Chapter 11 to 16

ALCOHOLS, PHENOLS AND ETHERS.

Q.1 Give the IUPAC name of the following.

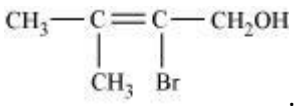
CH3-C (CH3) =CH-CH2OH

Ans:-3-Methyl But-2-en 1-ol

Q.2 Phenols are much more acidic than alcohols. Why

Ans:-Due to electron with drowning nature of ph-group.

Q3 **Give the IUPAC name of the following compound:**



.

Solution :

2 − Bromo-3-methyl-but-2-ene-1-ol.

Q.4 What happen when phenol is treated with excess of bromine(aq).

Ans It gives 2,4,6-tribromo phenol.

Q.5 Write chemical equation Williamson synthesis.

Ans- R-X+R- O- Na ---------→ R-O-R + NaCl

Q.6 Mention one uses of methanol.

Ans – (i) As a denaturant for ethanol

Q.7 The boiling point of ethanol is higher than that methoxy methane.

Ans-Ethanol has inter molecular hydrogen bonding, methoxymehane does not have H-bonding.

Q.8 **Name a substance that can be used as an antiseptic as well as a disinfectant**.

Ans:

Phenol can be used as an antiseptic as well as a disinfectant. 0.1% Soln of phenol is used as an antiseptic & 1% Soln of phenol is used as a disinfectant.

Q.9 Write the IUPAC name.

(CH3)3 C-OH

Ans- 2-methyl-2-propanol

Q.10 What is Nucleophiles.

Ans- The species which has high electrons density.

Q.11 Which catalyst are used in Friedel craft reaction?

Ans- Anh.AlCl3.

Q.12 Write a test to distinguish between primary, secondary and alcohols?

Ans Lucas test.

Q13 Write the IUPAC name of CH_3OH?

Ans- Methanol.

Q.14 Write the IUPAC name of CH_3-O-CH_3?

Ans- Methoxy methane.

Q.15.Write the IUPAC name of CH_3 CH_2-O-CH_3?

Ans- Ethoxy methane.

Short answers questions (2marks)

Q.1 Phenols are as a smaller dipole moment than methanol.

Ans:- Due to electron with drowning nature of ph-group-O bond is less polar.in case of methanol methyl group is electron releasing group So C-O bond is more polar.

Q.2 Explain why Phenol do not undergo substitution of OH group like alcohol.

Ans-C-O bond in phenol has some double bond characters due to resonance an hence cannot be easily replaced by Nu. In contrast the C-O bond in alcohol is pure single bond an hence can be easily released by Nu.

Q.3 Give a test to distinguish between phenol and Benzyl alcohol.

Ans- Phenols give violet colour with ferric chloride while benzyl alcohol does not give this coloure.

Q.4 Give a test to distinguish ethanol and phenol.

Ans- phenol turns blue litmus red,but Ethanol donot have effect on litmus paper.

Q.5Write theWilliamson synthesis reaction

Ans:- R-X +R-ONa----------→R-O-R +NaX

3marks questions

Q1. Write the reaction of phenol with Zn.

Ans: ph-OH +Zn----------→C_6H_6 +ZnO

Q2.Write the kolbes reaction?

Ans:Ph-oh +NaOH ------→ph-oNa +H_2O ---- (CO_2) -→ O- Hydroxy benzoic acid

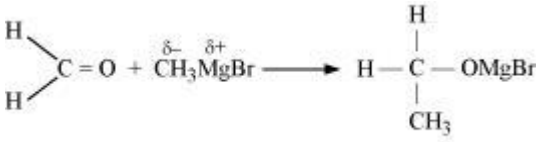
Q3.**(i) Explain the mechanism of Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.**

(ii) Explain the mechanism of Acid catalysed dehydration of an alcohol forming an alkene.

(iii)Explain the mechanism of Acid catalysed hydration of an alkene forming an alcohol.

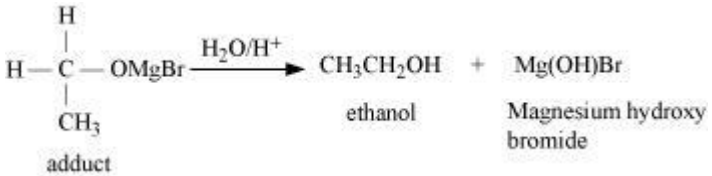
Ans:

(i) Grignard's reagent is an alkyl magnesium halide. The alkyl group has a partial negative charge, whereas the magnesium group has a partial positive charge. The alkyl group attacks the carbon of the carbonyl group to form an addition compound.



Methanal

Grignard's reagent acts as a nucleophilic agent & attacks electrophilic carbon atoms to yield a carbon – carbon bond. The addition to the nucleophile is an irreversible process due to the high pk_a value of the alkyl group.



adduct ethanol Magnesium hydroxy bromide

(ii) When heated with concentrated sulphuric acid, phosphoric acid or boric acid, alcohols undergo dehydration to form alkenes. The mechanism of this reaction involves the protonation of alcohol, followed by loss of a water molecule & a proton.

(a)

$$CH_3-CH_2-OH+H^+ \xleftrightarrow{\text{protonation}} CH_3-CH_2-\overset{+}{O}H_2$$

Oxonium ion

(b)

$$CH_3-CH_2-\overset{+}{O}H_2 \xleftrightarrow{-H_2O} CH_2-\overset{+}{C}H_2$$

Carbo cation

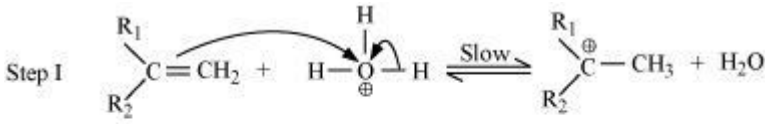
(c)

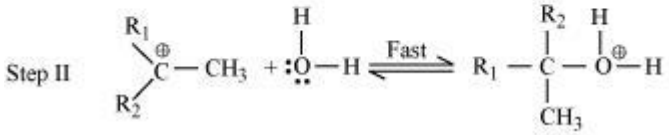
$$CH_3-\overset{+}{C}H_2 \xleftrightarrow{-H^+} H_2C=CH_2$$

Alkene

During the dehydration of alcohol, the intermediate carbocation may undergo re-arrangement, resulting in the formation of a stable carbocation.

(iii) Some reactive alkenes like 2 – methyl propene undergo direct hydration in the presence of mineral acids which act as catalysts. The addition of water to the double bond takes place in accordance with Markonikoff's rule.





Q.4(i) The bp. of ethanol is higher than that of methoxy methane.

(ii) Phenol is more acidic than ethanol.

(iii) O & p nitrophenol are more acidic than phenol.

Ans:-(i) Due to presence of a hydrogen attached to oxygen atom. As a result ethanol exists as associated molecules & hence it has higher bp. than methoxy methane which does not form hydrogen bond.

(ii) Because the phenoxide ion left after the release proton is stabilized by resonance but ethoxide. Moreover ethoxide ion is destabilized by +1 effect of ethyl group.

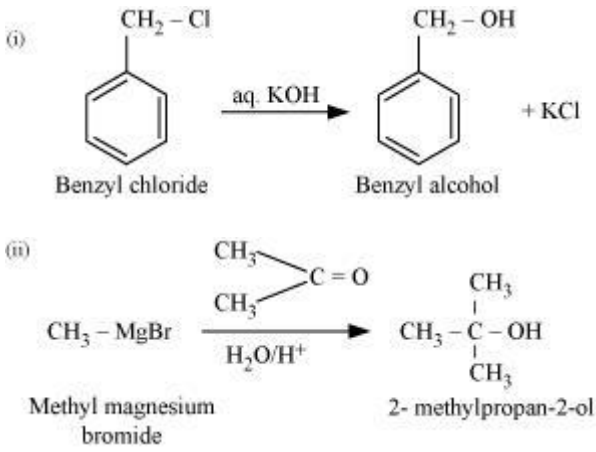
(iii) Due to I-effect or R-effect of NO_2 gp. The resulting phenolate ion is more destabilized by +1 effect of ethyl gp.

Q.5How are the following conversions carried out?

(i) Benzyl chloride to benzyl alcohol,

(ii) Methyl magnesium bromide to 2-methylpropan-2-ol

Ans:



5marks questions

Q.1 (a) An Organic compound ‘ A’ with molecular formula C_8H_8O gives positive DNP and iodoform test. It does not reduces Tollens or Fehling reagent and doesnotdecolourisesBr_2/H_2O also.On oxidation with chromic acid gives a carboxylic acid (B) with molecular formula $_{C7H6O2.}$Determine the structure of ‘A’ and ‘B’.

Ans-

A = Acetophenone B = Benzoic acid

(b) Complete the following reactions by identifying A ,B and C:

(I) A $+H_2(g)$------ $Pd/BaSO_4$----------→ (CH3)2 CHCHO

(II) $(CH_3)_3C\text{-}CO\text{-}CH_3$ + NaOI ----------→ B + C

Ans- (i) A= (CH3)2 CHCOCl

B= (CH3)3C-CO-Na + C = CHI3 Iodoform

Q.2 An Organic compound ‘ A’ with molecular formula C3H6 on treatment with aq.H2SO4 gives ‘B’ which on treatment with HCl/Zncl2 gives ‘C’. Thecompound ‘ C’ on treatment with ethanolic KOH gives back the compound ’A’ .Identify the compound A, B and C .

Ans: A=Propene, B=Propan-2-ol ,C=2-Chloropropane.

Aq.H2SO4 HCl/Zncl2 ethanolickoH

$CH_3\text{-}CH{=}CH_2$---------→$CH_3\text{-}CH(OH)\text{-}CH_3$----------→$CH_3\text{-}CH(Cl)\text{-}CH_2$----------→ $CH_3\text{-}CH{=}CH_2$

Hydration propan-2-ol Hydration propene

ALDEHYDES,KETONES AND CARBOXYLIC ACIDS

SECTION-A (Onemark Questions)

1. **Name one distinguishing test between aldehydes and ketones?**

Ans. Aldehydes and ketones can be distinguished by Tollen's test. Aldehydes give a silver mirror on reacting with Tollen's reagent whereas ketones will not react.

2. **Give reason why Formaldehyde does not undergo aldol condensation?**

Ans. Formaldehyde does not have any α -hydrogen and therefore it cannot show aldol condensation.

3. **Carboxylic acids have higher boiling points than alcohols of same no. of carbon atoms?**

Ans. Carboxylic acids have more extensive association of molecules through intermolecular hydrogen bonding than alcohols.

4. **Write IUPAC name .of $CH_3COCH_2COCH_3$.**

Ans.Pentane-2,4-dione.

5.What product is obtained when Ethylbenzene is oxidized with alkaline $KMnO_4$?

Ans. Benzoic acid is formed.

6Give chemical test to distinguish between acetaldehyde and benzaldehyde.

Ans.Acetaldehyde will respond to Iodoform test where asbenzaldehyde does not.

7.Write one chemical to distinguish between Formic acid and Acetic acid .

Ans.Formic acid gives silver mirror when treated with Tollen,'s reagent where as acetic acid does not.

8.Give two important uses of formalin.

Ans.Used as a preservative.

Used for the preparation of Bakelite.

9.How is formalin and trioxane related to methanal?

Ans.Formalin is 40%aqeous solution of methanalwhere astrioxane is trimer of methanal.

10.Complete the following reactionand give the name of the major product.

$HCHO + CH_3MgX$ ----------→ ?

Ans. $HCHO + CH_3MgX$ --------→$-CH_3CH_2OH + Mg(OH)X$

CH_3CH_2OH- Ethanol

11. Draw the structural formula of Hex-2-en4-yn-oic acid.

Ans. $CH_3-C\equiv C-CH=CHCOOH$

12. Arrange the following in the increasing order of acidic character.

$HCOOH$, $ClCH_2COOH$,CF_3COOH,Cl_3CCOOH

Ans. $CF_3COOH > CCl_3COOH > ClCH_2COOH > HCOOH$

13. Complete the reaction:-

$RCONH_2+4NaOH+Br_2$ --------→

Ans.$RCONH_2+4NaOH+Br_2$-------→ $RNH_2+ 2NaBr+ Na_2CO_3+2H_2O$.

14. Give one chemical test to distinguish between Phenol and benzoic acid.

Ans. On treatment with neutral $FeCl_3$ solution Phenol gives a violet color whereas Benzoic acid does not.

15. Most of the aromatic acids are solids while acetic acids and others of this series are liquids. Why?

Ans. Aromatic acids have higher molecular weights. Therefore more Vanderwaal's force of attraction as compared to aliphatic acids and hence they are solids .

SECTION –B (2 Mark Questions.)

1. Would you expect benzaldehyde to be more or less reactive in nucleophilic addition reaction 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 and hence is less reactive.

2. Describe the Transesterification reaction giving an example.

Ans. When an ester reacts with alcohol to form another ester and another alcohol, the process is called trans-esterification.

$CH_3COOC_2H_5 + CH_3OH$ ----------→ $CH_3COOC_2H_5 + C_2H_5OH$

3.Explain Hell- Volhard –Zelinsky reaction with an example.

Ans. Carboxylic acids having an a α hydrogen atom are halogenated at the α position on treatment with chlorine or bromine in the presence of small amount of red phosphorous to give α- halocarboxylic acids

$$RCH_2COOH \xrightarrow[(ii)\ H_2O/H^+]{(i)X_2/P(Red)} RCH(X)COOH.$$

4.Give simple chemical tests to distinguish between :-

(i) Pentan-2-one and Pentane-3-one
(ii) Ethanal and propanal

Ans. (i) Pentan-2-one gives Iodoform test on treatment with I_2/NaOHwhere as Pentane -3-one does not.

(ii)Ethanal gives Iodoform test whereas Propanal does not.

5.AlthoughPhenoxide ion has more number of resonating structures than Carboxylate ion, Carboxylic acids are more acidic than Phenol .Why?

Ans. In carboxylate ion (-)ve charge is delocalised over two oxygen atoms whereas in phenoxide ion (-)ve charge is delocalised over one oxygen atom .Therefore carboxylate ion is more stable than phenoxide ion .That is why Carboxylic acics are more acidic than Phenol.

6. Why is there a large difference in the boiling points of butanal and butan-1-ol?
Ans:-Butan-1-ol has higher boiling point due to intermolecular hydrogen bonding

7.Name the electrophile produced in the reaction of benzene with benzoyl chloridein the presence of anhydrous $AlCl_3$. Name the reaction also.

Ans: $C_6H_5\overset{\oplus}{C}O$ benzoyliumcation or $C_6H_5—\overset{\delta+}{\underset{\|}{C}}(=O)\cdots\cdots Cl\cdots\cdots \overset{\delta-}{AlCl_3}$. Friedel Craft's acylation reaction.

8. Arrange the following in decreasing order of their acidic strength and give reason for your answer.
CH_3CH_2OH, CH_3COOH, $ClCH_2COOH$, FCH_2COOH, $C_6H_5CH_2COOH$
Ans: $FCH_2COOH > ClCH_2COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2OH$
Due to +ve and –Ve inductive effects
9. Write the names associated with the following reactions:-
(i)

$$CH_3—\overset{\|}{\underset{O}{C}}—Cl + H_2 \xrightarrow{Pd\text{-}C/BaSO_4} CH_3—\overset{\|}{\underset{O}{C}}—H$$

(ii)

$$CH_3—CN \xrightarrow[(ii)\ H_2O/H^+]{(i)\ SnCl_2/HCl} CH_3CHO$$

Ans:- (i) Rosenmund Reduction
(ii)Stephens Reaction

10.

Complete the following reaction sequence.

$$CH_3—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} (A) \xrightarrow[Ether]{Na\ metal} (B) \xrightarrow{CH_3—Br} (C)$$

Ans:

$$A = CH_3—\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_3 \qquad B = CH_3—\overset{\overset{O^-Na^+}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_3 \qquad C = CH_3—\overset{\overset{O—CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_3$$

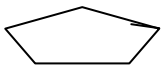
SECTION- C (THREE MARKS QUESTIONS)

1. What happens when :- (i) an aqueous solution of Sodium acetate is electrolysed
(ii) Calcium acetate is dry distilled
(iii) Sodium benzoate is heated with Sodalime

Ans. (i) $2CH_3COONa + 2H_2O \dashrightarrow C_2H_6 + 2CO_2 + 2NaOH + H_2$.

(ii)$CH_3COO)_2Ca \dashrightarrow CH_3COCH_3 + CaCO_3$

(iii)$C_6H_5COONa + NaOH(CaO) \dashrightarrow C_6H_6 + Na_2CO_3$

2. Write IUPAC names of the following Compounds:-
(i)$CH_3CO(CH_2)_4CH_3$ (ii) Ph-CH=CH-CHO (iii)OHC 

Ans. (i) Heptane -2-one (ii) 3-Phenylprop-2-en-1-al.(iii) Cyclopentanecarbaldehyde.

3.Complete the following equations:-

(i) $CH_3CONH_2 \xrightarrow{P2O5\text{-}/heat} ?$

(ii) $2CH_3CHO \xrightarrow{dil.\ NaOH} ?$

(iii)$C_6H_5COOH \xrightarrow{HNO3/H2SO4} ?$

Ans. (i)$CH_3CONH_2 \xrightarrow{P2O5\text{-}/heat} CH_3CN + H_2O$

(ii) $2CH_3CHO \xrightarrow{dil.\ NaOH} CH_3CH(OH)CH_2CHO$

(iii)$C_6H_5COOH \xrightarrow{HNO3/H2SO4} m\text{-}O_2N\text{-}C_6H_4\text{-}COOH$

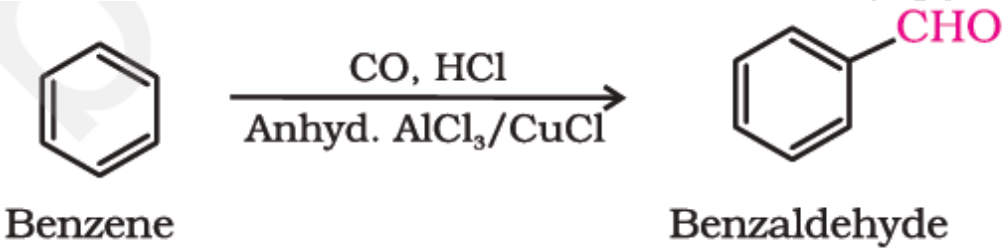
4.Explain the following:-

(i)Gatterman-Koch reaction

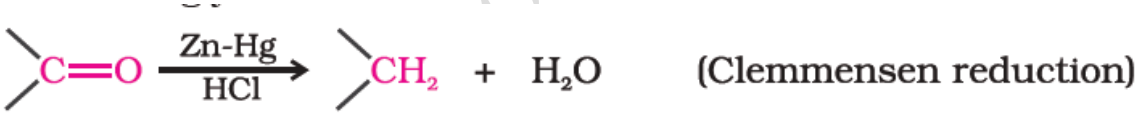
(ii) Clemensen reduction

(iii)Wolf-Kishner Reduction

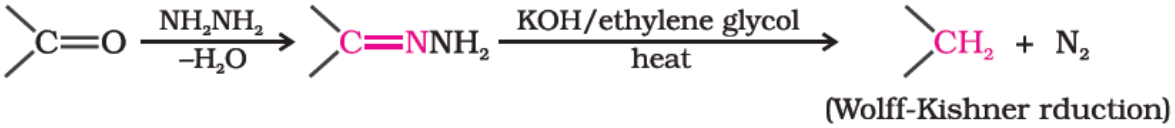
Ans(i) When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminiumchloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.This reaction is known as Gatterman-Kochreaction.



(ii)The carbonyl group of aldehydes and ketones is reduced to CH2 group on treatment with zincamalgam and concentrated hydrochloric acid called Clemensen Reduction.

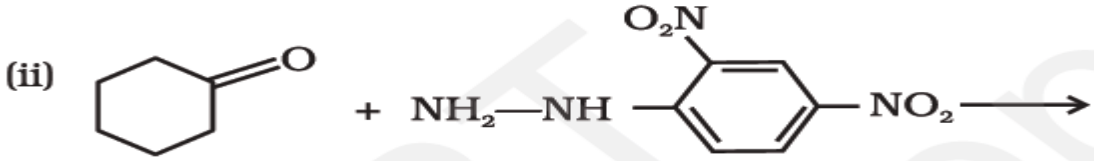


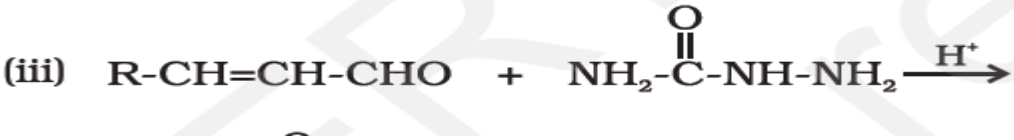
(ii)The carbonyl group of aldehydes and ketones is reduced to CH2 group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethyleneglycolcalled Wolff-Kishner reduction



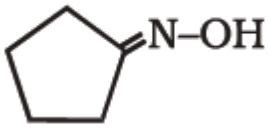
5. Predict the products of the following reactions

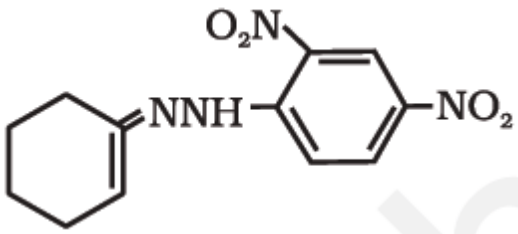
(i) 

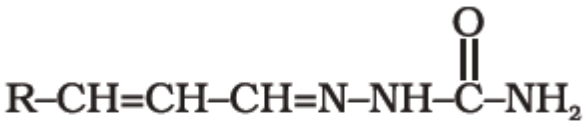
(ii) 

(iii) 

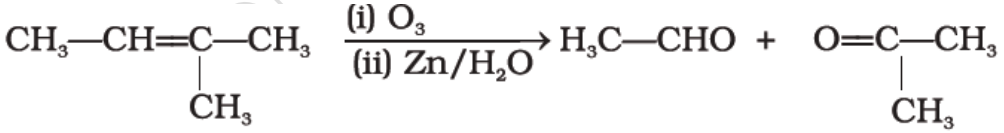
Ans:

(i) 

(ii) 

(iii) 

(6).An alkene 'A' (Mol. formula C5H10) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also forms iodoform on treatment with I2 and NaOH. Compound 'C' does not give Fehling's test but forms iodoform. Identify the compounds A, B and C. Write the reaction for ozonolysis and formation of iodoform from B and C



2-Methylbut-2-ene

(A) (B) (C)

Other isomers of 'A' will not give products corresponding to the given test.

Ans:

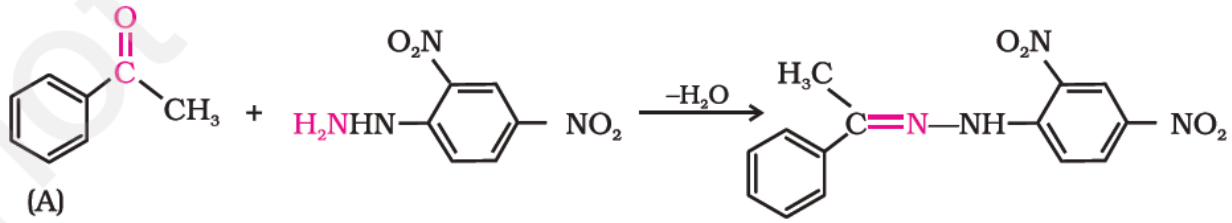
SECTION- D (FIVE MARKS QUESTIONS)

1.An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved.

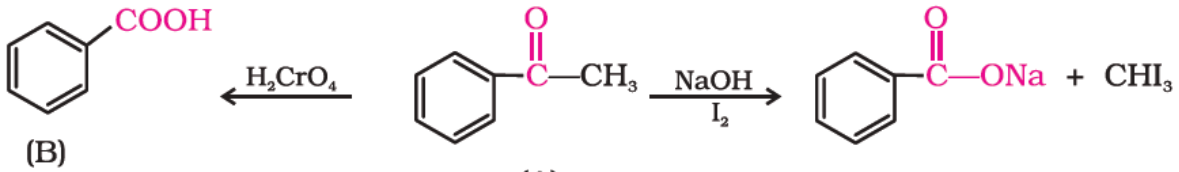
Ans:-(A) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Baeyer's reagent. This indicates

the presence of unsaturation due to an aromatic ring. Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a monosubstituted aromatic methyl ketone. The molecular formula of (A) indicates that it should be phenyl methyl ketone (acetophenone).

Reactions are as follows:



(A) C_8H_8O — 2, 4-Dinitrophenylhydrazine — 2, 4-DNP derivative



(B) $C_7H_6O_2$ — (A)

2 Write chemical reactions to affect the following transformations:

(i) Butan-1-ol to butanoic acid

(ii) Benzyl alcohol to phenylethanoic acid

(iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid

(iv) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid

(v) Cyclohexene to hexane-1,6-dioic acid

Ans:-

(i) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Jones reagent}]{CrO_3\text{-}H_2SO_4} CH_3CH_2CH_2COOH$

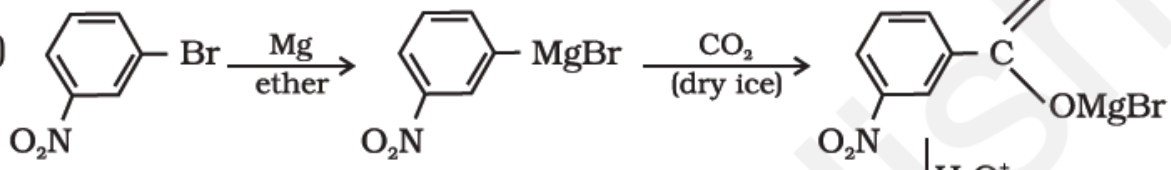
Butan-1-ol — Butanoic acid

(ii) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{KCN} C_6H_5CH_2CN$

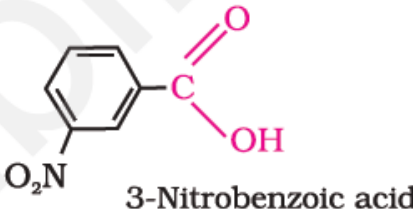
Benzyl alcohol — Benzyl bromide — Benzyl cyanide

$C_6H_5CH_2CN \xrightarrow[\Delta]{H_3O^+} C_6H_5CH_2COOH$

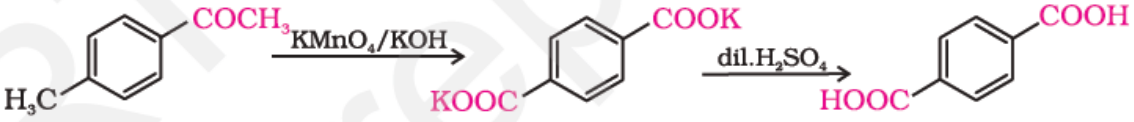
Phenylethanoic acid

(iii) 

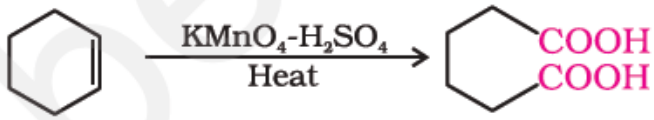
3-Nitrobromobenzene



3-Nitrobenzoic acid

(iv) 

4-Methylacetophenone — Dipotassium benzene-1, 4-dicarboxylate — Benzene-1, 4-dicarboxylic acid (Terephthalic acid)

(v) 

Cyclohexene — Hexane-1, 6-dioic acid (Adipic acid)

3. 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.

Element	%	At. Wt.	Relative no. of atoms	Divide by least
C	69.77	12	5.81	5.81/1.16=5
H	11.63	1	11.63	11.63/1.16=10
O	18.60	16	1.16	1.16/1.16=1

Empirical formula is $C_5H_{10}O$

Empirical formula mass = 86

N=86/86=1

Molecular formula is $C_5H_{10}O$

Since hydrogen atoms are double than carbon atoms, therefore, it is likely to be aldehyde or ketone. It does not reduce Tollen's reagent so it is a ketone.It reacts with $NaHSO_3$ and gives Iodoform test .Therefore it is Methylketone.On vigorous oxidation it gives ethanoic acid and propanoicacid .

The compound is Pentane-2-one.$CH_3COCH_2CH_2CH_3$

4.An organic compound (A) molecular formula $C_8H_{16}O_2$ was hydrolysed with dil. H_2SO_4 to give a carboxylic acid (B) and alcohol (C) . Oxidation of (C) with chromic acid produced (B).(C) on dehydration gives but-1-ene. Write equations for the reactions involved.

Ans. $CH_3CH_2CH_2COOCH_2CH_2CH2CH_3 + H_2O \xrightarrow{Dil\ H2SO4} CH_3CH_2CH_2COOH + CH_3CH_2CH_2CH_2OH$

(A) (B) (C)

$CH_3CH_2CH_2CH_2OH \xrightarrow{CrO3} CH_3CH_2CH_2COOH$

(C)

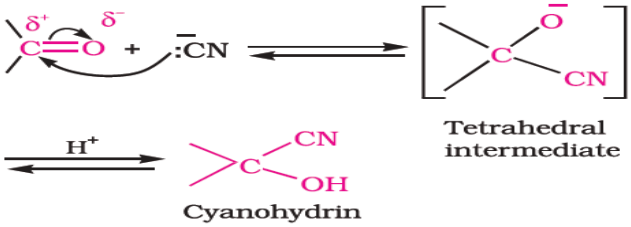
$CH_3CH_2CH_2CH_2OH \xrightarrow{Conc\ H2SO4} CH_3CH_2CH=CH_2$

(C)

5.What is meant by the following terms:-

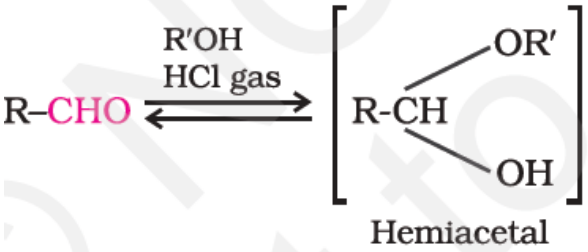
(a) Cyanohydrin (b) Semicarbazone (c)Hemiacetal (d)Ketal (d)2,4 –DNP derivative

Ans: (a).(a) When –CN and –OH groups are attached to the same carbon atom it is called cyanohydrin.e.g. $CH_3CH(OH)(CN)$.

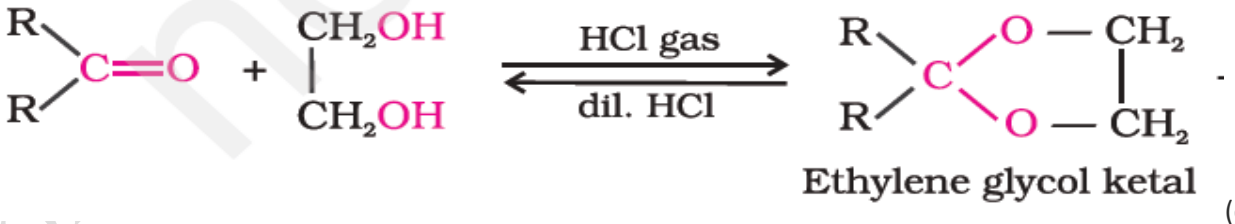


(b) When aldehyde or ketone react with semicarbazide the product formed is semicarbazone. E.g. H_3C-CH=N-$NHCONH_2$

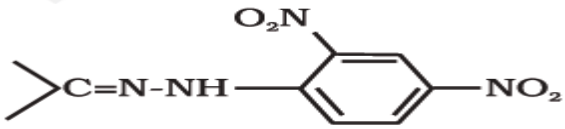
(c) When aldehyde reacts with one mole of alcohol in presence HCl gas Hemiacetal is formed. E.g. H_3C-CH(OH)-OCH_3



(d) When ketones react with two moles of alcohol /; Ethylene glycol in presence of HCl gas Ketal is formed.e.g.



(e)When aldehyde or ketone reacts with 2,4-DNP orange precipitate is formed.e.g.



: Kolkatta Region

AMINES

Q.1Give the IUPAC name of $H_2N - CH_2 - CH_2 - CH = CH_2$.

Soln: 4-amino-but-1-ene

Q.2 Write structure of methyl amine?

Ans- CH_3-NH_2

Q.3 Write the structure of methyl isocyanides?

Ans-CH_3NC

Q.4 Name the tests for Primary amine.

Ans- Carbylamines test

Q.5 Primary amines have higher b.p than tertiary amines.

Ans- Due to inter molecular hydrogen bonding.

Q.6 Why is alkyl amine more basic than ammonia?

Ans Due to +I effect of alkyl group.

Q.7 why do amine react as nucleophile.

Ans-due to lone pair of electron on nitrogen.

Q.8 Why are aqueous solution of amine basic in nature?

Ans- Because of high electron density on nitrogen it gains H+ from water.

Q.9 Name one test to distinguish between ethyl cynide and ethyl isocynide.

Ans- ethyl cynide on hydrolysis with acids form propionic acid, whereas ethyl isocynide with dilute HCl forms ethylamine and formic acid.

Q10.Identify A and B

$$C_6H_5NH_2 \xrightarrow{NaNO_2/HCL} A \xrightarrow{CuBr} B$$

Q11.Name the reaction in which amide directly converted into amines.

Ans:Hofmann'sbromamide reaction.

Q12.Complete the following:

$RNH_2 + CHCl_3 + 3KOH$----------→ ?

Q13. .Complete the following:

$RCONH_2 + Br_2 + 4\ NaOH$----------→ ?

Q14.Write the formula of hinsberg's reagent.

Ans:Benzoyl chloride.

Q15.What is meant by diazotization?

Ans:Conversion of primary aromatic amines into diazonium salts.

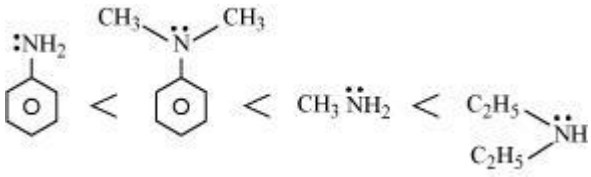
2marks questions

Q.1 In an increasing order of basic strength:

$C_6H_5NH_2$,$C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ & CH_3NH_2

Ans:

Basic strength:

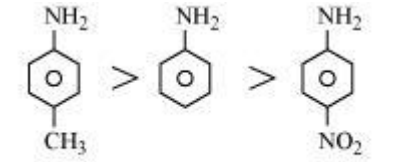


Aliphatic amines are stronger bases than aromatic amines due to the presence of lone pair of e- on nitrogen atom. In case of aromatic amines the lone pair gets delocalised by resonance. Diethyl amine has greater + I effect. Hence, e-density over the nitrogen atom is more in this case. Similarly N, N – dimethyl aniline has greater + I effect than aniline.

Q.2 In a decreasing order of basic strength:

Aniline, p-nitroaniline& p-toluidine

Ans-



p-toluidine aniline *p*-nitro aniline

Methyl ($-CH_3$) is an e- donating group. It increases the e- density on the ring. Therefore, the lone pair of nitrogen is available for donation. Hence, it is most basic. On the other h& nitro ($-NO_2$) is an e- withdrawing group. It decreases the e- density of the ring. Therefore, the lone pair is more delocalized in this case & is less available for donation. Thus, it will be least basic among the three.

Q.3 In an increasing order of pK_b values:

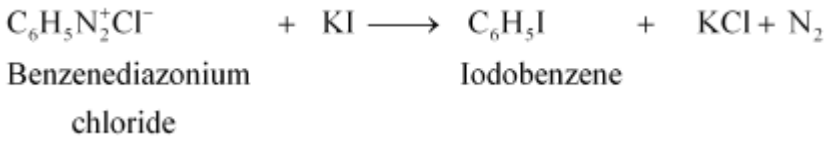
$C_2H_5NH_2$, C_6H_5 $NHCH_3$, $(C_2H_5)_2$ NH & $C_6H_5NH_2$

Ans-

Stronger the base is lesser is the pK_b value. $(C_2H_5)_2NH$ is the strongest base due to two e- releasing group followed by $C_2H_5NH_2$ which has only one e- releasing group. $C_6H_5NHCH_3$ is the next stronger base because of the presence of one e- releasing alkyl group & e- delocalising phenyl group. $C_6H_5NH_2$ is the least basic wherein the e- get delocalised by resonance.

Q.4.Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

Ans-:



Q.5Why is an alkylamine more basic than ammonia?

Ans:
An alkylamine is more basic than ammonia because of inductive effect (+I effect). Alkyl group or 'R' has an e-- releasing effect, which increases e- density over nitrogen atom. This increases its basicity.

3marks questions

Q.1Describe the Hofmann's bromamidereaction

Ans:

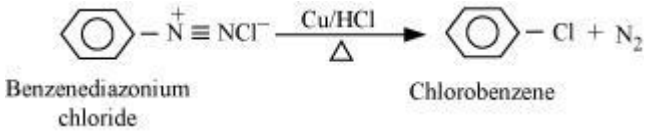
Hofmann's bromamidereaction: It involves the reaction of bromine with an acid amide in the presence of an alkali. It results in the formation of a primary amine with one carbon less than the parent compound. Here, the alkyl group migrates from carbonyl, with the elimination of CO_2. For example:

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + H_2O$$

Q.2Describe the Gattermanreaction

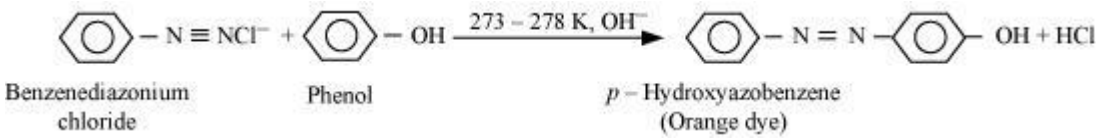
Ans- *Gattermanreaction*: This is a modification of *S&meyer* reaction in which benzenediazonium chloride is treated with copper powder & halogen acid to form aryl halides.



Q.3Describe the couplingreaction

Ans

Coupling reaction: It is the reaction of diazonium salts with phenols & aromatic amines to form *azo* compounds of the general formula Ar − N = N − Ar. The coupling of phenol takes place in a mildly alkaline medium.



Q.4pK_b for aniline is more than that for methylamine.

Ans:
In aniline, the lone pair of e- on the N atom is delocalised over the benzene ring. As a result, the e- density on the nitrogen atom decreases. In contrast, in CH_3NH_2, the +I effect of CH_3increases the e- density on the N atom. Therefore, aniline is a weaker base than methylamine. Hence, its pK_b value is higher than that of methylamine.

Q.5 Methylamine Soln in water reacts with ferric chloride Soln to give a precipitate of ferric hydroxide.

Ans- Being more basic than water, methylamine accepts a proton from water-liberating OH^- ions.

$$CH_3NH_2 + H_2O \longrightarrow CH_3NH_3OH^- \longrightarrow CH_3NH^+ + OH^-$$

These OH^- ions combine with Fe^{3+} ions present in H_2O to form a brown precipitate of hydrated ferric oxide.

$$FeCl_3 \rightarrow Fe^{3+} + 3\,Cl^-$$

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{\text{Hydrated ferric oxide (Brown ppt.)}}{2Fe(OH)_3}$$

5marks questions

Q1.An aromatic compound ' A' on treatment with aqueous ammonia and heating forms compound 'B ' which on heatiog with Br_2 and KOH forms a compound ' C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B andC.

Ans:-((A) Benzoic acid (B) Benzamide (c) Aniline

Q2.Complete the following reactions:

(i)$C_6H_5NH_2$ +$CHCl_3$ +alc.KOH---------→

(II)$C_6H_5N_2Cl$ +H_3PO_2 +H_2O----------→

(III)$C_6H_5NH_2$ +H_2SO_4(CONC)----------→

(IV)$C_6H_5N_2Cl$ +C_2H_5OH----------→

(V)$C_6H_5NO_2$ + Fe/HCl----------→

Ans:-

(i)$C_6H_5NH_2$ +$CHCl_3$ +alc.KOH----------→C_6H_5NC +3KCl +3H_2O

(II)$C_6H_5N_2Cl$ +H_3PO_2 +H_2O----------→C_6H_6 +H_3PO_3 +N_2 +HCl

(III)$C_6H_5NH_2$ +H_2SO_4(CONC)----------→NH_2-Ph-SO_3H +H_20

(IV)$C_6H_5N_2Cl$ +C_2H_5OH----------→C_6H_6 +N_2+CH_3CHO +HCl

(V)$C_6H_5NO_2$ + Fe/HCl----------→C_6H_5NH2

$$2Fe^{3+} + 6OH^- \longrightarrow \underset{\text{Hydrated ferric oxide}}{2Fe(OH)_3}$$
(Brown ppt.)

5marks questions

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(IV)$C_6H_5N_2Cl$ +C_2H_5OH----------→

(V)$C_6H_5NO_2$ + Fe/HCl----------→

Ans:-

(i)$C_6H_5NH_2$ +$CHCl_3$ +alc.KOH----------→C_6H_5NC +3KCl +$3H_2O$

(II)$C_6H_5N_2Cl$ +H_3PO_2 +H_2O----------→C_6H_6 +H_3PO_3 +N_2 +HCl

(III)$C_6H_5NH_2$ +H_2SO_4(CONC)----------→NH_2-Ph-SO_3H +H_20

(IV)$C_6H_5N_2Cl$ +C_2H_5OH----------→C_6H_6 +N_2+CH_3CHO +HCl

(V)$C_6H_5NO_2$ + Fe/HCl----------→C_6H_5NH2