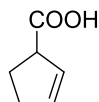
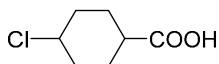
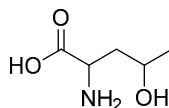
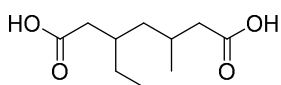
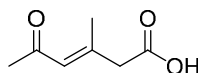
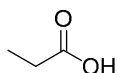


Chapter 13: Carboxylic Acids

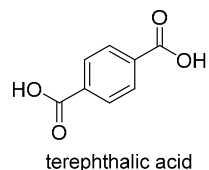
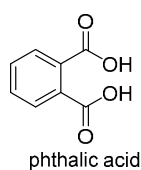
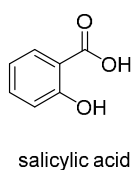
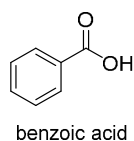
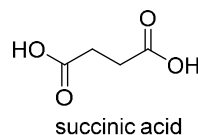
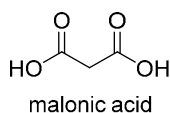
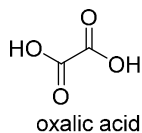
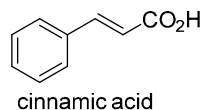
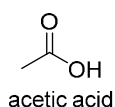
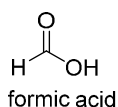
13.1 Nomenclature of Carboxylic Acids (IUPAC)

1. Find longest chain containing the carboxylic acid
2. Replace -e with -oic acid
3. Number the chain starting from the carboxylic acid carbon
4. Dicarboxylic acids are named by adding *di* to the suffix (dioic acid)
5. A carboxylic acid containing an aliphatic ring with the carboxylic acid directly bound to it is named by giving the name of the ring and adding carboxylic acid to it. Being the highest priority group, the ring carbon attached to the -CO₂H will be given the locant 1.
6. The simplest aromatic carboxylic acid is benzoic acid. Substituents can be added to the name with the appropriate locants. (Rules Chapter 9)
7. Aromatic dicarboxylic acids are named by adding *dicarboxylic acid* to *benzene*. Many have common names.



13.1

IUPAC and common names:



13.2

13.2 Properties of Carboxylic Acids**a) Hydrogen Bonding**

Strong H-bonding results in dimer formation in solids and non-polar solvents.

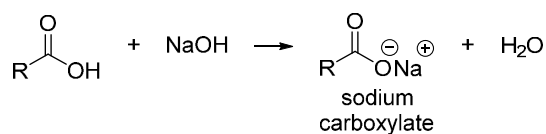
Significantly higher boiling points compared to alkanes or alkyl halides

Good solubility in polar solvents.

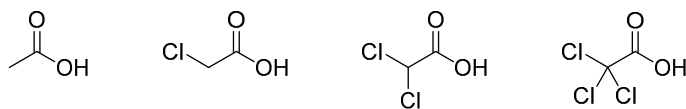
13.3

b) Acidity

Carboxylic acids are more acidic than alcohols due to resonance stabilization in the resulting carboxylate.

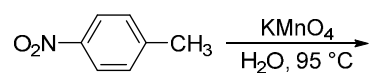
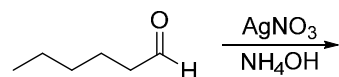
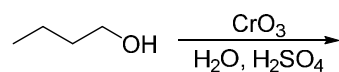


Electron-withdrawing groups increase the acidity through inductive effects:

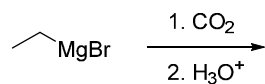


Benzoic acids are more acidic than aliphatic carboxylic acids.

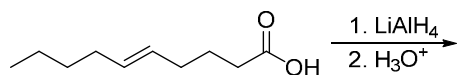
13.4

13.3 Synthesis of Carboxylic Acids**a) Oxidation of Benzylic Carbons gives Benzoic Acid Derivatives****b) Oxidation of Aldehydes with Silver(I)****c) Oxidation of Primary Alcohols to Carboxylic Acids**

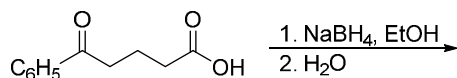
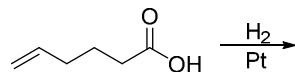
13.5

d) Addition of Grignard Reagents to Carbon Dioxide

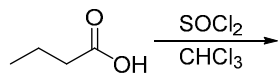
13.6

13.4 Reactions of Carboxylic Acids**a) Reduction of Carboxylic Acids to Primary Alcohols**

- Much slower than aldehyde or ketone reductions
 - LiAlH_4 must be used instead of NaBH_4
 - Attention: Any aldehydes, ketones, esters, acid chlorides or acid anhydrides will also be reduced
- Selective reductions of other functional groups in the presence of carboxylic acids.
- The carboxylic acid group is inert to hydrogenation.
 - Carboxylic acids are not reduced by NaBH_4 and LiBH_4

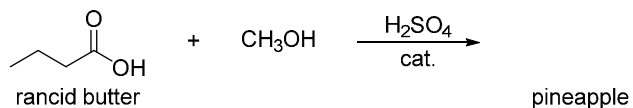


13.7

b) Conversion of Carboxylic Acids to Acid Chlorides

13.8

c) Conversion of Carboxylic Acids to Esters (Fischer Esterification)

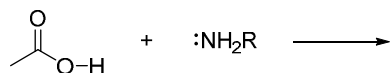


The Fischer esterification is reversible.

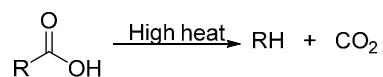
Removal of the resulting water byproduct draws the equilibrium to the side of the ester.

d) Conversion of Carboxylic Acids to Amides

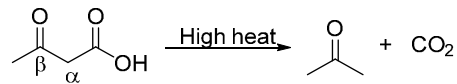
Direct conversion of carboxylic acids to amides is difficult because any amine will react with the carboxylic acid in an acid-base reaction.



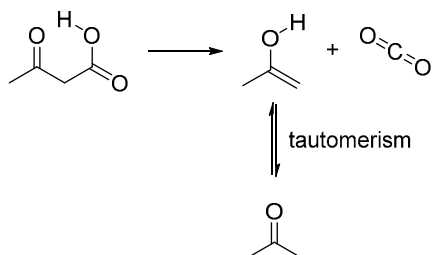
The most successful route is to first convert the carboxylic acid to an ester and then convert the ester to an amide. This is also how coupling agents (peptide synthesis) operate.

e) Decarboxylation Reactions

β-ketoacids are particularly prone to decarboxylate upon heating.

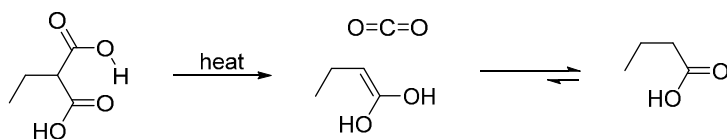


Mechanism:



13.11

β-dicarboxylic acid also decarboxylate easily:



13.12