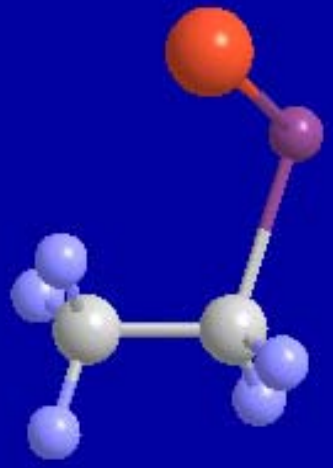
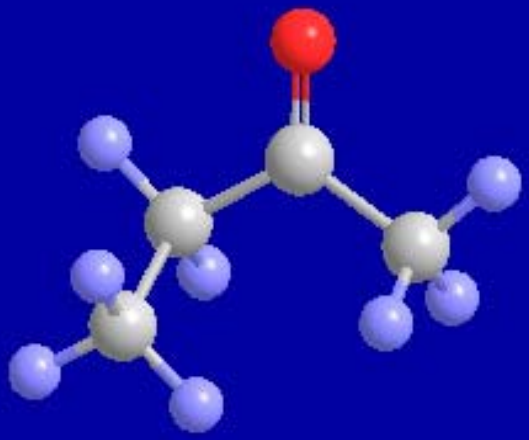
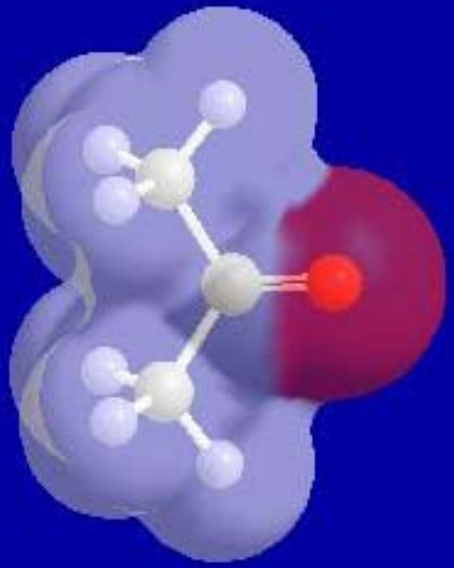
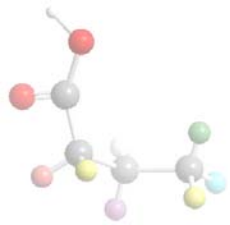




第十三章 取代酸和β-二羰基化合物

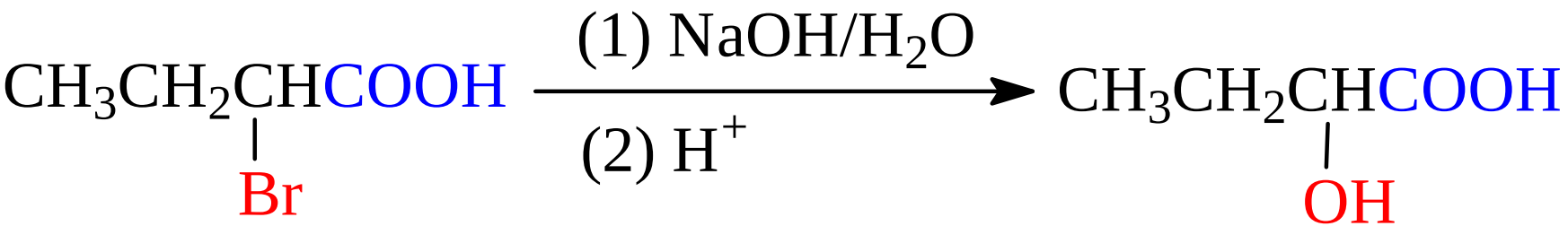


13.1 羟基酸



13.1.1 羟基酸的制备

1. 卤代酸水解



β-卤代酸水解易发生消除反应

2. 羟基腈水解

α-羟基酸

$$CH_3CH_2CH_2CHO \xrightarrow{HCN} CH_3CH_2CH_2CH(OH)CN$$

$$\xrightarrow{浓HCl} CH_3CH_2CH_2CH(OH)CO_2H$$

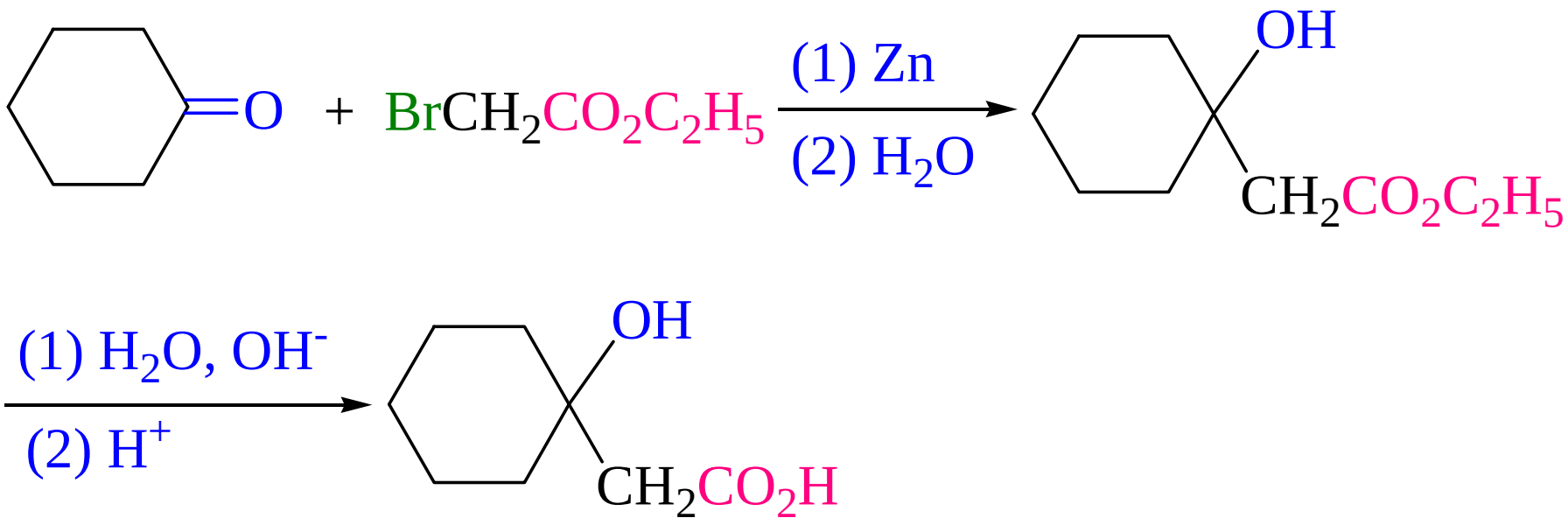
β-羟基酸

$$HOCH_2CH_2Cl + NaCN \longrightarrow HOCH_2CH_2CN$$

$$\xrightarrow{NaOH} \xrightarrow{H^+} HOCH_2CH_2CO_2H$$

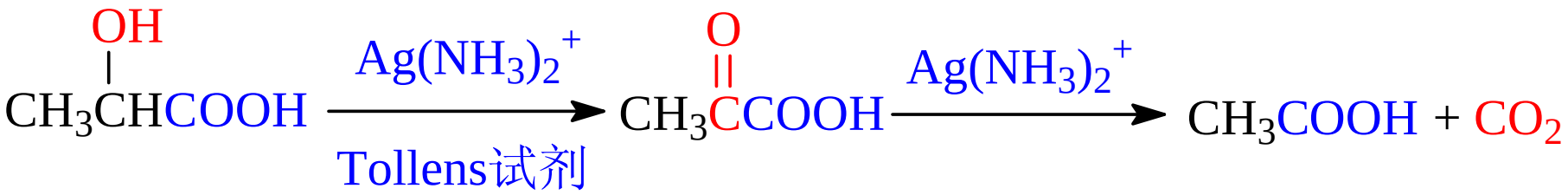
3. Reformatsky反应

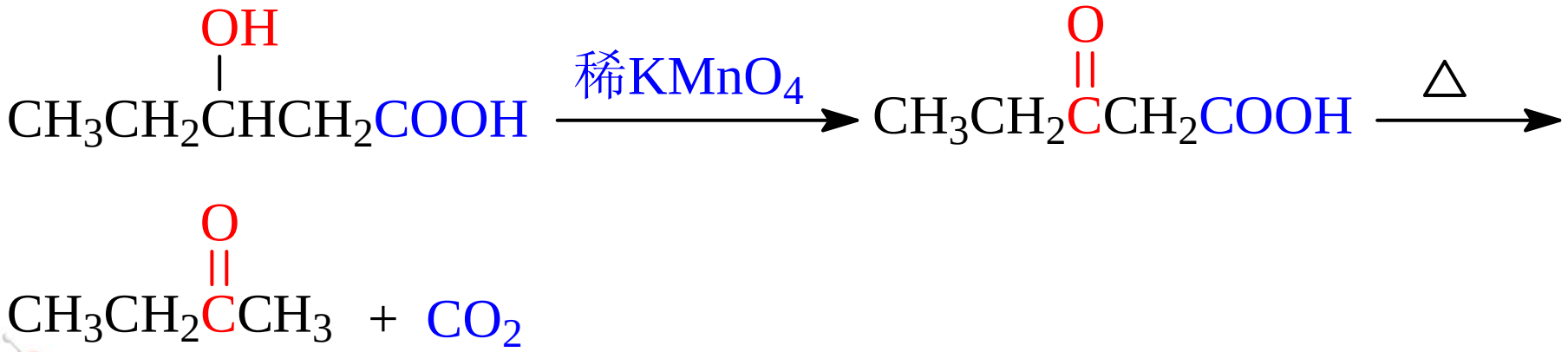
醛或酮与α-卤代酸酯在惰性溶剂（苯）中与锌粉反应，产物水解后得β-羟基酸。



13.1.2 羟基酸的反应

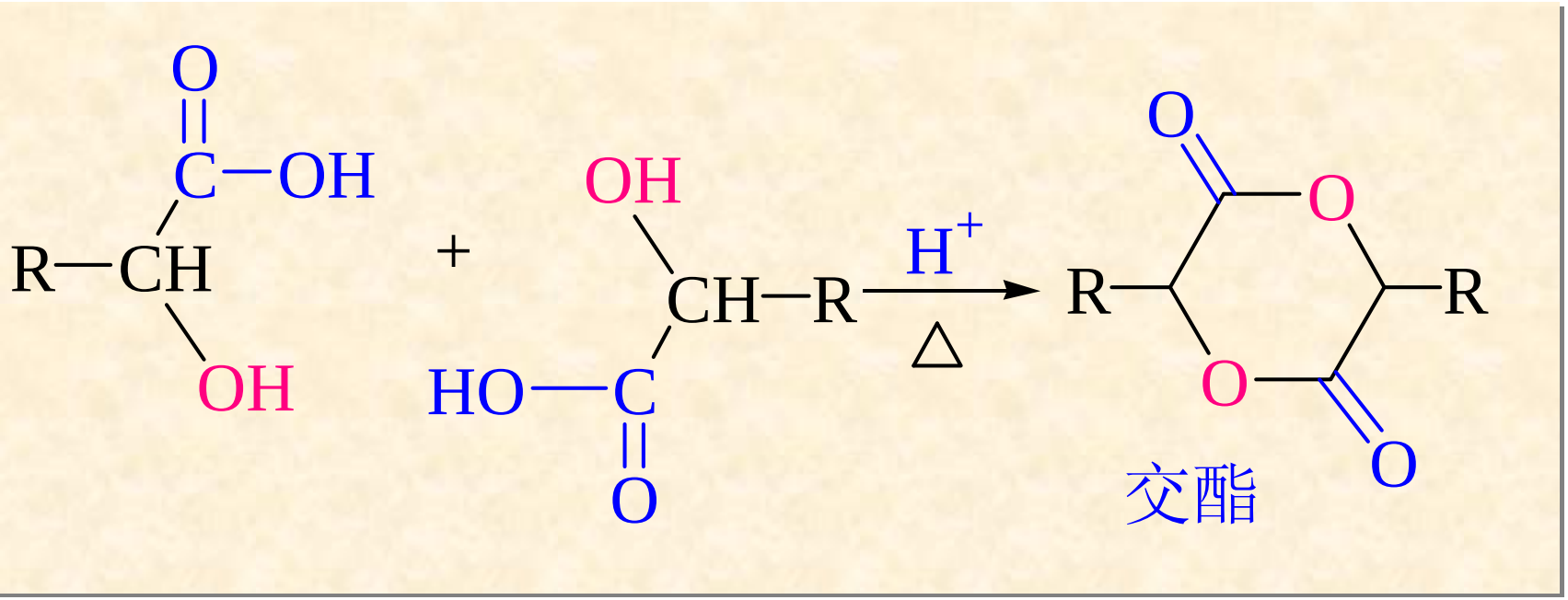
1. 氧化反应



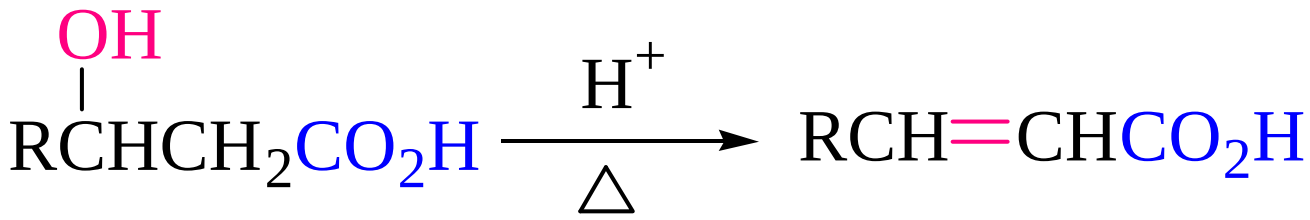


2. 脱水反应

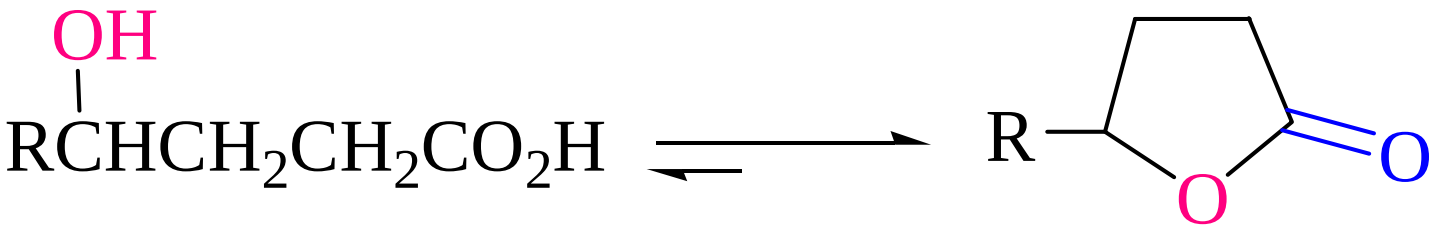
(1) α–羟基酸在酸存在下加热脱水形成交酯。



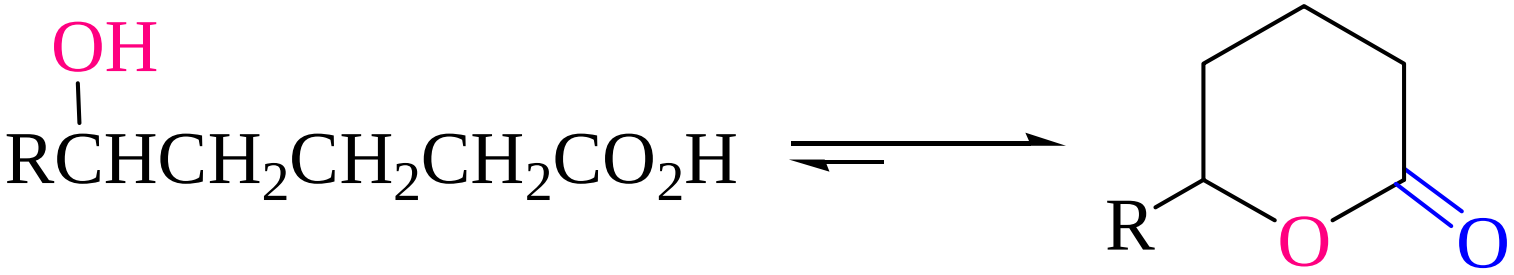
(2) β-羟基酸在酸存在下加热脱水形成 α,β-不饱和酸



(3) γ-和δ-羟基酸在酸作用下脱水形成内酯

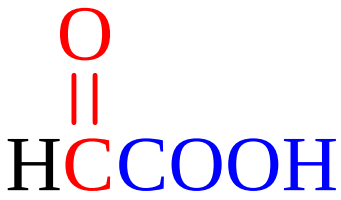


γ-羟基酸　　γ-内酯



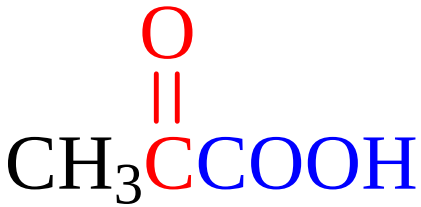
δ-羟基酸　　δ-内酯

13.2 羰基酸



氧代乙酸

（乙醛酸）

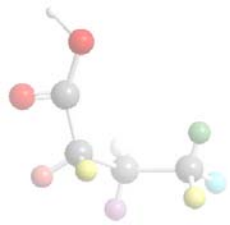


2-氧代丙酸

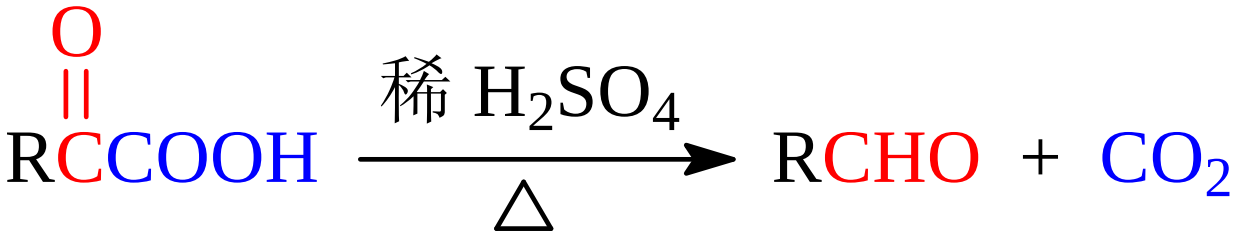
（丙酮酸）

3-氧代丁酸

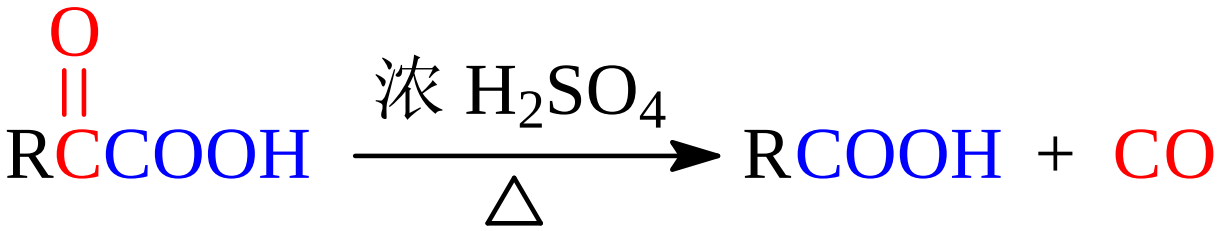
（乙酰乙酸）



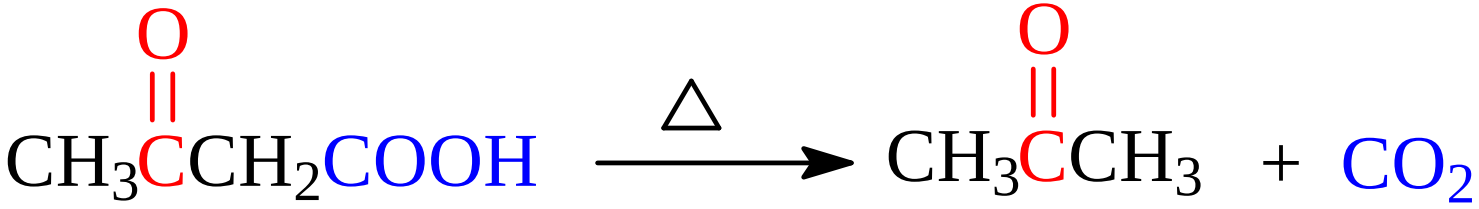
α-酮酸与稀硫酸共热，发生脱羧反应：



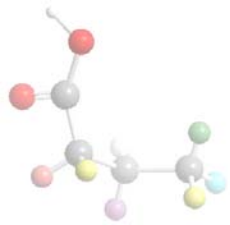
α-酮酸与浓硫酸共热，发生脱羰反应：



β-酮酸受热，发生脱羧反应：

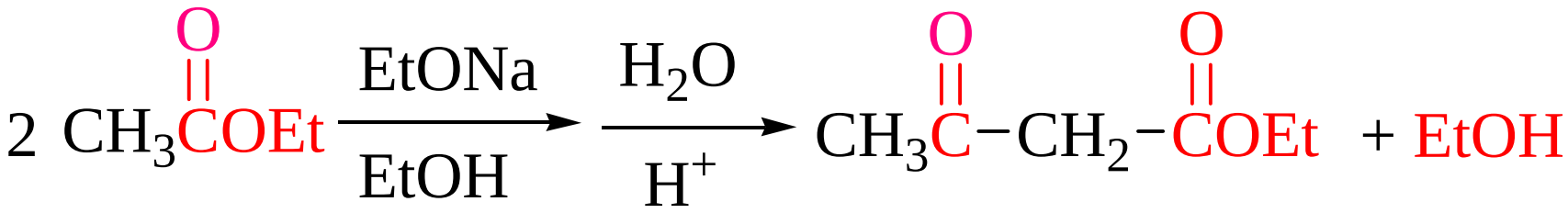


13.3 β-酮酸酯

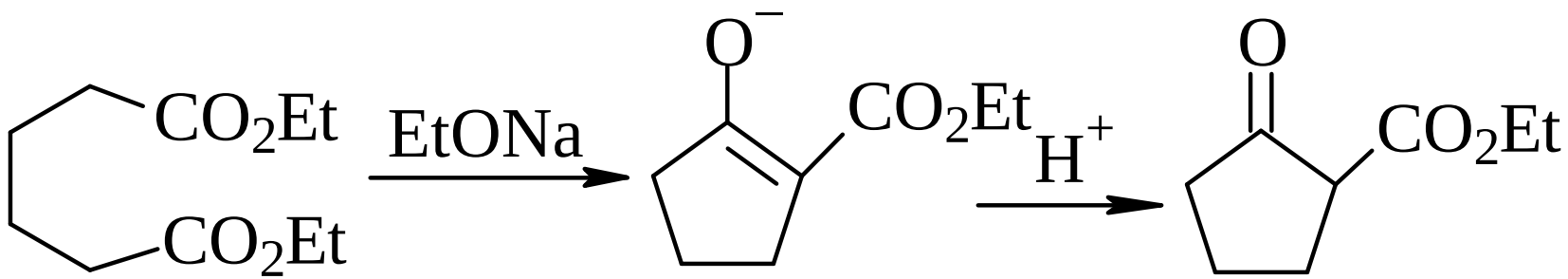


13.3.1 Claisen酯缩合反应

Claisen 酯缩合： 含α–氢的酯在碱的作用下，两分子酯发生缩合反应，生成 β–酮酸酯同时消去一分子醇。

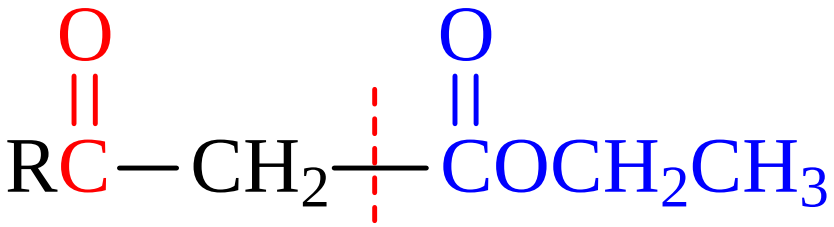


乙酸乙酯　　乙酰乙酸乙酯

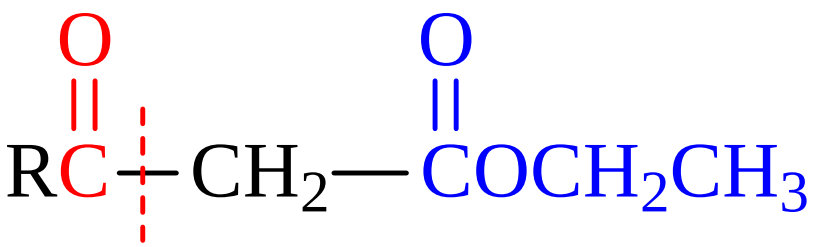


Dieckmann 缩合反应

13.3.2 β-酮酸酯的水解



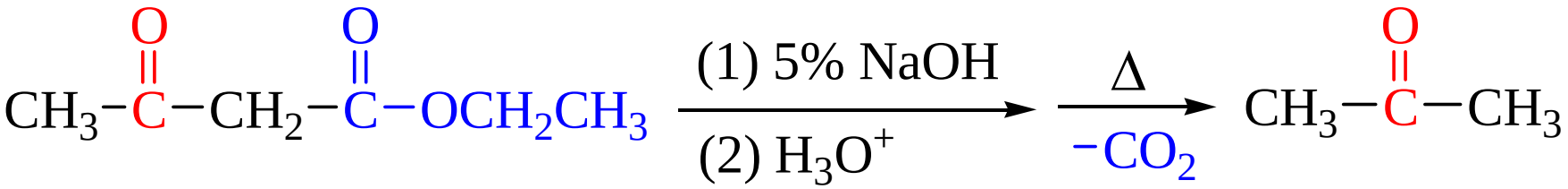
成酮水解



成酸水解

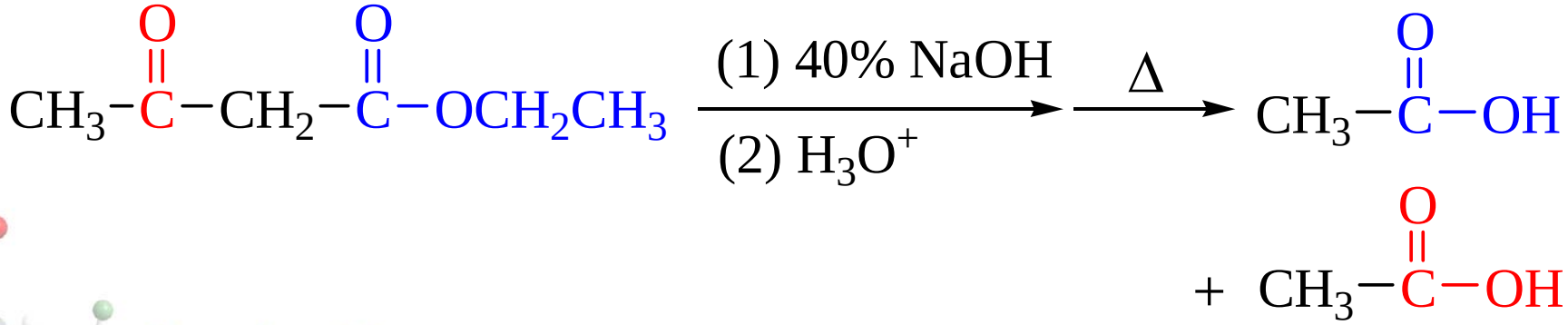
1. 成酮水解（酮式分解）

乙酰乙酸乙酯在稀碱溶液水解，酸化后加热脱羧得丙酮

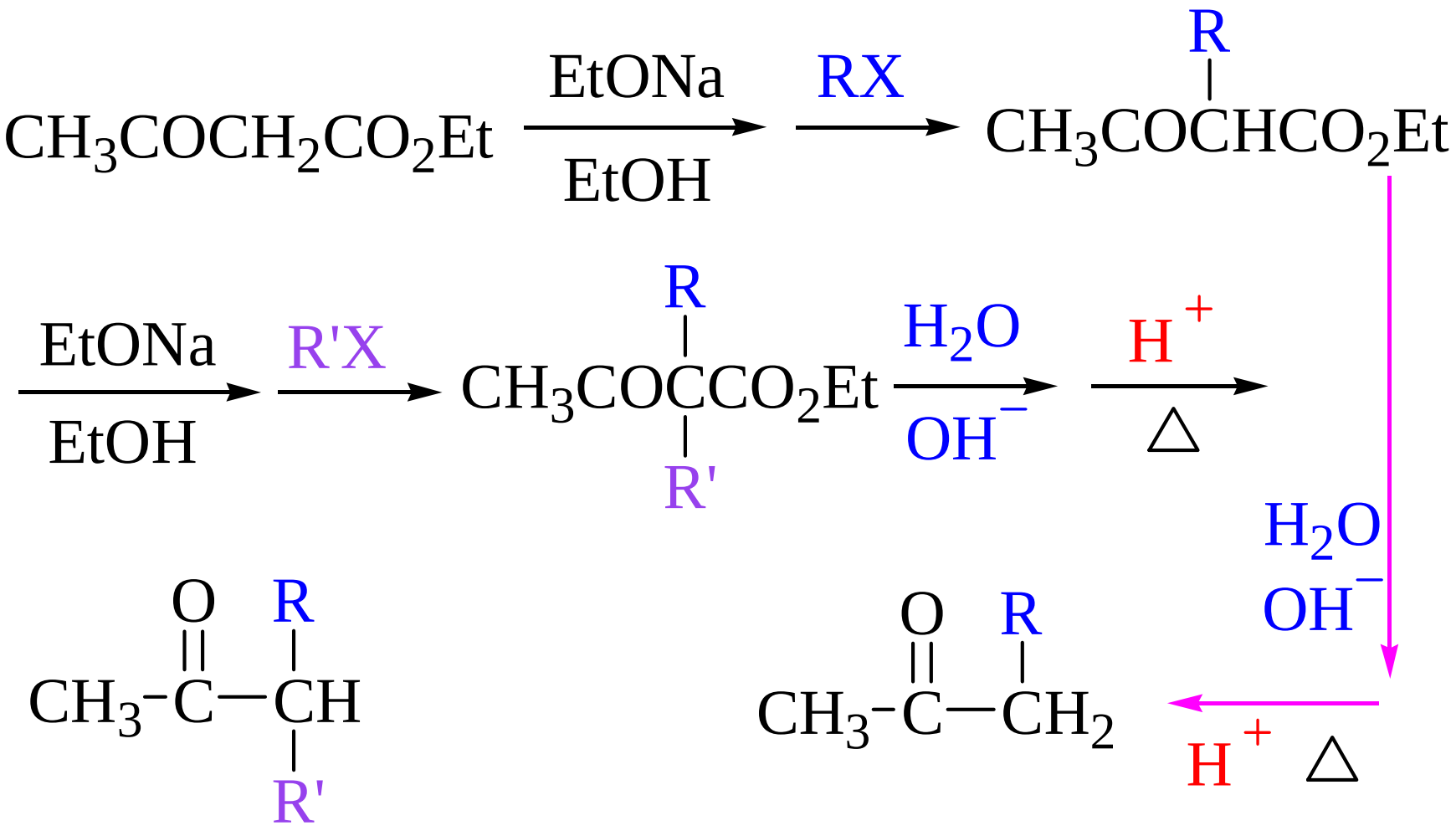


2. 成酸水解（酸式分解）

乙酰乙酸乙酯在浓碱溶液水解，发生$C_\alpha - C_\beta$键断裂，酸化后生成两个羧酸。

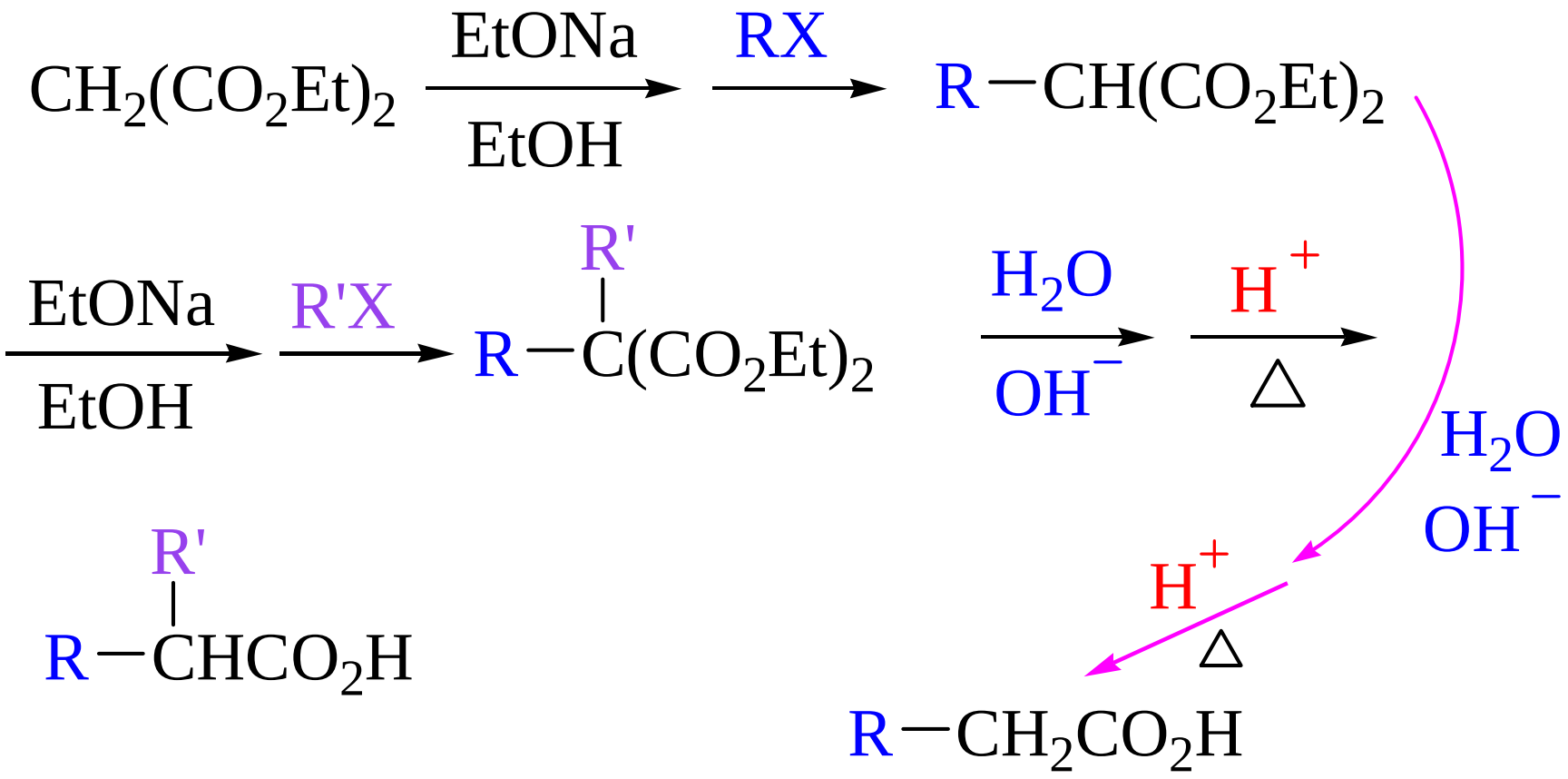


13.3.3 乙酰乙酸乙酯在合成上的应用



合成取代丙酮

13.3.3 丙二酸二乙酯在合成上的应用



合成取代乙酸