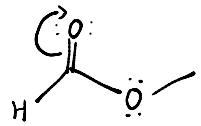
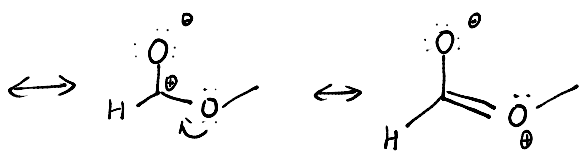
第11章 羧酸及其衍生物

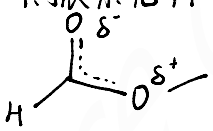
羧酸及其衍生物的结构

甲酸甲酯

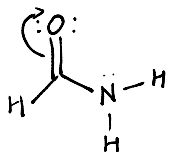


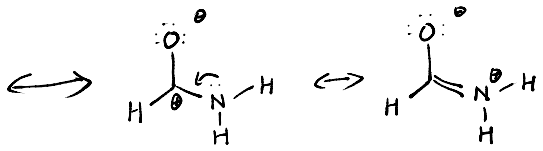


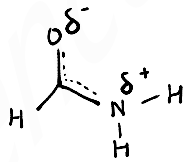
共振杂化体



甲酰胺





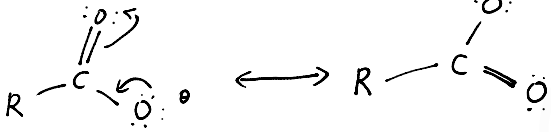


羧酸和酰胺的酸性

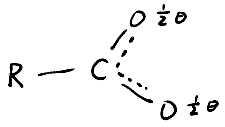
$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

共轭碱越稳定，酸性越强

酸根负离子



共振杂化体



诱导效应、共轭效应、氢键均会影响酸性

取代苯甲酸：一般邻位取代比对位取代苯甲酸的酸性强

对甲氧基的 +C 作用不利于稳定共轭碱

邻甲氧基的立体位阻不利于稳定酸，而 -I 作用利于稳定共轭碱

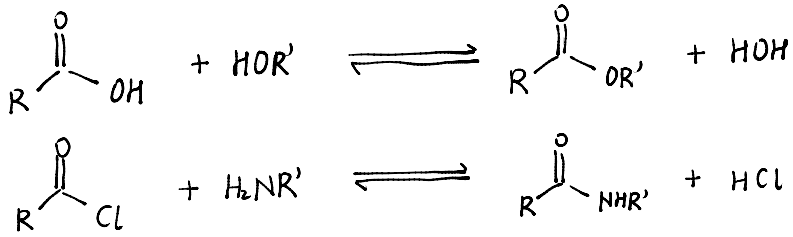
碳原子杂化类型对酸性的影响

	$C_2H_5CO_2H$	$CH_2=CHCH_2CO_2H$	$C_6H_5CH_2CO_2H$
pKa	4.87	4.34	4.30

S成分越多，电负性越大

why ?

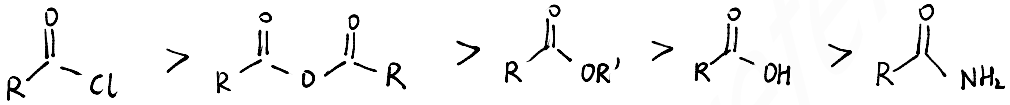
羧酸及其衍生物的亲核取代反应



相对反应活性的一般规律

离去基团离去的难易次序：$Cl^- > RCO_2H > ROH > H_2O > NH_3$

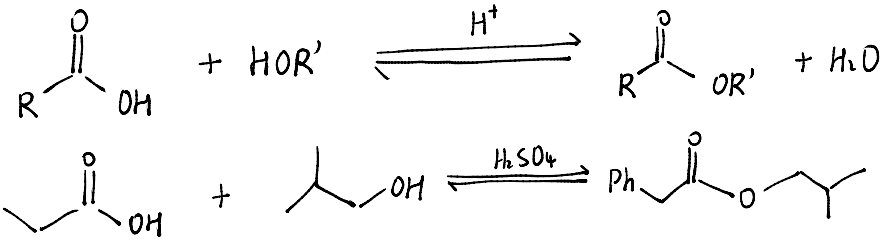
亲核取代速率由决速步（亲核加成）决定，给电子共轭效应越弱，吸电子诱导效应越强，反应速率越快



(1) 水作亲核试剂 —— 水解反应

(2) ROH 作亲核试剂 —— 醇解反应

酸的醇解 —— 酯化反应

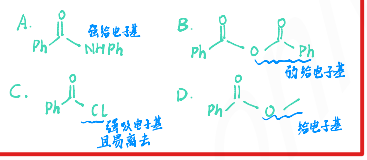


羧酸衍生物的亲核取代反应（如酯解）为"加成-消除"原理

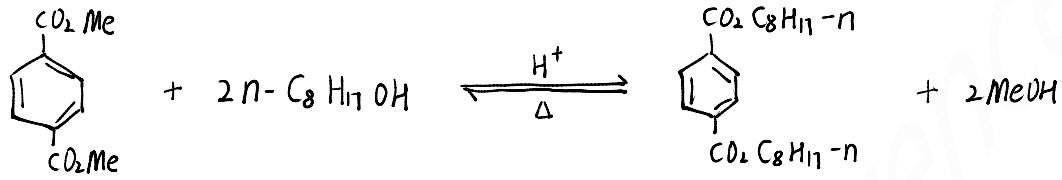
① 亲核试剂（醇的 O-H）对 羰基 C 的加成（羰基 C 缺电子性越强，越易加成）

② 消除离去基团（离去基团越易脱离，反应越快）

「23 24 Qdc118」
下列羧酸衍生物与醇发生亲核取代反应，活性最高的是（ ）



酯的醇解 —— 酯交换反应

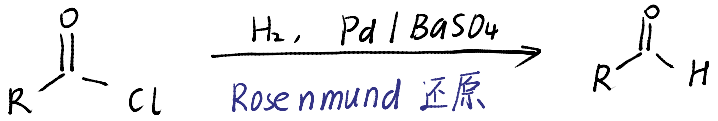


(3) 胺/氨作亲核试剂 —— 氨解反应（ammonolysis）

(4) 金属有机试剂作亲核试剂

羧酸及其衍生物的还原反应

催化氢化

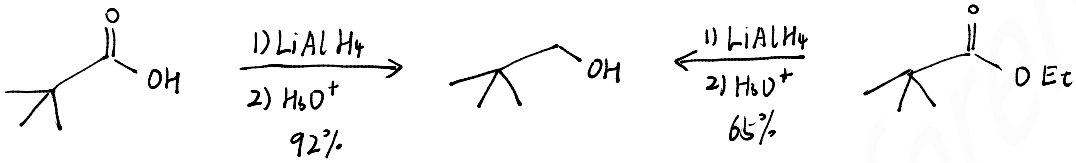


金属氢化物还原

氢化铝锂（$LiAlH_4$）还原

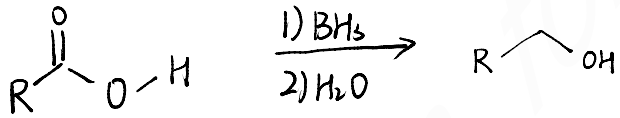
（酯基）

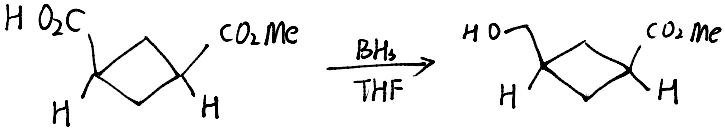
将羧酸中的羰基直接消去，并生成醇

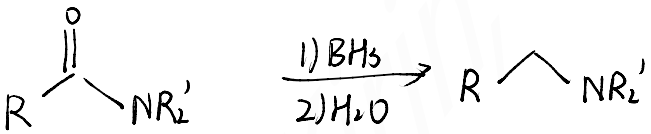


硼烷还原

将羧酸和酰胺还原







羧酸及其衍生物的其他反应

脱羧反应（逆 - ene 反应）

羧酸及其衍生物的制备

羧酸的制备

醇和醛的氧化

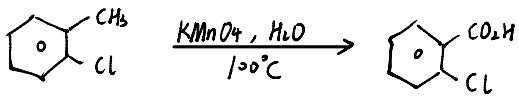
$$CH_3(CH_2)_8CH_2OH \xrightarrow[H_3O^+]{CrO_3} CH_3(CH_2)_8\overset{O}{\overset{\|}{C}}OH \quad 93\%$$

$$C_5H_{11}CHO \xrightarrow[NH_4OH]{Ag_2O} C_5H_{11}COOH$$

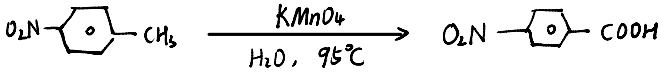
烯烃的氧化

$$RCH=CHR' \xrightarrow{KMnO_4} RCO_2H + R'CO_2H$$

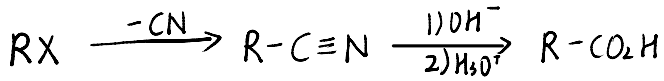
烷基苯的氧化



77%



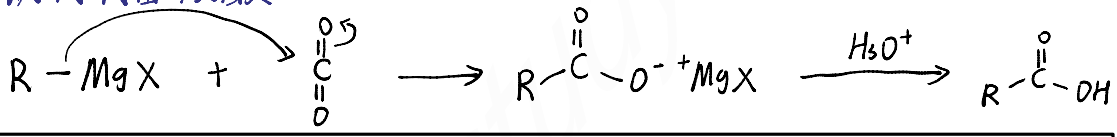
88%

腈的水解 

酰胺形成：

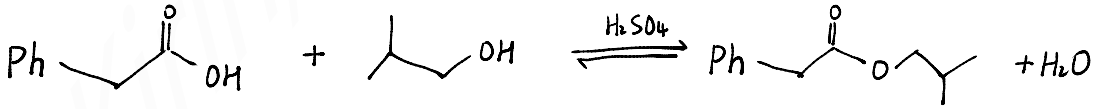
酰胺水解：

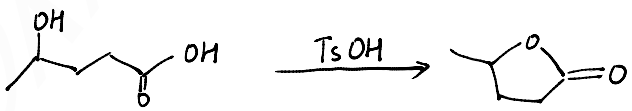
由格氏试剂制备羧酸：



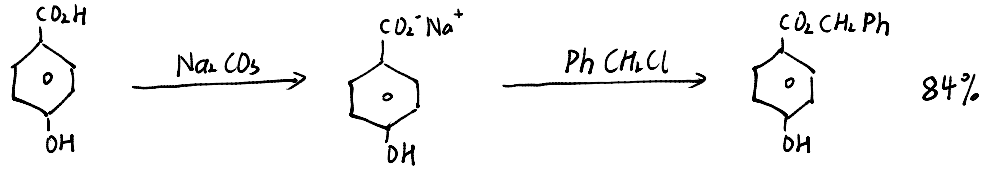
酯的制备

酯化反应

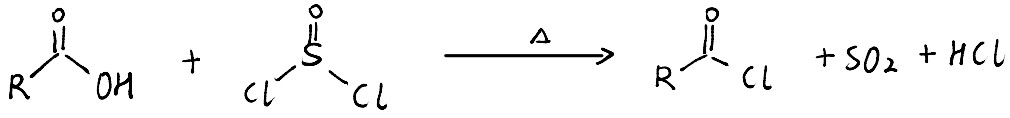


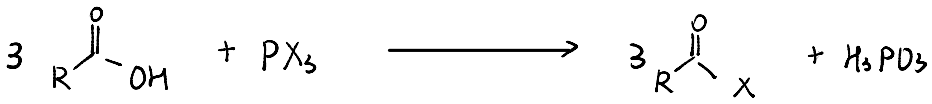


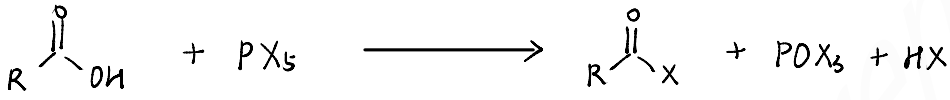
羧酸盐的亲核取代反应：S_N2 机理　适用于伯卤代烷



酰卤的制备

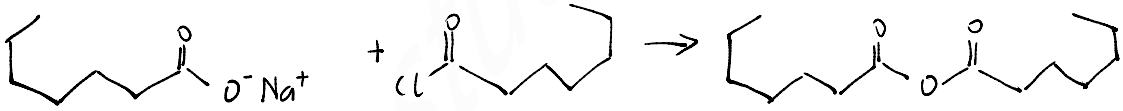




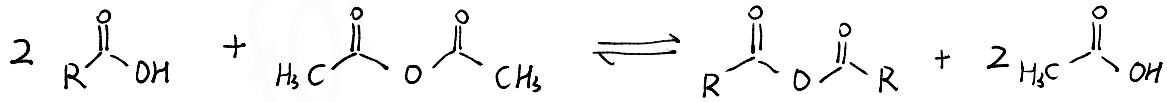


酸酐的制备

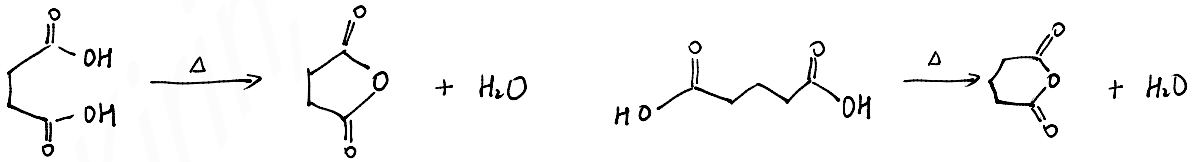
酰氯与羧酸的钠盐反应



酸酐交换反应

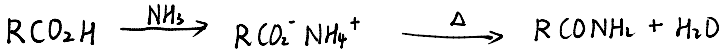


二元酸脱水

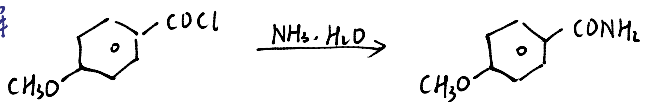


酰胺的制备

羧酸铵盐的氨解



酰氯 / 酸酐 / 酯的氨解



Beckmann 重排