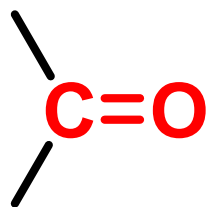


# Chapter 9

## 醛和酮

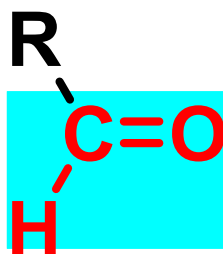
### *Reactions of Carbanions*

羰基化合物 (*carbonyl compounds*)。与羰基碳相连的原子如果有 **H** 原子，称为**醛**(*aldehydes*)，与羰基连接的原子都是碳原子则称为**酮** (*ketones*)。



羰基

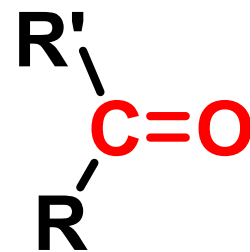
*carbonyl group*



—CHO 醛基

醛

*aldehyde*



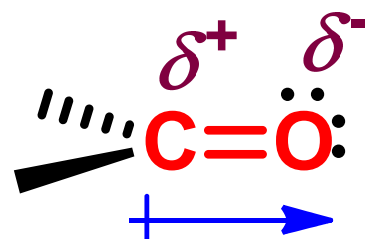
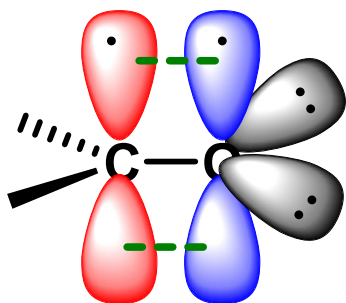
酮

*ketone*

# 第一节 结构、分类和命名

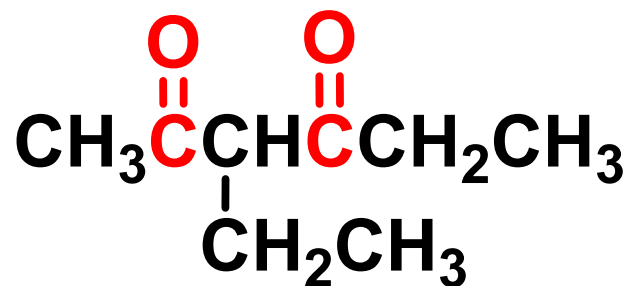
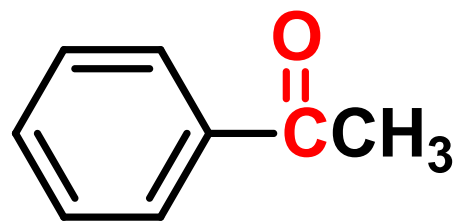
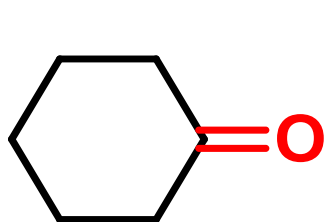
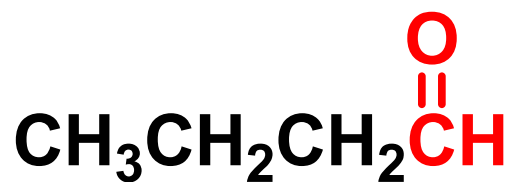
## 一、结构 (*Structure*)

碳原子  $sp^2$  杂化， $C=O$  双键平面构型，键角近  $120^\circ$ ， $C=O$  双键是不饱和极性键。



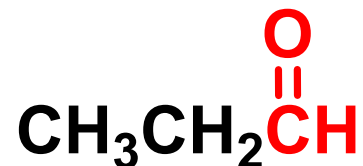
## 二、分类

脂肪族醛酮、脂环族醛酮、芳香醛酮；饱和醛酮、不饱和醛酮；一元、多元醛酮。



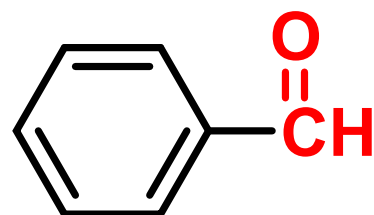
### 三、醛酮的命名

#### 1、普通命名法



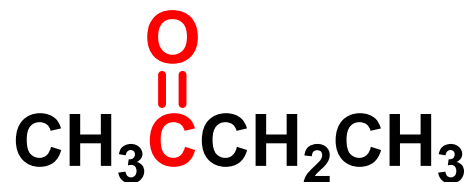
丙醛

propionaldehyde



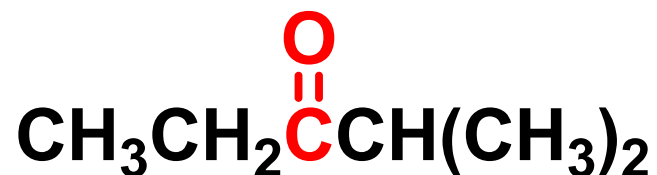
苯(基)甲醛

benzaldehyde



乙(基)甲(基)酮

ethyl methyl ketone

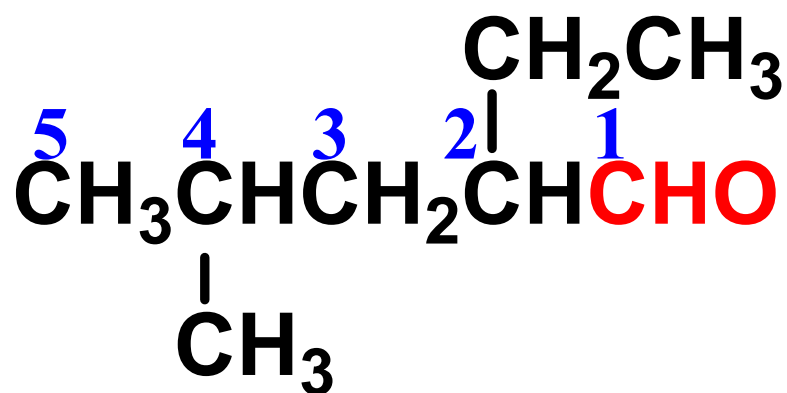


乙基异丙基酮

ethyl isopropyl ketone

## 2、系统命名法 (*IUPAC*)

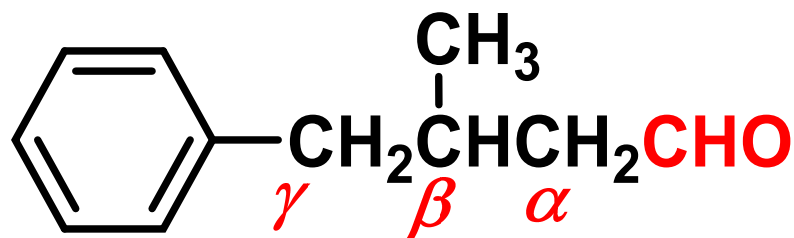
选择含有羰基碳的最长碳链为主链，编号使羰基碳位号最小，酮须指明羰基碳位号。



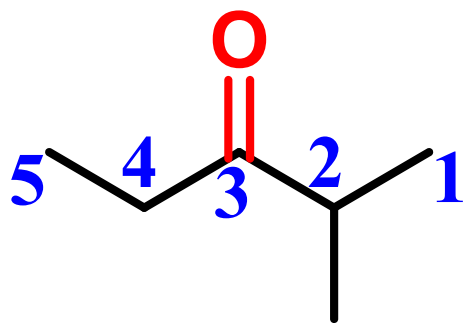
2-乙基-4-甲基戊醛

2-ethyl-4-methylpentanal

醛也可以用 $\alpha$ 、 $\beta$ 、 $\gamma$ 、 $\delta$ ...等标明。

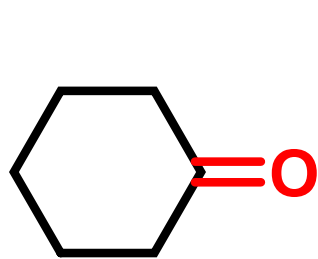


$\beta$ -甲基- $\gamma$ -苯基丁醛  
 $\beta$ -methyl- $\gamma$ -phenylbutanal



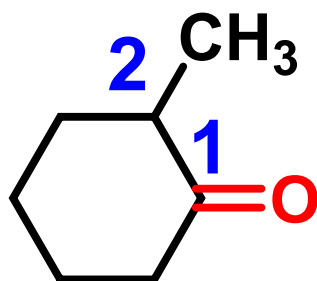
2-甲基戊-3-酮  
2-methylpentan-3-one

环酮的命名根据环上碳原子数称环某酮，环上有取代基时从羰基碳开始编号。羰基碳不在环上时，环作为取代基。



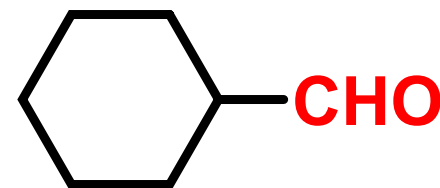
环己酮

cyclohexanone



2-甲基环己酮

2-methylcyclohexanone

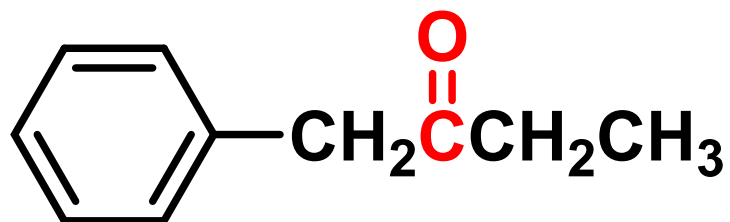


环己基甲醛

cyclohexylcarbaldehyde

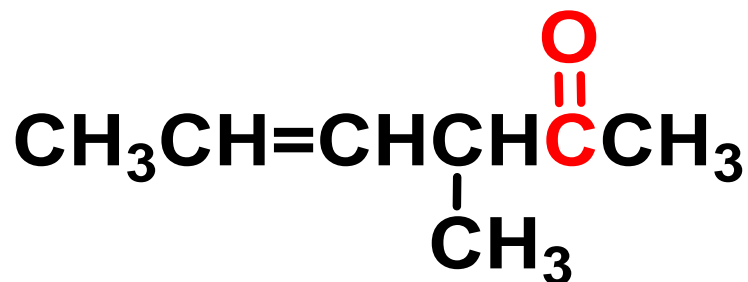


分子中含有苯环时，苯环作为取代基。



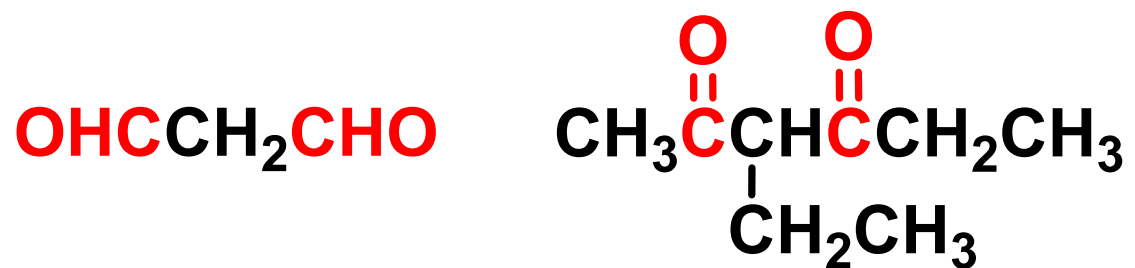
1-苯基丁-2-酮  
1-phenylbut-2-one

不饱和醛酮：以醛酮为母体，不饱和碳必须选在主链中，编号从靠近羰基一端开始。



3-甲基己-4-烯-2-酮  
3-methylhex-4-en-2-one

## 多元醛酮的命名

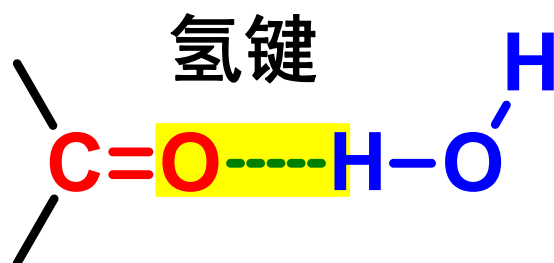
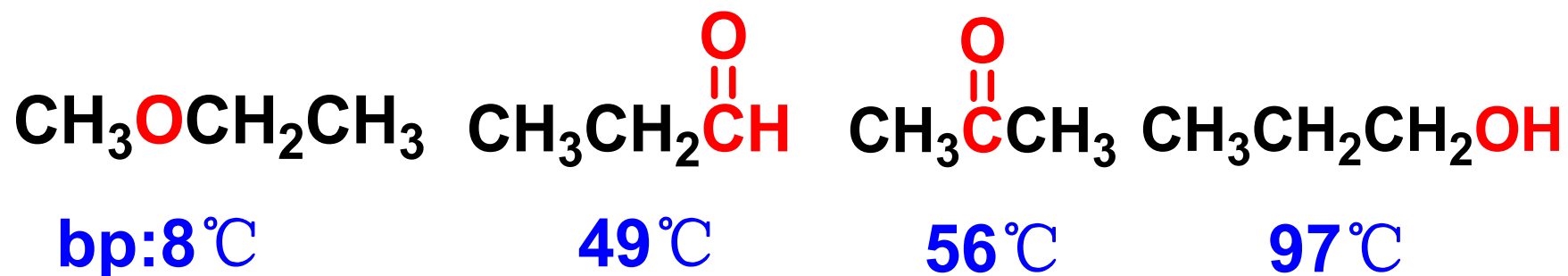


丙二醛  
**propanedial**

3-乙基己-2,4-二酮  
**3-ethylhexan-2,4-dione**

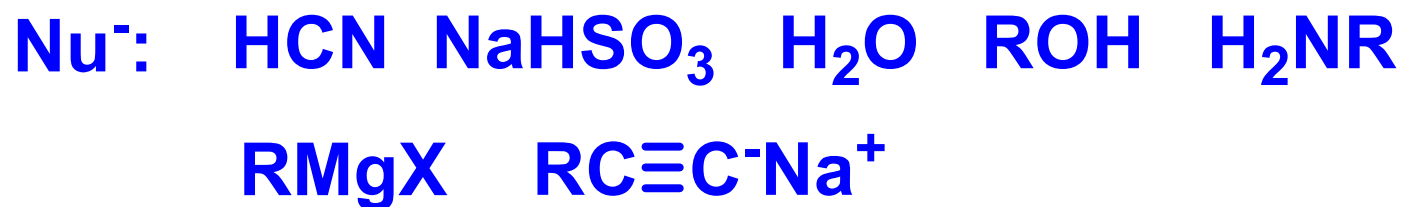
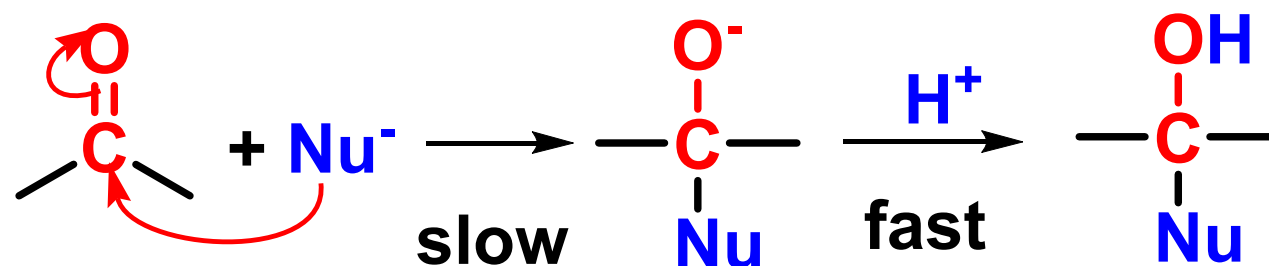
## 第二节 物理性质 (*physical property*)

熔沸点比分子量相近的醇低、比分子量相近的烃、醚等高，水溶性较大。

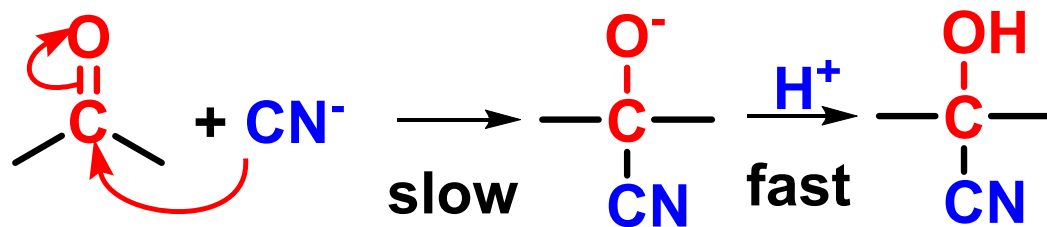
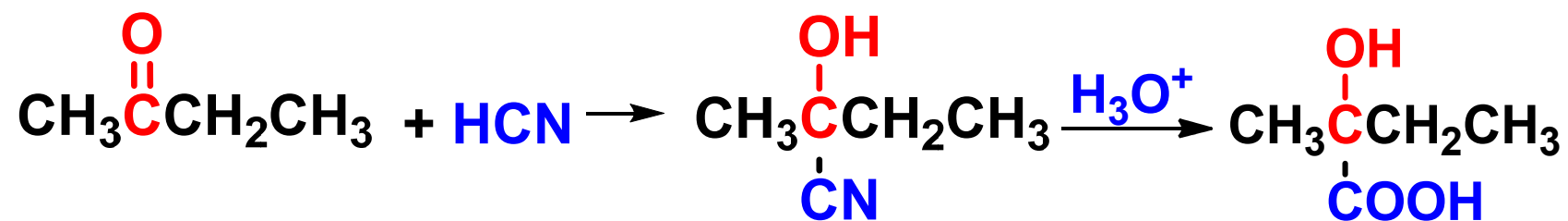
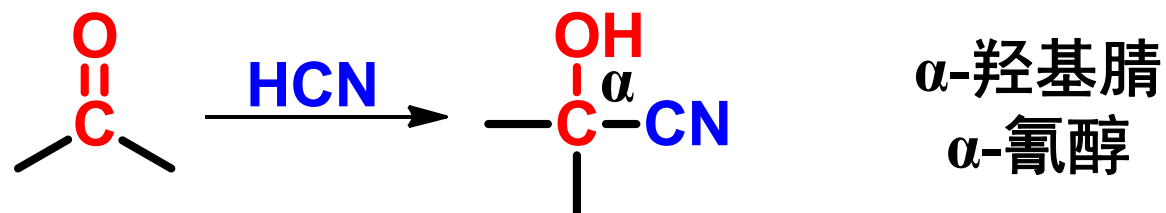


### 第三节 醛酮的化学性质

#### 一、亲核加成反应 (*Nucleophilic Addition Reaction*)



# 1、与氢氰酸加成



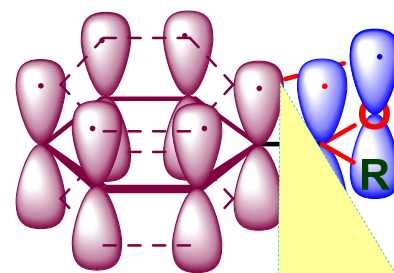
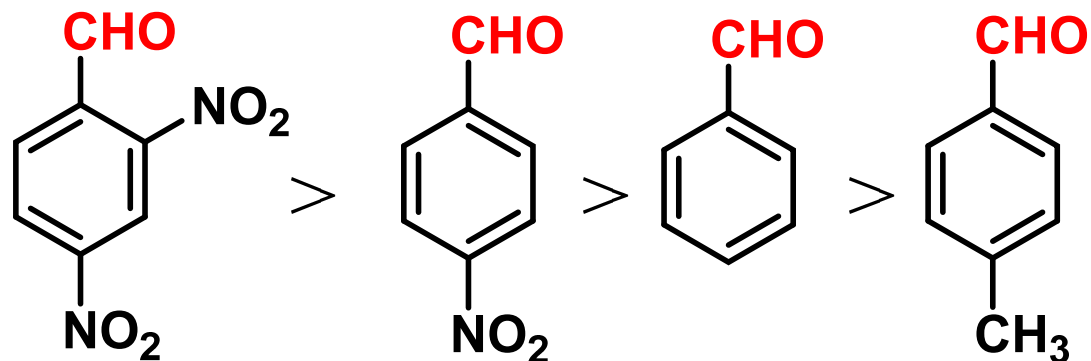
化合物	<i>K</i>	化合物	<i>K</i>
$\text{CH}_3\text{CHO}$	很大	$\text{CH}_3\text{COCH}(\text{CH}_3)_2$	38
$p\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$	1420	$\text{C}_6\text{H}_5\text{COCH}_3$	0.8
$\text{C}_6\text{H}_5\text{CHO}$	210	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$	很小

醛、脂肪族甲基酮、八碳以内环酮可以与HCN发生反应。

影响活性的因素：① 电性因素；② 空间位阻。

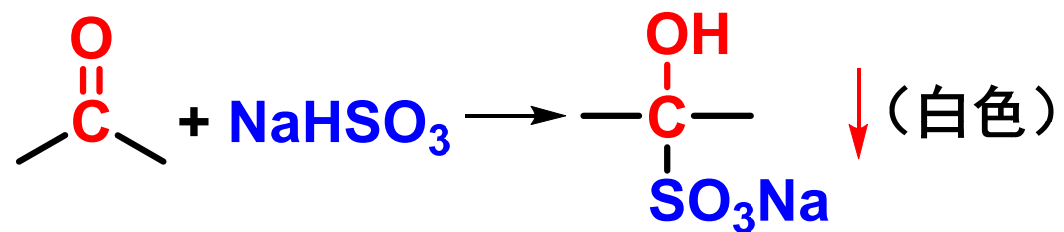


环酮只有八元环以下的能够与HCN反应。芳香酮活性较低。



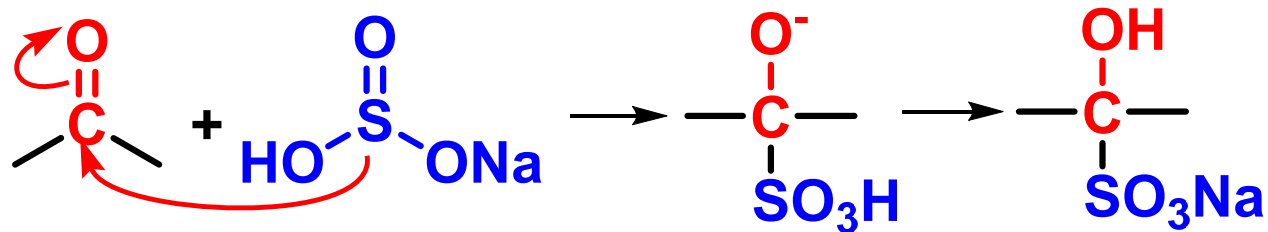
$\pi$ - $\pi$ 共轭  
正电荷密度降低

## 2、与亚硫酸氢钠 ( $\text{NaHSO}_3$ ) 加成

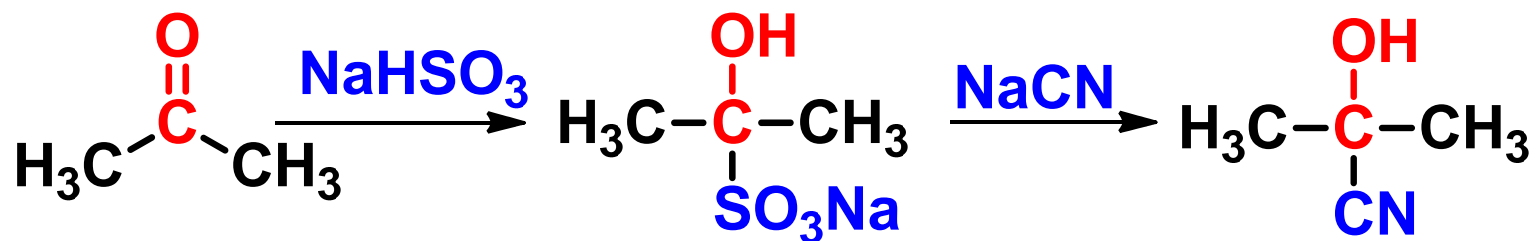
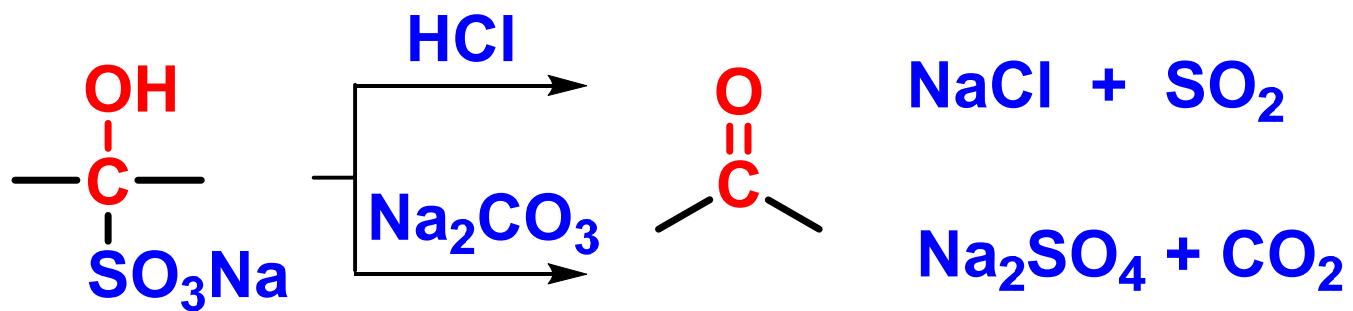


醛、脂肪族甲基酮和八个碳以下的环酮可以反应。

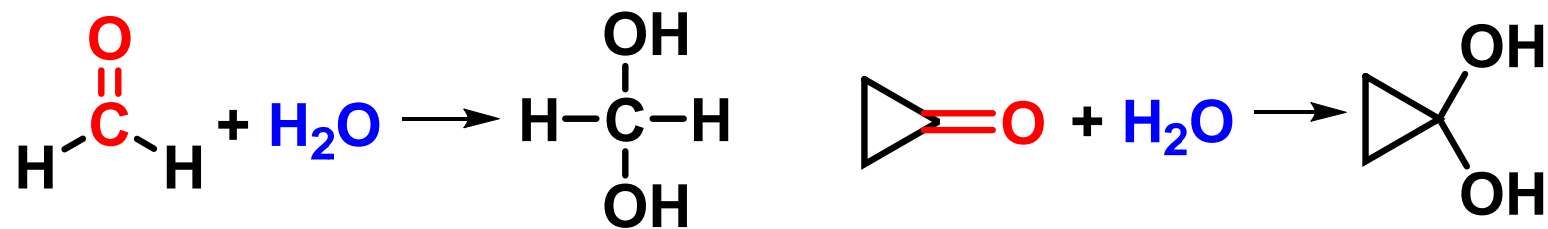
可以用于这些醛酮的分类鉴别和纯化。





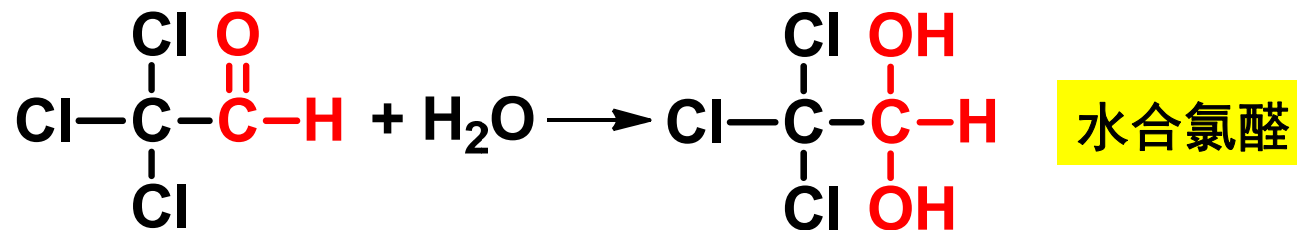


### 3、与 H<sub>2</sub>O 加成

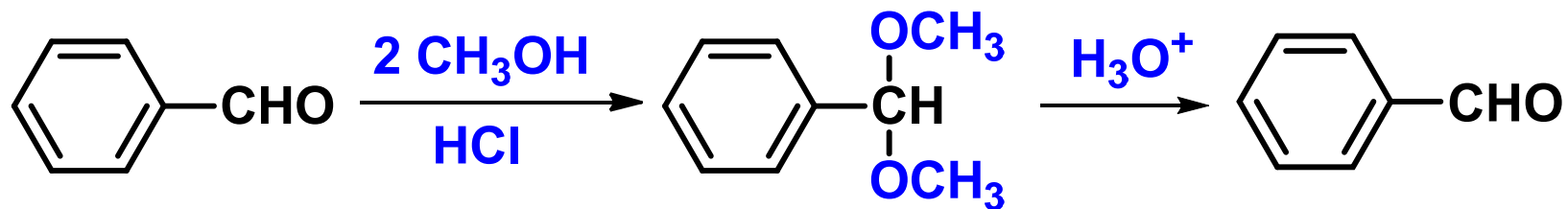
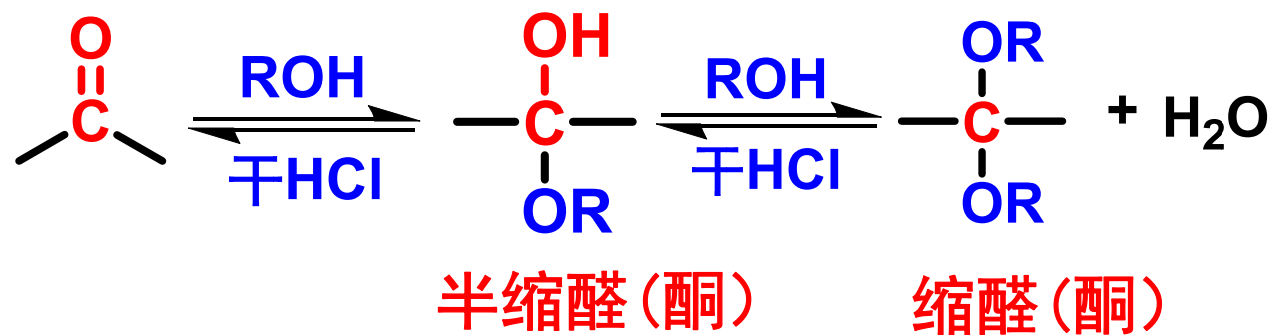


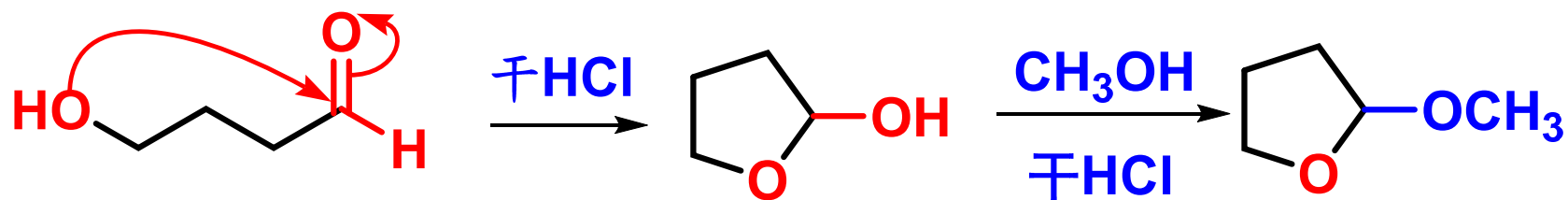
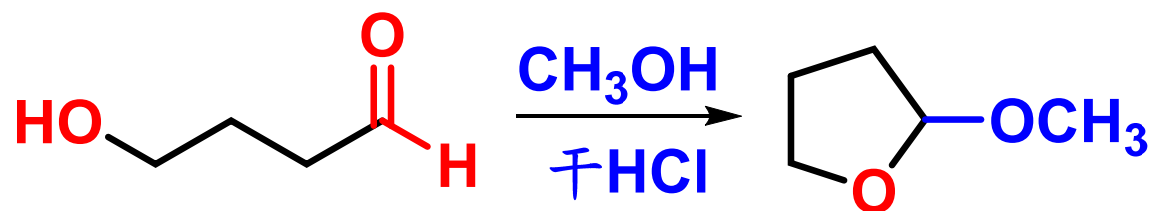
偕二醇

*geminal diol*

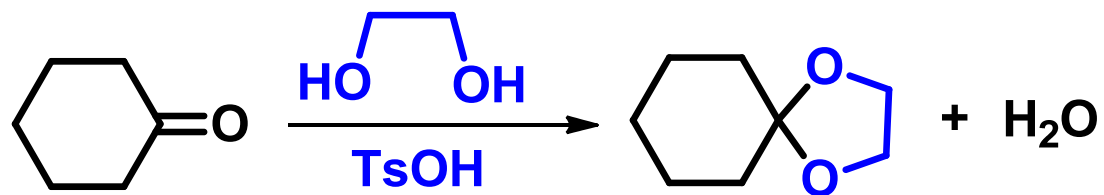


## 4、与醇加成

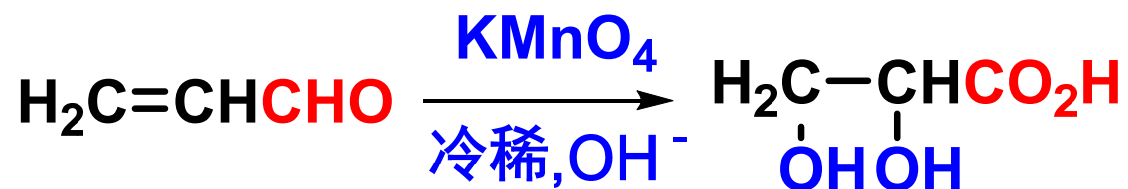
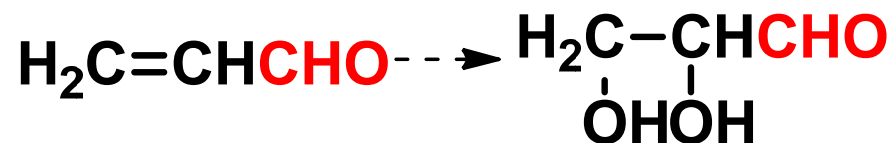


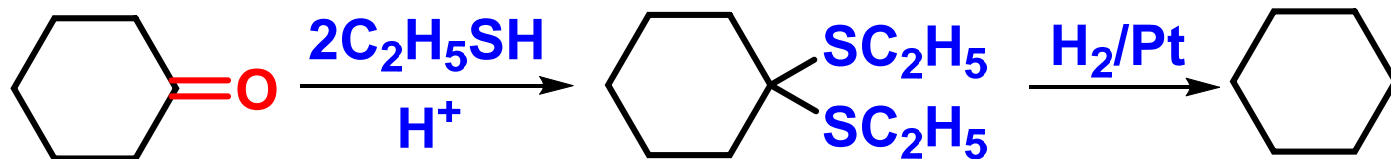
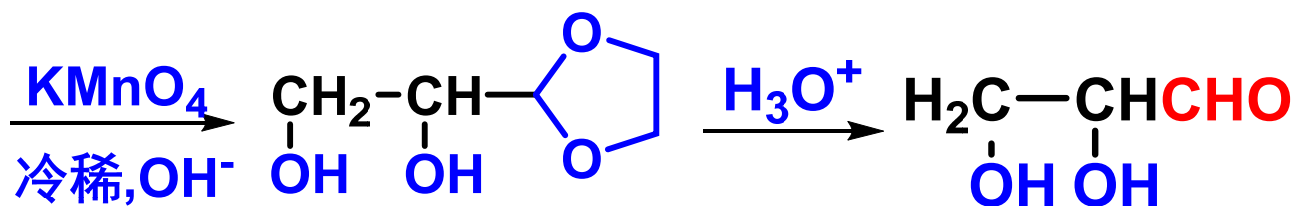
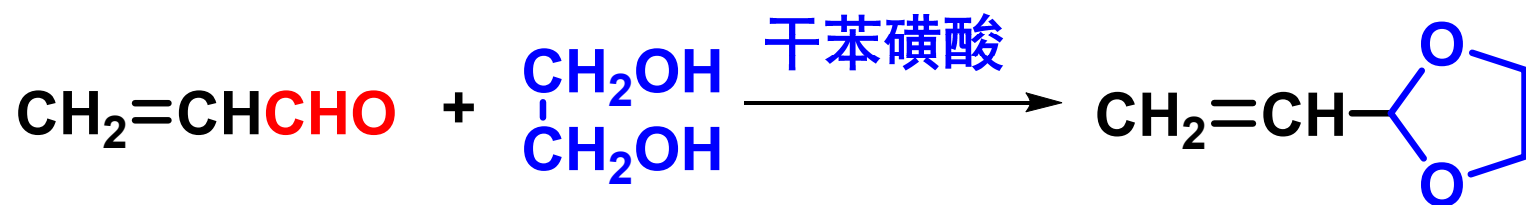


分子内形成半缩醛一般是5元或6元环



缩醛（酮）在碱性和中性水溶液中稳定，对于氧化还原剂稳定，用于保护醛酮羰基。



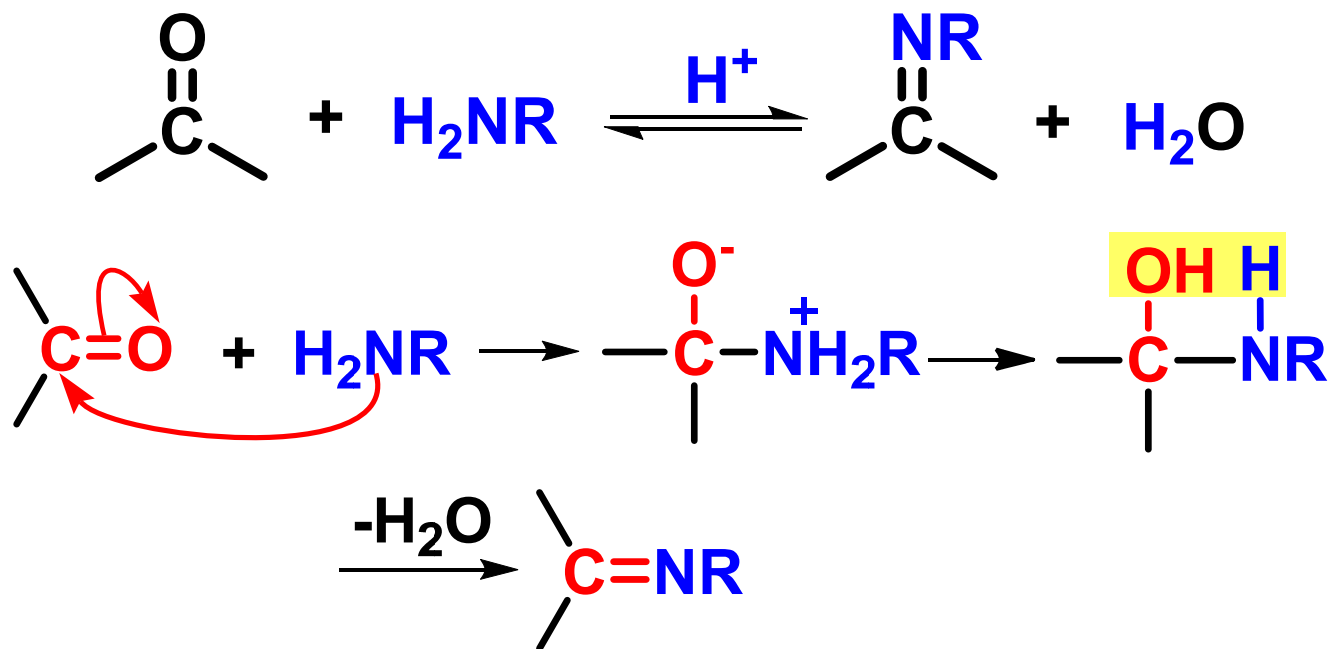


缩硫酮

## 5、加伯胺及胺的衍生物

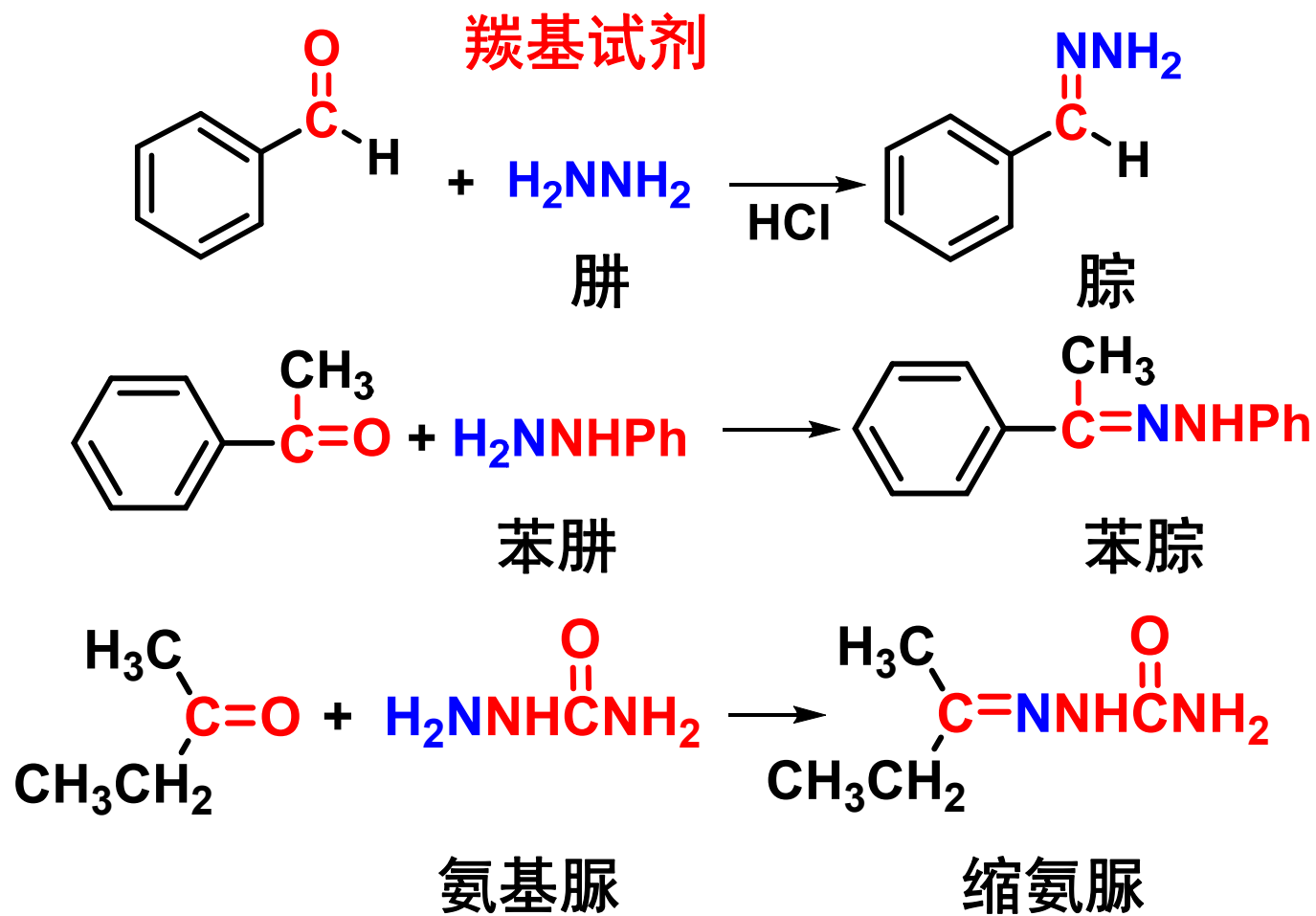
➤ 与伯胺的缩合

亚胺 (imine)  
席夫碱 (Schiff's base)

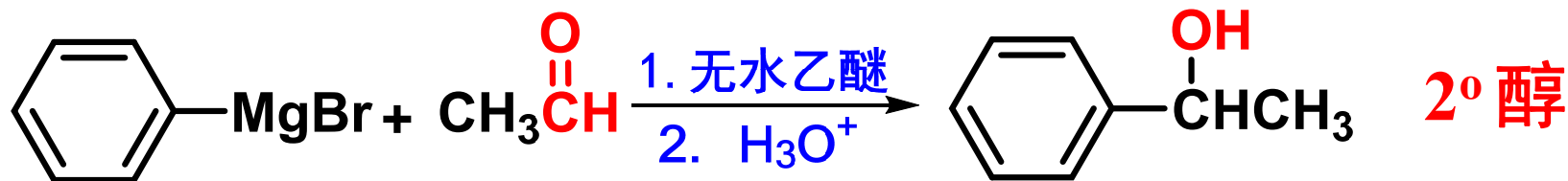
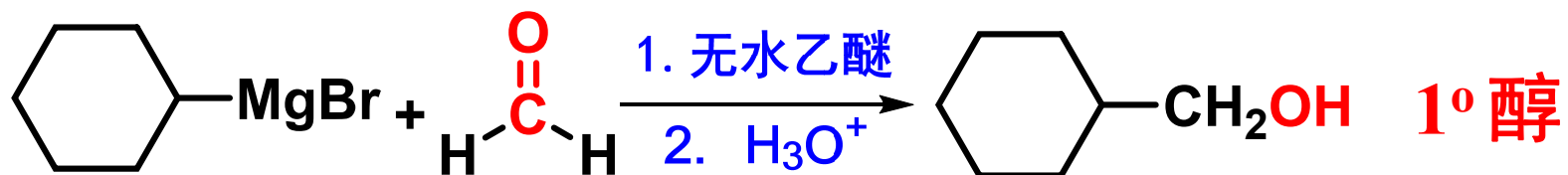
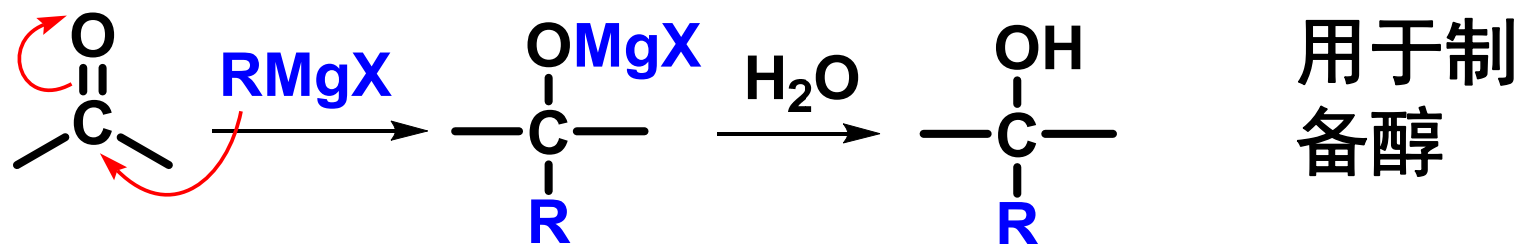


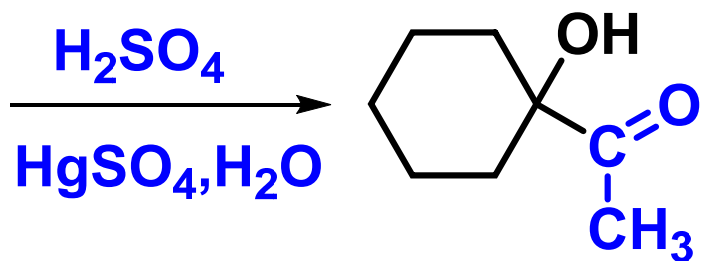
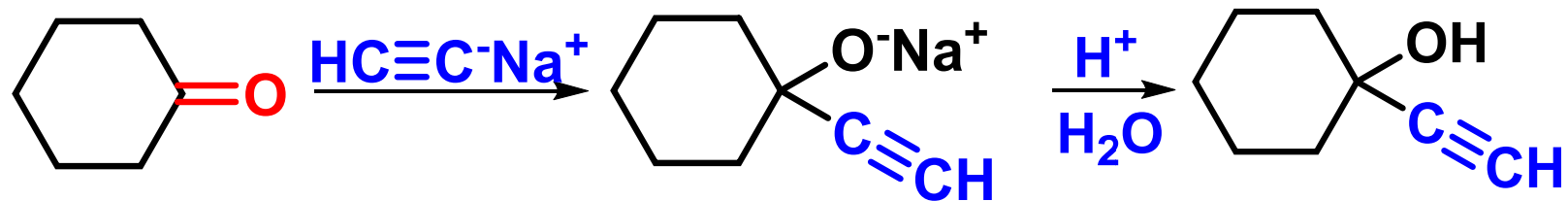
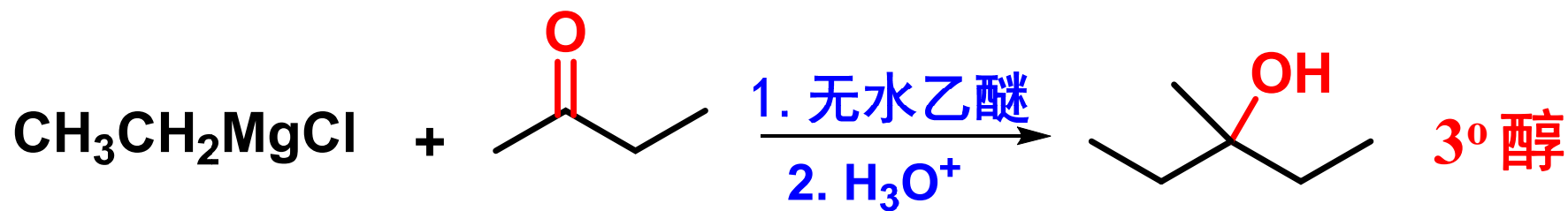






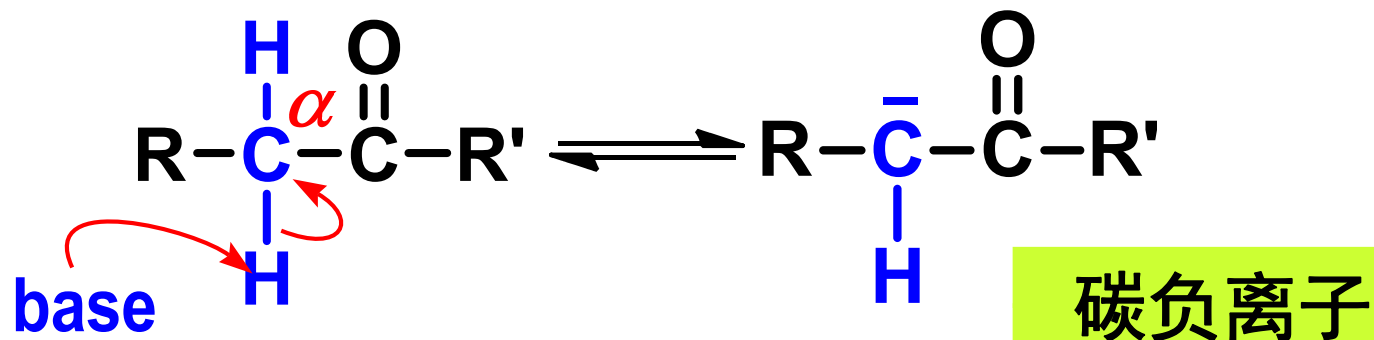
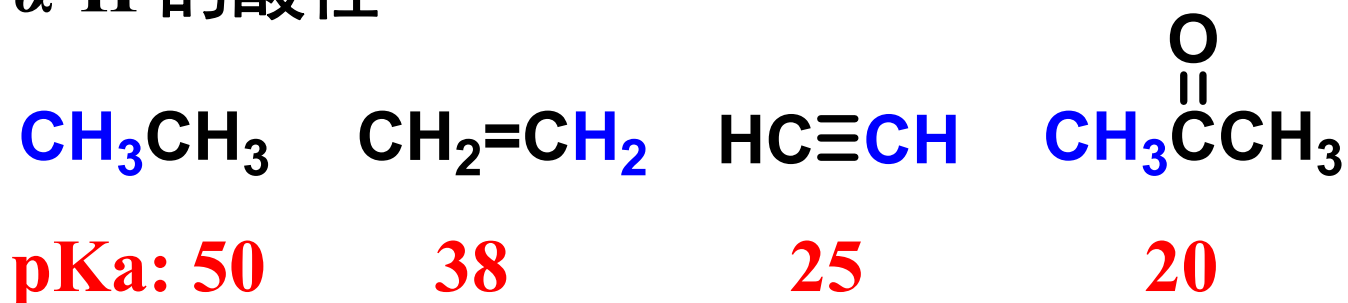
## 6、与金属有机化合物的加成反应

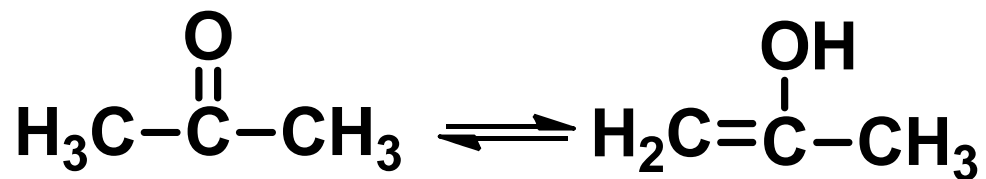
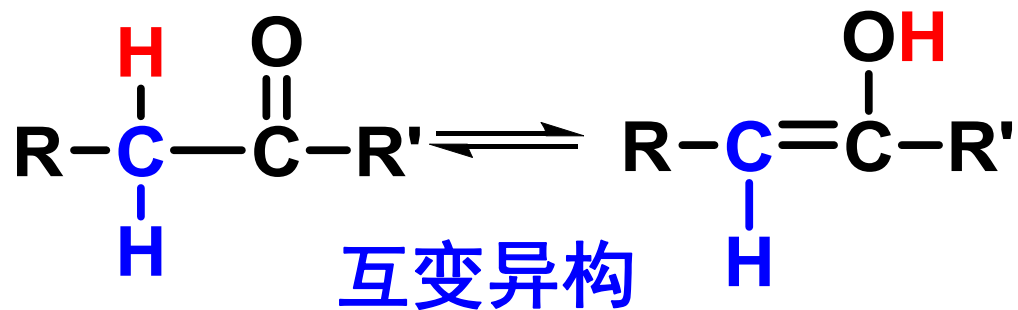
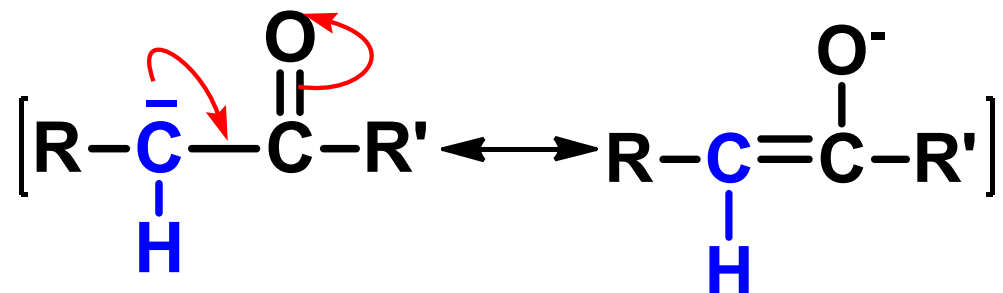




## 二、 $\alpha$ -H 的反应

### 1、 $\alpha$ -H 的酸性





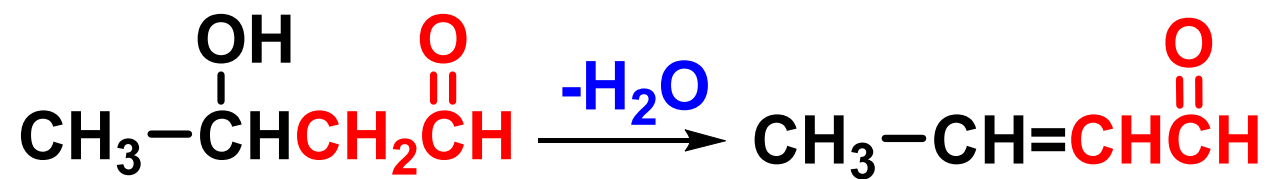
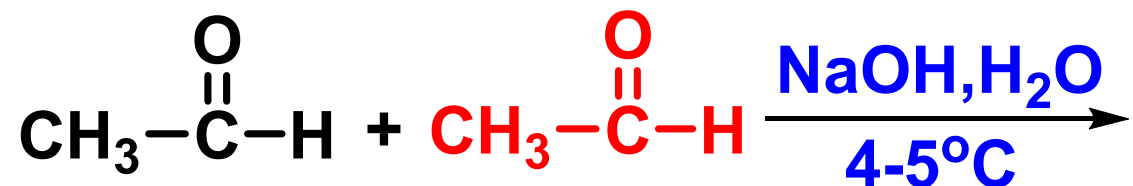
酮式 > 99.99%

烯醇式 < 0.01

化合物	pKa	化合物	pKa
$\text{CH}_3\text{NO}_2$	10.2	$\text{CH}_2(\text{NO}_2)_2$	3.57
$\text{CH}_3\text{COCl}$	16	$\text{CH}_3\text{COCH}_2\text{COCH}_3$	9
$\text{CH}_3\text{CHO}$	17	$\text{NCCH}_2\text{CO}_2\text{CH}_3$	9
$\text{CH}_3\text{COCH}_3$	20	$\text{NCCH}_2\text{CN}$	11.2
$\text{CH}_3\text{CO}_2\text{CH}_3$	25	$\text{CH}_3\text{COCH}_2\text{CO}_2\text{Et}$	11
$\text{CH}_3\text{CN}$	25	$\text{CH}_2(\text{CO}_2\text{Et})_2$	13

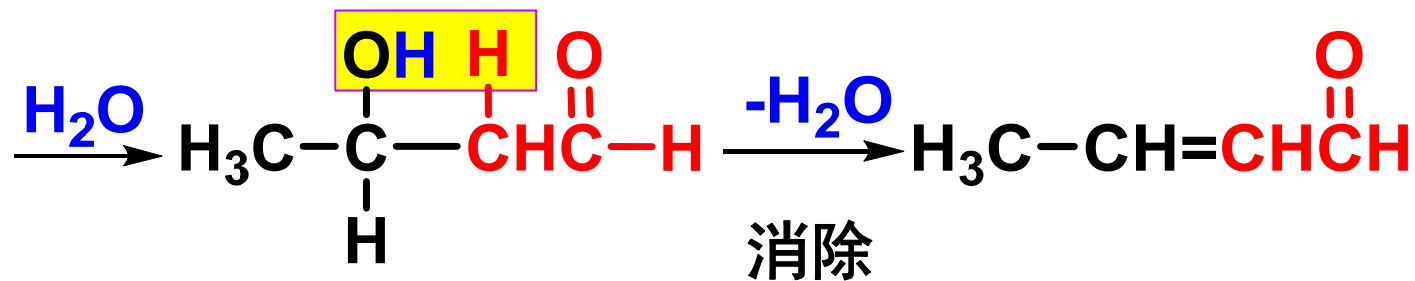
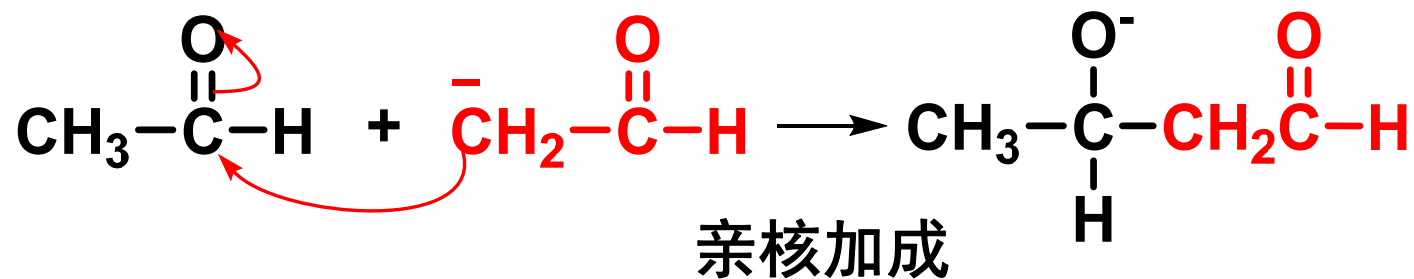
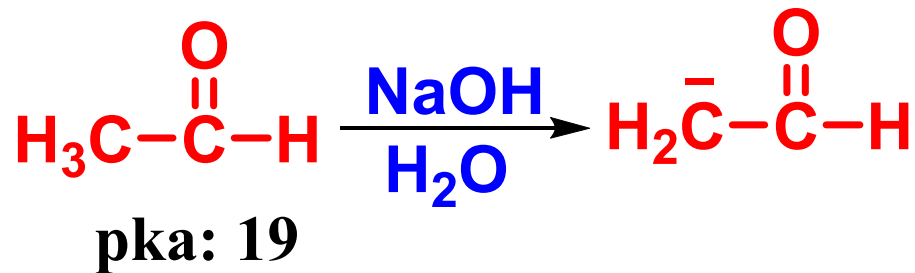
## 2、羟醛缩合反应 (*aldol condensation* )

### (1) 羟醛缩合反应

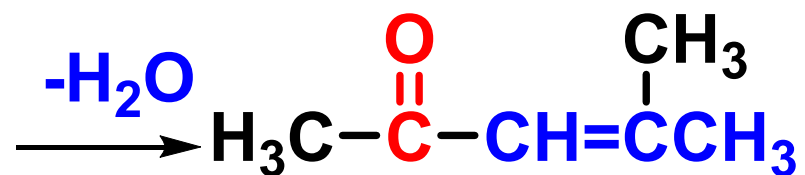
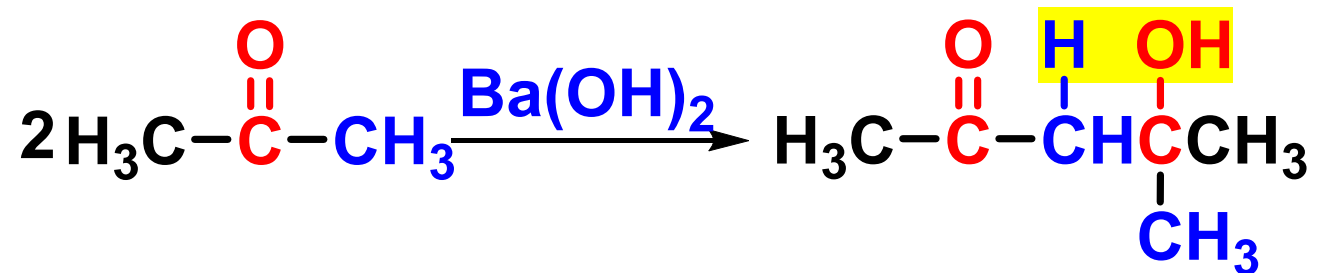
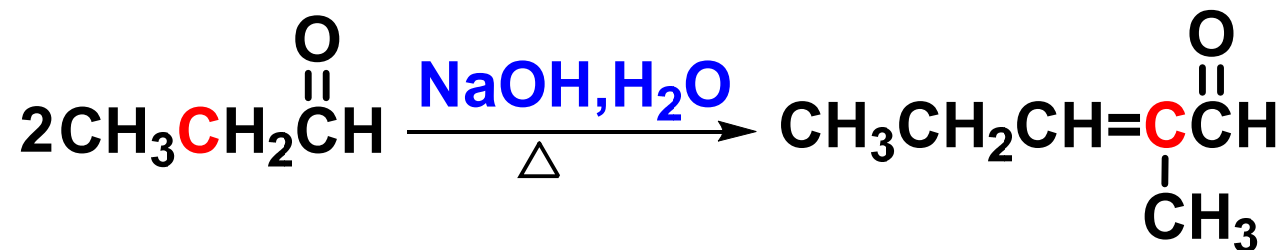


$\alpha, \beta$ -不饱和醛

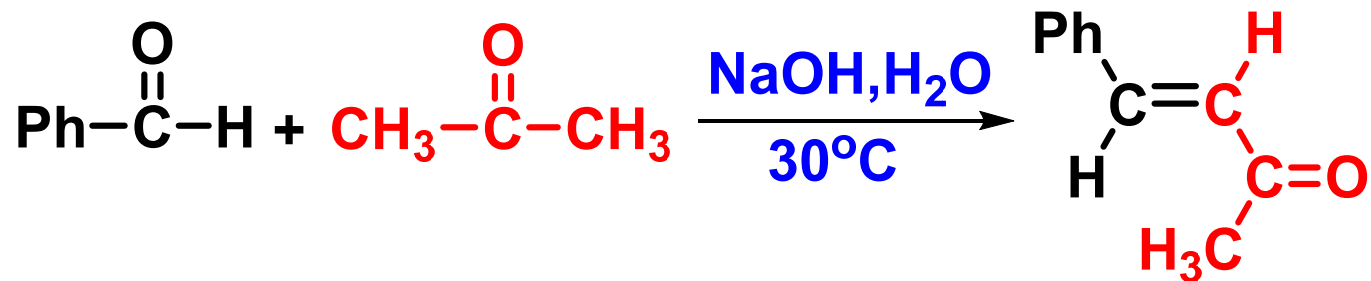
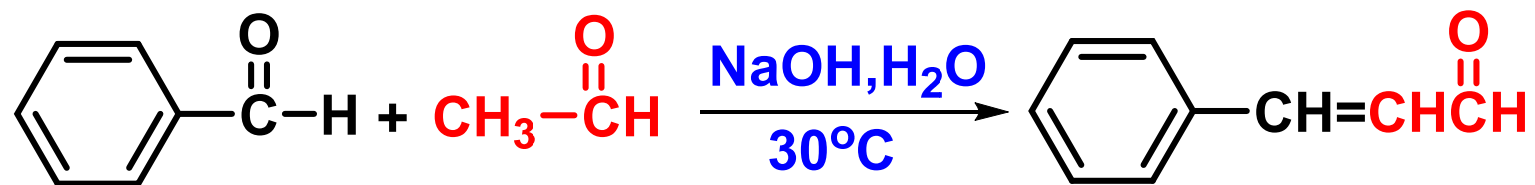
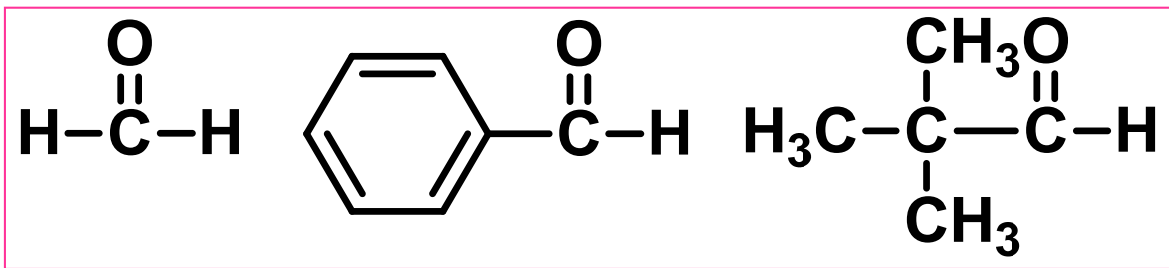
反应机理:





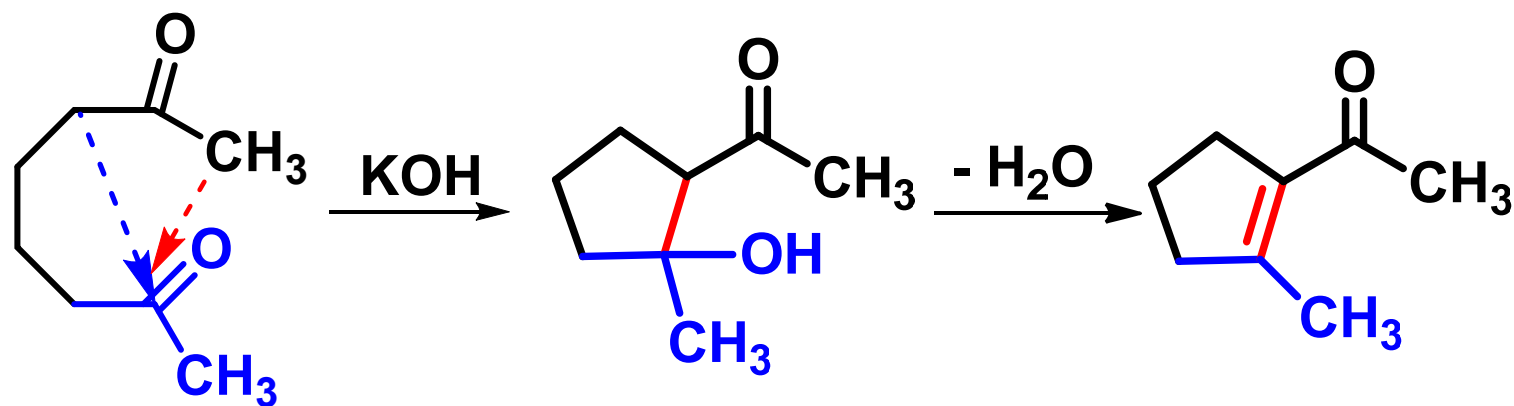




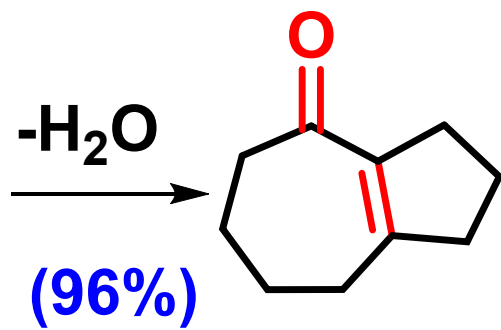
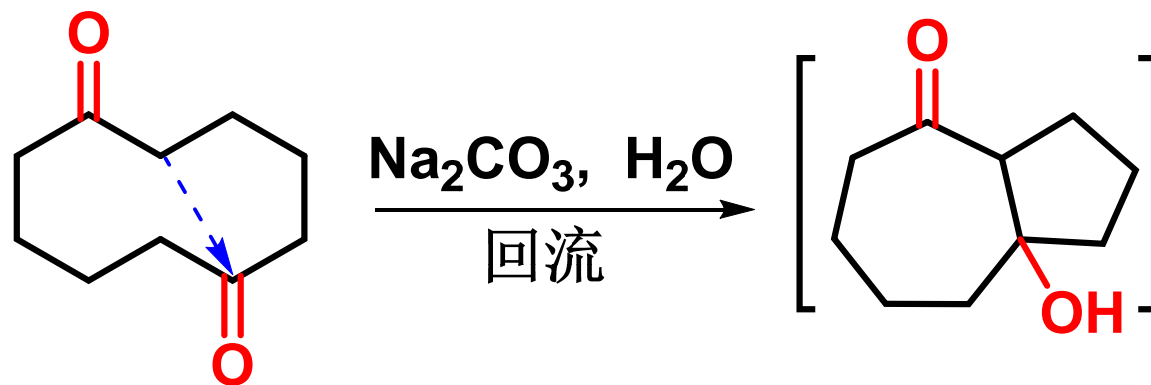


### (3) 分子内的羟醛缩合

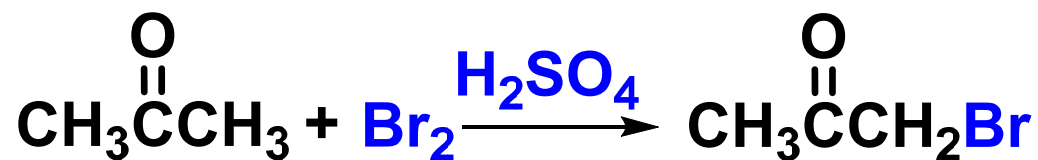
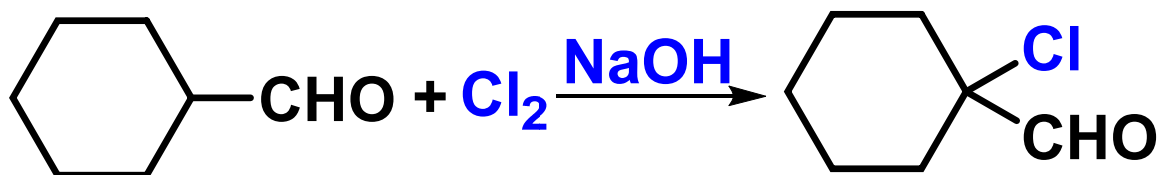
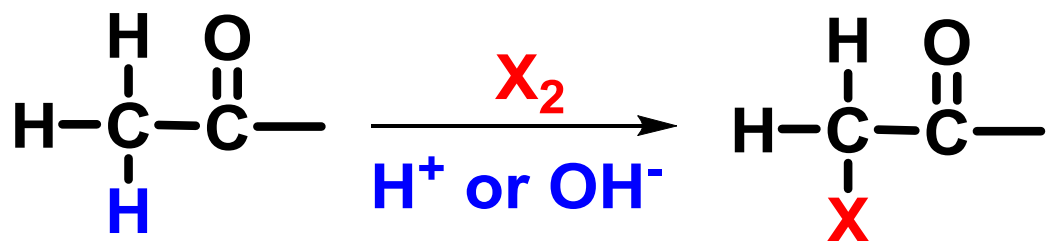
*(intramolecular aldol condensation)*



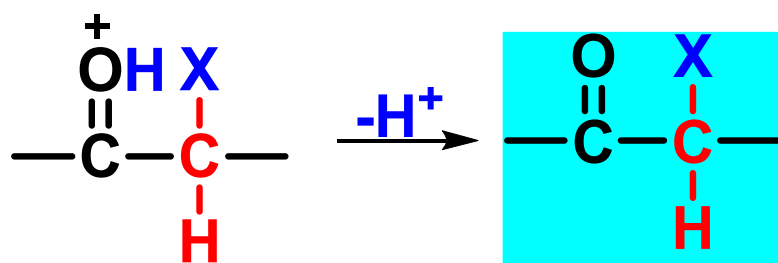
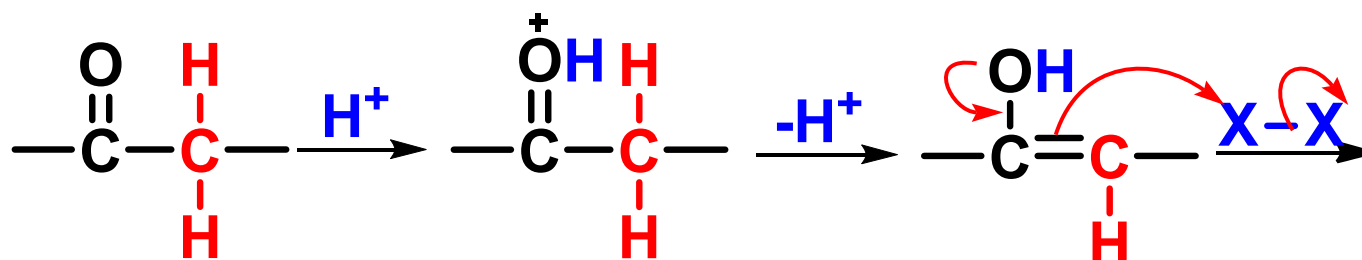
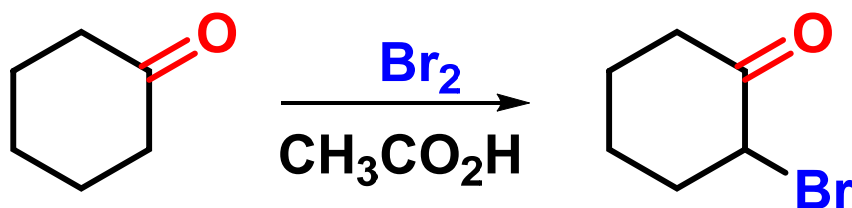
形成五元环或六元环



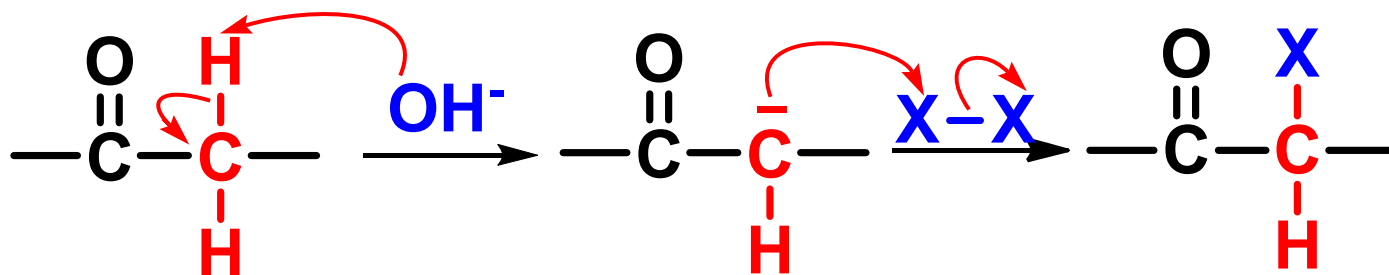
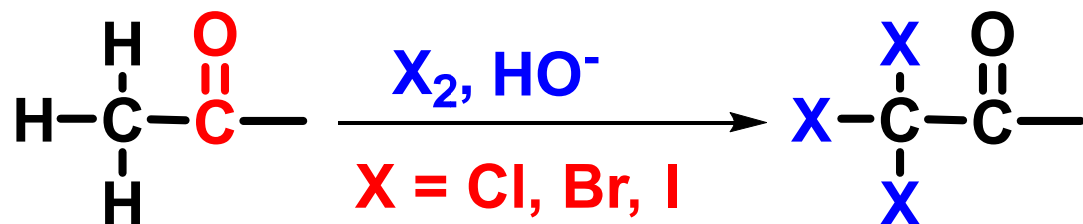
### 3、卤代反应和卤仿反应



● 酸催化卤代：单卤代

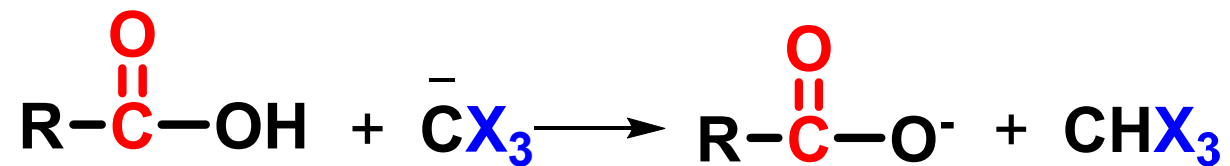
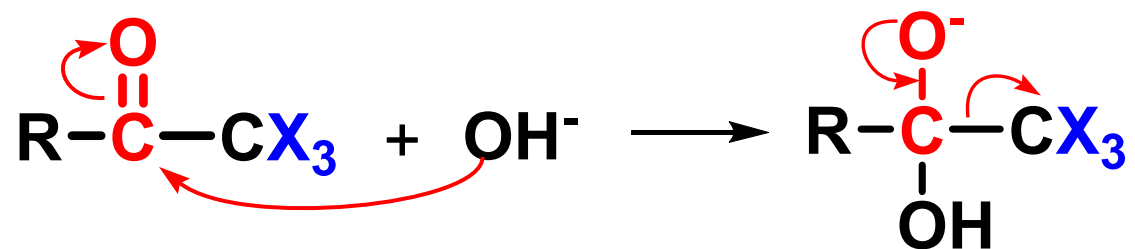
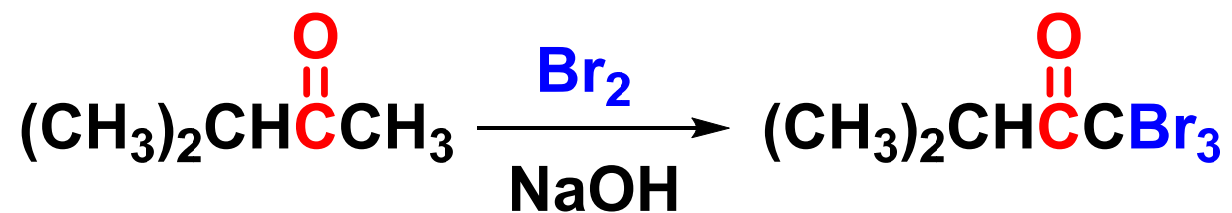


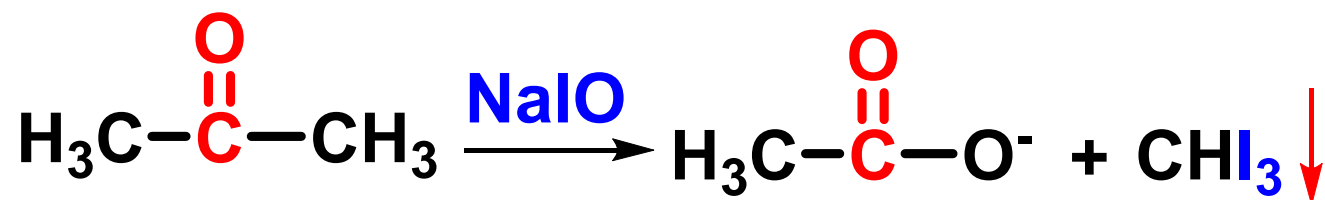
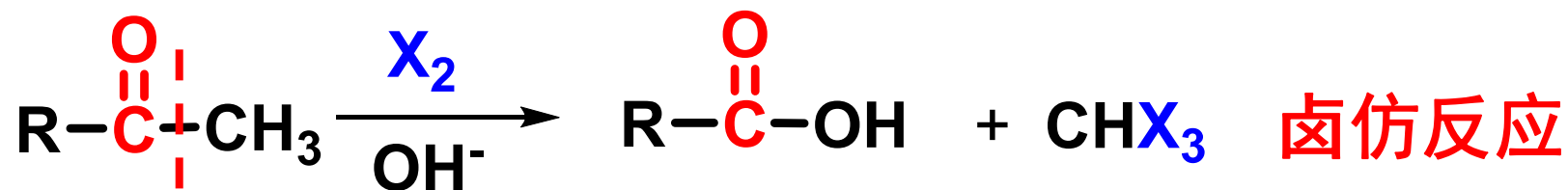
● 碱催化卤代：多卤代



产物 $\alpha$ -H的酸性比反应物强，更易取代，易得多取代产物。

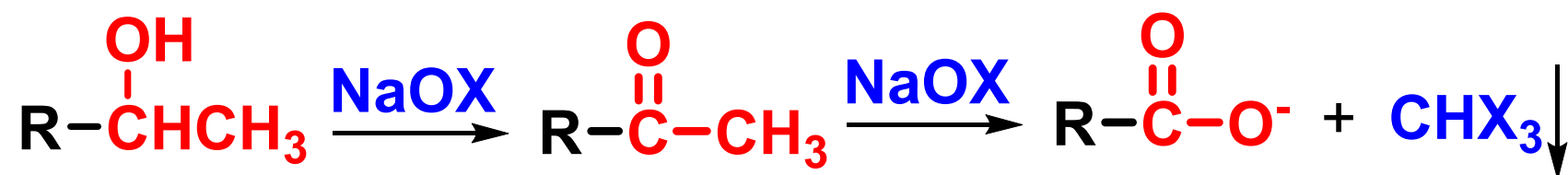






碘仿为有特殊臭味的黄色固体，且反应进行很快，可用于鉴别**乙醛**、**甲基酮**类化合物，称为碘仿反应。

$\alpha$ -碳原子上连有甲基的醇，可被次卤酸盐氧化成相应的羰基化合物。碘仿反应也可用于该种类型醇的鉴别。

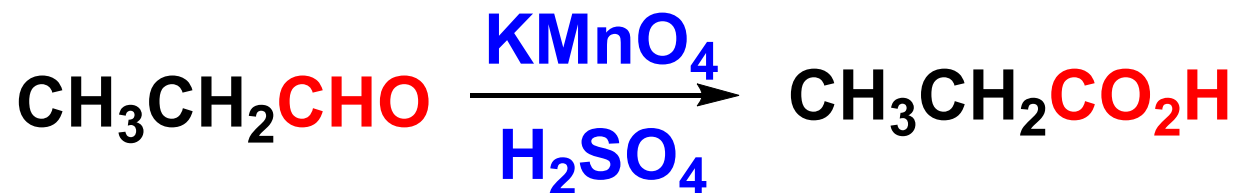
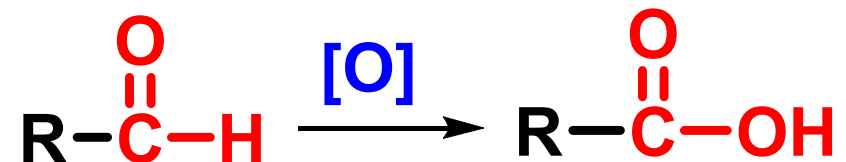


卤仿反应可用于鉴别：乙醛、甲基酮和部分具有特殊结构的醇。

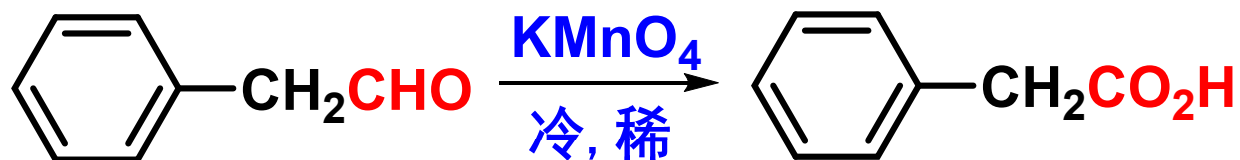
### 三、氧化反应

#### 1、醛的氧化

- 强氧化剂： $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ 等。



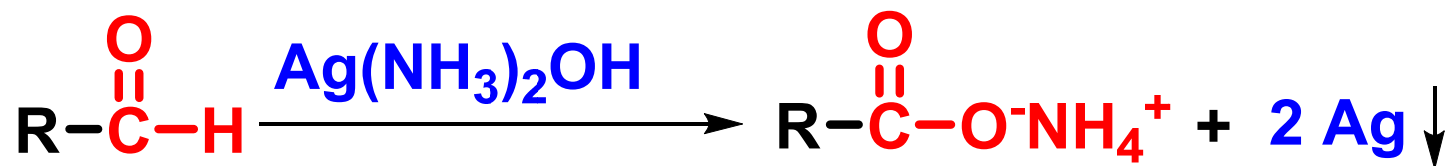
对强氧化剂敏感的基团如双键也被氧化。



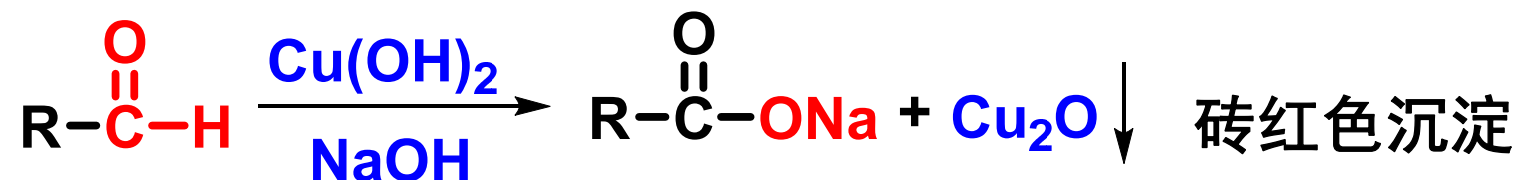
● 温和氧化剂:

AgNO<sub>3</sub>的氨水溶液 (Tollens 试剂)

CuSO<sub>4</sub>的酒石酸钠钾碱溶液 (Fehling试剂)

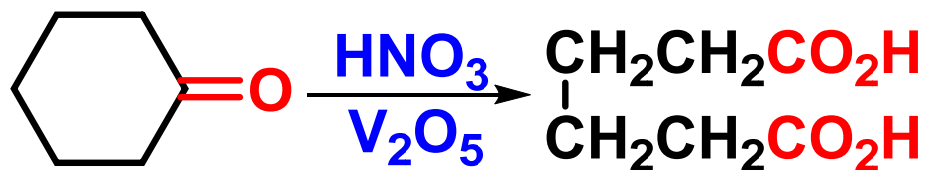


银镜反应



只与脂肪醛反应，不与芳香醛和酮反应，用于醛的氧化和鉴别。

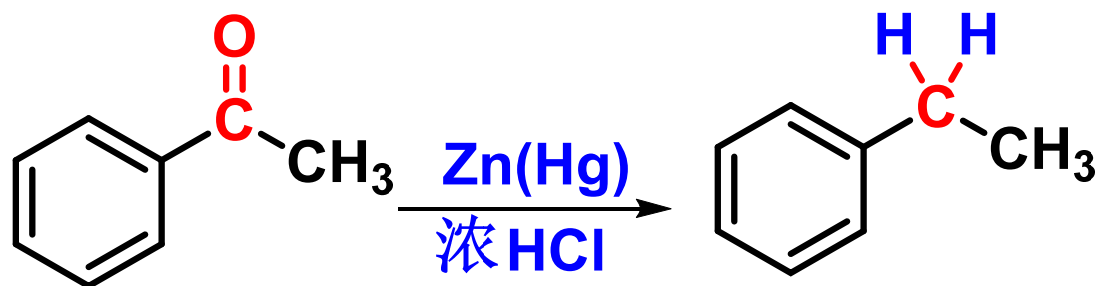
## 2、酮的氧化



## 四、还原反应

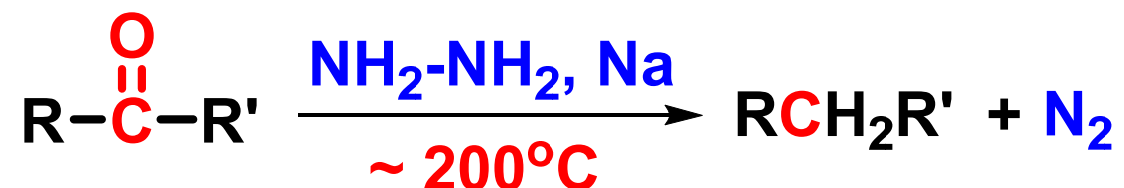
### 1、羰基还原甲叉基 ( $\text{CH}_2$ )

#### (1) 克莱蒙森 (*Clemmensen*) 还原

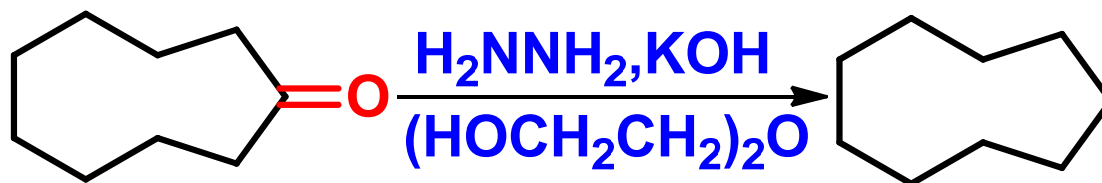
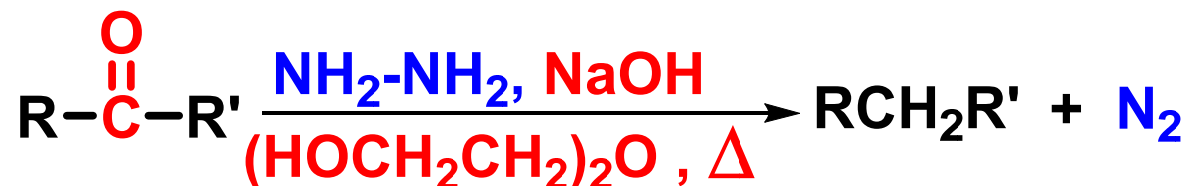


适用于对酸稳定的体系

## (2) 乌尔夫-凯惜纳 (*Wolff-Kishner*) 还原



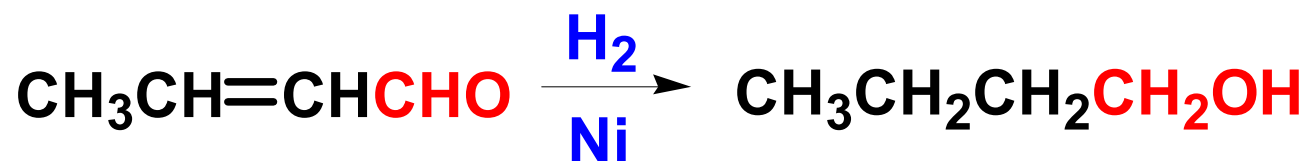
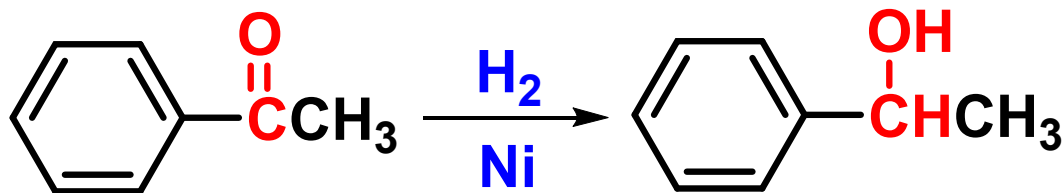
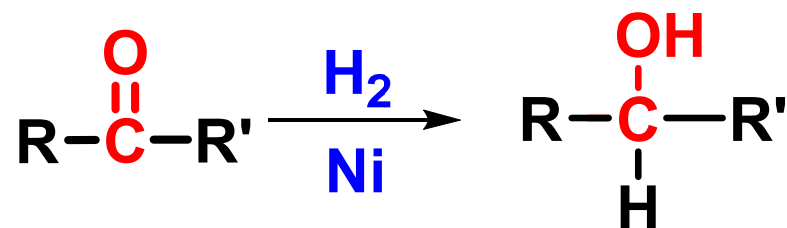
➤ 黄鸣龙改良法





## 2、羰基还原为醇羟基

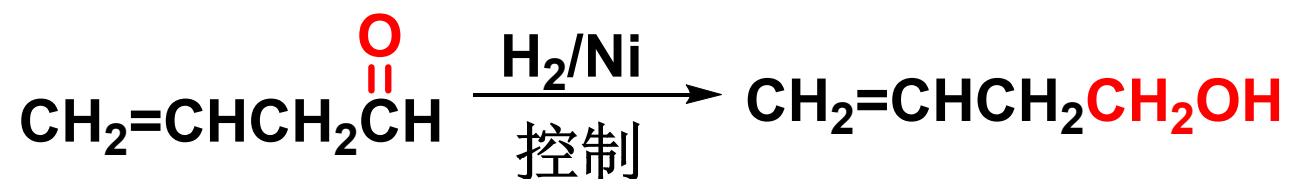
(1) 催化氢化



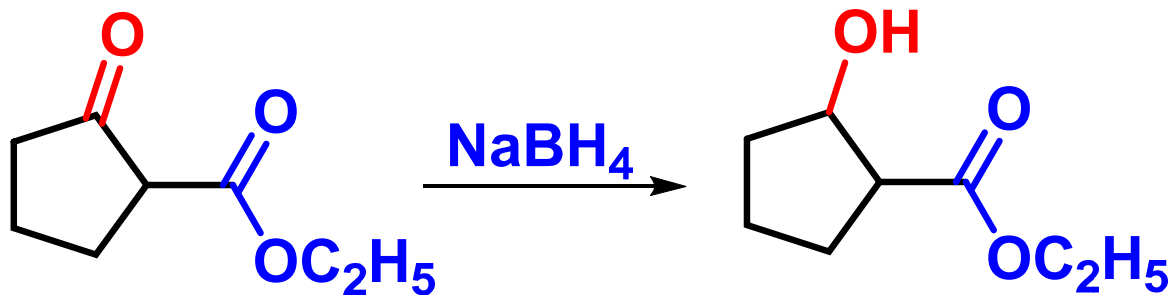
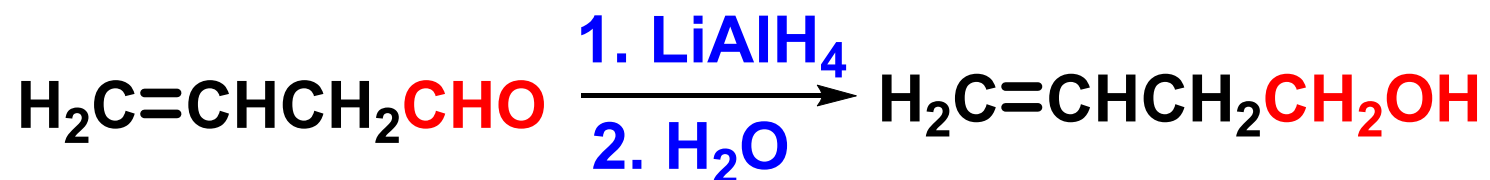
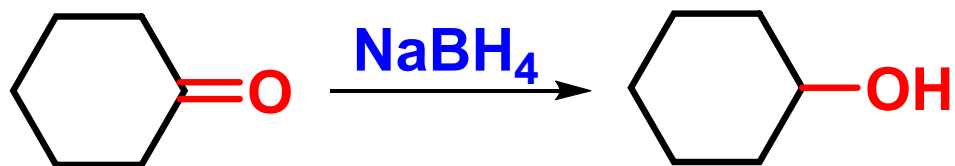
不饱和醛酮，官能团被还原活性为：

醛羰基 > 碳碳双键 > 酮羰基

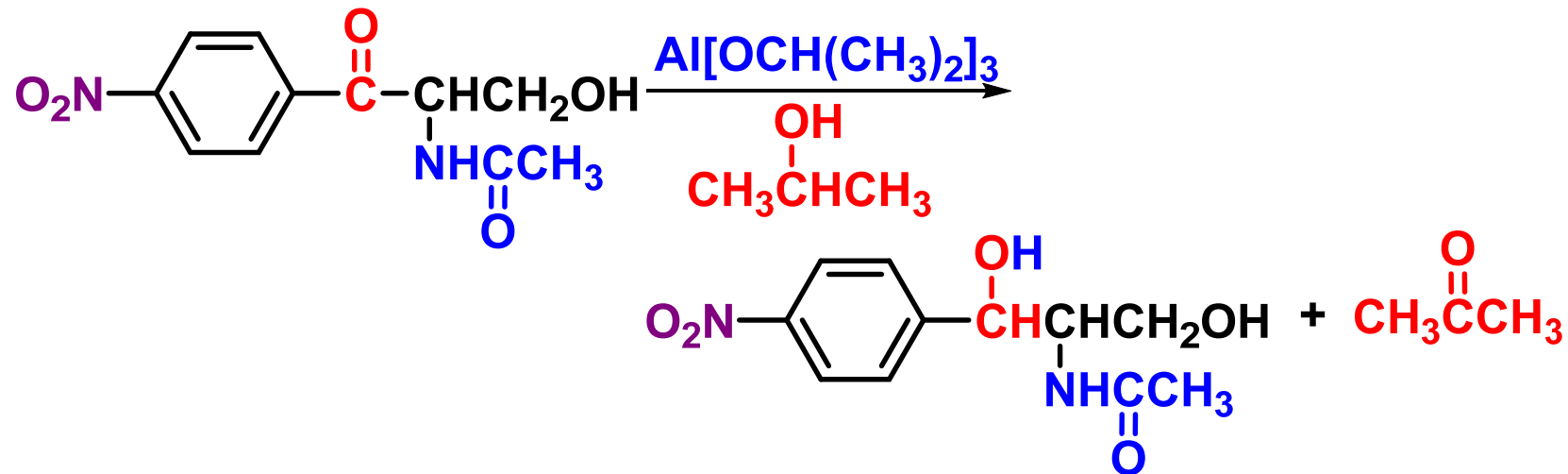
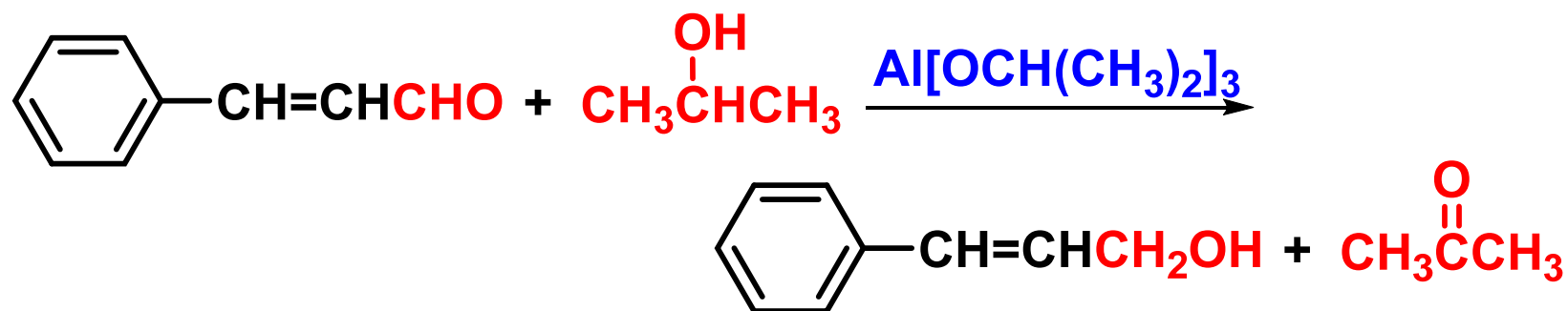
条件可以使活性高的基团优先被还原。



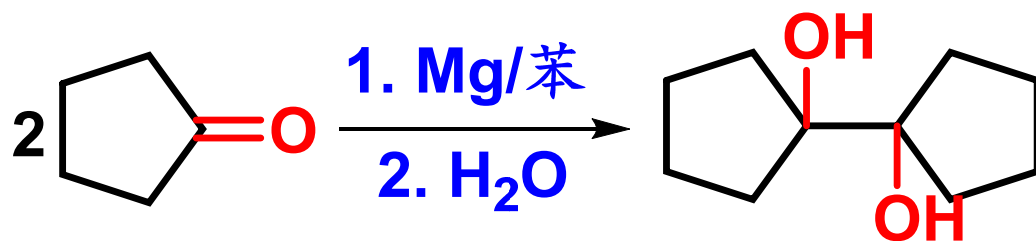
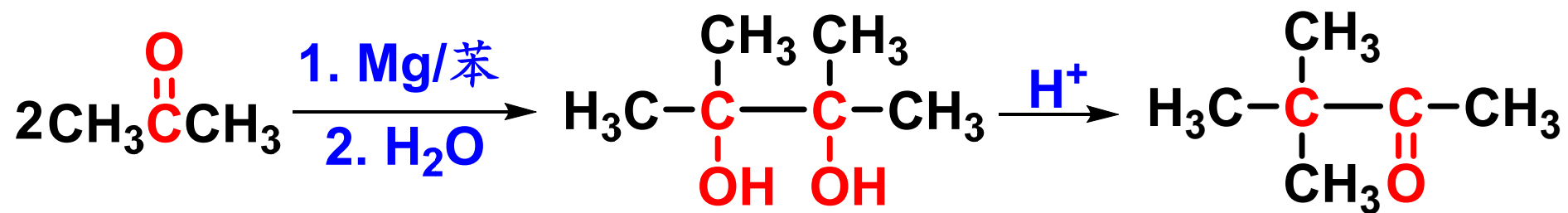
(2) 化学还原剂  $\text{NaBH}_4$ 、 $\text{LiAlH}_4$



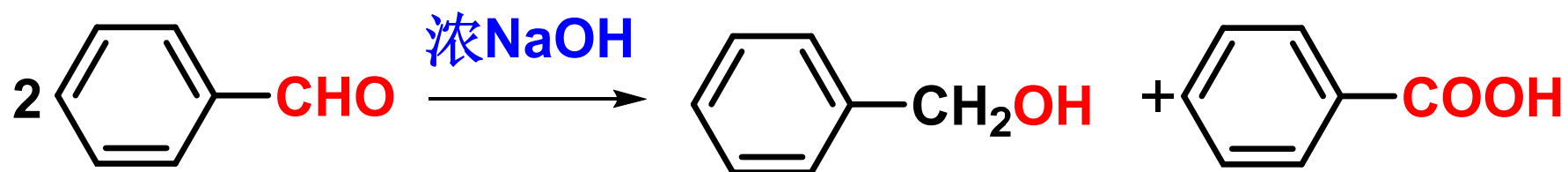
### (3) 迈尔外因-彭杜尔夫 (Meerwein-Ponndorf) 反应



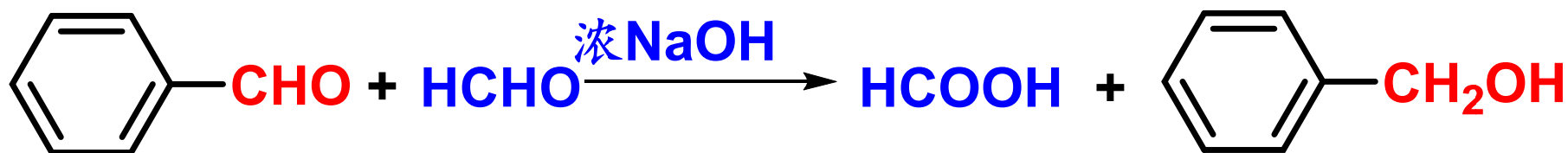
#### (4) 酮的双分子还原



### 3、康尼扎罗 (*Cannizzaro*) 反应



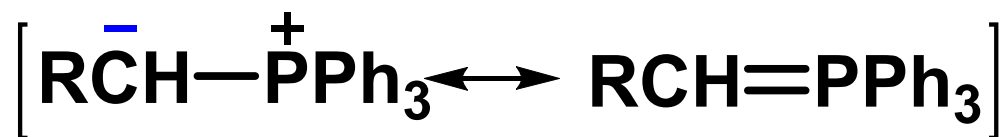
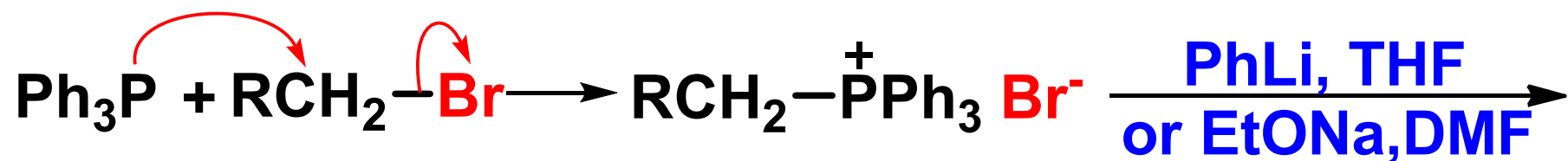
➤ 无 $\alpha$ -H的醛和甲醛（甲醛总是被氧化）



交叉康尼扎罗反应

## 五、其它反应

### 1、魏悌希 (*Wittig*) 反应



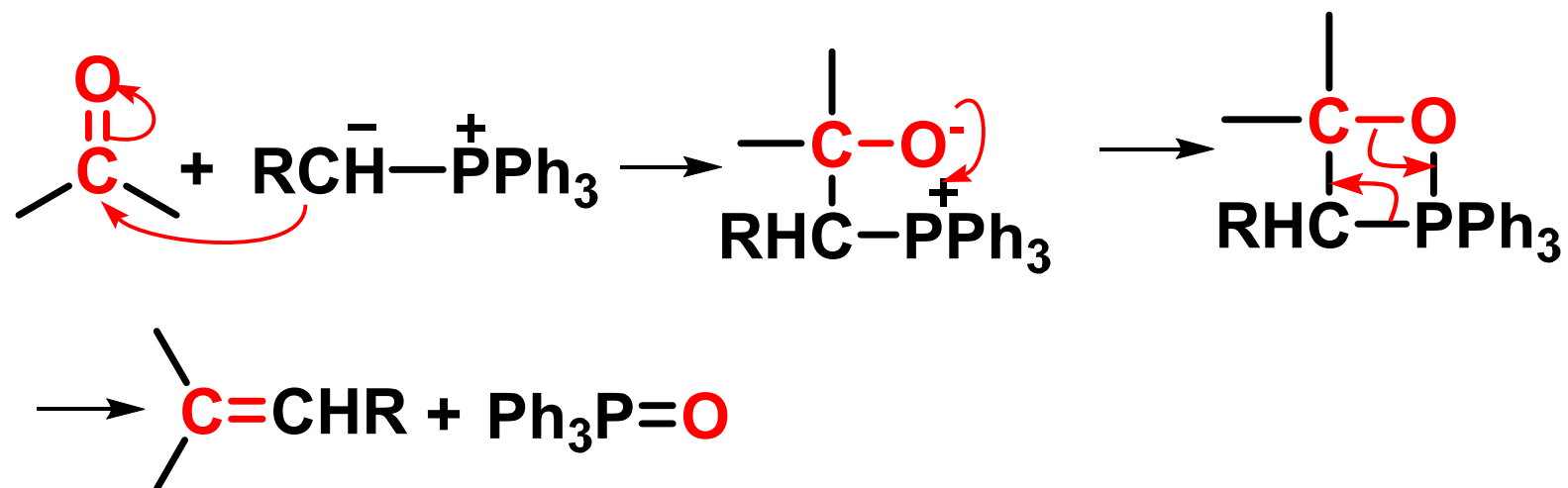
叶立德

**Ylide**

叶林

**Ylene**

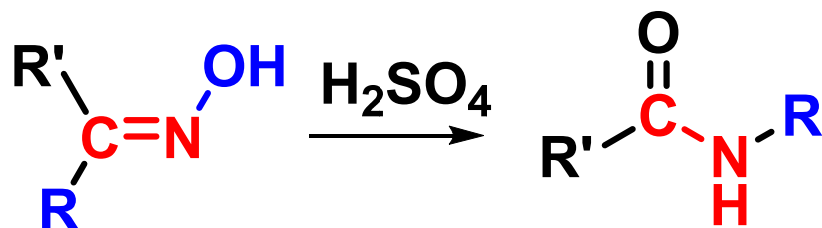
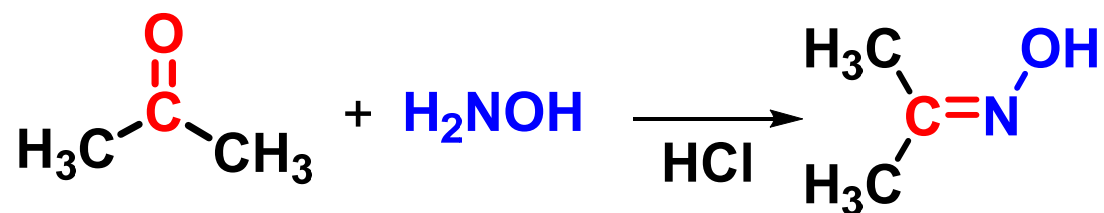
Wittig试剂



卤代烃是一级或二级卤代烃。反应试剂中可以有醚、酯、卤素、烯炔等官能团。

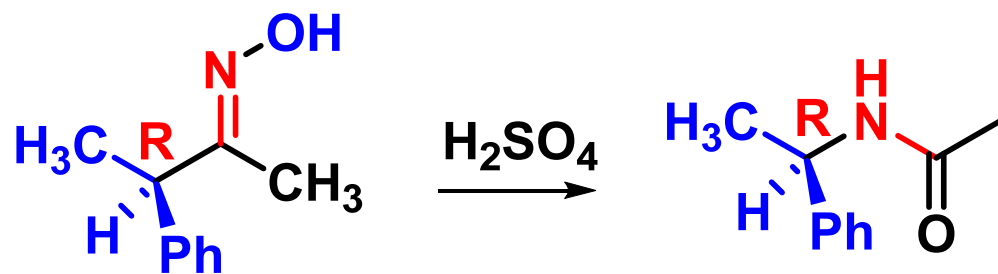
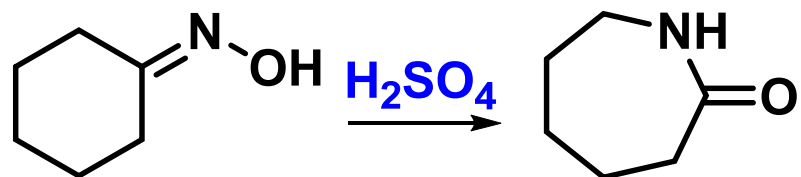
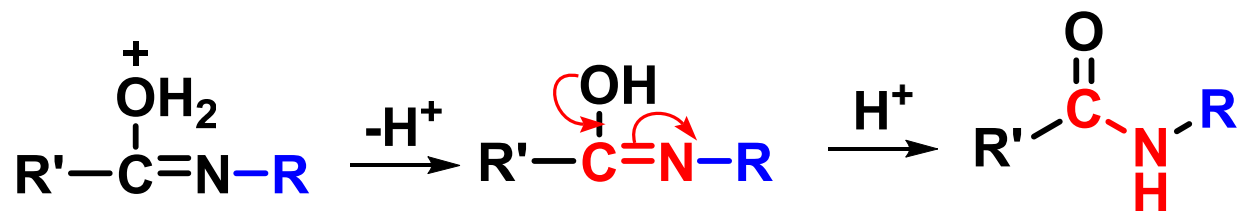
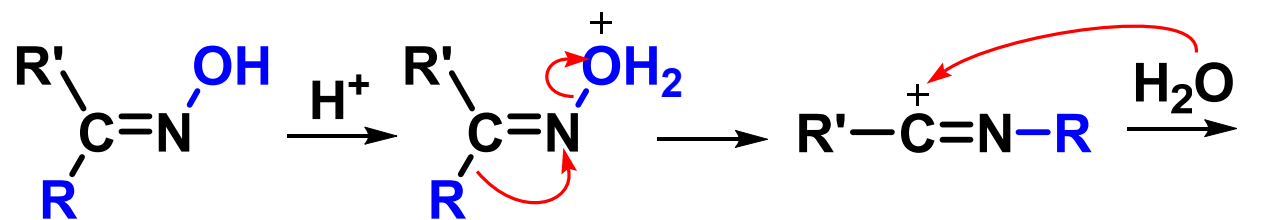


## 2、贝克曼 (*Beckmann*) 重排反应



R、R'：烷基、芳基。

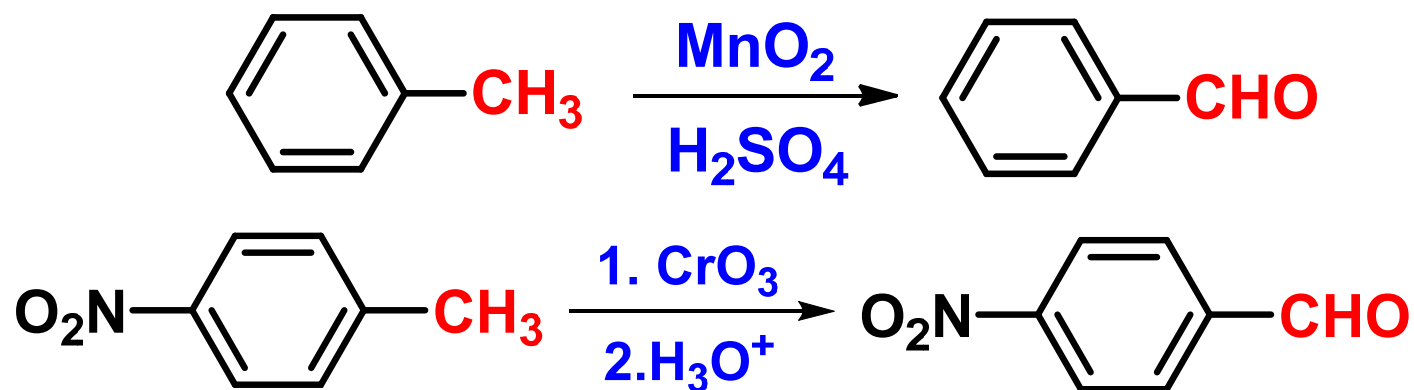
催化剂：硫酸、 $\text{SOCl}_2$ 、 $\text{PCl}_3$ 、路易斯酸等。



## 五、醛酮的制备

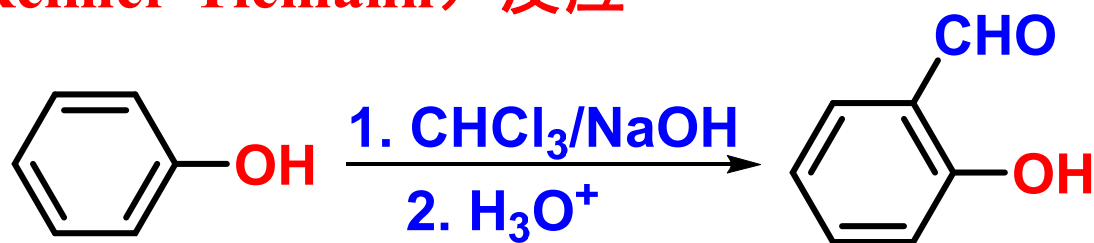
### 1、通过官能团转化制备

(1) 醇的氧化； (2) 烯烃的氧化和炔烃的水解； (3) 芳  
烃侧链氧化。

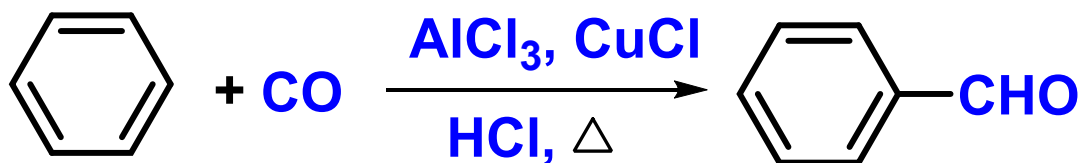


## 2、向分子中直接引入羰基

(1) 傅克酰化； (2) Fries重排； (3) 瑞默-梯曼  
(Reimer-Tiemann) 反应



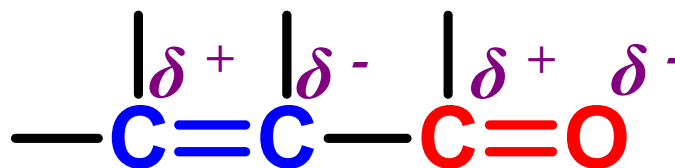
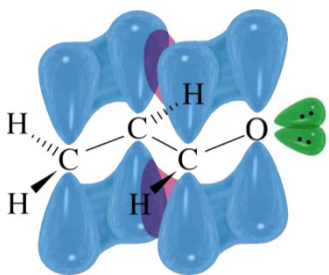
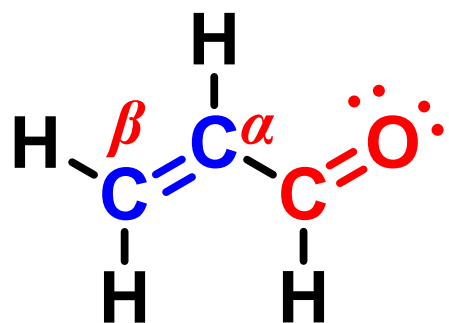
(4) 盖特曼-柯赫 (Gattermann-Koch) 反应



## 第五节 $\alpha, \beta$ -不饱和醛酮

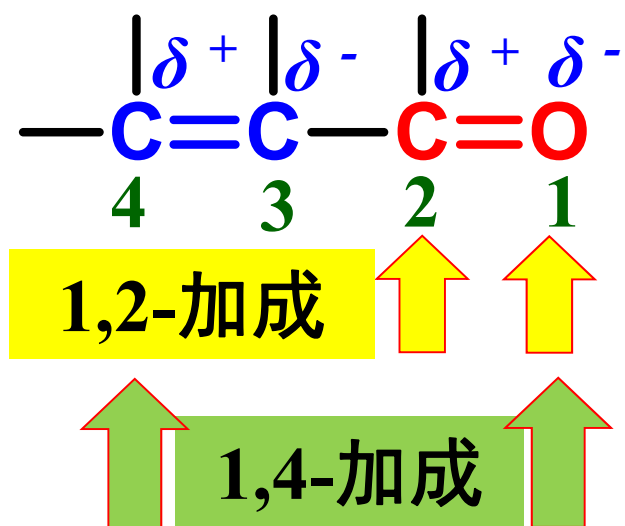
### 一、结构

$\alpha, \beta$ -不饱和醛酮分子中，碳碳双键和羰基共轭，形成一个  $\pi - \pi$  共轭体系。



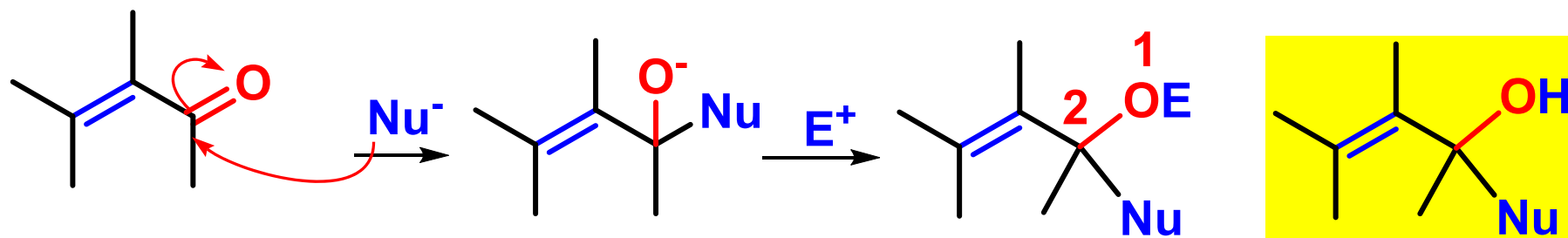
## 二、化学性质

### 1、亲核加成反应

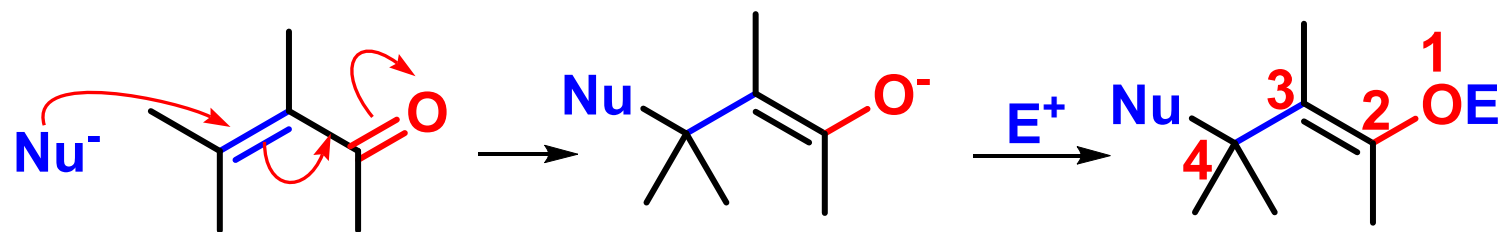


以哪种方式加成，取决于亲核试剂和醛酮的结构。

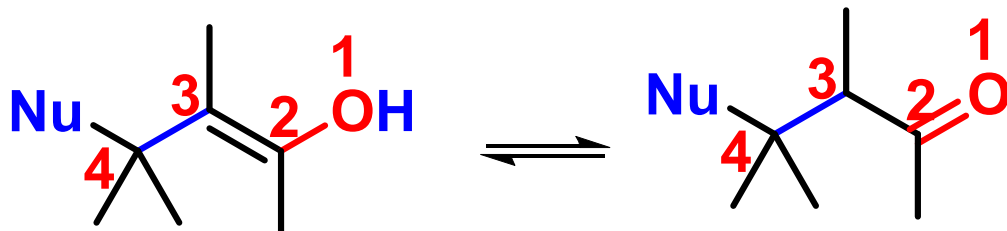
## 1,2-加成机理



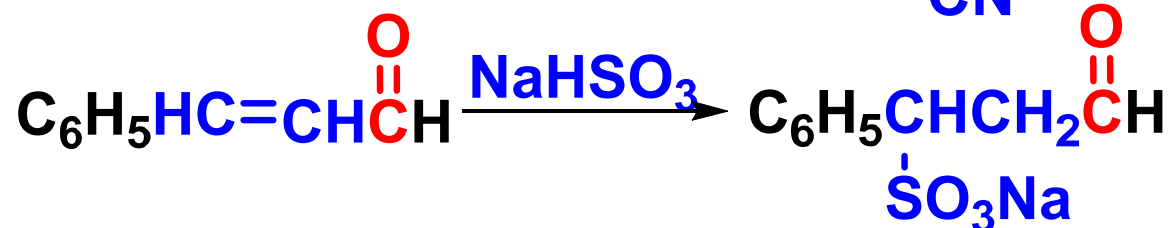
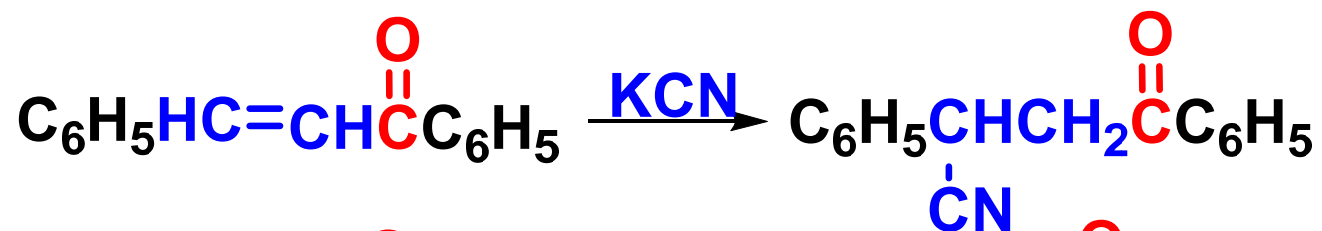
## 1,4-加成机理



烯醇

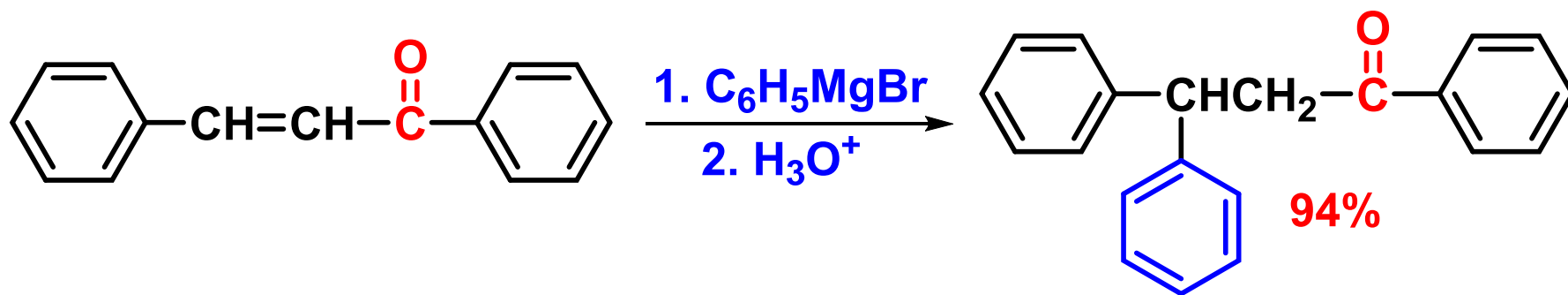
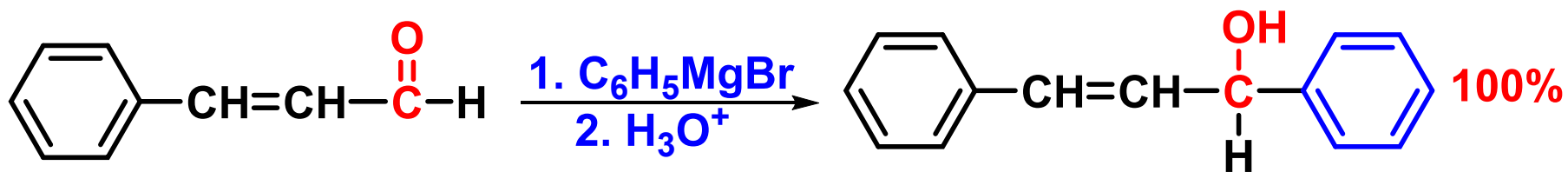


① HCN、NaHSO<sub>3</sub>、ROH、RNH<sub>2</sub> (胺、羟胺、苯肼) 等, 1,4-加成。

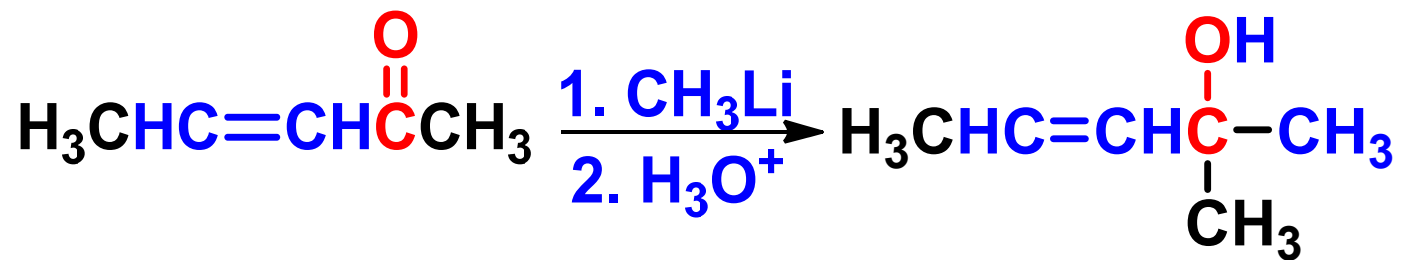
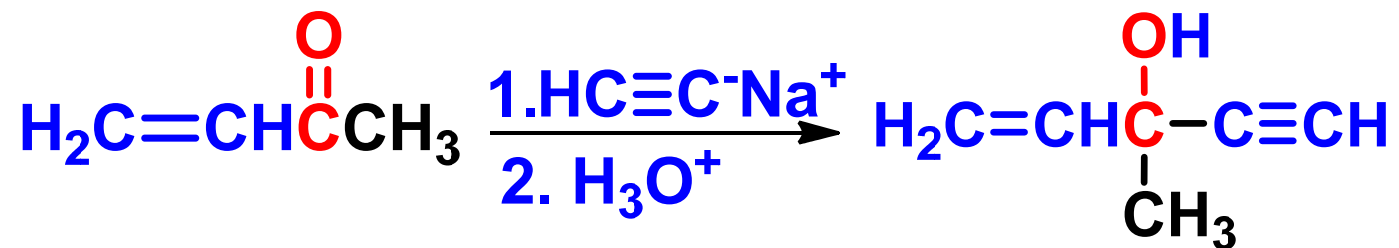




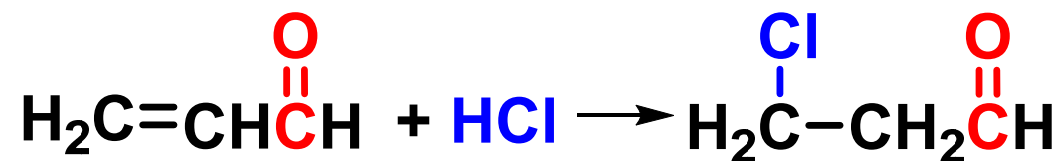
② 格氏试剂，1,2-和1,4-加成都有可能



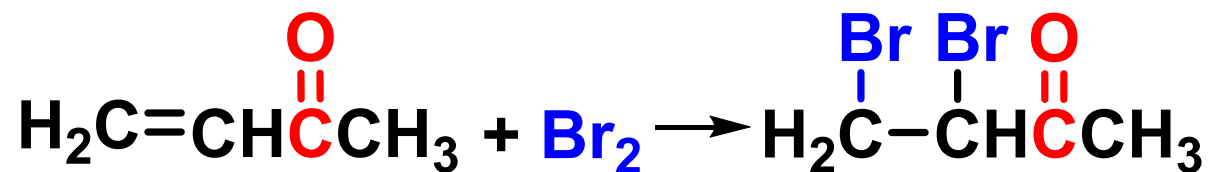
③有机锂、有机钠：1,2-加成



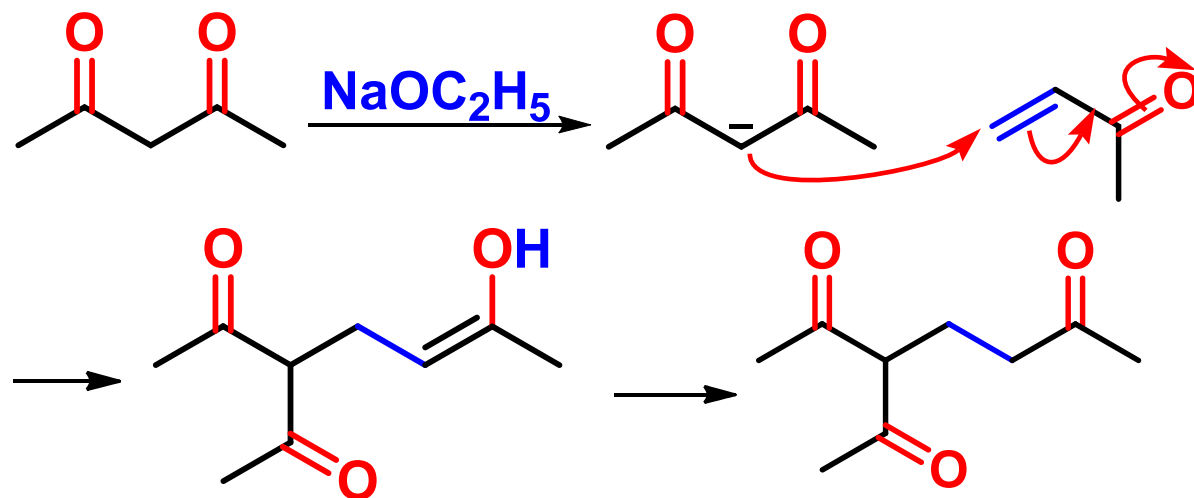
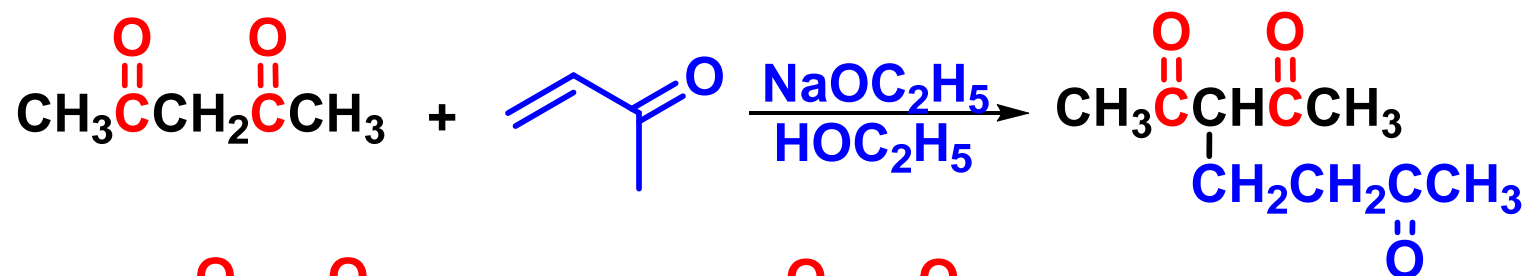
## 2、亲电加成反应：



卤素、次卤酸只在 C=C 上加成。



### 3、迈克尔加成反应 (Michael Addition Reaction)

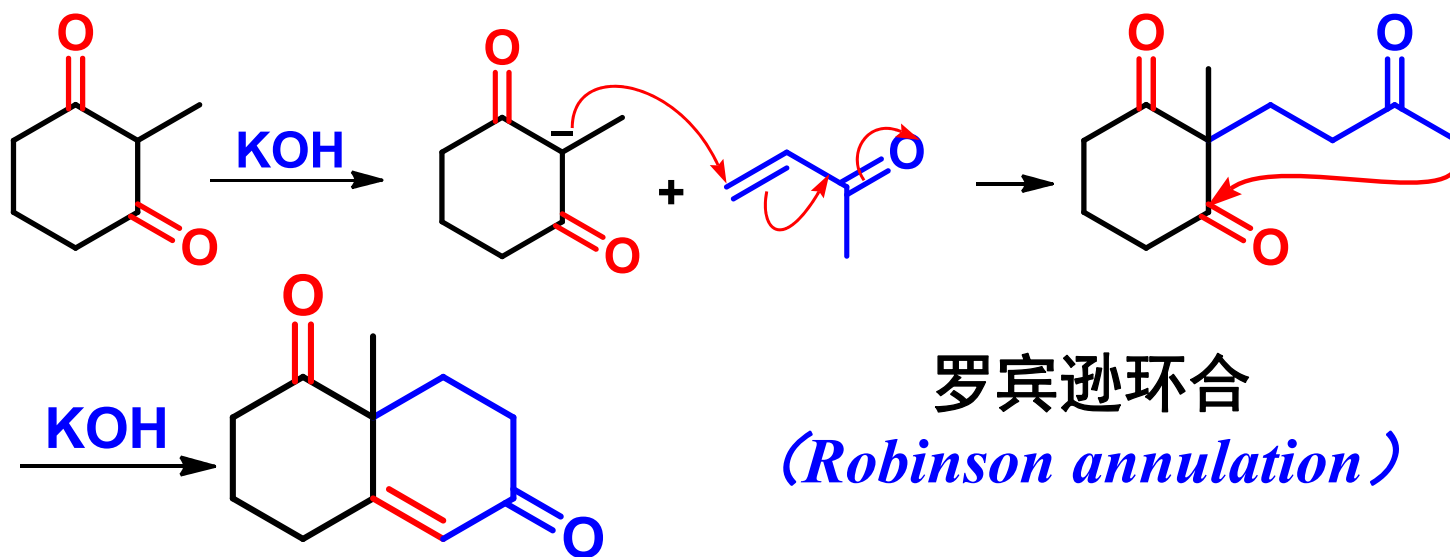
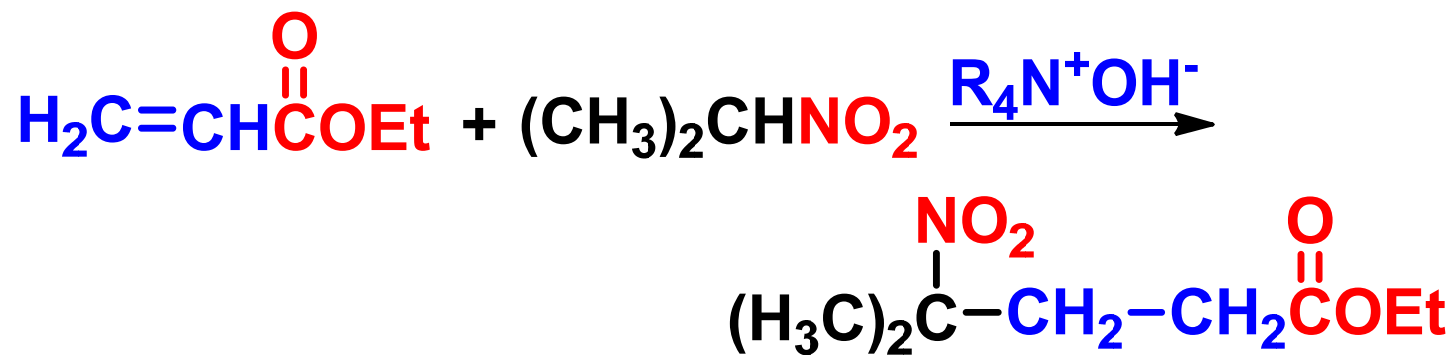




**A、B**为吸电子基团，如：**-CN、-NO<sub>2</sub>、-CO<sub>2</sub>Et、-COR**等。

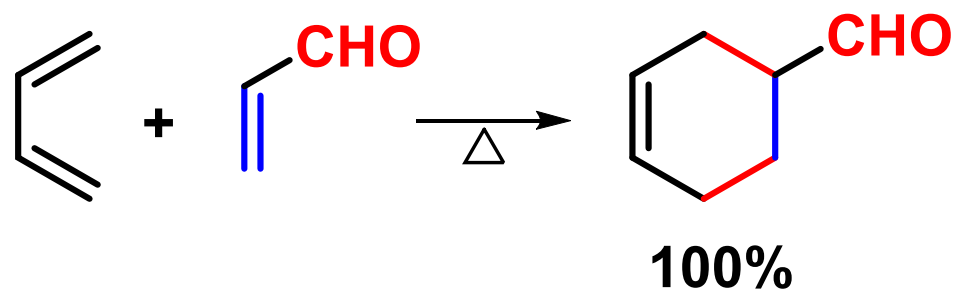
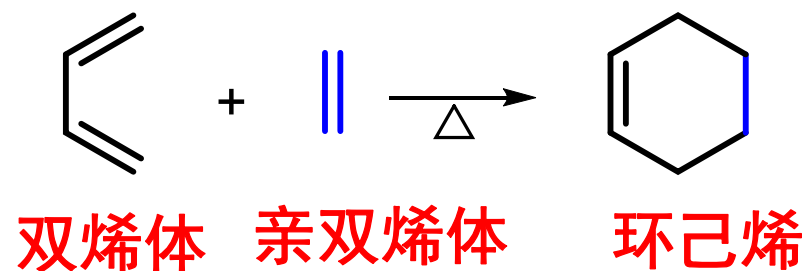
$\alpha$ 、 $\beta$ -不饱和化合物： $\alpha$ 、 $\beta$ -不饱和酸酯、腈、醛、酮等具有 $\alpha$ 、 $\beta$ -不饱和共轭体系的化合物。

碱为醇钠、KOH、NaOH、季铵碱、氨基钠、三乙胺、六氢吡啶等。

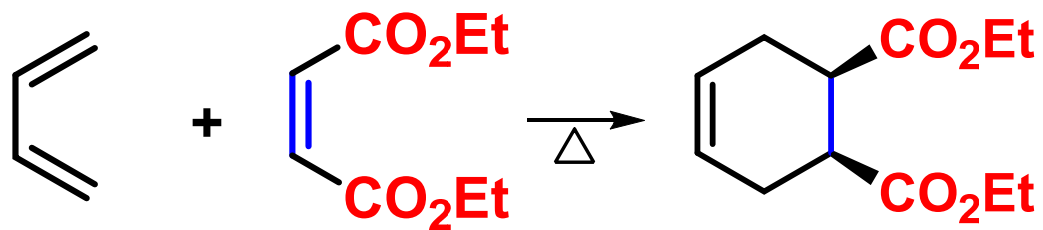
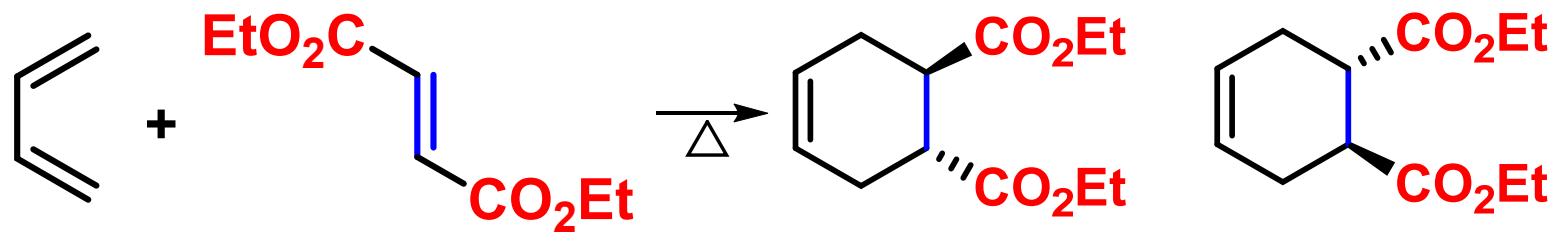


罗宾逊环合  
(*Robinson annulation*)

## 4、狄尔斯-阿尔德 (Diels-Alder) 反应

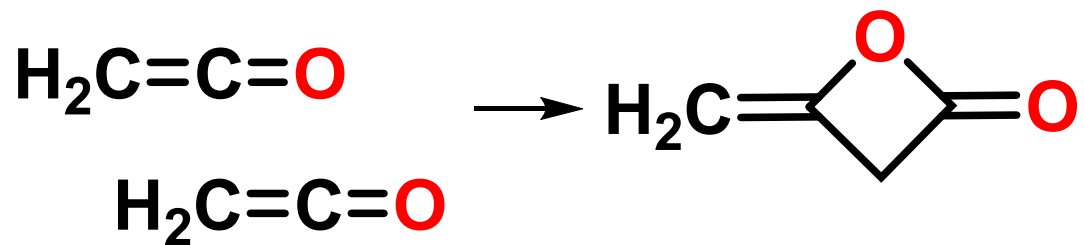


D-A反应是立体专一性反应，亲双烯体在反应过程中构型保持不变。





### 三、烯酮

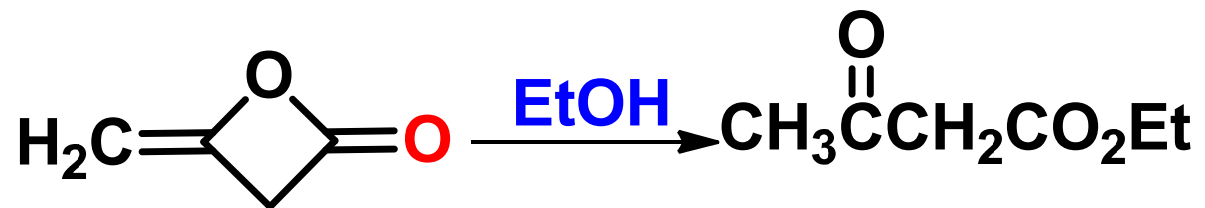
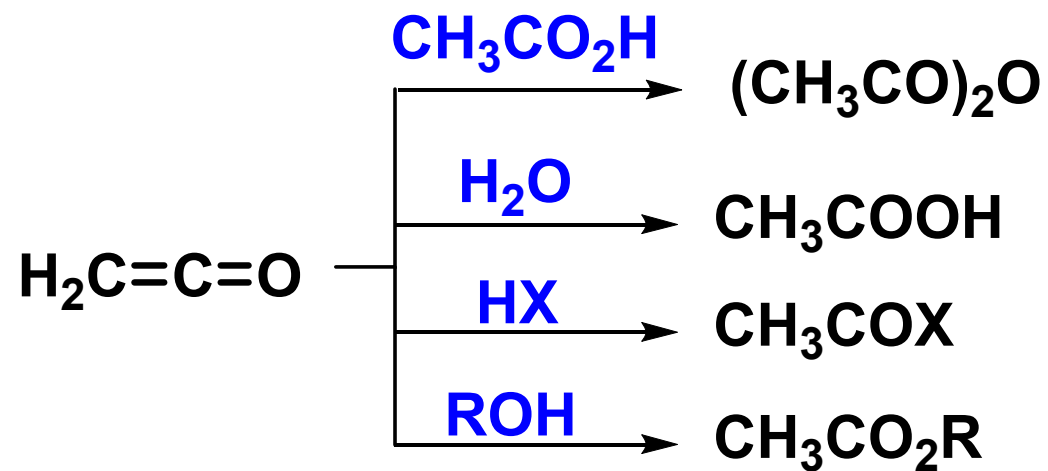


乙烯酮

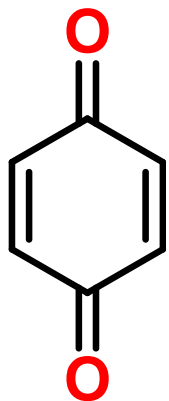
bp:  $-48^\circ\text{C}$

双乙烯酮

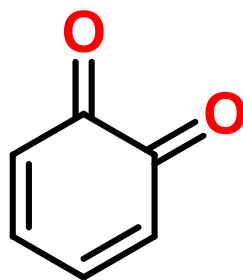
bp:  $128^\circ\text{C}$



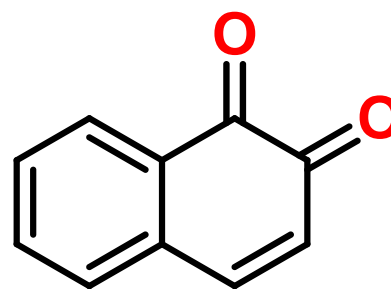
## 四、醌类化合物



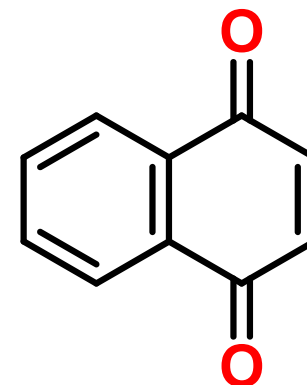
对苯醌  
(1,4-苯醌)



邻苯醌  
(1,2-苯醌)

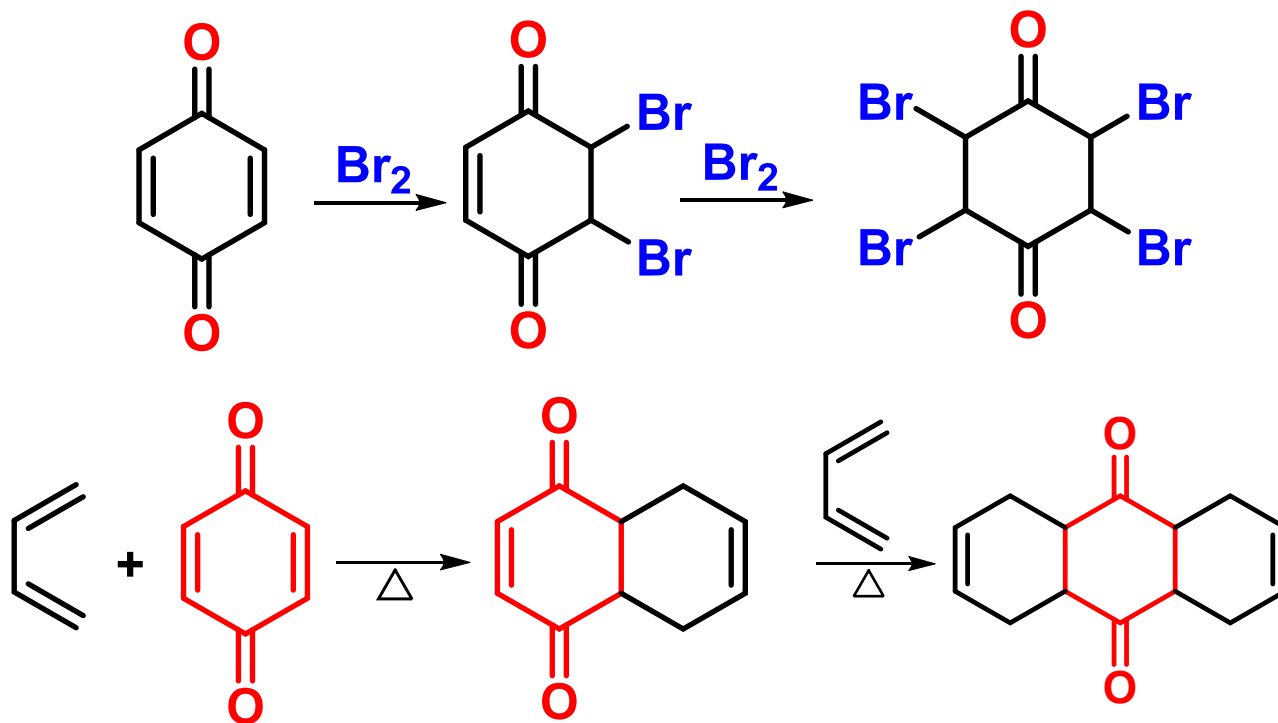


1,2-萘醌

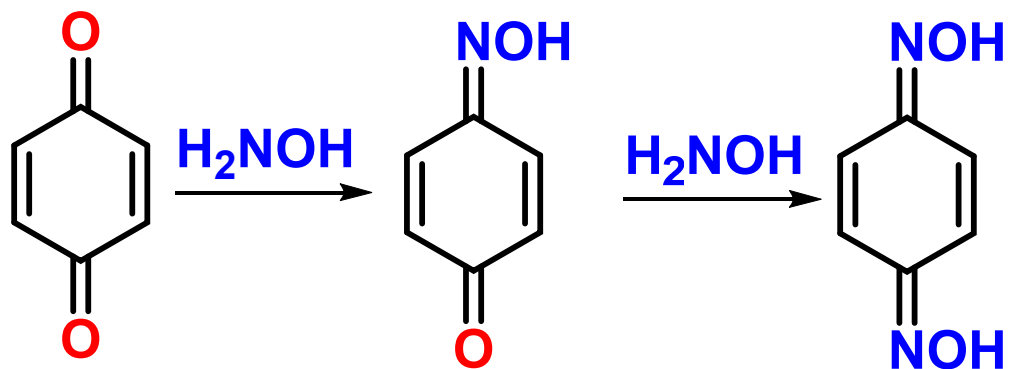


1,4-萘醌

## 烯键的加成反应



## 羰基与氨的衍生物反应



对苯醌单肟

对苯醌二肟

# 1,4-加成反应

