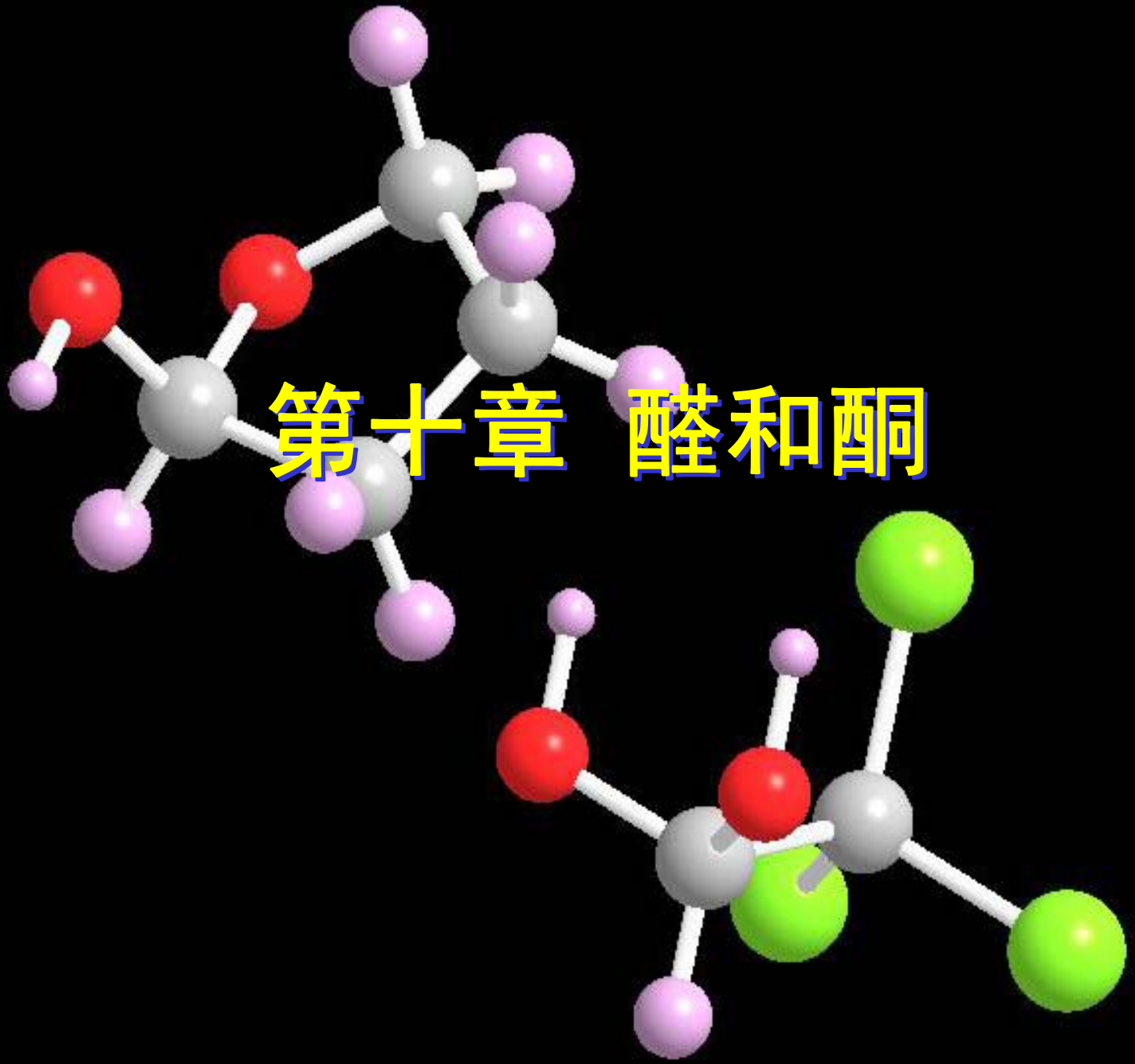
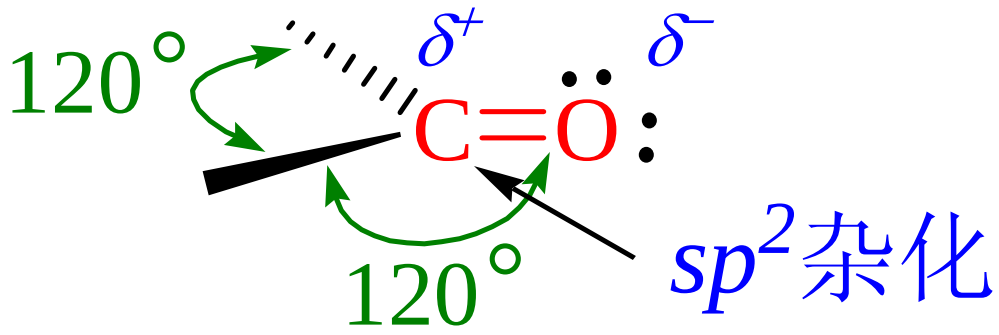


第十章 醛和酮

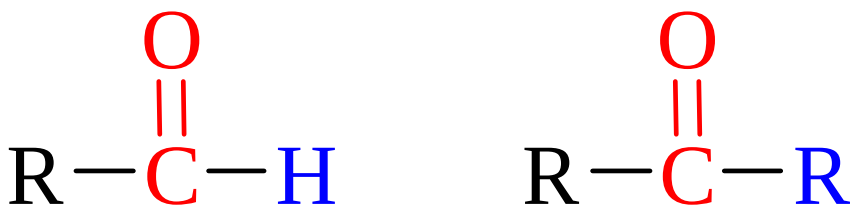
10.1 醛、酮的结构、命名和物理性质

10.1.1 醛酮的结构

醛、酮的官能团是羰基，羰基碳原子为sp^2杂化，带部分正电荷，是个极性官能团。

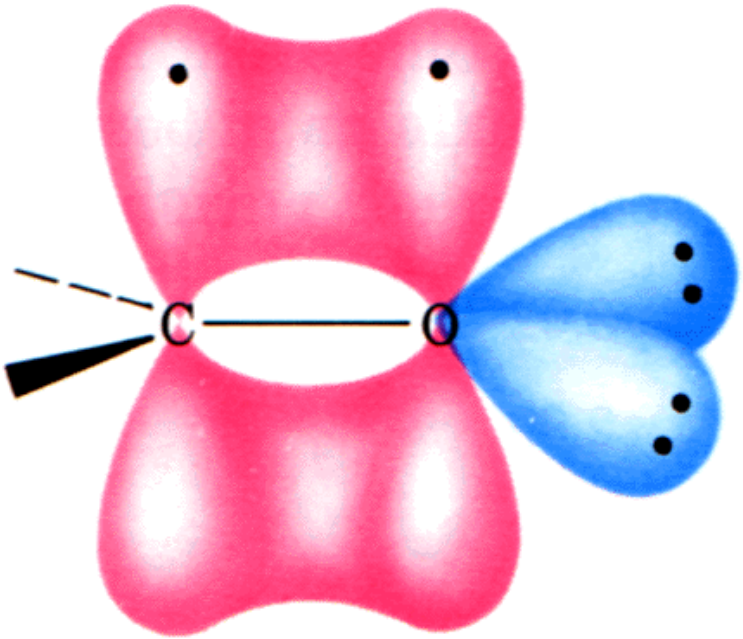


羰基

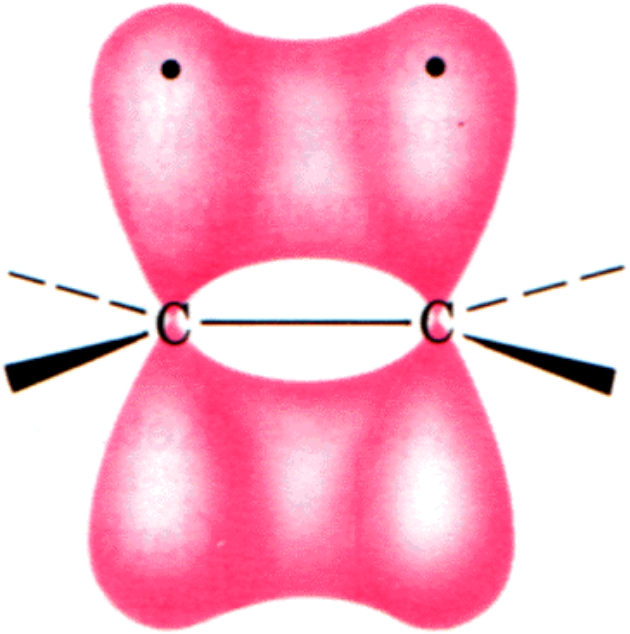


醛　　酮

羰基与烯烃结构的比较



羰 基



烯 烃

10.1.2 醛酮的命名

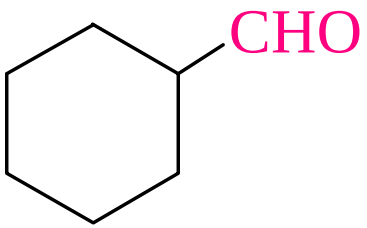
1.普通命名法（自学）
2.系统命名法

- 醛的羰基只能是在端基，不必标出羰基的位号

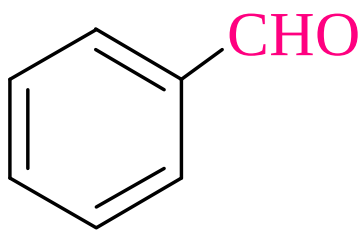
CH_3CHO　　$(CH_3)CHCHO$

乙醛　　2-甲基丙醛

- 羰基与环相连的醛，环名+甲醛

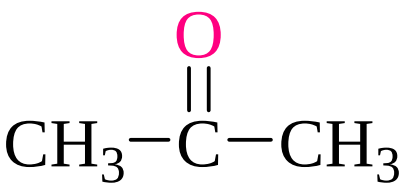


环己烷甲醛

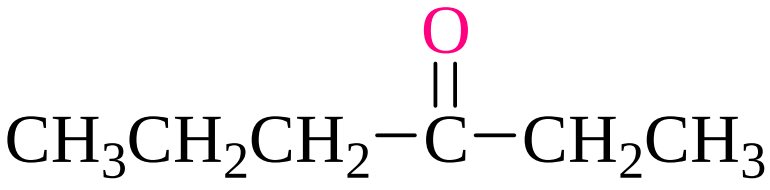


苯甲醛

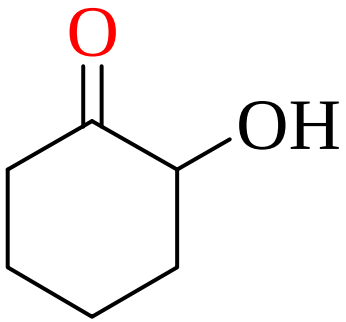
- 酮除羰基位置是唯一的情况外，一般应标位号
- 羰基在环上的，称为“环某酮”



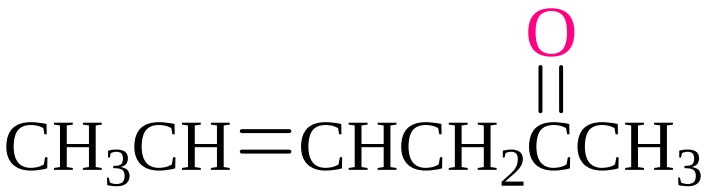
丙酮



3-己酮

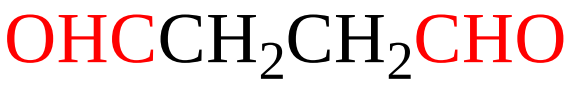


2-羟基环己酮

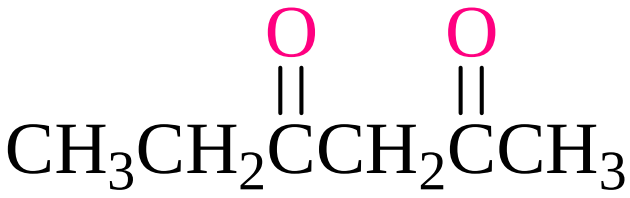


4-己烯-2-酮

- 二元醛（酮）称为“二醛”或“二酮”

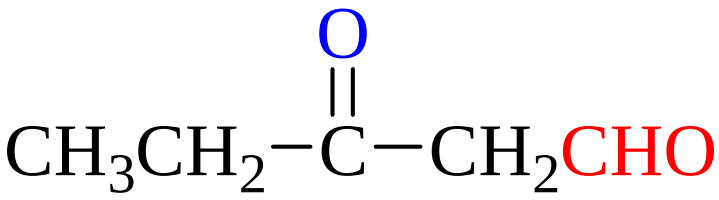


丁二醛



2,4-己二酮

- 羰基作为取代基时，羰基氧原子称为“氧代”

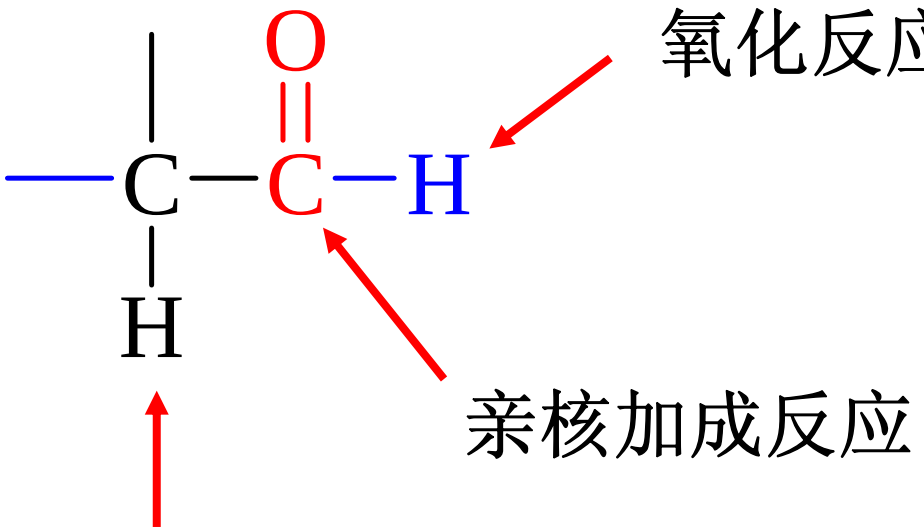


3-氧代戊醛

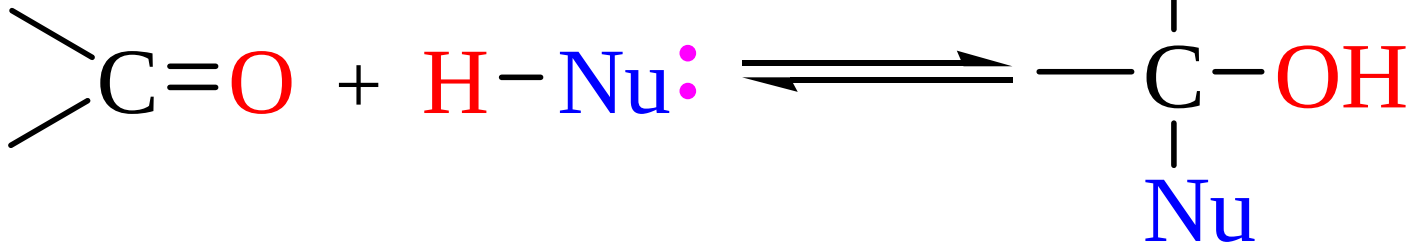
分子中既有醛又有酮羰基时，以醛为母体

10.1.3 醛酮的物理性质（自学）

10.2 醛酮的反应



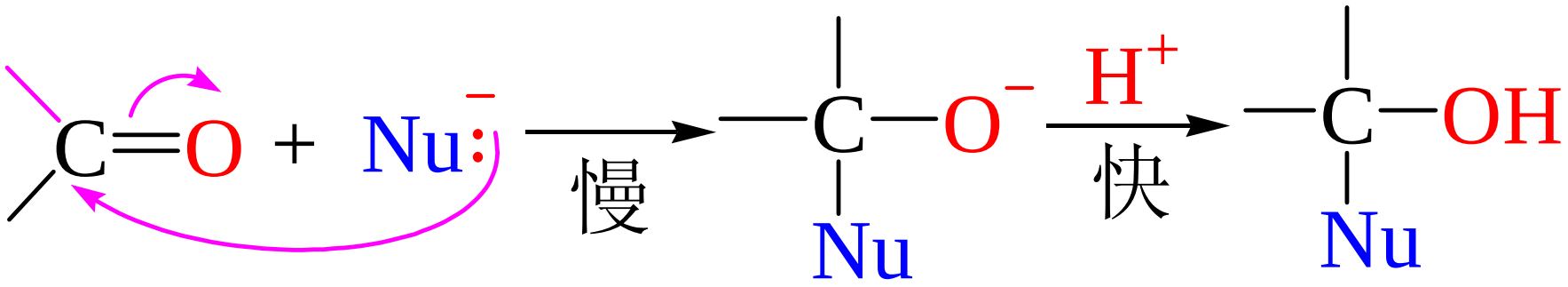
10.2.1 羰基的亲核加成



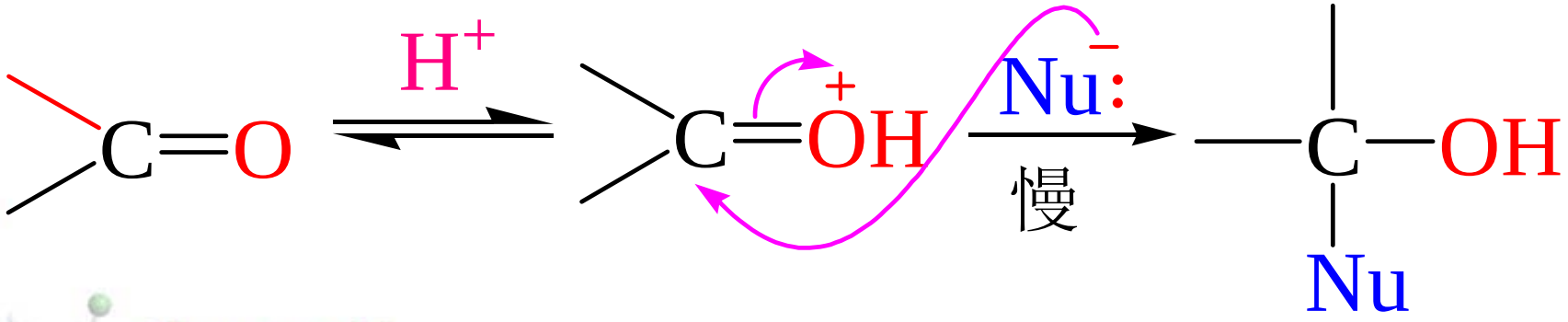
(1) 反应活性

醛 >环酮 > 脂肪酮 > 芳香酮

(2) 强亲核试剂的亲核加成机理



(3) 酸催化下的亲核加成机理



(4) 亲核试剂的分类

- 含碳的亲核试剂　　RMgX , HCN ,
- 含氮的亲核试剂　　RNH_2 , R_2NH , H_2N–G
- 含氧的亲核试剂　　H_2O . ROH
- 含硫的亲核试剂　　$NaHSO_3$

1. 与含碳亲核试剂的加成

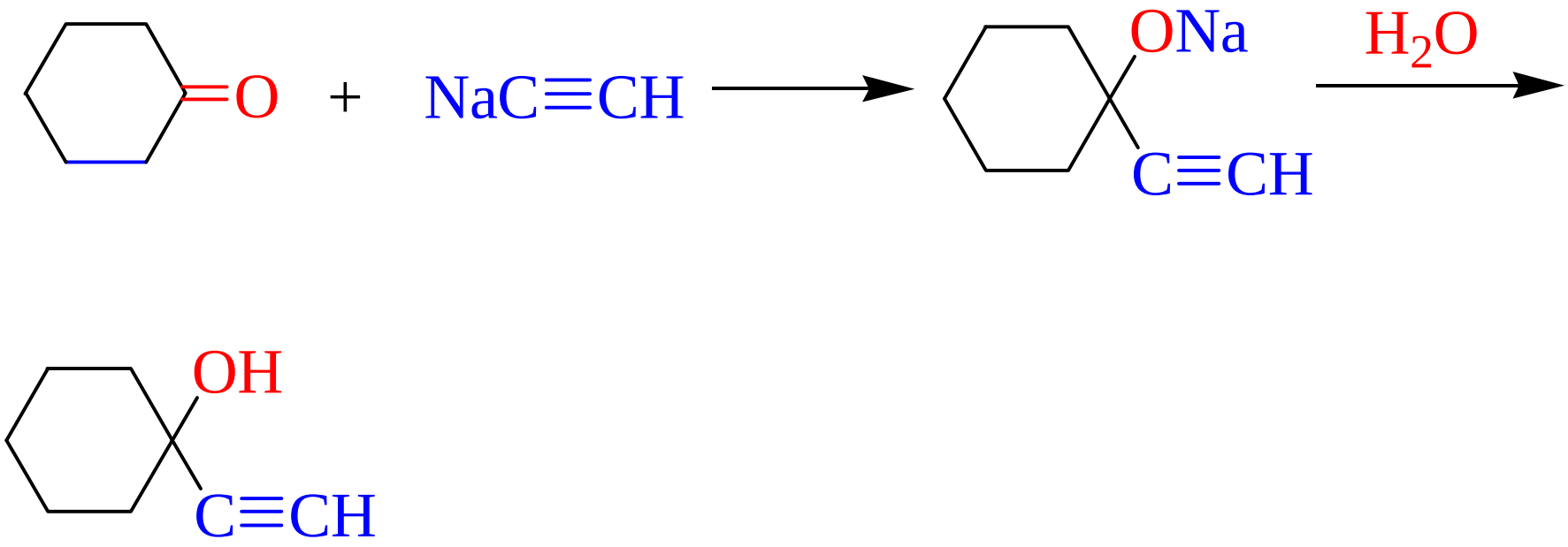
(1) 与Gringard试剂的加成

$$CH_2O \xrightarrow[\text{(2) } H_3O^+]{\text{(1) RMgX}} RCH_2OH \quad 1^\circ \text{ 醇}$$

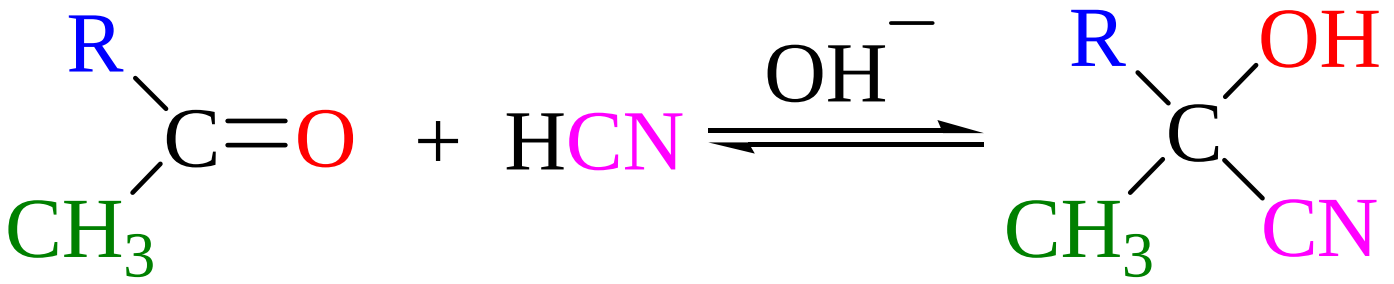
$$CH_3CHO \xrightarrow[\text{(2) } H_3O^+]{\text{(1) RMgX}} R\overset{\overset{\large OH}{|}}{C}HCH_3 \quad 2^\circ \text{ 醇}$$

$$CH_3\overset{\overset{\large O}{||}}{C}CH_3 \xrightarrow[\text{(2) } H_3O^+]{\text{(1) RMgX}} R\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large OH}{|}}{C}}CH_3 \quad 3^\circ \text{ 醇}$$

(2) 与炔化物加成



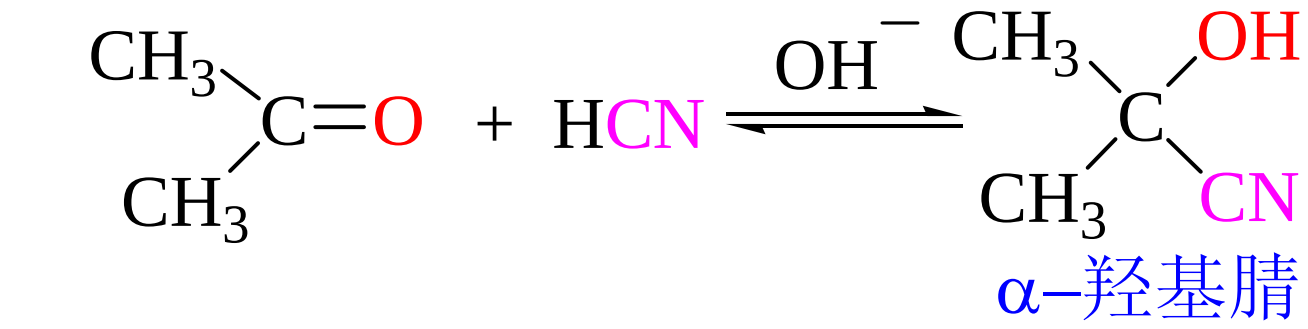
(3) 与HCN加成



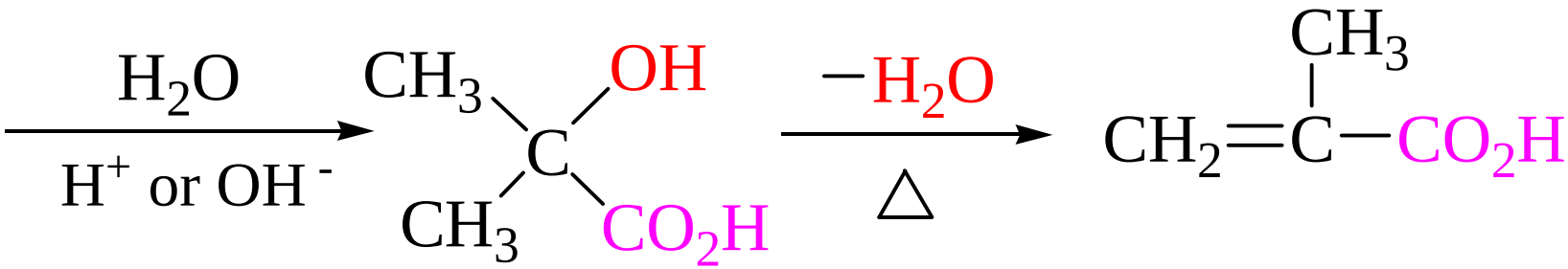
α–羟基腈

用途：

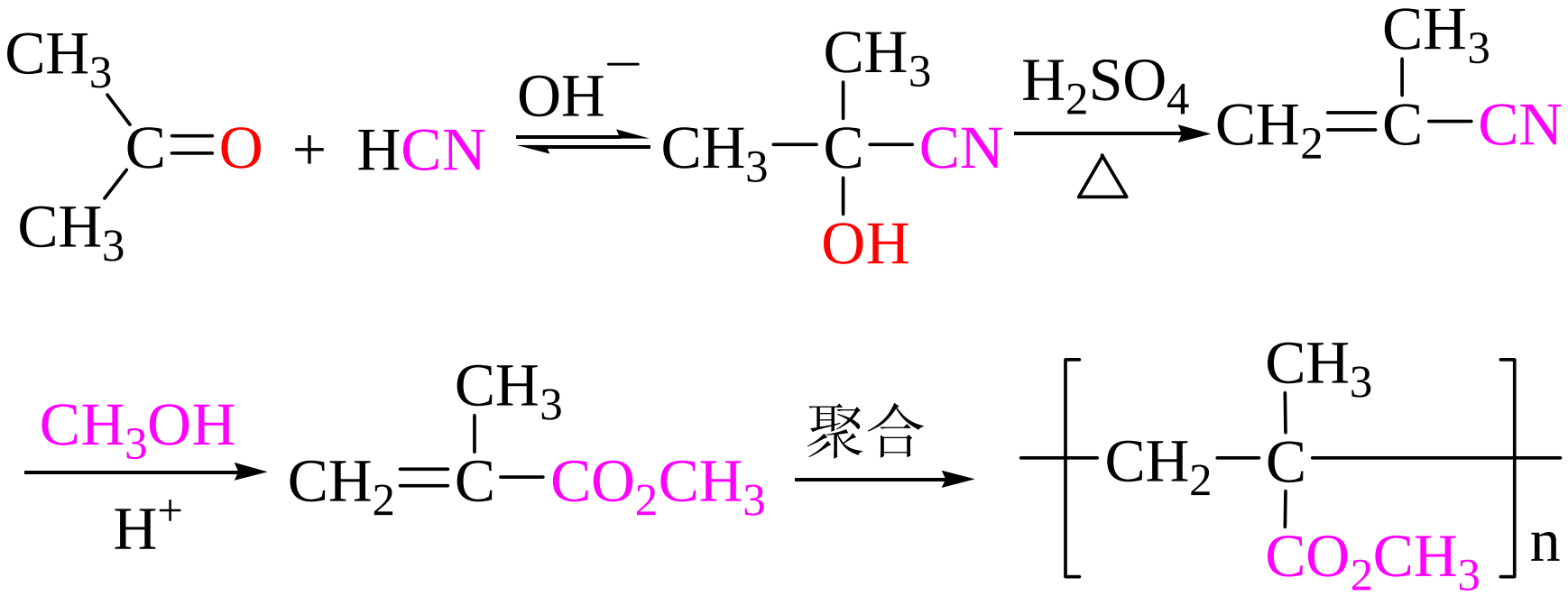
合成α–羟基腈、 α–羟基酸、α,β–不饱和酸。



α–羟基腈



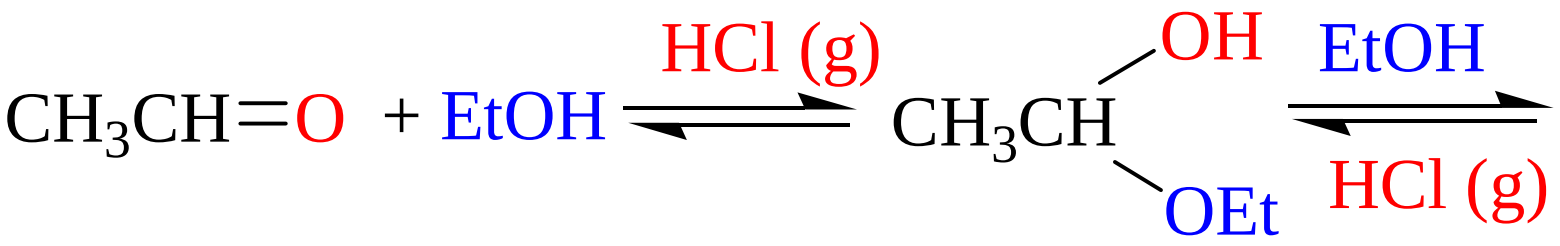
α–羟基酸　　α,β–不饱和酸



甲基丙烯酸甲酯　　有机玻璃

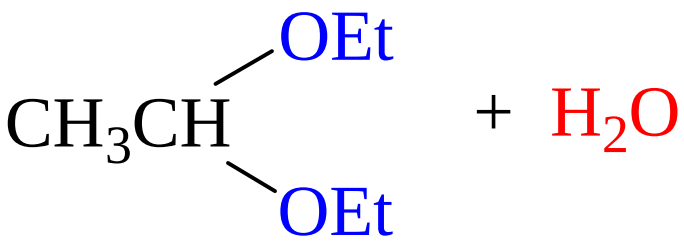
2. 与含氧亲核试剂的加成

(1)与醇的加成—— 形成半缩醛(酮)，缩醛(酮)



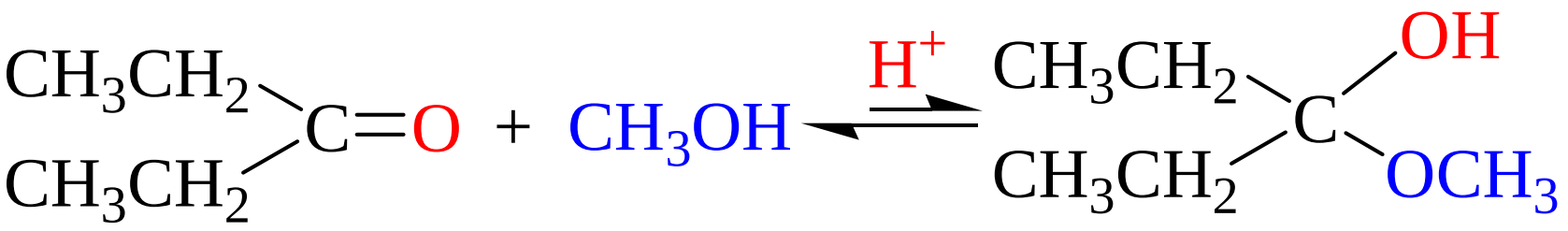
乙醛缩一乙醇

半缩醛

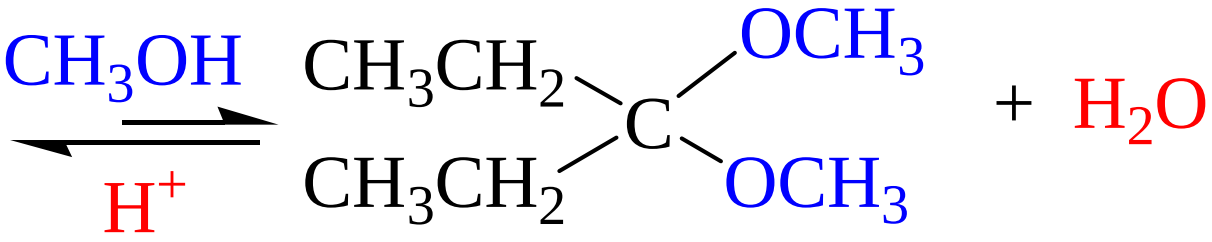


乙醛缩二乙醇

缩醛

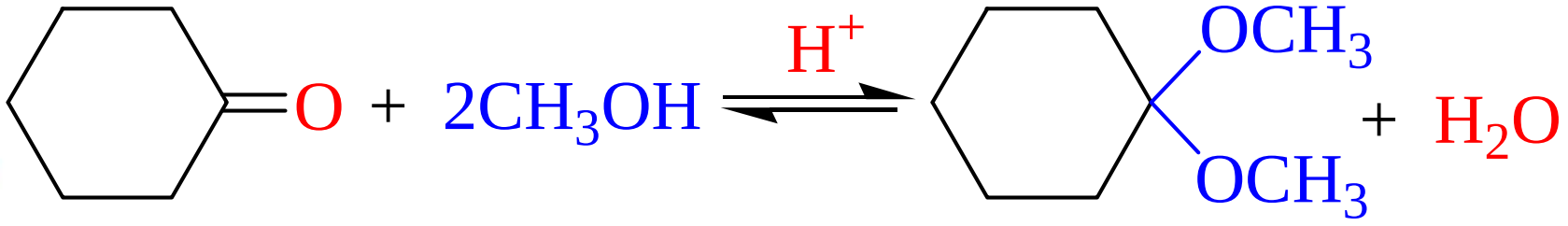


半缩酮

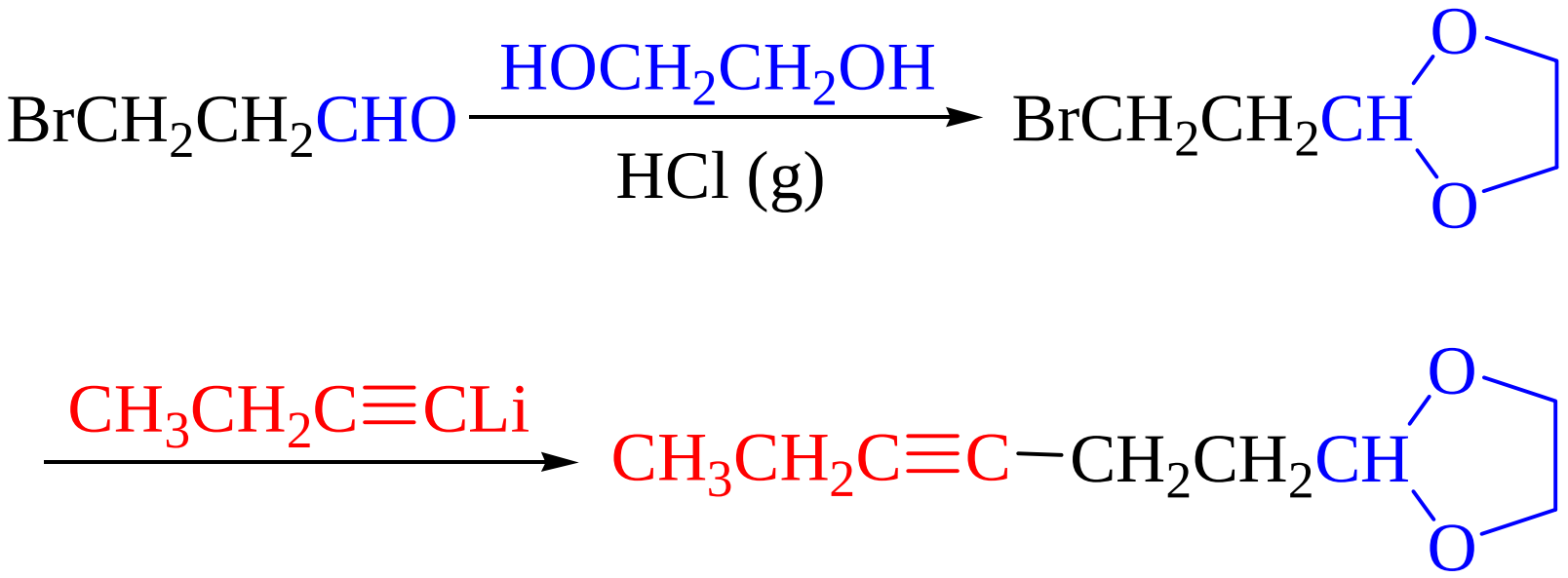


缩酮

环酮形成缩酮的产率较高：

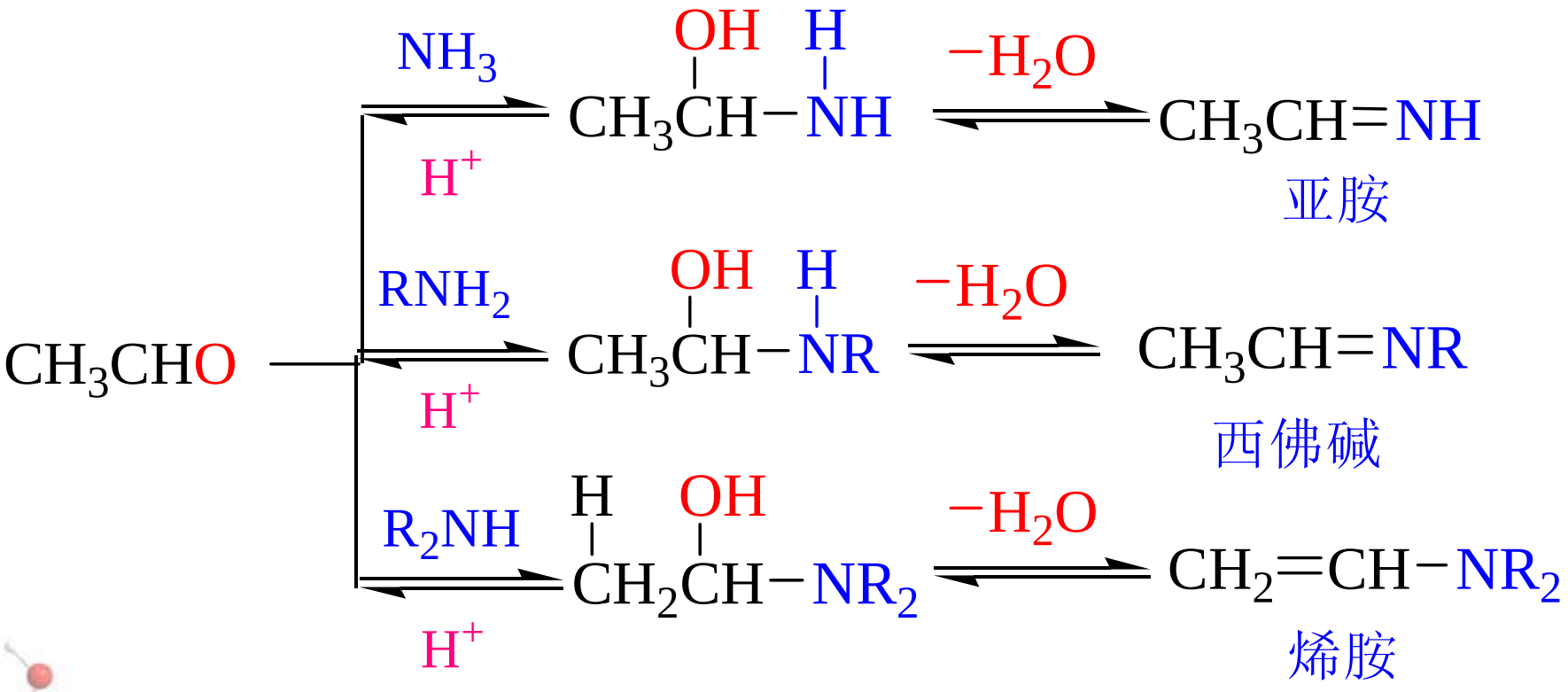


缩酮在合成中用于保护羰基：

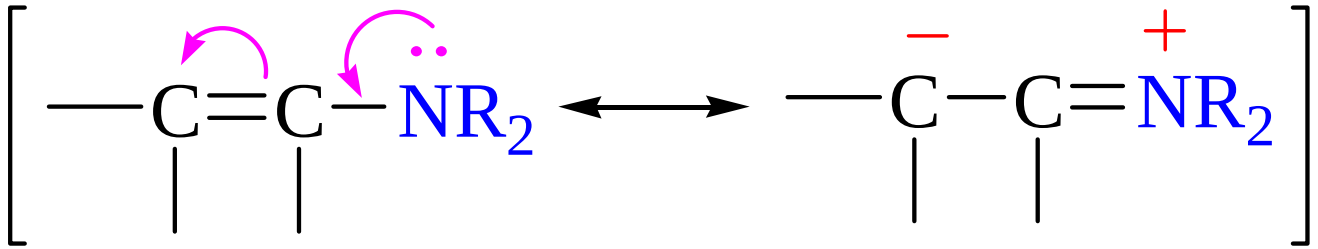


3. 与含氮亲核试剂的加成

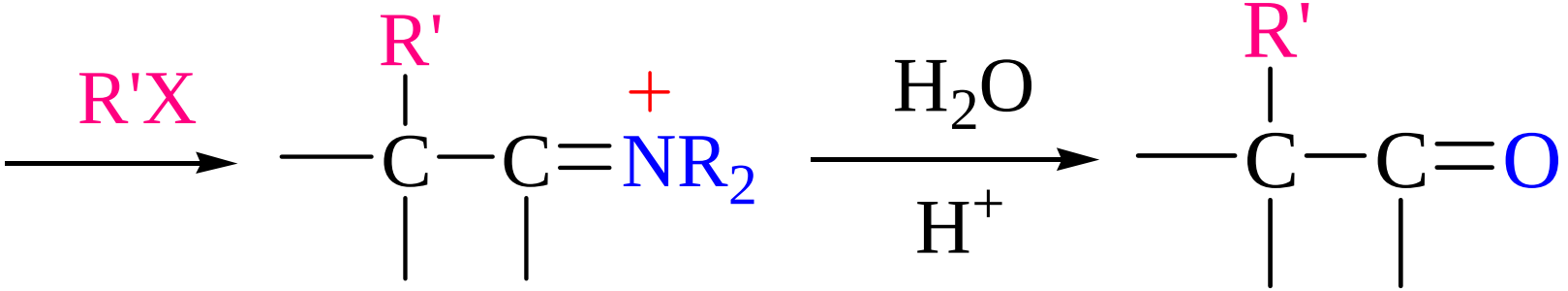
（1）与氨或胺的加成

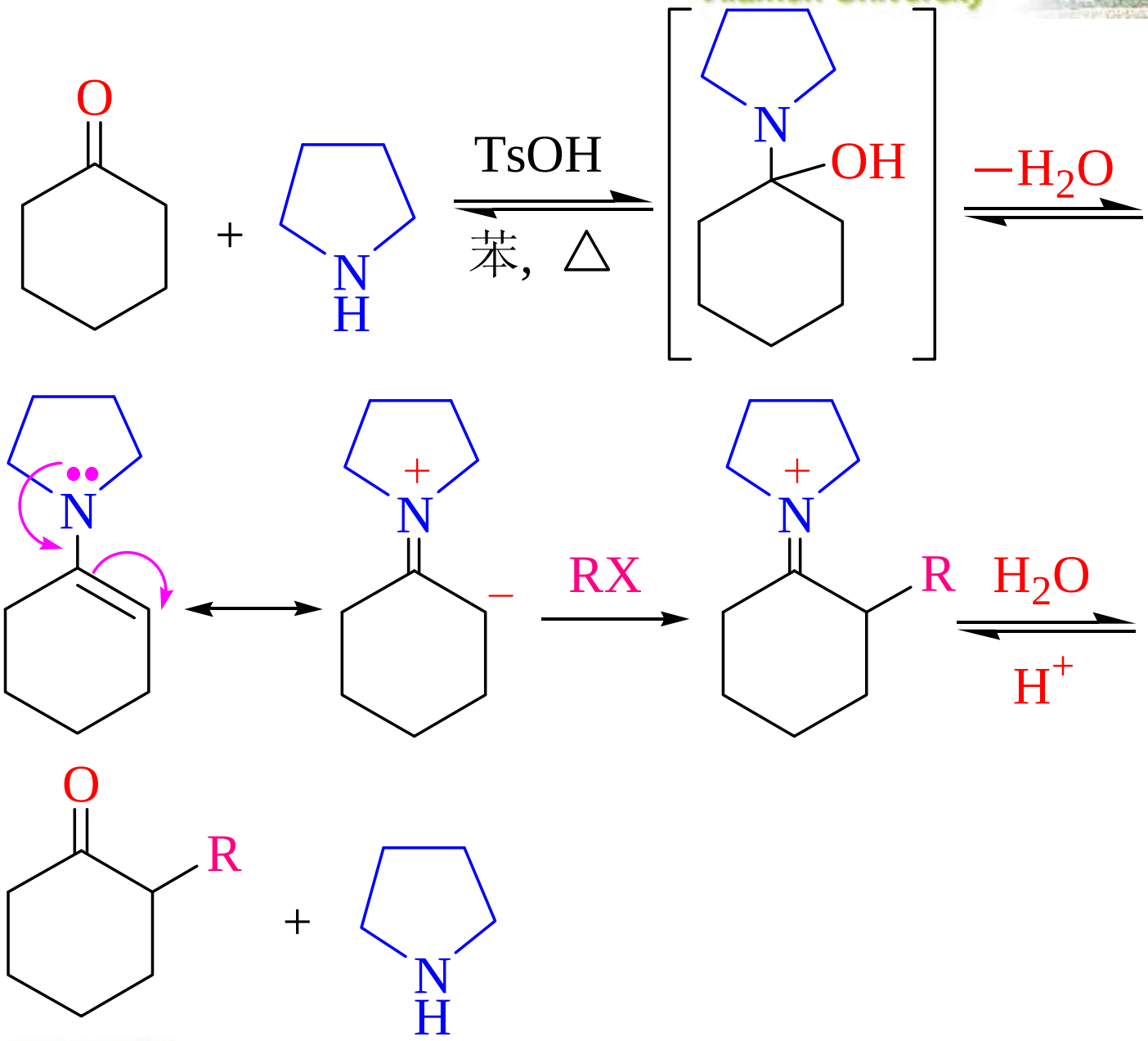


烯胺的性质及应用

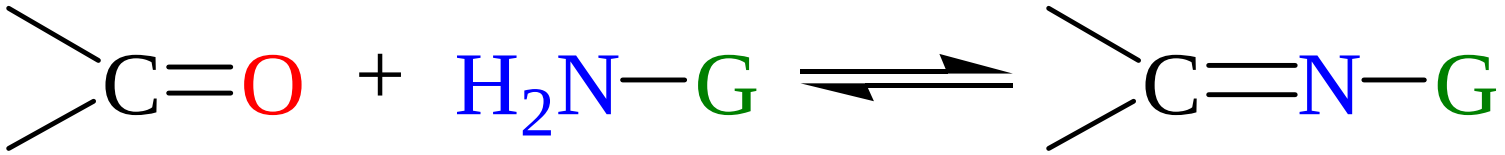


烯胺




O
+
N
H
TsOH
苯, △
N
OH
—H2O
N
+
N
–
RX
+
N
R
H2O
H+
O
R
+
N
H

（2）与氨的衍生物加成



$$G = OH\ ,\ NH_2\ ,\ NHAr\ ,\ NHCONH_2$$

羟氨　　肼　　苯肼　　氨基脲

$(CH_3)_2C{=}O + H_2N{-}OH \longrightarrow (CH_3)_2C{=}N{-}OH$

羟胺　　肟

$(CH_3)_2C{=}O + H_2N{-}NH_2 \longrightarrow (CH_3)_2C{=}N{-}NH_2$

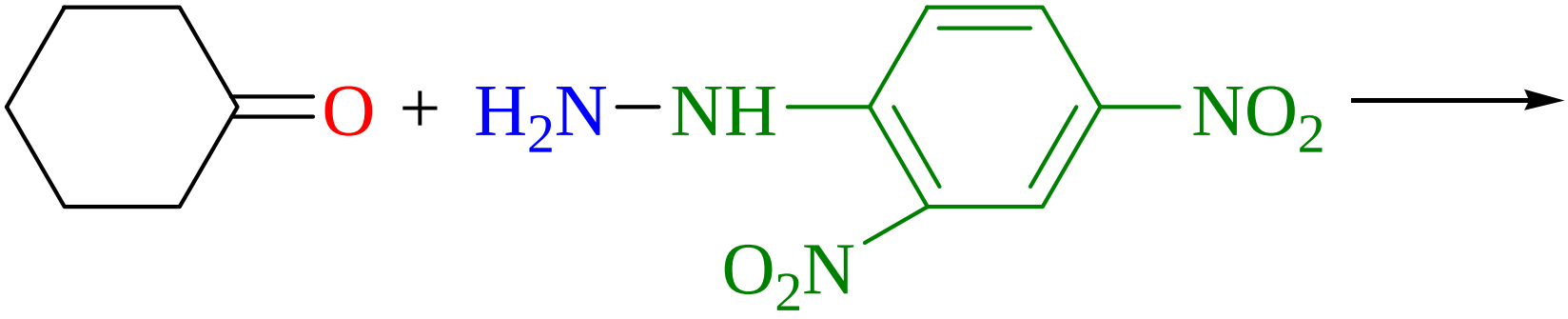
肼(联氨)　　腙

$(CH_3)_2C{=}O + H_2N{-}NH{-}C_6H_5 \longrightarrow$

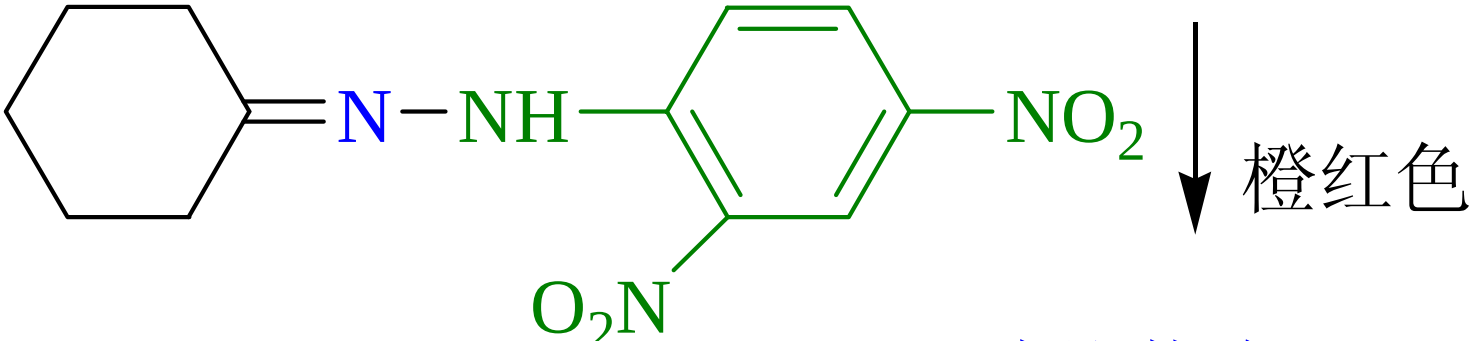
苯肼

$(CH_3)_2C{=}N{-}NH{-}C_6H_5$

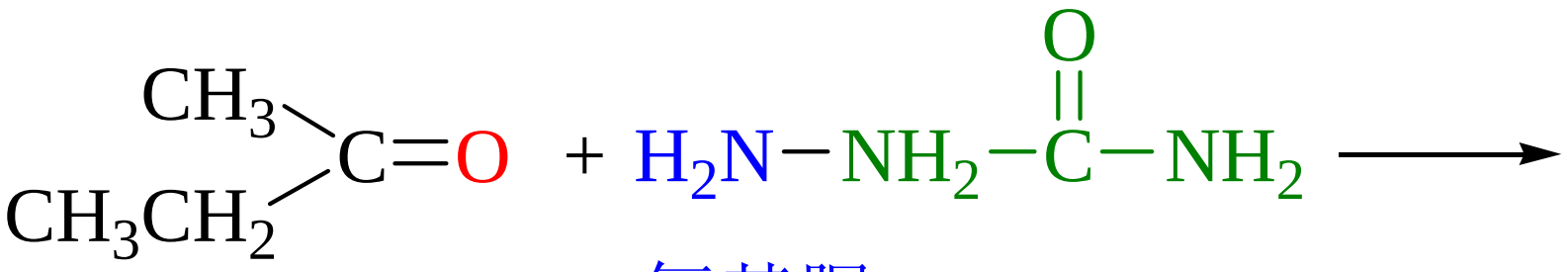
苯腙



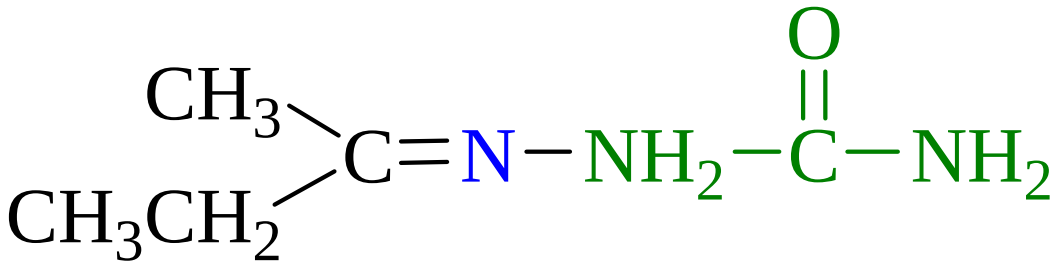
2,4－二硝基苯肼



2,4－二硝基苯腙



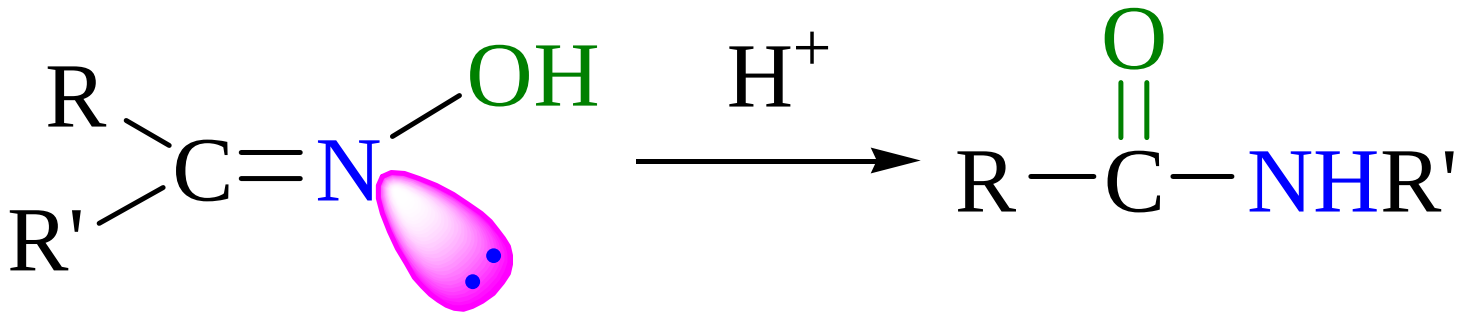
氨基脲



缩氨脲

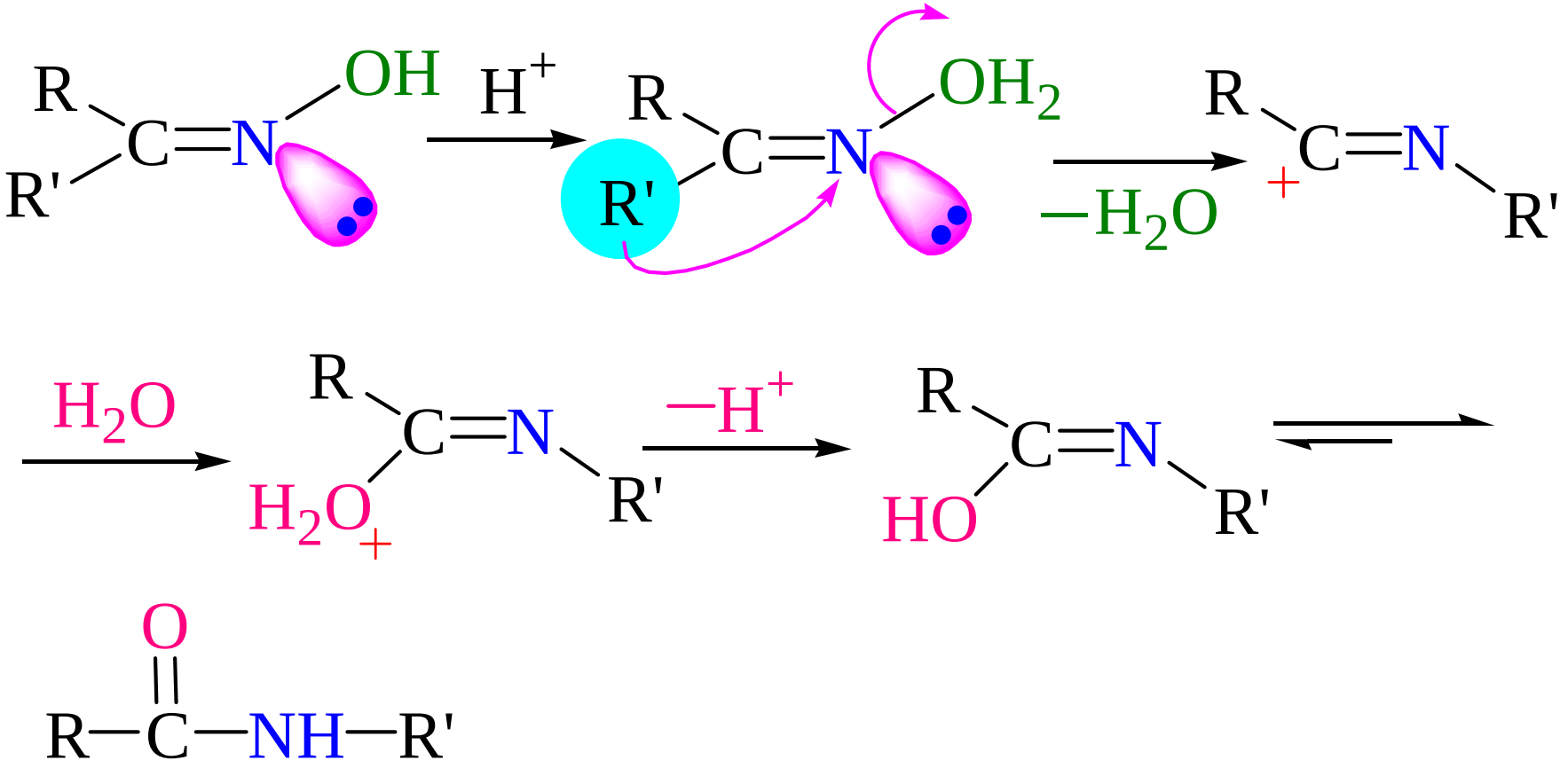
（3）Beckmann 重排

肟在酸作用下重排形成酰胺



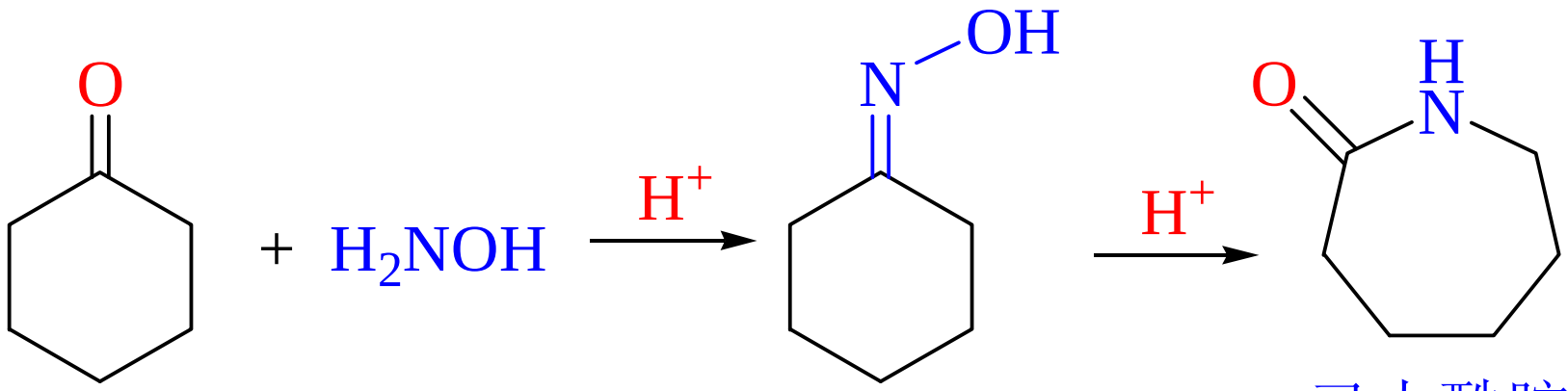
常用催化剂：H_2SO_4 , HCl (g) ,

反应机理

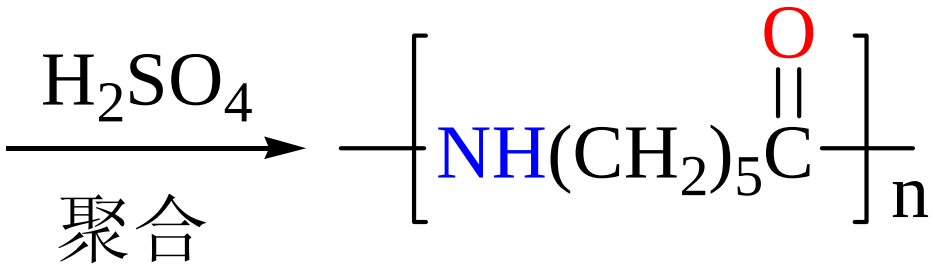


重排的应用

由酮制备酰胺

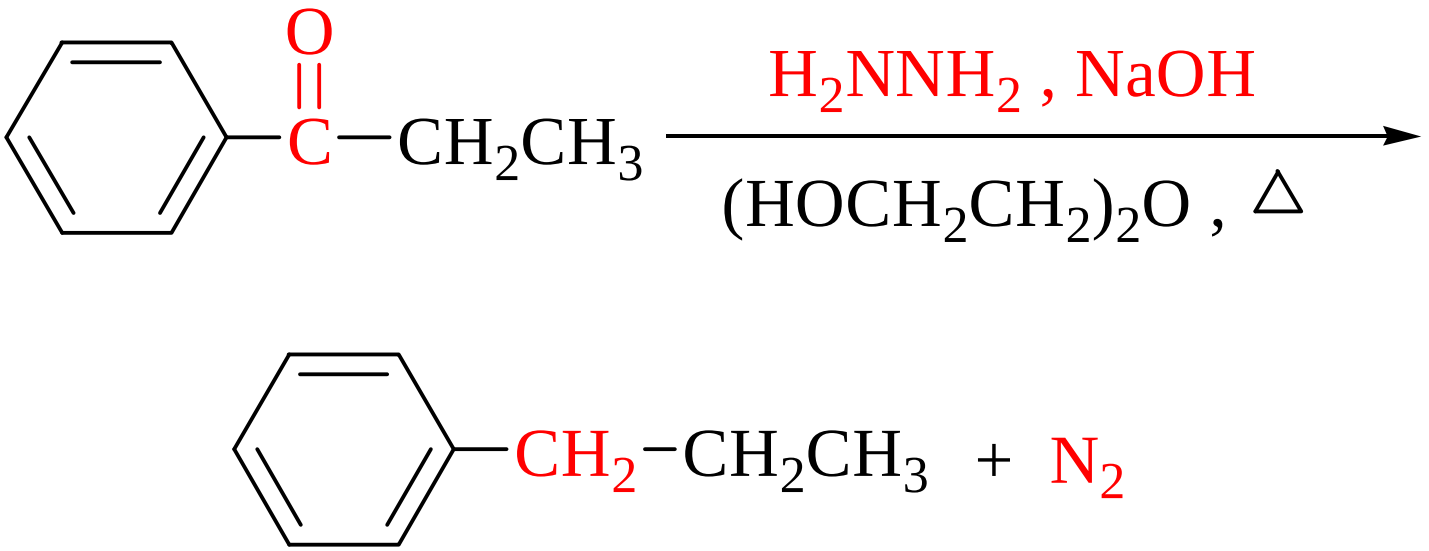


己内酰胺



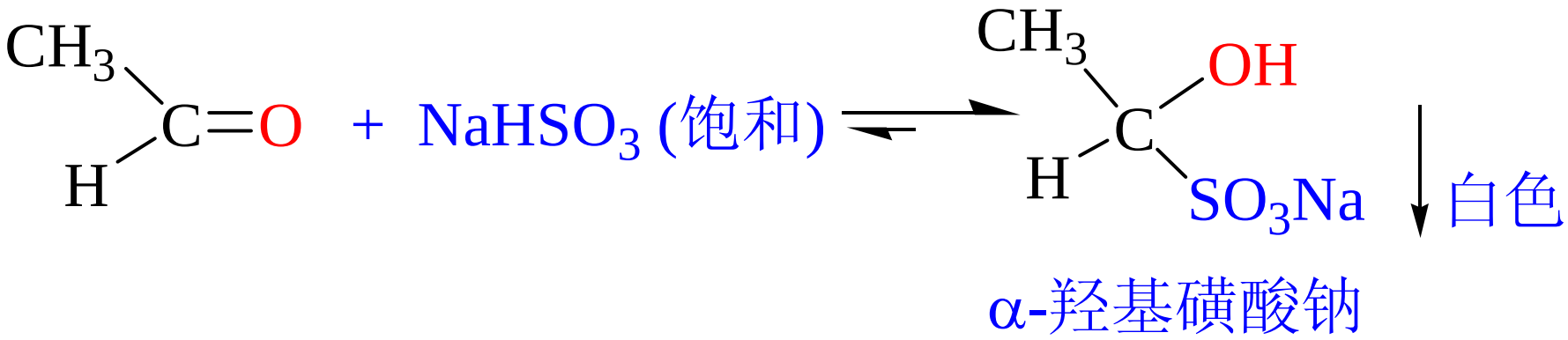
尼龙－6

（4） Wolff-Kishner-黄鸣龙 还原反应



4. 与含硫亲核试剂的加成

（1）与亚硫酸氢钠的反应

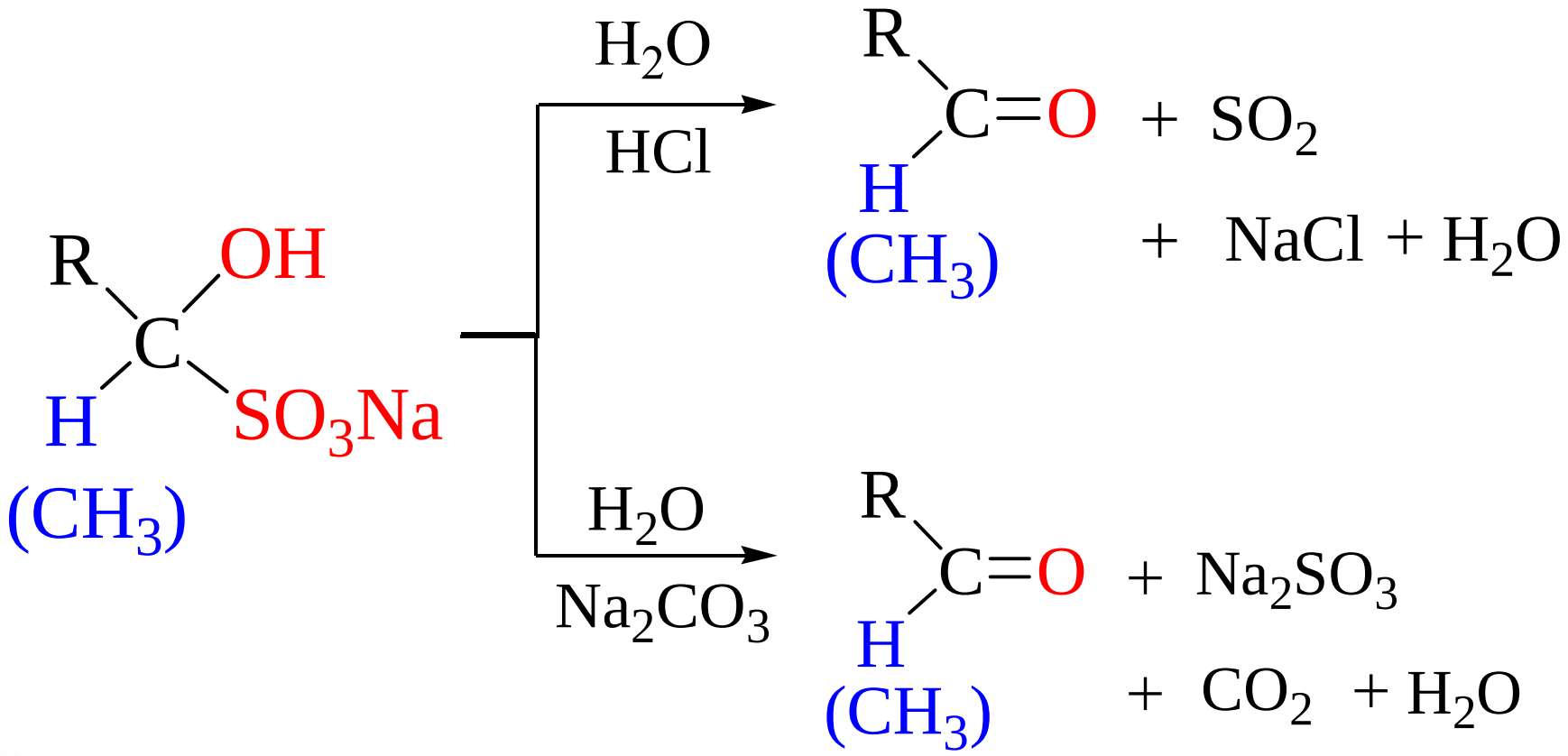


α-羟基磺酸钠

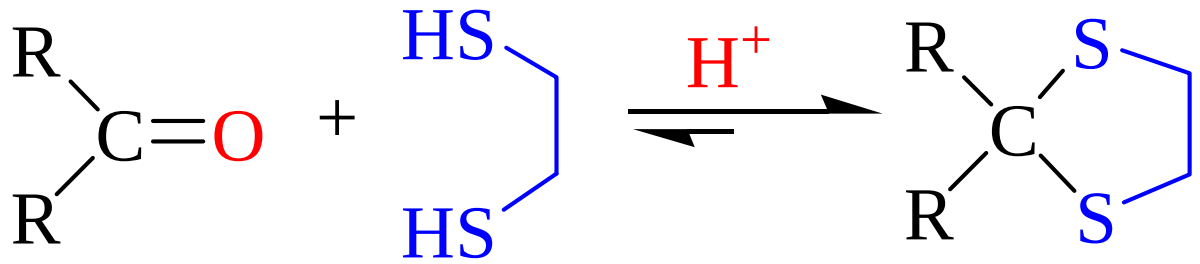
醛、脂肪族甲基酮、**C8**以下环酮能发生反应，其他酮不反应。

本反应可用于鉴别和分离提纯。

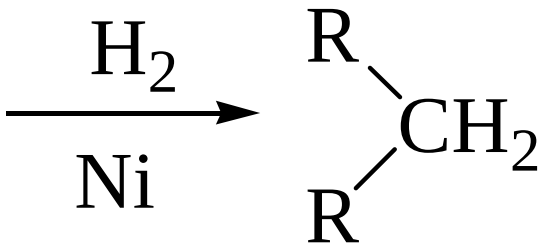
α-羟基磺酸钠与稀酸或稀碱加热发生水解：



(2) 与硫醇反应



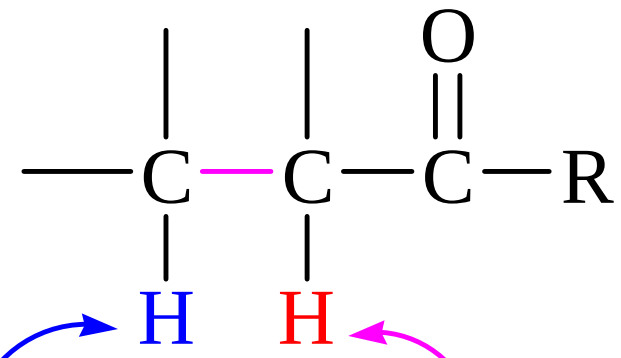
缩硫酮



缩硫酮氢解

10.3.2 α–活泼氢的反应

1. α-氢的活性

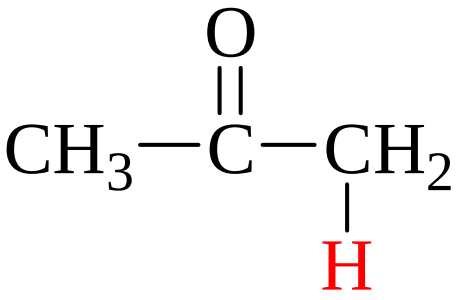


β–H

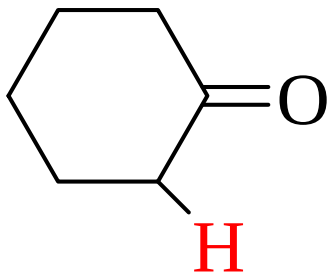
pK_a = 40 ~ 50

α–H

pK_a = 19 ~ 20

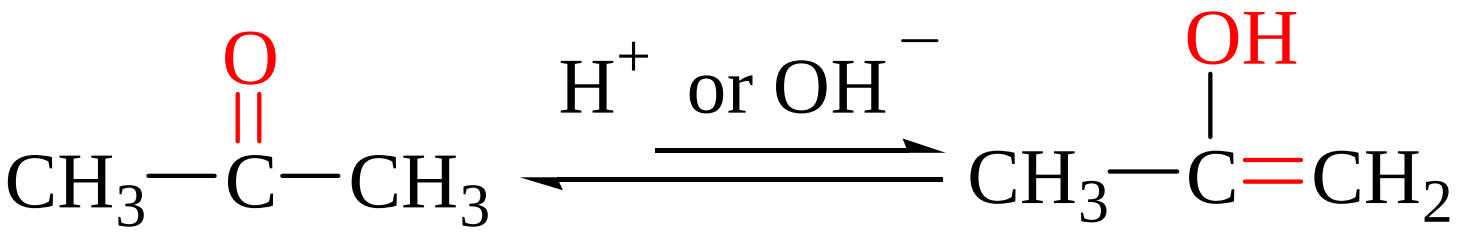


pK_a = 20.0

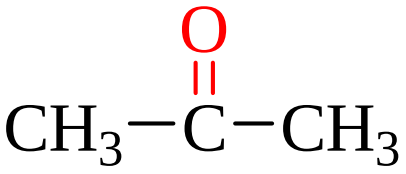


pK_a = 17.0

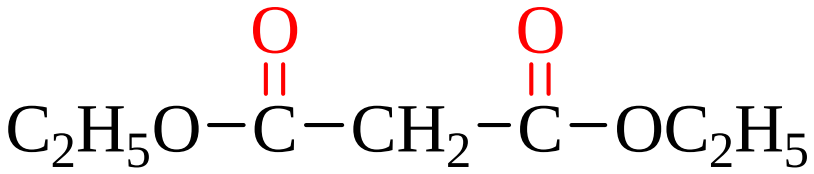
酮式和烯醇式—— 互变异构



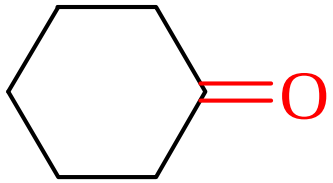
烯醇式含量



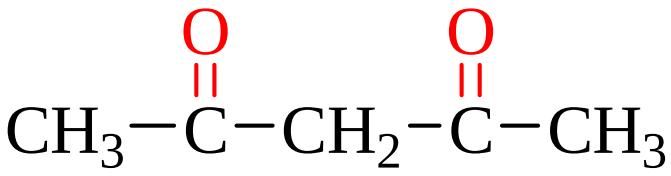
1.5 X 10^{-4}



7.7 X 10^{-3}

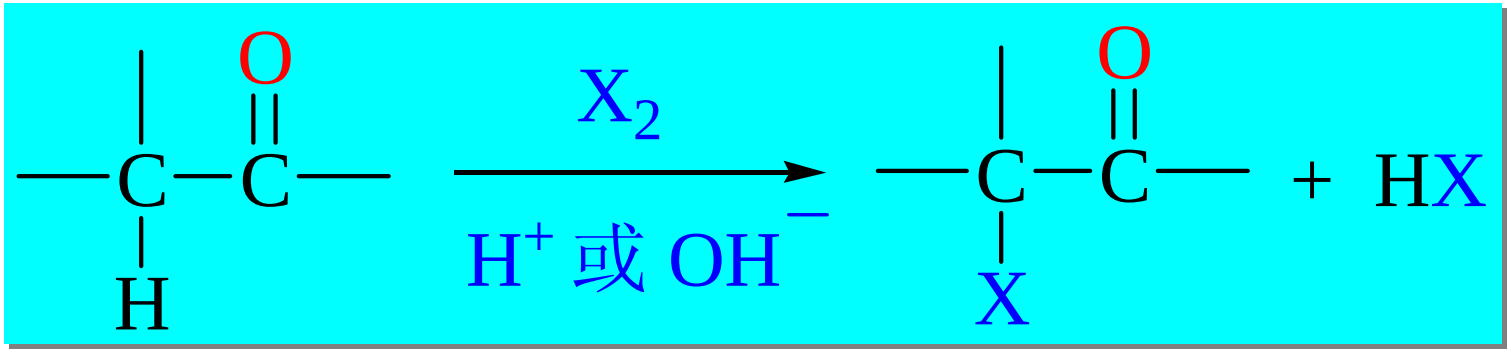


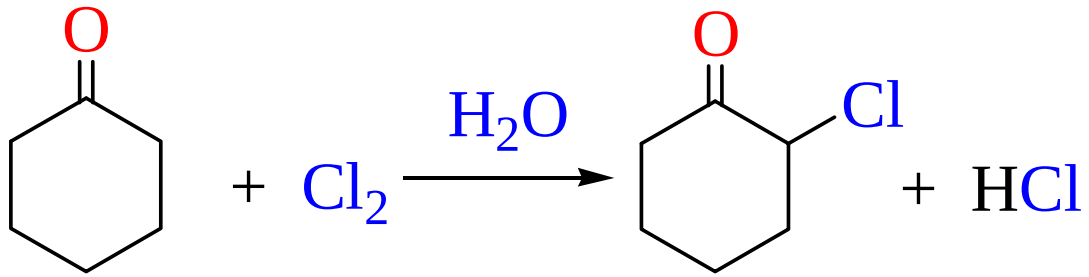
2.0 X 10^{-2}

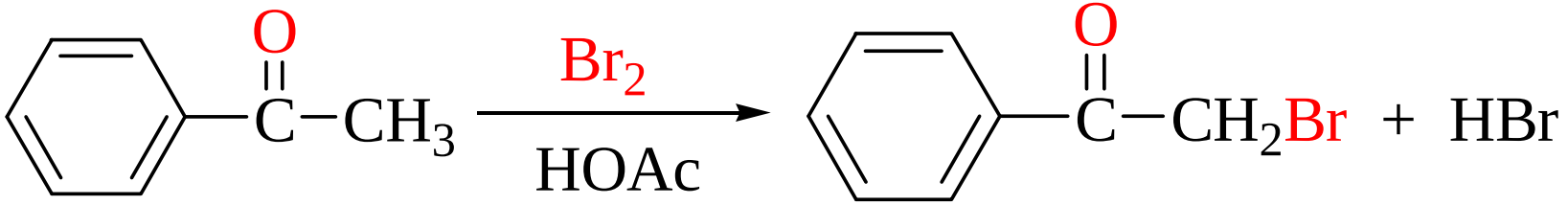


76.5

2. 醛酮的α-卤化



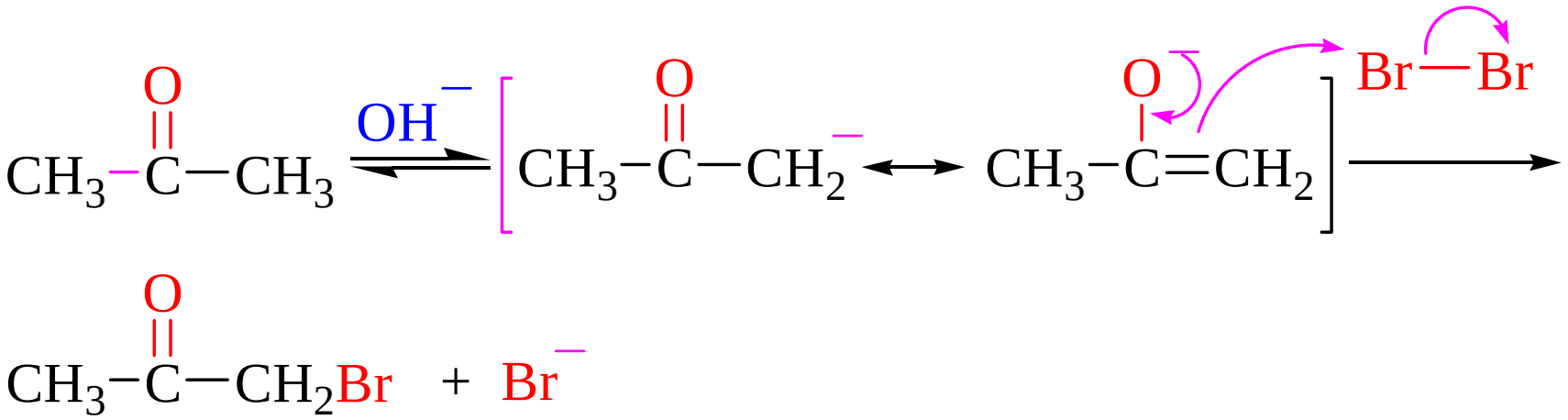




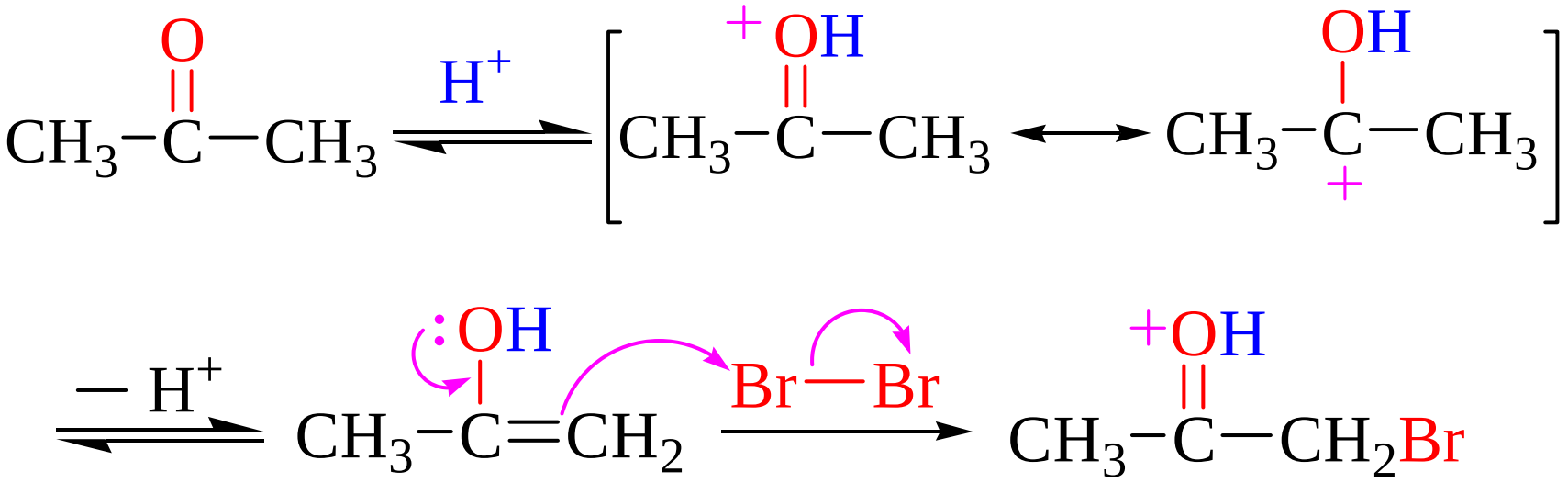
69 ~ 77%

反应机理

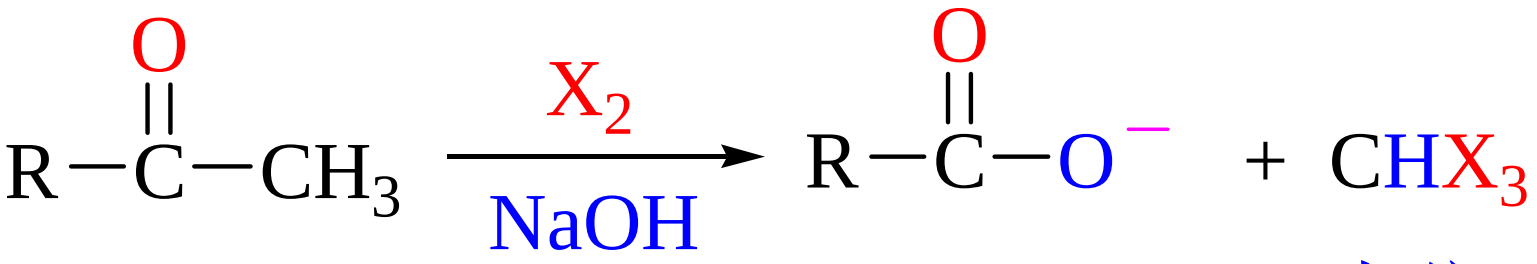
(1) 碱催化下的反应机理

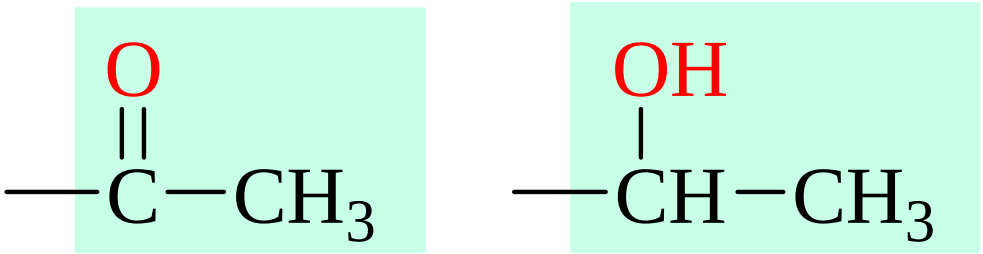


(2) 酸催化下的反应机理



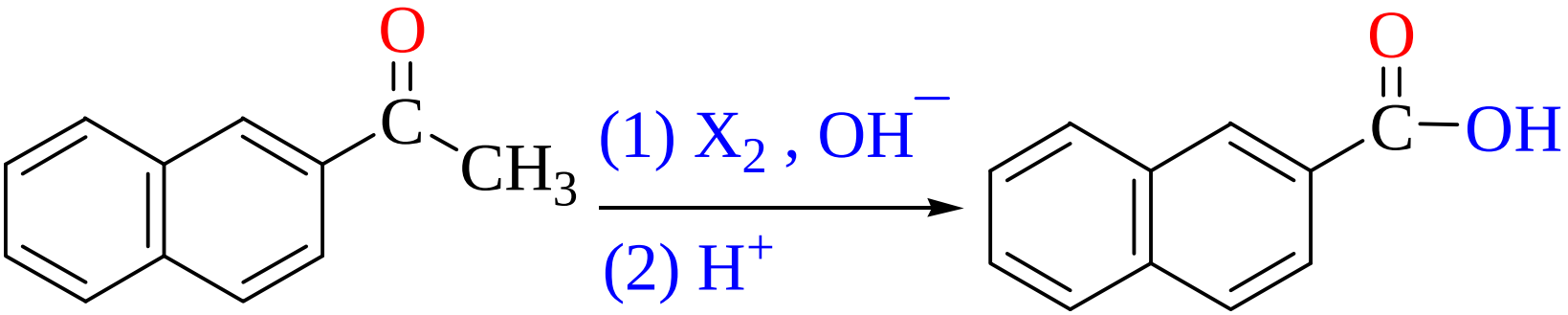
3. 卤仿反应

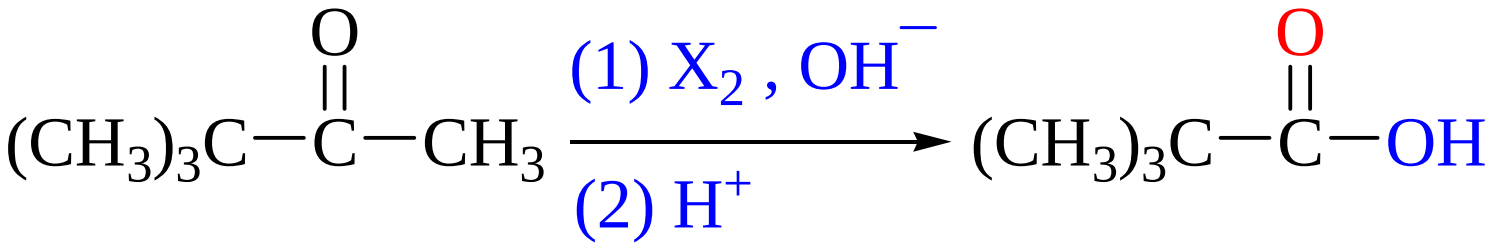


具有 

结构的化合物都能发生反应。碘仿反应可用于鉴别。

碘仿CHI_3↓ 黄色


O
C
CH3
(1) X2 , OH−
(2) H+
O
C
OH


O
(CH3)3C
C
CH3
(1) X2 , OH−
(2) H+
O
(CH3)3C
C
OH

4. 羟醛缩合

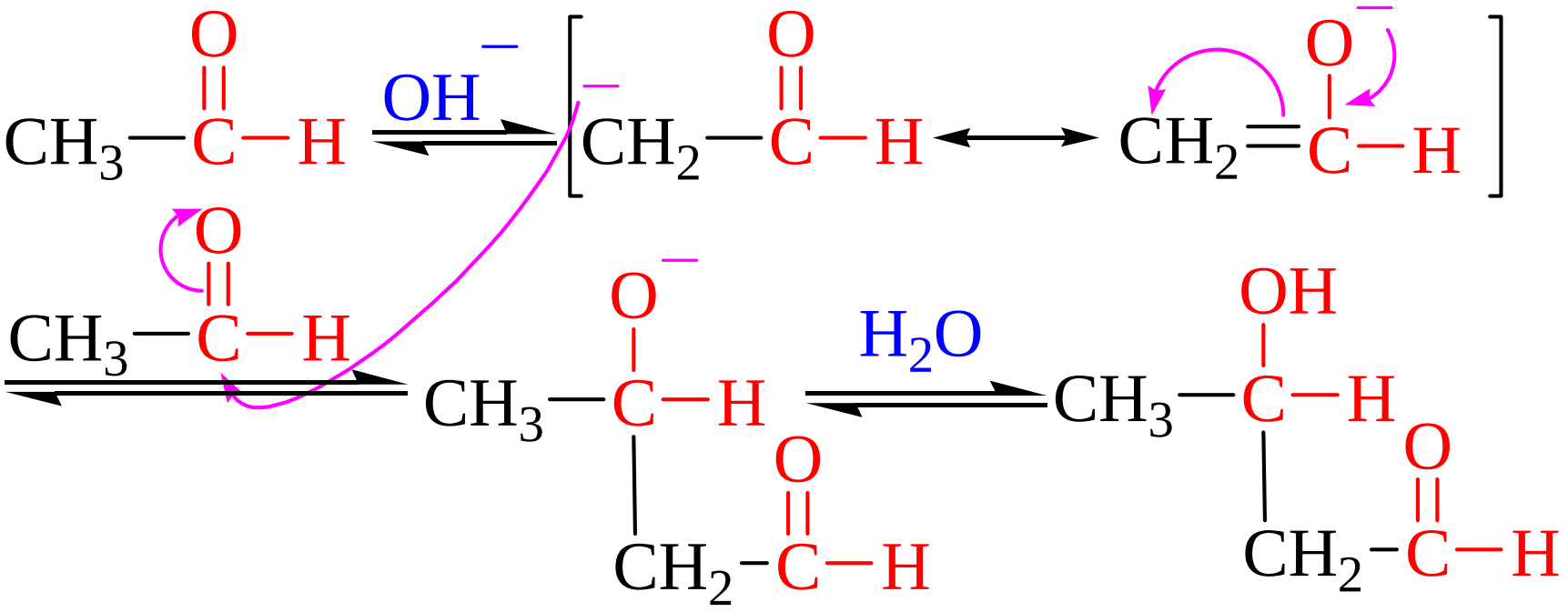
$$2\ CH_3CHO \xrightleftharpoons{OH^-} CH_3\underset{\displaystyle OH}{\underset{|}{C}}H-CH_2CHO$$

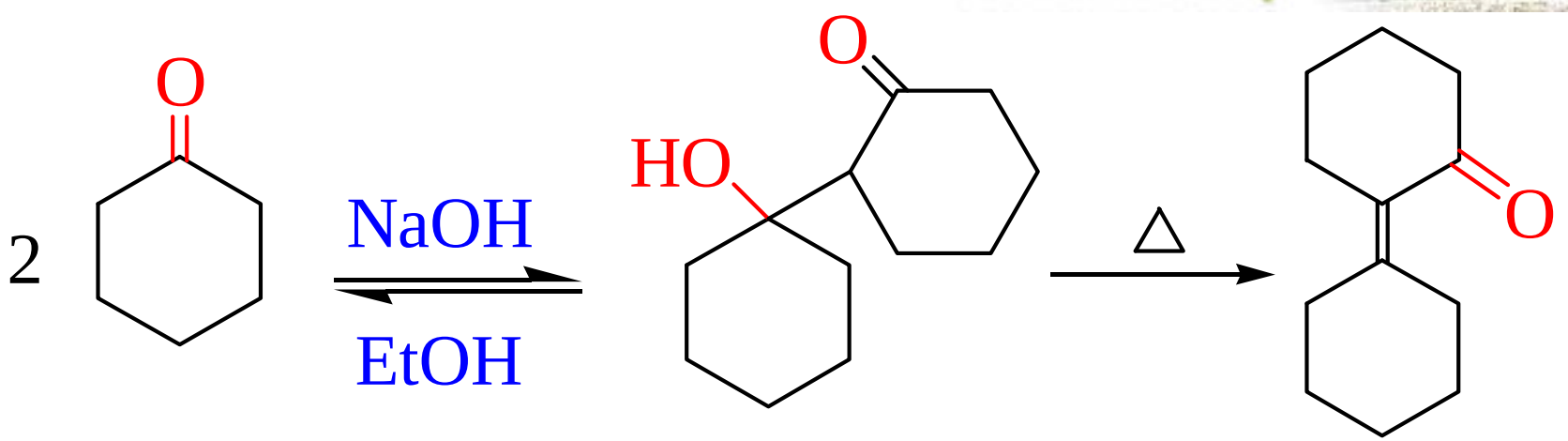
含有α-H的醛(酮)在稀碱的作用下，缩合生成β-羟基醛(酮)

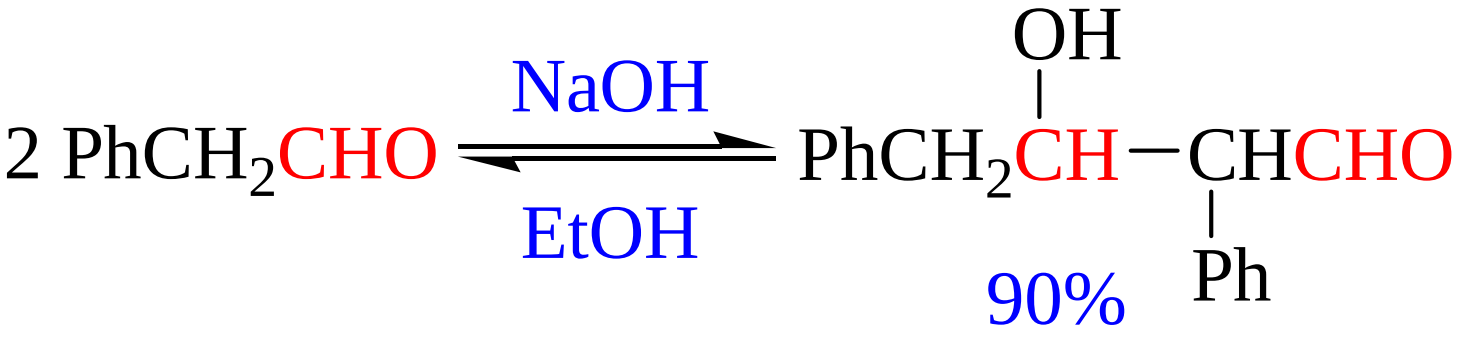
β-羟基醛(酮)易脱水形成α,β–不饱和醛(酮)：

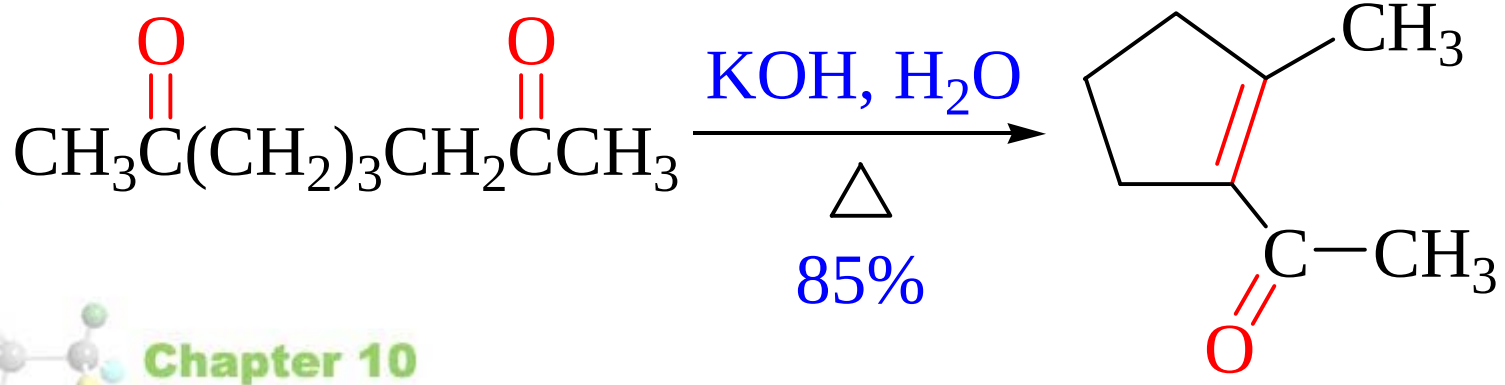
$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}H-CH_2CHO \xrightarrow{-H_2O} CH_3CH=CHCHO$$

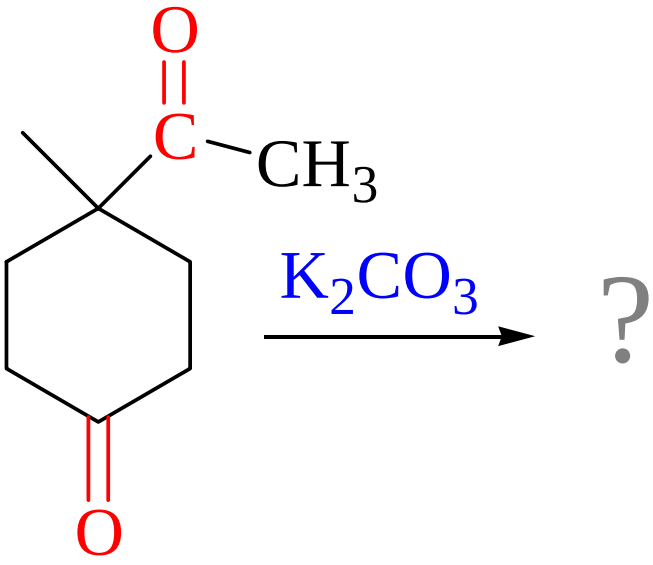
反应机理

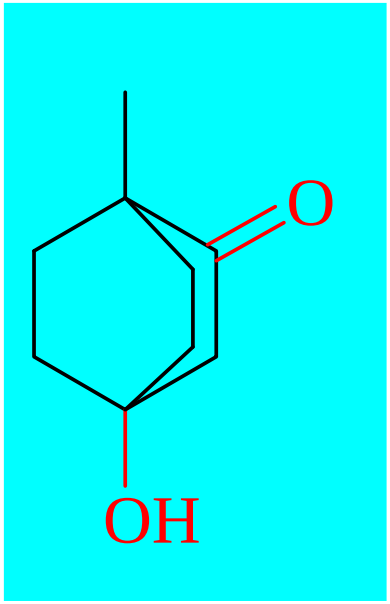


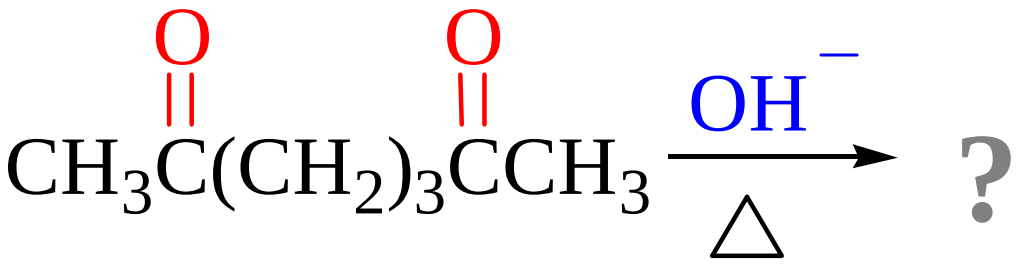

2
O
NaOH
EtOH
HO
O
△
O

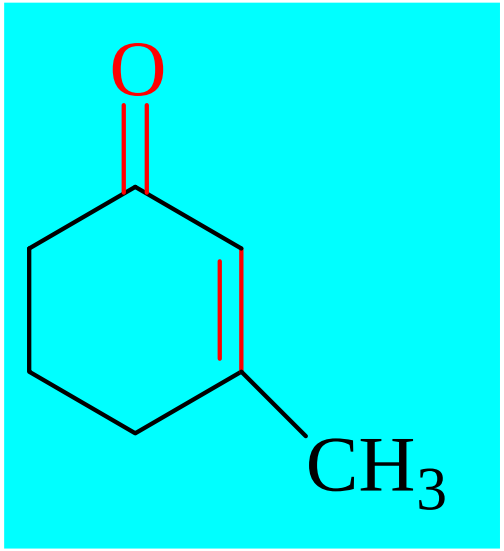

2 PhCH2CHO
NaOH
EtOH
OH
PhCH2CH—CHCHO
Ph
90%


O
O
CH3C(CH2)3CH2CCH3
KOH, H2O
△
85%
CH3
C—CH3
O


O
C
CH3
K2CO3
O
?


O
OH


O
O
CH3C(CH2)3CCH3
OH−
△
?


O
CH3

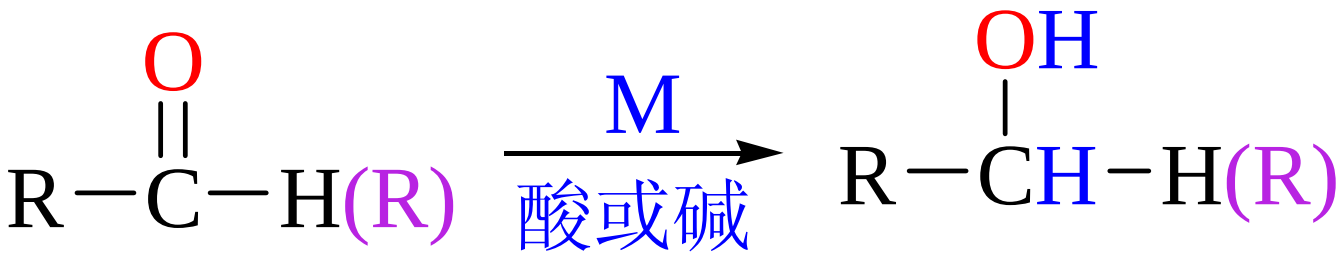
10.3.3 还原反应

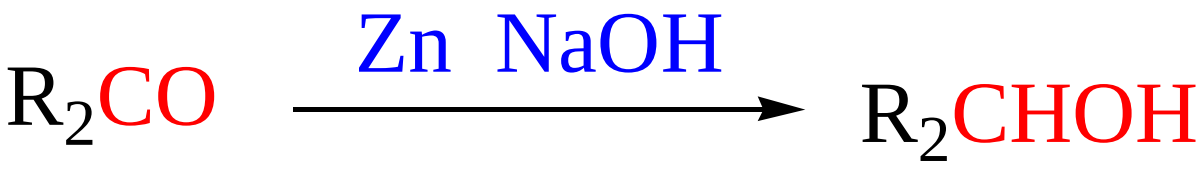
1. 催化氢化

$$RCHO + H_2 \xrightarrow[0.3\ MPa,\ 25℃]{Pt\ or\ Pd,\ Ni} RCH_2OH$$

$$R_2CO + H_2 \xrightarrow[0.3\ MPa,\ 25℃]{Pt\ or\ Pd,\ Ni} R_2CHOH$$

2. 金属还原剂

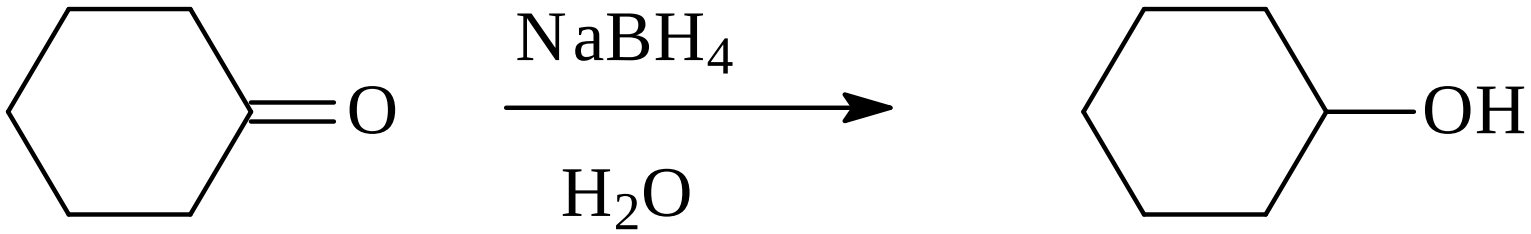




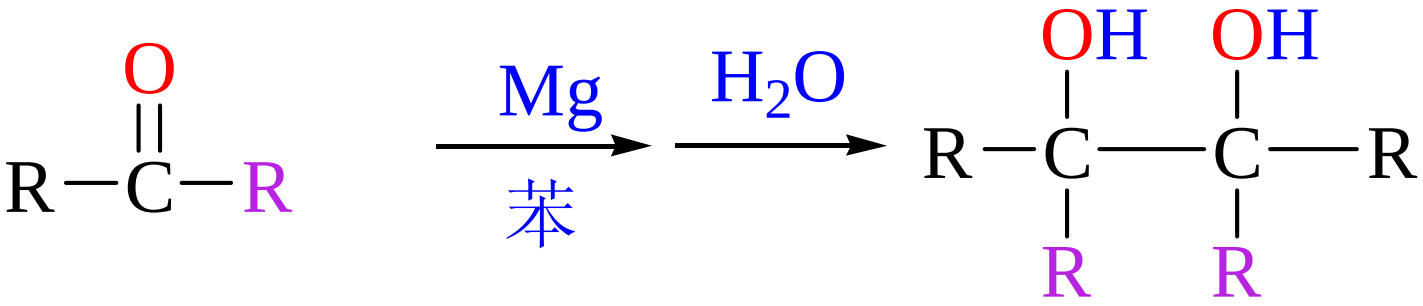
3. 用金属氢化物还原

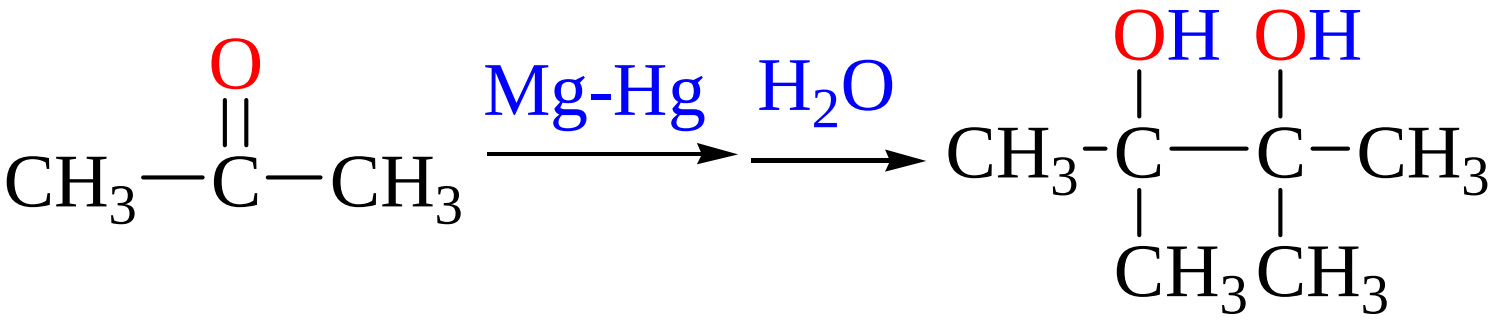
$LiAlH_4$　$NaBH_4$

$$4CH_3CH{=}CHCH_2CH_2CHO + LiAlH_4 \xrightarrow[(2)H_2O]{(1)Et_2O(\text{无水})} 4CH_3CH{=}CHCH_2CH_2CH_2OH$$

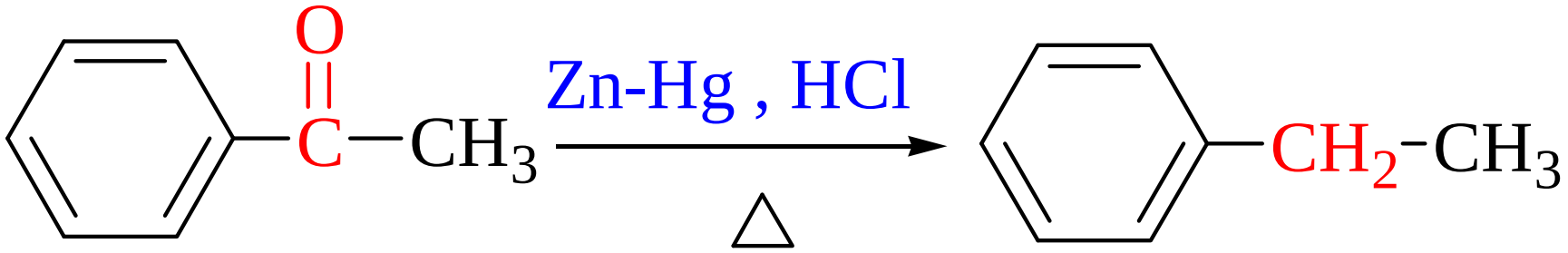


4. 双分子还原

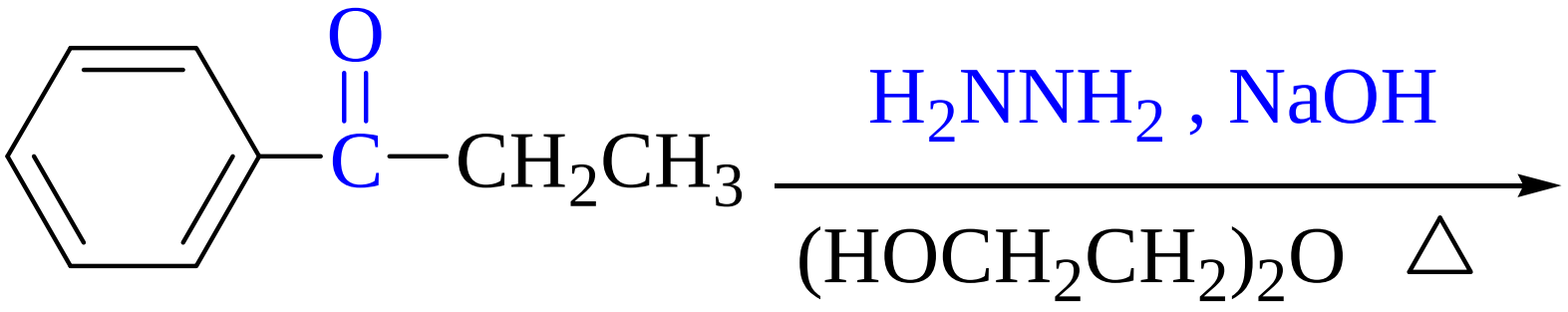

O
R—C—R
Mg
苯
H2O
OH OH
R—C—C—R
R R


O
CH3—C—CH3
Mg-Hg
H2O
OH OH
CH3-C—C-CH3
CH3 CH3

5 Clemmensen 还原



6 Wolff-Kishner-黄鸣龙还原



$$CH_2{-}CH_2CH_3 + N_2 + H_2O$$

10.3.4 氧化反应

1. 醛的氧化

$$RCHO \xrightarrow{[O]} RCO_2H$$

氧化剂：KMnO4, $K_2Cr_2O_7$, $H_2Cr_2O_7$, H_2CrO_4
RCO_3H , Ag_2O , H_2O_2, Br_2-H_2O ,

(1) 被Tollens 试剂氧化(银镜反应)

$$RCHO + Ag(NH_3)_2^+OH^- \longrightarrow RCO_2NH_4 + Ag\downarrow$$

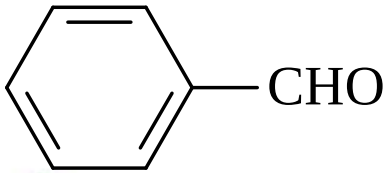
酮不发生反应

(2)被Fehling试剂氧化

$$RCHO + 2Cu^{2+} + NaOH \longrightarrow RCO_2Na + Cu_2O\downarrow$$

砖红

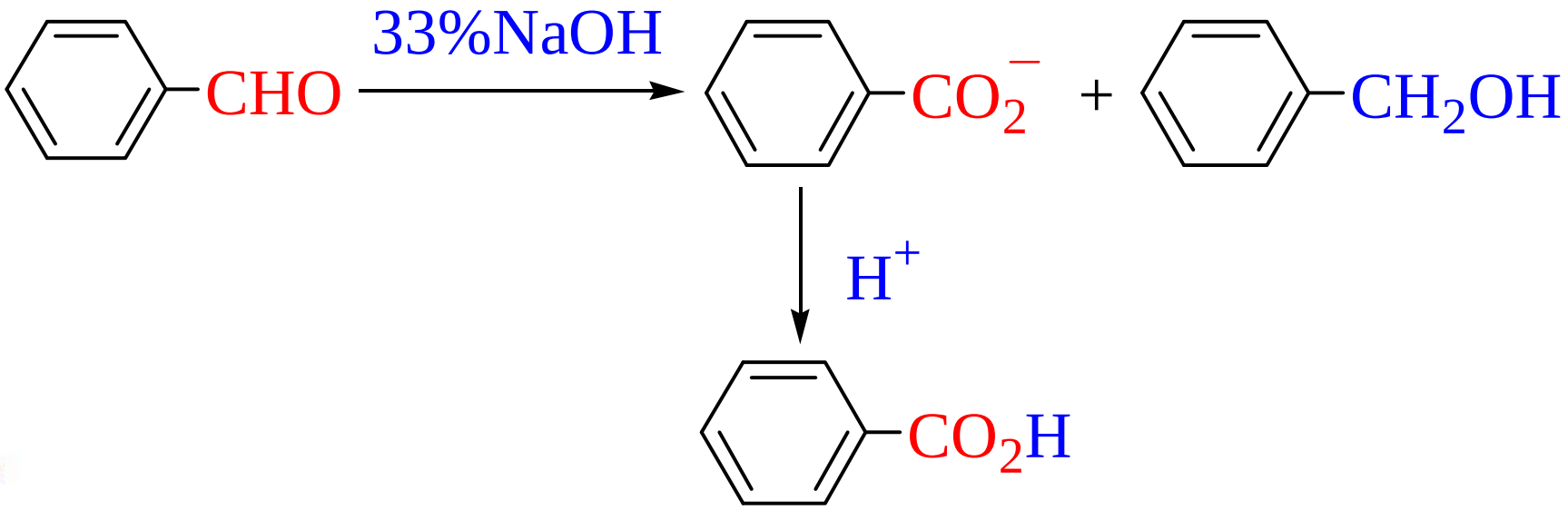
酮不发生反应



不被Fehling试剂氧化

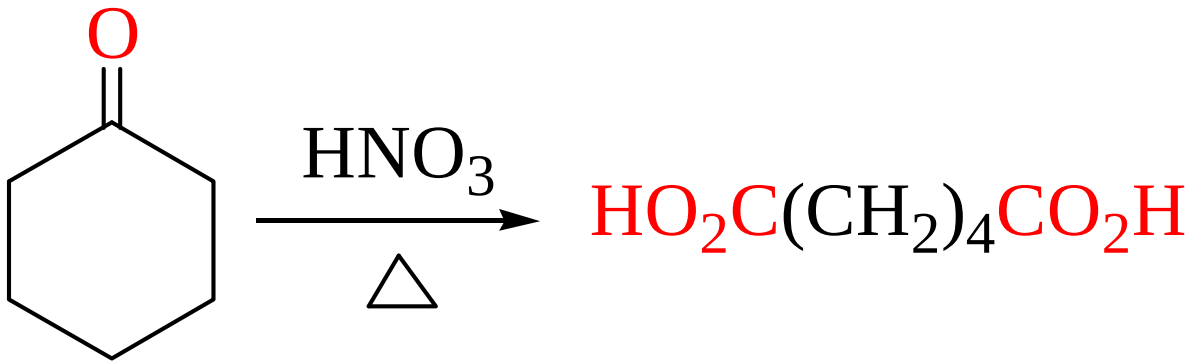
2. Cannizarro 反应

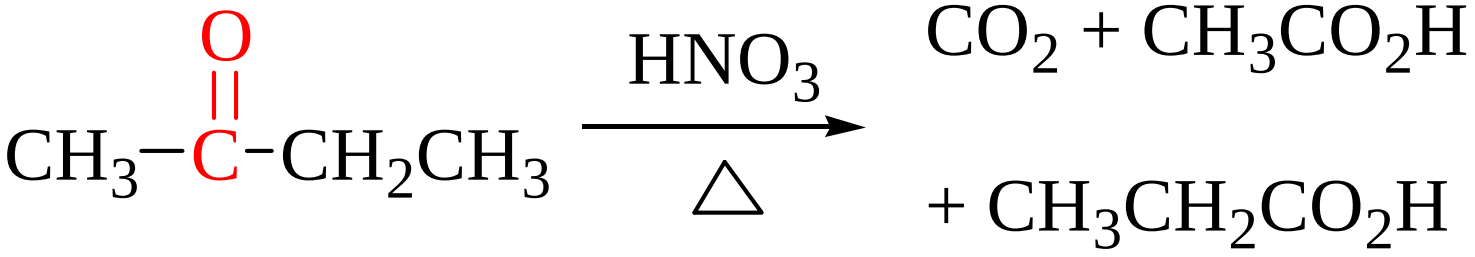
- 不含α–H的醛在浓碱作用下发生分子间的氧化－还原反应生成相应的醇和酸。



3. 酮的氧化

- 酮遇一般氧化剂时，不被氧化
- 酮遇强氧化剂时，发生碳链断裂，氧化成酸

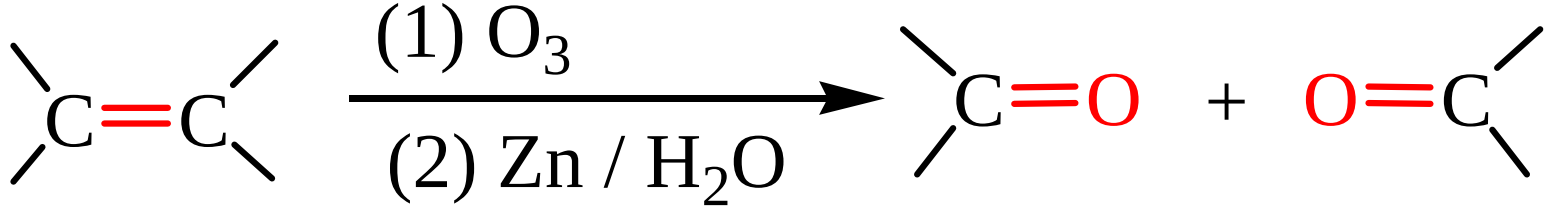


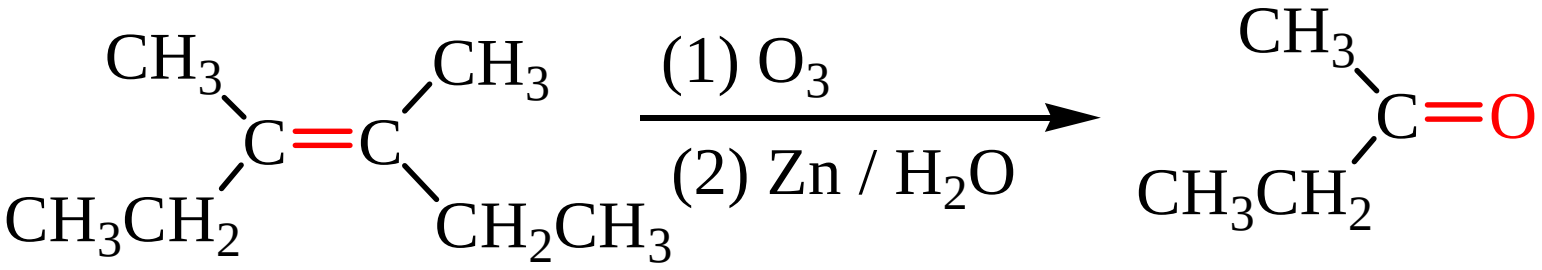


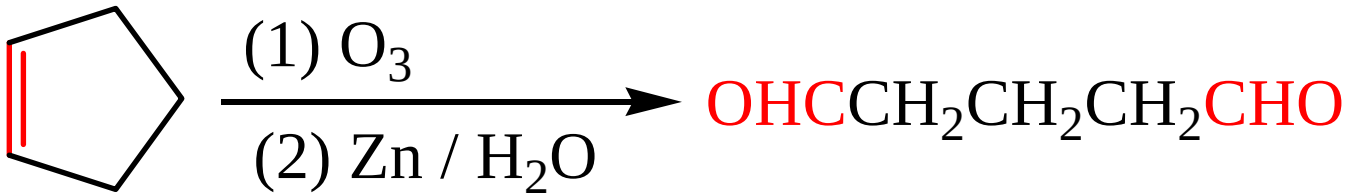
10.3 醛酮的制备

10.3.1 由烯烃制备

1. 臭氧解

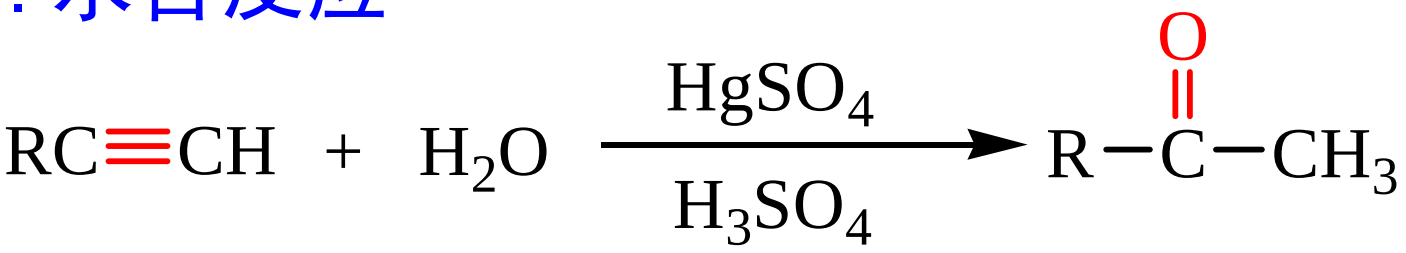




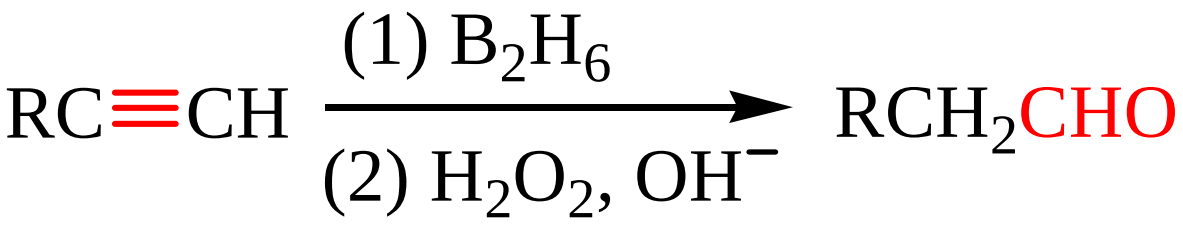


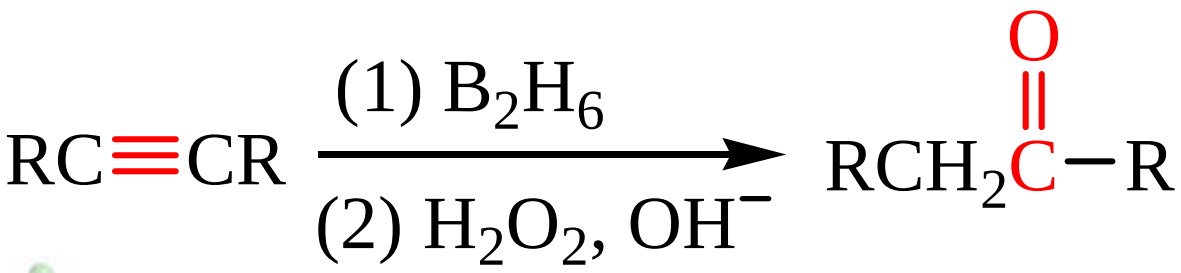
10.3.2 由炔烃制备

1. 水合反应



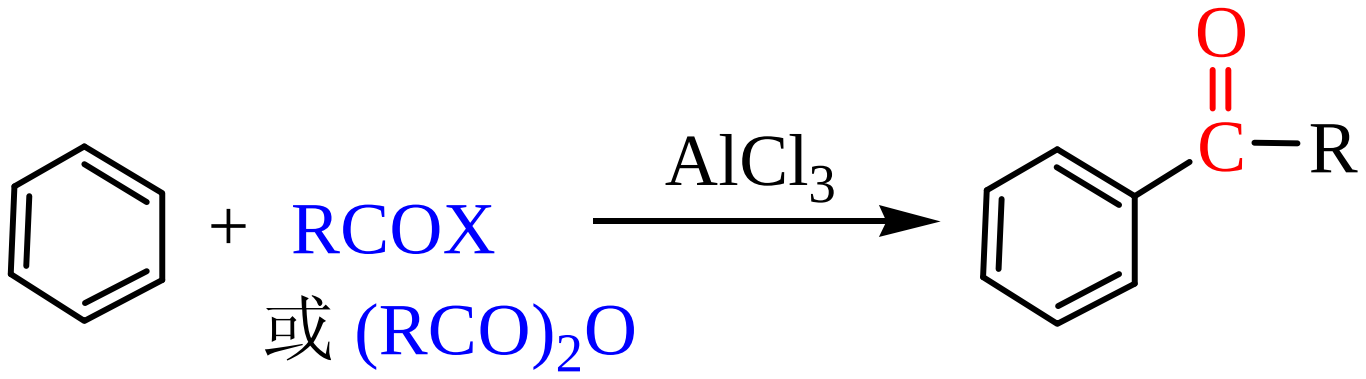
2. 硼氢化－氧化反应



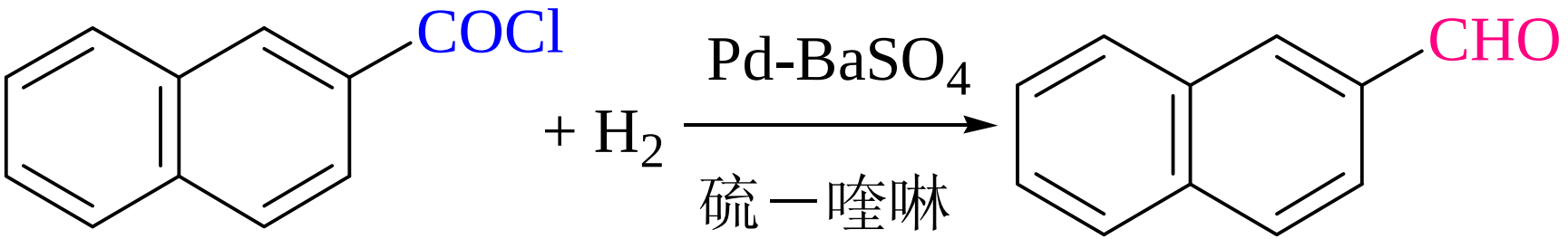


10.3.3 由芳烃制备

Freidel-Crafts 酰基化



10.3.4 由酰卤制备



Rosenmund 还原法

10. 3. 5 由醇制备

氧化

$$CH_3CH_2CH_2CH_2OH \xrightarrow[\triangle]{K_2Cr_2O_7\text{ - 稀}H_2SO_4} CH_3CH_2CH_2CHO$$

1°醇

$$CH_3\underset{OH}{\underset{|}{C}}HCH_2CH_3 \xrightarrow[\triangle]{K_2Cr_2O_7\text{ - 稀}H_2SO_4} CH_3\underset{O}{\underset{\|}{C}}CH_2CH_3$$

2°醇

$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}H(CH_2)_4CH_2OH \xrightarrow[CH_2Cl_2]{CrO_3\text{ - 吡啶}} CH_3CH_2\overset{CH_3}{\overset{|}{C}}H(CH_2)_4CHO$$