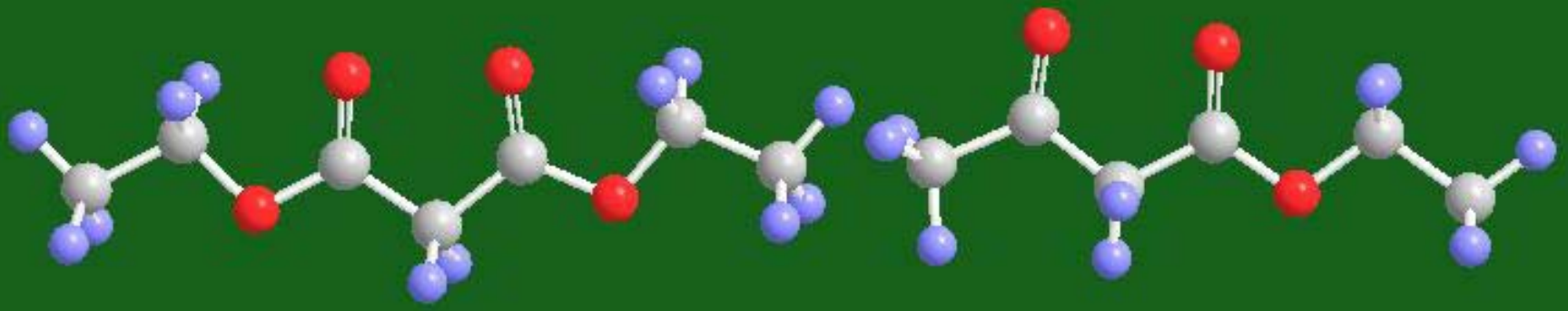
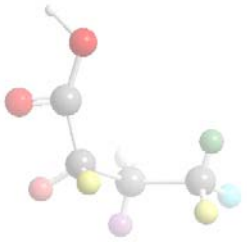
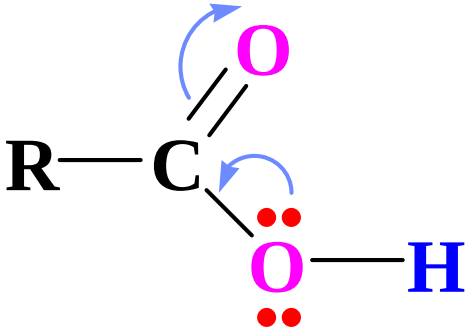
第十二章 羧酸及其衍生物

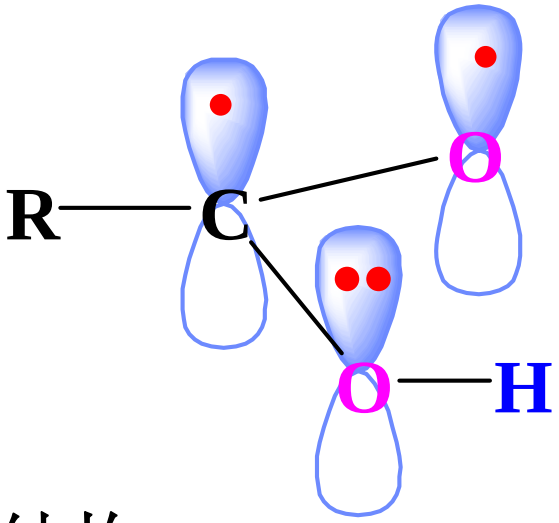


12.1 羧酸的结构、命名和物理性质

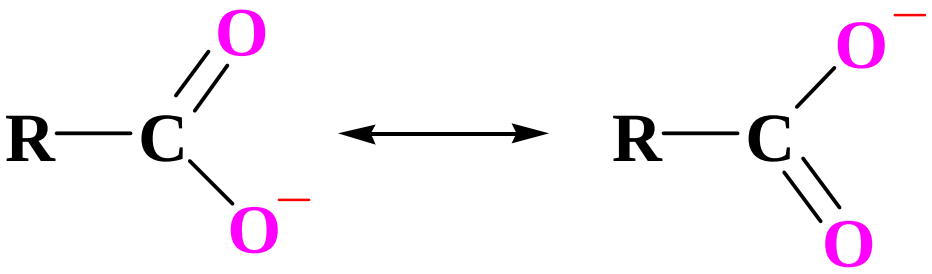


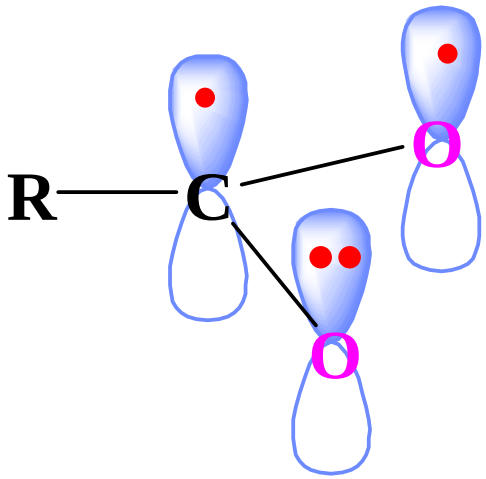
12.1.1 羧酸的结构



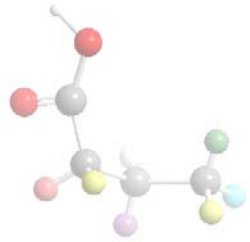


羧酸的结构





羧酸根的共振结构



12.1.2 羧酸的分类

- 按烃基分类

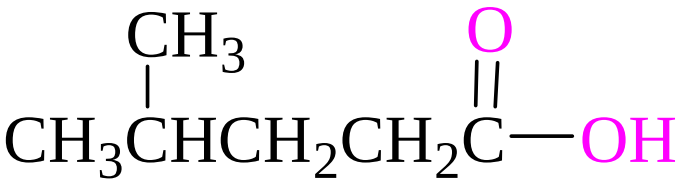
羧酸
- 脂肪酸
  - 饱和脂肪酸
  - 不饱和脂肪酸
- 芳香酸

- 按羧基数目分类

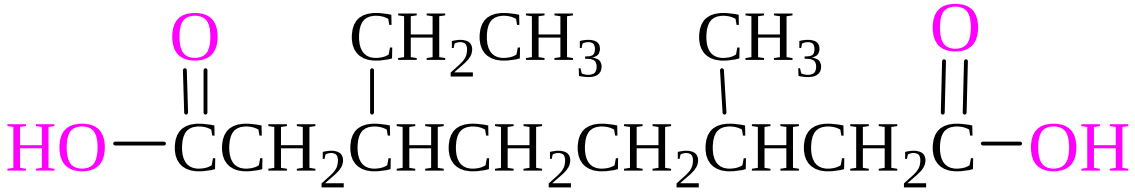
一元酸、二元酸、多元酸

12.1.3 羧酸的命名

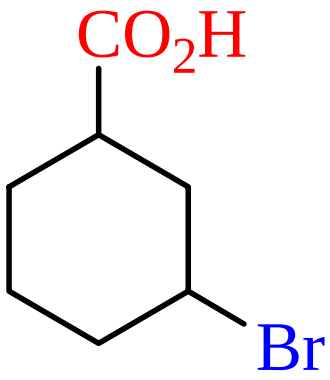
➢系统命名



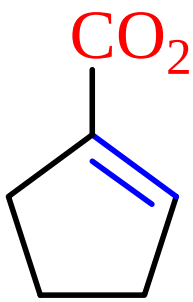
4-甲基戊酸



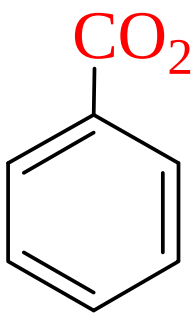
3-甲基-6-乙基辛二酸



3-溴环己烷羧酸



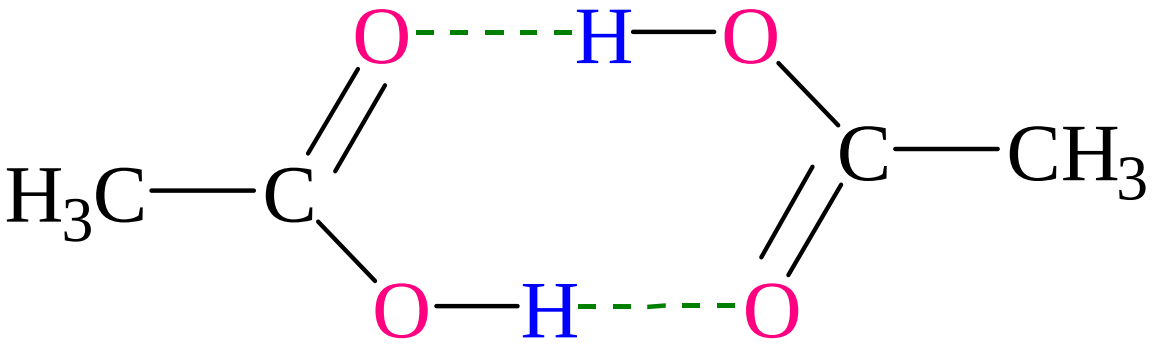
1-环戊烯羧酸



苯甲酸

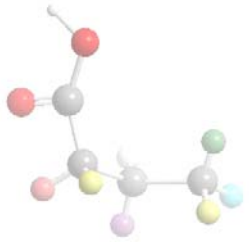
12.1.4 羧酸的物理性质（自学）

大多数羧酸在固态和液态时以二缔和体形式存在，沸点比相应的醇高



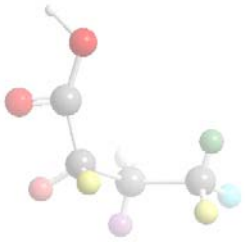
乙酸的二缔和体

12.2 羧酸的反应

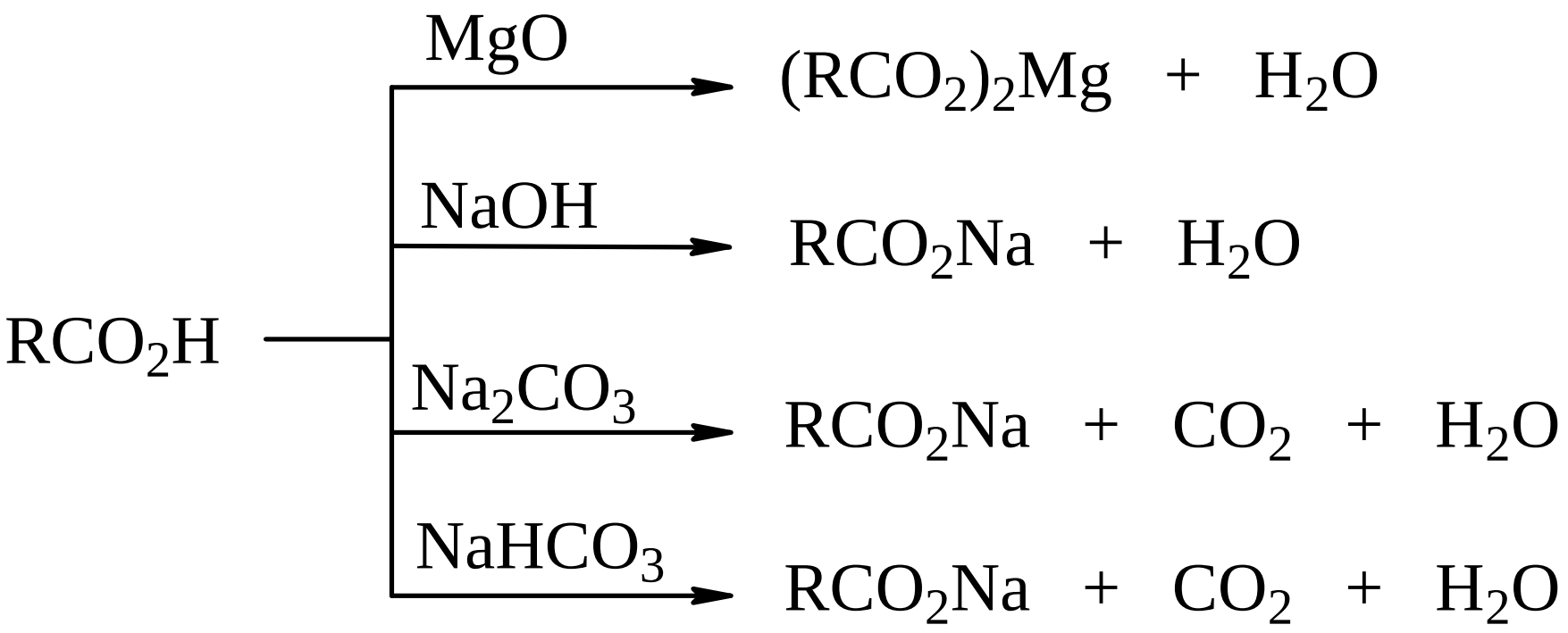


12.2.1 酸性

- 酸性比醇强得多
- 仍是一种弱酸
- 一元饱和脂肪族羧酸的*pKa*值一般在3~5之间

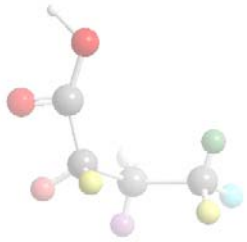


羧酸的酸性反应


RCO2H
MgO
(RCO2)2Mg + H2O
NaOH
RCO2Na + H2O
Na2CO3
RCO2Na + CO2 + H2O
NaHCO3
RCO2Na + CO2 + H2O

取代基对羧酸酸性的影响

- 吸电子取代基使酸性增强
- 给电子取代基使酸性减弱

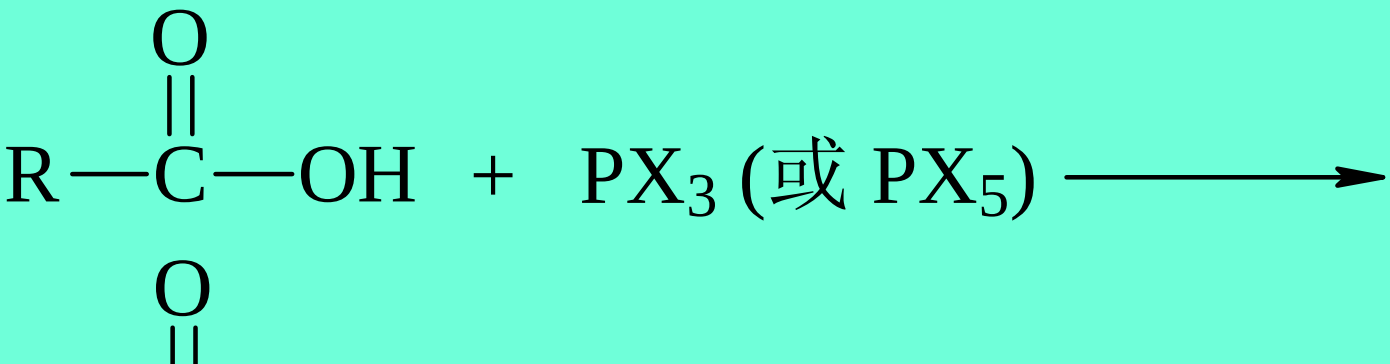


12.2.2 羰基的加成－消除反应

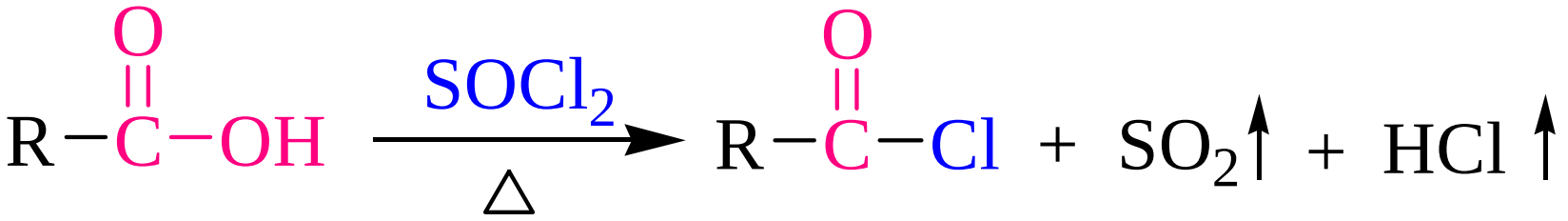
—— 形成羧酸衍生物

1. 形成酰卤

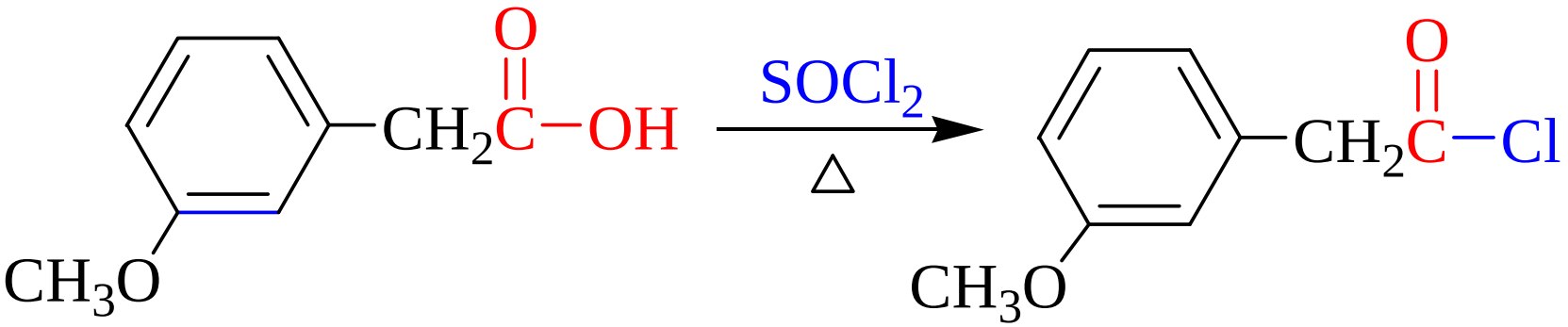
- PX_3 , PX_5
- $SOCl_2$



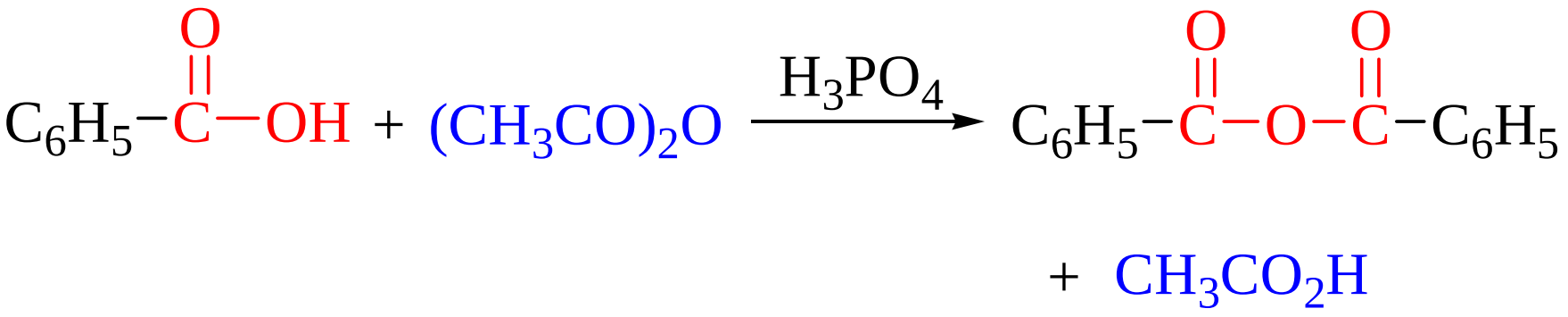
实验室制备酰氯一般用$SOCl_2$



产率高，纯度好。

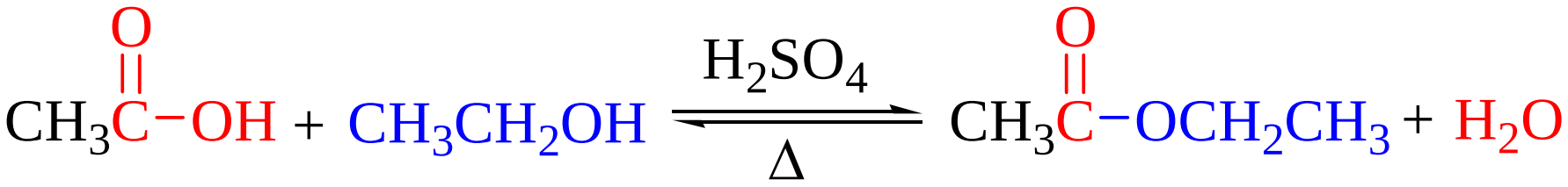


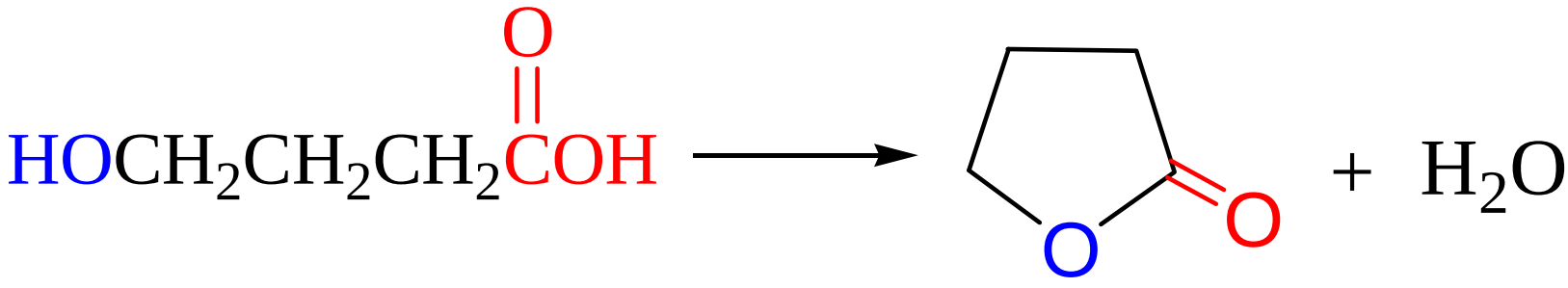
2. 形成酸酐


O
C6H5−C−OH + (CH3CO)2O
H3PO4
O
O
C6H5−C−O−C−C6H5
+ CH3CO2H

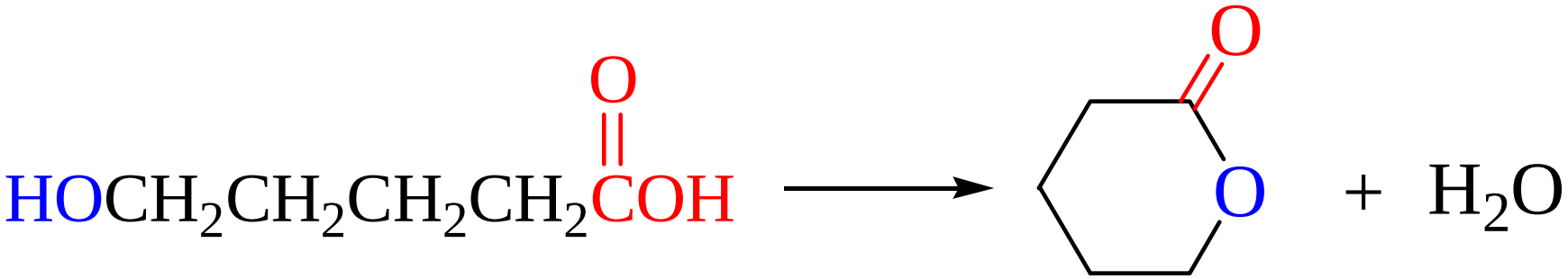

O
CH3CH2−C−OH
P2O5
O
O
CH3CH2−C−O−C−CH2CH3

3. 酯化反应





γ-丁内酯



δ-戊内酯

4. 形成酰胺和腈

$$CH_3CO_2H + NH_3 \longrightarrow CH_3CO_2^-NH_4^+$$

$$CH_3CO_2^-NH_4^+ \xrightarrow{100^\circ C} CH_3CONH_2 + H_2O$$

$$CH_3CONH_2 \xrightarrow[\triangle]{P_2O_5} CH_3CN$$

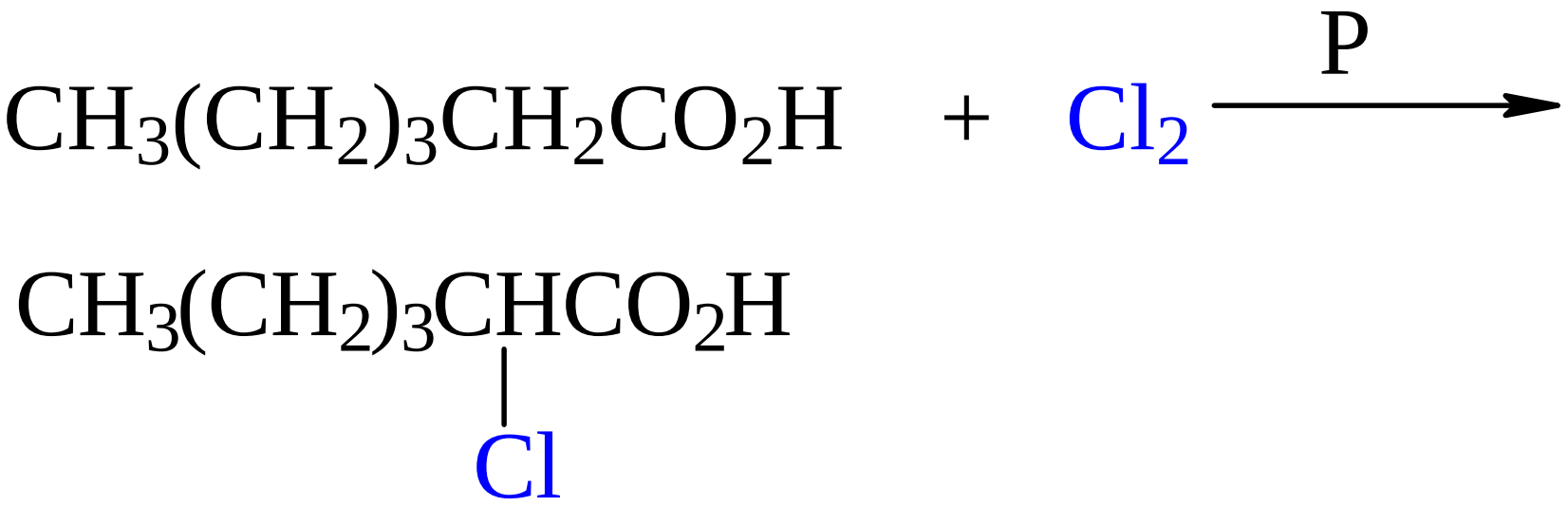
12.2.3 羧酸的还原反应

$$RCO_2H \xrightarrow[(2)H_3O^+]{(1)\ LiAlH_4} RCH_2OH$$

$$CH_3CH{=}CHCH_2CO_2H \xrightarrow[(2)H_3O^+]{(1)\ LiAlH_4} CH_3CH{=}CHCH_2CH_2OH$$

12.2.4 羧酸的α-卤代反应

与卤素在红磷或酰卤催化下发生α-卤代：



12.2.5 脱羧反应

- 羧酸在一定条件下失去羧基放出二氧化碳的反应称为脱羧反应。
- 当羧基的α-碳原子上连有吸电子基团时，可在适当的条件下发生脱羧反应。

$$A-CH_2CO_2H \xrightarrow{\text{适当条件}} A-CH_3 + CO_2$$

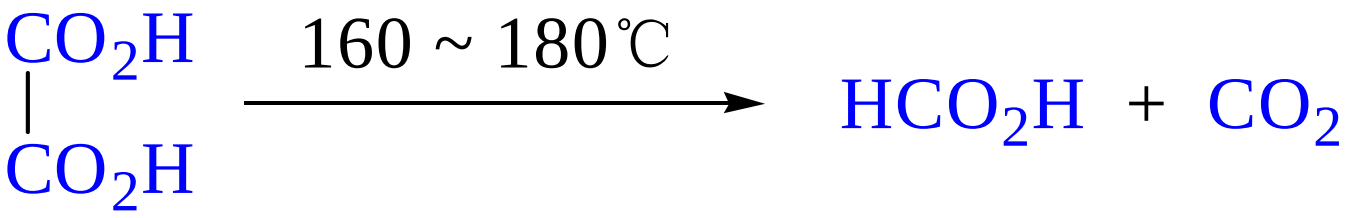
A = $-CO_2H$ $-CN$ $-COR$ $-NO_2$

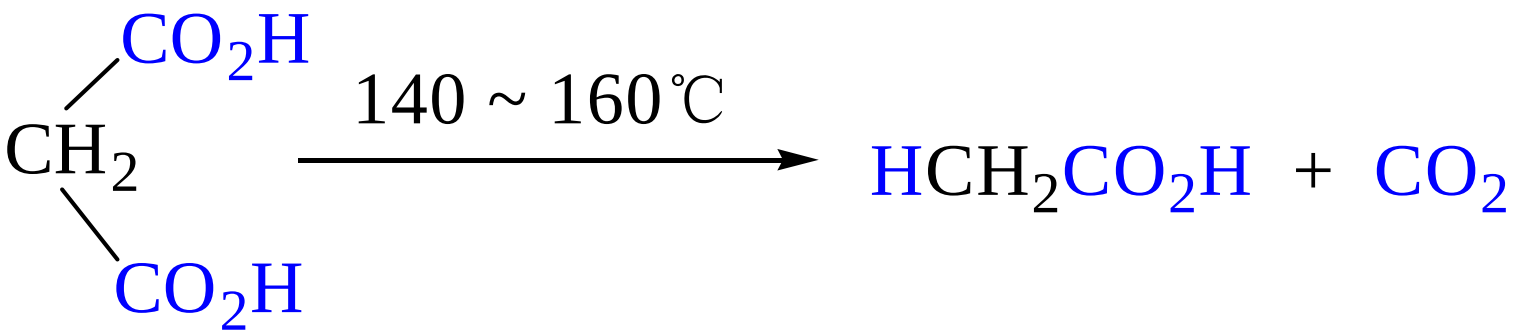
$-CX_3$ $\diagdown\!\!\diagup C=O$ $-C_6H_5$

适当条件：碱、热、特殊催化剂

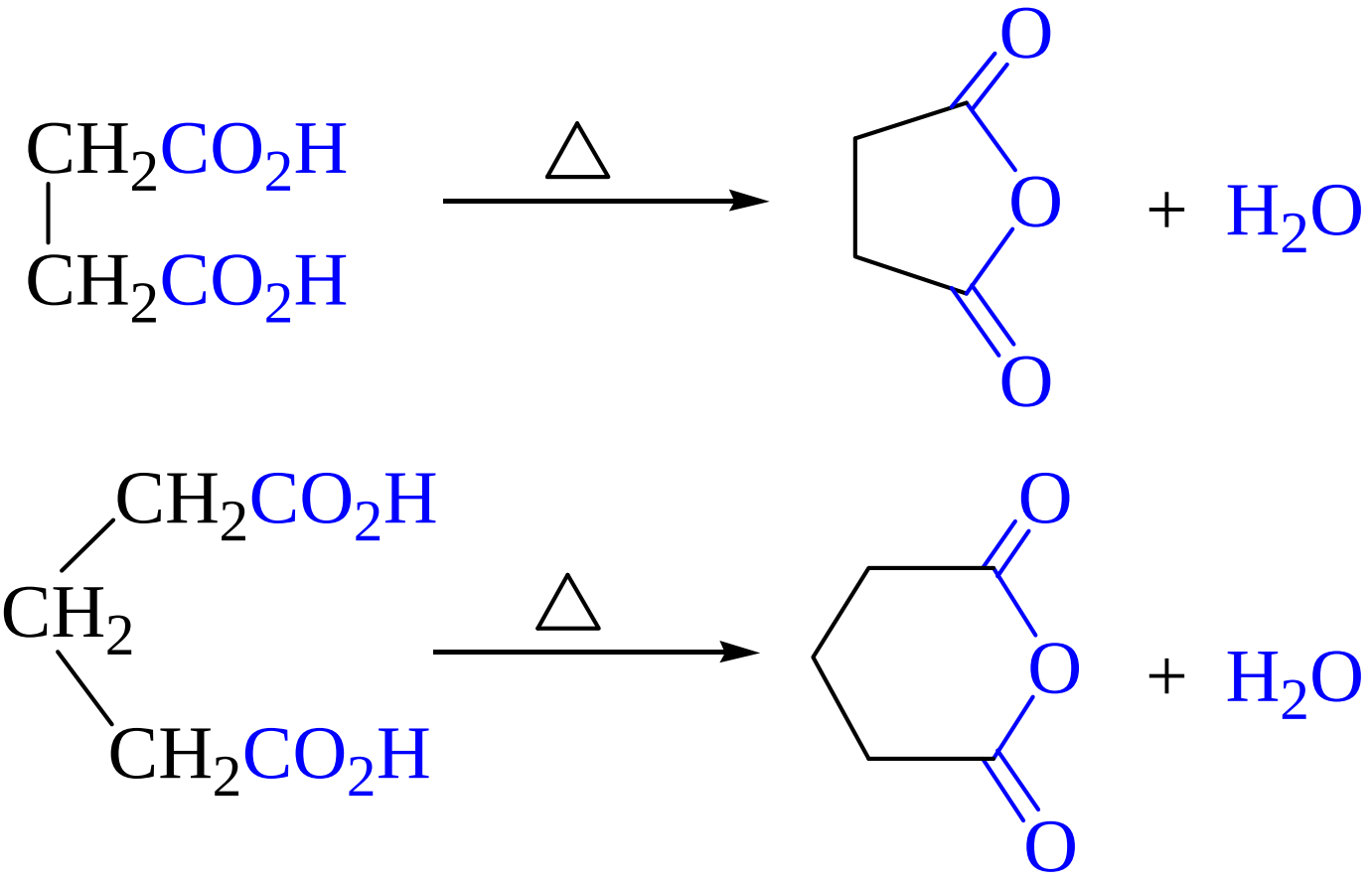
12.2.6 二元羧酸受热的反应

乙二酸、丙二酸受热发生脱羧反应生成一元羧酸；

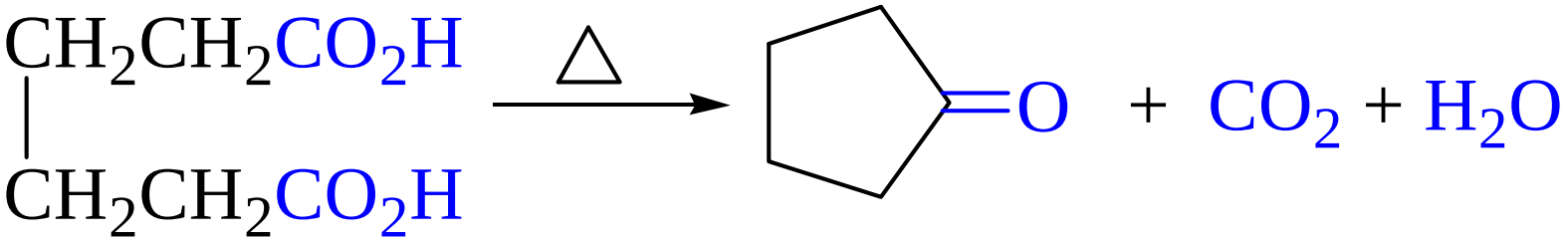


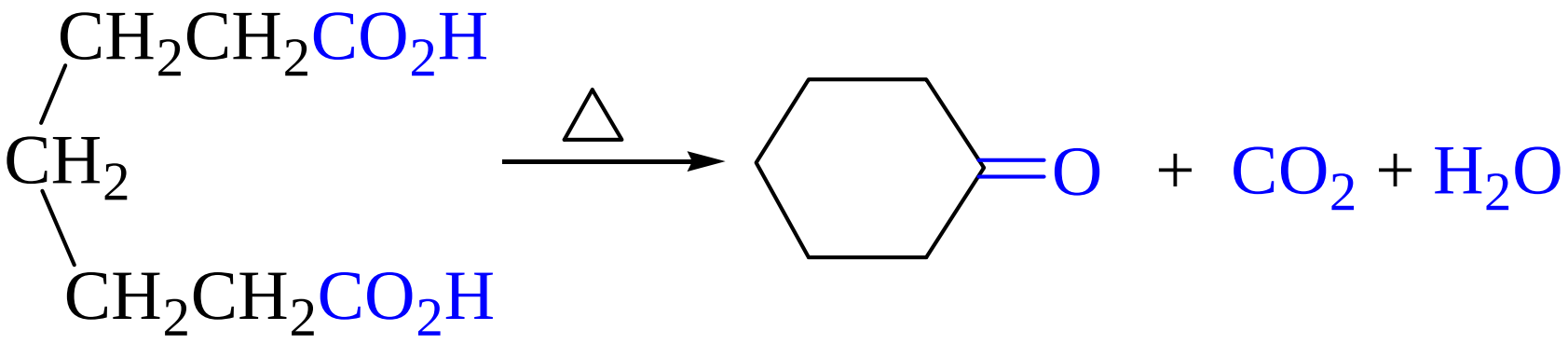


丁二酸、戊二酸受热发生脱水反应生成环状酸酐

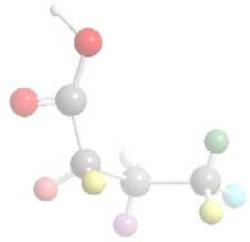


己二酸、庚二酸受热发生脱水兼脱羧反应生成环酮。

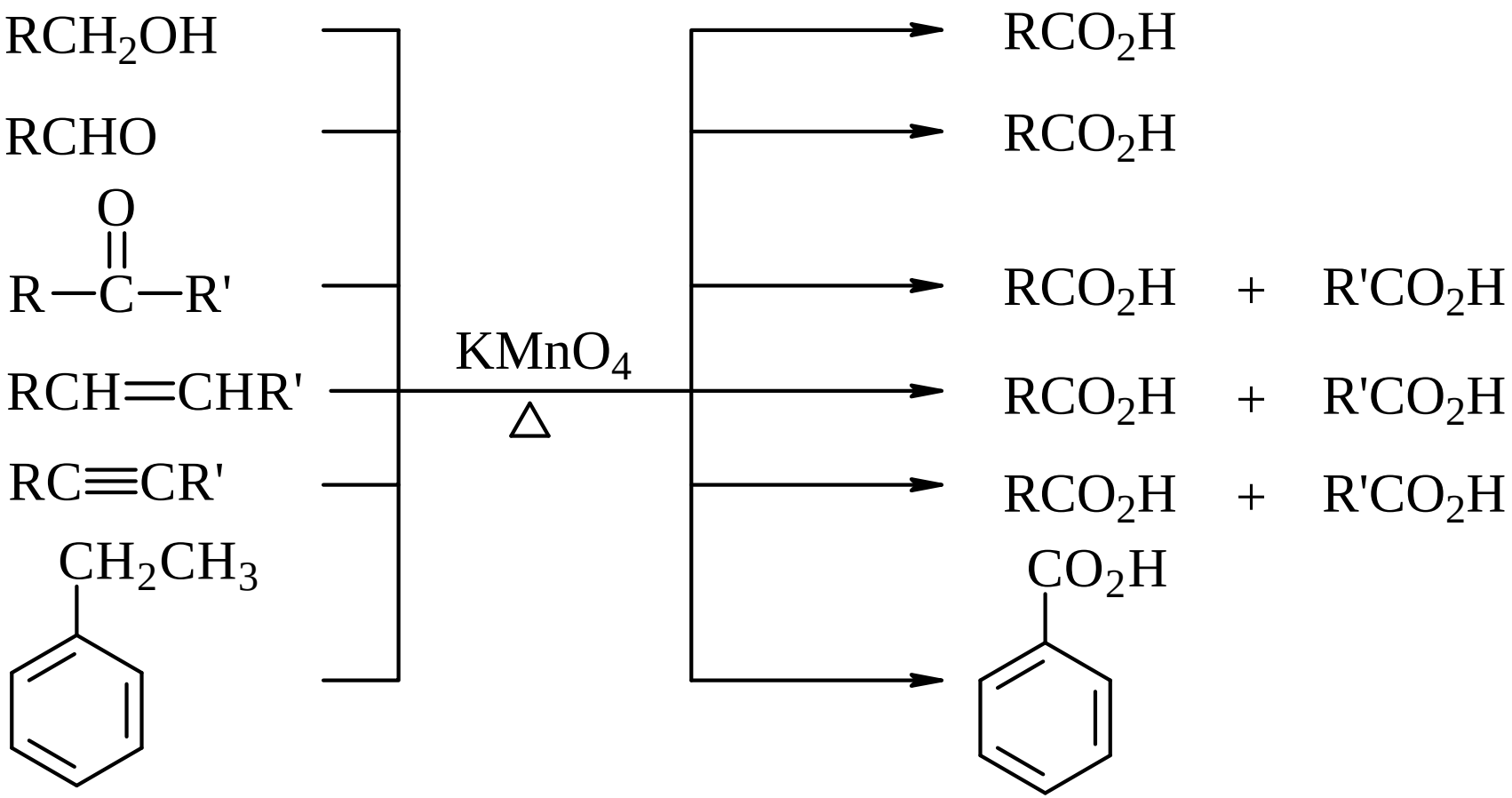




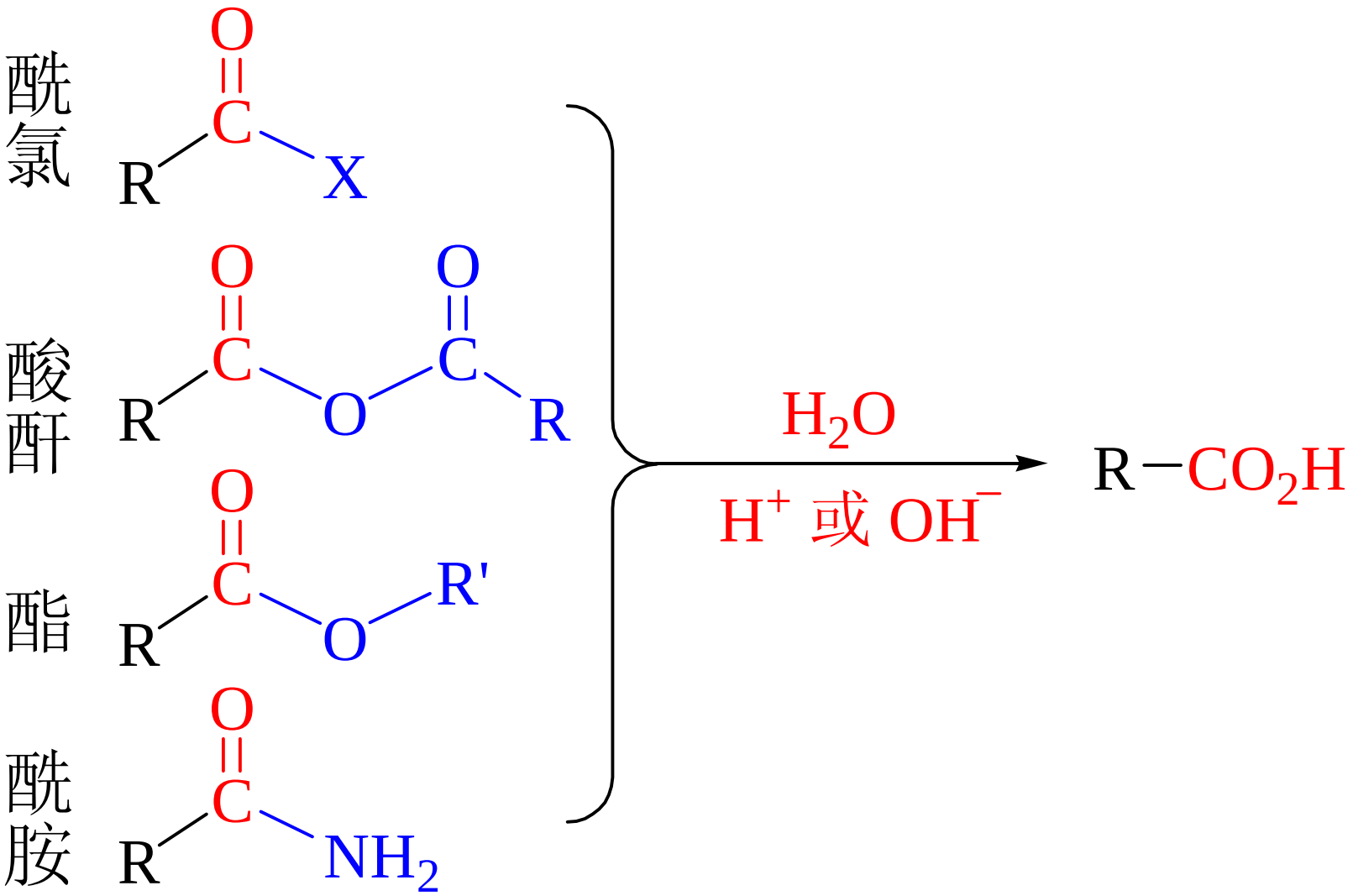
12.3 羧酸的制备



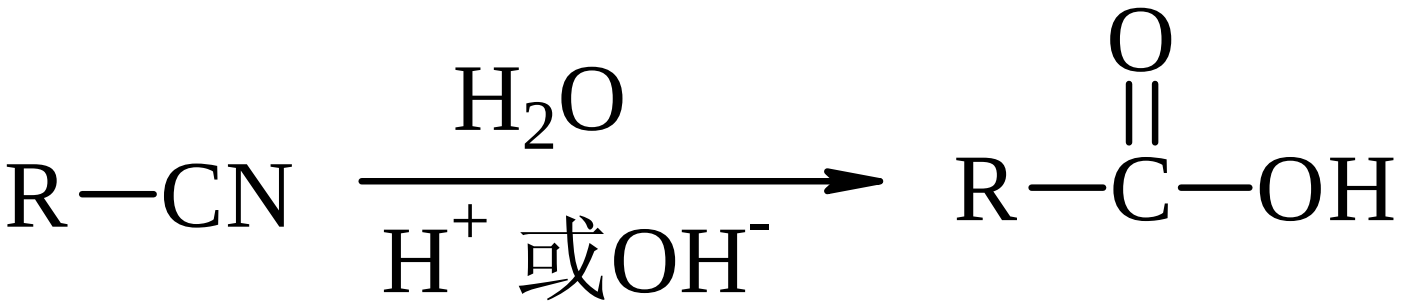
12.3.1 通过氧化反应制备



12.3.2 由羧酸衍生物水解



由腈水解



其中：

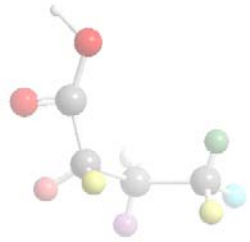
可由卤代烃制备增加一个碳原子的羧酸

12.3.3 有机金属化合物与二氧化碳反应制备

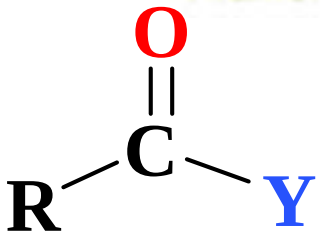
$$RMgX + CO_2 \longrightarrow RCO_2MgX$$

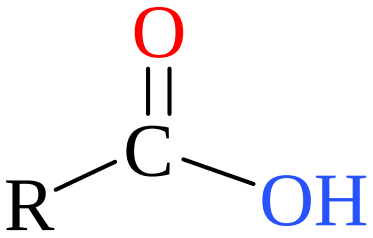
$$RCO_2MgX \xrightarrow[H^+]{H_2O} RCO_2H$$

12.4 羧酸衍生物

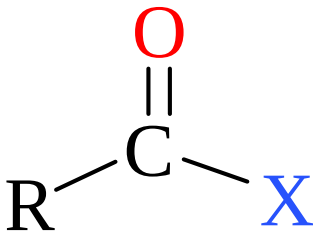


羧酸衍生物



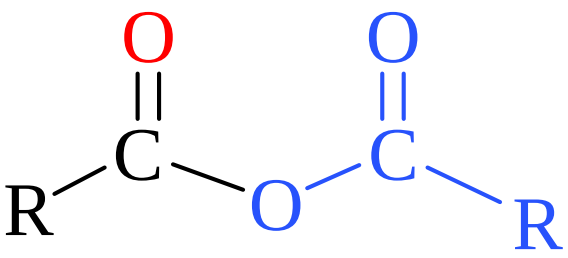


羧酸

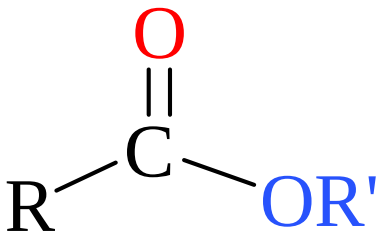


X = F, Cl, Br, I

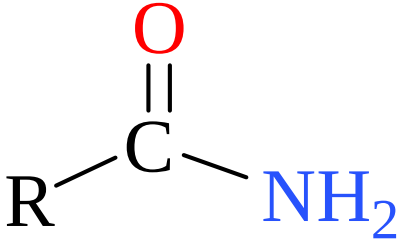
酰卤



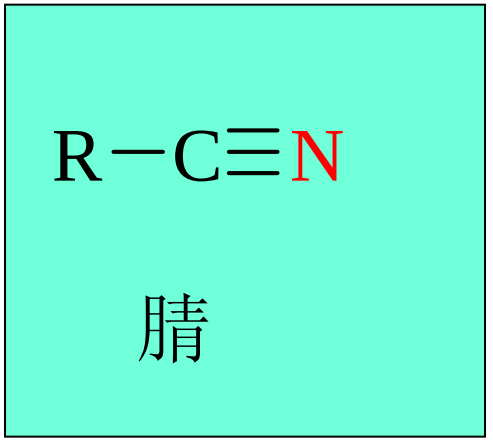
酸酐



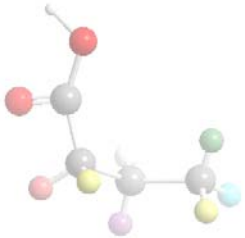
酯



酰胺



腈



12.4.1 羧酸衍生物的命名

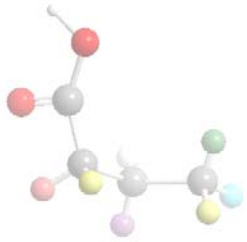
1. 酰卤的命名：RCOX

2. 酸酐的命名：RCO_2COR'

3. 酯的命名：RCO_2R'

4. 酰胺的命名：$RCONH_2$

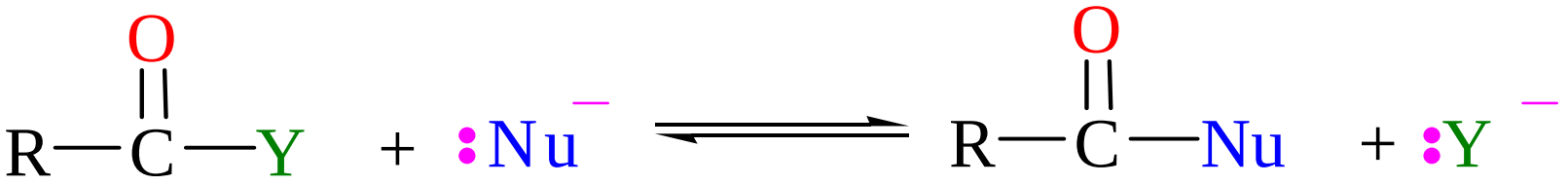
5. 腈的命名：RCN



12.4.2 羧酸衍生物的反应

一、亲核加成-消除反应

1. 反应机理



2. 水解反应

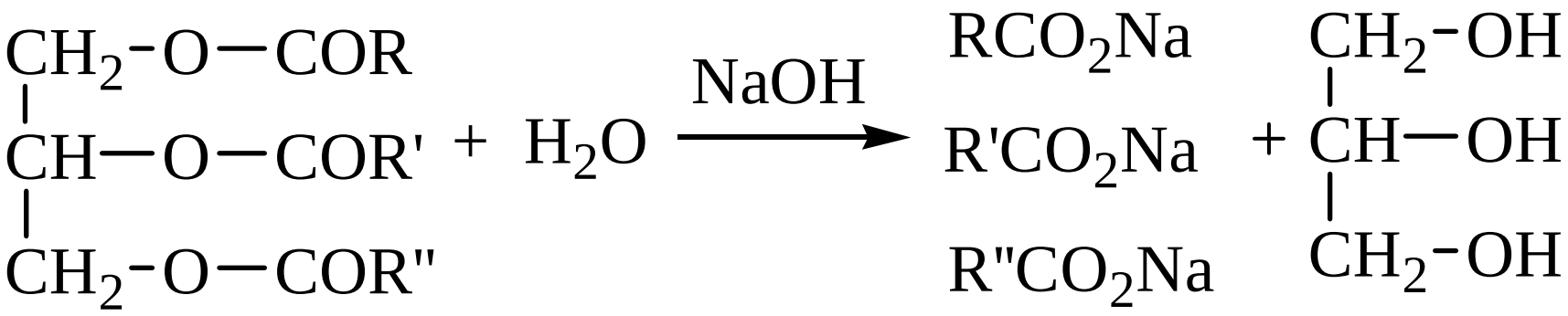
$$CH_3COCl + H_2O \longrightarrow CH_3CO_2H + HCl$$

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3CO_2H$$

$$CH_3CO_2C_2H_5 + H_2O \xrightarrow[\text{或}OH^-]{H^+} CH_3CO_2H + C_2H_5OH$$

$$CH_3CONH_2 + H_2O \xrightarrow[\text{或}OH^-]{H^+} CH_3CO_2H + NH_3$$

天然油脂的皂化反应

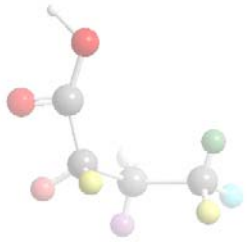

CH2-O—COR
CH—O—COR'
CH2-O—COR"
+ H2O
NaOH
RCO2Na
R'CO2Na
R"CO2Na
+
CH2-OH
CH—OH
CH2-OH

3. 醇解反应

$$CH_3COCl + C_2H_5OH \xrightarrow{\text{碱}} CH_3CO_2C_2H_5 + HCl$$

$$(CH_3CO)_2O + C_2H_5OH \xrightarrow{\text{碱}} CH_3CO_2C_2H_5 + CH_3CO_2H$$

$$CH_3CO_2CH_3 + C_2H_5OH \xrightarrow[\text{或}C_2H_5O^-]{H^+} CH_3CO_2C_2H_5 + CH_3OH$$



4. 氨解反应

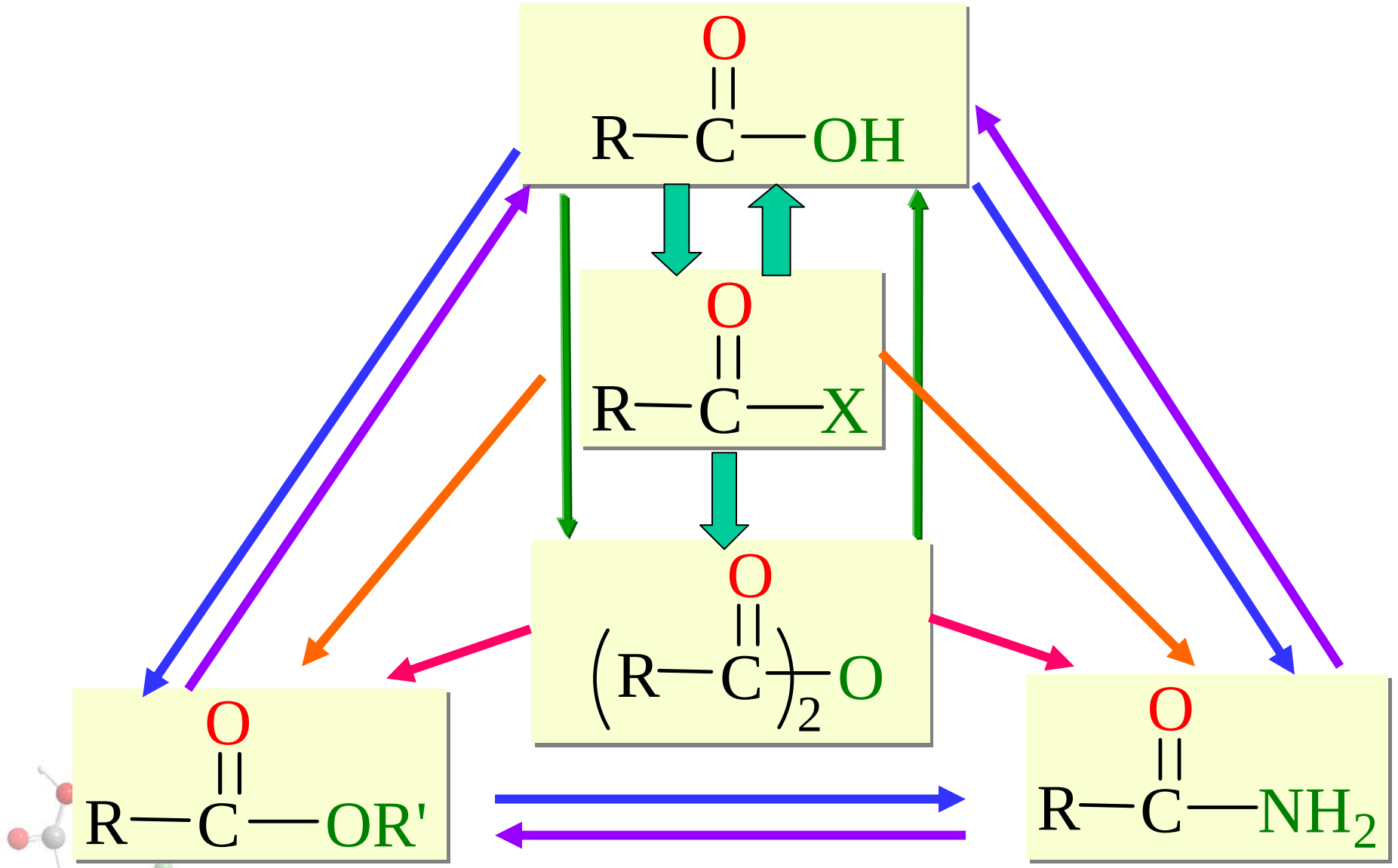
$$CH_3COCl + NH_3 \xrightarrow{碱} CH_3CONH_2 + HCl$$

$$(CH_3CO)_2O + (C_2H_5)_2NH \xrightarrow{碱} CH_3CON(C_2H_5)_2 + CH_3CO_2H$$

$$CH_3CO_2CH_2CH_3 + NH_3 \longrightarrow CH_3CONH_2 + CH_3CH_2OH$$

$$CH_3CONH_2 + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + NH_3$$

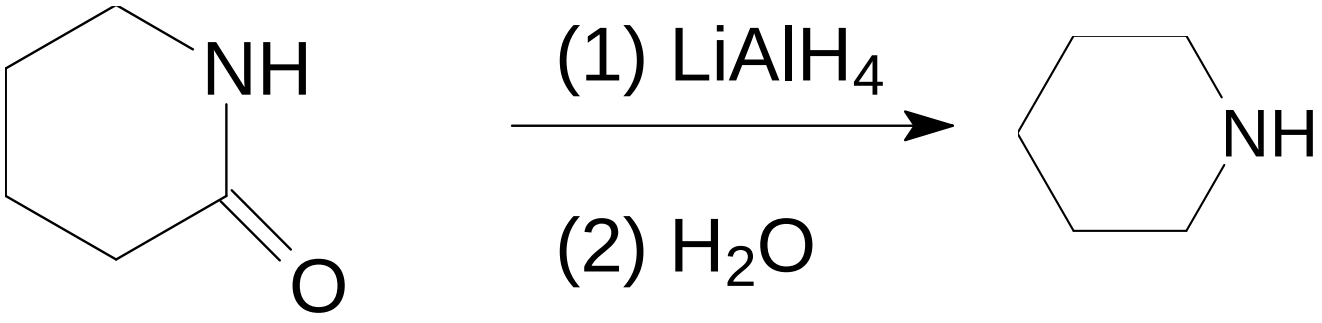
5. 羧酸衍生物的相互转化



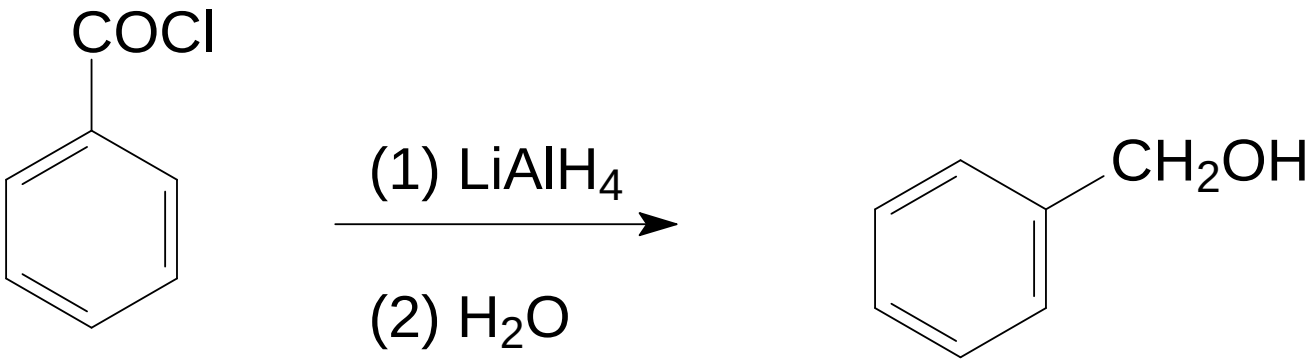
二、还原反应

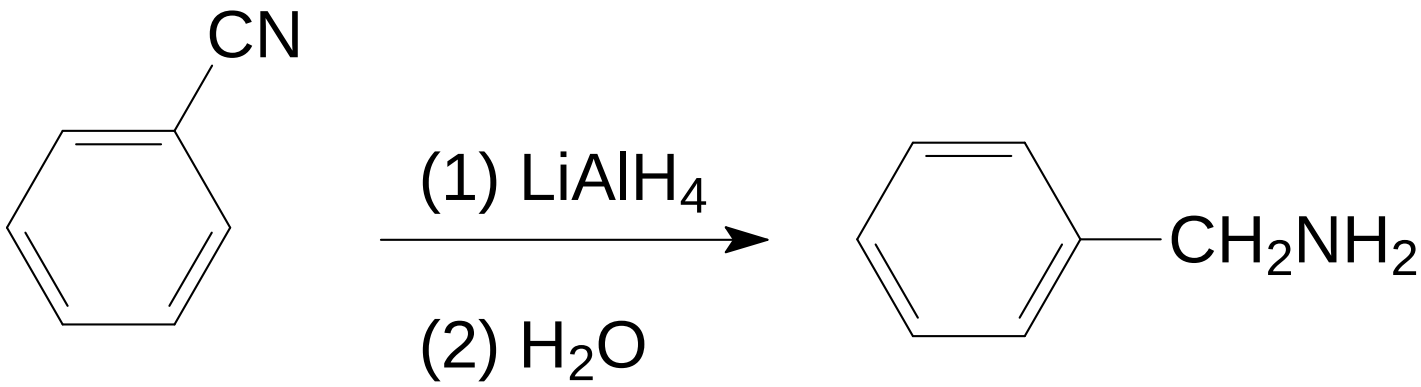
1. 用氢化铝锂($LiAlH_4$)还原：

$$C_{15}H_{31}COCl \xrightarrow[(2)H_2O]{(1)\ LiAlH_4} C_{15}H_{31}CH_2OH$$



$CH_3CH_2COOCH_2CH_2CH_3$ $\xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4}$ $CH_3CH_2CH_2OH$





2. 金属钠-醇还原

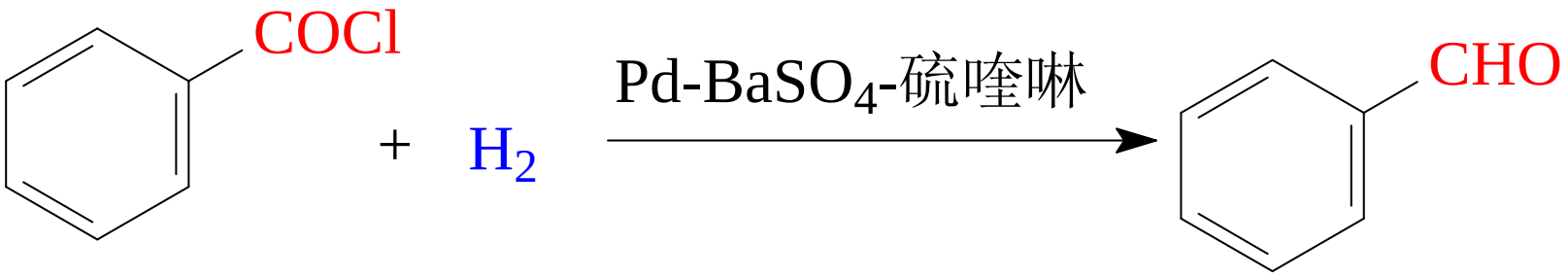
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOC_2H_5 \xrightarrow[CH_3CH_2OH]{Na}$$

油酸乙酯

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$$

油醇

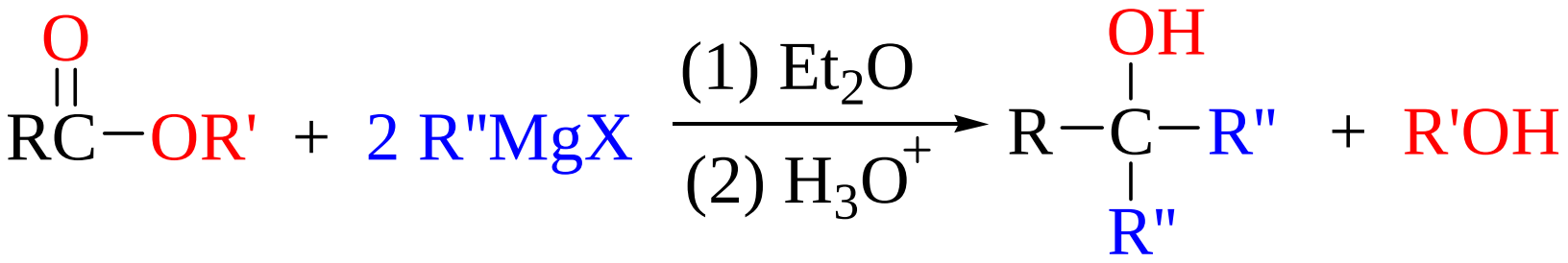
3. Rosenmund 还原

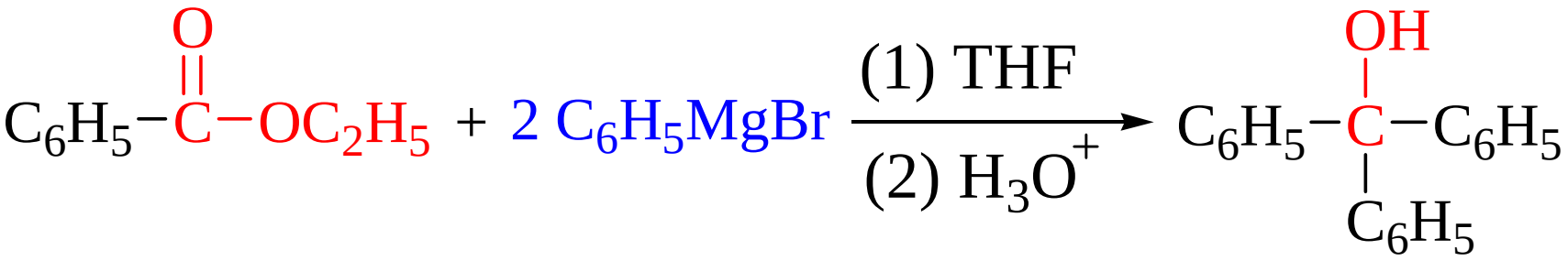


$$CH_3CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2COCl$$

$$CH_3CH_2COCl \xrightarrow[Pd\text{-}BaSO_4\text{-硫喹啉}]{H_2} CH_3CH_2CHO$$

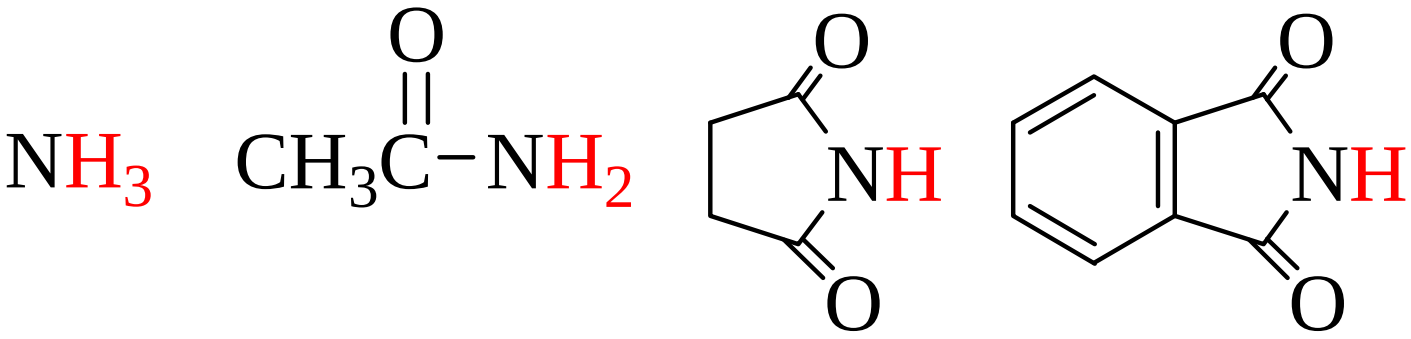
三、与有机金属化合物的反应





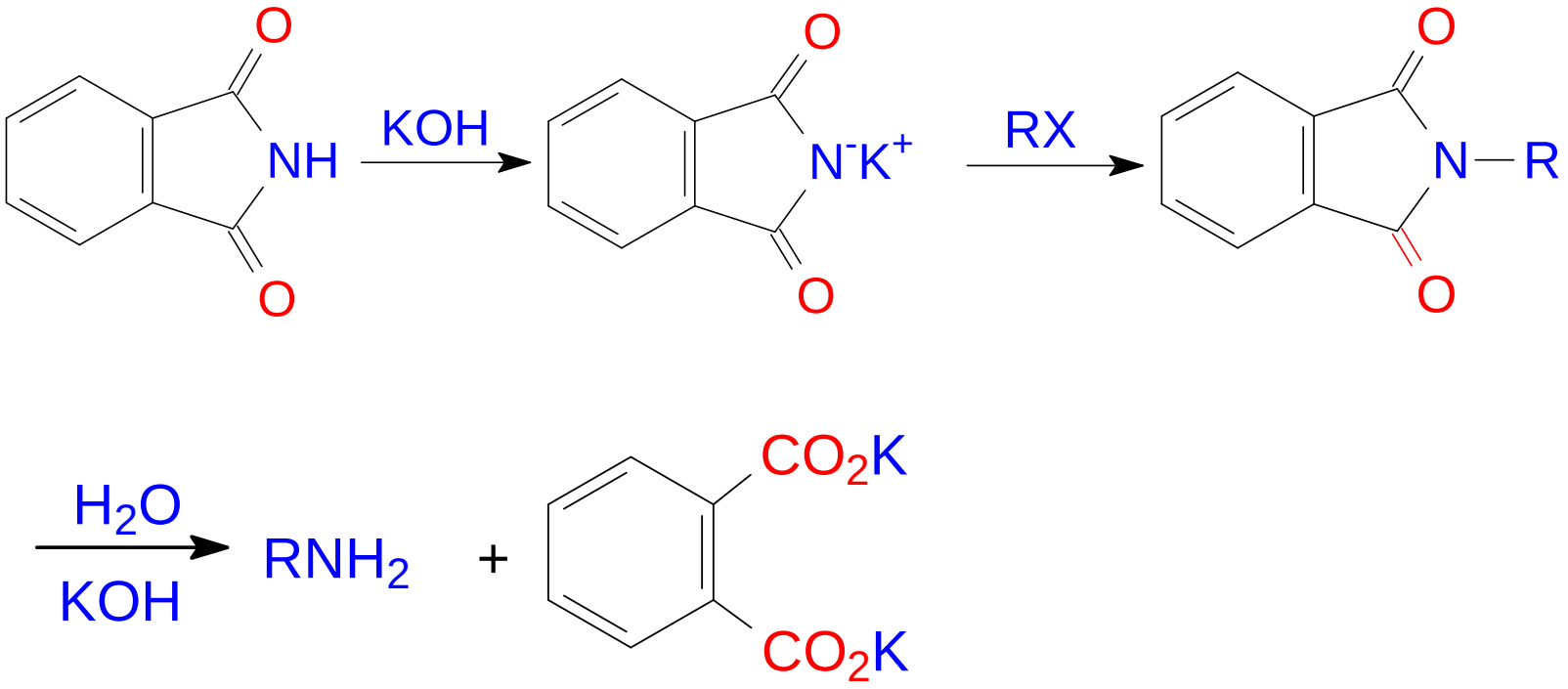
12.4.3 酰胺的特殊性质

1. 酰胺的酸碱性

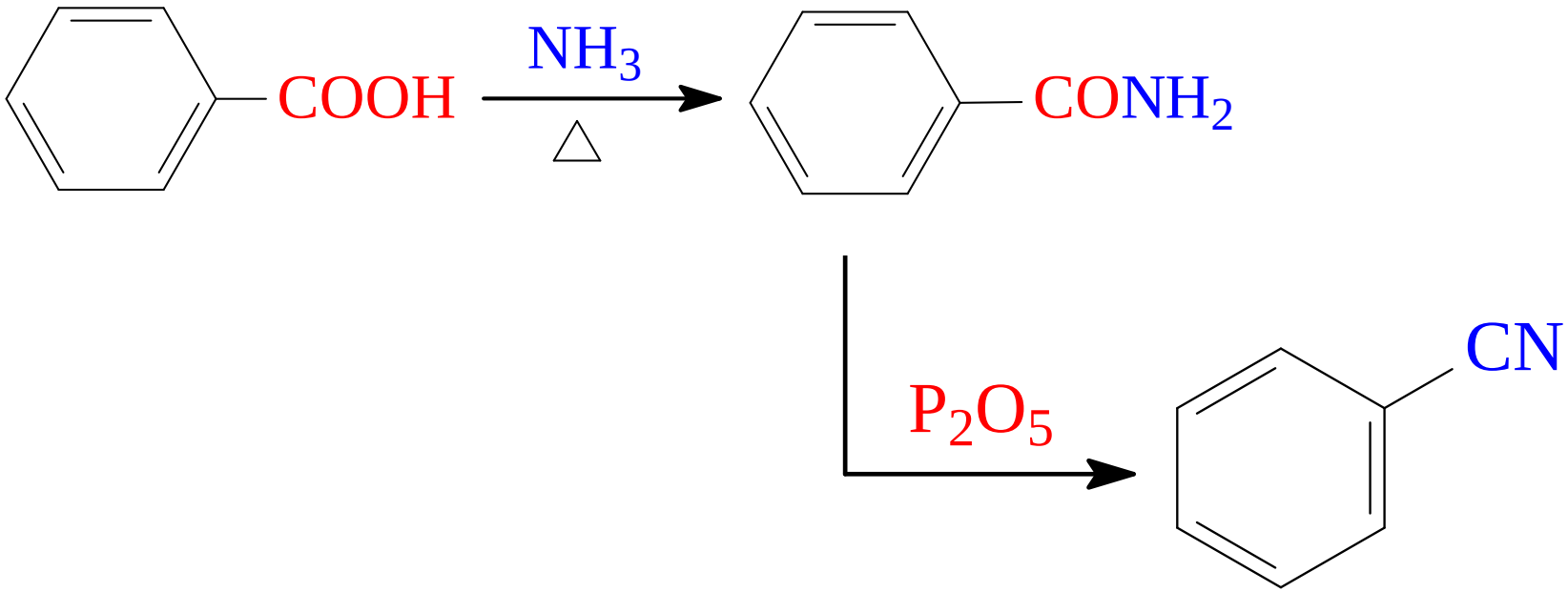


	NH_3	$CH_3C(=O)NH_2$		
pKa	34	~15.1	~9.6	~7.4

Gabriel反应——用于一级胺的制备：

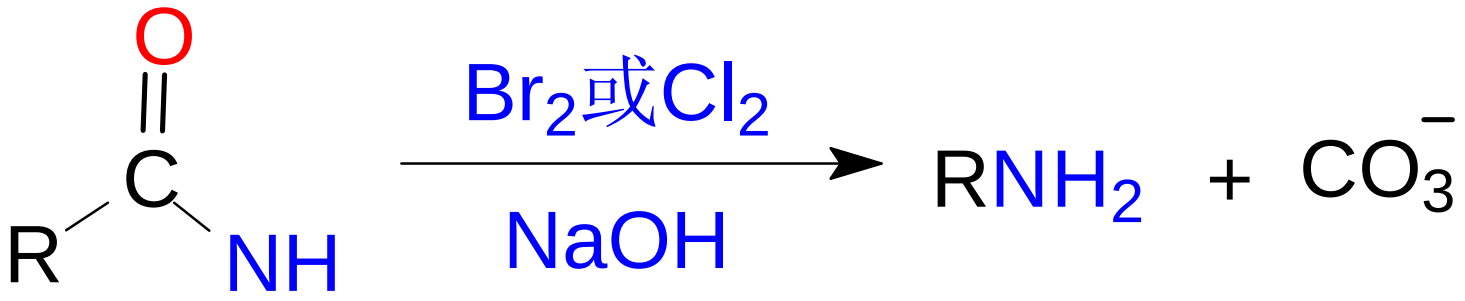


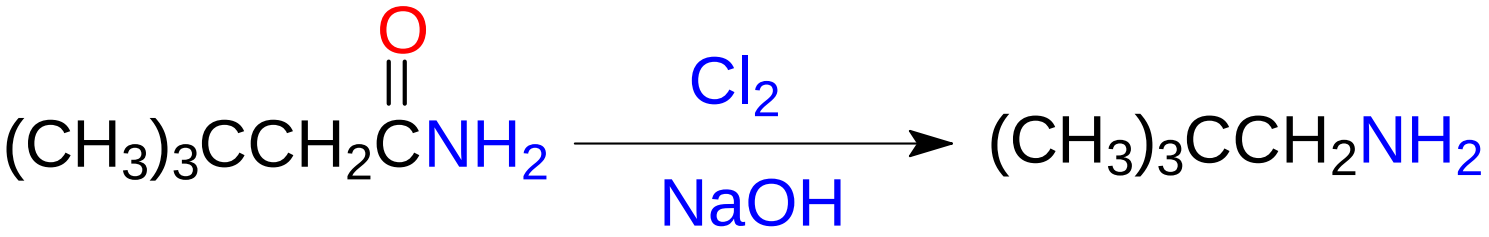
2. 酰胺的脱水

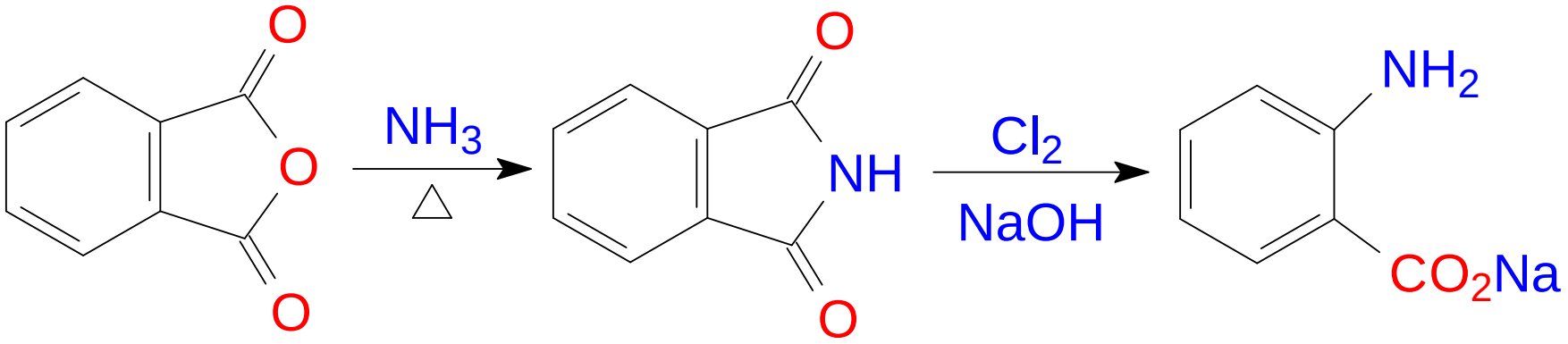


3.Hofmann降解反应

酰胺与溴或氯在碱溶液中作用，脱去羰基生成一级胺，使碳链减少一个碳原子的反应，通常称为**Hofmann降解反应**




O
(CH3)3CCH2CNH2
Cl2
NaOH
(CH3)3CCH2NH2


O
O
O
NH3
△
O
NH
O
Cl2
NaOH
NH2
CO2Na

12.4.4 重要的羧酸和衍生物

（自学）