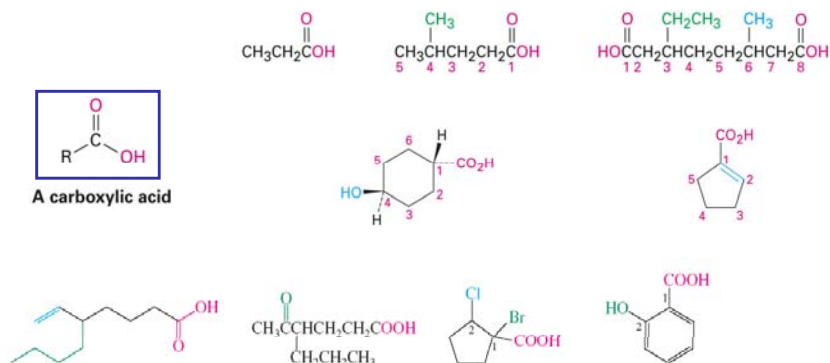


## Naming Carboxylic Acids

- Simple carboxylic acids derived from open-chain alkanes are systematically named by replacing the terminal  $-e$  with  $-oic$  acid; the  $-CO_2H$  carbon is numbered C1.
- Compounds with  $-CO_2H$  bonded to a ring are named using the suffix  $-carboxylic$  acid; the  $-CO_2H$  is attached to C1 and is not numbered itself.
- As a substituent, the  $CO_2H$  is called a **carboxyl group**.
- Acyl groups named by changing the  $-ic$  acid or  $-oic$  acid ending to  $-oyl$ .



17-1

## Common Names



Structure	Common Name	Acyl group
$HCO_2H$	Formic	Formyl
$CH_3CO_2H$	Acetic	Acetyl
$CH_3CH_2CO_2H$	Propionic	Propionyl
$CH_3CH_2CH_2CO_2H$	Butyric	Butyryl
$HO_2CCO_2H$	Oxalic	Oxalyl
$HO_2CCH_2CO_2H$	Malonic	Malonyl
$HO_2CCH_2CH_2CO_2H$	Succinic	Succinyl
$H_2C=CHCO_2H$	Acrylic	Acryloyl
$HO_2CCH=CHCO_2H$	Maleic (cis)	Maleoyl
	Benzoic	Benzoyl
	Phthalic	Phthaloyl

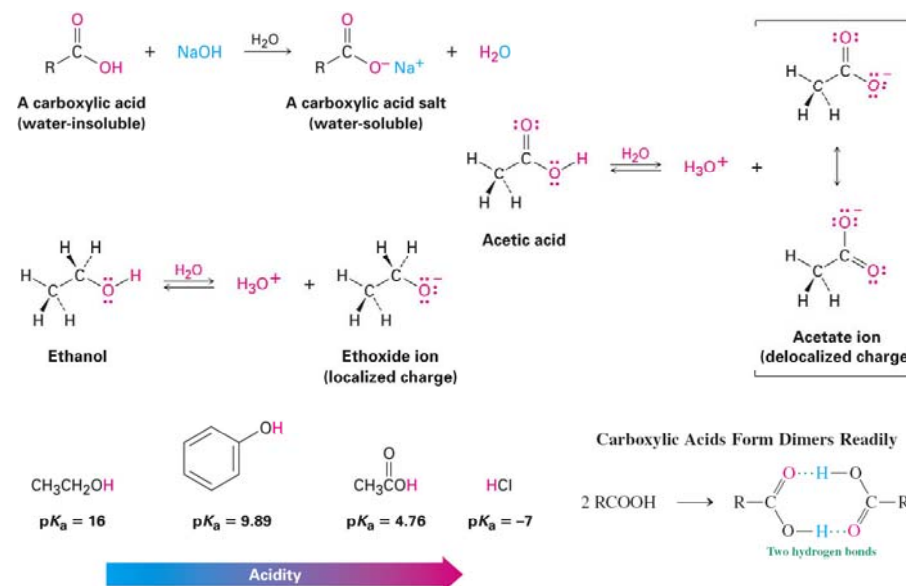
17-2

## Physical Properties of Carboxylic Acids

Derivative	Melting point (°C)	Boiling point (°C)
$CH_4$	-182.5	-161.7
$CH_3Cl$	-97.7	-24.2
$CH_3OH$	-97.8	65.0
HCHO	-92.0	-21.0
<b>HCOOH</b>	<b>8.4</b>	<b>100.6</b>
$CH_3CH_3$	-183.3	-88.6
$CH_3CH_2Cl$	-136.4	12.3
$CH_3CH_2OH$	-114.7	78.5
$CH_3CHO$	-121.0	20.8
<b><math>CH_3COOH</math></b>	<b>16.7</b>	<b>118.2</b>
$CH_3CH_2CH_3$	-187.7	-42.1
$CH_3CH_2CH_2Cl$	-122.8	46.6
$CH_3CH_2CH_2OH$	-126.5	97.4
$CH_3COCH_3$	-95.0	56.5
$CH_3CH_2CHO$	-81.0	48.8
<b><math>CH_3CH_2COOH</math></b>	<b>-20.8</b>	<b>141.8</b>

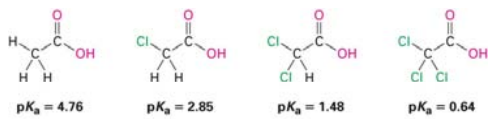
17-3

## Acidity of Carboxylic Acids

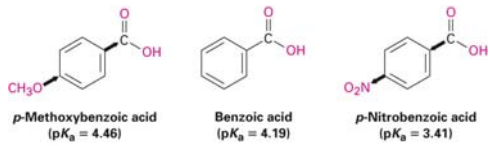


17-4

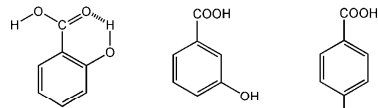
## Substituent Effects on Acidity



Acidity



Acidity



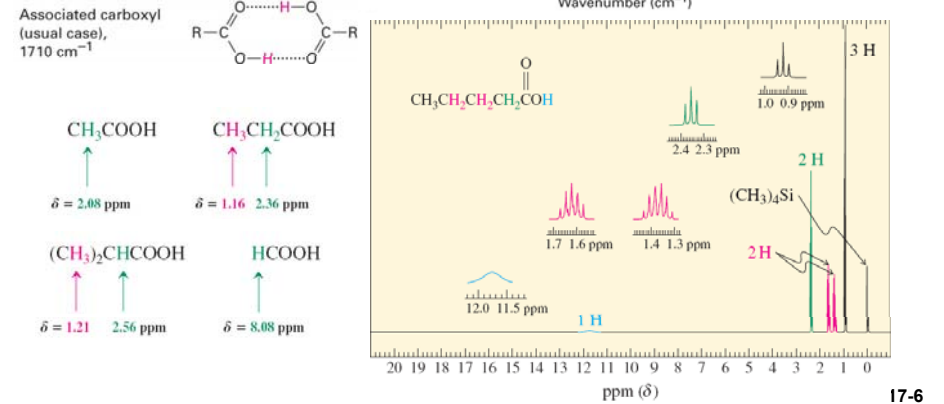
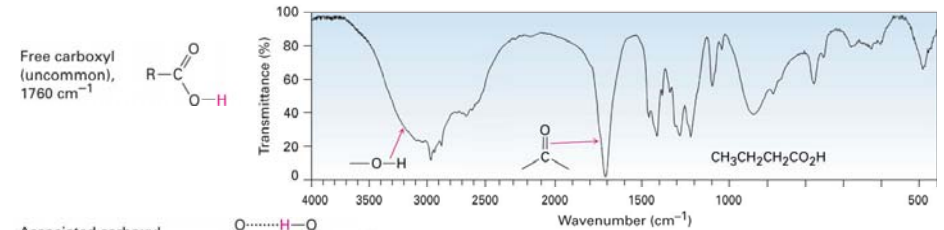
Y	$K_a \times 10^{-5}$	$pK_a$
-NO <sub>2</sub>	39	3.41
-CN	28	3.55
-CHO	18	3.75
-Br	11	3.96
-Cl	10	4.0
-H	6.46	4.19
CH <sub>3</sub>	4.3	4.34
-OCH <sub>3</sub>	3.5	4.46
-OH	3.3	4.48

Deactivating groups (top 5)

Activating groups (bottom 5)

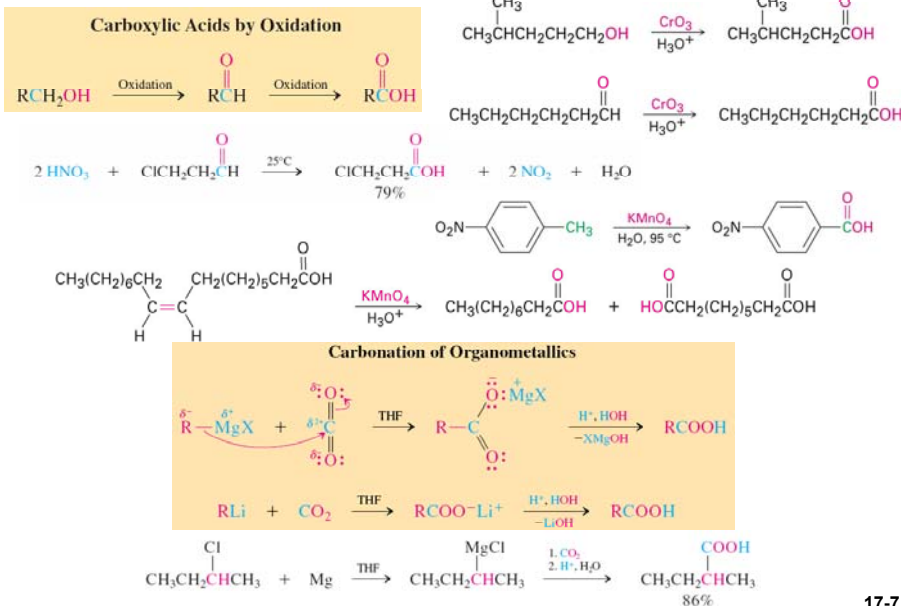
17-5

## IR and NMR Spectra of Carboxylic Acids



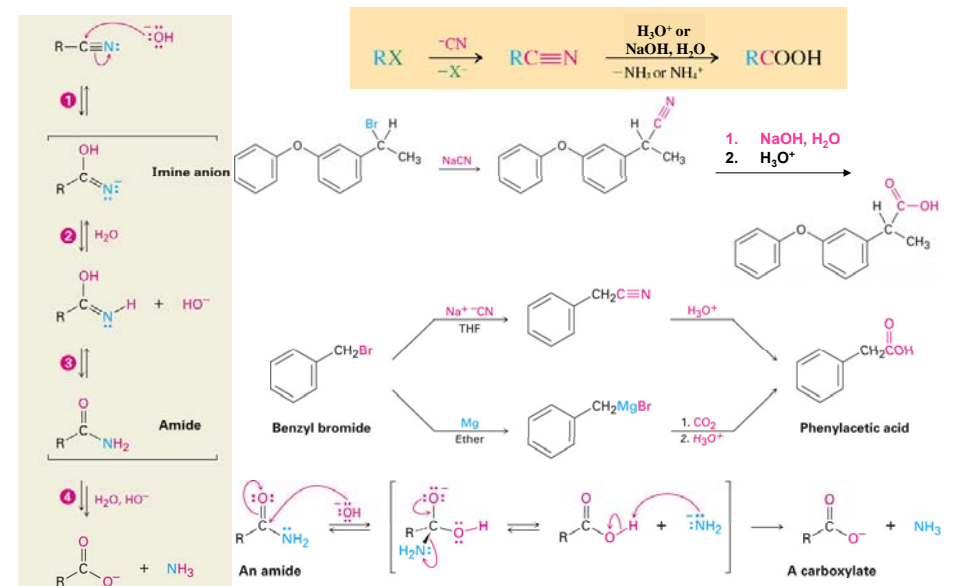
17-6

## Preparation of Carboxylic Acids



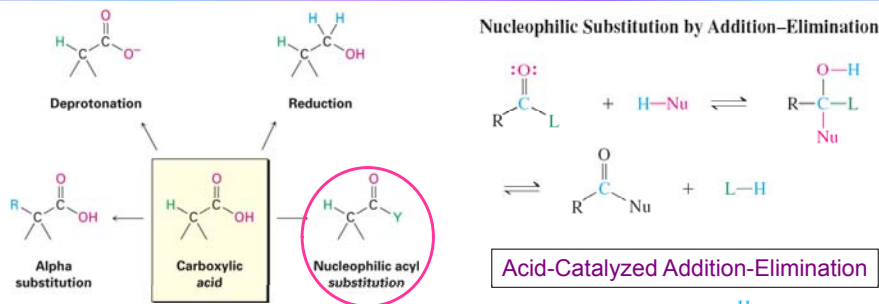
17-7

## Nitriles Hydrolyze to Carboxylic Acids



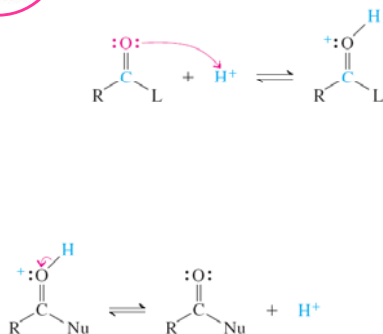
17-8

# Reactions of Carboxylic Acids



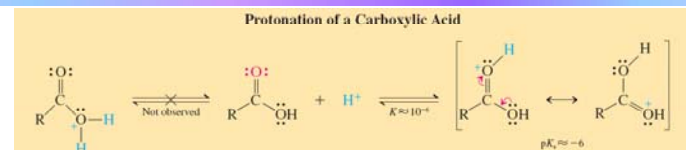
Step 1. Protonation  
Step 2. Addition-Elimination

Step 3. Deprotonation



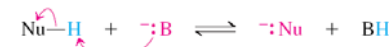
17-9

# Acid or Base-Catalyzed Addition-Elimination

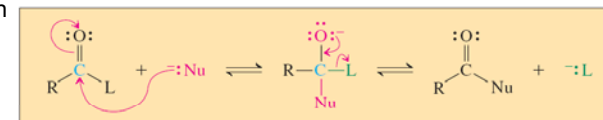


Base-Catalyzed Addition-Elimination

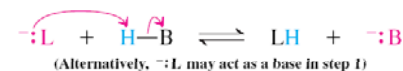
Step 1. Deprotonation of NuH



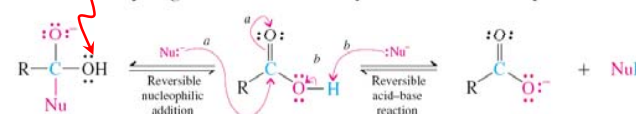
Step 2. Addition-Elimination



Step 3. Regeneration of Catalyst

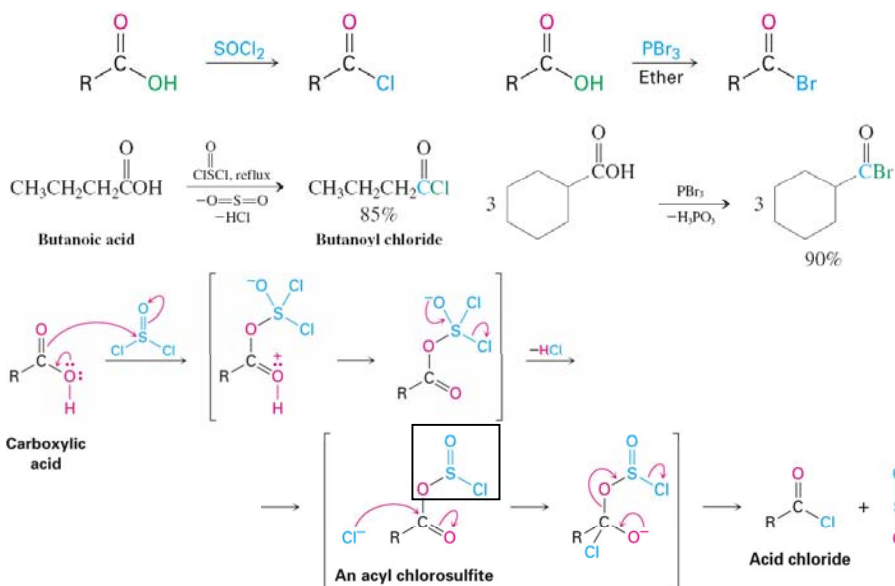


poor LG  
Competing Reactions of a Carboxylic Acid with a Nucleophile



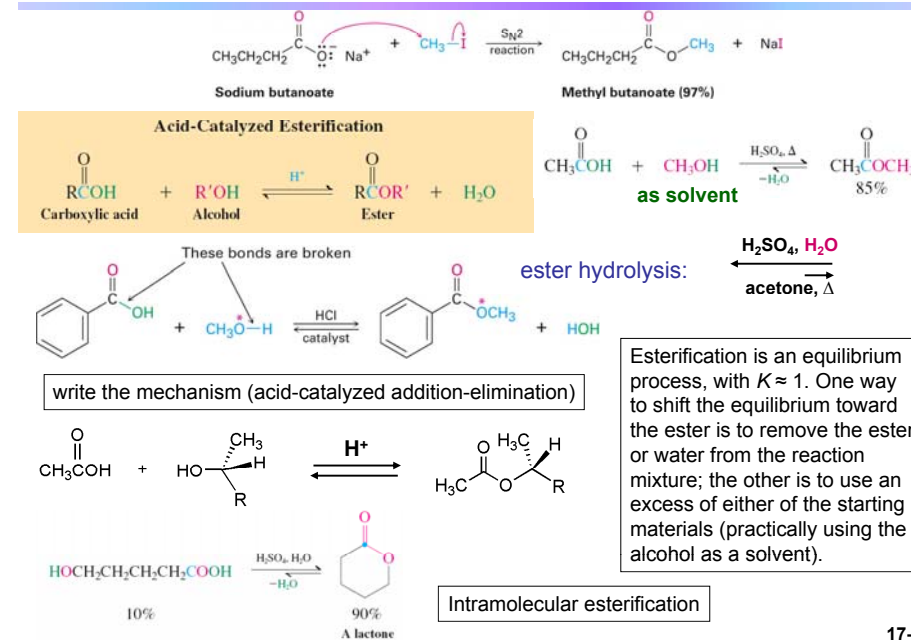
17-10

# Conversion of Carboxylic Acids into Acid Chloride



17-11

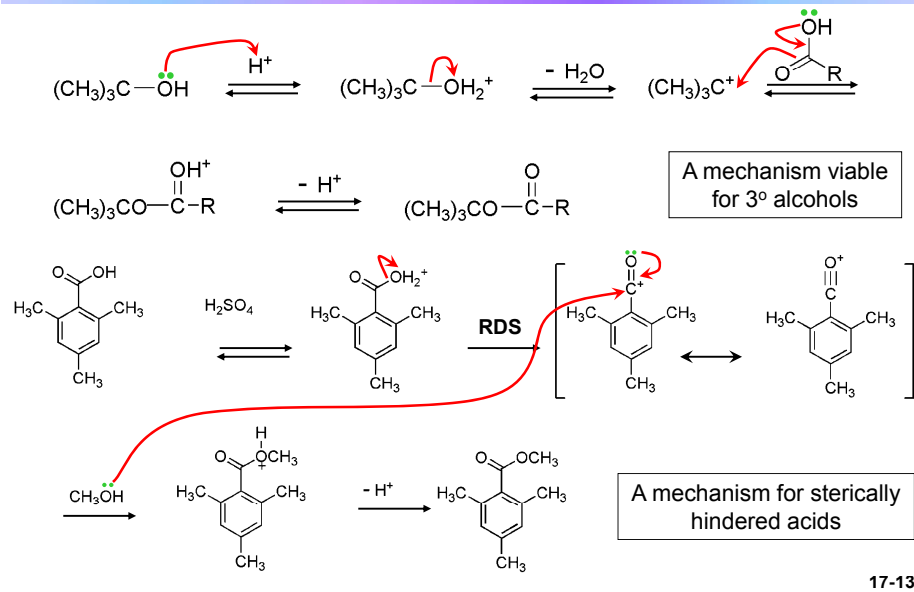
# Conversion of Carboxylic Acids into Esters



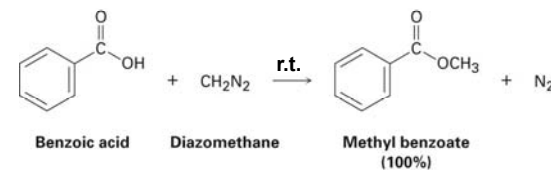
Esterification is an equilibrium process, with  $K \approx 1$ . One way to shift the equilibrium toward the ester is to remove the ester or water from the reaction mixture; the other is to use an excess of either of the starting materials (practically using the alcohol as a solvent).

17-12

## Alternative, Less Common Mechanisms of Esterification

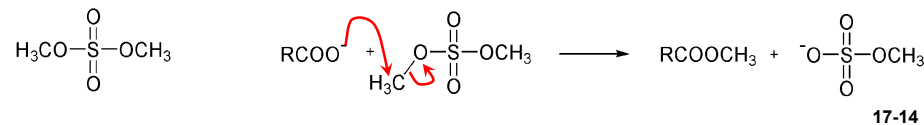


## Methylation of Carboxylic Acids

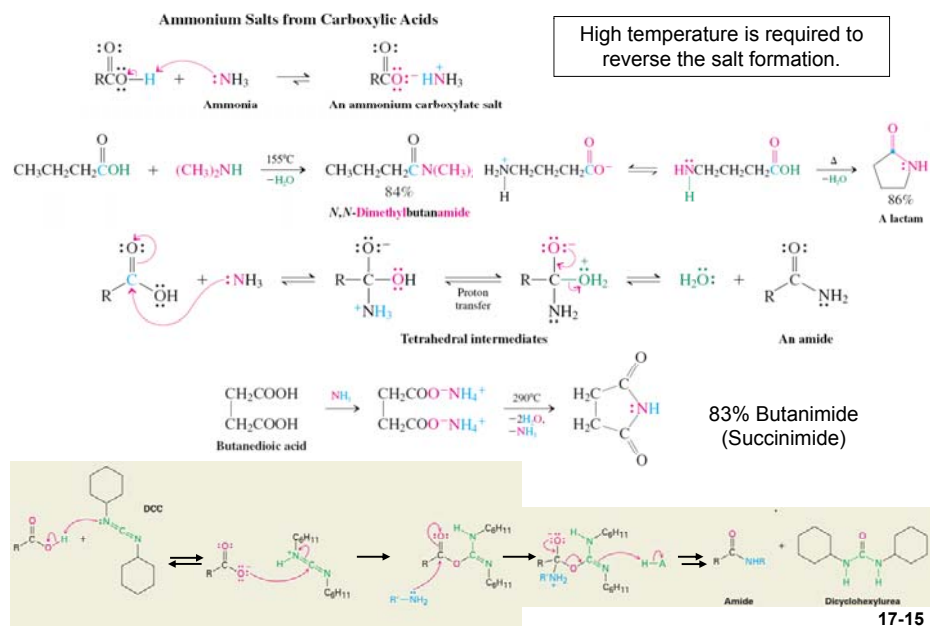


Very efficient methyl ester preparation method, but CH<sub>2</sub>N<sub>2</sub> is explosive and hazardous.

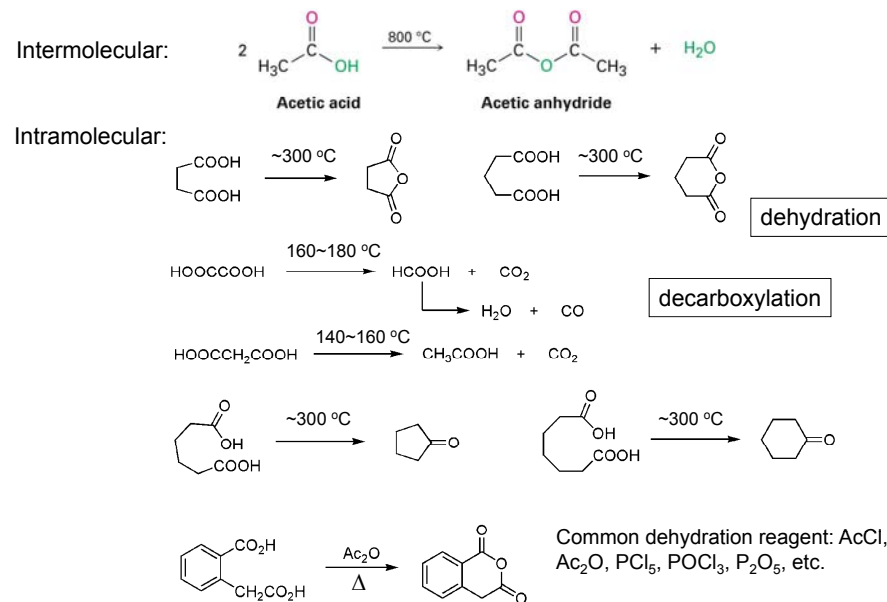
Dimethyl sulfate is a highly efficient methylation reagent, but toxic.



## Conversion of Carboxylic Acids into Amides

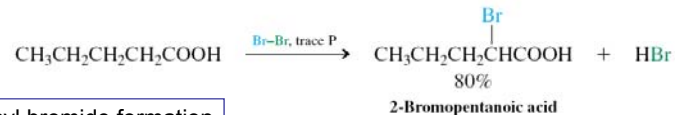


## Conversion of Carboxylic Acids into Anhydrides

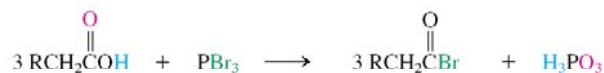


# α-Bromination of Carboxylic Acids

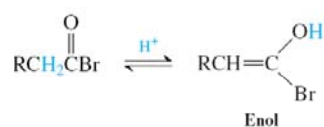
## A Hell-Volhard-Zelinsky\* Reaction



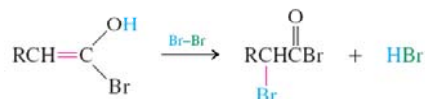
### Step 1. Acyl bromide formation



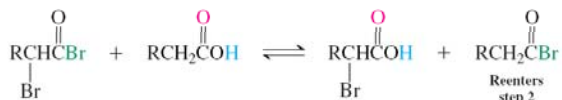
### Step 2. Enolization



### Step 3. Bromination

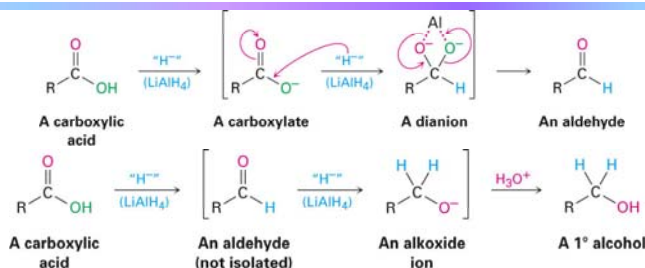


### Step 4. Exchange

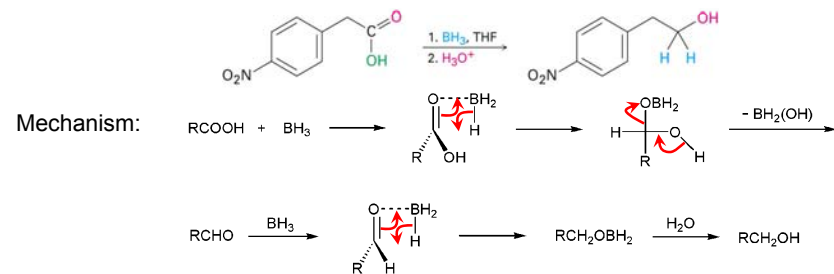


17-17

# Reduction of Carboxylic Acids

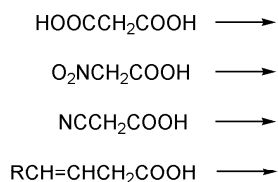
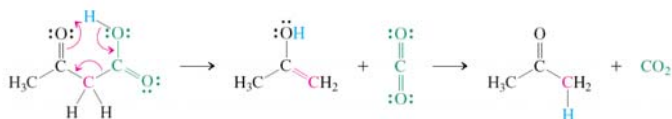
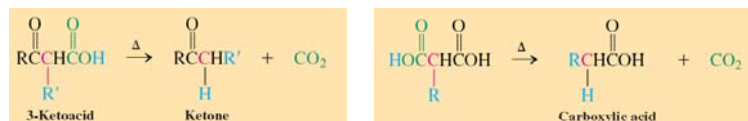


- Acid reduction requires higher temperatures (e.g., than aldehyde reduction) and extended reaction times due to the high-energy dianion intermediate;
- Aldehyde is not obtained as it is more reactive (prone to be reduced) than an acid.



# Various Decarboxylation Reactions

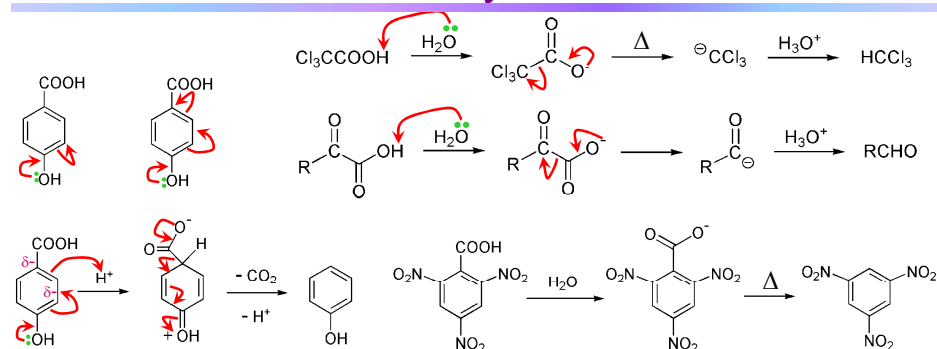
## β-ketoacid decarboxylation:



Draw mechanisms for these decarboxylation reactions.

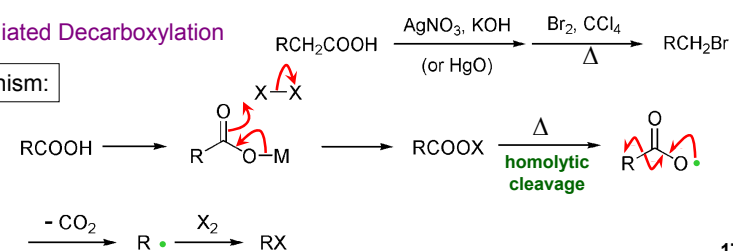
17-19

# Various Decarboxylation Reactions



## Radical Mediated Decarboxylation

### Mechanism:



17-20