

## **DISTINGUISH TESTS**

SL.NO	Name of the test	Identification of compounds
01	Neutral ferric chloride	Only phenols(violet or purple color)
02	Sodium bicarbonate	Only carboxylic acid(brisk effervescence)
03	Iodo form test	All 2-ketones,2-alohols,ethanal,ethanol(yellow color crystals)
04	Lucas test	To distinguish 1 <sup>o</sup> 2 <sup>o</sup> & 3 <sup>o</sup> alcohols
05	Hinsberg test	1 <sup>o</sup> 2 <sup>o</sup> & 3 <sup>o</sup> amines
06	Carbylamines test	Only primary amines
07	Sodium metal test	Alcohols(effervescence)
08	2,4 DNP test	Both aldehydes & ketones (yellow color crystals)
09	Tollen's test	Only aldehydes(silver mirror formation)
10	Fehiling's test	Only aldehydes(red ppt)
11	Schiff's test	Aldehydes & Ketones
12		

### **DISTINGUISH BETWEEN**

**How can we distinguish organic compounds?**

**Test for Hydrocarbons:** Unsaturation Test

- i) **With Bromine water:** Disappearance of orange-red colour of bromine water indicates unsaturation.
- ii) **Baeyer's test:** When alkaline KMnO<sub>4</sub> is added to an unsaturated hydrocarbon, disappearance of pink colour indicates unsaturation. In this process MnO<sub>2</sub> is formed( brown colour).

**Specific test for acetylene and all terminal alkynes.**

i) **with Tollen reagent:**  $\text{H-C}\equiv\text{C-H} + 2[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^- \rightarrow \text{Ag-C}\equiv\text{C-Ag} + 4\text{NH}_3 + 2\text{H}_2\text{O}$

ii) **With ammonical cuprous chloride:**

$\text{H-C}\equiv\text{C-H} + 2[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^- \rightarrow \text{Ag-C}\equiv\text{C-Ag} + 4\text{NH}_3 + 2\text{H}_2\text{O}$

Hint:

1. if one alkane and one unsaturated substance given, distinguish them with unsaturation test.
2. if one alkene and one alkyne given, distinguish them with specific test for alkynes.
3. if both alkynes are given, distinguish them with specific test.

**Test for Alcohols:**

1. **Ester test:** Alcohol form ester with carboxylic acid. Ester can be identified by sweet smelling.  $\text{R-CH} + \text{R}'\text{-COOH} \leftrightarrow \text{R-COOR}' + \text{H}_2\text{O}$

2. With Ceric ammonium nitrate, alcohol gives pink or red colour.

**Different types of Alcohol:**

Lucas Test: Alcohol treated with Lucas reagent. (HCl + ZnCl<sub>2</sub>)

If turbidity appears immediately --- Tertiary alcohol

If turbidity appears after 5 min --- Secondary alcohol

If turbidity not appears --- Primary alcohol

Iodoform test: ethyl alcohol and all 2-hydroxy alcohol gives this test.

Reactions:

Hint:

1. If one alcohol and one other compound is given, explain ester formation, ceric ammonium nitrate test for alcohol.
2. If primary, Sec, or Tert. Alcohol given, explain with Lucas test.
3. If both alcohol are same type ( either primary, sec or tert) use iodoform test to distinguish them.

**Test for Phenol:**

Phenol when reacts with neutral ferric chloride, it produces violet colour.

Imp: Acetic acid and Formic acid also gives this test but produces deep red colouration.

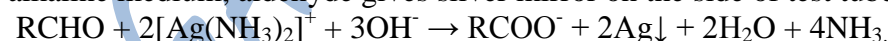
Test for aldehydes and Ketones:

**a) Test given by both aldehydes and ketones.**

- i). 2,4-dinitrophenyl hydrazine test: carbonyl compound react with 2,4-dinitrophenylhydrazine to form yellow or orange crystals.
- ii). Sodium bisulphate test: Aldehydes and ketones both form crystalline addition product with NaHSO<sub>3</sub>.
- iii). All aldehyde and ketones having CH<sub>3</sub>-C=O structure gives iodoform test positive.

**b) Test given by aldehydes only.**

i). Tollen Test: On warming with ammonical silver nitrate solution (Tollen reagent) in alkaline medium, aldehyde gives silver mirror on the side of test tube.

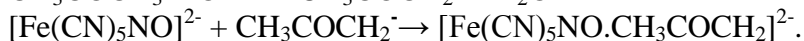
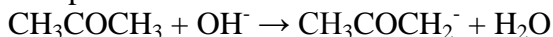


ii). Fehling solution Test: Fehling solution is alkaline solution of copper sulphate containing sodium potassium tartarate. Aldehydes gives reddish brown precipitate of Cu<sub>2</sub>O with Fehling solution.  $\text{RCHO} + 2\text{Cu}^{+2} + 5\text{OH}^- \rightarrow \text{RCOO}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$

**c) Test given by ketones only.**

i). m-dinitrobenzene test: Ketone gives violet colour with m-dinitrobenzene + NaOH solution.

ii). Sodium nitroprusside test: Ketone gives red colouration with sodium nitroprusside. In this process, the anion of the ketone formed by an alkali reacts with nitroprusside ion to form coloured ions.



Benzophenone does not give (+) test with m-dinitrobenzene and sodium nitroprusside.

Hint:

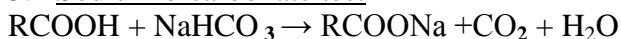
1. If one aldehyde and one ketone given, distinguish them by specific test.
2. If both are aldehyde or ketone, try to distinguish them by iodoform test.
3. Acetophenone and benzophenone: Acetophenone gives ketonic test whereas benzophenone does not.

**Test for Carboxylic acid:**

1. Litmus test (phenol also giving this test)

2. Ester test

3. Sodium bicarbonate test



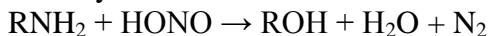
4. HCOOH and CH<sub>3</sub>COOH give test with neutral FeCl<sub>3</sub>.

**Test for Amines:**

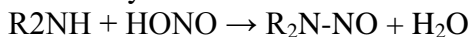
i). Litmus test

ii). Nitrous acid test:

Primary amine reacts with nitrous acid to give nitrogen gas.



Secondary amine reacts with nitrous acid to form a yellow oily nitrosamine.

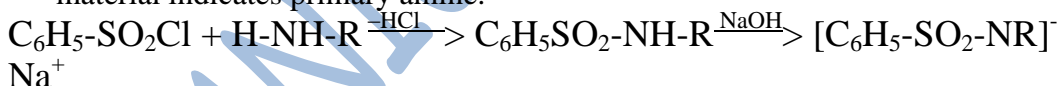


Tertiary amine reacts with nitrous acid to form soluble nitrite salt.



iii) Hinsberg Test: Amine when shaken with benzene sulphonyl chloride-

1. A clear solution in NaOH solution which on acidification gives an insoluble material indicates primary amine.



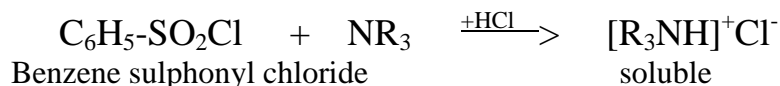
Benzene sulphonyl chloride  
sulphonamide (insoluble)

N-alkylbenzene

2. A precipitate (insoluble) which is insoluble in NaOH solution indicates secondary amine.



3. Tertiary amine does not react with benzene sulphonyl chloride. It forms soluble substance (addition product).



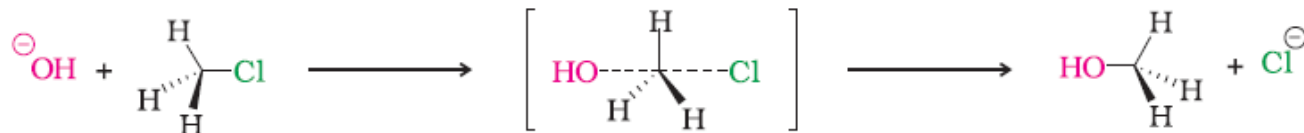
Specific test for Primary amine:

1. Azo-dye test: for aromatic primary amine only.

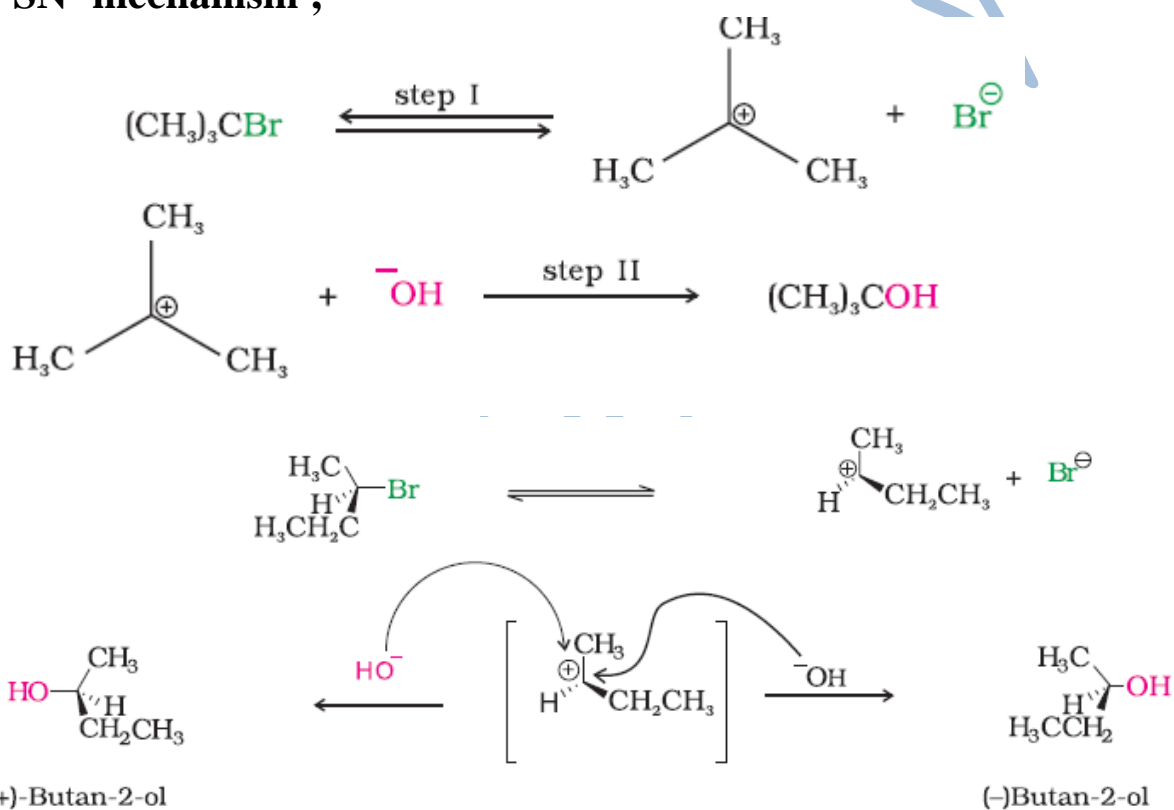


# Mechanism in Organic Chemistry

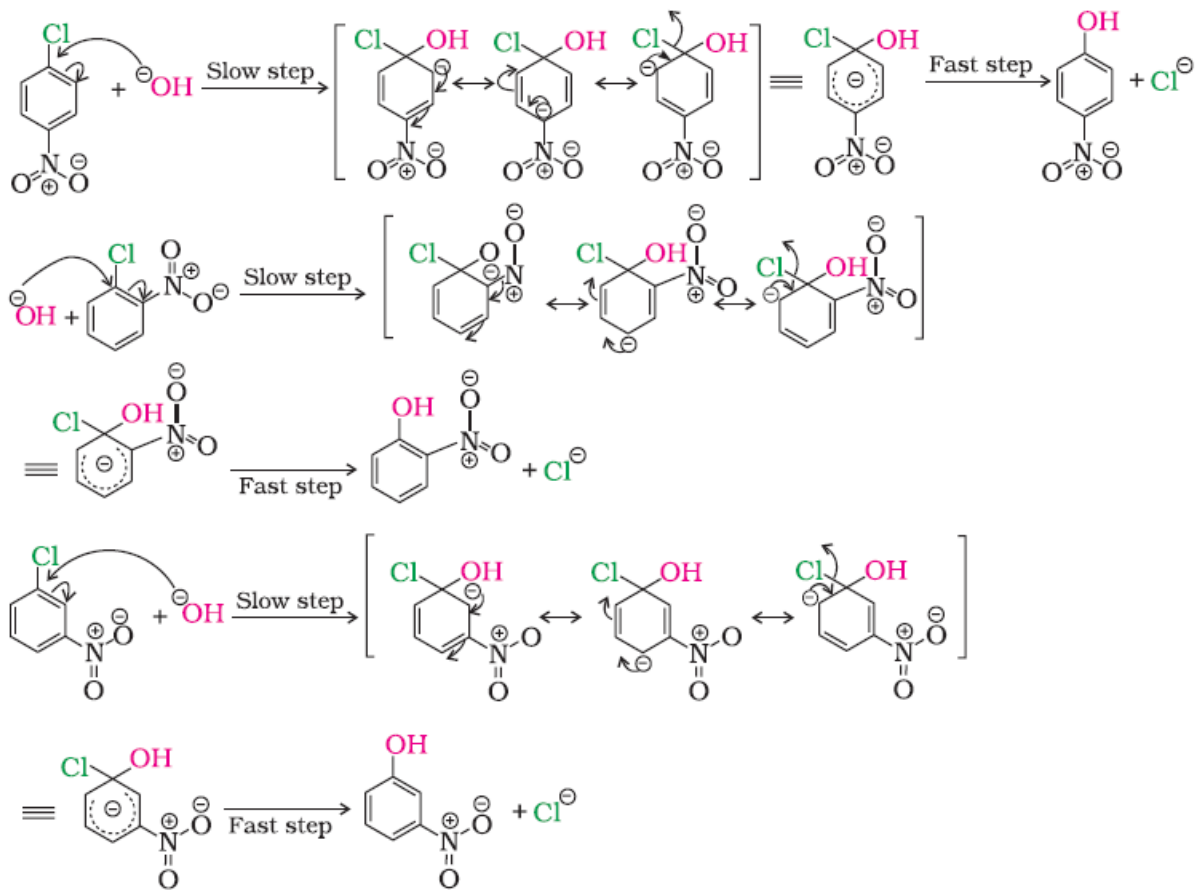
## 1. SN<sup>2</sup> Mechanism:



## 2. SN<sup>1</sup> mechanism ;



## 3. Effect of substituent on nucleophilic substitution on aryl halides



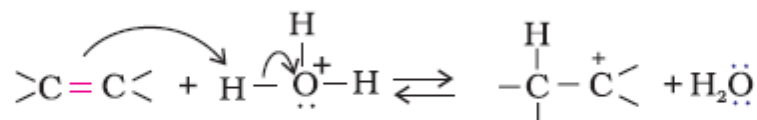
#### 4. Hydration of Alkenes:

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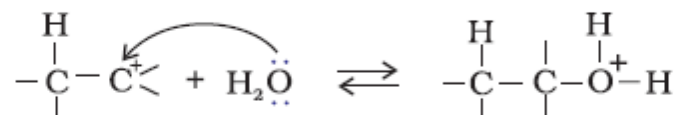
### Mechanism

The mechanism of the reaction involves the following three steps:

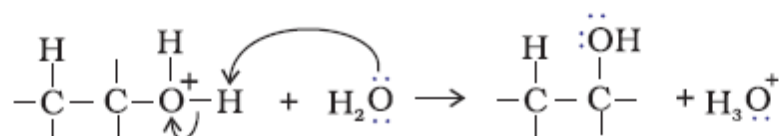
Step 1: Protonation of alkene to form carbocation by electrophilic attack of  $\text{H}_3\text{O}^+$ .



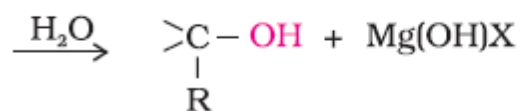
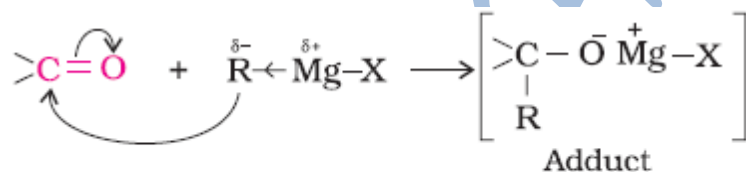
Step 2: Nucleophilic attack of water on carbocation.



Step 3: Deprotonation to form an alcohol.



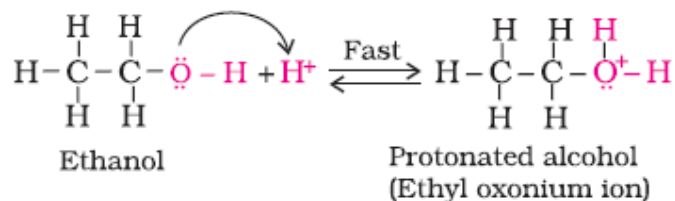
### 5. Addition of Grignard Reagent to Aldehydes & Ketones:



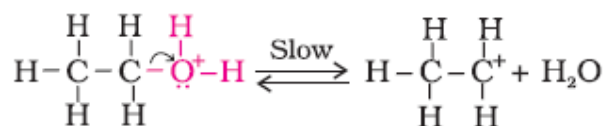
### 6. Dehydration of alcohols:

### Mechanism

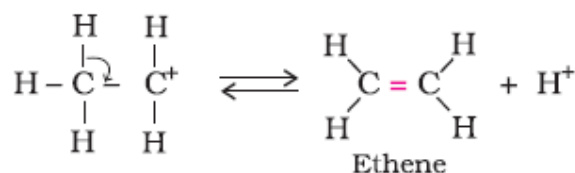
Step 1: Formation of protonated alcohol.



Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

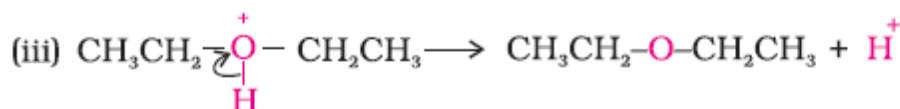
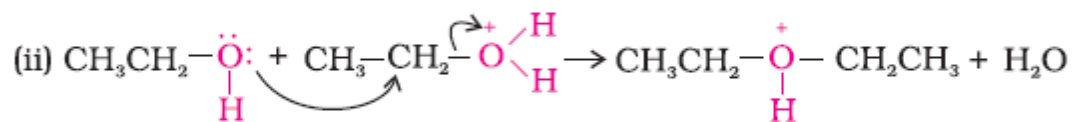
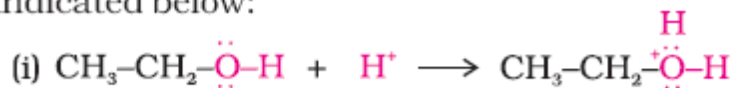


Step 3: Formation of ethene by elimination of a proton.



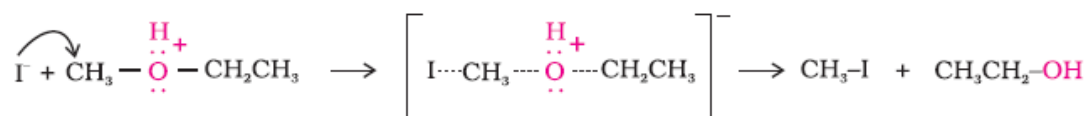
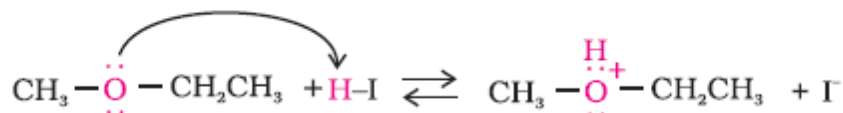
## 7. Dehydration of alcohols to give Ethers:

indicated below:



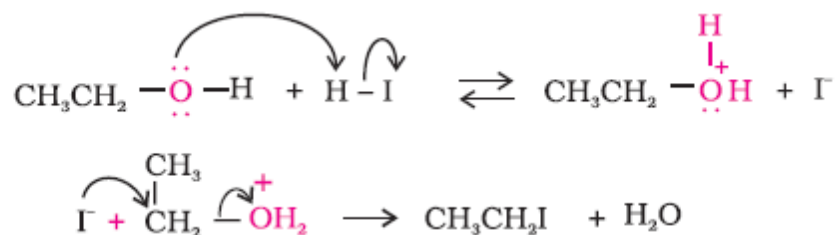
## 8. Reaction of ether with HI

Step 1:

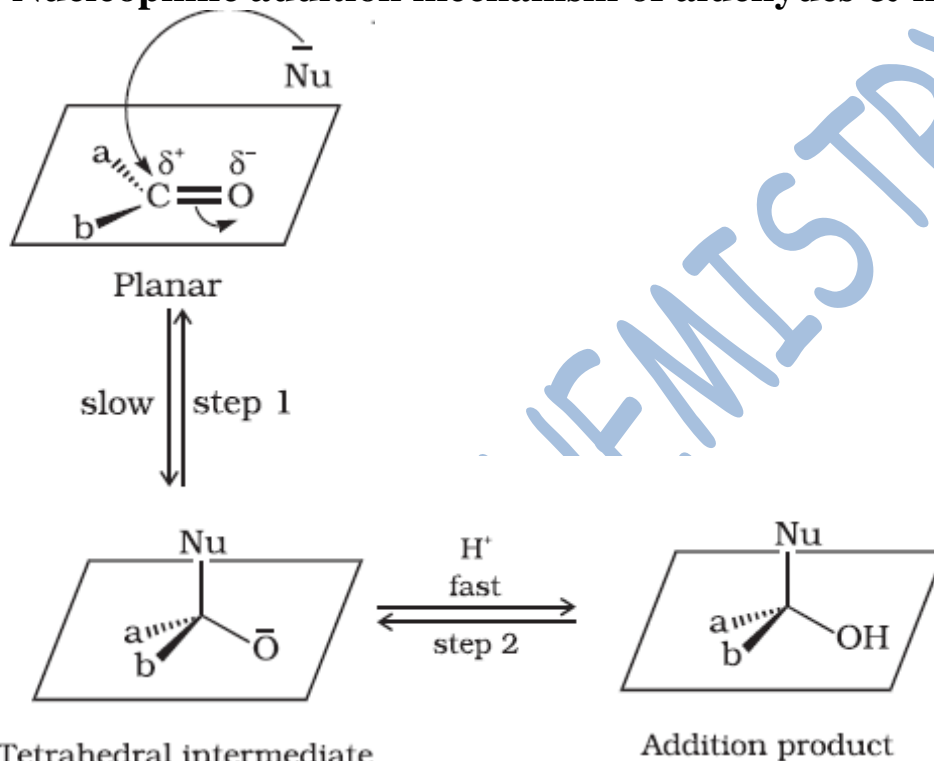




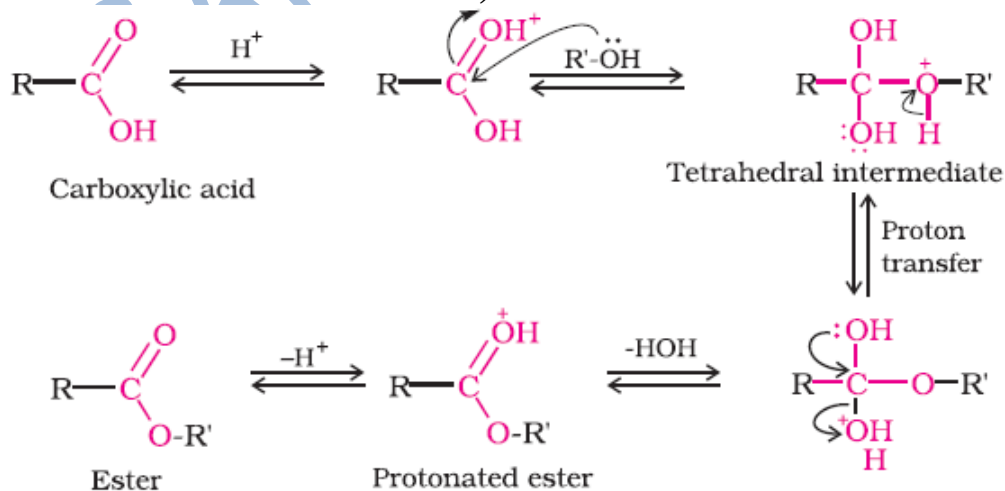
Step 3:



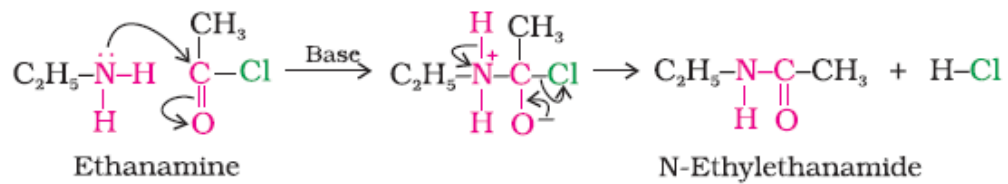
## 9. Nucleophilic addition mechanism of aldehydes & ketones.



## 10. Esterification mechanism;



## 11. Acylation of amines:



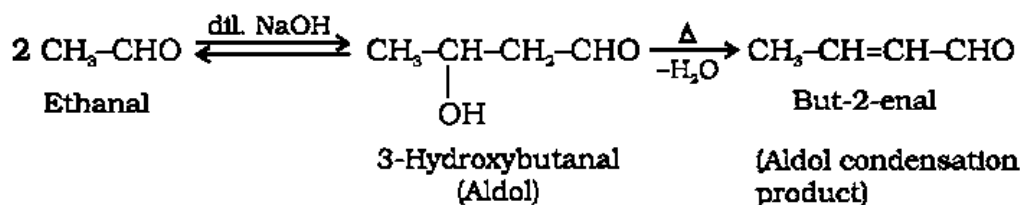
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# Organic Chemistry

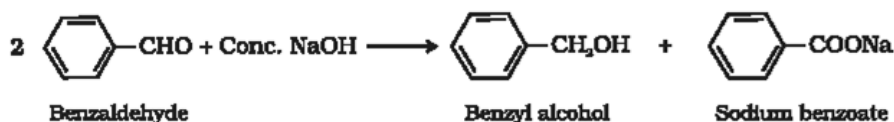
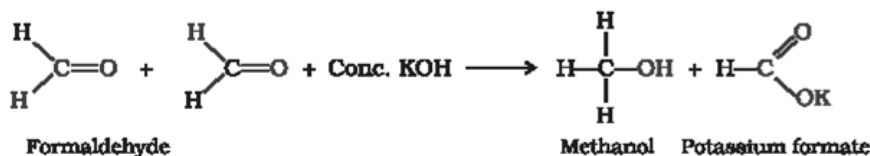
## Name Reactions

1. Aldol Condensation: condensation between two molecule of an aldehyde or a ketone having atleast one  $\alpha$ -hydrogen atom to form a  $\beta$ -hydroxyaldehyde or a  $\beta$ -hydroxyketone is known as aldol condensation.

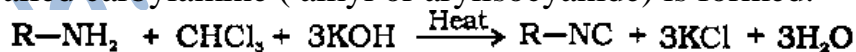


Aldol condensation takes place in presence of dil base.

2. Cannizzaro Reaction: The disproportionation (self-redox) of aldehydes lacking  $\alpha$ -hydrogen atom (as  $\text{C}_6\text{H}_5\text{CHO}$ ,  $\text{HCHO}$ ,  $\text{R}_3\text{C}\cdot\text{CHO}$  etc.) in presence of strong base to form salt of an acid & a primary alcohol is known as Cannizzaro reaction.

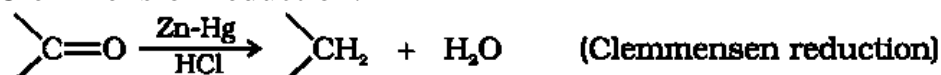


3. Carbylamine test: When a primary amine is heated with alcoholic caustic potash and chloroform, an offensive smelling compound called carbylamine (alkyl or arylisocyanide) is formed.

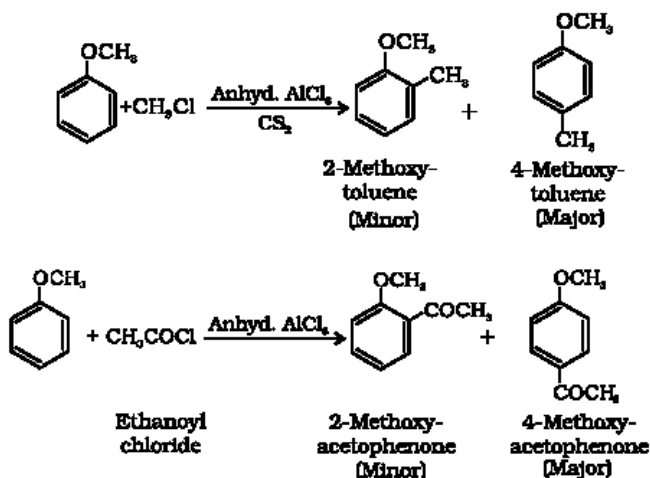


4. Claisen Condensation: The self condensation of ester containing  $\alpha$ -hydrogen atom in the presence of an alkoxide ( $\text{C}_2\text{H}_5\text{ONa}$ ) to give a  $\beta$ -ketoester is called Claisen condensation. Eg. Two molecule of ethylacetate condenses together to form ethyl  $\beta$ -ketobutanoate.

5. Clemmenson Reduction: The reduction of  $>\text{C}=\text{O}$  group to methyl group ( $>\text{CH}_2$ ) with amalgamated zinc and conc.  $\text{HCl}$  is known as Clemmenson reduction.



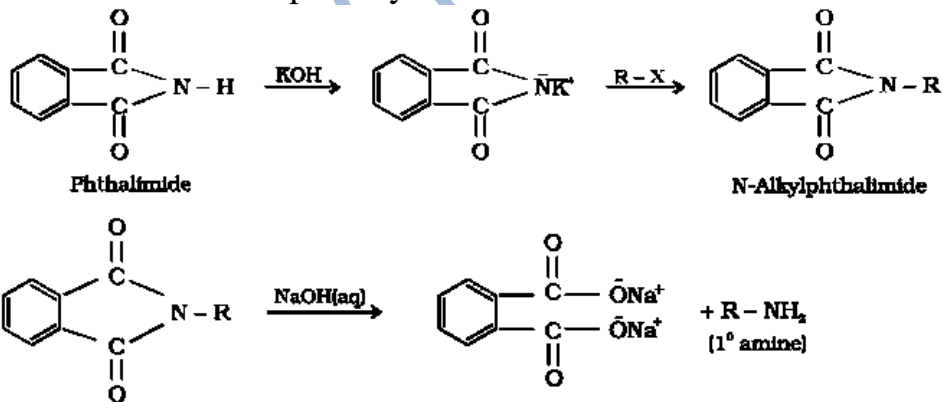




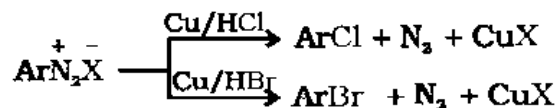
Introduction of an acyl group (RCO-) is called acylation.

11. Gabriel phthalimide synthesis: This method is used to prepare primary amine. The various steps involved are:

- i) phthalimide is treated with alcoholic solution of KOH to form potassium phthalimide.
- ii) The potassium salt is treated with an alkylhalide.
- iii) The product N-alkyl phthalimide is hydrolysed with dilute HCl to form a primary amine.

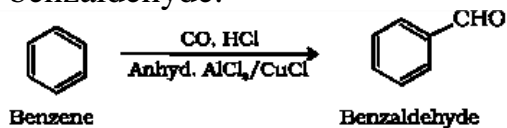


12. Gattermann Reaction: Gattermann reaction is used for obtaining chlorobenzene or bromobenzene from benzenediazonium chloride by treating it with Cu/HCl or Cu/HBr respectively.

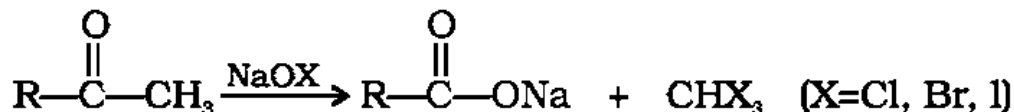


13. Gattermann-Koch Reaction: When benzene or its derivative is treated with carbon monoxide and HCl in the presence of

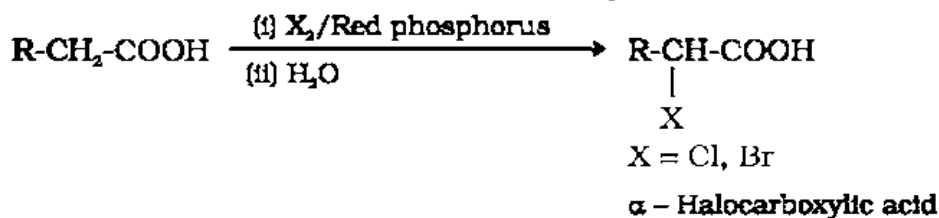
anhydrous aluminium chloride or CuCl, it gives benzaldehyde or substituted benzaldehyde.



14. Iodoform test: The compound containing methyl group bonded to carbonyl group (CH<sub>3</sub>-CO-) or (CH<sub>3</sub>-CH.OH-) reacts with aqueous NaOH and iodine solution gives yellow ppt of Iodoform.

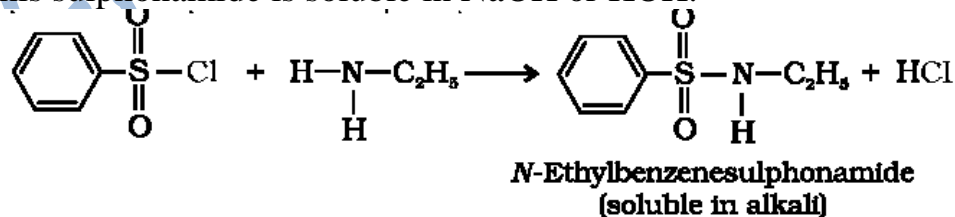


15. Hell-Volhard-Zelinsky Reaction: When aliphatic carboxylic acid containing  $\alpha$ -hydrogen are reacted with chlorine or bromine in presence of small amount of red phosphorous, the corresponding  $\alpha$ -haloacids are obtained.

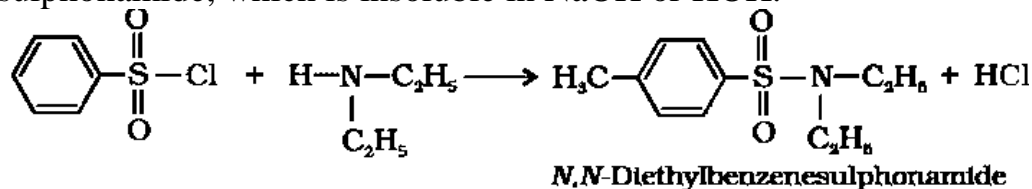


16. Hinsberg Test: Hinsberg test is employed to distinguish primary, secondary and tertiary amine. The reagent used in this test is benzene sulphonyl chloride. The tests are:

a) Primary amine:- It gives sulphonamide with hinsberg reagent, this sulphonamide is soluble in NaOH or KOH.

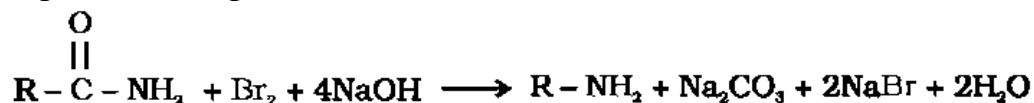


B) Secondary amine:-With hinsberg reagent,it forms sulphonamide, which is insoluble in NaOH or KOH.

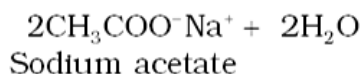


C) Tertiary amine:- Tertiary amine do not react with hinsberg reagent ,because it is not having replaceable hydrogen.

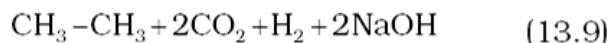
17. Hoffmann-Bromamide Reaction: When an amide is heated with bromine and an alkali, a primary amine containing one carbon less than the amide is obtained. This reaction is called Hoffmann-Bromamide reaction. This reaction is very useful for converting a higher homologue to next lower one.



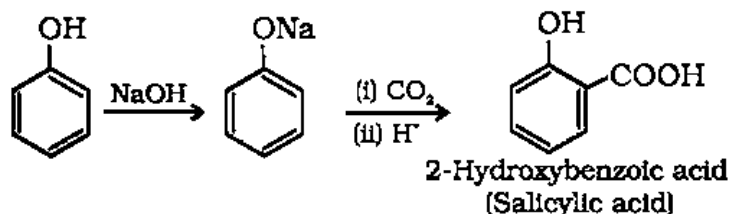
18. Kolbe's-Electrolysis process: Preperation of higher a;kanes by the electrolysis of sodium or potassium salt of lower fatty acids is called Kolbe's electrolysis reaction.



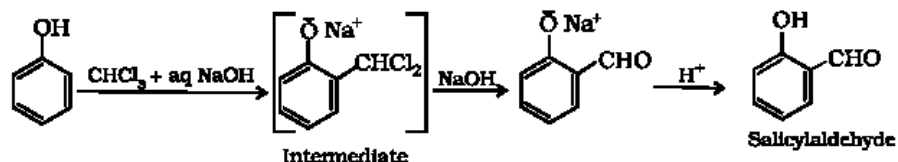
↓ Electrolysis



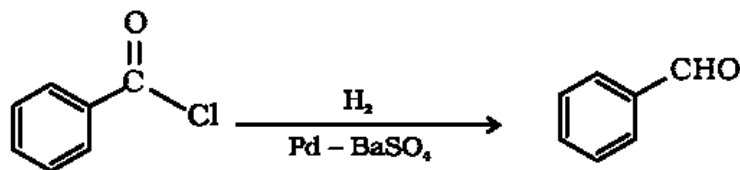
19. Kolbe,s Schmith process: This reaction gives the method for fixation of CO<sub>2</sub> in the benzene ring.Sodium phenoxide on heating that 120-140<sup>0</sup>C under 4-7 atm pressure with CO<sub>2</sub> gives sodium salicylate which on reaction with dil.HCl gives salicylic acid(2-hydroxy benzoic acid).



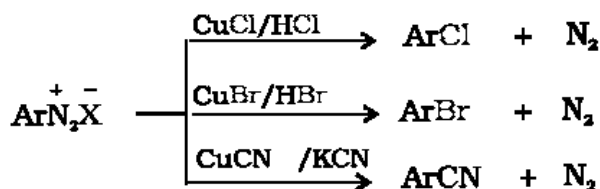
20. Riemer-Tiemann Reaction: The reaction of pheonal with chloroform or carbon-tetrachloride in the presence of aqueous alkali at 340k followed by hydrolysisof the resulting product gives salicyldehyde and salicylic acid respectively.



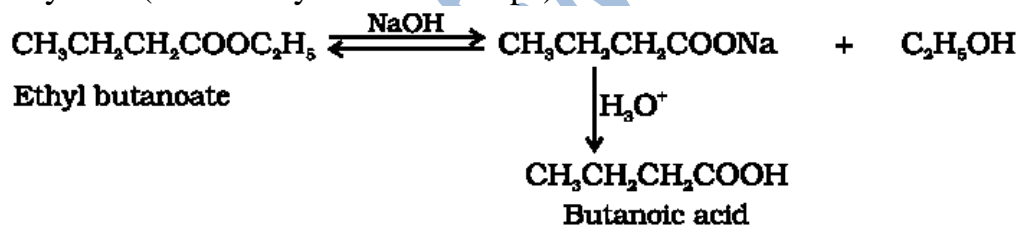
21. Rosenmund Reduction: Reduction of acid chloride (RCOCl)to the corresponding aldehyde with hydrogen using Pd/BaSO<sub>4</sub> as catalyst is known as rosenmund reaction.Here Pd/BaSO<sub>4</sub> used as negative catalyst and prevent further reduction to alcohol.



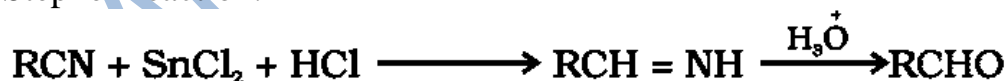
22. Sandmeyer Reaction: The conversion of benzene diazonium salt into halogen or cyano derivative of the parent aromatic hydrocarbon by treating it with a mixture containing the corresponding salt and the acid is called Sandmeyer reaction.



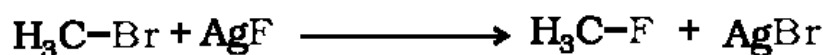
23. Saponification Process: Hydrolysis of esters in the presence of an alkali is known as saponification. In this process sodium salt of fatty acids (commonly called as soaps) are obtained.



24. Stephen Reaction: Nitriles can be reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde. This reaction is called Stephen reaction.

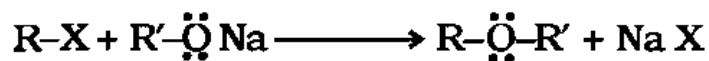


25. Swart's reaction: The synthesis of alkyl fluorides is accomplished by heating an alkyl chloride/ bromide in the presence of a metallic fluoride such as AgF, Hg<sub>2</sub>F<sub>2</sub> etc.



26. Williamson's synthesis: In Williamson synthesis, when an alkoxide or a phenoxide is made to react with an alkyl halide, an ether is obtained. In this method, haloarenes can not be used for the preparation of alkyl-aryl ethers because of the low reactivity of aryl halides.



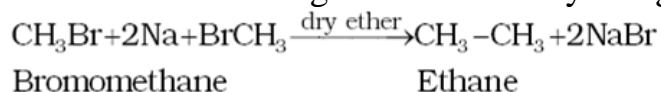


27. Wolf-Kishner reaction: A carbonyl compound on heating hydrazine and potassium hydroxide (KOH) in a high boiling polar solvent such as ethylene glycol, gets reduced to give a hydrocarbon.



(Wolf-Kishner reduction)

28. Wurtz-Fittig Reaction: This reaction is used for obtaining higher alkane from the halogen derivatives by using sodium.



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ORGANIC CHEMISTRY

## HALO ALKANES AND HALO ARENES

- Halo alkanes and Halo Arenes find wide applications in industry as well as in day-to-day life. They are used as solvents for relatively non-polar compounds and as starting materials for the synthesis of wide range of organic compounds. Chlorine containing antibiotic, *Chloramphenicol*, produced by soil microorganisms is very effective for the treatment of typhoid fever. Our body produces iodine containing hormone, *thyroxine*, the deficiency of which causes a disease called *goiter*. Synthetic halogen compounds, *viz.* Chloroquine is used for the treatment of malaria; halothane is used as an anaesthetic during surgery. Certain fully fluorinated compounds are being considered as potential blood substitutes in surgery.
- In halo alkanes as size of halogen increases C—X bond strength decreases hence reactivity increases.
- Preparation of Halo alkanes from alcohols using Thionyl chloride is preferred because the other two products are escapable gases.
- Preparation of Halo alkanes from alcohols using hydrogen halides, the order of reactivity of alcohols with a given halo acid is  $3^\circ > 2^\circ > 1^\circ$ .
- The above method is not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond.
- Iodination of Arenes with iodine is reversible in nature and requires the presence of an oxidizing agent ( $\text{HNO}_3$ ,  $\text{HIO}_4$ ) to oxidise the HI formed during iodination.
- Reactions of un saturated hydrocarbons with Bromine water yields colorless alkyl halides hence it is used as testing for un saturated hydro carbons.
- Markovnikov's rule: When un symmetrical alkene under goes addition with un symmetrical reagent, the major product of alkyl halide one in which, the negative part of addendum will be added to the carbon having less no. of hydrogen atoms.
- Anti Markovnikov's rule: (Peroxide Effect) (Kharasch Effect) When un symmetrical alkene under goes addition with un symmetrical reagent, the major product of alkyl halide one in which, the negative part of addendum will be added to the carbon having more no. of hydrogen atoms.
- Alkyl halides are having more boiling point as compare with hydro carbons of equal molecular mass it is due to dipole- dipole attractions present in it.
- For the same alkyl group, the boiling points of alkyl halides decrease in the order:  $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ . This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.
- The boiling points of isomeric halo alkanes decrease with increase in branching due to decrease in spherical surface area which in turn decreases vander waal's force.
- Boiling points of isomeric di halo benzenes are very nearly the same. However, the *para*-isomers are high melting as compared to their *ortho* and *meta*-isomers. It is due to symmetry of *para*-isomers that fits in crystal lattice better as compared to *ortho*- and *meta*-isomers.

- *The halo alkanes are only very slightly soluble in water, Energy released during dissolution is not sufficient to break the hydrogen bond between water molecules.*
- Groups like cyanides and nitrites possess two nucleophilic centres and are called *ambident nucleophiles*.
- Halo alkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. It is because KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.
- Nucleophilic substitution in alkyl halides follows two types of mechanisms, SN<sup>1</sup> (Substitution of Nucleophile follows first order kinetics) & SN<sup>2</sup> (Substitution of Nucleophile follows Second order kinetics).
- SN<sup>1</sup> reaction mechanism is followed by those alkyl halides whose carbo cation is stable like tertiary alkyl halides, Allyl halides & Benzyl halides. It forms carbo cation intermediate, which is triangular planar & SP<sup>2</sup> hybridized intermediate. If alkyl halide is optically active after substitution it forms racemic mixture.
- SN<sup>2</sup> reaction mechanism is followed by primary alkyl halide (whose carbanion is stable). It forms carbanion intermediate, which is sp<sup>3</sup>d hybridized and pentavalent. During SN<sup>2</sup> mechanism optical activity is reversed this is known as optical inversion.
- Molecules which are able to rotate plane polarized light are called optically active compounds.
- Light whose waves oscillate in only one plane is known as plane polarized light.
- Non super imposable mirror images are called Enantiomers.
- Substances which rotate plane polarized light are called dextro and one which rotates towards left is known as leavo rotatory compound.
- In a molecule if Carbon atom is surrounded by four different groups called asymmetric carbon or chiral carbon which is must for optical active compound.
- 1:1 ratio of dextro and leavo mixture is known as racemic mixture.
- The process of conversion of enantiomer into a racemic mixture is known as **racemisation**.
- Secondary alkyl halides undergoes both SN<sup>1</sup> & SN<sup>2</sup> mechanism.
- If there is possibility of formation of more than one alkene due to the availability of more than one α-hydrogen atoms, usually one alkene is formed as the major product. These form part of a pattern first observed by Russian chemist, Saytzeff who in 1875 formulated a rule which can be summarized as *“in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.”*
- An alkyl halide with α-hydrogen atoms when reacted with a base or a nucleophile has two competing routes: substitution (SN1 and SN2) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions. Thus, a bulkier nucleophile will prefer to act as a base and abstracts a proton rather than approach a tetravalent carbon atom (steric reasons) and *vice versa*.

- Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the Resonance effect (partial double bond), halogen bonded to  $sp^2$  carbon which is more electronegative and less bond length, instability of phenyl cation & repulsion between electron rich arenas, nucleophile.
- Nucleophilic substitution on aromatic rings becomes easy in the presence of electron withdrawing groups like nitro which stabilize the carbanion. This effect is not shown when nitro group is present at meta position.
- Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*-directing in electrophilic aromatic substitution reactions. Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilizes the intermediate carbocation formed during the electrophilic substitution. Through resonance, halogen tends to stabilize the carbocation and the effect is more pronounced at *ortho*- and *para*-positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho*- and *para* positions and hence makes the deactivation less for *ortho*- and *para* attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.
- Chloroform is slowly oxidized by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark colored bottles completely filled so that air is kept out.

## ALCOHOLS, PHENOLS & ETHERS

- The bond angle in alcohols is slightly less than the tetrahedral angle ( $109^\circ-28'$ ). It is due to the repulsion between the unshared electron pairs of oxygen.
- In phenols, the  $-OH$  group is attached to  $sp^2$  hybridised carbon of an aromatic ring. The carbon-oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to (i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring and (ii)  $sp^2$  hybridized state of carbon to which oxygen is attached.
- The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky ( $-R$ ) groups. The C-O bond length (141 pm) is almost the same as in alcohols.
- Hydroboration-oxidation of alkenes gives addition of water to alkene as per anti Markovnikov's rule.
- The boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers and hydrocarbons.
- Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups.
- Alcohols are weak Bronstead acids i.e. they can donate proton to a stronger base.

- The acidic character of alcohols is due to the polar nature of O–H bond. An electron-releasing group ( $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ) increases electron density on oxygen tending to decrease the polarity of O–H bond. This decreases the acid strength. Hence acidity of alcohols is  $1^\circ > 2^\circ > 3^\circ$  alcohols.
- Alcohols act as Bronsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.
- Alcohols and phenols react with Na metal gives hydrogen gas it supports the acidic nature. But Phenol even reacts with NaOH hence phenol is strong base than alcohol. It is due to the resonance stability of Phenoxide ion.
- Electron releasing groups on alcohol and phenol decrease acidity and electron withdrawing groups increase acidity. Because electron withdrawing groups stabilize the phenoxide/alkoxide ions. More  $K_a$  or Less  $P^K_a$  value indicates higher acidity.
- the relative ease of dehydration of alcohols follows the following order: Tertiary > Secondary > Primary it is due to stability of carbocation.
- The usual halogenation of benzene takes place in the presence of a Lewis acid, such as  $\text{FeBr}_3$ , which polarizes the halogen molecule. In case of phenol, the polarization of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of  $-\text{OH}$  group attached to the benzene ring.
- The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a color) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol.
- The dehydration of secondary and tertiary alcohols to give corresponding ethers is unsuccessful as elimination competes over substitution and as a consequence, alkenes are easily formed.
- The weak polarity of ethers do not appreciably affect their boiling points which are comparable to those of the alkanes of comparable molecular masses but are much lower than the boiling points of alcohols. The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.
- The miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water.
- The order of reactivity of hydrogen halides is as follows:  $\text{HI} > \text{HBr} > \text{HCl}$ .
- Reaction of anisole with HI gives Phenol & methyl iodide but not other products because there is a partial double bond character between Benzene ring and Oxygen.
- Tertiary butyl methyl ether react with HI gives Methanol and tertiary butyl Iodide it is due to stability of tertiary carbocation.
- $1^\circ, 2^\circ$  &  $3^\circ$  alcohols are distinguished by Lucas Test. Lucas reagent is  $\text{HCl} + \text{ZnCl}_2$  tertiary amines react with Lucas reagent and cloudiness forms immediately, secondary amines react with Lucas reagent and cloudiness forms after 5 mts, primary amines react with Lucas reagent and cloudiness forms only by heating.

## ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

- The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to 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 absence of intermolecular hydrogen bonding.
- The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bond with water. However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.
- The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance and hence it is less reactive than propanal.
- Sodium hydrogensulphite adds to aldehydes and ketones to form the addition products by equilibrium reaction. The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most ketones due to steric reasons. The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali. Therefore, these are useful for separation and purification of aldehydes.
- Addition of ammonia derivatives to the aldehydes & ketones takes place under controlled  $P^H$  because reaction takes place by acid catalyzed mechanism, if acidity is more it react with ammonia derivatives (bases).
- Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.
- Characteristic reactions of aldehydes and ketones are not given by carboxylic acids in spite of having  $C=O$  it is due to resonance stabilization of carboxylic group.
- Aliphatic carboxylic acids having 12 to 18 carbon atoms are known as fatty acids.
- The solubility decreases with increasing number of carbon atoms. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.
- Quantitatively acidity of carboxylic acids are compared by using  $K_a$  acid dissociation constant or  $P^K_a$  values. Higher  $K_a$  value or less  $P^K_a$  represents strong acids.
- Smaller the  $pKa$ , the stronger the acid ( the better it is as a proton donor). Strong acids have  $pKa$  values  $< 1$ , the acids with  $pKa$  values between 1 and 5 are considered to be moderately strong acids, weak acids have  $pKa$  values between 5 and 15, and extremely weak acids have  $pKa$  values  $>15$ .
- Carboxylic acids are weaker acids as compare with mineral acids like  $HCl$ ,  $H_2SO_4$ ,  $HNO_3$  but stronger acids than alcohol and phenol.
- Carboxylic acids are strong acids than Phenol it is due to high stability of carboxylate ion as compare to Phenoxide ion. Negative charge is distributed on

- two equally electronegative atoms where as in phenol it is distributed on two unequal atoms.
- Electron withdrawing groups increase the acidity of carboxylic acids by stabilizing the conjugate base through delocalization of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilizing the conjugate base.
  - The effect of the following groups in increasing acidity order is  
 $\text{Ph} < \text{I} < \text{Br} < \text{Cl} < \text{F} < \text{CN} < \text{NO}_2 < \text{CF}_3$
  - 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).

## AMINES

- In nature, Amines occur among proteins, vitamins, alkaloids and hormones. Synthetic examples include polymers, dyestuffs and drugs. Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure. Novocain, a synthetic amino compound, is used as an anesthetic in dentistry. Benadryl, a well known antihistaminic drug also contains tertiary amino group. Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes.
- Ammonolysis of alkyl halides gives amines, but it has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt. However, primary amine is obtained as a major product by taking large excess of ammonia. The order of reactivity of halides with amines is  $\text{RI} > \text{RBr} > \text{RCl}$ .
- Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.
- Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water.
- Equal molecular masses of amines & alcohols, alcohols are more polar than amines and form stronger intermolecular hydrogen bonds than amines.
- This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of

hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

**Primary > Secondary > Tertiary**

- Amines have an unshared pair of electrons on nitrogen atom due to which they behave as **Lewis base**. Basic character of amines can be better understood in terms of their  $K_b$  and  $pK_b$  values.
- Larger the value of  $K_b$  or smaller the value of  $pK_b$ , stronger is the base.
- Basicity of amines in gaseous state increased by +ve inductive effect, but in aqueous state apart from +I effect it also depends on hydration effect & steric effect.
- The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine >  $\text{NH}_3$ .
- The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:  
 $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$   
 $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
- $pK_b$  value of aniline is quite high than ammonia. It is because in aniline or other aryl amines, the  $-\text{NH}_2$  group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation.
- In case of substituted aniline, it is observed that electron releasing groups like  $-\text{OCH}_3$ ,  $-\text{CH}_3$  increase basic strength whereas electron withdrawing groups like  $-\text{NO}_2$ ,  $-\text{SO}_3$ ,  $-\text{COOH}$ ,  $-\text{X}$  decrease it.
- Reaction of nitrous acid with different amines gives different products. Primary aliphatic amines gives alcohols, primary aromatic amines gives diazonium chloride, secondary aliphatic and aromatic amines gives N-Nitroso amines, tertiary aliphatic amines gives quaternary ammonium nitrite where as tertiary aromatic amines gives p-nitroso aniline.
- $1^\circ, 2^\circ$  &  $3^\circ$  amines are distinguished by Hinsberg's test i.e. primary amine react with Hinsberg's reagent (**Benzene Sulphonyl Chloride**) and resulting compound is soluble in  $\text{KOH}$ , secondary amine react with B.S.C and resulting compound is insoluble in  $\text{KOH}$ , tertiary amines do not react with B.S.C.
- Aniline is more reactive for electrophilic substitution due to involvement of lone pair on nitrogen makes benzene ring activated towards electrophilic substitution. This effect is minimized by adding acyl group on nitrogen. The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below: Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of  $-\text{NHCOCH}_3$  group is less than that of amino group.
- Nitration aniline gives ortho, para & meta nitro aniline mixture of compounds. Though  $-\text{NH}_2$  is a o-p directing it forms substantial amount of meta product also it is due to in strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing. That is why besides the *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.
- Sulphonation aniline forms sulphonilic acid which forms zwitter ion.



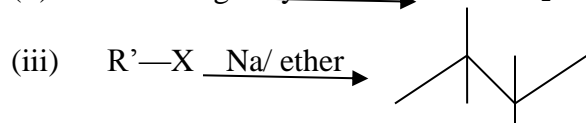
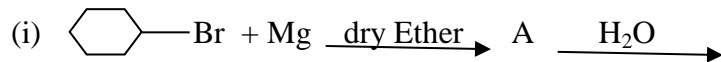
- The conversion of primary aromatic amines into diazonium salts by reacting with nitrous acid at  $0-5^{\circ}\text{C}$  is known as diazotization .
- Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yields *p*-amino azo benzene. This is an example of electrophilic substitution reaction.

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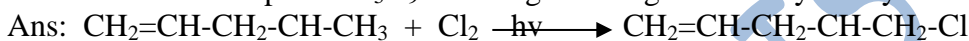
ORGANIC CHEMISTRY

## ORGANIC CONVERSIONS (text book)

1. Identify the A,B,C,D,E,R & R' in the following:

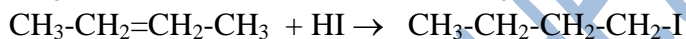
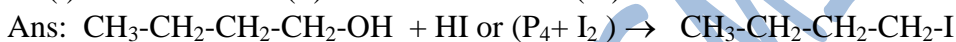


2. A hydrocarbon C<sub>5</sub>H<sub>10</sub> does not react with chlorine in dark but gives a single monochloro compound C<sub>5</sub>H<sub>9</sub>Cl in bright sun light. Identify the hydro carbon.

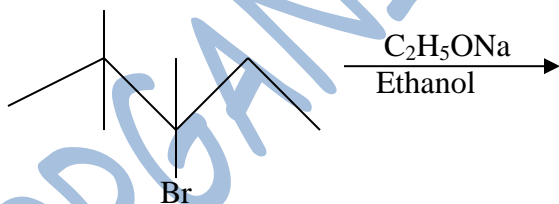
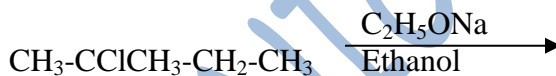
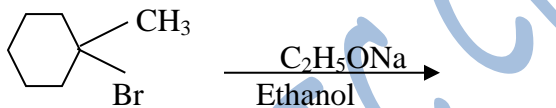


3. Write the equations for the preparation of 1-Iodo butane from :

(i) 1 – butanol    (ii) 1- chloro butane    (iii) But-1-ene



4. Predict the product from the following reactions:



1. How will you bring about following conversions:

- (i) Ethanol to but-1-yne
- (ii) Ethane to bromoethene
- (iii) Propene to 1-nitropropane
- (iv) Toluene to benzyl alcohol
- (v) Propene to propyne
- (vi) Ethanol to ethyl fluoride
- (vii) Bromomethane to propanone
- (viii) But-1-ene to but-2-ene
- (ix) 1-Chlorobutane to n-octane

- (x) Benzene to biphenyl.
- Propene to propan-1-ol
  - Ethanol to but-1-yne
  - 1-Bromopropane to 2-bromopropane
  - Toluene to benzyl alcohol
  - Benzene to 4-bromonitrobenzene
  - (vi) Benzyl alcohol to 2-phenylethanoic acid
  - Ethanol to propanenitrile
  - Aniline to chlorobenzene
  - 2-Chlorobutane to 3, 4-dimethylhexane
  - 2-Methyl-1-propene to 2-chloro-2-methylpropane
  - Ethyl chloride to propanoic acid
  - But-1-ene to n-butyliodide
  - 2-Chloropropane to 1-propanol
  - Isopropyl alcohol to iodoform
  - Chlorobenzene to *p*-nitrophenol
  - 2-Bromopropane to 1-bromopropane
  - Chloroethane to butane
  - Benzene to diphenyl
  - tert*-Butyl bromide to isobutyl bromide
  - Aniline to phenylisocyanide
  - Phenol into *o*-nitro Phenol
  - Phenol into Tri nitro phenol
  - Propene → Propan-2-ol.
  - Benzyl chloride → Benzyl alcohol.
  - Ethyl magnesium chloride → Propan-1-ol.
  - Methyl magnesium bromide → 2-Methylpropan-2-ol.
  - Propanone to Propene
  - Benzoic acid to Benzaldehyde
  - (Ethanol to 3-Hydroxybutanal
  - Benzene to *m*-Nitroacetophenone
  - Benzaldehyde to Benzophenone
  - Bromobenzene to 1-Phenylethanol
  - Benzaldehyde to 3-Phenylpropan-1-ol
  - Benzaldehyde to  $\alpha$ -Hydroxyphenylacetic acid
  - (ix) Benzoic acid to *m*- Nitrobenzyl alcohol
  - Benzene into aniline
  - (ii) Benzene into N, N-dimethylaniline
  - Cl-(CH<sub>2</sub>)<sub>4</sub>-Cl into hexan-1,6-diamine?
  - Ethanoic acid into methanamine
  - Hexanenitrile into 1-aminopentane
  - Methanol to ethanoic acid
  - (iv) Ethanamine into methanamine
  - Ethanoic acid into propanoic acid
  - Methanamine into ethanamine

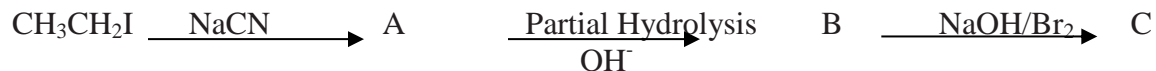
46. Nitromethane into dimethylamine
47. Propanoic acid into ethanoic acid?
48. Nitrobenzene to benzoic acid
49. Benzene to *m*-bromophenol
50. Benzoic acid to aniline
51. Aniline to 2,4,6-tribromofluorobenzene
52. Benzyl chloride to 2-phenylethanamine
53. Chlorobenzene to *p*-chloroaniline
54. Aniline to *p*-bromoaniline
55. Benzamide to toluene
56. Aniline to benzyl alcohol.

### Some Important Conversions

1. 2- Bromo Propane into 1 – Bromo Propane
2. Propan-2-ol into Propan -1- ol
3. Formaldehyde into Propan -1- ol
4. Acetaldehyde into Propan -2-ol
5. Acetone into t-Butyl alcohol
6. Aniline into Phenol
7. Cumene into Phenol
8. Phenol into salicylic Acid
9. Phenol into 2 – Acetoxy Benzoic Acid ( Aspirine)
10. Propan -1-ol into 2-Bromo Propane
11. Phenol into Benzaldehyde
12. Phenol into Salicylaldehyde
13. Ethane into diethyl ether
14. Ethyl chloride into propanal
15. Benzene into Benzaldehyde
16. Acetic acid to acetaldehyde
17. Acetic acid into acetone
18. Acetonitrile into Benzophenone
19. Acetaldehyde into lactic acid
20. Acetaldehyde into crotonaldehyde (But-2enal)
21. Acetaldehyde into Butan-1-ol
22. Acetaldehyde into But-2enoic acid
23. Acetaldehyde into Butane-2,4 diol
24. Acetone into 4-methyl pent-3-ene-2-one
25. Benzene into Benzoic acid
26. Benzoic acid into Aniline
27. Chloro Benzene into Benzoic acid
28. Benzyl alcohol into Phenyl ethanoic acid
29. 3-nitro Bromo Benzene into 3-nitro Benzoic acid

30. 4-methyl Acetophenone into terphthalic acid
31. cyclo hexane into adipic acid
32. Phthalic acid into phthalamide
33. Acetic acid into Malonic acid
34. Acetic Acid into Alanine
35. Benzene into methyl Benzoate
36. Benzene into m-nitro Benzoic acid
37. Benzene into p-nitro Benzoic acid
38. Benzene into Phynyl Acetic acid
39. Benzene into p-nitro Benzaldehyde
40. Benzene into Aneline
41. Ethyl chloride to propanamine
42. Ethyl amine into Ethyl Carbyl amine
43. Aneline into 4-bromo Aneline
44. Aneline into 4-Nitro Anelien
45. Aneline into Sulphanilic acid
46. Aneline into Acetanilide
47. Phenol into Phenyl Acetate
48. Aneline into Floro Benzene
49. Aneline into Nitro Benzene
50. Aneline into Phenol
51. Aneline into Benzoic Acid
52. Aneline into Benzene
53. 4-Nitro Toluene into 2-Bromo Benzoic Acid
54. 3-methyl Aneline into 3-Nitro Toluene
55. Acetic Acid to Methanol
56. Ethyl Bromide into Propan-1-ol
57. Benzamide into Toluene
58. Aneline into Benzyl alcohol
59. Benzoic Acid into Aneline
60. Benzene into m-bromo phenol
61. Propanoic acid into Ethanoic acid
62. Methanamine into Ethanamine
63. Ethanoic Acid into Propanoic Acid
64. Ethanamine into Methanamine
65. Benzoic Acid into m-nitro Benzyl alcohol
66. Benzaldehyde into alpha hydroxyl phenyl Acetic acid
67. Benzaldehyde into 3-Phenyl Propan-1-ol
68. Benzaldehyde into Benzophenone
69. Benzene into m-nitro Acetophenone
70. Propanone into Propene
71. Ethyl Chloride into Propanoic acid
72. Ethanol into Propanol
73. Ethanol into Propanoic Acid
74. Toluene into Benzyl alcohol
75. Ethanol into But-1-yne

76. Propene into Propyne



Diazonium Chloride into Benzamide

Ethyl Bromide into Propan-1-ol

Acetic Acid into Methanol

**SOME WORD PROBLEMS**

1. Write structural formulae of the organic compounds 'A', 'B', 'C' and 'D' in the following sequence of reactions: 'A' +  $\text{CH}_3\text{MgBr} \xrightarrow{-\text{H}_2\text{O}}$   $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3 \xrightarrow{\text{conc H}_2\text{SO}_4}$  'B'  $\xrightarrow{-\text{Br}_2}$  'C'  $\xrightarrow{\text{alc. KOH}}$  'D'
2. Etheral solution of an organic compound 'A' when heated with magnesium gave 'B'. 'B' on treatment with wthanal followed by acid hydrolysis gave 2-propanol. Identify the compound 'A'. what is 'B' known as?
3. A organic compound 'A' (molecular formula  $\text{C}_3\text{H}_6\text{O}$ ) is resistant to oxidation but forms a compound 'B' ( $\text{C}_3\text{H}_8\text{O}$ ) on reduction. 'B' reacts with  $\text{HBr}$  to form a bromide 'C' which on treatment with alcoholic  $\text{KOH}$  forms an alkene 'D' ( $\text{C}_3\text{H}_6$ ). Deduce the structures of A,B,C and D.
4. A compound 'A' which has characteristic odour, on treatment with  $\text{NaOH}$  forms two compounds 'B' and 'C'. compound 'B' has the molecular formula  $\text{C}_7\text{H}_8\text{O}$  which on oxidation gives back compound 'A'. Compound 'C' is the sodium salt of an acid, 'C' when heated with soda lime yields an aromatic hydrocarbon 'D'. Deduce the structures of A,B,C and D.
5. An organic compound 'A' has the molecular formula  $\text{C}_5\text{H}_{10}\text{O}$ . it does not reduce Fehling solution but forms a bisulphate compound. It also gives positive iodoform test. What are possible structures of 'A'?
6. A compound 'A' with molecular formula  $\text{C}_5\text{H}_{10}\text{O}$  gave a positive 2,4-DNP test but a negative Tollen,s test. It was oxidized to carboxylic acid 'B' with molecular formula  $\text{C}_3\text{H}_6\text{O}_2$ . Sodium salt of 'B' gave a hydrocarbon 'C' on Kolbe's electrolytic reduction. Identify A,B and C and write the chemical equations for the reaction.
7. When phenol heated with  $\text{Zn}$  it forms 'A'. 'A' converts in to 'B' when reacts with conc.  $\text{HNO}_3$  in presence of sulphuric acid. 'B' converts in to 'C' when it reacts with  $\text{Br}_2$ . 'C' converts into 'E' by hydrogenation followed by reaction with nitrous acid/ $\text{HCl}$ . Finally it converts into 'F' by acidic hydrolysis. Identify A,B,C,D,E and F.
8. An aliphatic compound 'A' with a molecular formula of  $\text{C}_3\text{H}_6\text{O}$  reacts with phenyl hydrazine to give compound 'B'. Reaction of 'A' with  $\text{I}_2$  in alkaline medium on warming, gives a yellow ppt 'C'. Identify compound A,B and C.

9. Two moles of organic compound 'A' on treatment with a strong base gives two compound B and C. Compound 'B' on hydrogenation with Cu gives 'A' while acidification of C yields carboxylic acid 'D', having molecular formula of  $\text{CH}_2\text{O}_2$ . identify the compounds A,B,C and D.

10. An organic compound 'A' having molecular formula  $\text{C}_8\text{H}_{16}\text{O}$  was hydrolysed with dilute sulphuric acid to give a carboxylic acid 'B' and an alcohol 'C'. oxidation of 'C' with chromic acid produces 'B'. Write IUPAC names for possible structures of 'A' and equations for the reactions involved.

11. A compound 'A' of molecular formula  $\text{C}_3\text{H}_7\text{O}_2\text{N}$  on reaction with Fe and conc.HCl gives a compound 'B' of molecular formula  $\text{C}_3\text{H}_9\text{N}$ . compound 'B' on treatment with  $\text{NaNO}_2$  and HCl gives another compound 'C' of molecular formula  $\text{C}_3\text{H}_8\text{O}$ . Compound 'C' gives effervescence with Na. on oxidation with  $\text{CrO}_3$ , the compound 'C' gives a saturated aldehyde containing three carbon atoms. Deduce the structures of A,B and C and write the equations for the reactions involved.

12. A compound 'X' having molecular formula  $\text{C}_3\text{H}_7\text{NO}$ , reacts with  $\text{Br}_2$  in presence of NaOH gives compound 'Y'. the compound 'X' reacts with  $\text{HNO}_2$  to form ethanol and  $\text{N}_2$  gas. Identify the compound X and Y and write the reactions involved.

13. An aliphatic compound 'A' with molecular formula  $\text{C}_2\text{H}_3\text{Cl}$  on treatment with AgCN gives two isomeric compounds of unequal amounts with the molecular formula  $\text{C}_3\text{H}_3\text{N}$ . The minor of these two products on complete reduction with  $\text{H}_2$  in the presence of Ni gives a compound 'B' with a molecular formula  $\text{C}_3\text{H}_9\text{N}$ . identify the compounds A,B and write the reactions involved.

14. Iodomethane reacts with KCN to form a major product 'A'. Compound 'A' on reduction in presence of  $\text{LiAlH}_4$  forms a higher amine 'B'. Compound B on treatment with  $\text{CuCl}_2$  forms a blue colour complex 'C'. Identify the compounds A,B and C.

15. An organic compound 'A' having molecular formula  $\text{C}_2\text{H}_3\text{N}$  on reduction gave another compound 'B'. The Compound 'B' on treatment with  $\text{HNO}_2$  gave ethyl alcohol. 'B' on warming with  $\text{CHCl}_3$  and alcoholic potash gave an offensive smelling substance 'C'. Identify A,B and C.

16. Two isomeric compounds A and B having molecular formula  $\text{C}_4\text{H}_{11}\text{N}$ , both lose  $\text{N}_2$  on treatment with  $\text{HNO}_2$  and gives compound C and D respectively. C is resistant to oxidation but immediately responds to Lucas reagent, whereas 'D' responds to Lucas reagent after 5 minutes and gives a positive iodoform test. Identify A and B.

Primary alkyl halide  $\text{C}_4\text{H}_9\text{Br}$  (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d),  $\text{C}_8\text{H}_{18}$  which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

An organic compound with the molecular formula  $\text{C}_9\text{H}_{10}\text{O}$  forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

An organic compound (A) (molecular formula  $\text{C}_8\text{H}_{16}\text{O}_2$ ) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation

of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br<sub>2</sub> and KOH forms a compound 'C' of molecular formula C<sub>6</sub>H<sub>7</sub>N. Write the structures and IUPAC names of compounds A, B and C.

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ORGANIC CHEMISTRY



S.No.	Reagent	Function
1	$\text{PCl}_3, \text{PBr}_3, \text{PI}_3$	Alcohols into Alkyl halides
2	$\text{SOCl}_2, \text{PCl}_5$	Alcohols into Alkyl chlorides & Carboxylic acids into Acid Chlorides
3	$\text{HCl}/\text{ZnCl}_2, \text{HBr}, \text{HI}$	Alcohols into alkyl halides
4	$\text{Cl}_2/\text{Fe}$ or $\text{FeCl}_3$	Cl group substituting on Benzene
5	$\text{NaNO}_2 / \text{HCl}$ $0-5^\circ\text{C}$	Diazotisation
6	$\text{CuCl}, \text{CuBr}, \text{CuCN}, \text{KI}, \text{H}_2\text{O}, \text{H}_3\text{PO}_2$	Diazonium Chloride into Chlor Benzene, Bromo Benzene, Benzo nitrile, Iodo Benzene, Phenol, Benzene respectively
7	$\text{HBF}_4$ or $\text{NaBF}_4$	Diazonium Chloride into Fluoro Benzene
8	$\text{AgF}$ or $\text{Hg}_2\text{F}_2$ or $\text{SbF}_3$ or $\text{CoF}_2$	Alkyl halides into alkyl fluorides
9	$\text{Na}$ / dry ether	Alkyl halides into alkanes
10	$\text{NaOH}$ 623/443/368K	Chloro benzene to phenol
11	$\text{Br}_2 / \text{FeBr}_3$	Bromination of Benzene
12	$\text{Cl}_2 / \text{FeCl}_3$	Chlorination of Benzene
13	$\text{CH}_3\text{Cl} / \text{AlCl}_3$	alkylation of benzene and its derivatives
14	$\text{CH-CO-Cl} / \text{AlCl}_3$	Acylation on benzene
15	$\text{H}_2\text{SO}_4 / \text{HNO}_3$	Nitration of benzene
16	$(\text{CHCO})_2\text{O} / \text{AlCl}_3$	O – Acylation of Phenol
17	$\text{H}_2\text{SO}_4$	Sulphonation on Benzene
18	$\text{H}_2\text{O} / \text{H}_2\text{SO}_4$	alkenes into alcohols
	Aq KOH	Alkyl halide into alcohol
19	$\text{BH}_3 / \text{H}_2\text{O}_2 / \text{OH}^-$	Alkenes into alcohols (Anti Markownikoff product)
20	$\text{NaBH}_4 / \text{LiAlH}_4 (\text{LAH})$	Aldehydes, ketones, acids into alcohols, Nitriles & Cyanides, Isocyanides into amines
21	$\text{H}_2 / \text{Ni}$ or $\text{H}_2 / \text{Pd}$	reduction of aldehydes, ketones and cyanides
22	$\text{RMgX} / \text{H}_3\text{O}^+$	Aldehydes, ketones into alcohols
23	$\text{O}_2 / \text{H}^+$	Cumene to phenol
24	$\text{Na}$	Alcohol or phenol into Sodium alkoxide/Phenoxide
25	$(\text{CHCO})_2\text{O} / \text{CH-CO-Cl}$	O acylation on phenol or N acylation on Aniline or amine
26	Conc. $\text{H}_2\text{SO}_4 / 443\text{K}$	Conversion of primary alcohols into Alkenes
27	Conc. $\text{H}_2\text{SO}_4 / 410\text{K}$	Conversion of alcohols into Ethers

28	85% H <sub>3</sub> PO <sub>4</sub> / 440K	Secondary alcohol into alkene
29	20% H <sub>3</sub> PO <sub>4</sub> /358K	Tertiary alcohol into alkene
	Alcoholic KOH	Alkyl halide into alkene
30	CrO <sub>3</sub> /KMnO <sub>4</sub> or K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> in acidic medium	oxidation of alcohols into acids
31	Cu /573k	dehydrogenation of alcohols gives 1 <sup>o</sup> alcohols into aldehydes and 2 <sup>o</sup> alcohols into ketones & 3 <sup>o</sup> alcohols into alkenes
32	Dil. HNO <sub>3</sub>	Mono nitration of Phenol
33	Conc.HNO <sub>3</sub>	tri nitration of phenol
34	Br <sub>2</sub> /H <sub>2</sub> O	tri bromination of phenol
35	Br <sub>2</sub> /CS <sub>2</sub>	mono bromination of phenol
36	NaOH /CO <sub>2</sub>	Phenol to salicylic acid
37	CHCl <sub>3</sub> /NaOH	Phenol to salicylaldehyde
38	Zn dust	Phenol to Benzene
39	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /H <sub>2</sub> SO <sub>4</sub> or air	Phenol to Benzo quinone
40	Zn/Cr <sub>2</sub> O <sub>3</sub> 200to 300 atm 573 – 673K	CO & H into methanol
41	Invertase	Sucrose into Glucose or Fructose
42	Zymase	Glucose or Fructose into ethanol
43	HI	Ether into alcohol & alkyl halide
44	PCC	alcohol to aldehyde
45	Pd /BaSO <sub>4</sub> ,H <sub>2</sub>	acid chloride into aldehyde
46	SnCl <sub>2</sub> /HCl/H <sub>3</sub> O <sup>+</sup>	Cyanides into aldehydes
47	AlH(i-Bu) <sub>2</sub> /H <sub>2</sub> O	Cyanides into aldehydes
48	DIBAL-H/H <sub>2</sub> O	Esters into aldehydes
49	CrO <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O	Toluene to aldehyde
50	CrO <sub>3</sub> /((CH <sub>3</sub> CO) <sub>2</sub> O	Toluene into Benzaldehyde
51	Cl <sub>2</sub> /hv	Chlorination on alkyl group of Benzene or alkane
52	CO, HCl anhydrous AlCl <sub>3</sub>	Benzene to Benzaldehyde
53	(CH <sub>3</sub> ) <sub>2</sub> Cd	acid chloride into ketones
54	RMgX/H <sub>3</sub> O <sup>+</sup>	Cyanides into ketones
55	HCN	Carbonyl compound into cyanohydrin
56	NaHSO <sub>3</sub>	addition to aldehyde and ketone
57	H <sub>2</sub> NOH	carbonyl compound into oxime
58	H <sub>2</sub> N-NH <sub>2</sub>	carbonyl compound into hydrazone
59	H <sub>2</sub> N-NH-Ph	carbonyl compound into Phenyl hydrazone

60	2,4DNP	carbonyl compound into 2,4 dinitro phenyl hydrazone
61	$\text{H}_2\text{N-NH-CO-CH}_3$	carbonyl compound into semi carbazide
62	ROH/HCl	Aldehydes & ketones into hemiacetal and acetal
63	$\text{HO-CH}_2\text{-CH}_2\text{-OH/HCl}$	Aldehyde or ketone into ethelene glycol ketone
64	Zn-Hg/HCl	carbonyl compound into alkane
65	$\text{H}_2\text{N-NH}_2/\text{KOH}$	carbonyl compound into alkane
66	$\text{KMnO}_4/\text{OH}^-/\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ or $\text{HNO}_3$	Ketones into mixture of carboxylic acids on prolonged oxidation
67	$(\text{Ag}(\text{NH}_3)_2)\text{NO}_3+\text{NaOH}$	Tollen's test
68	$\text{Cu}(\text{OH})_2$	Fehiling's test
69	$\text{NaOH}+\text{I}_2$	Iodoform
70	$\text{NaOH}$ or $\text{Ba}(\text{OH})_2$	aldal condensation
71	Conc KOH or NaOH	Cannizaro's reaction
72	$\text{KMnO}_4/\text{KOH}$	Toluene/alkyl Benzene into Benzoic Acid
73	$\text{H}_2\text{O}/\text{H}^+$	Cyanides into carboxylic acids, amides into carboxylic acids, esters into carboxylic acid and alcohols, acid chlorides or anhydrides into carboxylic acids
74	NaOH	Saponificaiton of ester, acid into salt of acid
75	$\text{Na}_2\text{CO}_3$ or $\text{NaHCO}_3$	Carboxylic acid test
76	$\text{P}_4\text{O}_{10}$ or $\text{P}_2\text{O}_5$	Dehydration of acids into anhydride, amides into nitriles
77	ROH/conc $\text{H}_2\text{SO}_4$	Caroxylic acids into esters
78	$\text{PCl}_3$ , $\text{SOCl}_2$ , $\text{PCl}_5$	Carboxylic acids into acid chlorides
79	$\text{NH}_3$ heating	Carboxylic acids into amides
80	$\text{NaOH}/\text{CaO}$	Decarboxylation (acids into alkanes)
81	$\text{LiAlH}_4$	Carboxylic acids into alcohols, amides into amines
82	$\text{Cl}_2/\text{red.P}_4$	HVZ reaction
83	$\text{Sn}/\text{HCl}$ or $\text{Fe}/\text{HCl}$ , $\text{H}_2/\text{Pd}$	Reduction of nitro compounds into amines
84	$\text{NH}_3$	Alkyl halides into amines
85	$\text{H}_2/\text{Ni}$ or $\text{H}_2/\text{Pd}$ $\text{LiAlH}_4$	Amides into cyanindes
86	$\text{KOH}/\text{R-X}$	Phthalamide into amine

87	NaOH /Br <sub>2</sub>	Hoffman bromamide, amide into amine with one 'C' less
88	KOH,CHCl <sub>3</sub>	Amines into Carbyl amines
89	NaNO <sub>2</sub> /HCl	1 <sup>o</sup> aliphatic amines into alcohols
90	NaNO <sub>2</sub> /HCl 0 – 5 <sup>o</sup> C	Aniline into diazonium chloride
91	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> Cl	Distinguishing 1 <sup>o</sup> ,2 <sup>o</sup> & 3 <sup>o</sup> amines
92	Br <sub>2</sub> /H <sub>2</sub> O	Aniline into tri bromo aniline
93	Br <sub>2</sub> / CH-CO-Cl /(CHCO) <sub>2</sub> O	Aniline into Bromo Aniline
94	HNO <sub>3</sub> / CH-CO-Cl /(CHCO) <sub>2</sub> O	Nitro aniline
95	H <sub>2</sub> SO <sub>4</sub>	Sulphonation on aniline
96	CuCl,CuBr,CuCN,KI,H <sub>2</sub> O, H <sub>3</sub> PO <sub>2</sub> or CH <sub>3</sub> -CH <sub>2</sub> -OH	Diazonium Chloride into Chlor Benzene, Bromo Benzene, Benzo nitrile, Iodo Benzene , Phenol,Benzene respectively

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ORGANIC CHEMISTRY

## REASONING QUESTIONS IN ORGANIC CHEMISTRY

### TEXT EXERCISE

1. Why is sulphuric acid is not used during reaction of alcohols with KI?

Ans: Sulphuric acid converts the KI into HI and then oxidizes into I<sub>2</sub>

2. Arrange each set of compounds in order of increasing boiling points.

(i) Bromo Ethane, Bromoform, Chloro methane, Dibromo methane

(ii) 1-Chloro Propane, Isopropyl chloride, 1-chloro butane

Ans: Chloro Methane(CH<sub>3</sub>Cl) < Bromo Ethane(CH<sub>3</sub>-CH<sub>2</sub>-Br) < Dibromo Methane(CH<sub>2</sub>Br<sub>2</sub>) < Bromoform (CHBr<sub>3</sub>)

CH<sub>3</sub>CHCl-CH<sub>3</sub> < CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>Cl < CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Cl

As atomic mass increases boiling point increases. And branching compounds has less spherical contact as compare with straight chain compounds. Hence bp less for branching chain alkyl halides.

3. Which of the following undergo SN<sup>2</sup> faster?



Ans: -CH<sub>2</sub>Cl is more faster under go SN<sup>2</sup> because it is Primary alkyl halide

-I is more faster to under go SN<sup>2</sup> mechanism because I is better leaving group due to its large size.

4. Predict the order of reactivity of the following compounds in SN<sup>1</sup> & SN<sup>2</sup> reactions.

(i) The four isomeric bromo butanes

(ii) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)Br, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>(CH<sub>3</sub>)Br, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)Br

Ans: CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Br < CH<sub>3</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-Br < CH<sub>3</sub>-CH<sub>2</sub>-CHBr-CH<sub>3</sub> < C(CH<sub>3</sub>)<sub>3</sub>Br order for SN<sup>1</sup> mechanism

CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Br > CH<sub>3</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-Br > CH<sub>3</sub>-CH<sub>2</sub>-CHBr-CH<sub>3</sub> > C(CH<sub>3</sub>)<sub>3</sub>Br order for SN<sup>2</sup> mechanism

C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br order for SN<sup>1</sup> mechanism

C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br < C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)Br < C<sub>6</sub>H<sub>5</sub>CH(C<sub>6</sub>H<sub>5</sub>)Br < C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)Br

Order for SN<sup>1</sup> mechanism

C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br > C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)Br > C<sub>6</sub>H<sub>5</sub>CH(C<sub>6</sub>H<sub>5</sub>)Br > C<sub>6</sub>H<sub>5</sub>C(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)Br

Order for SN<sup>2</sup> mechanism

5. Although Chlorine is an electron withdrawing group yet it is ortho para directing in electrophilic aromatic substitution reactions. Why?

Ans: Cl is electron withdrawing by inductive effect, and it electron releasing by resonance and creates negative charge at ortho and para positions. And here resonance effect is more as compare with inductive effect.

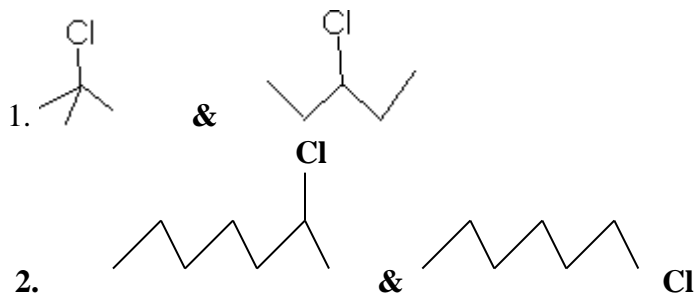
6. Which alkyl halide from the following pairs would you expect to react more rapidly by an SN<sup>2</sup> mechanism? Explain your answer?

1. CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Br & CH<sub>3</sub>-CH<sub>2</sub>-CHBr-CH<sub>3</sub>

2. CH<sub>3</sub>-CH<sub>2</sub>-CHBr-CH<sub>3</sub> & C(CH<sub>3</sub>)<sub>3</sub>Br

3. CH<sub>3</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>2</sub>-Br & CH<sub>3</sub>-CH<sub>2</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-Br

- Ans: 1.  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$  primary alkyl halide is more reactive than secondary alkyl halide
2.  $\text{CH}_3\text{-CH}_2\text{-CHBr-CH}_3$  Secondary alkyl halide is more reactive than Tertiary alkyl halide
3.  $\text{CH}_3\text{-CHCH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$  As methyl group is far from Br it will less stabilize the carbo cations and facilitate the  $\text{SN}^2$  mechanism.
7. Which of the following compound go faster  $\text{SN}^1$  reaction:



- Ans: 1. first compound is more stable because tertiary is more reactive than secondary alkyl halide for  $\text{SN}^1$  mechanism.
2. first compound is more stable because Secondary is more reactive than primary for  $\text{SN}^1$  mechanism.

8. Which one of the following has highest boiling point;  
 $\text{CH}_2\text{Cl}_2$   $\text{CHCl}_3$   $\text{CCl}_4$

Ans: net Dipole moment of  $\text{CH}_2\text{Cl}_2$  &  $\text{CCl}_4$  is zero due to cancellation dipole moment of bonds due to its symmetric structure. Where as net dipole moment of  $\text{CHCl}_3$  is not zero. Because its structure is not symmetric.

9. Which compound in each of the following pairs react faster in  $\text{SN}^2$  reaction with  $\text{OH}^-$ ?  
 (i)  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$  (ii)  $(\text{CH}_3)_3\text{CCl}$  or  $\text{CH}_3\text{Cl}$

Ans:  $\text{CH}_3\text{I}$  is faster reactive by  $\text{SN}^2$  mechanism because C-I bond strength is less than C-Br bond

$\text{CH}_3\text{Cl}$  is faster reactive than  $(\text{CH}_3)_3\text{CCl}$  by  $\text{SN}^2$  mechanism because  $1^\circ$  alkyl halide more reactive by  $\text{SN}^2$  mechanism.

10. Halo alkanes react with  $\text{KCN}$  to form alkyl cyanides as main product while  $\text{AgCN}$  forms isocyanides as the chief product. Explain.

Ans:  $\text{KCN}$  is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs. The attack takes place mainly through carbon atom not through nitrogen atom since C—C is more stable than C—N bond. However,  $\text{AgCN}$  is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

11. Why does  $\text{NO}_2$  group show its effect only at ortho and para positions and not at meta positions?

Ans: The presence of  $\text{NO}_2$  group at ortho and para positions with draws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on halo arene. The carbanion thus formed is stabilized through resonance. The negative charge appeared at ortho and para positions with respect to the halogen substituent is stabilized by  $\text{NO}_2$  group while in case of meta nitro benzene, none of the resonating structures bear the negative charge on carbon atom bearing the  $\text{NO}_2$  group. Therefore the presence of nitro group at meta position does not stabilize the

negative charge and no effect on reactivity is observed by the presence of  $\text{NO}_2$  group at meta position.

12. The dipole moment of chloro benzene is lower than that of cyclohexyl chloride. Why?

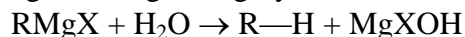
Ans: It is due to electron withdrawing effect of phenyl group which decreases dipole moment of chloro benzene.

13. Alkyl halides, though polar, are immiscible with water. Explain.

Ans: Due to absence of hydrogen bond in alkyl halides with water.

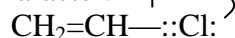
14. Grignard reagent should be prepared under anhydrous conditions. Give reason.

Ans: Grignard reagent highly reacts with water to form alkanes.



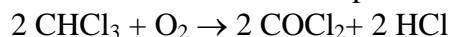
15. Vinyl chloride is less reactive towards nucleophilic substitution. Explain.

Ans: Due to resonance between C—Cl bond in vinyl chloride showing partial double bond character.



16. Chloroform is stored in dark colored bottles by completely filling it. Explain.

Ans: Chloroform reacts with air in the presence of sunlight to form poisonous phosgene.



17. Out of  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  &  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$  which is more easily hydrolyzed by KOH?

Ans: The second compound is more resonance stabilized hence easily forms a carbocation and reacts faster by  $\text{S}_\text{N}1$  mechanism.

18. The treatment of alkyl halides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH alkenes are major products. Explain.

Ans: Substitution of alkyl halide gives alcohols and elimination gives alkenes and there is a competition between substitution and elimination. In the presence of a low polarity solvent like alcohol, elimination is favored, whereas in the presence of a high polarity solvent like water, substitution is favored.

19. Bond angle of ethers is slightly greater than tetrahedral bond angle. Explain.

Ans: Due to repulsion of bulky alkyl groups in ethers, bond angles are slightly greater than tetrahedral bond angle.

20. Arrange the following sets of compounds in order of their increasing boiling points:

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Ans: (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

21. Acidity of alcohols is as follows explain?  $1^\circ > 2^\circ > 3^\circ$

Ans: An electron-releasing group ( $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ) increases electron density on oxygen, tending to decrease the polarity of O-H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:

22. Arrange the following compounds in increasing order of their acid strength:

Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

Ans: Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol,

2,4, 6-trinitrophenol.

23. The reaction of alcohols with carboxylic acid or anhydrides to form esters conc.  $\text{H}_2\text{SO}_4$  is added, and the reaction with alcohol and acid chloride base like pyridine is used. Explain.

Ans:  $\text{R-OH} + \text{RCOOH}/\text{RCOOCOR} \leftrightarrow \text{RCOOR} + \text{H}_2\text{O}$

$\text{R-OH} + \text{RCOCl} \leftrightarrow \text{RCOOR} + \text{HCl}$

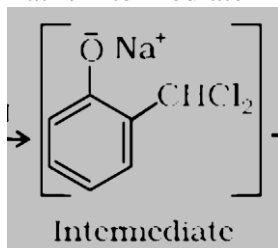
Sulphuric acid removes the water and prevent back ward reaction,

Base like pyridine removes the acid HCl and prevent back ward reaction.

24. The relative dehydration of alcohols is Tertiary>Secondary>Primary give reason.

Ans: Dehydration carryout by carbocation mechanism, and stability of carbocation is tertiary>Secondary>Primary

25. What is intermediate in Riemer –Tiemann reaction.



Ans:

26. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

Ans: Due to hydrogen bond

27. Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in benzene ring.

Ans: Methoxy group on Benzene ring donates the electrons and activate the ring and creates -ve charge on the ortho and para positions hence electrophile is attracted at these positions.

28. Arrange the following compounds in the increasing order of their boiling points:

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{H}_5\text{C}_2\text{-O-C}_2\text{H}_5$ ,  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Ans:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 < \text{H}_5\text{C}_2\text{-O-C}_2\text{H}_5 < \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} < \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

Alcohols with hydrogen bond has more bp, Ethers have less dipole dipole moment as compare with aldehydes and alkanes least with weak vander waals forces.

29. Aldehydes and ketones are soluble in water.

Ans: They soluble in water due to formation of H bond between carbonyl compounds and water.

30. Toluene with  $\text{CrO}_3$  and Acetic anhydride forms benzaldehyde. Explain.

Ans: Toluene forms Benzylidene diacetate intermediate with  $\text{CrO}_3$  and Acetic anhydride.

31. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

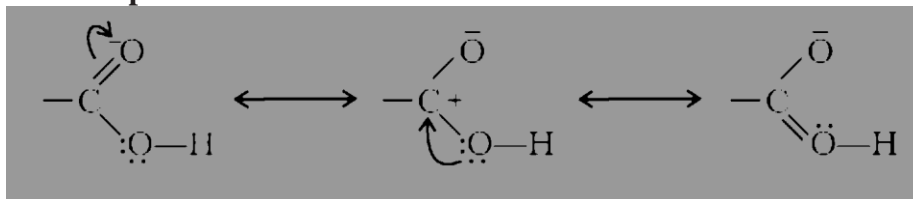
Ans: The carbon atom of the carbonyl group of benzaldehyde is less



electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.

32. Carbonyl carbon of carboxylic acid is less electrophilic than aldehydes and ketones give reason.

Ans: The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:



33. Carboxylic acids are having higher boiling points than aldehydes, ketones and even alcohols of comparable molecular masses. Explain.

Ans: Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase. In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.

34. Carboxylic acids are stronger acids than phenol though both possess resonance stabilization of respective anions.

Ans: The higher acidity of carboxylic acids as compared to phenols can be understood similarly. The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The conjugate base of phenol, a 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 delocalised over two electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion. Thus, the carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols.

35.

Which acid of each pair shown here would you expect to be stronger?

(i)  $\text{CH}_3\text{CO}_2\text{H}$  or  $\text{CH}_2\text{FCO}_2\text{H}$                       (ii)  $\text{CH}_2\text{FCO}_2\text{H}$  or  $\text{CH}_2\text{ClCO}_2\text{H}$

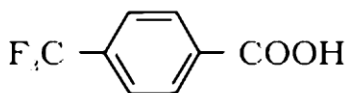
(iii)  $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$  or  $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$

(iv)  $\text{F}_2\text{C}-\text{C}_6\text{H}_4-\text{COOH}$  or  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$

Ans:  $\text{CH}_2\text{FCO}_2\text{H}$  because -ve inductive effect by F

$\text{CH}_2\text{FCO}_2\text{H}$  -ve inductive effect of F is more than Cl

$\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$  If -ve inductive group near to  $\text{COOH}$  more acidic.



-ve inductive effect of three F atoms

36. Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-

Trimethylcyclohexanone does not.

(ii) There are two  $\text{-NH}_2$  groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

Ans: Due to steric effect and electron releasing effect.

The other two  $\text{NH}_2$  groups involve resonance with  $\text{C}=\text{O}$

To prevent back ward reaction

37. Aryl amines cannot be prepared by Gabriel Phthalamide synthesis. Explain.

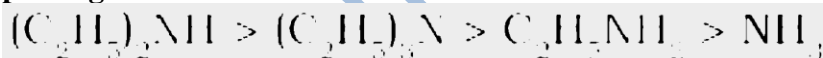
Ans: Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

38. Boiling point of Primary, secondary and tertiary amines is different give reason.

Ans: This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary

39. The basic strength of amines in aqueous solutions is different from gaseous phase give reason.



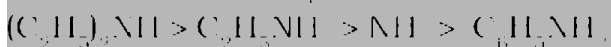
It is due to inductive effect, hydrogen bond and hydration effect

40.

Arrange the following in decreasing order of their basic strength:

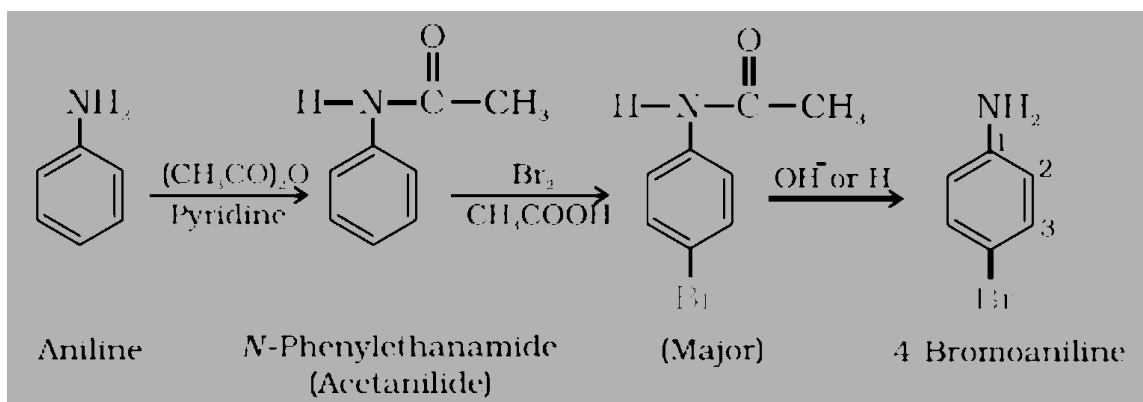


The decreasing order of basic strength of the above amines and ammonia follows the following order:



41. Generally aniline direct bromination gives tri substituted product to get mono substituted product what is to be done.

Ans: This can be done by protecting the  $\text{-NH}_2$  group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

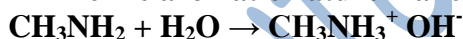


42. Account for the following:

- (i)  $pK_b$  of aniline is more than that of methylamine.
- (ii) Ethylamine is soluble in water whereas aniline is not.
- (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (iv) Although amino group is *o*- and *p*- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
- (v) Aniline does not undergo Friedel-Crafts reaction.
- (vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- (vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Ans: More  $P_{kb}$ , less basic, less basicity of aniline is due to involvement of lone pair in resonance.

In Aniline aromatic nature makes insoluble in water.



These hydroxide ions can make Ferric hydroxide.

in the strongly acidic medium, aniline is protonated to form the anilinium ion which is *meta* directing.

Aryl amines can not under go nucleophilic substitution.

43. Give plausible explanation for each of the following:

- (i) Why are amines less acidic than alcohols of comparable molecular masses?
- (ii) Why do primary amines have higher boiling point than tertiary amines?
- (iii) Why are aliphatic amines stronger bases than aromatic amines?

Ans: Nitrogen is less Electronegative than Oxygen which makes less polarization of N—H bond as compare with O—H bond.

There is no H bond in Tertiary amines.

In aromatic amines lone pair involve in resonance.

## REASONING QUESTIONS IN ORGANIC CHEMISTRY

### OTHER QUESTIONS

44. Preparation of ethers by dehydration of alcohols is not suitable for the using of secondary and tertiary alcohols give reason.

Ans: dehydration of secondary and tertiary alcohols to give corresponding ethers is successful as elimination competes over substitution and as a consequence, alkenes are easily formed.

45. The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.

(i) What would be the major product of this reaction ?

(ii) Write a suitable reaction for the preparation of t-butylethyl ether.



Ans: (i) The major product of the given reaction is 2-methylprop-1-ene.

It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus elimination reaction predominates over substitution.



46. Which of the following is appropriate for the preparation of anisole?

a) Bromo Benzene & Sodium Methoxide b) Phenoxide &  $\text{CH}_3\text{Br}$

Ans: Set b is appropriate because nucleophilic substitution on aromatic ring is difficult due to partial double bond character.

47. The bond angle in alcohol is slightly less than the tetrahedral bond angle (109.5°). Why? Is it so?

Ans: It is due to the repulsion between the unpaired electron pairs of oxygen.

48. Carbon oxygen bond length in phenol is less than the alcohol?

Ans: It is due to the partial double bond character between C and O in phenol.

49. Boiling point of the alcohol is more than the alkenes. Comment?

Ans: due to intermolecular hydrogen in alcohols it has high boiling point.

50. Branched alcohols are having low boiling point compare with normal straight chain alcohols? Explain. OR

Boiling point t-Butyl alcohol is less than the n-Butyl alcohol? Explain.

Ans: As branching increases surface area decreases and Vander wall's force decreases, hence boiling point decreases. And also in branched alcohols due to electron releasing effect strength of hydrogen decreases.

51. Arrange the following compounds in increasing order of their boiling points?



Ans: molecular of these compounds are similar; ethanol is having intermolecular H-bond hence more boiling point. Among acetaldehyde and ether, acetaldehyde has strong dipole attractions than the ethers.

Propene is weak van der Waals' forces. Hence the boiling point order is



52. Arrange the following in increasing order of their reactivity towards nucleophilic addition reactions.



Ans:  $\text{CH}_3\text{-CO-CH}_3 < \text{CH}_3\text{-CHO} < \text{H-CHO}$

Electron releasing effect

Steric effect

53. Ethers have low boiling point compare with corresponding alcohols.

**Give reasons**

**Ans:** Alcohols can form intermolecular H-bond, where as ethers do not. Hence alcohols are having high boiling point than ethers.

**54. Alcohols are Bronsted bases or Proton acceptors. Explain?**

**Ans.** It is due to presence of unshared electron pair over oxygen atom which makes alcohols proton acceptors. Proton acceptors are known as Bronsted bases.

**55. Alcohols are weak acids than water. Explain?**

**Ans.** In both the cases due to polar O-H bond, behave as acids. But in alcohols due to presence of alkyl groups, which are electron releasing hence O-H bond is less polarized, shows weak acidic character.

**56. Arrange the acidity order for 1, 2 & 3 Isomeric alcohols (C<sub>4</sub>H<sub>10</sub>O)?**

**Ans.** Always electron releasing effect destabilizes the anion and decrease the acidity.

**57. Phenol is stronger acid than alcohol. Explain.**

**(Or)**

**Phenol is weak proton acceptor than alcohol. Explain.**

**Ans.** Acidity of the substance depends on stability of anion after losing H<sup>+</sup> ion. Since phenoxide ion undergoes resonance stabilization compare to alkoxide, phenol is more acidic than alcohol.

**58. Arrange the following compounds in increasing order of their acidic strength.**

**Propan-1-ol, 4-Methyl phenol, Phenol, 3,5 dinitrophenol, 2,4,6 Trinitrophenol.**

**Ans.** Propan-1-ol < 4-Methoxy phenol < Phenol < 3,5 dinitrophenol < 2, 4, 6 Trinitrophenol

**Phenol is more than alcohol due to resonance stability of phenoxide ion.**

**Electron releasing groups like (O-CH<sub>3</sub>) methoxy decreases acidity.**

**Electron withdrawing groups like (-NO<sub>2</sub>) nitro groups increases acidity.**

**More number of electron withdrawing groups more acidity.**

**59. O-nitro phenol & p-nitro phenol can be separated by distillation? Explain.**

**Or**

**Boiling point of p-nitro phenol is more than the o-nitro phenol. Explain?**

**Ans.** O-nitro phenol is a steam volatile due to intermolecular Hydrogen bond where as p-nitro phenol is having inter molecular Hydrogen bond.

**Inter molecular hydrogen bond decreases Boiling point**

**Inter molecular hydrogen bond increases Boiling point**

**60. The usual halogenations of Benzene takes place of in presence of Lewis acid catalyst like AlCl<sub>3</sub>, where as phenol can directly react with Bromine? Explain?**

**Ans.** In case of Halogenations of benzene Br<sub>2</sub> is polarized by FeBr<sub>3</sub>, but in case of phenol the polarization of Br<sub>2</sub> takes place by phenol due to highly activating effect of OH group present on the benzene ring.

**61. Primary alkyl halide reacts with sodium alkoxide and forms ethers in good yield**

but t-alkyl halides yield fewer amounts of ethers. Explain?

Ans. Since tertiary carbocation is more stable and it will form alkenes instead of ether. 20. Explain the fact that in aryl alkyl ethers (i) alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho & para position ?

Ans. Alkoxy group is electron releasing to the benzene ring (+ve mesomeric effect) and by resonance -ve charge obtained at ortho & para positions only. Hence electrophile attracts at ortho & para positions. And due to +ve mesomeric effect ring became activated.

62. t- Butyl methyl ether reacts with HI forms methanol & t- butyl iodide explain?

Ans. Since tertiary carbocation is more stable and reaction is following carbocation

mechanism it gives t- Butyl iodide.

63. The commercial ethanol is mixed with copper sulphate & pyridine. Explain.

Ans. Commercial ethanol is mixed with  $\text{CuSO}_4$  & pyridine to make it unfit for drinking. It is known as denaturation of alcohol.

64. Explain why are alcohols comparatively more soluble in water than the corresponding hydrocarbons?

Ans. It is due to Hydrogen Bond formation with water.

65. Explain how does the -OH group to a carbon of benzene ring activates it towards electrophilic substitution?

Ans. OH group donates its non bonded electrons to resonance with benzene and creates negative charge at o-p positions hence ring is activated towards electrophilic substitution.

66. Explain the fact that in aryl alkyl ethers (i) alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho & para position ?

Ans. Alkoxy group is electron releasing to the benzene ring (+ve mesomeric effect) and by resonance -ve charge obtained at ortho & para positions only. Hence electrophile attracts at ortho & para positions. And due to +ve mesomeric effect ring became activated.

67. Unlike phenols, alcohols are easily protonated. Give reason.

Ans. Alcohols act as proton acceptors or Bronsted bases. It is due to presence of unshared electron pair over oxygen. In case of phenol lone pair is involving in resonance. Hence, it can not be protonated easily.

68. Reaction of alcohols with hydrogen halides (HX) is of the following order.

Explain.

$3^\circ$  alcohols  $2^\circ$  alcohols  $1^\circ$  alcohols

Ans. This reaction takes place through carbocation mechanism since the stability of carbocation is  $3 > 2 > 1$ . The reactivity order is also same.

69. Anisole react with HI gives phenol & methyl iodide but not iodo benzene and methanol. Explain.

Ans. Nucleophilic substitution on aromatic ring is difficult due to partial double Bond character between oxygen and carbon of benzene ring.

70. Name the intermediate or electrophile formed during Reimer-Tiemann reaction?

Ans. Dichloro carbon -  $:CCl_2$

71. Phenol reacts with bromine in the presence of carbon disulphide to give monobromophenol whereas with water it gives tribromophenol. Explain.

Ans.  $CS_2$  is a non-polar solvent whereas water is a polar solvent. In the presence of a polar solvent phenol polarizes and gives more electrophilic substitution.

72. Ethers made of similar kind of polar bonds (symmetric) also possess some net dipole moment. Explain.

Ans. Due to its bent structure.

73. While separating a mixture of ortho & para nitro phenols by steam distillation, name the isomer which is steam volatile. Give reasons?

Ans: O-nitro phenol is steam volatile due to intermolecular hydrogen bond.

74. Explain why O-nitro phenol is more acidic than O-methoxy phenol?

Ans: Nitro group is an electron withdrawing group which increases acidity whereas methoxy group is an electron releasing group which decreases acidity.

75. Phenol is more active towards electrophilic substitution than benzene. Explain?

Ans: OH group present on the phenol is electron releasing and activates the benzene ring through resonance.

76. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reasons?

Ans: Secondary and tertiary alcohols will give alkenes easily by dehydration.

77. Explain why is propanal higher boiling than butane?

Ans: Due to intermolecular hydrogen bond present in alcohols, they possess high boiling point.

78. Explain why are alcohols comparatively more soluble in water than the corresponding hydrocarbons?

Ans: Due to presence of intermolecular hydrogen bond in alcohols.

79. Aldehydes and ketones possess more dipole moment than ethers. Explain?

Ans: Due to presence of double bond more polarity which increases dipole moment.

34. Arrange the following compounds in increasing order of their boiling points?

$CH_3-CHO$  ,  $CH_3-CH_2-OH$  ,  $CH_3-O-CH_3$  ,  $CH_3-CH_2-CH_3$

Ans: Their molecular masses are almost all similar but

$CH_3-CH_2-OH > CH_3-CHO > CH_3-O-CH_3 > CH_3-CH_2-CH_3$   
Inter molecular H-bond      more polar than ethers      presence of polarization      no H-bond &

80. Why is it necessary to use sulphuric acid in nitration of benzene?

Ans: Sulphuric acid is helping in formation of  $NO_2$  electrophile which is easy to substitute on benzene.

81. Acetic acid is halogenated in the presence of red P and  $Cl_2$  but formic acid cannot be halogenated in the same way. Explain?

Ans. There is no alpha hydrogen in formic acid.

82. Carboxylic acids are having more boiling point than alcohols of same molecular

mass. explain

Ans. In carboxylic acids strength of H bond is stronger than alcohols and forms dimer in carboxylic acids which increases boiling point.

83. Carboxylic acid can not give characteristic reactions of aldehydes and ketones though both are having carbonyl group CO?

Ans. Carbonyl group in carboxylic acid is resonance stabilized as carboxylate ion. Hence it can not give nucleophilic addition reactions given by carbonyl group.

84. Formaldehyde gives Cannizzaro's reaction but acetaldehyde cannot. Explain

Ans. Cannizzaro's reaction is given by any aldehydes without alpha hydrogen hence acetaldehyde cannot give this reaction.

85. Why do aldehydes and ketones have high dipole moment?

Ans. Due to presence of polarisable C=O bond in it.

86. Phenol is acidic but do not react with sodium bicarbonate solution. Explain?

Ans. Phenol is a weak acid hence it can not react with weak base like sodium bicarbonate.

87. Boiling point of glycol is higher than alcohol of same molecular mass. Explain?

Ans. As the number of -OH groups increases strength of H bond increases and boiling point also increases.

88. Nitration of phenol is easier than benzene. Explain?

Ans. Due to presence of -OH group which causes electron releasing effect, ring is activated and electrophilic substitution is easier.

89. Why methyl amine has lower boiling point than methanol?

Ans. Amines possess weak hydrogen bond than alcohols, hence methanol has higher boiling point.

90. Why is it difficult to prepare pure amines by ammonolysis of alkyl halides?

Ans. Reaction of alkyl halides with ammonia gives mixture of amines because secondary and tertiary amines also behave as nucleophilic and undergoes substitution with alkyl halides.

91. Electrophilic substitution in case of aromatic amines takes place more readily than benzene. Explain?

Ans. NH<sub>2</sub> group present on the benzene is electron releasing and activates ring. Hence electrophilic substitution is easy.

92. Why does silver chloride dissolve in methyl amine solution?

Ans. Methyl amine forms a complex compound with silver chloride and that is soluble in water



93. Tertiary amines do not undergo acylation. Explain?

Ans. As these are not having hydrogen on nitrogen they can not give acylation reaction with acid chlorides.

94. Why is diazotization of aniline carried in ice cold solution?

Ans. Diazonium salts are stable at cold conditions only.

95. Why are amides less basic than amines?

Ans. Lone pair present in amides is involved in resonance hence it is less basic than amines.



96. Why is ethyl amine more basic than amines?

Ans. In ethyl amine lone pair is not involved in resonance where as in aniline lone pair is involved in resonance. Hence ethyl amine more basic than amines

97. Acid catalyzed dehydration of t- butanol is faster than n-butanol why?

Ans. Dehydration is taking place through carbon cation mechanism as tertiary carbo cation is more stable .hence t- butanol is faster than n-butanol

98. Sodium bisulphate is used for preparation of aldehydes and ketones?

Ans. Mixture of aldehydes and ketones react with NaHSO<sub>3</sub> aldehydes preferably react to form salts as compare with ketones, hence they are separated.

99. Hydrazones of acetaldehyde are not prepared in highly acidic medium?

Ans. Hydrazones are prepared from hydrazenes and it is basic in nature. In highly acidic medium it forms salt.

100. Why are amides amphoteric in nature>

Ans. Lone pair present in N of amides in involving in resonance and less available for donating hence behave as weak bases. And during resonance it forms +ve charge on nitrogen which has tendency to loose proton and behave as acidic . So amides are amphoteric in nature.

101. Highly branched carboxylic acids are less than unbranched acids .Why?

Ans.As branching increases,electron releasing effect increases,which decreases acidity.

102. Aniline dissolves in aq.HCl,why?

Ans.Aniline is basic in nature.hence,it is soluble in acids like HCl.

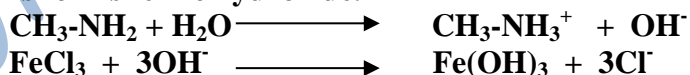
103. A weakly basic solution favours coupling of benzene diazonium chloride with phenol.Explain?

104. Why are aryl diazonium ion more stable than diazonium ion?

Ans. Aryl diazonium ion is stabilized by resonance but in alkyl diazonium ion ,no resonance for stabilization.

105. Methyl amine in water reacts with ferric chloride to precipitate ferric hydroxide.Why?

Ans.Methyl amine is a proton acceptor from water and forms hydroxyl ion which reacts with ferric ions forms ferric hydroxide.



106. Ethers possess a dipole moment even if the alkyl radicals in the molecule are identical.Explain?

Ans.Due to Sp<sup>3</sup> hybridisation ,ethers posses bent structure hence net dipole moment is not zero and will not cancel.

107. Why di-tertiary butyl ethers cannot be prepared by Williamson's synthesis?

Ans. As tertiary carbocation is more stable,it has less tendency to undergo Nucleophilic substitution.Hence it cannot be prepared.

108. Treatment of C<sub>6</sub>H<sub>5</sub>-CHO with HCN gives a mixture of two isomers which cannot

be separated even by very careful fractional distillation?

**Ans.** This reaction gives racemic mixture of two optical isomers which are having almost all same boiling point and similar chemical properties. Hence they cannot be separated by fractional distillation.

**109.** Electrophilic substitution on nitro benzene is difficult compare with benzene. explain?

**Ans.** Nitro group present on the benzene is electron withdrawing and deactivates the ring for substitution. Hence it is difficult.

**110.** The presence of electron withdrawing groups on benzene facilitates nucleophilic substitution. Explain?

**Ans.** Due to electron withdrawing effect it will stabilize the carbanion intermediate.



**111.** Tertiary amines are having low boiling point compare with primary and secondary amines. Explain?

**Ans.** Due to absence of Hydrogen bond in tertiary amines, they possess low boiling point as compare with primary and secondary.

**112.** In solutions, basic strength of amines is secondary > tertiary > primary. Explain?

**Ans.** Basic strength of amines depends on ammonium cation in solutions. Ammonium stability not only depends on electron releasing effect but also H-bonding, steric factor. Hence the above order of basic strength is correct.

**113.** In gas phase, basic strength of amines is tertiary > secondary > primary. Explain?

**Ans.** In gas phase, there is no solvation effect. It only depends on electron releasing effect. Hence the above order is correct for basic strength in gas phase.

**114.** Acylation on amines and phenols takes place directly, whereas acylation on benzene requires  $\text{AlCl}_3$  catalyst. Give reasons?

**Ans.** Reaction of amines and phenol with acid chlorides is nucleophilic substitution, which takes place directly due to presence of lone pair on both oxygen and Nitrogen. Whereas acid chloride on reaction with benzene is electrophilic substitution which requires a catalyst like  $\text{AlCl}_3$  catalyst to form an electrophile.

**115.** Acid chlorides give pungent smell in air. Explain?

**Ans.** Acid chlorides undergo hydrolysis with atmospheric moisture and gives HCl fumes, which are pungent.

**116.** Nitration of benzene gives substantial amount of meta product, though  $-\text{NH}_2$  is o-p directing group?

**Ans.** Nitration takes place in the presence of  $\text{H}^+$  ions which protonates on Amine and forms which behaves as electron withdrawing group, hence it forms some amount of meta product.

**117.** Before nitration, Aniline is acylated. Explain?

**Ans.** To protect  $-\text{NH}_2$  group from oxidation and to prevent meta product.

**118. Reactivity order of carboxylic acid derivatives are  
Acid chlorides>Anhydrides>Esters>Amides.Explain the reason?**

**Ans.I) Basicity of leaving group**

**II) Resonance effect**

**74.Explain cyanides are soluble in water whereas isocyanides are insoluble.**

**Ans.Cyanides can form hydrogen bond with water whereas Isocyanides cannot.**

**119. Preparation of Alkyl halides from alcohols by using SOCl<sub>2</sub> is preferable.Explain?**

**Ans.When SOCl<sub>2</sub> is used,side products are gases and forms pure alkyl halides.**



**120. Alkyl halides react with nitrites whereas AgNO<sub>2</sub> gives Nitro alkanes.Explain?**

**Ans. KNO<sub>2</sub> is an ionic compound and forms NO<sub>2</sub><sup>-</sup> which is an ambidentate nucleophile.It can form bond with nitrogen and oxygen.Since C-O bond is stable,it forms alkyl nitrites whereas AgNO<sub>2</sub> is covalent compound.Here oxygen is not free.only bonding takes through nitrogen and forms nitroalkanes.**

**121. During preparation of esters by reaction of carboxylic acids and alcohols,the ester formed is distilled out as soon as it is formed.Explain?**

**Ans.Formation of ester is a reversible reaction.To prevent backward reaction,it is distilled out immediately.**

**122. Electrophilic substitution on Benzoic acid takes place at meta position?**

**Ans.Since COOH group is electron withdrawing group,it acts as meta directing group in resonance,it creates positive charge on ortho and para position.And electrophile is positive and feel repulsion at ortho and para position.Hence it goes to the meta position.**

### **SOME REASONING QUESTIONS asked in CBSE Board**

2006- DELHI

1. Electrophilic substitution in case of amines takes place more readily than benzene.
2. CH<sub>3</sub>CONH<sub>2</sub> is a weaker base than CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>.
3. Nitro compounds have higher boiling points than hydrocarbons having almost same molecular mass.

2006- AISSCE

1.  $\sigma$ -nitrophenol is more acidic than  $\sigma$ -methoxyphenol.
2. Glycerol is used in cosmetics.
3. Explain the observed Kb order: Et<sub>2</sub>NH > Et<sub>3</sub>N > EtNH<sub>2</sub>, in aqueous solution.

2006- FOREIGN

1. Aldehydes are more reactive than ketones towards nucleophilic reaction.

2. Electrophilic substitution in benzoic acid takes place at meta position.

2005-DELHI

1. Why are primary amines higher boiling than tertiary amines/
2. Alkylamines are stronger base than arylamine.
3. Acetanilide is preferred as good solvent in organic chemistry.
4. Carboxylic acid do not gives characteristic reactions of carbonul group.
5. Treatment of benzaldehyde with HCN gives a mixture of two isomers which can be separated even by fractional distillation.
6.  $\text{NaHSO}_3$  is used for purification of aldehydes and ketone.

AISSCE

1. How is the basic strength of aromatic amine affected by the presence of an electron releasing group on the benzene ring?
2. How an  $-\text{OH}$  group attached to a carbon in the benzene ring activates benzene towards electrophilic substitution?
3. Nitrobenzene does not undergo Friedelcraft,s reaction.
4. Methylamine in water reacts with  $\text{FeCl}_3$  to precipitate  $\text{Fe}(\text{OH})_3$ .
5. Methylamine is stronger base than ammonia.

FOREIGN

1. Why are primary amine higher boiling than tertiary amine?
2. Aldehydes are more reactive than ketones towards.
3. Carboxylic acids have much higher acidity than phenol.
4. In aquous solution, secondary amines are more basic than tertiary amines.
5. Amines are more basic than comparable alcohol.

2004- DELHI

1. Aromatic amines are less basic than ammonia and aliphatic amines.
2. Draw the structure of a carbonyl group and indicate clearly a) hybridized state of carbon, b)  $\sigma$ -and  $\pi$ - bond present c) electrophilic and nucleophilic centres in it.
3. Aldehydes are more reactive than ketone towards nucleophilic reaction.
4. Chloroacetic acid is stronger than acetic acid.

AISSCE

1. Even in mild condition, aniline on bromination gives 2,4,6-tribromoaniline.
2. Diazonium ion acts as electrophile.
3. Nucleophilic substitution of p-nitrochlorobenzene is easier than that of chlorobenzene.
4. Amines are more basic than comparable alcohol.
5. It is difficult to prepare pure amines by ammonolysis of R-X.
6. Electrophilic substitution in case of aromatic amines takes place more readily than in benzene.
7. In contrast to arenas, aliphatic hydrocarbons do not undergo nitration.
8. Ethers possess a net dipole moment even if the alkyl radicals in the molecule is identical.
9. Sodium bisulphate is used for purification of aldehydes and ketones.
10. Most aromatic acids are solid but the aliphatic acids are liquid.
11. Aniline is a weaker base than cyclohexyl amine.
12. Benzoic acid is stronger than acetic acid.