

第十三章

(Chapter 13)

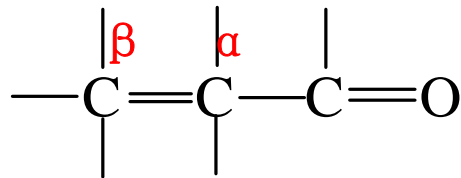


不饱和醛酮及取代醛酮

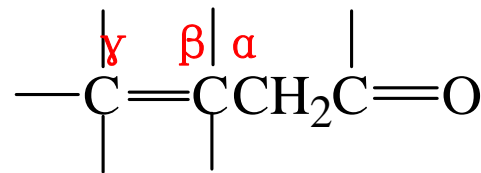
Unsaturated aldehydes and ketones and aldehydes
and ketones with substituent

§ 13.1 α , β -不饱和醛酮

α , β -unsaturated aldehydes and ketones

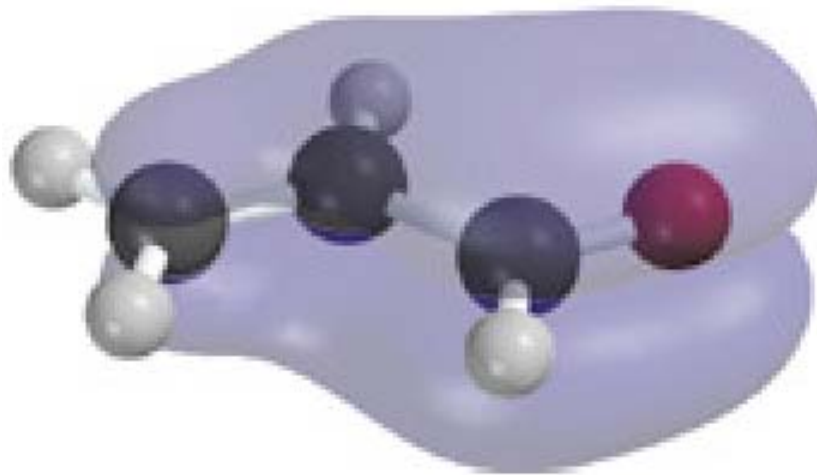


α , β -不饱和醛酮



β , γ -不饱和醛酮

较稳定

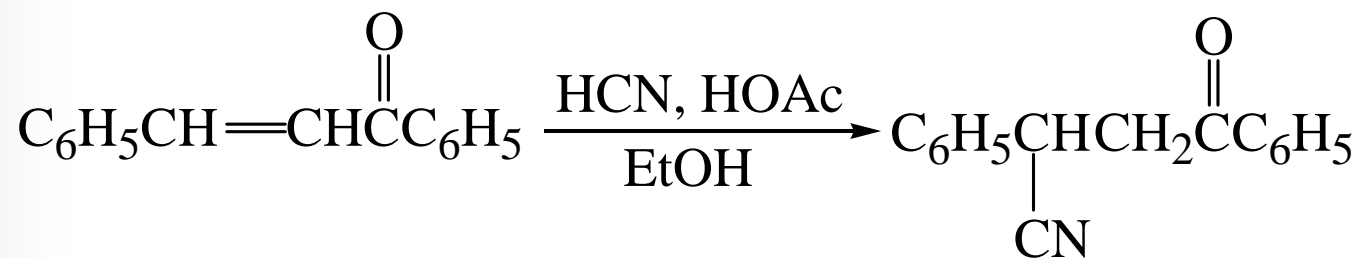


丙烯醛 (Acrolein, $\text{H}_2\text{C}=\text{CHCH}=\text{O}$)

一、 α , β -不饱和醛酮的反应 (Reactions of α , β -unsaturated aldehydes and ketones)

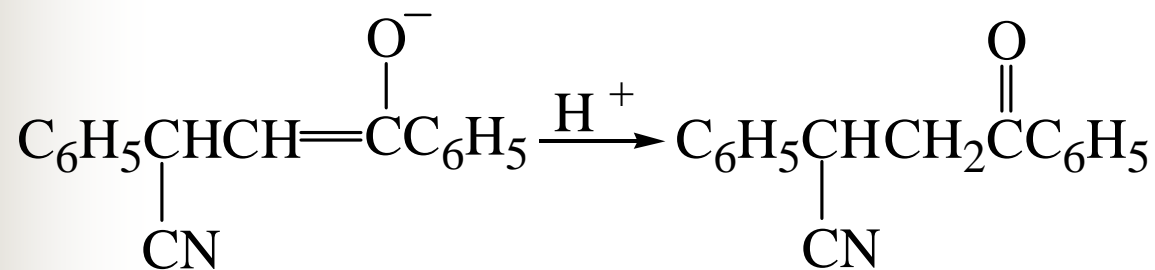
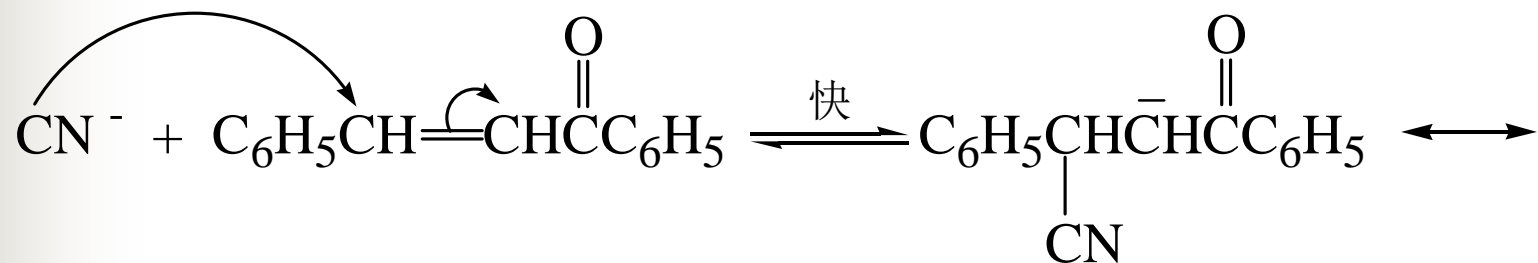
1. 加氢氰酸 (Addition of hydrogen cyanide)

一般只生成1,4-加成 (1, 4-addition, conjugate addition) 产物



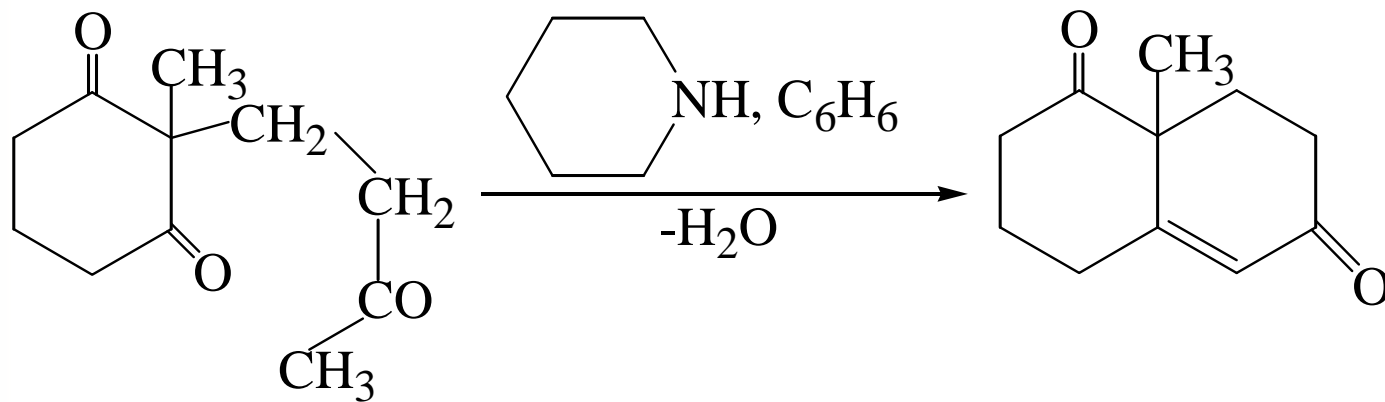
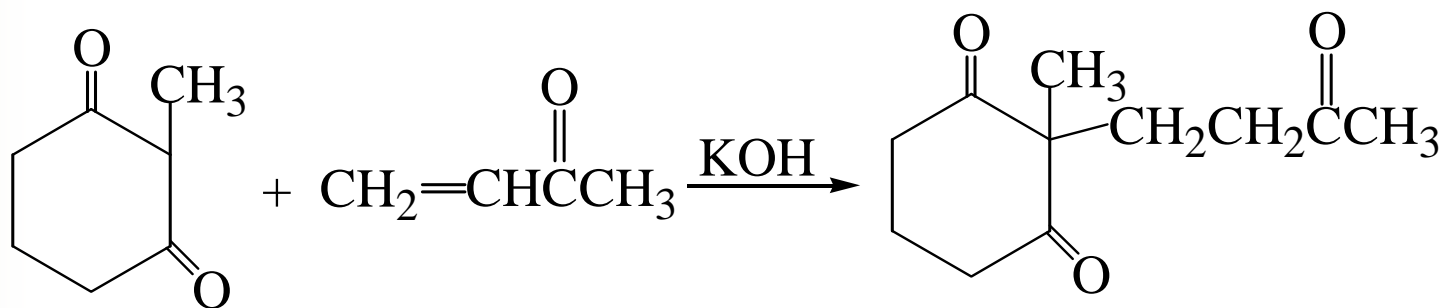
1,3-Diphenyl-2-propen-1-one 4-Oxo-2,4-diphenylbutanenitrile

机理 (Mechanism):



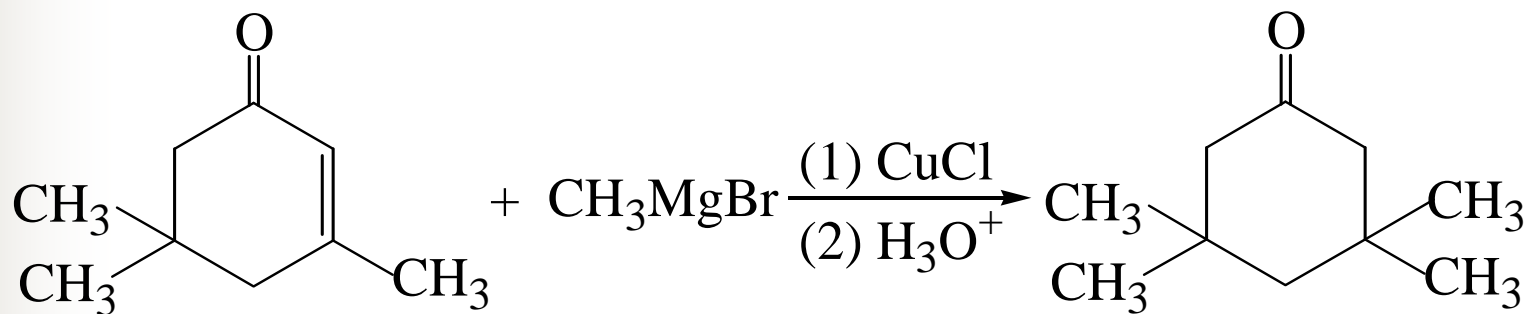
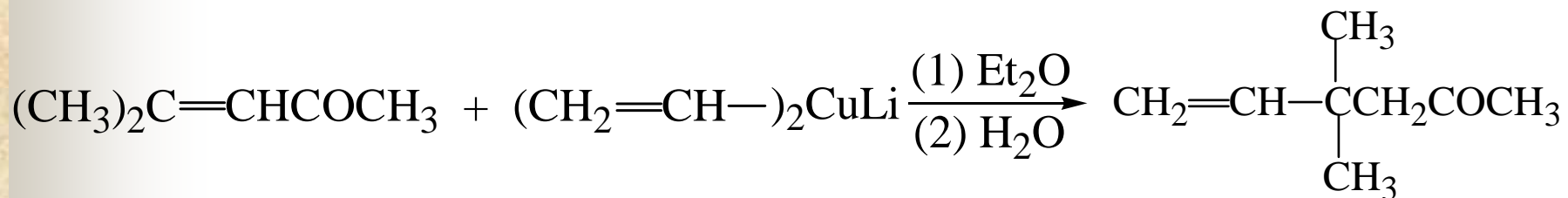
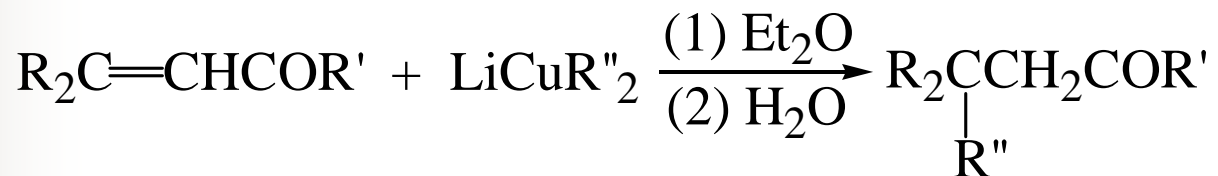
2. 迈克尔反应 (The Michael reaction)

烯醇负离子与 α, β -不饱和羰基化合物的1,4-加成称为迈克尔反应。



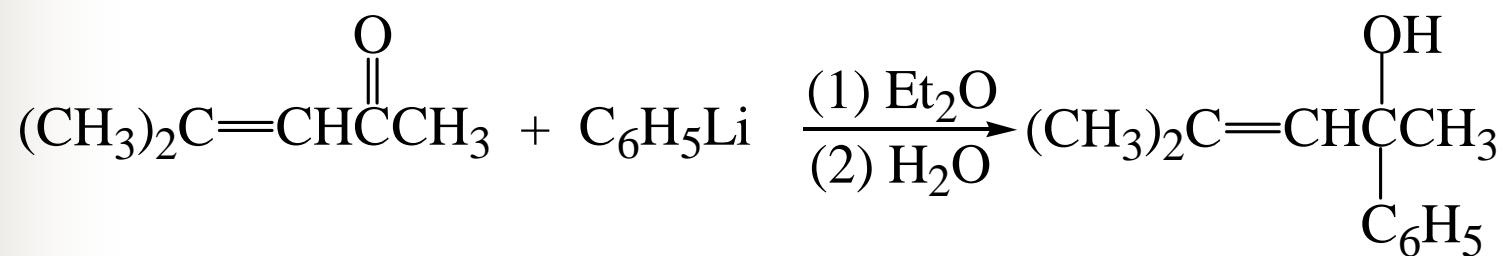
3. 与二烷基铜锂的反应 (Addition of lithium dialkylcuprates)

1,4-加成

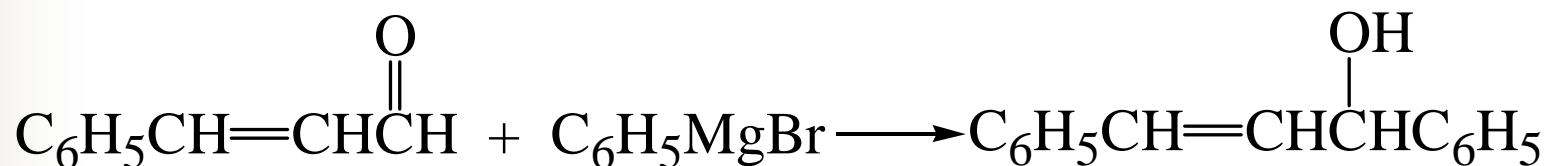


4. 与烷基锂和格利雅试剂的反应 (Addition of alkyllithium or Grignard reagents)

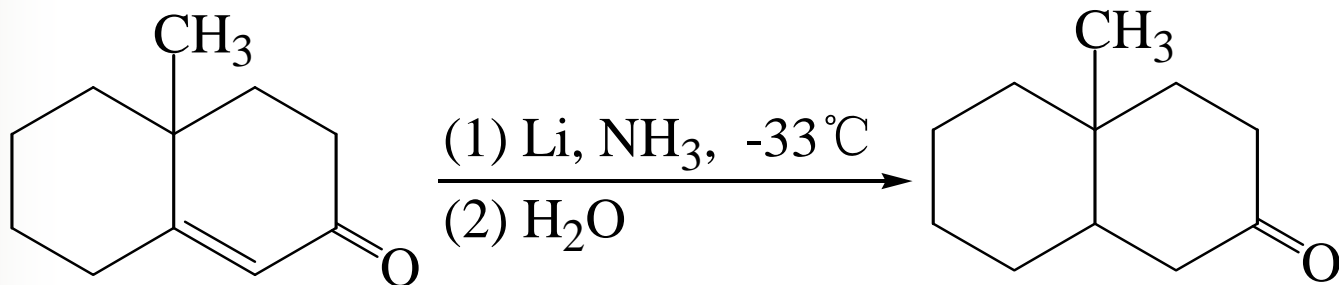
烷基锂与 α, β -不饱和醛酮起1, 2-加成反应(1, 2-addition, direct addition)



用高纯度的镁制备的格利雅试剂与 α, β -不饱和醛酮起1, 2-加成反应

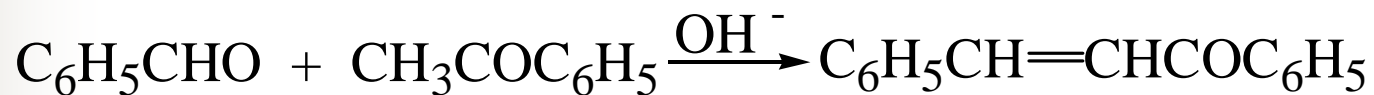


5. 还原 (Reduction of α, β -unsaturated aldehydes and ketones)



二、 α , β -不饱和醛酮的制法 (Preparation of α , β -unsaturated aldehydes and ketones)

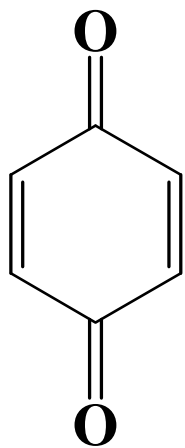
醛酮的羟醛缩合反应



§ 13.2 醌 (Quinones)

是一类特殊的环酮。

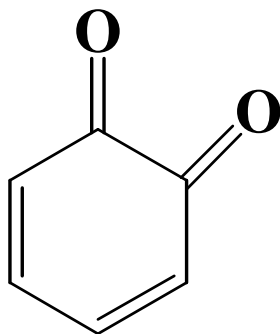
一、醌的命名 (Nomenclature of quinones)



对苯醌

1,4-苯醌

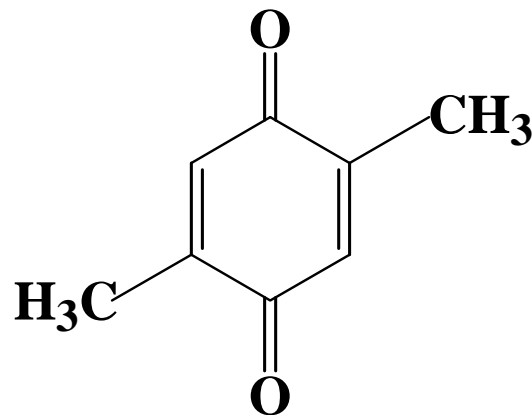
(1,4-benzoquinone)



邻苯醌

1,2-苯醌

(1,2-benzoquinone)



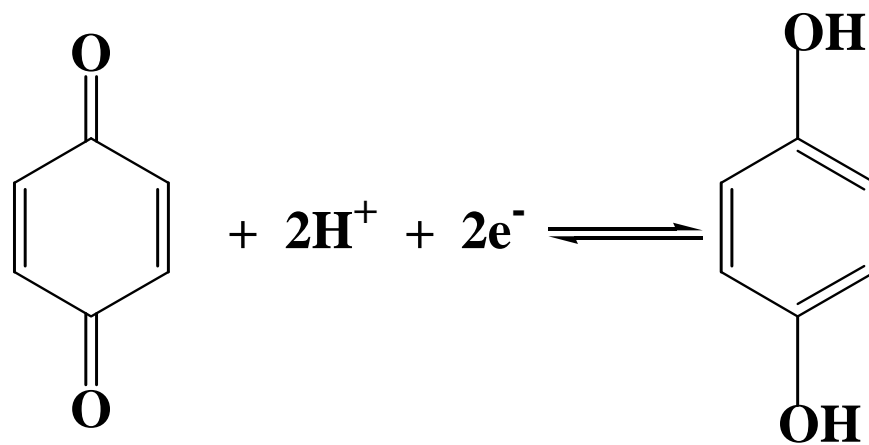
2,5-二甲基-1,4-苯醌

2,5-Dimethyl-1,4-
benzoquinone

醌为结晶固体，一般有颜色。

二、醌的反应 (Reaction of quinones)

1. 还原



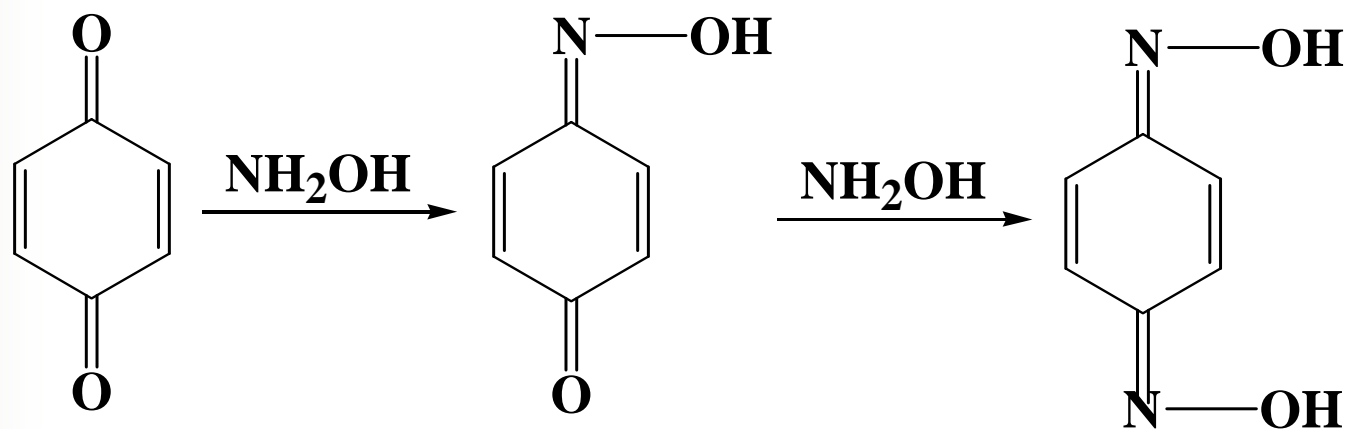
对苯醌
(氧化剂)

对苯二酚
(氢醌)

组成一个电化学氧化-还原体系

2. 加成反应

(1) 对苯醌与羟胺作用生成一肟或二肟:



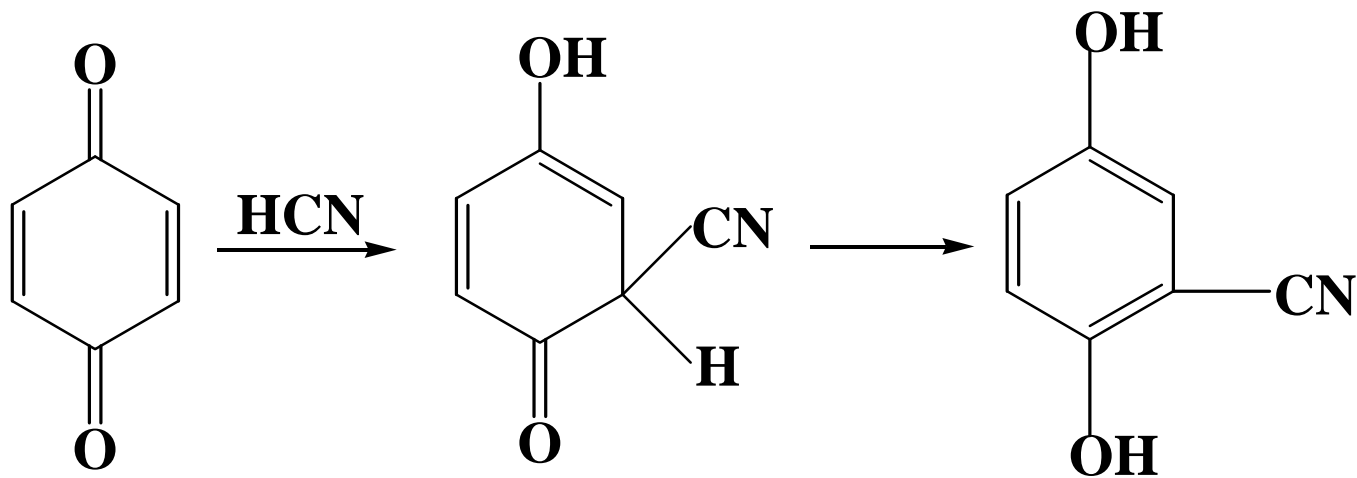
对苯醌

对苯醌一肟

苯醌二肟

反应必须在酸性溶液中进行

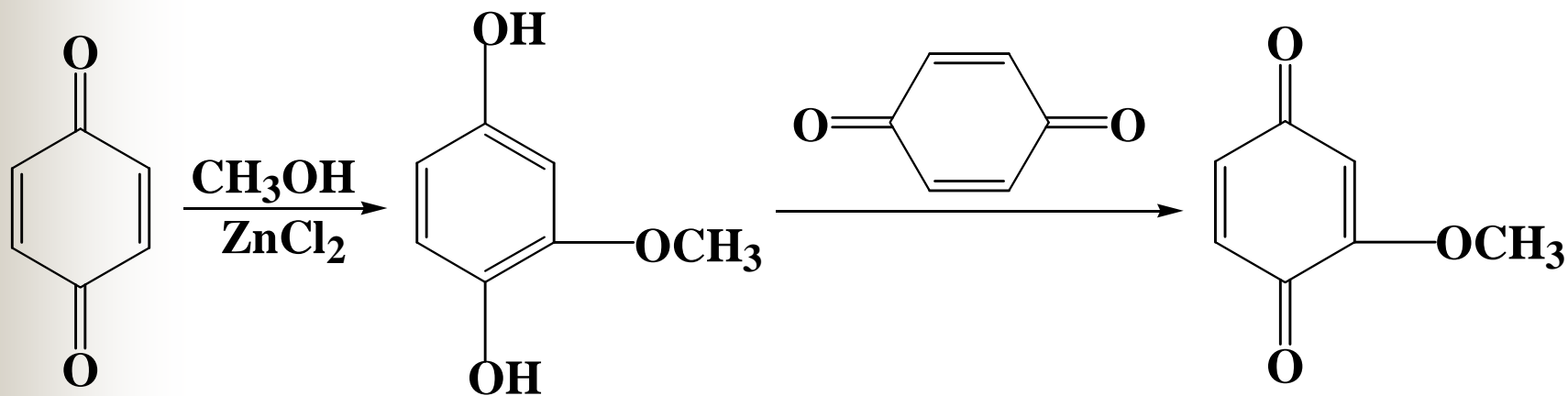
(2) 对苯醌与氢氰酸加成:



对苯醌

2-氰基-1,4-苯二酚

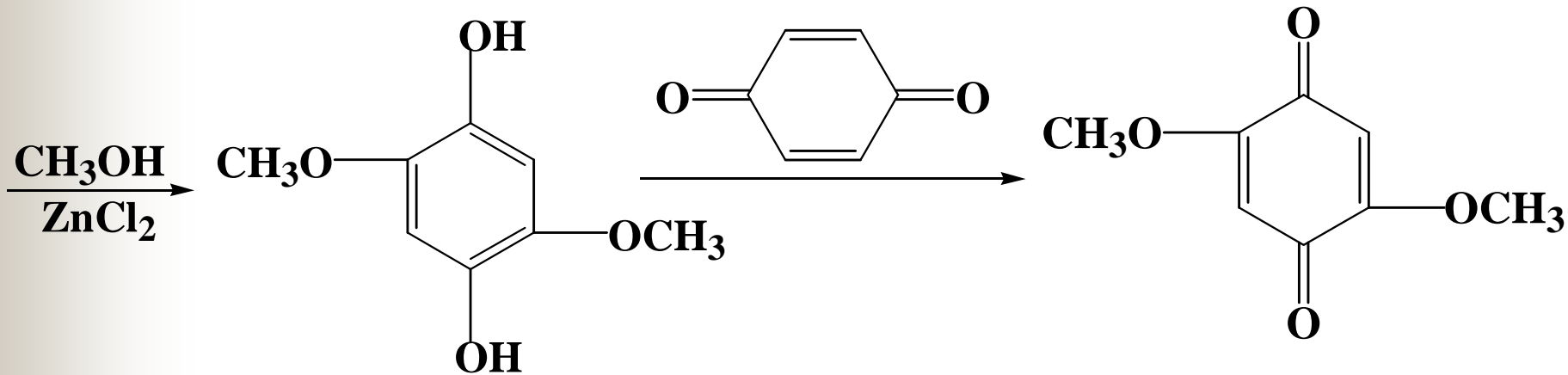
(3) 对苯醌与甲醇加成:



对苯醌

2-甲氧基-1,4-苯二酚

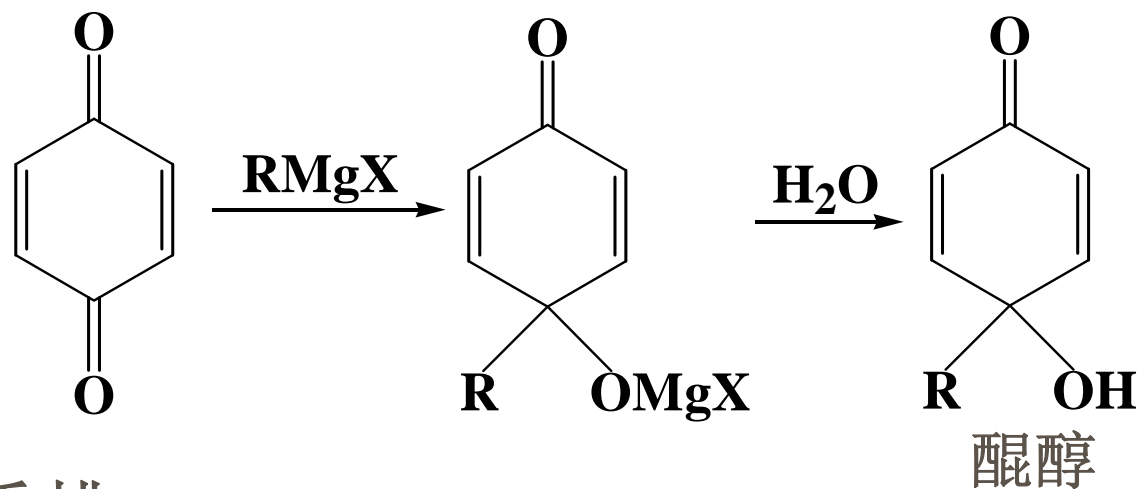
2-甲氧基-1,4-苯醌



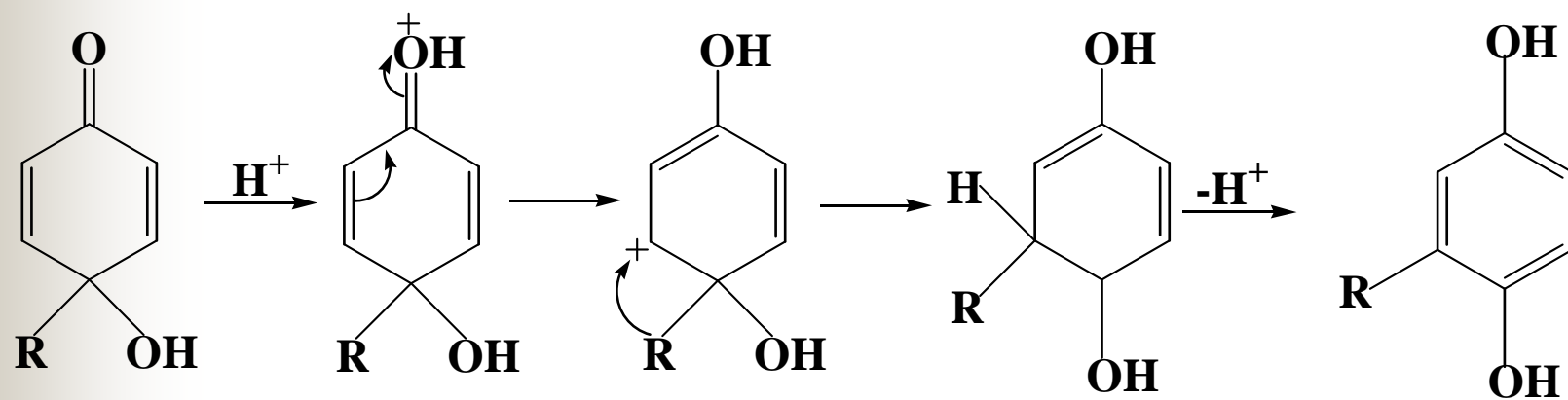
2,5-二甲氧基-1,4-苯二酚

2,5-二甲氧基-1,4-苯醌

(3) 苯醌与格式试剂反应:

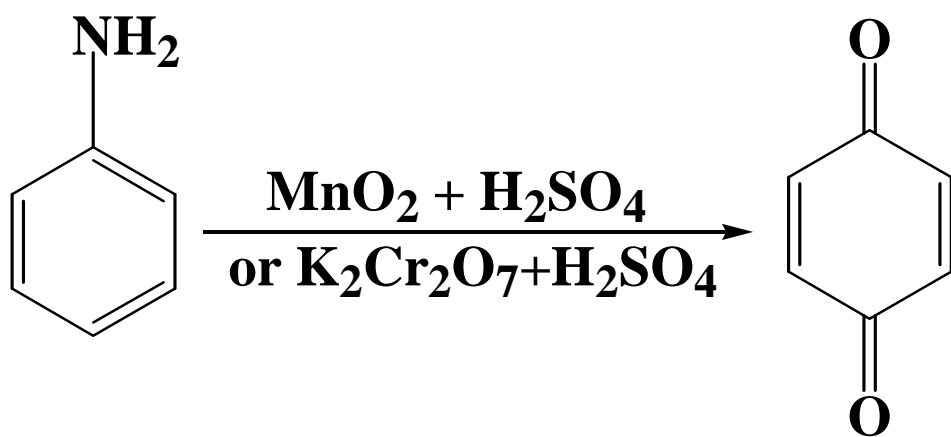


醌醇重排:



三、醌的制法 (Preparation of quinones)

一般由芳香族化合物氧化制备



对苯醌

§ 13.3 羟基醛酮 (Hydroxy aldehydes and hydroxy ketones)

一、羟基醛酮的反应 (Reaction of hydroxy aldehydes and hydroxy ketones)

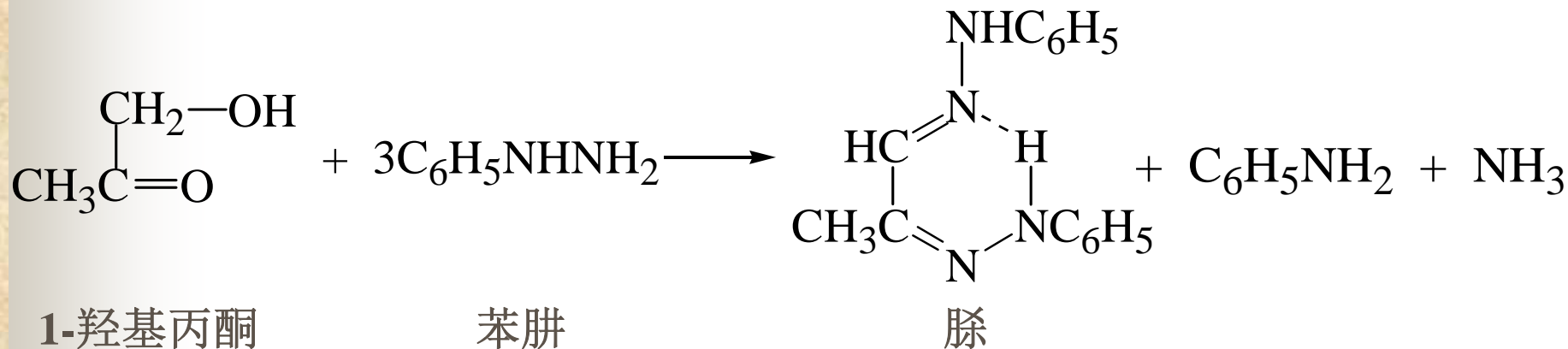
1. α -羟基醛酮

α -羟基醛与相应的 α -羟基酮可以互变

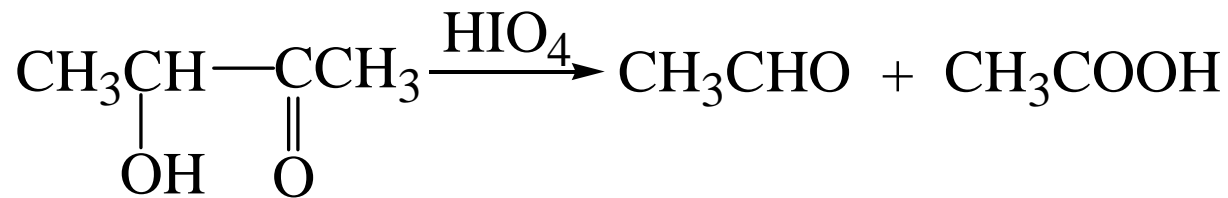


还原酮：烯二醇与碱生成的盐

α -羟基醛酮与苯肼作用生成脎

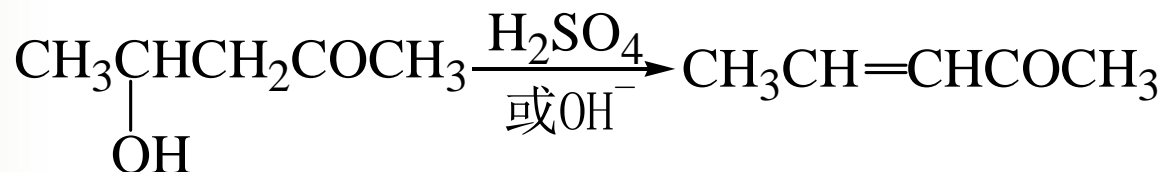


α -羟基醛酮能被高碘酸裂解

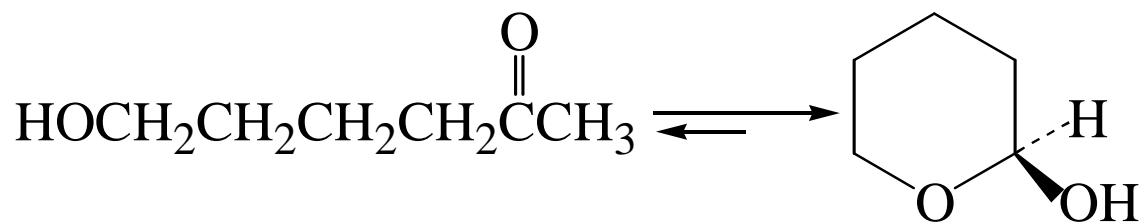
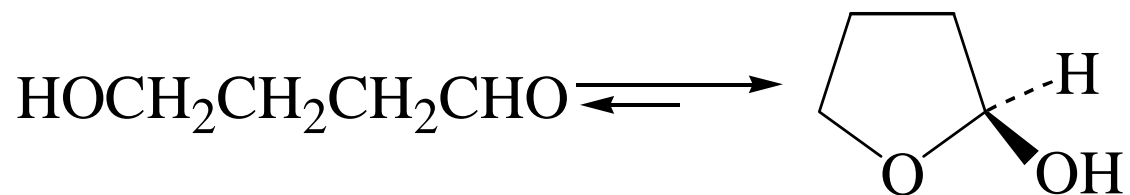


2. β -羟基醛酮

易脱水



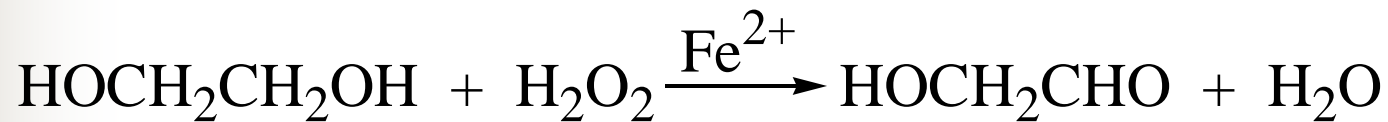
3. γ -和 δ -羟基醛酮 与环状半缩醛形成动态平衡



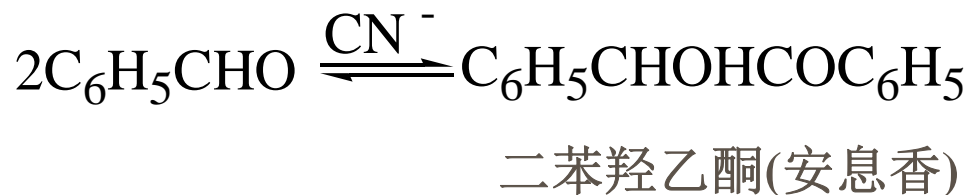
既有羟基醛酮 的反应， 又有环状半缩醛的反应

二、羟基醛酮的制法 (Preparation of hydroxy aldehydes and hydroxy ketones)

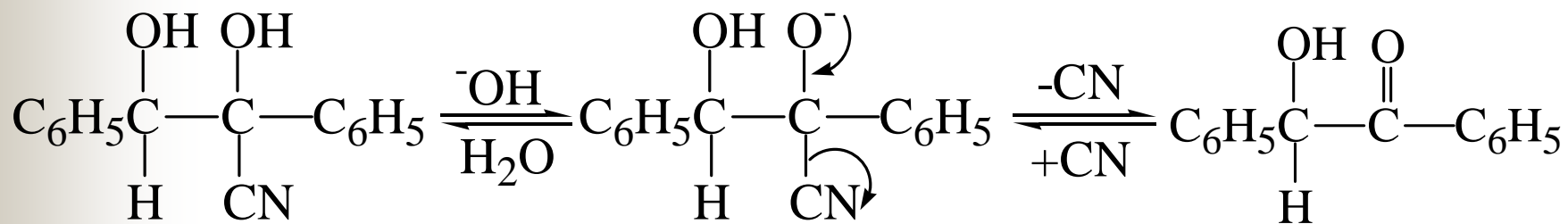
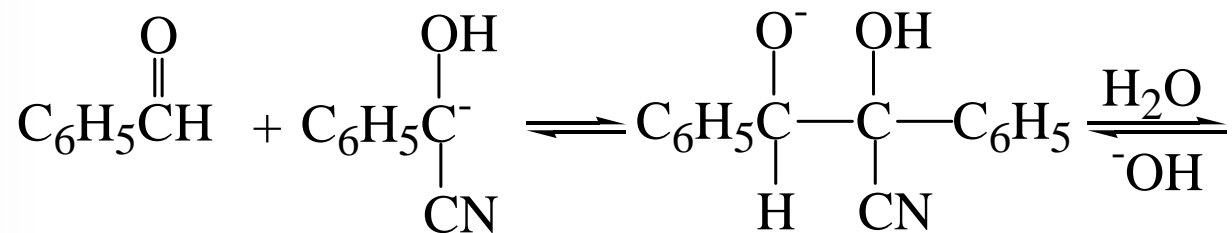
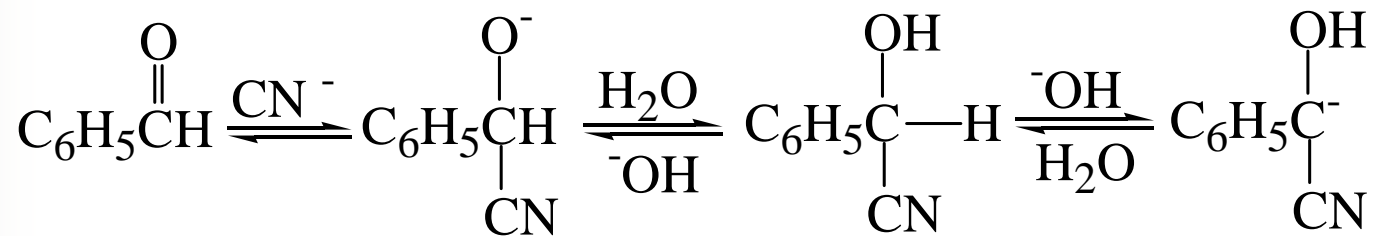
1. 1, 2-二醇的氧化



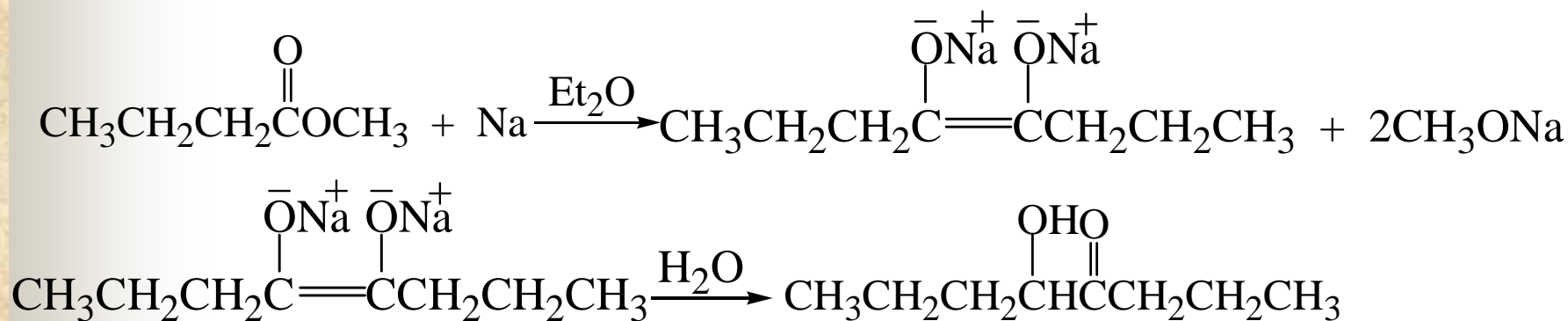
2. 安息香缩合



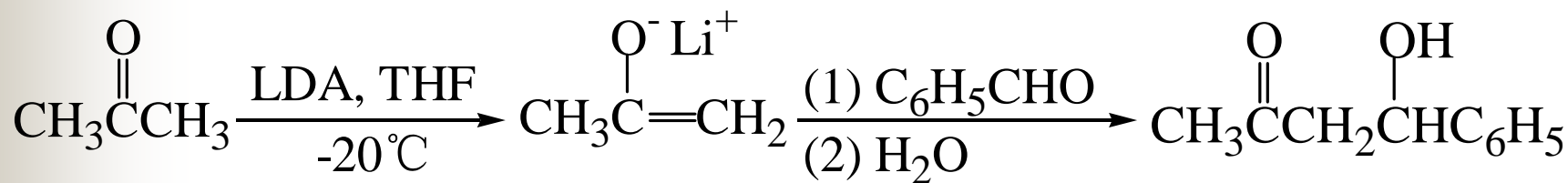
机理:



3. 酮醇缩合



4. 烯醇盐与醛缩合



LDA: 二异丙基氨基锂 $[(\text{CH}_3)_2\text{CH}]_2\text{N}\cdot\text{Li}^+$

§ 13.4 紫外光谱 (Ultraviolet Spectroscopy)

一、紫外光谱的一般特性

紫外光: $\lambda = 4\sim 400\text{nm}$ $\left\{ \begin{array}{l} \text{近紫外区: } \lambda = 200\sim 400\text{nm} \\ \text{远紫外区: } \lambda = 4\sim 200\text{nm} \end{array} \right.$

紫外光谱图: 横坐标—波长 (nm)

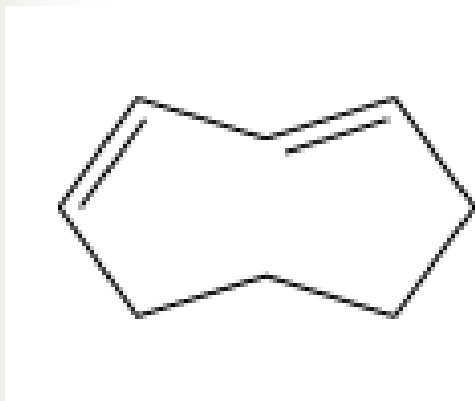
纵坐标—吸光度 $A = \log \frac{I_0}{I}$

吸收带

对甲苯乙酮 $\lambda_{\text{max}}^{\text{CH}_3\text{OH}} 252\text{nm}, \quad \epsilon = 12,300$

ϵ 的定义: $\log \frac{I_0}{I} = \epsilon \cdot c \cdot l \quad A = \log \frac{I_0}{I} = \epsilon \cdot c \cdot l$

$$\epsilon = \frac{A}{c \cdot l}$$



cis, trans-1,3-Cyclooctadiene

$\lambda_{\text{max}}^{\text{ethanol}}$ 230 nm

$\epsilon_{\text{max}}^{\text{ethanol}}$ 2630

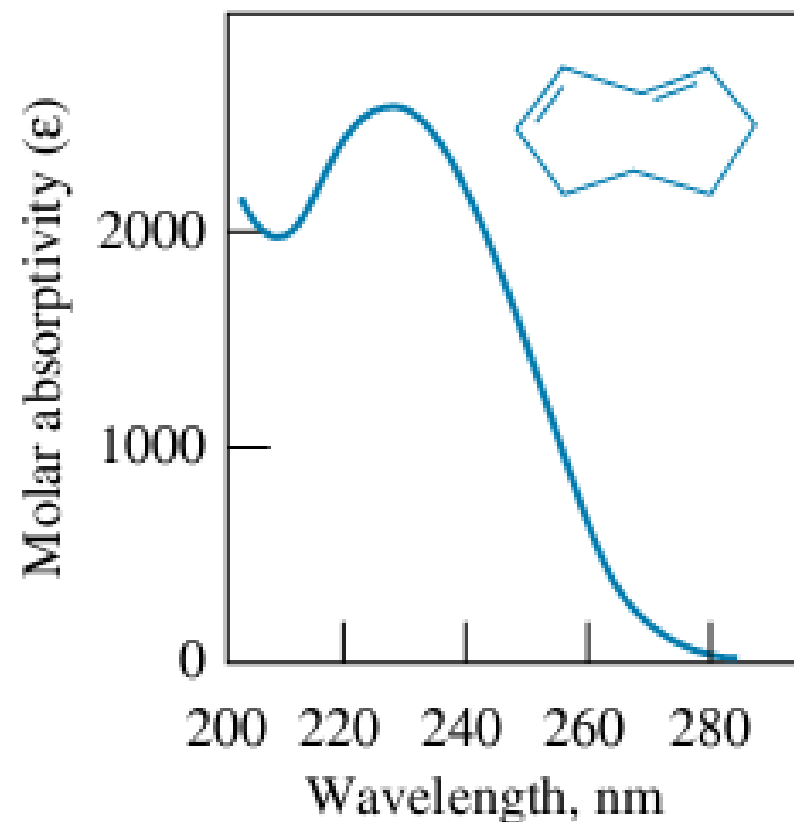
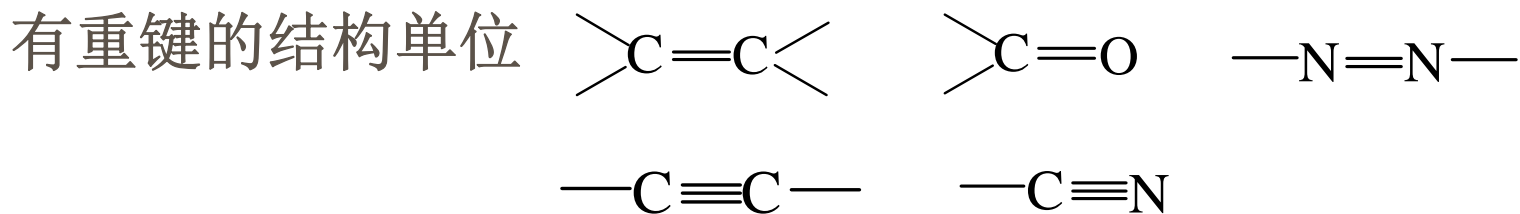
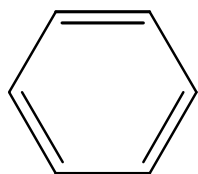


FIGURE 13.32 The ultraviolet spectrum of *cis,trans*-1,3-cyclooctadiene.

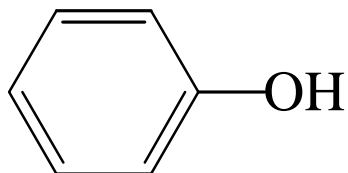
发色团: 能够吸收可见光及(或)紫外光(800~200nm)的孤立官能团



助色团: 在波长200nm以上无吸收带, 但与发色团连接时能使吸收带向长波方向移动, 并使吸收强度增加的官能团



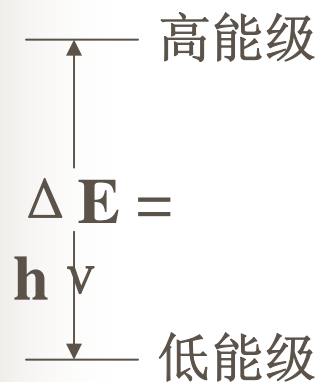
$$\lambda_{\max} 256\text{nm}, \quad \varepsilon = 200$$



$$\lambda_{\max}^{\text{H}_2\text{O}} 270\text{nm}, \quad \varepsilon = 1450$$

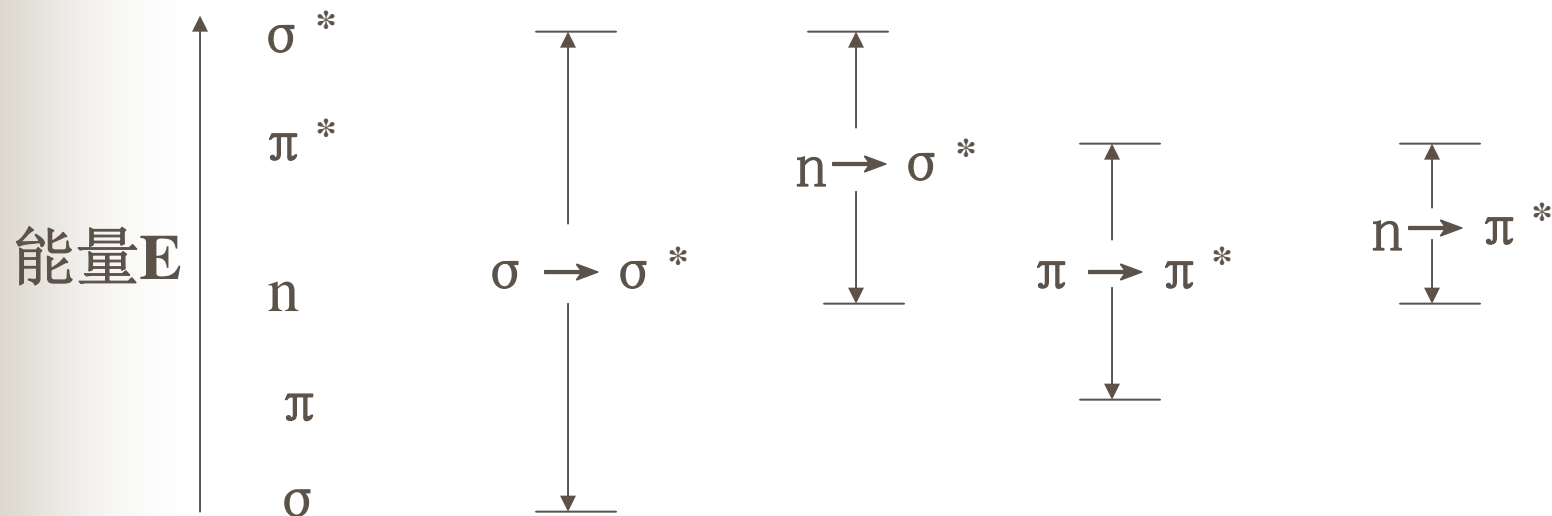
根据化合物的紫外光谱可以推测它所含的发色团

二、紫外光谱的基本原理



电子的振动和转动能级

1. 跃迁的分类



电子跃迁的类型及能量示意图

跃迁类型

吸收能量的近似范围



~150nm



<200nm



<200nm



200~400nm



200~400nm

有机物的电子跃迁类型

饱和烃: $\sigma \rightarrow \sigma^*$

不饱和烃: $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ (孤立)
特征

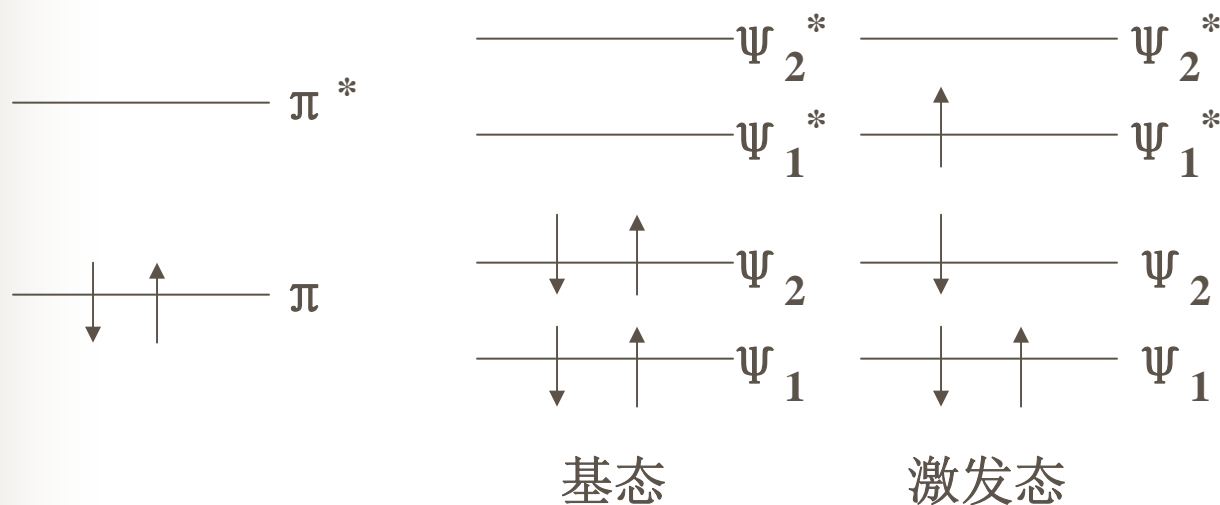
含有 $\text{—}\ddot{\text{N}}\text{—}$, $\text{—}\ddot{\text{O}}\text{—}$, $\text{—}\ddot{\text{X}}$ 等基团的有机物的电子跃迁类型:

(1) $\text{>C—}\ddot{\text{O}}$ 单键型: $\sigma \rightarrow \sigma^*$, $\mathbf{n \rightarrow \sigma^*}$ (特征)

(2) $\text{>C=}\ddot{\text{O}}$ 双键型、 $\text{CH}_2=\text{CH—}\ddot{\text{O}}\text{—}$ 共轭型:

$\mathbf{n \rightarrow \sigma^*}$, $\mathbf{n \rightarrow \pi^*}$, $\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$

二、共轭的影响



乙烯

$$\lambda_{\max} 165\text{nm}$$

$$\varepsilon = 15000 \text{ (蒸气)}$$

丁二烯

$$\lambda_{\max}^{\text{己烷}} 256\text{nm}$$

$$\varepsilon = 21000$$

向红移动：共轭双键数目增加，吸收带向波长增加的方向移动的现象。



紫外光谱可用于顺反异构体构型的测定：

反式异构体 λ_{\max} > 顺式异构体 λ_{\max}