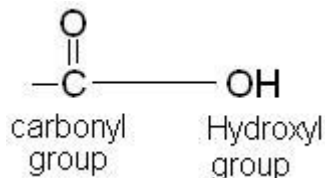


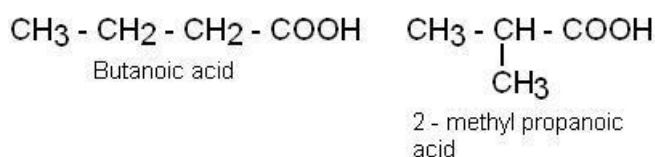
CARBOXYLIC ACIDS

Organic compounds containing carboxylic group $-\text{COOH}$ are called carboxylic acids.



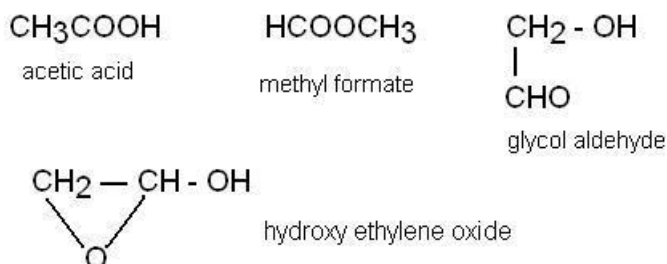
ISOMERISM IN CARBOXYLIC ACIDS

- (i) Chain isomerism: This is due to the difference in the structure of carbon chain



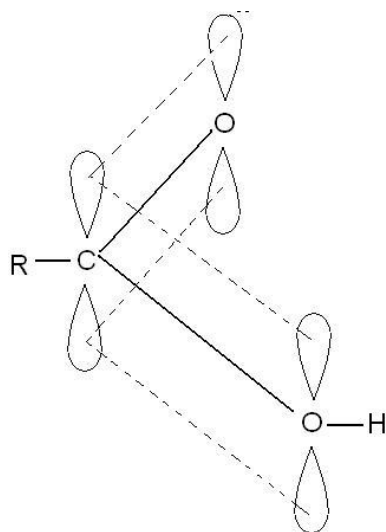
- (ii) Functional isomerism : Monocarboxylic acids show functional isomerism with esters of the acids, hydroxyl carbonyl compounds and hydroxyl oxiranes.

Example : $\text{C}_2\text{H}_4\text{O}_2$



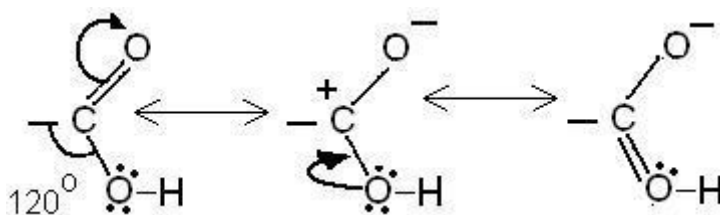
STRUCTURE OF CARBOXYLIC ACID

- Carbon atom of carboxyl group is sp^2 – hybridized and forms one σ - bond with hydrogen or carbon atom depending upon the structure of carboxylic acid. Half filled p-orbital of each oxygen atom and unhybridised p-orbital of carbon atom lies in the same plane and overlaps to form a π - bonds, one carbon and two oxygen atoms



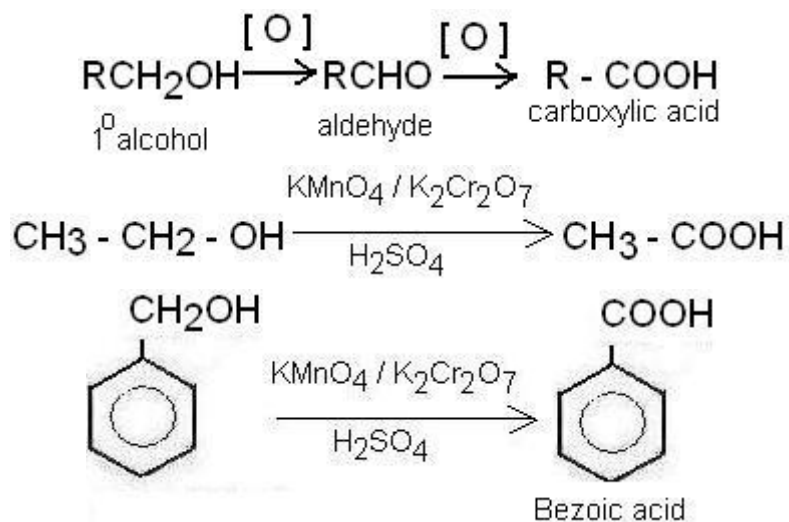
- In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120° . The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below.

CARBOXYLIC ACID



GENERAL METHOD OF PREPARATION OF CARBOXYLIC ACIDS

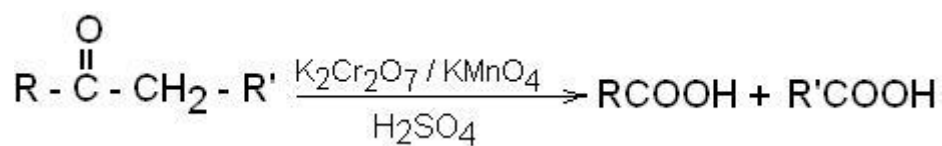
1. Oxidation of alcohols



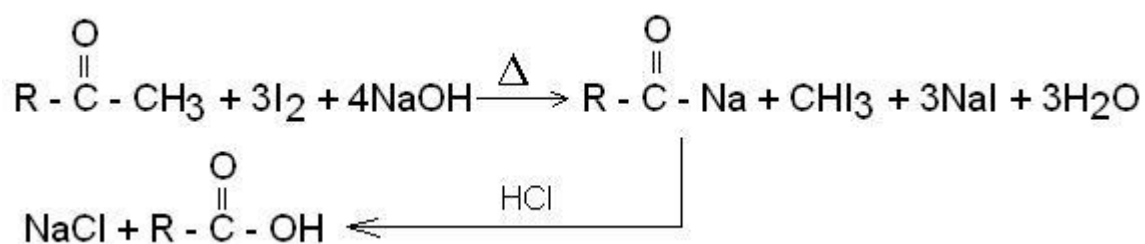
2. Oxidation of carbonyl compounds



Ketones can only be oxidized with strong oxidizing agents to mixture of carboxylic acid with lesser number of carbon atoms

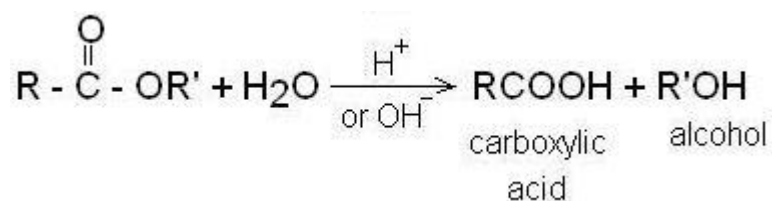


3. Haloform reaction

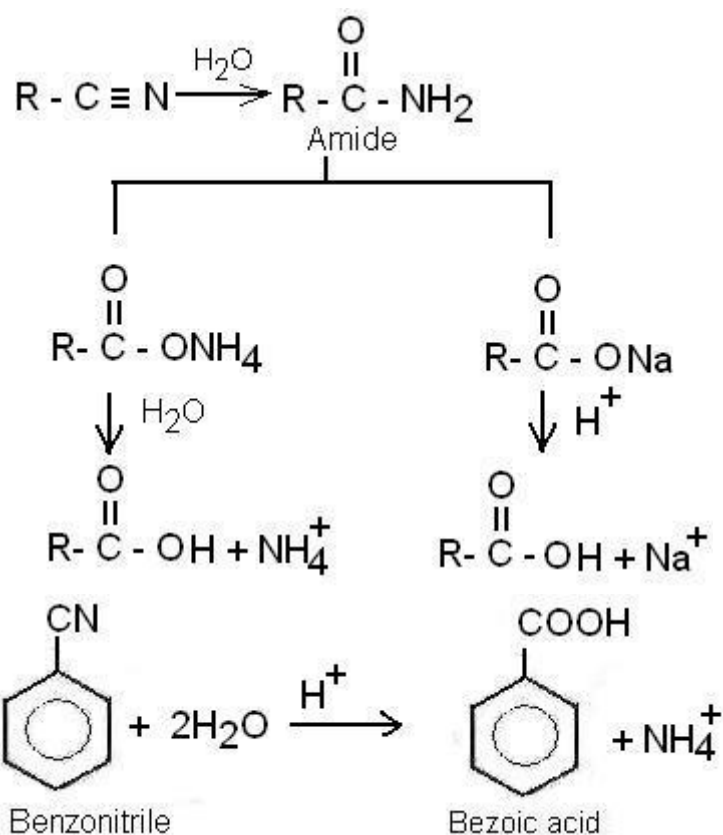


4. Hydrolysis of ester

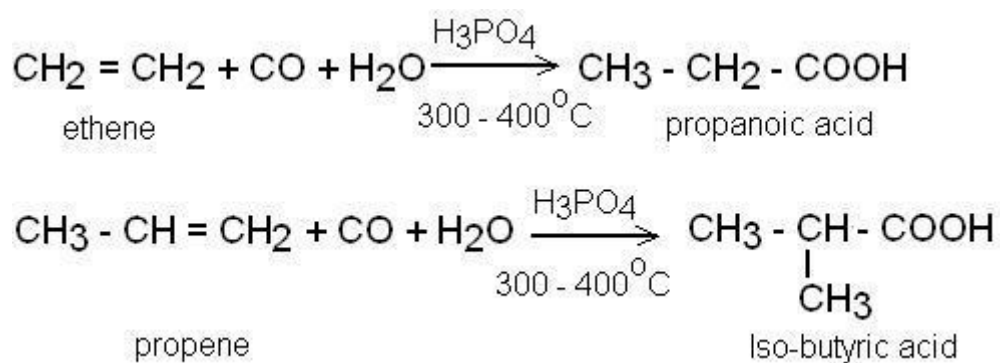
CARBOXYLIC ACID



5. Hydrolysis of nitriles



6. Koch reaction

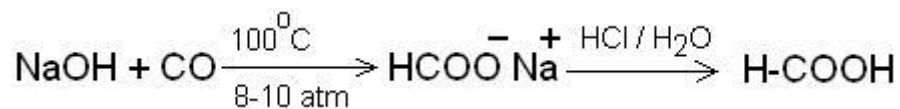


7. Carbonation of sodium alkoxide

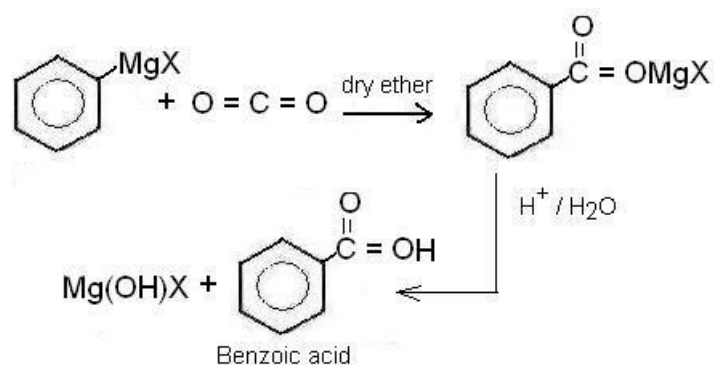
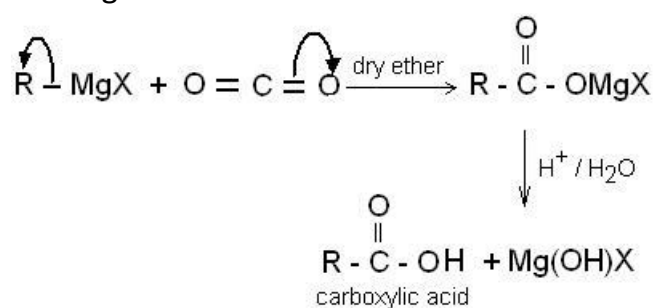
CARBOXYLIC ACID



Formic acid can be produced by carbonation of NaOH

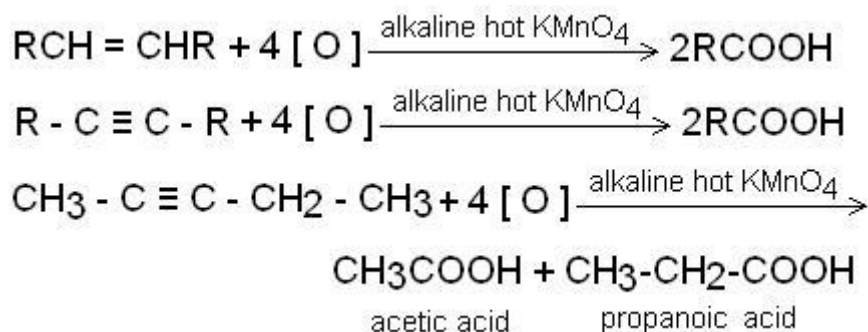


8. Carbonation of Grignard reagent

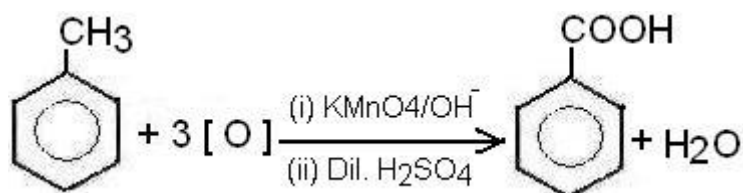


9. Oxidative cleavage of alkenes and alkynes

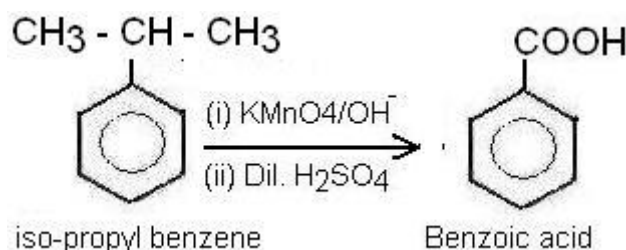
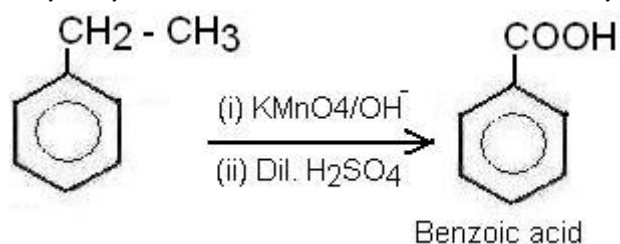
CARBOXYLIC ACID



10. Oxidation of alkyl benzene



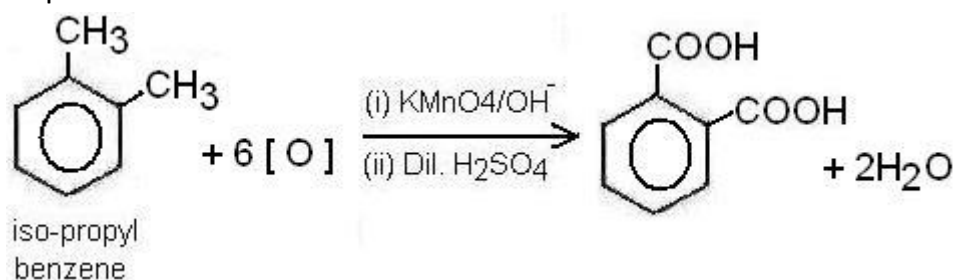
- During oxidation side chain is oxidised to $-\text{COOH}$ group irrespective of the length of the chain
- Only primary and secondary alkyl side chain are oxidized to carbonyl group



Greater the number of benzylic hydrogen atoms, greater is the ease of oxidation.

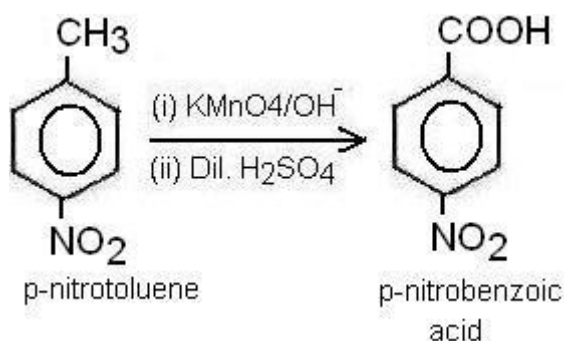
Thus order of ease of oxidation is $1^\circ > 2^\circ > 3^\circ$

If two alkyl groups are attached to benzene ring then each side chain is oxidized to carboxylic group

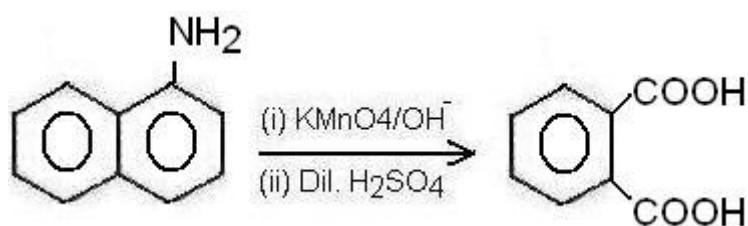


If an electron withdrawing group is present it stabilizes the benzene ring and oxidation produces substituted benzoic acid.

CARBOXYLIC ACID

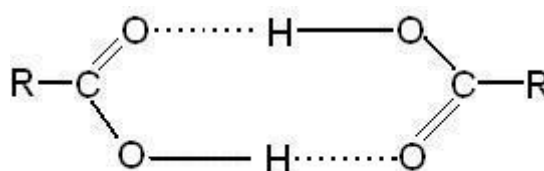


Whereas electron releasing group like $-\text{OH}$, $-\text{NH}_2$ destabilize the benzene ring and make it susceptible to oxidation.



PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

- First three members are colourless, pungent smelling liquids. Next members butyric acid has odour of rancid butter, whereas next five members (C_5 to C_9) have goat like odour. But higher member (above C_{10}) are colourless and odourless waxy solids due to low volatility acids are colourless, odourless solids.
- Lower aliphatic carboxylic acids ($\text{C}_1 - \text{C}_4$) are soluble in water due to H-bonding. Solubility decreases with increased molecular weight and $\text{C}_6\text{H}_{13}\text{COOH}$ is fairly soluble in water. Aromatic acids are nearly insoluble in water due to large hydrocarbon part.
- Carboxylic acid are polar in nature and exist as dimer in vapour state or in aprotic solvents due to formation of H-bonding.



Dimer of carboxylic acid

- Carboxylic acids have higher boiling point than hydrocarbons, aldehydes and ketones and alcohols comparable molecular hydrogen bonding.
- Carboxylic acids having even number of carbon atoms have higher melting points as compare to homologous member just above or below in the series containing odd number of carbon atoms. This is because of zig-zag carbon chain of

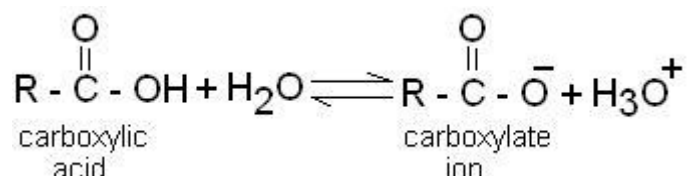
CARBOXYLIC ACID

even number of carbon atoms fit closely in crystal lattice, so that intermolecular forces of attraction increase and also melting point.

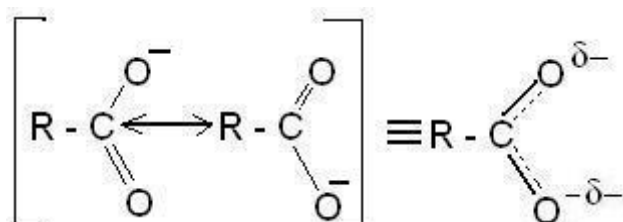
- Aromatic acids have higher melting and boiling point than aliphatic acids of comparable molecular weight due to close packing in crystal lattice.

ACIDIC STRENGTH OF CARBOXYLIC ACIDS

Carboxylic acids ionize in aqueous solution and exists in equilibrium with carboxylate ion.



Carboxylate ion is stabilized by resonance



Strength of carboxylic acids is expressed in terms of dissociation constant K_a

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}][\text{H}_2\text{O}]}$$

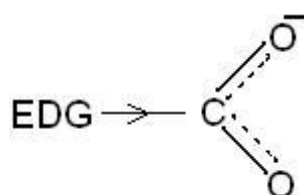
Greater the value of K_a , greater is the tendency to ionize and hence stronger the acid

$$\text{p}K_a = -\log K_a$$

Greater the value of K_a , smaller the value of $\text{p}K_a$ and hence stronger is the carboxylic acid.

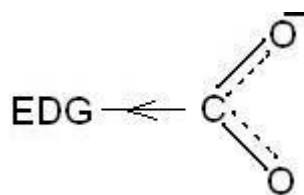
EFFECT OF SUBSTITUENT ON ACIDIC STRENGTH OF CARBOXYLIC ACIDS

Electron donating group (+I effect) destabilizes the carboxylate ion by intensifying the negative charge and thus decreases the acidic strength

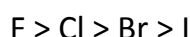


CARBOXYLIC ACID

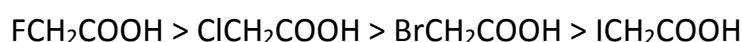
Electron withdrawing group (-I effect), stabilizes the carboxylate ion by dispersing negative charge on carboxylate ion and hence increases the acid strength



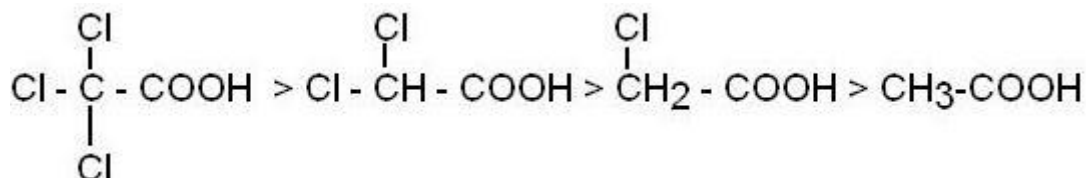
- Halogens are electron withdrawing nature and hence increase the acidic strength. -I effect of halogens decreases in the order.



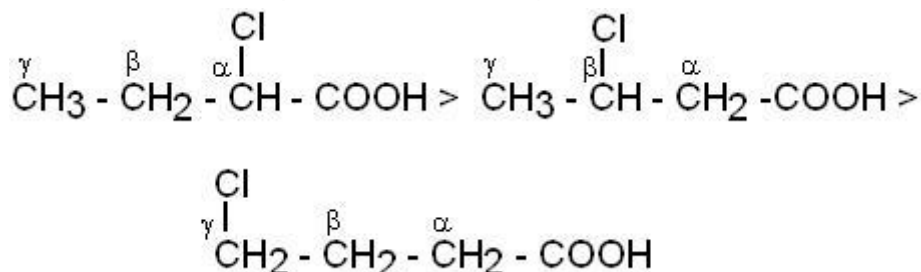
Hence acidic strength of α - haloacids decreases in the order



- Greater the number of electron withdrawing groups or halogens greater is the acidic strength thus



Effect of halogen group decrease as its distance from $-COOH$ group increases. Thus α - haloacid are more stronger than β - haloacids and γ - haloacids.



$CH \equiv C - CH_2COOH$ is stronger acid than $CH_2 = CH - CH_2COOH$ because in $C \equiv C$ bond carbon is sp hybridized which is more electronegative than sp^2 hybridised carbon of $-C=C-$.

Hence $-C \equiv C -$ exerts better electron withdrawing effect (-I) effect than $C = C$.

RELATIVE ACIDIC STRENGTH OF UNSUBSTITUTED ALIPHATIC AND AROMATIC ACIDS

Acidic strength of un-substituted aliphatic acid follows the order



Phenyl group directly attached to carboxyl group exerts -I effect which is weaker than +I effect of CH_3 of an alkyl group and hence acidic strength follows the order:

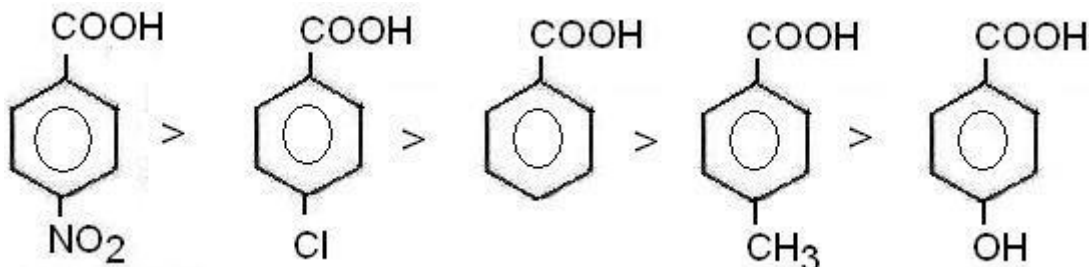


CARBOXYLIC ACID

But phenyl group attached to carboxyl group through some saturated carbon atom exerts weak electron withdrawing inductive effect (-I effect), so the acidic strength follows the order: Benzoic acid > phenyl acid > acetic acid.

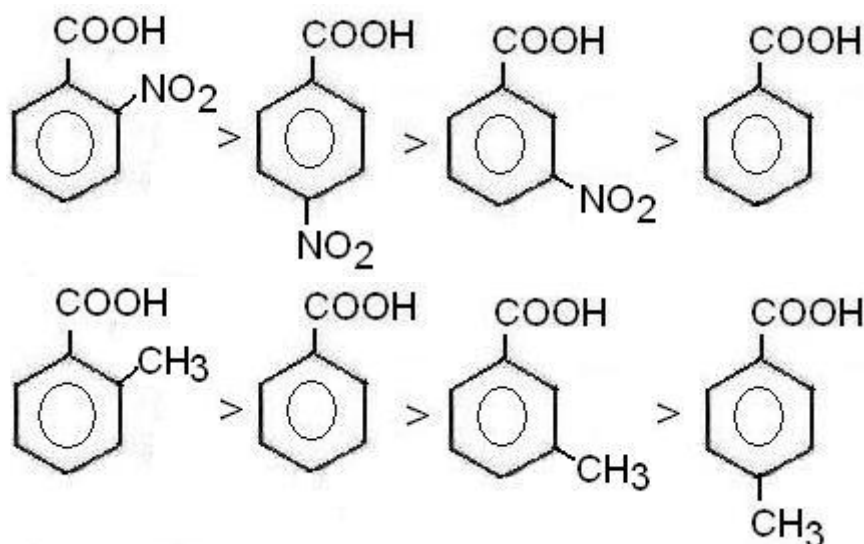
RELATIVE ACIDIC STRENGTH OF SUBSTITUTED AROMATIC ACIDS

Electron donating substituent (+I effect) decrease the acidic strength whereas electron withdrawing group (-I effect) increase the acidic strength of substituted benzoic acid thus,



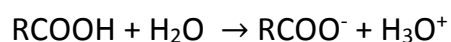
Ortho substituted acids are stronger than benzoic acid irrespective of the nature of the substituent.

Effect of any substituent is more pronounced at para-position than meta-position.

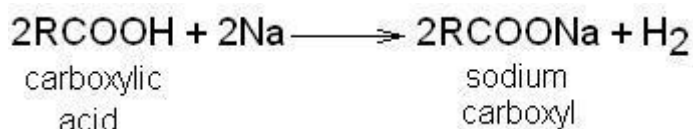


CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

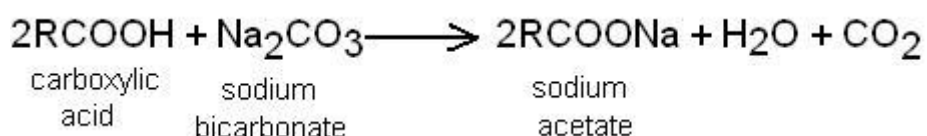
(A) Reactions due to H-atom of carboxyl group



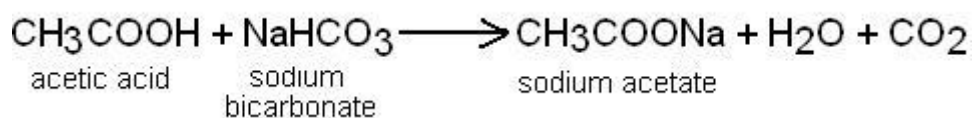
(1) Reaction with metals



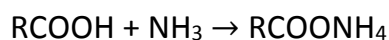
(2) Reaction with metal carbonates and bicarbonates



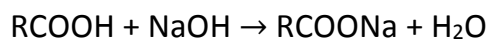
CARBOXYLIC ACID



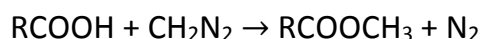
(3) Reaction with ammonia



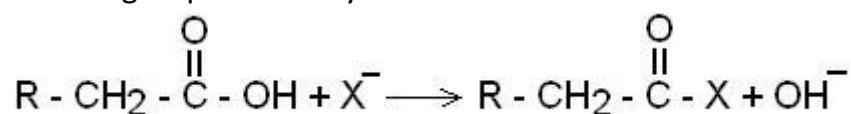
(4) Reaction with alkali



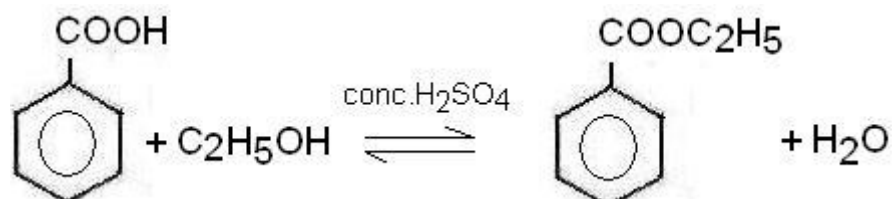
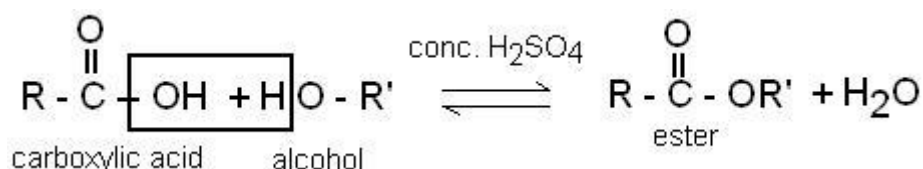
(5) Reaction with diazomethane (ester formation)



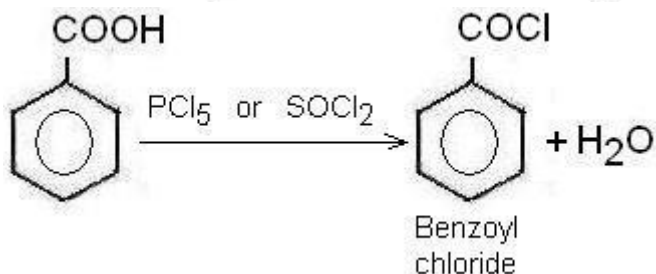
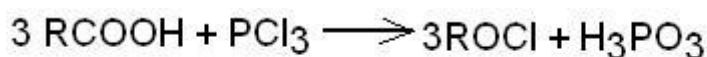
(B) Reactions due to -OH group of carboxylic acids



1. Formation of ester (esterification)



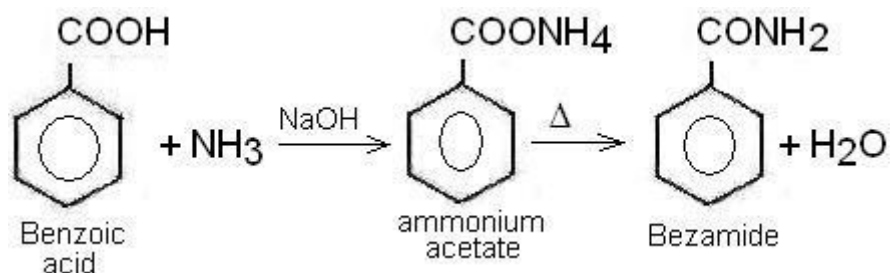
2. Formation of acid chloride



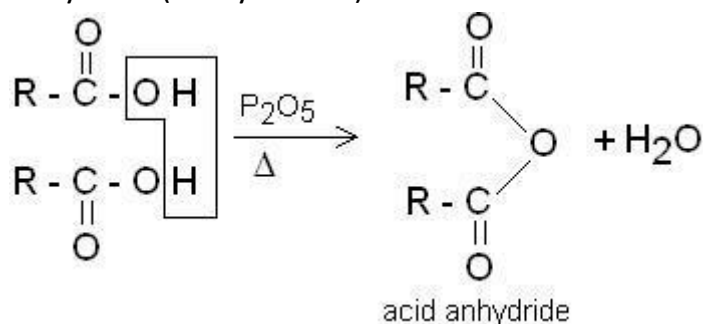
3. Formation of amides



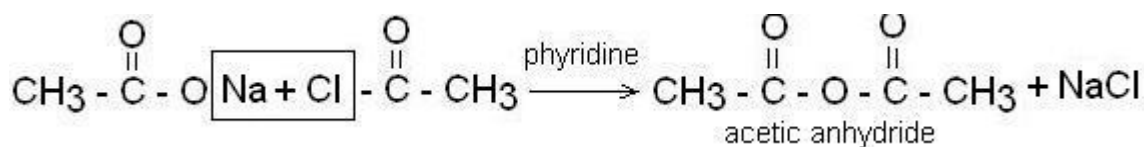
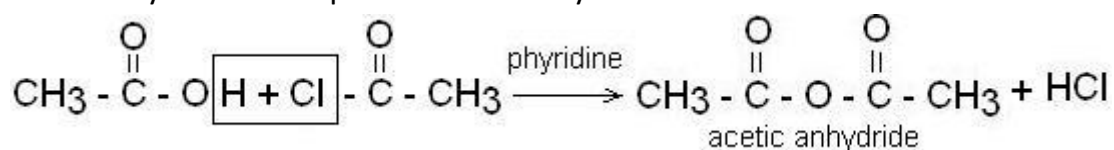
CARBOXYLIC ACID



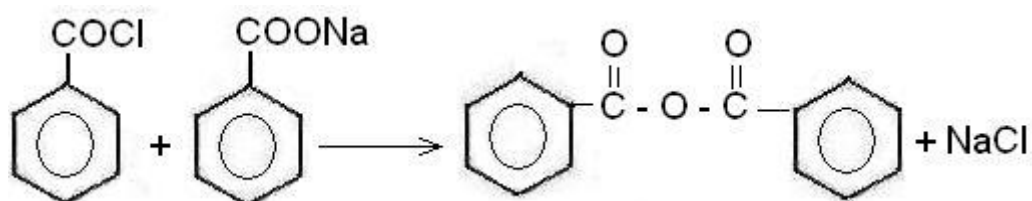
4. Formation of acid anhydride (Dehydration)



Acid chloride on reaction with carboxylic acid in presence of pyridine or with sodium salt of carboxylic acid also produce acid anhydride.



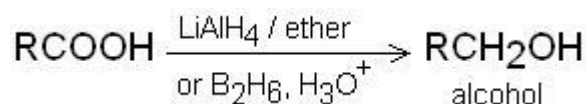
Aromatic carboxylic acid produces anhydride by reaction of acid chloride



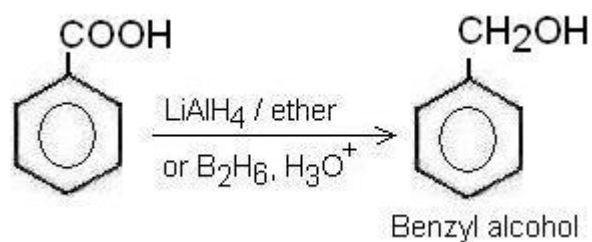
(C) Reactions due to carboxylic group as a whole

1. Reduction

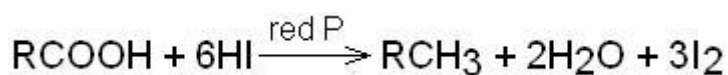
(i) Reduction to alcohols



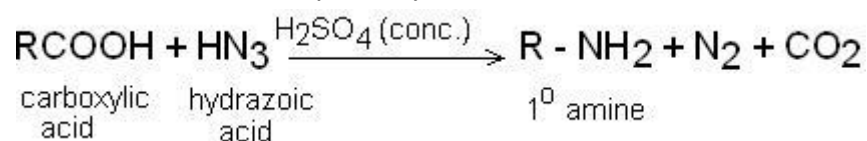
CARBOXYLIC ACID



(ii) Reduction to alkanes

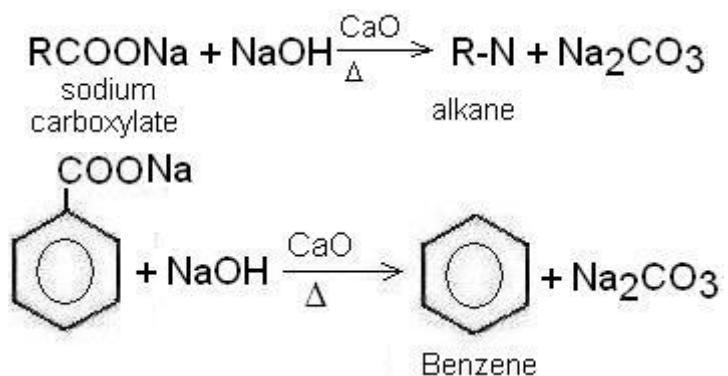


2. Schmidt's reaction (Formation of primary amines)



3. Decarboxylation

(i) Decarboxylation with sodalime

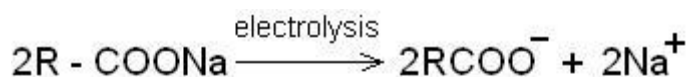


NaOH and CaO should be in the ratio of 3:1

Presence of an electron withdrawing group favours decarboxylation.

(ii) Kolbe's reaction (Electrolytic decarboxylation)

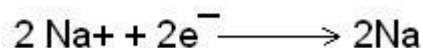
CARBOXYLIC ACID



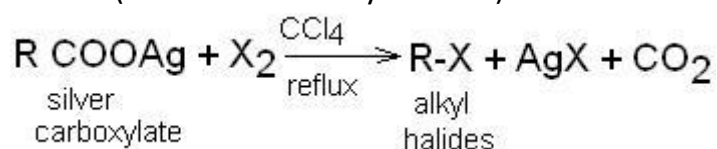
At anode:



At cathode:

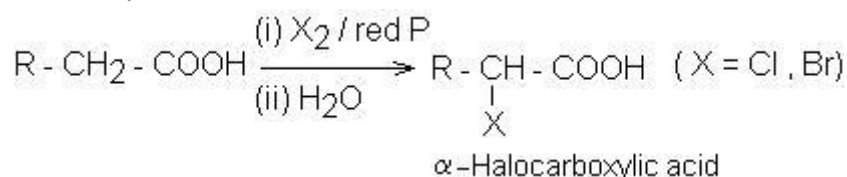


(iii) Hunsdiecker reaction (Formation of alkyl halides)



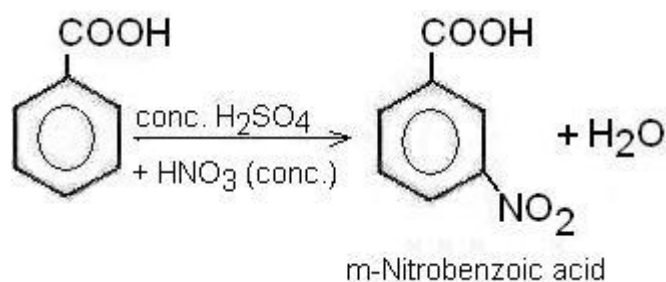
(D) Reactions due to alkyl group of carboxylic acids

1. Hell –Volhard-Zelinsky reaction

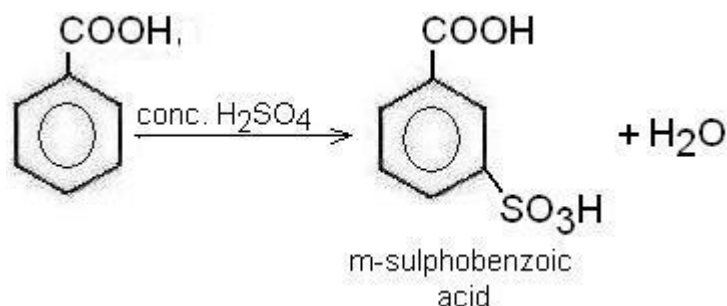


2. Electrophilic aromatic substitution reaction

(i) Nitration

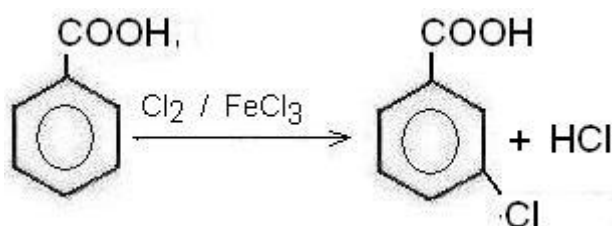


(ii) Sulphonation



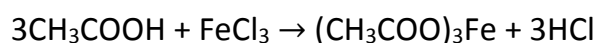
CARBOXYLIC ACID

(iii) Chlorination

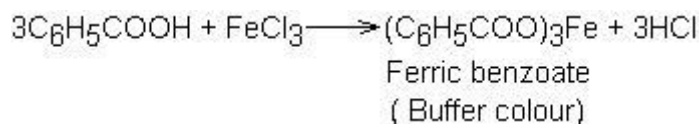


GENERAL TESTS FOR CARBOXYLIC GROUP

- (i) The aqueous solution of the acid turns blue litmus red
- (ii) The aqueous solution of the acid gives brisk effervescence of carbon dioxide with sodium bicarbonate or sodium carbonate (sodium bicarbonate test)
- (iii) On heating with alcohol and concentrated sulphuric acid, a fruity smell of ester is formed.
- (iv) Acetic acid gives blood-red or wine-red colour on treatment with ferric chloride; formation of ferric acetate; formation of ferric acetate takes place in this reaction.



- (v) Neutral solution of formic acid gives red precipitate with Fehling's solution, black precipitate with Tollen's reagent.
- (vi) Benzoic acid gives buff colour on treatment with neutral ferric chloride.



USE OF CARBOXYLIC ACIDS

- (i) Acetic acid is used as vinegar and in the manufacture of pickles
- (ii) Acetic acid is used in the manufacture of plastics, rayon and silk industries
- (iii) Acetic acid is used in the manufacture in antiknocking agent.
- (iv) Salts of benzoic acid is used as urinary antiseptics.
- (v) Benzoic acid is used in the treatment of skin diseases like eczema
- (vi) Formic acid is used in the preservation of fruits
- (vii) Formic acid is used as reducing agent.

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