

Chapter-12

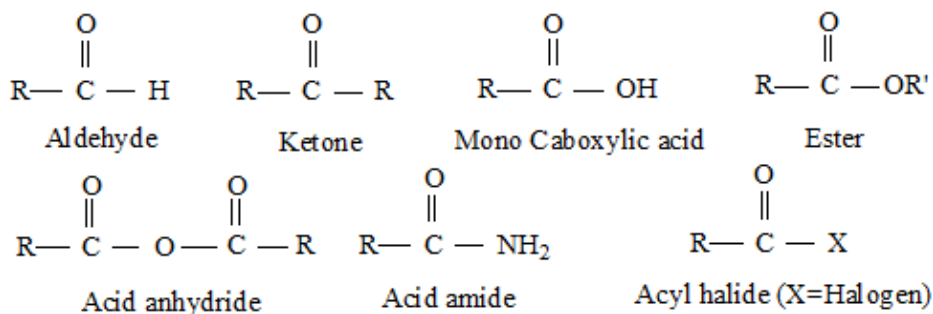
Aldehydes, Ketones and Carboxylic Acids

Lecture 01

Organic compounds containing carbon-oxygen double bond ($>C=O$) called carbonyl group, which is one of the most important functional groups in organic chemistry.

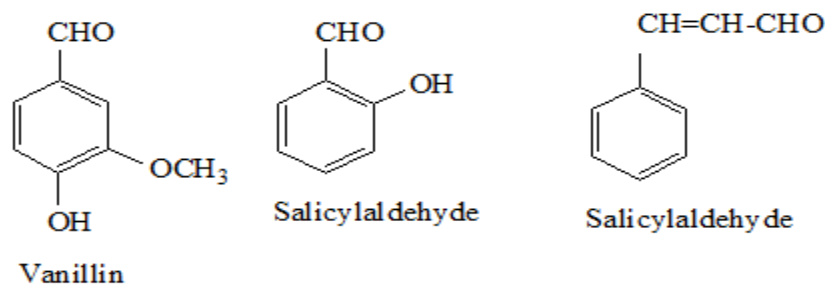
(i) In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones, it is bonded to two carbon atoms.

(ii) The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides) while in compounds where carbonyl group is attached to nitrogen and halogens are called amides and acyl halides respectively. The general formulas of these classes of compounds are given below:

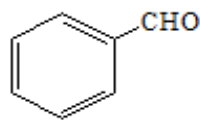
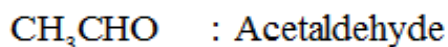


(iii) Aldehydes, ketones, and carboxylic acids are widespread in plants and animal kingdom. They play an important role in the biochemical processes of life.

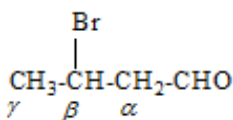
(iv) They add fragrance and flavor to nature. Ex: vanillin (from vanilla beans), salicylaldehyde (from meadowsweet) and cinnamaldehyde (from cinnamon) have very pleasant fragrances.



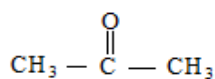
(v) They are used in many food products and pharmaceuticals to add flavors. Some of these families are manufactured for use as solvents (i.e., acetone) and for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics, etc.



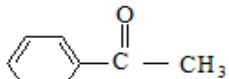
Benzaldehyde

 β -Bromobutyraldehyde

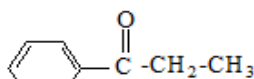
Nomenclature and Structure of Carbonyl Group:



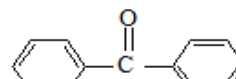
Acetone



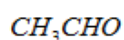
Acetophenone



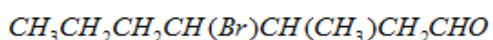
Propiophenone



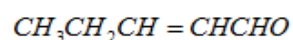
Benzophenone



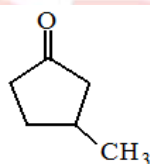
Acetaldehyde



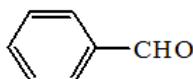
4-Bromo-3-methylheptanal



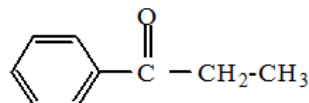
Pent-2-enal



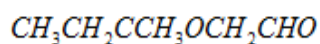
3-Methylcyclopentanone



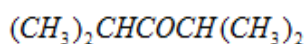
Benzaldehyde



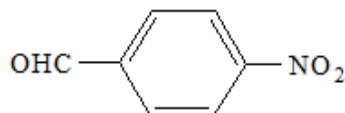
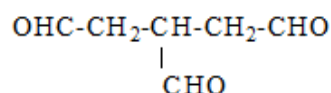
1-Phenylpropan-1-one



3-Oxopentanal



2,4-Dimethylpentan-3-one

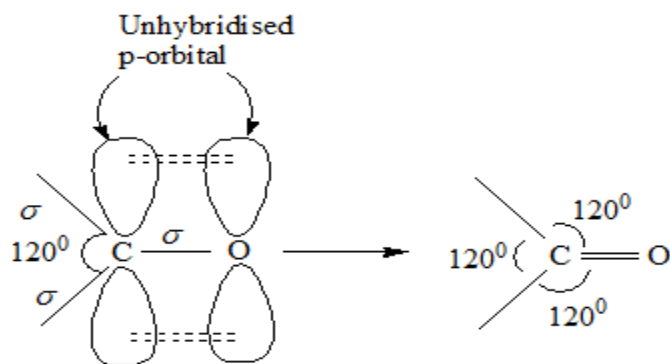
4-Nitrobenzaldehyde
or 4-Nitrobenzenecarbaldehyde

Propane-1,2,3-tricarbaldehyde

Structure of the Carbonyl Group:

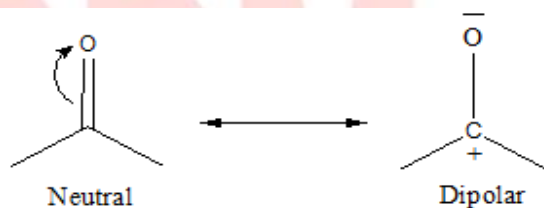
(i) The carbonyl carbon atom is sp^2 -hybridized and forms three sigma bonds with three surrounding atoms.

(ii) Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the pi-electron cloud is above and below the plane. The bond angles are approximately 120° as expected of a trigonal coplanar structure.



(iii) The carbon-oxygen double bond is polarised due to the higher electronegativity of oxygen relative to carbon. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a nucleophilic (Lewis base) center.

(iv) Carbonyl compounds have permanent dipole moments and are polar. The high polarity of the carbonyl group is explained based on resonance as:



LECTURE-02

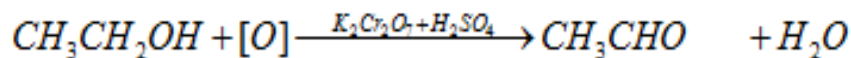
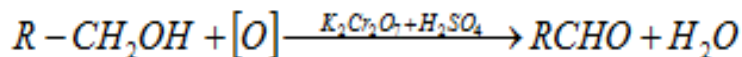
Preparation of Aldehydes and Ketones:

Preparation of Aldehydes:

1. By oxidation of alcohols
2. By dehydrogenation of alcohols
3. From alkenes by ozonolysis.
4. From alkynes by hydration.
5. From acyl chloride (acid chloride)
6. From nitriles and esters
7. By oxidation of methylbenzene
8. By side-chain chlorination followed by hydrolysis
9. By Gatterman – Koch reaction

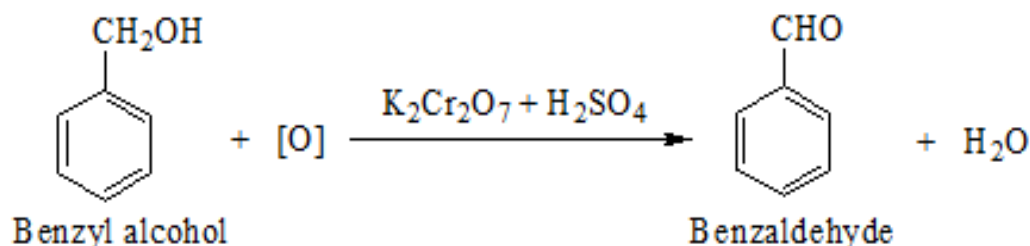
1. By oxidation of alcohols:

Aldehydes can be obtained by the oxidation of primary alcohols with oxidizing agents like acidified $K_2Cr_2O_7$, aqueous or alkaline $KMnO_4$ solution.



Ethyl alcohol

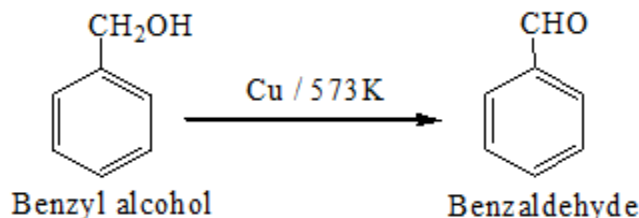
Acetaldehyde



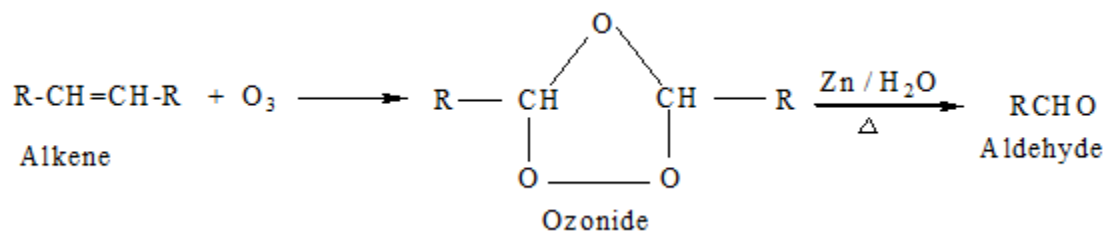
In this method aldehydes are removed as soon as they formed otherwise they will be oxidized to corresponding carboxylic acids. Some special oxidizing agents are also used to prepare aldehydes from alcohol. These are i) Collins reagent ($\text{CrO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$) ii) PCC (Pyridiniumchlorochromate $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl} \cdot \text{CrO}_3 / \text{CH}_2\text{Cl}_2$ iii) Anhydrous CrO_3

2. By dehydrogenation of alcohols:

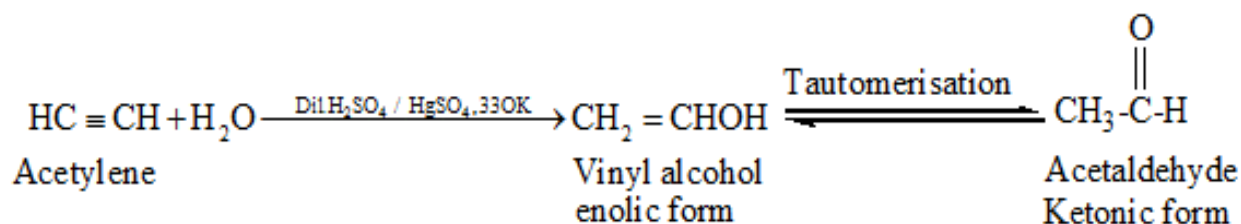
Aldehydes are easily obtained by passing vapors of primary alcohol overheated copper at 573K.



3. By ozonolysis of alkenes: Aldehydes are obtained by the ozonolysis of alkenes like $\text{RCH}=\text{CHR}$.

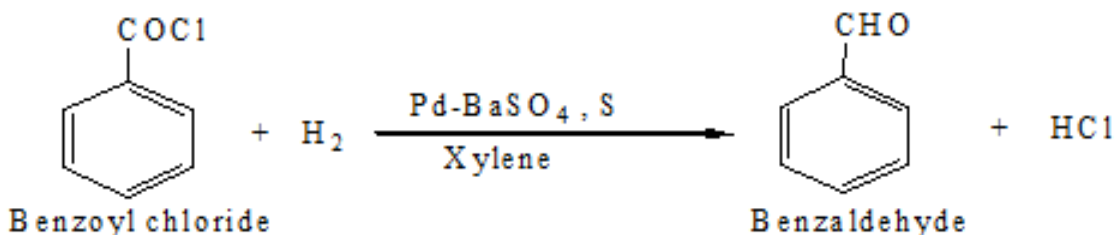
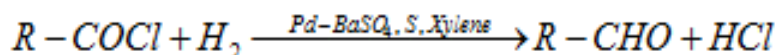


4. By hydration of alkynes: Acetylene on hydration in presence of dil. sulphuric acid and mercuric sulphate at 330K gives acetaldehyde.



5. From acyl chloride / acid chloride (Rosenmund Reduction):

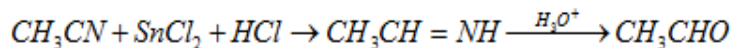
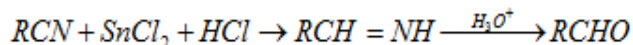
When acid chloride is reduced with hydrogen in the presence of a Palladium catalyst deposited on barium sulphate and partially poisoned by the addition of sulphur or quinoline using xylene as the solvent, it gives the corresponding aldehyde. It is called **Rosenmund Reduction**.



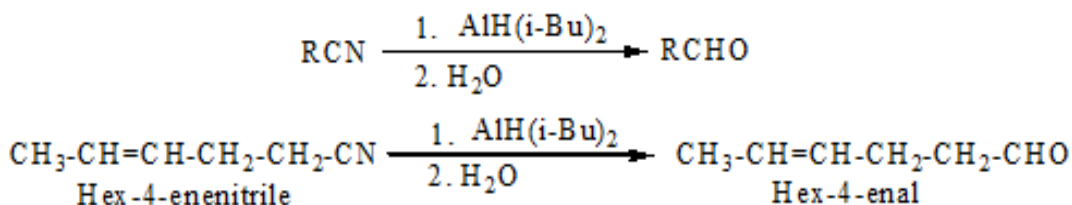
Formaldehyde cannot be prepared by this method because HCOCl (Formyl chloride) is quite unstable.

6. From nitriles and esters:

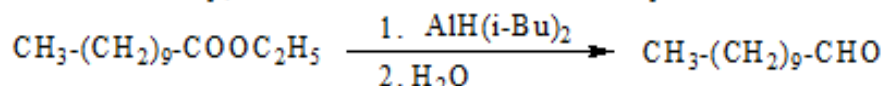
(i) Nitriles are reduced to the corresponding imine with stannous chloride in the presence of HCl , which on hydrolysis gives the corresponding aldehyde. This reaction is called **Stephen reaction**.



(ii) Nitriles are also selectively reduced by di isobutyl aluminum hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:

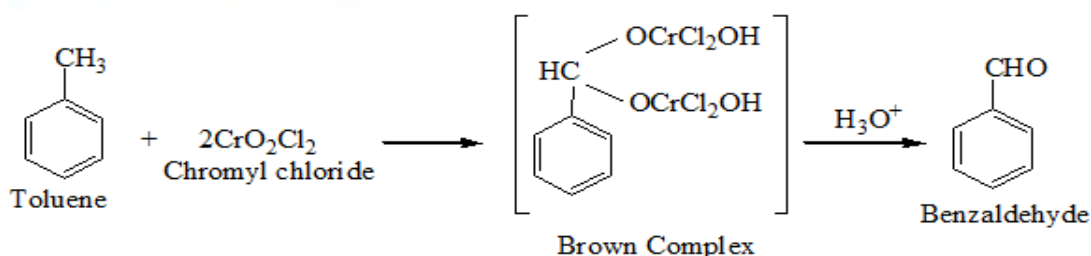


Similarly, esters are also reduced to aldehydes with DIBAL -H.



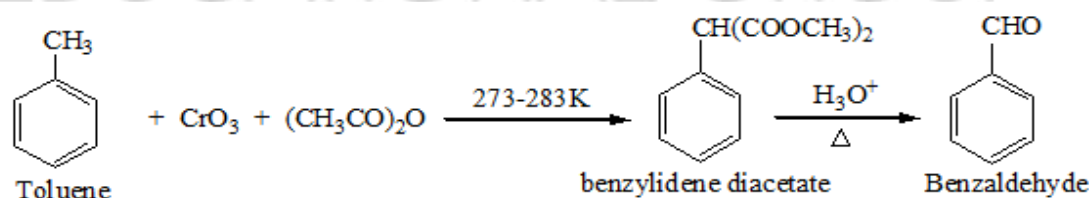
6. By oxidation of methylbenzene (Etard reaction):

When methylbenzene is treated with a solution of Chromyl chloride in CCl_4 a brown complex is formed which is separated and decomposed with water to give benzaldehyde. This reaction is called the **Etard reaction**.



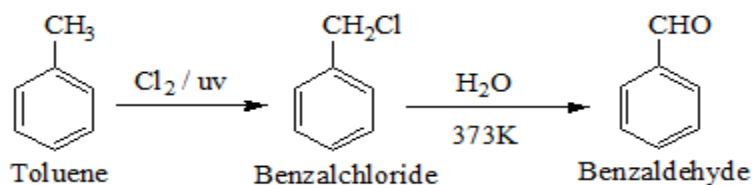
Use of chromic oxide (CrO₃):

Toluene or substituted toluene is converted to benzylidenediacetate on treating with chromic oxide in acetic anhydride. The benzylidenediacetate can be hydrolyzed to corresponding benzaldehyde with aqueous acid.



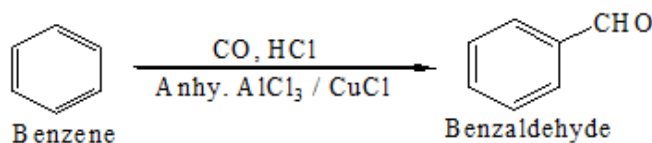
7. By side-chain chlorination followed by hydrolysis:

Sidechain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This is a commercial method of manufacture of benzaldehyde.



8. By Gatterman – Koch reaction:

When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminum chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



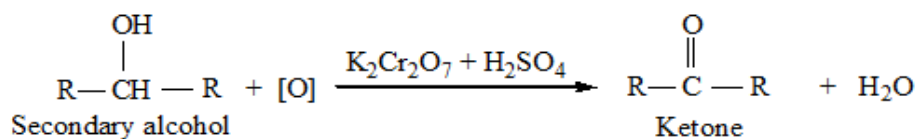
This reaction is known as the Gatterman-Koch reaction.

Preparation of Ketones:

1. By oxidation of alcohols
2. By dehydrogenation of alcohols
3. From alkenes by ozonolysis
4. From alkynes by hydration
5. From benzene or substituted benzenes
4. From acyl chloride (acid chloride)
5. From nitriles.

1. By oxidation of alcohols:

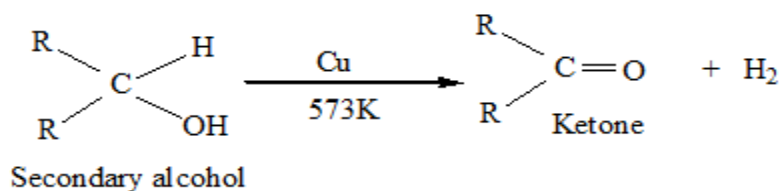
Ketones can be easily prepared by the oxidation of secondary alcohols with acidified potassium dichromate or potassium permanganate.



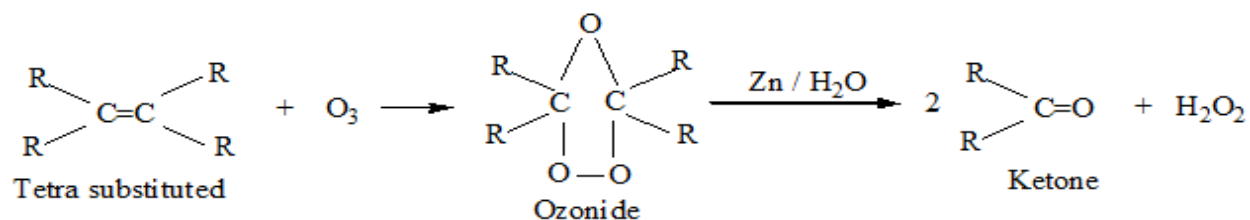
Ketones are not easily oxidized further.

2. By dehydrogenation of alcohols:

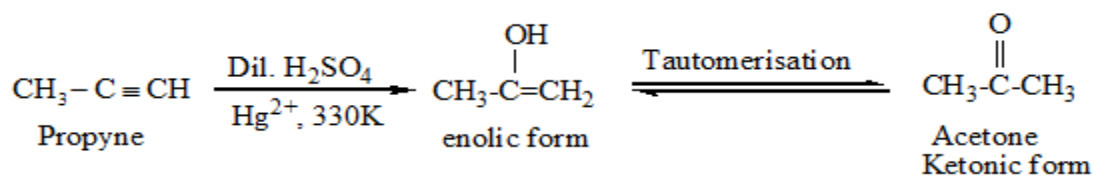
Ketones are produced by passing vapors of secondary alcohol over heated copper at 573K.



3. By ozonolysis of alkenes: Ketones are obtained by the ozonolysis of tetrasubstituted alkenes ($\text{R}_2\text{C}=\text{CR}_2$).

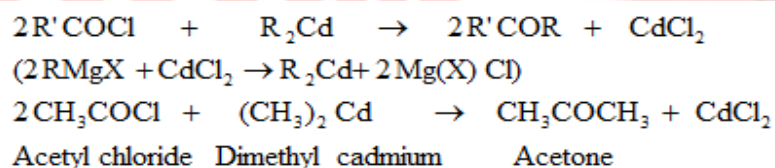


4. By hydration of alkynes: Alkynes (Except acetylene) on hydration in presence of dil. sulphuric acid and mercuric sulphate at 330K give ketone.



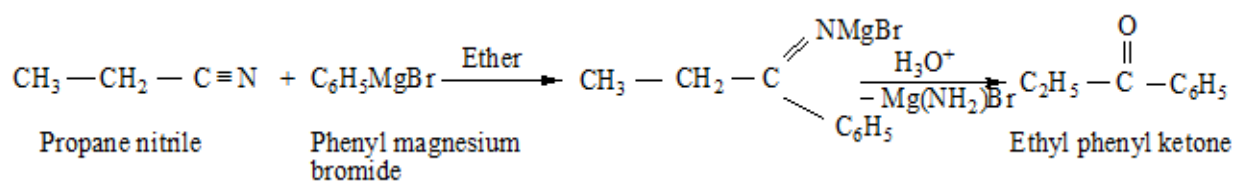
5. From acyl chloride (acid chloride):

Treatment of acyl chlorides with dialkylcadmium, prepared by the reaction of cadmium chloride with Grignard reagent, gives ketones.

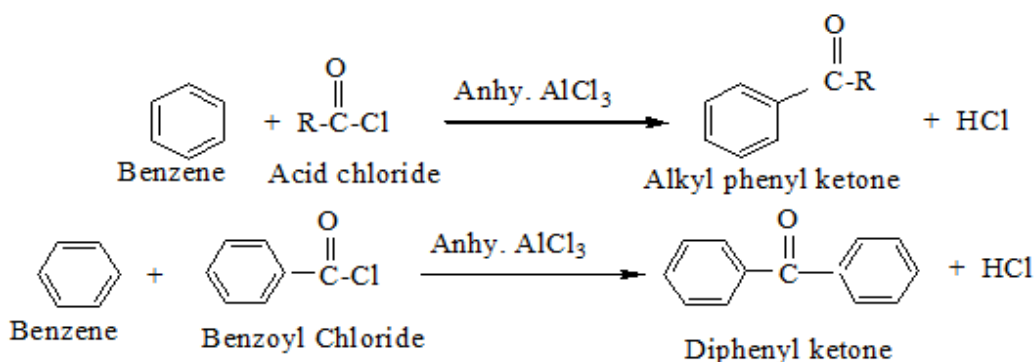


6. From nitriles:

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



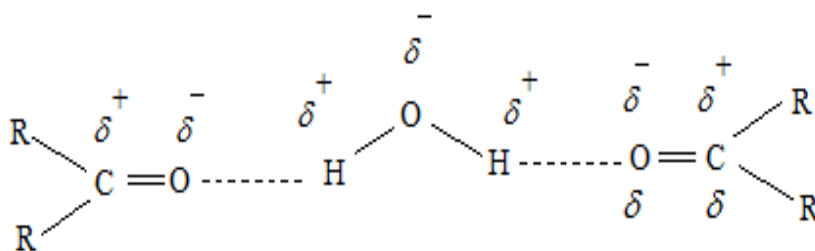
7. From benzene or substituted benzenes: When benzene or substituted benzene is treated with an acid chloride in the presence of anhydrous aluminum chloride, then the corresponding ketone is formed. This reaction is known as the Friedel-Crafts acylation reaction.



LECTURE-03

Physical Properties:

1. Methanal is a gas at room temperature.
2. Ethanal is a volatile liquid.
3. Other aldehydes and ketones are liquid or solid at room temperature.
4. The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to the weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to the absence of intermolecular hydrogen bonding.
5. The lower members of aldehydes and ketones such as methanal, ethanal, and propanone are miscible with water in all proportions because they form a hydrogen bond with water.



6. However, the solubility of aldehydes and ketones decreases rapidly in increasing the length of the alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc. The lower aldehydes have sharp pungent odors. As the size of the molecule increases, the odour becomes less pungent and more fragrant.

Chemical Reactions:

1. Nucleophilic addition reactions

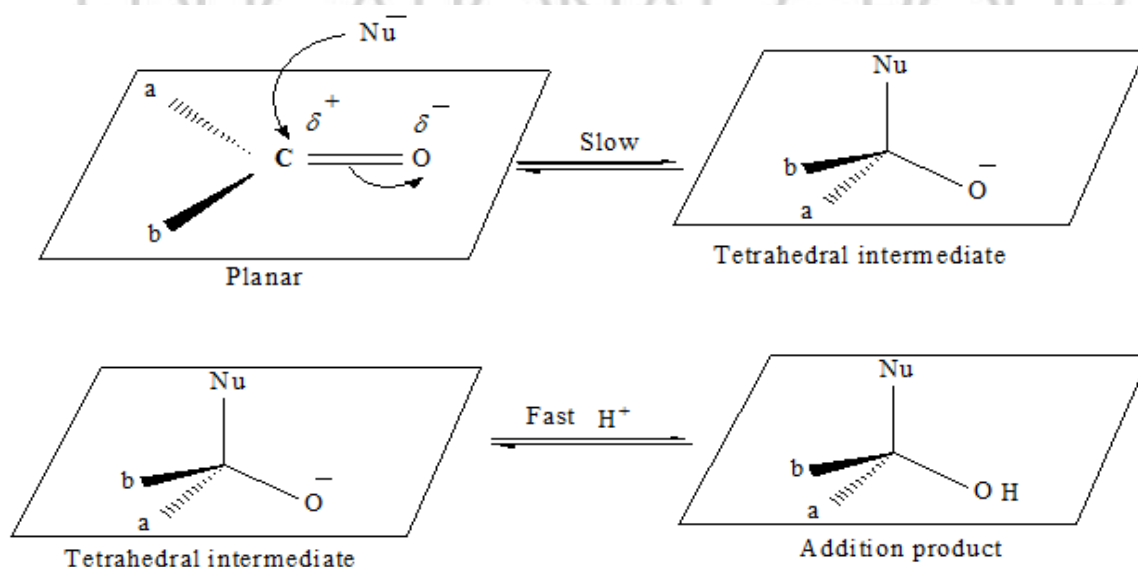
2. Reaction with HCN
3. Reaction with NaHSO_3
4. Reaction with Grignard reagent
5. Reaction with alcohols
6. Reaction with ammonia and its derivatives
7. Reduction
8. Oxidation
9. Reaction due to alpha hydrogen (Aldolcondensation)
10. Cannizzaro Reaction
11. Electrophilic substitution reaction

1. Nucleophilic addition reactions:

The aldehydes and ketones undergo nucleophilic addition reactions.

Mechanism of nucleophilic addition reactions:

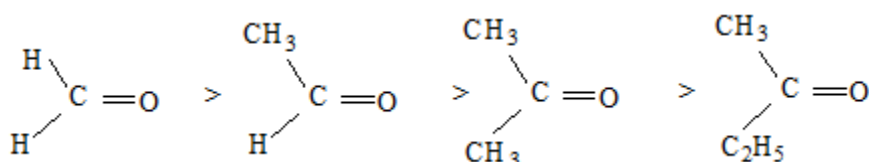
1. A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridized orbitals of carbonyl carbon.
2. The hybridization of carbon changes from **sp^2 to sp^3** in this process and a tetrahedral alkoxide intermediate is produced.
3. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is the addition of Nu^- and H^+ across the carbon-oxygen double bond.



Reactivity:

- a) Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.

- b) The presence of two relatively large substituents in ketones hinders the approach of a nucleophile to carbonyl carbon than in aldehydes having only one such substituent.
- c) Electronically, aldehydes are more reactive than ketones because two alkyl groups in ketone reduce the electrophilicity of the carbonyl carbon more effectively.
- d) Hence the order of reactivity of aliphatic carbonyl compounds towards Nucleophilic substitution reaction is



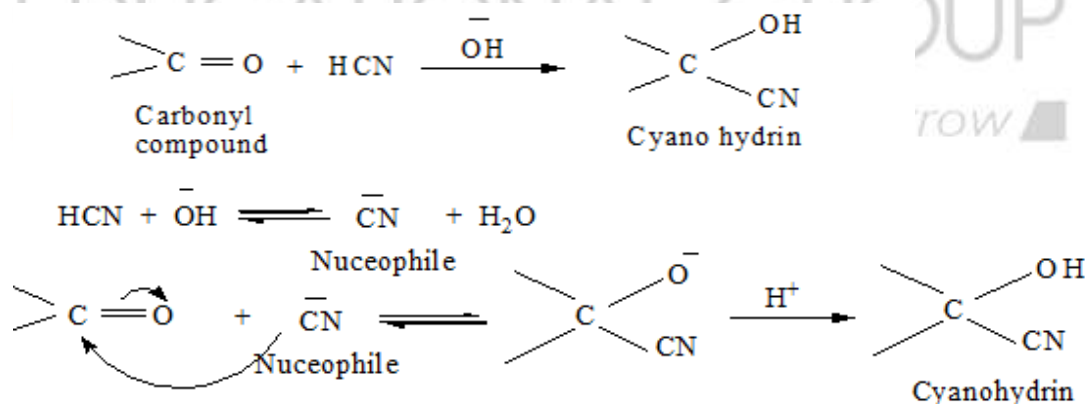
Aromatic aldehydes and ketones are less reactive than the aliphatic aldehydes and ketones. Because the +R-effect of the aromatic ring dominates over -I-effect of the aromatic ring which deactivates the carbonyl group.

The order of reactivity is $\text{C}_6\text{H}_5\text{CHO} > \text{C}_6\text{H}_5\text{COCH}_3 > \text{C}_6\text{H}_5\text{COC}_6\text{H}_5$

Some important examples of nucleophilic addition and nucleophilic addition-elimination reactions:

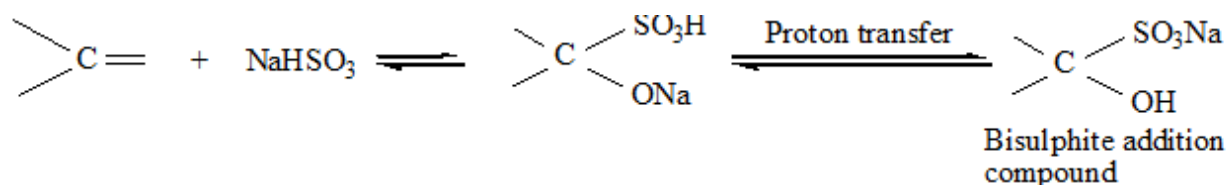
2. Addition of hydrogen cyanide (HCN):

Aldehydes and ketones react with hydrogen cyanide (HCN) to yield cyanohydrins. This reaction occurs very slowly with pure HCN. Therefore, it is catalyzed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily adds to carbonyl compounds to yield the corresponding cyanohydrin.

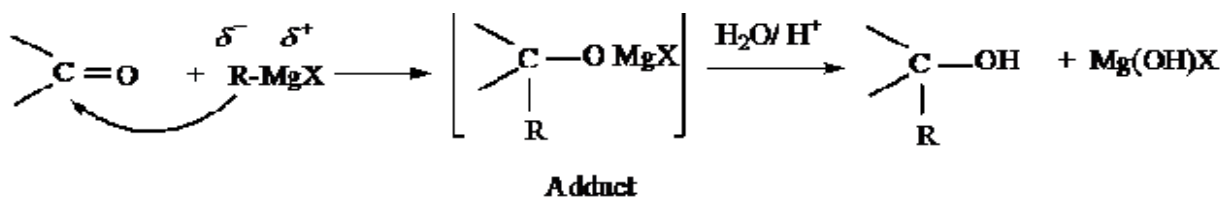


3. Addition of sodium hydrogensulphite:

Aldehydes and ketones are added with Sodium hydrogensulphite to form corresponding crystalline sodium bisulphite.

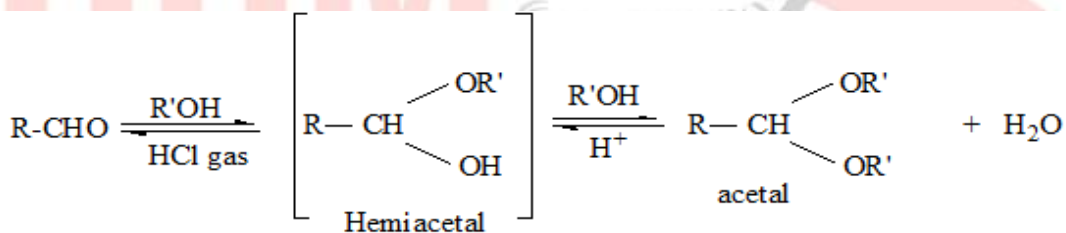


4. Addition of Grignard reagents: Aldehydes and ketones added with the Grignard reagent to form alcohols.

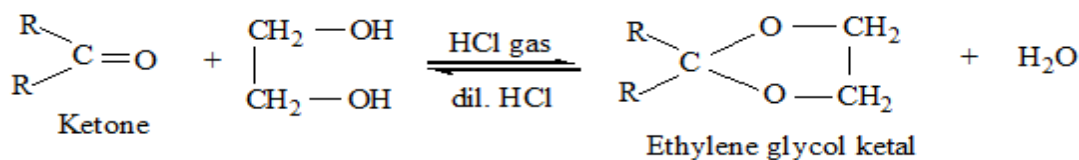


LECT-4

5. Addition of alcohol: Aldehydes react with monohydric alcohol in the presence of dry HCl gas to form alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molecule of alcohol to give a gem-alkoxy compound known as acetal.



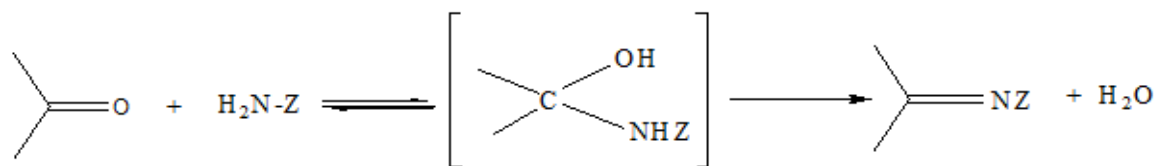
Ketones do not react with monohydric alcohols readily but react with diols like ethylene glycol under similar conditions to form cyclic ketals. Acetals and ketals are hydrolyzed with aqueous mineral acids to yield corresponding aldehydes and ketones respectively.



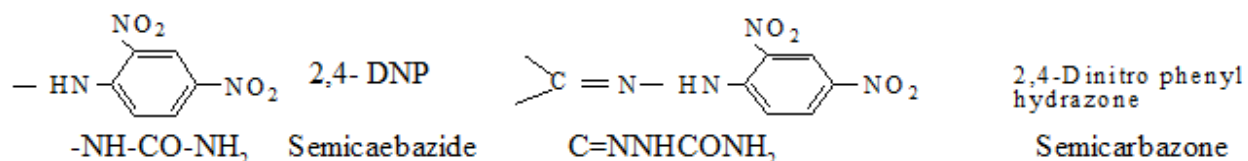
6. Nucleophilic addition Elimination reactions(Addition with Ammonia and its derivatives)

Nucleophiles, such as ammonia and its derivatives H₂N-Z add to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalyzed by the acid of pH around 3.5. The equilibrium favors the product formation due to rapid dehydration of the intermediate to form >C=N-Z.

Z = Alkyl, aryl, OH, NH₂, C₆H₅NH, NHCONH₂, etc.



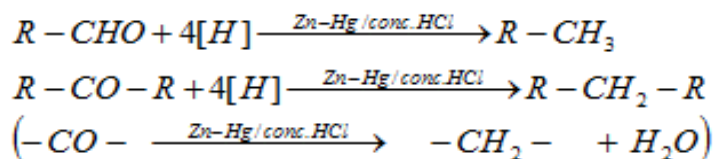
Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	C=NH	Imine
-R	Amine	C=NR	Schiff's Base
-OH	Hydroxylamine	C=NOH	Oxime
-NH ₂	Hydrazine	C=NNH ₂	Hydrazone
-NH-C ₆ H ₅	Phenyl hydrazine	C=NNHC ₆ H ₅	Phenylhydrazone



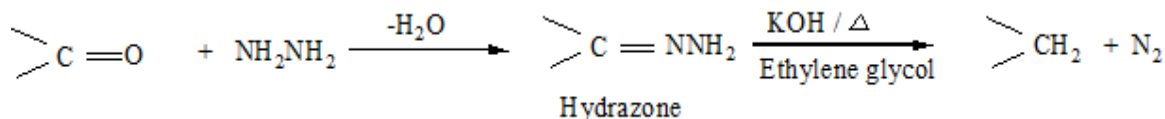
7. Reduction

(i) Reduction to hydrocarbon (Clemmensen reduction):

The carbonyl group of aldehydes and ketones is reduced to the CH₂ group on treatment with zinc amalgam and concentrated hydrochloric acid.

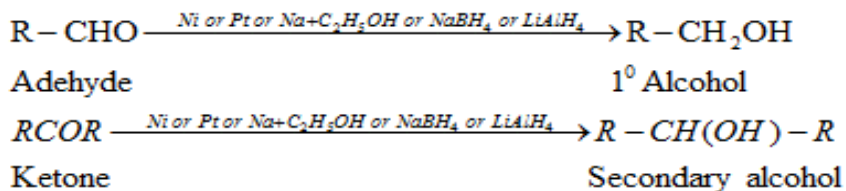


(ii) Reduction to hydrocarbon (Wolff-Kishner reduction): The carbonyl group of aldehydes and ketones is reduced to CH₂ group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in a high boiling solvent such as ethylene glycol.



(iii) Reduction to alcohols:

Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride (NaBH₄) or lithium aluminum hydride (LiAlH₄) as well as by catalytic hydrogenation.



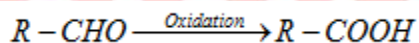
LECTURE 05

8. Oxidation of Aldehydes and Ketones:

(i) Aldehydes are easily oxidized to carboxylic acids on treatment with common oxidizing agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidizing agents, mainly Tollens' reagent and Fehlings' reagent also oxidize aldehydes.

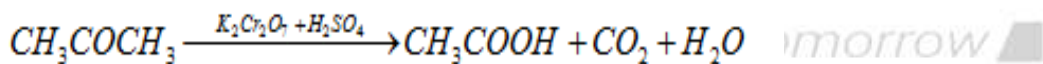
(ii) Ketones are generally oxidized under vigorous conditions, i.e. strong oxidizing agents and at elevated temperatures. Their oxidation involves C-C bond cleavage to give a mixture of carboxylic acids having a lesser number of carbon atoms than the parent ketone.

Oxidation of Aldehydes and Ketones: Aldehydes are easily oxidized to carboxylic acids on treatment with common oxidizing agents like nitric acid, pot. Permanganate, pot.dichromate etc.

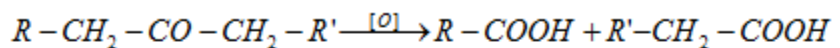


Oxidation of Ketone:

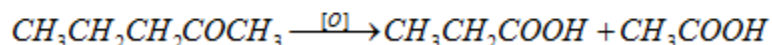
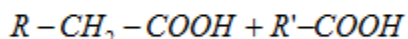
Ketones are not oxidized by mild oxidizing agents like Fehling solution or Tollen's reagent because of the absence of a C-H bond. Oxidation of ketones possible in presence of strong oxidizing agents like acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$.



The oxidation of mixed ketones takes place according to **Popoff's rule** (The carbonyl group remains along with the smaller alkyl group).

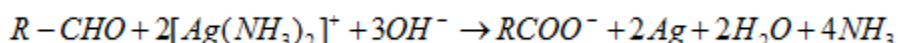


or



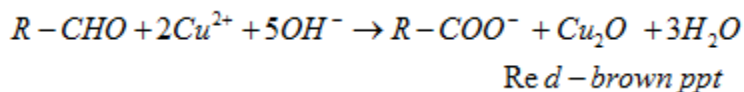
Tollens' test:

On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidized to corresponding carboxylate anion. The reaction occurs in an alkaline medium.

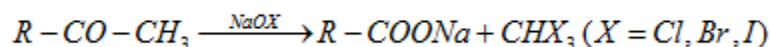


Fehling's test:

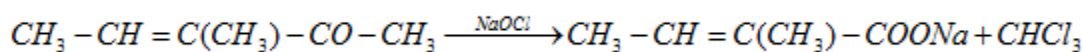
Fehling solutions are the mixture of Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartrate (Rochelle salt). On heating an aldehyde with Fehling's reagent, a reddish-brown precipitate of cuprous oxide is obtained. Aldehydes are oxidized to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.



Oxidation of methyl ketones by haloform reaction: Aldehydes and ketones having methyl ketone group on treatment with halogens in presence of aqueous alkali or sodium hypohalite give haloform. This is known as the haloform reaction.



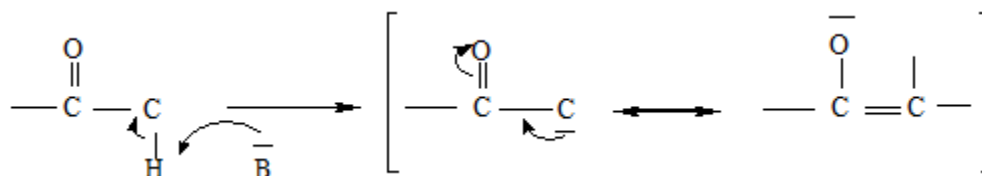
This oxidation does not affect C=C present in the molecule.



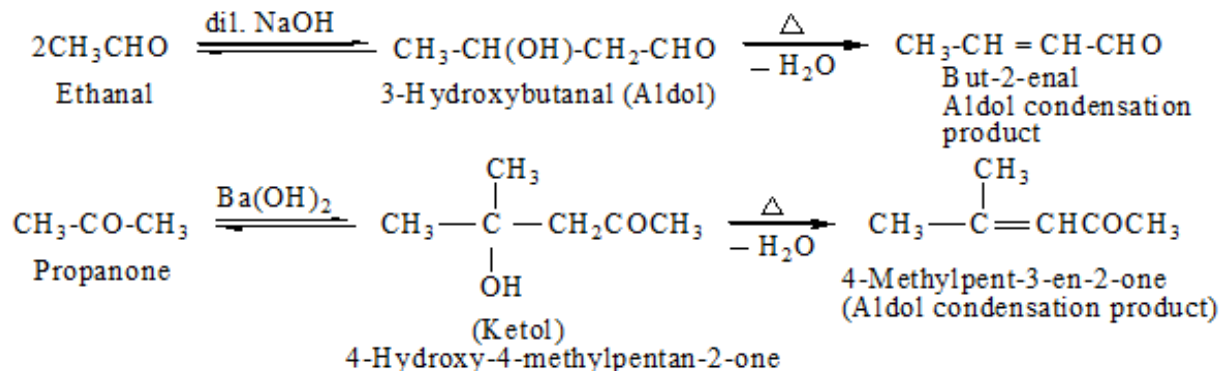
Iodoform reaction with NaOI is also used for the detection of the CH₃CO group or CH₃CHO group.

9. Reactions due to -hydrogen**The acidity of -hydrogens of aldehydes and ketones:**

The acidity of alpha-hydrogen atoms of carbonyl compounds is due to the strong electron-withdrawing effect of the carbonyl group and resonance stabilization of the conjugate base.



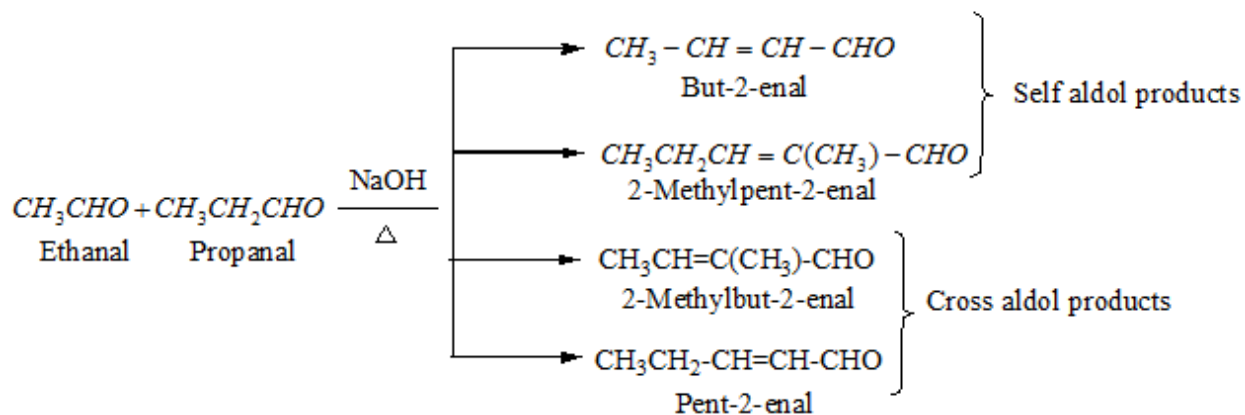
(i) Aldol condensation: Aldehydes and ketones having at least one alpha-hydrogen undergo a reaction in the presence of dilute alkali as a catalyst to form beta-hydroxy aldehydes (aldol) or beta-hydroxy ketones (ketol), respectively. This is known as the Aldol reaction.



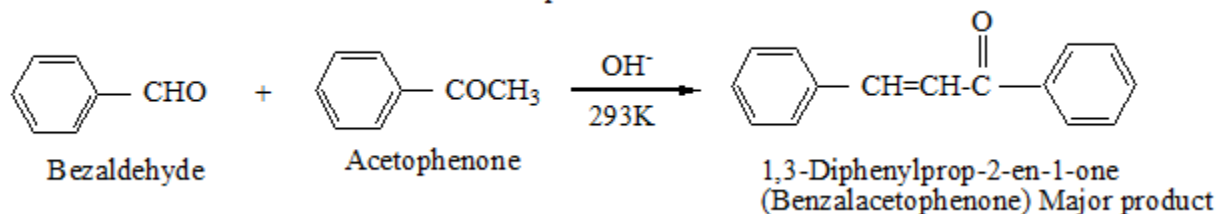
The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give, -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called Aldol condensation. Though ketones give ketols (compounds containing keto and alcohol groups), the general name aldol condensation still applies to the reactions of ketones due to their similarity with aldehydes.

(ii) Cross aldol condensation:

When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain α -hydrogen atoms, it gives a mixture of four products.



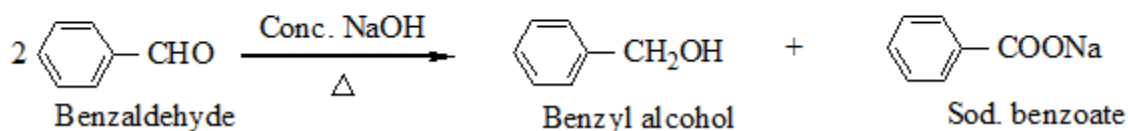
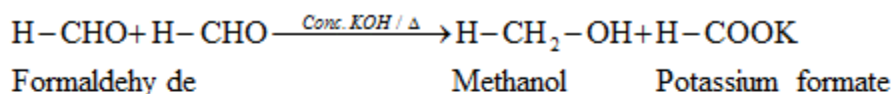
Ketones can also be used as one component in the cross aldol reactions.



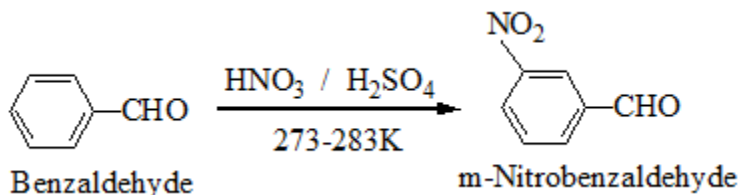
LECTURE-06

10. Cannizzaro reaction:

Aldehydes which do not have α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidized to carboxylic acid salt.

**11. Electrophilic substitution reaction:**

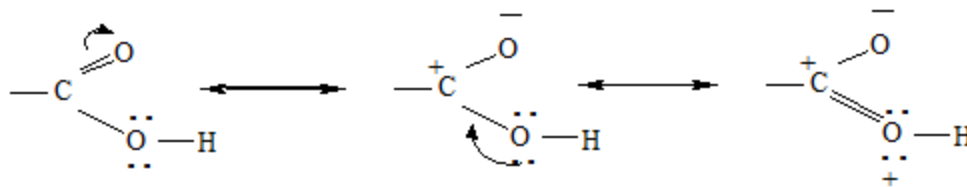
Aromatic aldehydes and ketones undergo electrophilic substitution to form the *m*-substituted product.

**Uses of Aldehydes and Ketones:**

- (a) In the chemical industry aldehydes and ketones are used as solvents, starting materials and reagents for the synthesis of other products.
- (b) Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare bakelite (a phenol-formaldehyde resin), urea-formaldehyde glues and other polymeric products.
- (c) Acetaldehyde is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers, and drugs.
- (d) Benzaldehyde is used in perfumery and dye industries.
- (e) Acetone and ethyl methyl ketone are common industrial solvents.

Structure of Carboxyl Group:

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 resonance structure shown below:

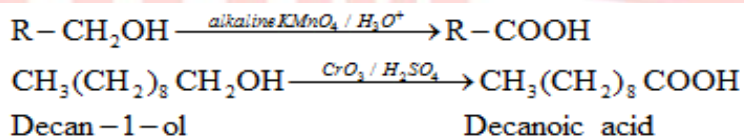


Methods of Preparation of Carboxylic Acids:

1. From primary
2. Aldehydes
3. From alkylbenzenes
4. From nitriles and amides
5. From Grignard reagents
6. From acyl halides and anhydrides
6. From esters

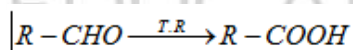
1. From primary alcohols:

Primary alcohols are readily oxidized to carboxylic acids with common oxidizing agents such as potassium permanganate (KMnO_4) in neutral, acidic, or alkaline media or by potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and chromium trioxide (CrO_3) in acidic media (Jones reagent).



2. From aldehydes:

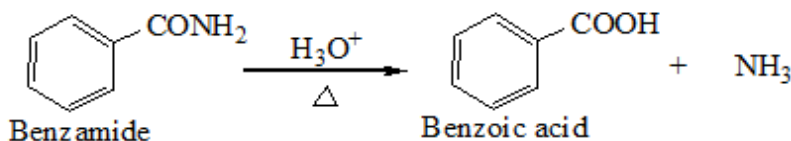
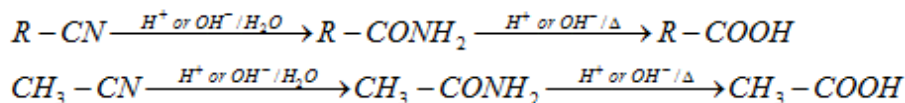
Carboxylic acids can be prepared from aldehydes by using mild oxidizing agents.



LECTURE-07

2. From nitriles and amides:

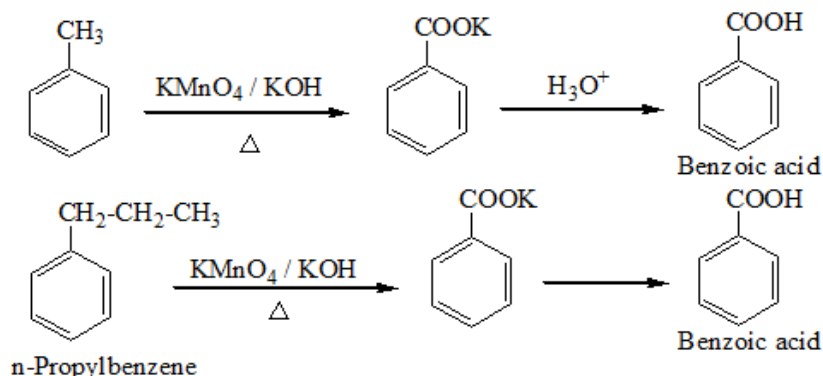
Nitriles are hydrolyzed to amides and then to acids in the presence of H^+ or OH^- as a catalyst.



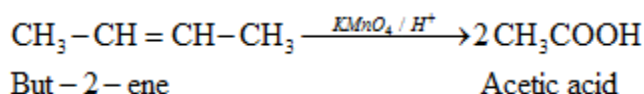
3. From alkylbenzenes:

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkylbenzenes with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidized to the

carboxyl group irrespective of the length of the side chain. Primary and secondary alkyl groups are oxidized in this manner while the tertiary group is not affected.

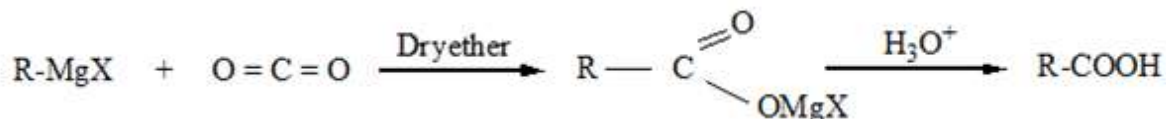


Substituted alkenes are also oxidized to carboxylic acids with these reagents.



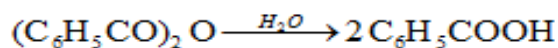
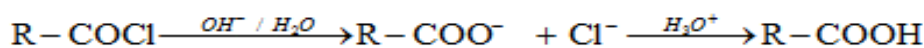
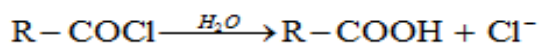
4. From Grignard reagents:

Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with a mineral acid.

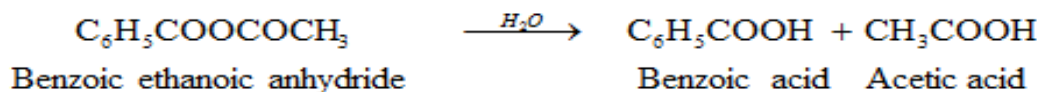


5. From acyl halides and anhydrides:

Acid chlorides when hydrolyzed with water give carboxylic acids or more readily hydrolyzed with an aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides on the other hand are hydrolyzed to corresponding acid(s) with water.

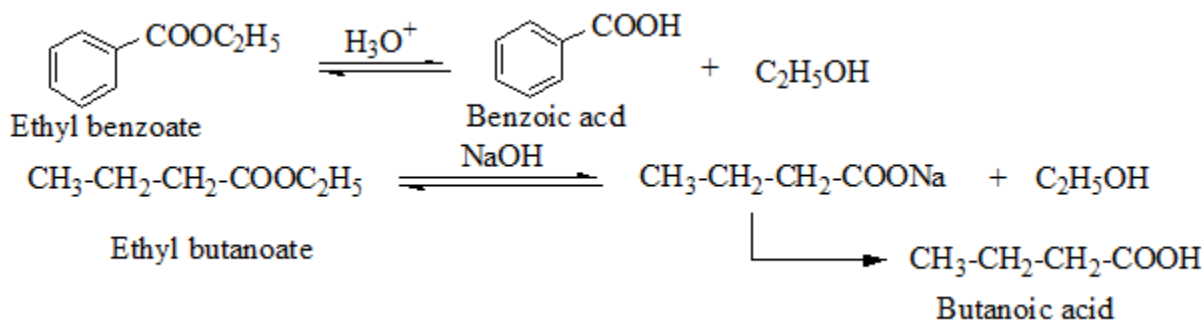


Benzoic anhydride Benzoic acid



6. From esters:

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids

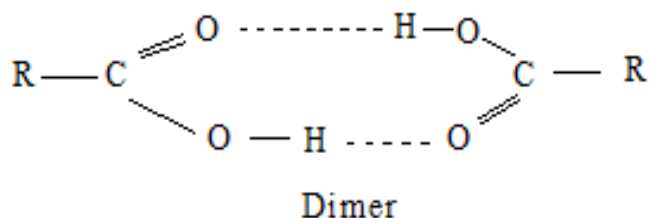


LECTURE-08

Physical Properties:

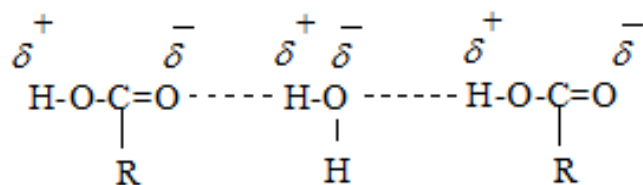
Physical state: Aliphatic carboxylic acids upto nine carbon atoms are colorless liquids at room temperature with unpleasant odors. The higher acids are wax-like solids and are practically odorless due to their low volatility.

Boiling point: Carboxylic acids are higher boiling liquids than aldehydes, ketones, and even alcohols of comparable molecular masses. This is due to intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapor phase. Most carboxylic acids exist as a dimer in the vapor phase or the aprotic solvents. Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.



Solubility:

The solubility of lower members of carboxylic acids is due to the formation of intermolecular hydrogen bonding with water molecules. It decreases with an increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of the hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic acid is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.



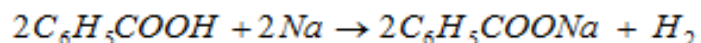
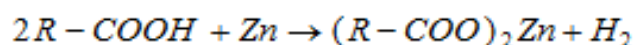
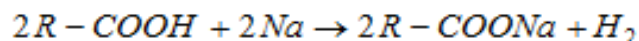
Hydrogen bonding

Chemical Reactions:

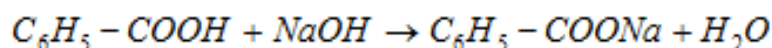
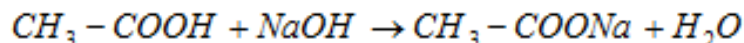
1. Reactions Involving Cleavage of O–H Bond(Acidity)
2. Reactions involving cleavage of C-OH bond
 - (a) Formation of anhydride
 - (b) Esterification
 - (c) Reaction with PCl_5 , PCl_3 , and SOCl_2
 - (d) Reaction with ammonia
3. Reactions involving -COOH group
 - (a) Reduction
 - (b) Decarboxylation
4. Substitution Reaction in the Hydrocarbon part.
 - (a) Halogenation (HVZ Reaction)
 - (b) Ring Substitution.

1. Reactions Involving Cleavage of O–H Bond(Acidity):**(a) Reactions with metals.**

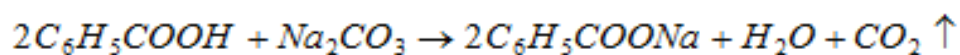
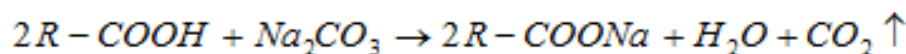
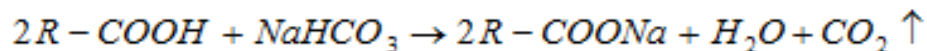
Carboxylic acids react with active metals like Na, Mg, Ca, Zn to evolve Hydrogen. This indicates the acidity of carboxylic acids.

**(b) Reaction with NaOH:**

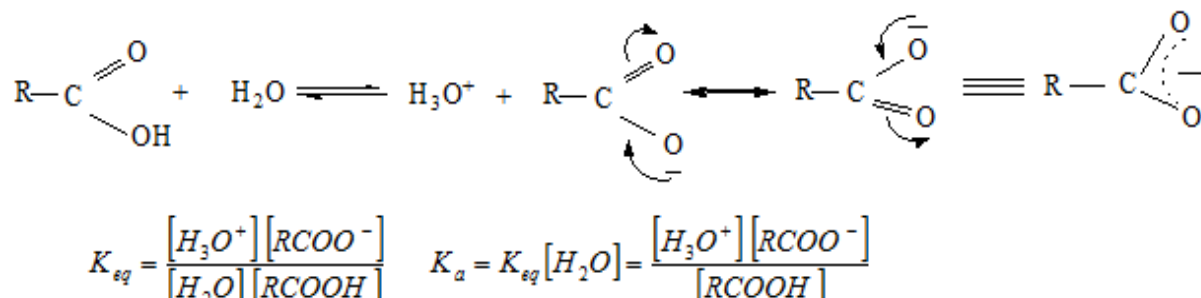
Carboxylic acids neutralize caustic alkalies to form salt and water.

**(c) Reaction with alkali metal carbonates and bicarbonates:**

Carboxylic acids decompose carbonates and bicarbonates with the liberation of CO_2 with brisk effervescence.



Carboxylic acids dissociate in water to give resonance stabilized carboxylate anions and the hydronium ion.



Where K_{eq} is equilibrium constant and K_a is the acid dissociation constant. The strength of an acid is generally indicated by its pK_a value rather than its K_a value.

$$pK_a = -\log K_a$$

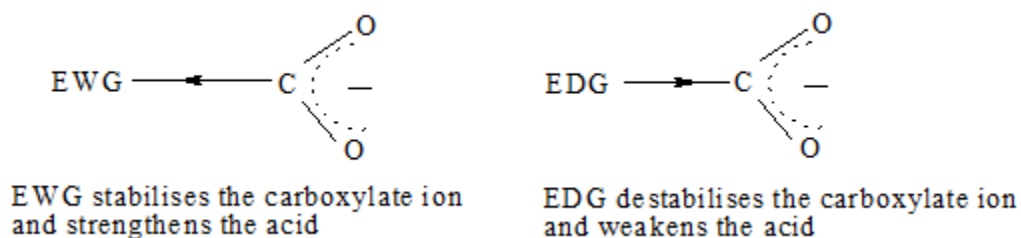
Smaller the pK_a , the stronger the acid (the better proton donor). Strong acids have pK_a values <1 , the acids with pK_a values between 1 and 5 are considered to be moderately strong acids, weak acids have pK_a values between 5 and 15, and extremely weak acid have pK_a values >15 .

Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols (pK_a is ~ 16 for ethanol and 10 for phenol). Carboxylic acids are amongst the most acidic organic compounds. Carboxylic acids are stronger than phenols. It can be explained as :

The conjugate base of carboxylic acid, (carboxylate ion) is stabilized by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. Whereas the conjugate base of phenol, (phenoxide ion) has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom. Therefore, resonance in phenoxide ion is not as important as it is in carboxylate ion. Further, the negative charge is delocalized over two electronegative oxygen atoms in carboxylate ion. whereas it is less effectively delocalized over one oxygen atom and less electronegative carbon atoms in phenoxide ion. Thus, the carboxylate ion is more stabilized than phenoxide ion, so carboxylic acids are more acidic than phenols.

Effect of substituents on the acidity of carboxylic acids:

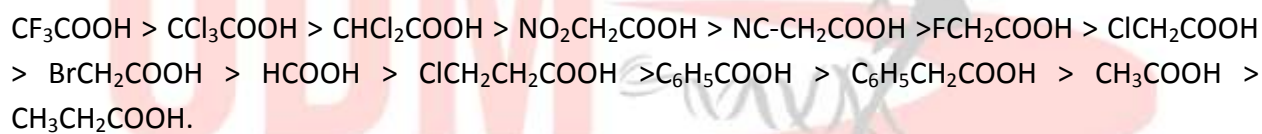
Substituents affect the acidity of the carboxylic acids. Because they affect the stability of the conjugate base. Electron withdrawing groups increase the acidity of carboxylic acids by stabilizing the conjugate base by inductive or resonance effects. But electron-donating groups decrease the acidity by destabilizing the conjugate base.



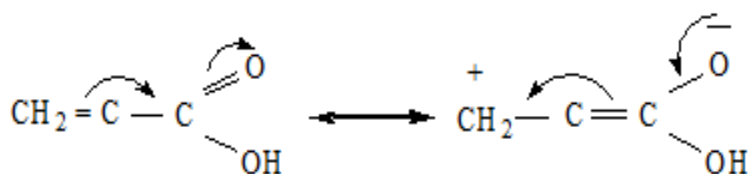
The effect of the following groups in increasing acidity order is



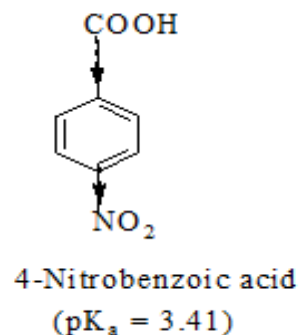
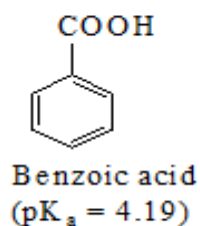
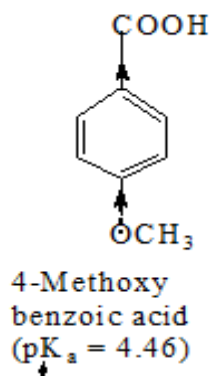
Order of acidic strength of some acids are:



The presence of phenyl or vinyl group to the carboxylic acid decreases acidity expected due to the resonance effect. This is due to the greater electronegativity of sp^2 hybridized carbon of carboxyl carbon.



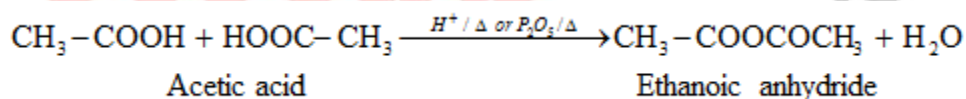
The presence of an electron-withdrawing group at the p-position of aromatic carboxylic acid increases acidity while electron-donating groups at p-position decrease acidity.



Reactions Involving Cleavage of C–OH Bond:

(a) Formation of anhydride:

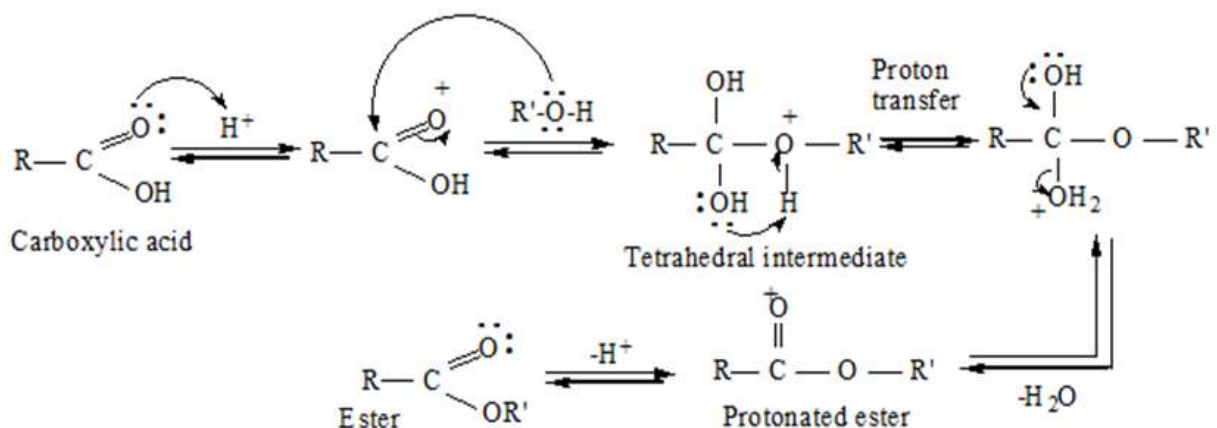
Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give the corresponding anhydride.



(b) Esterification:

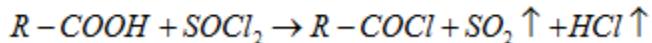
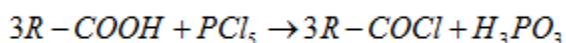
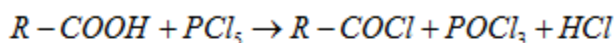
Carboxylic acids are esterified with alcohols or phenols in the presence of a mineral acid such as concentrated H_2SO_4 or HCl gas as a catalyst.





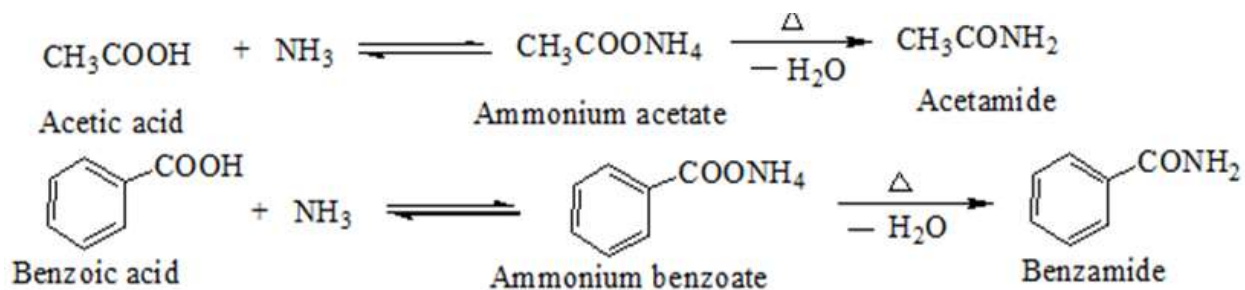
(c) Reaction with PCl_5 , PCl_3 , and $SOCl_2$

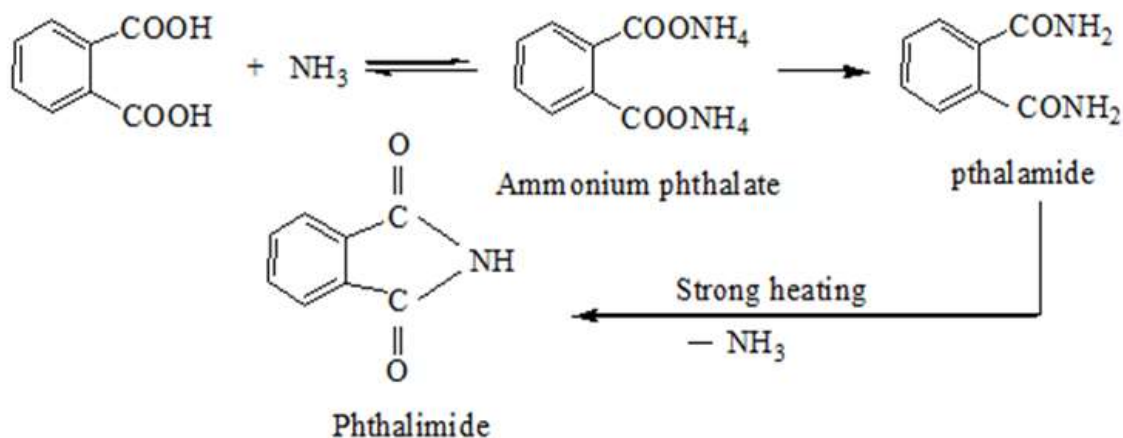
The hydroxyl group of carboxylic acids behaves like that of alcohol and is easily replaced by chlorine atom on treating with PCl_5 , PCl_3 , or $SOCl_2$. Thionyl chloride ($SOCl_2$) is preferred because the other two products are gaseous and escape the reaction mixture making the purification of the products easier.



(d) Reaction with ammonia:

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides.



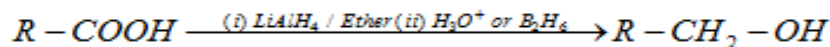


LECTURE-09

3. Reactions involving -COOH group:

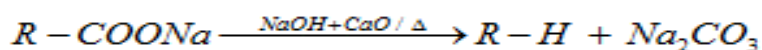
(a) Reduction:

Carboxylic acids are reduced to primary alcohols by lithium aluminum hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.



(b) Decarboxylation:

Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3: 1). The reaction is known as decarboxylation.

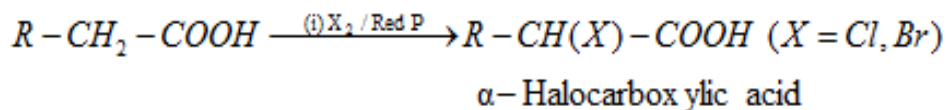


Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid. The reaction is known as **Kolbe electrolysis**.

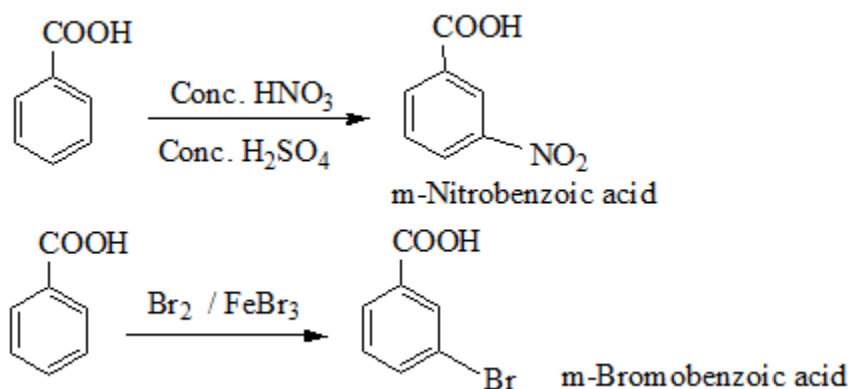
4. Substitution Reaction in the Hydrocarbon part:

(a) Halogenation (HVZ Reaction):

Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of a small amount of red phosphorus to give α -halocarboxylic acids. The reaction is known as the **Hell-Volhard-Zelinsky reaction**.

**(b) Ring Substitution:**

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta-directing group. They, however, do not undergo **Friedel-Crafts reaction** because the carboxyl group is deactivating and the catalyst aluminum chloride (Lewis acid) gets bonded to the carboxyl group.

**Uses:**

Methanoic acid is used in rubber, textile, dyeing, leather, and electroplating industries. Ethanoic acid is used as a solvent and as vinegar in the food industry. Hexanedioic acid is used in the manufacture of nylon-6, 6. Esters of benzoic acid are used in perfumery. Sodium benzoate is used as a food preservative. Higher fatty acids are used for the manufacture of soaps and detergents.