

CH 318 N

LECTURE 13

Textbook Assignment: Chapter 16

Homework (for credit): POW 6 posted

Today's Topics: Carboxylic Acids

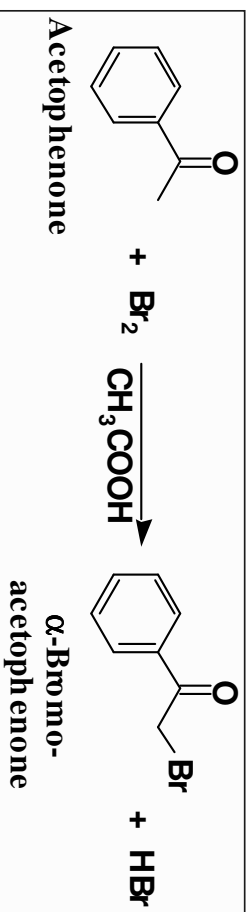
Notice & Announcements:

ORGANIC LECTURE SERIES

Aldehydes And Ketones

α -Halogenation

➤ α -Halogenation: aldehydes and ketones with at least one α -hydrogen react at an α -carbon with Br_2 and Cl_2



– reaction is catalyzed by both acid and base

– **Caution!! These are lachrymators**

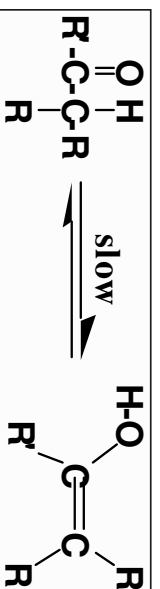


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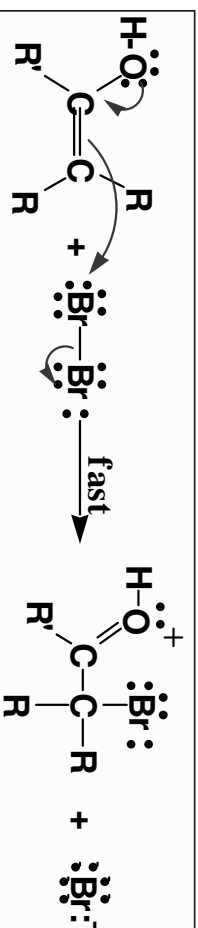
α -Halogenation

• **Acid-catalyzed** α -halogenation

Step 1: acid-catalyzed enolization - forms the **enol**



Step 2: nucleophilic attack of the enol on halogen



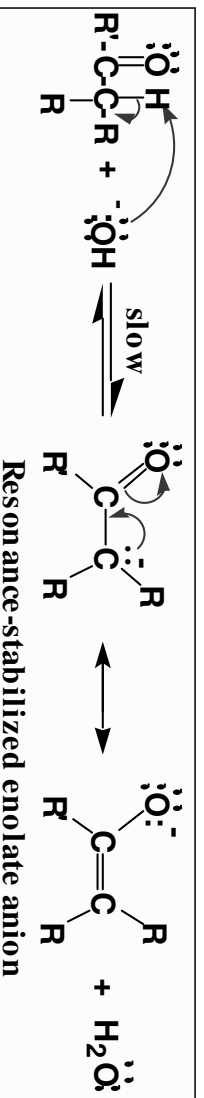
Step 3: (not shown) proton transfer to solvent completes the reaction

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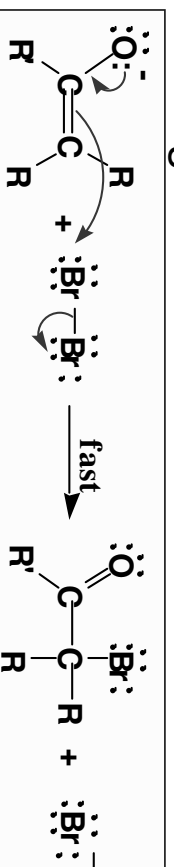
α -Halogenation

- **Base-promoted α -halogenation**

Step 1: formation of an enolate anion



Step 2: nucleophilic attack of the enolate anion on halogen



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α -Halogenation

- **Acid-catalyzed α -halogenation:**
 - introduction of a second halogen is slower than the first
 - introduction of the electronegative halogen on the α -carbon decreases the basicity of the carbonyl oxygen toward protonation
- **Base-promoted α -halogenation:**
 - each successive halogenation is more rapid than the previous one
 - the introduction of the electronegative halogen on the α -carbon increases the acidity of the remaining α -hydrogens and, thus, each successive α -hydrogen is removed more rapidly than the previous one

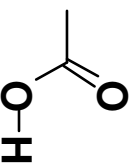
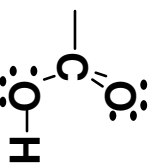
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Carboxylic Acids

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Structure

- The functional group of a carboxylic acid is a carboxyl group



Alternative representations for a carboxyl group

- the general formula for an aliphatic carboxylic acid is RCOOH ; that for an aromatic carboxylic acid is ArCOOH

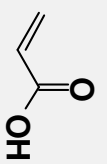
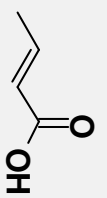
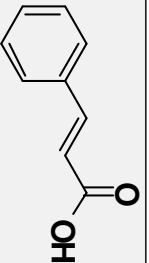
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Nomenclature

- IUPAC names: drop the -e from the parent alkane and add the suffix -oic acid


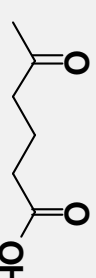

| | | |
|---------------------------------|--------------------------------|--|
| <chem>HCOOH</chem> | <chem>CH3COOH</chem> |  |
| Methanoic acid (Formic acid) | Ethanoic acid (Acetic acid) | 3-Methylbutanoic acid (Isovaleric acid) |

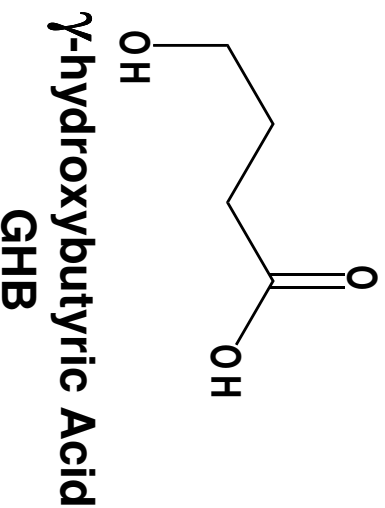
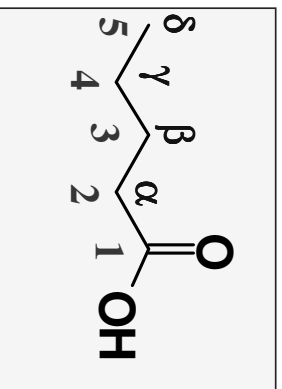
– if the compound contains a carbon-carbon double bond, change the infix -an- to -en-

| | | |
|---|---|--|
|  |  |  |
| Propenoic acid (Acrylic acid) | <i>trans</i> -2-Butenoic acid (Crotonic acid) | <i>trans</i> -3-Phenylpropenoic acid (Cinnamic acid) |

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- The carboxyl group takes precedence over most other functional groups

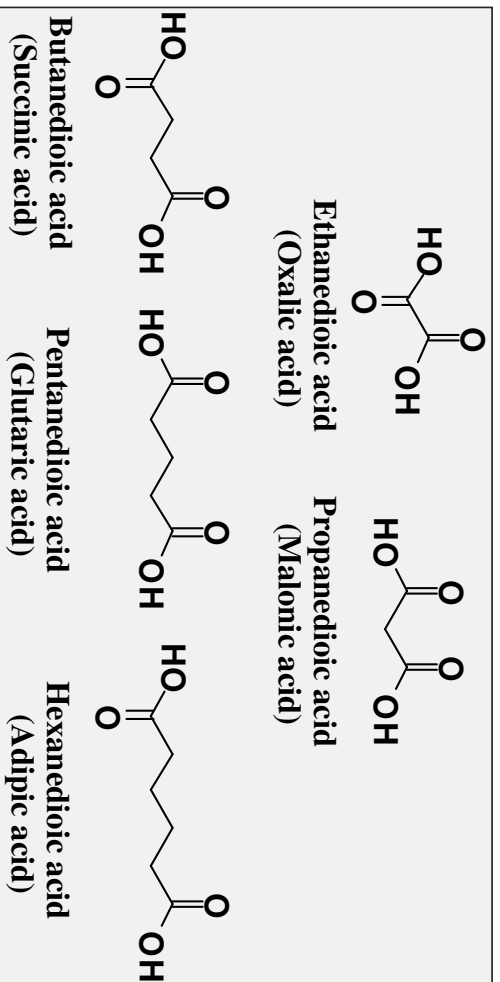
| | | |
|---|---|---|
|  |  |  |
| (<i>R</i>)-5-Hydroxyhexanoic acid | 5-Oxohexanoic acid | 4-Aminobutanoic acid |



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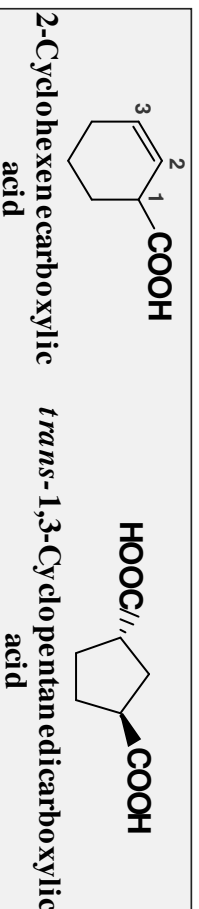
Nomenclature

- dicarboxylic acids: add the suffix -dioic acid to the name of the parent alkane containing both carboxyl groups

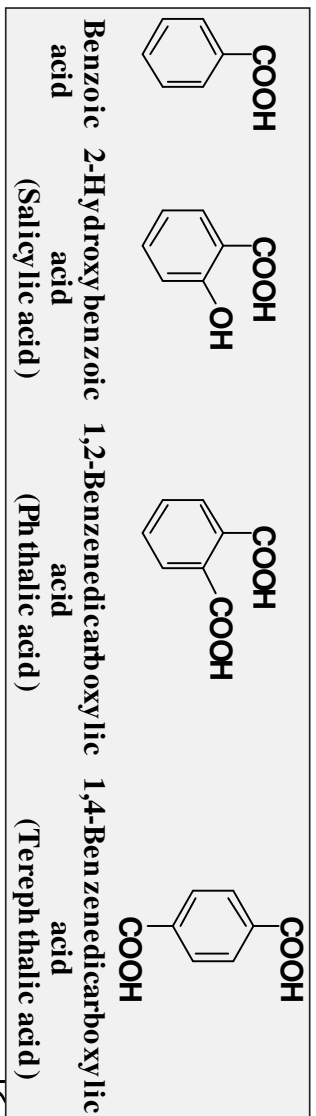


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- if the carboxyl group is bonded to a ring, name the ring compound and add the suffix -carboxylic acid



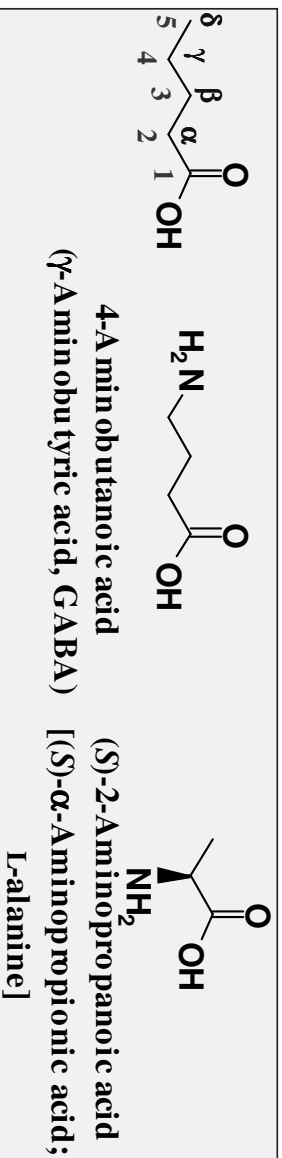
- benzoic acid is the simplest aromatic carboxylic acid
- use numbers to show the location of substituents



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Nomenclature

–when **common names** are used, the letters α , β , γ , δ , etc. are often used to locate substituents



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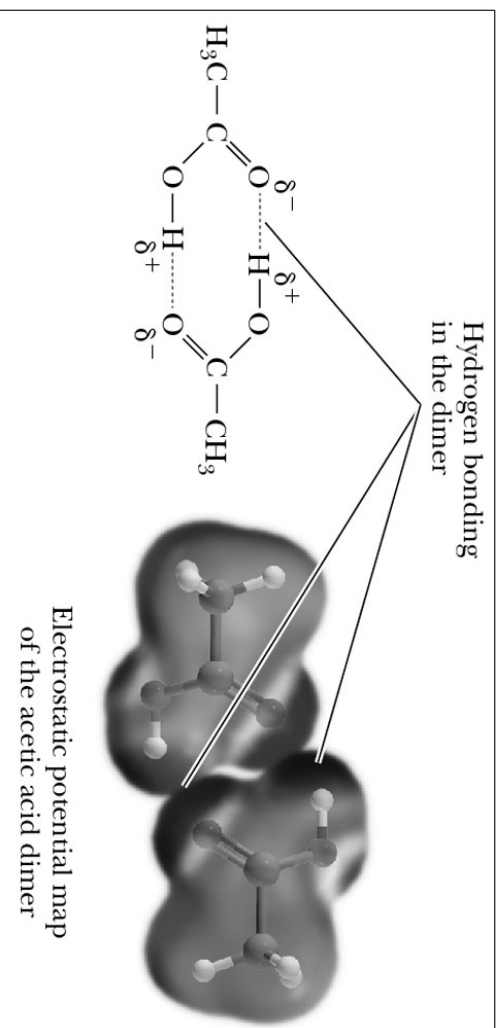
Spectral Properties

- **IR:** Broad O-H stretch (s) 3300-2500 cm^{-1}
Carbonyl (s) 1720-1705 cm^{-1}
C-O (m) 1440-1395 cm^{-1}
- **NMR:** Acidic proton is a singlet δ 10-15
- **^{13}C NMR:** carbonyl carbon 150-185 ppm
- **MS:** Peaks @ M-17 (OH) and M-45 (COOH); these are α cleavage products

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Physical Properties

- In the liquid and solid states, carboxylic acids are associated by hydrogen bonding into dimeric structures



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Physical Properties

- Carboxylic acids have significantly **higher boiling points** than other types of organic compounds of comparable molecular weight
 - they are polar compounds and form very strong intermolecular hydrogen bonds

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Physical Properties

- Carboxylic acids **are more soluble in water than alcohols**, ethers, aldehydes, and ketones of comparable molecular weight
 - they form hydrogen bonds with water molecules through their C=O and OH groups

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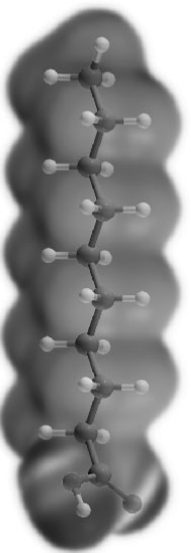
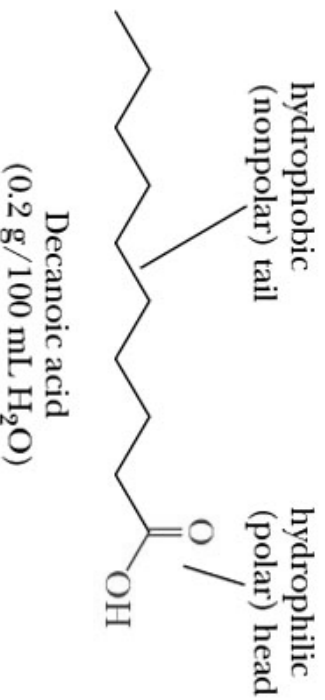
Physical Properties

| Structure | Name | Molecular Weight (g/mol) | Boiling Point (°C) | Solubility (g/100 g H ₂ O) |
|--|---------------|--------------------------|--------------------|---------------------------------------|
| CH ₃ COOH | Acetic acid | 60.1 | 118 | Infinite |
| CH ₃ CH ₂ CH ₂ OH | 1-Propanol | 60.1 | 97 | Infinite |
| CH ₃ CH ₂ CHO | Propanal | 58.1 | 48 | 16 |
| | | | | |
| CH ₃ (CH ₂) ₂ COOH | Butanoic acid | 88.1 | 163 | Infinite |
| CH ₃ (CH ₂) ₃ CH ₂ OH | 1-Pentanol | 88.1 | 137 | 2.3 |
| CH ₃ (CH ₂) ₃ CHO | Pentanal | 86.1 | 103 | Slight |
| | | | | |
| CH ₃ (CH ₂) ₄ COOH | Hexanoic acid | 116.2 | 205 | 1.0 |
| CH ₃ (CH ₂) ₅ CH ₂ OH | 1-Heptanol | 116.2 | 176 | 0.2 |
| CH ₃ (CH ₂) ₅ CHO | Heptanal | 114.1 | 153 | 0.1 |

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Physical Properties

water solubility decreases as the relative size of the hydrophobic portion of the molecule increases

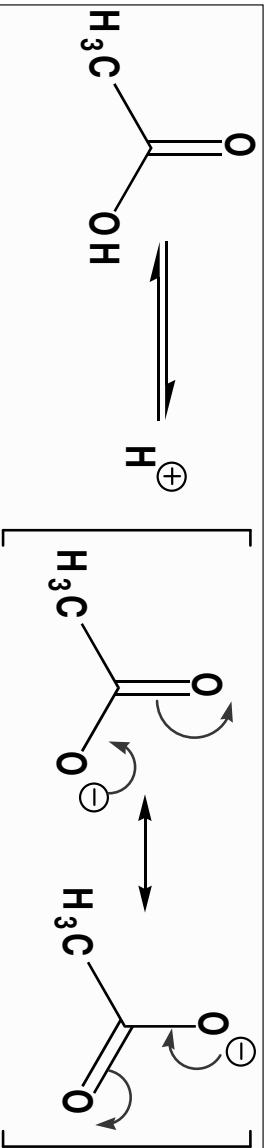


Electrostatic potential map

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Acidity

- Carboxylic acids are **weak acids**
 - values of pK_a for most aliphatic and aromatic carboxylic acids fall within the range 4 to 5
- The greater acidity of carboxylic acids relative to alcohols (both compounds that contain an OH group) is due to resonance stabilization of the carboxylate anion



Acidity

–electron-withdrawing substituents near the carboxyl group increase acidity through their inductive effect

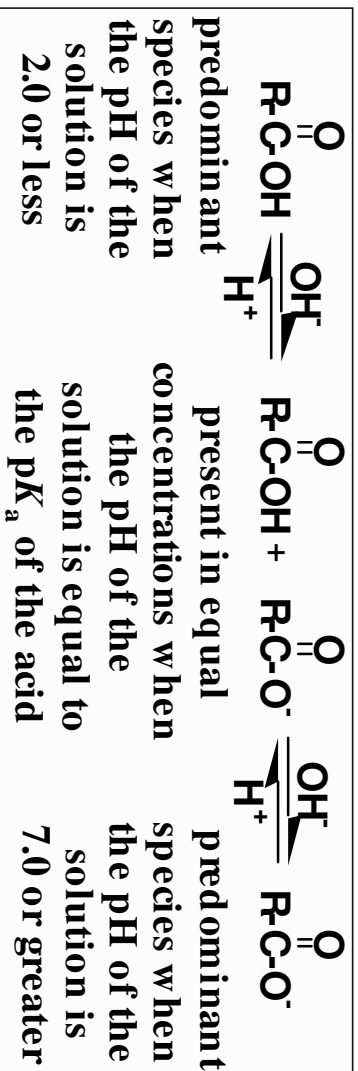
| Formula: | CH ₃ COOH | ClCH ₂ COOH | Cl ₂ CHCOOH | Cl ₃ CCOOH |
|-------------------|---|------------------------|------------------------|-----------------------|
| Name: | Acetic acid | Chloroacetic acid | Dichloroacetic acid | Trichloroacetic acid |
| pK _a : | 4.76 | 2.86 | 1.48 | 0.70 |
| | Increasing acid strength  | | | |



Note: the pK_a scale is a logarithmic scale

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the form of a carboxylic acid present in aqueous solution depends on the pH of the solution:



$$\text{pH} = pK_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

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For organic acids in equilibrium:



Henderson-Hasselbalch equation:

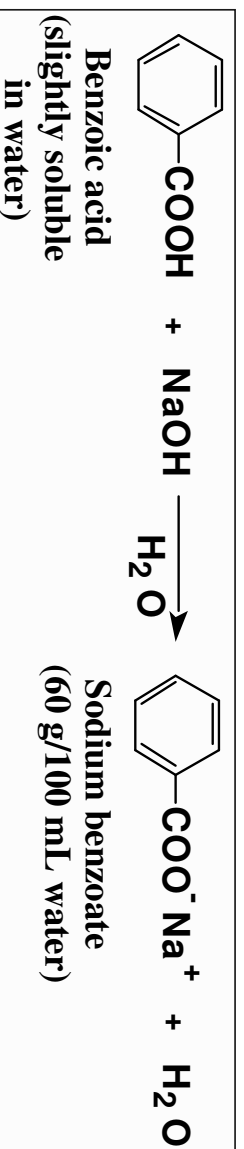
$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$$

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Reaction with Bases

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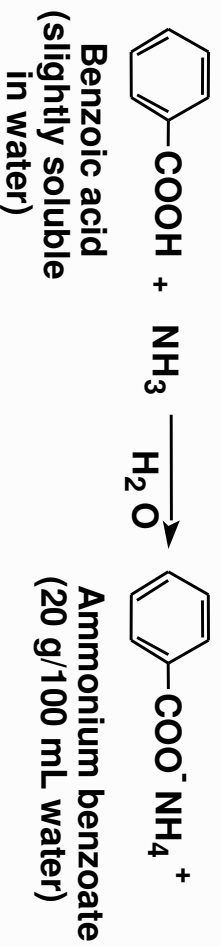
Carboxylic acids, whether soluble or insoluble in water, react with NaOH, KOH, and other strong bases to give water-soluble salts



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Reaction with Bases

- They also form water-soluble salts with ammonia and amines

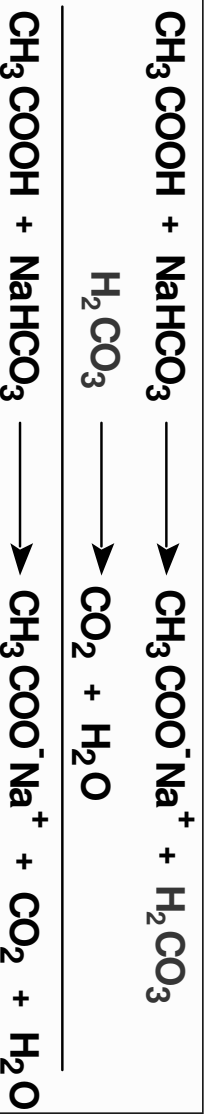


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Reaction with Bases

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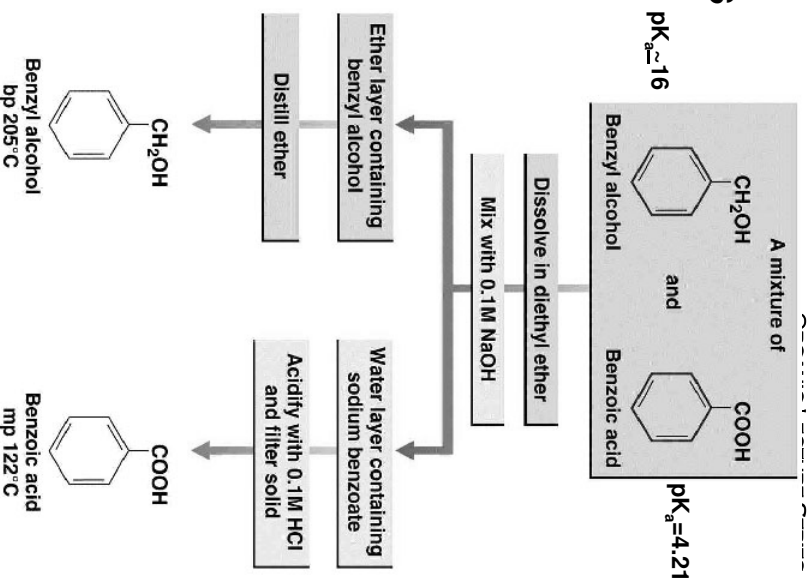
- Carboxylic acids react with sodium bicarbonate and sodium carbonate to form water-soluble salts and carbonic acid
 - carbonic acid, in turn, breaks down to carbon dioxide and water



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Exploiting pKa differences

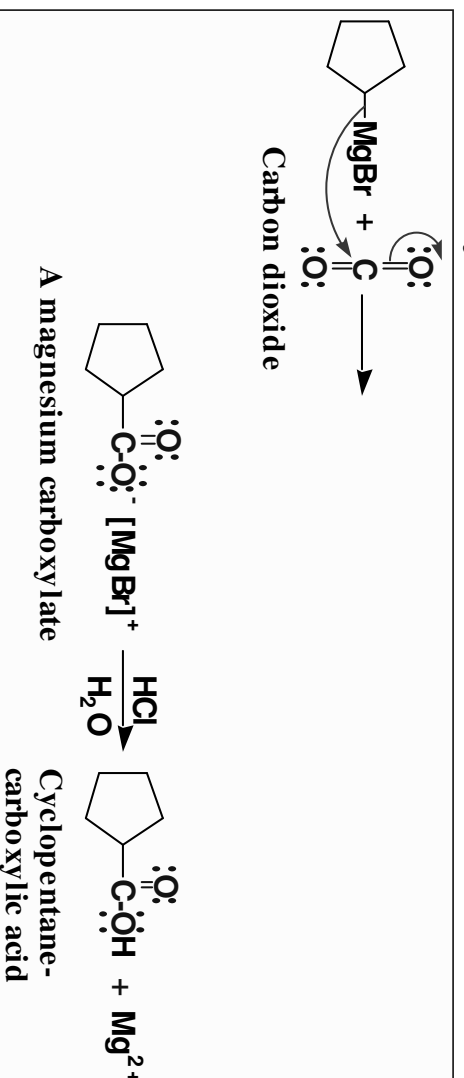
- Reaction with bases
 - the acid-base properties of carboxylic acids allow an easy separation of carboxylic acids from water-insoluble nonacidic compounds



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Preparation

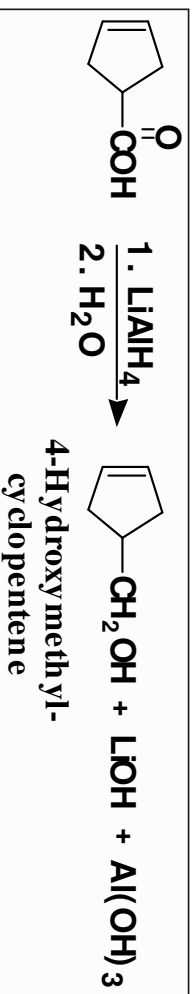
- Carbonation of Grignard reagents
 - treatment of a Grignard reagent with carbon dioxide followed by acidification gives a carboxylic acid



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Reduction

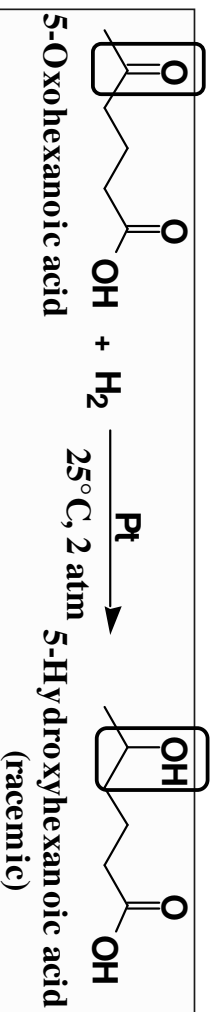
- The carboxyl group is very resistant to reduction
 - it is not affected by catalytic hydrogenation under conditions that easily reduce aldehydes and ketones to alcohols, and reduce alkenes and alkynes to alkanes; it is not reduced by NaBH_4
- **Lithium aluminum hydride reduces a carboxyl group to a 1° alcohol**
 - reduction is carried out in diethyl ether, THF, or other nonreactive, aprotic solvent



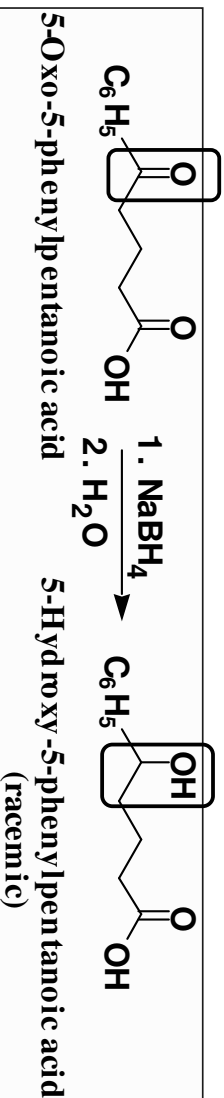
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Selective Reduction

- carboxyl groups are not affected by catalytic reduction under conditions that reduce aldehydes and ketones

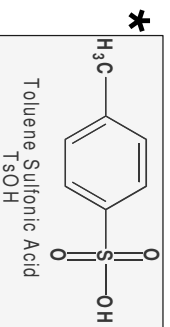
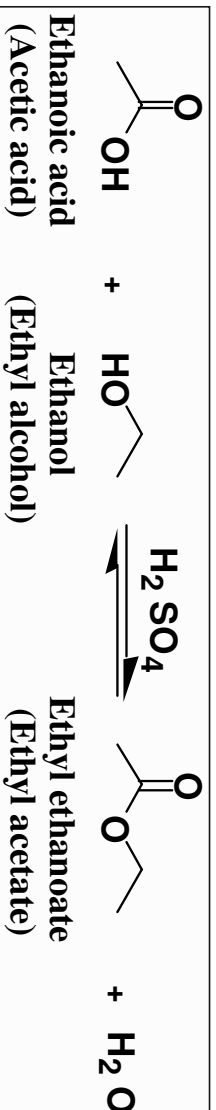


- nor are carboxyl groups reduced by NaBH_4



Fischer Esterification

- Esters can be prepared by treating a carboxylic acid with an alcohol in the presence of an acid catalyst, commonly H_2SO_4 , ArSO_3H^* , or gaseous HCl



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Fischer Esterification

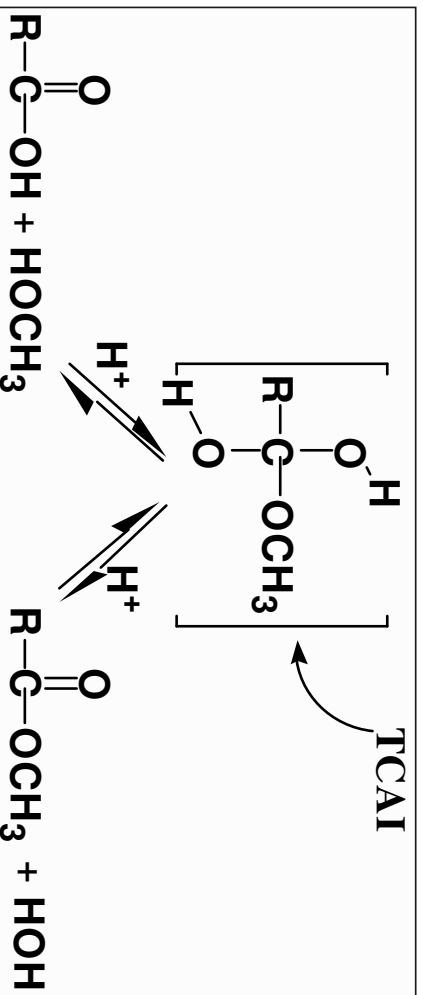
Fischer esterification is an equilibrium reaction

- by careful control of experimental conditions, it is possible to prepare esters in high yield
- if the alcohol is inexpensive relative to the carboxylic acid, it can be used in excess to drive the equilibrium to the right
- alternatively, water can be removed by azeotropic distillation and a Dean-Stark trap

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Fischer Esterification

– a key intermediate in Fischer esterification is the tetrahedral carbonyl addition intermediate formed by addition of ROH to the C=O group



(refer to mechanism worksheet)