

## REASONING QUESTIONS IN ORGANIC CHEMISTRY

### TEXT EXERCISE

1. Why is sulphuric acid 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>)

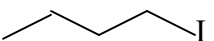
CH<sub>3</sub>CHCl-CH<sub>3</sub> < CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>Cl < CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Cl

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 < 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>CH<sub>2</sub>(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>CH<sub>2</sub>(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

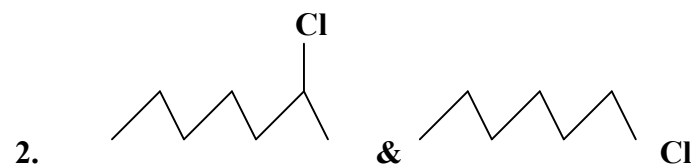
3. CH<sub>3</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>2</sub>-Br & CH<sub>3</sub>-CH<sub>2</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-Br

Ans: 1. CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Br primary alkyl halide is more reactive than secondary alkyl halide

2. CH<sub>3</sub>-CH<sub>2</sub>-CHBr-CH<sub>3</sub> Secondary alkyl halide is more reactive than Tertiary alkyl halide

3. CH<sub>3</sub>-CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>2</sub>-Br As methyl group is far from Br it will less stabilize the carbo cations and facilitate the SN<sup>2</sup> mechanism.

7. Which of the following compound go faster SN<sup>1</sup> 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;



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?

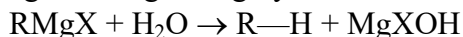
Ans: It is due to electron withdrawing effect of phenyl group which decrease dipole moment of chloro benzene.

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

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

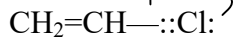
14. Grignard reagent should be prepared under anhydrous conditions. Give reason.

Ans: Grignard reagent highly react with water to alkanes.



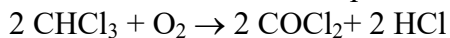
15. Vinyl chloride is less reactive towards nucleophilic substitution. Explain.

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



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

Ans: Chloroform react with air in presence of sun light it forms poisonous phosgene.



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

Ans; The second compound is more resonance stabilized hence easily forms carbo cation and react faster by  $\text{SN}^1$  mechanism.

18. The treatment of alkyl halides with aqueous  $\text{KOH}$  leads to the formation of alcohols but in the presence of alcoholic  $\text{KOH}$  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 low polarity solvent like alcohol favours elimination where as in the presence of high polarity solvent like water substitution 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 is 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?  $1^0 > 2^0 > 3^0$

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

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

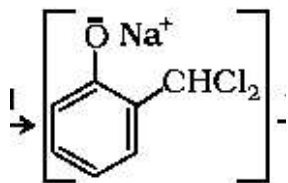
Sulphuric acid removes the water and prevent back ward reaction,

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.



Intermediate

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.

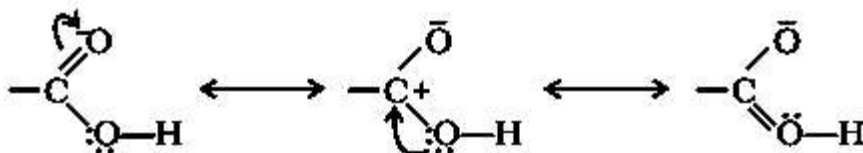
31. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

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 electronegative 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.

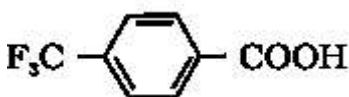
35.

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)  $\text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$  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.

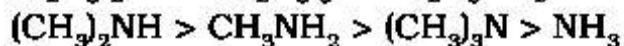
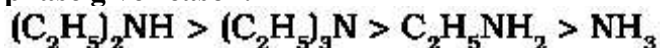
Ans: Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

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

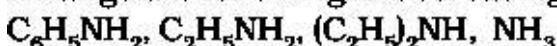
39. The basic strength of amines in aqueous solutions is different from gaseous phase give reason.



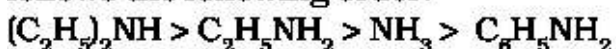
It is due to inductive effect, hydrogen bond and hydration effect

40.

Arrange the following in decreasing order of their basic strength:

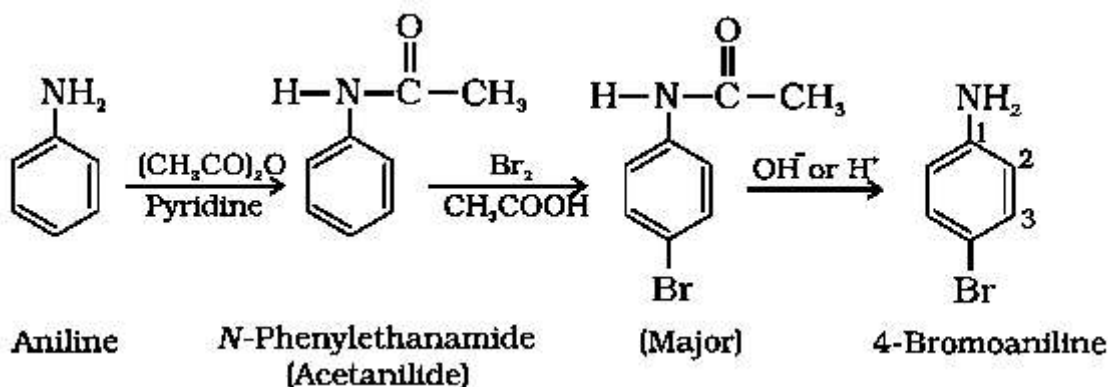


The decreasing order of basic strength of the above amines and ammonia follows the following order:



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 -NH<sub>2</sub> group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

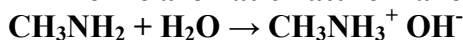


42. Account for the following:

- (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 ( $109^\circ 28'$ ). 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.

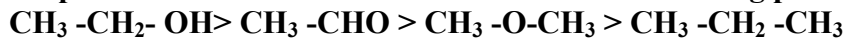
Ans: As branching increases surface area decreases and Vander wall's force decreases, hence boiling point decreases. And also in branched alcohols due to electron releasing effect strength of hydrogen decreases.

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



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

Propene is weak vanderwaal's 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 CuSO<sub>4</sub> & 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 react with bromine in the presence of carbon disulphide gives monobromophenol whereas with water gives tribromophenol. Explain.  
 Ans.  $CS_2$  is a non-polar solvent whereas water is a polar solvent. In the presence of polar solvent phenol polarizes and gives mole 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 inter molecular hydrogen bond.
74. Explain why O-nitro phenol is more acidic than O-methoxy phenol?  
 Ans: Nitro group is an electron withdrawing which increases acidity whereas methoxy group is an electron releasing 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 isopropanol 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



$\text{CH}_3\text{-CH}_2\text{-OH} > \text{CH}_3\text{-CHO} > \text{CH}_3\text{-O-CH}_3 > \text{CH}_3\text{-CH}_2\text{-CH}_3$   
 Inter molecular H-bond      more polar than ethers      presence of polarization      no H-bond &

80. Why it is necessary to use sulphuric acid in nitration of benzene?  
 Ans: sulphuric acid is helping in formation of  $\text{NO}_2$  electrophile which is easy To substitute on benzene.
81. Acetic acid is halogenated in the presence of red P and  $\text{Cl}_2$  but formic acid cannot be halogenated in the same way . Explain?  
 Ans. There is no alpha hydrogen in formic acid.
82. Carboxylic acid 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  $\text{CO}$ ?  
 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 Polarizable  $\text{C}=\text{O}$  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  $-\text{OH}$  group's 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  $-\text{OH}$  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.  $\text{NH}_2$  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  

$$2\text{CH}_3\text{NH}_2 + \text{AgCl} \rightarrow [\text{Ag}(\text{CH}_3\text{NH}_2)_2] \text{Cl}$$
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 carbocation mechanism as tertiary carbocation 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 is involved 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 lose 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.

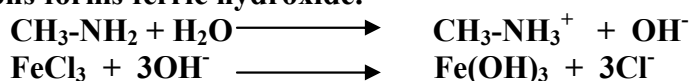
103. A weakly basic solution favours coupling of benzene diazonium chloride with phenol. Explain?

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

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 to form 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 possess 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

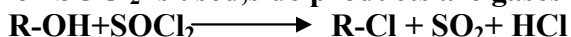
II) Resonance effect

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  $\text{SOCl}_2$  is preferable. Explain?

Ans. When  $\text{SOCl}_2$  is used, side products are gases and forms pure alkyl halides.



120. Alkyl halides react with nitrites whereas  $\text{AgNO}_2$  gives Nitro alkanes. Explain?

Ans.  $\text{KNO}_2$  is an ionic compound and forms  $\text{NO}_2^-$  which is an ambidentate nucleophile. It can form bond with nitrogen and oxygen. Since C-O bond is stable, it forms alkyl nitrites whereas  $\text{AgNO}_2$  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  $\text{COOH}$  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.  $\text{CH}_3\text{CONH}_2$  is a weaker base than  $\text{CH}_3\text{CH}_2\text{NH}_2$ .

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  $K_b$  order:  $\text{Et}_2\text{NH} > \text{Et}_3\text{N} > \text{EtNH}_2$ , 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 aqueous 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.

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