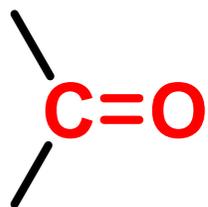


Chapter 9

醛和酮

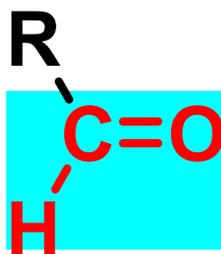
Reactions of Carbanions

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

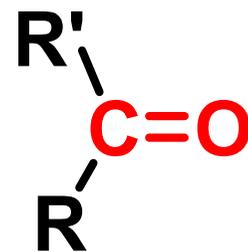
carbonyl group



—CHO 醛基

醛

aldehyde



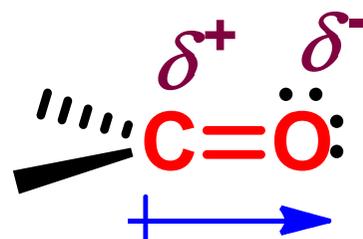
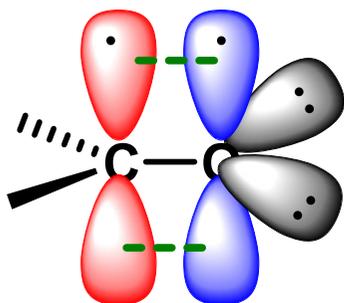
酮

ketone

第一节 结构、分类和命名

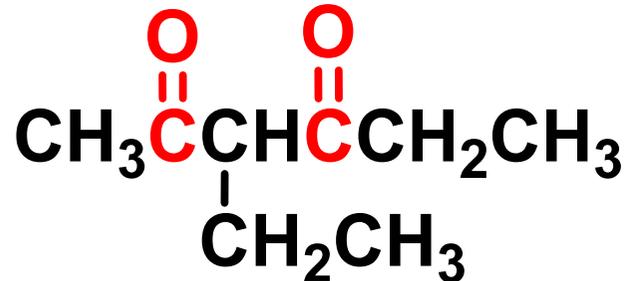
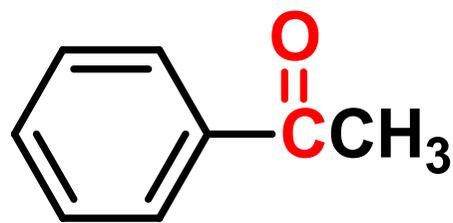
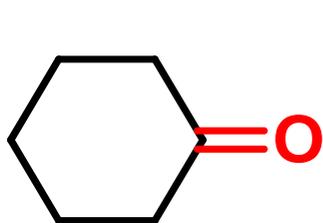
一、结构 (*Structure*)

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



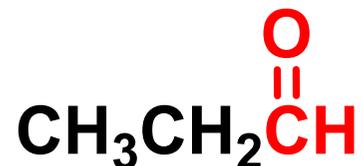
二、分类

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。



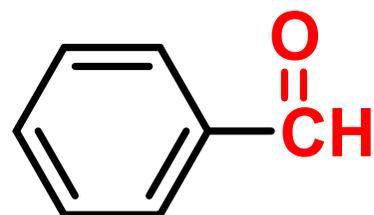
三、醛酮的命名

1、普通命名法



丙醛

propionaldehyde



苯(基)甲醛

benzaldehyde



乙(基)甲(基)酮

ethyl methyl ketone

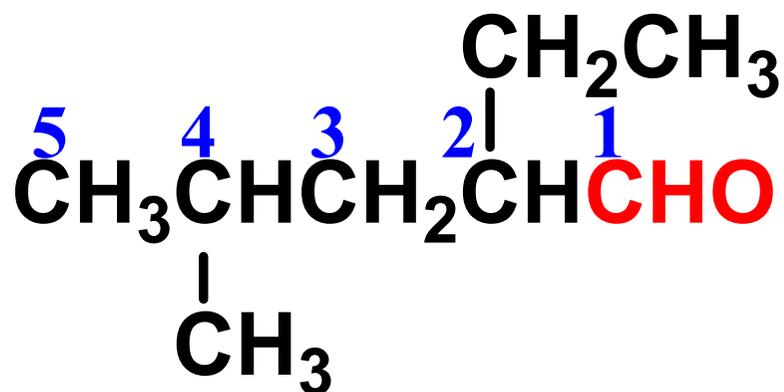


乙基异丙基酮

ethyl isopropyl ketone

2、系统命名法 (*IUPAC*)

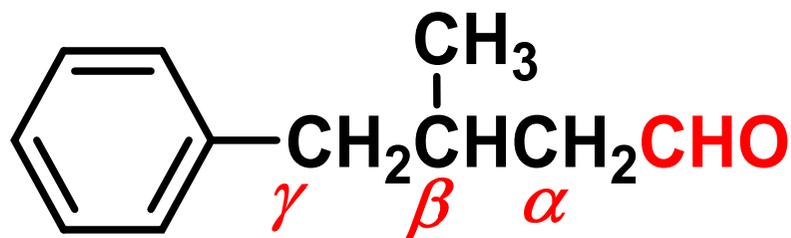
选择含有羰基碳的最长碳链为主链，编号使羰基碳位号最小，酮须指明羰基碳位号。



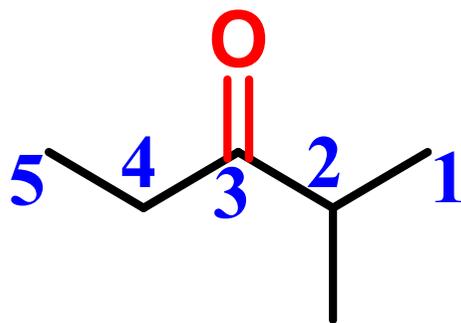
2-乙基-4-甲基戊醛

2-ethyl-4-methylpentanal

醛也可以用 α 、 β 、 γ 、 δ ...等标明。

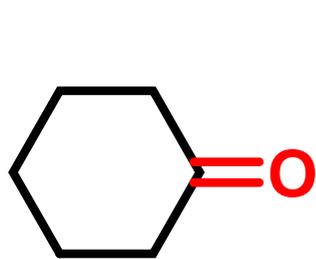


β -甲基- γ -苯基丁醛
 β -methyl- γ -phenylbutanal



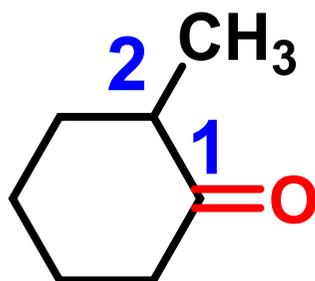
2-甲基戊-3-酮
2-methylpentan-3-one

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。



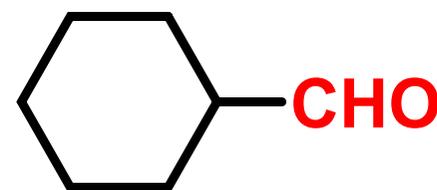
环己酮

cyclohexanone



2-甲基环己酮

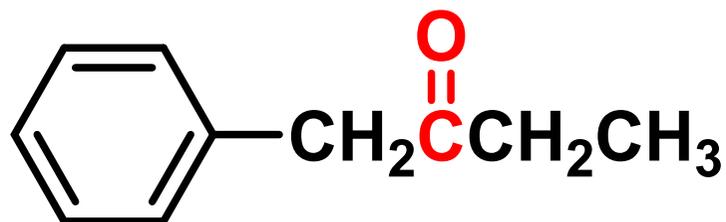
2-methylcyclohexanone



环己基甲醛

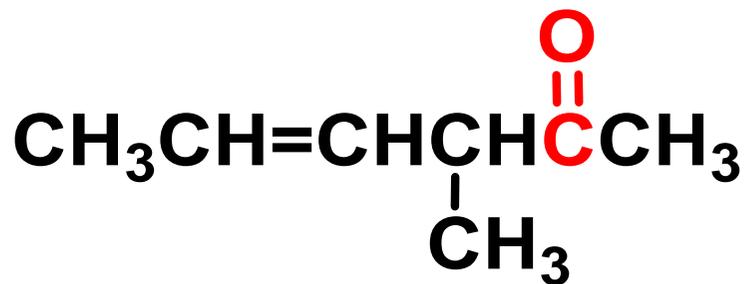
cyclohexylcarbaldehyde

分子中含有苯环时，苯环作为取代基。



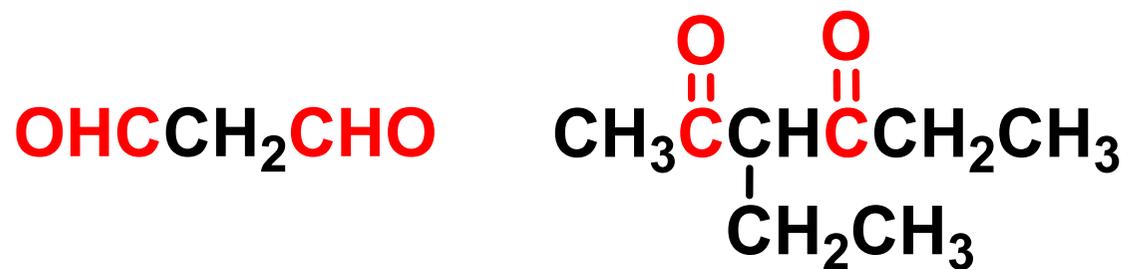
1-苯基丁-2-酮
1-phenylbut-2-one

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

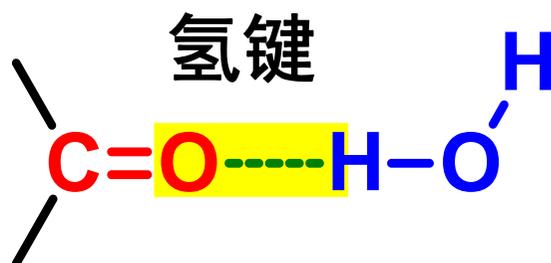
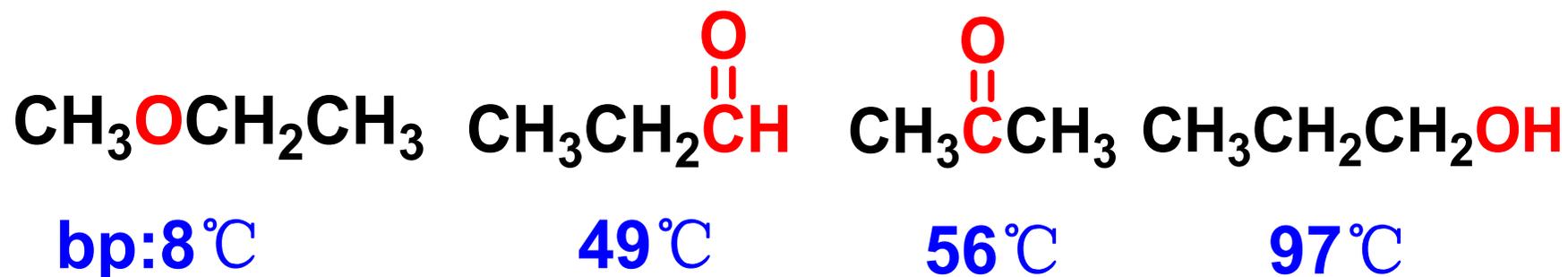


丙二醛
propanedial

3-乙基己-2,4-二酮
3-ethylhexan-2,4-dione

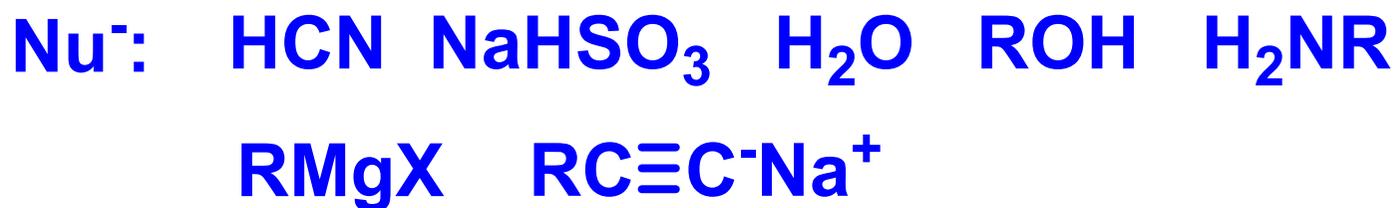
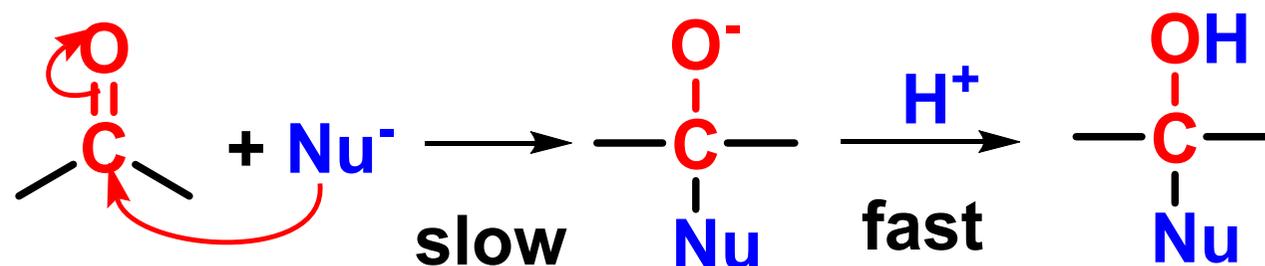
第二节 物理性质 (*physical property*)

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。

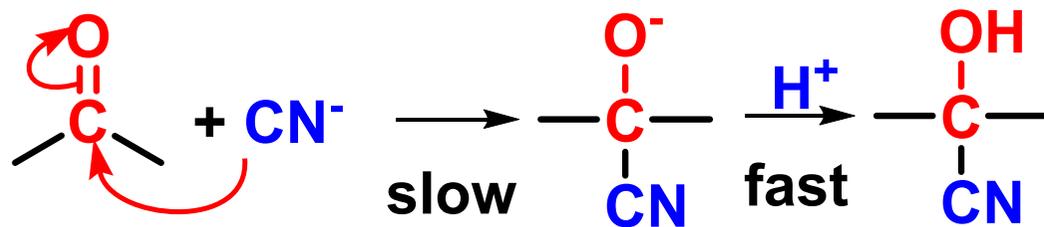
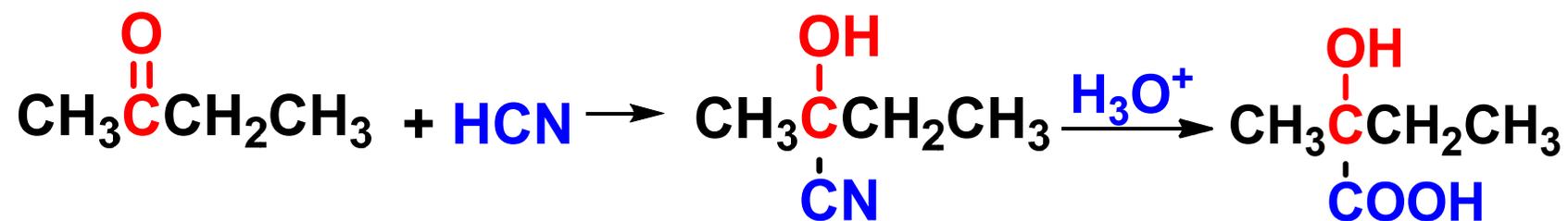
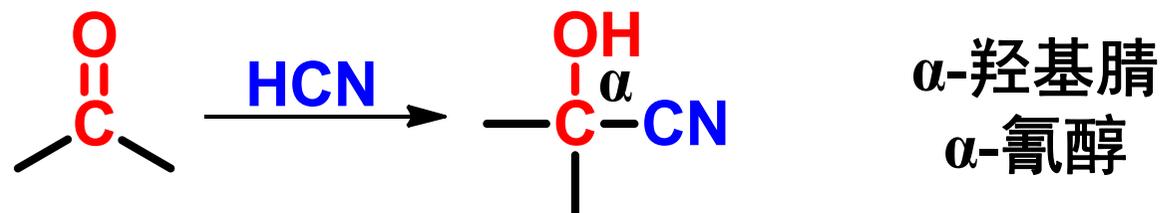


第三节 醛酮的化学性质

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



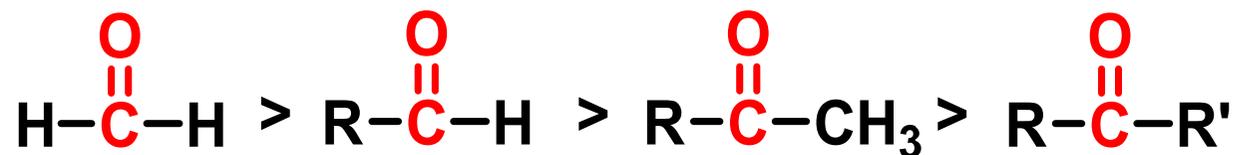
1、与氢氰酸加成



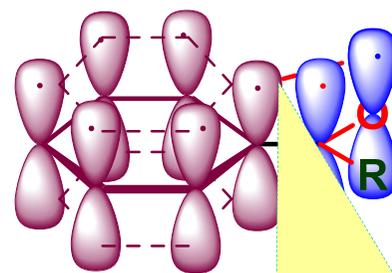
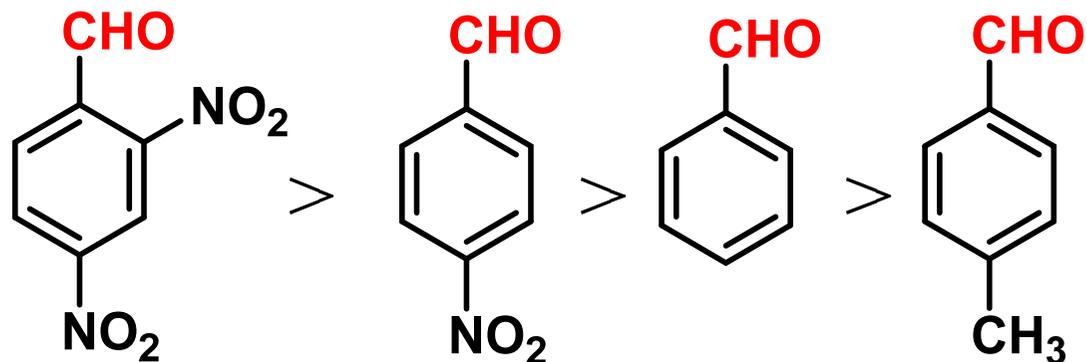
化合物	<i>K</i>	化合物	<i>K</i>
CH_3CHO	很大	$\text{CH}_3\text{COCH}(\text{CH}_3)_2$	38
$p\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$	1420	$\text{C}_6\text{H}_5\text{COCH}_3$	0.8
$\text{C}_6\text{H}_5\text{CHO}$	210	$\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$	很小

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。

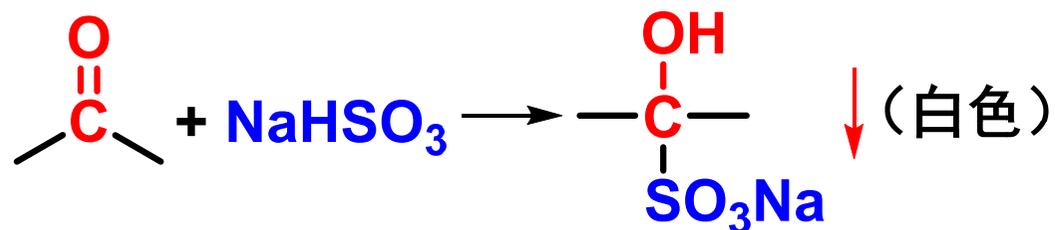


环酮只有八元环以下的能够与HCN反应。芳香酮活性较低。



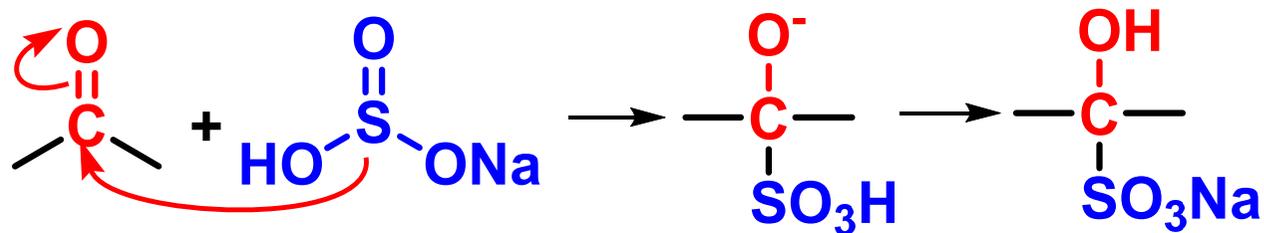
π - π 共轭
正电荷密度降低

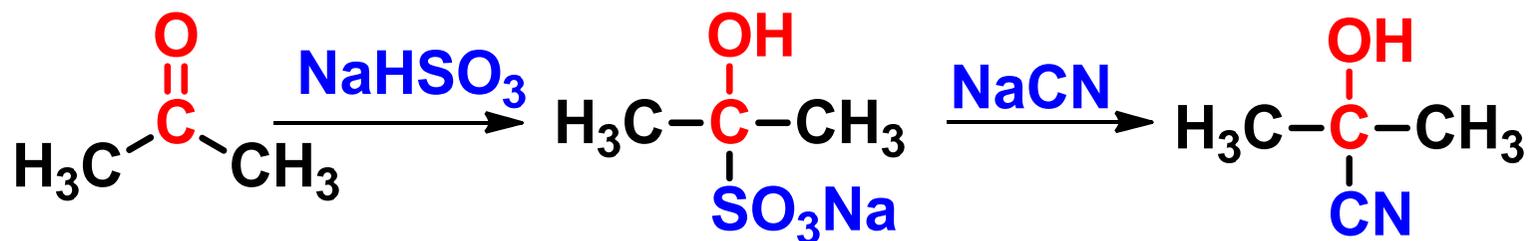
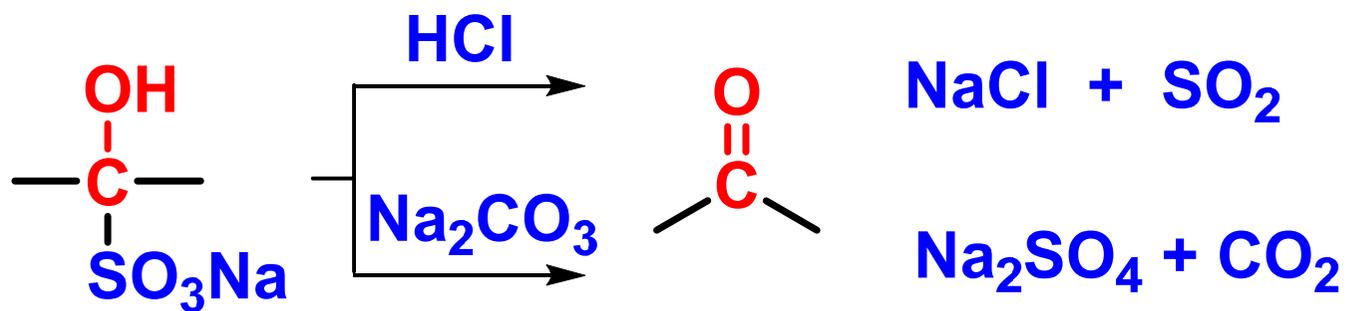
2、与亚硫酸氢钠 (NaHSO_3) 加成



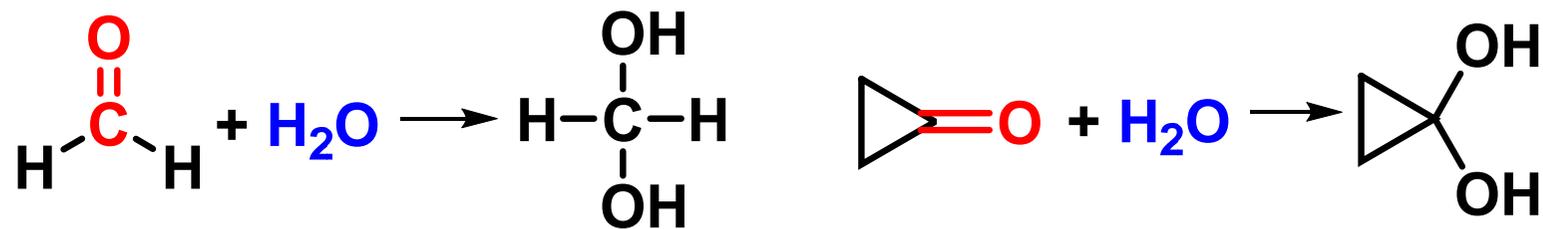
醛、脂肪族甲基酮和八个碳以下的环酮可以反应。

可以用于这些醛酮的分类鉴别和纯化。



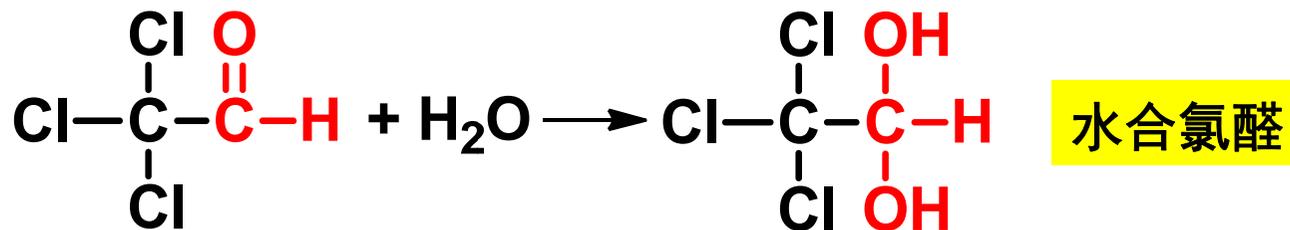


3、与 H₂O 加成

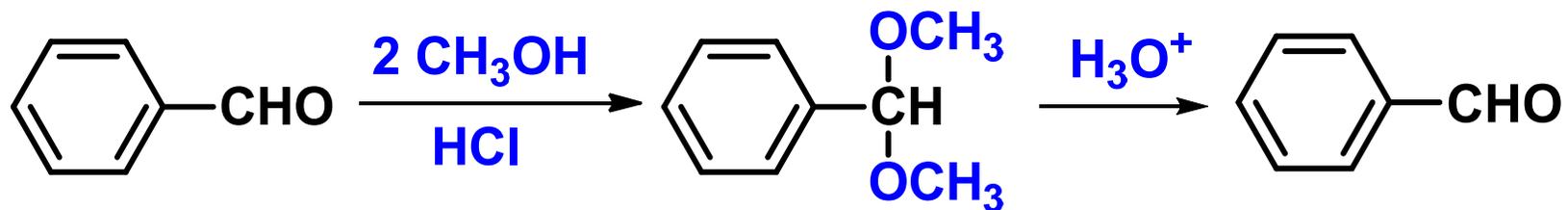
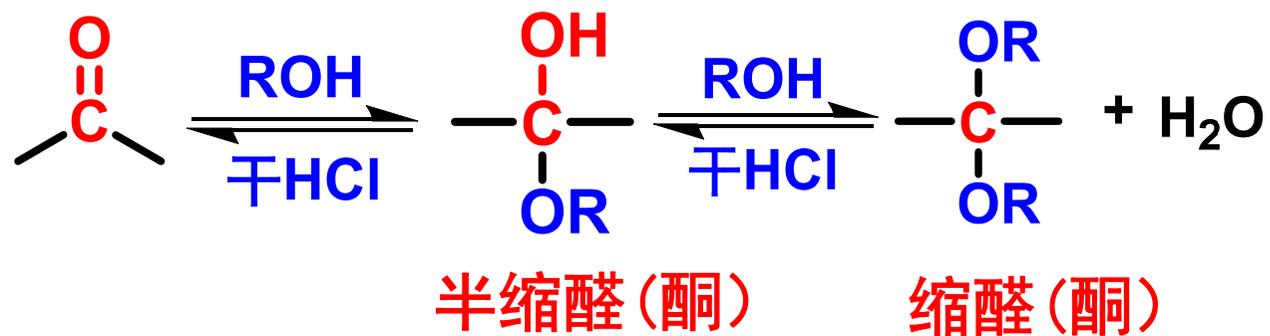


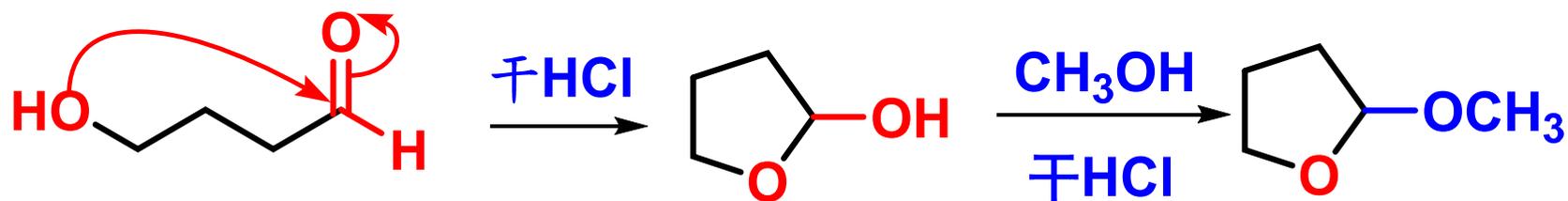
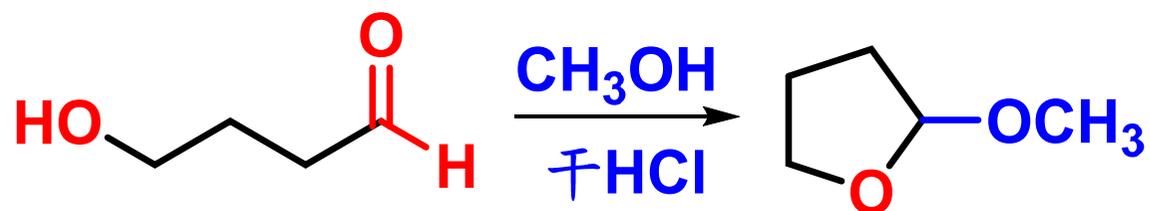
偕二醇

geminal diol

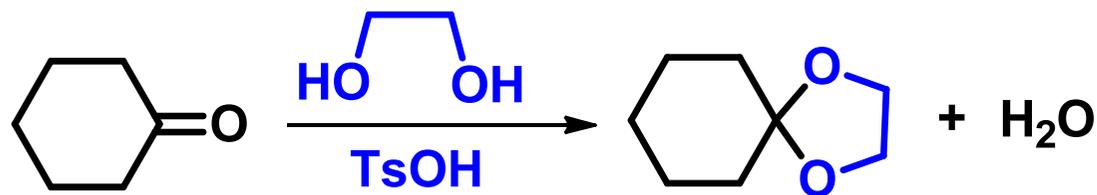


4、与醇加成

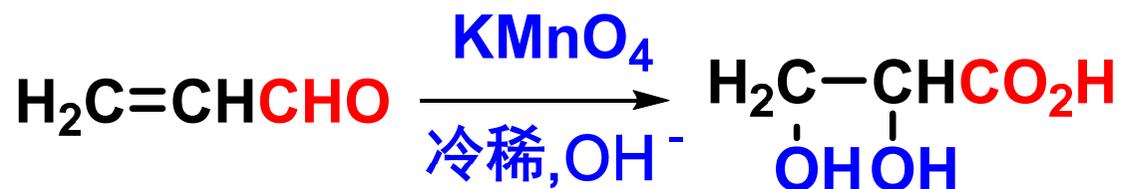
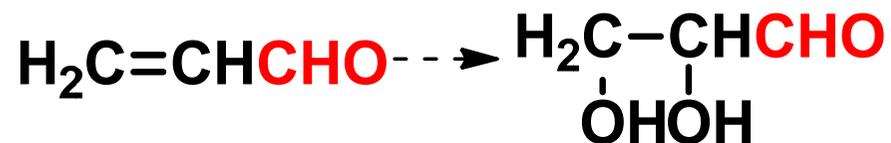


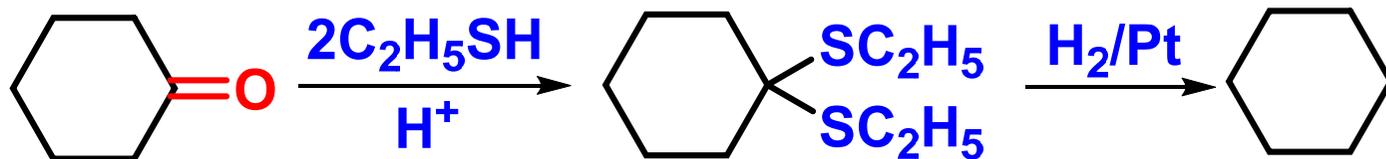
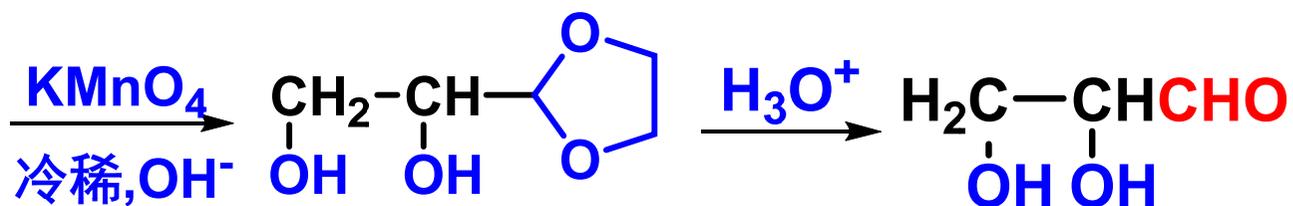
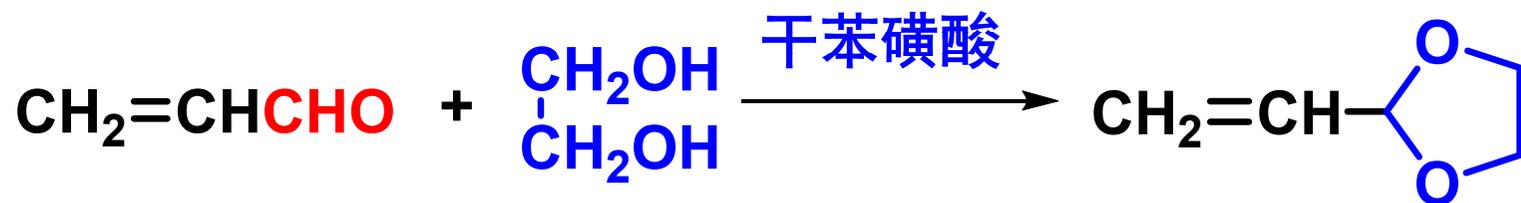


分子内形成半缩醛一般是5元或6元环



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。



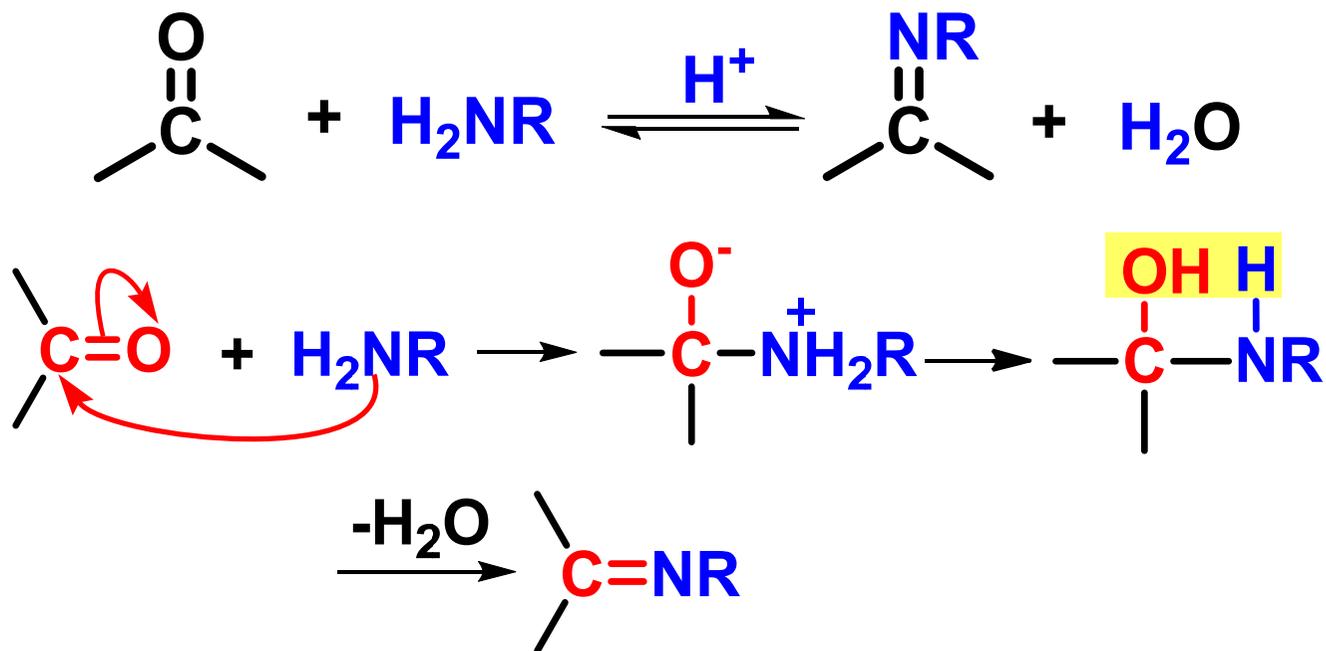


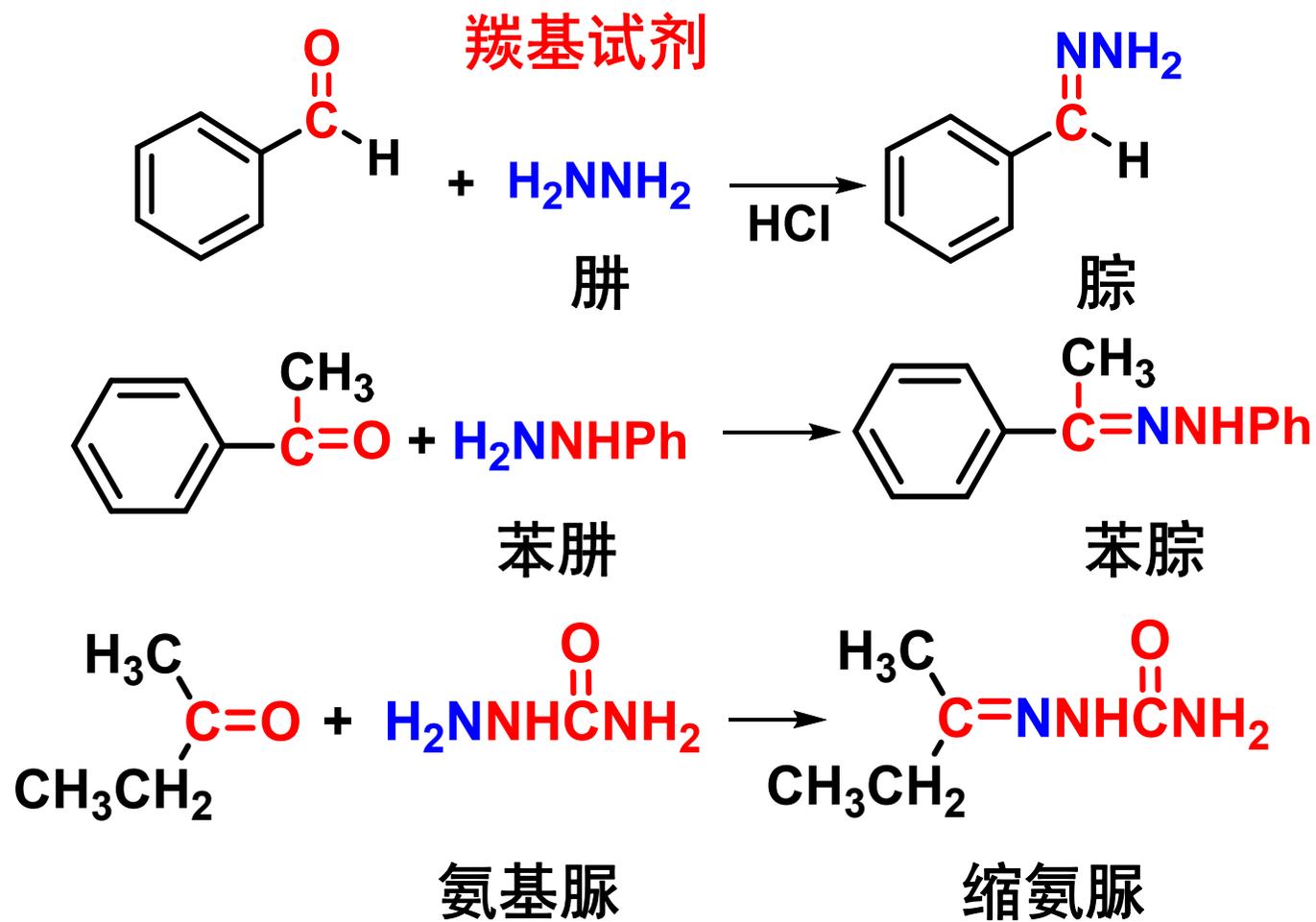
缩硫酮

5、加伯胺及胺的衍生物

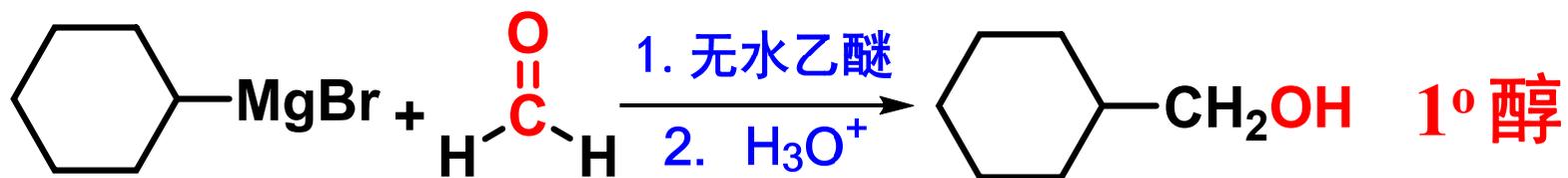
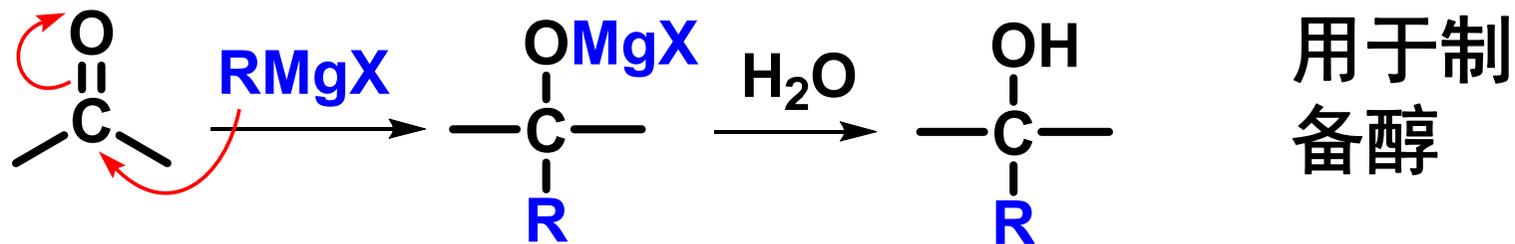
➤ 与伯胺的缩合

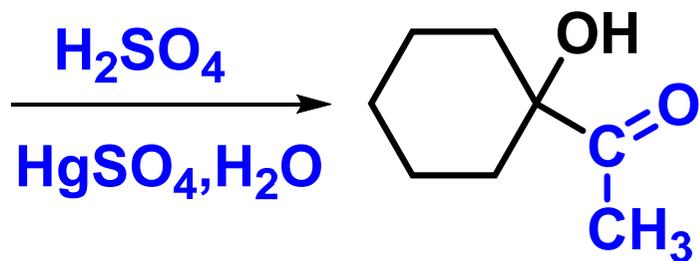
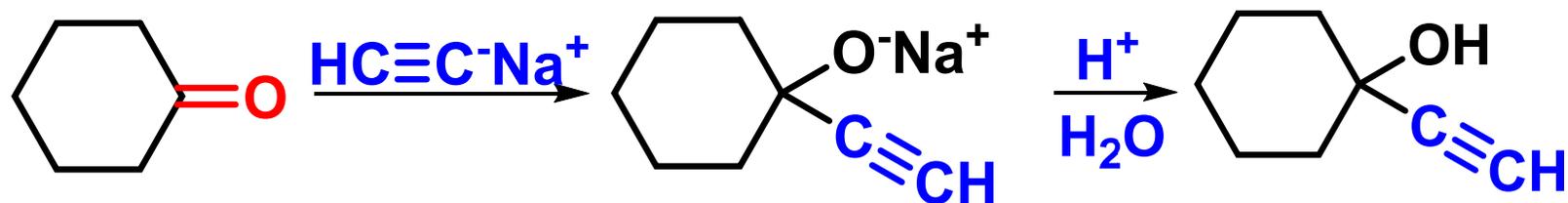
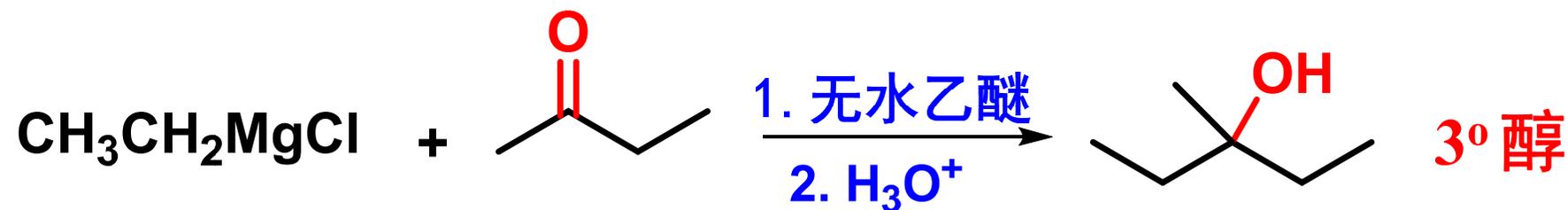
亚胺 (imine)
席夫碱 (Schiff's base)





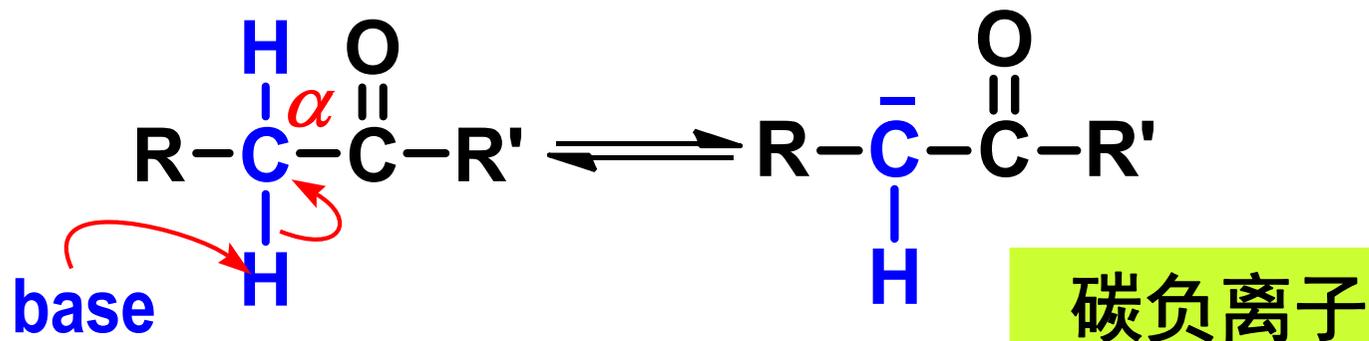
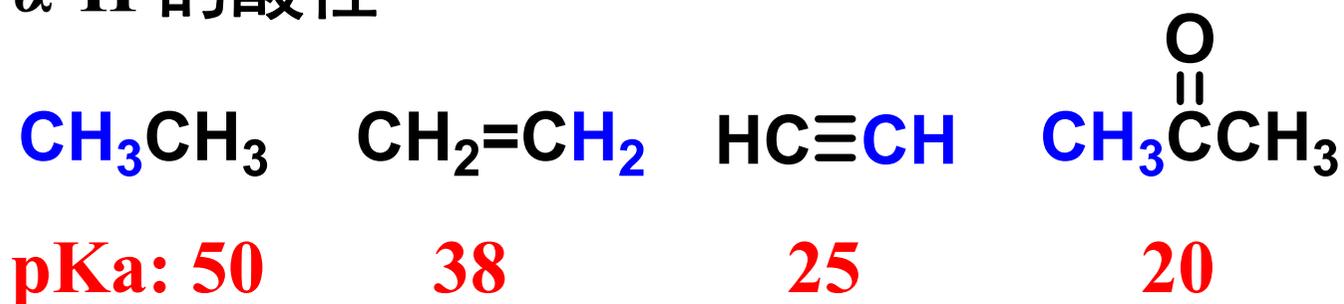
6、与金属有机化合物的加成反应

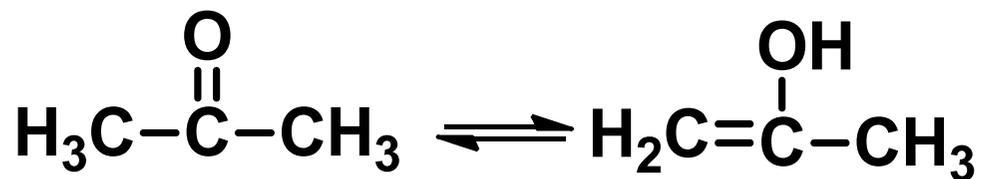
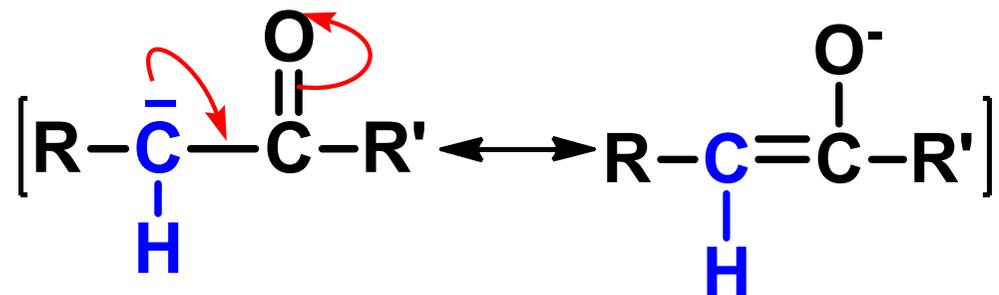




二、 α -H 的反应

1、 α -H 的酸性





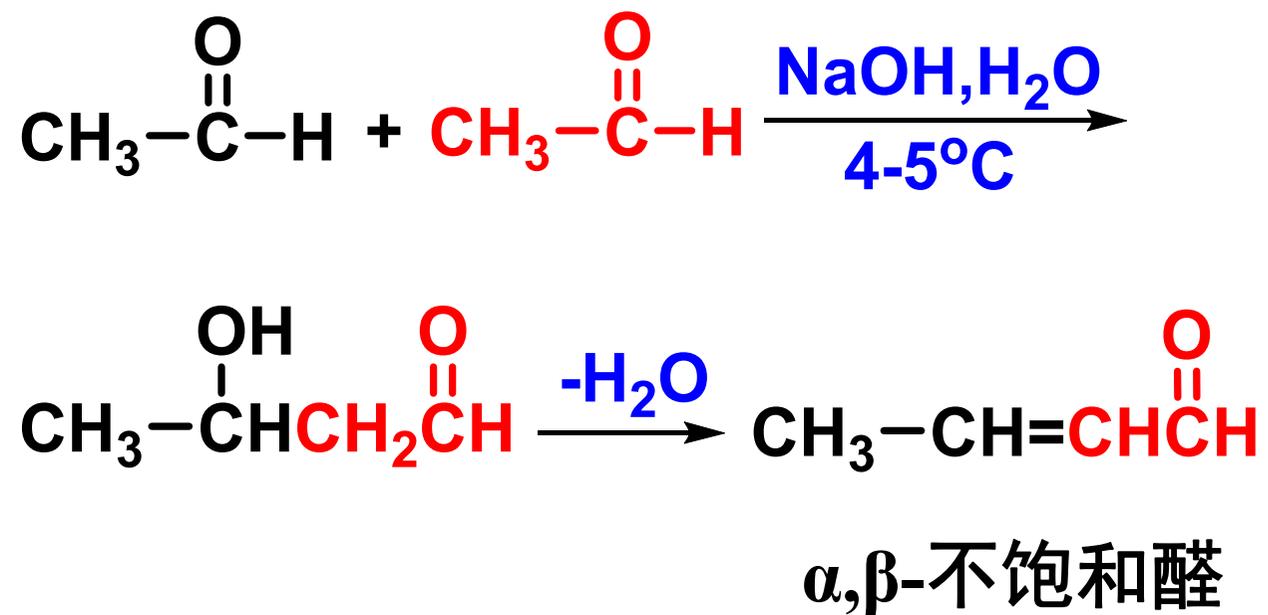
酮式 > 99.99%

烯醇式 < 0.01

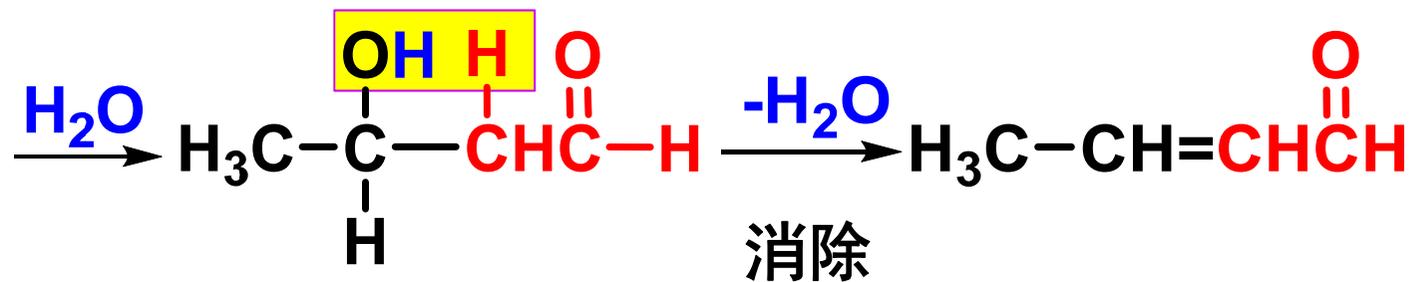
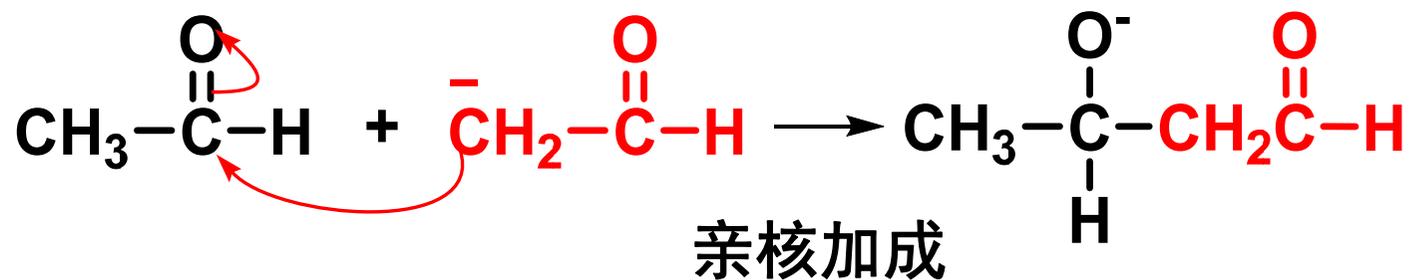
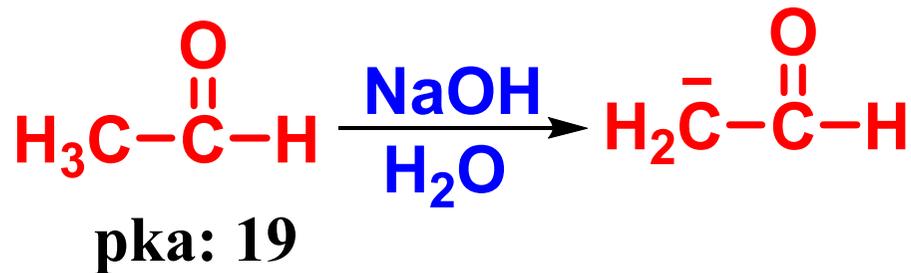
化合物	pKa	化合物	pKa
CH_3NO_2	10.2	$\text{CH}_2(\text{NO}_2)_2$	3.57
CH_3COCl	16	$\text{CH}_3\text{COCH}_2\text{COCH}_3$	9
CH_3CHO	17	$\text{NCCH}_2\text{CO}_2\text{CH}_3$	9
CH_3COCH_3	20	NCCH_2CN	11.2
$\text{CH}_3\text{CO}_2\text{CH}_3$	25	$\text{CH}_3\text{COCH}_2\text{CO}_2\text{Et}$	11
CH_3CN	25	$\text{CH}_2(\text{CO}_2\text{Et})_2$	13

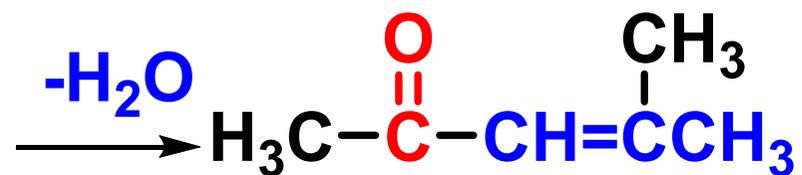
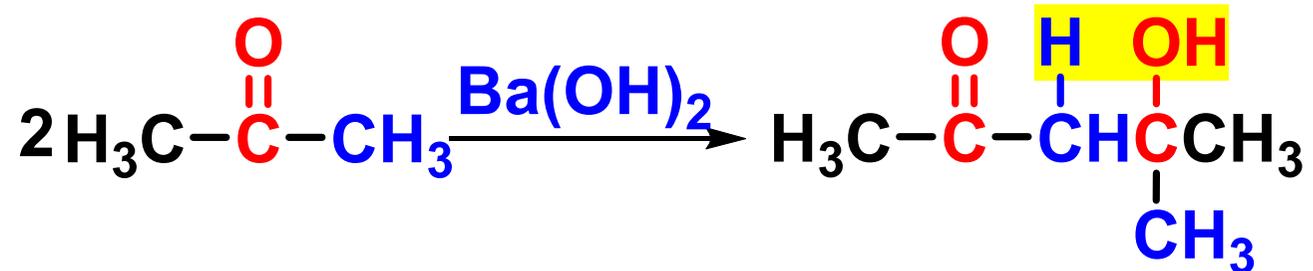
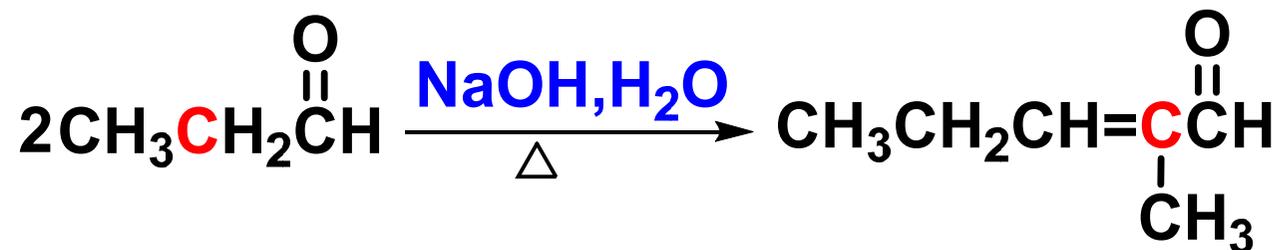
2、羟醛缩合反应 (*aldol condensation*)

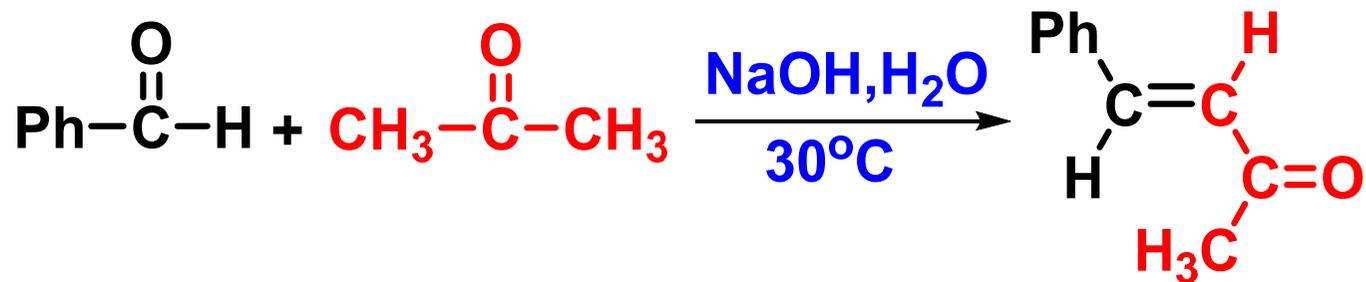
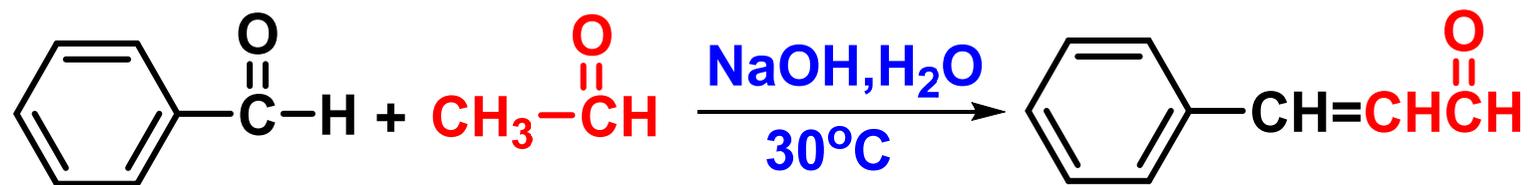
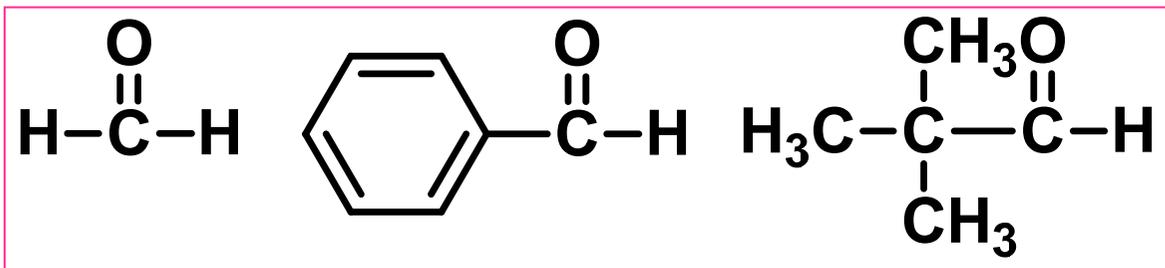
(1) 羟醛缩合反应



反应机理:

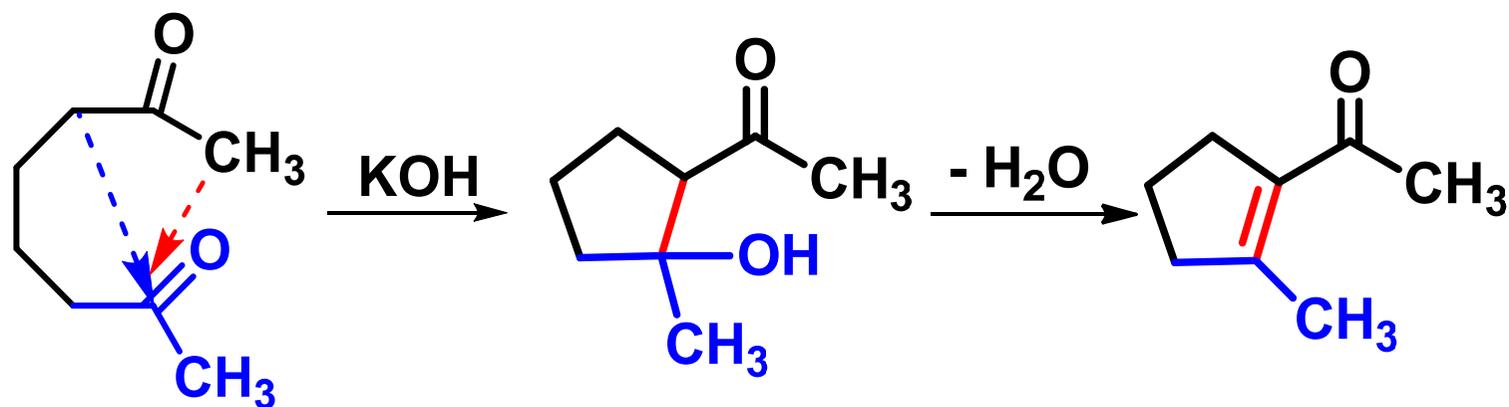




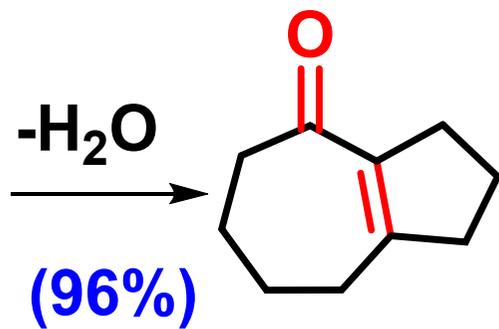
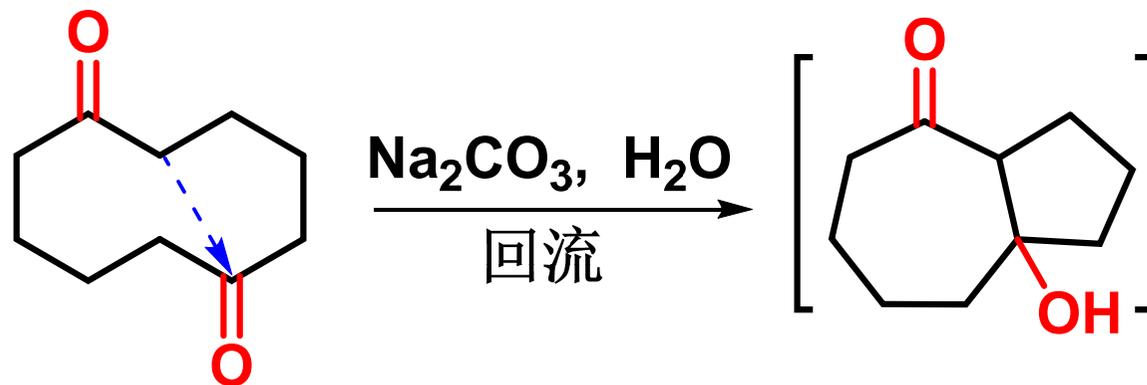


(3) 分子内的羟醛缩合

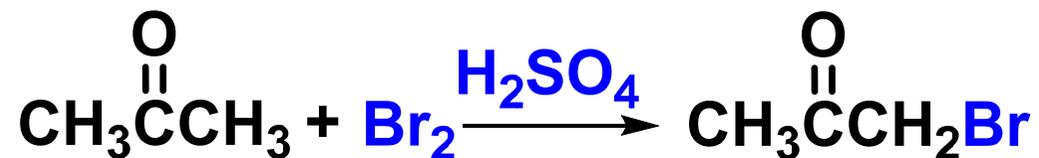
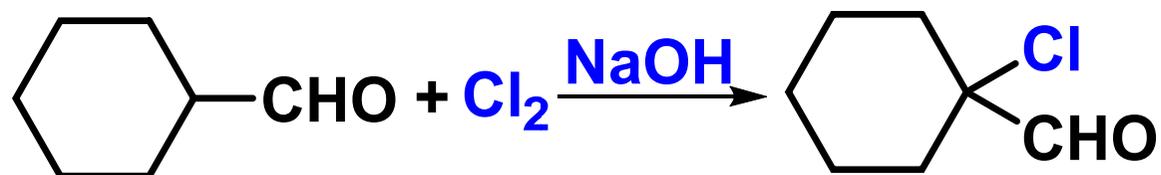
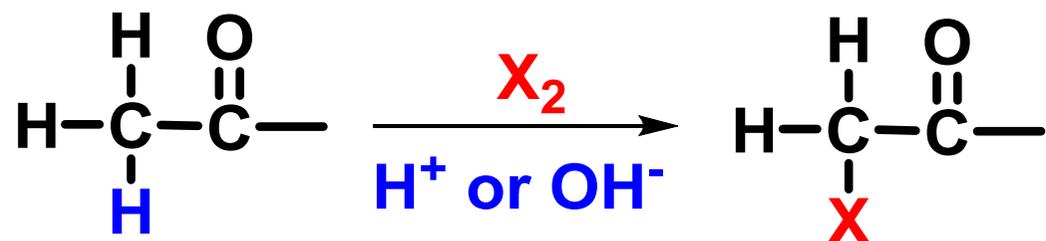
(intramolecular aldol condensation)



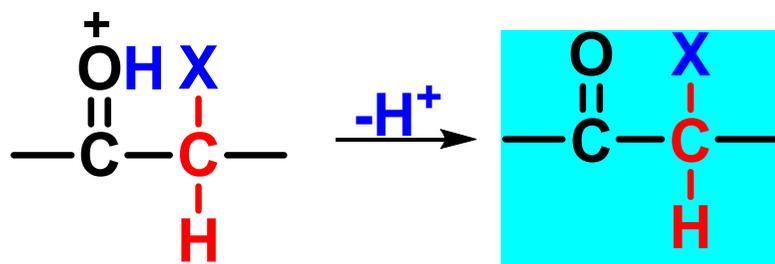
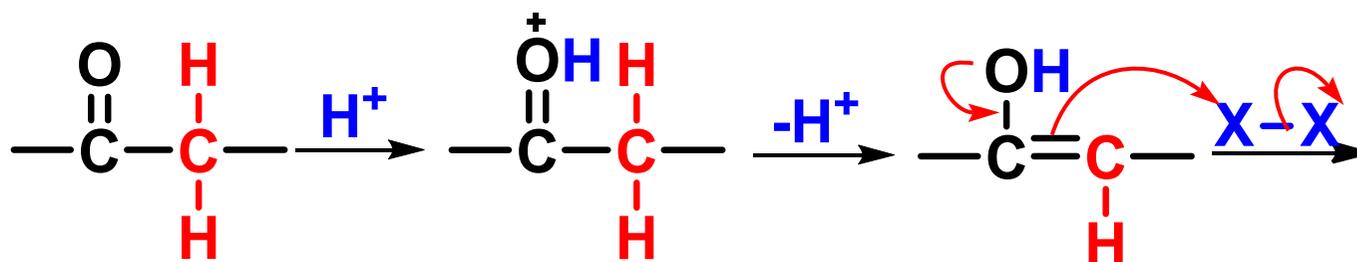
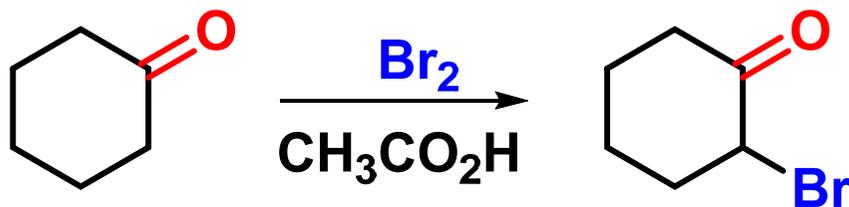
形成五元环或六元环



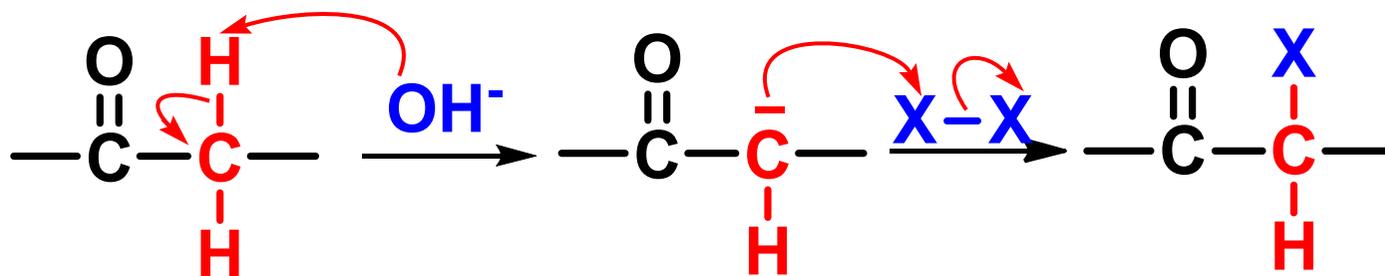
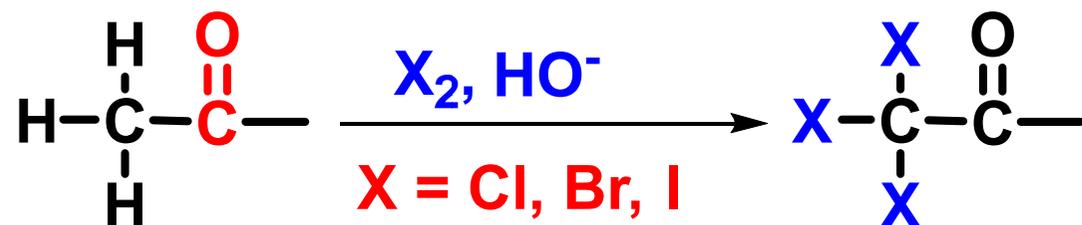
3、卤代反应和卤仿反应



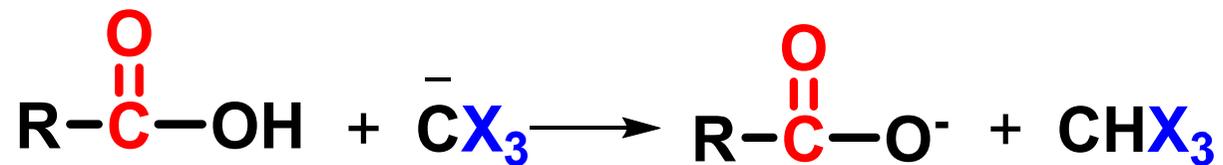
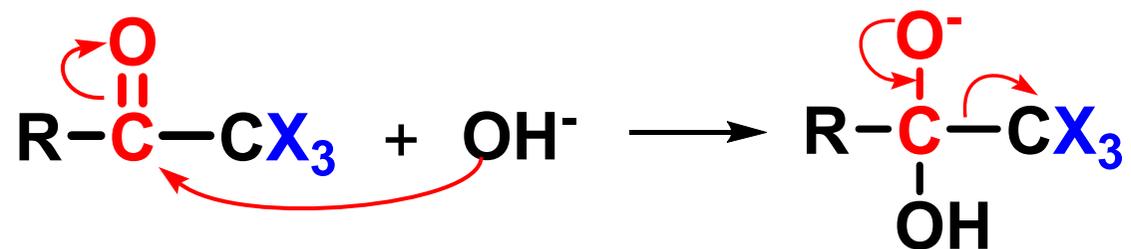
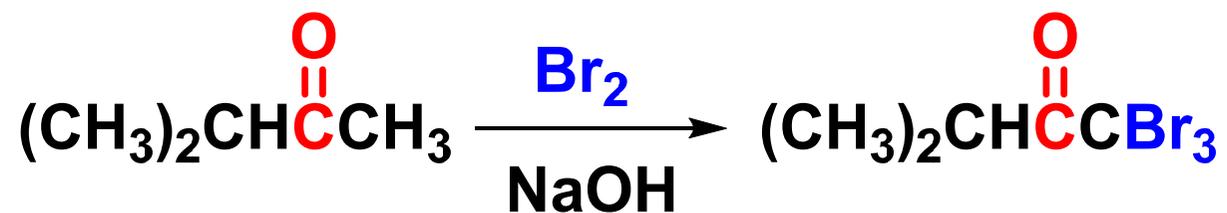
● 酸催化卤代：单卤代

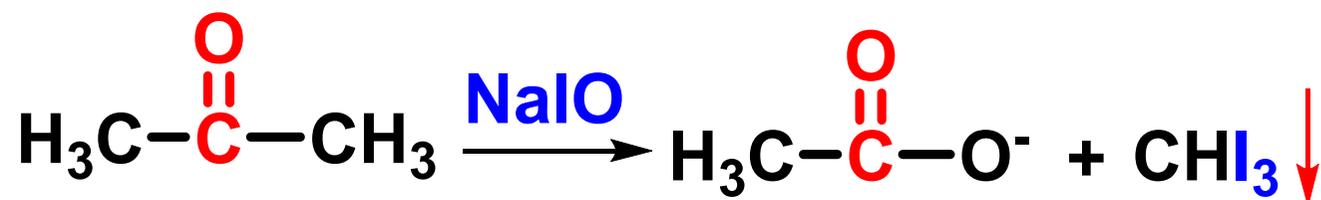
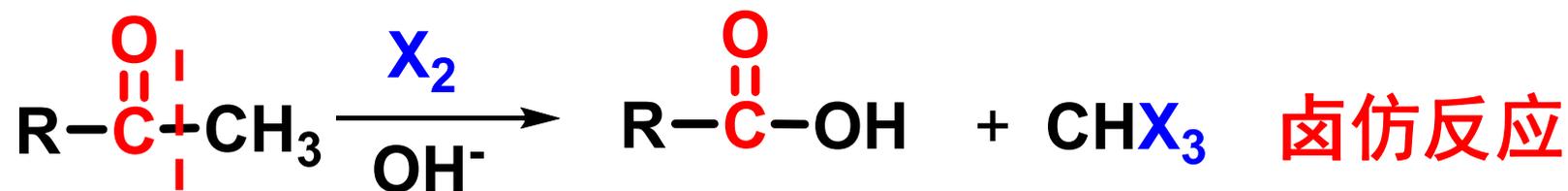


● 碱催化卤代：多卤代



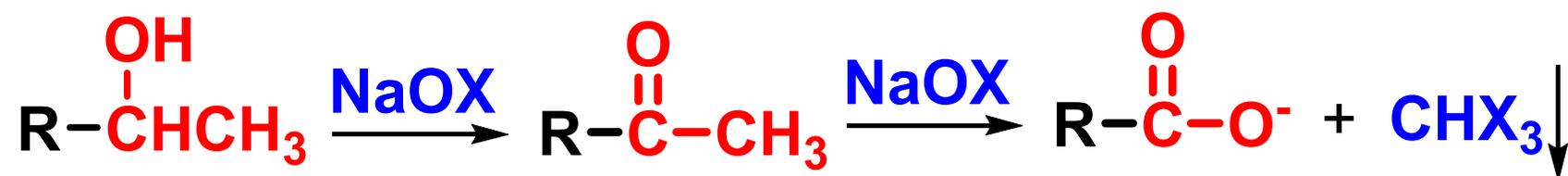
产物 α -H的酸性比反应物强，更易取代，易得多取代产物。





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。

α -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。

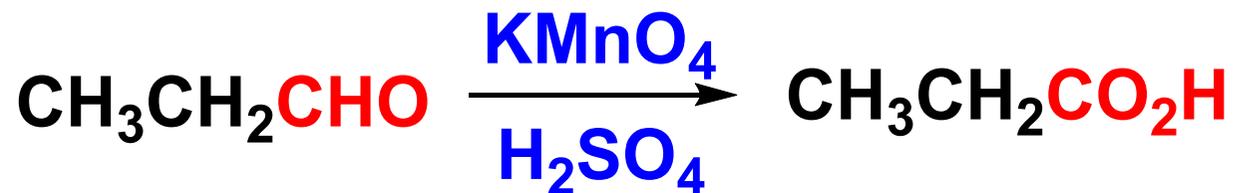
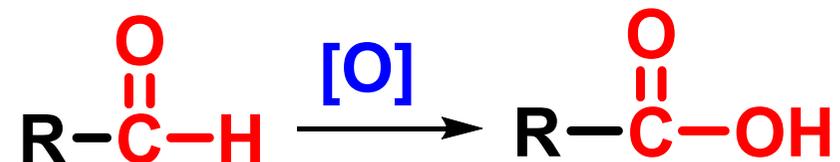


卤仿反应可用于鉴别：乙醛、甲基酮和部分具有特殊结构的醇。

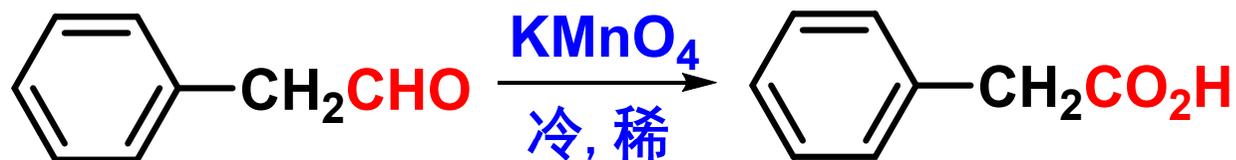
三、氧化反应

1、醛的氧化

- 强氧化剂： KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, HNO_3 等。



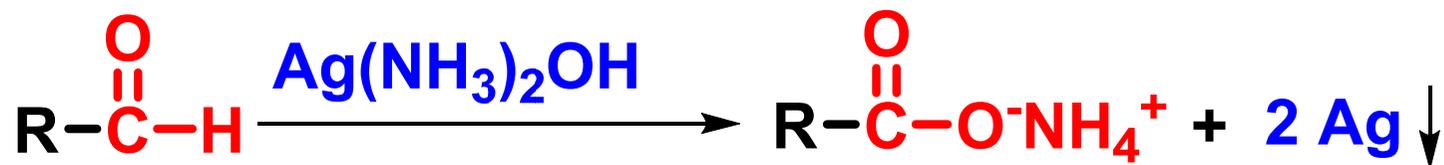
对强氧化剂敏感的基团如双键也被氧化。



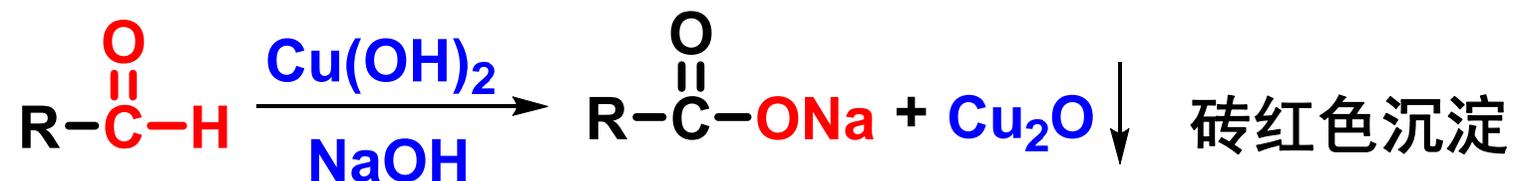
● 温和氧化剂:

AgNO₃的氨水溶液 (Tollens 试剂)

CuSO₄的酒石酸钠钾碱溶液 (Fehling试剂)

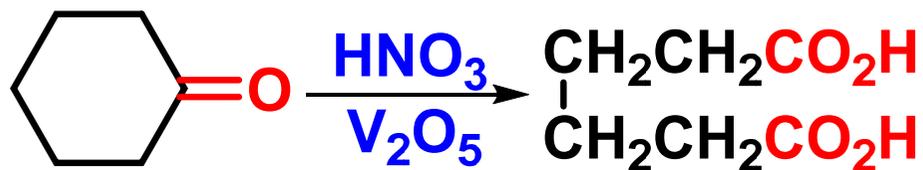


银镜反应



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。

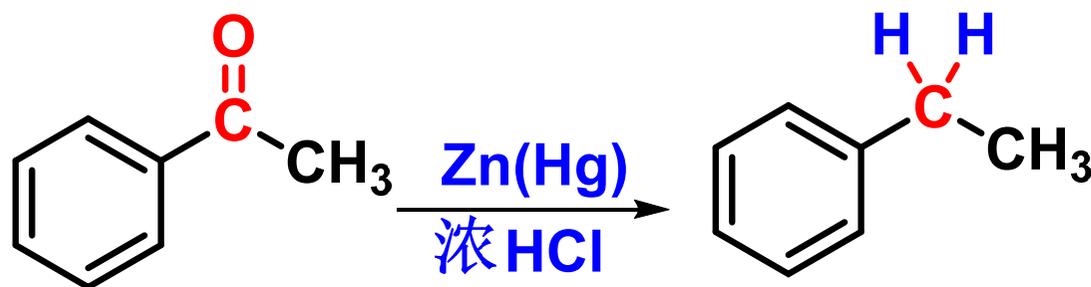
2、酮的氧化



四、还原反应

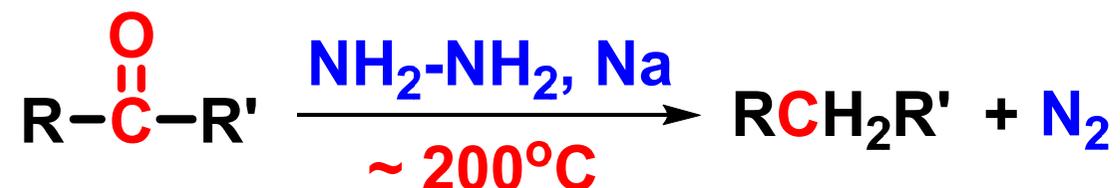
1、羰基还原甲叉基 (CH_2)

(1) 克莱蒙森 (*Clemmensen*) 还原

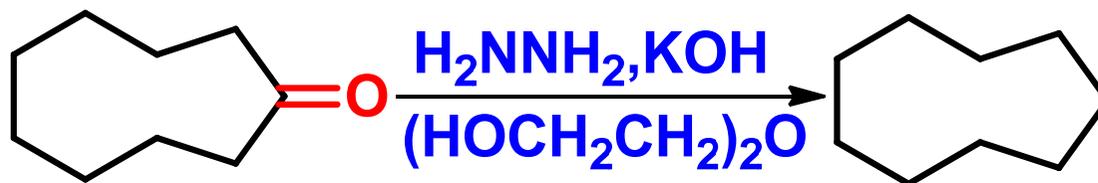
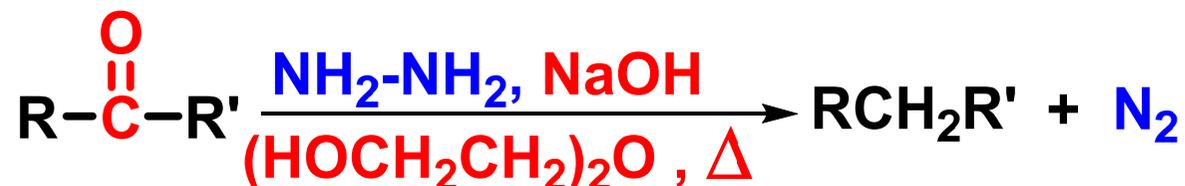


适用于对酸稳定的体系

(2) 乌尔夫-凯惜纳 (*Wolff-Kishner*) 还原

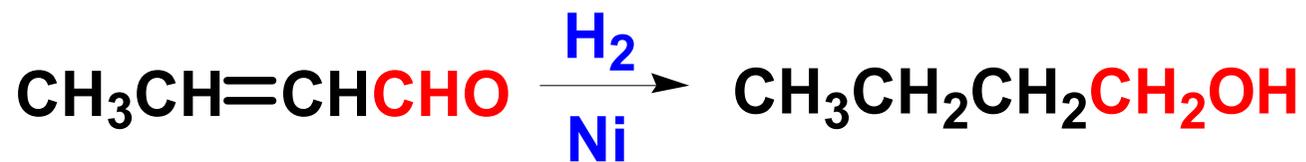
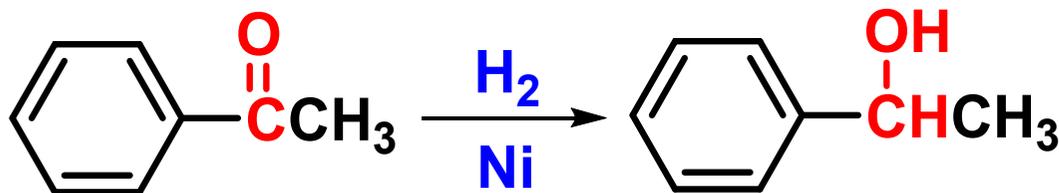
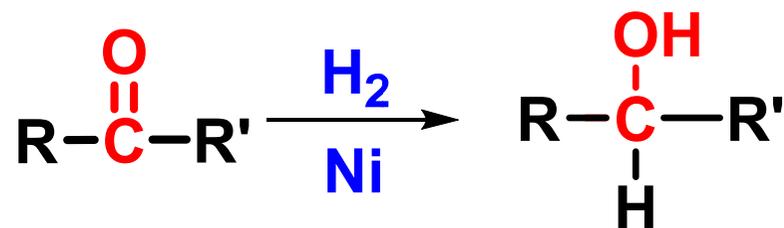


➤ 黄鸣龙改良法



2、羰基还原为醇羟基

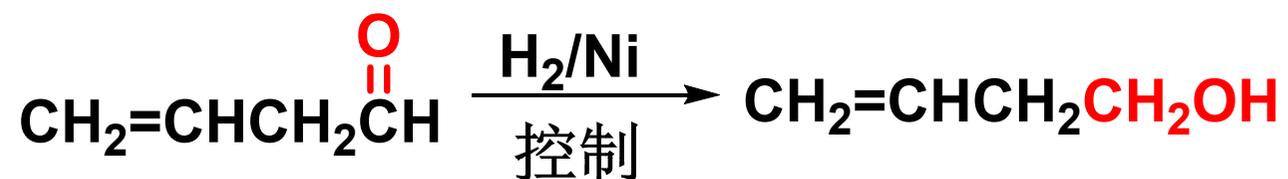
(1) 催化氢化



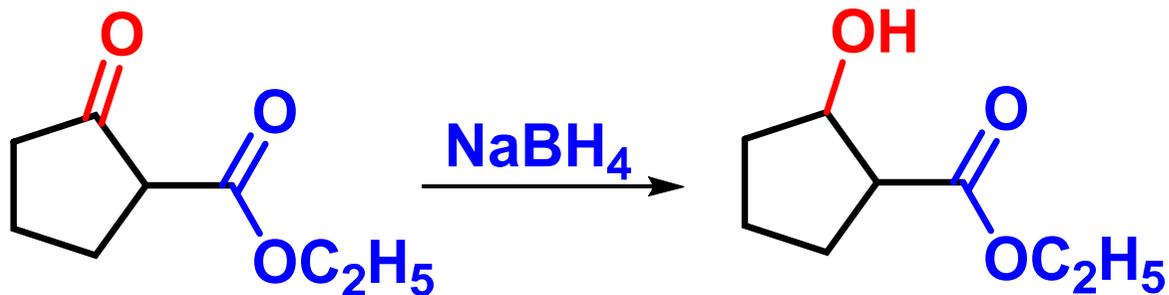
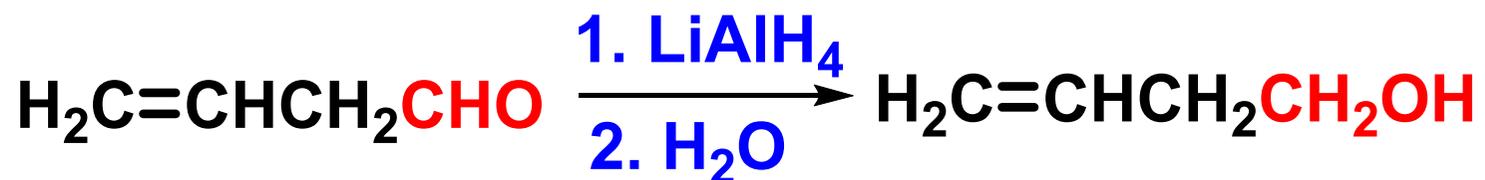
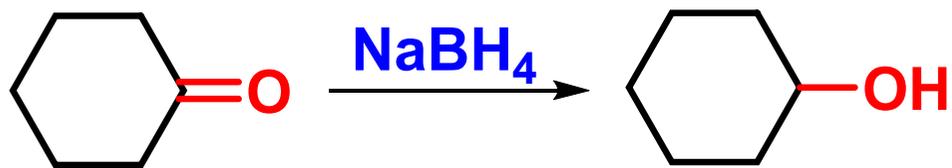
不饱和醛酮，官能团被还原活性为：

醛羰基 > 碳碳双键 > 酮羰基

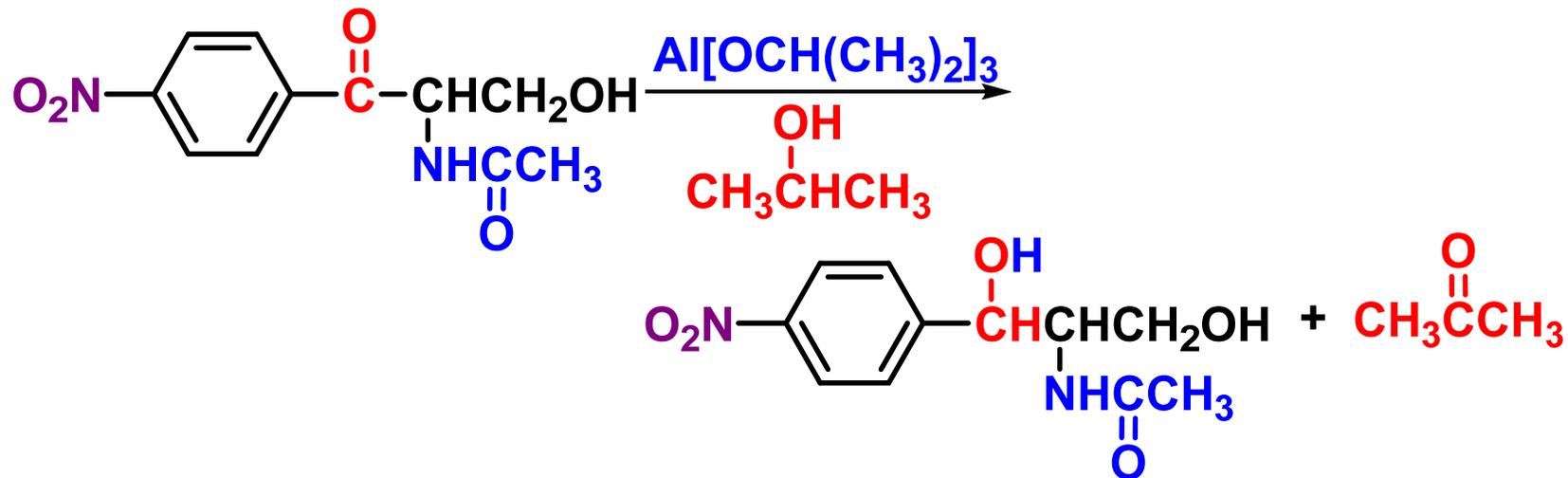
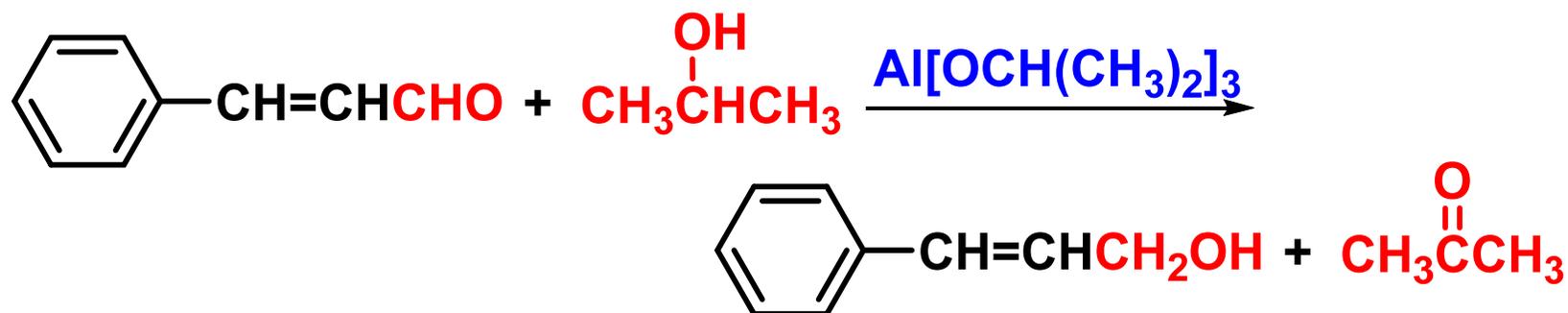
条件可以使活性高的基团优先被还原。



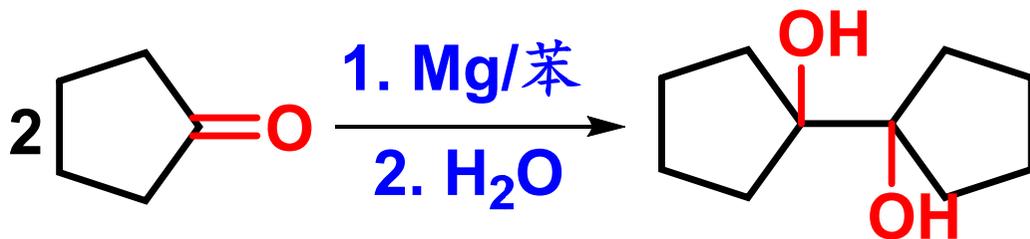
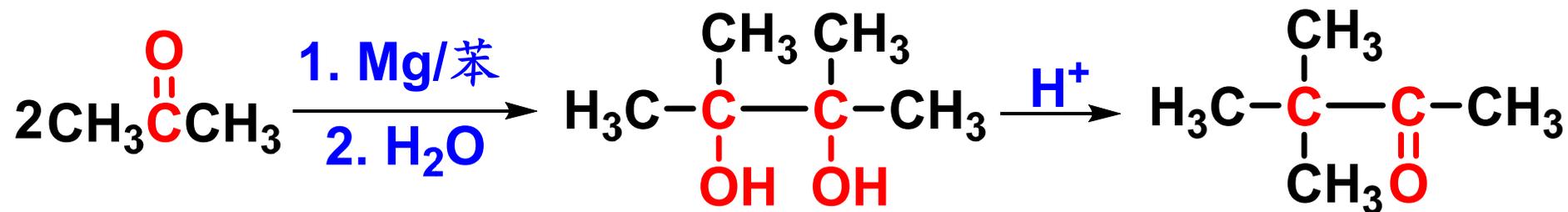
(2) 化学还原剂 NaBH_4 、 LiAlH_4



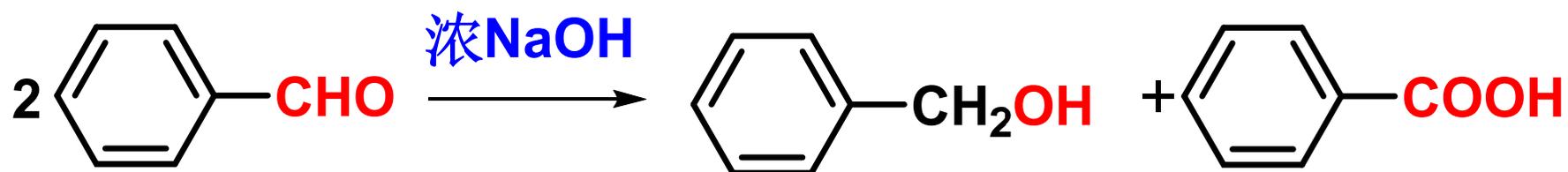
(3) 迈尔外因-彭杜尔夫 (Meerwein-Ponndorf) 反应



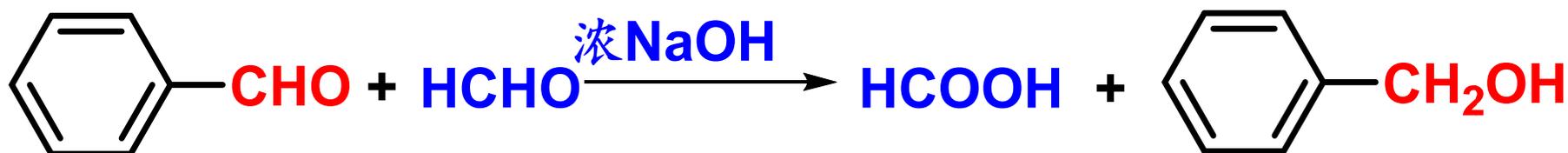
(4) 酮的双分子还原



3、康尼扎罗 (*Cannozzaro*) 反应



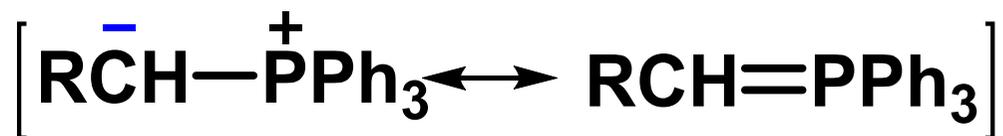
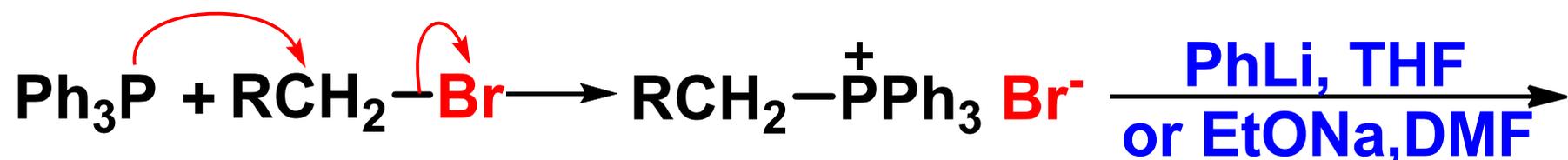
➤ 无 α -H的醛和甲醛（甲醛总是被氧化）



交叉康尼扎罗反应

五、其它反应

1、魏悌希 (*Wittig*) 反应



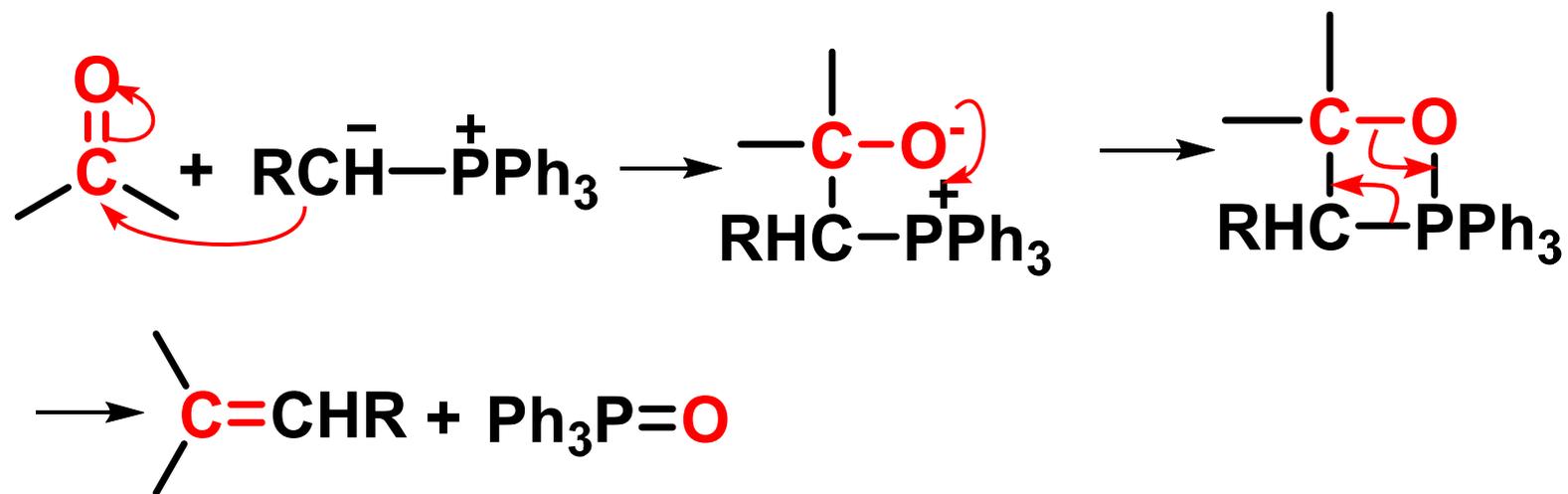
叶立德

Ylide

叶林

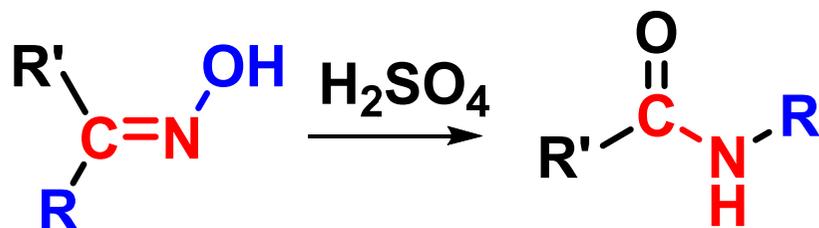
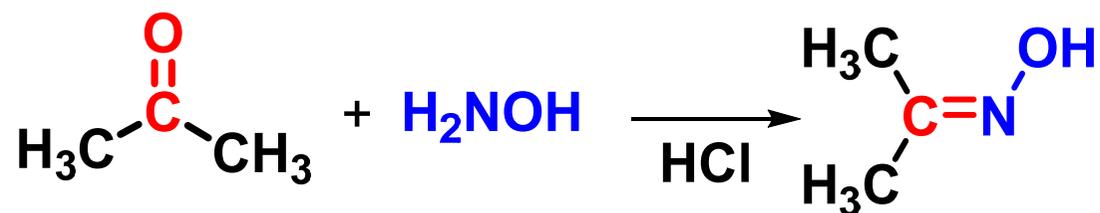
Ylene

Wittig试剂



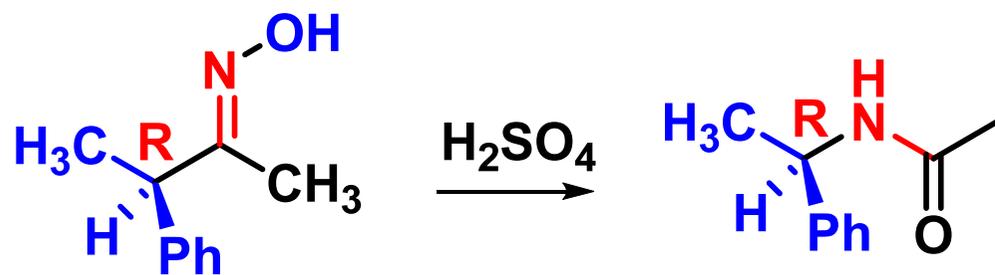
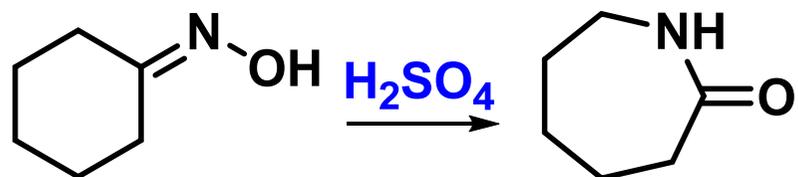
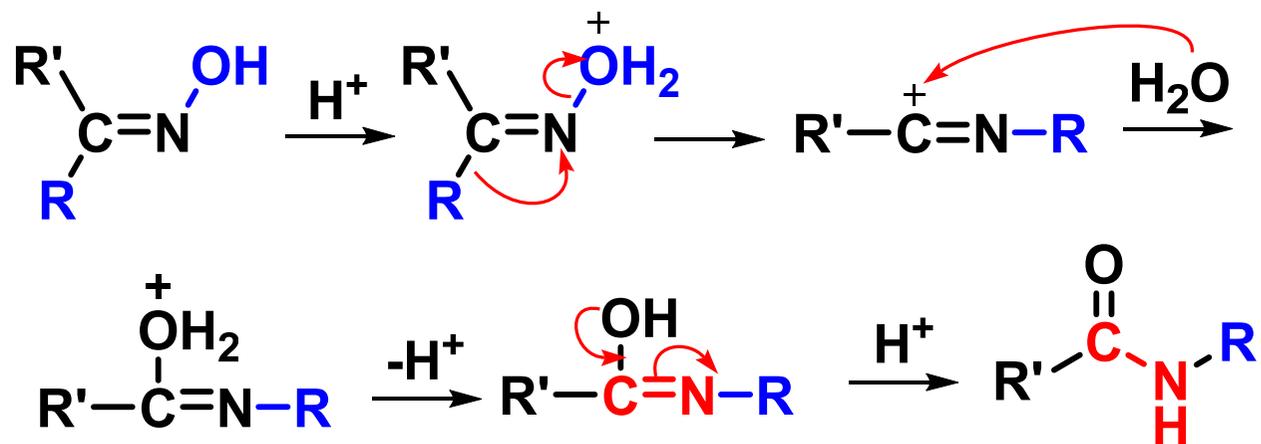
卤代烃是一级或二级卤代烃。反应试剂中可以有醚、酯、卤素、烯炔等官能团。

2、贝克曼 (*Beckmann*) 重排反应



R、R'：烷基、芳基。

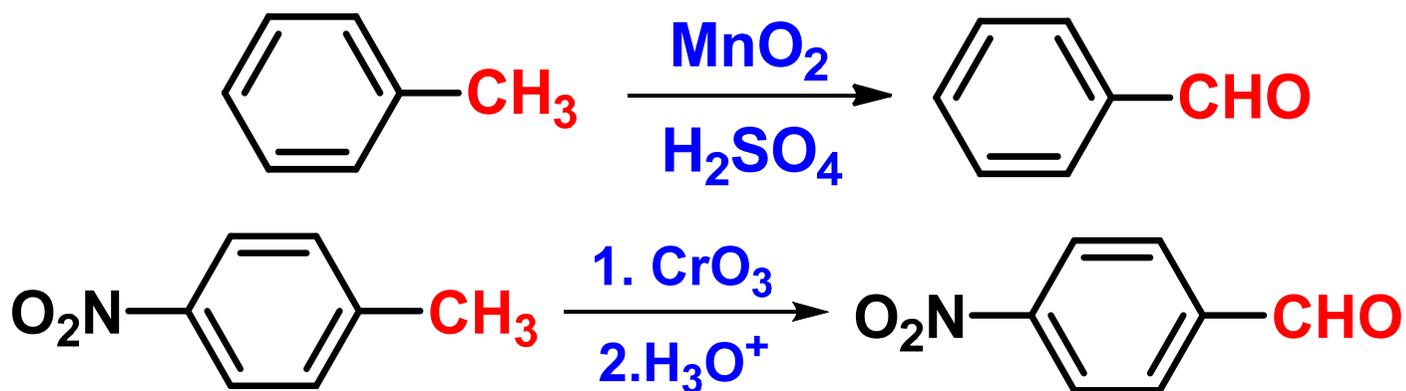
催化剂：硫酸、 SOCl_2 、 PCl_3 、路易斯酸等。



五、醛酮的制备

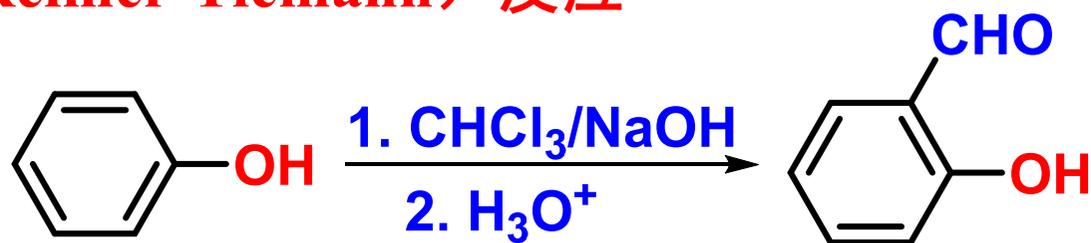
1、通过官能团转化制备

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

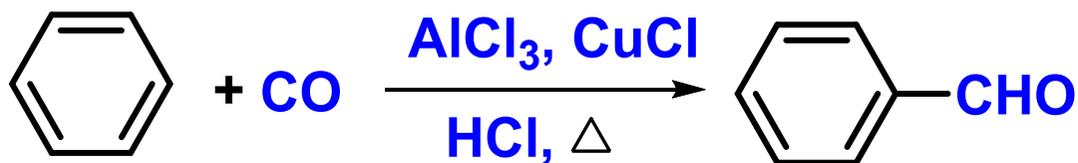


2、向分子中直接引入羰基

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



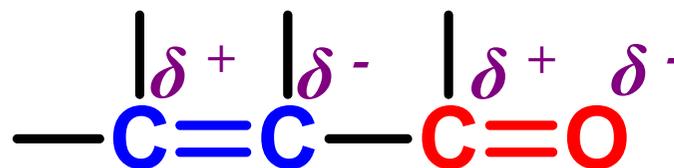
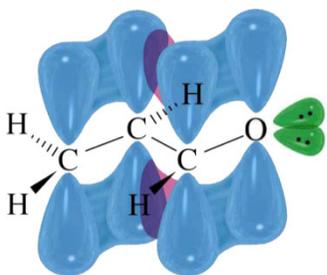
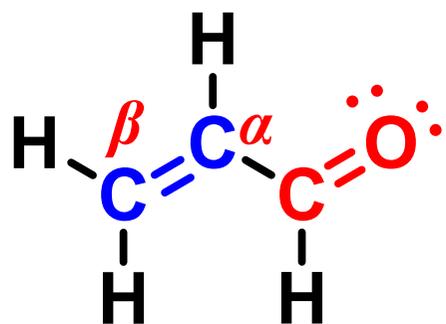
(4) 盖特曼-柯赫 (Gattermann-Koch) 反应



第五节 α, β -不饱和醛酮

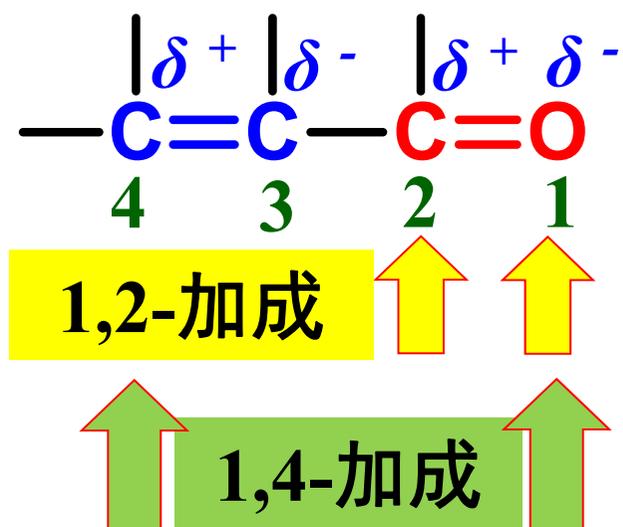
一、结构

α, β -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。



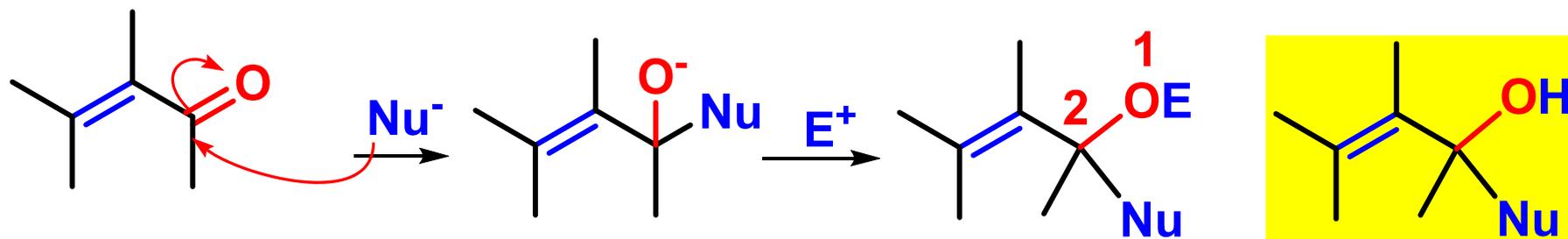
二、化学性质

1、亲核加成反应

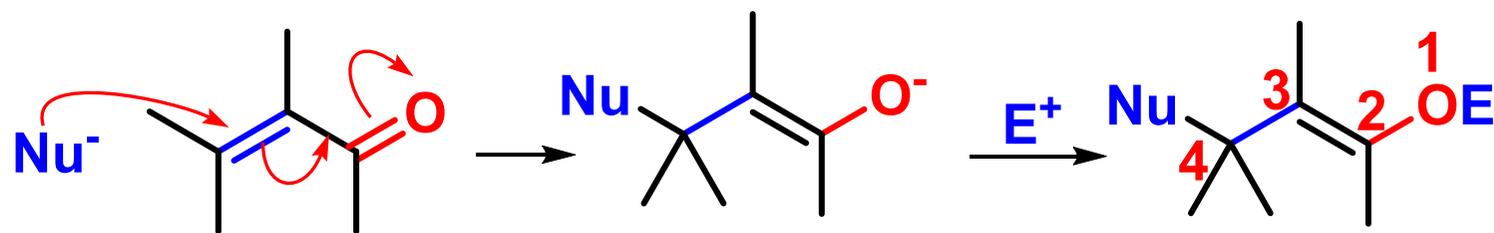


以哪种方式加成，取决于亲核试剂和醛酮的结构。

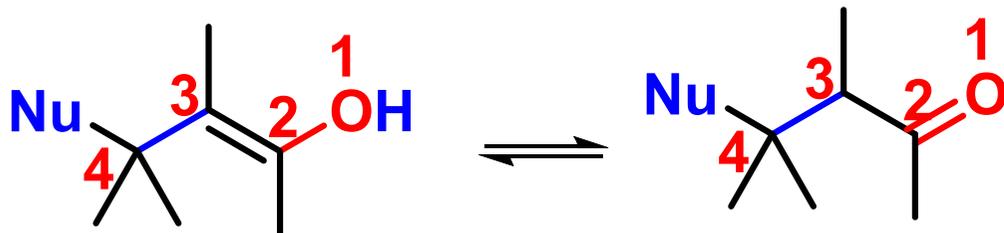
1,2-加成机理



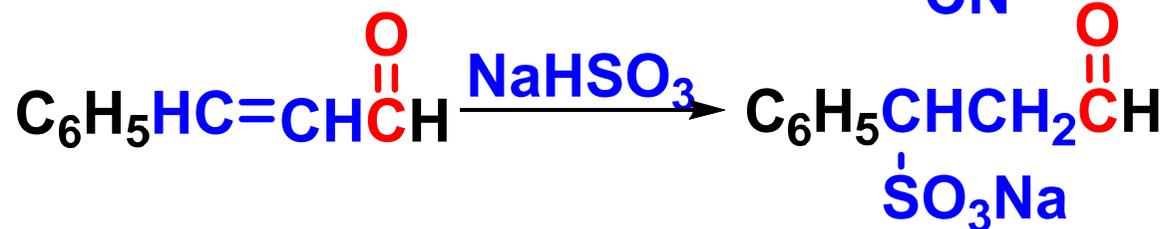
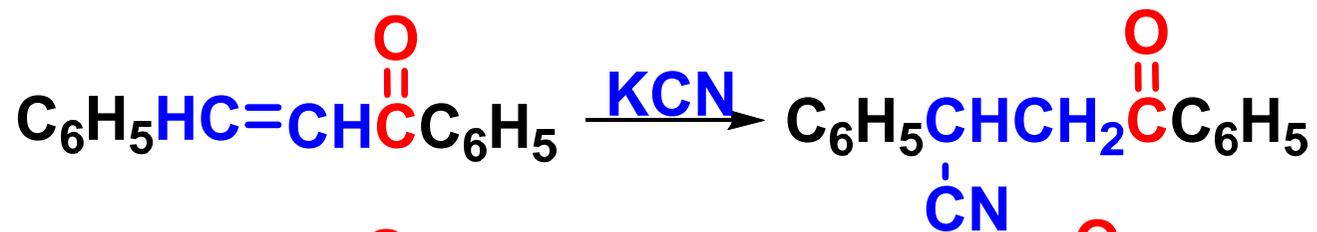
1,4-加成机理



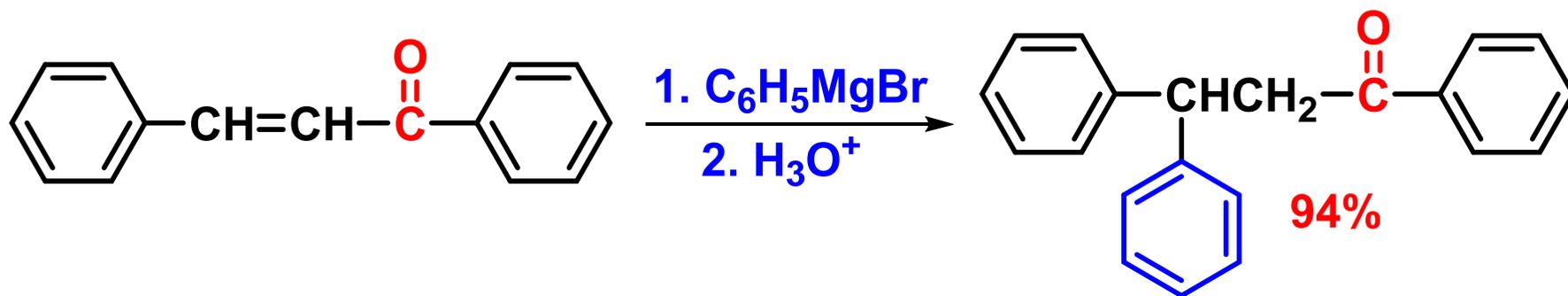
烯醇



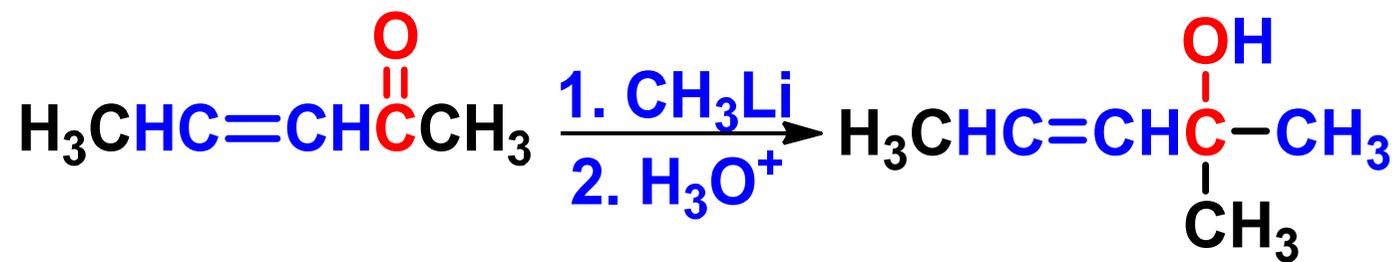
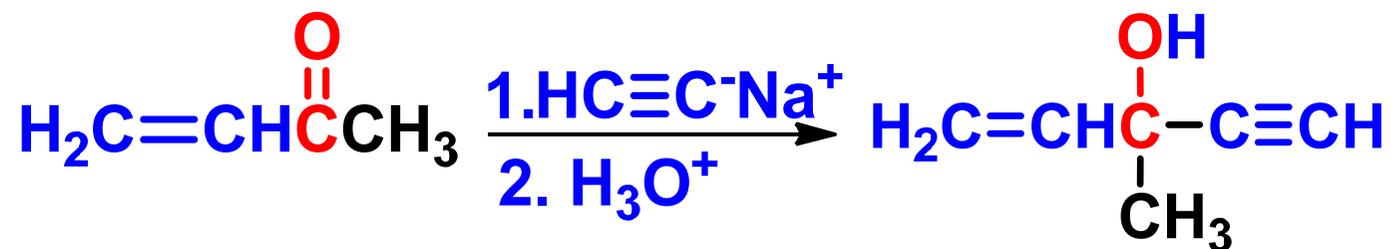
① HCN、NaHSO₃、ROH、RNH₂ (胺、羟胺、苯肼) 等, 1,4-加成。



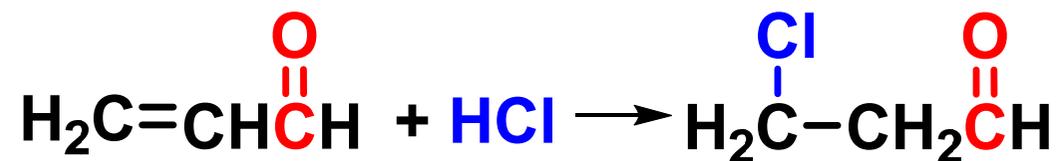
② 格氏试剂，1,2-和1,4-加成都有可能



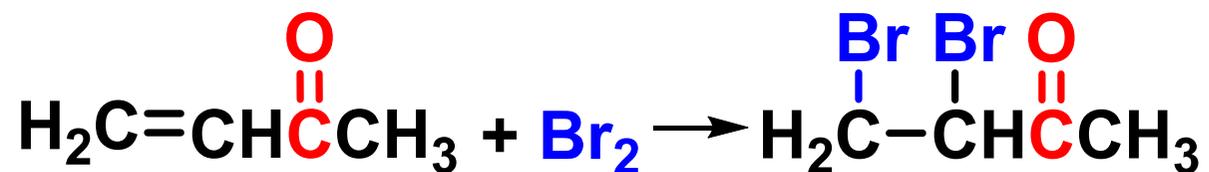
③ 有机锂、有机钠：1,2-加成



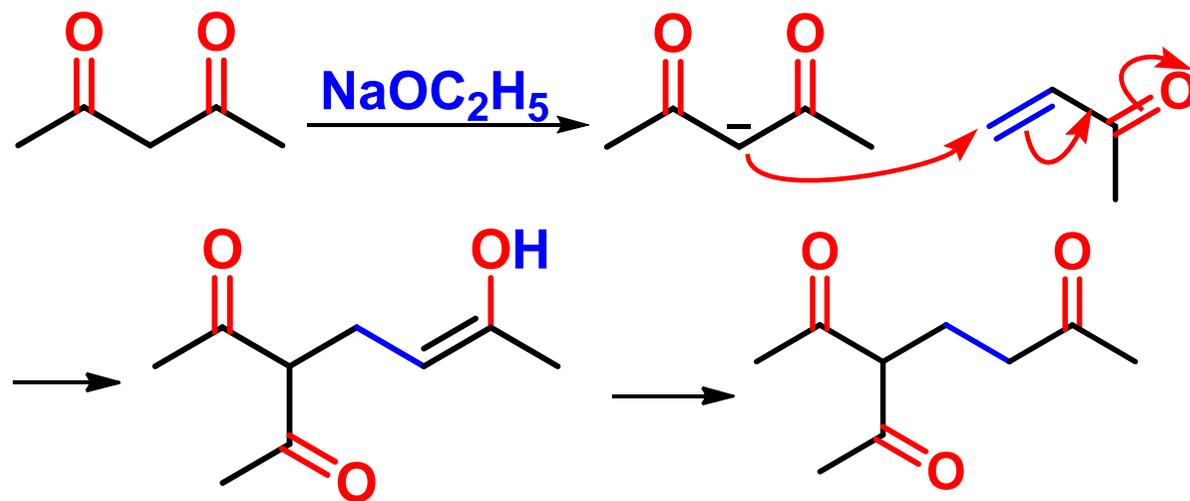
2、亲电加成反应：



卤素、次卤酸只在 C=C 上加成。



3、迈克尔加成反应 (Michael Addition Reaction)

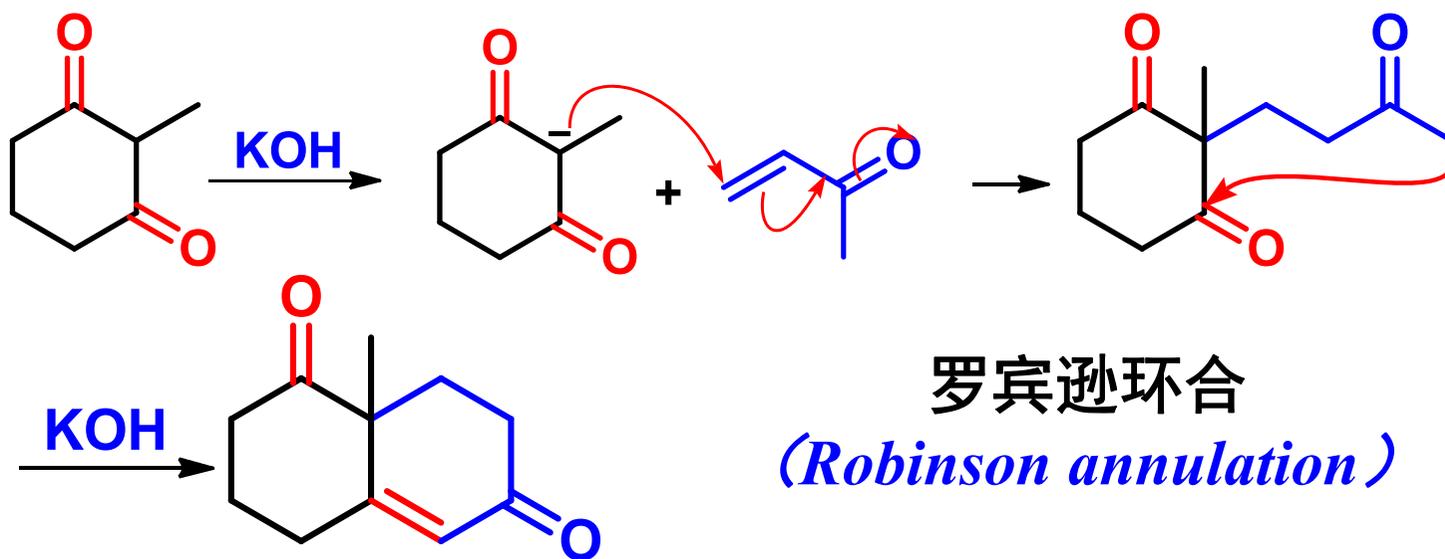
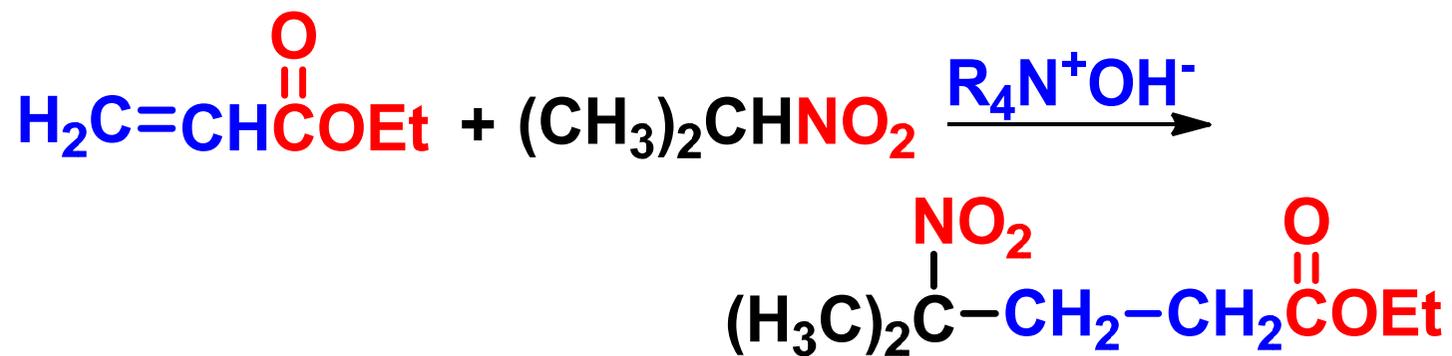




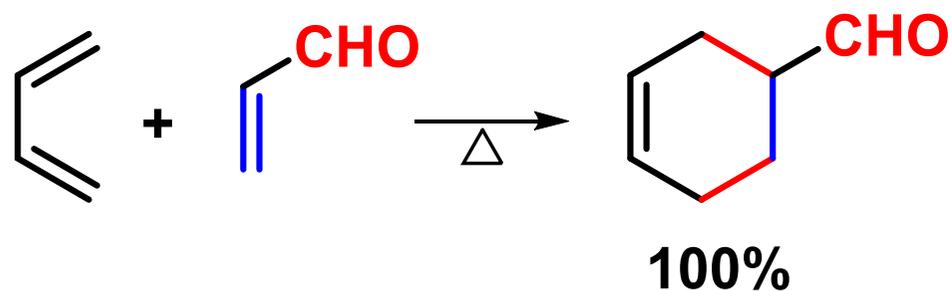
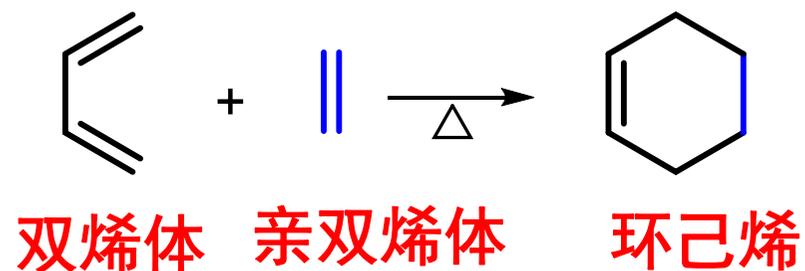
A、B为吸电子基团，如：**-CN、-NO₂、-CO₂Et、-COR**等。

α , β -不饱和化合物: α 、 β -不饱和酸酯、腈、醛、酮等具有 α , β - 不饱和共轭体系的化合物。

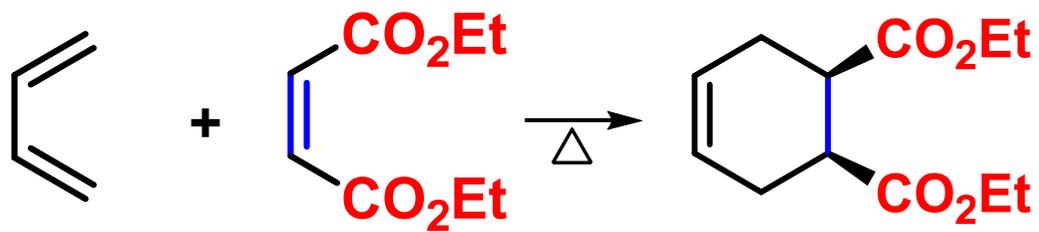
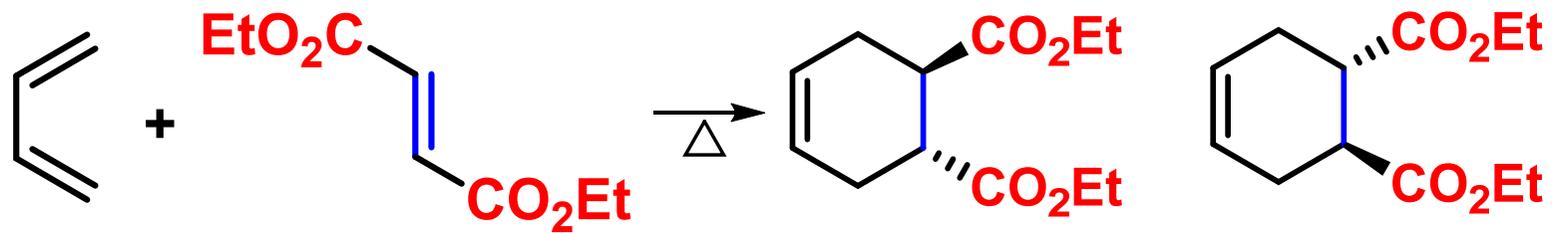
碱为醇钠、KOH、NaOH、季铵碱、氨基钠、三乙胺、六氢吡啶等。



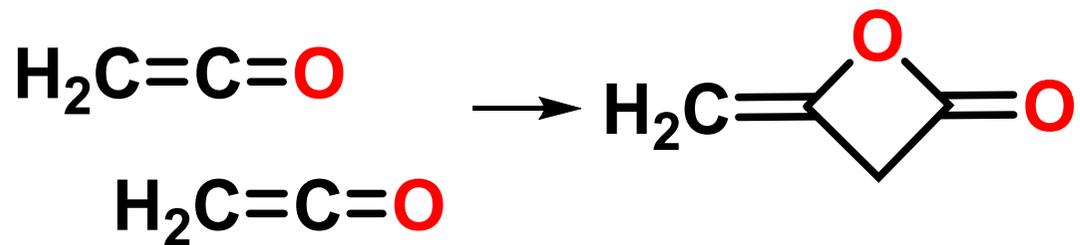
4、狄尔斯-阿尔德 (Diels-Alder) 反应



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

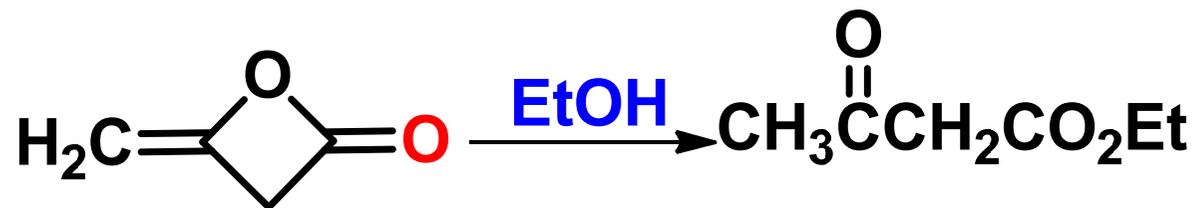
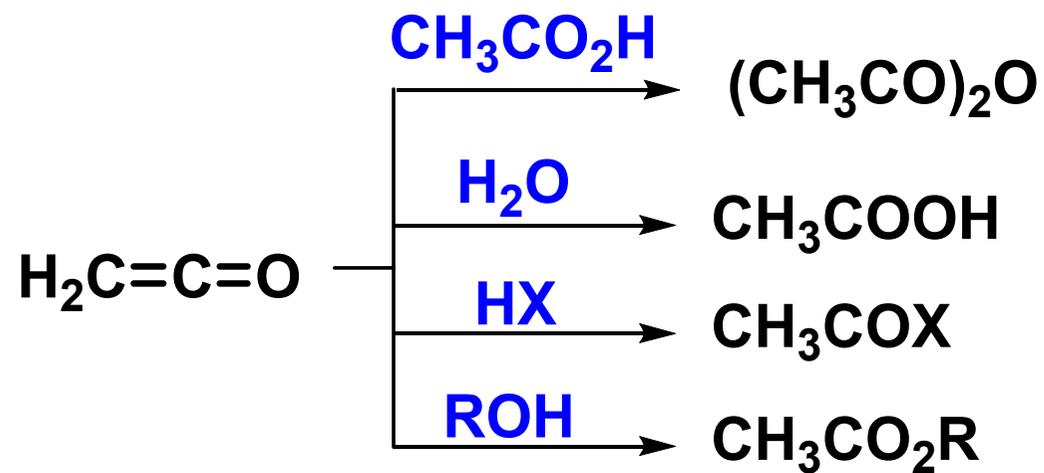


乙炔酮

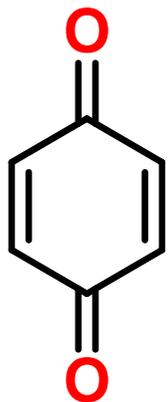
bp: -48°C

双乙炔酮

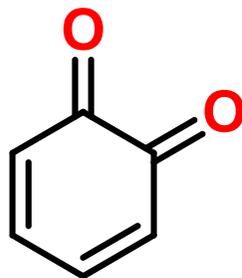
bp: 128°C



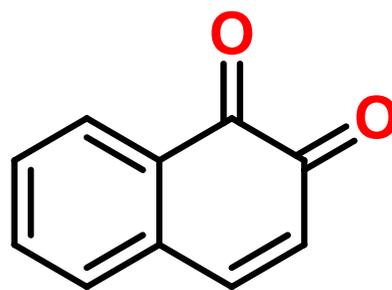
四、醌类化合物



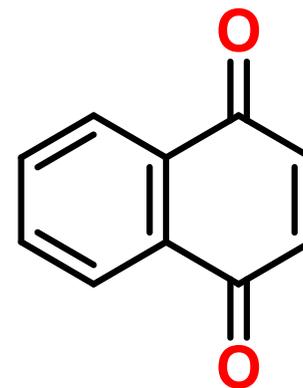
对苯醌
(1,4-苯醌)



邻苯醌
(1,2-苯醌)

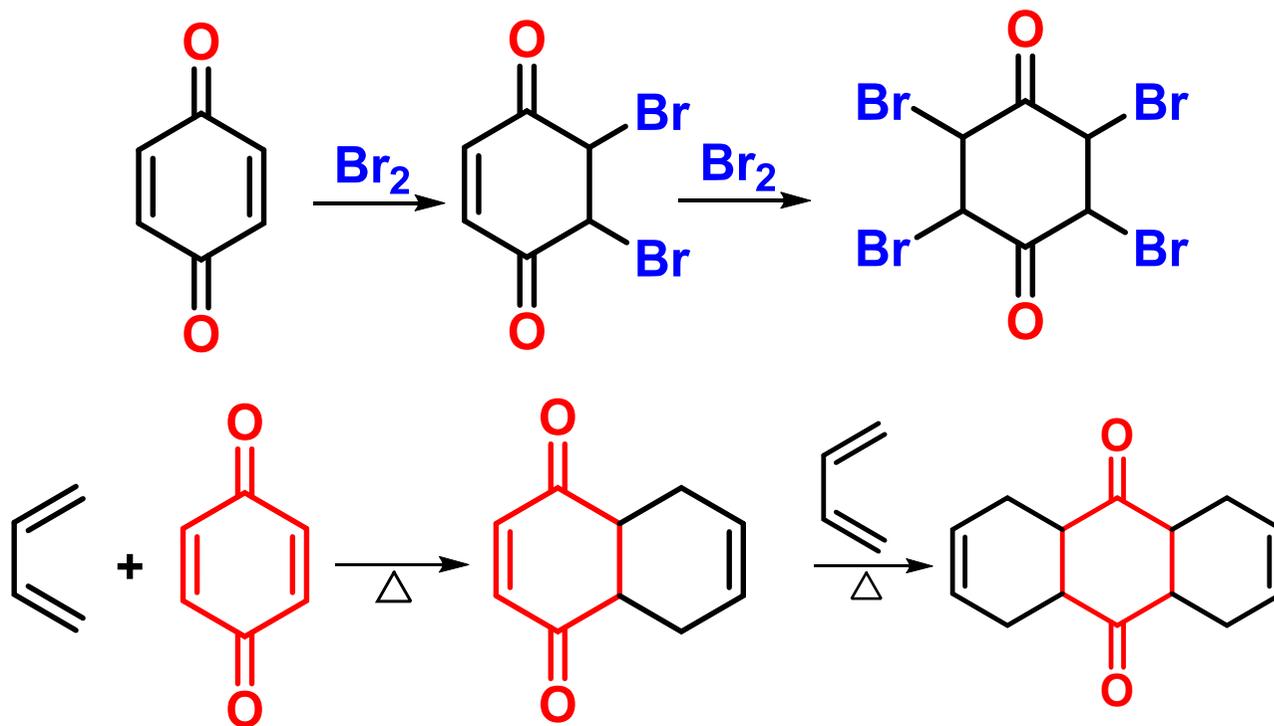


1,2-萘醌

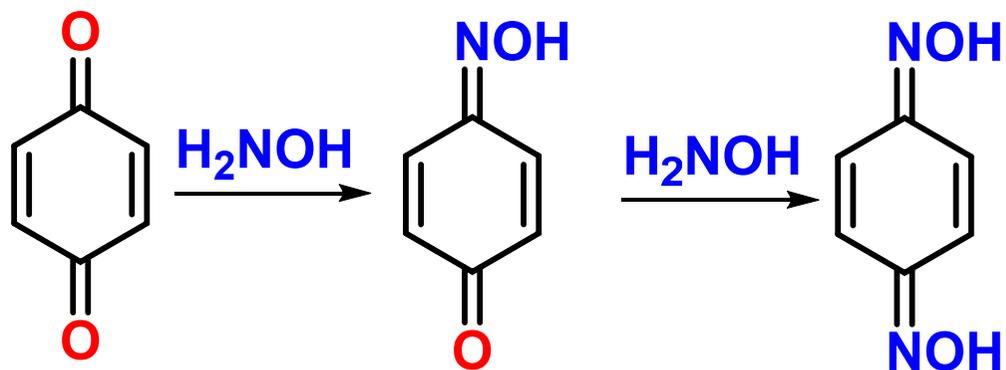


1,4-萘醌

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

