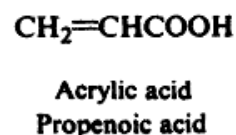
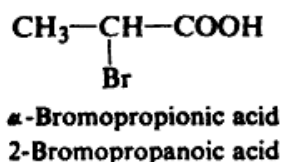
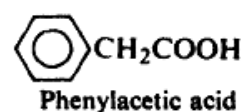
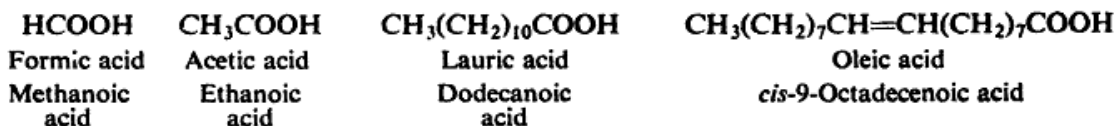




Carboxylic Acids

Structure

These compounds contain the carboxyl group attached to either an alkyl group (RCOOH) or an aryl group (ArCOOH). For example:



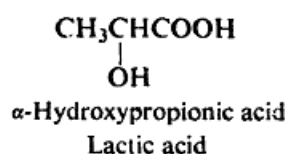
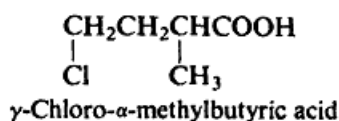
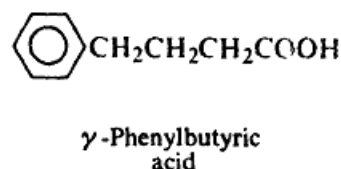
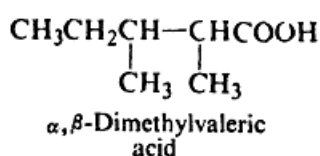
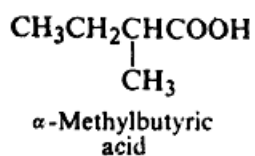
Nomenclature

The aliphatic carboxylic acids have been known for a long time, and as a result have common names that refer to their sources rather than to their chemical structures. For example: formic acid, acetic acid, butyric acid etc.

Branched-chain acids and substituted acids are named as derivatives of the straight chain acids. To indicate the position of attachment, the Greek letters α -, β -, γ -, δ - etc., are used; the α -carbon is the one bearing the carboxyl group,

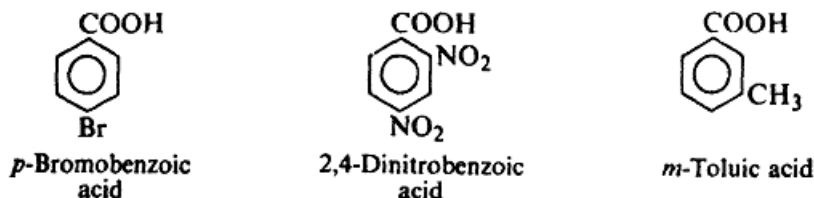


For example:

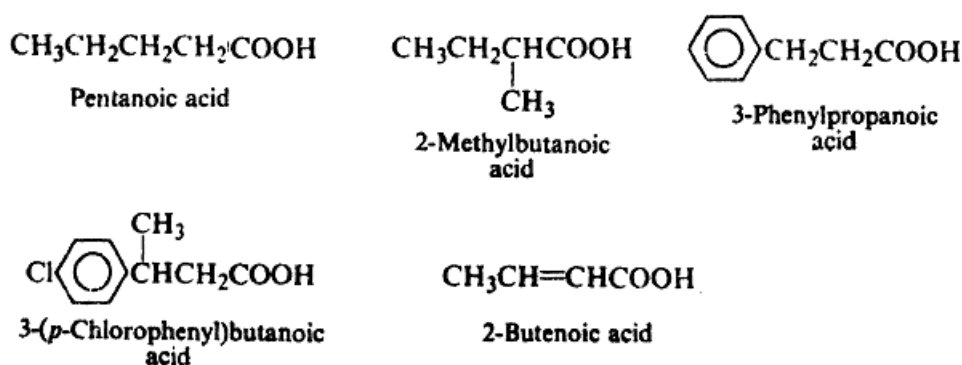




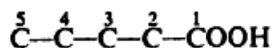
Aromatic acids, ArCOOH , are usually named as derivatives of the parent acid, benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$. The methyl benzoic acids are given the special name of toluic acids.



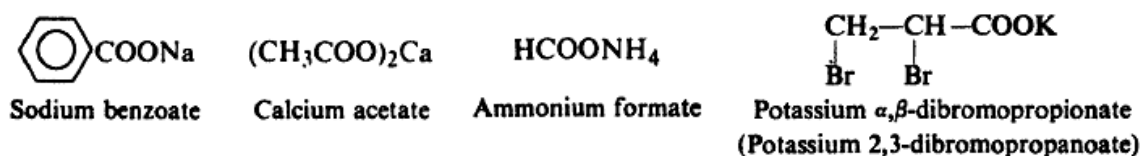
The IUPAC names follow the usual pattern. The longest chain carrying the carboxyl group is considered the parent structure, and is named by replacing the -e of the corresponding alkane with -oic acid. For example:



The position of a substituent is indicated as usual by a number. We should notice



The name of a salt of a carboxylic acid consists of the name of the cation (sodium, potassium, ammonium, etc.) Followed by the name of the acid with the ending -ic acid changed to -ate. For example:



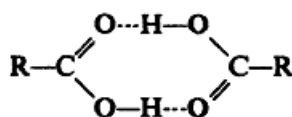
Physical properties

Carboxylic acid molecules are polar and like alcohol molecules can form hydrogen bonding with each other and with other kinds of molecules. The aliphatic acids therefore show very much the same solubility behavior as the alcohol: the first four are miscible with water, the five -carbon acid is partly soluble, and the higher acids are virtually insoluble. Water



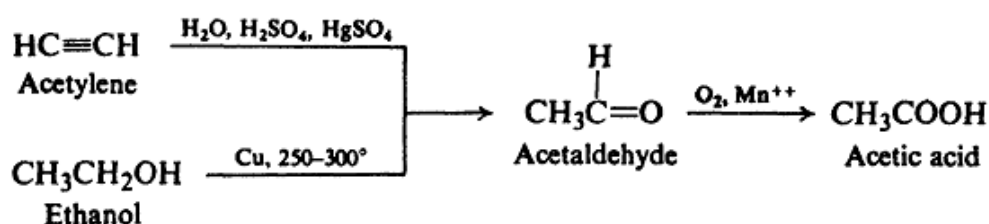
solubility undoubtedly arises from hydrogen bonding between the carboxylic acid and water. The simplest aromatic acid, benzoic acid, contains too many carbon atoms to show appreciable solubility in water. Carboxylic acids are soluble in less polar solvents like ether, alcohol, benzene, etc.

We can see that the carboxylic acids are even higher boiling than alcohols. For example, propionic acid (B.P. 141) boils more than twenty degrees higher than the alcohol of comparable molecular weight, n-butyl alcohol (b.p.118). These very high boiling points are due to the fact that a pair of carboxylic acid molecules is held together not by one but by two hydrogen bonds:



Industrial source

Acetic acid, by far the most important of all carboxylic acids, is prepared by air oxidation of acetaldehyde, which is readily available from the hydration of acetylene or the dehydrogenation of ethanol.

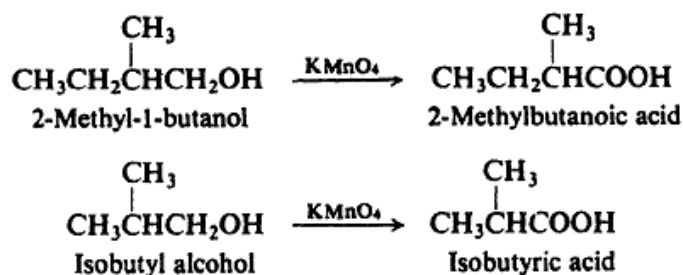


The most important sources of aliphatic carboxylic acids are the animal and vegetable fats. From fats there can be obtained, in purity of over 90%, straight-chain carboxylic acids of even carbon number ranging from six to eighteen carbon atoms.

Preparation

1. Oxidation of primary alcohols.

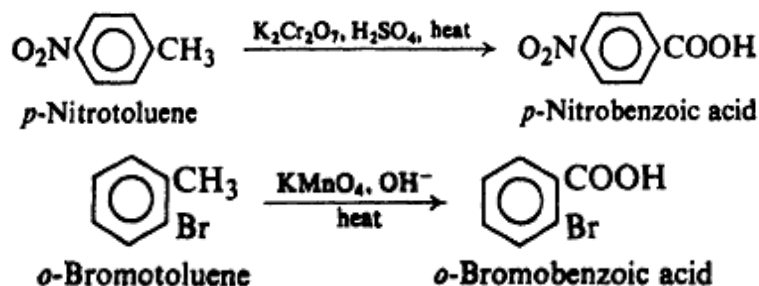
Examples:





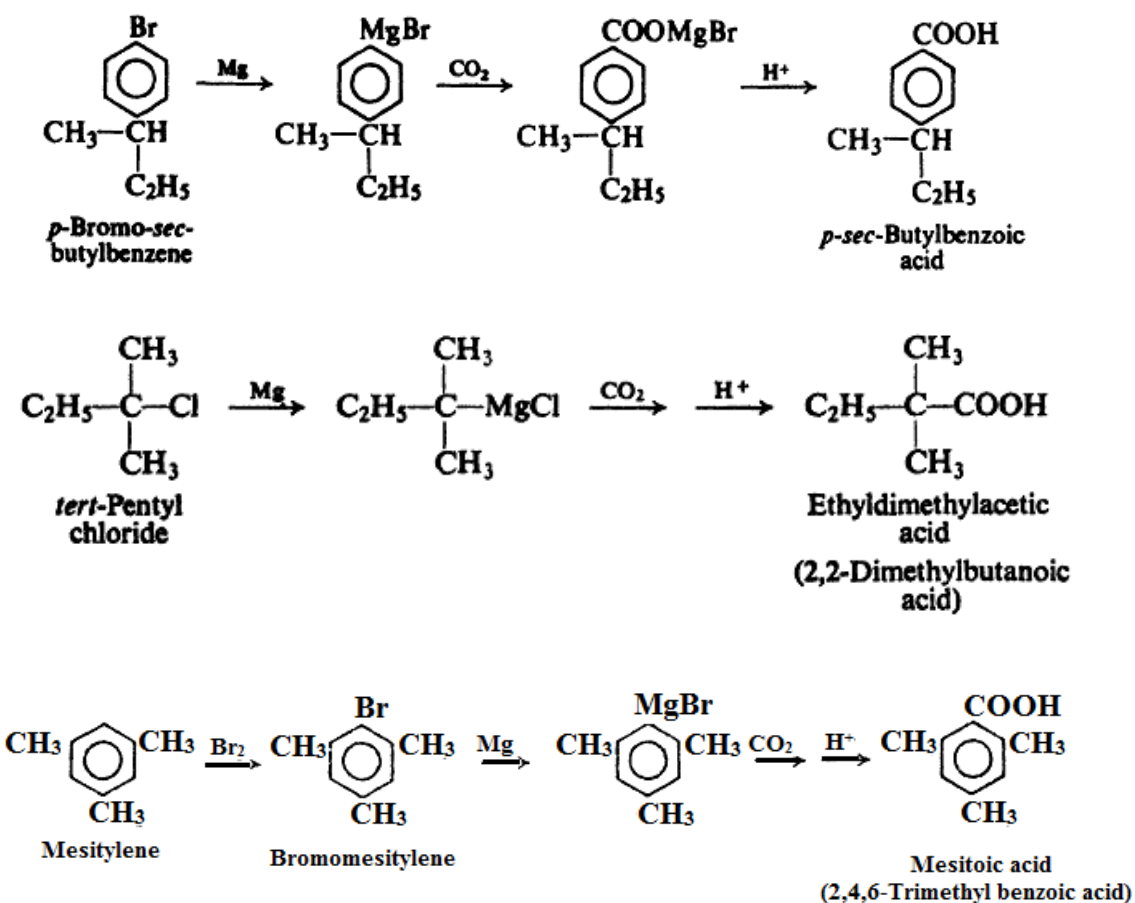
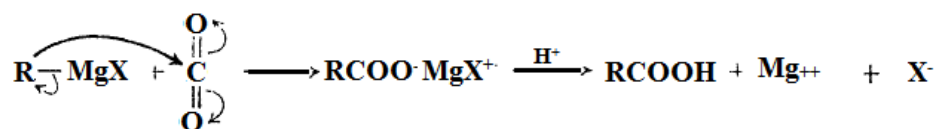
2. Oxidation of alkyl benzenes.

Examples:



3. Carbonation of Grignard reagents.

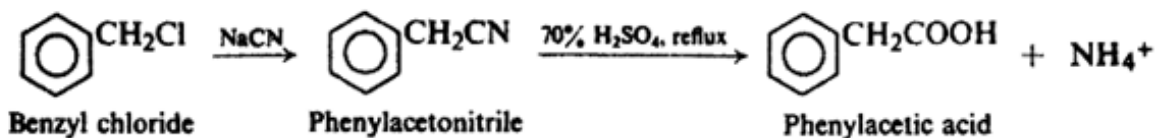
The Grignard reagent adds to the carbon-oxygen double bond just as in the reaction with aldehydes and ketones. The product is the magnesium salt of the carboxylic acid, from which the free acid is liberated by treatment with mineral acid.



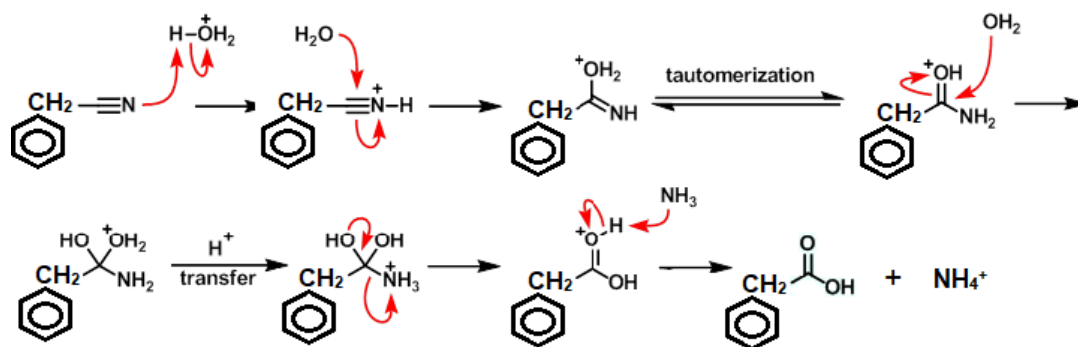


4. Hydrolysis of nitrites.

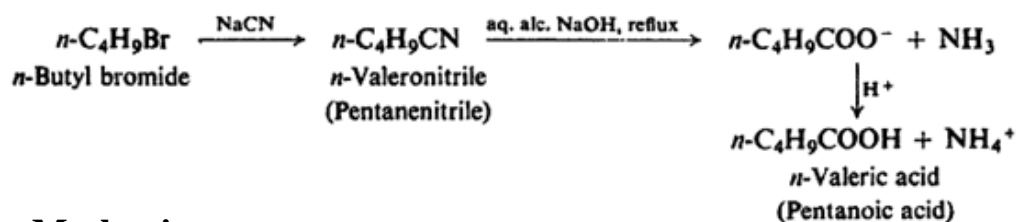
a- acidic hydrolysis of nitriles



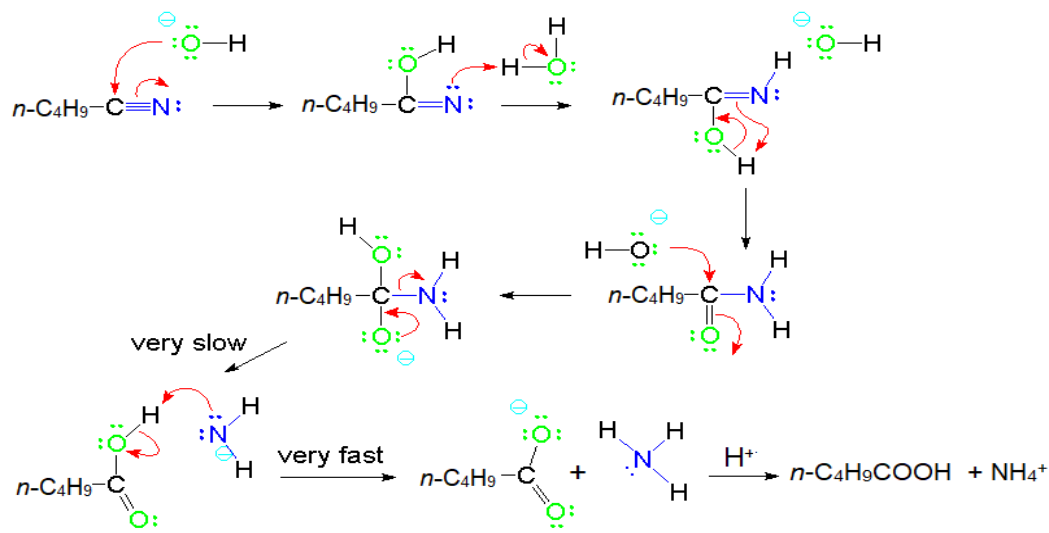
mechanism:



b- basic hydrolysis of nitriles



Mechanism:



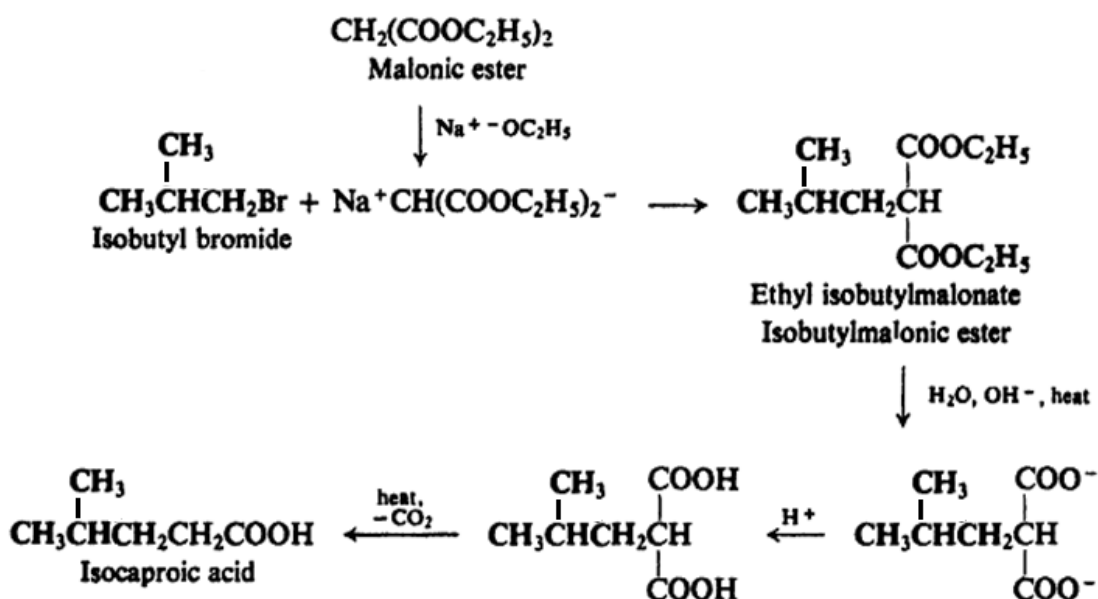


5. Malonic ester synthesis.

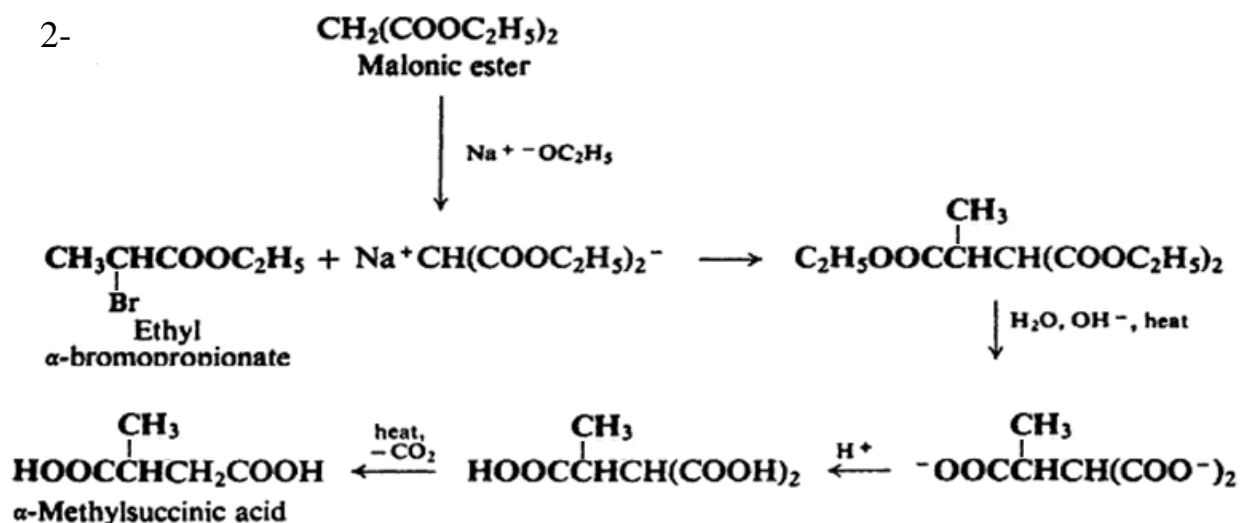
One of the most valuable methods of preparing carboxylic acids makes use of ethyl malonate (Malonic ester) $\text{CH}_2(\text{COOC}_2\text{H}_5)_2$ and is called the **malonic ester synthesis**. This reaction involves nucleophilic attack on the alkyl halide by the carbanion $\text{CH}(\text{COOC}_2\text{H}_5)_2^-$, and, gives highest yields primary alkyl halides, lower yields with secondary alkyl halides, and is worthless for tertiary alkyl halides and for aryl halides .

Examples:

1-



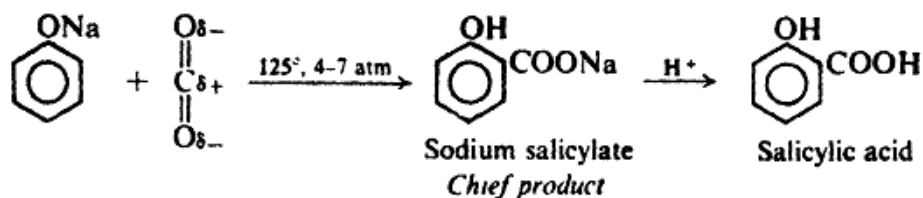
2-





6. Kolbe reaction. Synthesis of phenolic acids

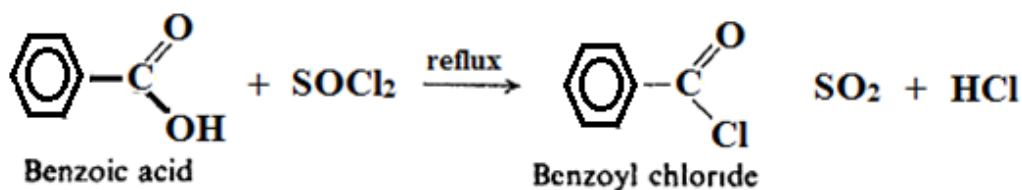
Treatment of the salt of a phenol with carbon dioxide brings about substitution of the carboxyl group, -COOH, for hydrogen of the ring. This reaction is known as the Kolbe reaction; its most important application is in the conversion of phenol itself into *P*-hydroxy benzoic acid



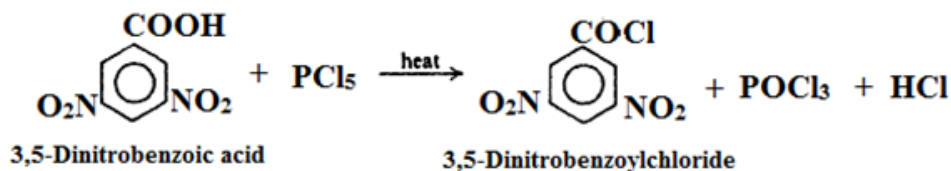
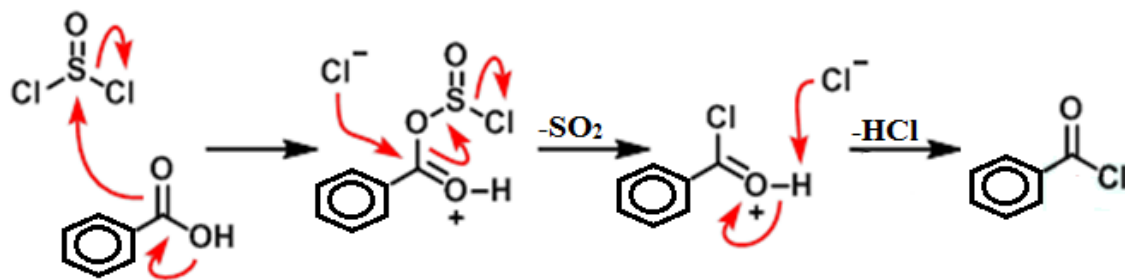
Reactions of Carboxylic acids

1. Conversion into functional derivatives

(a) Conversion into acid chlorides.



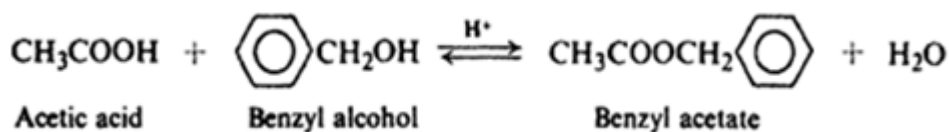
The mechanism:



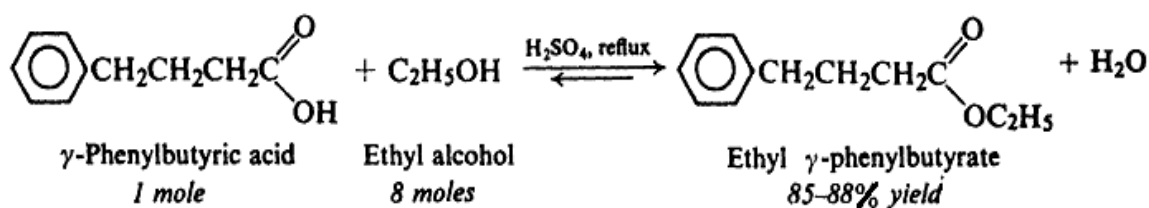
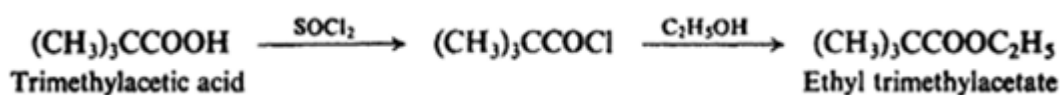
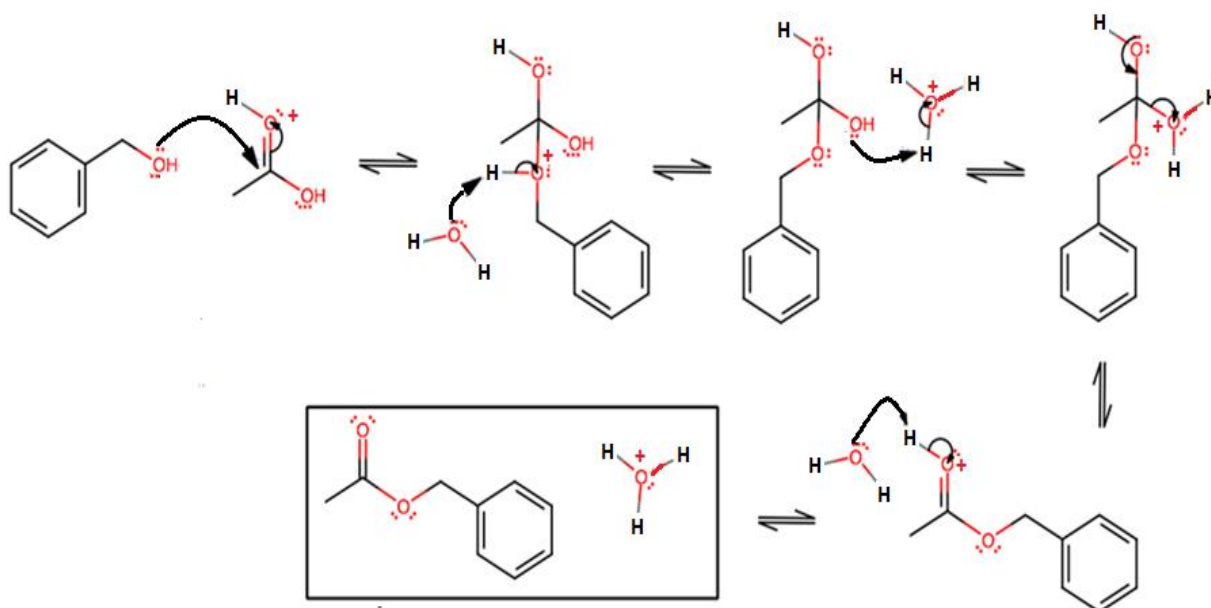
(b) Conversion into esters

A carboxylic acid is converted directly into an ester when heated with an alcohol in the presence of a little mineral acid, usually concentrated sulfuric acid or dry hydrogen chloride. This reaction is reversible, and

generally reaches equilibrium when there are appreciable quantities of both reactants and products present.

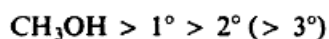


The mechanism:



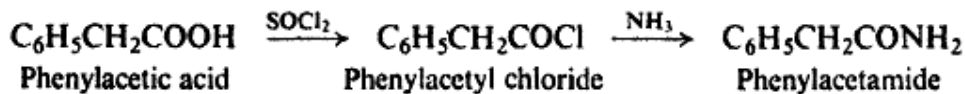
The presence of bulky groups near the site of reaction, whether in the alcohol or in the acid, slows down esterification (as well as its reverse, hydrolysis).

**Reactivity
in esterifi-
cation**





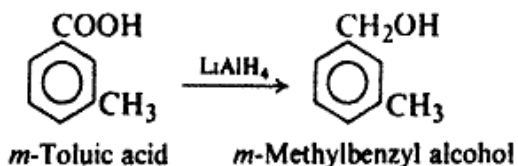
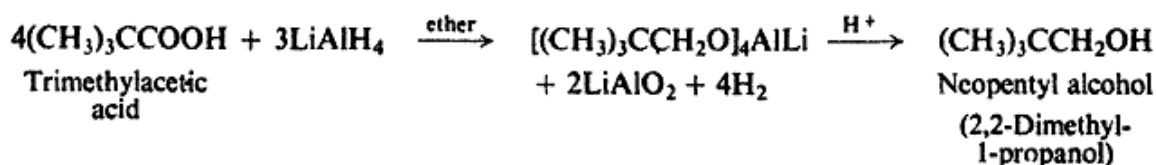
(c) Conversion into amides.



2. Reduction.

(a) Reduction of acids to alcohols

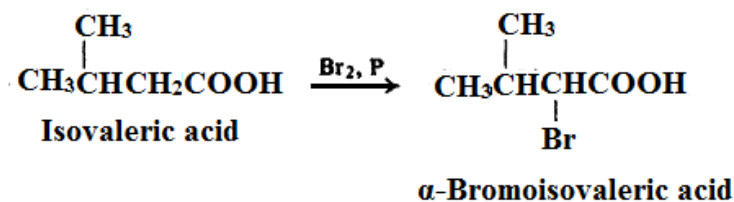
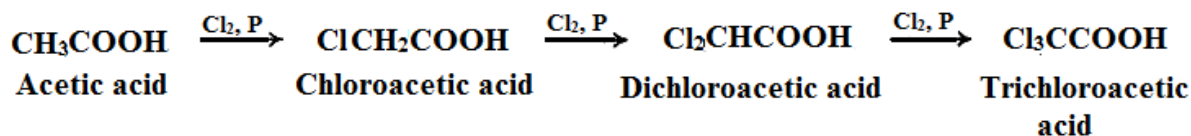
Lithium aluminum hydride LiAlH_4 is one of the few reagents that can reduce an acid to an alcohol; the initial product is an alkoxide from which the alcohol is liberated by hydrolysis:



3. Substitution in alkyl or aryl group

(a) Alpha-halogenation of aliphatic acids. Hell-Volhard-Zelinsky reaction.

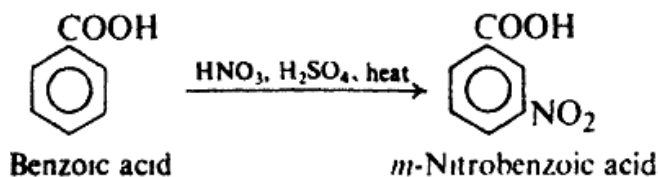
In the presence of a small amount of phosphorus, aliphatic carboxylic acids react smoothly with chlorine or bromine to yield a compound in which α -hydrogen has been replaced by halogen.





(b) Ring substitution in aromatic acids.

-COOH: deactivates, and directs meta in electrophilic substitution.



Dicarboxylic acids

If the substituent is a second carboxyl group, we have a dicarboxylic acid .

For example:

