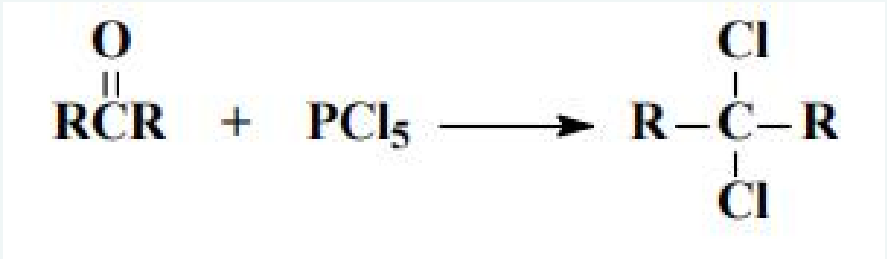
Vitamin B_1



酸性氢

相当于 N≡C⊖

15.与PCl_5的反应



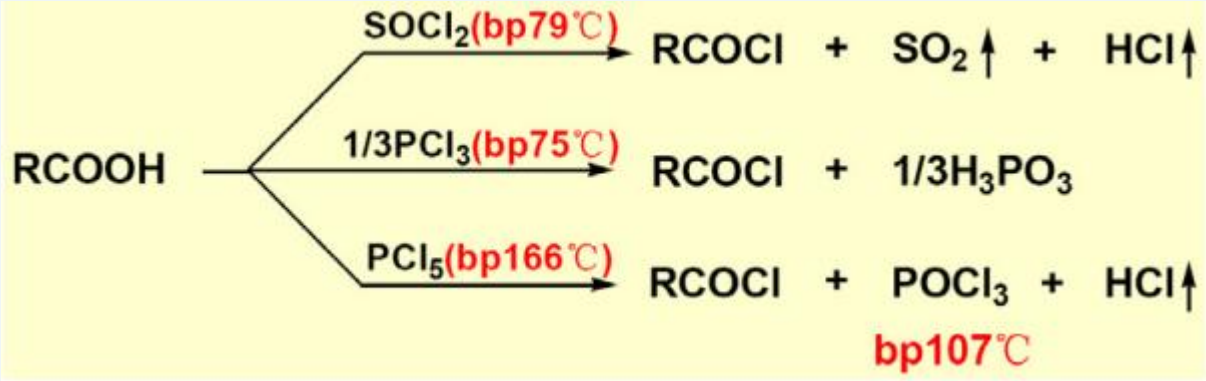
时光不负有心人

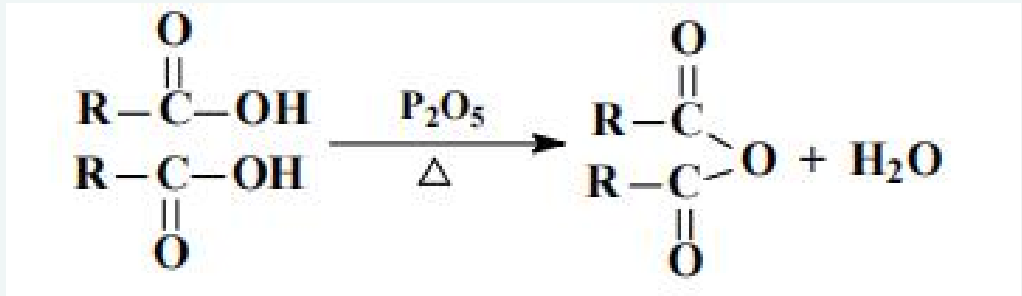
人总会上岸的

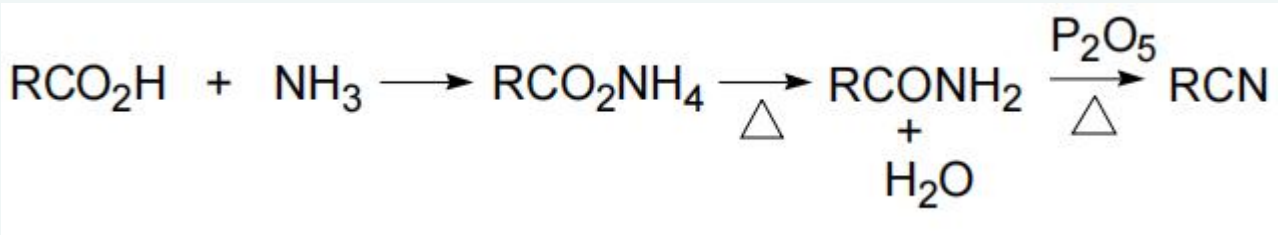
高中有机化学知识拓展

10 羧酸

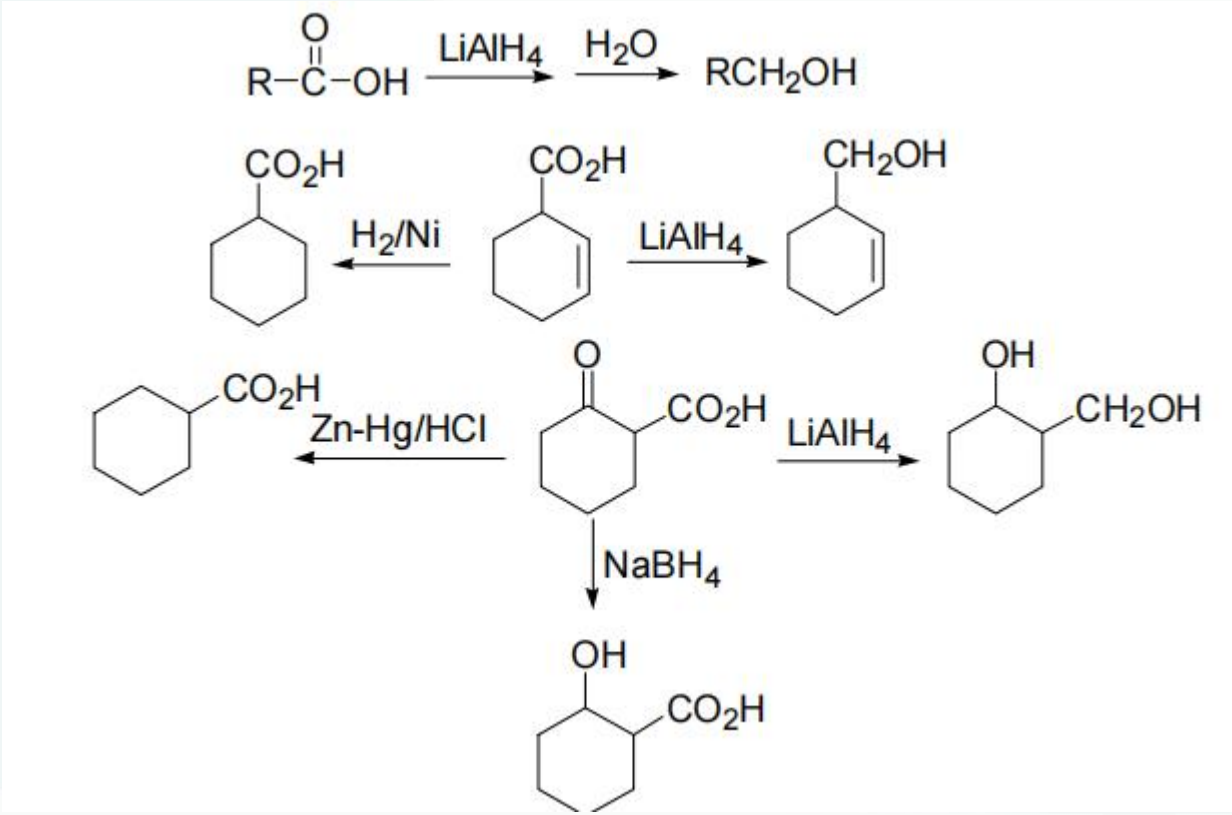
1.羧酸形成衍生物


RCOOH
SOCl2(bp79℃)
RCOCl + SO2↑ + HCl↑
1/3PCl3(bp75℃)
RCOCl + 1/3H3PO3
PCl5(bp166℃)
RCOCl + POCl3 + HCl↑
bp107℃

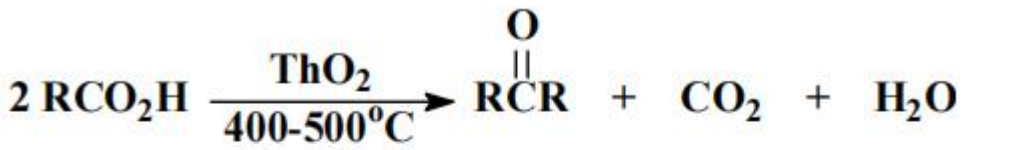

R—C(=O)—OH
R—C(=O)—OH
P2O5
△
R—C(=O)
R—C(=O)
O + H2O


RCO2H + NH3 → RCO2NH4 △ RCONH2 + H2O P2O5 △ RCN

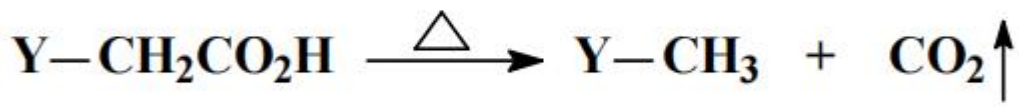
2.羧酸的还原


R–C(=O)–OH
LiAlH4
H2O
RCH2OH
CO2H
H2/Ni
LiAlH4
CH2OH
Zn-Hg/HCl
NaBH4
OH

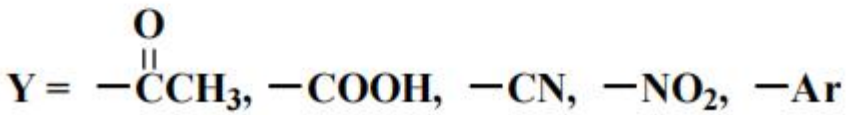
3.脱羧反应



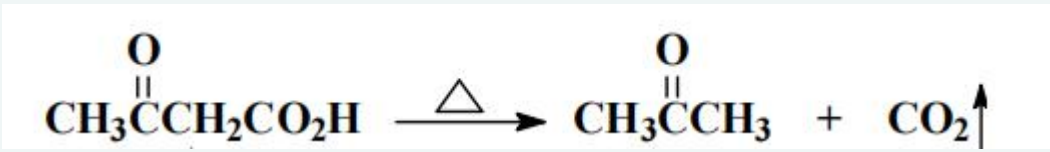
$$2\,RCO_2H \xrightarrow[400\text{-}500^{o}C]{ThO_2} R\overset{\overset{O}{\|}}{C}R + CO_2 + H_2O$$



$$Y-CH_2CO_2H \xrightarrow{\triangle} Y-CH_3 + CO_2\uparrow$$



$$Y = -\overset{\overset{O}{\|}}{C}CH_3,\ -COOH,\ -CN,\ -NO_2,\ -Ar$$



$$CH_3\overset{\overset{O}{\|}}{C}CH_2CO_2H \xrightarrow{\triangle} CH_3\overset{\overset{O}{\|}}{C}CH_3 + CO_2\uparrow$$

3.脱羧反应

$$RCO_2M + X_2 \xrightarrow[\triangle]{} RX + CO_2 + MX$$

M = Ag^+, Hg^{2+}, Pb^{2+}; X = Br, I

$$RCO_2Ag + Br_2 \xrightarrow[\triangle]{} RBr + CO_2 + AgBr$$

$$RCO_2H \xrightarrow[\triangle]{Pb(O_2CCH_3)_4/LiCl} RCl + CO_2$$

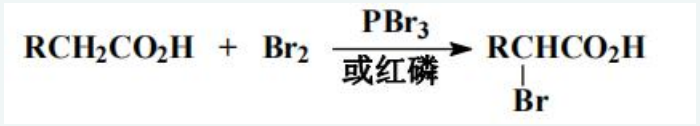
$$\xrightarrow[\triangle]{Pb(O_2CCH_3)_4/I_2} RI + CO_2$$

$$\xrightarrow[\triangle]{HgO/Br_2} RBr + CO_2$$

$$2\,RCO_2Na + H_2O \xrightarrow{电解} R\text{-}R + CO_2 + H_2 + NaOH$$

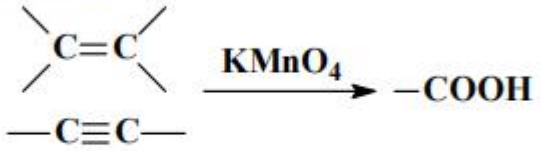
$$C_2H_5O_2CCH_2CH_2CH_2CO_2K + H_2O \xrightarrow{电解} C_2H_5O_2C(CH_2)_6CO_2C_2H_5$$

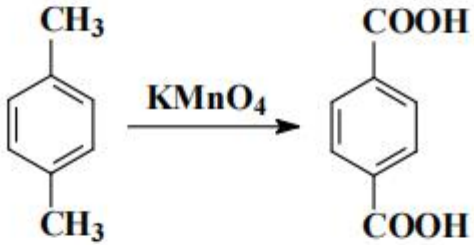
4.α-卤代酸

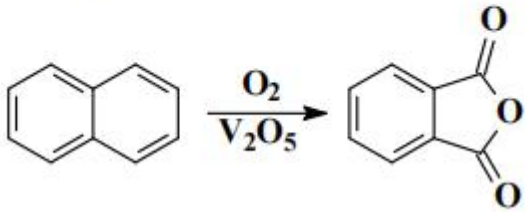


5.羧酸的制备

(1) 烃的氧化

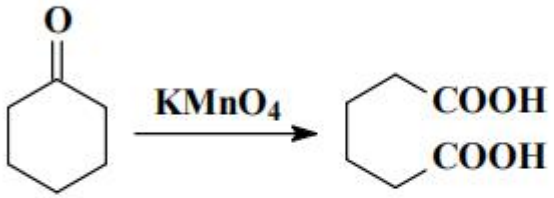






(2) 含氧化合物的氧化

$$\begin{matrix} RCH_2OH \\ RCHO \end{matrix} \xrightarrow{[O]} RCOOH$$



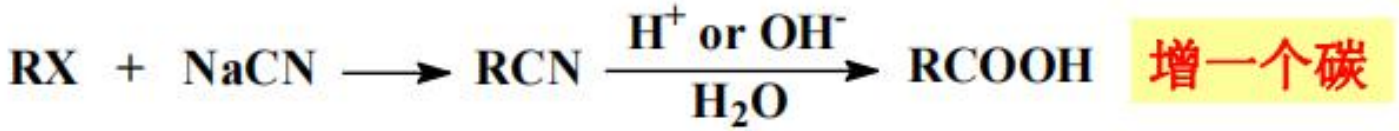
$$RCH{=}CHCHO \xrightarrow[\text{or Fehling}]{\text{Tollens reagent}} RCH{=}CHCOOH$$

$$RCH{=}CHC(=O)CH_3 \xrightarrow[(2)\ H^+]{(1)\ X_2/OH^-} RCH{=}CHCOOH$$

少一个碳

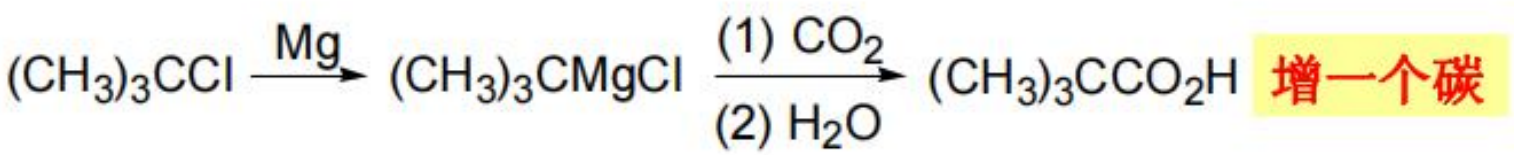
5.羧酸的制备

(1) 腈水解法



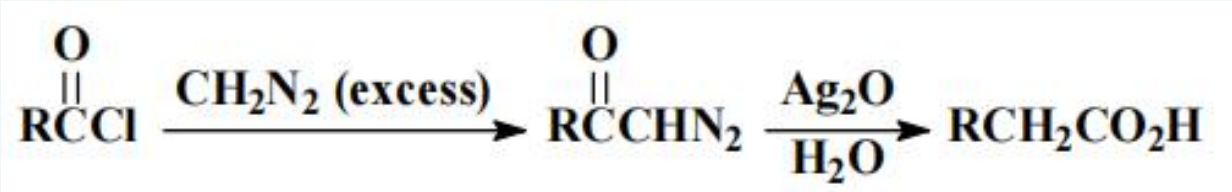
增一个碳

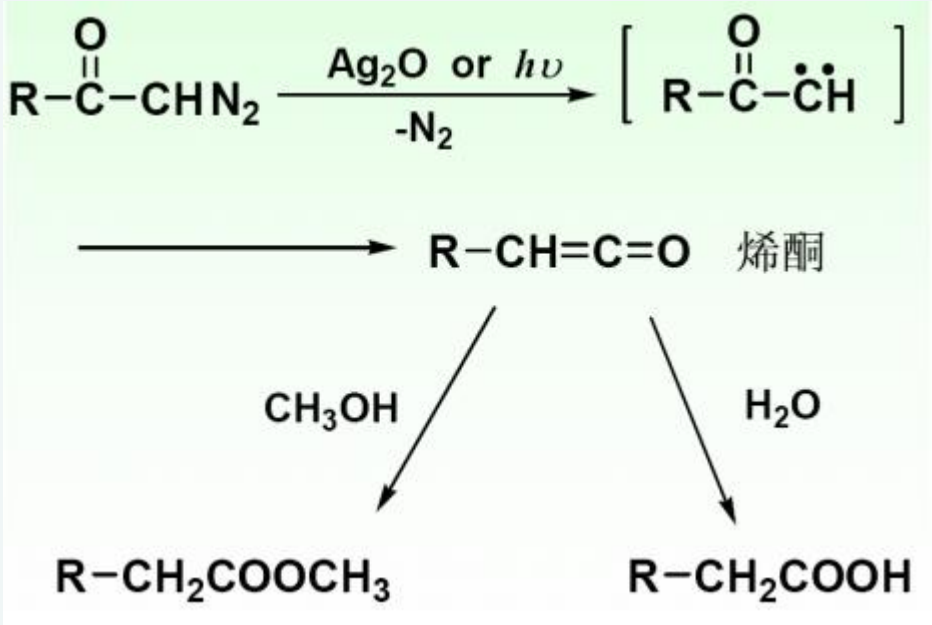
(2) 格氏试剂法



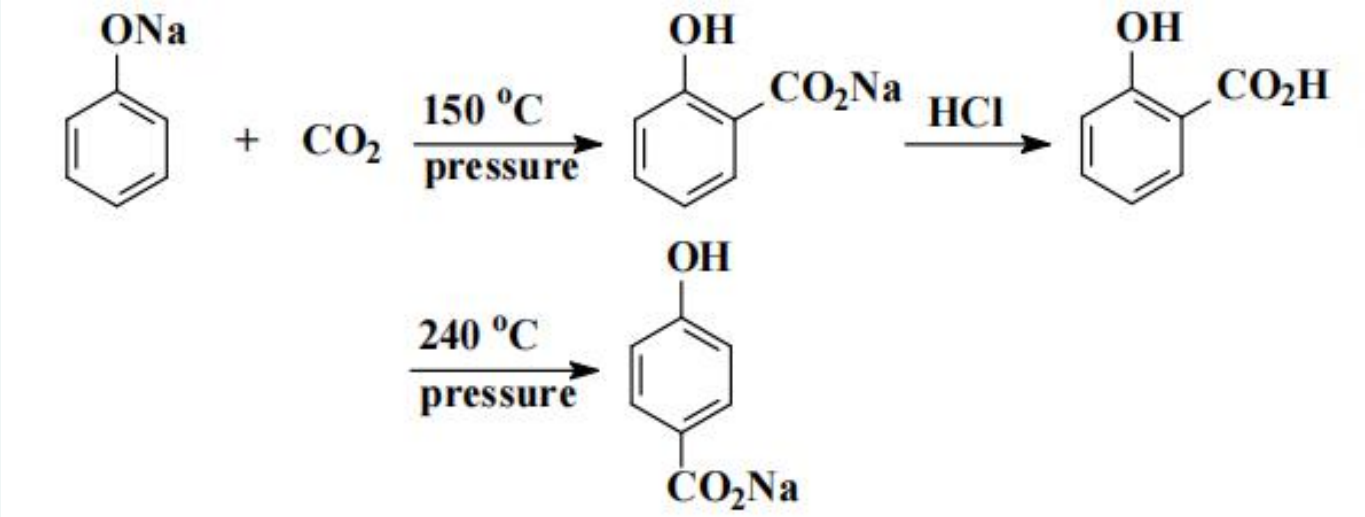
增一个碳

5.羧酸的制备


O
RCCl
CH2N2 (excess)
O
RCCHN2
Ag2O
H2O
RCH2CO2H

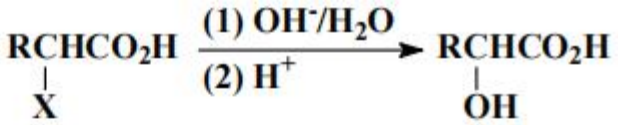

O
R–C–CHN2
Ag2O or hυ
-N2
O
R–C–CH
R–CH=C=O
烯酮
CH3OH
H2O
R–CH2COOCH3
R–CH2COOH

5.羧酸的制备

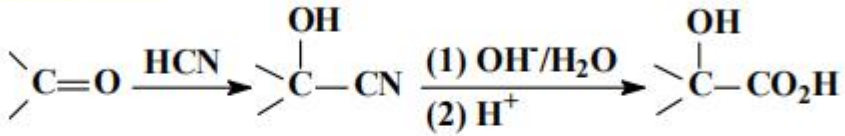

ONa
+ CO2
150 °C
pressure
OH
CO2Na
HCl
OH
CO2H
240 °C
pressure
OH
CO2Na

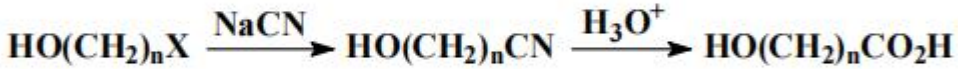
6.羟基羧酸的制备

(a) α-卤代酸水解

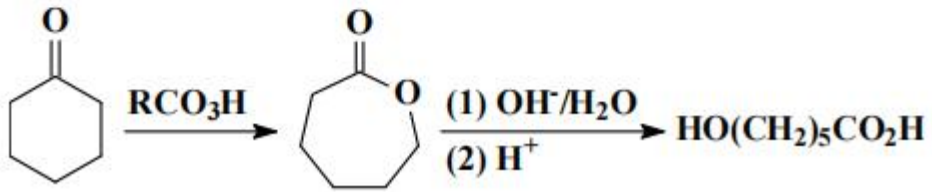


(b) 羟基腈水解

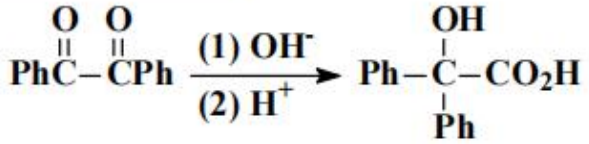




(c) 内酯水解

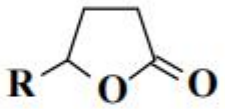


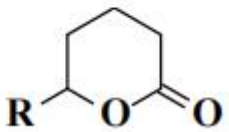
(d) 由邻二酮制备



7.羟基羧酸的反应

β 位：$RCHCH_2CO_2H \xrightarrow[\triangle]{H^+} RCH{=}CHCO_2H$（OH）　消除

γ 位：$RCHCH_2CH_2CO_2H \xrightarrow[\triangle]{H^+}$  （OH）

δ 位：$RCH(CH_2)_3CO_2H \xrightarrow[\triangle]{H^+}$  （OH）

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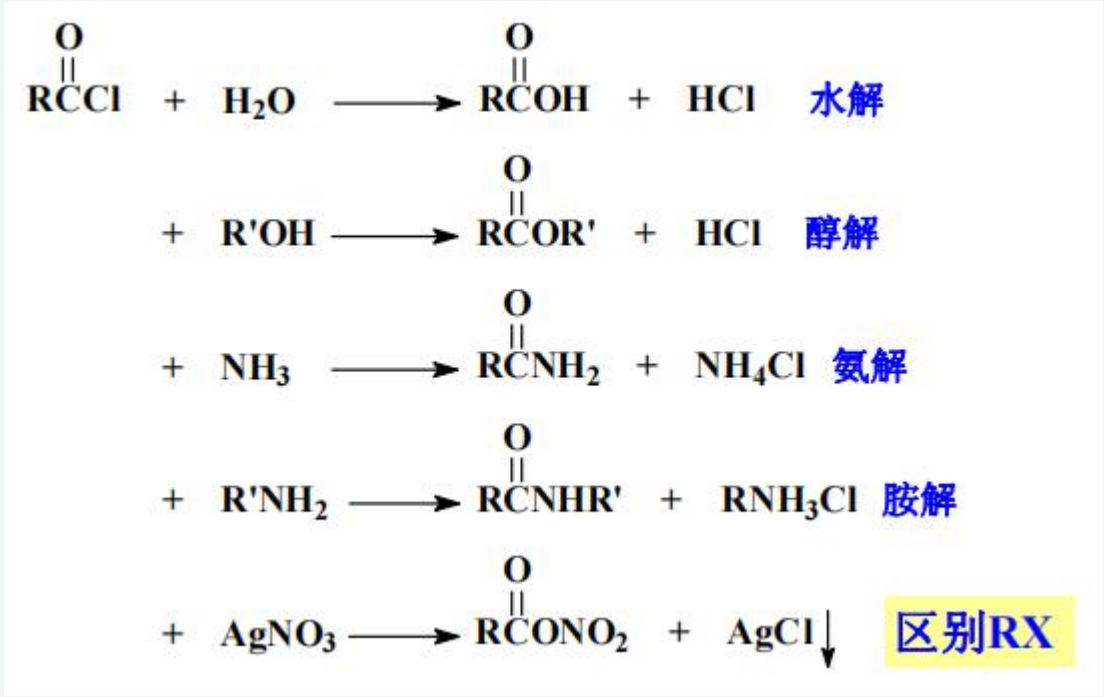
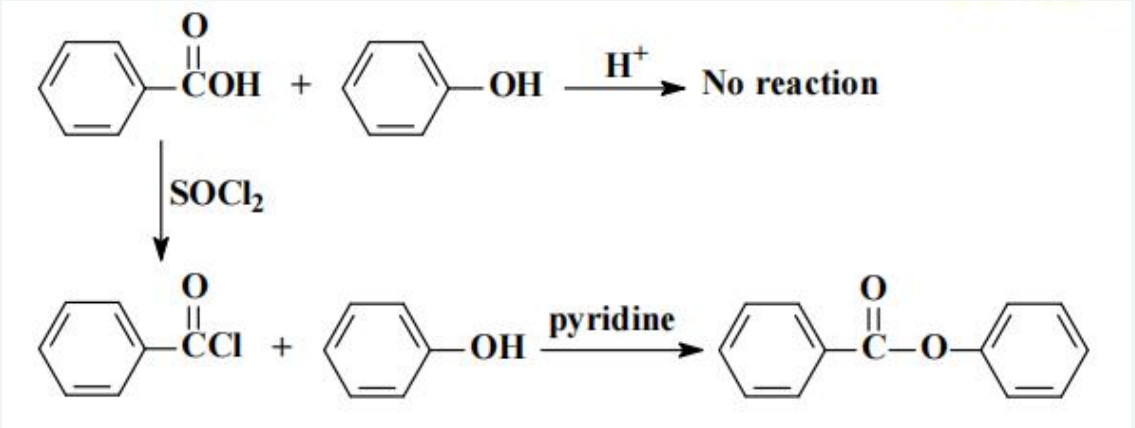
高中有机化学知识拓展

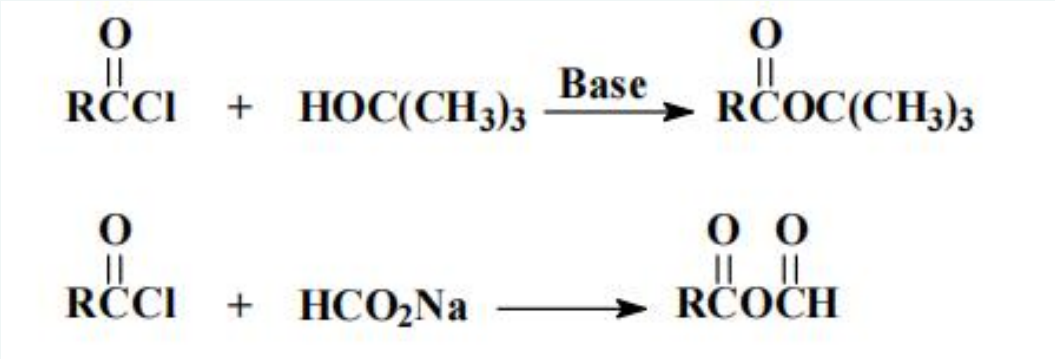
11 羧酸衍生物

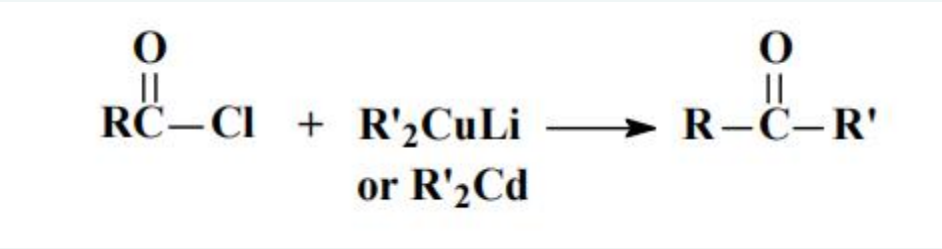
1.酰卤的反应


RCCl + H2O → RCOH + HCl 水解
+ R'OH → RCOR' + HCl 醇解
+ NH3 → RCNH2 + NH4Cl 氨解
+ R'NH2 → RCNHR' + RNH3Cl 胺解
+ AgNO3 → RCONO2 + AgCl↓ 区别RX

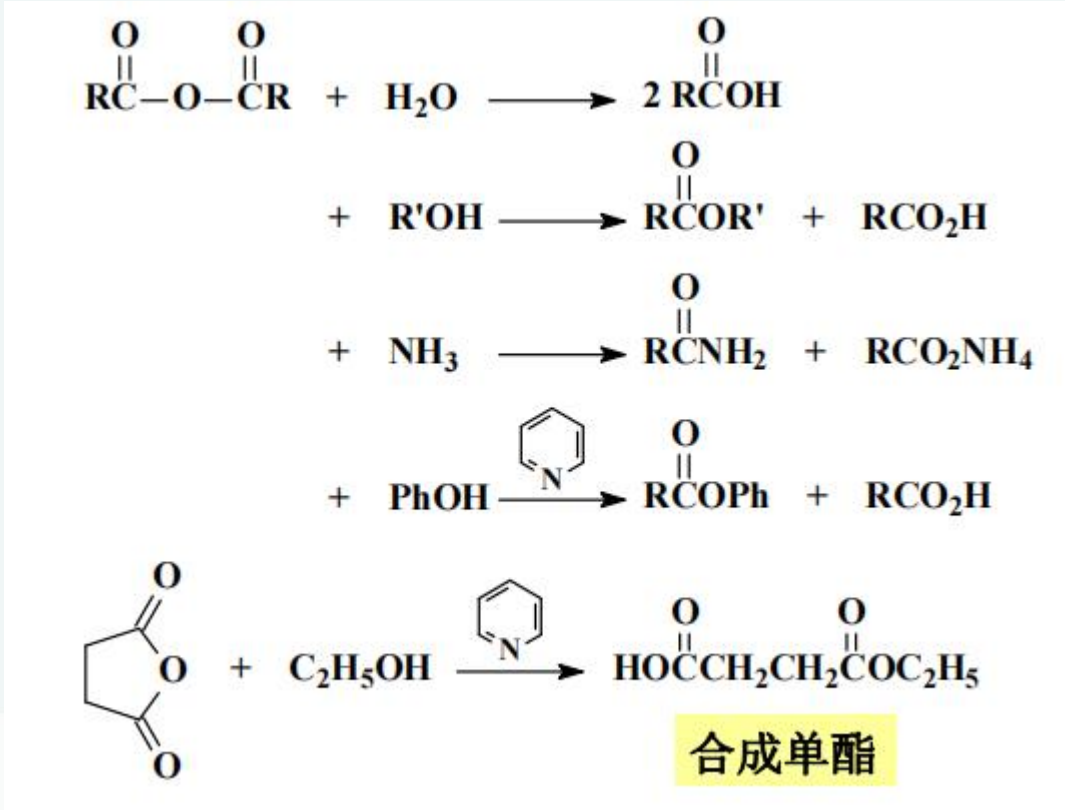

COH + OH
H+
No reaction
SOCl2
CCl + OH
pyridine
C–O

1.酰卤的反应

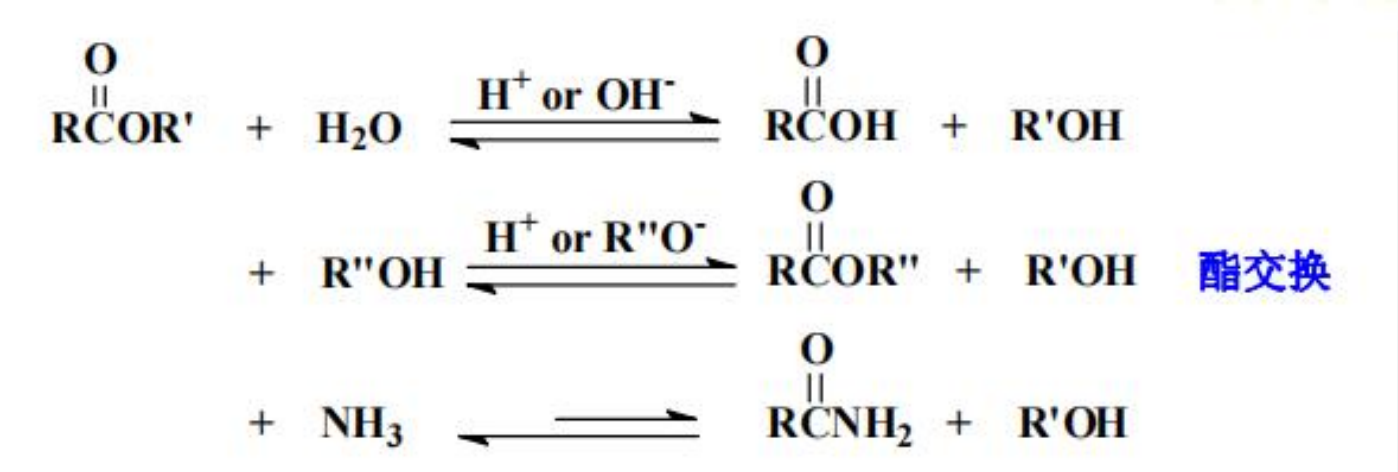

RCCl + HOC(CH3)3 Base RCOC(CH3)3
RCCl + HCO2Na RCOCH

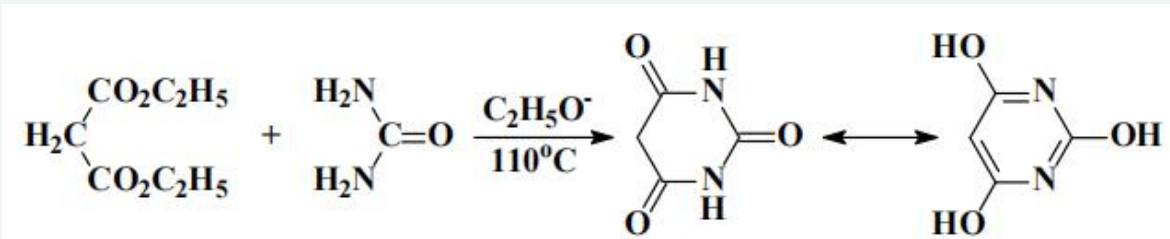

RC—Cl + R'2CuLi or R'2Cd R—C—R'

2.酸酐的反应


RC(=O)–O–C(=O)R + H2O → 2 RCOH
+ R'OH → RCOR' + RCO2H
+ NH3 → RCNH2 + RCO2NH4
+ PhOH → RCOPh + RCO2H
+ C2H5OH → HOCCH2CH2COC2H5
合成单酯

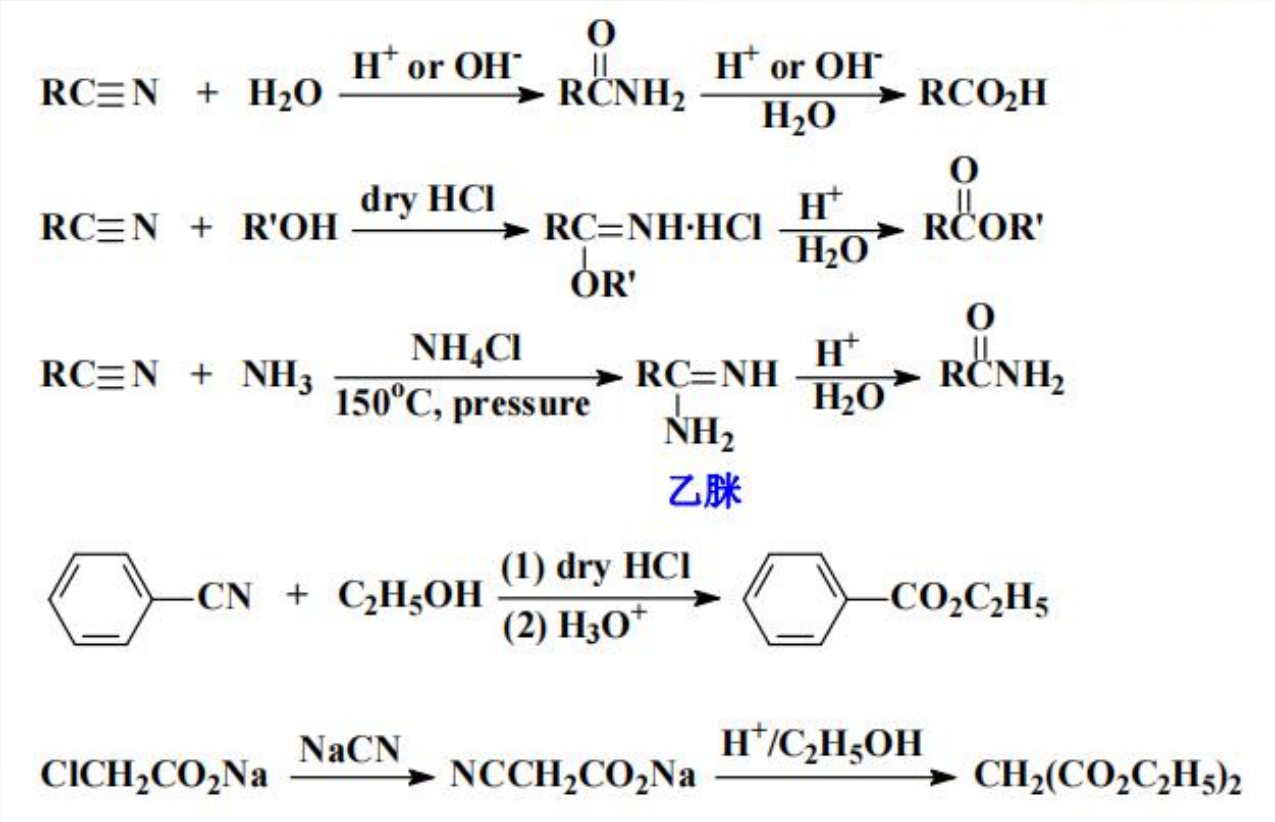
3.酯的反应



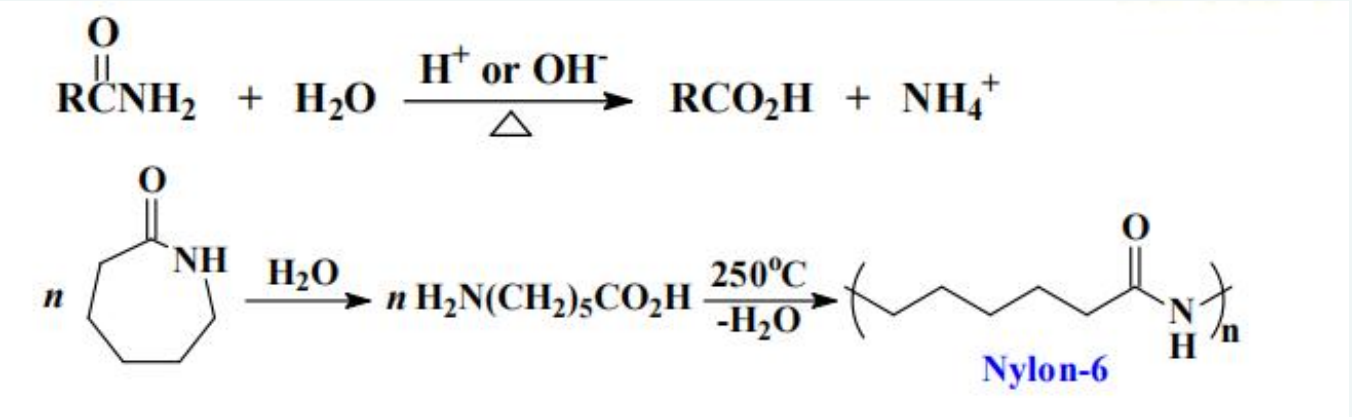


巴比妥酸 (2,4,6-三羟基嘧啶)
barbituric acid

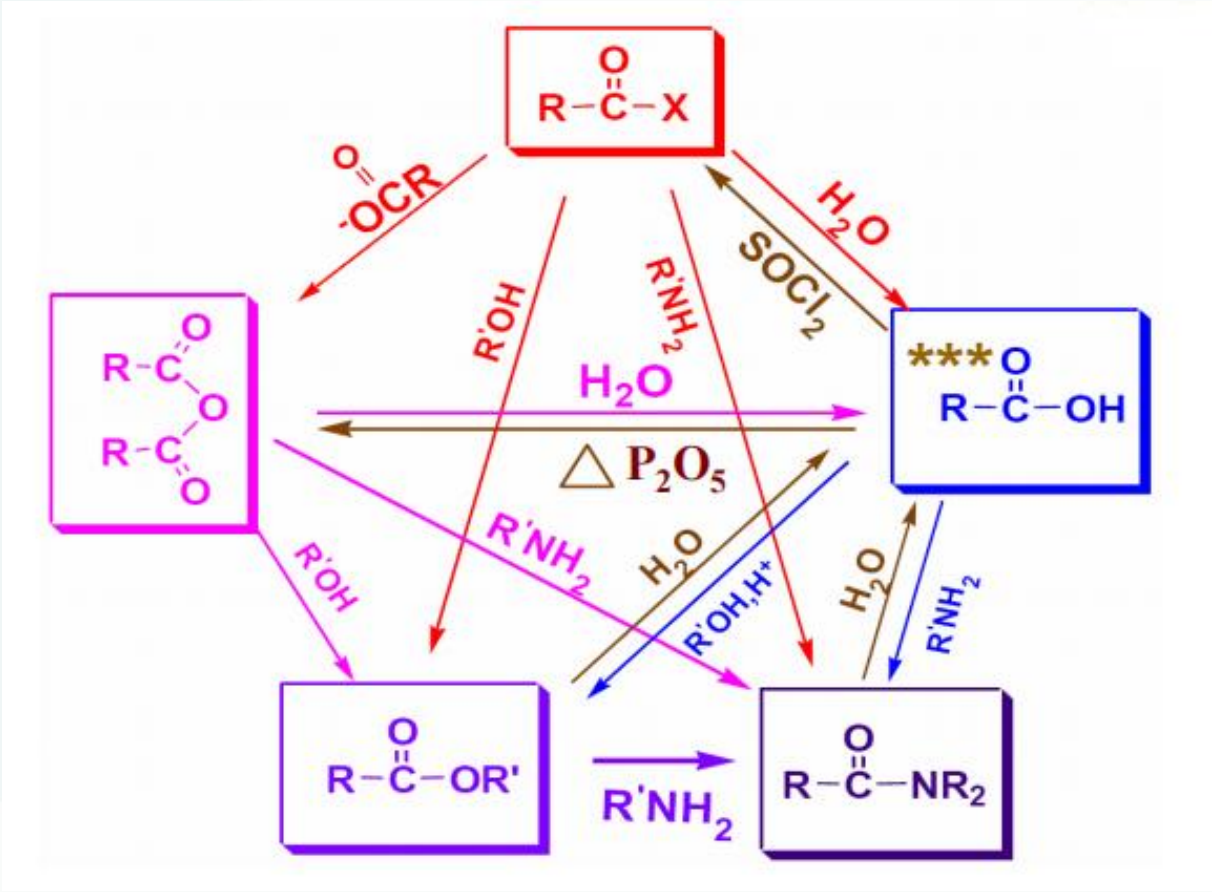
4.腈的反应


RC≡N + H2O
H+ or OH-
RCNH2
H+ or OH-
H2O
RCO2H
RC≡N + R'OH
dry HCl
RC=NH·HCl
OR'
H+
H2O
RCOR'
RC≡N + NH3
NH4Cl
150°C, pressure
RC=NH
NH2
H+
H2O
RCNH2
乙脒
CN + C2H5OH
(1) dry HCl
(2) H3O+
CO2C2H5
ClCH2CO2Na
NaCN
NCCH2CO2Na
H+/C2H5OH
CH2(CO2C2H5)2

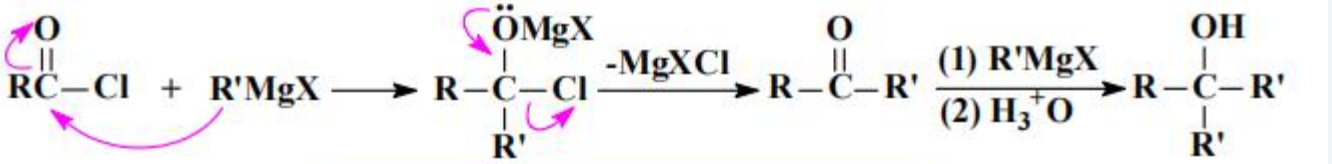
5.酰胺的反应


RCNH2 + H2O
H+ or OH-
RCO2H + NH4+
n
NH
H2O
n H2N(CH2)5CO2H
250°C
-H2O
N
H
n
Nylon-6

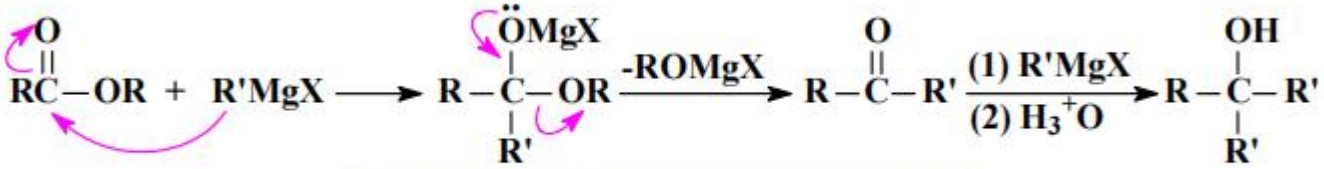
6.羧酸衍生物的关系


R–C(=O)–X
O=OCR
R'OH
R'NH2
SOCl2
H2O
R–C(=O)–O–C(=O)–R
H2O
△ P2O5
***R–C(=O)–OH
R'NH2
R'OH
H2O
R'OH,H+
H2O
R'NH2
R–C(=O)–OR'
R'NH2
R–C(=O)–NR2

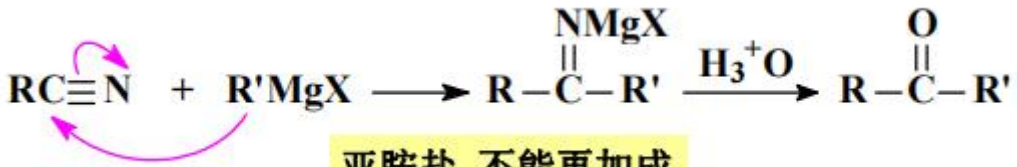
7.格氏试剂的反应



酰氯羰基比酮羰基活泼，可停于此

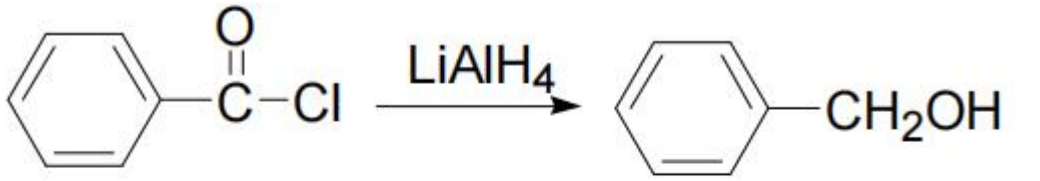


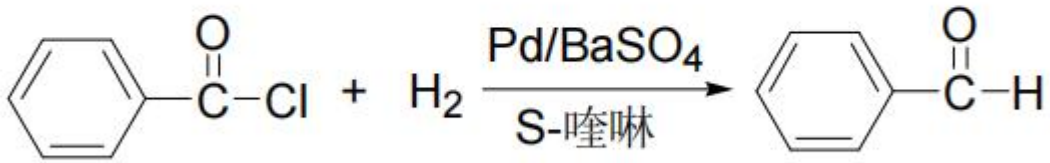
酮羰基比酯羰基活泼，不能停于此

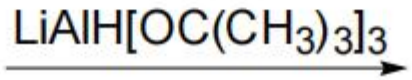


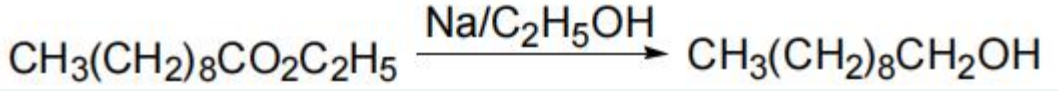
亚胺盐，不能再加成

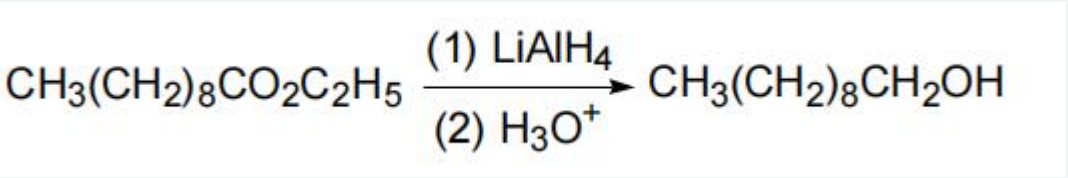
8.还原反应

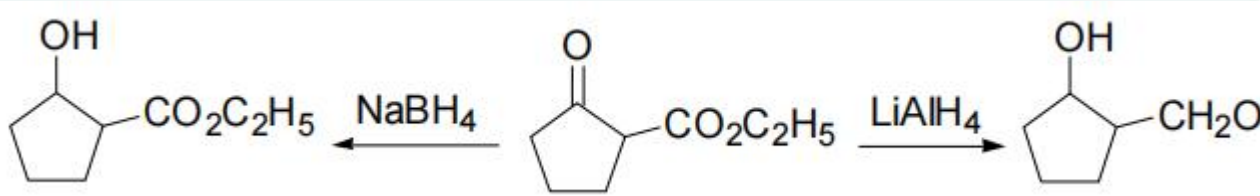

O
C–Cl
LiAlH4
CH2OH


O
C–Cl
+
H2
Pd/BaSO4
S-喹啉
O
C–H

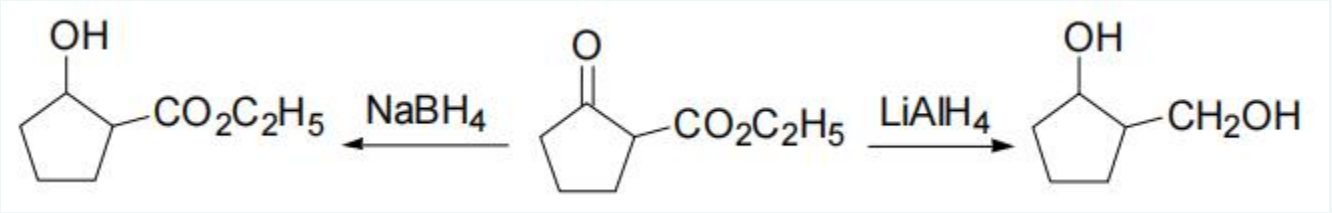

LiAlH[OC(CH3)3]3


CH3(CH2)8CO2C2H5
Na/C2H5OH
CH3(CH2)8CH2OH


CH3(CH2)8CO2C2H5
(1) LiAlH4
(2) H3O+
CH3(CH2)8CH2OH

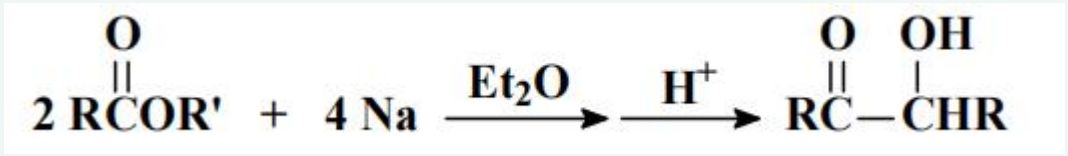

OH
CO2C2H5
NaBH4
O
CO2C2H5
LiAlH4
OH
CH2O

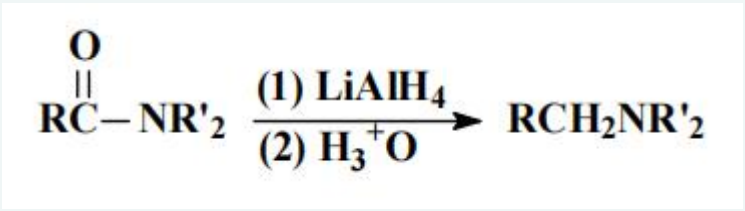
8.还原反应

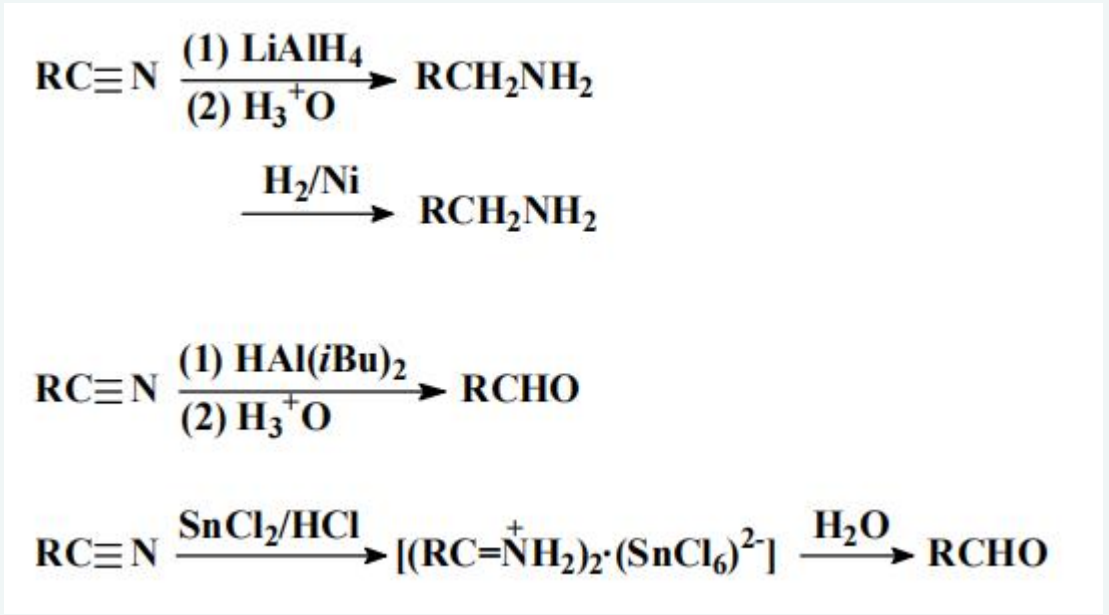

OH
$CO_2C_2H_5$
$NaBH_4$
O
$CO_2C_2H_5$
$LiAlH_4$
OH
CH_2OH


O
O
O
$LiAlH_4$
$HOCH_2CH_2CH_2CH_2OH$
O
O
O
C_2H_5OH
O
O
$C_2H_5OCCH_2CH_2COH$
Na/C_2H_5OH
O
$HOCH_2CH_2CH_2COH$
选择性还原

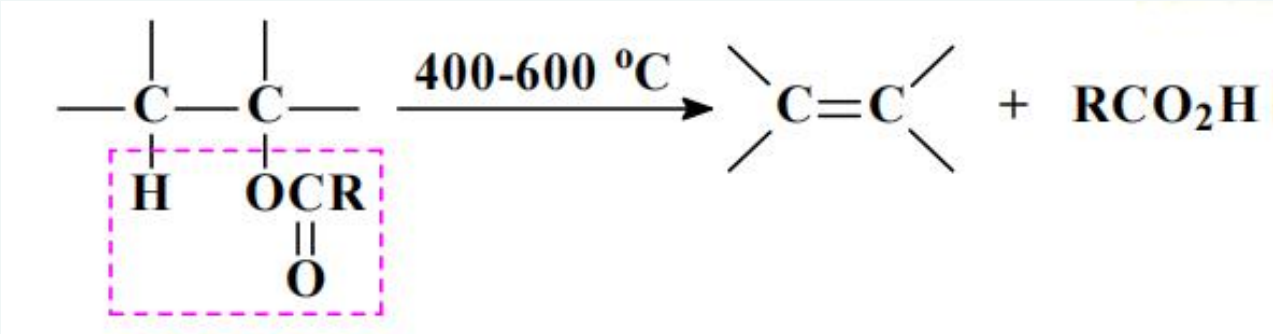
8.还原反应


O
2 RCOR' + 4 Na
Et2O
H+
O OH
RC—CHR


O
RC—NR'2
(1) LiAlH4
(2) H3+O
RCH2NR'2


RC≡N
(1) LiAlH4
(2) H3+O
RCH2NH2
H2/Ni
RCH2NH2
RC≡N
(1) HAl(iBu)2
(2) H3+O
RCHO
RC≡N
SnCl2/HCl
[(RC=NH2+)2·(SnCl6)2-]
H2O
RCHO

9.消去反应



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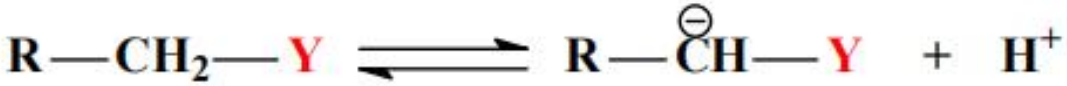
12 羧酸衍生物涉及碳负离子的反应

1.羧酸衍生物α-C上面氢的酸性



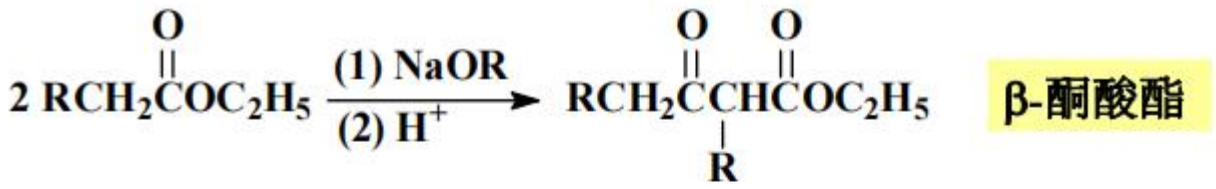
	pK_a		pK_a
RCH_2CONMe_2	30	$NCCH_2CN$	11.8
RCH_2CN	25	$CH_3COCH_2CO_2C_2H_5$	10.7
RCH_2CO_2R	24.5	$PhCOCH_2COCH_3$	9.4
$RCOCH_2R$	20~21	$CH_3COCH_2COCH_3$	8.9
$PhCOCH_2R$	19	$CH_3CH_2NO_2$	8.6
RCH_2CHO	17	CH_3COCH_2CHO	5.9
RCH_2COCl	~16	$HCOCH_2CHO$	5
$CH_2(CO_2C_2H_5)_2$	13	$O_2NCH_2NO_2$	3.6

酸性:	CH_3CO_2H >	H_2O >	ROH >	$CH_3C{\equiv}CH$ >	NH_3 >	$CH_2{=}CH_2$ >	CH_3CH_3
p*K*a	4.8	15.7	16~19	25	34	44	50

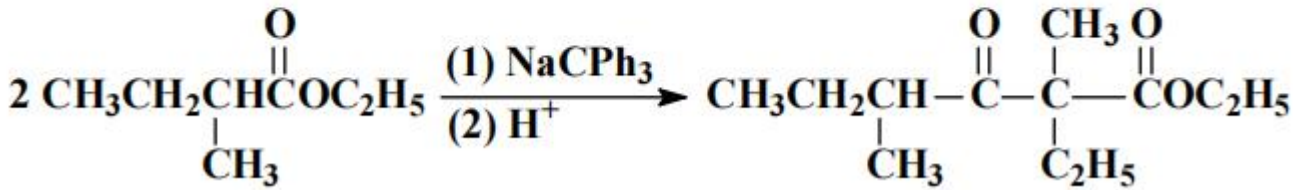
2.缩合反应（取代反应）

适用范围：

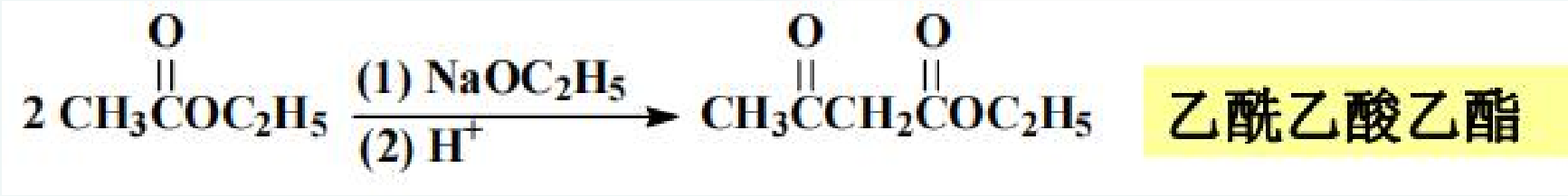
- 只要有两个α氢的酯，就可以缩合
- 只有一个α氢的酯，醇钠碱性不够强，用更强的碱才能缩合
- 双重α氢不能进行酯缩合

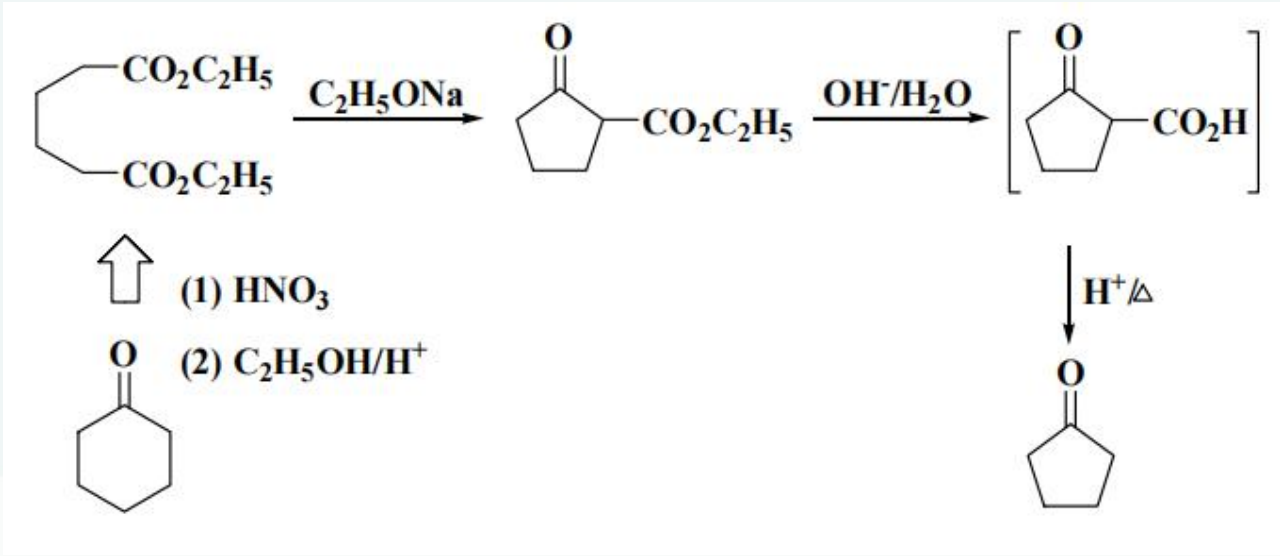


β-酮酸酯

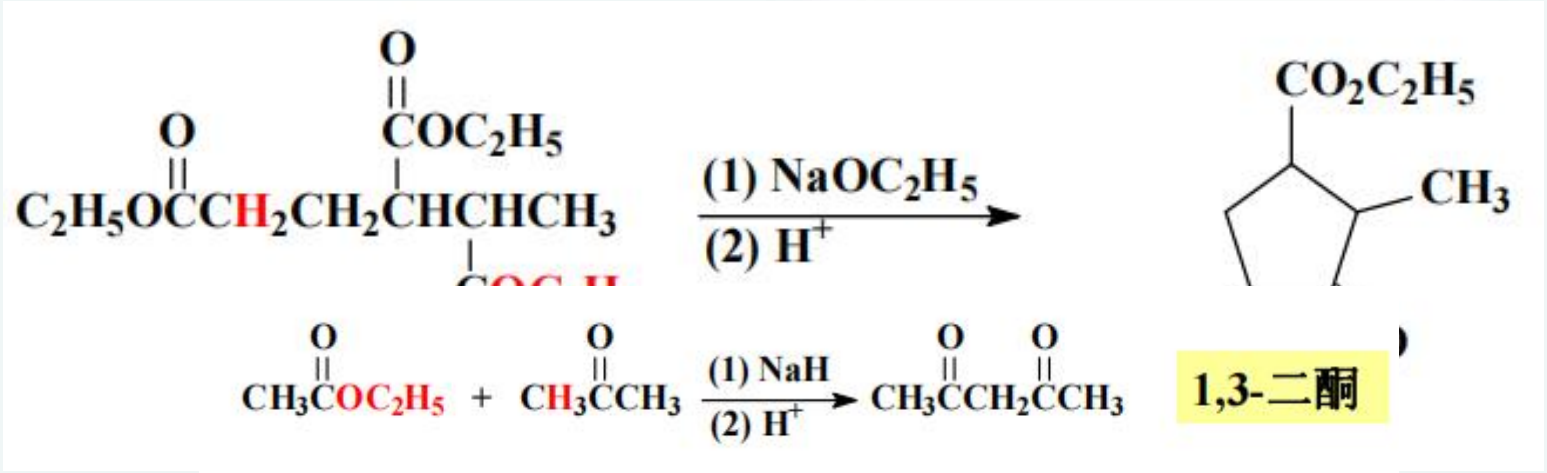


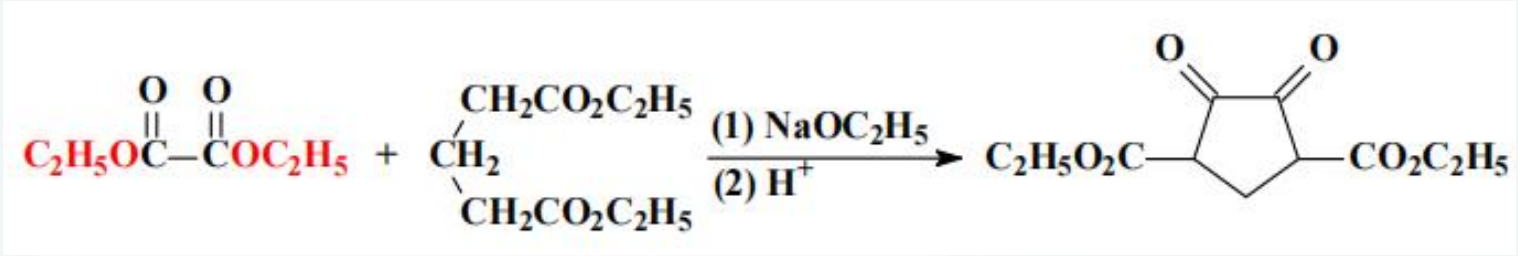
2.缩合反应（取代反应）


2 CH3COC2H5
(1) NaOC2H5
(2) H+
CH3CCH2COC2H5
乙酰乙酸乙酯

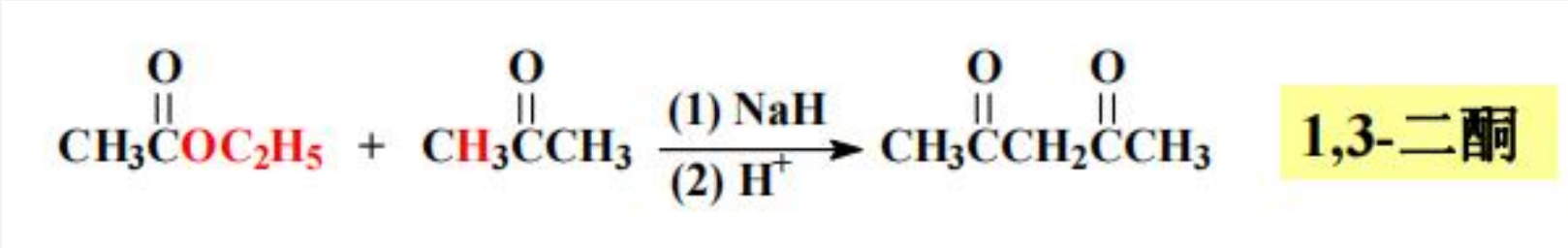

CO2C2H5
CO2C2H5
C2H5ONa
CO2C2H5
OH-/H2O
CO2H
(1) HNO3
(2) C2H5OH/H+
H+/△

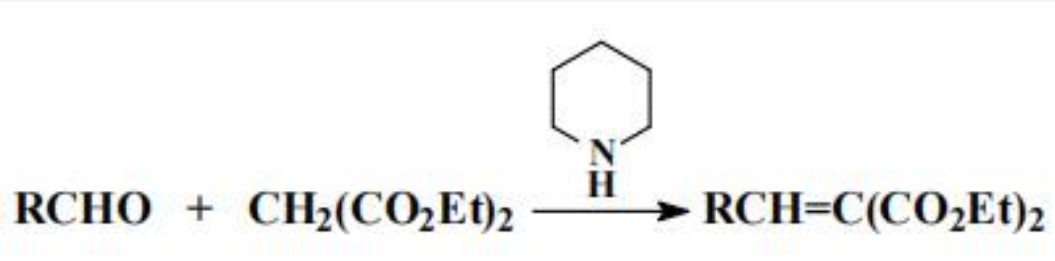
2.缩合反应（取代反应）


(1) NaOC2H5
(2) H+
CO2C2H5
CH3
(1) NaH
(2) H+
1,3-二酮


CH2CO2C2H5
CH2
CH2CO2C2H5
(1) NaOC2H5
(2) H+
C2H5O2C
CO2C2H5

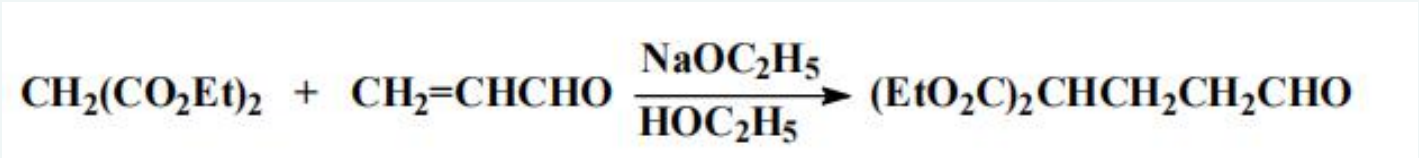
2.缩合反应（取代反应）

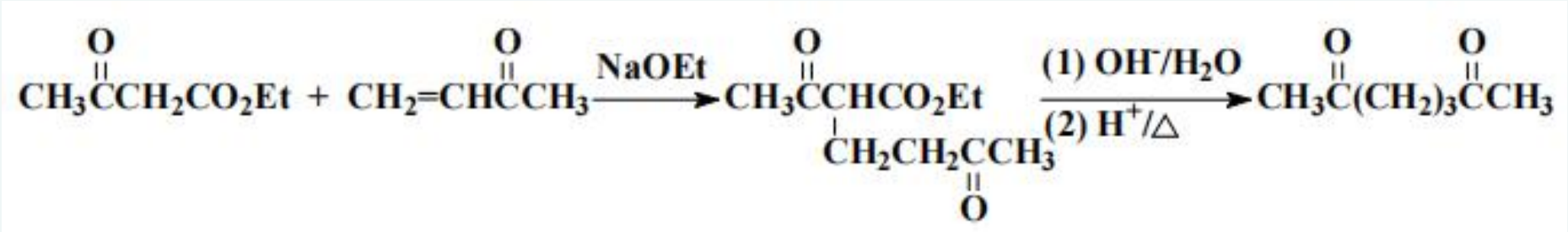

O
O
O
O
CH3COC2H5 + CH3CCH3
(1) NaH
(2) H+
CH3CCH2CCH3
1,3-二酮


N
H
RCHO + CH2(CO2Et)2
RCH=C(CO2Et)2

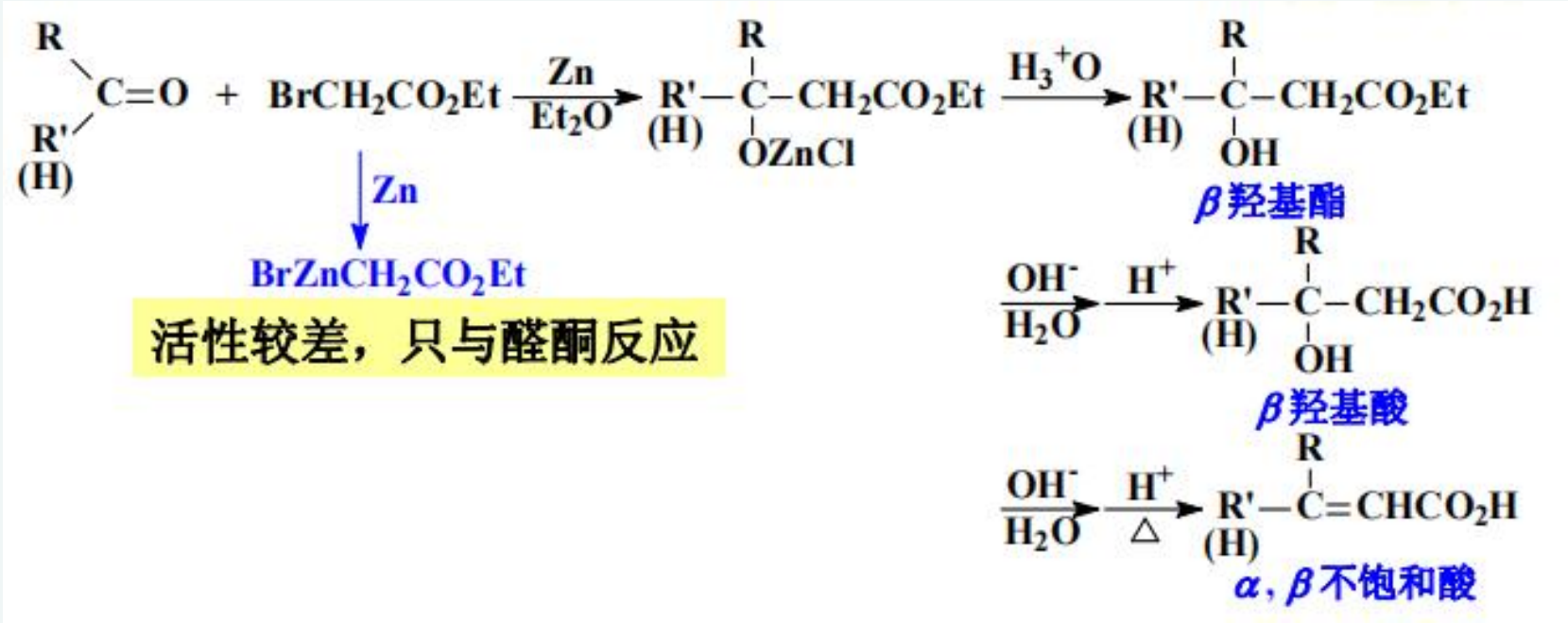

O O
PhCHO + CH3COCCH3
CH3COONa
△
PhCH=CHCO2H + CH3CO2H

3.加成反应

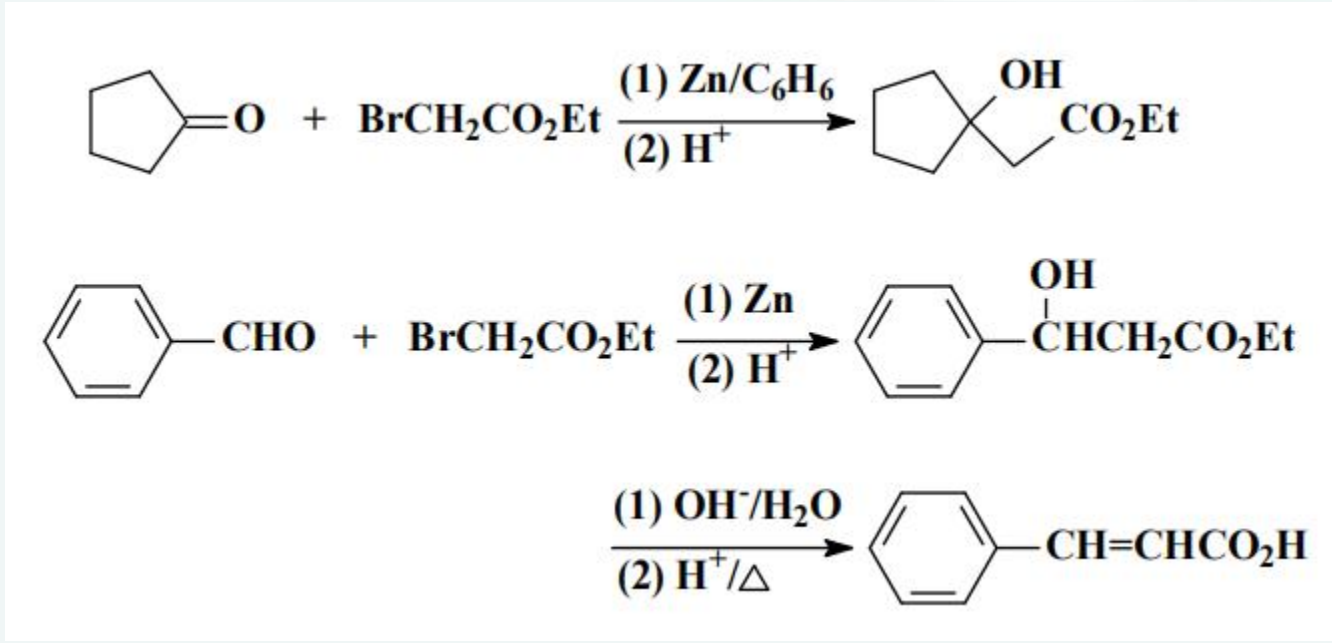

CH2(CO2Et)2 + CH2=CHCHO
NaOC2H5
HOC2H5
(EtO2C)2CHCH2CH2CHO

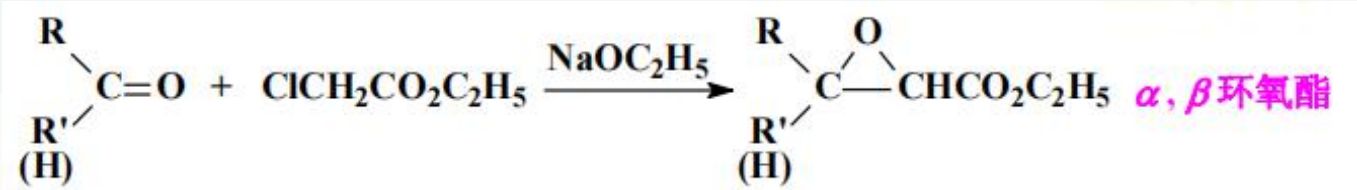

CH3CCH2CO2Et + CH2=CHCCH3
NaOEt
CH3CCHCO2Et
CH2CH2CCH3
(1) OH-/H2O
(2) H+/△
CH3C(CH2)3CCH3

3.加成反应


R
C=O
R'
(H)
+ BrCH2CO2Et
Zn
Et2O
R'—C—CH2CO2Et
(H)
OZnCl
H3+O
OH
β羟基酯
Zn
BrZnCH2CO2Et
活性较差，只与醛酮反应
OH-
H2O
H+
R'—C—CH2CO2H
β羟基酸
△
R'—C=CHCO2H
α，β不饱和酸

3.加成反应


(1) Zn/C6H6
(2) H+
OH
CO2Et
CHO
BrCH2CO2Et
(1) Zn
(2) H+
OH
CHCH2CO2Et
(1) OH-/H2O
(2) H+/△
CH=CHCO2H


R
C=O
R'
(H)
ClCH2CO2C2H5
NaOC2H5
O
CHCO2C2H5
α,β环氧酯

时光不负有心人

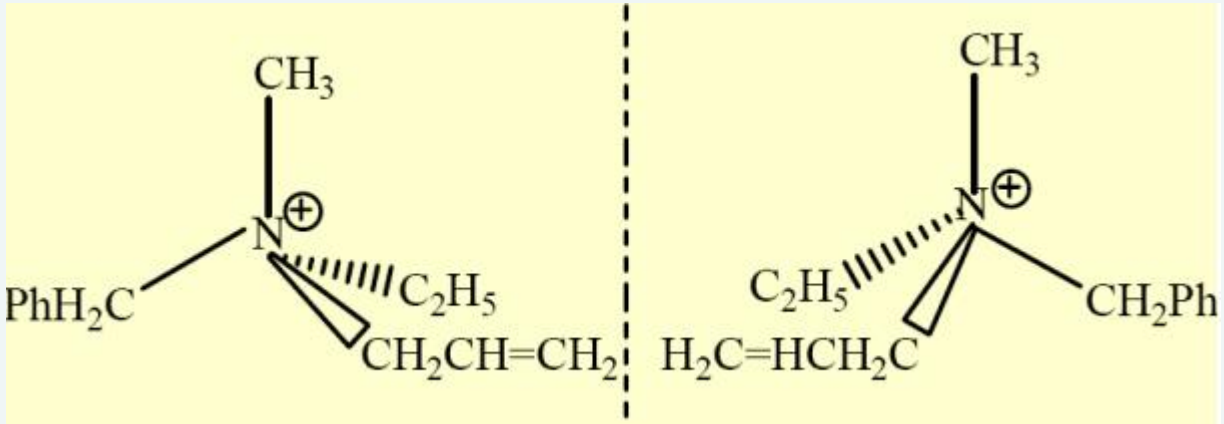
人总会上岸的

高中有机化学知识拓展

13 胺

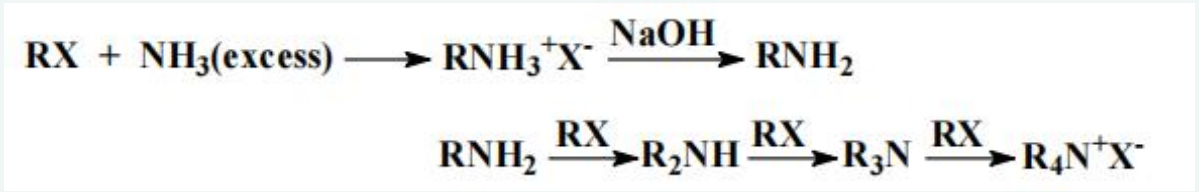
1.胺的分类与手性

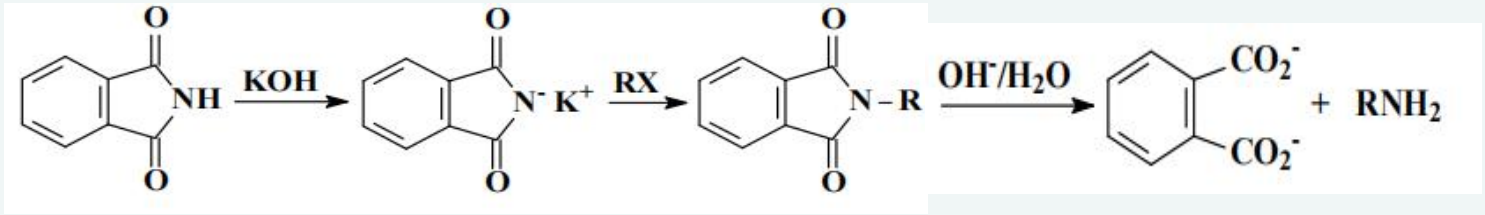
NH_3	RNH_2	R_2NH	R_3N	$R_4N^+X^-$	$R_4N^+OH^-$
氨	伯胺(1°)	仲胺 (2°)	叔胺(3°)	季铵盐	季铵碱

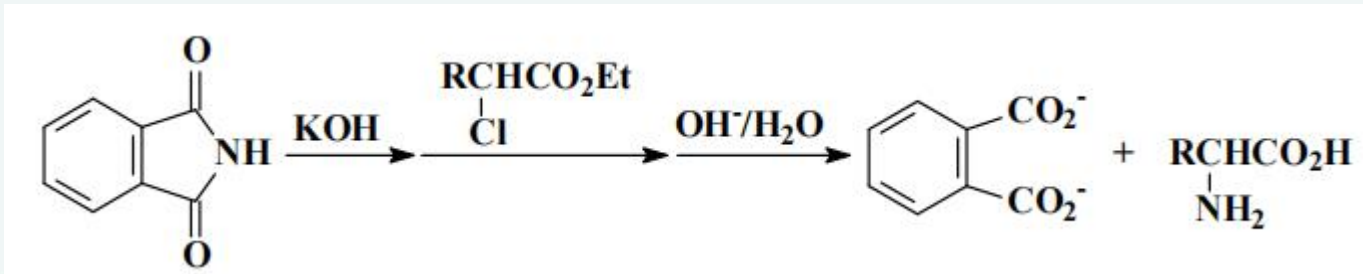


生成季铵盐以后，N的四个sp^3全部用来成键，当四个基团不同时，存在对映异构体

2.制备胺

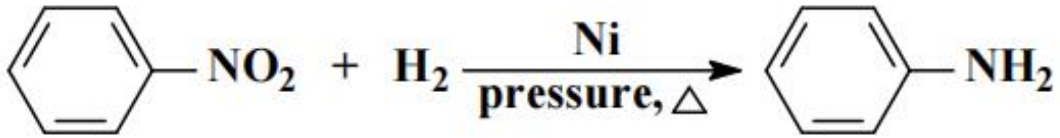


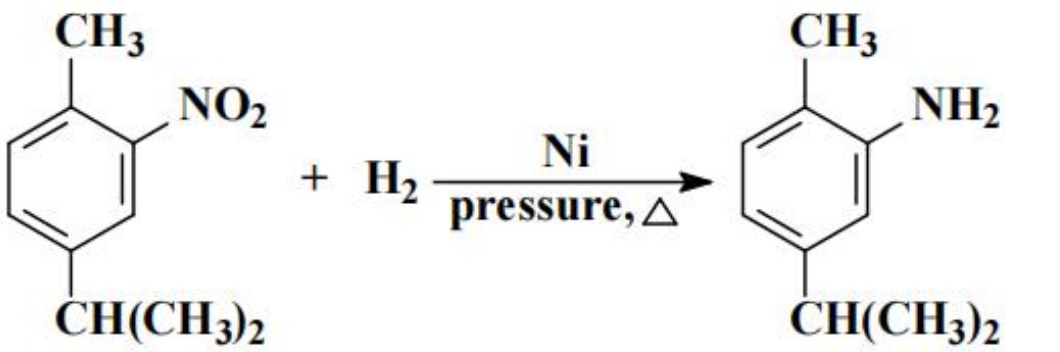


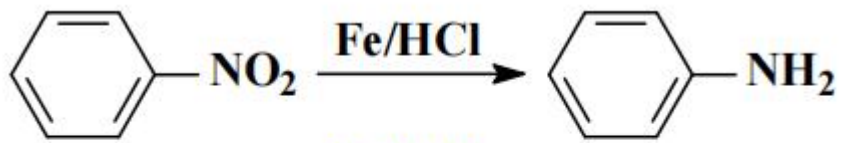


制备伯胺和氨基酸

2.硝基还原制备胺

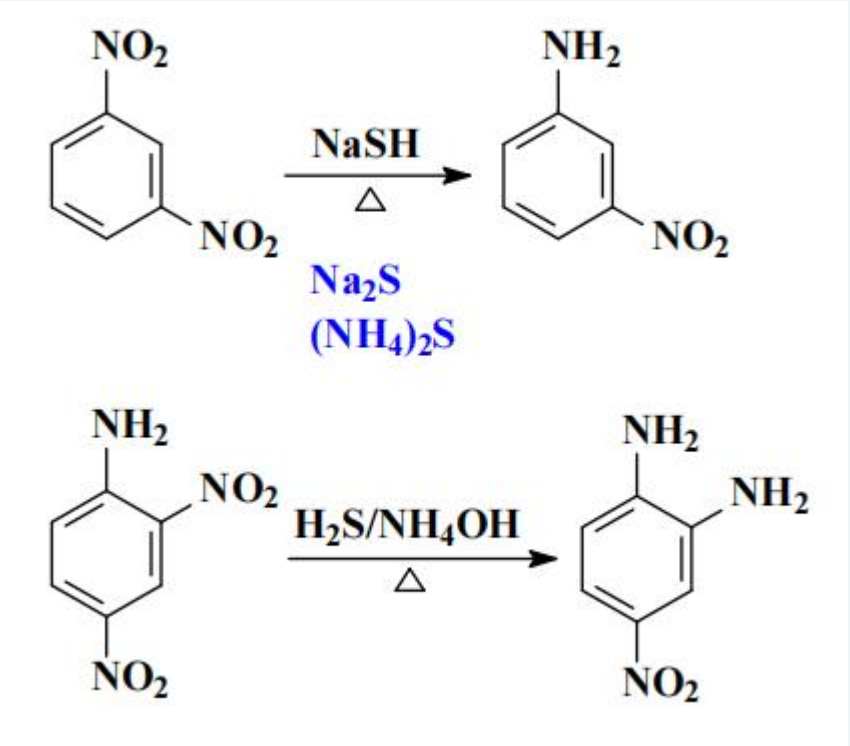




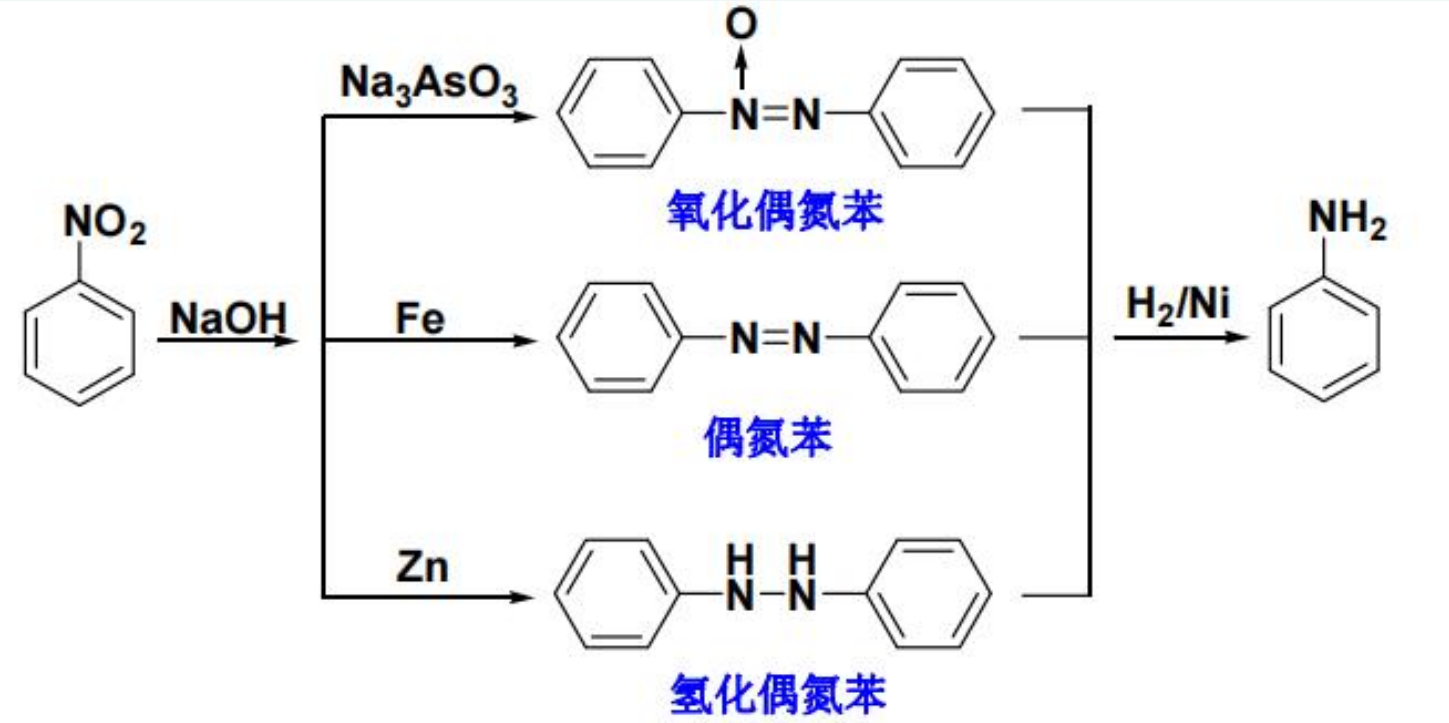


Zn/HCl
$SnCl_2$/HCl
$FeCl_2$/HCl

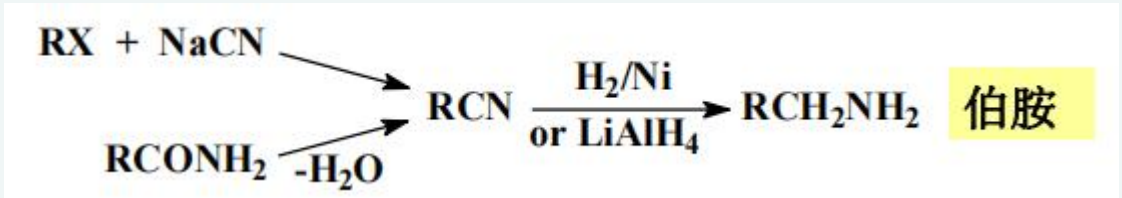
2.硝基还原制备胺（选择性还原）

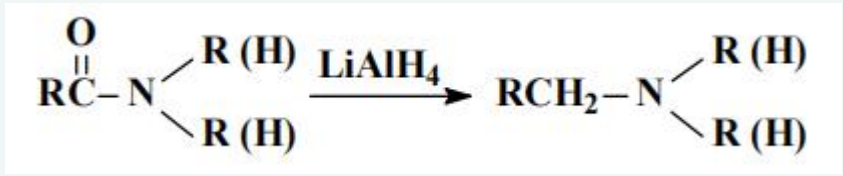


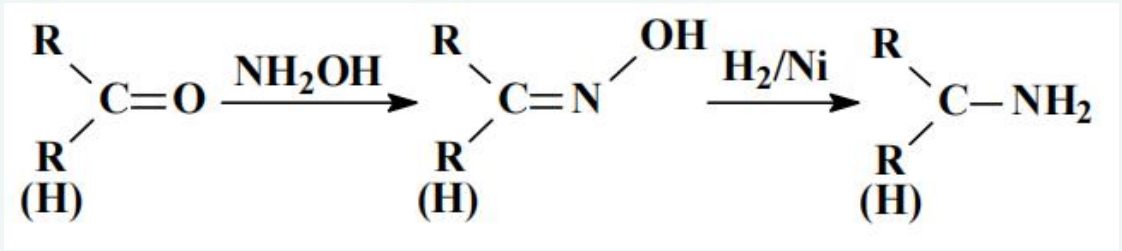
2.碱性还原制备胺

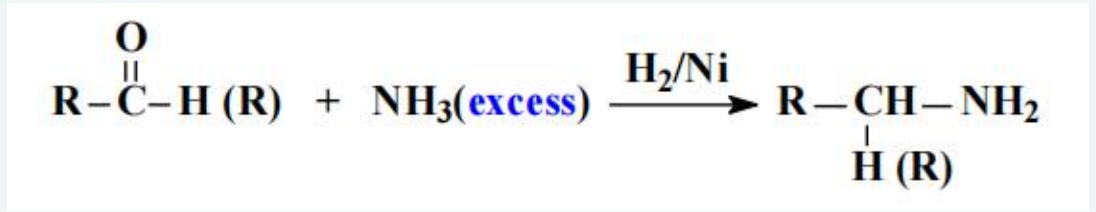


2.其他含氮化合物还原制备胺

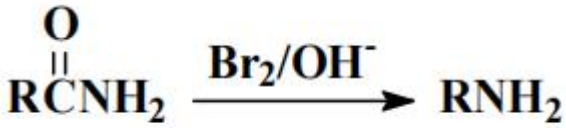




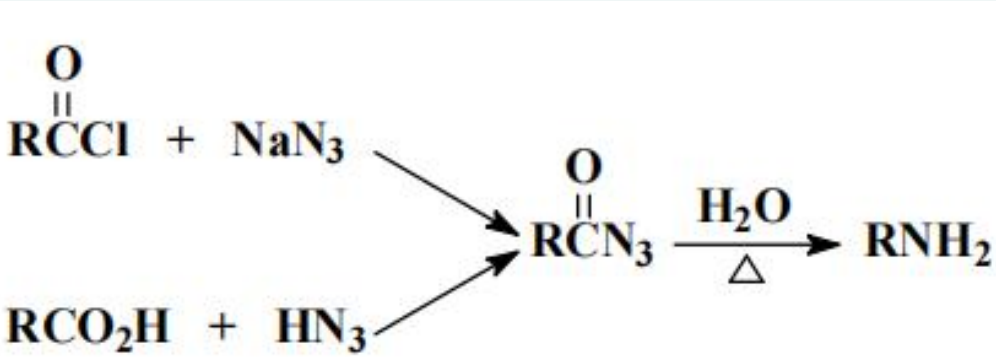




3.Hoffman重排



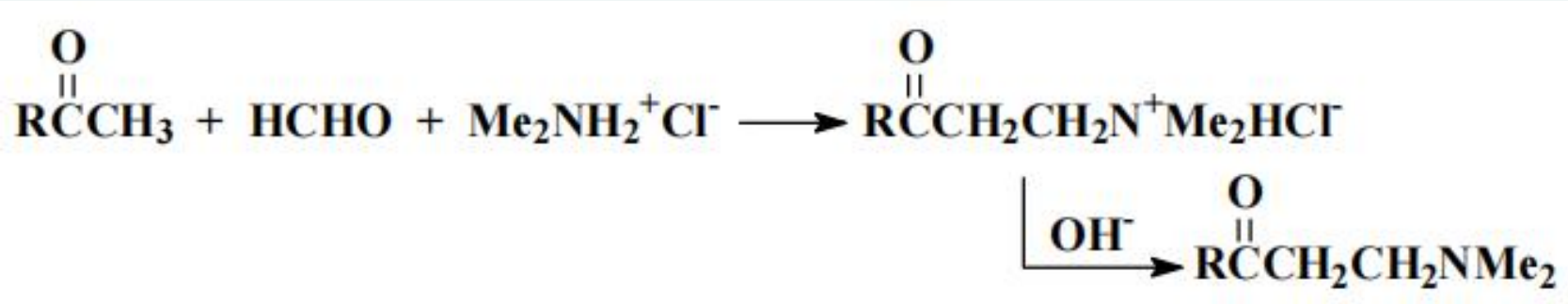
由酰胺制备少一个碳原子的胺

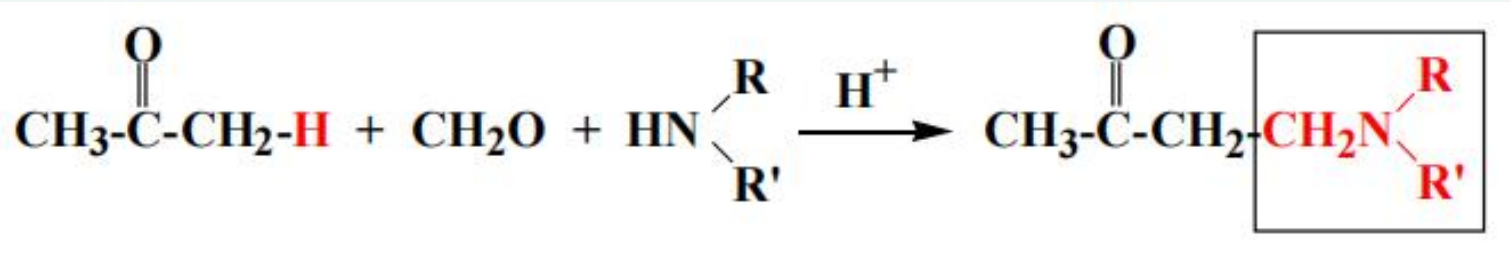


由羧酸、酰氯制备少一个碳原子的胺

4.Mannich反应

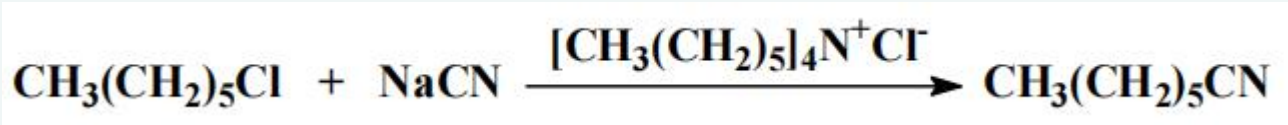
含有α-H的酮与甲醛等简单脂肪醛及铵盐水溶液反应，生成β氨基酮。



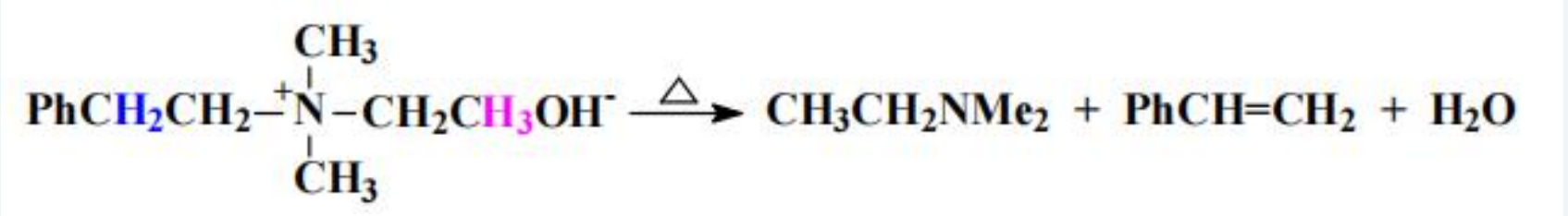


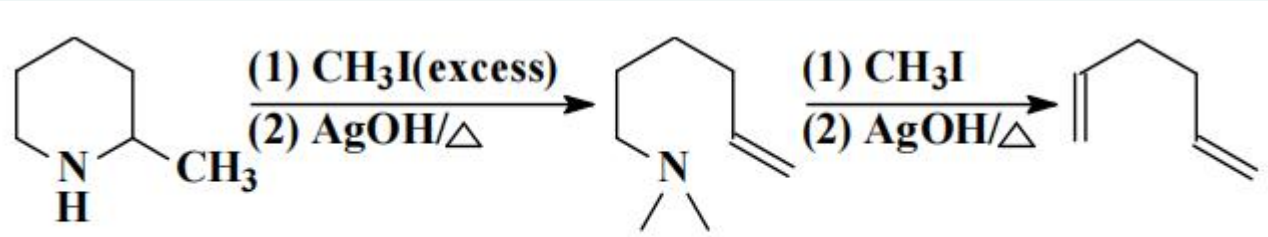
5.相转移催化剂

相转移催化剂常为季铵盐，可以帮助反应物从一相转移到能够发生反应的另一相当中，从而加快异相系统反应速率的一类催化剂。一般在相转移催化的反应中，存在水溶液和有机溶剂两相，离子往往可溶于水相，不溶于有机相，而有机底物则可溶于有机溶剂之中。不存在相转移催化剂时，两相相互隔离，反应物仅在界面接触，反应进行得很慢。相转移催化剂可以与水相中的离子所结合，并利用自身对有机溶剂的亲和性，将水相中的反应物转移到有机相中，促使反应发生。



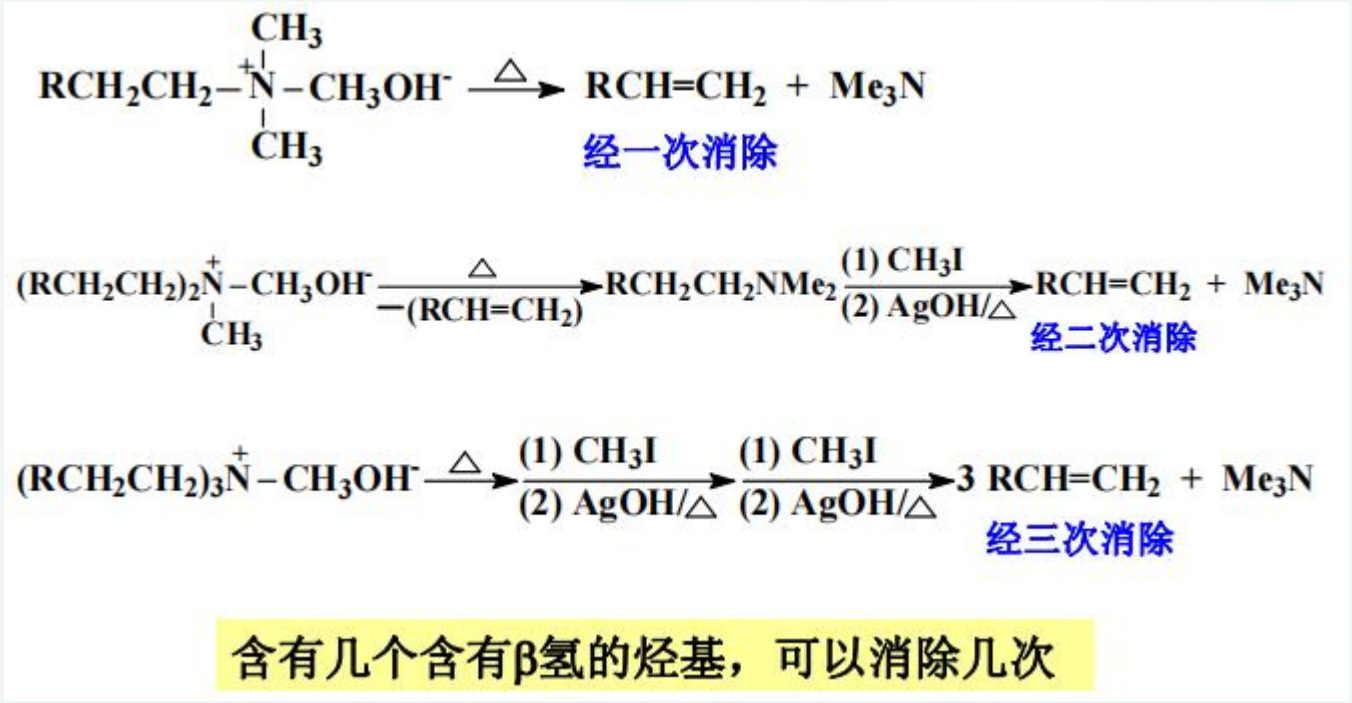
6.消去反应



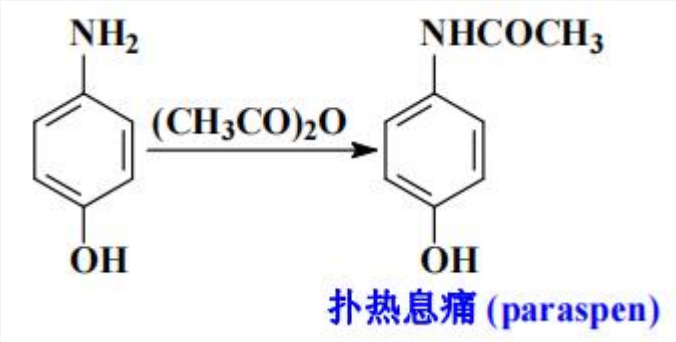


环状仲胺可以消除2次，生成二烯

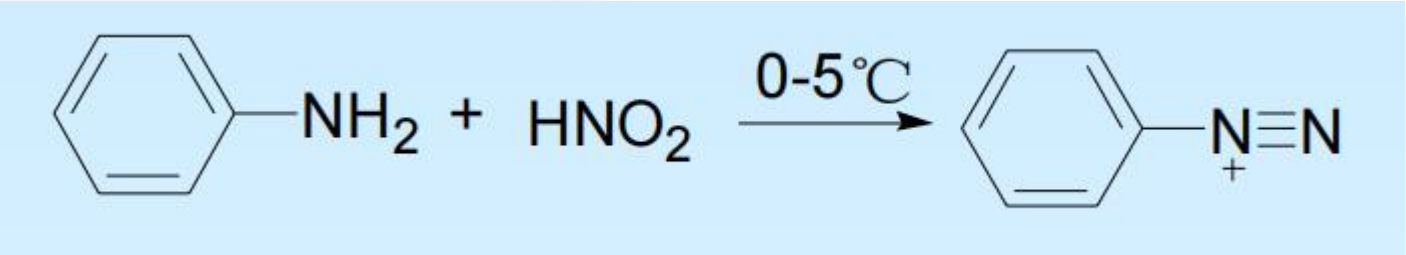
6.消去反应

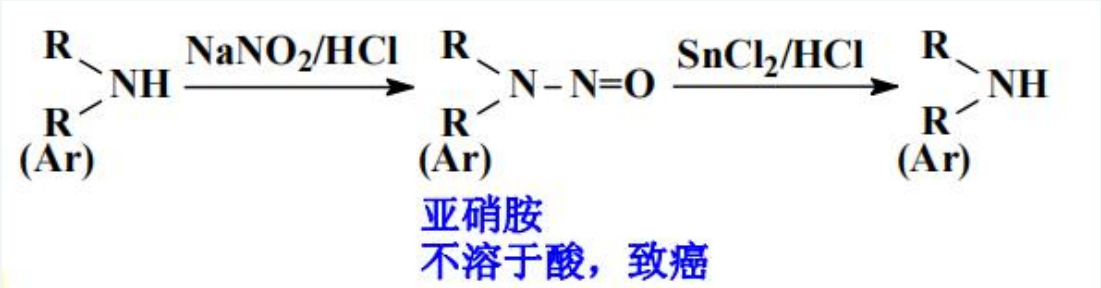

RCH2CH2–N+(CH3)2–CH3OH- △→ RCH=CH2 + Me3N
经一次消除
(RCH2CH2)2N+–CH3OH- △ −(RCH=CH2) RCH2CH2NMe2 (1) CH3I (2) AgOH/△ RCH=CH2 + Me3N
经二次消除
(RCH2CH2)3N+–CH3OH- △ (1) CH3I (2) AgOH/△ (1) CH3I (2) AgOH/△ 3 RCH=CH2 + Me3N
经三次消除
含有几个含有β氢的烃基，可以消除几次

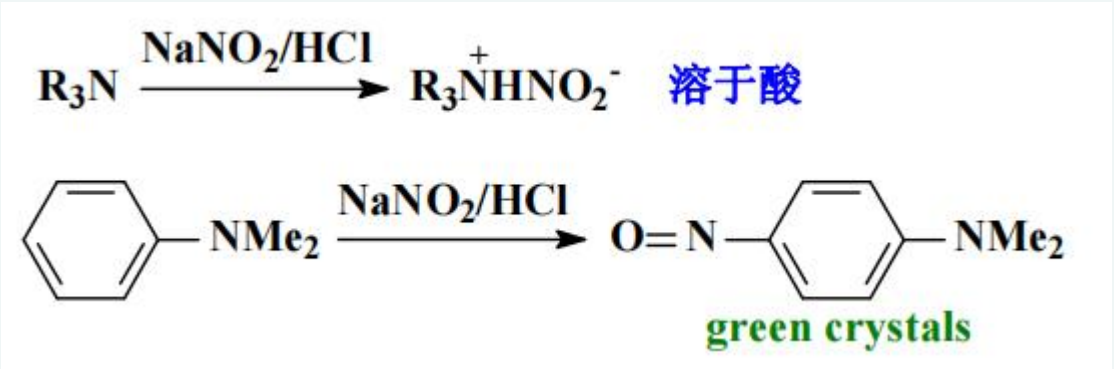
7.取代反应



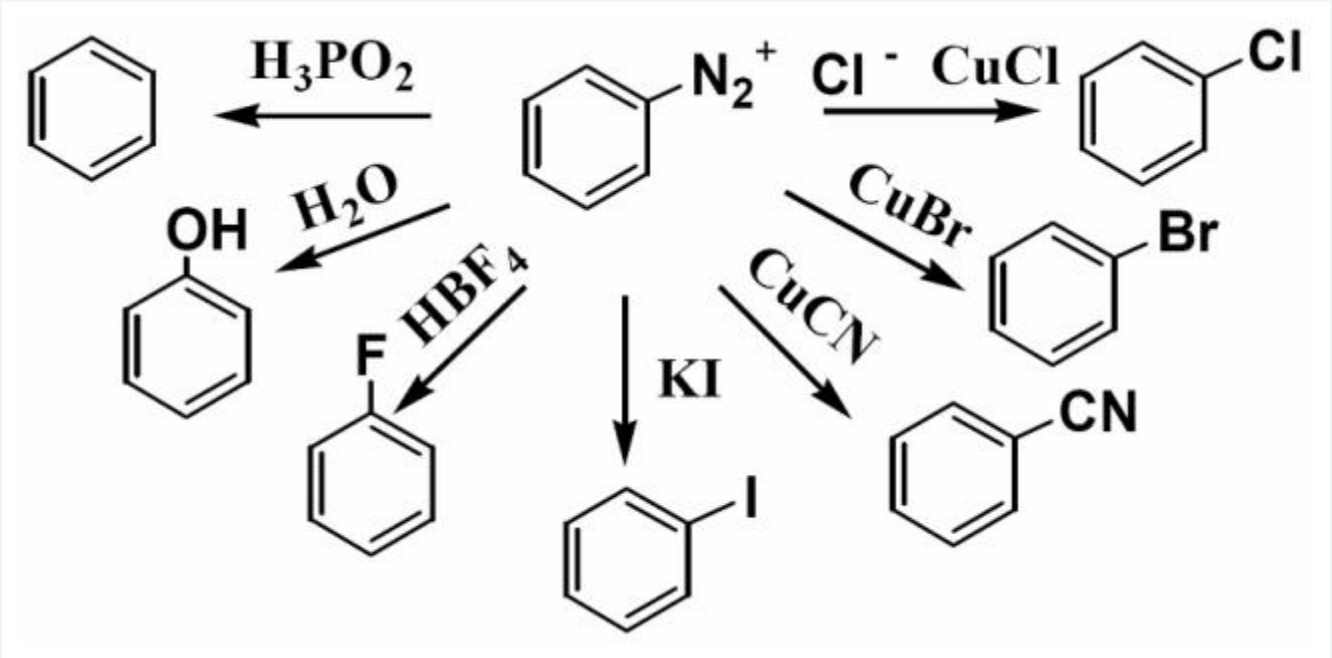
8.重氮盐


NH2 + HNO2
0-5℃
N≡N
+

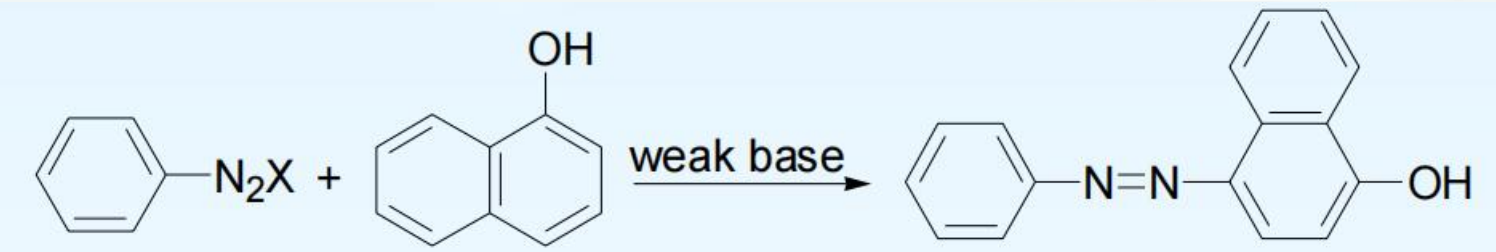

R
NH
R
(Ar)
NaNO2/HCl
N-N=O
SnCl2/HCl
亚硝胺
不溶于酸，致癌


R3N
NaNO2/HCl
R3NHNO2-
溶于酸
NMe2
O=N
green crystals

8.重氮盐



9.偶氮化合物



苏丹红1号：1-苯基偶氮-2-萘酚

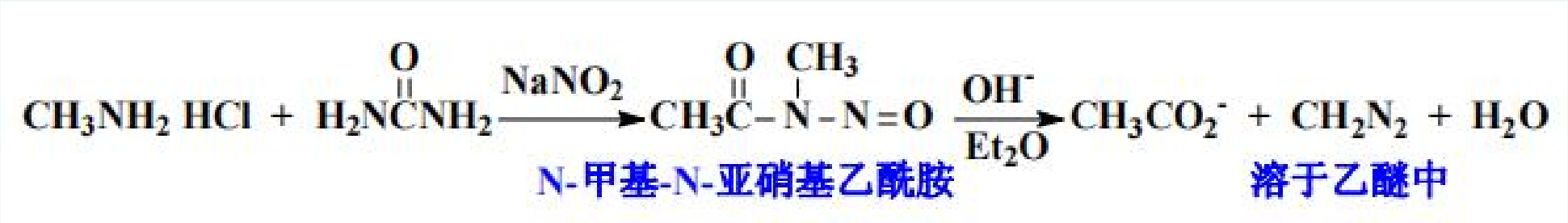
苏丹红2号：1-[(2,4-二甲基苯)偶氮]-2-萘酚

苏丹红3号：1-[4-(苯基偶氮)苯基]偶氮-2-萘酚

苏丹红4号：1-2-甲基-4-[(2-甲基苯)偶氮]苯基偶氮-2-萘酚

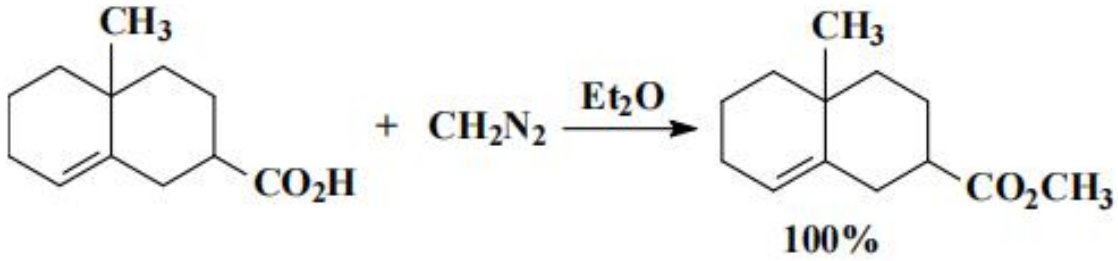
10.重氮甲烷

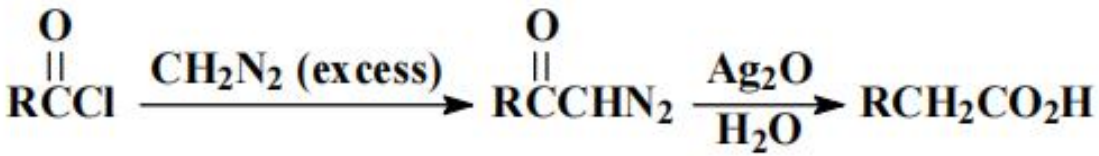
黄色有毒气体，易爆，沸点-23℃，在有机合成中常用其乙醚溶液。



10.重氮甲烷

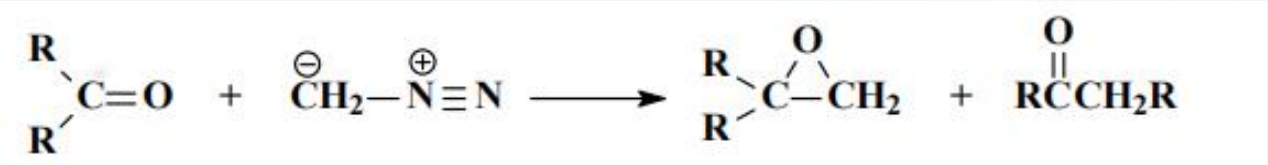
与酸、酚、烯醇等反应生成甲酯或甲基醚

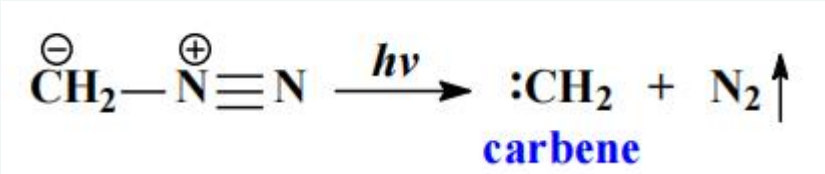


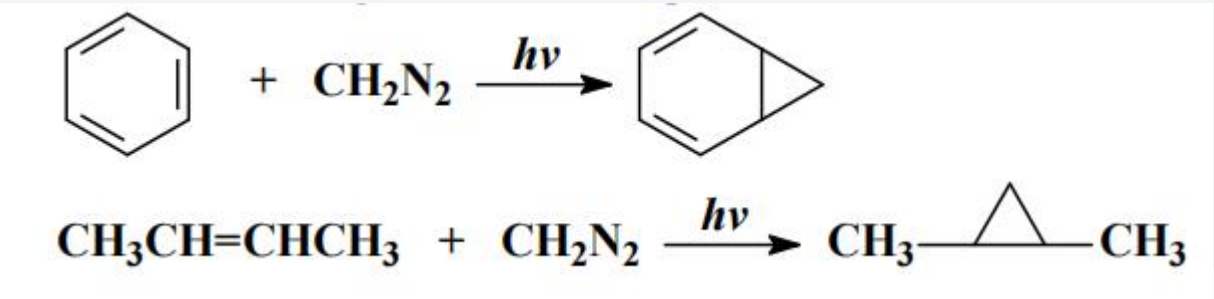


增一个碳

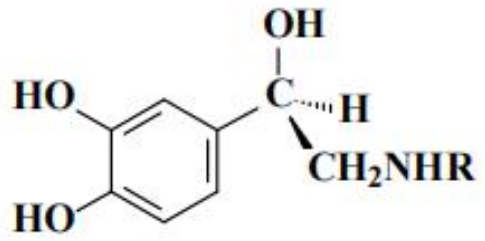
10.重氮甲烷



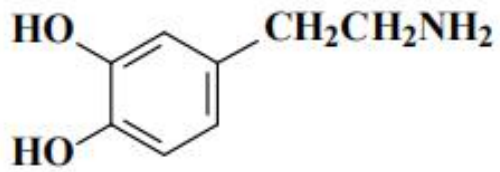




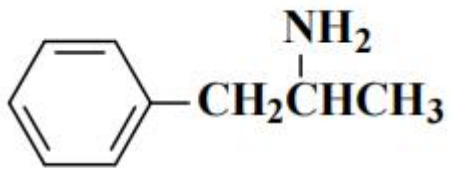
12.苯乙胺类化合物



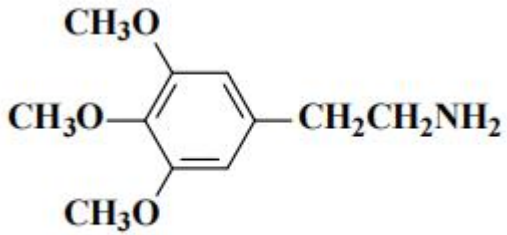
R = CH_3, Adrenaline 肾上腺素 (预警)
R = H, Noradrenaline 去甲肾上腺素



Dopamine 多巴胺 (大脑中)



冰毒 (摇头丸)



Mescaline 酶斯卡灵 (致幻剂)

时光不负有心人

人总会上岸的