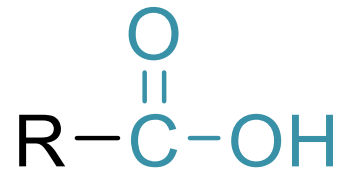
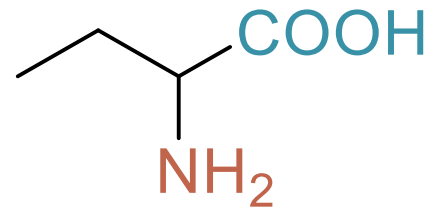
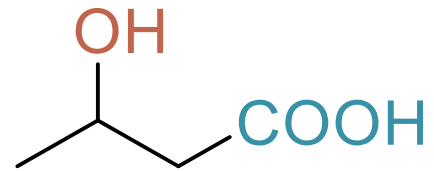
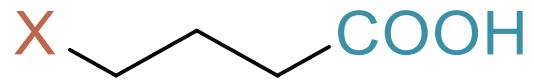


° 十一章 羧酸与取代羧酸



羧酸

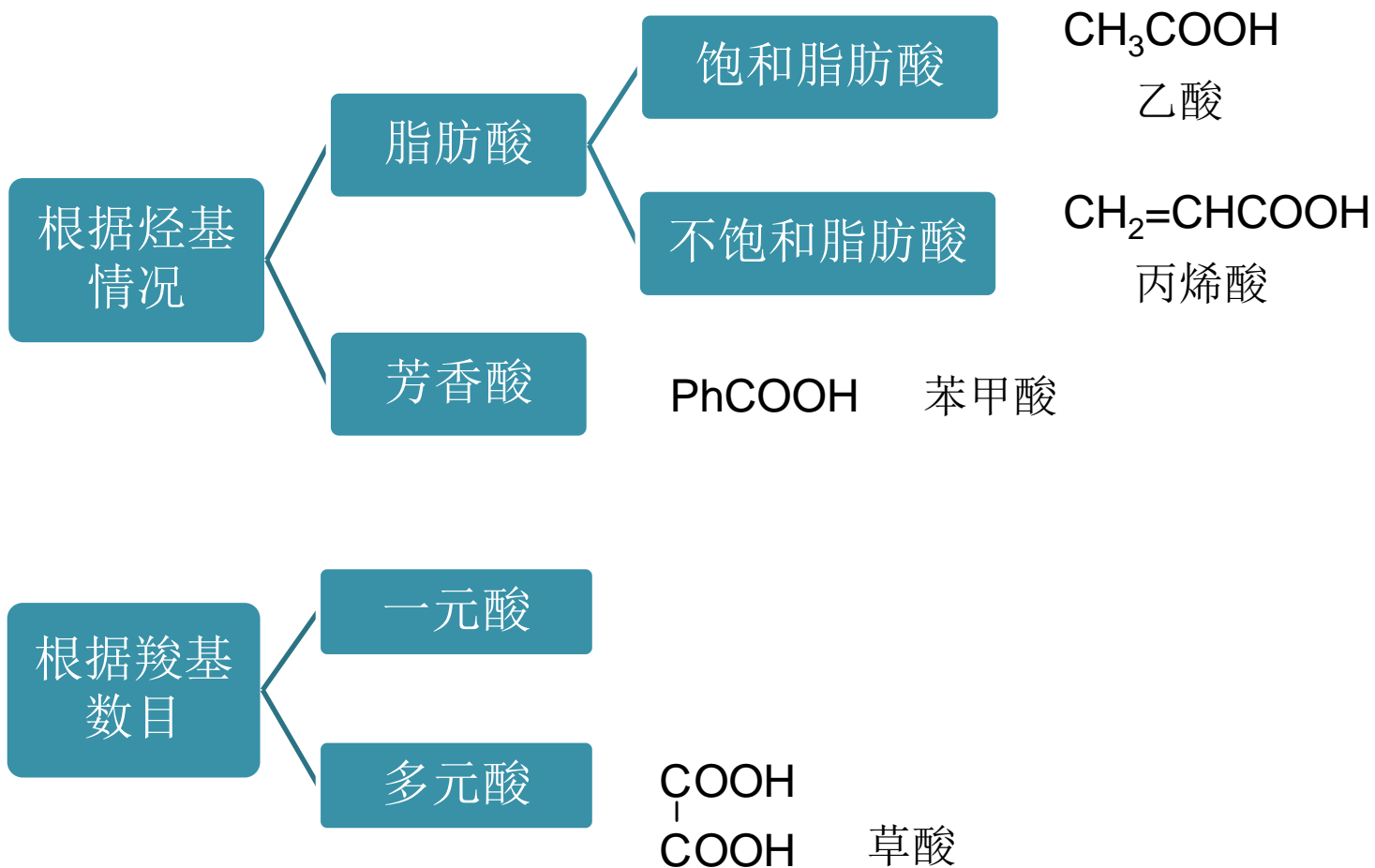


取代羧酸

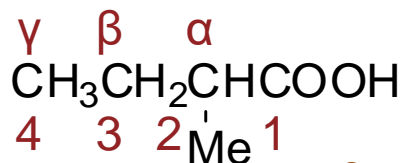
第十一章 羧酸与取代羧酸

第一节 羧酸

羧酸的分类



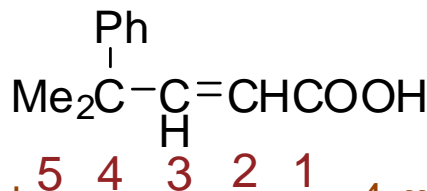
羧酸的命名



α-甲基丁酸

2-甲基丁酸

2-methylbutanoic acid



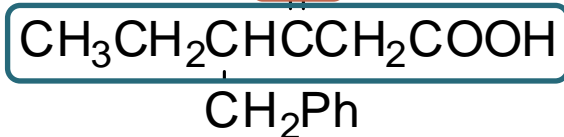
4-甲基-4-苯基

戊-2-烯酸

4-methyl-4-phenylpent-2-enoic acid

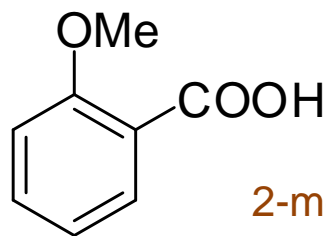
取代基 

母体



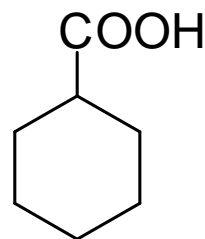
4-苄基-3-氧亚基己酸

4-benzyl-3-oxohexanoic acid



邻甲氧基苯甲酸

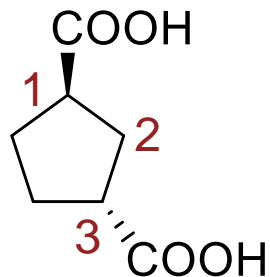
2-methoxybenzoic acid



环己基甲酸

环己烷甲酸

cyclohexanecarboxylic acid

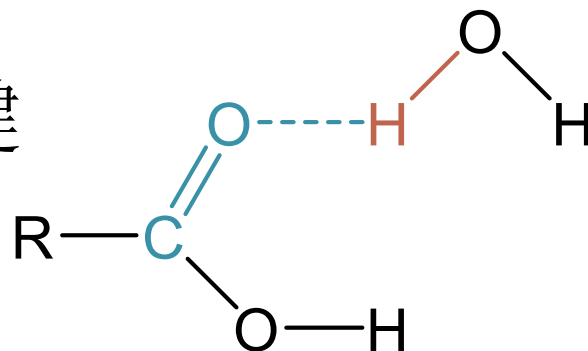


(1R,3R)-环戊烷-1,3-二甲酸

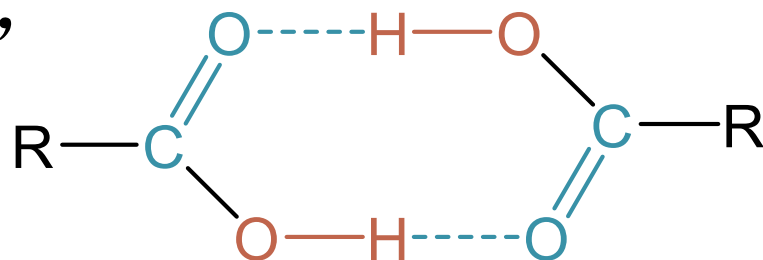
(1R,3R)-cyclopentane-1,3-dicarboxylic acid

羧酸的物理性质

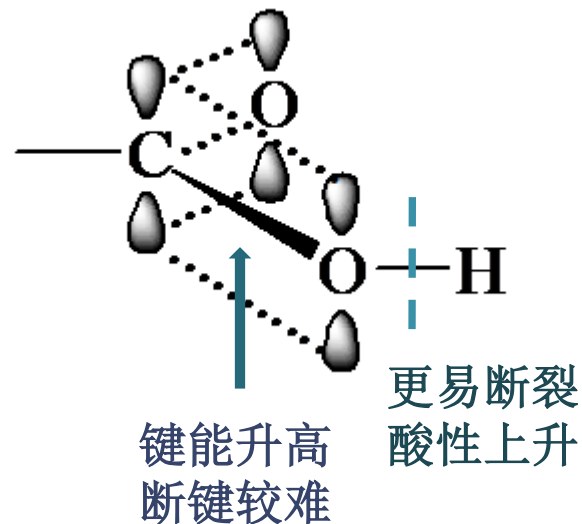
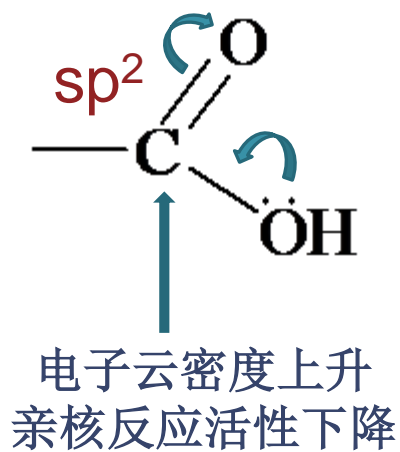
- 与水之间可以形成氢键
——水溶性好



- 分子间可形成氢键，
构成二缔合体
——沸点高



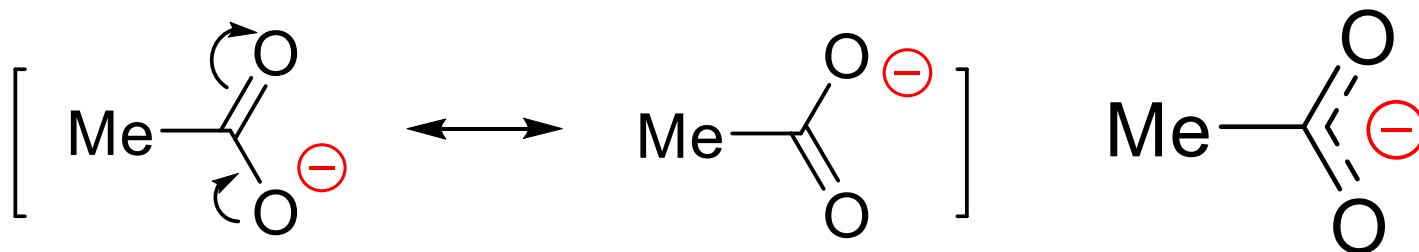
羧基的结构



羧酸的酸性



	NH_3	$\text{RC}\equiv\text{CH}$	ROH	H_2O	PhOH	H_2CO_3	RCOOH
pKa	~35	~25	16-19	15.7	10	6.4	~5



两个能量相同的共振极限式，羧酸根负离子稳定性很高

脂肪酸的酸性

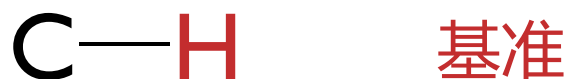
		+I	+I -I sp ³ 杂化, 无共轭
	CH ₃ COOH	CH ₃ CH ₂ COOH	HOCH ₂ COOH
pKa	4.76	4.87	3.83
	-I	-I	-I
	BrCH ₂ COOH	ClCH ₂ COOH	O ₂ NCH ₂ COOH
	2.94	2.86	1.08



Y吸电子：负离子稳定性上升，酸性增强

Y给电子：负离子稳定性下降，酸性减弱

• 诱导效应复习

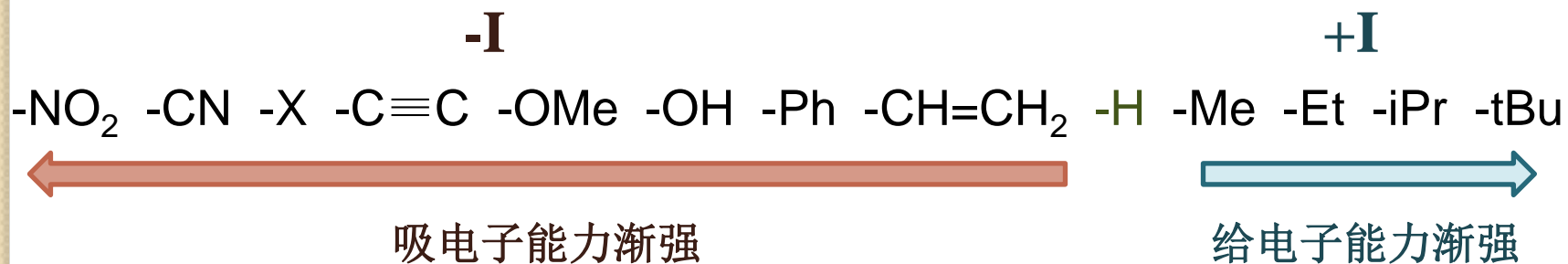


A: $-\text{X}$ 、 $-\text{OH}$ 、 $-\text{OR}$ 、 $-\text{NH}_2$ 、
 $-\text{CH}=\text{CH}_2$ 、 $-\text{C}\equiv\text{CH}$ 、 $-\text{Ph}$
 $-\text{CX}_3 \dots$

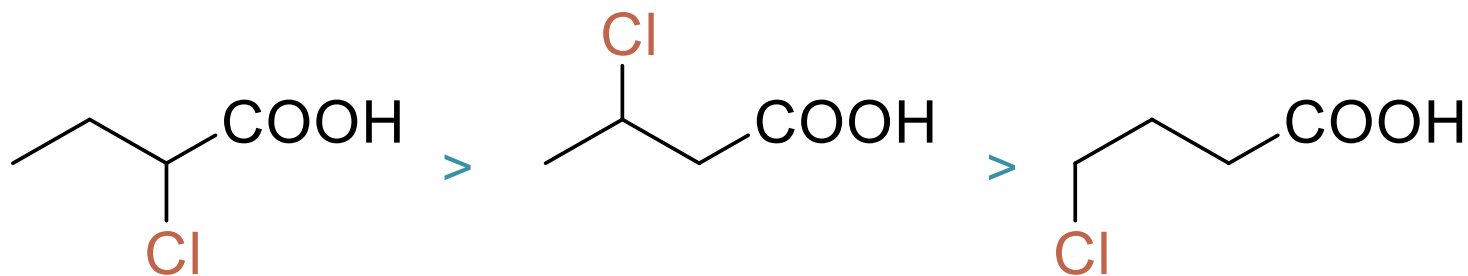


B: $-\text{R}$

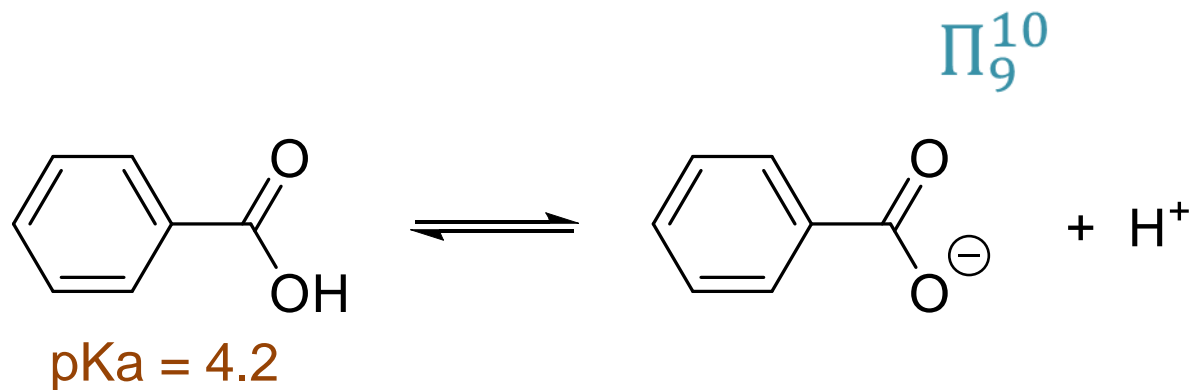
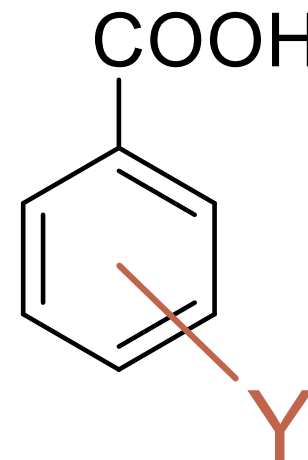
- 常见基团诱导效应强弱



脂肪酸的酸性

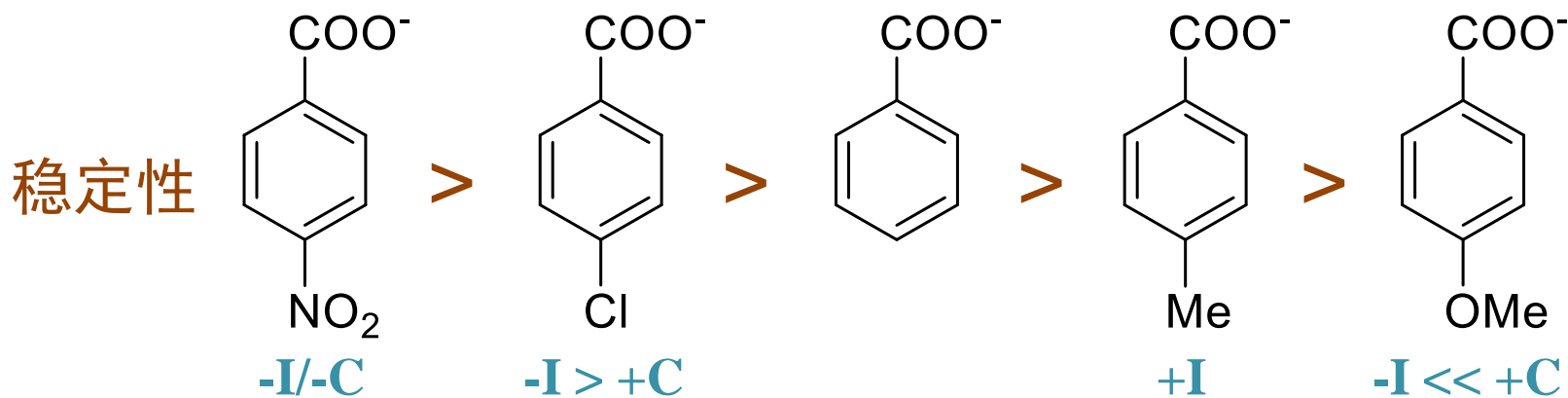
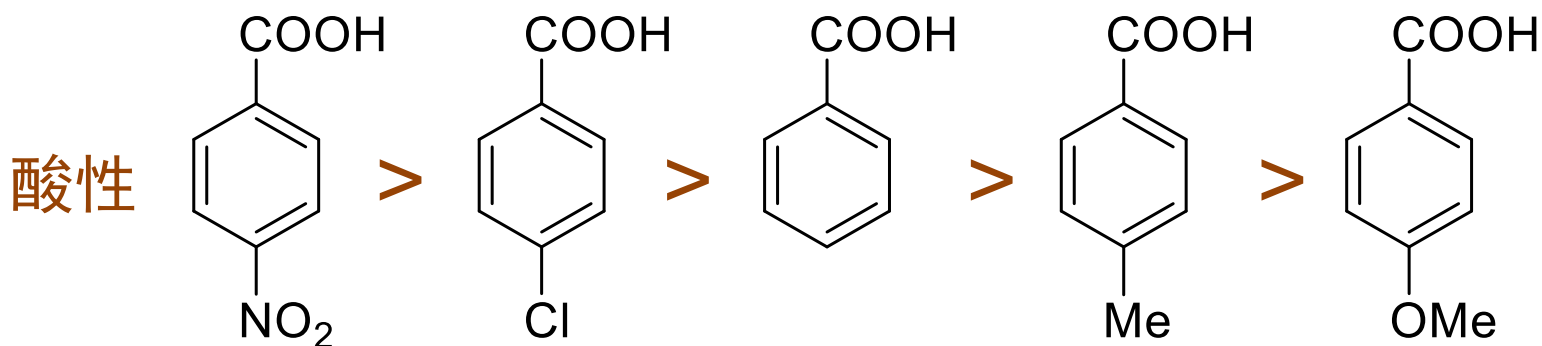


芳香酸的酸性

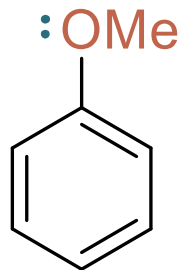
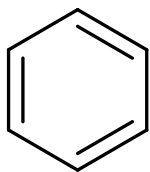


酸性: $\text{HCOOH} > \text{PhCOOH} > \text{RCOOH}$

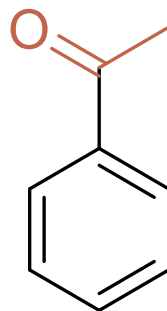
取代苯甲酸的酸性



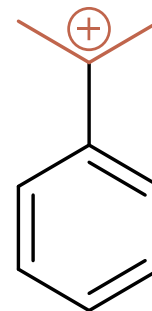
• 共轭效应复习



提供电子对参与共轭
母体电子云密度上升
+C

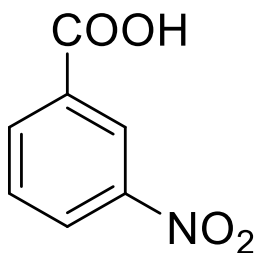


提供单电子参与共轭
基团内有杂原子
母体电子云密度下降
-C

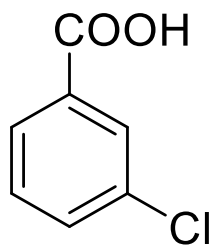


提供空轨道参与共轭
母体电子云密度下降
-C

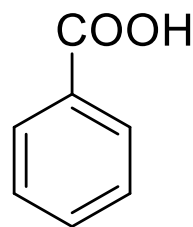
取代苯甲酸的酸性



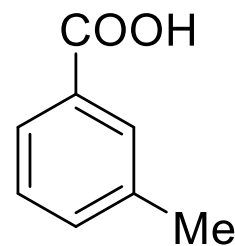
pKa 3.49



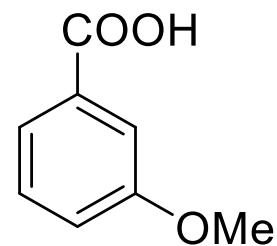
3.83



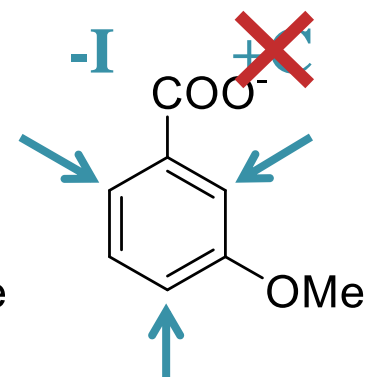
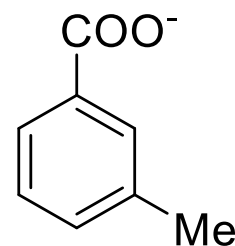
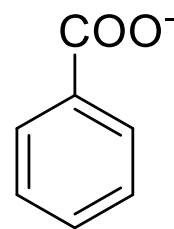
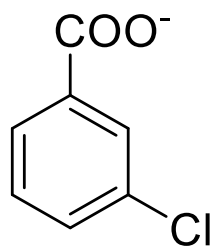
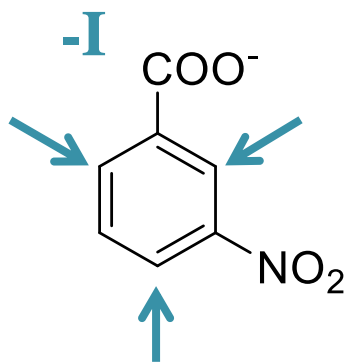
4.20



4.27

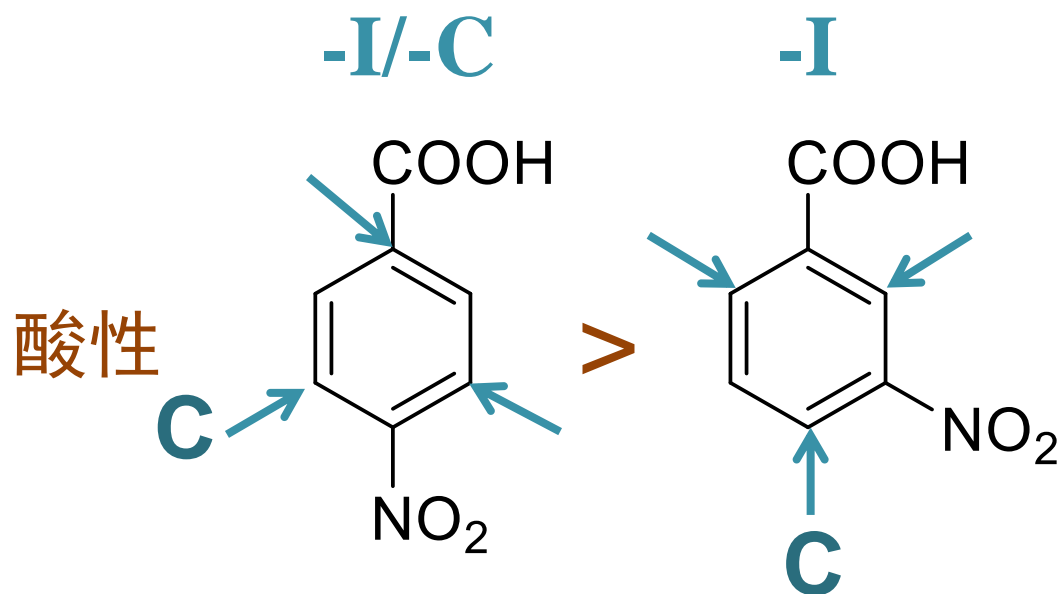


4.09

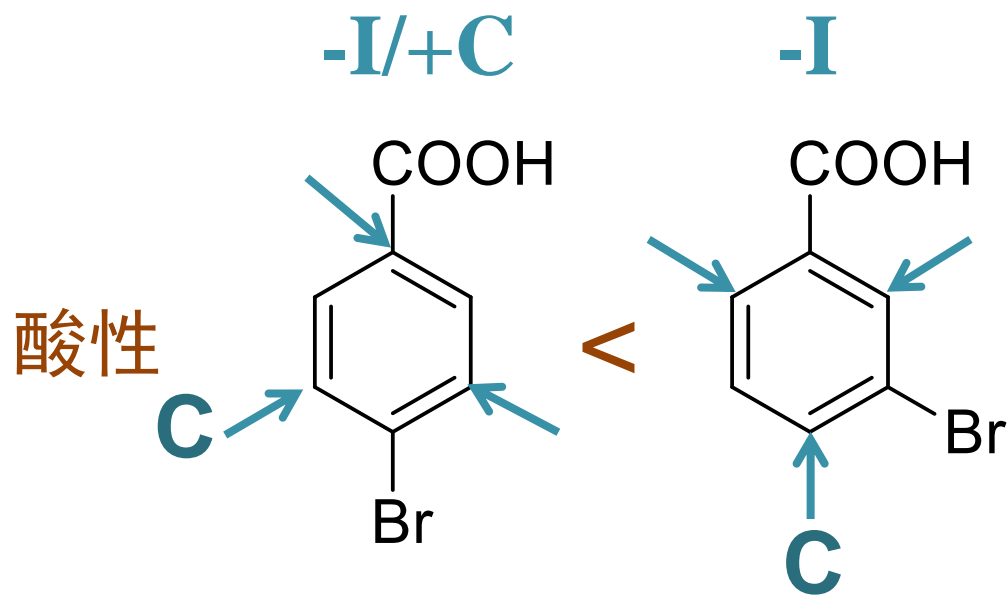


共轭效应
主要影响
邻对位

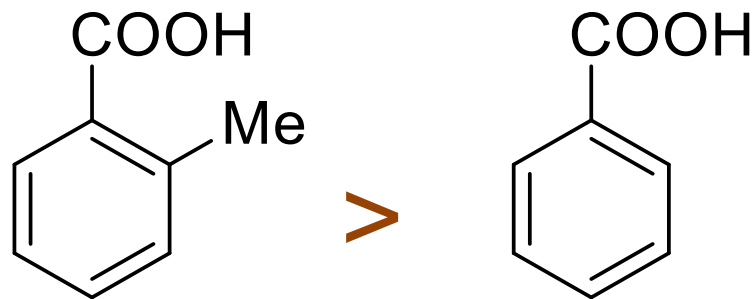
取代苯甲酸的酸性



取代苯甲酸的酸性

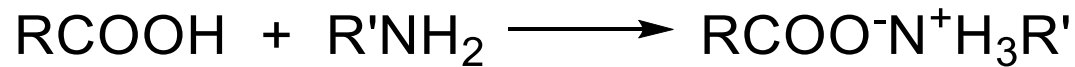
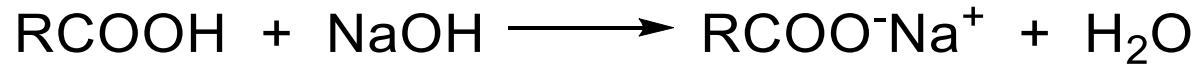


取代苯甲酸的酸性



邻位效应

成盐反应



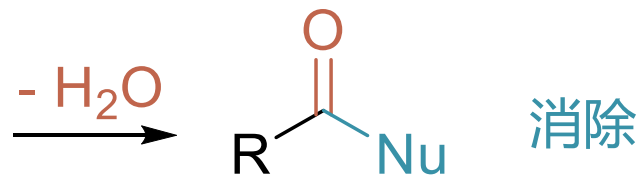
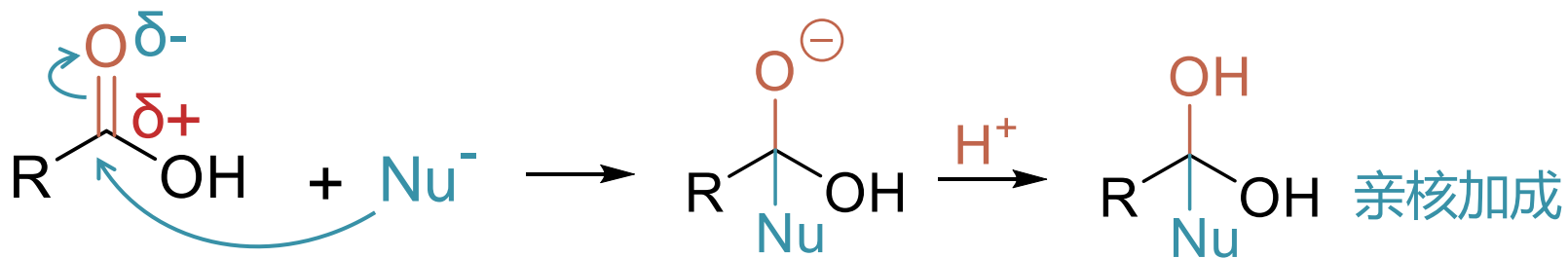
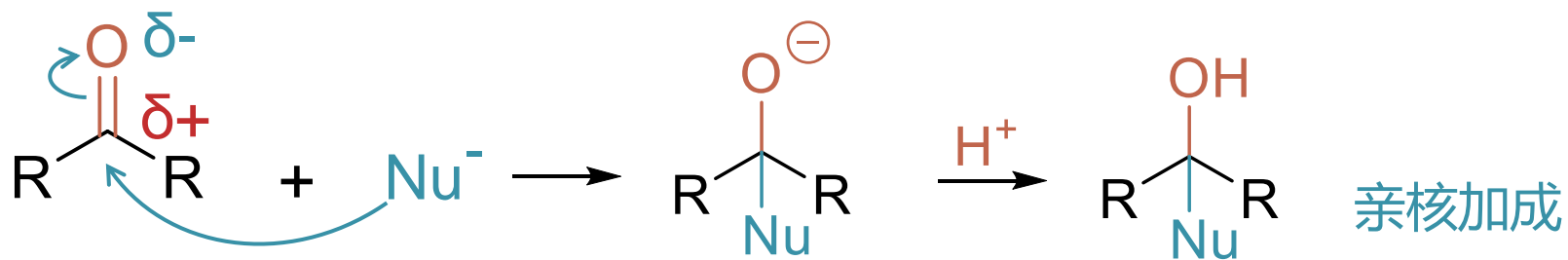
憎水基

亲水基

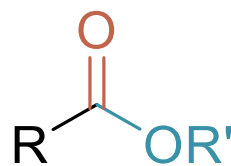
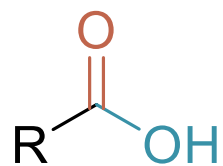


软脂酸钠

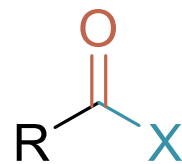
羧基的亲核反应



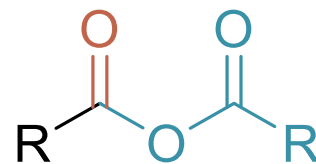
羧基的亲核反应



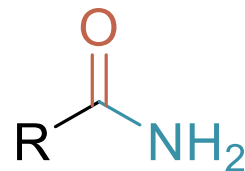
酯



酰卤



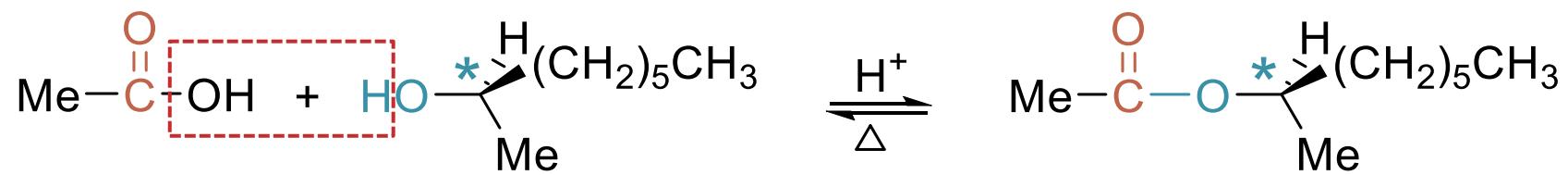
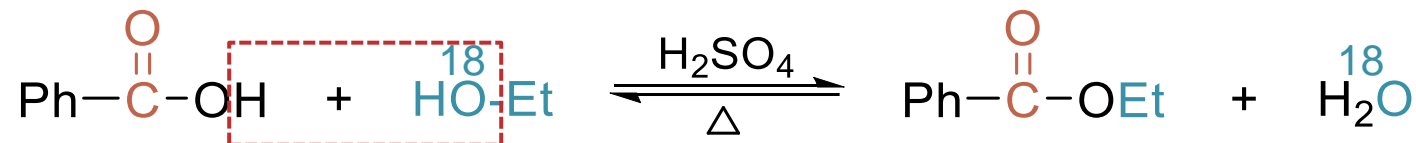
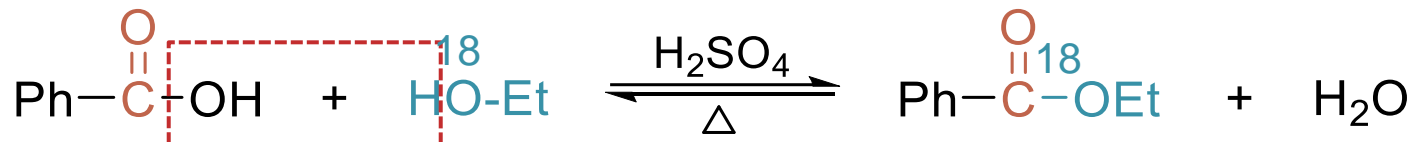
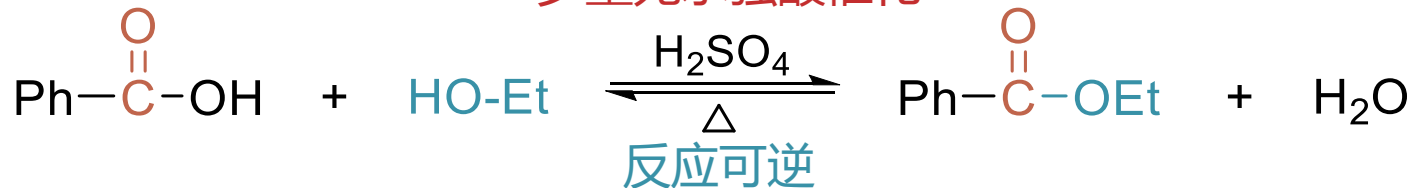
酸酐



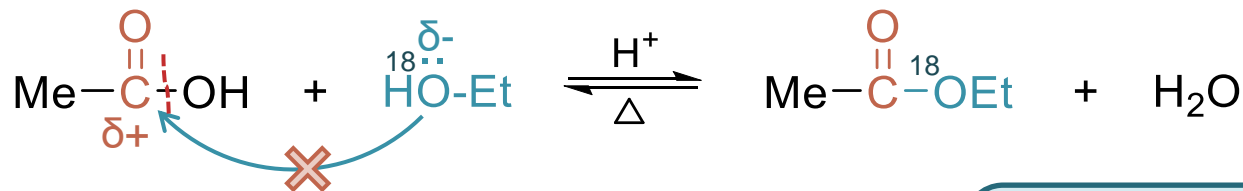
酰胺

羧酸的酯化反应

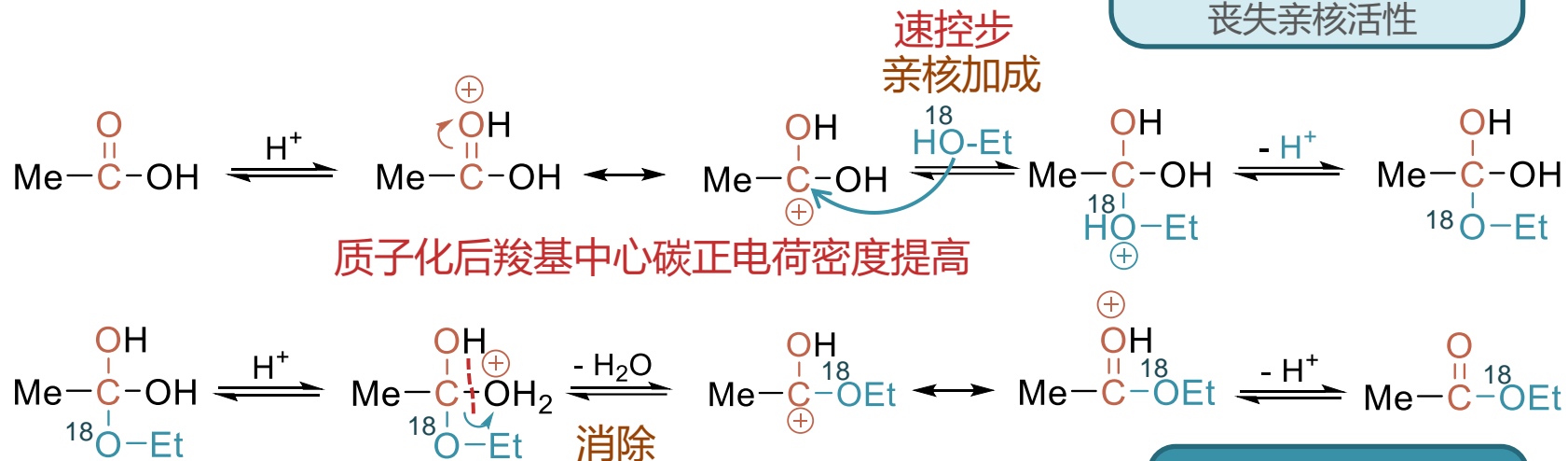
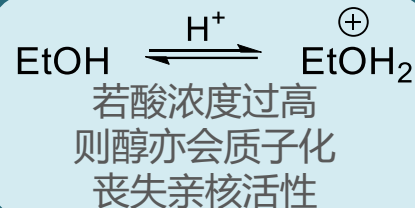
少量无水强酸催化



羧酸的酯化反应：机理



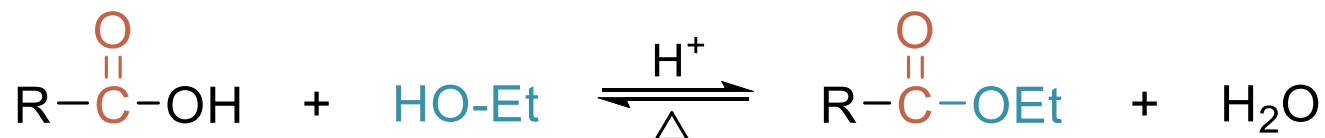
羧基中心碳正电荷密度有限
醇无法直接进攻



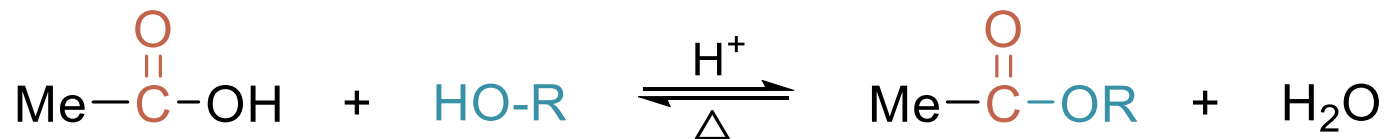
- 亲核加成-消除
- 酰氧断裂

羧酸的酯化反应：机理

- 位阻影响反应速率



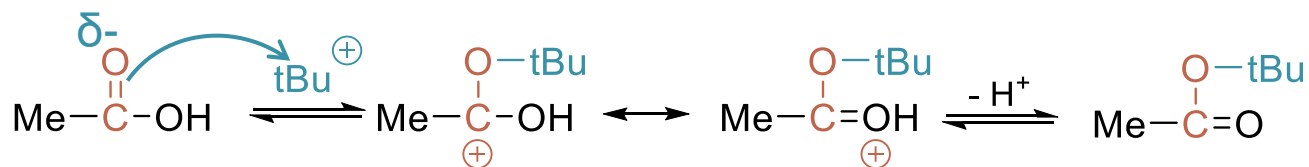
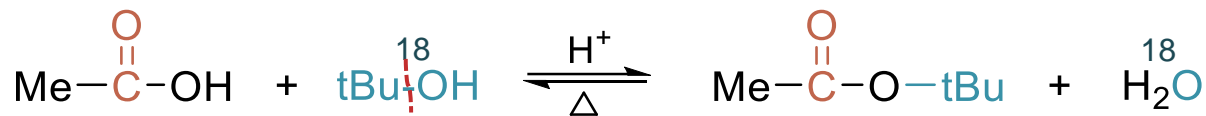
v: $\text{HCOOH} > \text{MeCOOH} > \text{MeCH}_2\text{COOH} > \text{Me}_2\text{CHCOOH} > \text{Me}_3\text{CCOOH}$



v: $\text{CH}_3\text{OH} > \text{MeCH}_2\text{OH} > \text{Me}_2\text{CHOH}$

$\text{Me}_3\text{COH} ?$

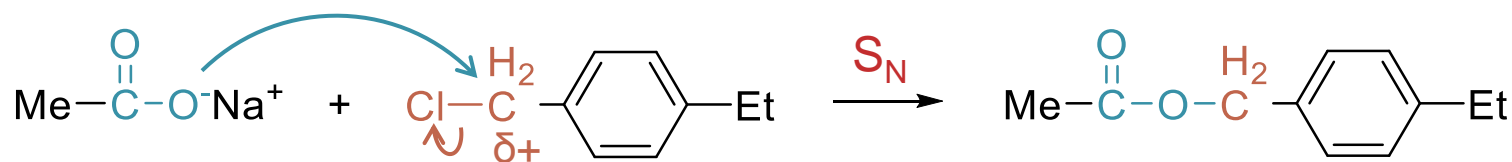
羧酸的酯化反应：机理



- 碳正离子
- 烷氧断裂

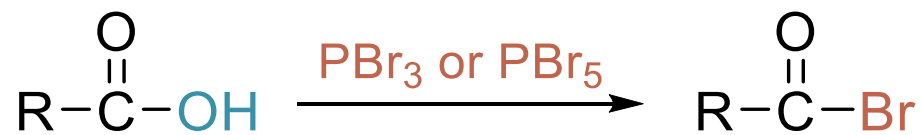
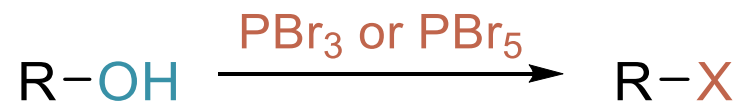
叔醇：一般通过碳正离子历程
其它醇：一般通过亲核加成-消除历程

羧酸制备酯的其它方法

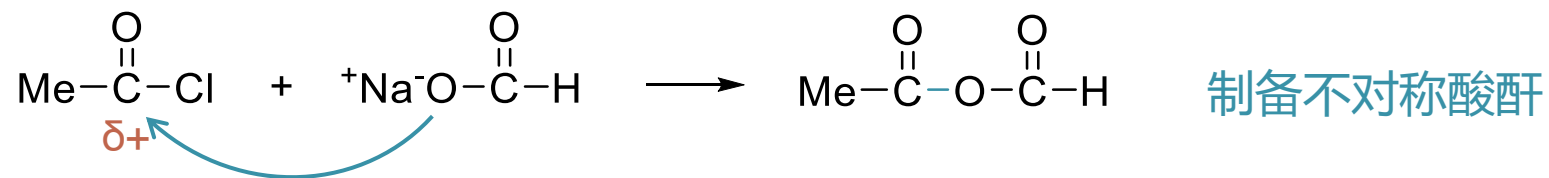
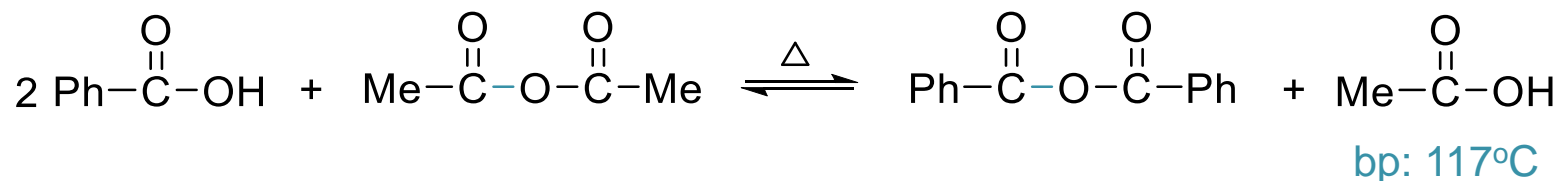
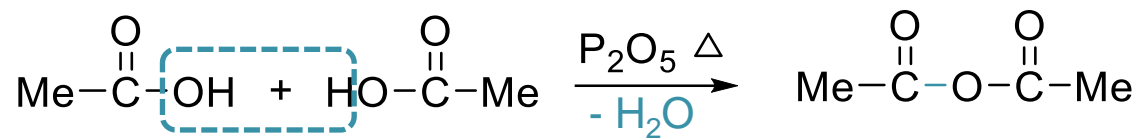


羧酸盐可作为亲核试剂
在合成中具有独特的价值

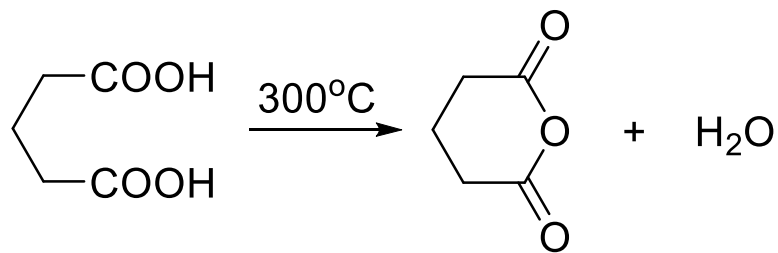
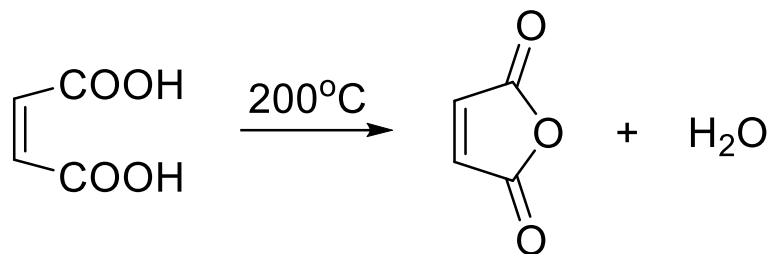
酰卤的生成



酸酐的生成

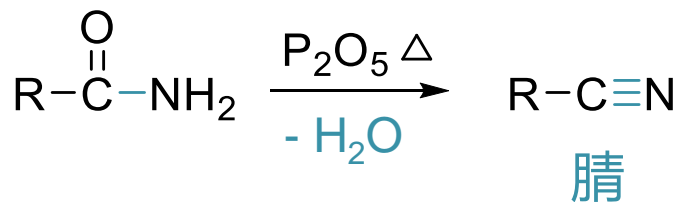
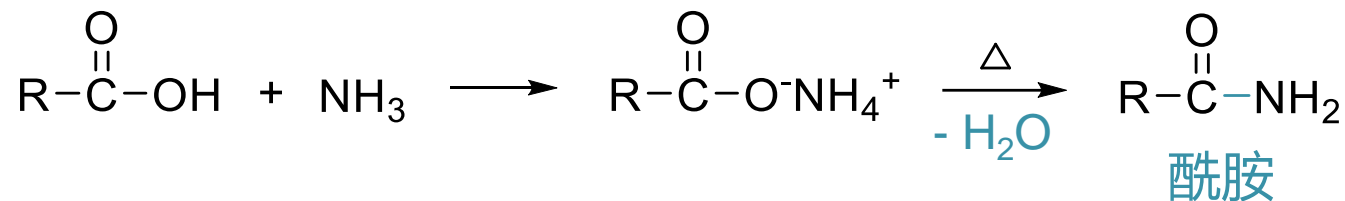


酸酐的生成



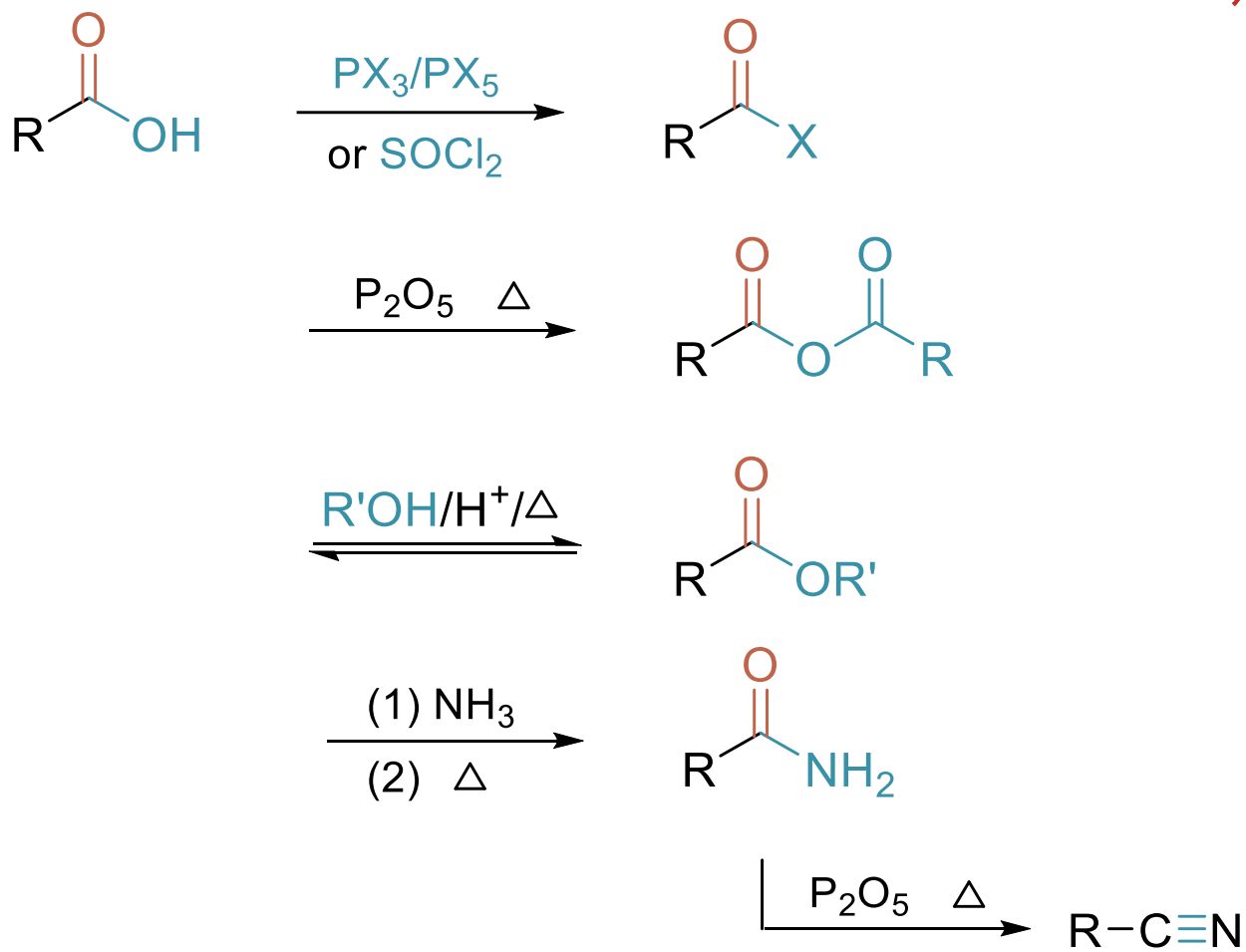
结构合适的二元酸易分子内脱水得到环状酸酐

酰胺的生成



羧基的亲核反应

羧酸衍生物



酰卤

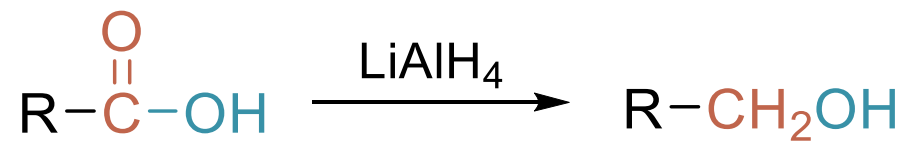
酸酐

酯

酰胺

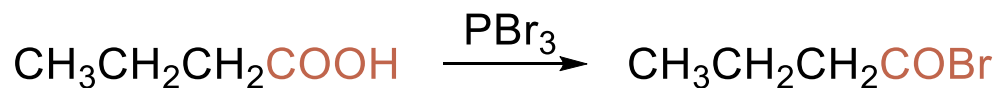
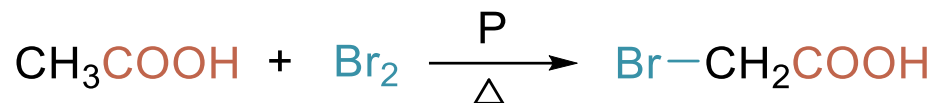
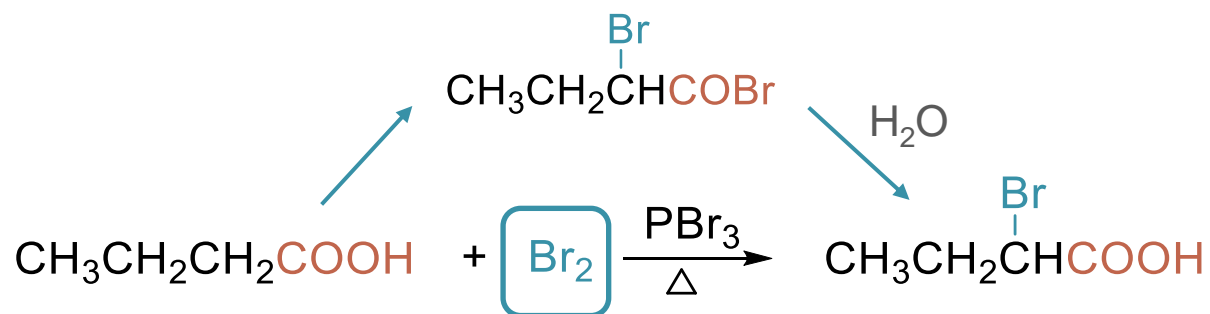
腈

羧酸的还原

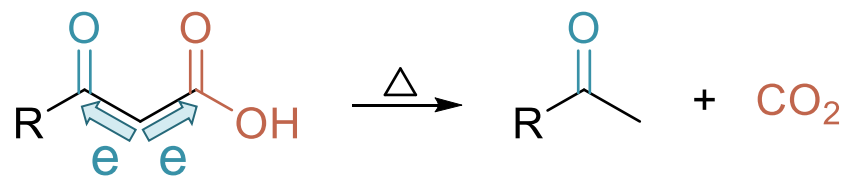


合成价值不高，较少使用

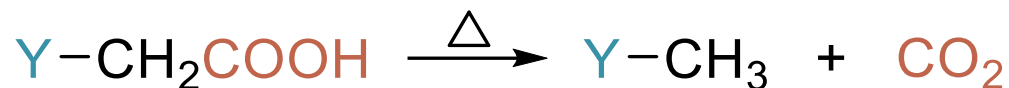
羧酸的 α -卤代



脱羧反应

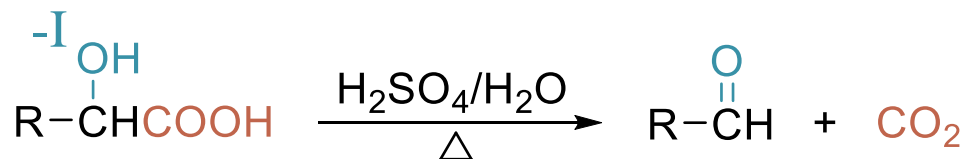


两侧基团拉电子
导致C-COOH键能下降

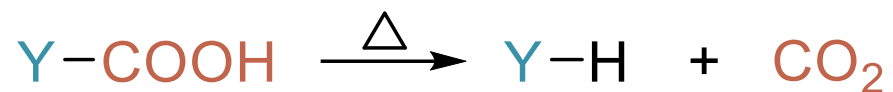


羧基 α -位连接吸电子基团往往易发生脱羧

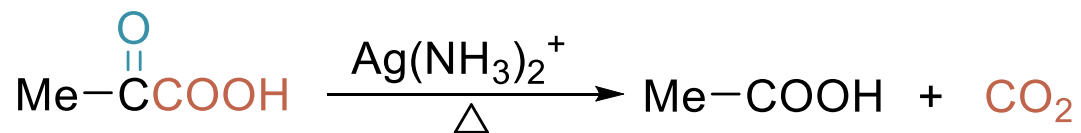
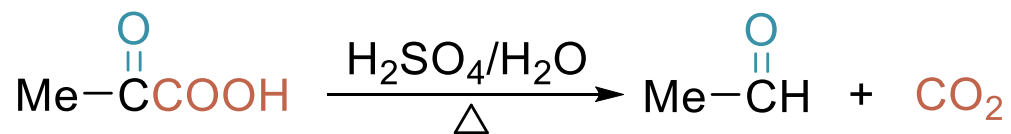
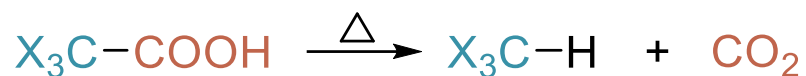
Y: -COR、-COOH、-CN、-NO₂……



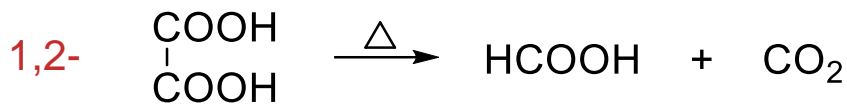
脱羧反应



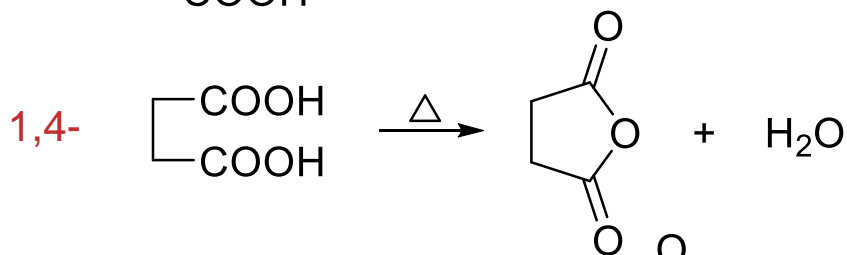
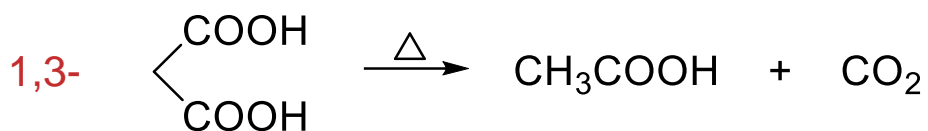
羧基上直接连接吸电子基团亦容易发生脱羧



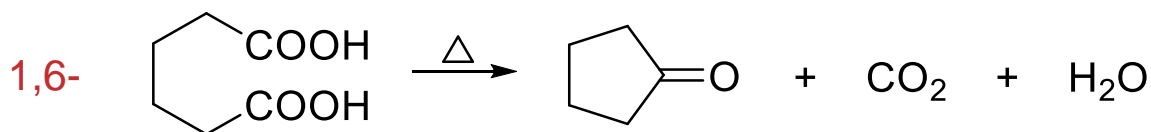
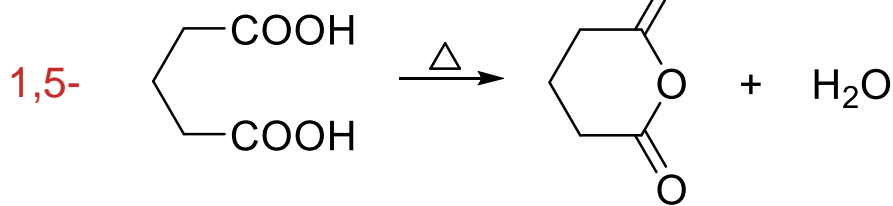
二元酸的热分解



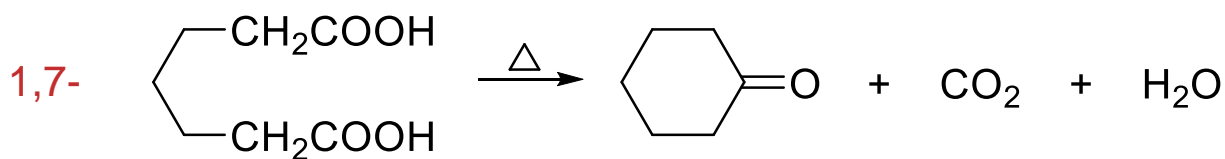
脱羧



失水



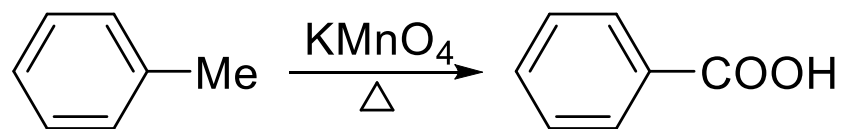
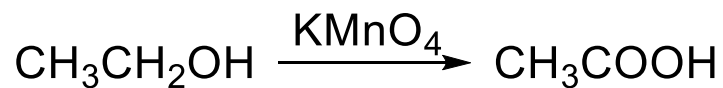
脱羧+失水



Blanc规则

羧酸的制备

- 氧化法

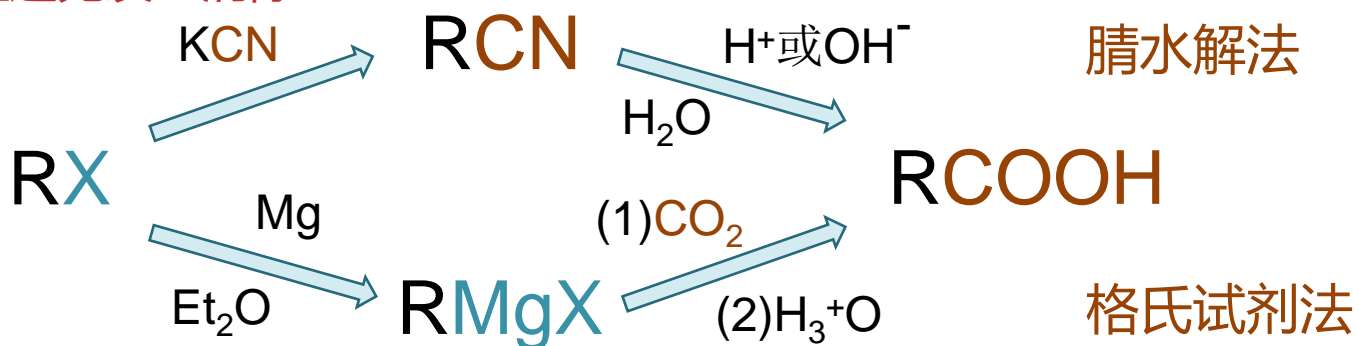


一般条件较剧烈，产率受影响

羧酸的制备

- 腈水解法与格氏试剂法

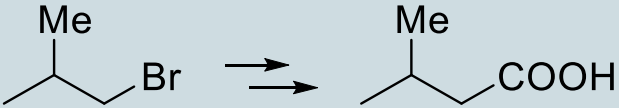
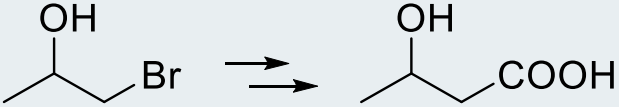
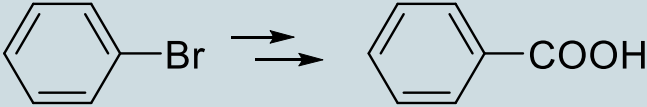
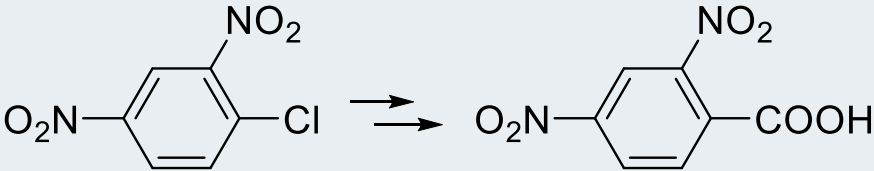
需尽量避免发生消除



需保证底物中基团
不与格氏试剂冲突

两种方法均可由卤代烃制备多一碳羧酸
可互为补充

羧酸的制备

	腈水解法	格氏试剂法
 <p><chem>CC(C)CBr >> CC(C)C(=O)O</chem></p>	✓	✓
 <p><chem>CC(C)(O)CBr >> CC(C)C(=O)O</chem></p>	✓	
 <p><chem>c1ccccc1Br >> c1ccccc1C(=O)O</chem></p>		✓
 <p><chem>O=[N+]([O-])c1cc(Cl)ccc1[N+](=O)[O-] >> O=[N+]([O-])c1cc(C(=O)O)ccc1[N+](=O)[O-]</chem></p>	✓	