

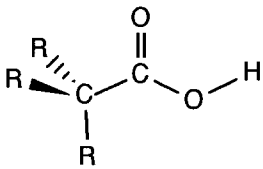
**CHAPTER 20: Carboxylic Acids** (RCOOH, RCO<sub>2</sub>H)

aliphatic acids -

aromatic acids -

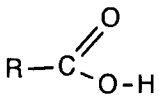
fatty acids -

**STRUCTURE:**

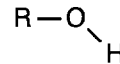


**PHYSICAL PROPERTIES:**

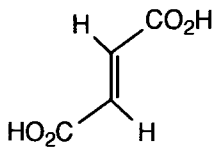
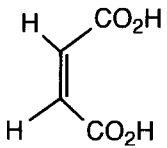
I. Boiling Point (> alkanes, ethers, aldehydes/ ketones)



vs



II. Melting Point - crystal packing efficiency is important  
- presence of double bonds, especially cis-double bonds, lowers MP



Stearic acid (C<sub>17</sub>, saturated)

Linoleic acid (C<sub>17</sub>, two cis =)

III. Solubility in H<sub>2</sub>O - greater solubility than alcohols

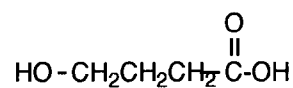
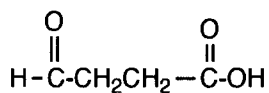
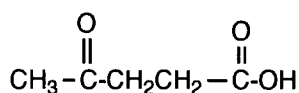
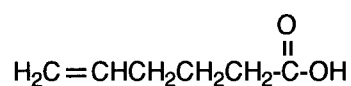
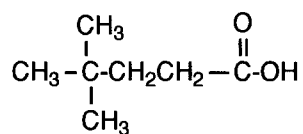
- more than 6 carbons - only slightly soluble in water
- the salts of most carboxylic acids are water soluble

## CARBOXYLIC ACID NOMENCLATURE

I. Open chain (acyclic): drop "e" from alkane/alkene/alkyne name, add "oic acid"

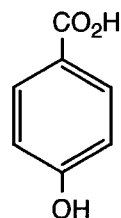
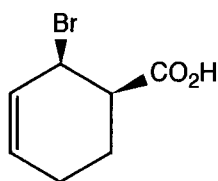
- COOH carbon is always # 1

- priority over all functional groups studied so far (see table p. 985)

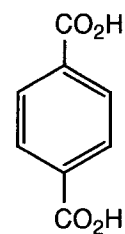
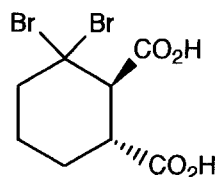
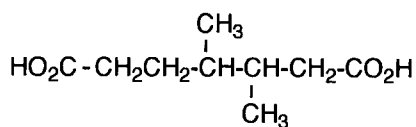


II. Cyclic: add "carboxylic acid" to the cycloalkane or cycloalkene name

- C-COOH is always # 1

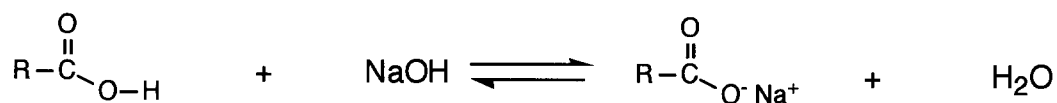
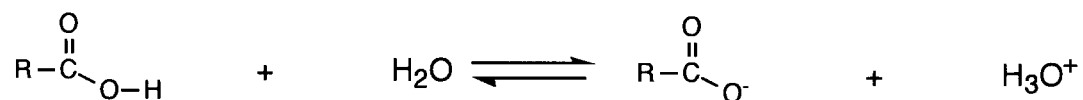


III. Dicarboxylic acids: add "dioic acid" (acyclic) or "dicarboxylic acid" (cyclic)



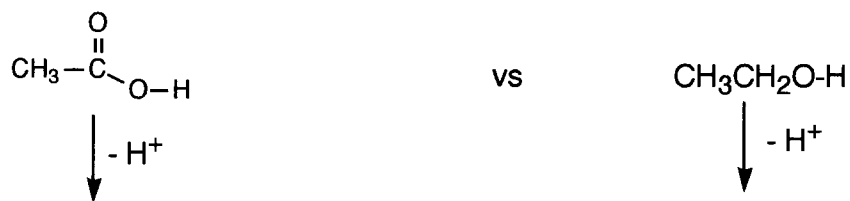
## ACIDITY OF CARBOXYLIC ACIDS

I. Strength: weak acids:

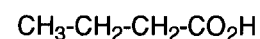
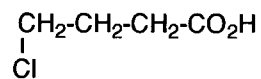
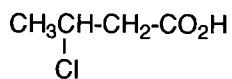
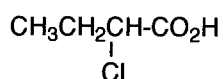
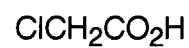
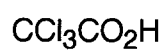
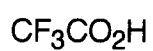


II. Factors that Affect Acidity:  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

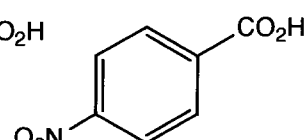
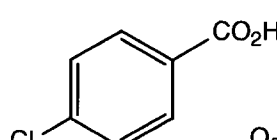
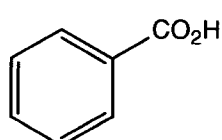
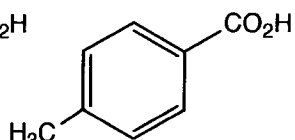
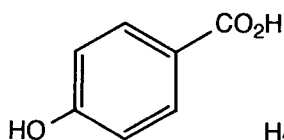
A. Resonance



B. Electron withdrawing groups -

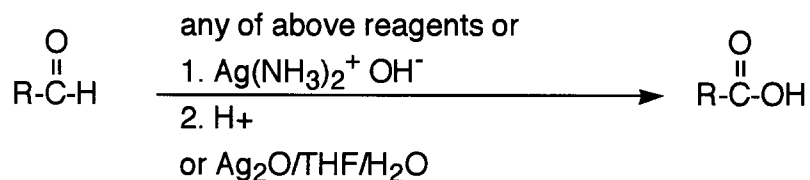
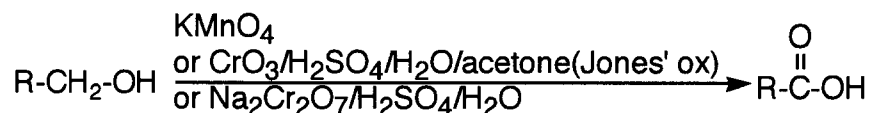


C. Electron donating groups -

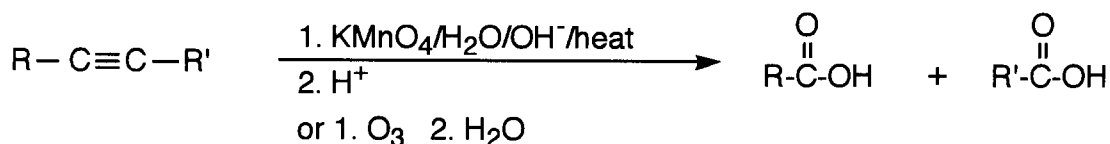
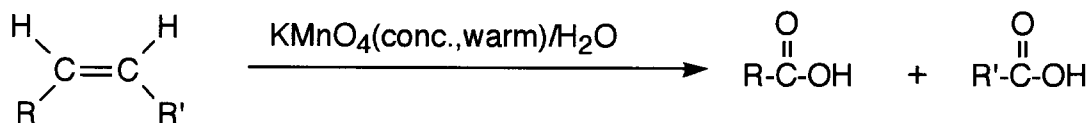


## Synthesis of Carboxylic Acids (Review)

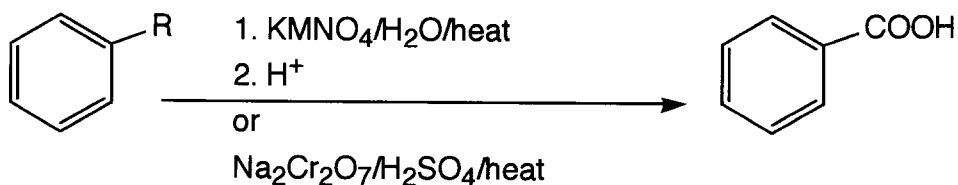
### I. Oxidation of 1° alcohols and aldehydes:



### II. Oxidative cleavage of alkenes and alkynes:

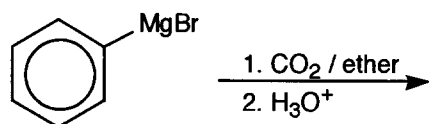
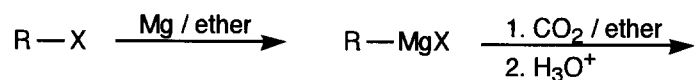


### III. Oxidation of alkylbenzene side chains:

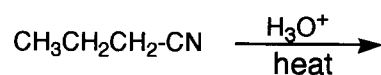
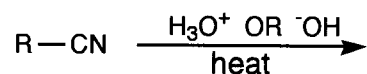


NOTE: These conditions oxidize other oxidizable functional groups!

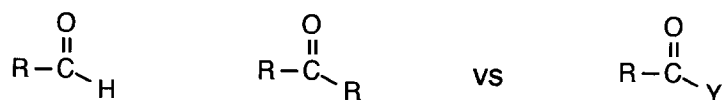
## IV. Carboxylation of Grignard Reagents



## V. Hydrolysis of Nitriles (NEW!, mechanism in Ch. 21)



## OVERVIEW OF REACTIONS OF CARBOXYLIC ACIDS AND THEIR DERIVATIVES



acyl compounds:

Y = OH

Y = Cl, Br

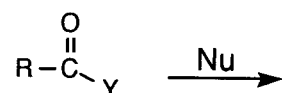
Y = OR

Y = NH<sub>2</sub>, NHR, NR<sub>2</sub>Y = O -  $\overset{\text{O}}{\parallel}{C}$  - R

The carbonyl carbon in an acyl compound does not react by the same mechanism as the carbonyl in an aldehyde or ketone.

aldehyde / ketone:

acyl compound:



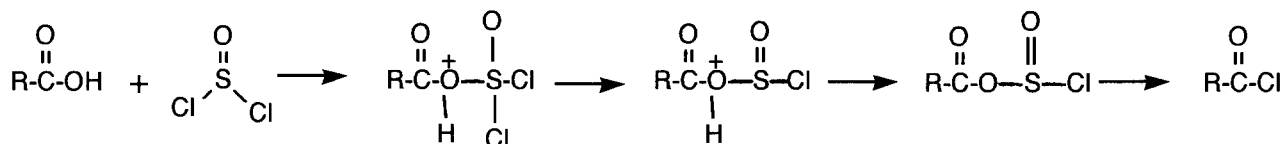
## REACTIONS OF CARBOXYLIC ACIDS

### I. Synthesis and Reactions of Acid Chlorides:

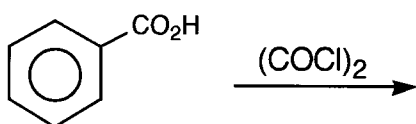
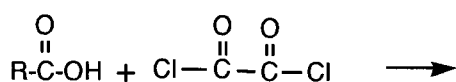


#### A. Synthesis:

##### 1. (Review) Most common reagent and mechanism - thionyl chloride

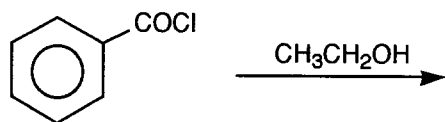
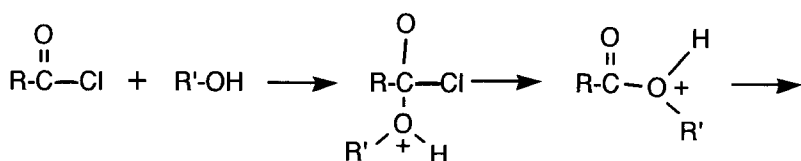


##### 2. oxalyl chloride - better yields but expensive

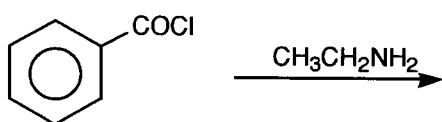
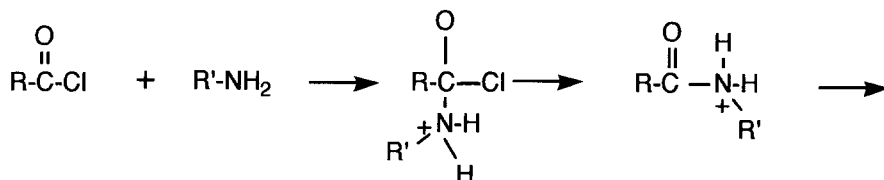


#### B. Reactions of Acid Chlorides (more later)

##### 1. (Review) Ester formation

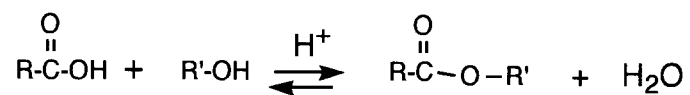


##### 2. Amide formation - BEST method

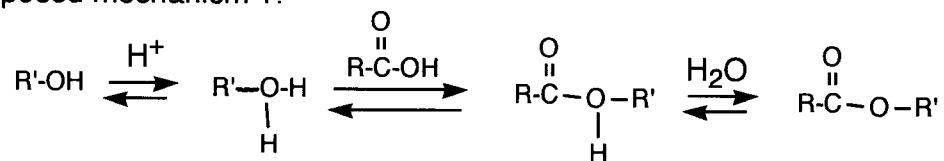


## II. Synthesis of Esters

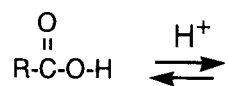
### A. (Review) Fischer Esterification



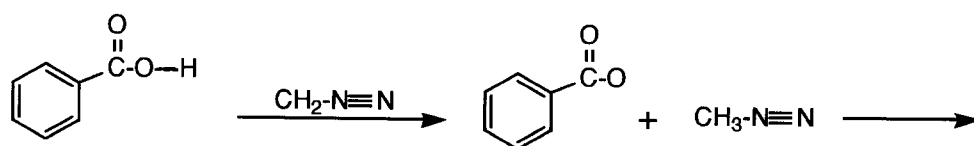
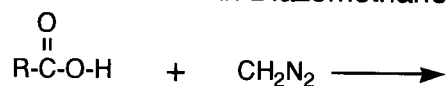
Proposed mechanism 1:



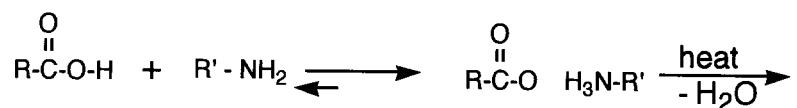
Proposed mechanism 2:



### B. Esterification with Diazomethane

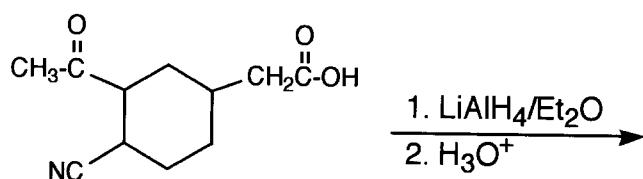
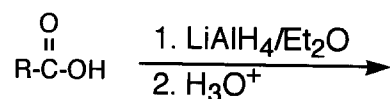


### III. Direct Amide Synthesis

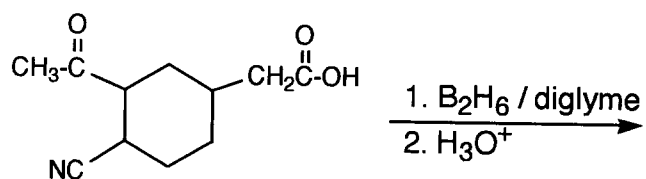


### IV. Reduction of RCO<sub>2</sub>H

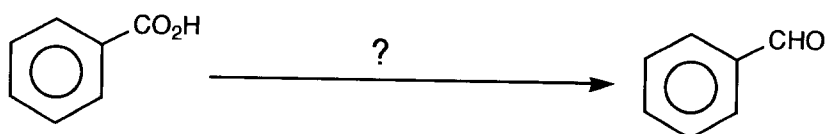
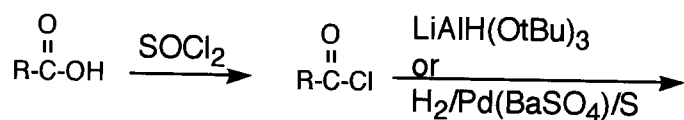
#### A. (Review) LAH reduction - not selective



#### B. Diborane reduction - very selective! - CO<sub>2</sub>H reacts faster with B<sub>2</sub>H<sub>6</sub> than any other functional group

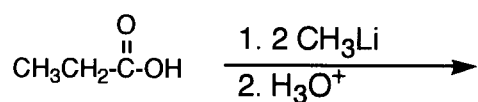
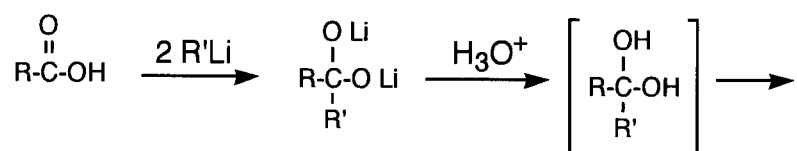


#### C. (Review) Reduction to aldehydes

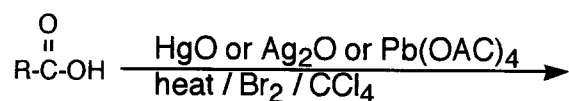




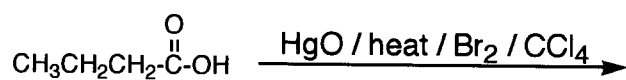
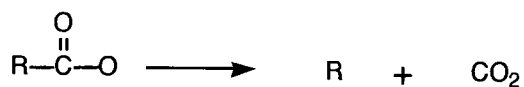
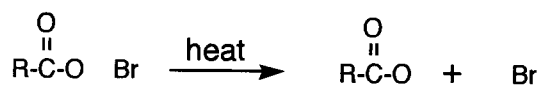
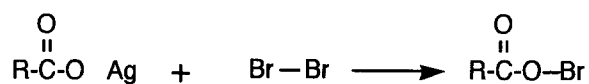
## V. Ketone Formation (Review)



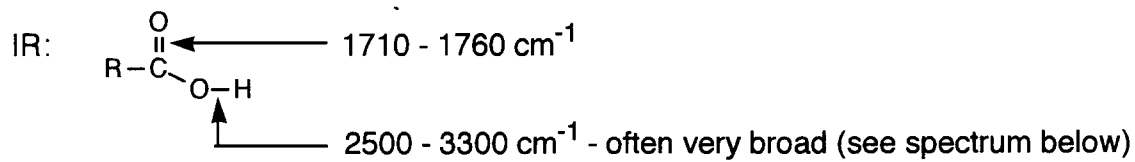
VI. Decarboxylation - The Hunsdiecker Reaction - converts heavy metal salts of  $\text{RCO}_2\text{H}$  into alkyl halides with 1 less carbon



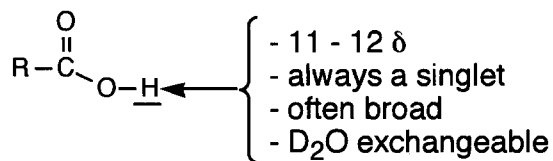
Mechanism: first - carboxylic acid salt is formed with metal then:



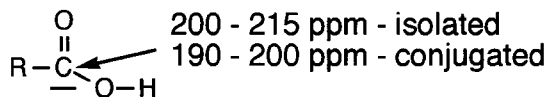
## SPECTROSCOPY SUMMARY



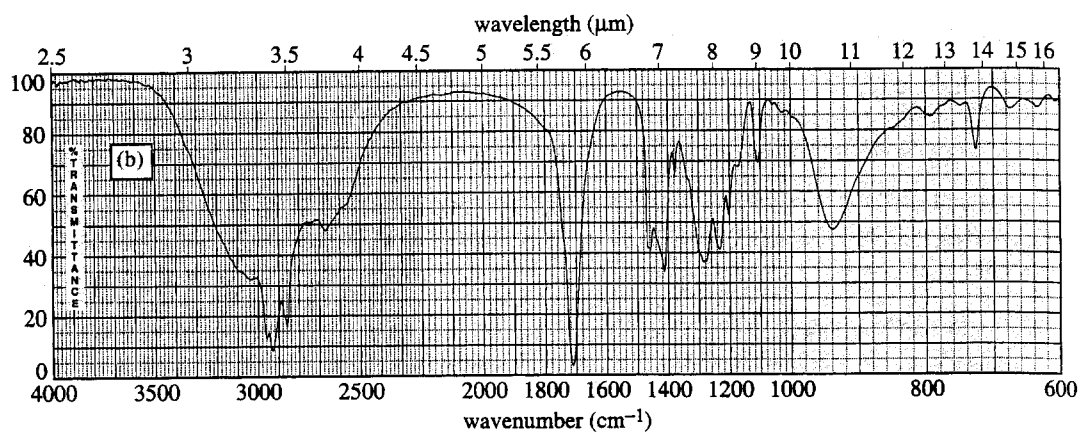
$^1\text{H}$  NMR:



$^{13}\text{C}$  NMR:



sample IR



unknown  
 $\text{C}_4\text{H}_6\text{O}_2$

