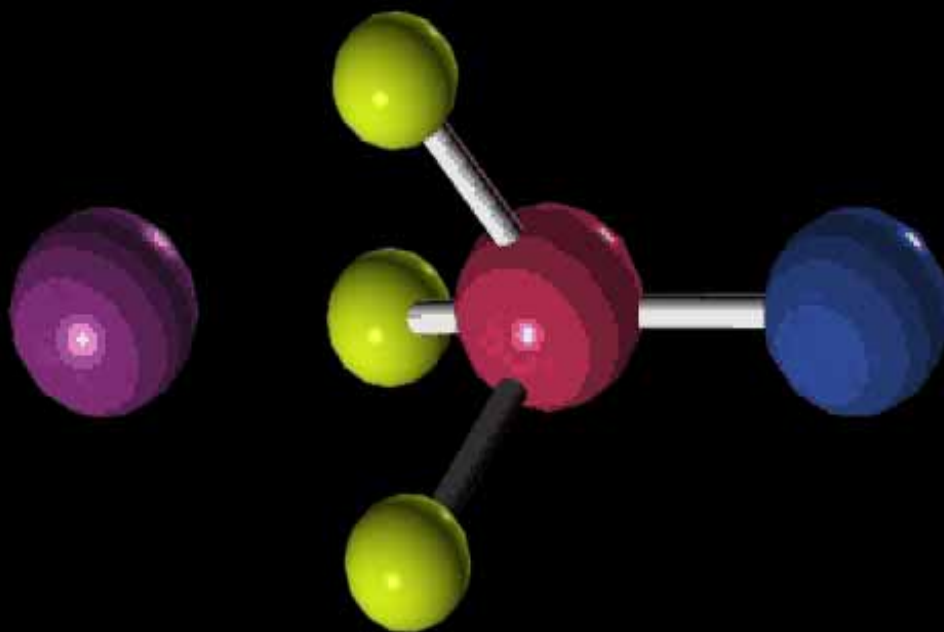
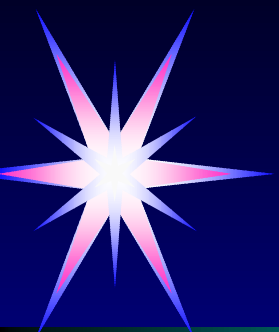


# 有机化学

( Organic Chemistry )

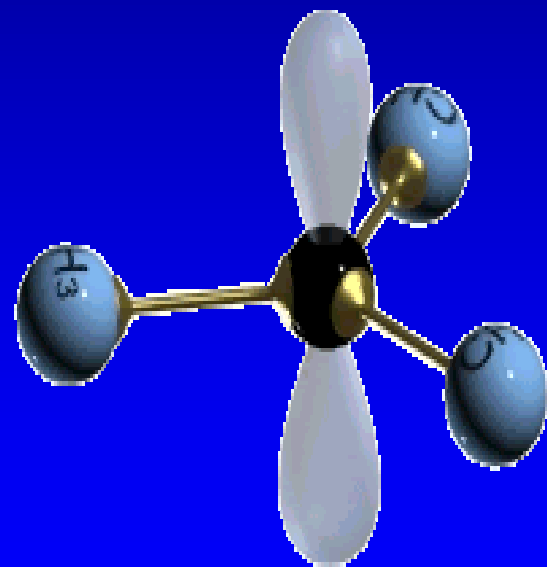


制作：付蕾 朱凤岗

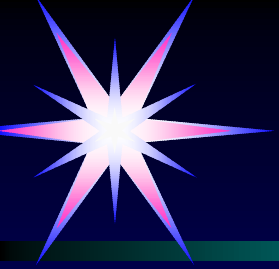


# 有机化学

( Organic Chemistry )



制作：付蕾 朱凤岗



# 第九章 醛 酮 醌

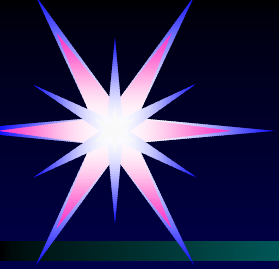
( Aldehydes , ketones , quinones )

第一节 醛和酮

( Aldehydes , ketones )

第二节 醌

( Quinones )



# 第一节 醛和酮

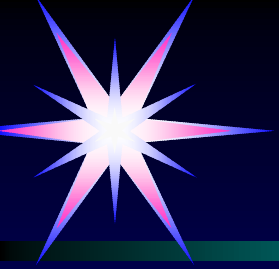
( Aldehydes , ketones )

## 一、分类和命名

( Classification and nomenclature )

## 二、化学性质

( Reactions of aldehydes , ketones )



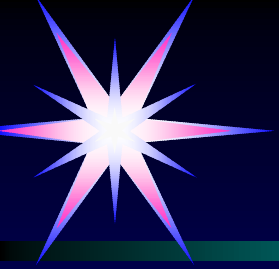
# 一、分类和命名

## ( Classification and nomenclature )

### 1. 分类 ( Classification )

**烃基：** 脂肪族醛酮；芳香族醛酮

**羰基数目：** 一元醛酮；二元醛酮



## 2. 命名 (Nomenclature)

系统法

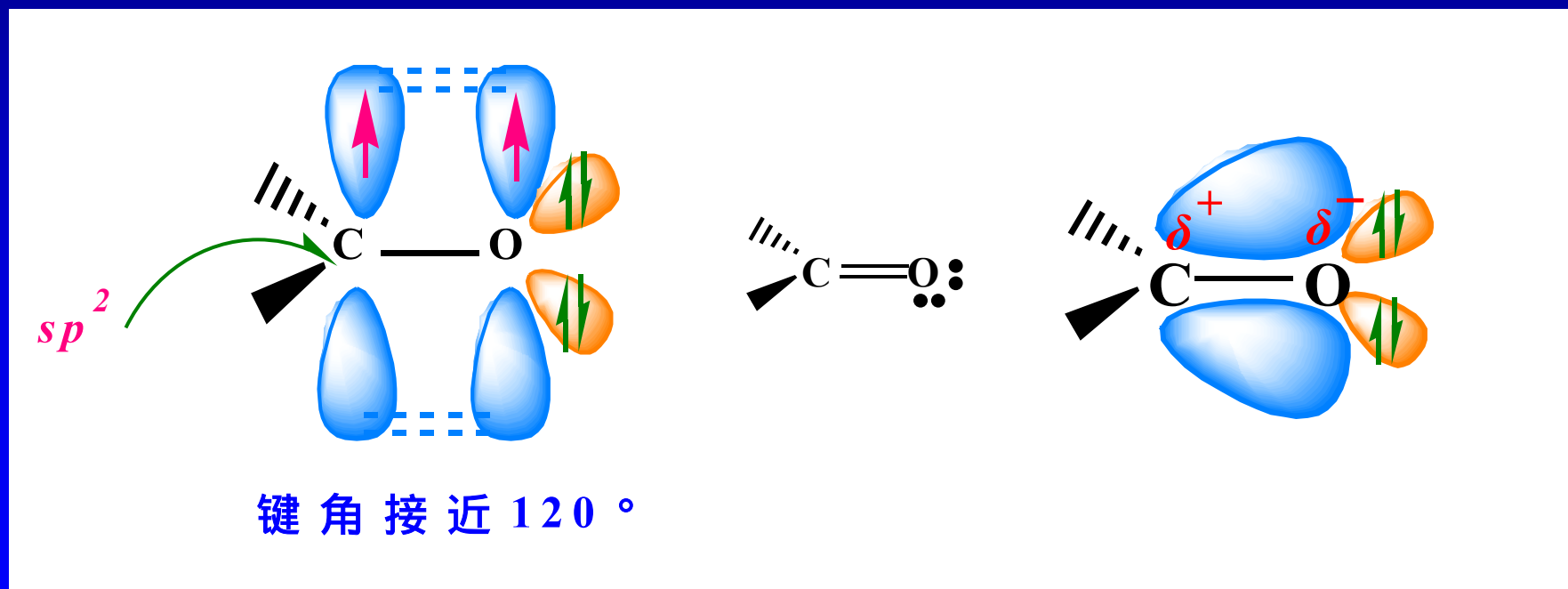
选主链：含羰基和重键  
Ar- 取代基

编号：近羰基端（阿，希），  
指明羰基位置和数目

## 二、化学性质

### ( Reactions of aldehydes , ketones )

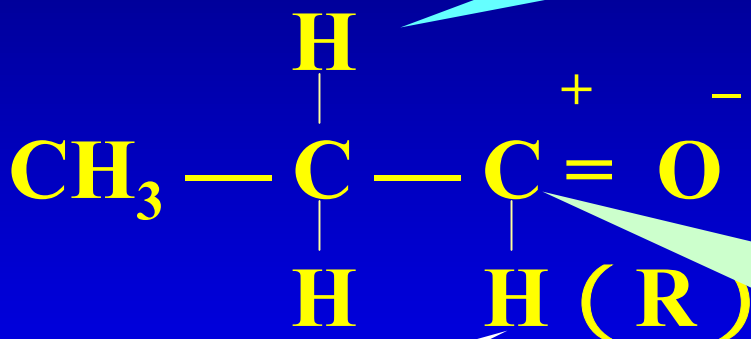
结构分析：



## 二、化学性质

( Reactions of aldehydes , ketones )

- H反应



碱和亲核试剂进攻部位

醛基的特殊反应

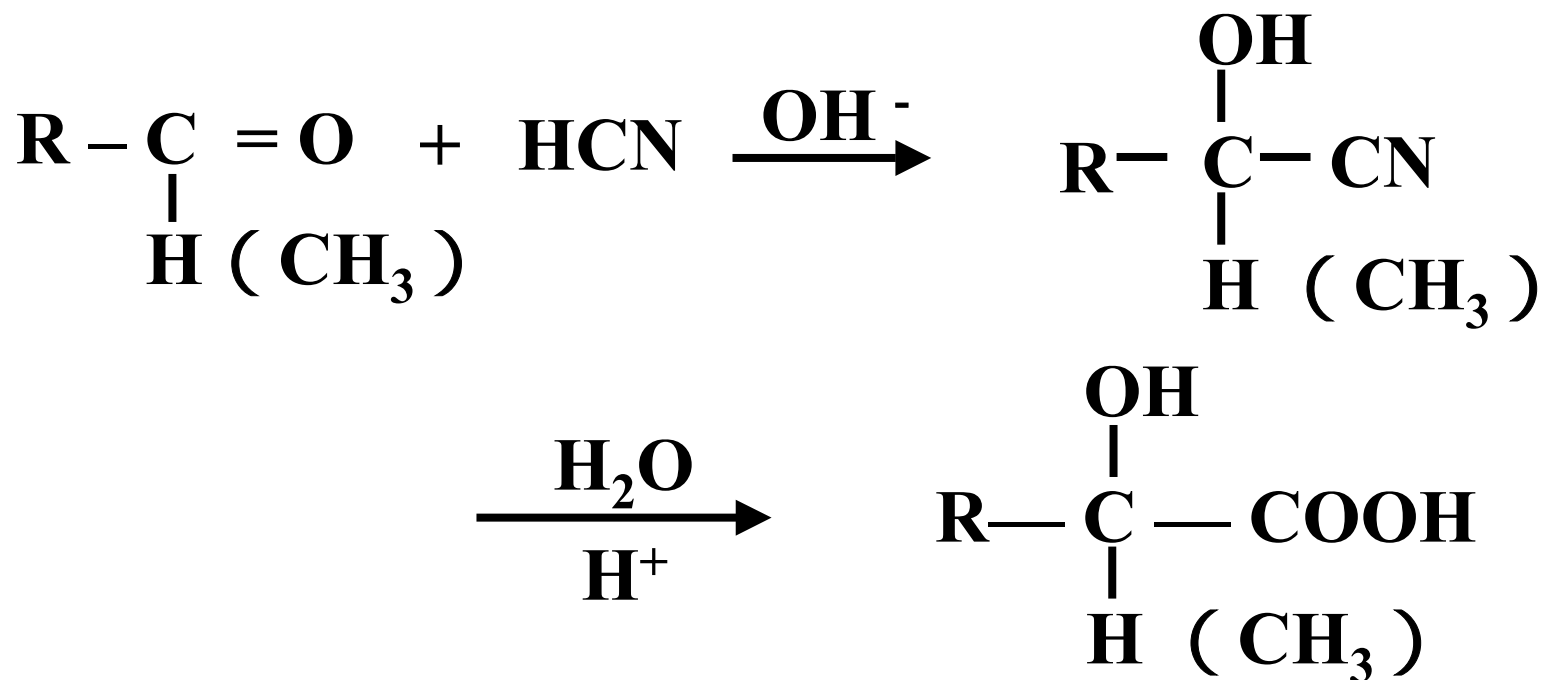




# 1. 羰基的加成反应

(1) 与HCN加成：

醛、甲基酮，C<sub>8</sub>以下环烷酮

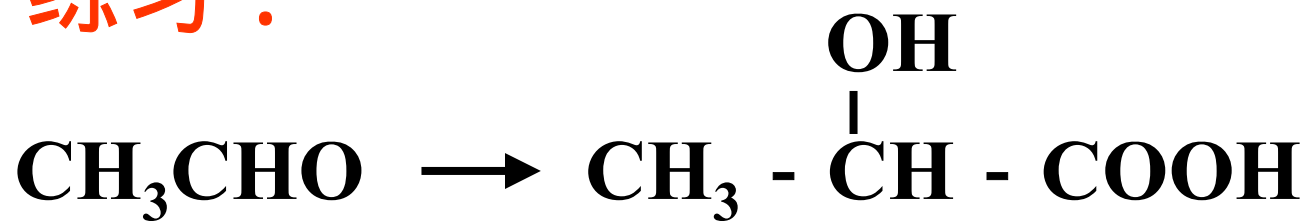




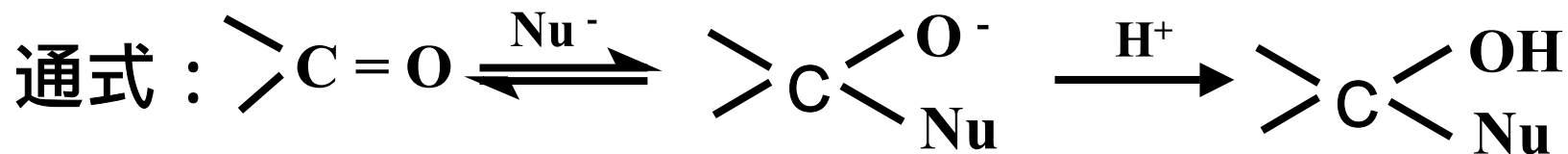
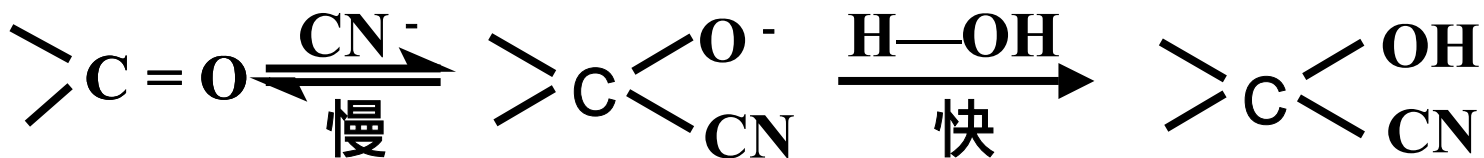
讨论：

用途：增碳反应

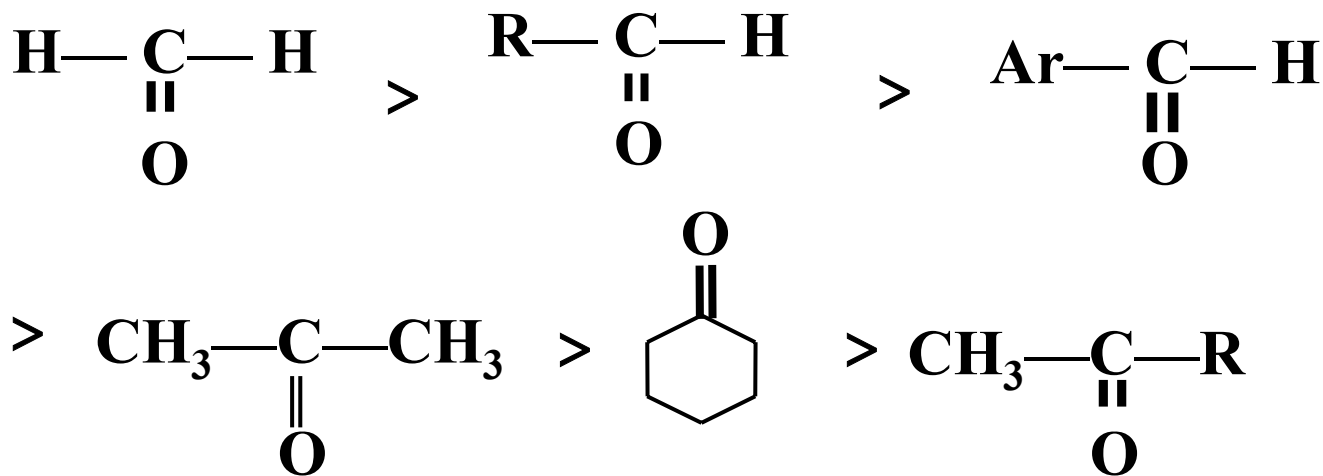
练习：



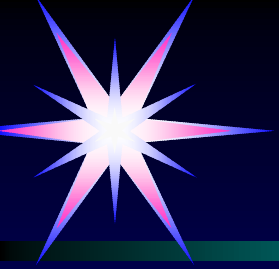
# 讨论： 历程：



# 讨论： 活性：



解释：R 越多越大，空间位阻越大；  
+  
C 电子密度越大，速度越慢。

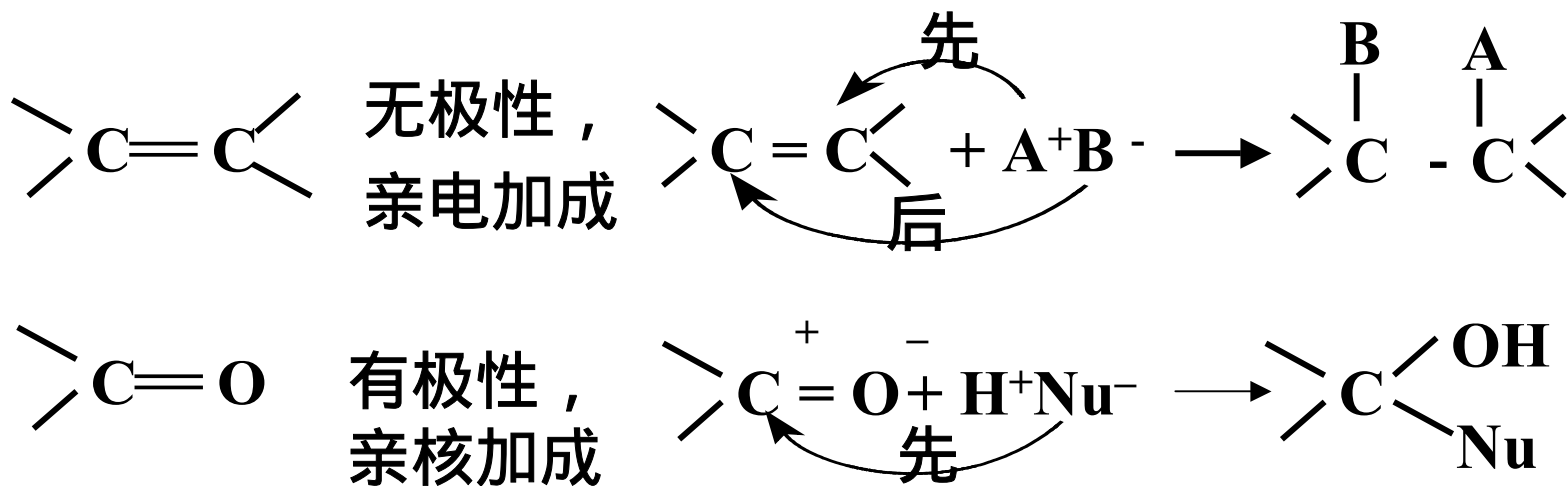


# 讨论：亲电加成与亲核加成的区别

相同点：

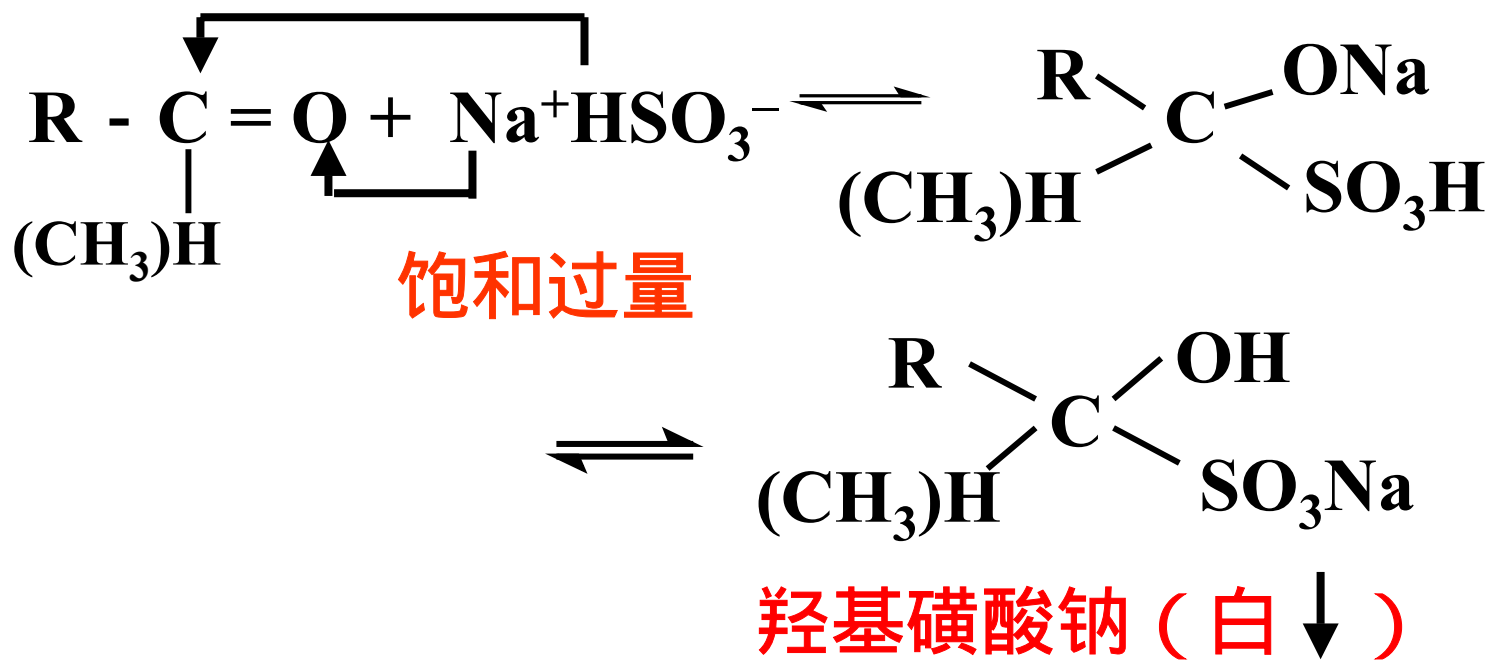
共价键的组成相同 { 一个 键  
                                  一个 键：加成

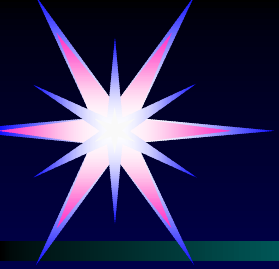
不同点：



## (2) 与NaHSO<sub>3</sub>加成：

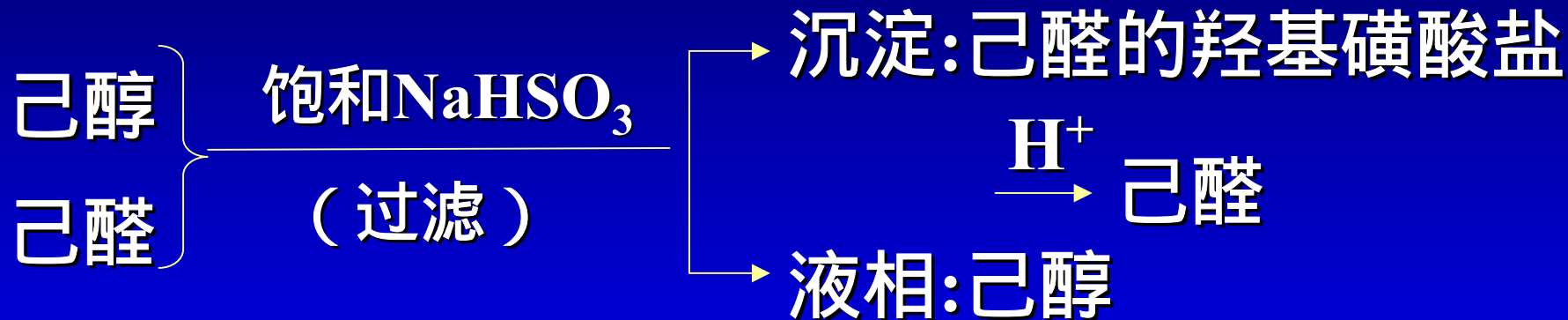
醛、甲基酮，C<sub>8</sub>以下环烷酮





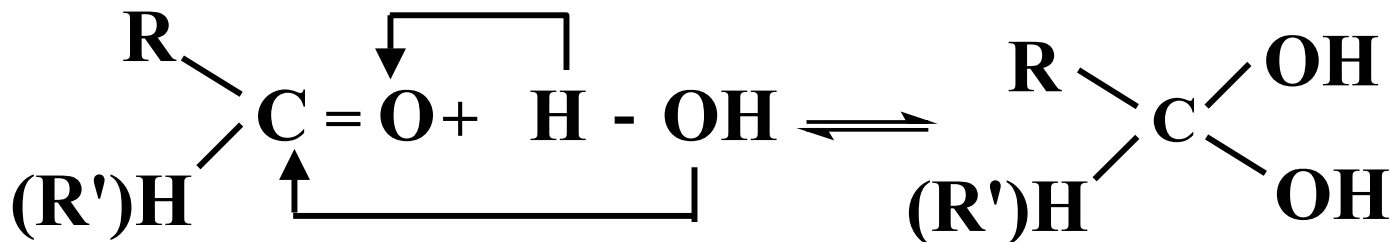
# 用途：

## 分离提纯



鉴别：白色↓ 醛、甲基酮等。

### (3) 与H<sub>2</sub>O加成 醛与酮

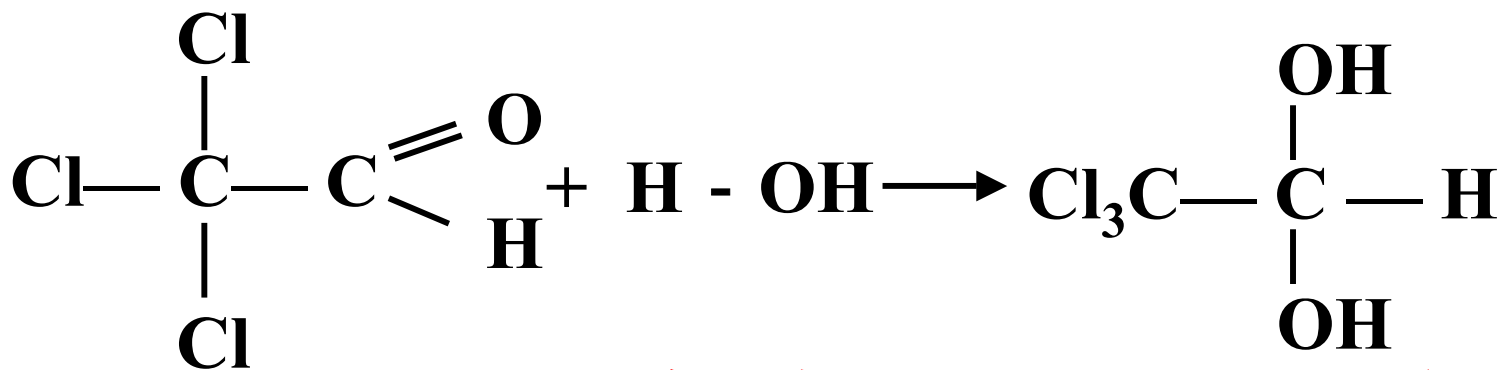


讨论： 双二醇不稳定

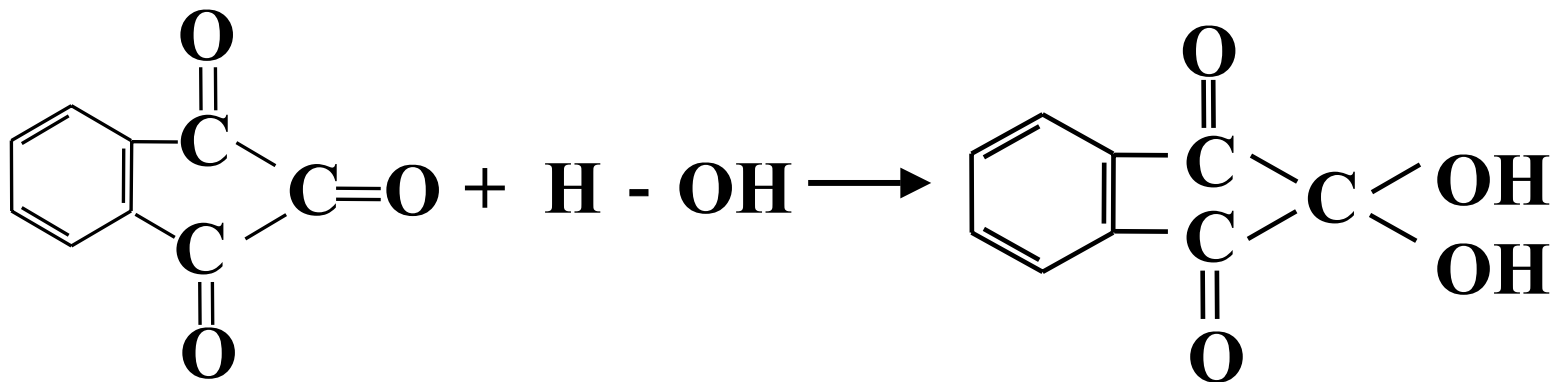
但R上连有吸电子基时，电子云密度得到分散，产物可稳定



### (3) 与H<sub>2</sub>O加成 醛与酮



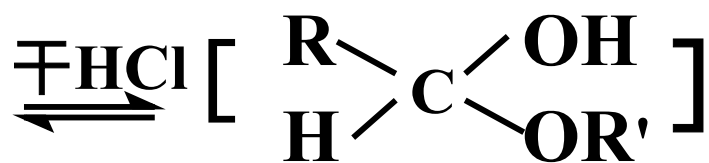
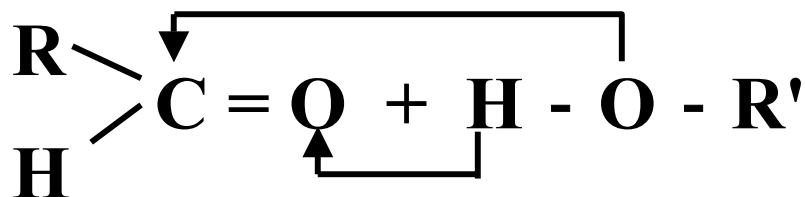
水合三氯乙醛 (催眠、止痛)



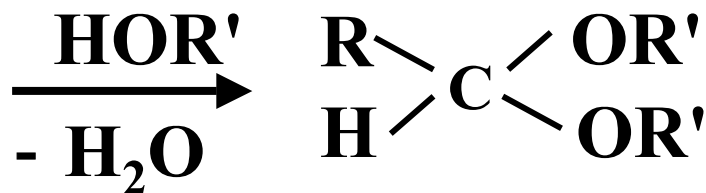
水合茛三酮 (鉴别 -氨基酸)

# (4) 与ROH加成

# 醛



半缩醛 { 羟基醚  
不稳定



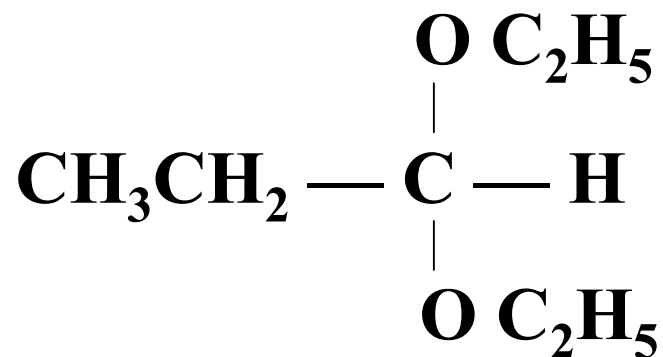
缩醛 { 双二醚  
性质稳定



## 用途：保护醛基

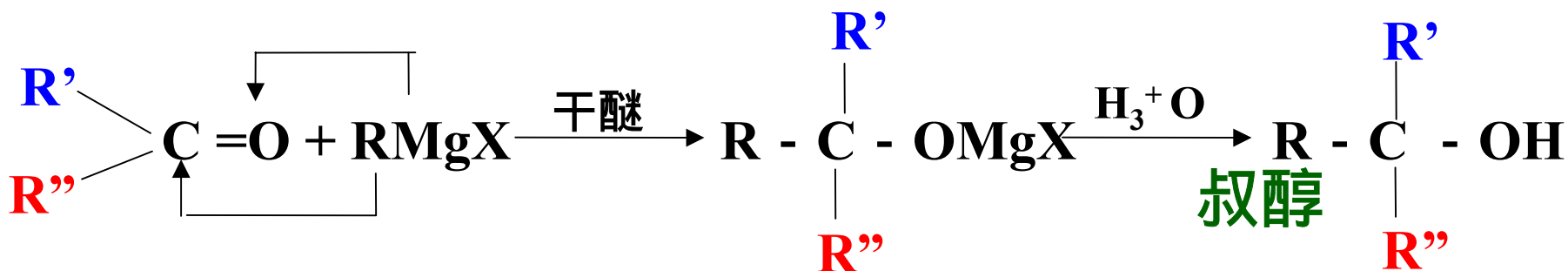
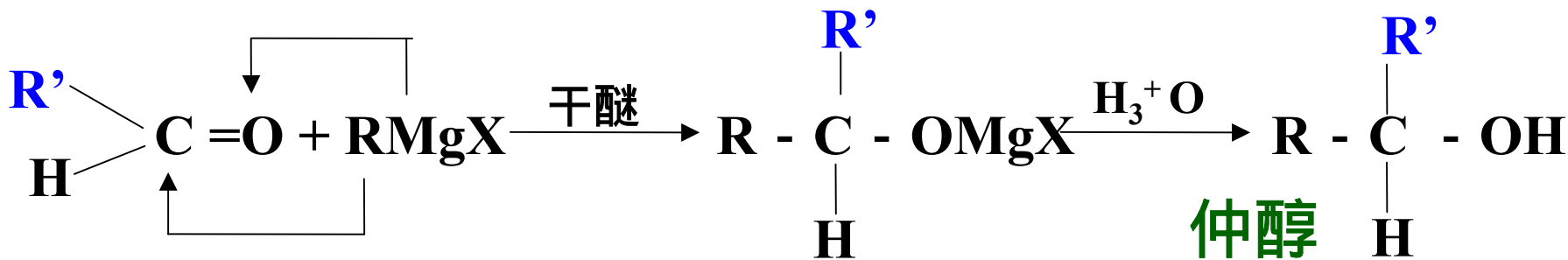
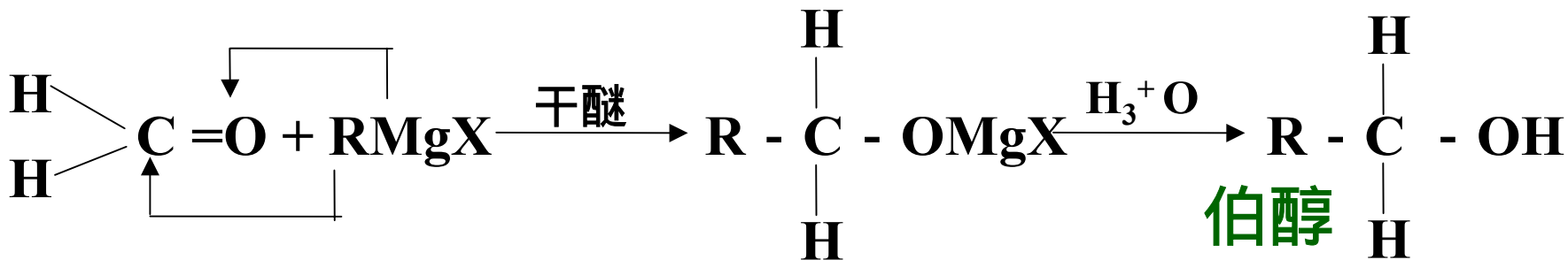
例如： $\text{HOCH}_2\text{CHO} \rightarrow \text{OHC}-\text{COOH}$

缩醛命名：



二乙醇缩丙醛  
(1, 1-二乙氧基丙烷)

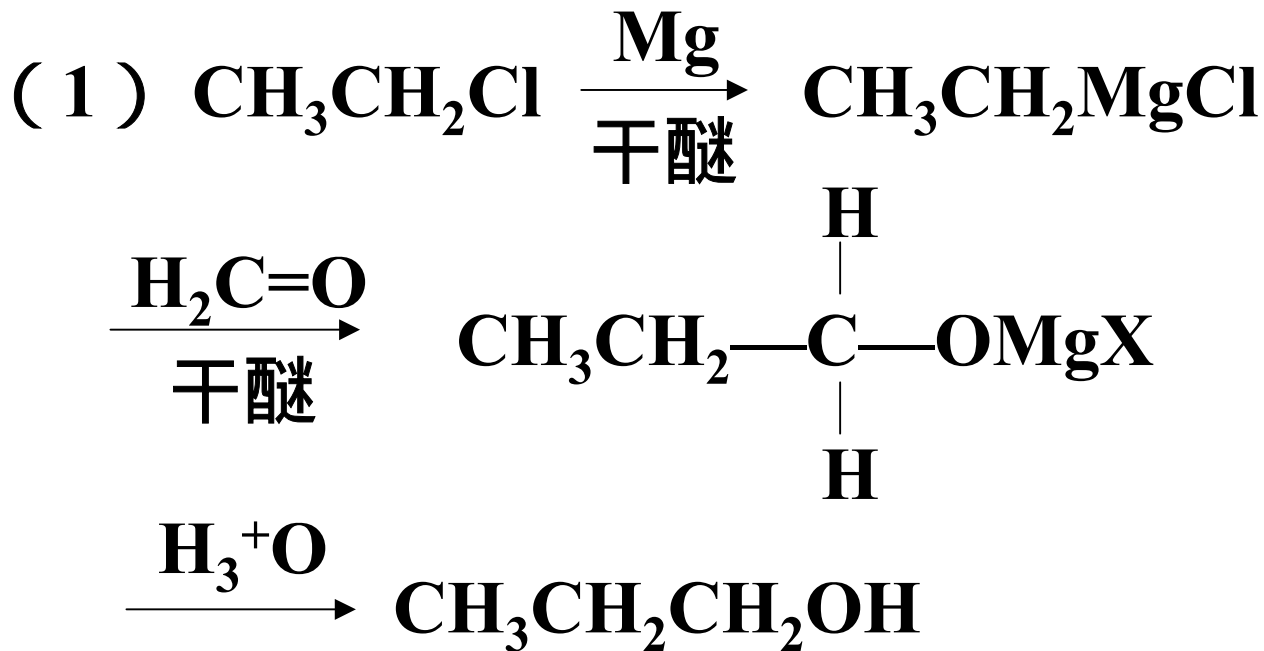
# (5) 与R - MgX 加成



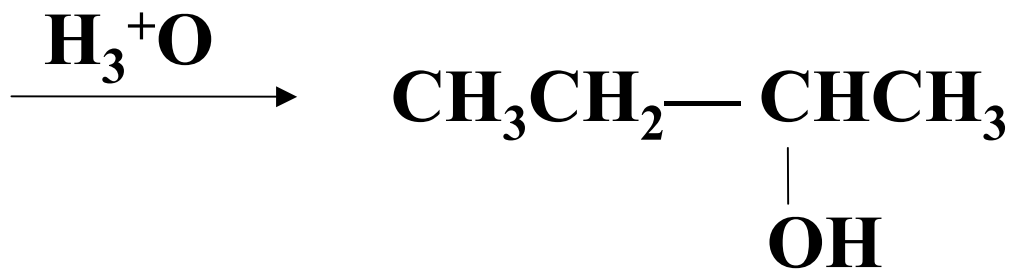
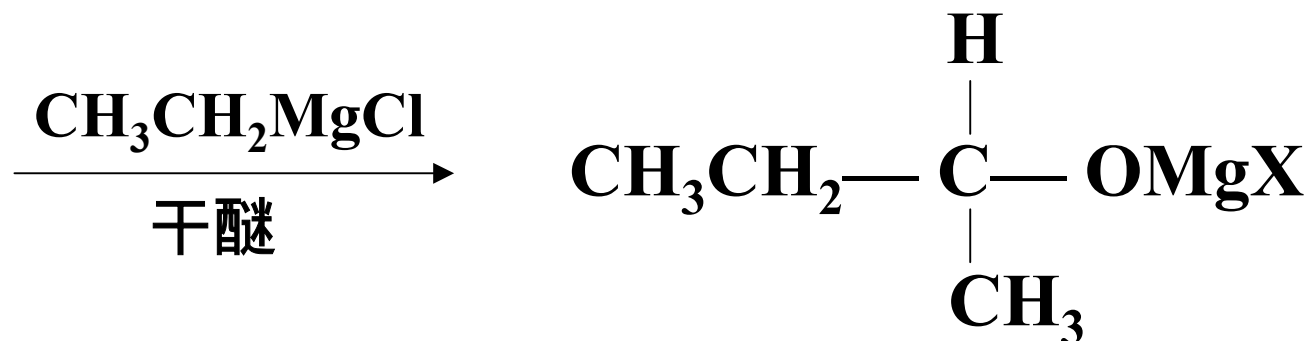
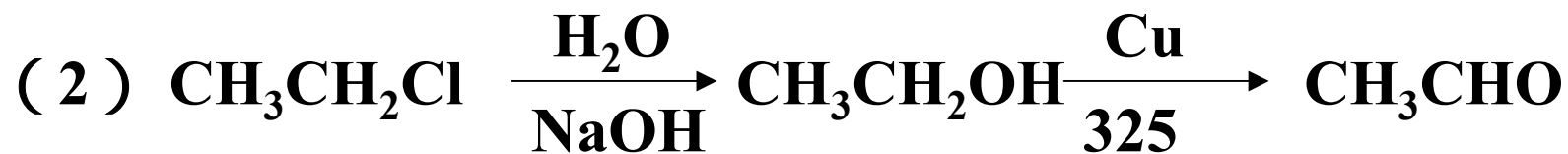


# 练习：

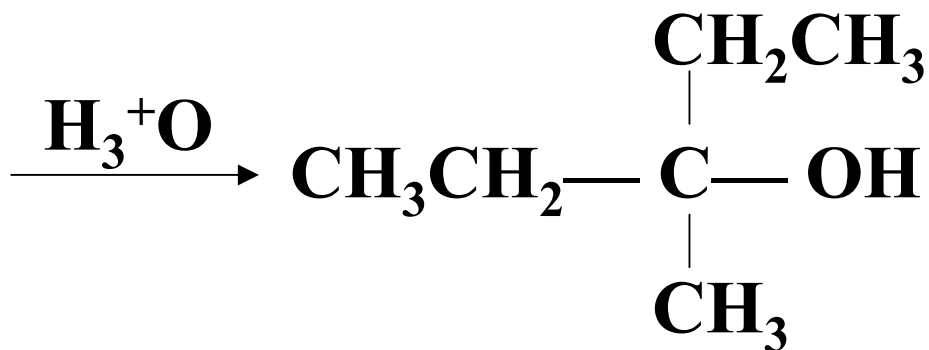
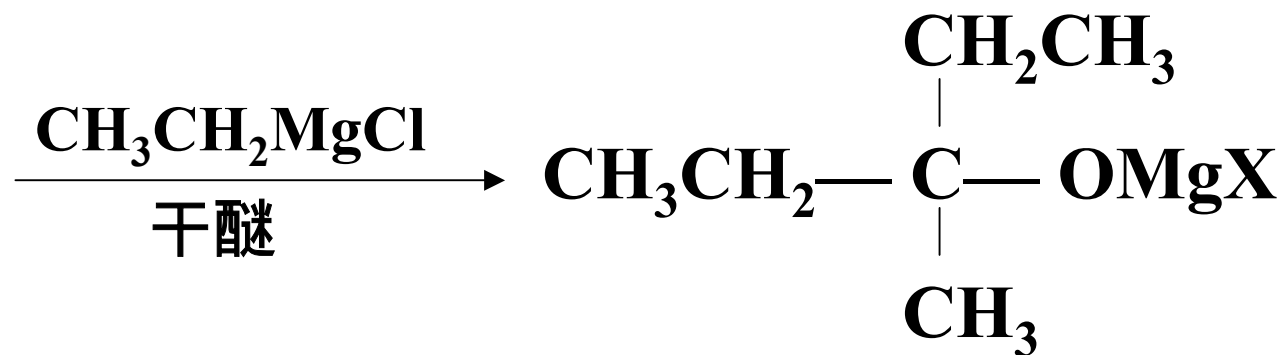
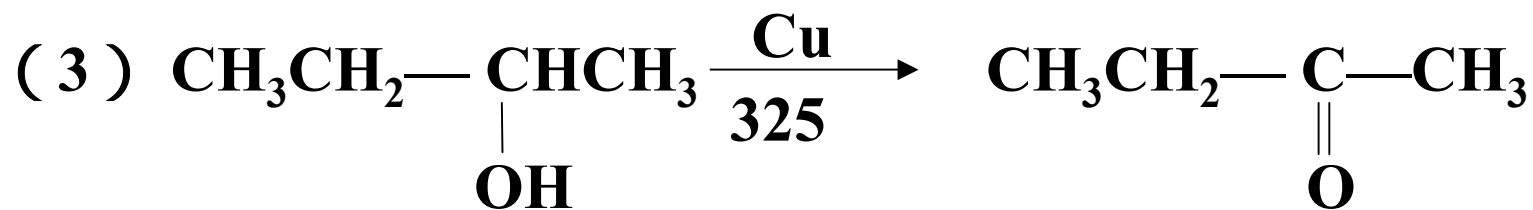
写出由氯乙烷合成丙醇、2 - 丁醇、3 - 甲基 - 3 - 戊醇的反应式。

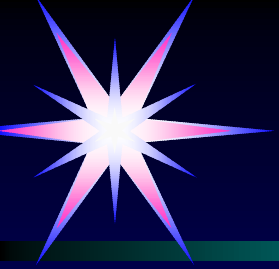


## 2 - 丁醇



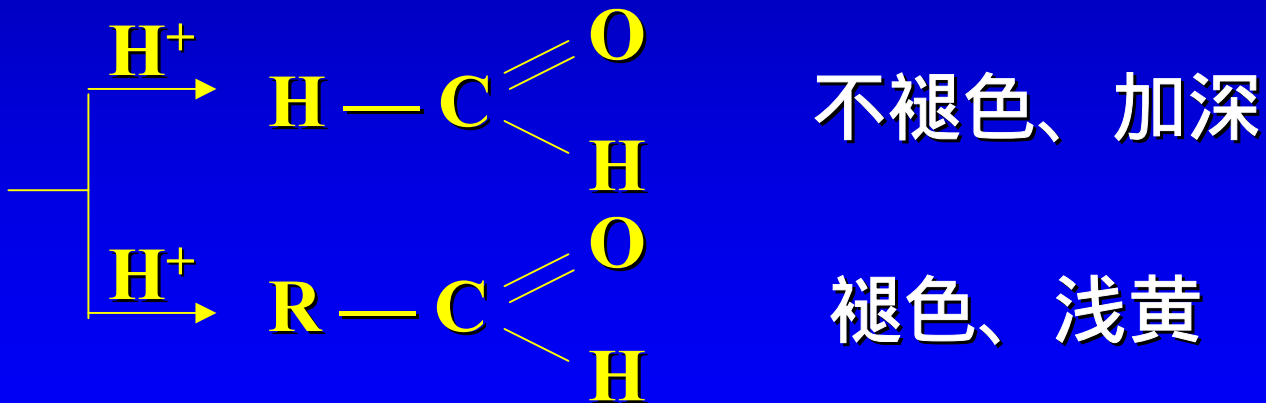
# 3 - 甲基 - 3 - 戊醇





## (6) 与品红试剂反应

希夫试剂： 品红溶液  $\xrightarrow{\text{SO}_2}$  品红试剂  
(红) (无)

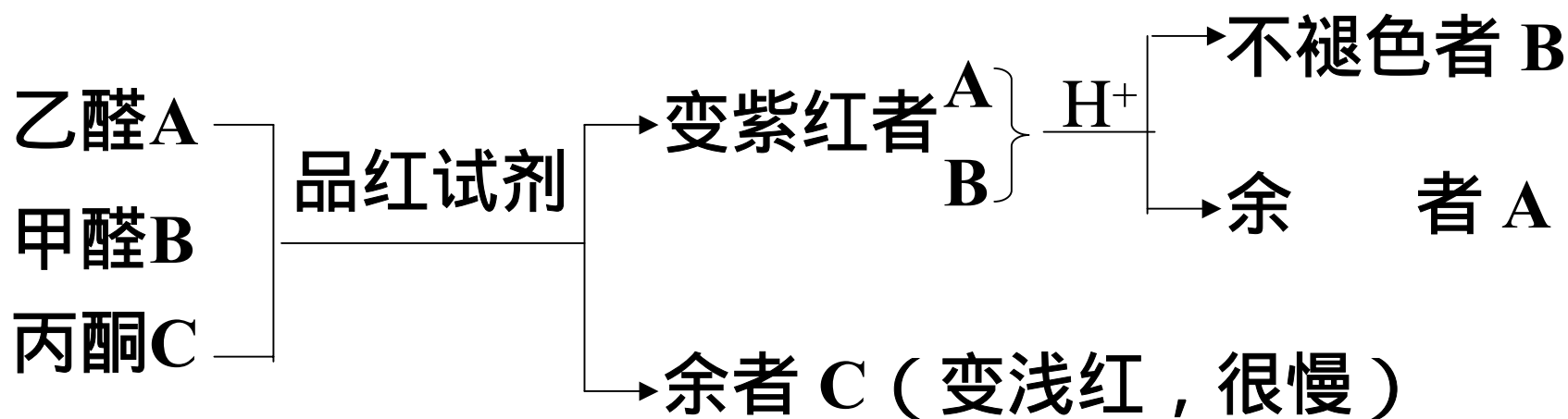




# 用途：

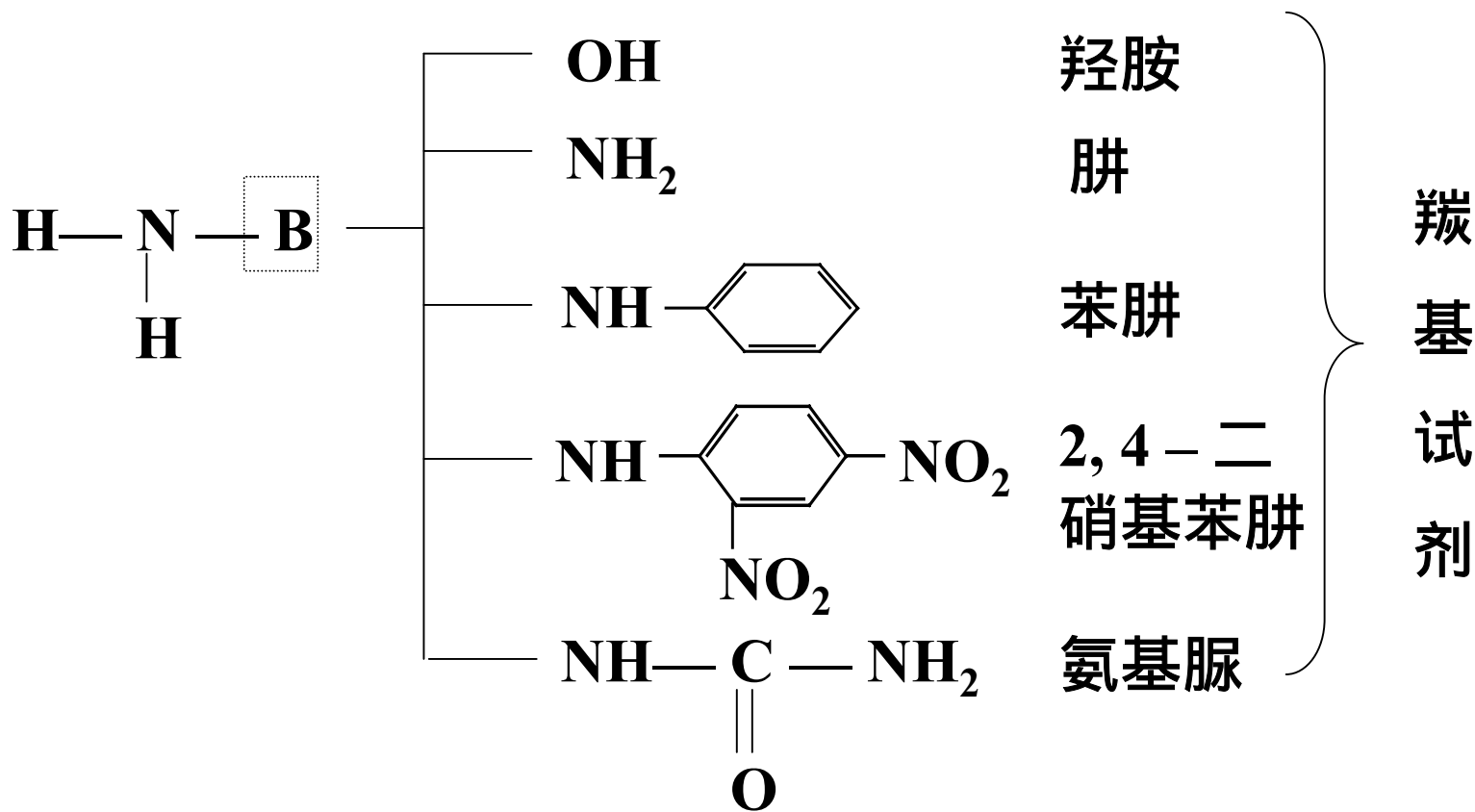
## 鉴别醛，区别甲醛与他醛

用化学方法鉴别下列化合物：

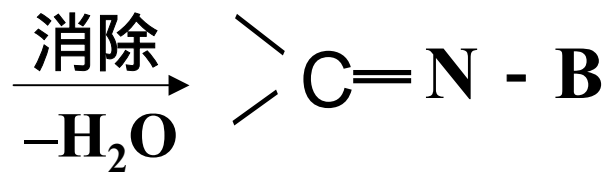
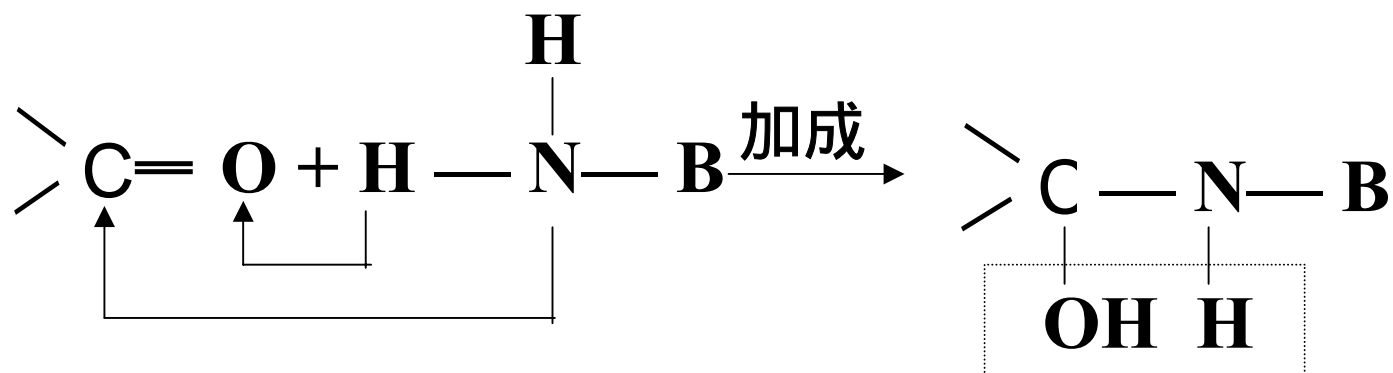


## 2、加成—消除反应

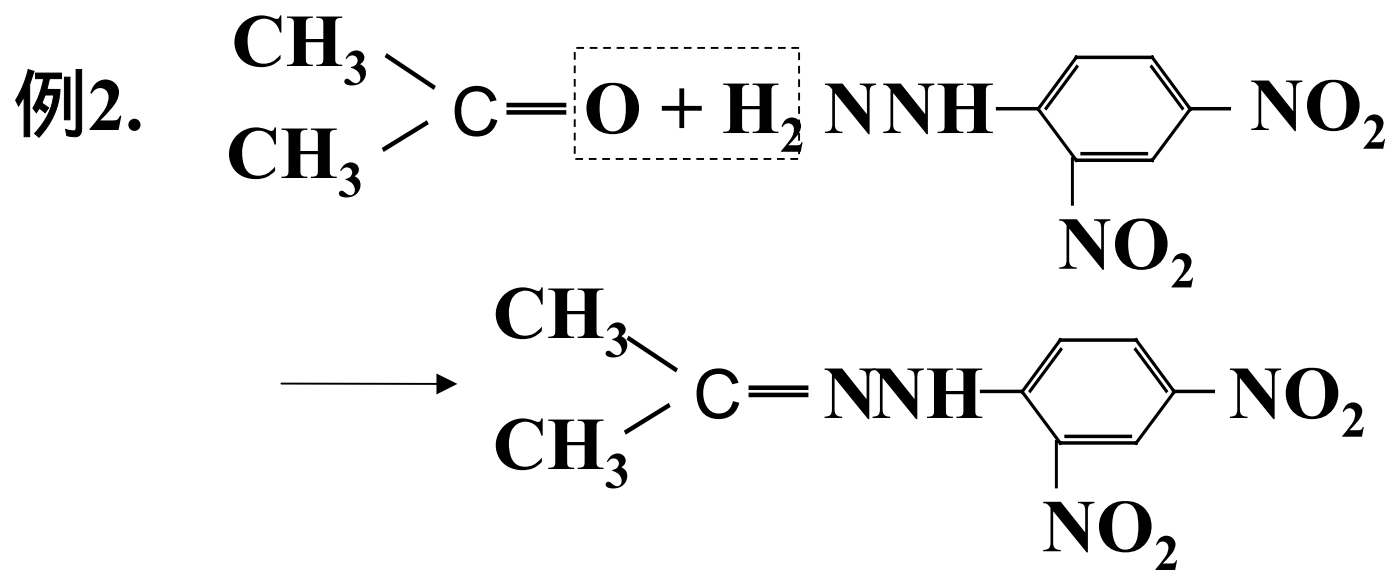
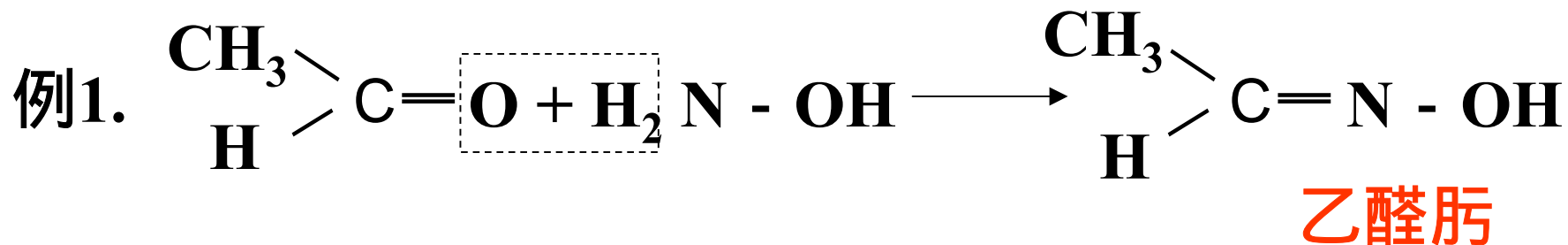
## 醛 酮



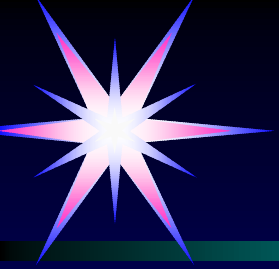
通式：



# 例题



丙酮-2, 4 - 二硝基苯腙

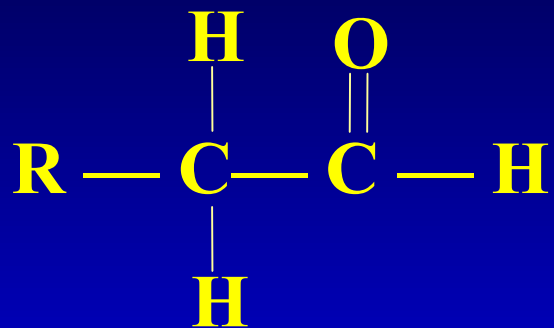


## 用途：

- (1) 鉴别：白 ，黄↓ (2,4-二硝基苯肼)
- (2) 分离提纯



### 3、 — 活泼氢的反应

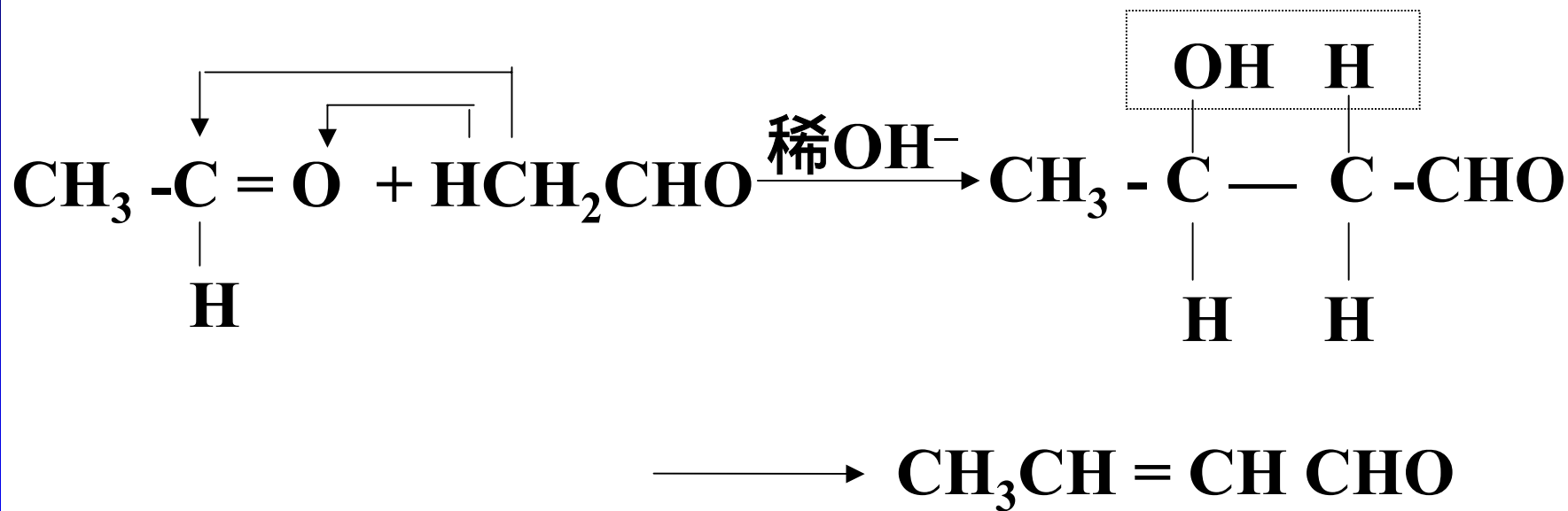


活泼原因： $-I$ ， $\sigma-\pi$



# (1) 羟醛缩合反应

## 相同分子间缩合



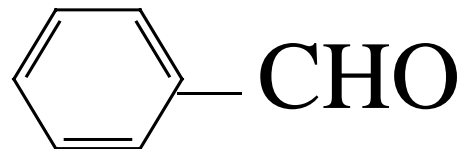
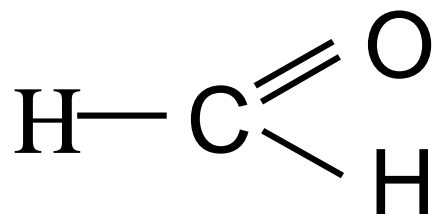
用途：制不饱和醛，增碳反应。



# 条件：

- 一分子有  $\text{>C=O}$ ；
- 另一分子有  $\text{-H}$ 。

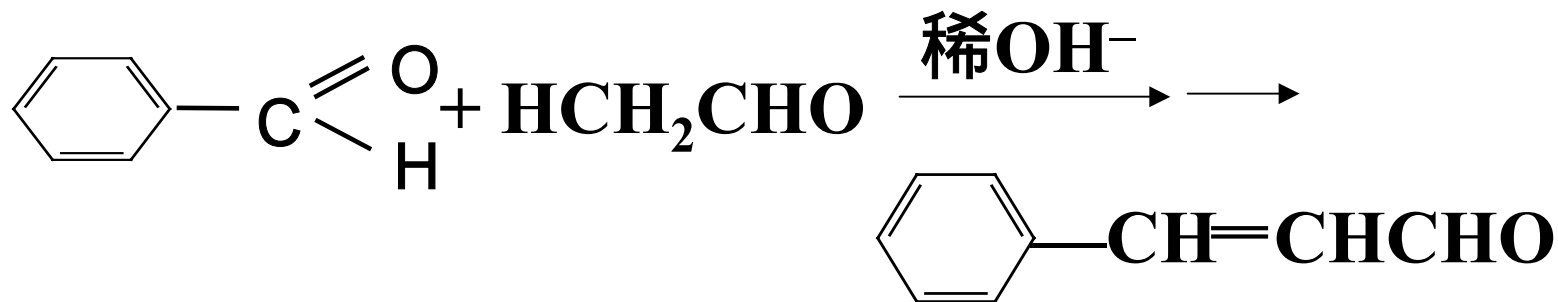
如：



$\text{OHC}-\text{CHO}$  等本身不能缩合



# 不同分子间交叉缩合



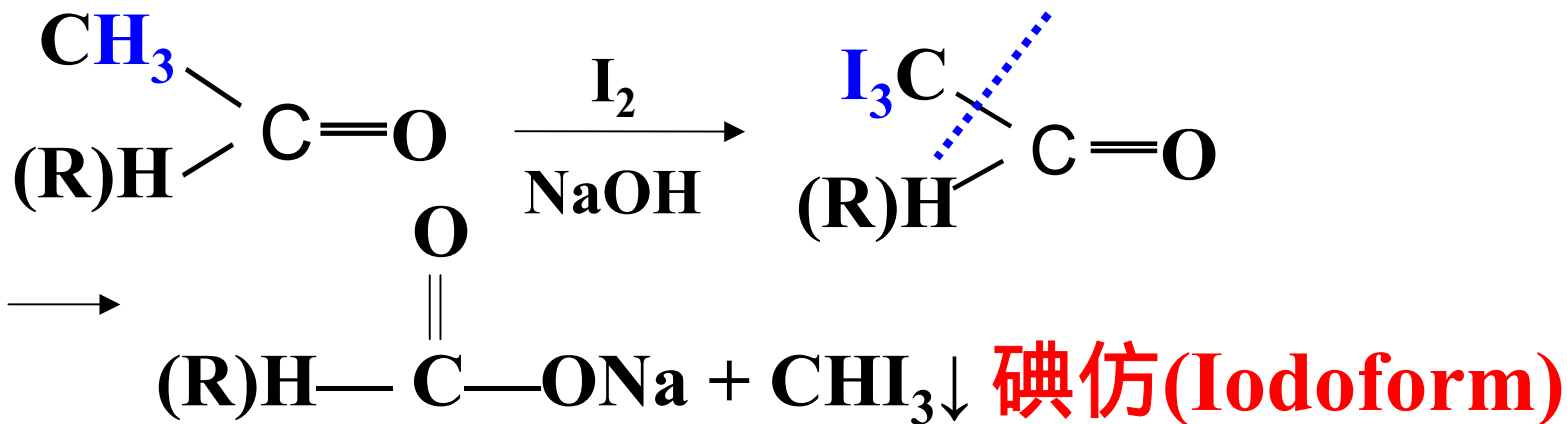
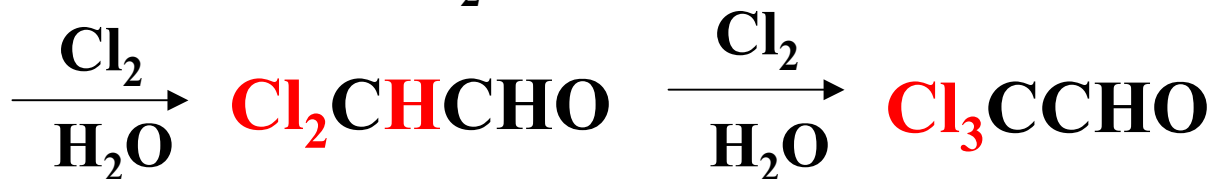
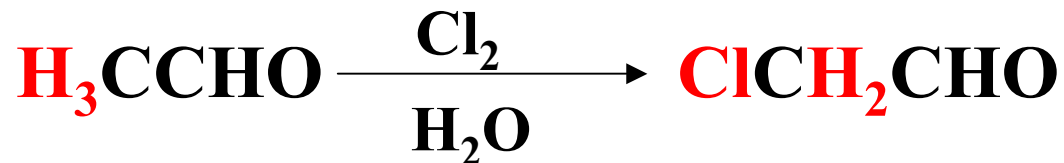
用途：增碳反应

生物体：磷酸二羟丙酮和磷酸甘油

醛交叉缩合成果糖

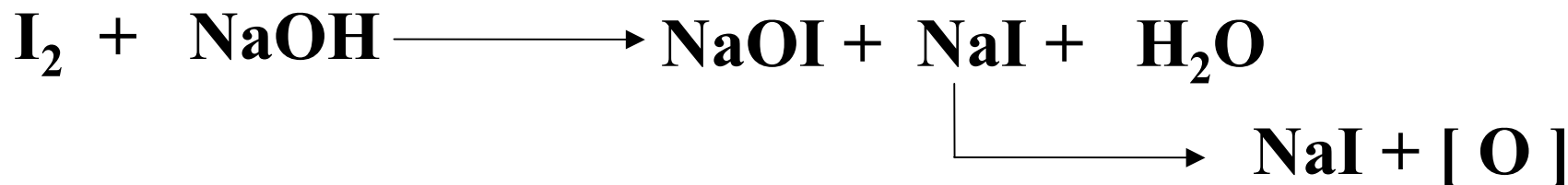
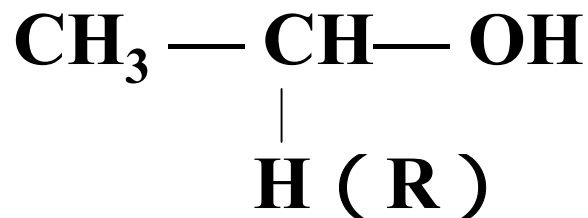
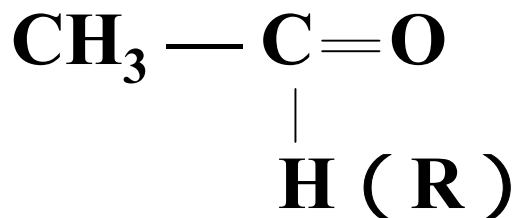
制作：付蕾 朱凤岗

## (2) 卤代反应





# 范围



用途： 减碳反应

鉴别：淡黄↓



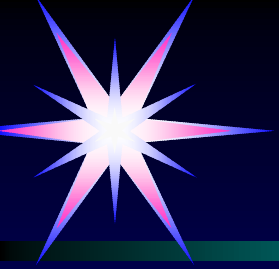
## 4、氧化还原反应

(1) 氧化反应 醛用弱氧化剂氧化

多伦试剂 (Tollens) 适用于所有醛

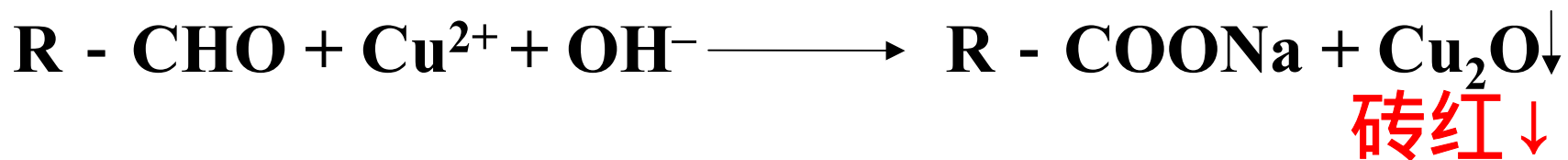


金属银



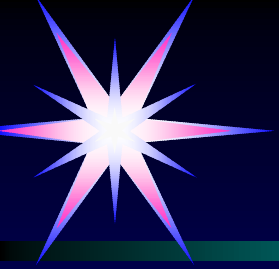
# 氧化反应

斐林试剂 (Fehling) 芳醛不反应



斐林试剂 {  
A.  $\text{CuSO}_4$   
B.  $\text{NaOH}$  + 酒石酸钾钠

用时等体积混合



# 氧化反应

## 班乃狄克试剂 (Benedict)

成份： $\text{Na}_2\text{CO}_3$   $\longrightarrow$   $\text{NaOH}$

柠檬酸钠  $\longrightarrow$  酒石酸钾钠

试剂较稳定，短时间内合在一起可使用。



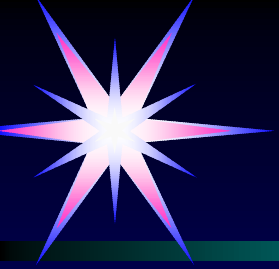
用途：

鉴别醛类

制备不饱和酸



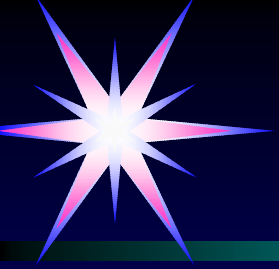
只氧化醛基，不影响双键。



练习：

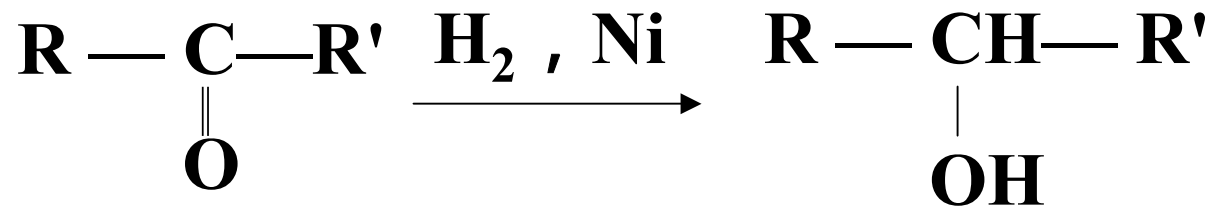
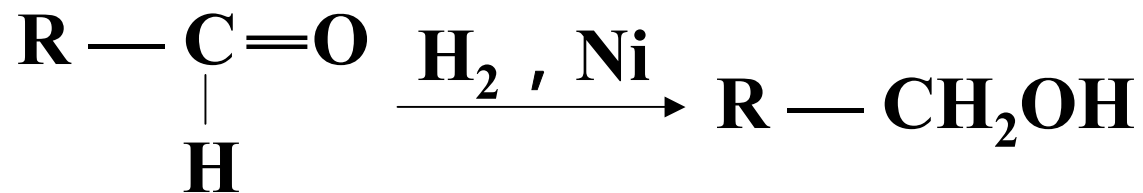






## (2) 还原反应 (醛、酮)

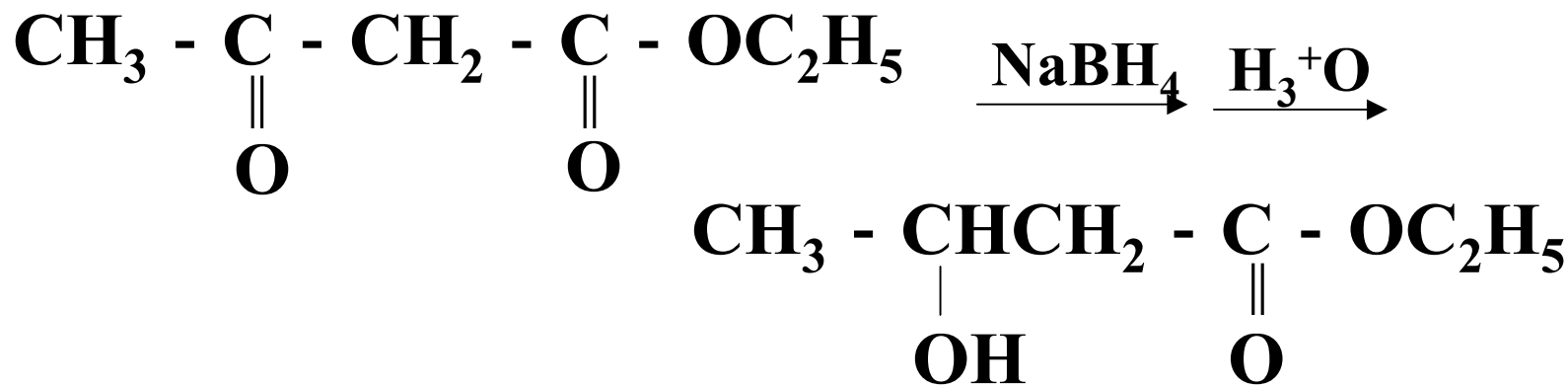
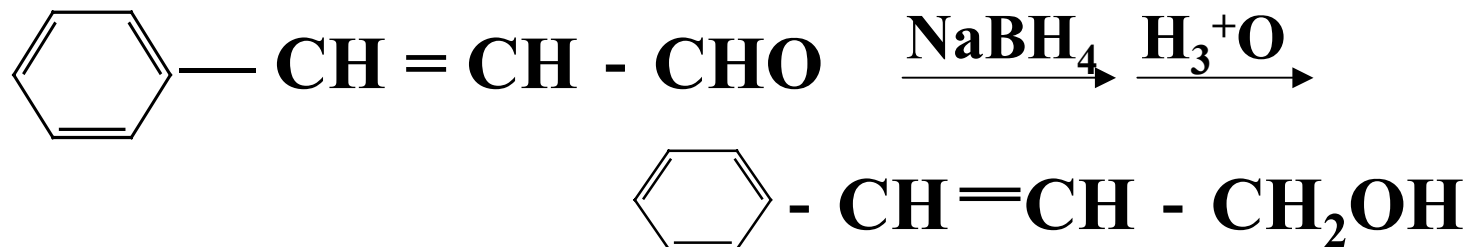
催化氢化：无选择性， $C=C$ ，  
 $C-N$ ， $C=O$ 均可还原



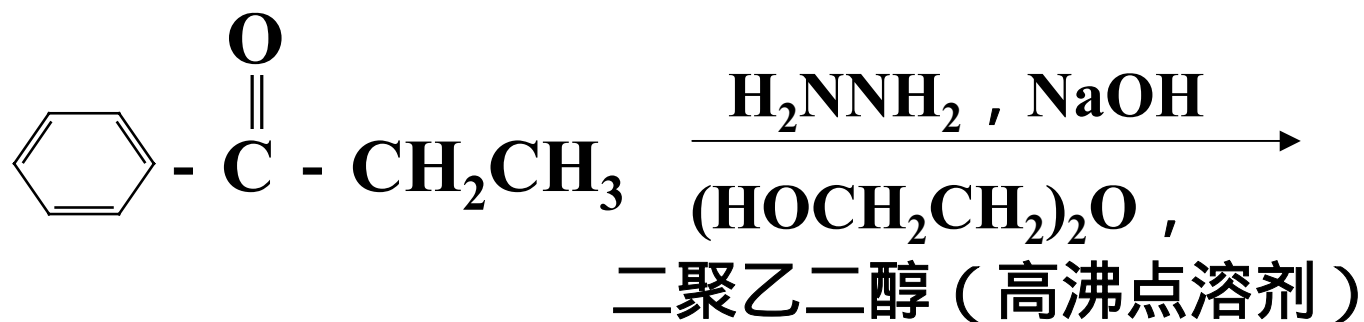
# 金属氢化物

# NaBH<sub>4</sub> (硼氢化钠)

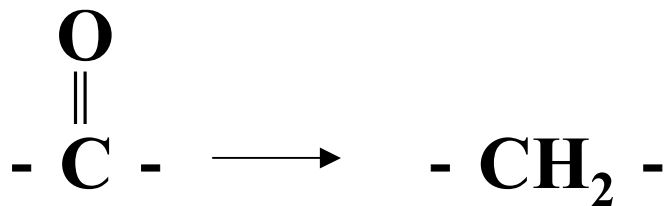
优点：缓和，选择性好，效果好，只还原  $\text{>C=O}$



# 沃尔夫—凯惜纳—黄鸣龙反应



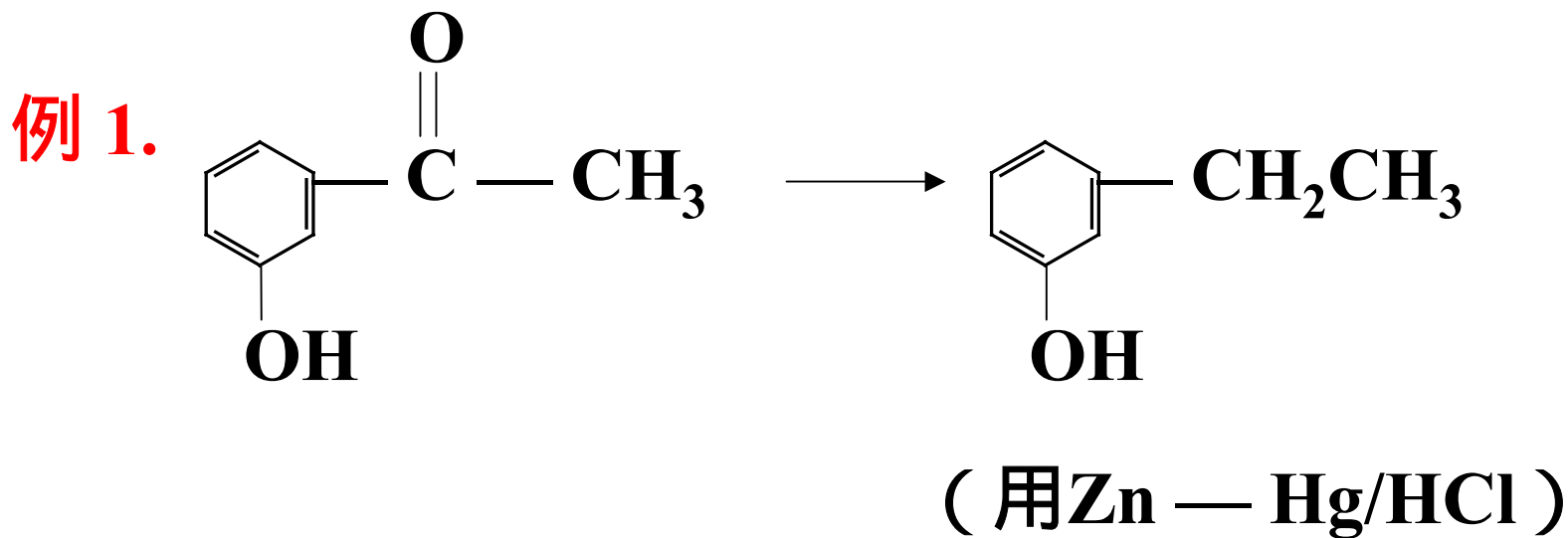
反应部位



# 克莱门森还原法 (Zn - Hg / HCl)

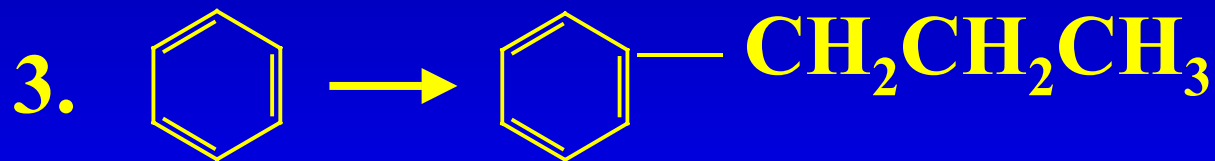
对碱敏感时可用克莱门森还原法 (锌汞齐)

如：酚羟基 (—OH), 双键



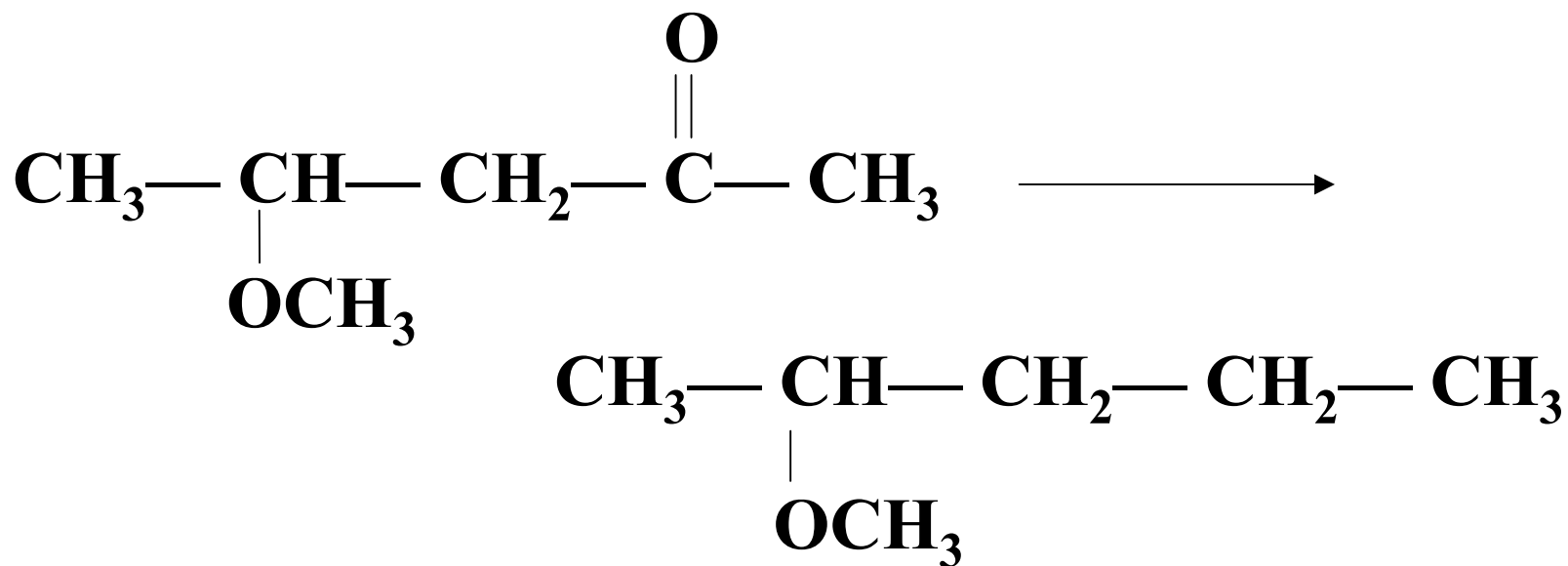


# 练习：





# 练习：



(用沃尔夫—凯惜纳—黄鸣龙试剂)

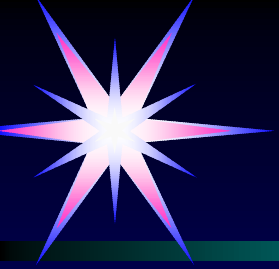


### (3) 岐化反应 (Cannizzaro)

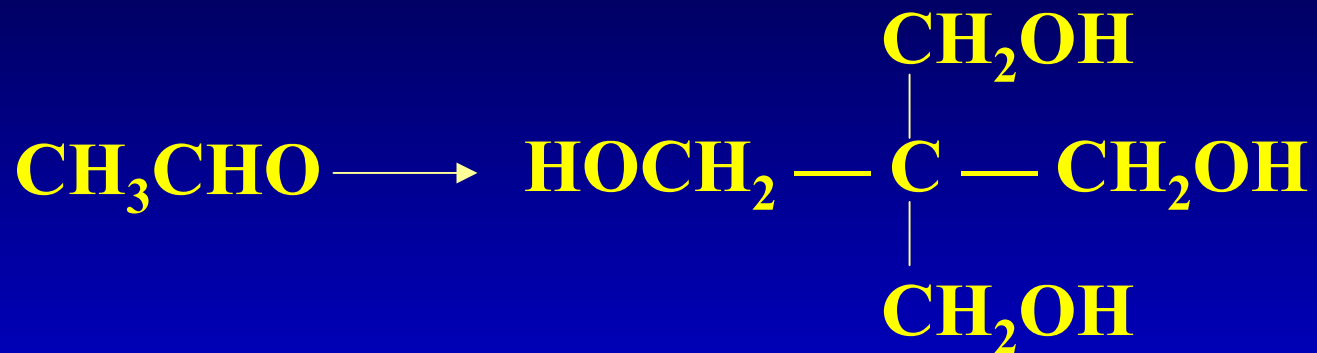
条件：无  $\alpha$ -H 的醛



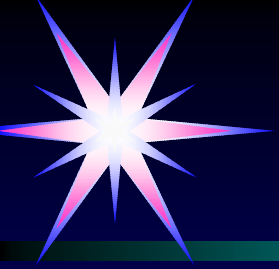
大分子还原    小分子氧化



# 练习：







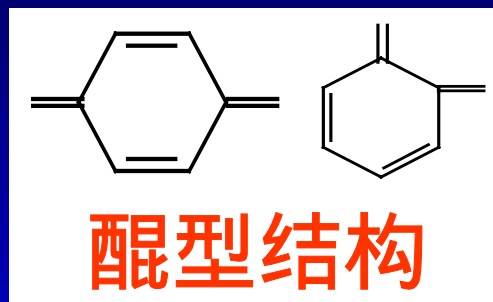
## 第二节 醌 (Quinones)

- 一、醌的结构和命名  
( Structure and nomenclature )
- 二、醌的化学性质  
( Reactions of quinones )

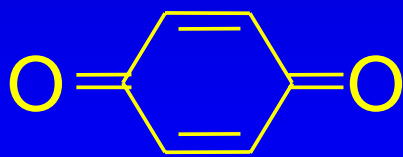
# 一、醌的结构和命名

## ( Structure and nomenclature )

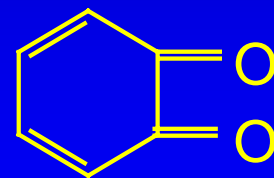
结构：特殊的环状  
不饱和二酮



命名：位置—芳环名称—醌



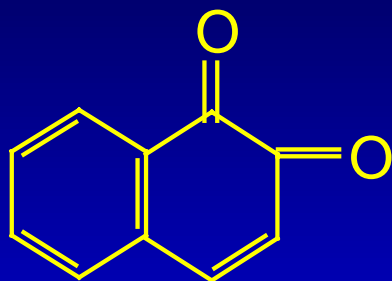
1,4-苯醌



1,2-苯醌

# 一、醌的结构和命名

## ( Structure and nomenclature)



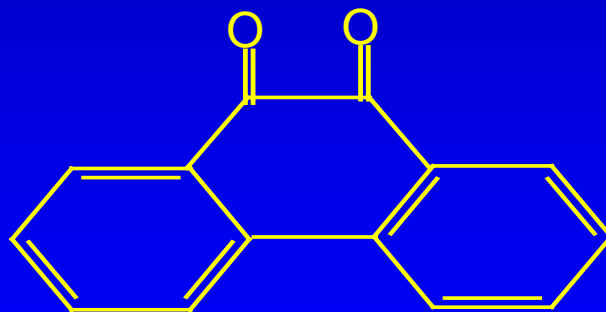
1, 2 - 萘醌



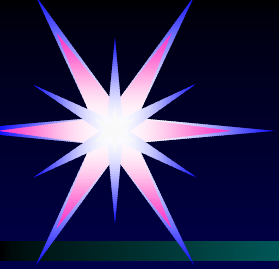
1, 4 - 萘醌



9, 10 - 蒽醌



9, 10 - 菲醌



## 二、化学性质

### ( Reactions of quinones)

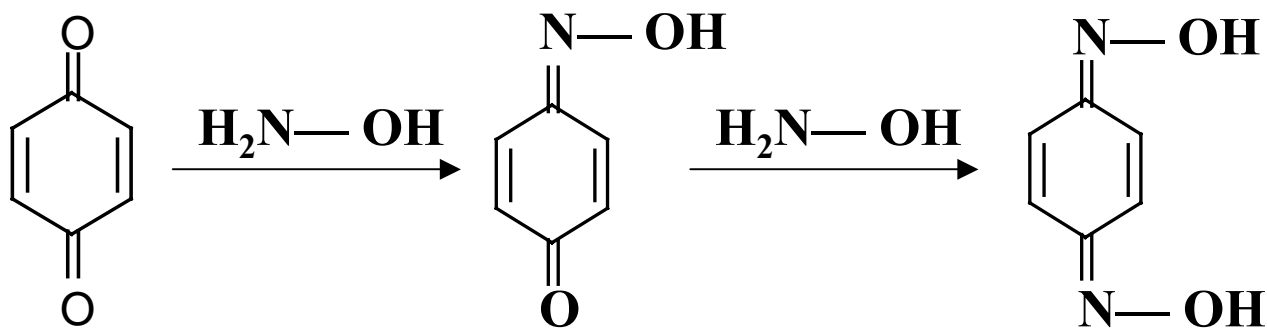
结构分析：



具羰基和烯的性质

# 1、加成反应

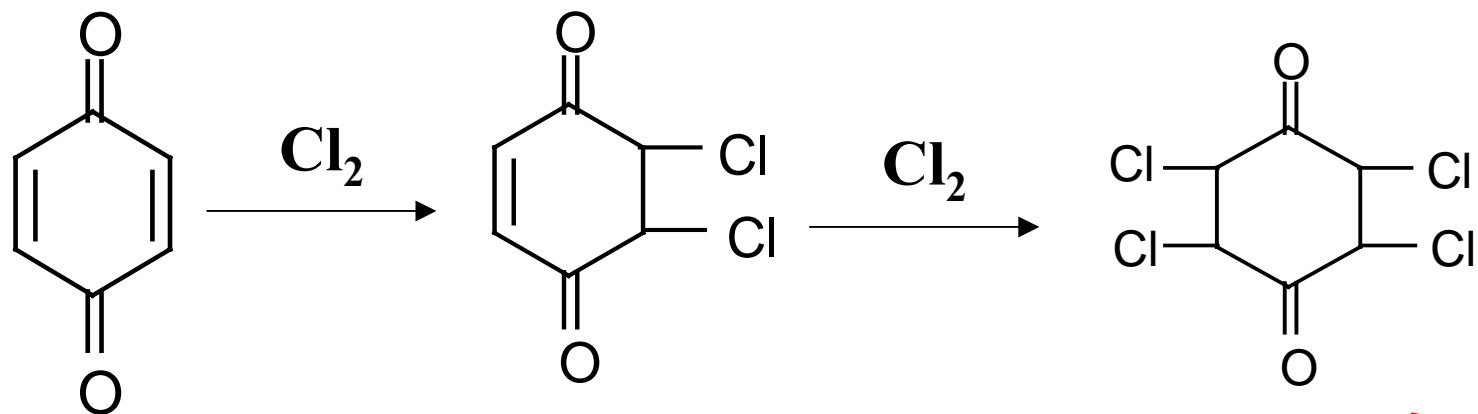
## (1) 羰基加成



对苯醌单肟

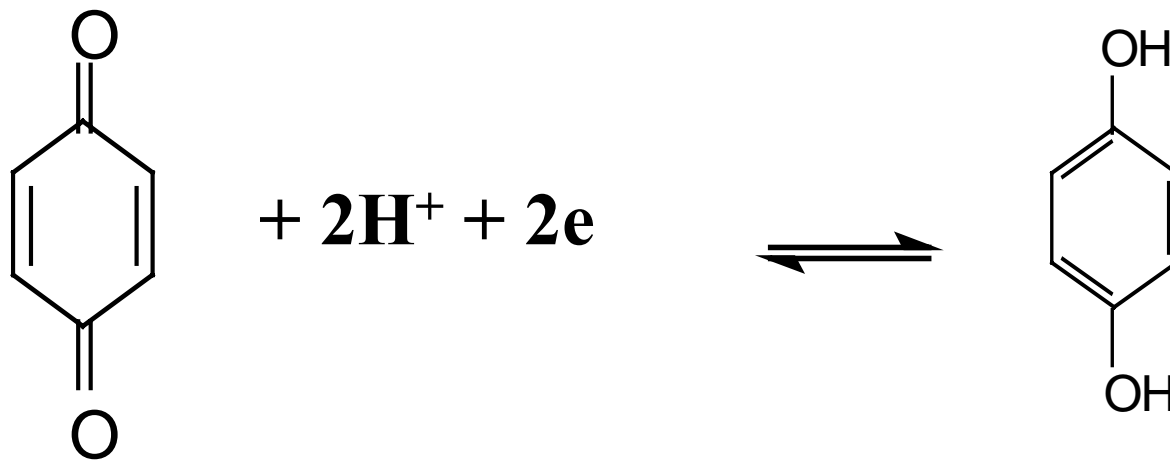
对苯醌双肟

## (2) 烯键加成

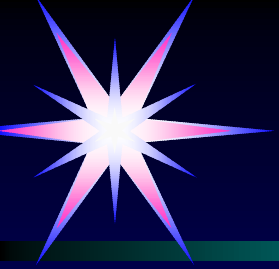


2, 3, 5, 6 - 四氯  
-1, 4 - 环己二酮

## 2、还原反应



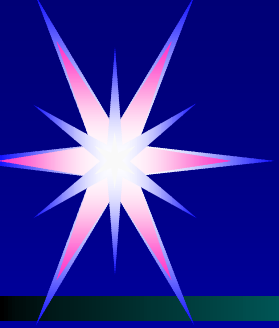
用途：在生物氧化过程中起传递氢的作用。



# 第八章 重点讲解问题

1. 醛和酮的命名
2. 醛和酮的化学性质
3. 醌的结构、命名和化学性质





再见  
Good-bye

