

博学 求真 厚德 正人

有机化学

第十四章 β -二羰基化合物



聊城大学化学化工学院

Liaocheng University





β -二羰基化物：两个羰基被一个碳原子隔开的化合物

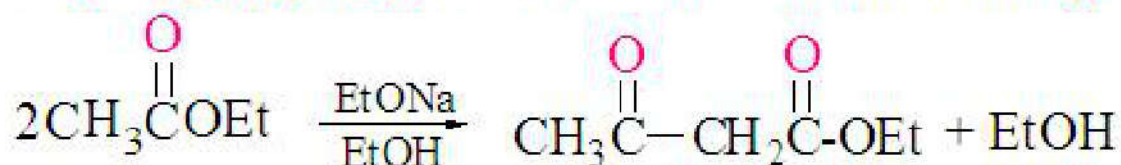


14.1 乙酰乙酸乙酯 (EAA) 及应用

14.1.1 制备

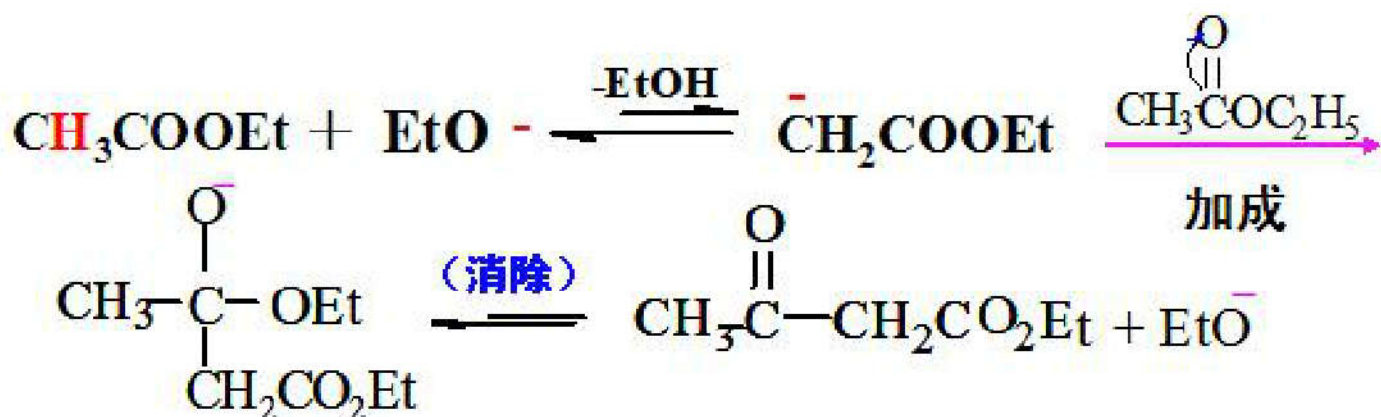
一、Claisen酯缩合

含 α -氢的酯在碱作用下，分子间缩合生成 β -酮酸酯



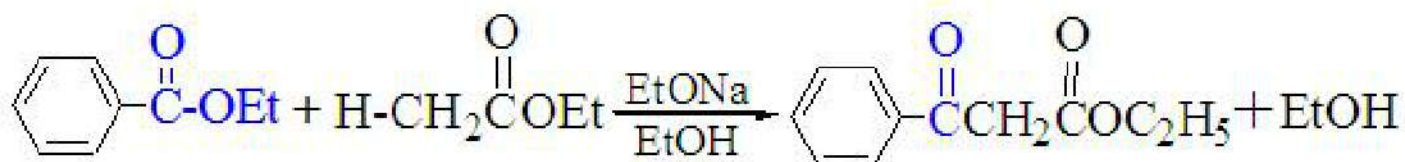
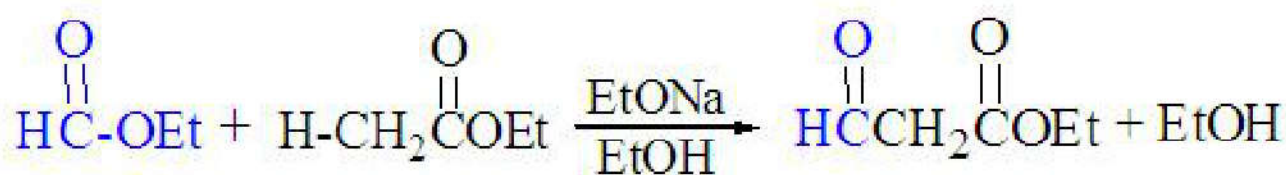
反应历程





二、交错酯缩合

含 α -氢和不含 α -氢的酯在碱作用下分子间缩合

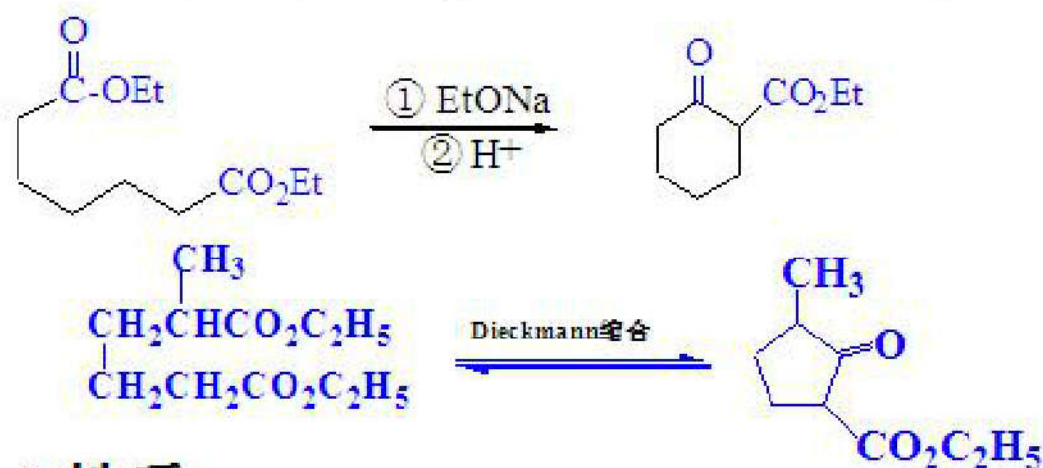




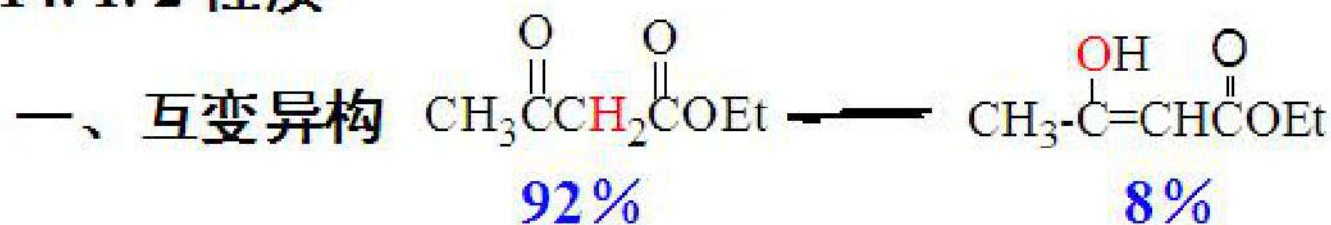
无 α -氢酯: HCOOR 、 PhCOOR 、 $(\text{COOR})_2$ 等

三、Dieckmann反应

含 α -氢二元酸酯在碱作用下分子内缩合

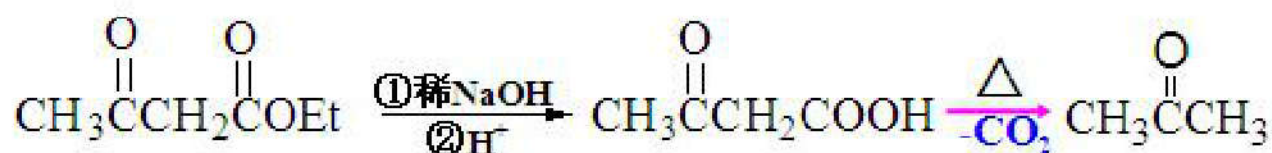


14.1.2 性质



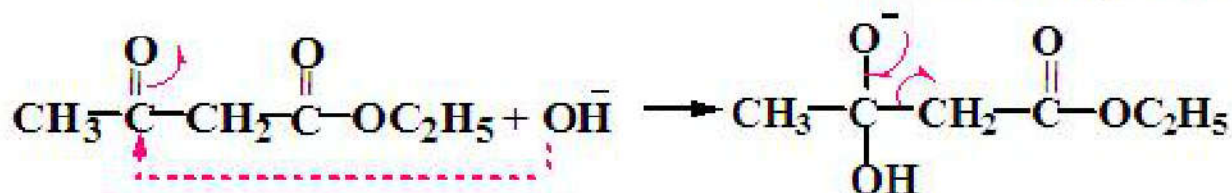
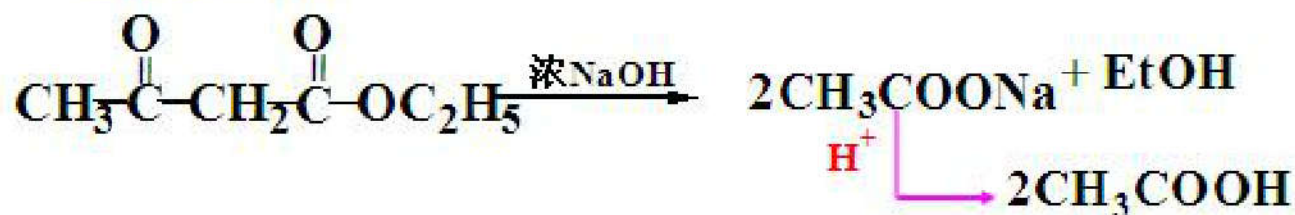


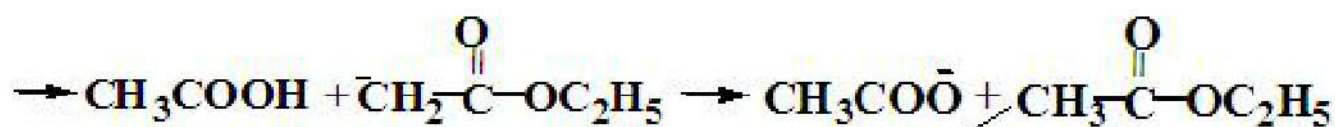
2、酮式分解



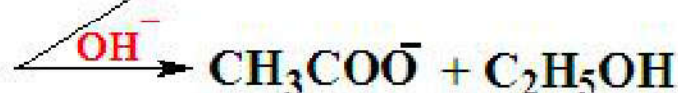
3、酸式分解

历程:

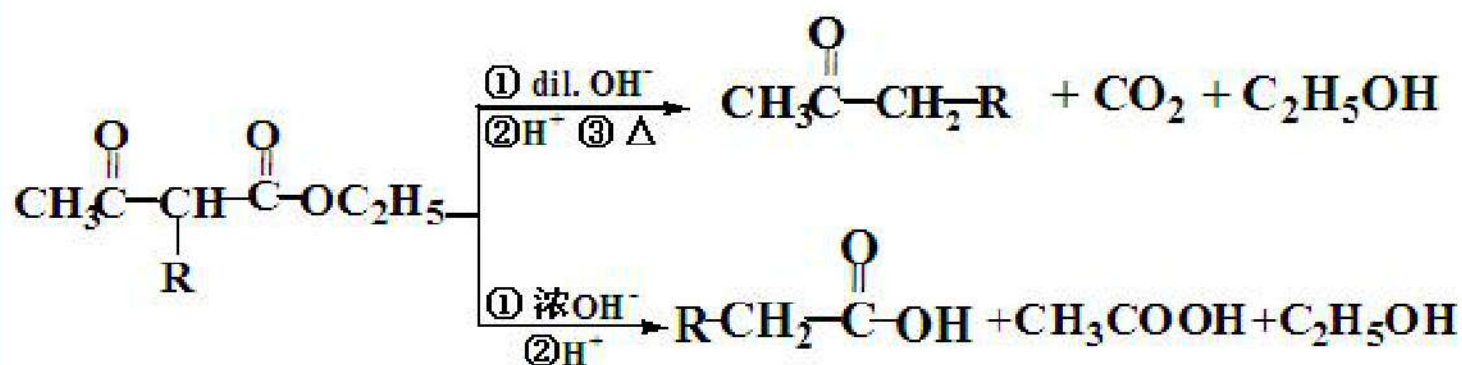
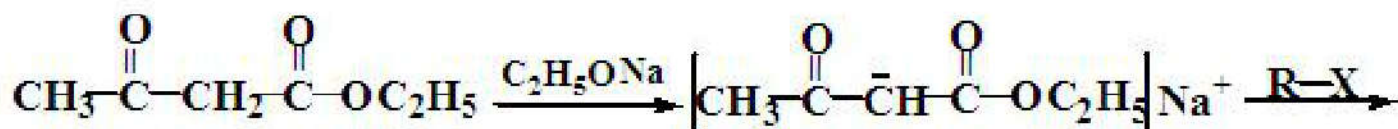


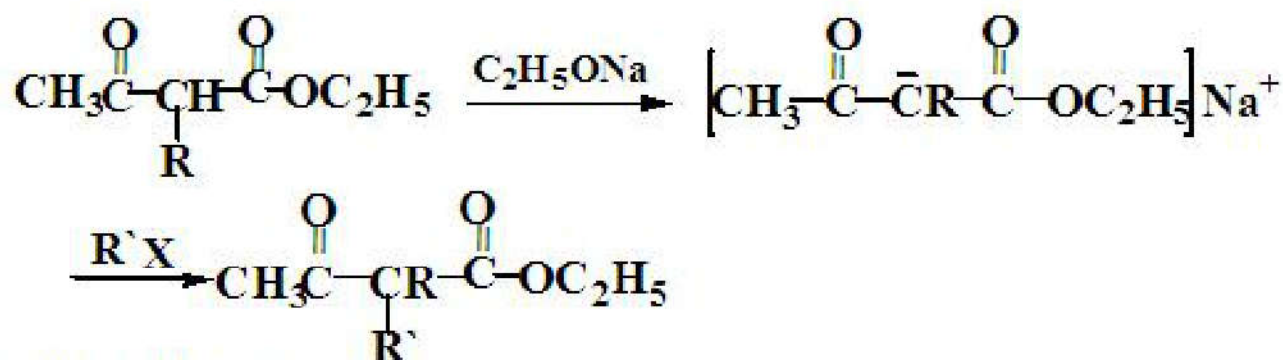


* 4、活泼亚甲基上反应



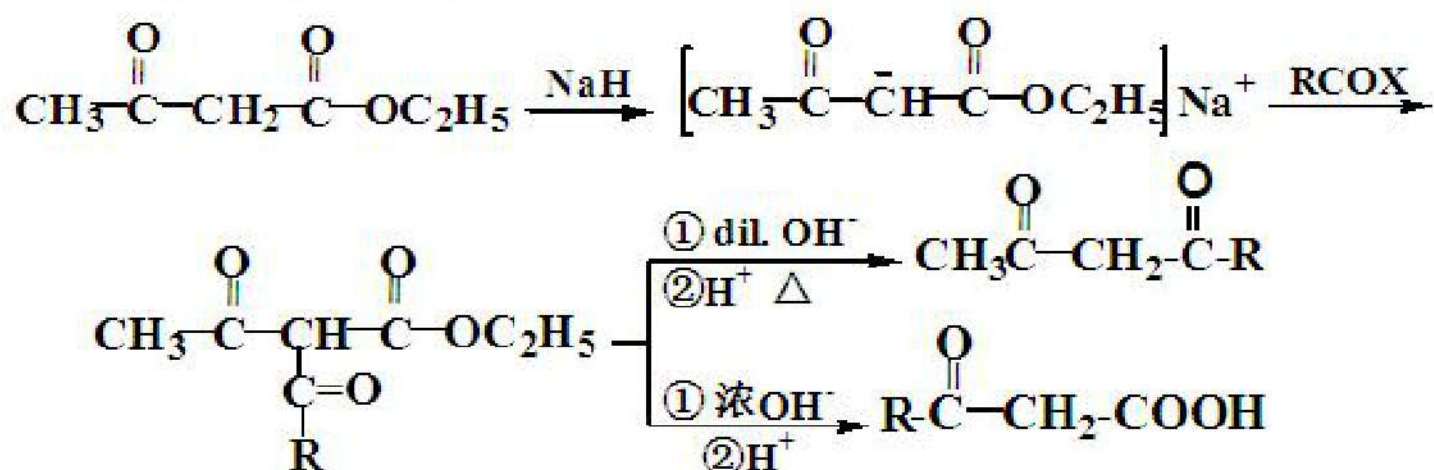
(1) 烃基化: RX (1°)、 RCOCH_2X 、 XCH_2COOR





二、酰基化反应

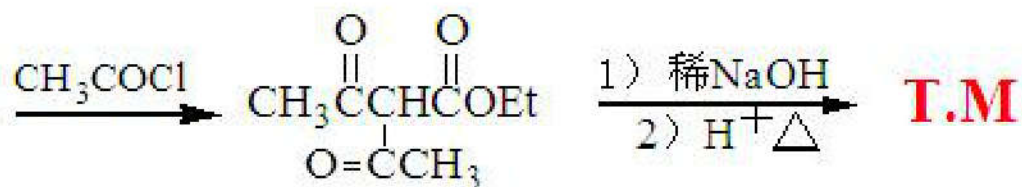
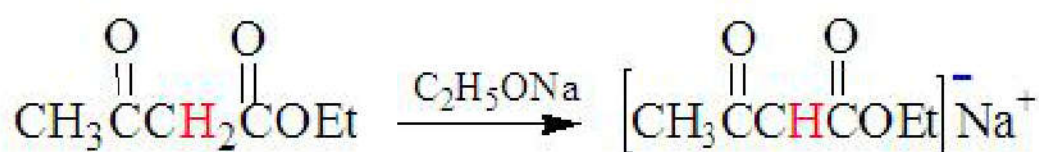
酰基化试剂: RCOX、酸酐等



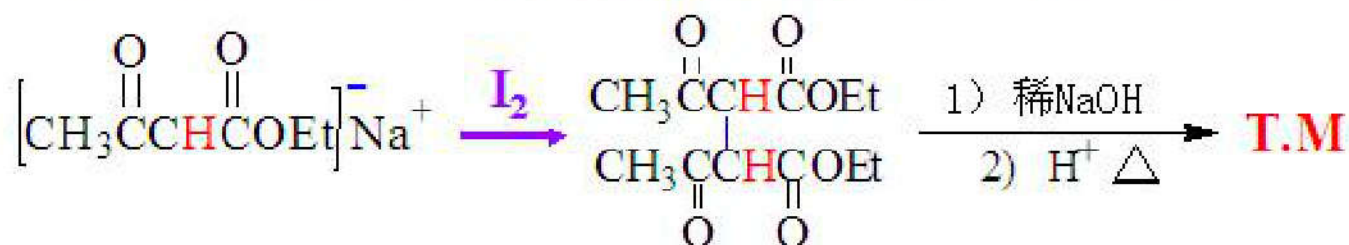


二、合成二羰基化合物

例3: $\text{CH}_3\text{COCH}_2\text{-COCH}_3$

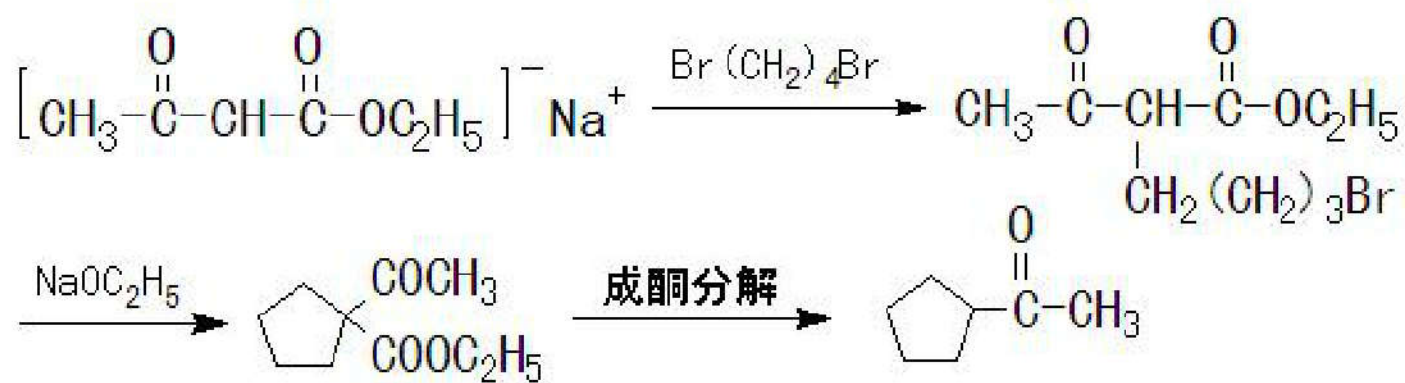


注意: EAA 的碳负离子与 I_2 的偶合反应





例4：合成环酮



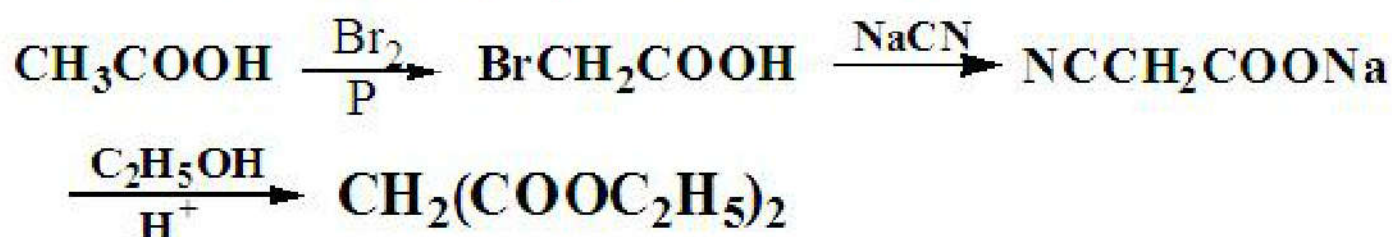
三、合成一元羧酸

例5：合成2-甲基丙酸



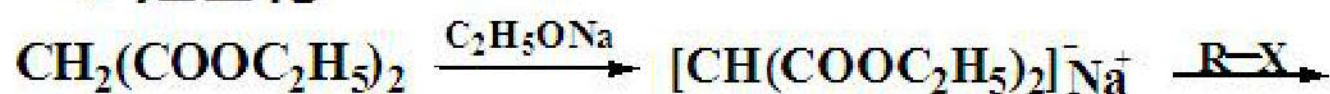
14.2 丙二酸二乙酯及其在有机合成中的应用

14.2.1 丙二酸二乙酯的制备



14.2.2 性质

一、烷基化

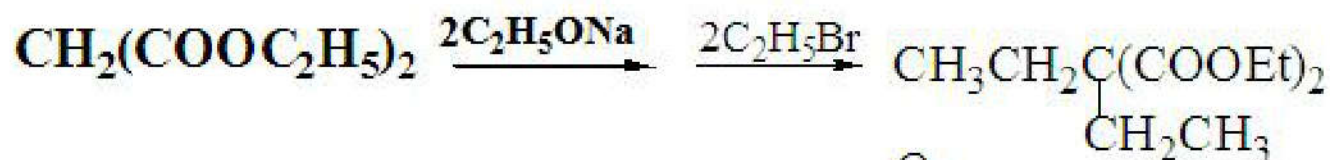
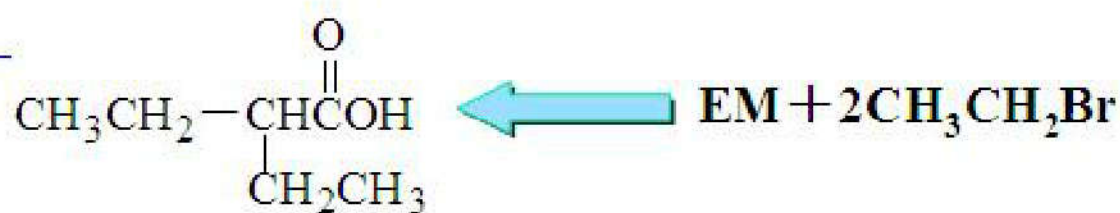
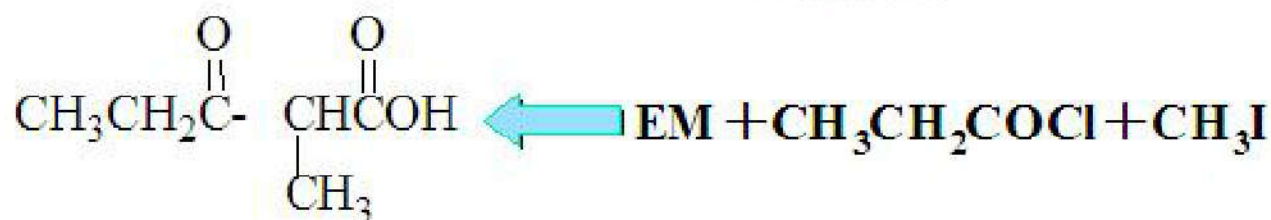
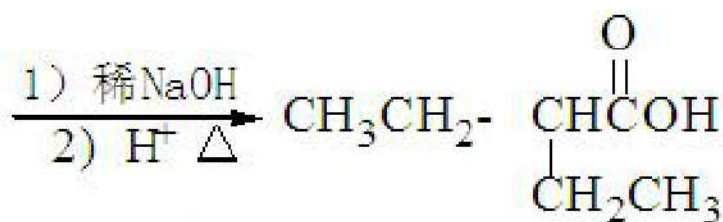


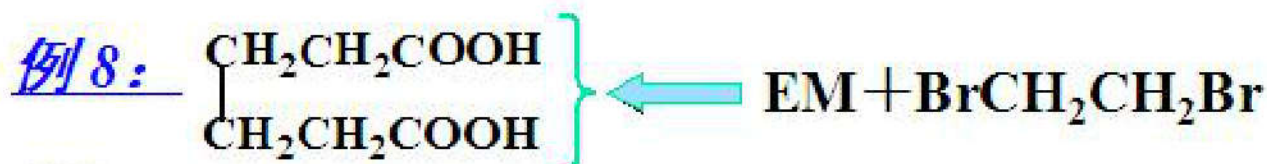
二、酰基化 (略)



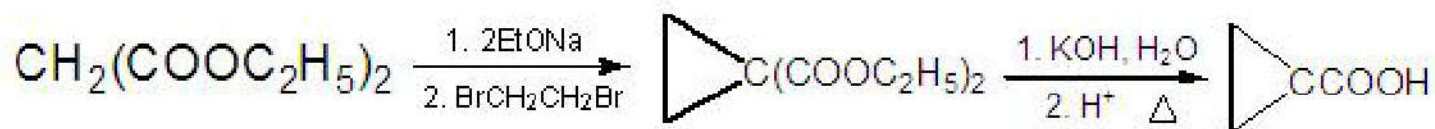


14. 2. 3丙二酸二乙酯在有机合成中的应用

例 6:例 7:



例 9:



例 10:

