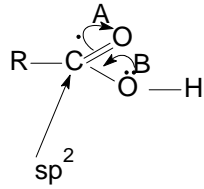


# 第十一章 羧酸及其衍生物

## 11. 1 结构、命名和物性

### 1. 结构:



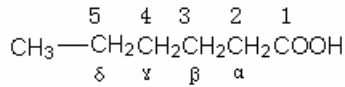
羰基原子电正性减弱, 不利于亲核反应

羟基氧原子上电子云密度减低, 氢原子易解离--有酸性

### 2. 命名

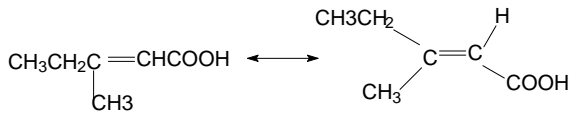
分类: 芳香, 脂肪; 饱和, 不饱和; 一元, 多元。

命名: 命名不饱和羧酸时, 选择含有羧酸和不饱和键的最长碳链为主链, 按碳原子数称为某烯酸。



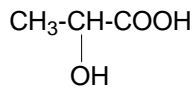
eg.  $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$

2( $\alpha$ )-甲基丁酸



3-甲基-2-戊烯酸

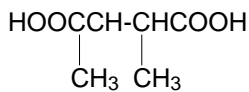
$\beta$ -甲基- $\alpha$ -戊烯酸



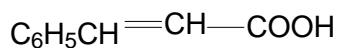
2-羟基丙酸 (乳酸)



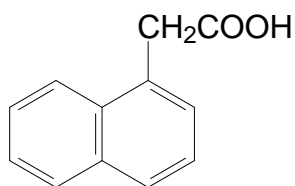
(2)-丁烯二酸



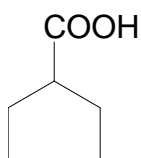
2-甲基-3-乙基丁二酸



3-苯基丙烯酸（肉桂酸）



$\alpha$ -萘乙酸



环戊烯甲酸

### 3. 物性

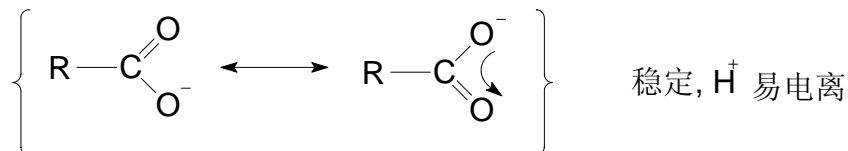
溶解度：低级溶于水，随分子量增大而逐渐减小，低级二元羧酸溶于水，不溶于有机溶剂（氢键）

B. P.：高，大于同分子量的醇

M. P.：偶大于前后相临的奇数碳原子的熔点。

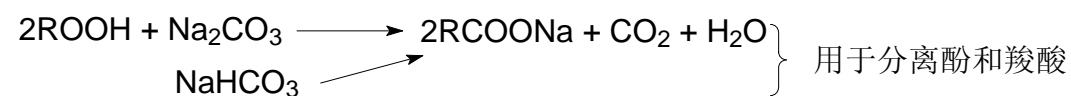
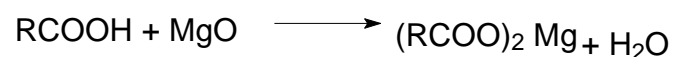
## 11. 2 化性

### 1. 酸性

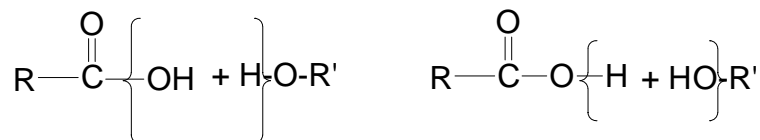
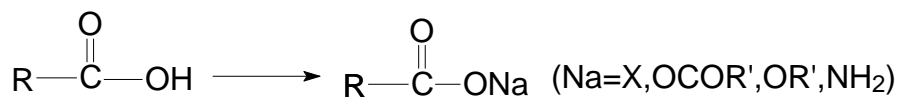


$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

$PK_a = -\lg K_a, PK_a$  较小



2. 羧酸衍生物的生成



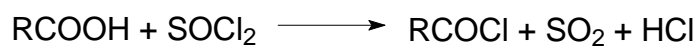
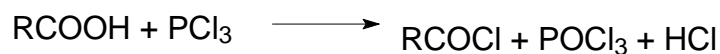
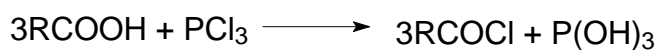
(1)

(2)

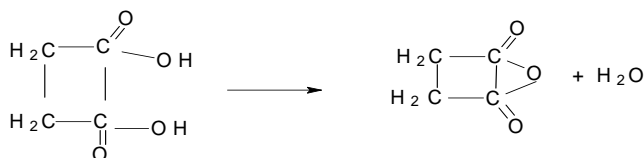
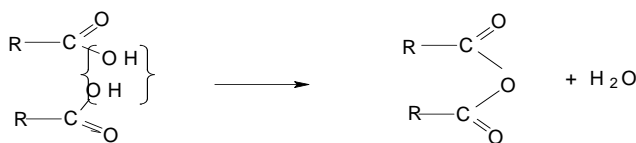
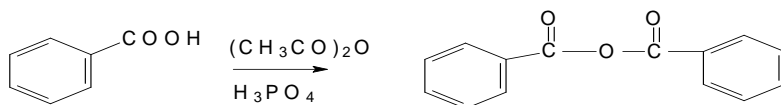
酰氧键断裂

烷氧键断裂

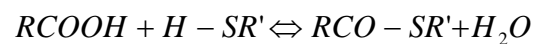
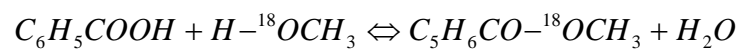
一般以方式1进行,只有叔醇按方式2进行



或成酸酐如下:



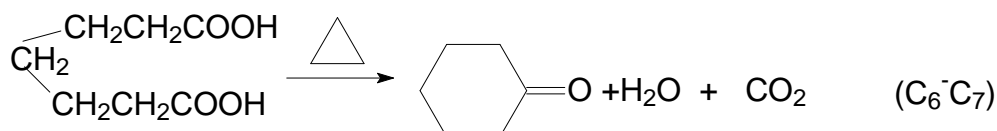
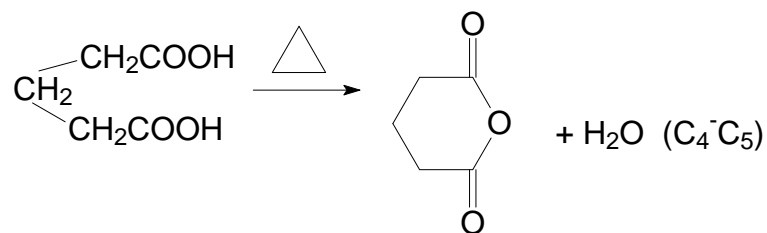
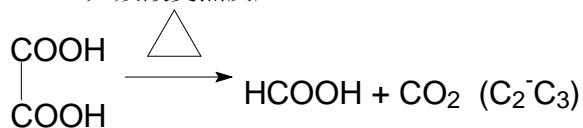
或生成酯



历经加成-消除



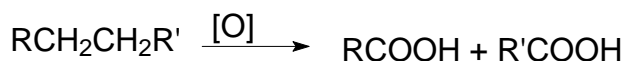
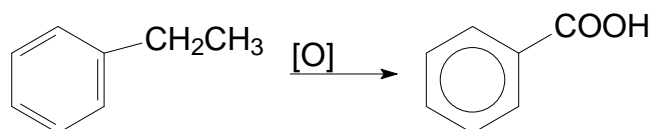
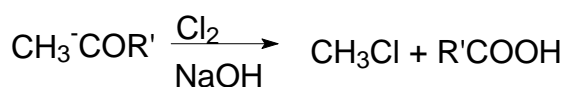
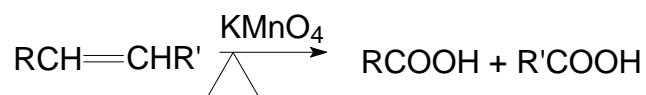
### 6. 二元羧酸受热反应



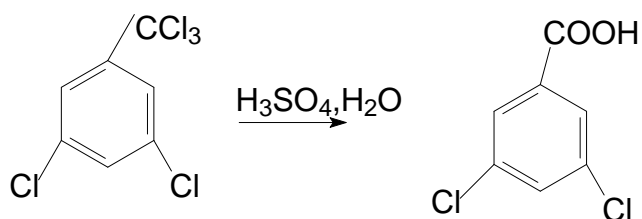
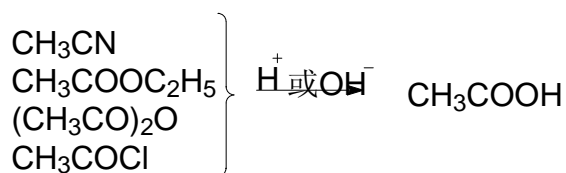
### 11. 3 制备

高级脂肪酸一般由动植物的油脂中得到。

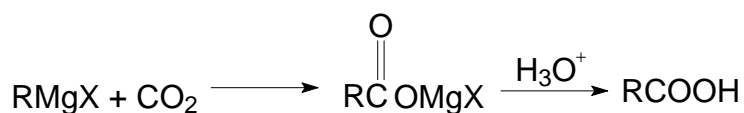
#### 1. 氧化法



#### 2. 水解法



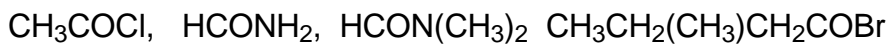
#### 3. 由 GRIGNARD 试剂与 $\text{CO}_2$ 作用, 增加 1 个 C。



#### 11. 4 羧酸衍生物命名与性质

##### 1. 命名

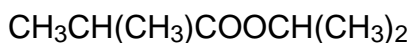
酰卤酰胺按照酰基命名



##### 2. 酸酐按照形成酐的羧酸命名



##### 3. 酯，某酸某酯，(羧酸+醇)



异丁酸异丙酯

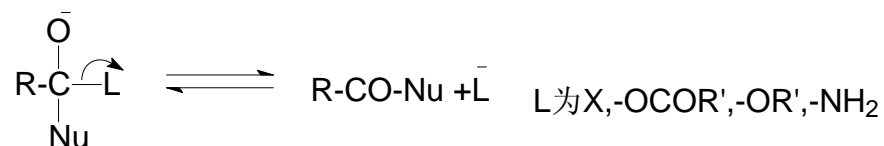
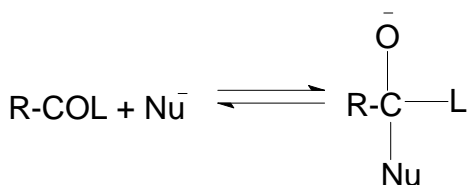
##### 4. 结构复杂时，P330。

物性 (P331)

#### 11. 5 化性

亲核加成反应

##### 1) 历程



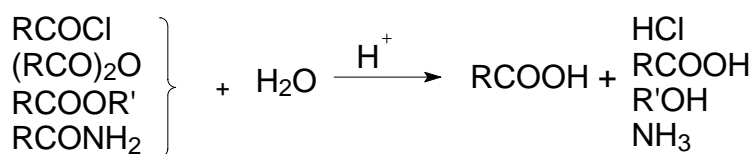
(-J) 吸电子能力  $-\text{X} > -\text{OCOR}' > -\text{OR}' > -\text{NH}_2$

(+C)  $-\text{X} < -\text{OCOR}' < -\text{OR}' < -\text{NH}_2$

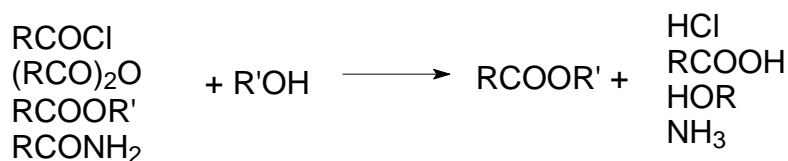
所以,烷基C上的正电性为  $\text{RCOX} > \text{RCOOCOR}' > \text{RCOOR}' > \text{RCONH}_2$

活性为 酰卤 > 酸酐 > 酯 > 酰胺

##### 2) 水解



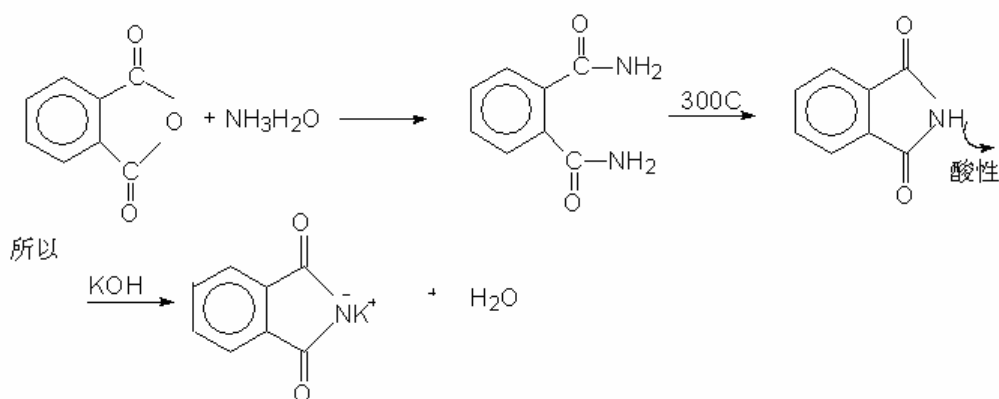
##### 3) 醇解



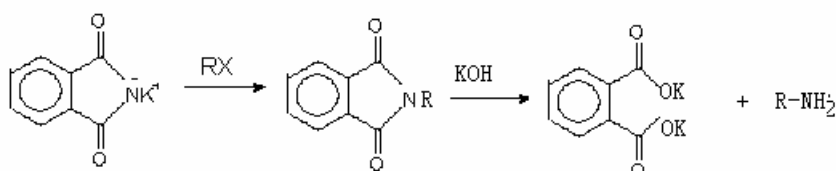


## 11.6 酰胺的特殊性质

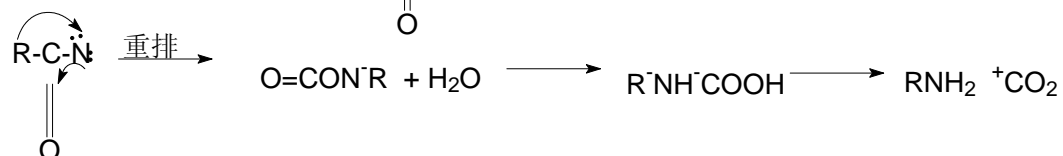
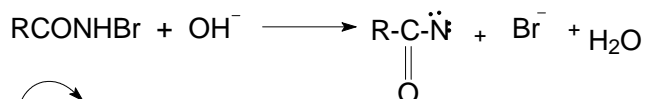
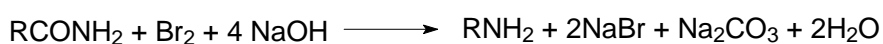
### 1) 酸碱性-----中性



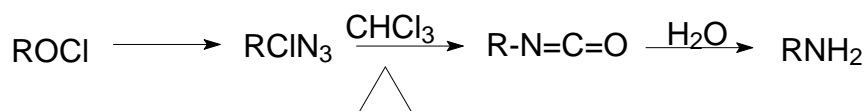
### Gabriel 反应



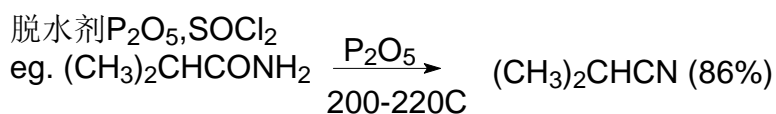
### 2) Hoffman 重排 (降级)



### CURBIUS 重排



### 3) 脱水反应



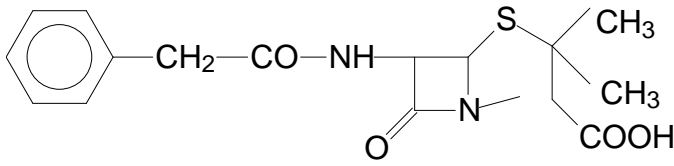
腈分子的偶极距较大, 极性大, 分子间吸引力大, B.P.高, 溶解度大(水), 例如, 乙腈能溶于水, 是一种常用的非质子极性溶剂。



## 11.7 重要的羧酸及衍生物

前列腺素

青霉素如下：



## 11.8 磺酸及其衍生物

1) 定义

HO-SO-OH  
亚硫酸

RSO-OH  
亚磺酸

RO-SO-OH  
亚硫酸氢酯

RO-SO-OR'  
亚硫酸酯

HO-SO<sub>2</sub>-OH

硫酸

RSO<sub>2</sub>-OH

磺酸

ROSO<sub>2</sub>-OH

硫酸氢酯

RO-SO<sub>2</sub>-OR'

硫酸酯

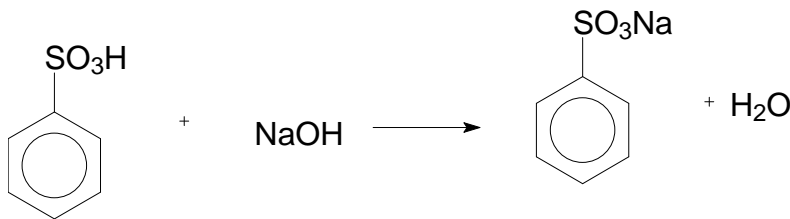
取代-OH为磺酸,取代-H叫酯

2) 物性

强酸，酸性与硫酸相当，稀湿性强，易溶于水，其钙、镁、银盐都溶于水

3) 化性

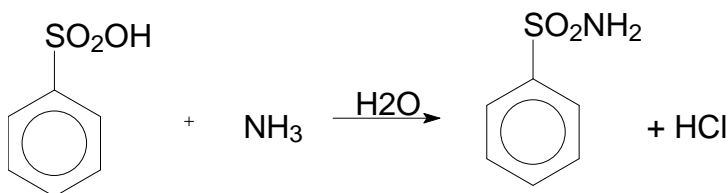
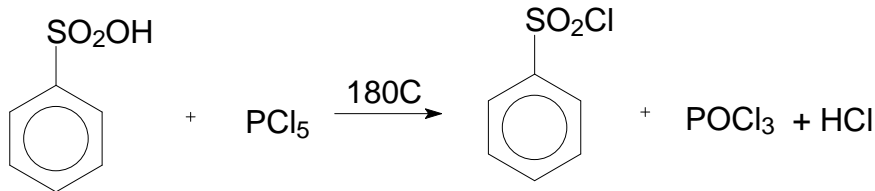
酸性强

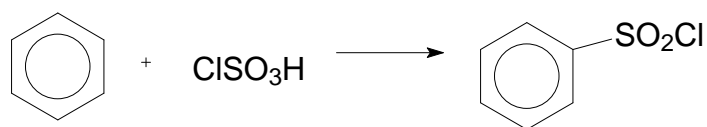
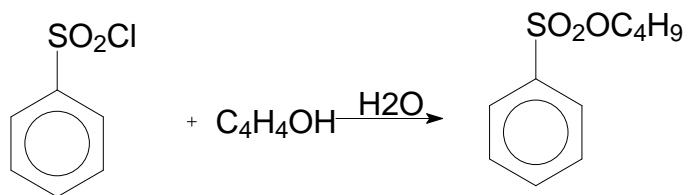


可代替硫酸催化酯水解，醇分子内或外脱水，羧酸和醇的酯化及异丙苯氧化丙酮和苯酚。

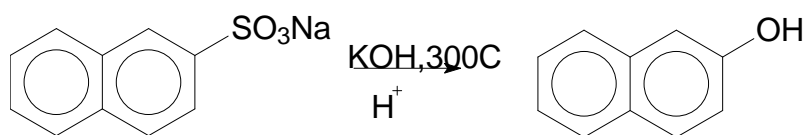
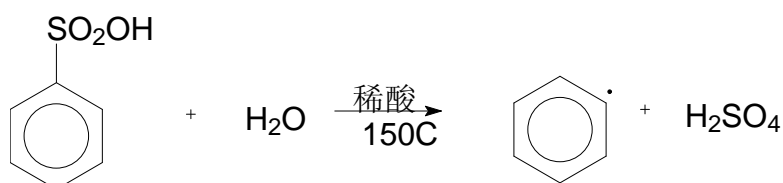
如使用 PE 碳酸型阳离子树脂，具有分离方便，不腐蚀设备，不污染环境，反应条件温和，副产物少，产品纯度高的特点。

羧基键取代：

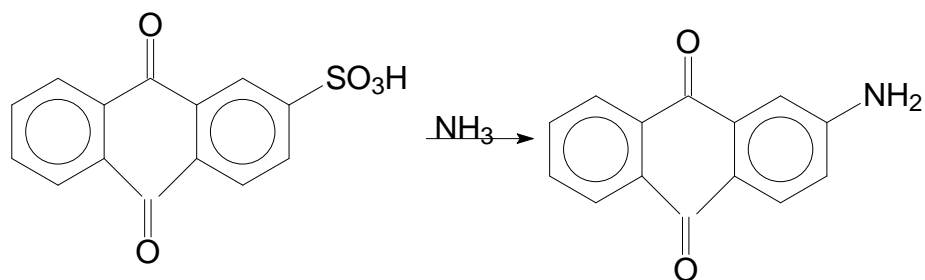
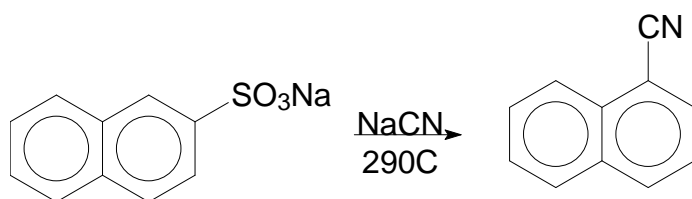




磺酸基被取代:

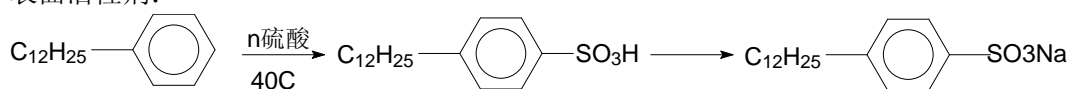


其他亲核取代:

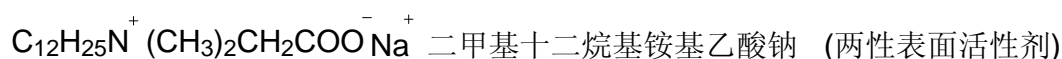
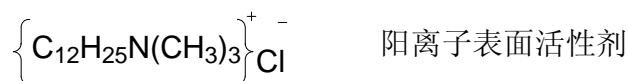


4) 应用:

表面活性剂:

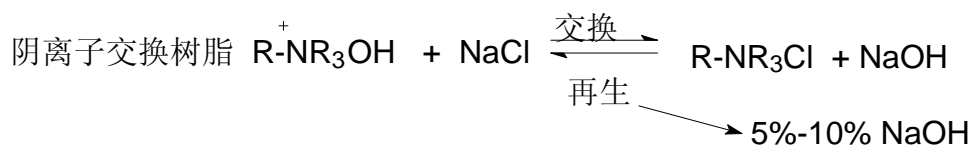
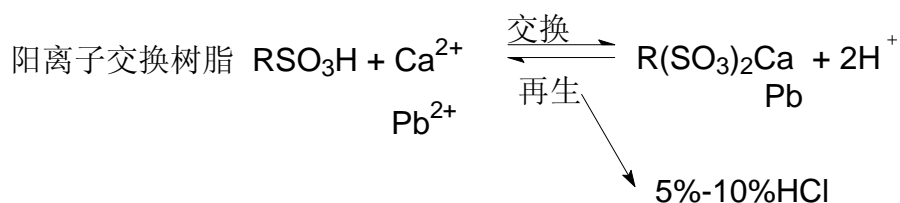


其钙盐, 镁盐均溶于水, 而肥皂为高级脂肪酸钠, 则不能在硬水中使用。  
这类表面活性剂为阴离子表面活性剂,



(聚氧乙烯烷基醚) 非离子表面活性剂 (不起泡)

离子交换树脂:



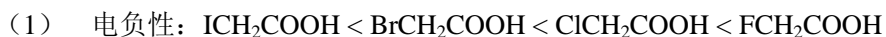
### 3) 磺胺类药物 P278

## § 11.3 取代酸的酸性

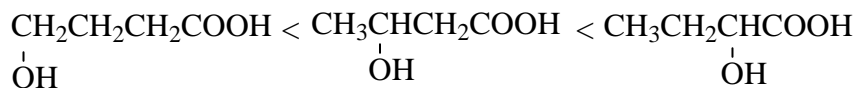
羧酸分子中烃基上的氢原子被取代——取代酸 (substituted acid)

$\left\{ \begin{array}{l} \text{卤代酸} \\ \text{羟基酸} \\ \text{羰基酸} \end{array} \right.$

1. I效应对酸性的影响:



(2) 距离:



Pka

4.70

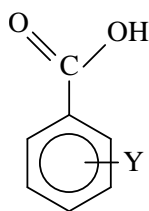
4.50

3.86

(3) 烷基斥电子:



(4) 苯环:



P323. 表 11.2

$\left\{ \begin{array}{l} \text{I: 邻>间>对} \\ \text{C: 对>间} \quad (\text{eg. 间硝基苯甲酸} < \text{对硝基苯甲酸酸性}) \end{array} \right.$

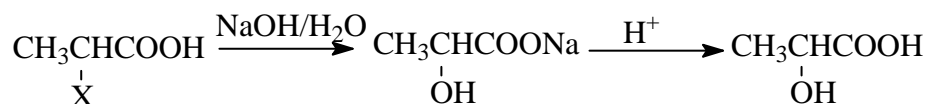
### § 11.3.1 羟基酸 $\left\{ \begin{array}{l} \text{醇酸} \\ \text{酚酸} \end{array} \right.$

一. 命名: 羧基为母体, 羟基为取代基。(P345)

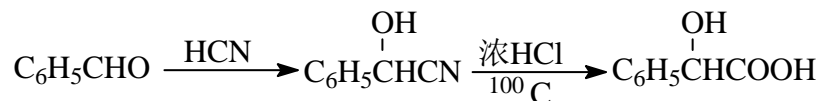
物性: m.p., b.p., 溶解度一般大于相应的羧酸, 一般有旋光性。

二. 醇酸的制法:

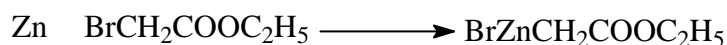
1. 卤代酸水解:  $\alpha$ -卤代酸



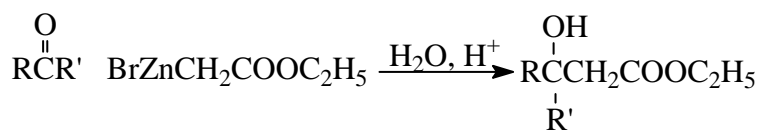
2. 氰醇水解:



3. Reformatsky 反应:



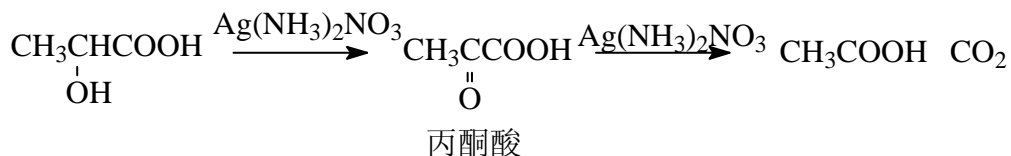
( $\alpha$ -卤代酸酯)



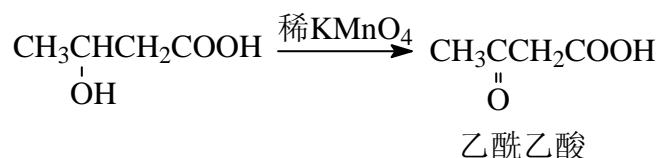
( $\beta$ -羟基酸)

三. 反应: 具有酚羟基何羧基的典型反应

1. 氧化:  $\alpha$ -羟基酸比一般醇羟基易于被氧化

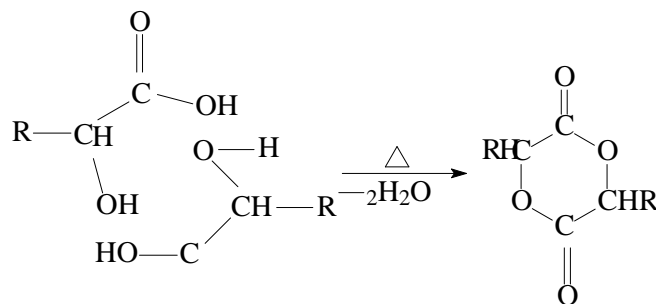


其它:

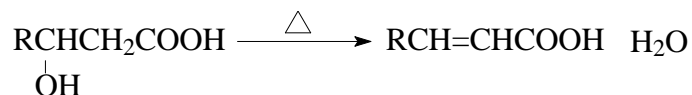


2. 脱水:

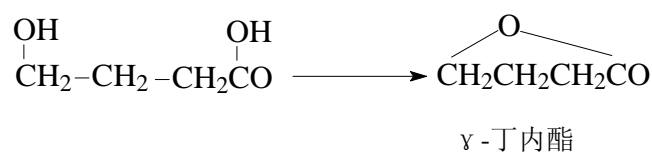
(1)  $\alpha$ -羟基酸——六元环的内酯



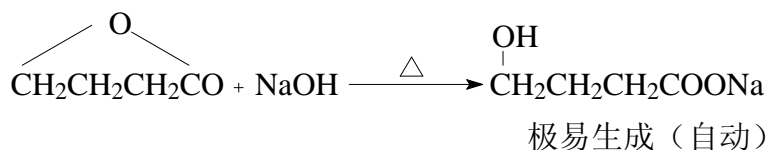
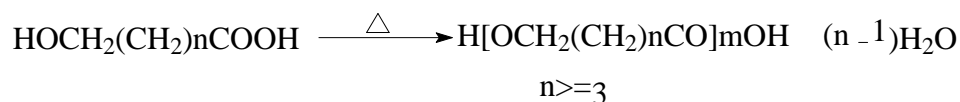
(2)  $\beta$ -羟基酸—— $\alpha$   $\beta$  不饱和酸



(3)  $\delta$ - $\delta$ - ——分子内酯化产生内酯。(五元或六元环)



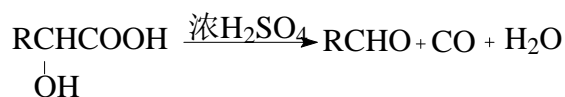
(4) 四个 C 以上——分子间脱水生成链状聚酯。



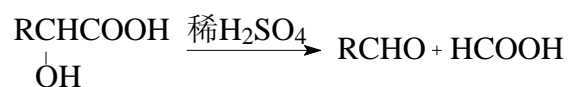
$\therefore$  内酯类药物要在中性溶液中保持，偏酸或偏碱会引起开环而失效。

3. 分解反应:

$\alpha$ -羟基酸



P346

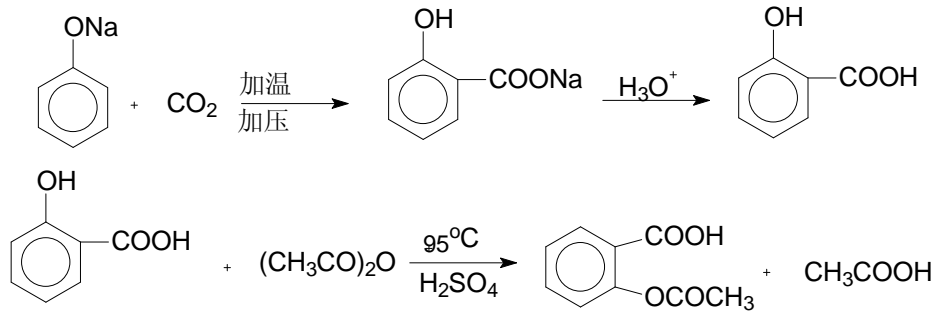


四. 重要的醇酸。P349

1. 苹果酸  $\alpha$ -羟基丁二酸
2. 酒石酸 2,3-二羟基丁二酸
3. 柠檬酸 3-羧基-3-羟基戊二酸

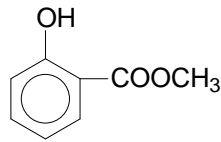
## 五. 酚酸。P350

### 1. 水杨酸

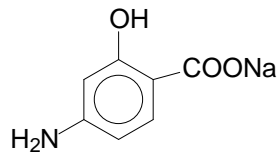


阿司匹林

Aspirin + 非那西丁 (phenacetin) + 咖啡因 (caffeine) —— 复方阿司匹林

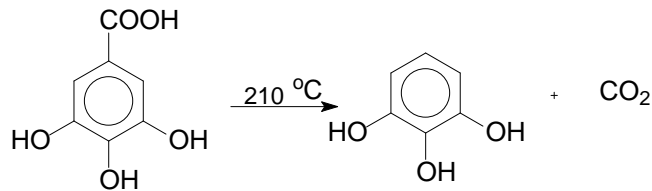


——冬青油 (冷烫伤)



——PAS (冷肺结核)

### 2. 没食子酸 (gallic acid) 存在于茶、五倍子中, 是鞣质的一个组成部分。

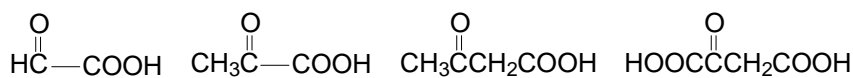


焦性没食子酸 (磺胺增效剂)

## § 11.3.2 羧基酸——酮酸 (ketoacid)

### 一. 命名

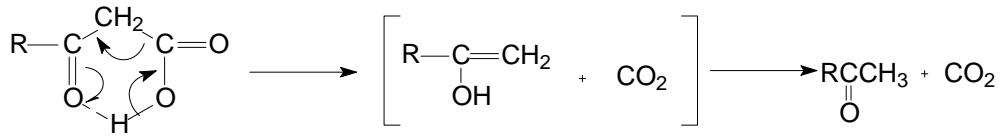
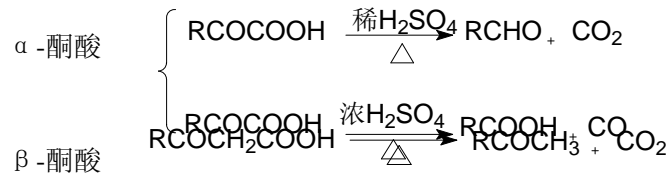
以羟基为母体, 用  $\alpha$ 、 $\beta$ 、 $\gamma$ ……或 1、2、3……标出羧基的位置, 其中,  $\alpha$ 、 $\beta$ ——酮酸较重要, 是人体内糖, 脂肪和蛋白质的代谢产物。



乙醛酸       $\alpha$ -氧代丙酸      3-丁酮酸      丁酮二酸  
 (氧代乙酸)                      ( $\beta$ -丁酮酸)      ( $\alpha$ -氧代丁二酸)

酮酸较重要, 是光合作用生成糖类的中间体。

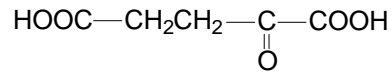
二. 性质:



三. 重要的羧基酸: p352.

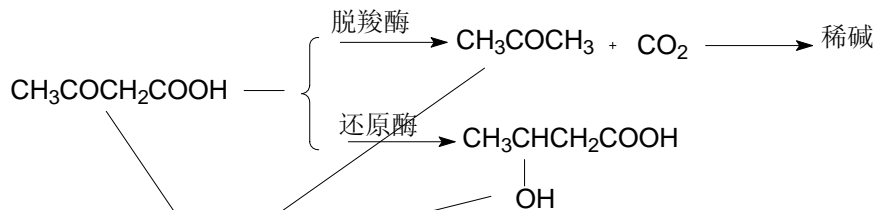
1. 乙醛酸 未成熟的水果中。

2. 丙酮酸



3.  $\alpha$ -酮戊二酸

4.  $\beta$ -丁酮酸:  $\text{CH}_3\text{COCH}_2\text{COOH}$  乙酰乙酸, 是体内脂肪代谢的中间产物。



统称为酮体 (ketone body), 大量存在于糖尿病患者的尿和血液中。