

CH 310 N

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LECTURE 11

Textbook Assignment: Chapter 16 Continue

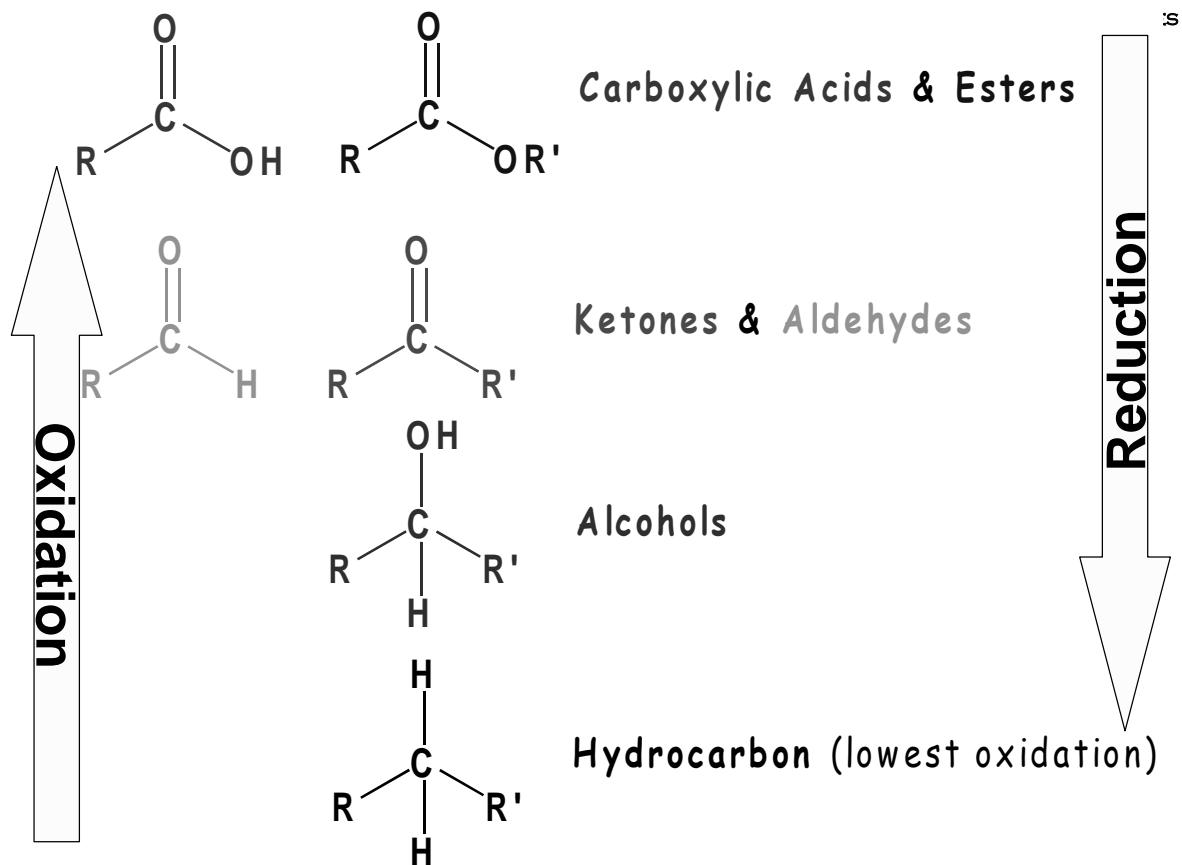
Homework (for credit): POW 5 posted

Today's Topics: Aldehydes & Ketones (cont'd)

Notice & Announcements:

ORGANIC LECTURE SERIES

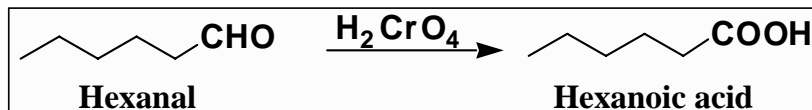
Aldehydes And Ketones



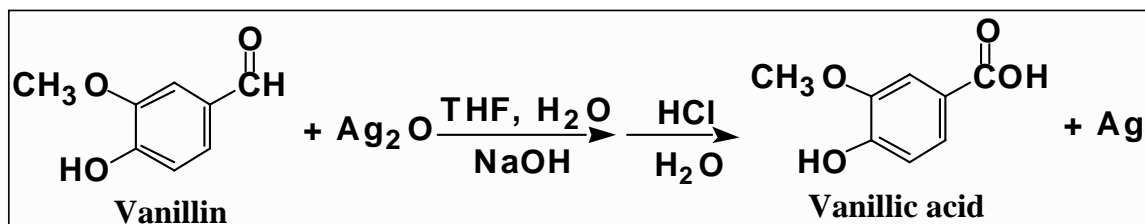
ORGANIC LECTURE SERIES

Oxidation of Aldehydes

- Aldehydes are oxidized to carboxylic acids by a variety of oxidizing agents, including H_2CrO_4



- They are also oxidized by Ag(I)
 - in one method, a solution of the aldehyde in aqueous ethanol or THF is shaken with a slurry of silver oxide

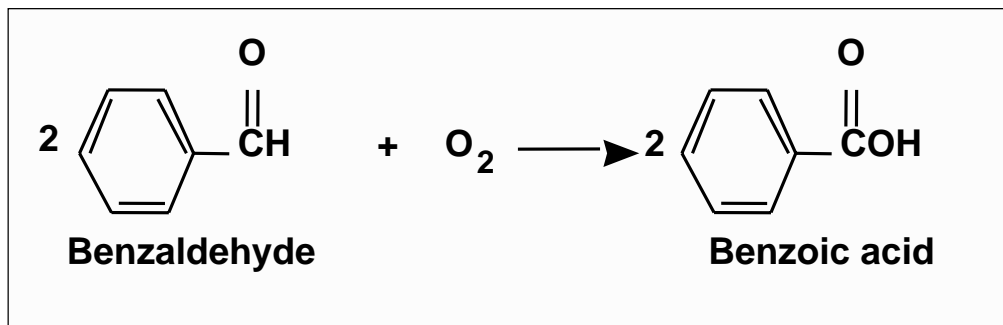


* See 10.8 for Jones reagent & PCC: pyridine \cdot CrO $_3$

Oxidation of Aldehydes

Aldehydes are oxidized by O_2 in a radical chain reaction

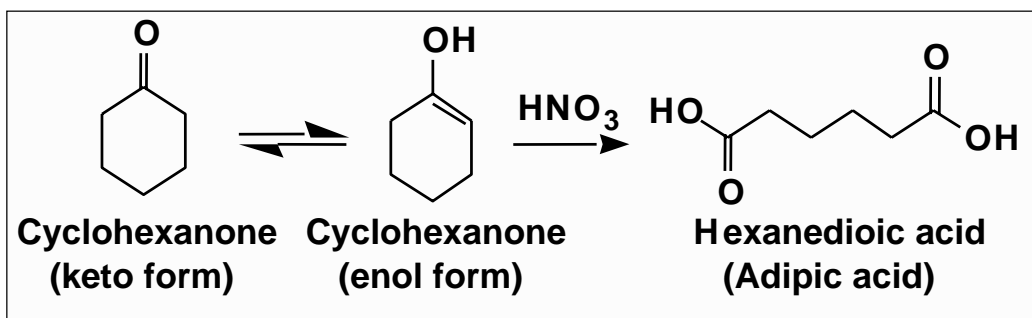
- liquid aldehydes are so sensitive to air that they must be stored under N_2



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“Oxidation” of Ketones

- ketones are **not** normally oxidized by chromic acid (H_2CrO_4)
- they are oxidized by powerful oxidants at high temperature and high concentrations of acid or base

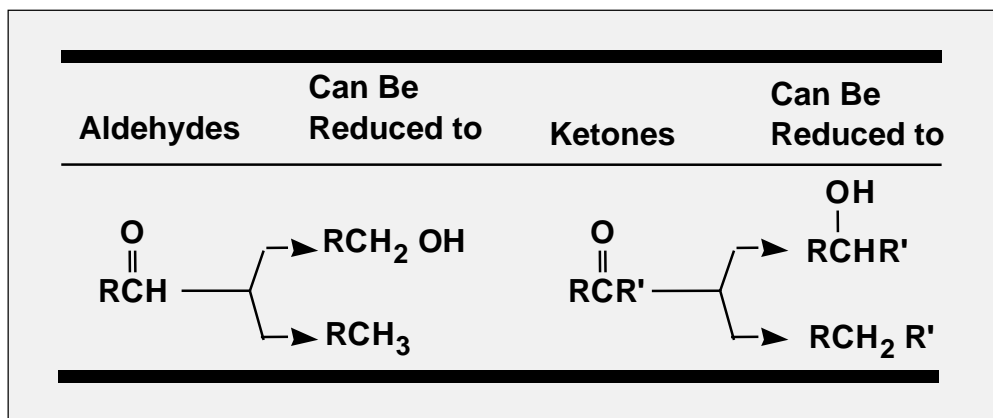


One of the starting materials for Nylon 6,6

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Reduction

- aldehydes can be reduced to 1° alcohols
- ketones can be reduced to 2° alcohols
- the C=O group of an aldehyde or ketone can be reduced to a -CH₂- group

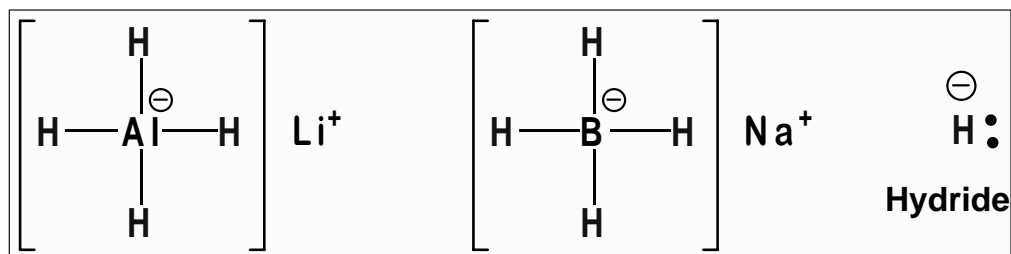


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Metal Hydride Reduction

The most common laboratory reagents for the reduction of aldehydes and ketones are NaBH₄ and LiAlH₄

- both reagents are sources of hydride ion, H:^- a very powerful nucleophile



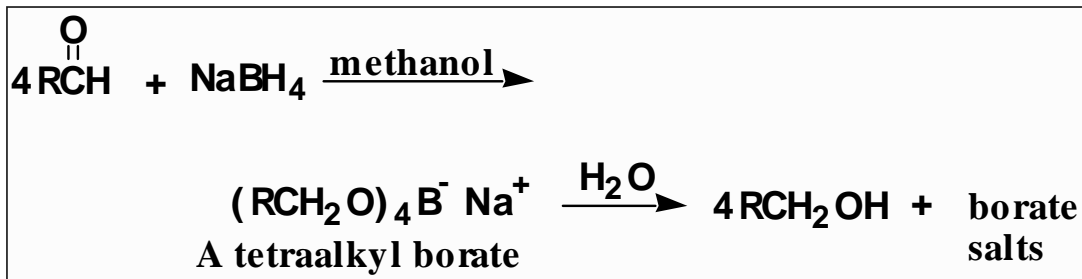
Lithium Aluminum Hydride
LAH

Sodium Borohydride
NaBH₄

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Sodium Borohydride Reduction

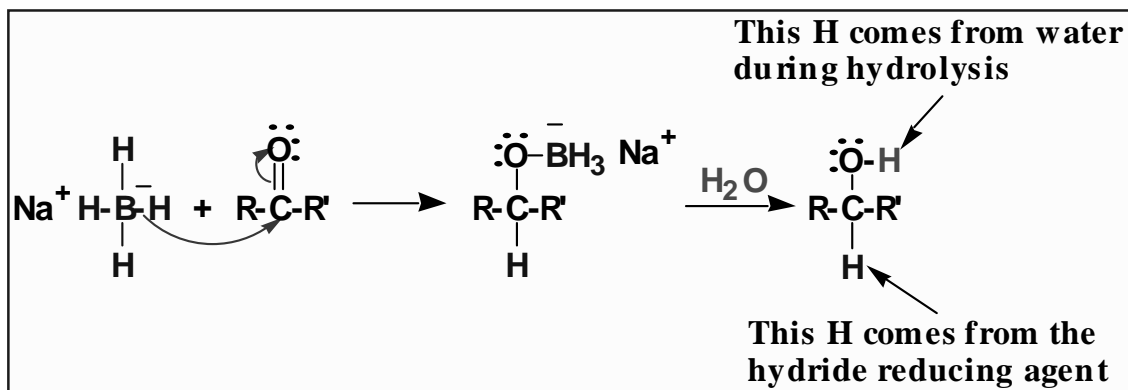
- reductions with NaBH_4 are most commonly carried out in aqueous methanol, in pure methanol, or in ethanol
- one mole of NaBH_4 reduces four moles of aldehyde or ketone



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Sodium Borohydride Reduction

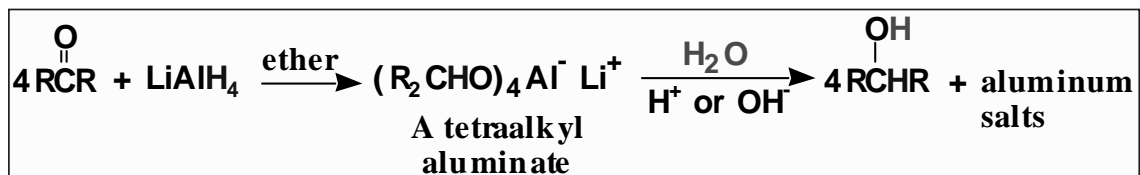
- The key step in metal hydride reduction is transfer of a hydride ion to the $\text{C}=\text{O}$ group to form a tetrahedral carbonyl addition compound



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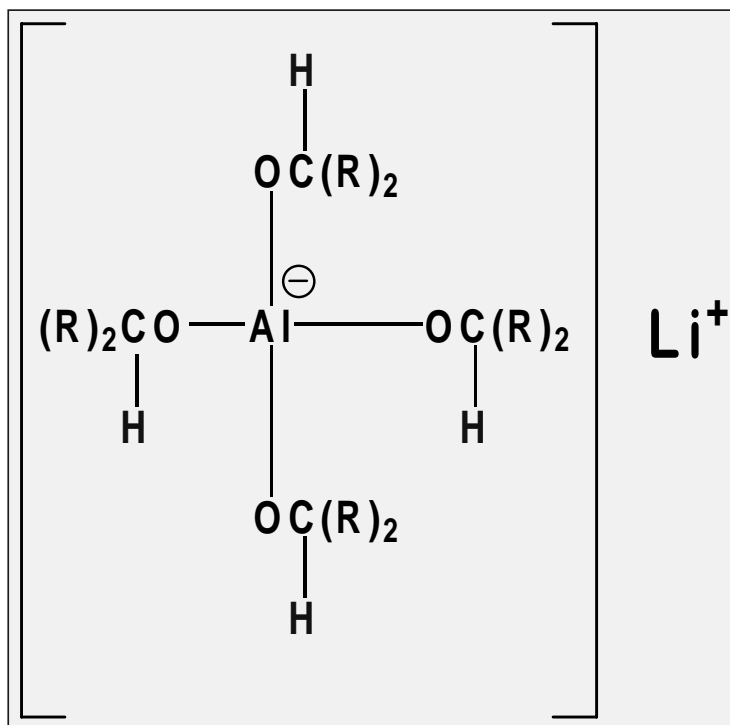
LAH Reduction

- unlike NaBH_4 , LiAlH_4 reacts violently with **water, methanol**, and other protic solvents
- reductions using it are carried out in dry (anhydrous) diethyl ether or tetrahydrofuran (THF)



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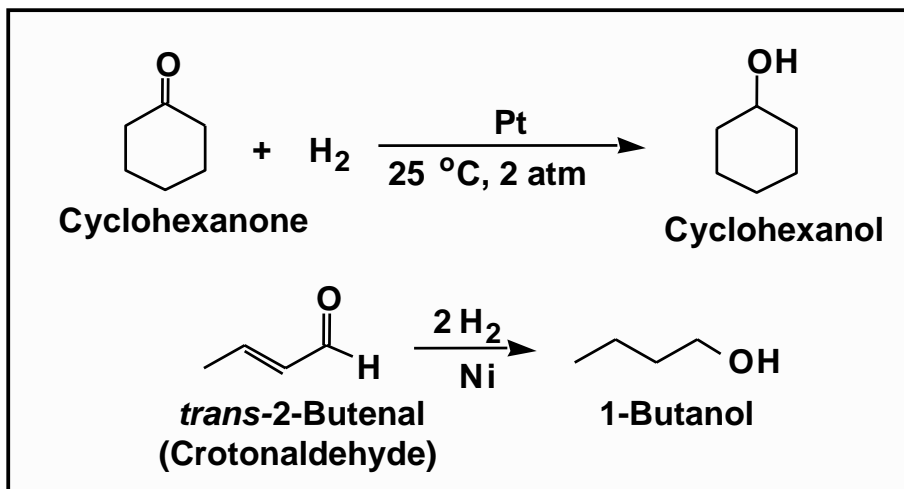
Lithium tetra-alkyl aluminate



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Catalytic Reduction

- Catalytic reductions are generally carried out at from 25° to 100°C and 1 to 5 atm H₂

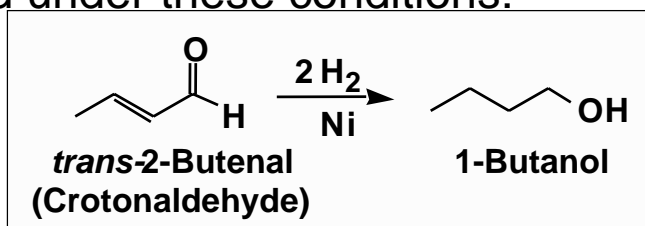


Note: Both the olefin and the carbonyl are reduced

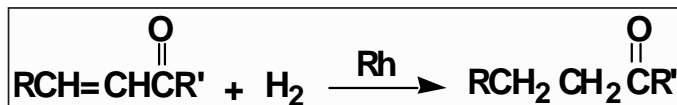
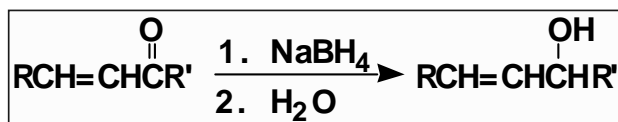
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Catalytic Reduction

- A carbon-carbon double bond may also be reduced under these conditions:



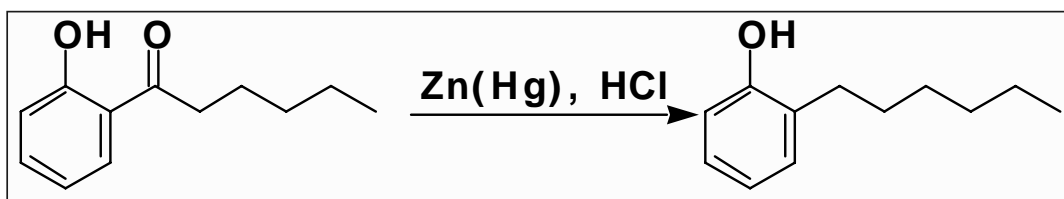
- by careful choice of experimental conditions, it is often possible to selectively reduce a carbon-carbon double bond in the presence of an aldehyde or ketone



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Clemmensen Reduction

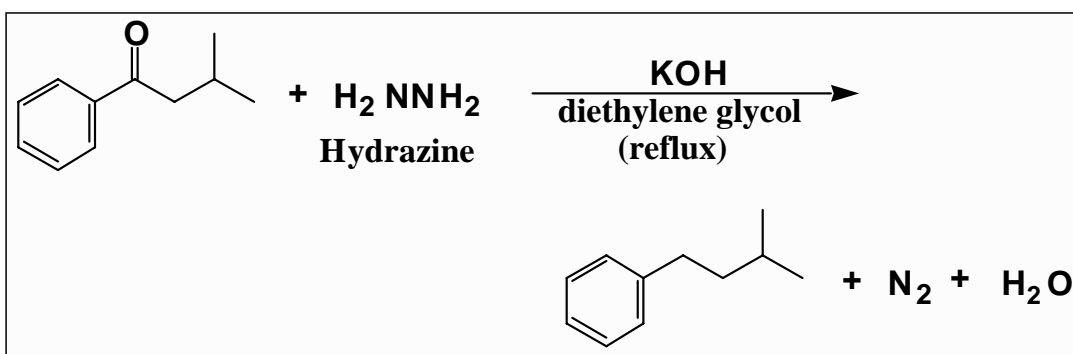
- refluxing an aldehyde or ketone with amalgamated zinc in concentrated HCl converts the carbonyl group to a methylene group
- Classic reaction but harsh conditions limit its use



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Wolff-Kishner Reduction

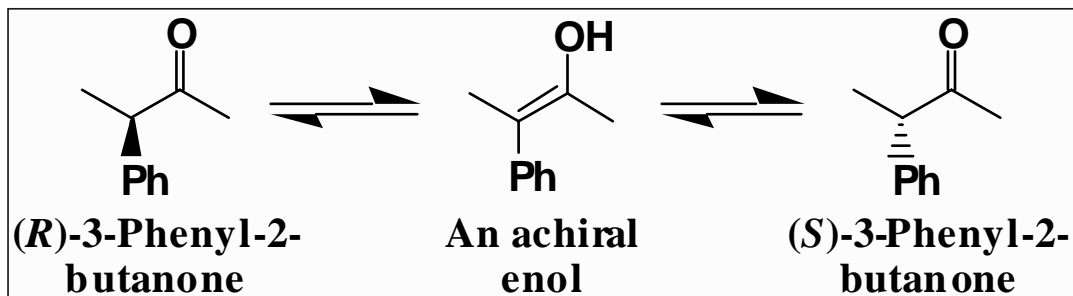
- in the original procedure, the aldehyde or ketone and hydrazine are refluxed with KOH in a high-boiling solvent
- the same reaction can be brought about using hydrazine and potassium *tert*-butoxide in DMSO (Di-methyl sulfoxide)



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Racemization

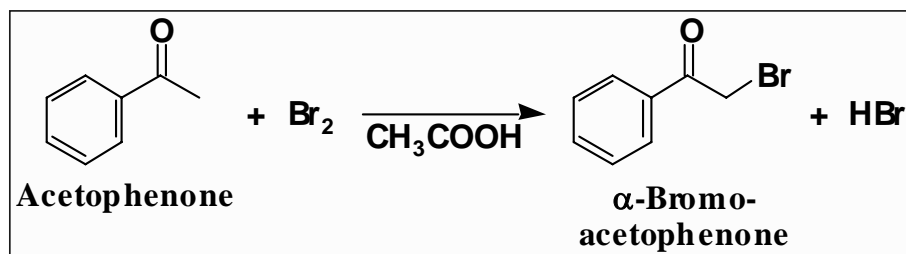
- Racemization at an α -carbon may be catalyzed by either acid or base
- Once stereochemistry is set, this is usually an undesirable side reaction.



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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**

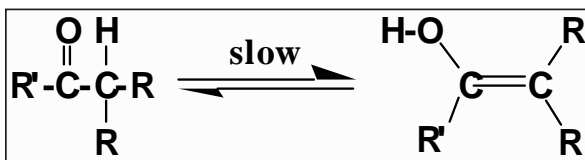


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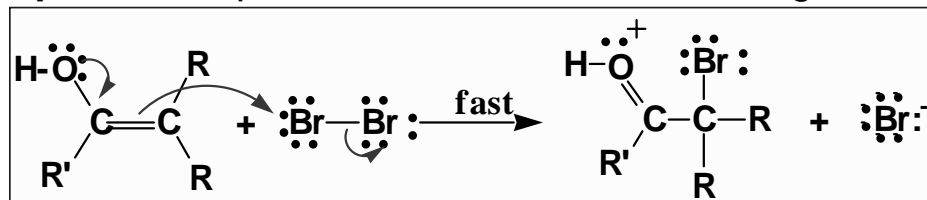
α -Halogenation

- **Acid-catalyzed** α -halogenation

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



Step 2: nucleophilic attack of the enol on halogen

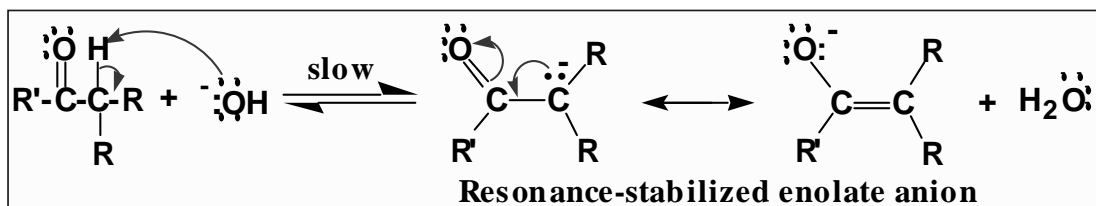


Step 3: (not shown) proton transfer to solvent completes the reaction

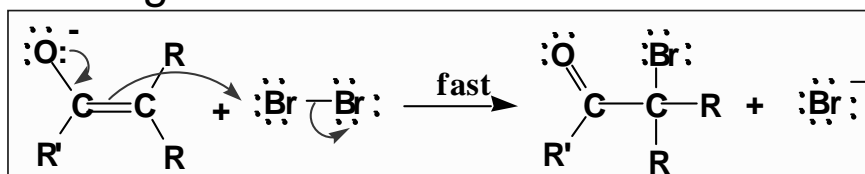
α -Halogenation

- **Base-promoted** α -halogenation

Step 1: formation of an **enolate anion**



Step 2: nucleophilic attack of the enolate anion on halogen



- **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

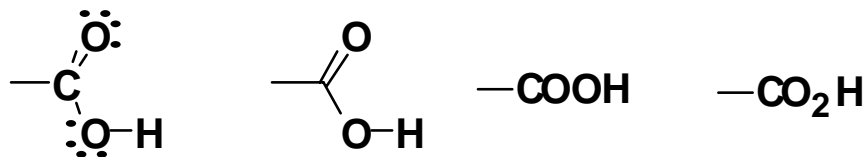
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Carboxylic Acids

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Structure

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



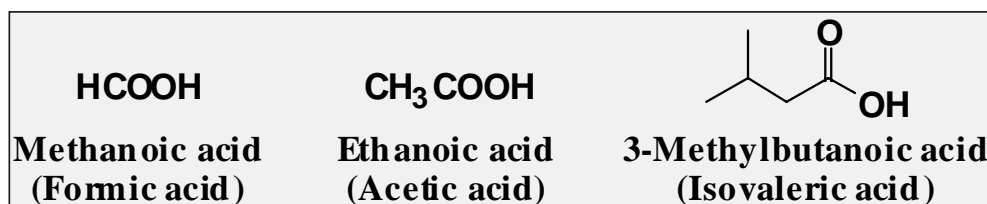
Alternative representations for a carboxyl group

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

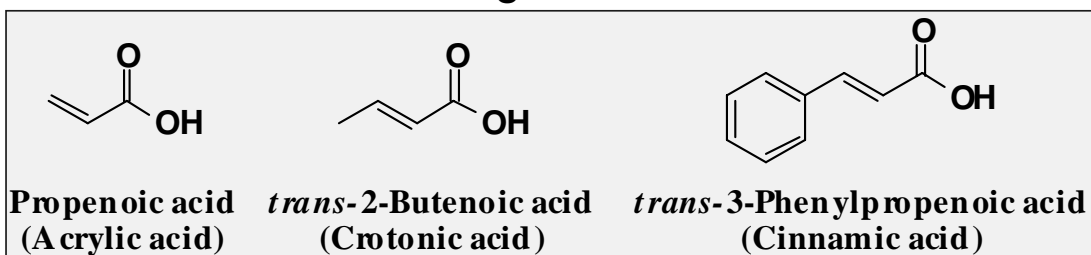
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Nomenclature

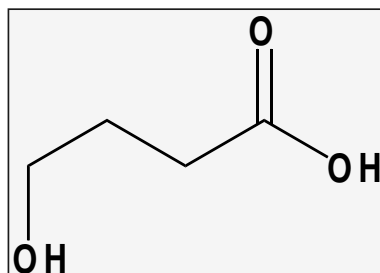
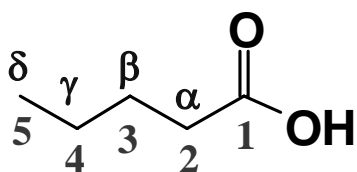
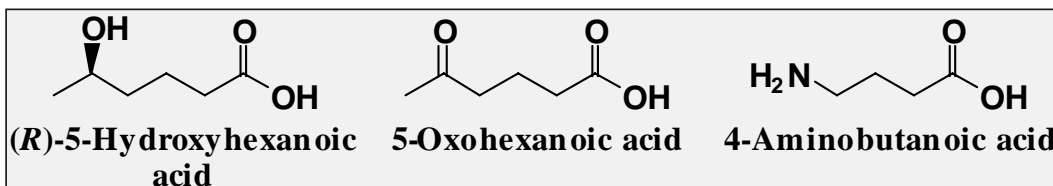
- IUPAC names: drop the -e from the parent alkane and add the suffix -oic acid



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



- The carboxyl group takes precedence over most other functional groups

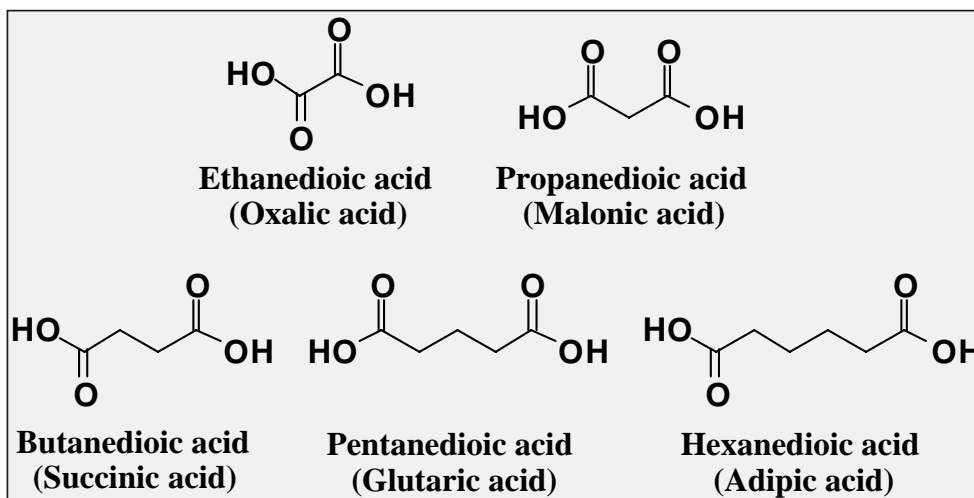


**γ -hydroxybutyric Acid (GHB)-
anesthetic; hypnotic**

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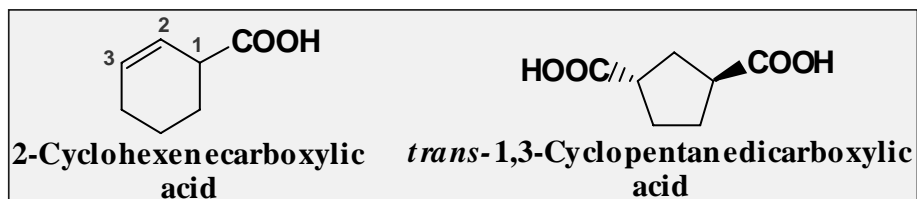
Nomenclature

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

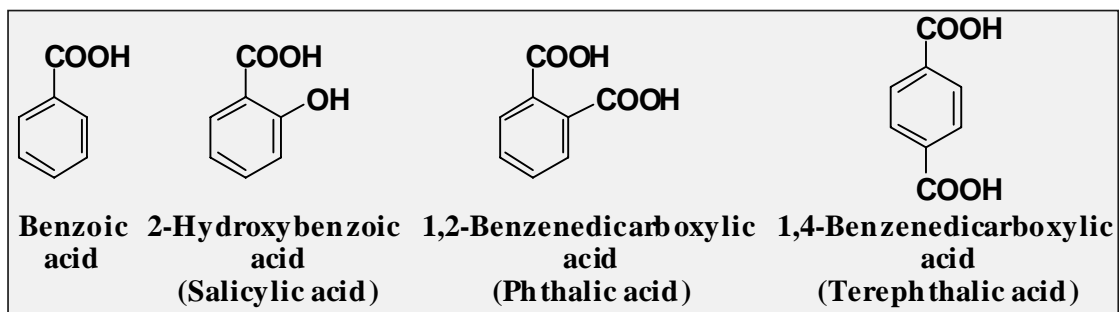


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- if the carboxyl group is bonded to a ring, name the ring compound and add the suffix -carboxylic acid

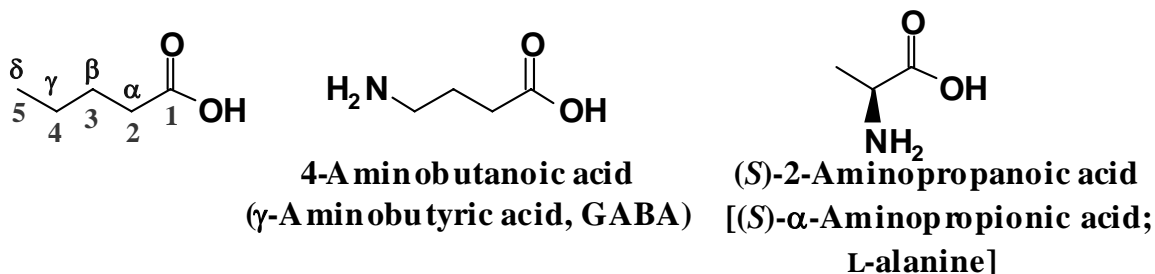


- **benzoic acid** is the simplest aromatic carboxylic acid
- use numbers to show the location of substituents



Nomenclature

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



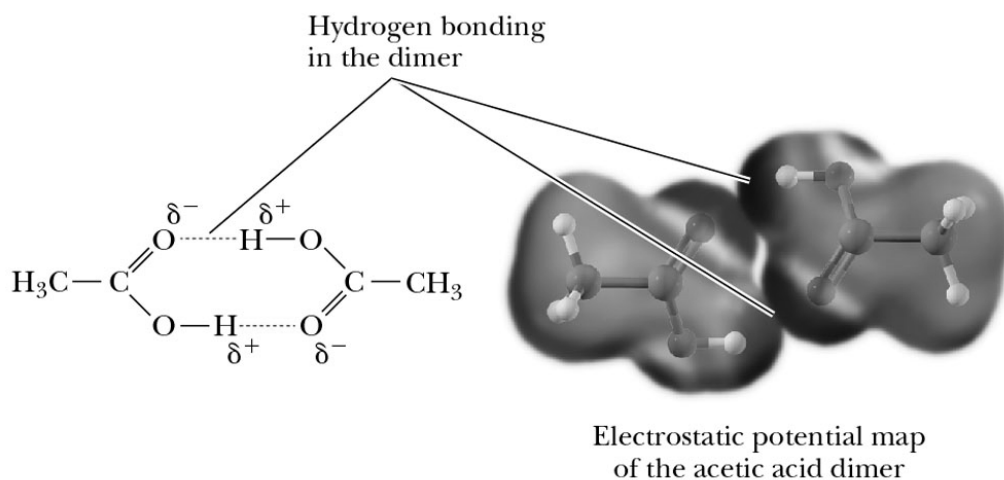
Spectral Properties

- **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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