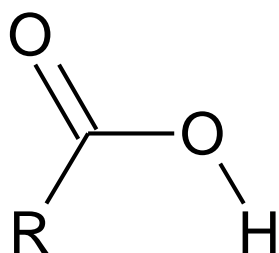


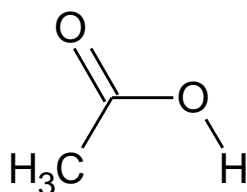
CHM 224 – ORGANIC CHEMISTRY I

CARBOXYLIC ACID AND DERIVATIVES

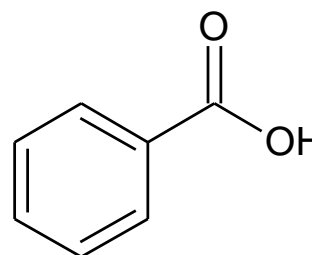
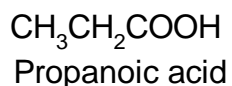
Alkanoic acids also known as carboxylic acids combine both carbonyl and a hydroxyl groups on the same carbon called a carbonyl group. Because they are distinctly acidic, they are called carboxylic acids.



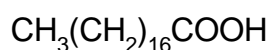
Structure and general formular of carboxylic Acid



Ethanoic (acetic) acid



benzoic acid



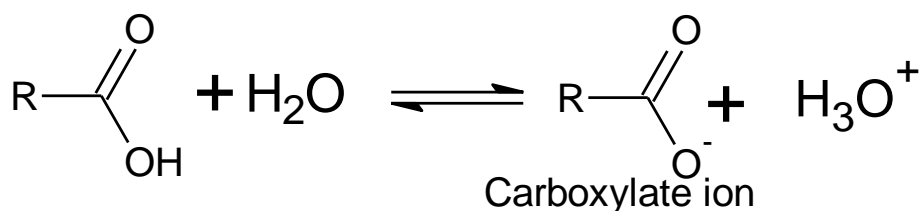
Stearic acid (fatty acid)

Note

Fatty acids are long chain aliphatic acids with even number of carbon atoms derived from the hydrolysis of fats and oils.

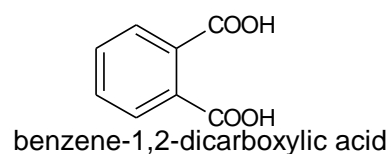
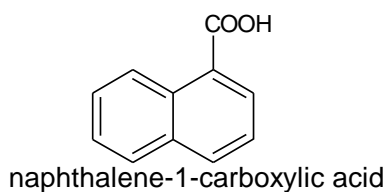
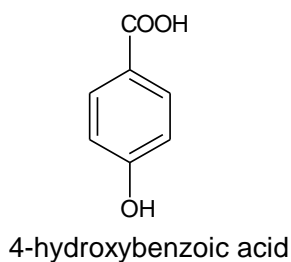
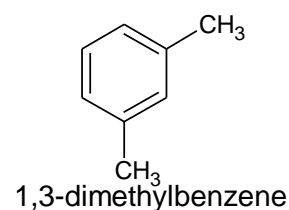
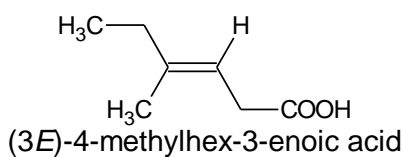
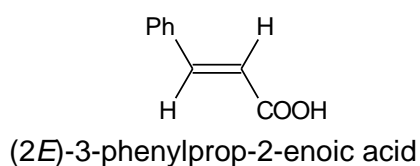
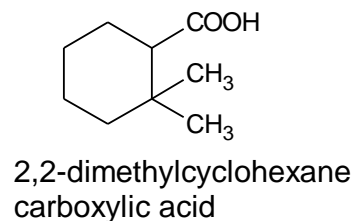
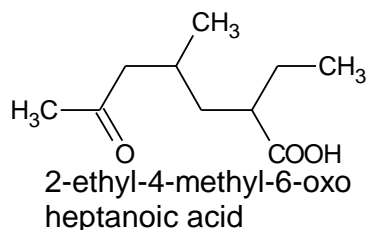
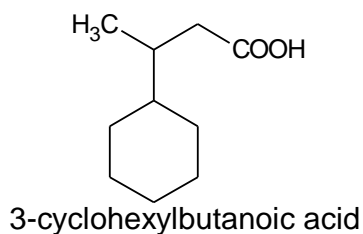
Acidity of Carboxylic acids

The acidity of carboxylic acids depends on the electrophilic character of the carbonyl carbon. If this character is decreased, the acidity of the carboxylic acid will also decrease. Similarly, an increase in its electrophilicity will increase the acidity of the acid. Acetic acid is ten times weaker an acid than formic acid.



NOMENCLATURE

In naming carboxylic acids, IUPAC rule is used, and the carboxyl group takes priority over any of the other functional groups. Some examples are given below:



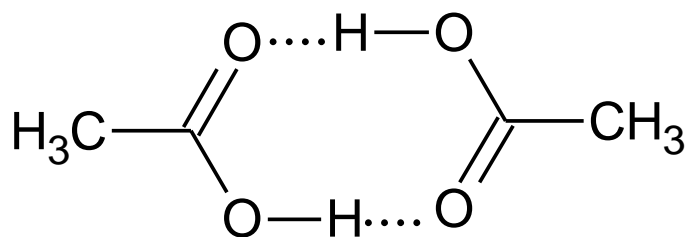
STRUCTURE

Formic acid is the most stable -COOH and the entire molecule is planar. i.e. the sp^2 hybrid carbonyl carbon is planar, with nearly trigonal bond angles. The -OH bond lies in this plane with the C=O bond.

PROPERTIES OF CARBOXYLIC ACIDS

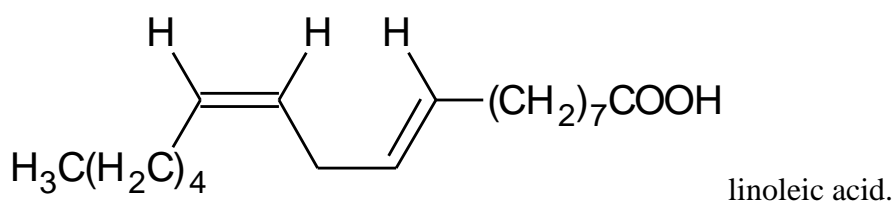
BOILING POINTS

COOH boils at considerably higher temperatures than alcohols, aldehydes and ketones of similar molecular weights. Example, acetic acid (MW 60) boils at 118 °C, 1-propanol and propanal both boils at 97 °C and 49 °C respectively. This can be explained from the formation of a stable, hydrogen bonded dimer which contain an 8-membered ring joined by 2 hydrogen bonds, effectively doubling the MW of the molecule leaving the liquid phase.



MELTING POINTS

Acids containing more than eight carbon atoms are generally solids, except they contain double bonds. The presence of double bonds (especially cis) in a long chain impedes formation of a stable crystal lattice, resulting in a lower melting point. Example, both stearic (octadecanoic) acid and linoleic (cis, cis-9,12-octadecenoic acid) have 18 carbon atoms. But stearic melts at 70 °C while linoleic acid melts at -5 °C.



Note:

The melting point of diacids are relatively high because the forces of hydrogen bonding are particularly strong.

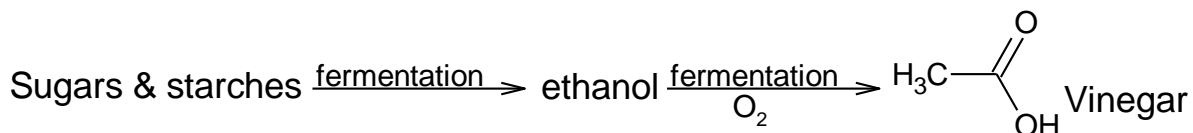
SOLUBILITIES

COOHs form hydrogen bonds with water. The lower MW acids (up through 4 carbon atoms) are miscible with water. As the length of the HC chain increases, water solubility decreases until acids with more than 10 carbon atoms are nearly insoluble in water.

COOHs are very soluble in alcohols because the acids form hydrogen bonds with alcohols. Also, most COOHs are quite soluble in relatively non-polar solvents such as chloroform because they continue to exist in their dimeric form in the non-polar solvent.

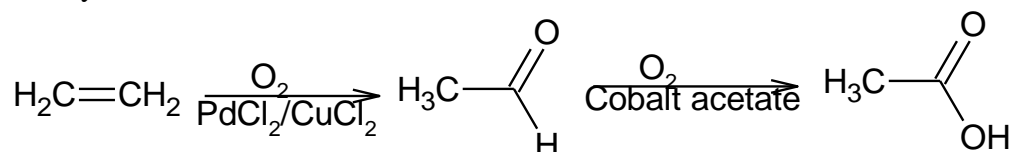
PREPARATIONS

1. The most important commercially aliphatic acid is acetic acid. Vinegar (5% aq. solution of acetic acid) used in cooking and in prepared foods such as ketchup and salad dressings is produced by fermentation of sugar and starches.



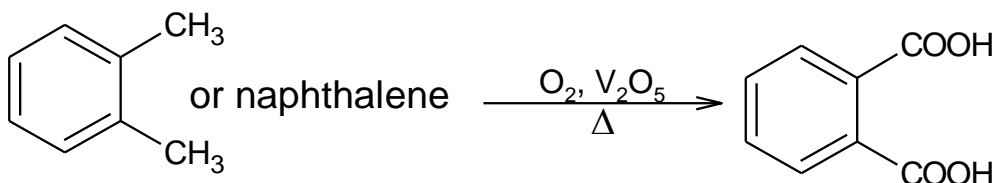
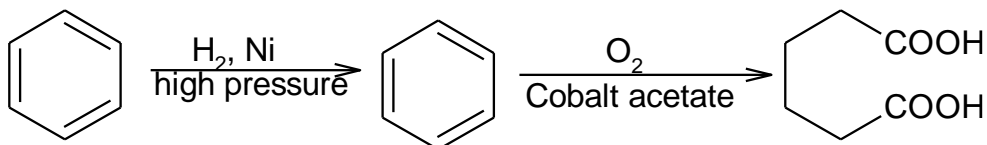
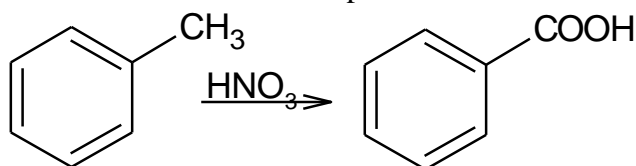
2. Oxidations

- a. Catalytic oxidation of alkenes

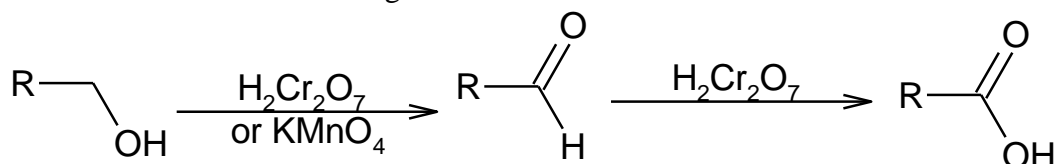


- b. Oxidative cleavage of alkenes

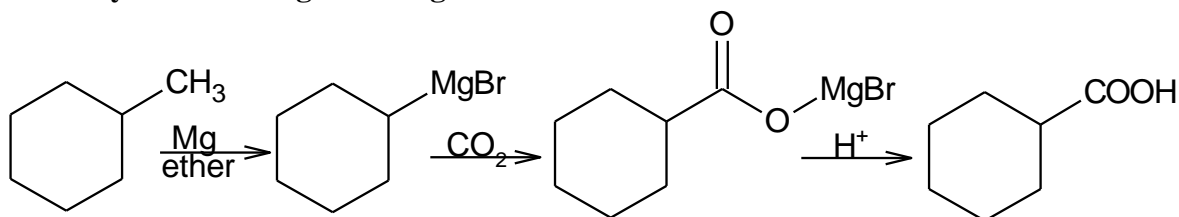
- c. Oxidation of Aromatic compounds



- d. Oxidation of primary alcohols – oxidation of primary alcohol gives an aldehyde which when further oxidised gives an acid.

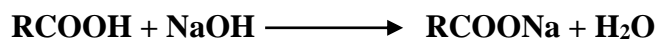
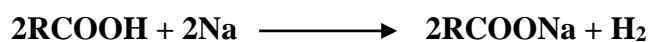


3. Carboxylation of Grignard reagents



REACTIONS OF COOHS & DERIVATIVES

1. Reactions involving the cleavage of O-H bond.



2. Reactions involving the cleavage of C-O bond – Nucleophilic substitution reactions:

a. **ESTER FORMATION**

b. **AMIDE FORMATION**

c. **ACID HALIDE FORMATION**

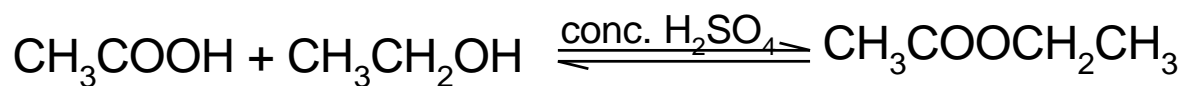
d. **ACID ANHYDRIDE FORMATION**

e. **ACID NITRILE**

3. Reactions involving the cleavage of the whole carbonyl group.

4. Reactions involving the alkyl group of the carbonyl compound.

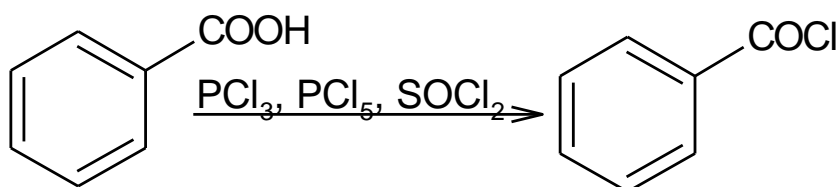
ESTER FORMATION



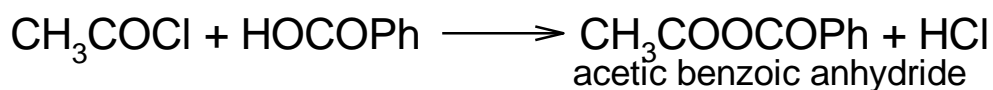
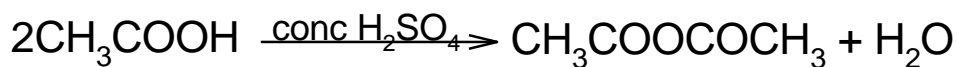
Amide formation



Acid halide formation



Formation of acid anhydride



Formation of Acid Nitrile

