Carboxylic Acids

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Lect. 15

Introduction

- The functional group of carboxylic acids consists of a C=O with -OH bonded to the same carbon.
- Carboxyl group is usually written -COOH.
- Aliphatic acids have an alkyl group bonded to -COOH.
- Aromatic acids have an aryl group.
- Fatty acids are long-chain aliphatic acids.

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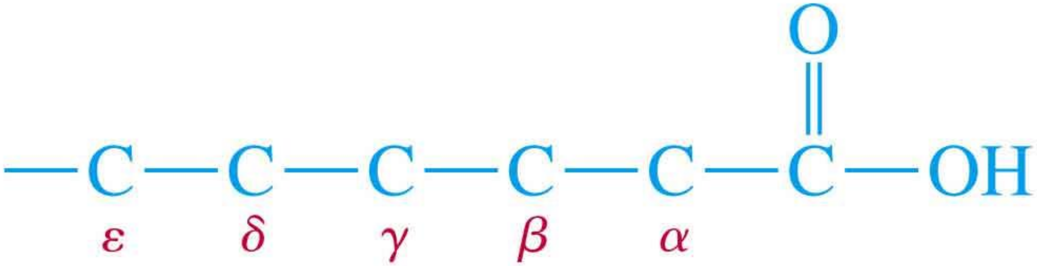
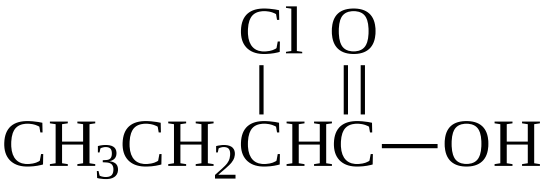
Common Names

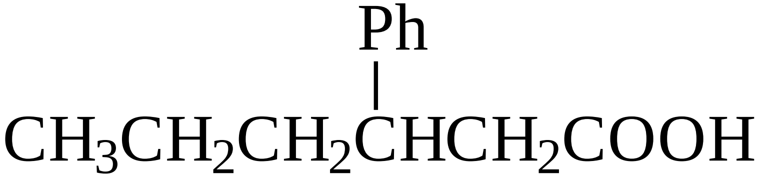
- Many aliphatic acids have historical names.
- Positions of substituents on the chain are labeled with Greek letters.





$CH_3CH_2\overset{\overset{Cl}{|}}{C}H\overset{\overset{O}{\|}}{C}{—}OH$

α-chlorobutyric acid



$CH_3CH_2CH_2\overset{\overset{Ph}{|}}{C}HCH_2COOH$

β-phenylcaproic acid

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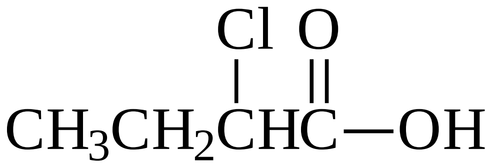
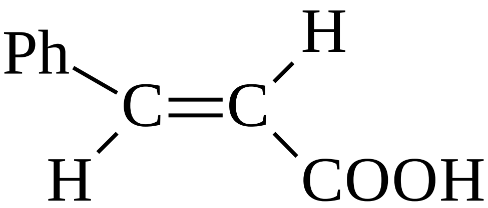
IUPAC Names

- Remove -*e* from alkane (or alkene) name, add -*oic acid*.
- The carbon of the carboxyl group is #1.



$$\mathrm{CH_3CH_2}\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-OH}$$

2-chlorobutanoic acid



trans-3-phenyl-2-propenoic acid (cinnamic acid)

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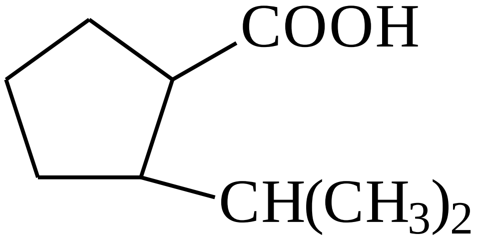
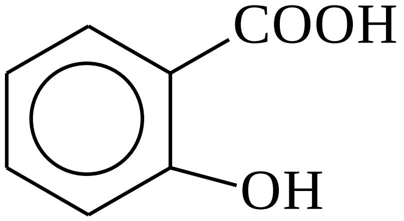
Naming Cyclic Acids

- Cycloalkanes bonded to -COOH are named as cycloalkanecarboxylic acids.
- Aromatic acids are named as benzoic acids.



2-isopropylcyclopentanecarboxylic acid



o-hydroxybenzoic acid
(salicylic acid)

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Dicarboxylic Acids

- Aliphatic diacids are usually called by their common names (to be memorized).
- For IUPAC name, number the chain from the end closest to a substituent.
- Two carboxyl groups on a benzene ring indicate a phthalic acid.

$$HOOCCH_2\overset{\overset{\displaystyle Br}{|}}{C}HCH_2CH_2COOH$$

3-bromohexanedioic acid

β-bromoadipic acid

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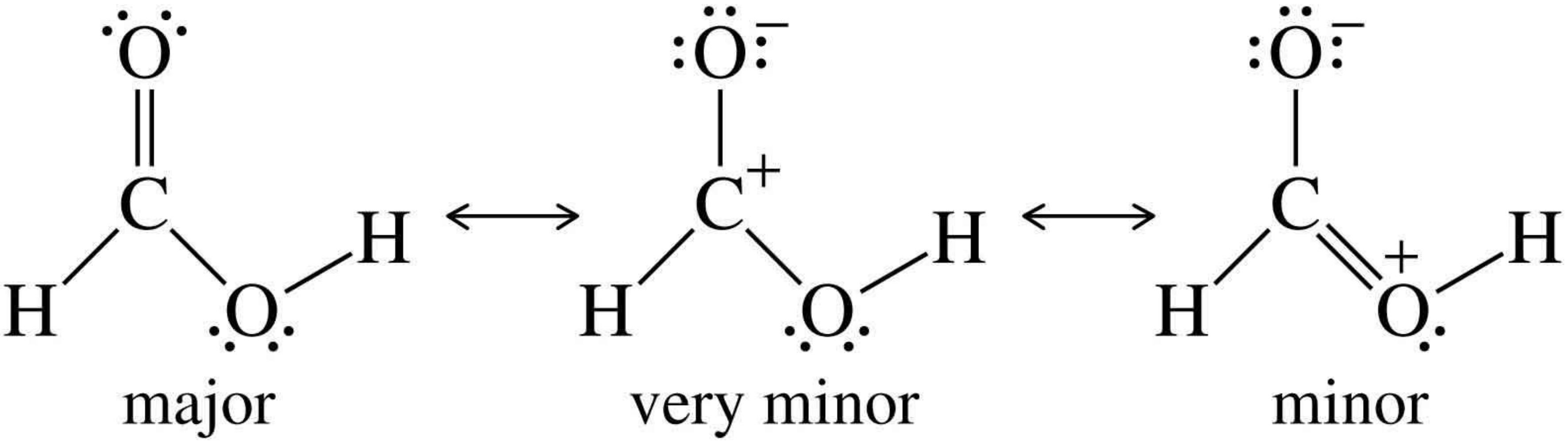
Structure of Carboxyl

- Carbon is *sp*^{2} hybridized.
- Bond angles are close to 120°.
- O-H eclipsed with C=O, to get overlap of π orbital with orbital of lone pair on oxygen.



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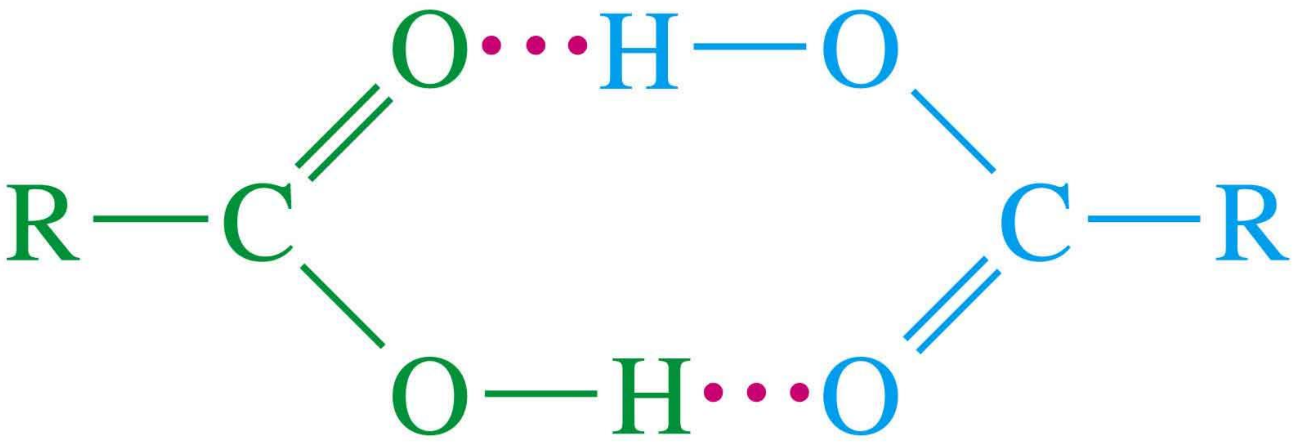
Boiling Points

Higher boiling points than similar alcohols, due to dimer formation.



hydrogen-bonded acid dimer

Acetic acid, b.p. 118°C

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Melting Points

- Aliphatic acids with more than 8 carbons are solids at room temperature.
- Double bonds (especially cis) lower the melting point. Note these 18-C acids:
  - Stearic acid (saturated): 72°C
  - Oleic acid (one cis double bond): 16°C
  - Linoleic acid (two cis double bonds): -5°C

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Solubility

- Water solubility decreases with the length of the carbon chain.
- Up to 4 carbons, acid is miscible in water.
- More soluble in alcohol.
- Also soluble in relatively nonpolar solvents like chloroform because it dissolves as a dimer.

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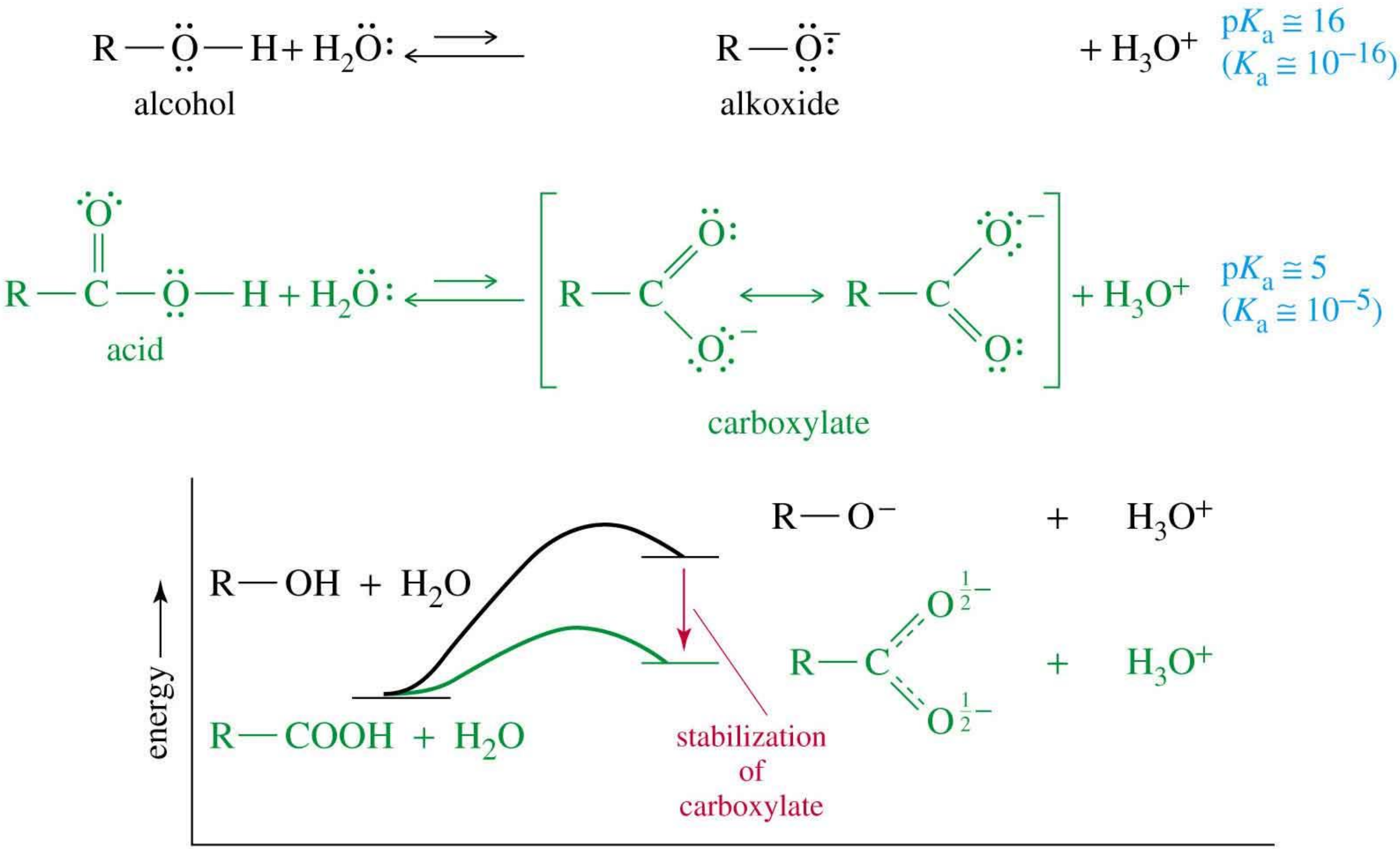
Acidity


R—O—H + H2O ⇌ R—O⁻ + H3O⁺
alcohol
alkoxide
pKa ≅ 16
(Ka ≅ 10⁻¹⁶)
R—C(=O)—O—H + H2O ⇌ [R—C(=O)—O⁻ ⟷ R—C(—O⁻)=O] + H3O⁺
acid
carboxylate
pKa ≅ 5
(Ka ≅ 10⁻⁵)
energy
R—OH + H2O
R—O⁻ + H3O⁺
R—COOH + H2O
R—C(O½⁻)(O½⁻) + H3O⁺
stabilization of carboxylate

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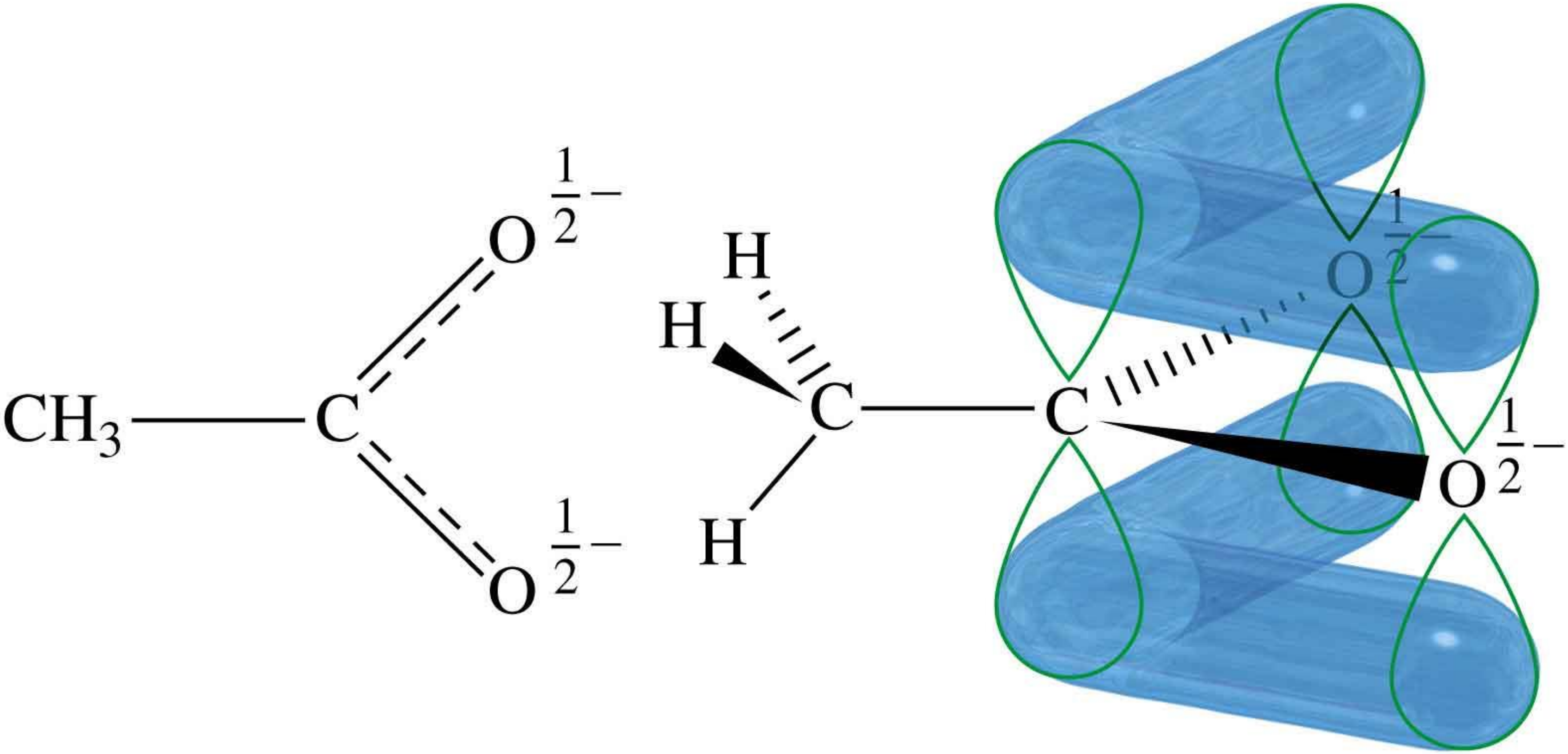
Resonance Stabilization



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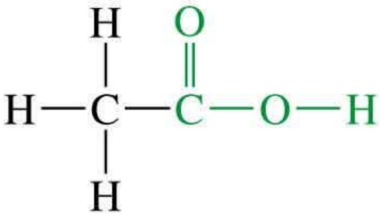
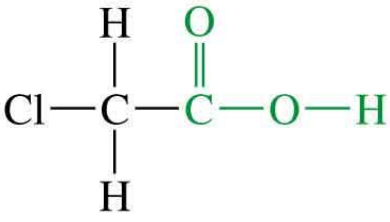
Substituent Effects on Acidity



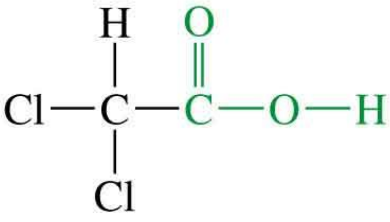
acetic acid

pK_a = 4.74



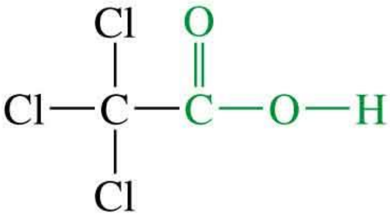
chloroacetic acid

pK_a = 2.86



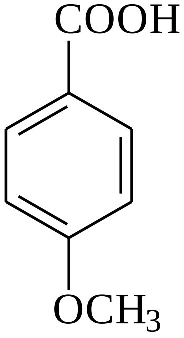
dichloroacetic acid

pK_a = 1.26



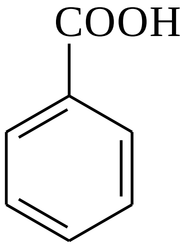
trichloroacetic acid

pK_a = 0.64



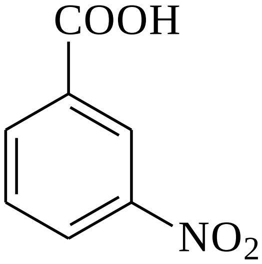
p-methoxy

pK_a = 4.46



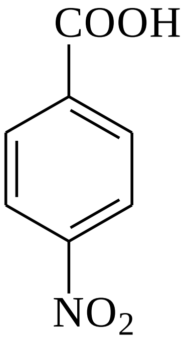
benzoic acid

pK_a = 4.19



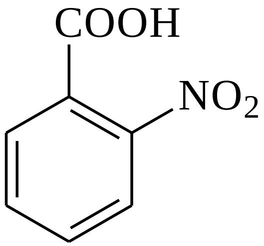
m-nitro

pK_a = 3.47



p-nitro

pK_a = 3.41



o-nitro

pK_a = 2.16

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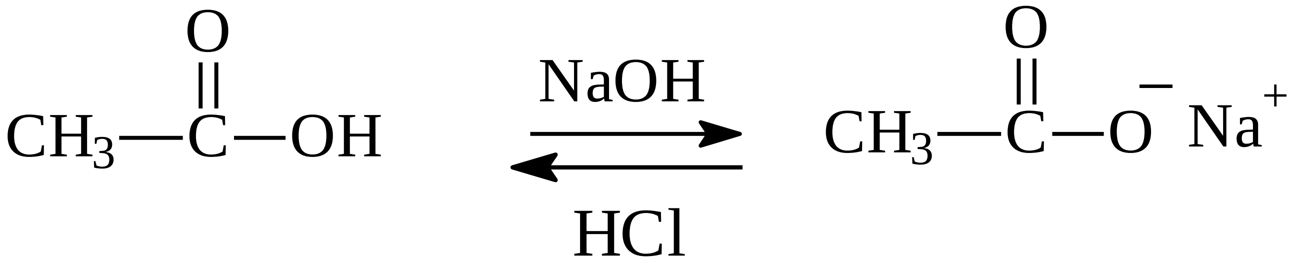
Salts of Carboxylic Acids

- Sodium hydroxide removes a proton to form the salt.
- Adding a strong acid, like HCl, regenerates the carboxylic acid.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \underset{HCl}{\overset{NaOH}{\rightleftarrows}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^{-}\ Na^{+}$$

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Naming Acid Salts

- Name the cation.
- Then name the anion by replacing the -ic acid with -ate.

$$CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_2COO^- K^+$$

potassium β-chlorovalerate
potassium 3-chloropentanoate

=>

Properties of Acid Salts

- Usually solids with no odor.
- Carboxylate salts of Na^+, K^+, Li^+, and NH_4^+ are soluble in water.
- Soap is the soluble sodium salt of a long chain fatty acid.
- Salts can be formed by the reaction of an acid with $NaHCO_3$, releasing CO_2.

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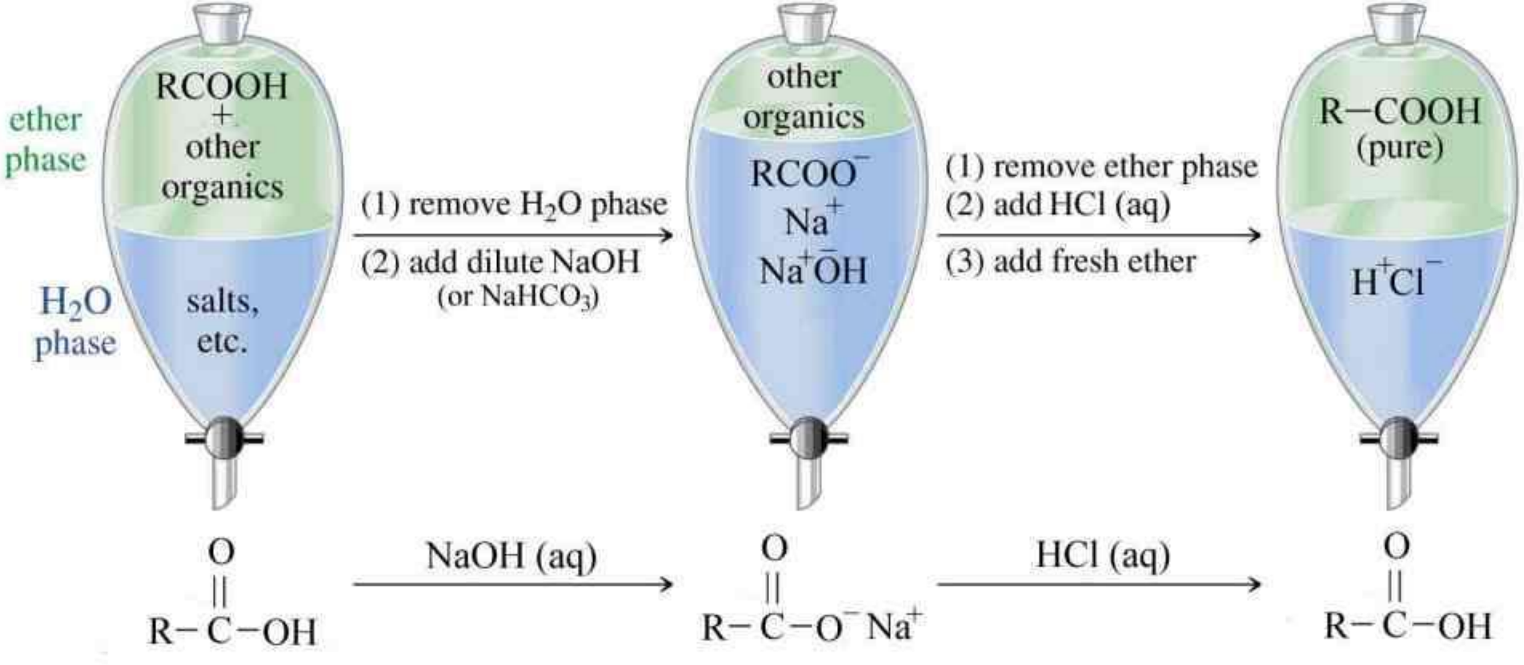
Purifying an Acid



Some Important Acids

- Acetic acid is in vinegar and other foods, used industrially as solvent, catalyst, and reagent for synthesis.
- Fatty acids from fats and oils.
- Benzoic acid in drugs, preservatives.
- Adipic acid used to make nylon 66.
- Phthalic acid used to make polyesters.

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Synthesis Review

- Oxidation of primary alcohols and aldehydes with chromic acid.
- Cleavage of an alkene with hot $KMnO_4$ produces a carboxylic acid if there is a hydrogen on the double-bonded carbon.
- Alkyl benzene oxidized to benzoic acid by hot $KMnO_4$ or hot chromic acid.

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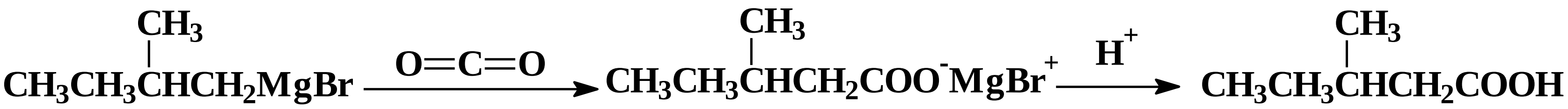
Grignard Synthesis

Grignard reagent + CO_2 yields a carboxylate salt.



$$CH_3CH_3\overset{CH_3}{\overset{|}{C}}HCH_2MgBr \xrightarrow{O{=}C{=}O} CH_3CH_3\overset{CH_3}{\overset{|}{C}}HCH_2COO^{-}MgBr^{+} \xrightarrow{H^{+}} CH_3CH_3\overset{CH_3}{\overset{|}{C}}HCH_2COOH$$

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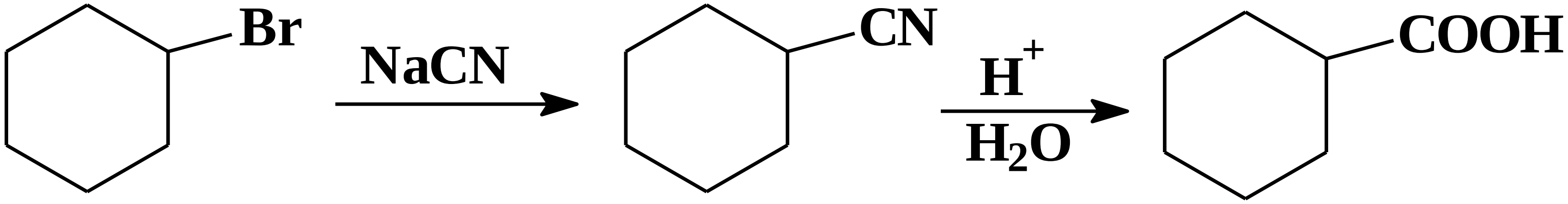
Hydrolysis of Nitriles

Basic or acidic hydrolysis of a nitrile produces a carboxylic acid.



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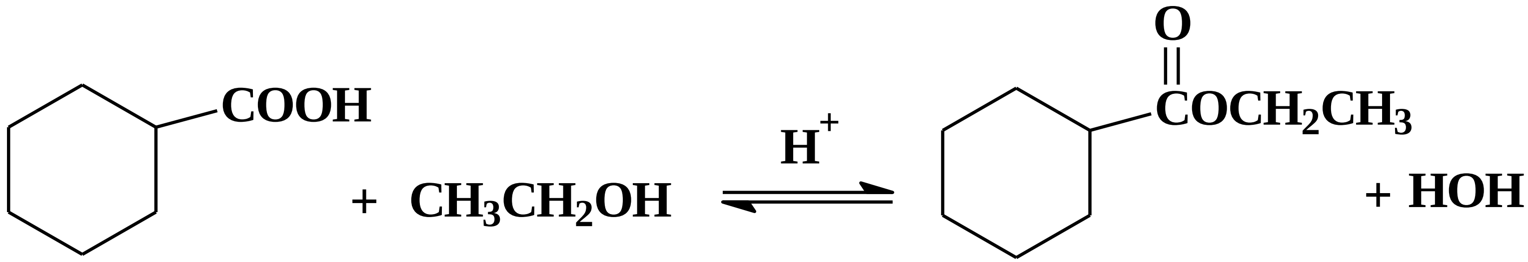
Acid Derivatives

- The group bonded to the acyl carbon determines the class of compound:
  - -OH, carboxylic acid
  - -Cl, acid chloride
  - -OR’, ester
  - -NH_2, amide
- These interconvert via nucleophilic acyl substitution. =>

Fischer Esterification

- Acid + alcohol yields ester + water.
- Acid catalyzed for weak nucleophile.
- All steps are reversible.
- Reaction reaches equilibrium.



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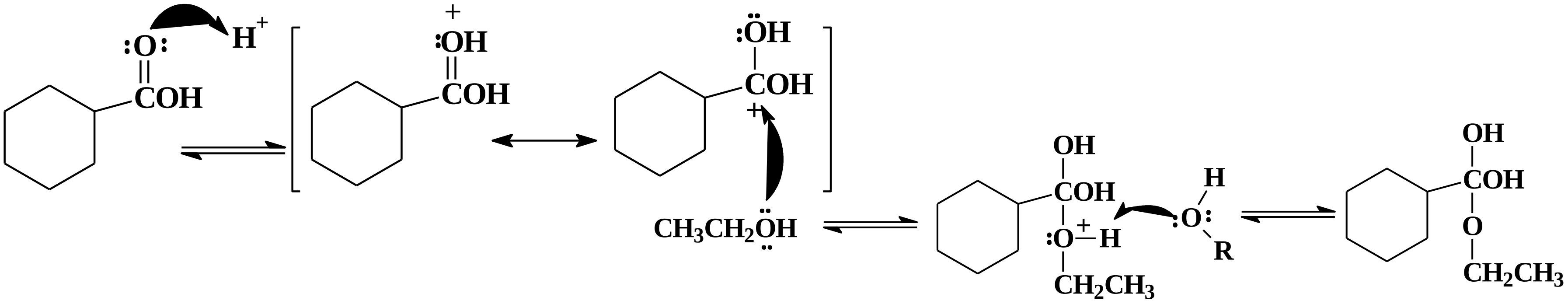
Fischer Mechanism (1)

Protonation of carbonyl and attack of alcohol, a weak nucleophile.



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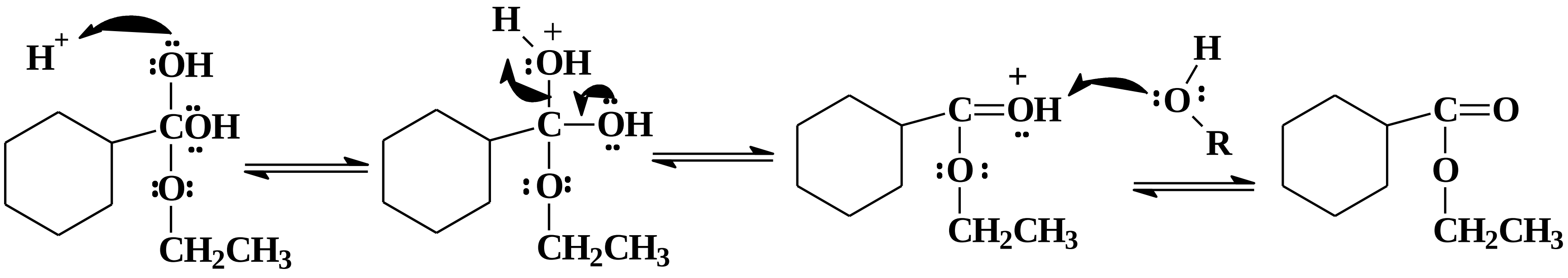
Fischer Mechanism (2)

Protonation of -OH and loss of water.



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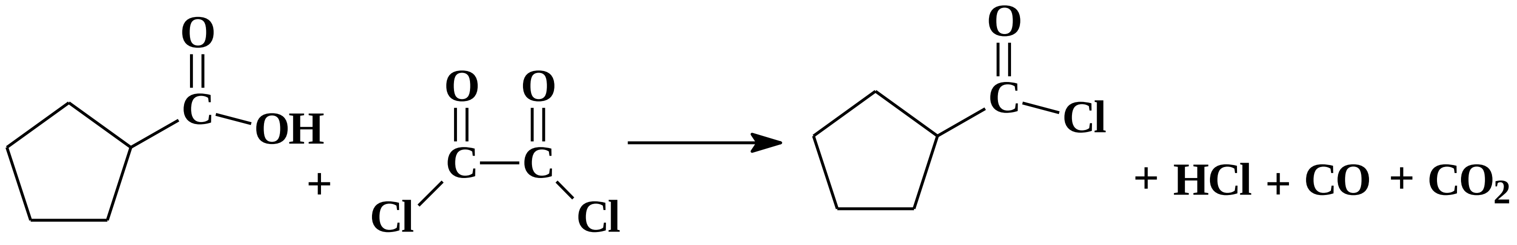
Acid Chlorides

- An activated form of the carboxylic acid.
- Chloride is a good leaving group, so undergoes acyl substitution easily.
- To synthesize acid chlorides use thionyl chloride or oxalyl chloride with the acid.



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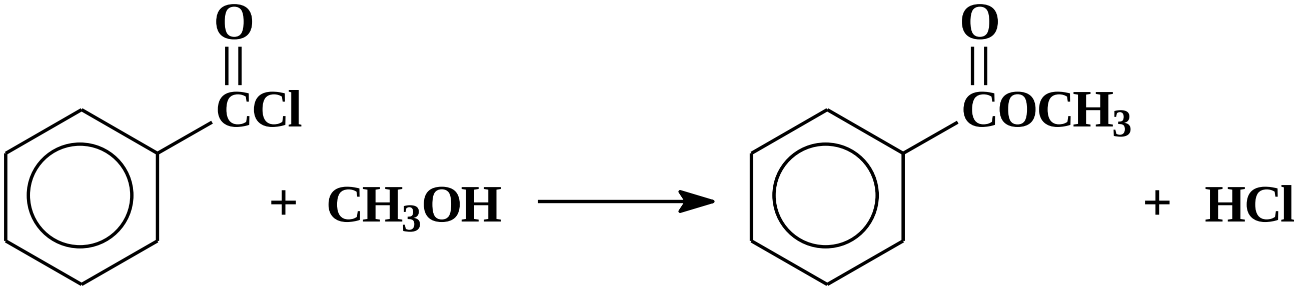
Esters from Acid Chlorides

- Acid chlorides react with alcohols to give esters in good yield.
- Mechanism is nucleophilic addition of the alcohol to the carbonyl as chloride ion leaves, then deprotonation.



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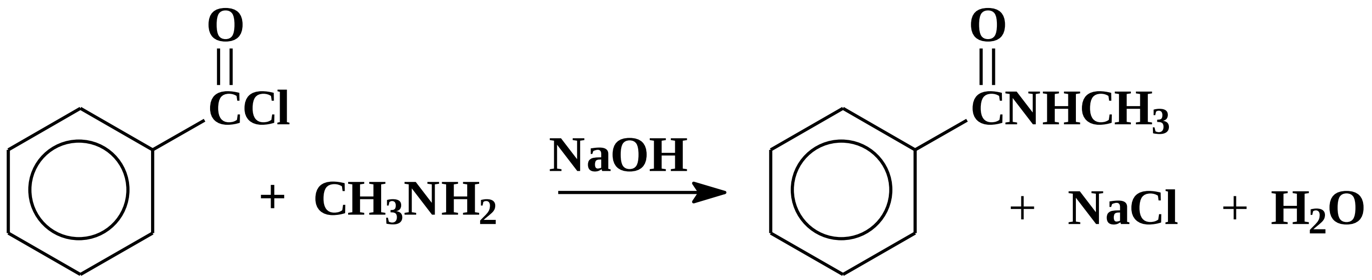
Amides from Acid Chlorides

- Acid chlorides react with ammonia and amines to give amides.
- A base (NaOH or pyridine) is added to remove HCl by-product.



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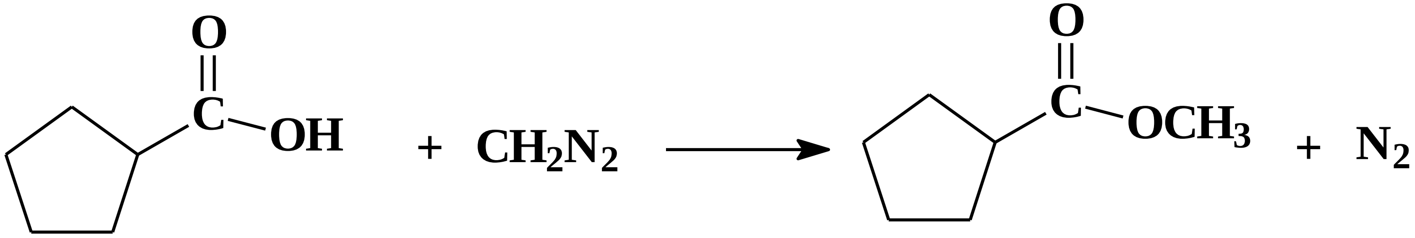
Diazomethane

- CH_2N_2 reacts with carboxylic acids to produce methyl esters quantitatively.
- Very toxic, explosive. Dissolve in ether.



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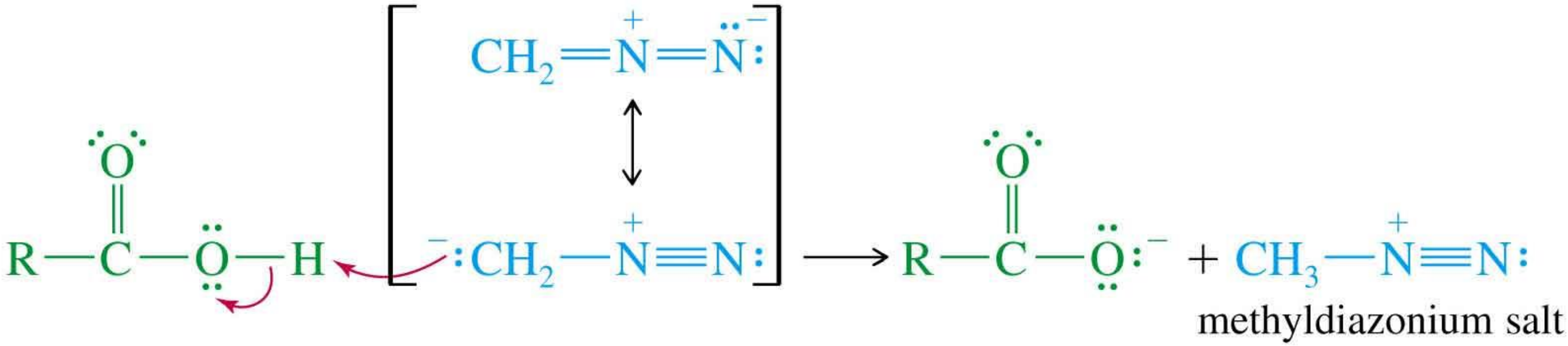
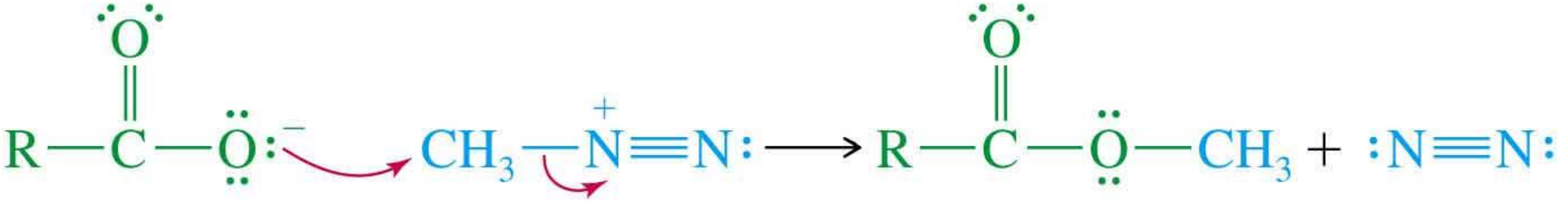
Mechanism for Diazomethane

Step 1: Proton transfer



Step 2: Nucleophilic attack on the methyl group



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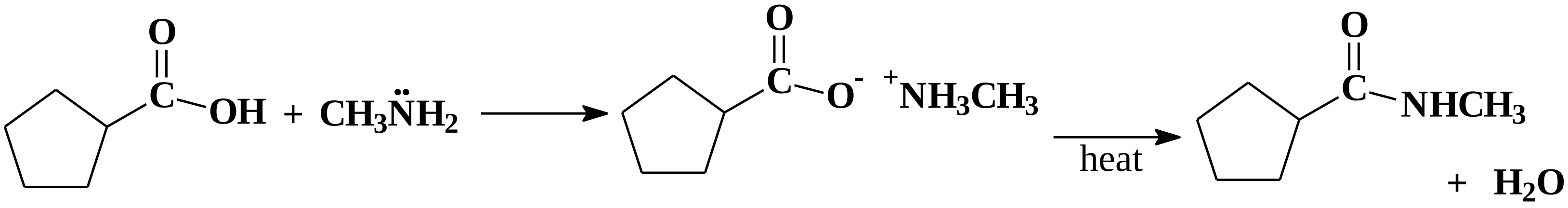
Amides from Acids

- Amine (base) removes a proton from the carboxylic acid to form a salt.
- Heating the salt above 100°C drives off steam and forms the amide.



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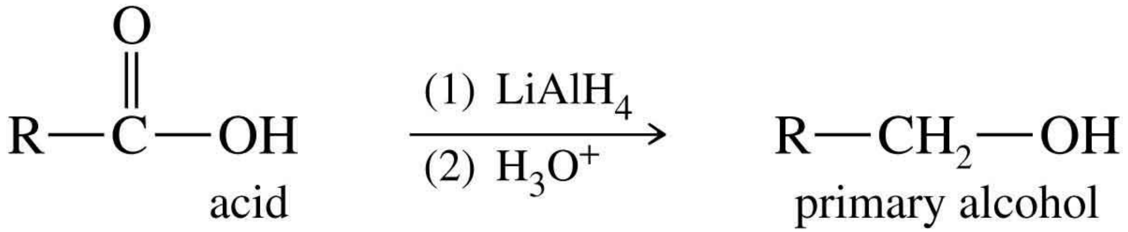
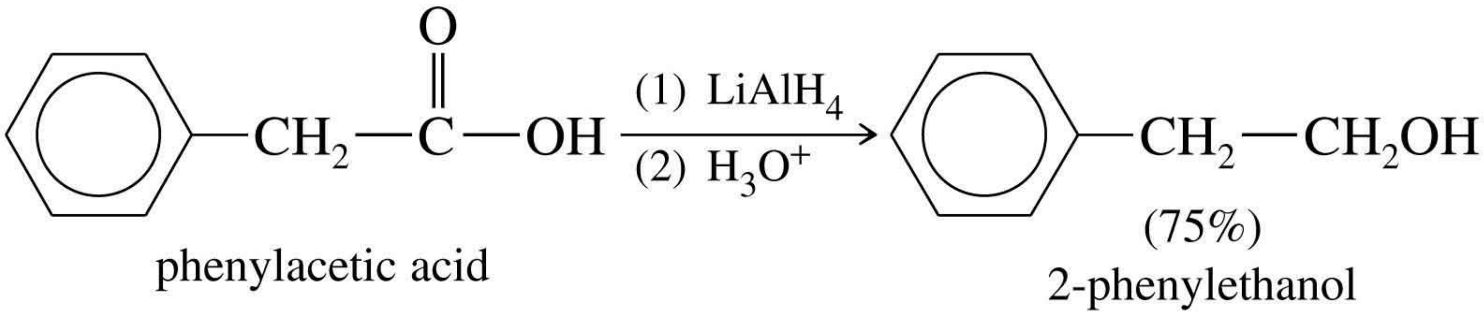
Reduction to 1° Alcohols

- Use strong reducing agent, $LiAlH_4$.
- Borane, BH_3 in THF, reduces carboxylic acid to alcohol, but does not reduce ketone.



$$R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[(2)\ H_3O^+]{(1)\ LiAlH_4} R-CH_2-OH$$

Example



phenylacetic acid

2-phenylethanol

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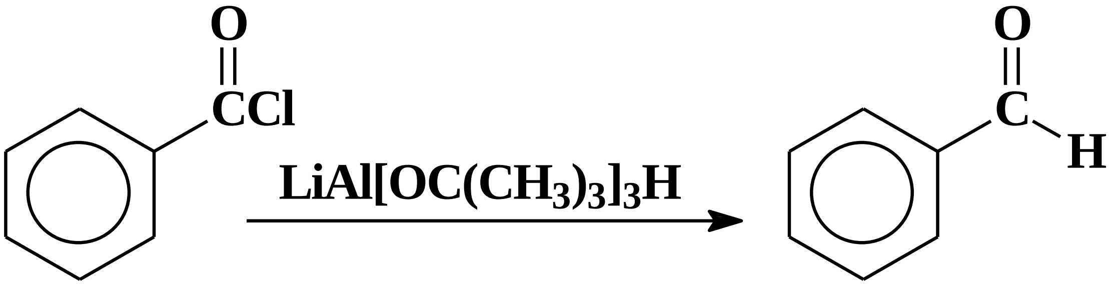
Reduction to Aldehyde

- Difficult to stop reduction at aldehyde.
- Use a more reactive form of the acid (an acid chloride) and a weaker reducing agent, lithium aluminum tri(*t*-butoxy)hydride.



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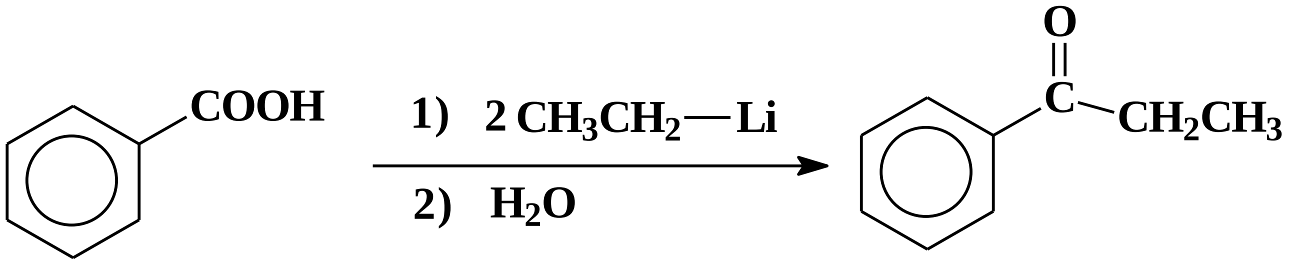
Alkylation to Form Ketones

React 2 equivalents of an organolithium reagent with a carboxylic acid.



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