

## ARMY PUBLIC SCHOOL JAMMU CANTT

### HOLIDAYS HOMEWORK (2019-20)

CLASS- 12

**SUB- CHEMISTRY**

**DO THESE QUESTIONS ON CLASS WORK NOTEBOOK.**

#### **Haloalkanes and Haloarenes – (4 MARKS)**

1. Give one example each of:

- a) Markwonikov's addition. b) Kharasch effect. c) Sand Meyer reaction d) Diazotisation reaction  
e) Finkelstein reaction f) Swarts reaction g) Wurtz reaction h) Wurtz Fittig reaction i) Fittig reaction  
j) Friedel's craft acylation reaction of chloro benzene k) Friediel craft's alkylation reaction. of chloro benzene.  
l) nitration of chloro benzene. m) sulphonation of chloro benzene. n) Dehydro halogenation ( $\beta$  -elimination reaction) o) Zatsev rule. p) chlorination of chloro benzene.

2. Explain the classification of halo alkanes based on

- a) number of halogen atoms.  
b) compounds having  $sp^3$  C-X bond  
c) compounds having  $sp^2$  C-X bond  
d) dihalides. Give one example each and their IUPAC names.

3. Account for the following:

- a) Halo alkanes have higher boiling point than the corresponding parent alkane.  
b) Boiling point of halo alkanes  $RI > RBr > RCl > RF$   
c) Boiling point of 1-Bromo butane  $> 2$ -Bromo butane  $> 1$ -Bromo- 2-methyl propane  $> 2$ -Bromo- 2-methyl propane.  
d) Melting point of p-Dichlo benzene is higher than its ortho and meta isomer.  
e) Halo alkanes are polar in nature but sparingly soluble in water.  
f) Iodo alkane can not be prepared by the reaction of alcohol with KI and sulphuric acid. Phosphoric acid is used in place of sulphuric acid.  
g) Order of reactivity of alcohol with HX is tert alcohol  $>$  sec alcohol  $>$  primary alcohol..  
h) Halo arenes can not be prepared by treating phenol with HX or NaX in the presence of sulphuric acid.

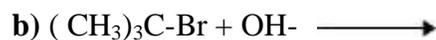
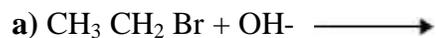
- i) Iodination of benzene is carried out in the presence of  $\text{HIO}_3$  or  $\text{HNO}_3$ .
- j) Propane on chlorination gives 2-chloro propane as a major product and not 1-chloro propane.
- k) Kharasch effect is possible only with  $\text{HBr}$  and not with  $\text{HCl}$  and  $\text{HI}$ .
- l) Alcohol reacts with thionyl chloride to give pure halo alkane.
- m) Finkelstein reaction of halo alkane is carried out in the presence of dry acetone.
- n) Order of reactivity of halo alkanes as per substitution bimolecular nucleophilic is primary halide > secondary halide > tertiary halide.
- o) Order of reaction as per substitution unimolecular is tertiary halide > secondary halide > primary halide.
- p) Benzylic halides and allylic halides are more reactive towards nucleophile than halo alkanes.
- q) Chloro ethene is less reactive towards nucleophile than chloro ethane.
- r) Halo arenes are less reactive towards nucleophile than halo alkanes.
- s)  $\text{S}_{\text{N}}1$  mechanism is ruled out in the reaction of halo arenes with nucleophile.
- t) Electron withdrawing groups like  $\text{NO}_2$  at ortho and para position with respect to halogen facilitates nucleophilic substitution reaction.
- u) Electron withdrawing groups like  $\text{NO}_2$  at meta position with respect to halogen has no effect on nucleophilic substitution reaction.
- v) Halo arenes are less reactive towards electrophile than benzene.
- w) Although chlorine atom has electron withdrawing effect electrophilic substitution occurs at ortho and para position.
- x) Order of reactivity of alkyl halide  $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
- y) Halo alkanes react with  $\text{KCN}$  to give alkyl cyanide as a major product while it gives alkyl isocyanide as a major product with  $\text{AgCN}$ .
- z) Halo alkanes give nitro alkane with  $\text{KNO}_2$  while nitro alkane with  $\text{AgNO}_2$ .
- za)  $\text{CH}_3\text{I}$  undergoes  $\text{S}_{\text{N}}2$  reaction faster than  $\text{CH}_3\text{Cl}$ .

4. Explain the following with suitable examples:

- a) chiral and chirality   b) enantiomers   c) racemic mixture  
d) retention of configuration   e) inversion of configuration.

5. Mention the differences between  $\text{SN}^1$  and  $\text{SN}^2$  mechanism of halo alkane.

6. Give the products and explain the mechanisms of the following reactions:



7. Carry out the following conversions:

a. Propene to i) Propan-1-ol ii) Propan-2-ol b. Ethanol to but-1-yne

c. 1-Bromo propane to 2-Bromo propane and vice versa. d. Toluene to benzyl alcohol.

e. Benzene to i) 4-bromonitro benzene ii) 3-bromonitro benzene.

f. Benzyl alcohol to 2-phenyl ethanoic acid. g. Ethanol to a) Propane nitrile b) Ethyl isocyanide.

h. Aniline i) Chloro benzene ii) Bromo benzene iii) Iodo benzene.

i. 2-Chloro butane to 3,4- dimethylhexane. j. 2-Methyl-1-propene to 2-chloro-2-methylpropane.

k. Ethyl chloride to propanoic acid. l. But-1-ene to n-butyl iodide.

m. 2-chloropropane to propan-1-ol n. Isopropyl alcohol to iodoform.

o. Chloro benzene to i) p-nitro phenol ii) p-chloronitro benzene iii) p-chloro  
iv) p- chloro acetophenone. v) p-chloro benzene sulphonic acid vi) 1,4-Dichloro benzene. vii) biphenyl.

p. Chloroethane to butane. q. tert-butyl bromide to isobutyl bromide.

r. Aniline to phenylisocyanide.

s. Propene to i) 2,3-dimethyl butane ii) n-hexane.

t. Tert-butyl bromide to 2-methyl prop-1-ene.

8. What happens when:

a) n-butyl chloride is treated with alcoholic KOH.

b) bromobenzene is treated with Mg in the presence of dry ether.

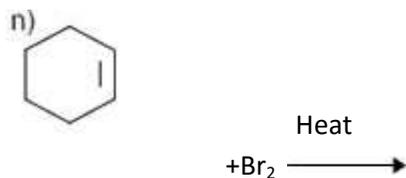
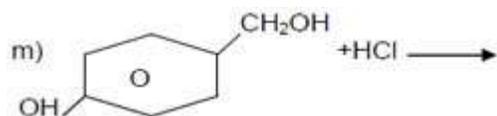
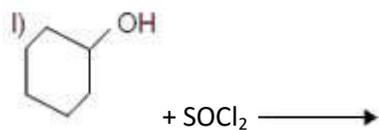
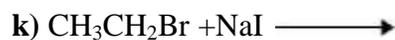
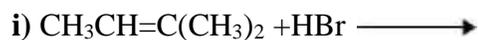
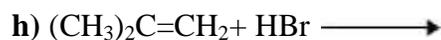
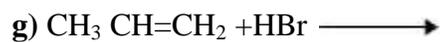
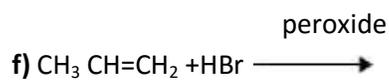
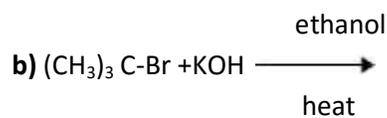
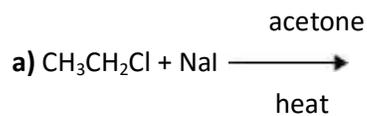
c) chlorobenzene is subjected to hydrolysis.

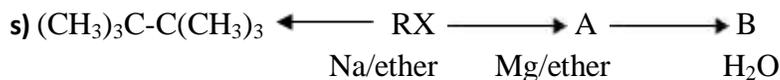
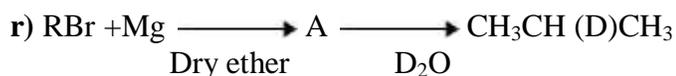
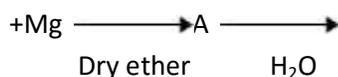
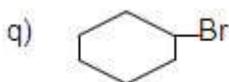
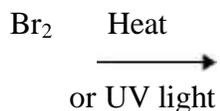
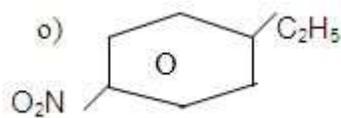
d) ethyl chloride is treated with aqueous KOH.

e) methyl bromide is treated with Na in the presence of dry ether.

f) methyl chloride is treated with i) KCN ii) AgCN iii)  $\text{KNO}_2$  iv)  $\text{AgNO}_2$

9. Write the structure of the major organic product in each of the following reactions:





10. Arrange the compounds of each set in order of decreasing reactivity towards a)  $\text{SN}^2$  displacement. b)  $\text{SN}^1$  displacement.

- 2-bromo-2-methylbutane, 1-bromopentane, 2-bromo pentane
- 1-bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane
- 1-bromo butane, 1-bromo-2-methyl propane, 1-bromo-2-phenyl propane.
- Methyl chloride, Methyl bromide and Methyl iodide.

11. Primary halide A ( $\text{C}_4\text{H}_9\text{Br}$ ) with alcoholic KOH gives a compound B. B on treatment with HBr gives C which is an isomer of A. A on treatment with Na in dry ether gives a compound D which is different from when n-butyl bromide is reacted with Na in dry ether. Give the structural formula of A. Write the equations of the reactions involved.

12. An alkyl halide  $\text{C}_7\text{H}_{15}\text{Br}$  is optically active. It reacts with KOH solution to give racemic mixture. Explain the mechanism of the reaction.

13. Distinguish chemically between:

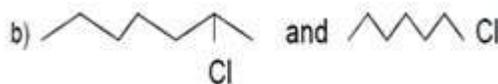
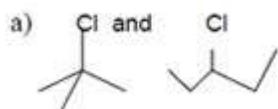
- a)  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$       b) Chloro benzene and chloro methane  
c) chloro benzene and benzyl chloride      d)  $\text{CHCl}_3$  and  $\text{CCl}_4$

14. Primary alkyl halide A ( $\text{C}_4\text{H}_9\text{Br}$ ) reacts with alcoholic KOH to give B. B reacts with HBr to give C which is an isomer of A. When A is treated with sodium in dry ether it gives a compound D  $\text{C}_8\text{H}_{18}$  which is different from the compound when n-butyl bromide is treated with sodium. Give the structural formula of A and complete the reaction.

15. Which alkyl halide from the following pairs would you expect to react more rapidly by  $\text{S}_\text{N}^2$  Mechanism? Explain your answer.

- a) 1-Bromo butane and 2-Bromo butane.      b) 2-Bromo butane and 2-Bromo-2-methyl propane.  
c) Cyclo hexyl chloro methane and chloro cyclo hexane.      d) Iodo butane and chloro butane.

16. Which alkyl halide from the following pairs would you expect to react more rapidly by  $\text{S}_\text{N}^1$  Mechanism? Explain your answer.



17. Predict the order of reactivity of the following compounds in  $\text{S}_\text{N}^1$  and  $\text{S}_\text{N}^2$  mechanism.

- a)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$       b)  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$       c)  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$       d)  $\text{C}_6\text{H}_5(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$ . Explain your answer.

18. Arrange the following in the increasing order of boiling point.

- a) Bromomethane, Bromoform, Chloromethane and Dibromomethane.  
b) 1-Chloropropane, 1-Chlorobutane and isopropyl chloride.

19. Among the isomeric alkanes  $\text{C}_5\text{H}_{12}$ , identify the one that on photochemical chlorination yields

- a) A single monochloride molecule      b) Three isomeric monochloride molecules  
c) Four isomeric monochlorides.

### ALCOHOLS, PHENOLS AND ETHERS – (4 MARKS)

1. Write the equations of the following named reactions:

- a) Hydro boration  
b) williamson's synthesis  
c) cumene phenol process  
d) Kolbe's reaction  
e) Riemier Tiemann reaction

2. Explain Lucas test with suitable examples

**3.** Distinguish chemically between the following pairs of organic compounds

- a)** Phenol and methanol
- b)** methanol and ethanol
- c)** propan-1-ol and propan-2-ol
- d)** pentan-3-ol and 2-Methyl butan 2-ol

**4.** Account for the following:

- a)** COH bond angle in alcohol is less than tetrahedral angle of  $109.5^\circ$
- b)** COC bond angle in ether is more than tetrahedral angle of  $109.5^\circ$
- c)** C-O bond length in phenol is less than that of alcohol.
- d)** Phenol has lower dipole moment than alcohol.
- e)** Phenol undergoes electrophilic substitution at ortho and para position
- f)** Alcohol acts as a Brønsted acid as well as Brønsted base.
- g)** Phenol is more acidic than alcohol.
- h)** Acidity of alcohol is primary alcohol > sec alcohol > tert alcohol.
- i)** Basicity of alcohol is tert alcohol > sec alcohol > primary alcohol.
- j)** In Williamson's synthesis sec and tert halide can not be used.
- k)** para nitro phenol is less steam volatile than ortho nitro phenol.
- l)** Presence of nitro group at ortho and para position makes phenol more acidic.
- m)** Alcohols and phenols have higher boiling point.
- n)** Boiling point of alcohol is higher than its isomeric ether.
- o)** Boiling point of glycerol > ethylene glycol > ethanol.
- p)** Grignard reagent is a versatile reagent in organic chemistry.
- q)** Cresol is less acidic than phenol.
- r)** In esterification reaction, water is removed as soon as it is formed.
- s)** Order of reactivity of HX with alcohol is  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
- t)** Alcohol reacts with  $\text{SOCl}_2$  to give pure halo alkane.

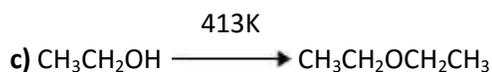
- u)** Ease of dehydration of alcohol is tert alcohol > sec alcohol > primary alcohol.
- v)** Phenol and anisole undergoes bromination reaction even in the absence of halogen carrier.
- w)** Methyl phenyl ether reacts with HI to give phenol and methyl iodide and not methanol and iodo benzene.
- x)** Methoxy ethane reacts with HI to give methyl iodide and ethanol and not ethyl iodide and methanol.
- y)** Tert butyl methyl ether reacts with HI to give tert butyl iodide and methanol and not not methyl iodide and tert butyl alcohol.
- z)** Anisole undergoes electrophilic substitution at ortho and para position.
- aa)** Boiling point of butan-1-ol is higher than tert butyl alcohol.
- bb)** Alcohol, phenol and ether are soluble in water.
- cc)** In the reaction between acid chloride and alcohol a small amount of pyridine is added.
- dd)** Alcohol behaves as nucleophile as well as electrophile.
- ee)** Water is a stronger acid than alcohol.

**5.** Carry out the following conversions:

- a)** Ethanal to ethanol.
- b)** Acetone to propan-2-ol.
- c)** Ethanoic acid to ethanol.
- d)** Ethene to ethanol.
- e)** Propene to propan-2-ol.
- f)** Methanal to ethanol.
- g)** Methanal to benzyl alcohol.
- h)** Ethanal to propan-2-ol.
- i)** Acetone to 2-methyl propan-2-ol.
- j)** But-1-ene to butan-1-ol.
- k)** But-2-ene to butan-2-ol.
- l)** Chloro benzene to phenol.

- m)** Aniline to phenol.
- n)** Benzene to phenol.
- o)** Ethanol to ethyl ethanoate.
- p)** Ethanol to ethene.
- q)** Ethanol to ethanal.
- r)** Tert butyl alcohol to 2-methyl prop-1-ene.
- s)** Propan-2-ol to acetone.
- t)** Phenol to
  - i)** phenyl ethanoate.
  - ii)** 2-Acetoxy benzoic acid.
  - iii)** ortho and para nitro phenol.
  - iv)** 2,4,6-trinitro phenol
  - v)** para bromo phenol
  - vi)** 2,4,6- tri bromo phenol
  - vii)** salicylic acid
  - viii)** salicylaldehyde
  - ix)** anisole
  - x)** benzene
  - xi)** benzo quinone.
- u)** Ethyl iodide to diethyl ether
- v)** Methyl bromide to 2 methoxy 2 methyl propane.
- w)** Benzyl chloride to benzyl alcohol
- x)** Ethyl magnesium chloride to propan-1-ol
- y)** Cumene to phenol
- z)** Anisole to
  - i)** phenol
  - ii)** ortho and para hydroxyl aceto phenone
  - iii)** para bromo anisole
  - iv)** ortho and para methyl anisole
  - v)** ortho and para methoxy aceto phenone
  - vi)** ortho and para nitro anisole
  - vii)** Ethene to ethane-1,2-diol

6. Explain the mechanism of the following reactions:



d) Explain the mechanisms of the reactions in which alcohol acts as

a) nucleophile

b) electrophile

7. How is ethanol prepared from

a) ethene

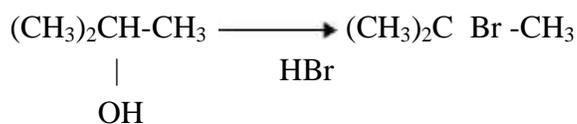
b) cane sugar? Mention 2 uses of ethanol.

8. How is methanol commercially? Mention 2 uses of the same.

9. How is phenol prepared commercially? Mention 2 uses of the same.

10. An organic compound A reacts with NaOH under drastic conditions to give B. B reacts with  $\text{Br}_2(\text{aq})$  to give C. C on zinc dust distillation gives 1,3,5-Tribromobenzene. Identify the compounds and write the equations of the reactions involved.

11. Give the mechanism for the reaction:



12. Write the equations of the following reactions:

a) Friedel-Craft's alkylation of anisole.

b) Friedel-Craft's acylation of anisole.

c) Nitration of anisole.

d) Bromination of anisole in ethanoic acid medium.

e) Oxidation of Propan-1-ol with alkaline  $\text{KMnO}_4$  solution

f) Phenol with  $\text{Br}_2$  in  $\text{CS}_2$

g) Phenol with dilute  $\text{HNO}_3$

h) Phenol with chloroform in the presence of aqueous NaOH.

13. Write the equation of reaction of HI with:

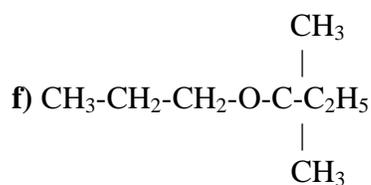
a) 1-Propoxy propane

b) Methoxy benzene

c) benzyl ethyl ether.

d)  $\text{CH}_3-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2\text{OCH}_2-\text{CH}_3$

e)  $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_5$

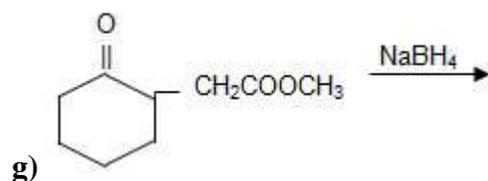
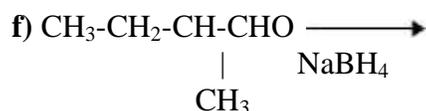
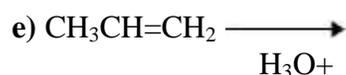
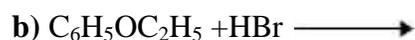


14. Name the reagent used in the following reactions:

- Oxidation of primary alcohol to carboxylic acid.
- Oxidation of primary alcohol to aldehyde.
- Bromination of phenol to 2,4,6-Tribromophenol.
- Benzyl alcohol to benzoic acid.
- Dehydration of Propan-2-ol to propene.
- Butan-2-one to Butan-2-ol.

15. You are given benzene, concentrated sulphuric acid and NaOH. Write the equation involved in the preparation of phenol using these reagents.

16. Give the products of the following reactions:



17. Give the structure and IUPAC names of the products expected from the following reactions:

- Catalytic reduction of butanal
- Hydration of propene in the presence of dilute sulphuric acid.
- Reaction of propanone with methyl magnesium bromide followed by hydrolysis.

18. The following is not the appropriate reaction for the preparation of tert-butyl ethyl ether.  
$$\text{C}_2\text{H}_5\text{ONa} + (\text{CH}_3)_3\text{C-Cl} \longrightarrow (\text{CH}_3)_3\text{COC}_2\text{H}_5$$

- a) What would be the major product for this reaction ?  
b) Write the reaction for the preparation of tert-butyl ethyl ether.

19. Give the structure of the product you would expect when each of the following alcohol react with

- i) HBr      ii)  $\text{SOCl}_2$       iii)  $\text{ZnCl}_2 + \text{HCl}$

- a) Butan-1-ol      b) 2-Methylbutan-2-ol

20. Predict the major product in the acid catalysed dehydration of

- a) butan-1-ol      b) 1-Methylcyclohexanol.

21. Draw the resonance structures of phenoxide ion of ortho and para nitrophenols.

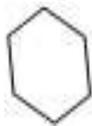
22. Write the structure of major products formed in the following reactions:

- a) Mono nitration of 3-methylphenol.  
b) Dinitration of 3-methylphenol.  
c) Mononitration of phenyl methanoate.

23. How are the following alcohols prepared by the reaction of Grignard reagent with HCHO?

- a)  $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$

- b)  $\text{CH}_2\text{OH}$



24. Arrange the following compounds in the order of properties mentioned:

- a) Pentan-1-ol, Pentan-2-ol, ethanol, Propan-1-ol and methanol.(increasing order of boiling point.  
b) Pentan-1-ol, n-butane, Pentanal and ethoxyethane.(increasing order of boiling point.)  
c) Propan-1-ol, 2,4,6-Trinitrophenol, 3-Nitrophenol, 3,5-Dinitrophenol, Phenol and 4-Methylphenol ( increasing order of acidity)

## ALDEHYDE, KETONE AND CARBOXYLIC ACID – (6 MARKS)

1. Write equations for the following named reactions:

- a) Nucleophilic addition reaction.                      b) Clemmensen reduction.                      c) Wolff-Kishner reduction.  
d) Aldol condensation.                      e) Crossed aldol condensation                      f) Cannizzaro reaction.  
g) Rosenmund's reduction.                      h) Kolbe's electrolysis                      i) Stephen reaction.  
j) Etard reaction.                      k) Decarboxylation.                      l) Acylation.                      m) Schotten-Baumann reaction.  
n) Friedel-Crafts acylation.                      o) Esterification.                      p) Gattermann-Koch reaction.  
q) Hell-Volhard-Zelinsky reaction.

2. Explain:

- a) Fehling's test                      b) Tollen's reagent test with suitable examples.

3. Distinguish chemically between the following pairs of organic compounds:

- a) Methanal and ethanal.                      b) Ethanal and propanone.                      c) Pentan-2-one and pentan-3-one.  
d) Acetophenone and benzophenone.                      e) Formic acid and acetic acid.  
f) Benzoic acid and ethyl benzoate.                      g) Phenol and benzoic acid.                      h) Ethanal and propanal.  
i) Propanal and diethyl ether.                      j) Benzaldehyde and acetophenone.                      k) Ethanal and propanone

4. Account for the following:

- a) Aldehyde and ketone are polar in nature.  
b) Aldehyde and ketones have higher boiling point than hydrocarbons of comparable molar mass.  
c) Aldehyde and ketones have lower boiling point than alcohols of comparable molar mass.  
d) Ketone has higher boiling point than aldehyde of comparable molar mass.  
e) Oxidation of primary alcohol to aldehyde is carried out using PCC as an oxidizing agent.  
f) Rosenmund's reduction of acid chloride to aldehyde is carried out using quinoline and sulphur.  
g) Aldehyde is more reactive than ketone towards nucleophile.  
h) Butanone is less reactive than propanone.

- i)** 2,2,6-Tri methyl cyclo hexanone is less reactive towards nucleophile than cyclo hexanone.
- j)** Para nitro benzaldehyde is more reactive towards nucleophile than benzaldehyde.
- k)** Para methyl benzaldehyde is less reactive towards nucleophile than benzaldehyde.
- m)** Reaction of aldehyde with alcohol to give acetal is carried out in the presence of HCl(g).
- n)** Formaldehyde and benzaldehyde undergoes cannizaro reaction and not aldol condensation.
- o)** Acetaldehyde undergoes aldol condensation and not cannizaro reaction.
- p)** Aromatic aldehyde and ketones undergoes electrophilic substitution at meta position.
- q)** Carboxylic acid do not show the reactions of aldehyde and ketone though it has  $>C=O$  group.
- r)** Carboxylic acid has higher boiling point than aldehyde, ketone and alcohol of comparable molar mass.
- s)** In semi carbazide, only one  $NH_2$  group is involved in the formation of semi carbazone.
- t)** Aldehyde, ketone and carboxylic acid are soluble in water.
- u)** In oxidation of primary alcohol to carboxylic acid is not carried out using acidified potassium dichromate.
- v)** Carboxylic acid is more acidic than alcohol.
- w)** Carboxylic acid is more acidic than phenol.
- x)** Acidity of  $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$ .
- y)** Acidity of  $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$ .
- z)**  $\alpha$  chloro propanoic acid is more acidic than  $\beta$  chloro propanoic acid.
- aa)** Acetic acid is less acidic than formic acid.
- bb)** Pure acid halide is prepared by the reaction of carboxylic acid with thionyl chloride.
- cc)** Carbon in carbonyl group of aldehyde and ketone acts as Lewis acid (electrophile) while oxygen acts as Lewis base ( nucleophile).
- dd)** Benzoic acid does not undergo Friedel craft alkylation reaction.

**5.** How is

- a)** HCHO
- b)**  $CH_3CHO$

c)  $C_6H_5CHO$  prepared commercially? Mention two uses of each.

6. How is

a)  $HCOOH$

b)  $CH_3COOH$

c)  $C_6H_5COOH$  prepared commercially? Mention two uses of each.

7. Carry out the following conversions:

a) Ethanol to ethanal.

b) Methanol to methanal.

c) Propan-2-ol to propanone.

d) Methanal to

i) ethanol

ii) benzyl alcohol.

e) Ethanal to

i) propan-2-ol

ii) acetone.

f) Acetone to

i) tert butyl alcohol

ii) 2-Methyl prop-1-ene.

g) Benzaldehyde to

i) alpha- hydroxy phenyl acetic acid

ii) 3-phenyl propan-1-ol

iii) 1- phenyl ethanol.

iv) benzyl alcohol and sodium benzoate.

v) cinnamaldehyde.

vi) 1,3-Diphenyl prop- 2-en-1-one

vii) benzo phenone

- viii)** m-nitro benzaldehyde
- ix)** benzal acetophenone.
- h)** Butan-1-ol to butanal.
- i)** Cyclo hex-2-en-1-ol to cyclo hex-2-en 1-one.
- j)** Pentan-3-en-2-ol to pent-3-en-2-one.
- k)** But-2-ene to ethanal
- l)** Para nitro toluene to para nitro benzaldehyde.
- m)** Ethanal to butan-2-one.
- n)** Ethanal to butane- 1,3- diol.
- o)** Ethanal to but-2-enal
- p)** Ethanal to but-2-enoic acid.
- q)** Ethanal to butan-1-ol
- r)** Ethanal to butanoic acid.
- s)** Propanone to propene.
- t)** Propanal to butanone.
- u)** Ethanal to 2-hydroxy butanal.
- v)** Benzaldehyde to benzo phenone.
- w)** Benzoic acid to benzaldehyde.
- x)** Propanoic acid to propenoic acid.
- y)** Benzene to m-nitro aceto phenone.
- z)** Bromo benzene to 1-phenyl ethanol.
- aa)** Benzoic acid to m- nitro benzoic acid.
- bb)** Benzoic acid to benzyl amine.
- cc)** Para nitro benzoic acid to para nitro aniline.
- dd)** Hexanoic acid to hexane nitrle.

- ee)** Hexanoic acid to 1-amino pentane.
- ff)** Hept-1-ene to heptanal
- gg)** Hept-1-ene to hexanal.
- hh)** Hept-1-ene to heptanoic acid.
- ii)** Hept-1-ene to hexanoic acid.
- jj)** Ethene to ethanal.
- kk)** Propene to acetone.
- ll)** 2, 3- dimethyl but-2-ene to acetone.
- mm)** Ethanal to lactic acid.
- nn)** Ethanal to ethane.
- oo)** Ethanal to Ethanoic acid.
- pp)** Acetone to 4-hydroxy-4-methyl pentan-2-one.
- qq)** Benzaldehyde to benzyl alcohol and sodium benzoate.
- rr)** Methanal to methanol and sodium methanoate.
- ss)** Toluene to benzaldehyde.
- tt)** Ethyl benzene to benzoic acid.
- uu)** But-2-ene to ethanoic acid.
- v v)** Ethane nitrile to ethanoic acid.
- ww)** Methyl magnesium bromide to ethanoic acid.
- xx)** Para methyl aceto phenone to benzene-1,4- dicarboxylic acid.
- yy)** Cyclo hexene to hexane-1,6-dicarboxylic acid.
- zz)** Ethanoic acid to ethanol.
- aaa)** Propanoic acid to  $\alpha$ - chloro propanoic acid.
- bbb)** Methanol to Ethanoic acid.
- ccc)** Benzoic acid to m-nitro benzoic acid.

**ddd)** Benzoic acid to m-bromo benzoic acid.

**eee)** Acetyl chloride to acetaldehyde.

**fff)** Benzoyl chloride to benzaldehyde.

**mmm)** Benzene to aceto phenone.

**nnn)** Benzene to benzo phenone.

**ooo)** Ethanoic acid to ethanoyl chloride.

**sss)** Ethanoic acid to ethanoic anhydride.

**tft)** Ethanoic acid to ethyl ethanoate.

**a)** Ethanoic acid to ethanamine.

**b)** Hexane nitrile to 1-amino pentane.

**c)** Benzoic acid to benzo phenone.

**d)** Benzoic acid to

**i)** aceto

**ii)** benzaldehyde

**iii)** benzophenone

phenone.

**e)** Benzene to methyl benzoate.

**f)** Benzene to m- nitro benzoic acid.

**g)** Benzene to p- nitro benzoic acid.

**h)** Benzene to p- nitro benzaldehyde.

**i)** Benzene to phenyl acetic acid.

**j)** Ethanoyl chloride to propanone.

**k)** Benzene to benzaldehyde

**l)** Ethane nitrile to

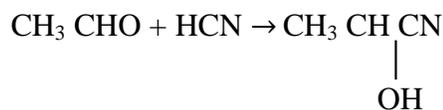
**i)** ethanal

**ii)** propanal

**m)** vinyl cyanide to prop2-enal

- n) p-fluoro toluene to p-fluoro benzaldehyde.
- o) cyclo hexanol to cyclohexanone.
- p) Hexan-1-ol to hexanal
- q) Butan-1-ol to butanoic acid.
- r) Benzyl alcohol to phenyl ethanoic acid.
- s) 3-nitro bromo benzene to 3-nitro benzoic acid
- t) 4- methyl acetophenone to benzene-1,4-dicarboxylic acid.
- u) Butanal to butanoic acid.
- v) Ethyl butanoate to ethanoic acid.
- w) cyclo hexane to Hexane-1,6-dicarboxylic acid.
- x) Benzene-1,4-dicarboxylic acid to phthalimide

8. Explain the mechanism of the following reaction:



9. An organic compound A(C<sub>8</sub>H<sub>8</sub>O) gives orange red precipitate with 2,4-DNP reagent. It responds to iodoform test. It does not respond to Tollen's reagent test. It does not decolorise bromine water. A on oxidation using CrO<sub>3</sub> give B. Identify the compounds and write the equations of the reactions involved.

10. An organic compound C<sub>9</sub>H<sub>10</sub>O forms 2,4-DNP derivative, reduces Tollen's reagent and Undergoes cannizaro reaction. On vigorous oxidation it gives Benzene-1,2-dicarboxylic acid. Identify the compound.

11. An organic compound contain 69.77% C and 11.63% H and the remaining O. Molecular mass of the compound is 86 u. It does not reduce Tollen's reagent, gives positive iodoform test and respond to sodium bisulphate test. On oxidation it gives acetic acid and propanoic acid. Give the structure of the organic compound.

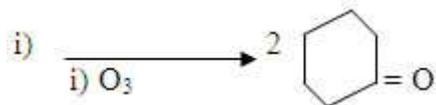
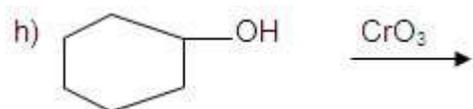
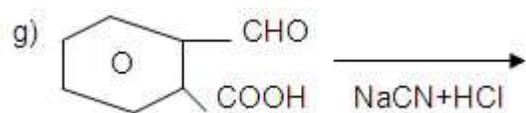
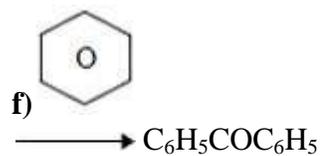
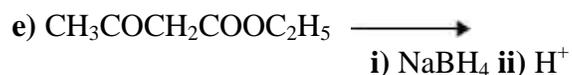
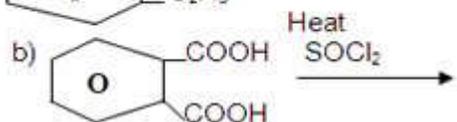
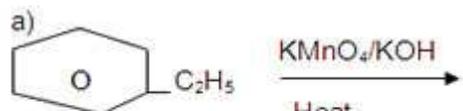
12. Arrange the following in the increasing order of property mentioned:

- a) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone( reactivity with HCN)
- b) 2-Bromo butanoic acid, 3-Bromo butanoic acid, Butanoic acid, 3-Methyl propanoic acid (acid strength)
- c) Benzoic acid, 4-Nitro benzoic acid, 3,4-Dinitro benzoic acid, 4-Methoxy benzoic acid (acid strength)
- d) Ethanal, Propanal, Propanone, Butanone( increasing order of reactivity towards nucleophile)

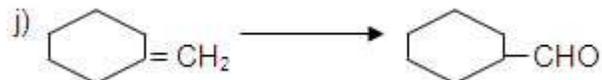
e) Benzaldehyde, p-Tolualdehyde, p-Nitro benzaldehyde, Acetophenone(increasing order of reactivity towards nucleophile)

f) Butanal, Butanol, Ethoxy ethane and Butane (increasing order of boiling point)

13. Complete each synthesis by giving missing starting material, reactant or product.



ii)  $\text{Zn} / \text{H}_2\text{O}$



14. Which acid of each pair would you expect to be stronger?

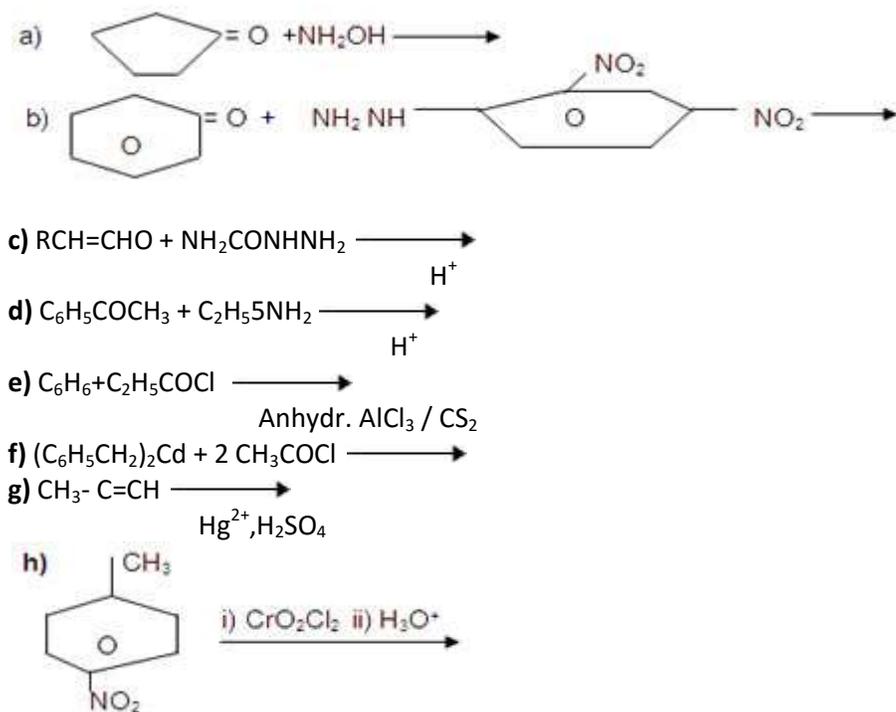
- a) Ethanoic acid and fluoro ethanoic acid
- b) Fluoro ethanoic acid and chloro ethanoic acid
- c) 4- Fluoro butanoic acid and 3-Fluoro butanoic acid
- d) p-Trifluoro benzoic acid and p- Methyl benzoic acid.

15. Arrange the following in the increasing order of boiling point: Ethanal, Ethanol, Ethoxy ethane and Propane

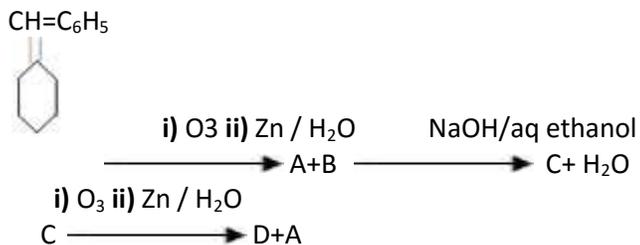
16. Predict the product formed when cyclohexanecarbaldehyde reacts with

- a)  $\text{PhMgBr} + \text{H}_3\text{O}^+$
- b) Tollens' reagent
- c) Semicarbazide and weak acid
- d) excess ethanol and acid.
- e) Zinc amalgam and dilute HCl

17. Give the products of the following reactions:



18. Identify the compounds A,B,C and D in the following reactions:



### Amines - 4 Marks Questions

1. Give one example each of the following named reactions:

- Sand meyer reaction
- Gabriel pthalimide synthesis.
- Coupling reaction
- Diazotisation reaction.
- Gatterman reaction
- Hoffmann bromamide reaction

2. Explain the following tests with suitable examples:

- Carbylamine test
- Hinsberg test.

3. Account for the following:

- Methyl chloride reacts with  $\text{AgNO}_2$  to give nitro methane as a major product where as it gives nitrito methane as a major product with  $\text{KNO}_2$
- C-N bond in aniline is shorter than in aliphatic amines.
- In ammonolysis of halo alkane , primary amine is the only product when large excess of ammonia is used while quaternary ammonium salt is the only product when halo alkane is in excess.
- Primary and sec amines have higher boiling point than tert amine.
- Amines have lower boiling point than alcohol of comparable molar mass.

- f)** Amines are soluble in water. Solubility of amines p.amines>sec amines>tert amines
- g)** Amines are less soluble in water than alcohol.
- h)** Basicity of amines in aqueous solution is sec amine>tert amine>p.amine.
- i)** Basicity of amines in vapor phase tert amine>sec amine>p.amine.
- j)** Aniline is a weaker base than aliphatic amine.
- k)** Electron repelling group at ortho and para position increases the basicity while electron withdrawing group at ortho and para position decreases the density of aniline.
- l)** Ammonolysis of halo alkane is carried out in the presence of a base.
- m)** Unlike alkylation of amines acylation stops after first step.
- n)** Tert amines do not react with acid derivatives.
- o)** Aniline undergoes bromination even in the absence of halogen carrier.
- p)** Nitration of aniline gives 47% meta nitro aniline.
- q)** P-toluidine is more basic than aniline.
- r)** Amines are less acidic than alcohol.
- s)** Halo alkane reacts with KCN to give alkyl cyanide as a major product while it gives alkyl isocyanide as a major product with AgCN.
- t)** Aniline does not undergo Friedel craft's reaction.
- u)** Aniline can't be prepared by Gabriel phthalimide synthesis.
- v)**  $\text{ArN}_2\text{X}$  is more stable than  $\text{RN}_2\text{X}$  at lower temperature.
- w)** Aniline is a weaker base than ammonia.
- x)** Order of basicity  $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$
- y)** Order of basicity  $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
- Z)** Bromination of aniline after acylation gives only para bromo aniline.
- aa)** Sandmeyer reaction is preferred over Gatterman reaction to prepare halo arenes from aniline.
- bb)** Ethyl amine is soluble in water but not aniline.
- cc)** Aqueous solution of methyl amine with ferric chloride solution gives brown precipitate of ferric hydroxide..

**dd)** Gabriel phthalimide synthesis is preferred to prepare primary amine.

**ee)** p-nitro aniline is less basic than aniline.

**4.** Carry out the following conversions:

**a)** Ethanoyl chloride to

**i)** ethanamine.

**ii)** N-methyl amino ethane.

**b)** Ethanoyl chloride methanamide

**c)** Methanamine to

**i)** N-methyl ethanamide.

**ii)** methyl iso cyanide.

**d)** Dimethyl amine to N,N dimethyl amine.

**e)** Ethane nitrile to

**i)** ethanoic acid.

**ii)** methyl ethanoate.

**iii)** acetone.

**iv)** ethanamine.

**f)** Benzo nitrile to

**i)** benzoic acid

**ii)** aniline

**g)** Aniline to

**i)** chloro benzene.

**ii)** bromo benzene.

**iii)** fluoro benzene

**iv)** iodo benzene .

**v)** phenol

**vi)** benzene.

**vii)** benzoic acid.

**viii)** para hydroxyl azo benzene.

**ix)** para amino azo benzene.

**x)** Nitro benzene

**xi)** 1,3,5-tribromo benzene

**xii)** p-bromo aniline

**xiii)** 2,4,6-tribromo aniline

**xiii)** benzyl alcohol

**h)** 4-nitro toluene to 2-bromo benzoic acid.

**i)** 3-methyl aniline to 3-nitro toluene.

**j)** Ethanoic acid to

**a)** ethanamine

**b)** methanamine

**k)** Methanol to ethanoic acid.

**l)** Ethanamine to methanamine

**m)** Methanamine to ethanamine.

- n) Nitro methane to dimethyl amine.
  - o) Propanoic acid to ethanoic acid.
  - p) Ethanoic acid to propanoic acid.
  - q) Nitro benzene to benzoic acid.
  - r) Benzene to m-bromo phenol.
  - s) Benzoic acid to aniline.
  - t) Aniline to 2,4,6- tribromo fluorobenzene
  - u) Benzyl chloride to 2-phenyl ethanamine.
  - v) Chloro benzene to p-chloro aniline.
  - w) Benzamide to toluene
6. Distinguish chemically between
- a) Methyl amine and aniline
  - b) methyl amine and dimethyl amine.
  - c) Aniline and benzyl amine
  - d) Aniline and N- methyl aniline.
  - e) dimethyl amine and trimethyl amine.

7. An organic compound

A on reaction with NaOH and Br<sub>2</sub> gives

B. B on diazotization gives

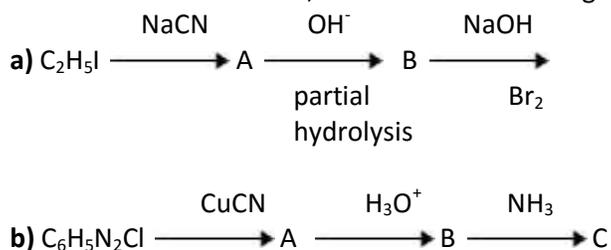
C. C when warmed with water gives

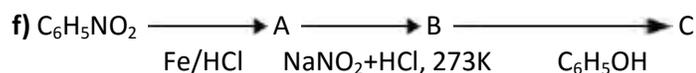
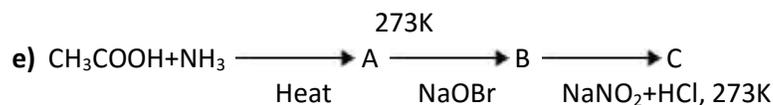
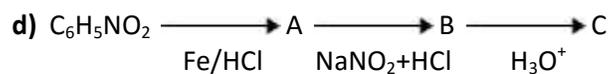
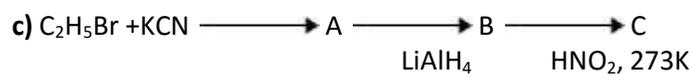
D. D gives violet coloration with neutral ferric chloride solution. Identify the compounds and write the equations of the reactions involved.

8. Give equation for the following reactions:

- a) ethanolic NH<sub>3</sub> with C<sub>2</sub>H<sub>5</sub>Cl
- b) ammonolysis of benzyl chloride followed by reaction with 2 moles of methyl chloride.
- c) sulphonation of aniline
- d) reaction of aniline with acetic anhydride.
- e) reaction of aniline with aqueous bromine.

9. Give the structure of A,B and C in the following reactions:





10. An organic compound A on heating with aqueous ammonia forms B. B on treatment with  $Br_2$  and KOH gives C of molecular formula  $C_6H_7N$ . Give the structure of the compounds A, B and C. Write IUPAC name of the each compound.

11. Give the equations of the reactions involved when aniline is reacted with

- $CHCl_3 + KOH$
- Conc sulphuric acid
- aqueous bromine
- acetic anhydride

12. Give the equation of the reaction involved when benzene diazonium chloride is treated with

- $H_3PO_2 + H_2O$
- i)  $HBF_4$  followed by  $NaNO_2 / Cu$

13. Arrange the following:

- increasing order of  $pK_b$  values-  $C_2H_5NH_2$ ,  $(C_2H_5)_2NH$ ,  $C_6H_5NHCH_3$ ,  $C_6H_5NH_2$
- increasing order of basic strength
  - $C_6H_5NH_2$ ,  $C_6H_5N(CH_3)_2$ ,  $(C_2H_5)_2NH$ ,  $CH_3NH_2$
  - Aniline, para nitro aniline, para toluidine
  - Aniline, N-Methyl aniline, benzyl amine
  - Aniline, methyl amine, dimethyl amine, trimethyl amine, benzyl amine
  - Aniline, ethyl amine, diethyl amine, triethyl amine.

c) decreasing order of basic strength in gas phase  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $(\text{C}_2\text{H}_5)_3\text{N}$ ,  $\text{NH}_3$

d) increasing order of boiling point-  $\text{C}_2\text{H}_5\text{OH}$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $\text{C}_2\text{H}_5\text{NH}_2$

e) increasing order of solubility in water- Aniline, ethyl amine, Diethyl amine

**14.** Write the reaction of final alkylation product with excess of ethyl iodide in the presence of Sodium carbonate solution.

**15.** Write the chemical reaction of aniline with benzoyl chloride and give the IUPAC name of the product formed.