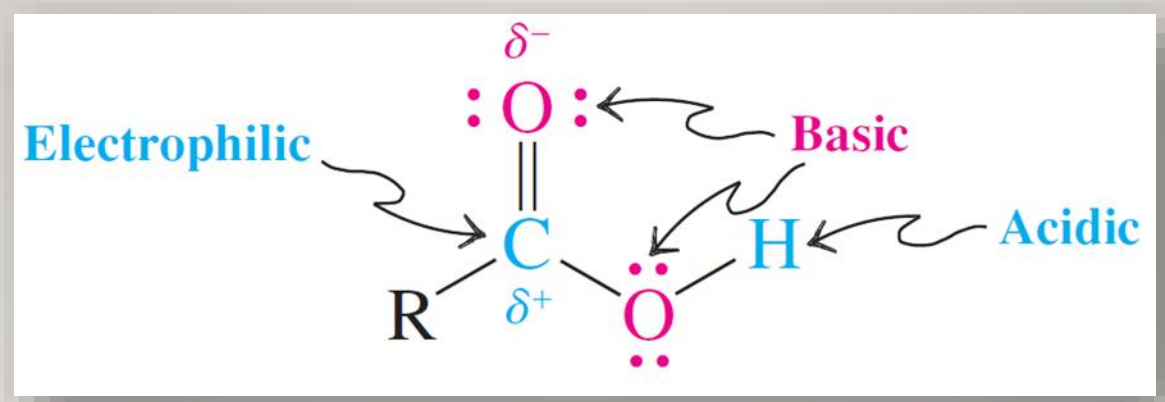
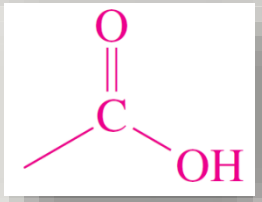
CHM-134 ORGANIC CHEMISTRY
CHAPTER-10: CARBOXYLIC ACIDS & DERIVATIVES



Carboxy group: -COOH, -CO_2H,



Order of Precedence of Functional Groups

RCOH	RCOCR	RCOR′	RCX	$RCNR'_2$	RCN	RCH	RCR′	ROH	RSH	RNH_2
Carboxylic acid	Anhydride	Ester	Acyl halide	Amide	Nitrile	Aldehyde	Ketone	Alcohol	Thiol	Amine

Increasing precedence in naming

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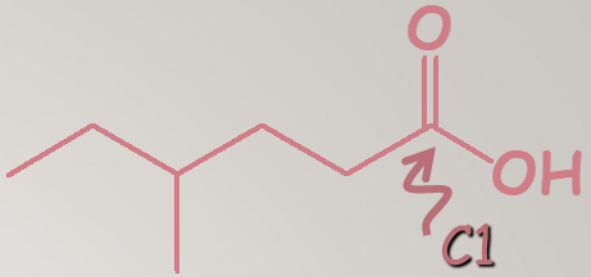
10.1 NOMENCLATURE RULES

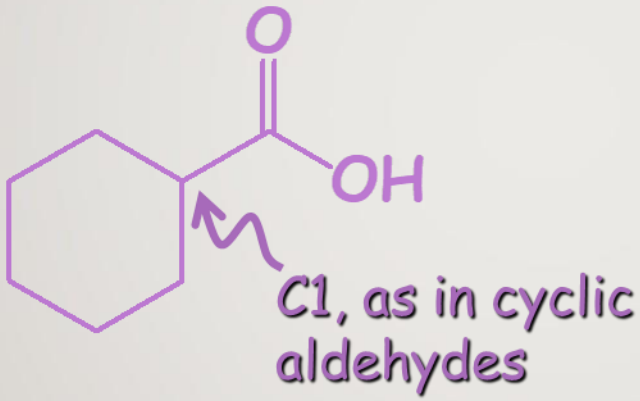
IUPAC: Replace –e of alkane name with –oic acid

$HCOOH$ Methanoic acid—Formic acid accepted
CH_3COOH Ethanoic acid—Acetic acid accepted
CH_3CH_2COOH Propanoic acid
Etc.

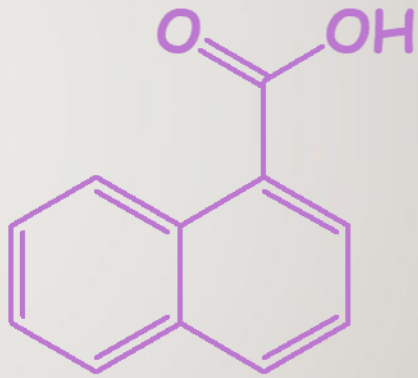


4-Methylhexanoic acid

Cyclic: Cycloalkanecarboxylic acids



Cyclohexanecarboxylic acid



1-Naphthalenecarboxylic acid

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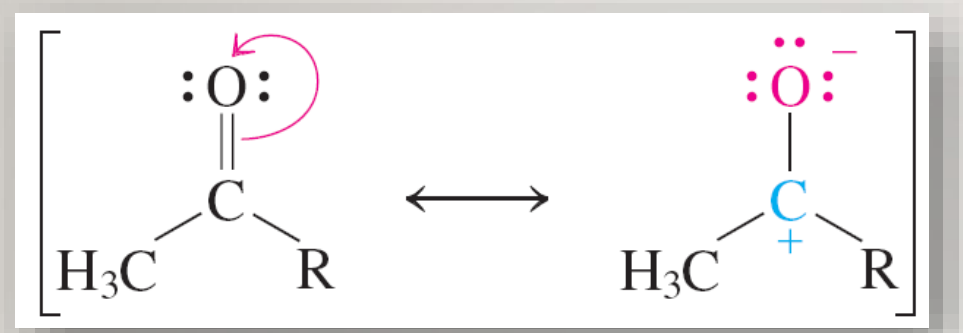
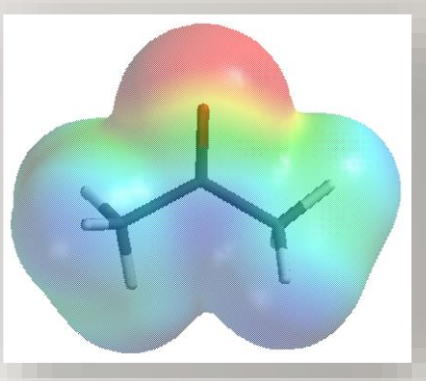
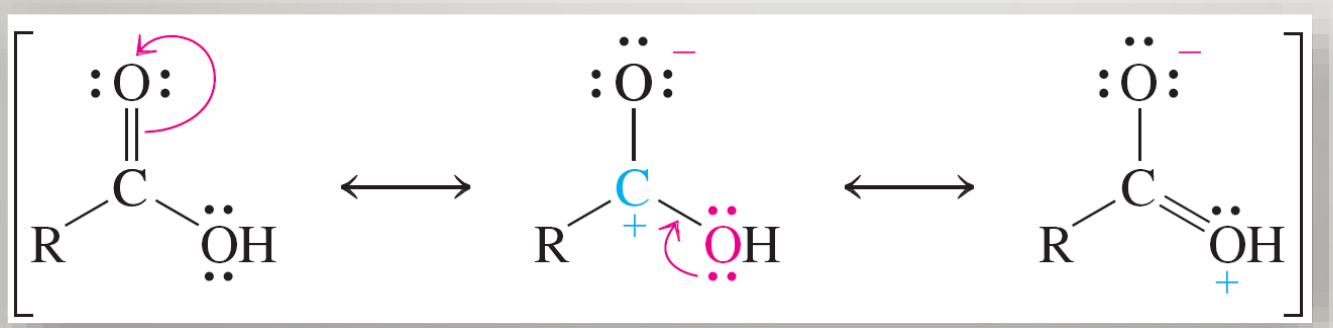
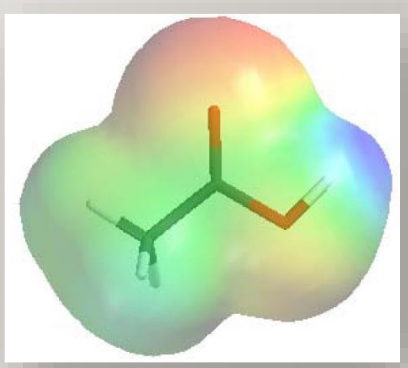
10.2 RESONANCE

Ketones versus Carboxylic Acids:









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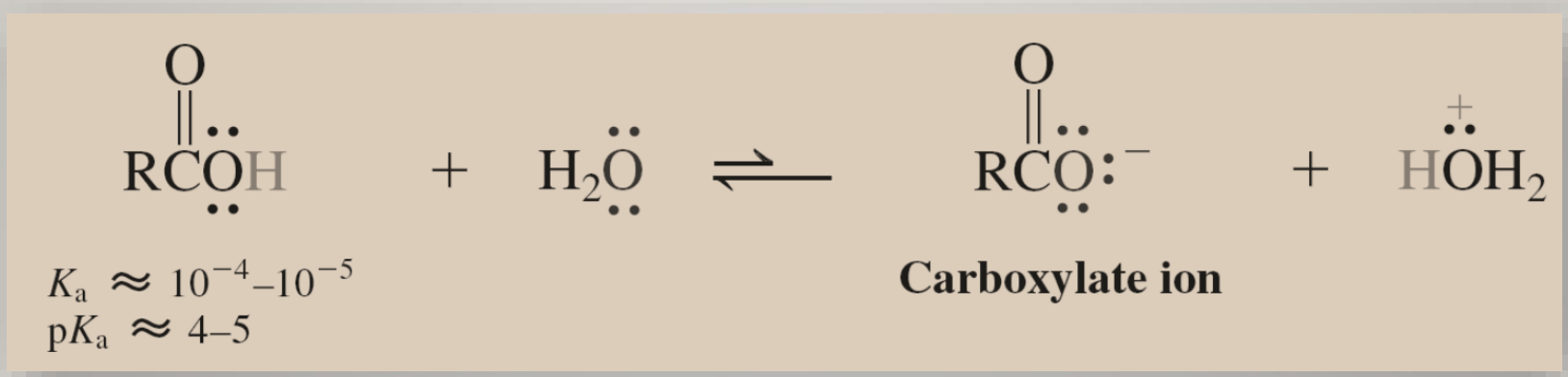
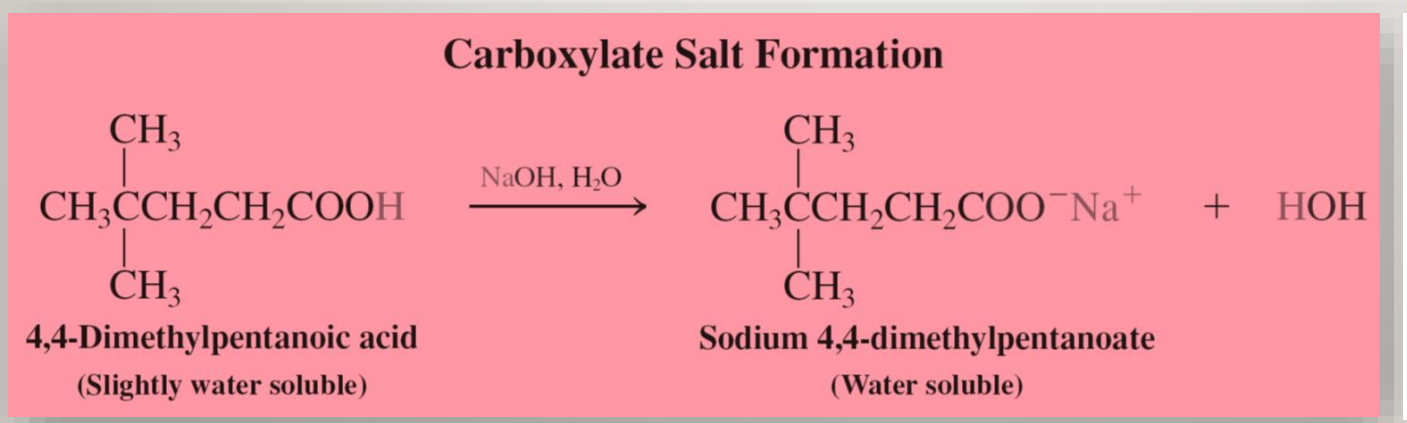
10.2 ACIDITY

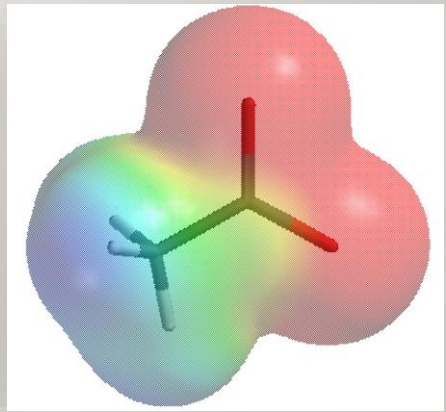
The carboxy group is relatively acidic:



Reasons:

1. Carbonyl carbon is inductively strongly electron withdrawing,
2. Carboxylate ion is stabilized by resonance.





Acetate ion

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10.2 ACIDITY

Electron withdrawing groups increase the acidity (decrease pK_a):

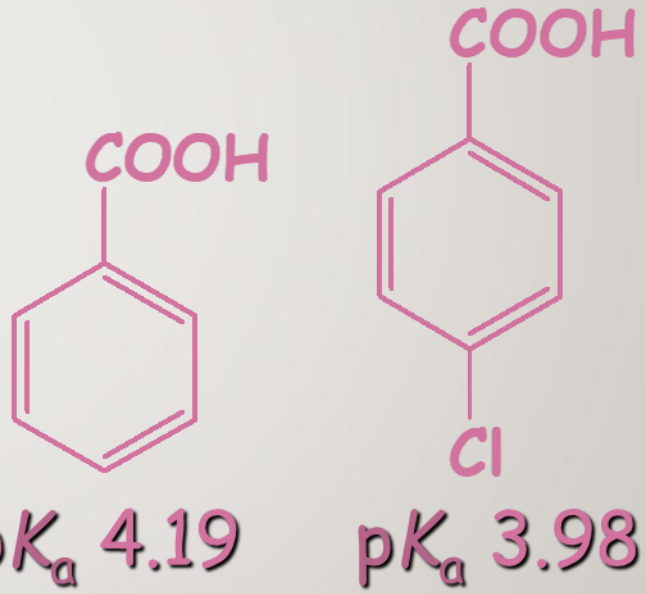
CH_3COOH pK_a = 4.76

CF_3COOH pK_a = 0.23

Compound	pK_a
$ClCH_2COOH$	2.82
$Cl_2CHCOOH$	1.26
Cl_3CCOOH	0.63

Distance affects acidity:

Compound	pK_a
$CH_3CH_2CHClCOOH$	2.84
$CH_3CHClCH_2COOH$	4.06
$ClCH_2CH_2CH_2COOH$	4.52



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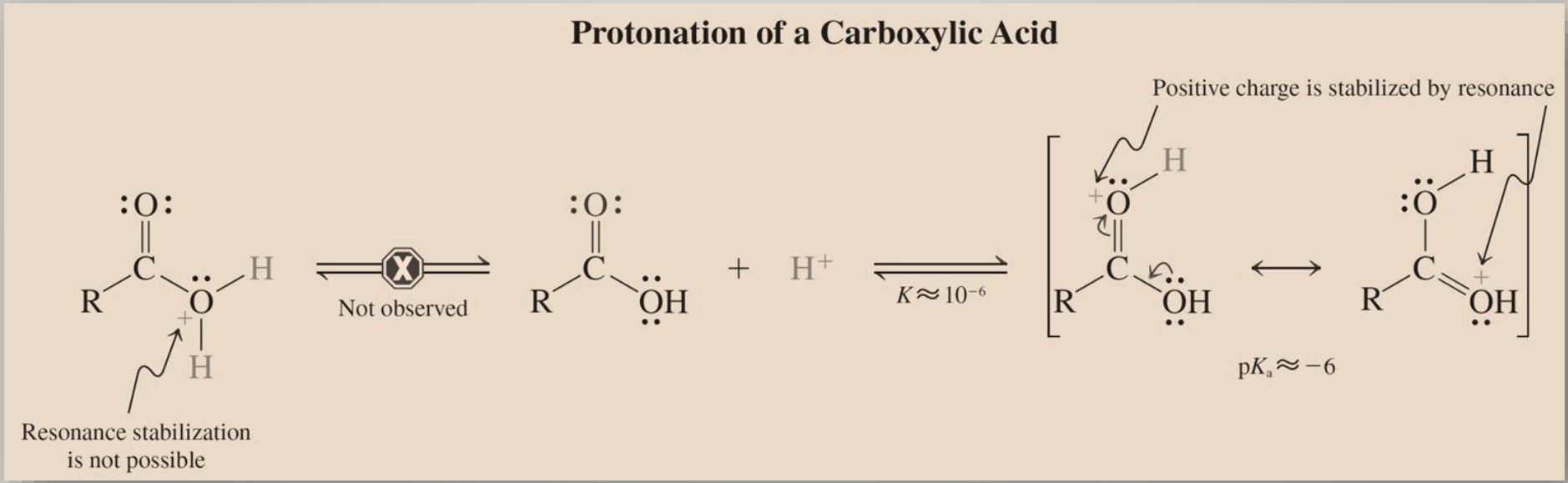
10.3 BASICITY



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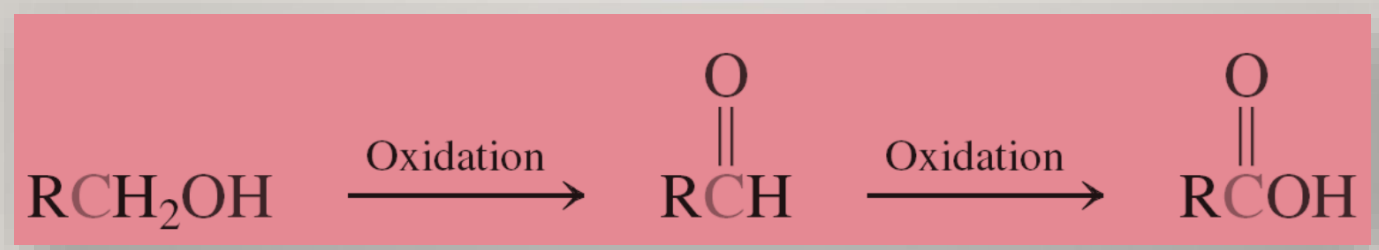
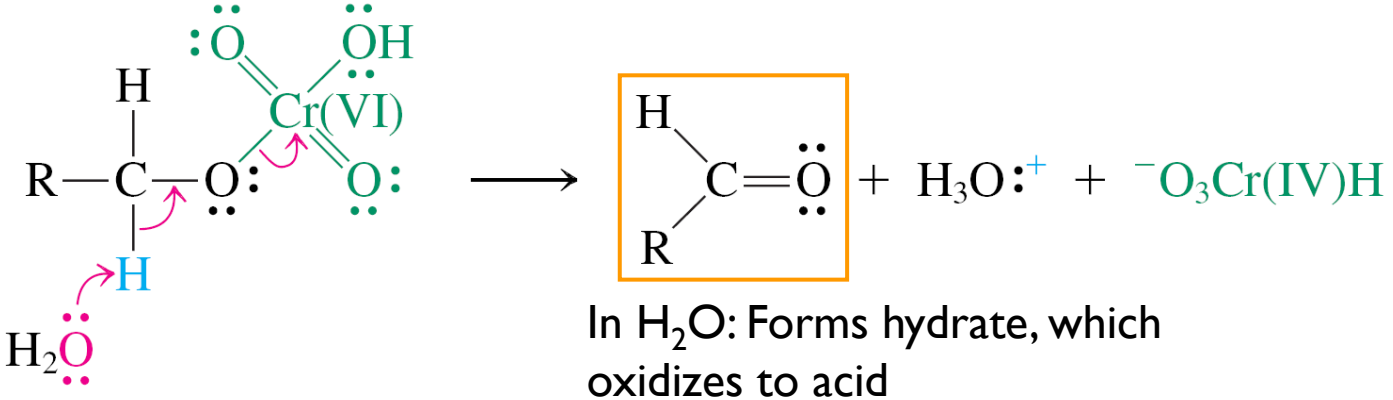
10.4 SYNTHESIS OF CARBOXYLIC ACIDS

1. Oxidation of primary alcohols and aldehydes



With $KMnO_4$; or CrO_3, H_2O; or HNO_3; or H_2O_2
Recall Cr(VI) oxidation:

Aldehyde Formation from a Chromic Ester



In H_2O: Forms hydrate, which oxidizes to acid

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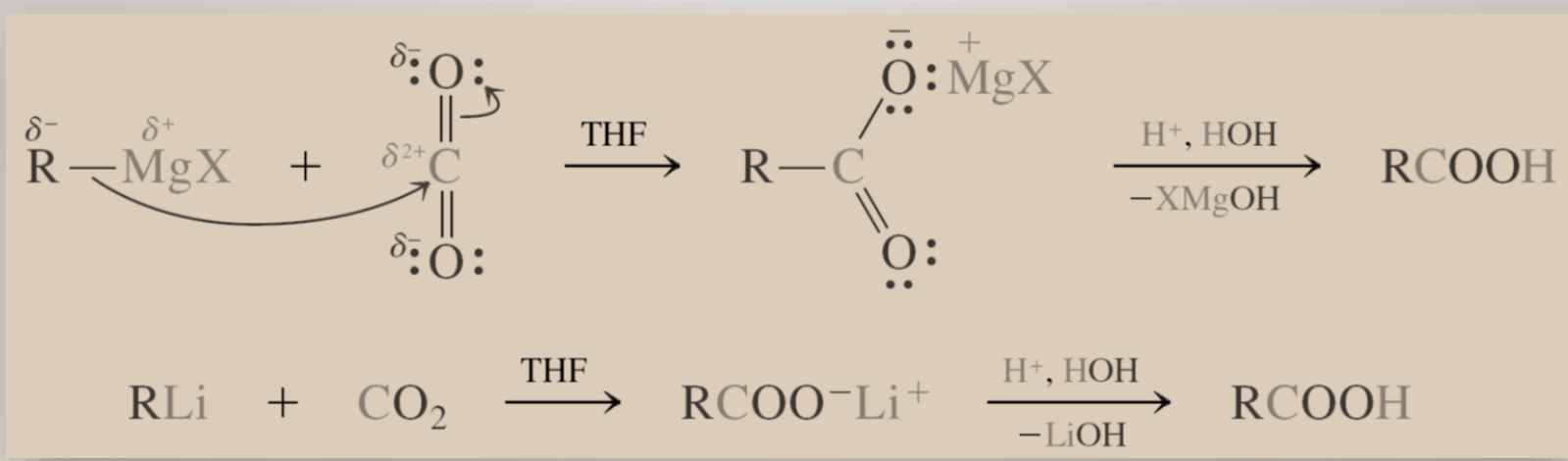
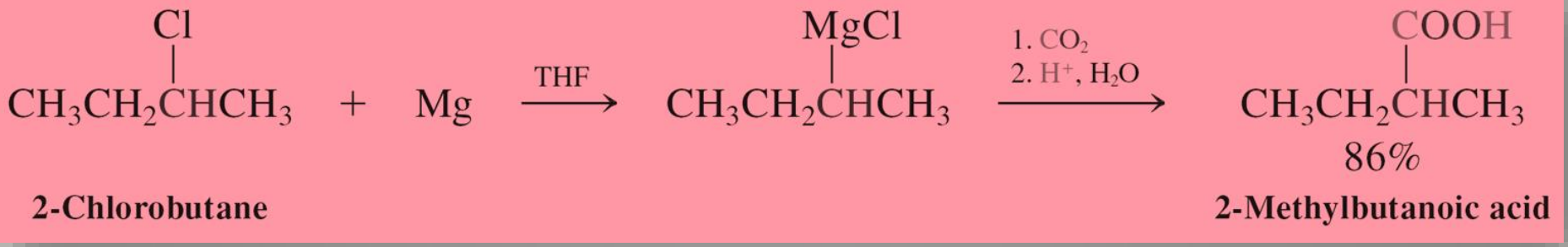
10.4 SYNTHESIS OF CARBOXYLIC ACIDS

2. Carbonation: Organometallic reagents and carbon dioxide





Synthetic strategy: RH → RX → RMgBr → RCO_2H

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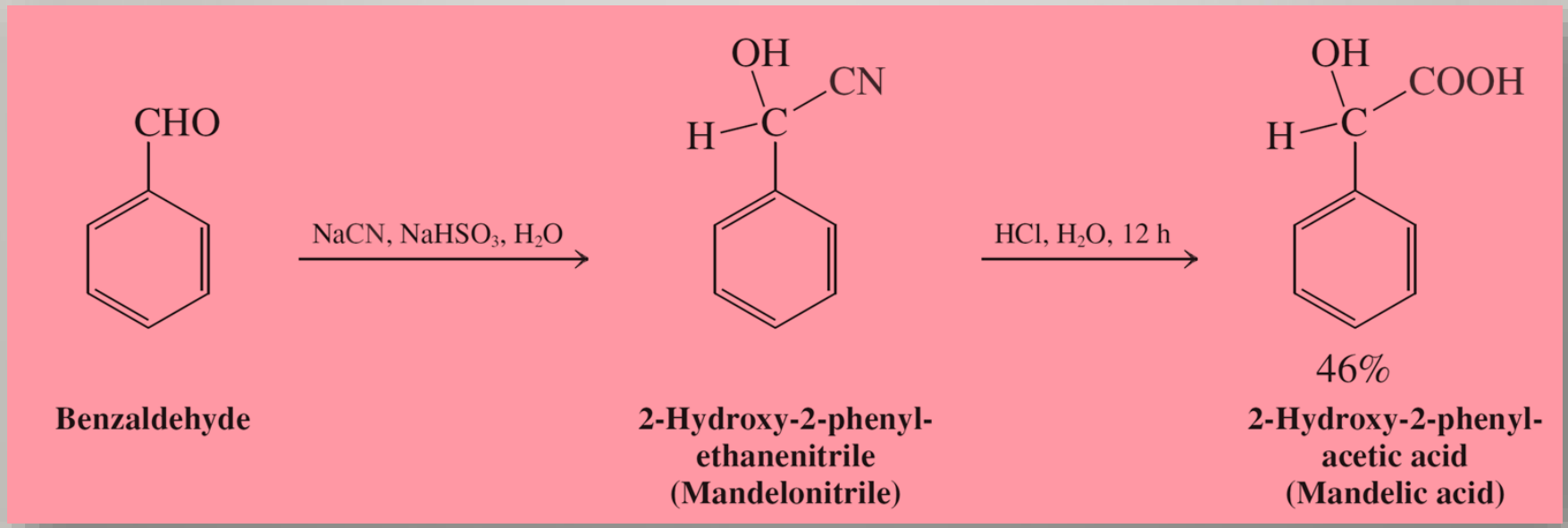
10.4 SYNTHESIS OF CARBOXYLIC ACIDS

3. Nitrile hydrolysis

With aqueous acid or base, e.g. NaOH, H_2O:

Carboxylic Acids from Haloalkanes Through Nitriles

$$RX \xrightarrow[-X^-]{^-CN} RC{\equiv}N \xrightarrow[-NH_3 \text{ or } NH_4^+]{1.\ HO^-;\ 2.\ H^+, H_2O} RCOOH$$



Benzaldehyde

2-Hydroxy-2-phenyl-ethanenitrile (Mandelonitrile)

2-Hydroxy-2-phenyl-acetic acid (Mandelic acid)

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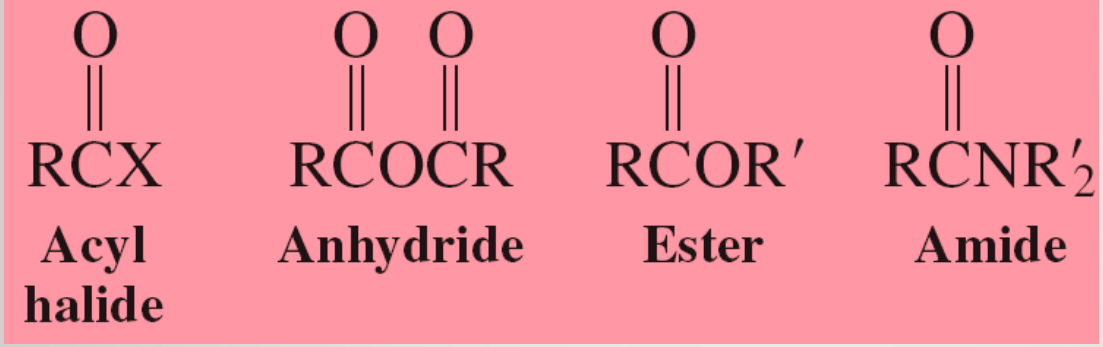
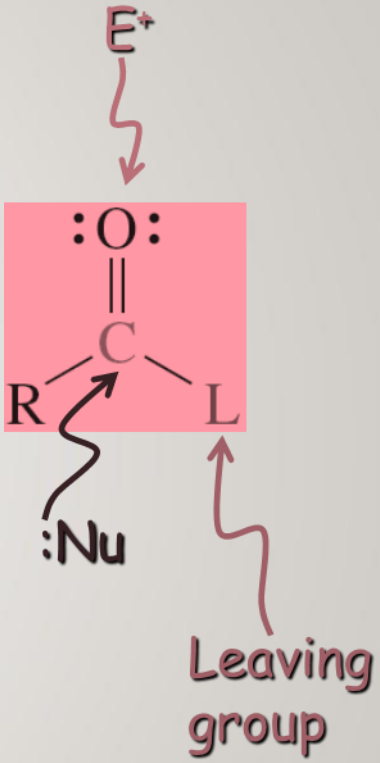
10.5 REACTIONS OF CARBOXYLIC ACIDS

Carboxylic Acid Derivatives



Nucleophilic substitution occurs by addition-elimination



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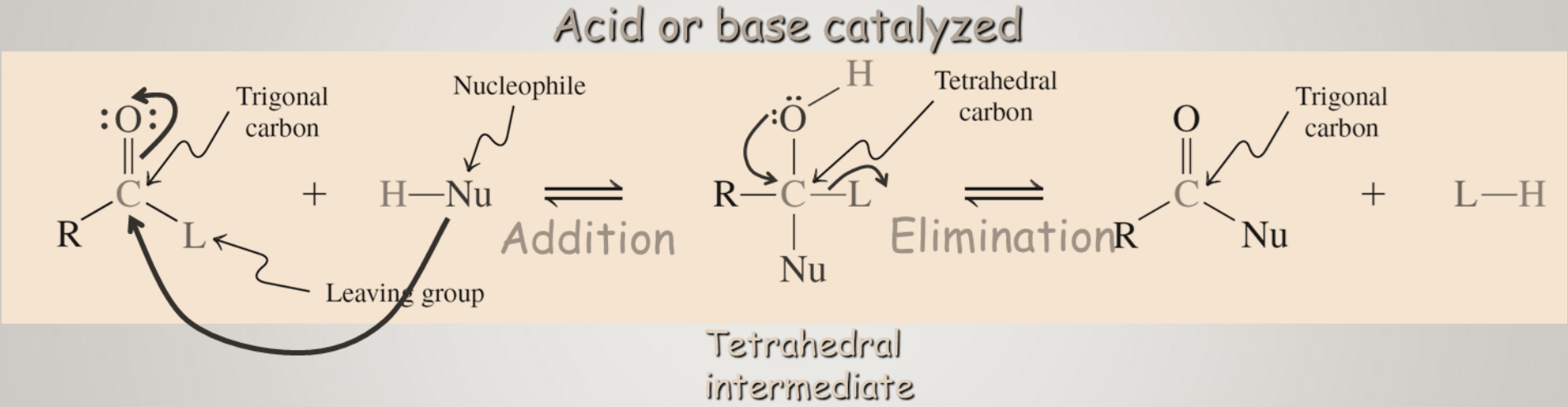
10.5 REACTIONS OF CARBOXYLIC ACID DERIVATIVES



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10.6 SYNTHESIS OF CARBOXYLIC ACID DERIVATIVES

A. Acyl Halides:

More stable

Poor Nu

Less stable

Bad leaving group, strong base, good Nu

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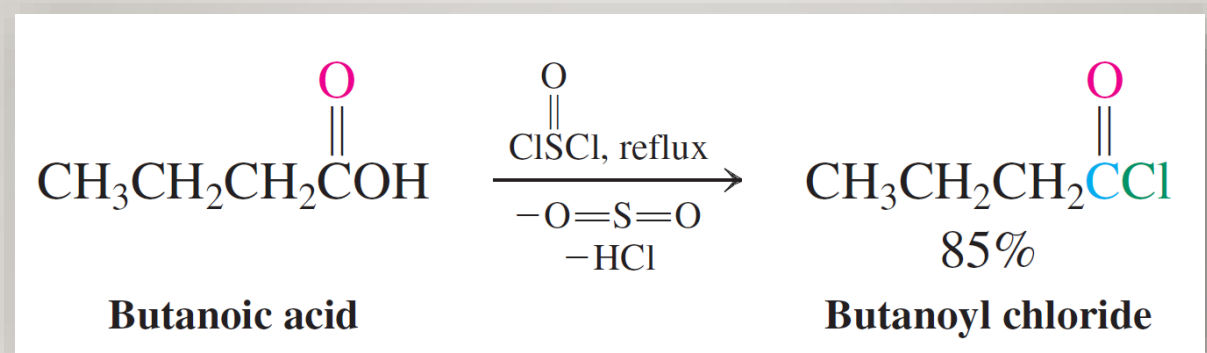
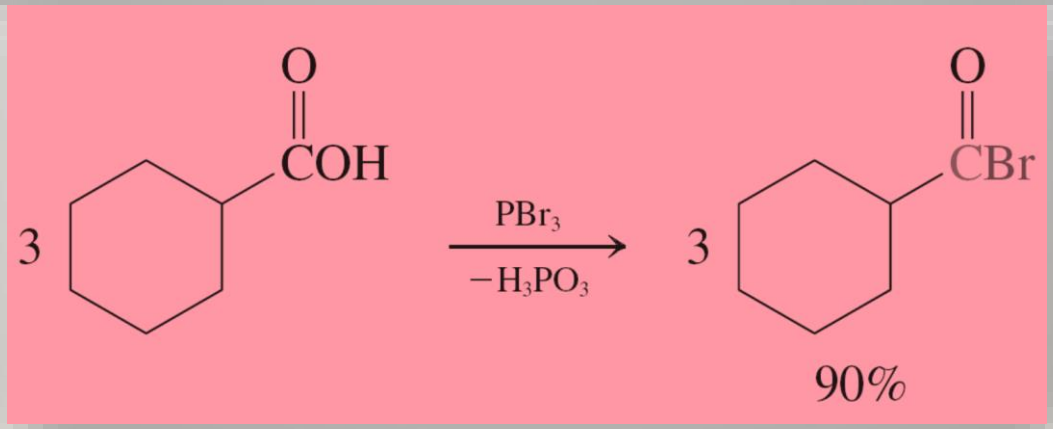
10.6 SYNTHESIS OF CARBOXYLIC ACID DERIVATIVES

A. Acyl Halides:

Therefore use other reagents: $SOCl_2$, PCl_5, PBr_3





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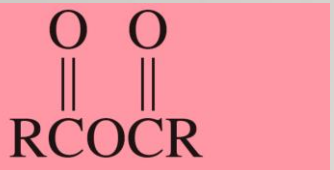
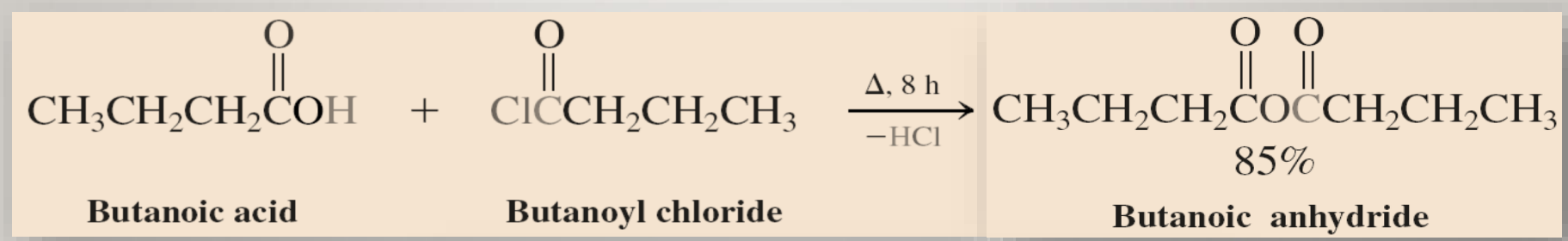
10.6 SYNTHESIS OF CARBOXYLIC ACID DERIVATIVES

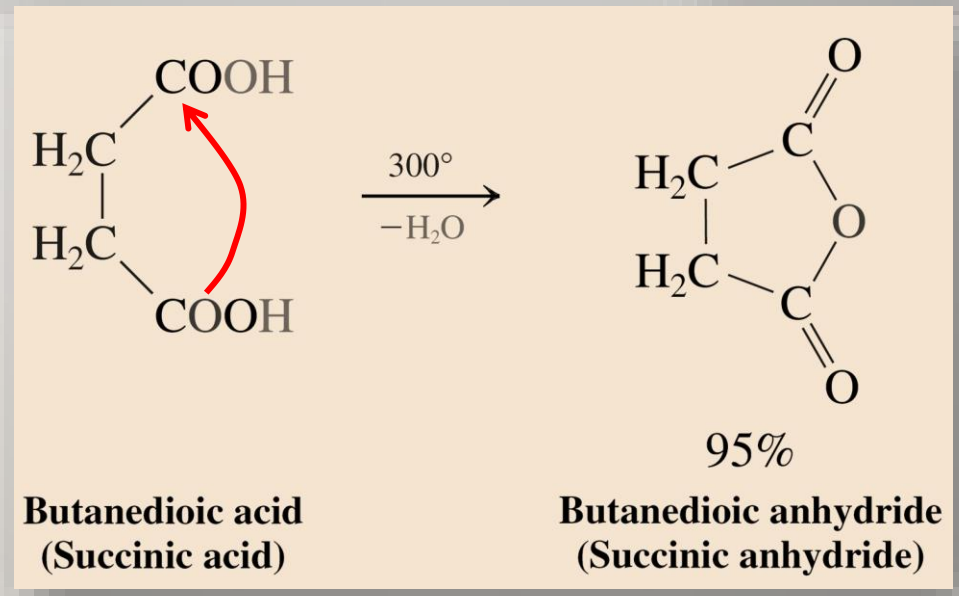
B. Anhydrides



Carboxylic anhydride



Butanoic acid **Butanoyl chloride** **Butanoic anhydride**



Butanedioic acid (Succinic acid) **Butanedioic anhydride (Succinic anhydride)**

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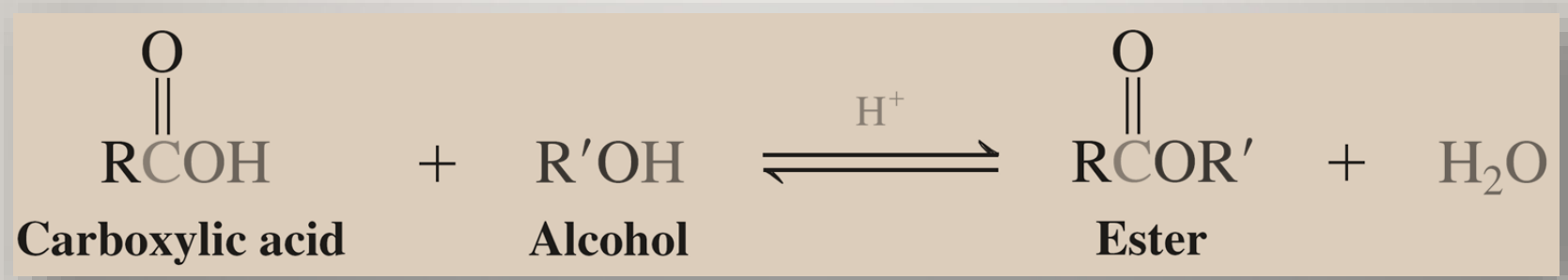
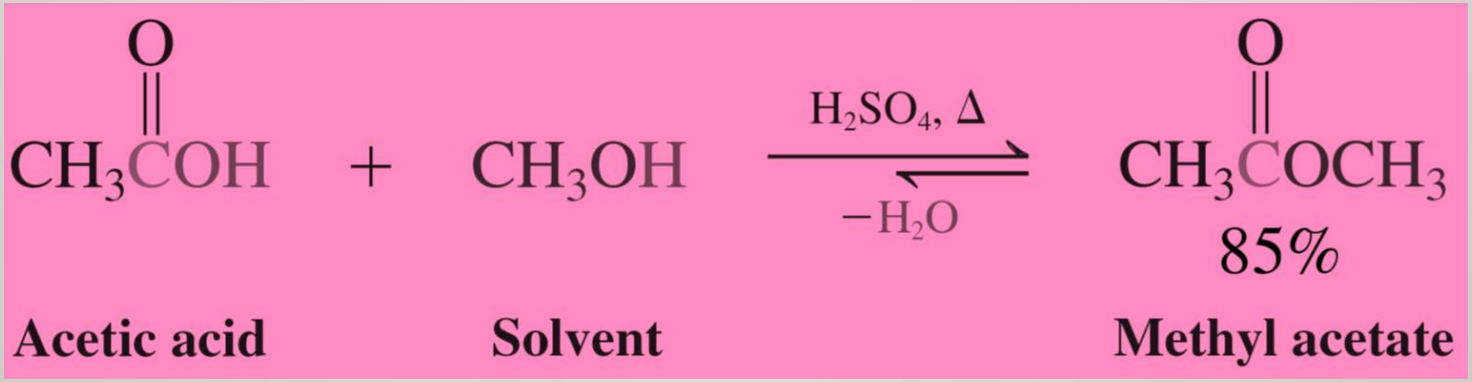
10.6 SYNTHESIS OF CARBOXYLIC ACID DERIVATIVES

C. Esters:

Alcohols + carboxylic acids, cat. mineral acid, reversible





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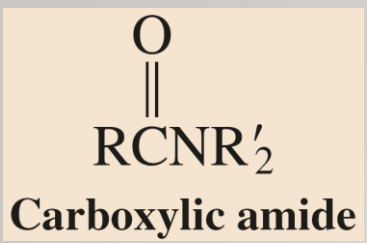
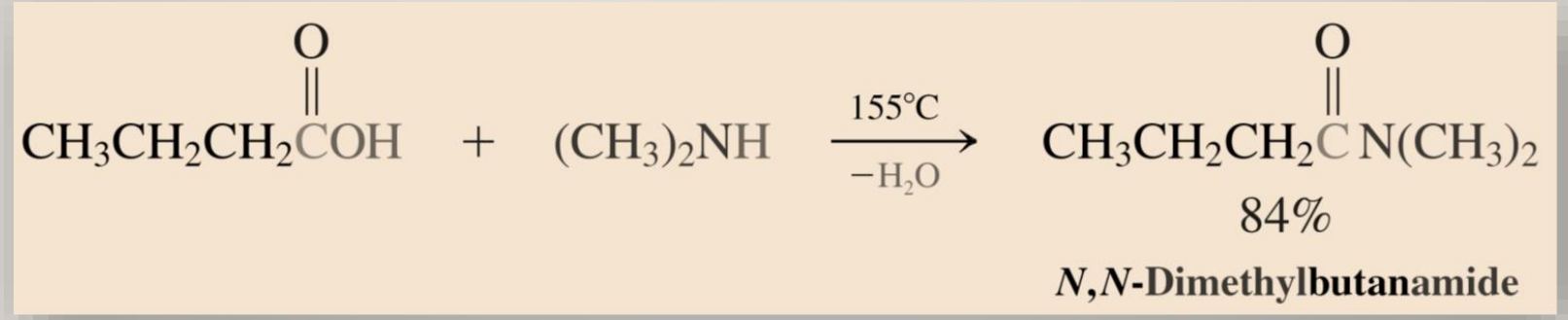
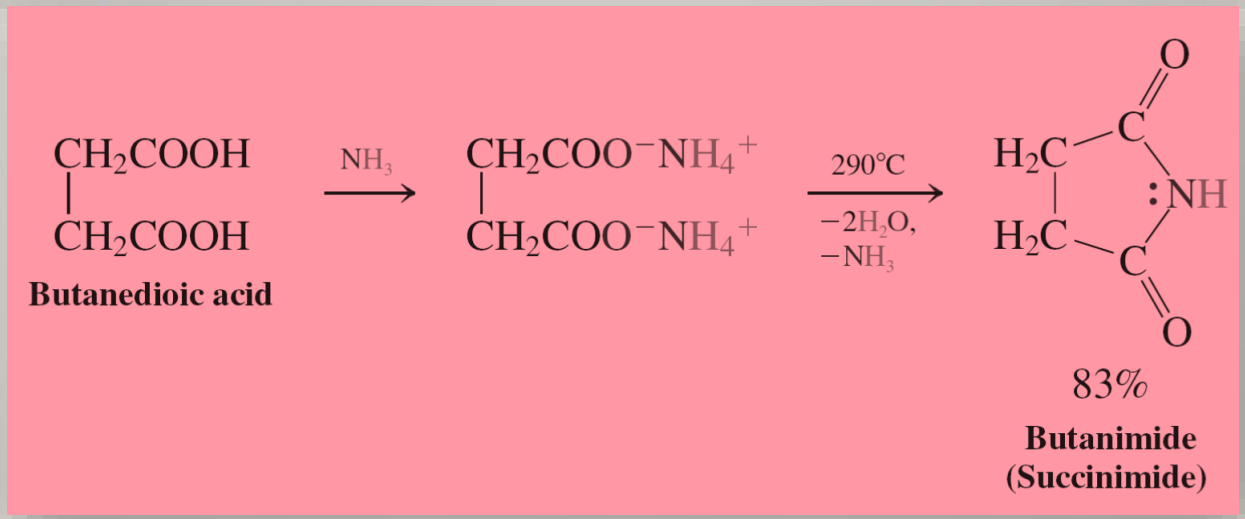
D. Amides



Heat carboxylic acid with an amine:





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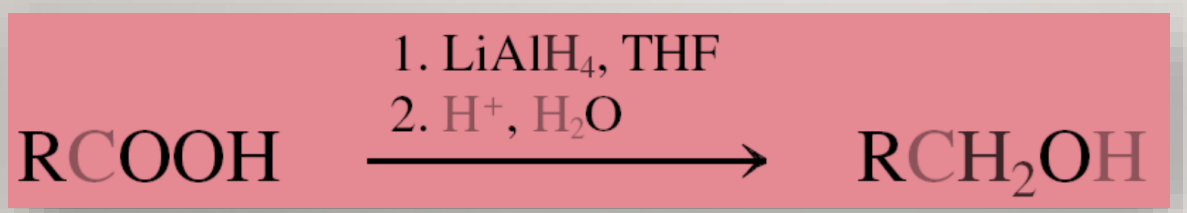
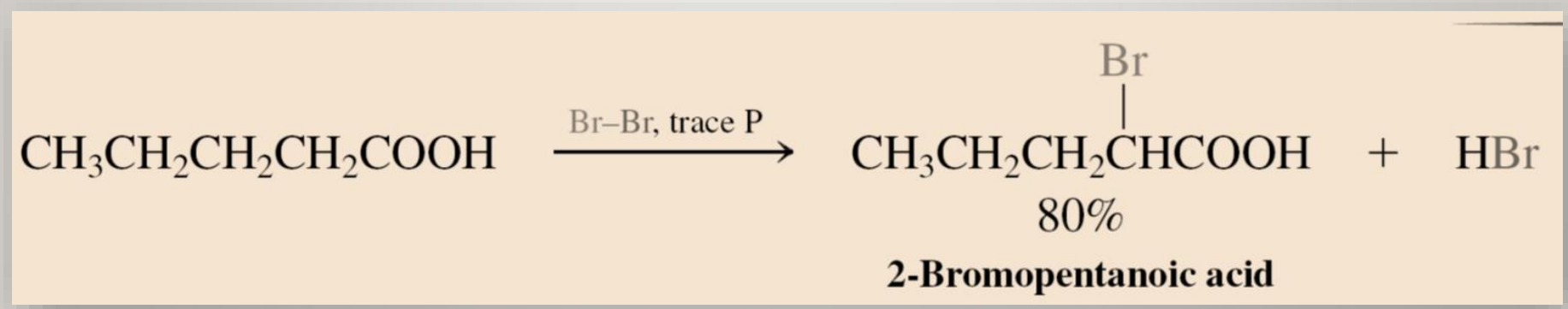
10.6 OTHER REACTIONS OF CARBOXYLIC ACIDS

1. Reduction by $LiAlH_4$



2. Hell-Volhard-Zelinsky Reaction



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