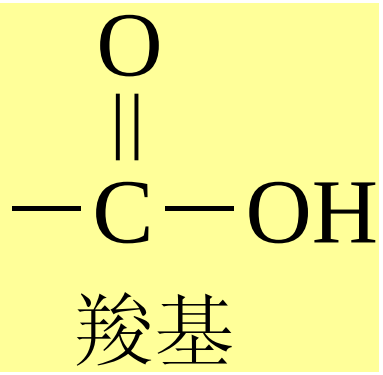
第十一章　羧酸

概述



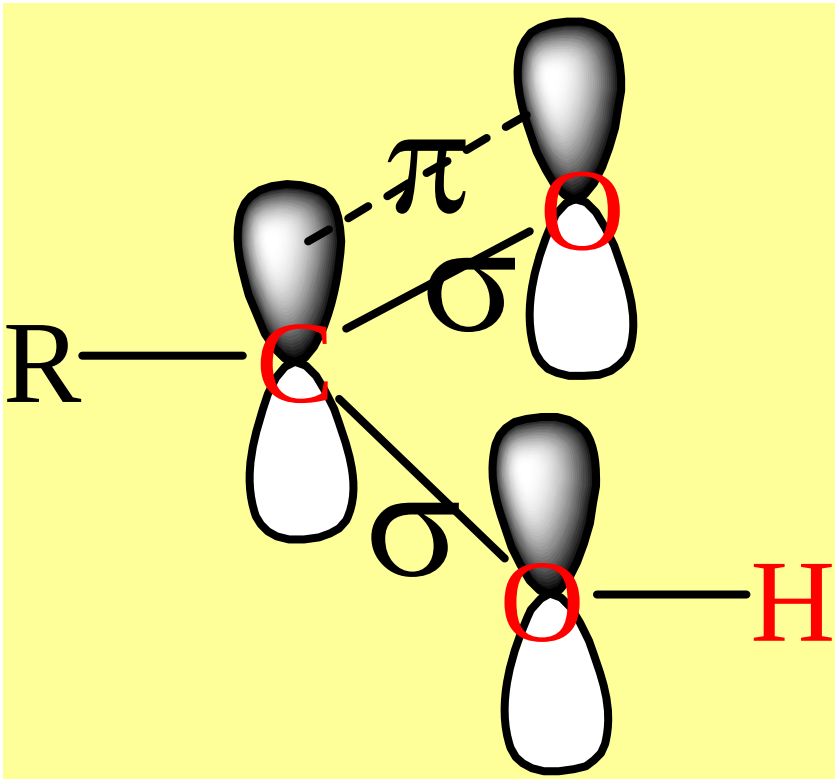
- 羧酸
  - 脂肪酸
    - 饱和酸
    - 不饱和酸
  - 芳香酸
- 一元酸
- 二元酸
- 多元酸

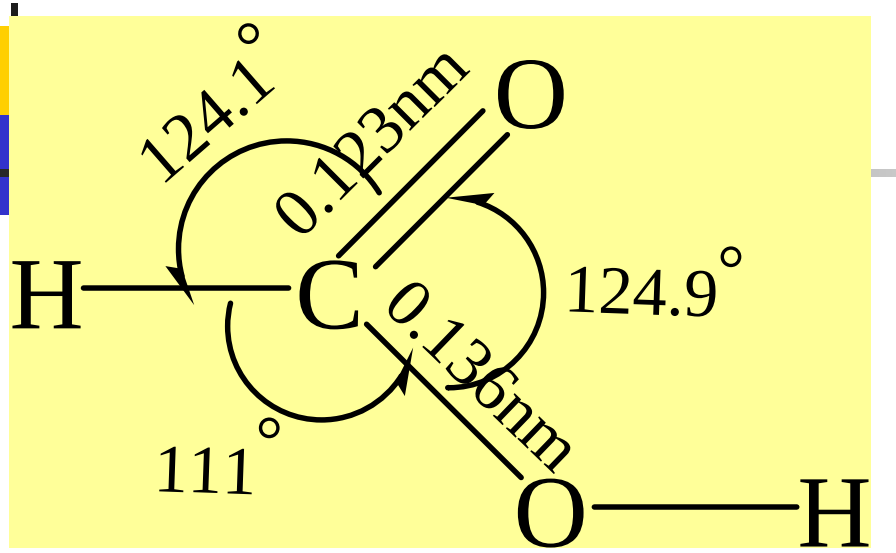
食用醋：2％乙酸水溶液

§11.1 羧酸的结构、命名和物理性质

一、羧酸的结构

C：sp^2杂化

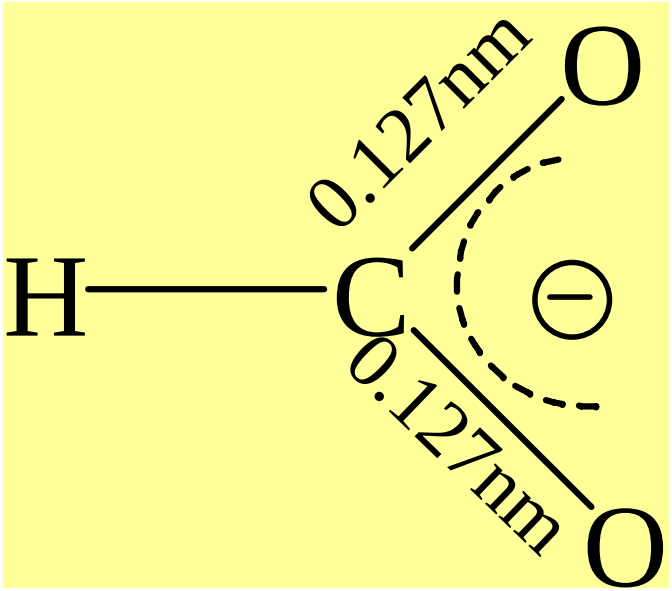




键长平均化

C = O　0.122nm

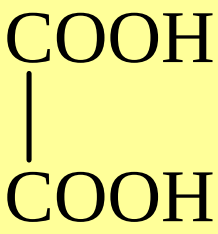
C – O　0.143nm



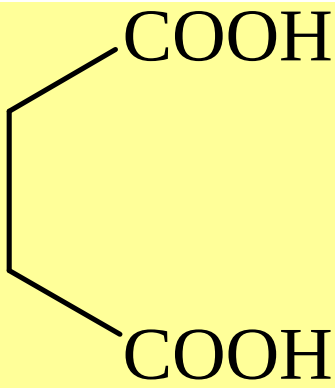
二、羧酸的命名

与醛的命名原则相同

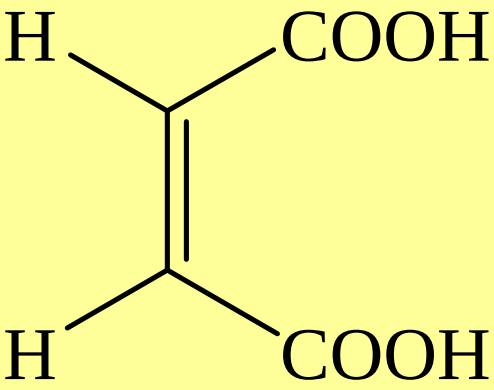
$HCOOH$	甲酸（蚁酸）
CH_3COOH	乙酸（醋酸）
$CH_3CH=CHCOOH$	2－丁烯酸（巴豆酸）
$n\text{-}CH_3(CH_2)_{10}COOH$	十二酸（月桂酸）
$n\text{-}CH_3(CH_2)_{14}COOH$	十六酸（软脂酸）
$n\text{-}CH_3(CH_2)_{16}COOH$	十八酸（硬脂酸）
$PhCOOH$	苯甲酸（安息香酸）



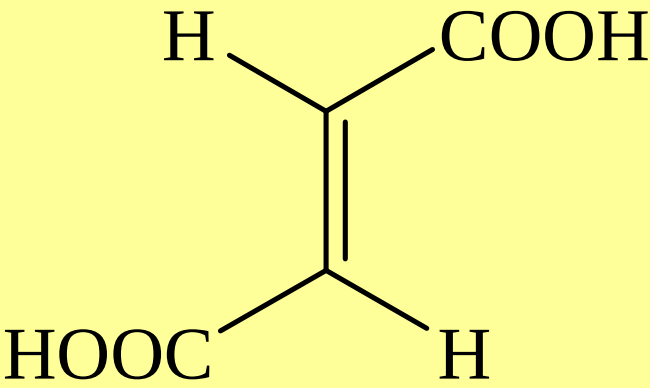
乙二酸
草酸



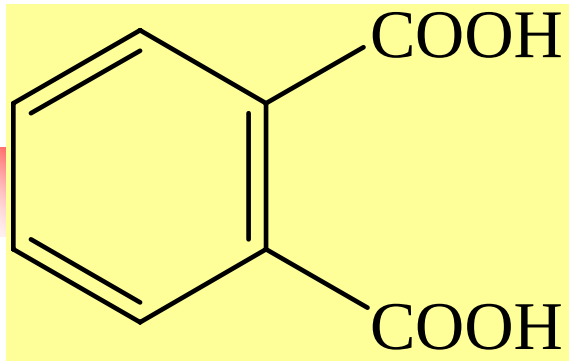
1,4-丁二酸
琥珀酸



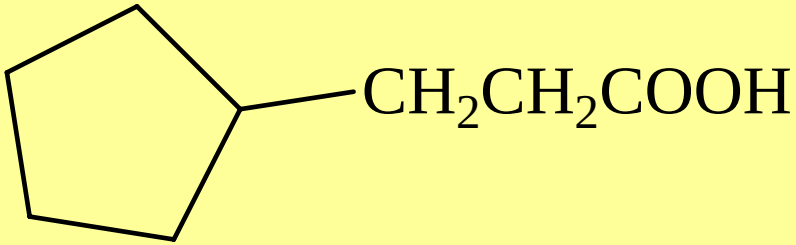
顺-丁烯二酸
马来酸



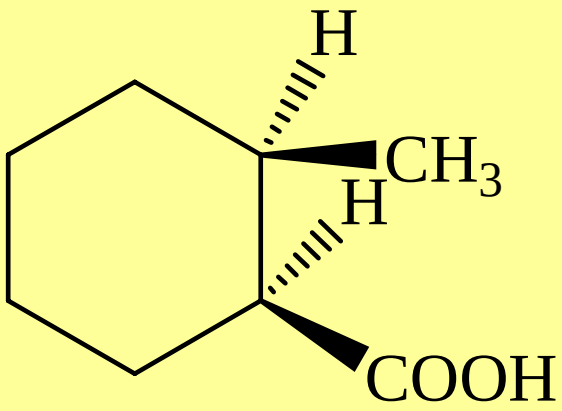
反-丁烯二酸
富马酸



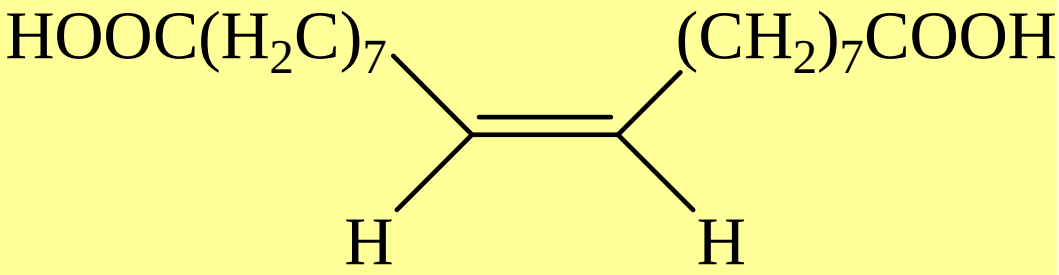
邻苯二甲酸



3-环戊基丙酸
β-环戊基丙酸



顺-2-甲基环己基甲酸

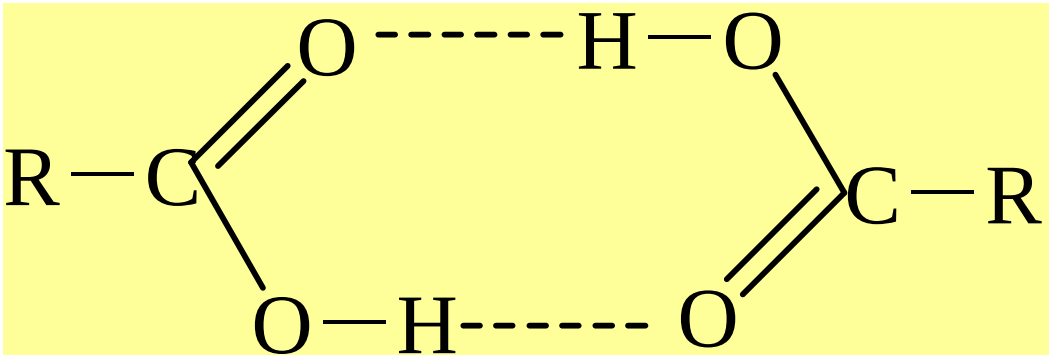


顺-十八碳-9-烯二酸

三、羧酸的物理性质

1. b.p. 高于分子量相近的醇

	Mw	b.p.(°C)
HCOOH	46	100.5
CH_3CH_2OH	46	78.4
CH_3COOH	60	118
$CH_3CH_2CH_2OH$	60	97.2



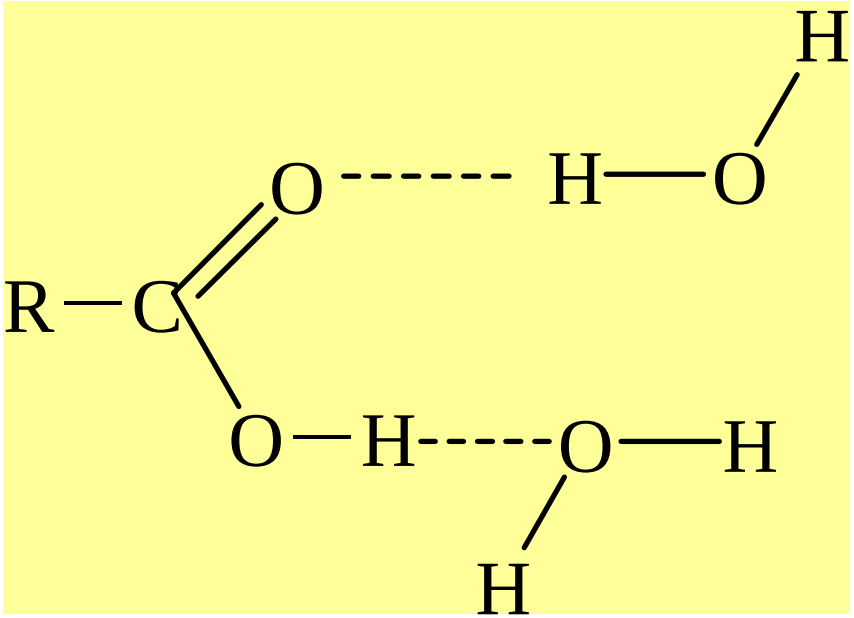
双分子缔合体

2. 溶解度

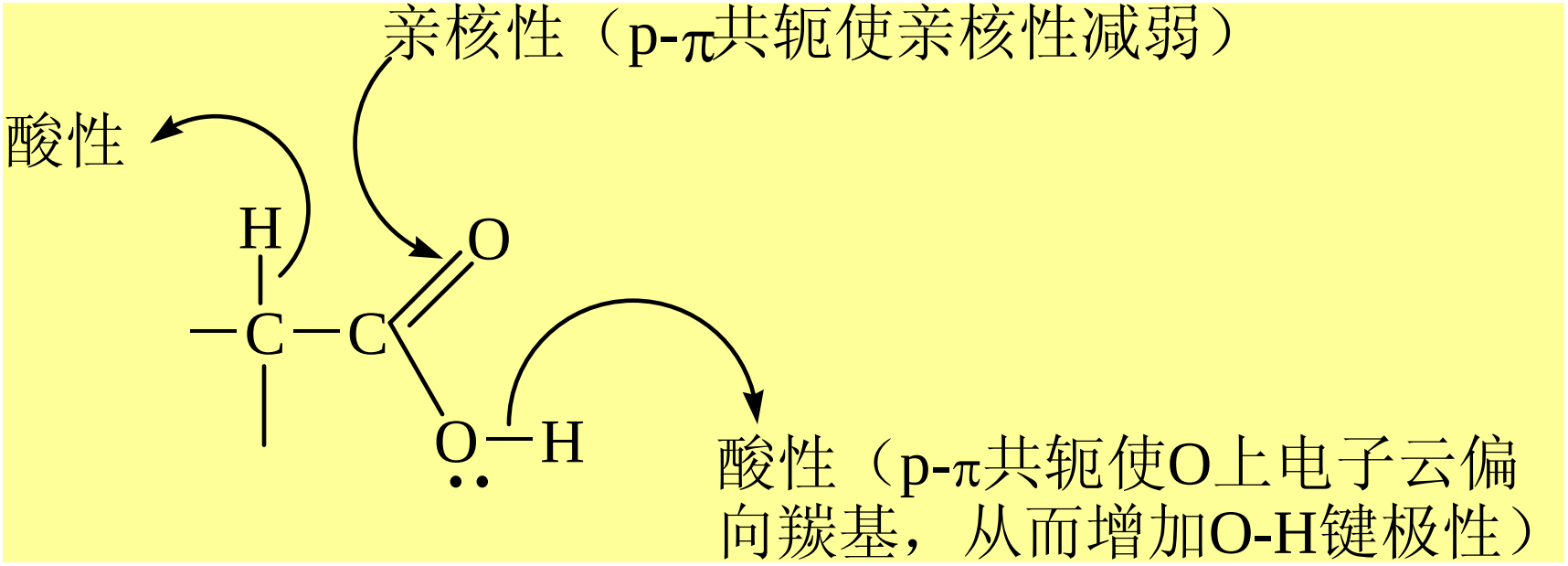
C1~C4：与H_2O互溶

随着碳数增加，在水中溶解度减小

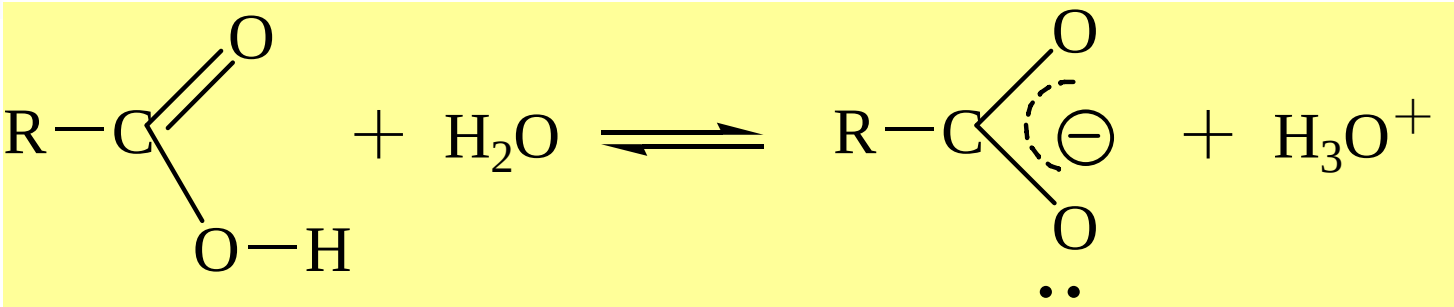
芳香羧酸在水中溶解度小



§11.2 羧酸的化学性质



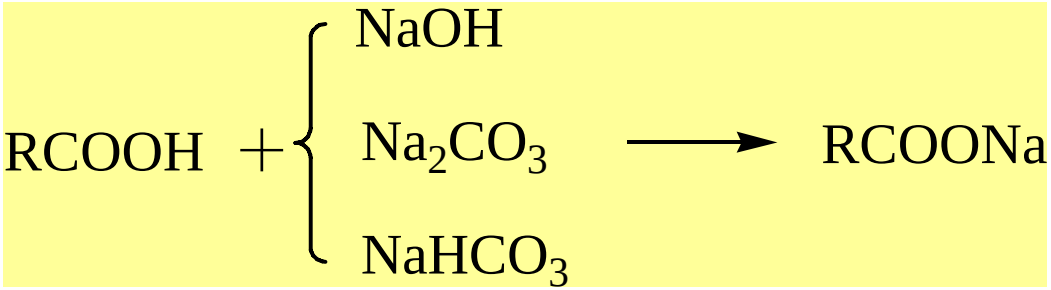
一、酸性



pKa＝3～5
弱酸性

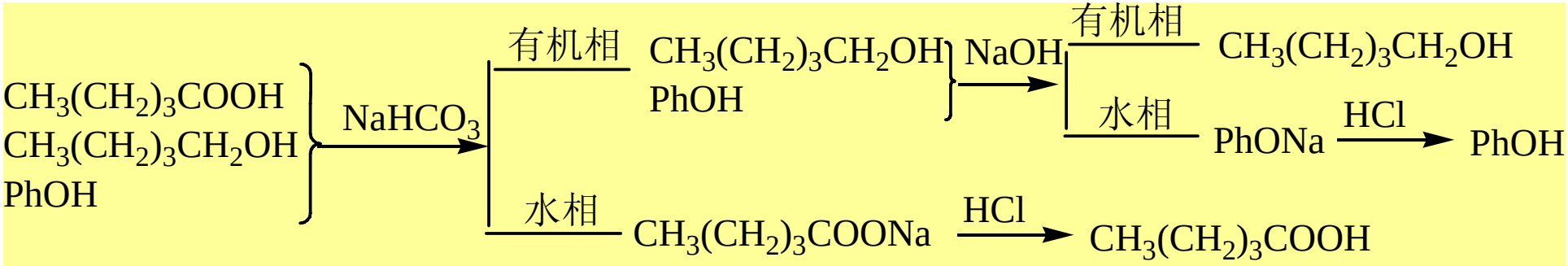
	pKa
无机酸	~ 1
H_2CO_3	6.38
PhOH	~ 10

1. 成盐反应

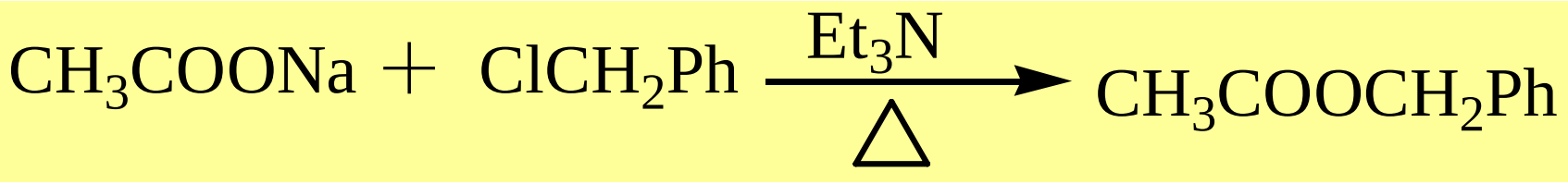


应用

A. 分离、提纯



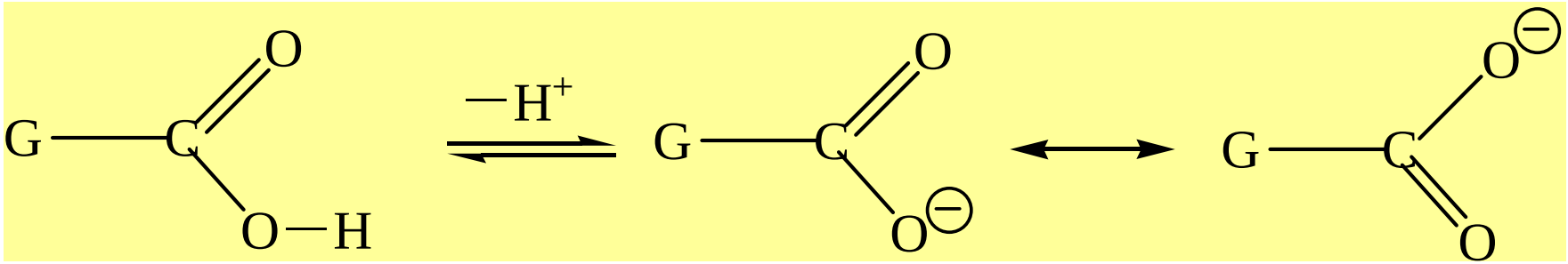
B. 合成酯



伯卤代烷

2. 影响羧酸酸性的因素

A. 取代基的电子效应



G: 吸电子，有利于负电荷的分散，酸性增加

推电子，使负电荷密度增加，降低负离子稳定性，酸性降低

脂肪酸的酸性

	FCH_2COOH	$ClCH_2COOH$	$BrCH_2COOH$	ICH_2COOH	CH_3COOH
pKa	2.66	2.80	2.90	3.18	4.76

	$CH_3CH_2CHClCOOH$	$CH_3CHClCH_2COOH$	$ClCH_2CH_2CH_2COOH$	$CH_3CH_2CH_2COOH$
pKa	2.82	4.41	4.70	4.82

	CH_3COOH	CH_3CH_2COOH	$(CH_3)_2CHCOOH$	$(CH_3)_3CCOOH$
pKa	4.76	4.87	4.86	5.26
	+C(3)	+C(2)	+C(1)	
	+I	+I	+I	+I

芳香酸的酸性

G	-o	-m	-p
H	4.20	4.20	4.20
CH_3	3.91	4.27	4.32
Br	2.85	3.0	3.92
OH	2.70	4.08	4.07
OCH_3	4.09	4.09	4.40
NO_2	2.21	3.49	3.42

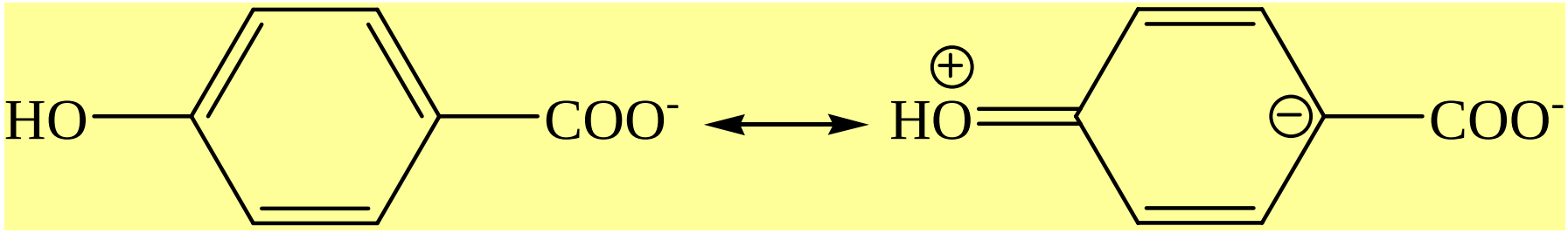
a) 邻位效应：取代基(吸电子、推电子)处于羧基邻位，使酸性增加

b) 酸性：间位>对位

如：-Me：-p(σ-p、+I）-m(+I)

-Br：-p(+C、-I）-m(-I)

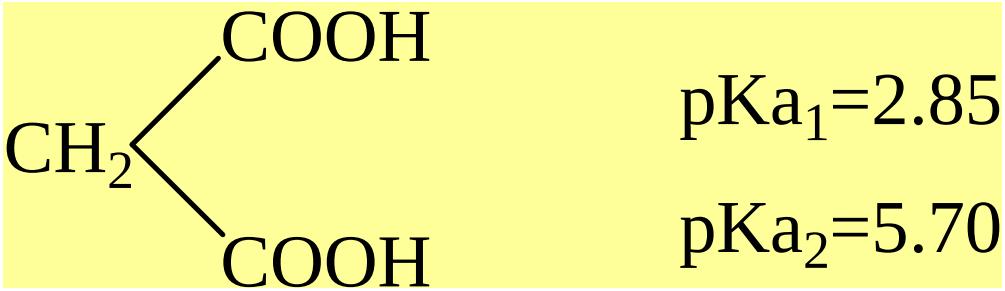
-OH: -p(+C、-I）-m(-I)



c) 酸性：对位>间位

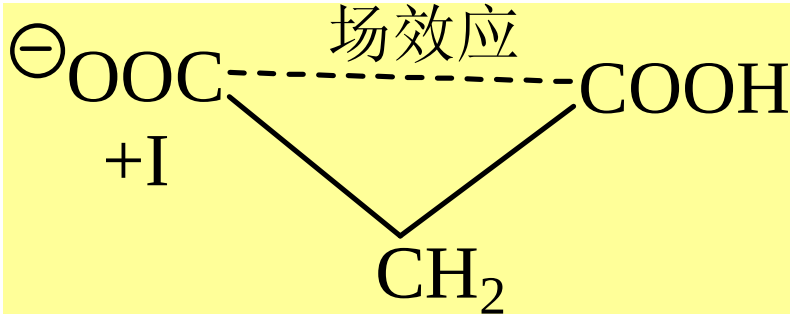
如：-NO_2：-p(-C、-I）-m(-I)

B. 场效应



$pKa_1=2.85$

$pKa_2=5.70$



场效应：空间的静电作用

$-COO^-$产生的电场对另一反应中心有影响（使另一羧基上质子不易离去）

二、羧羟基的取代反应

1. 酯化反应

$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$

A. 反应特点

a) 可逆

	CH_3COOH	+	C_2H_5OH	$\rightleftharpoons$	$CH_3COOC_2H_5$	+	H_2O
投料	1		1				
平衡					2/3		2/3

b) 反应慢

室温放置**16**年，达到平衡

150°C下，需要几天

c) 采取措施

提高反应速度:

加热：每增加10度，速度增加1倍

加催化剂：H_2SO_4、HCl、对甲苯磺酸

固体酸：分子筛等

提高产率:

增加反应物浓度

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

1	2	86%
1	8	97%

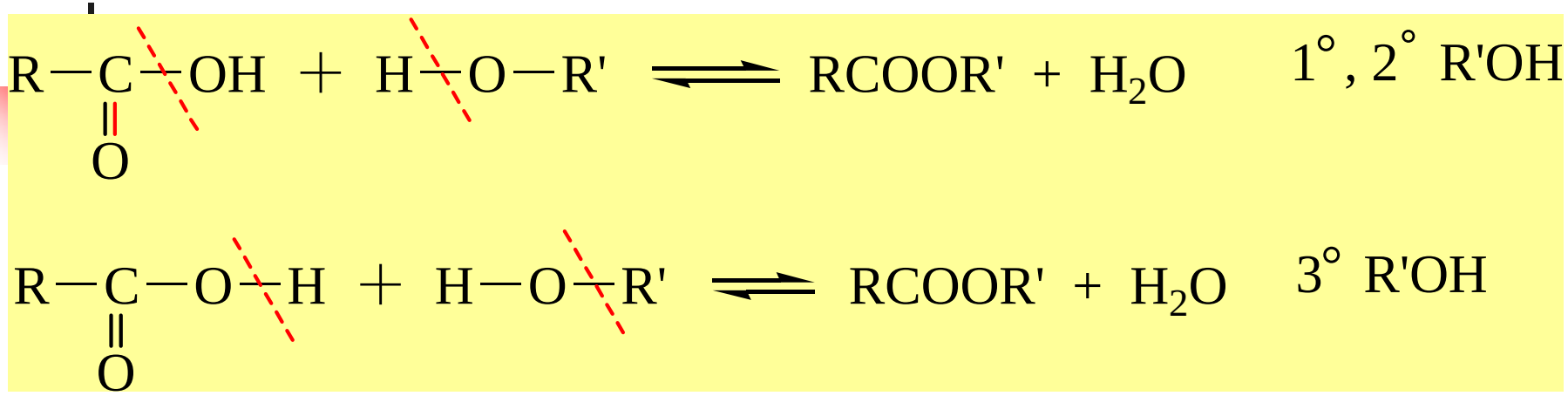
分出某种产物

共沸蒸馏：产物沸点低于醇及酸

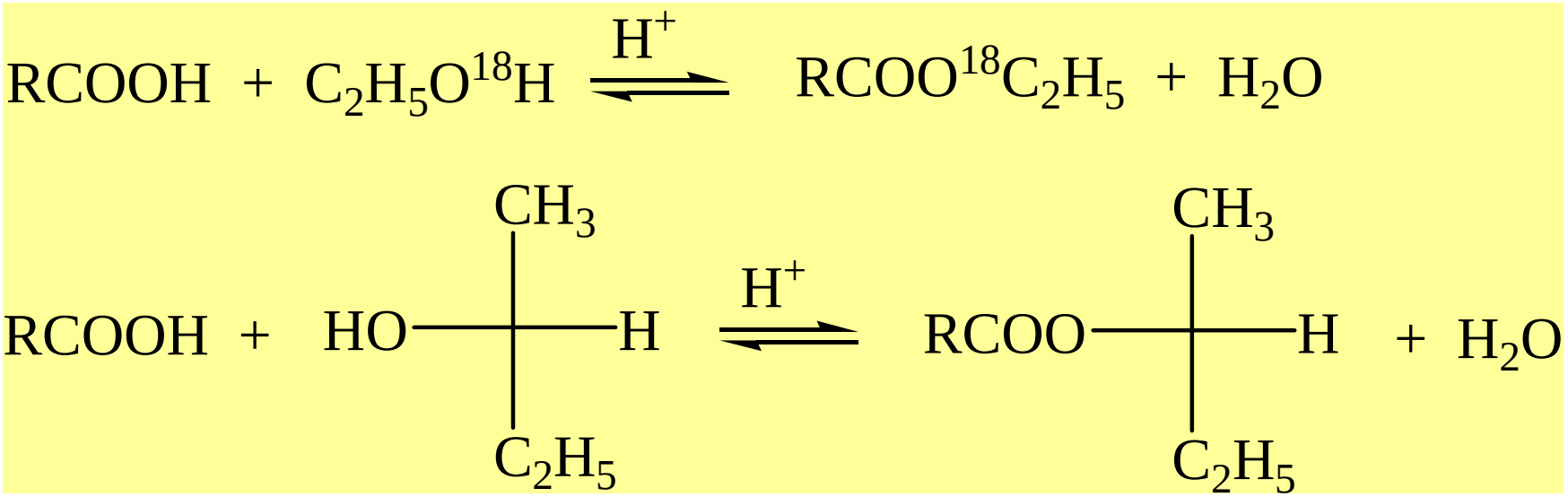
乙酸乙酯/水（**91.9/8.1)**

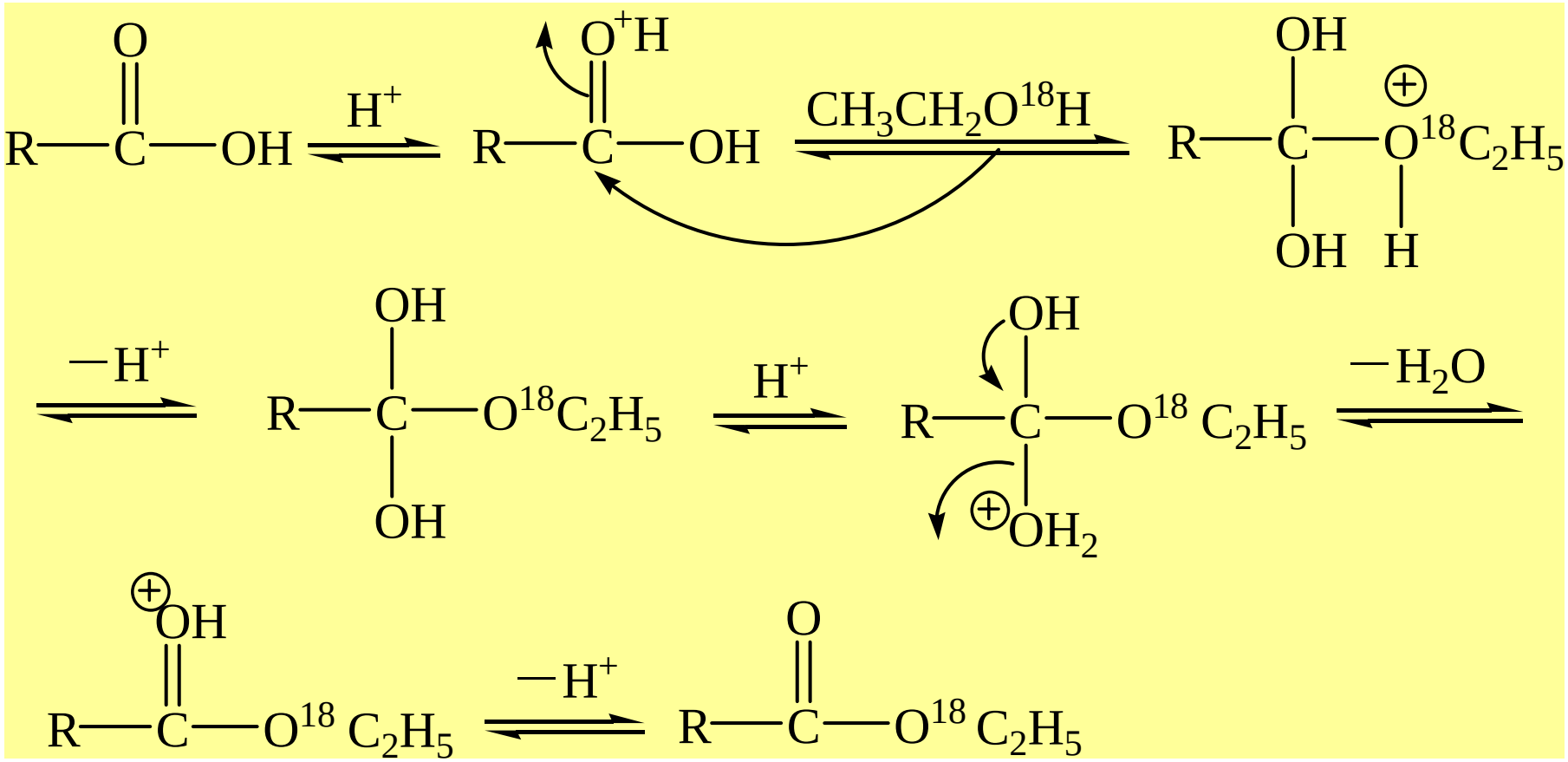
加脱水剂：苯、甲苯（油水分离）

B. 反应机理

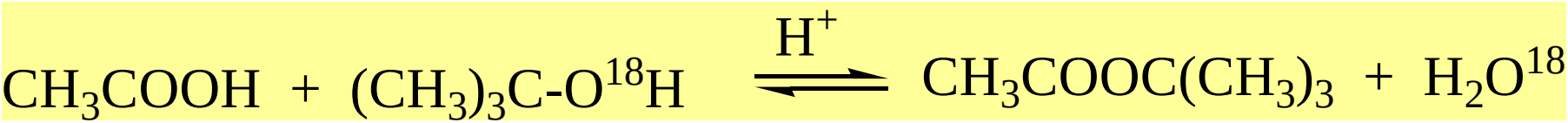

R—C—OH + H—O—R' ⇌ RCOOR' + H2O
O
1°, 2° R'OH
R—C—O—H + H—O—R' ⇌ RCOOR' + H2O
O
3° R'OH

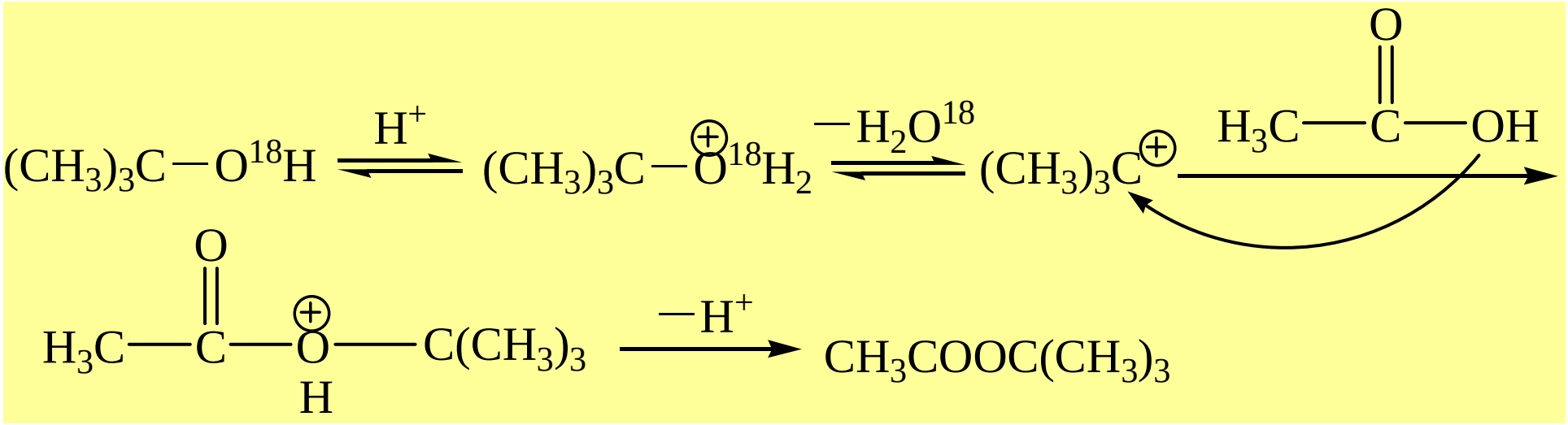
a) 酰氧断键


RCOOH + C2H5O18H ⇌ RCOO18C2H5 + H2O
H+
RCOOH + HO—C(CH3)(C2H5)—H ⇌ RCOO—C(CH3)(C2H5)—H + H2O
H+


R—C(=O)—OH
H+
R—C(=O+H)—OH
CH3CH2O18H
R—C(OH)(OH)—O18C2H5
H
−H+
R—C(OH)2—O18C2H5
H+
R—C(OH)—O18C2H5
OH2
−H2O
R—C(=OH+)—O18C2H5
−H+
R—C(=O)—O18C2H5

b) 烷氧断键


CH3COOH + (CH3)3C-O18H
H+
CH3COOC(CH3)3 + H2O18


(CH3)3C—O18H
H+
(CH3)3C—O18H2
—H2O18
(CH3)3C
O
H3C—C—OH
O
H3C—C—O—C(CH3)3
H
—H+
CH3COOC(CH3)3

c) 酯化反应速率

与CH_3OH反应

	CH_3COOH	CH_3CH_2COOH	$(CH_3)_2CHCOOH$	$(CH_3)_3CCOOH$
相对速率	1	0.84	0.33	0.037

空阻越大，酯化反应越慢

与RCOOH反应

相对速率　1° > 2° > 3°ROH

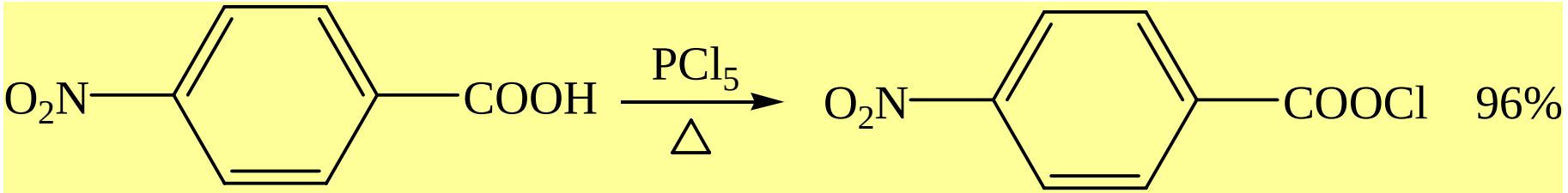
3°ROH通常用酰卤或酸酐酯化

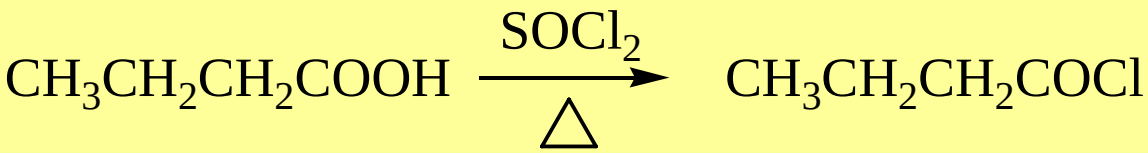
2. 生成酰卤的反应

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$RCOOH + PCl_3 \longrightarrow RCOCl + H_3PO_3$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$





3. 生成酰胺的反应

$$RCOOH + NH_3 \rightleftharpoons RCOO^-NH_4^+ \xrightarrow[\triangle]{} RCONH_2 + H_2O$$

$$CH_3CH_2CH_2COOH + NH_3 \xrightarrow{185^\circ C} CH_3CH_2CH_2CONH_2 + H_2O \quad 85\%$$

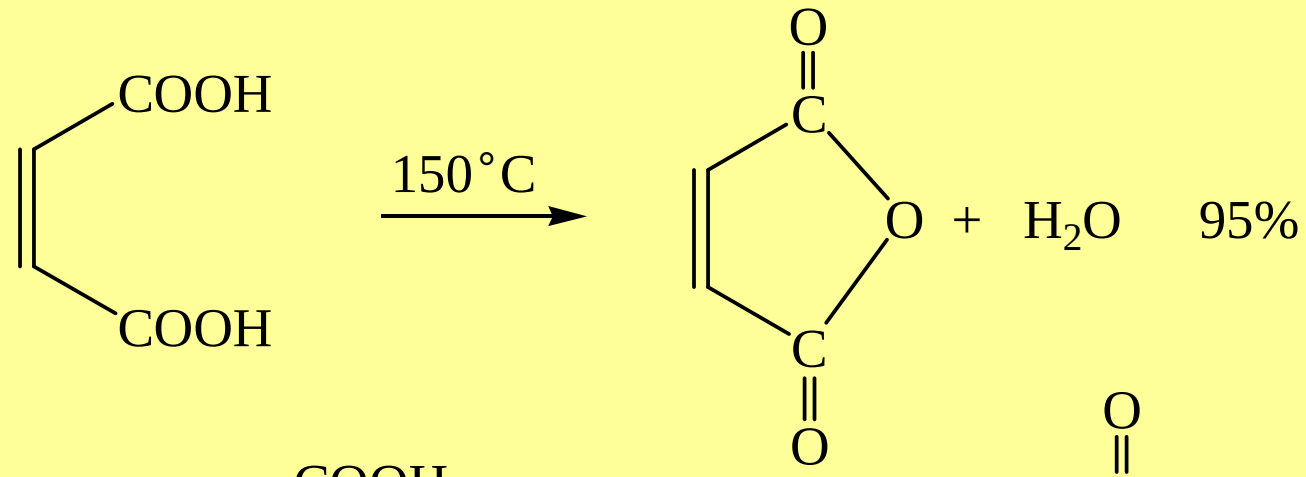
$$PhCOOH + PhNH_2 \xrightarrow{225^\circ C} PhCONHPh + H_2O \quad 80\sim84\%$$

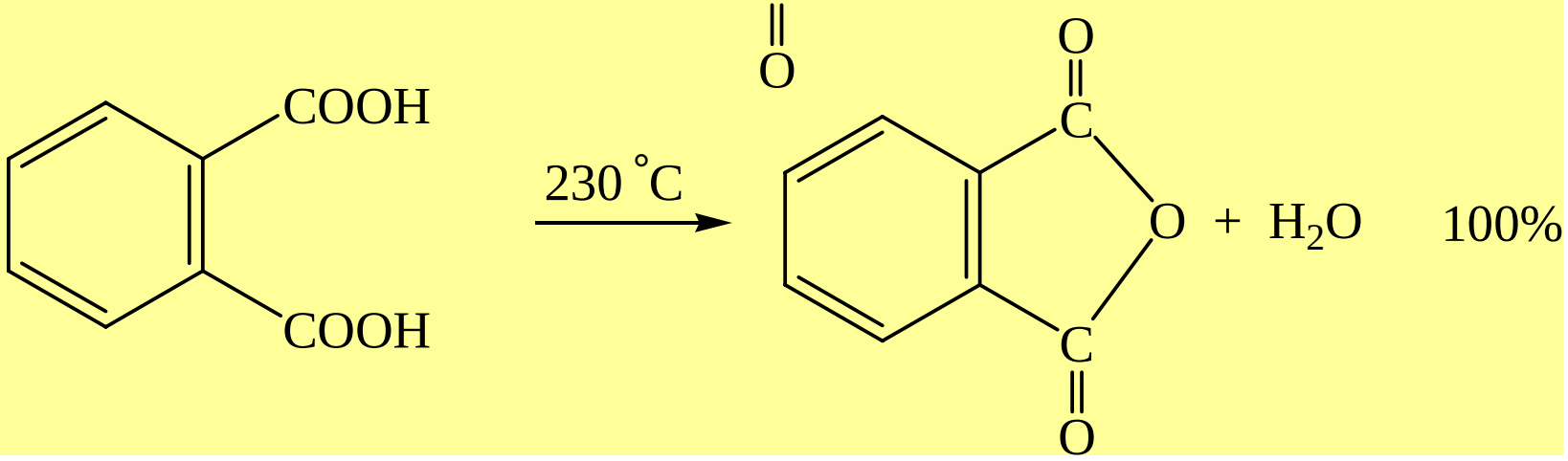
4. 生成酸酐的反应

$$2\ RCOOH \xrightarrow[\triangle]{P_2O_5} (RCO)_2O$$

$$2\ CF_3COOH \xrightarrow[\triangle]{P_2O_5} (CF_3CO)_2O \quad 74\%$$

$$PhCOOH + (CH_3CO)_2O \xrightarrow[\triangle]{} (PhCO)_2O + CH_3COOH \quad 74\%$$



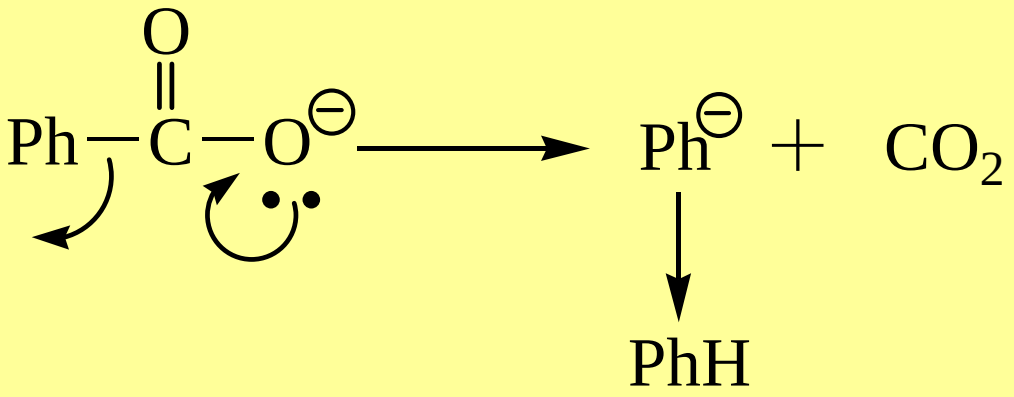


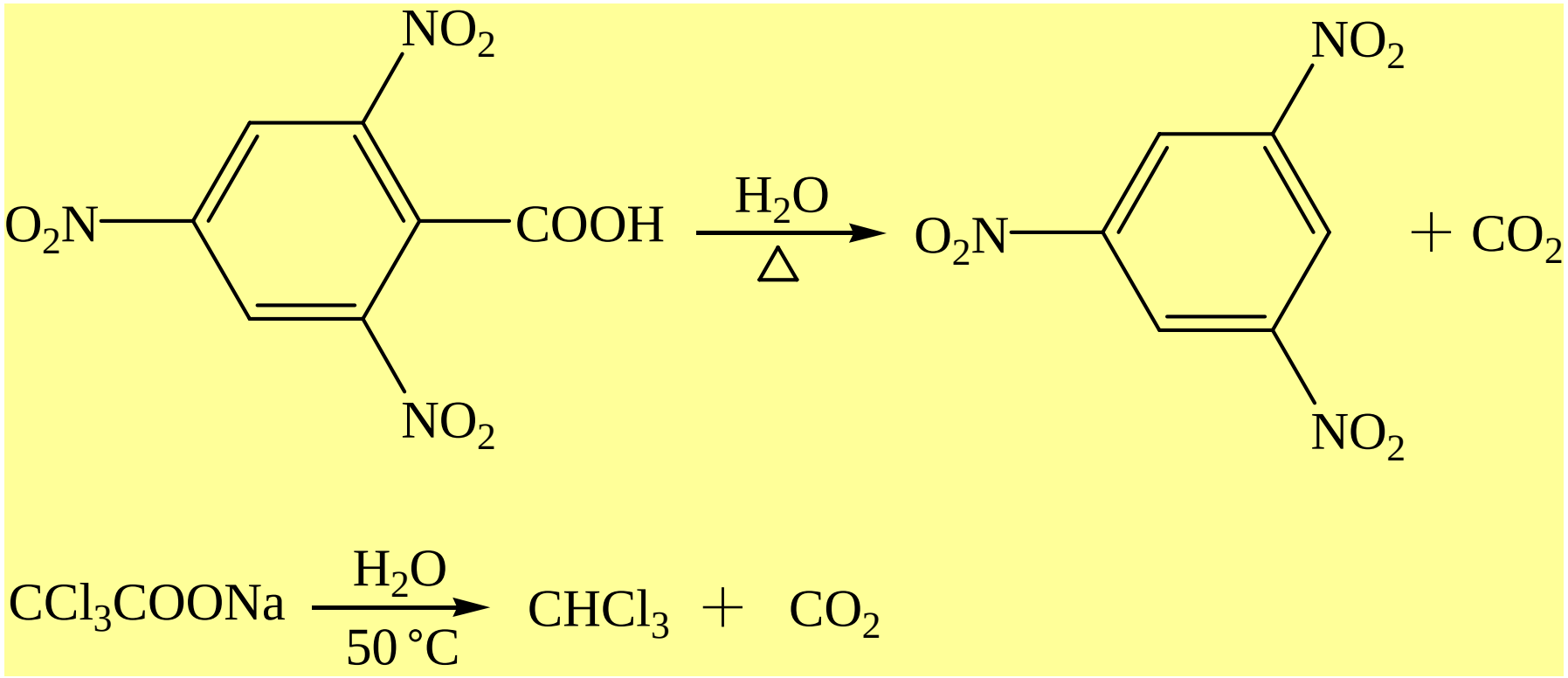
三、脱羧反应

1. 饱和脂肪酸、芳香酸

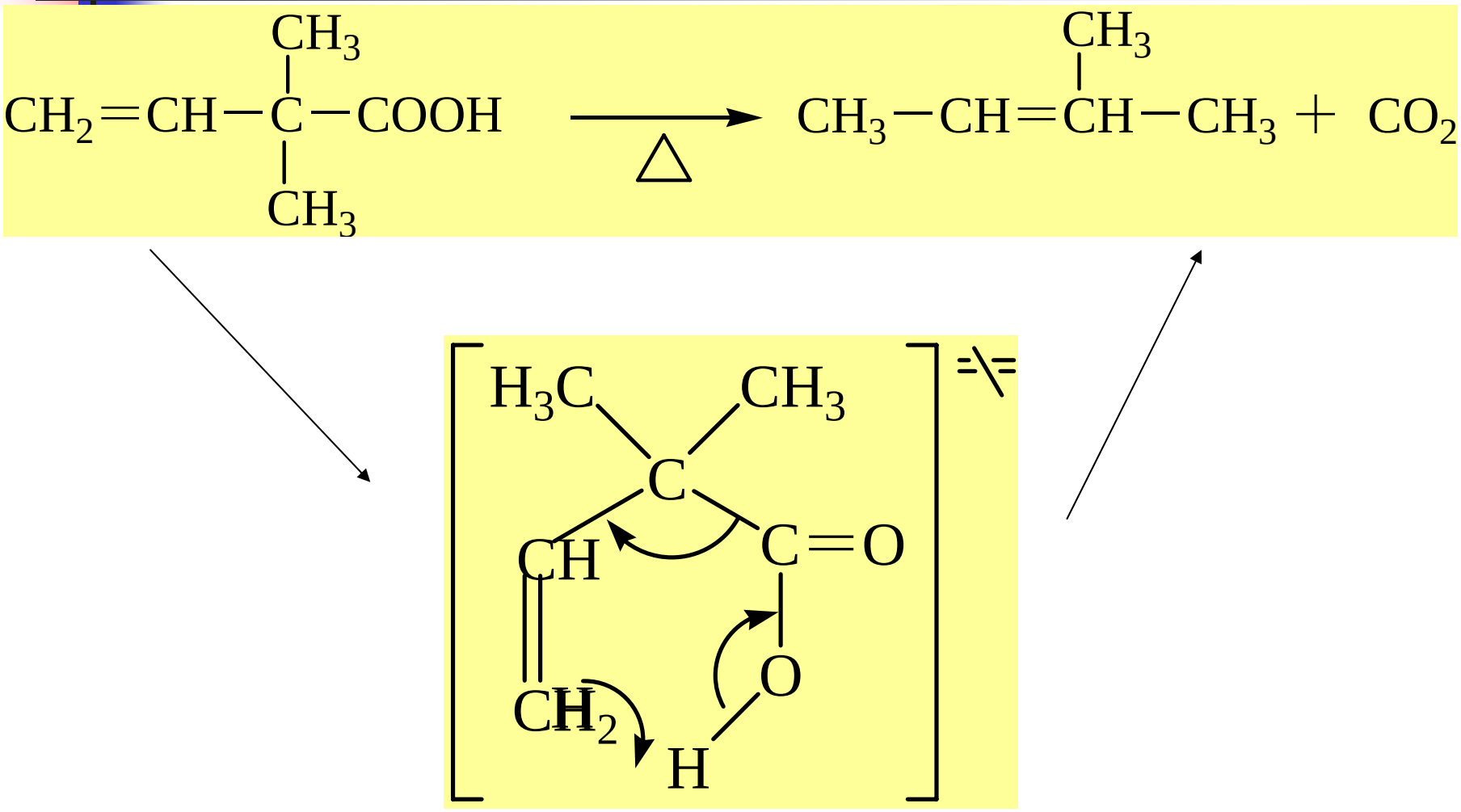
$$CH_3COONa + NaOH(CaO) \xrightarrow[\triangle]{} CH_4 + Na_2CO_3$$

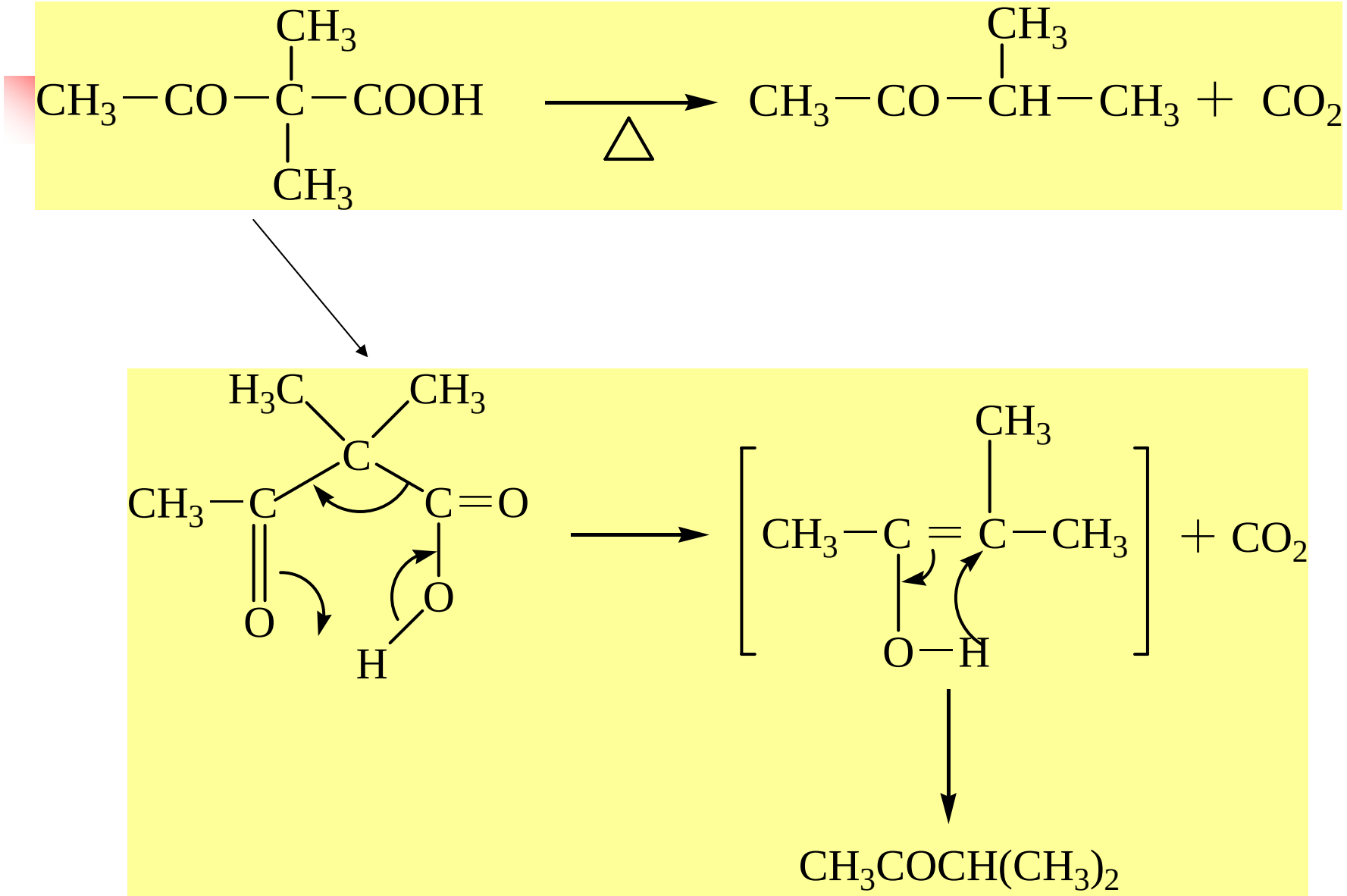
$$PhCOONa + NaOH(CaO) \xrightarrow[\triangle]{} PhH + Na_2CO_3$$




NO2
O2N
COOH
H2O
Δ
NO2
O2N
NO2
+ CO2
NO2
CCl3COONa
H2O
50 °C
CHCl3 + CO2

2. β,γ-不饱和酸



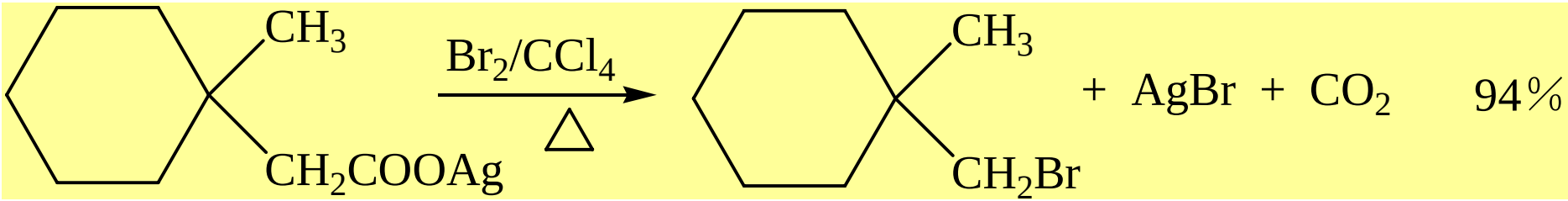

CH3
CH3—CO—C—COOH
CH3
△
CH3
CH3—CO—CH—CH3 + CO2
H3C
CH3
C
CH3—C
C=O
O
O
H
CH3
CH3—C=C—CH3
+ CO2
O—H
CH3COCH(CH3)2

3. 脱羧卤代

A. Hunsdiecke（汉斯狄克）反应

$$RCOOAg \xrightarrow[\triangle]{Br_2/CCl_4} RBr + AgBr + CO_2$$

制备1°RBr



银盐的纯度要求高，且需要无水条件。改进:

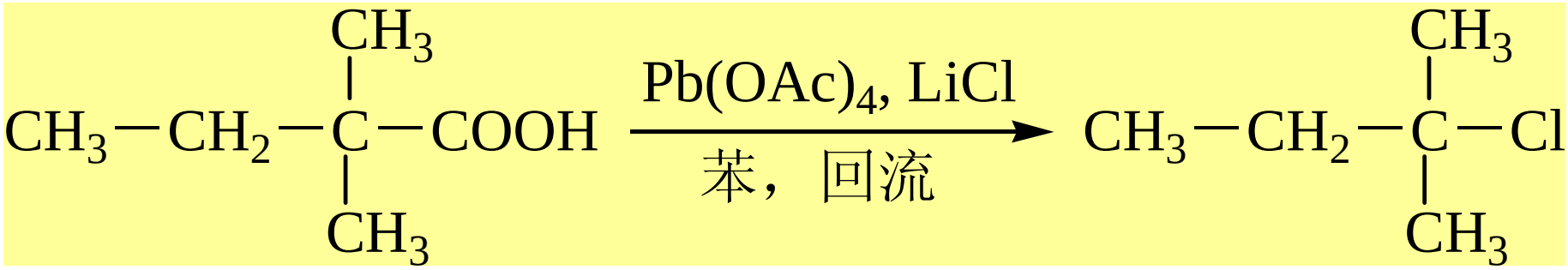
$$RCOOH + HgO + Br_2 \xrightarrow{CCl_4} RBr + HgBr + CO_2 + H_2O$$

B. Kochi（柯齐）反应

$$RCOOH + Pb(OAc)_4 + LiCl \longrightarrow$$

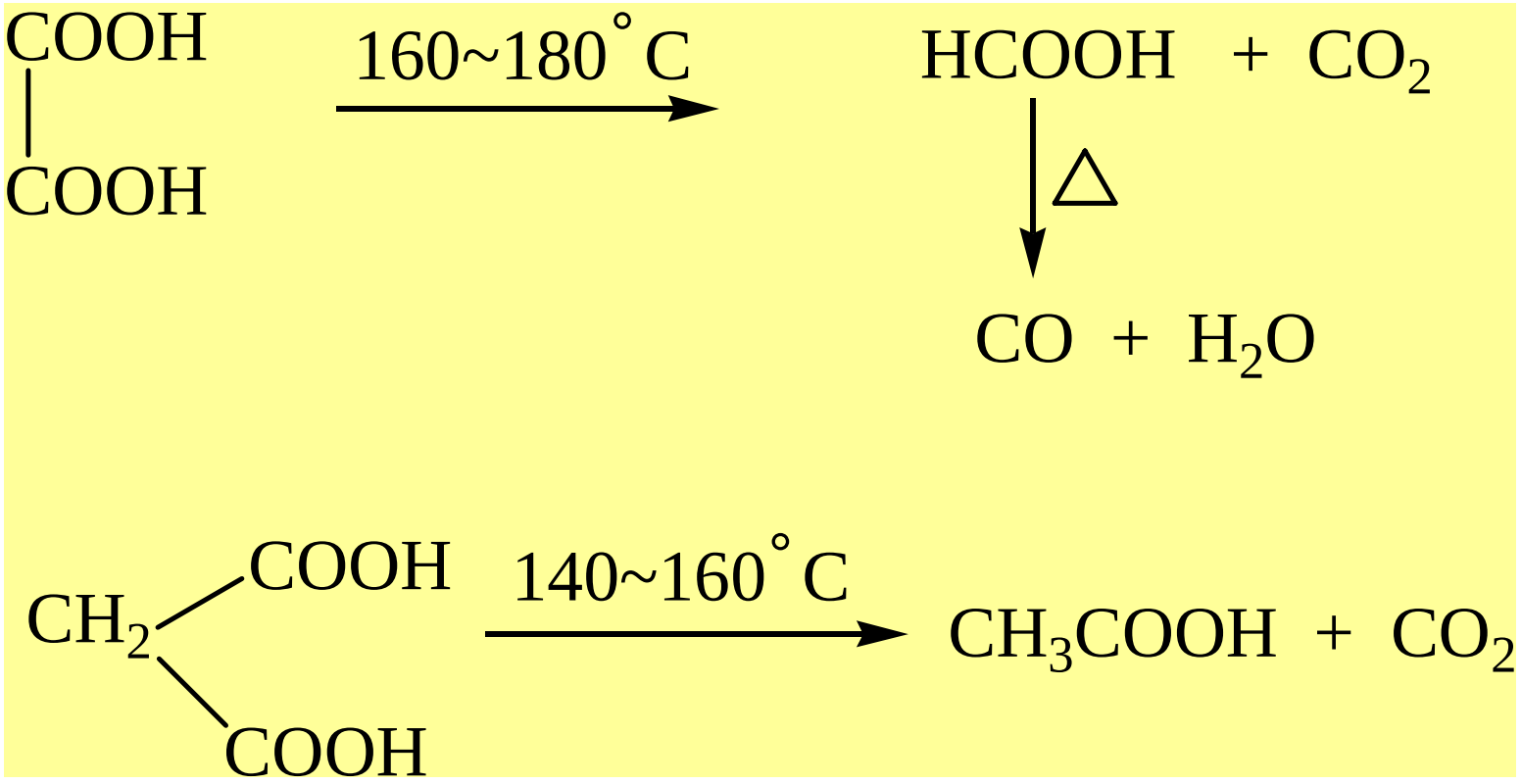
$$RCl + Pb(OAc)_2 + LiOAc + CO_2 + HOAc$$

制备1°、2°、3°RCl

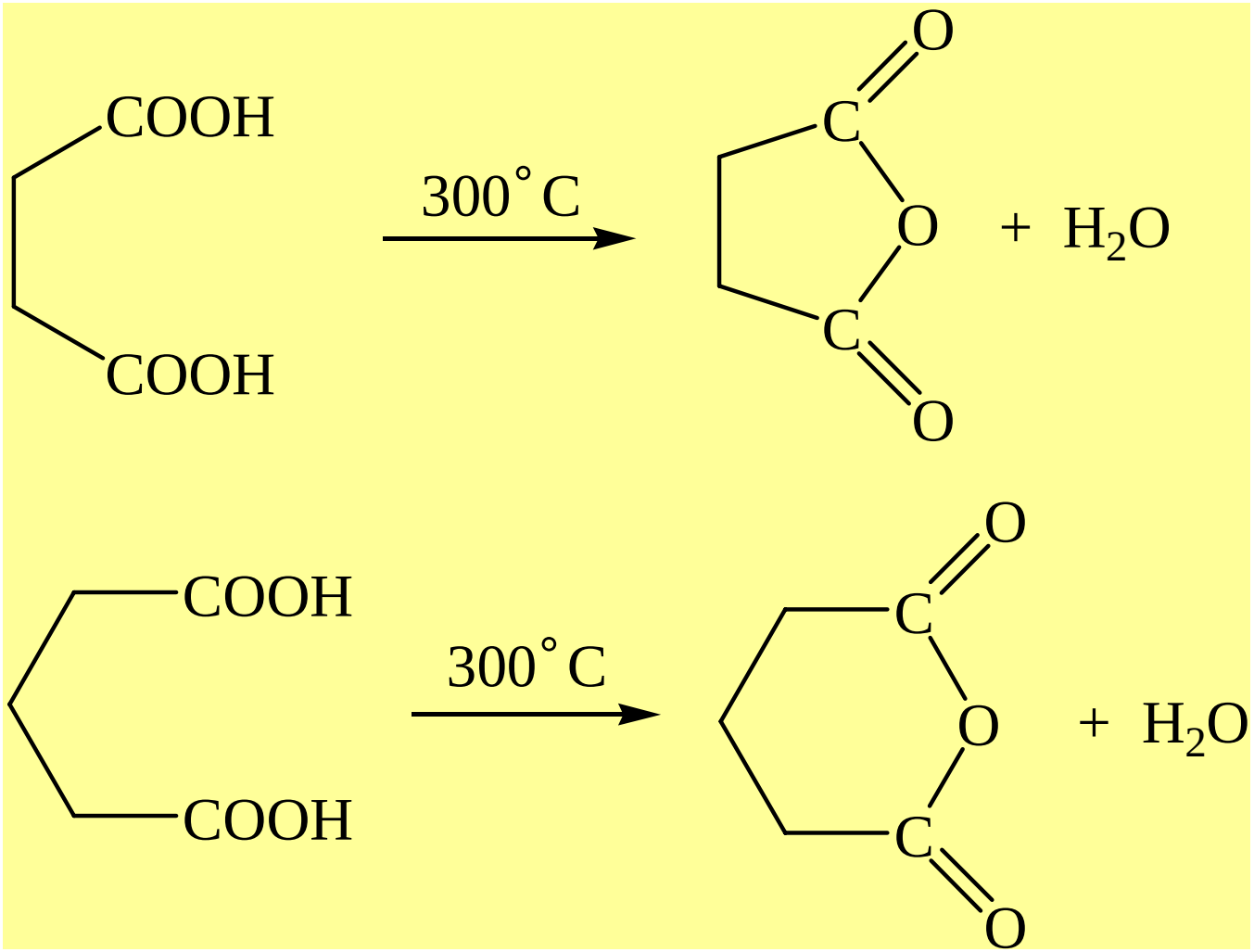


四、二元 脱羧的受热反应

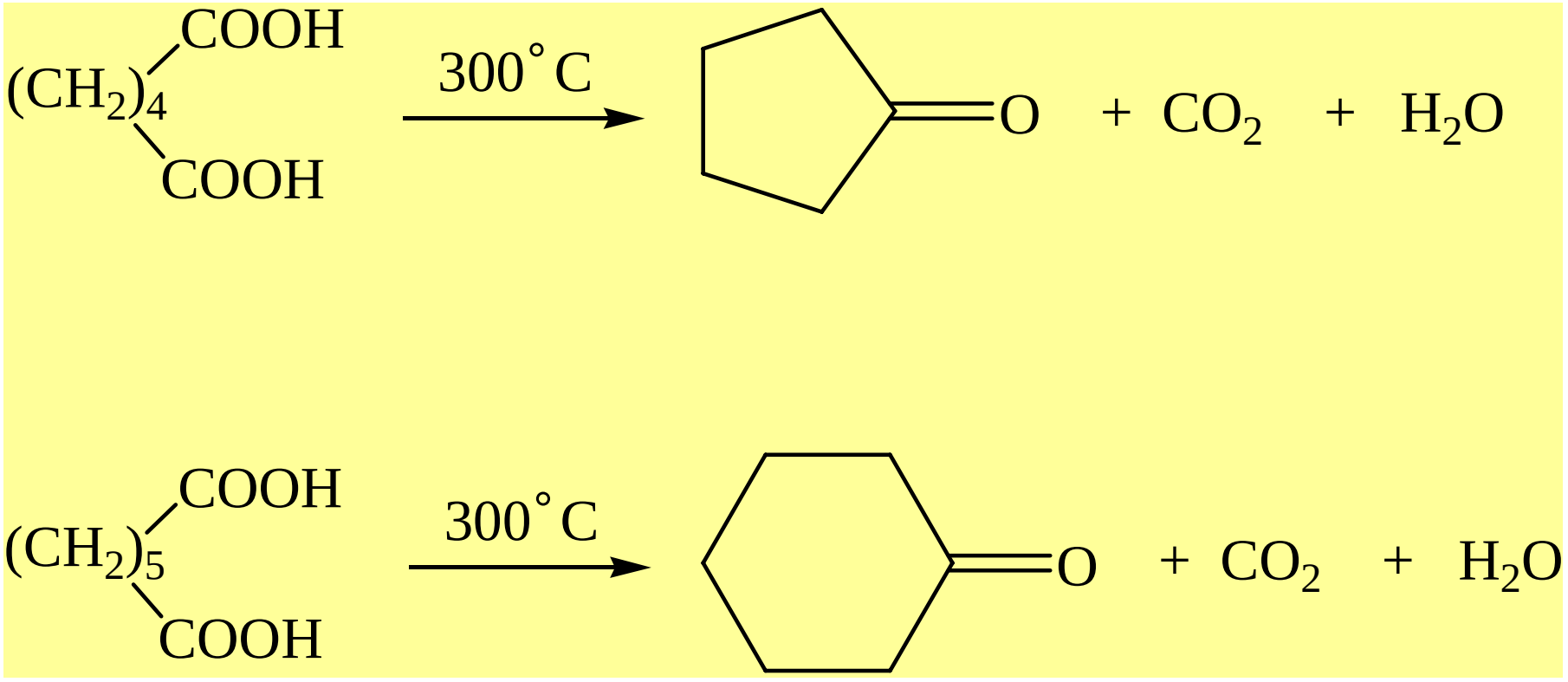
1. 1,2或1,3-二羧酸：脱CO_2



2. 1,4或1,5-二羧酸：脱H_2O



3. 1,6或1,7-二羧酸：脱CO_2、H_2O

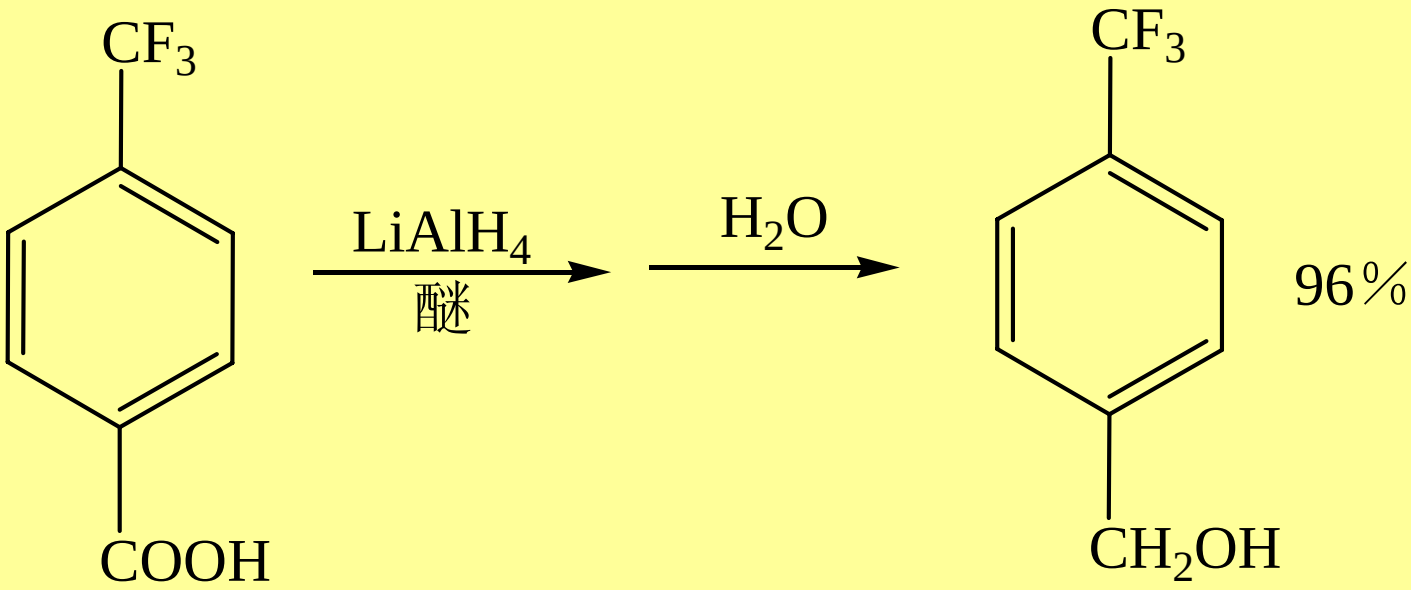


五、还原反应

$$RCOOH + H_2 \xrightarrow{Cat.} \text{难还原}$$

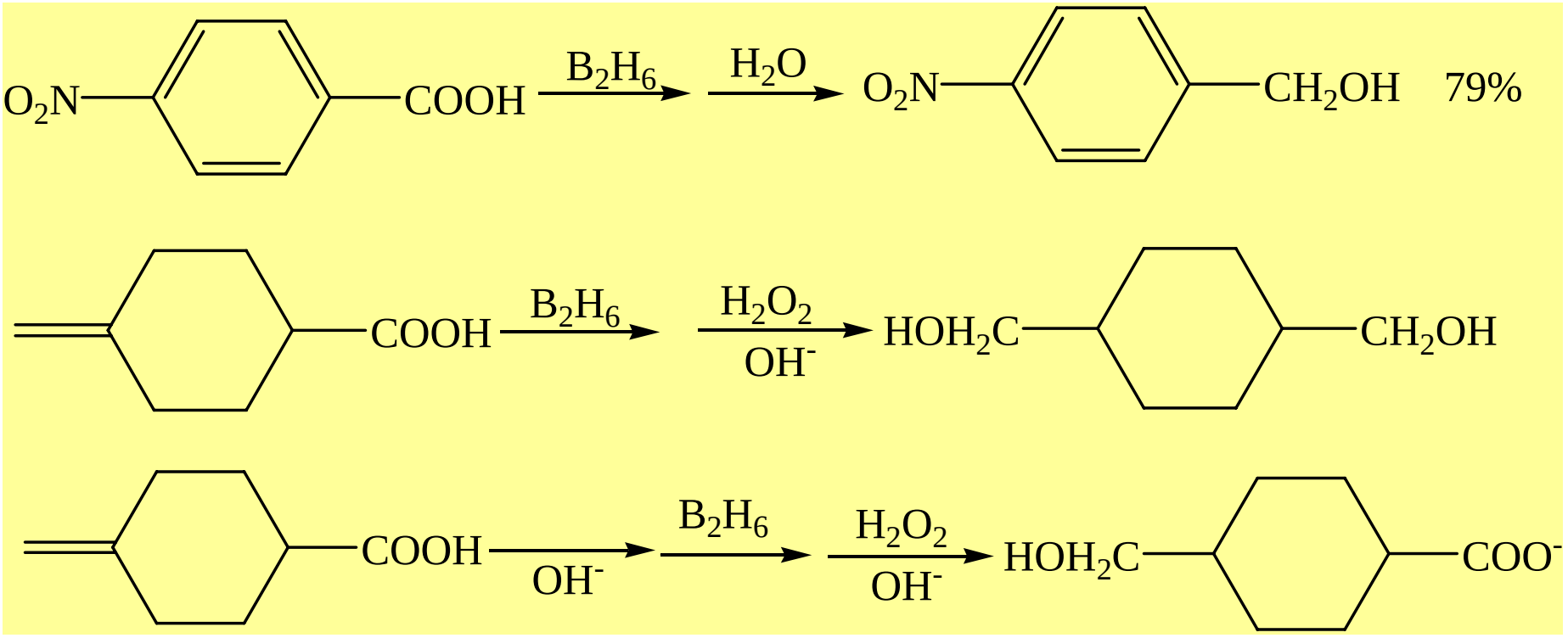
1. $LiAlH_4$

$$(CH_3)_3CCOOH \xrightarrow[\text{醚}]{LiAlH_4} \xrightarrow{H_2O} (CH_3)_3CCH_2OH \quad 92\%$$

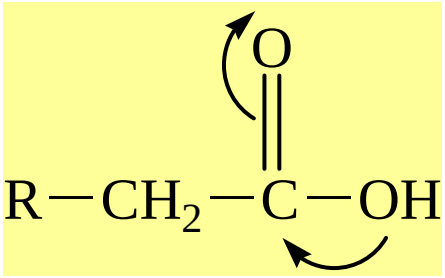


$$CH_2{=}CHCH_2COOH \xrightarrow[\text{醚}]{LiAlH_4} \xrightarrow{H_2O} CH_2{=}CHCH_2CH_2OH$$

2. B_2H_6


O2N
COOH
B2H6
H2O
O2N
CH2OH
79%
COOH
B2H6
H2O2
OH-
HOH2C
CH2OH
COOH
OH-
B2H6
H2O2
OH-
HOH2C
COO-

六、卤代反应

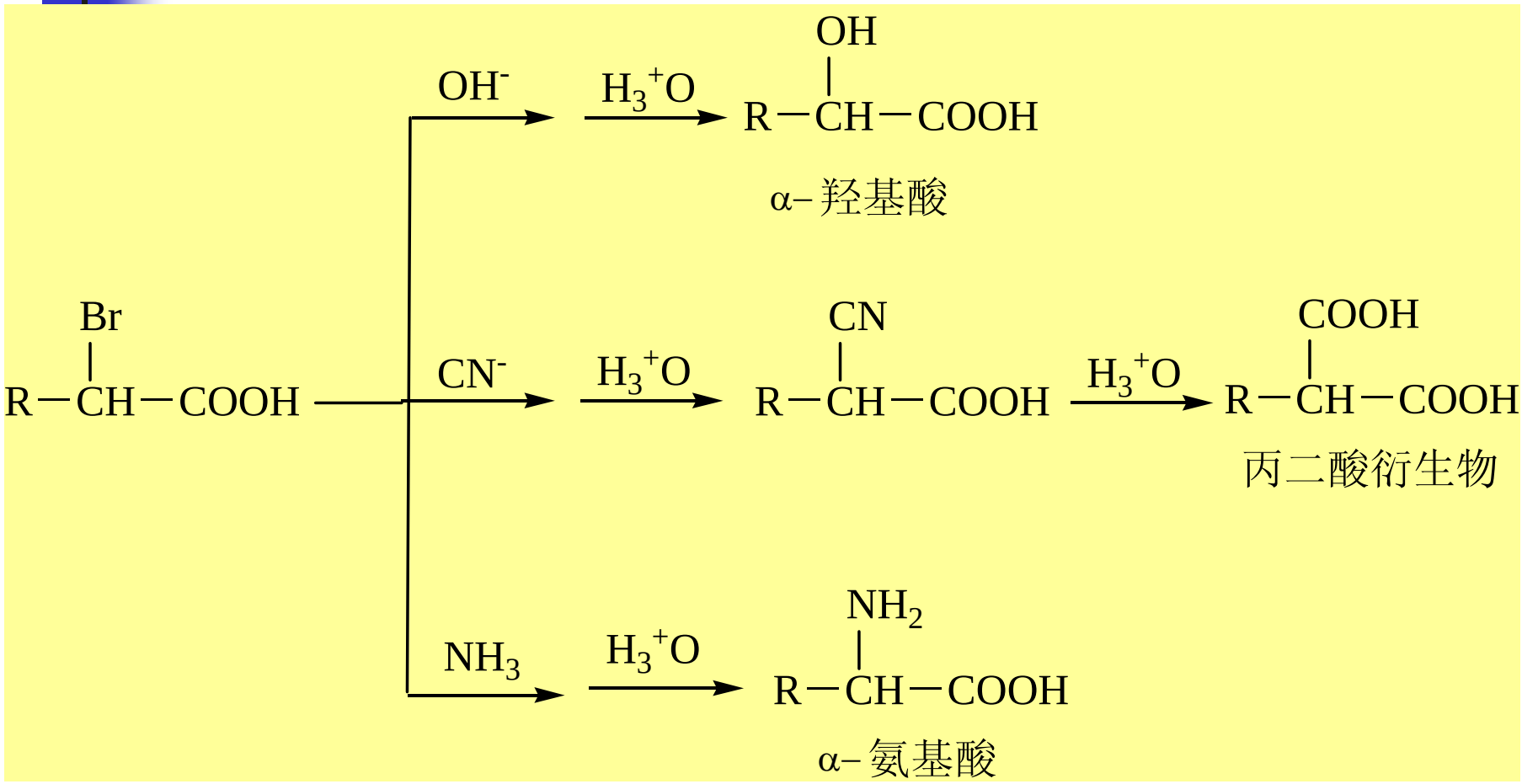


p-π共轭使α-H卤代变慢

$$CH_3CH_2CH_2COOH \xrightarrow[\text{光照或加热}]{Cl_2} \begin{matrix} CH_3CH_2CHClCOOH & 5\% \\ CH_3CHClCH_2COOH & 64\% \\ CH_2ClCH_2CH_2COOH & 31\% \end{matrix}$$

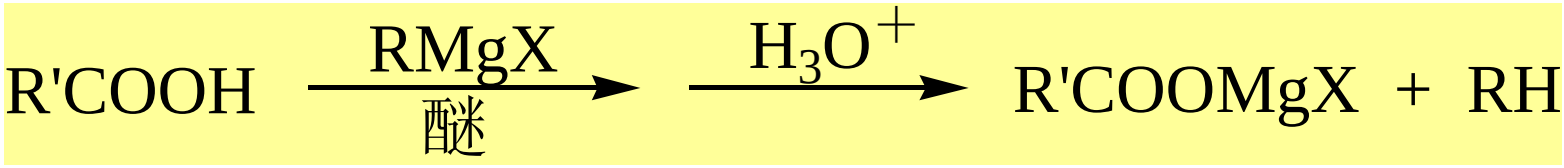
$$CH_3CH_2CH_2CH_2COOH \xrightarrow[70\,^{\circ}C]{P,\ Br_2} CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCOOH \quad 80\%$$

应用：

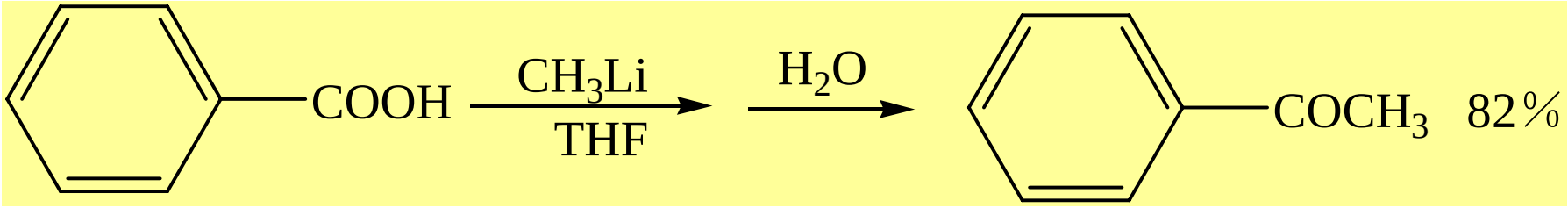

OH
OH⁻
H₃⁺O
R—CH—COOH
α–羟基酸
Br
R—CH—COOH
CN
CN⁻
H₃⁺O
R—CH—COOH
H₃⁺O
COOH
R—CH—COOH
丙二酸衍生物
NH₂
NH₃
H₃⁺O
R—CH—COOH
α–氨基酸

七、与金属有机化合物反应

1. 与RMgX反应

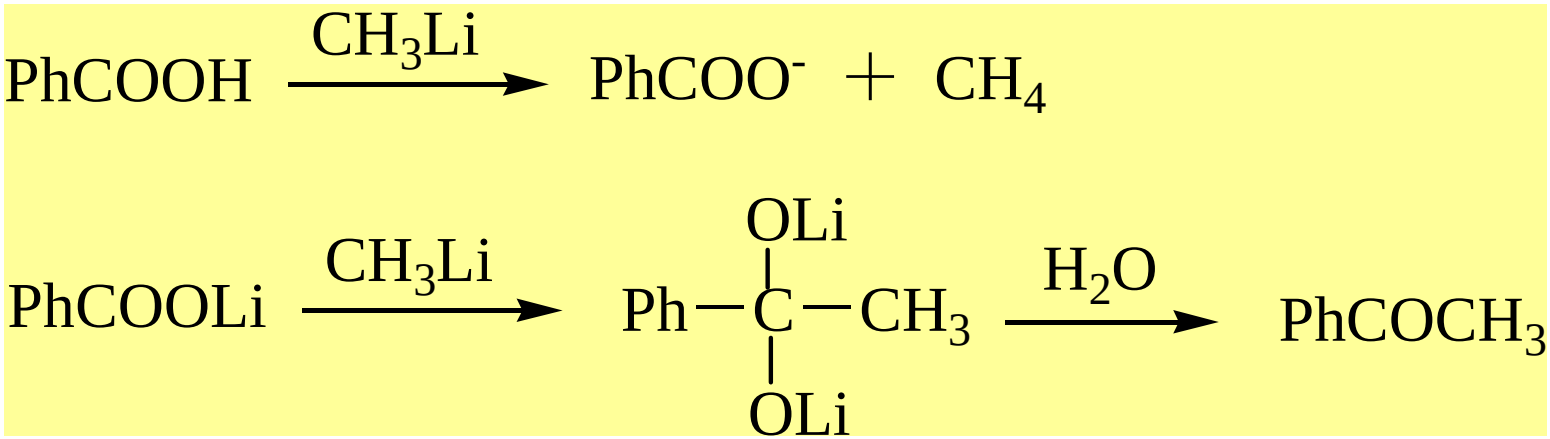


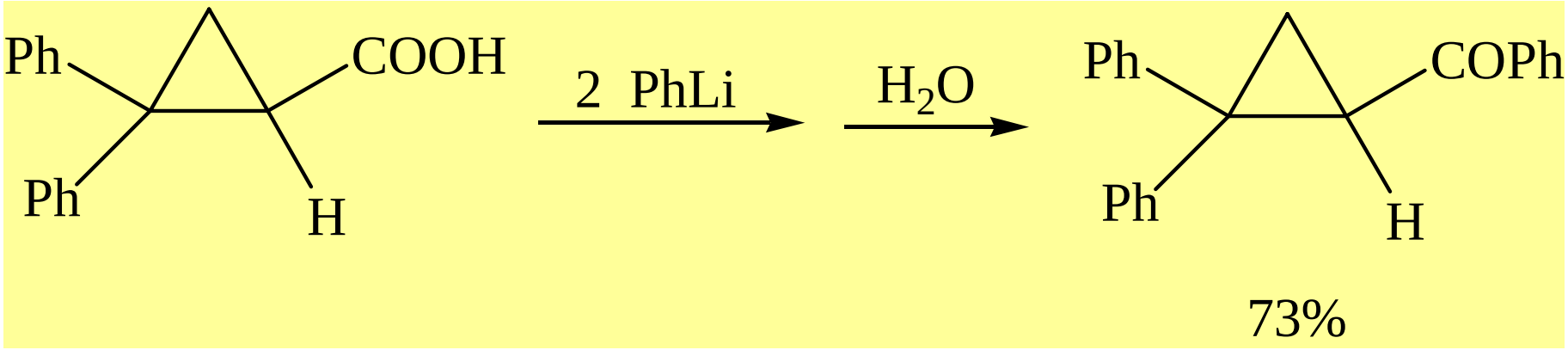
2. 与RLi反应



制备酮

反应机理:


PhCOOH
CH3Li
PhCOO- + CH4
PhCOOLi
CH3Li
OLi
Ph
C
CH3
OLi
H2O
PhCOCH3


Ph
COOH
Ph
H
2 PhLi
H2O
Ph
COPh
Ph
H
73%

§11.3 羧酸的制备

一、氧化反应

$$RHC{=}CHR' \xrightarrow{KMnO_4/H^+} RCOOH + R'COOH$$

$$RC{\equiv}CR' \xrightarrow{KMnO_4/H^+} RCOOH + R'COOH$$

$$ArCHRR' \xrightarrow{KMnO_4/H^+} ArCOOH$$

$$RCH_2OH \xrightarrow{KMnO_4/H^+} RCOOH$$

$$RCHO \xrightarrow{KMnO_4/H^+} RCOOH$$

二、腈的水解：制备增加C1羧酸

$$RCN \xrightarrow[\triangle]{H_3{+}O} RCOOH$$

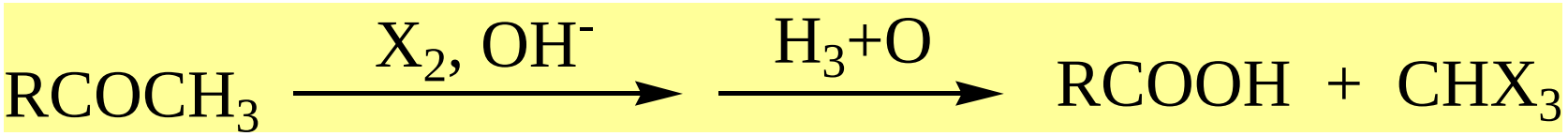
$$RCH_2Cl \xrightarrow{CN^-} \xrightarrow[\triangle]{H_3{+}O} RCH_2COOH$$

三、RMgX的羧化：制备增加C1羧酸

$$RMgX \xrightarrow{CO_2} \xrightarrow{H_3{+}O} RCOOH$$

$$(CH_3)_3C\text{-}Cl \xrightarrow{Mg} \xrightarrow{CO_2} \xrightarrow{H_3{+}O} (CH_3)_3C\text{-}COOH \quad 80\%$$

四、卤仿反应：制备减少C1羧酸



本章要点

羧酸酸性
酯化反应及其机理
卤代及脱羧卤代反应
脱羧反应及其机理
二元羧酸的受热反应
还原反应
羧酸与RLi反应

作业

P538　12-4　iii, v
P541　12-7　iii, vii
P549　12-11　i, iii, iv, v
P553　12-14　iii, iv
P554　12-15　i, ii, iii, iv
P568　12-23　v, vi