UNIT 11

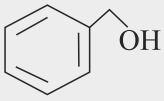
Alcohols, Phenols and Ethers

Points to Remember

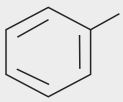
Classification of Alcohols:

(a) Containg sp^3 C-OH bond. (i)-CH_2-OH (1^0), (ii) > CH-OH(2^0), (iii)$-\overset{\backslash}{\underset{/}{C}}-$ OH (3^0)

Allylic: CH_2 =CH-CH_2-OH

(iv)Benzylic:  OH

(b) Containg sp^2 C-OH bond - Vinylic (i) CH_2=CH-OH

(ii)Phenols:  OH

Classification of ethers:

Simple/Symmetric: Alkyl/aryl groups attached to oxygen are same e.g. $CH_3CH_2OCH_2CH_3$

Mixed/Unsymmetric: Two different alkyl/aryl groups attached to oxygen e.g. $CH_3OCH_2CH_3$

Classification and Nomenclature of Alcohols and ethers

Nomenclature:

Alcohols: Common names (Alkyl group + alcohol)

IUPAC (Alkan+ol, substituting -e by - ol e.g. ethanol)

Phenols: Common names (as derivatives of phenol with position like ortho-, meta-,para-)

IUPAC (Derivatives of phenols with numbers like 1,2-, 1,3-e.g.

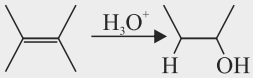
2-Nitrophenol or o-nitrophenol)

Ethers: Common names (alkyl/aryl groups in alphabetical order followed by ether e.g. ethyl methyl ether) IUPAC (In alkyl/aryl group - e is replaced by oxy followed by parent hydrocarbon e.g. methoxyethane)

Preparation of Alcohols

1. From alkenes:

a) By acid catalyzed hydration(Markonikov's addition)



b) By hydroboration-Oxidation(Anti-Markonikov)

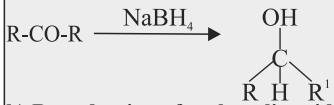
$3CH_3\text{-}CH{=}CH_2 + (H\text{-}BH_2)_2 \rightarrow (CH_3\text{-}CH_2\text{-}CH_2)_3B.$

$\xrightarrow[H_2O]{H_2O_2, OH^-} 3CH_3\text{-}CH_2\text{-}OH + B(OH)_3$

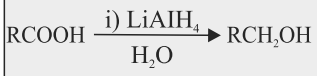
2. From carbonyl compounds

a) By reduction of aldehydes and ketones

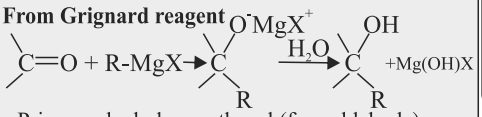
$R\text{-}CHO + H_2 \xrightarrow{Pd} RCH_2OH$



b) By reduction of carboxylic acids and esters



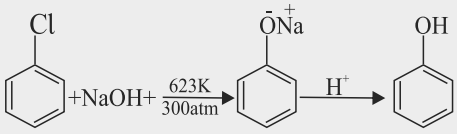
3. From Grignard reagent



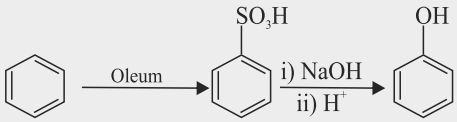
For Primary alcohol→ methanal (formaldehyde)
Secondary → aldehydes other than methanal
Tertiary → Ketones are used with appropriate Grignard reagent

Preparation of Phenol

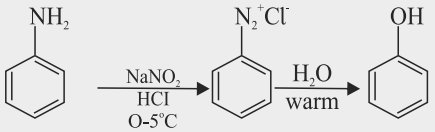
1. From Haloalkanes



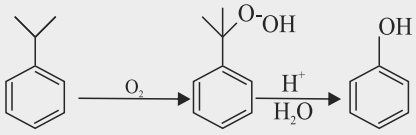
2. From Benzene sulphonic acid



3. From Diazonium salts



4. From Cumene



Preparation of Alcohols, Phenols and Ethers

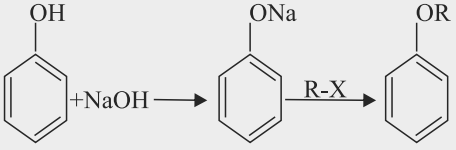
Preparation of Ethers

1. By dehydration of alcohols

$CH_3CH_2OH \xrightarrow[413K]{H_2SO_4} CH_3CH_2OCH_2CH_3$

2. Williamsons Synthesis

$RX + R'\text{-}ONa \longrightarrow R\text{-}O\text{-}R^1$



Physical Properties and Reactions of Alcohols and phenols

(a) Physical properties:

- Boiling point increases with increase of cabon chain
- Solubility decreases with increase in size of alkyl aryl group

(b) Chemical properties:

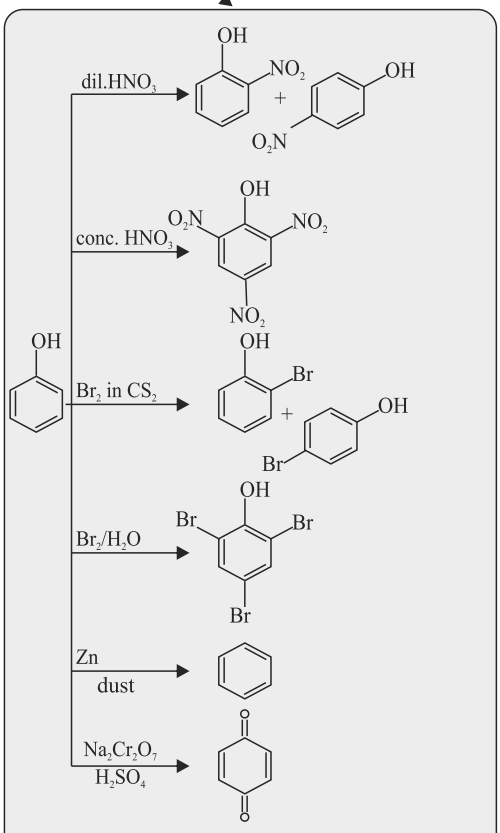
(i) $2R\text{-}O\text{-}H + 2Na \longrightarrow 2\ R\text{-}\overset{-}{O}\overset{+}{N}a + H_2$;
Acidity-primary>secondary>tertiary

(ii) $Ar/RO\text{-}H + R^1\text{-}COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR^1 + H_2O$ (Esterification)
$ROH + HX \longrightarrow R\text{-}X + H_2O$(withAnhydrous $ZnCl_2$+HCl, Lucas Test)
Order: Primary < Secondary < Tertiary

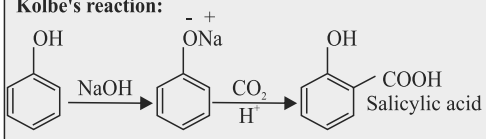
(iii) $C_2H_5OH \xrightarrow[443K]{H_2SO_4} CH_2{=}CH_2 + H_2O$:
Order: Primary<secondary<tertiary

(iv) $RCH_2OH \xrightarrow[\text{or PCC}]{CrO_3} RCHO \longrightarrow R\text{-}COOH$

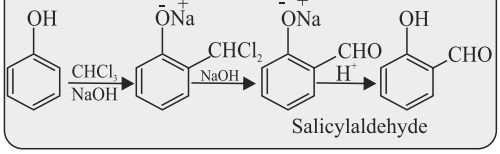
$KMnO_4$



Kolbe's reaction:

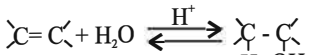


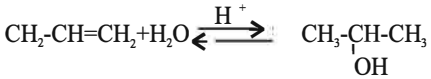
Reimer Tiemann reaction:



Mechanisms:

a) Hydration of Alkenes

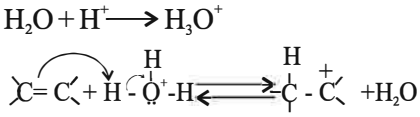




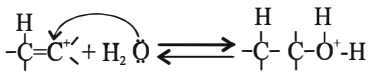
Mechanism of hydration of ethene

The mechanism of the reaction involves the following three steps:

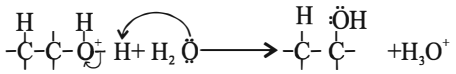
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.



Step 2: Nucleophilic attack of water on carbocation.

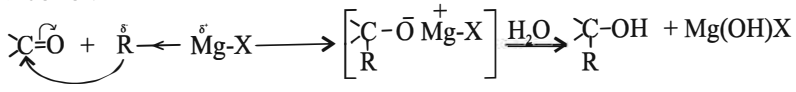


Step 3: Deprotonation to form an alcohol.



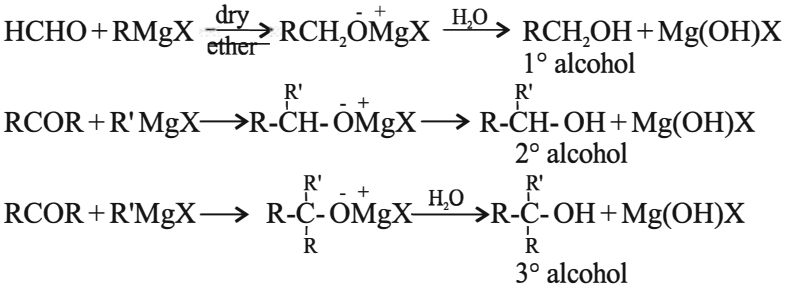
b) Reaction of Grignard reagent

The first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct. Hydrolysis of the adduct yields an alcohol.



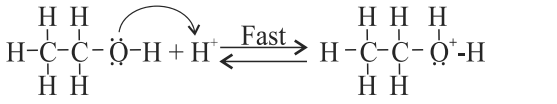
Adduct

The overall reactions using different aldehydes and ketones in dry ether medium are as follows:



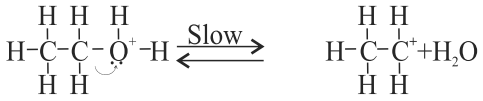
c) Dehydration of Alcohols (Mechanism)

Step 1: Formation of protonated alcohol.

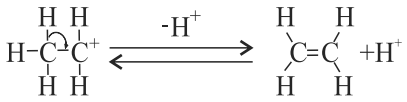


Ethanol — Protonated alcohol (Ethyl oxonium ion)

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



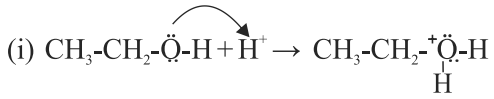
Step 3: Formation of ethene by elimination of a proton.



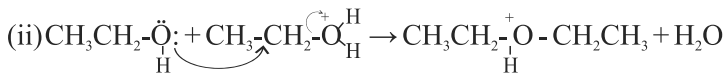
The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

d) Dehydration of alcohol at 413K to form Ether : Mechanism

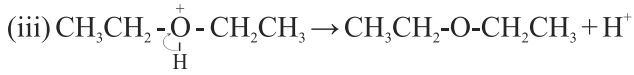
The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:



(i) $CH_3\text{-}CH_2\text{-}\ddot{O}\text{-}H + H^+ \rightarrow CH_3\text{-}CH_2\text{-}{}^{+}\ddot{O}\text{-}H$ (H)



(ii) $CH_3CH_2\text{-}\ddot{O}\text{:} + CH_3\text{-}CH_2\text{-}{}^{+}O(H)H \rightarrow CH_3CH_2\text{-}{}^{+}O(H)\text{-}CH_2CH_3 + H_2O$



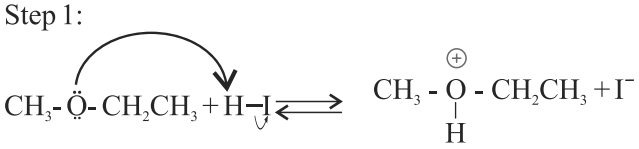
(iii) $CH_3CH_2\text{-}{}^{+}O(H)\text{-}CH_2CH_3 \rightarrow CH_3CH_2\text{-O-}CH_2CH_3 + H^+$

Acidic dehydration of alcohols at 443 K to give an alkene is also associated with substitution reaction to give an ether.

c) Reaction of ethers with HI: (Mechanism)

The reaction of an ether with concentrated HI starts with with protonation of ether molecule.

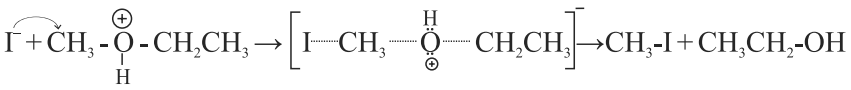
Step 1:



Step 2:

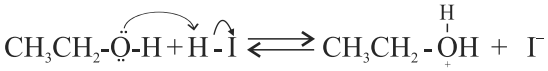
Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaccs an alcohol molecule by S_N2 mechanism.

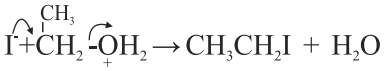
Thus, in the cleavage of mixed ethers with two different alkyl groups. The alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).



When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

Step 3:





OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. Arrange the following compound in decreasing order of boiling point?

   (i) Propan-1-ol

   (ii) Butan-2-ol

   (iii) Butan-1-ol

   (iv) Pentan-1-ol

   (a) i>iii>ii>iv (b) i>ii>iii>iv

   (c) iv>iii>ii>i (d) iv>ii>iii>i

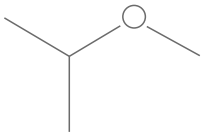
2. What is the correct order of reactivity of alcohols in the following reaction?

   $R-OH + HCl \xrightarrow{\text{Anhy. } ZnCl_2} R-Cl + H_2O$

   (a) 1°>2°>3° (b) 1°>3°>2°

   (c) $3° > 1^0 > 2°$ (d) 3° > 2° > 1°

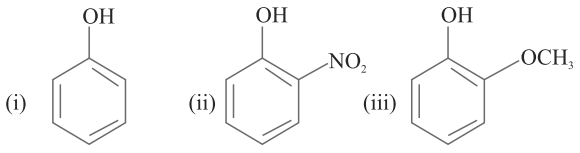
3. IUPAC name of the compound :



   (a) 1-Methoxy- 1 -methylethane (b) 2-Methoxy-2-methylethane

   (c) 2-Methoxypropane (d) Isopropylmethyl ether

4. The correct order of decreasing acid strength of the following compound is:



(a) i>ii>iii (b) iii>ii>i

(c) ii>i>iii (d) ii>iii>i

5. The major product obtained on reaction of phenol with NaOH followed by CO_2 and acidification is:

(a) Benzoic acid (b) Salicylaldehyde

(c) Salicylic acid (d) Phthalic acid

6. Which of the following alcohol on dehydration with conc. H_2SO_4 gives but-2-ene?

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

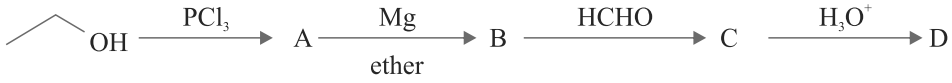
(c) 2-Methylpropan-l-ol (d) Both (a) and (b)

7. Which of the following alcohol give iodoform test?

(a) Butan-1-ol (b) Propan-1-ol

(c) Propan-2-ol (d) Pentan-3-one

8. In the following sequence of reaction. The product D is



(a) n-Butyl alcohol (b) n-Propyl alcohol

(c) Propanal (d) Butanal

9. Correct statement in case of n-butanol and t-Butanol is:

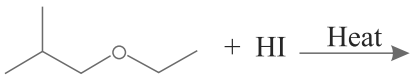
(a) both are having equal solubility in water

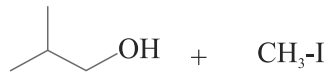
(b) 1-Butanol is more soluble in water

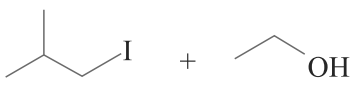
(c) boiling point of t-butanol is lower than n-butanol

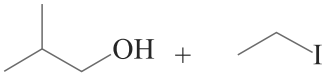
(d) boiling point of n-butanol is lower than t-butanol

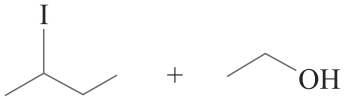
10. The major products of following reaction are:



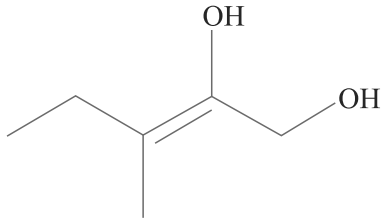
(a) 

(b) 

(c) 

(d) 

11. Write the IUPAC name of the compound given below.



(a) 3-Methylpent-2-ene-1,2-diol

(b) 2-Methylp ent-2-ene-1,2-diol

(c) 3-Methylpent-3-ene-2,3-diol

(d) 3-Methylpent-3-ene-4,5-diol

12. Which of the following are used to convert RCHO into RCH_2OH ?

(a) H_2/Pd (b) $LiAlH_4$

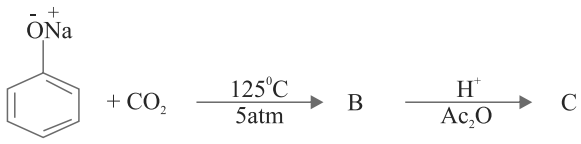
(c) $NaBH_4$ (d) All of the above

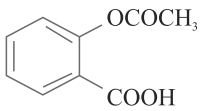
13. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields-

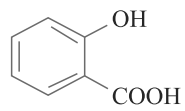
(a) *o*-cresol (b) *m*-cresol

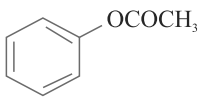
(c) 2,4-Dihydroxytoluene (d) Benzyl alcohol

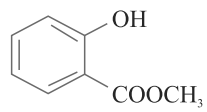
14. The product **C** in given reaction will be

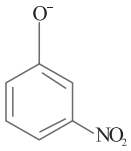


(a) 

(b) 

(c) 

(d) 

15. Which of the following species can act as the strongest base?
    (a) ^{-}OH
    (b) ^{-}OR
    (c) $^{-}OC\text{-}_6H_5$
    (d) 

16. CH_3CH_2OH can be converted into CH_3CHO by.....
    (a) catalytic hydrogenation
    (b) treatment with $LiAlH_4$
    (c) treatment with pyridinium chlorochromate (PCC)
    (d) treatment with $KMnO_4$
17. Which of the following reactions will yield phenol?
    (a) Fusion of chlorobenzene with NaOH at 300 atm.
    (b) Diazotization of aniline followed by heating with water.
    (c) Sulphonation of benzene followed by treatment with NaOH then acidification.
    (d) All of the above
18. Williamson's synthesis is used to prepare
    (a) alcohol (b) ethers (c) Aldehydes (d) Amines
19. Which of the following compound will be most readily attacked by electrophile?
    (a) Chlorobenzene (b) Benzene (c) Phenol (d) Toluene

II FILL IN THE BLANKS

1. Phenol on reaction with bromine water gives white precipitate of.....
2. Ethanoic acid on reaction with $LiAlH_4$ forms.....
3. Reaction of.....with Grignard reagent gives primary alcohols.
4. Phenols are commercially manufactured by oxidation followed by acidification of.....
5. Reaction of alcohols/phenols with carboxylic acids is termed as.....
6. .....test is used to distinguish primary, secondary and tertiary alcohols.
7. Dehydration of tertiary alcohols is .....than primary alcohols.
8. Dehydration of alcohols to form ether is ..... type reaction.
9. Benzyl alcohol on reaction with $KMnO_4$ followed by acidification forms.....
10. $SOCl_2$ converts Propan-1 -ol to .....

III ASSERTION REASON TYPE QUESTIONS

In the following questions a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

(A) Assertion and reason both are correct and reason is correct explation of assertion

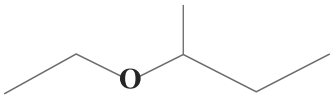
(B) Both assertion and reason are correct statement but reason is not correct explation of assertion.

(C) Assertion is correct statement but reason is wrong statement.

(D) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION :** *p*-Nitrophenol is more acidic than phenol.
   REASON : Nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance.

2. **ASSERTION :** IUPAC name of the compound is 2-Ethoxy-2-methylethane.



   REASON : In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by -OR or -OAr group [where, R= alkyl group and Ar = aryl group].

3. **ASSERTION :** Bond angle in ethers is slightly less than the tetrahedral angle.
   REASON : There is a repulsion between the two bulky (-R) groups.

4. **ASSERTION :** *o*-Nitrophenol is less soluble in water than the *m*– and *p*-isomers.
   REASON: *m*– and *p*-Nitrophenols exist as associated molecule.

5. **ASSERTION :** Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid .
   REASON: Lewis acid polarises the bromine molecule.

6. **ASSERTION :** Ethanol is a weaker acid than phenol.
   REASON : Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

7. **ASSERTION :** Phenols give *o*-and *p*-Nitrophcnol on nitration with dil. HNO_3.
   REASON : -OH group in phenol is *o*-,*p*- directing.

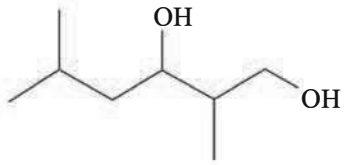
8. **ASSERTION :** $(CH_3)_3$ C- O-CH_3 gives $(CH_3)_3$ C-I and CH_3OH on treatment with HI.
   REASON : The reaction occur by S_N1 mechanism
9. **ASSERTION :** Protonation of phenol is difficult than ethanol.
   REASON : Ethyl group in ethanol is electron releasing.
10. **ASSERTION :** Tertiary alcohols gives turbidity almost immediately on treatment with $ZnCl_2$ /HCl.
    REASON : Tertiary carbocation formed is very stable and undergoes substitution easily.

IV **ONE WORD TYPE QUESTIONS**

1. Which reagent used to convert primary alcohol to carboxylic acid?
2. Out of *ortho* and *para*- Nitrophenol which is more steam volatile?
3. Write the major product of bromination of anisole?
4. Give name reaction used to convert phenol to salicylaldehyde?
5. Out of picric acid and phenol, which is more acidic?
6. Which reagent could be used to reduce aldehyde selectively in presence of ester group?
7. Name the reagent(s) used to convert propene to propan-l-ol?
8. Out of primary, secondary and tertiary alcohols which is most acidic?
9. Write IUPAC of the product formed, when phenol is treated with conc. HNO_3 .
10. Draw structure of hex-1-en-3-ol.
11. Give a name of chemical test to distinguish between pentan-3-one and pentan-2-one.
12. _____ bonding is responsible for solubility of ethanol in water.
13. Name the product fromed when phenol is treated with $Na_2Cr_2O_7/H_2SO_4$
14. Write IUPAC name of aspirin.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

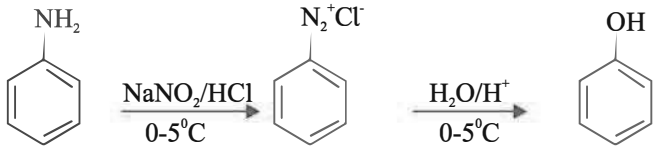
1. Write IUPAC name of the following compound:



Ans: 2,5-Dimethylhexane1,3-diol

2. How is phenol obtained from aniline ?

Ans:



3. Why phenol is acidic in nature ?

Ans: Due to stability of phenoxide ion by resonance

4. Among HI, HBr and HCI which is most reactive towards alcohols. Why?

Ans: Due to lowest bond dissociation enthalpy of HI, it is most reactive.

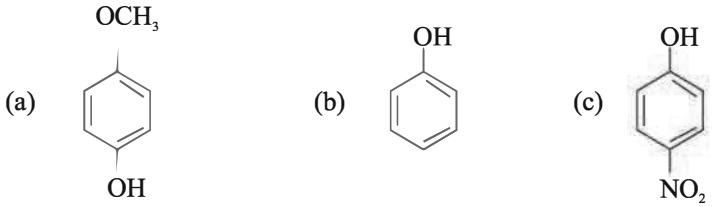
5. Name a compound which is used as antiseptic as well as disinfectant'.

Ans: Solution of phenol : 0.2% antiseptic, 2% disinfectant

6. What is nitrating mixture for monosubstitution of phenol?

Ans: Dilute HNO_3

7. Arrange the following in decreasing order of their acidic character:

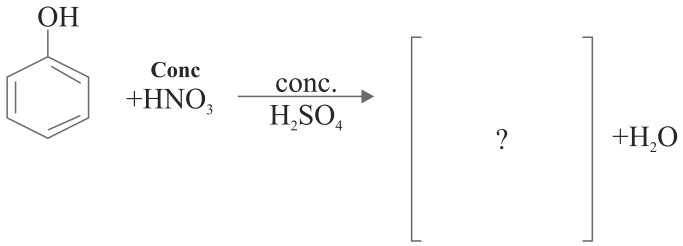


Ans: (c) > (b) > (a)

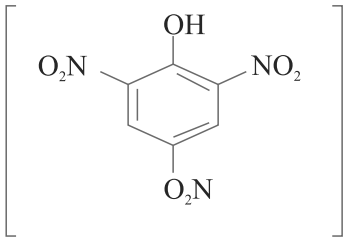
8. Why lower alcohols are soluble in water while higher alcohols are not?

Ans: Due to formation of hydrogen bonds, lower alcohols are soluble but increase in hydrophobic chain decreases solubility.

9. Complete the following reaction :



Ans:



10. What happens when CH_3CH_2OH heated with red P and HI ?

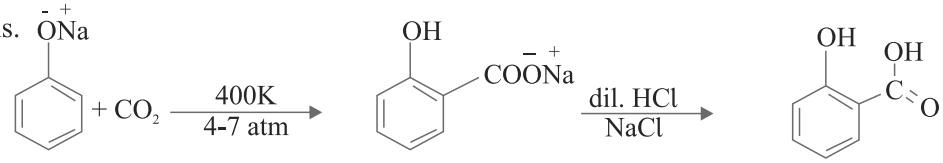
Ans:.

11. Ethanol has higher boiling point than Methoxymethane. Give reason.

Ans : Because of intermolecular H- bonding in ethanol.

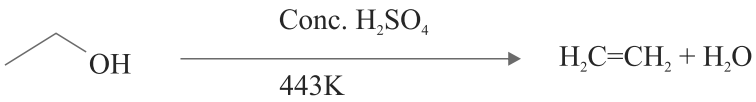
12. Explain Kolbe's reaction with example.

Ans.



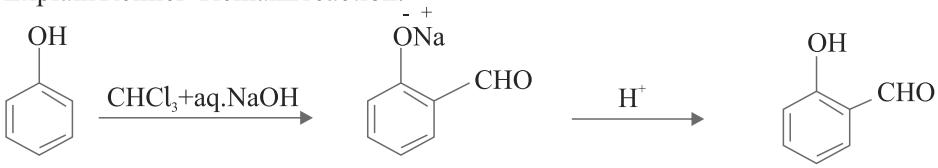
13. How could you convert ethanol to ethene ?

Ans .

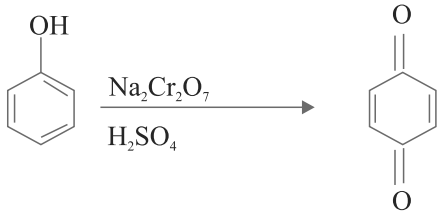


14. Explain Reimer-Tiemann reaction.

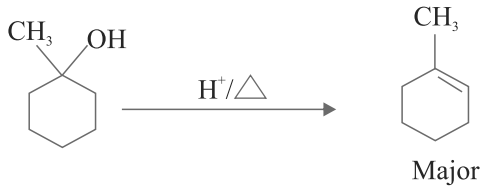
Ans.



15. How will you get benzoquinone from phenol?

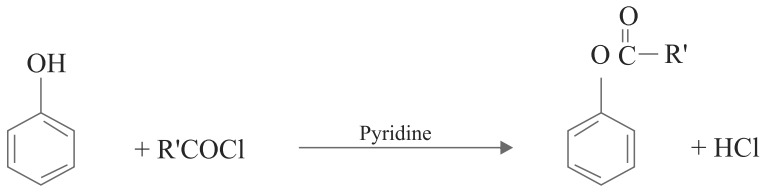
Ans. 

16. Predict the major product of acid catalysed dehydration of 1-Methylcyclohexanol

Ans. 

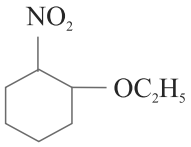
Major

17. What is the significance of pyridine in following reaction.



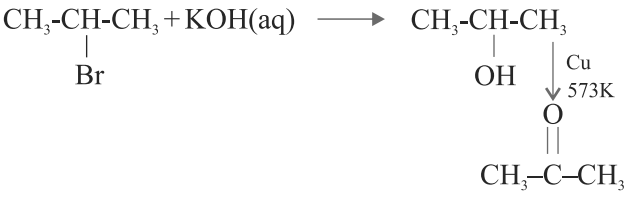
Major

Ans. To remove HCl from product side and shift the reaction in forward direction.

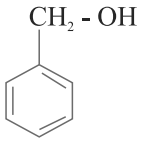
18. Write the IUPAC name of 

Ans: 1-Ethoxy-2-nitrocyclohexane.

19. How is acetone obtained from 2- bromopropane ?

Ans. 

20. Which alcohol contain the -OH group attach to a sp^3 hybridised carbon atom next to an aromatic ring.

Ans. Benzyl alcohol 

21. Which chemical is used as wood spirit ?

Ans. Methanol CH_3OH

22. Why boiling point of ethers are much lower than those of alcohols of comparable molecular masses.

Ans. There is no H-bonding in ethers which is present in alcohol.

23. Which test is used to distinguish between phenol and benzyl Alcohol.

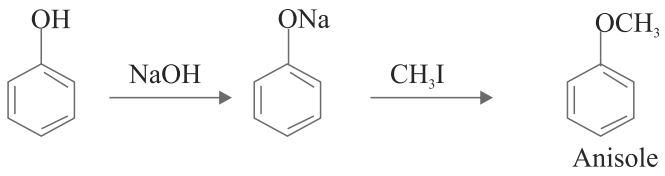
Ans. Neutral $FeCl_3$

Phenol gives violet colour with aq. $FeCl_3$ while benzyl alcohol does not.

24. Why does phenol not undergo protonation easily.

Ans. In phenol, there is positive charge, in its resonation structure, therefore does not undego protonation.

25. Write the steps involved in conversion of phenol to anisole.

Ans. 

Anisole

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. Out of t-Butyl alcohol and n-Butanol, which one will undergo acid catalysed dehydration faster and why?

Ans: t-Butyl alcohol will undergo dehydration faster due to formation of stable tertiary carbocation intermediate.

2. Carry out the following conversions:
   (a) Phenol to salicaldehyde
   (b) t-Butylchloride to t-butyl ethyl ether
   (c) Propene to propan-l-ol

3. Write the steps involved in the mechanism for the formation of ethanol from ethene.

Ans. Refer Points to remember

4. Predict the reagent for carrying out the following conversions:

   (a) Phenol to benzoquinone

   (b) Anisole to *p*-bromoanisole

   (c) Phenol to 2,4,6-tribromophenol

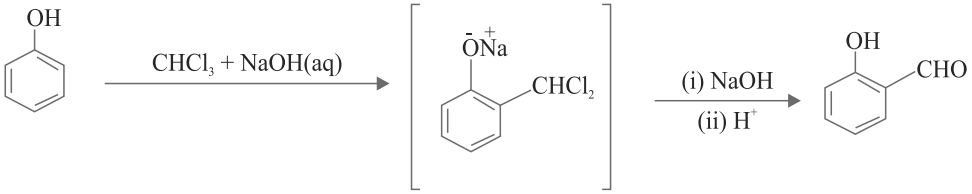
Ans. (a) $Na_2Cr_2O_7/H^+$ (b) Br_2/CH_3COOH (c) Br_2/H_2O

5. Write one chemical reaction to illustrate the following:

   (a) Reimer-Tiemann reaction

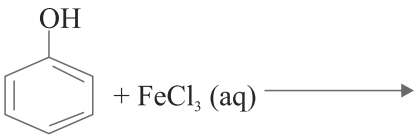
   (b) Williamson synthesis

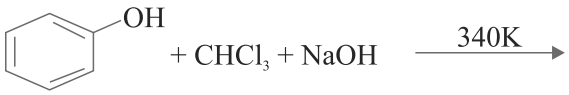
Ans:

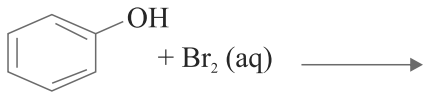
(a) 

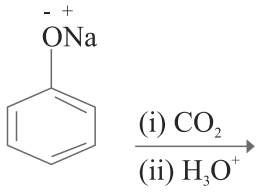
(b) 

6. Complete the following the equations and name the products:

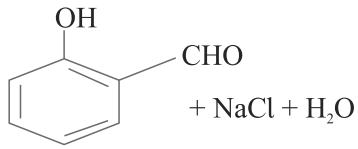
(i) 

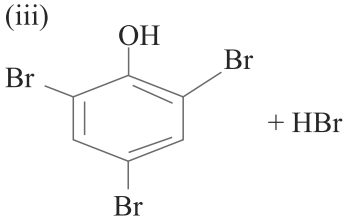
(ii) 

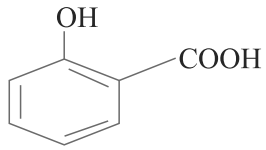
(iii) 

(iv) 

Ans: (i) $[Fe(C_6H_5O)_3]^{3-}$+HC1

(ii) 

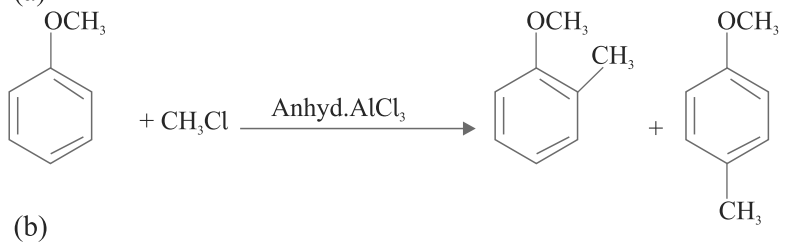
(iii) 

(iv) 

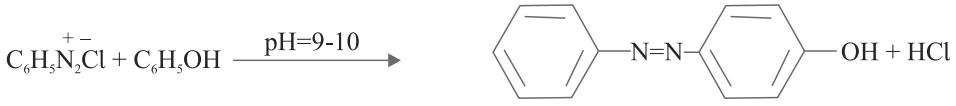
7. Write an example for the following name reactions :

(a) Friedel-Crafts alkylation of anisole (b) Coupling reaction

Ans: (a)



(b)



8. Account for the following:
   (a) Phenol has a smaller dipole moment than methanol.
   (b) Phenol undergoes electrophilic substitution reactions faster than benzene.

Ans: (a) Due to delocalization of electrons of oxygen in phenol.
   (b) Due to +R effect of -OH group in phenol which activates phenyl nucleus by increasing electron density as compared to benzene.

9. Give one reaction of alcohol involving cleavage of :
   (a) C-O bond (b) O-H bond

Ans: (a)

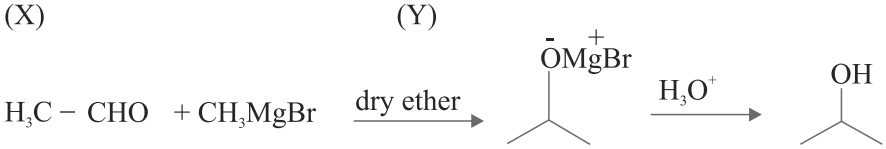
(b)

10. Ethereal solution of an organic compound 'X' when heated with Mg gave 'Y' which on treatment with CH_3CHO followed by acid hydrolysis gave 2-Propanol. Identify the compound 'X'. What is 'Y' known as ?

Ans:

$$CH_3Br + Mg \xrightarrow{\text{dry ether}} CH_3MgBr$$

(X) (Y)



11. Phenol is more acidic than alcohol: Give reason.

Ans: Due to resonance stabilised phenoxide ion.

12. While separating a mixture of *o*- and *p*-nitrophenols by steam distillation, name the isomer which is steam volatile? Give reasons.

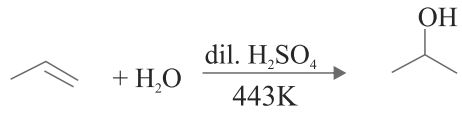
Ans: *o*-Nitrophenol is steam volatile because it is not stabilized by intermolecular hydrogen bonding.

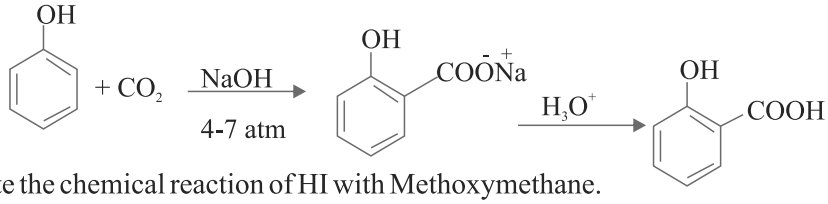
13. Write the reactions and conditions involved in the conversion of:

(a) Propene to propan-2-ol

(b) Phenol to salicylic acid

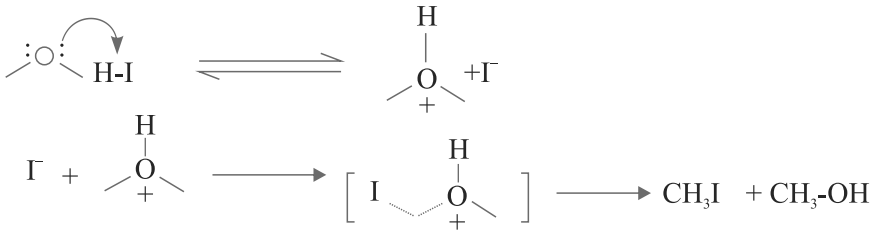
Ans:

(a) 

(b) 

14. Write the chemical reaction of HI with Methoxymethane.

Ans:



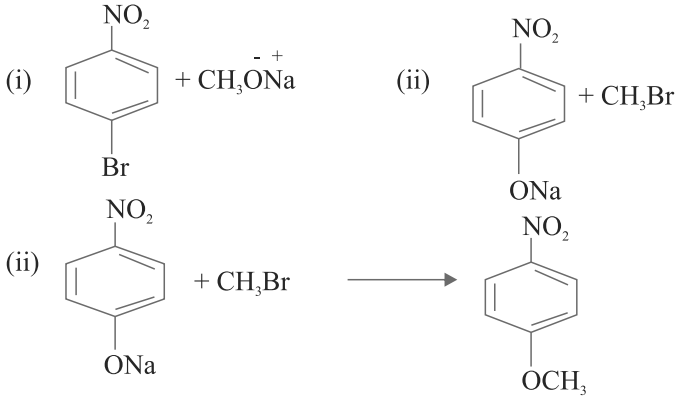
15. Ethers are relatively inert. Justify

Ans: Due to absence of any active site in their molecules, divalent oxygen is linked to carbon atoms on both sides (C-O-C).

16. How will you distinguish between CH_3OH and C_2H_5OH?

Ans: $C_2H_5OH + 4I_2 + 3Na_2CO_3 \xrightarrow{heat} CH_3I + HCOONa + 5NaI + 2H_2O + 3CO_2$

17. Which of the following is an appropriate set of reactants for the preparation of 1-Methoxy-4- nitrobenzene and why?

Ans: 

Haloarene undergoes nucleophilic substitution reactions in drastic conditions hence correct option is (i).

18. Arrange in order of boiling points :

(a) C_2H_5-O-C_2H_5, C_4H_9COOH, C_4H_9OH

(b) C_3H_7CHO, $CH_3COC_2H_5$, $C_2H_5COOCH_3$, $(CH_3CO)_2O$

Ans: (a) $C_4H_9COOH > C_4H_9OH > C_2H_5$-O-$C_2H_5$

(b) $(CH_3CO)_2O > C_2H_5COOCH_3 > CH_3COC_2H_5 > C_3H_7CHO$

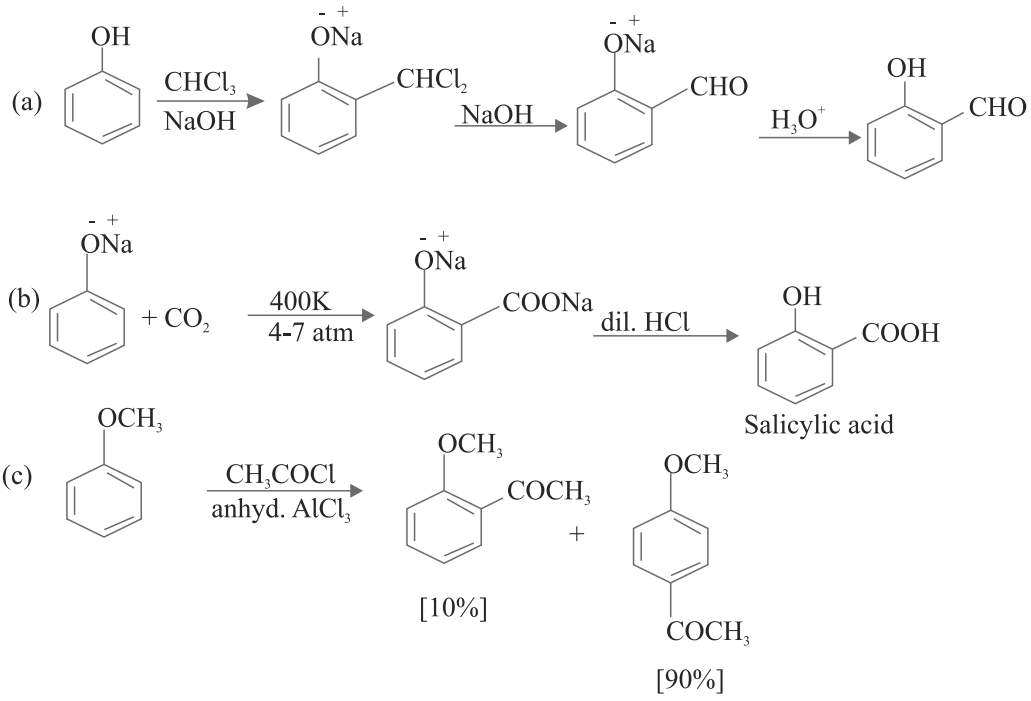
19. Describe the following reactions with examples :

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

(c) Friedel Crafts acylation of anisole

Ans:

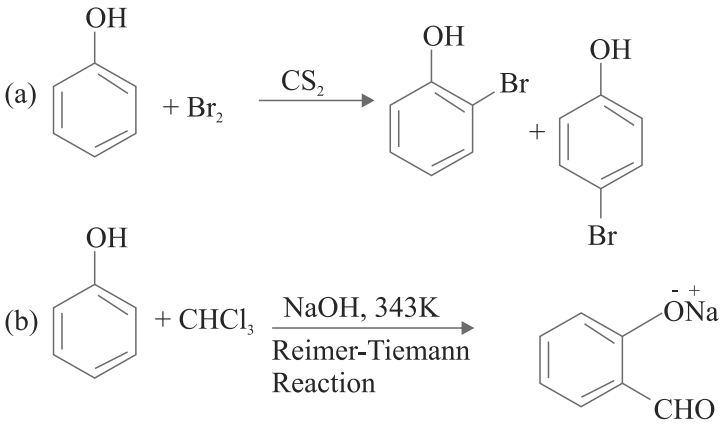


20. Give equations of the following reactions:

(a) Bromine in CS_2 with phenol

(b) Treating phenol with chloroform in presence of aqueous NaOH

(c) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.



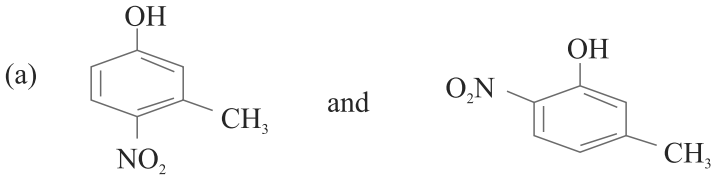
21. Write the structure of the major products of the following:

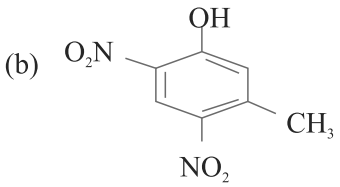
(a) Mononitration of 3-Methylphenol

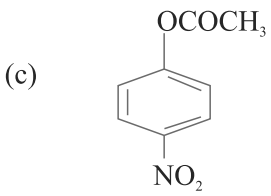
(b) Dinitration of 3-Methylphenol

(c) Mononitration of phenyl ethanoate

Ans : -OH and -CH_3 are *o*-and *p*-directing groups. The products are:







22. Dehydration of alcohols to form an alkene is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3. Explain.

Ans: In acidic medium alcohols are protonated then loses H_2O to form a carbocation. If HCl is used which is strong nucleophile causes nucleophilic substitution and HNO_3 causes oxidation.

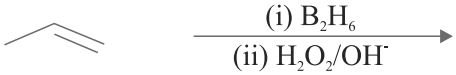
23. Name the reagents which arc used in the following conversions:
    (a) Primary alcohol to an aldehyde
    (b) Butan-2-one to Butan-2-ol
    (c) Phenol to 2,4,6-Trinitrophenol

Ans: (i) PCC, a complex of chromium trioxide with pyridine and HCl.
    (ii) $NaBH_4$, sodium borohydride
    (iii) Conc $HNO_3 + H_2SO_4$

24. Write major products of following reactions:

(i) 

(ii) 

(iii) 

(iv) C_6H_5OH $\xrightarrow[\text{(ii) } CO_2,\ H^+]{\text{(i) aq. NaOH}}$

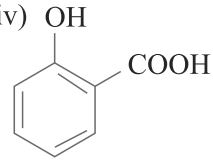
(v) $CH_2Br\text{-}CH_2Br$ $\xrightarrow{KOH\ (aq)}$

(vi) $C_6H_5NH_2$ $\xrightarrow[\text{(ii) } 0\text{-}5^oC]{\text{(i) } NaNO_2/HCl}$

Ans: (i) $CH_3CH_2CH_2CH_2OH$

(ii) $CH_3CH=CHCHO$

(iii) $CH_3CH_2CH_2OH$

(iv) 

(v) $CH_2OH\text{-}CH_2OH$

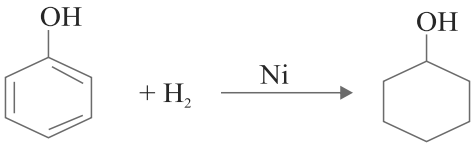
(vi) CH_3CH_2OH

25. How will you carry out following conversion :

(a) Phenol to Cyclohexanol

(b) Benzyl chloride to Benzyl alcohol

(c) Anisole to phenol

Ans: (a) 

(b) 

(c) 

LONG ANSWER TYPE QUESTIONS (5 Marks)

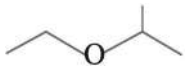
1. An alcohol 'A' ($C_4H_{10}O$) on oxidation with acidified $K_2Cr_2O_7$ gives carboxylic acid 'B' ($C_4H_8O_2$). Compound 'A' when dehydrated with conc. H_2SO_4 at 443K gives compound 'C' with aqueous H_2SO_4. 'C' gives compound 'D' ($C_4H_{10}O$) which is an isomer of 'A'. Compound 'D' is resistant to oxidation but compound 'A' can be easily oxidised. Identify A, B, C and D and write their structure.

Ans: A: $(CH_3)_2CHCH_2OH$ C: $(CH_3)_2C=CH_2$

B: $CH_3CH(CH_3)COOH$ D: $(CH_3)_3C\text{-}OH$

2. An ether 'A' ($C_5H_{12}O$) when heated with excess of hot conc. HI produced two alkyl halides which on hydrolysis form compound 'B' and 'C' . Oxidation of B gives an acid 'D' whereas oxidation of 'C' gave a ketone 'E'. Deduce the structure of A, B, C, D and E.

Ans:

A. 

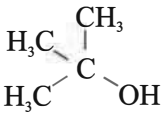
B. 

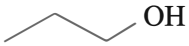
C. 

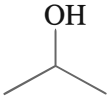
D. CH_3- COOH

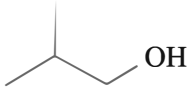
E. 

3. a) Which of the following compounds gives fastest reaction with HBr and why?

(i) 

(ii) 

(iii) 

(iv) 

Ans: (i) $(CH_3)_3C\text{-}OH$

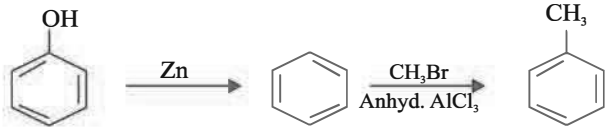
Due to formation more stable of carbocation

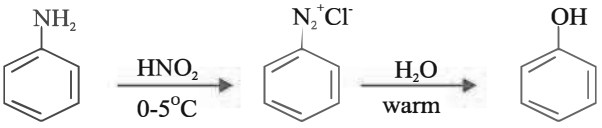
b) Convert the following:

(i) Toluene from Phenol

(ii) Phenol from Aniline.

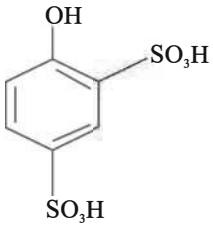
Ans. (i)

(i) 

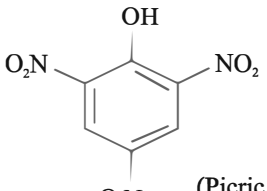
(ii) 

4. Phenol, C_6H_5OH when reacts with concentrated sulphuric acid, forms 'Y'. The compound, 'Y' is reacted with concentrated nitric acid to form 'Z'. Identify 'Y' and 'Z' Explain why phenol is not converted commercially to 'Z' by reacting it with conc. HNO_3

Ans:



(Y)

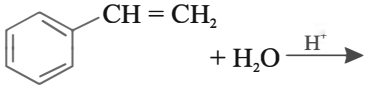


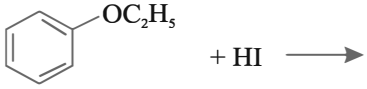
(Picric acid)

(Z)

Reason: Picric acid yield is very poor.

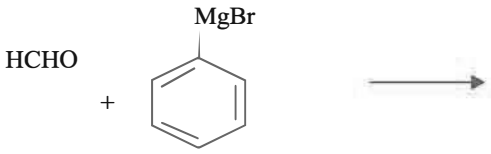
5. Write the strucutre of the main product in the following reactions:

(i) 

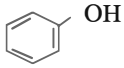
(ii) 

(iii) 

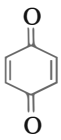
(iv) 

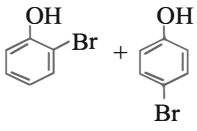
(v) 

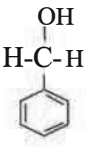
Ans. (i) C_6H_5-CH(OH)-CH_3

(ii) 

+ CH_3CH_2I

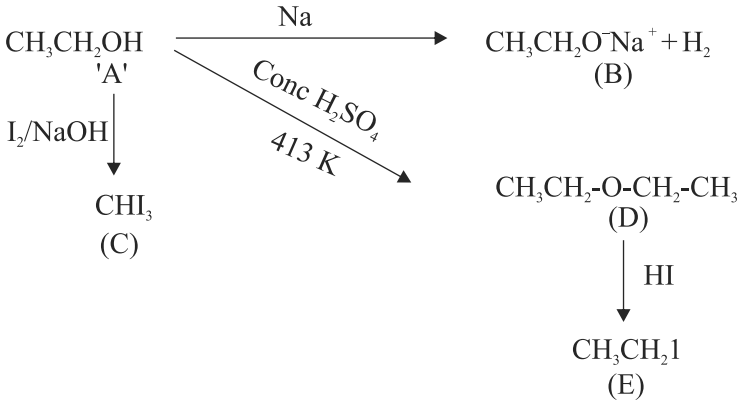
(iii) 

(iv) 

(v) 

6. An organic compound 'A' (C_2H_6O) reacts with sodium to form a compound 'B' with the evolution of H_2. 'A' gives a yellow compound 'C' on reacting with Iodine and NaOH. When heated with conc. H_2SO_4 form 'D' which on reaction with conc. HI at 373 K gives compound 'E'. The compound 'D' is also obtained when 'B' is heated with 'E'. Identify A, B, C, D, E . Write the equation for the reactions involved.

Ans. A-CH_3CH_2OH



7. Two compounds [A] and [B] have molecular formula C_2H_6O on reacting with HI, [A] gives alkyl iodide and water while [B] give alkyl iodide and alcohol. Identify compounds [A] and [B] write the reaction involved.

Ans. A-$C_2H_5OH + HI \longrightarrow C_2H_5I$

B- $CH_3OCH_3 + HI \longrightarrow CH_3I + CH_3OH$

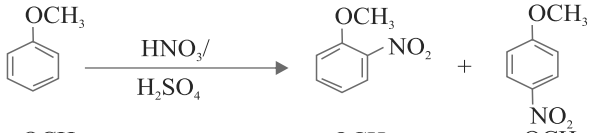
8. A compound [A]$C_4H_{10}O$ is found to be soluble in sulpheric acid . [A] does not react with Na or $KMnO_4$. On heating with excess of HI, it is converted into single alkyl halide, Identify compound [A]

Ans. [A]- $CH_3CH_2O\text{-}CH_2CH_3 + HI \longrightarrow 2\,CH_3CH_2I$

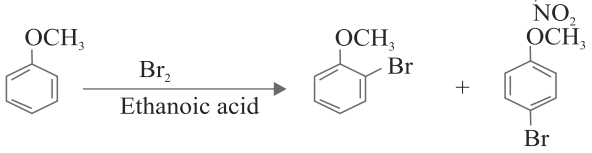
9. (a) Write the chemical equation for the following reaction
(i) Friedel-Craft alkylation in anisole
(ii) Nitration of anisole
(iii) Bromination of anisole in ethanolic medium
(b) Explain alkyl aryl ether directs the incoming substituents towards ortho and para position in the ring

Ans. (a) (i)

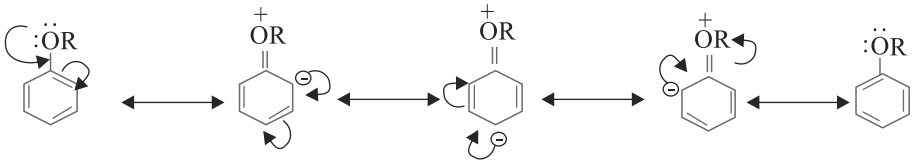
(ii)



(iii)



(b) Due to resonane



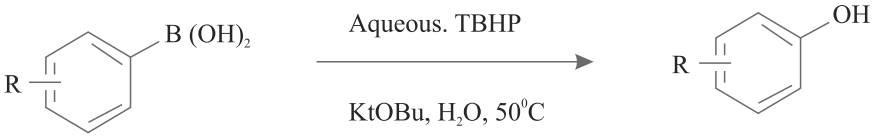
10. (i) Write the chemical test to distinguish between following pairs of compounds
(a)Ethanol and Propan-2-ol
(b) Butan-1-ol and Phenol
(c) Propan-2-ol and pentan-3-ol
(d)Phenol and Anisole
(ii) Write reagent(s) to carry out following conversions:
(a) Dehydrogeration of ethanol to ethanal
(b) Phenol to Benzene

Ans. (i) (a) Lucas Test (anhy $ZnCl_2$ + HCl)
(b) aq. $FeCl_3$ solution
(c) Iodoform test
(c) Neutral $FeCl_3$ solution
(d) Neutral $FeCl_3$ test
(ii) (a) Cu/573K
(b) zinc dust

CASE-STUDY BASED QUESTIONS

1. **Read the passage and answer the following questions:**

In the past few decades, phenols have received great attention in modern synthetic chemistry since ever Runge and Laurent made the first discovery in 1834 and 1841, respectively with regard to this motif, which is frequently found in natural products, flavonoids and pharmaceutically important compounds associated with certain bioactivities, such as antibacterial, antifungal, antibiotic, anti-inflammatory, antiviral, anxiolytic and antioxidant activities. Conventional methods for the large-scale synthesis of phenols include the Hock process, diazotization of aromatic amines and nucleophilic substitution reactions. Academicians have focused on the development of alternative approaches, for example, C-H activation of arenes and oxidation of C-Si bonds and C-halo bonds. Recently, the direct hydroxylation of aryl boronic acids to phenols has gained a lot of attention. In this context, a variety of oxidative methods employing metal catalysts, $Cu(OAc)_2$-H_2O_2, $CuSO_4$-phenanthroline, $CuC1_2$-miceller systems, Cu_2O-NH_3, $[Ru(bpy)_3C1_2]$-$6H_2O$, Al_2O_3-H_2O_2, and H_3BO_3-H_2O_2 has been developed. On the other hand, the metal-free oxidative process are also competitive, Oxone, nBu_4NHSO_5, NH_2OH, H_2O_2-poly(N-vinylpyrrolidone), I_2-H_2O_2, Amberlite IR-120-H_2O_2, N-oxides, MCPBA, $NaClO_2$, photoredox catalysis, electrochemical oxidation, $(NH_4)_2S_2O_8$, PEG-400-H_2O_2, WERSA-H_2O_2, WEBPA-H_2O_2, nanoparticles of Ag, Cu_2O, and Fe_2O_3/silica gel and TBHP/$C1_3CCN$. Despite these efficient oxidative processes, developing a new methodology free from metal oxidants and organic solvents is highly desirable. As part of our research interest involving metal-free oxidation reactions herein, a new protocol for the direct hydroxylation of aryl boronic acids with TBHP in the aqueous medium is reported (Scheme 1).



Scheme 1: Hydroxylation of aryl boronic acids.

Reference : Tanveer MahmadAlli Shaikh, **Synthesis of Phenols via Metal-Free Hydroxylation of Aryl Boronic Acids with Aqueous TBHP**, *Journal of Chemistry*, vol. **2020**, Article ID 1543081, 7 pages, 2020. https://doi.org/10.1155/2020/1543081

(A) Which of the following method of preparation of phenols is least likely to take place at 298K?

(i) Nucleophilic substitution in chlorobenzene

(ii) Reaction of diazonium salt with water.

(iii) Oxidation followed by acidification of cumene

(iv) Reaction of benzene sulphonic acid with NaOH followed by acidification

(B) In which of the following haloarene, nucleophilic substitution will be fastest to yield corresponding phenol?

(i) Chlorobenzene

(ii) *p*-Chloronitrobenzene

(iii) *p*-Cholrotoluene

(iv) *p*-Chloroanisole

(C) Aniline on reaction with $NaNO_2$ + HCl forms (X). (X) converts to (Y) on reaction with KI. (X) and (Y) are respectively-

(i) Benzene diazonium chloride, iodobenzene

(ii) Iodobenzene, Ethoxybenzene

(iii) Iodobenzene, Benzene

(iv) Benzene diazonium chloride, Phenol

(D) Phenols on reaction with bromine water forms-

(i) Colourless, 2-Bromophenol

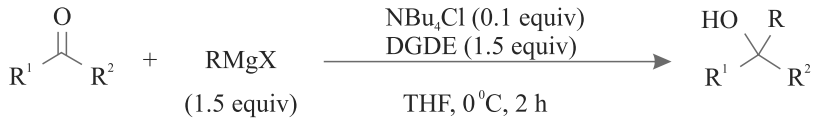
(ii) Dark coloured mixture of 2-Brornophenol and 4-Bromophenol

(iii) White precipitate of 2,4,6-Tribromophenol

(iv) Yellow colouration of 2,4-Dibromophenol

2. **Read the passage and answer the following questions:**

On the basis of the investigation of the combinational effect of quaternary ammonium salts and organic bases, an added-metal-free catalytic system for nucleophilic addition reactions of a variety of Grignard reagents to diverse ketones in the solvent has been developed to produce tertiary alcohols in good to excellent yields. By using tetrabutylammonium chloride (NBu_4C1) as a catalyst and diglyme (DGDE) as an additive, this system strongly enhances the efficiency of



R^1=Aryl and alkyl
R^2=Aryl and alkyl

R=alkyl and allyl
X=Br, Cl

good to excellent yields

addition at the expense of enolization and reduction. NBu_4C1 should help to shift the Schlenk equilibrium of Grignard reagents to the side of dimeric Grignard reagents to favor the additions of Grignard reagents to ketones via a favored six-membered transition state to form the desired tertiary alcohols, and DGDE should increase the nucleophilic reactivities of Grignard reagents by coordination. This catalytic system has been applied in the efficient synthesis of Citalopram, an effective U.S. FDA-approved antidepressant, and a recyclable version of this catalytic synthesis has also been devised.

Reference : Hua Zong, Huayin Huang, Junfeng Liu, Guangling Bian, and Ling Song **Added-Metal-Free Catalytic Nucleophilic Addition of Grignard Reagents to Ketones** *J. Org. Chem.* **2012**, 77, 10, 4645-4652

(A) Which ketone and Grignard reagent can be used to form 2-methylbutan-2-ol ?

(B) Write structure and IUPAC name of product formed reaction of allyl magnesium bromide with acetophenone?

(C) Which reaction will take place at faster rate and why?

(i) Benzaldehyde + Propyl magnesium bromide

(ii) Propanal + Benzyl magnesium bromide

(D) Why Grignard reagent is stored under anhydrous conditions?

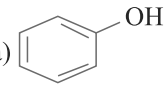
3. **Read the passage and answer the following questions:**

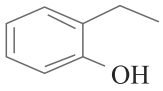
Phenols are compounds that possess a hydroxyl group directly attached to an aromatic. carbocyclic nucleus. Phenol is the trivial name for monohydroxybenzene. The *o*-, *m*-, and *p*-cresols are monohydroxytoluenes ($CH_3.C_6H_4OH$) and are distinct in their properties and reactions from the isomeric side-chain hydroxy compound, benzyl alcohol ($C_6H_5.CH_2OH$), which is a typical aromatic alcohol. Simple monohydric phenols are either corrosive liquids or low melting solids. The dihydric and trihydric phenols are solids. The mono-hydroxy compounds are only slightly soluble in water but are miscible with organic solvents. Water solubility increases and solubility in organic solvents

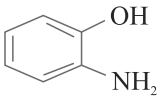
decreases with the introduction of additional hydroxyl groups. They are all characterized by, and distinguished from, the aliphatic or aromatic alcohols by their ready solubility in aqueous alkali. Phenols and the cresols are widely used as antiseptics and disinfectants; the cresols are contained in the wood preserving fluid, creosote. Many phenols have wide application in the industrial production of plastics, dyestuffs, insectides, selective weedkillers, and germicides.

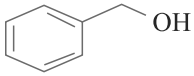
Reference : P.W.G. Smith, A.R. Tatchell, **Phenols**, *Aromatic Chemistry*, 1969

(A) Which of the following is not a phenol?

(a) 

(b) 

(c) 

(d) 

(B) Which of the following phenol has highest pK_a value?

(a) Phenol (b) *p*-Nitrophenol

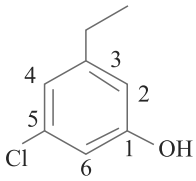
(c) *o*-Nitrophenol (d) *o*-cresol

(C) Phenols may be characterized by the reaction with-

(a) $FeCl_3$ (b) Br_2 water

(c) $NaHCO_3$ (d) Both $FeC1_3$ and $NaHCO_3$

(D) Write IUPAC name of following phenol.



ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. (c) 2. (d) 3. (c) 4. (c) 5. (c) 6. (d) 7. (d) 8. (b) 9. (c) 10. (c)
11. (a) 12. (d) 13. (d) 14. (a) 15. (b) 16. (c) 17. (d) 18. (b) 19. (c)

II FILL IN THE BLANKS

1. 2.4,6-Tribrornophenol
2. Ethanol
3. Methanal
4. Cumene
5. Esterification
6. Lucas
7. Easier
8. S_N2
9. Benzoic acid
10. 1 -Chloropropane

III ASSERTION REASON TYPE QUESTIONS

1. (A) 2. (D) 3. (D). 4. (C) 5. (D) 6. (C) 7. (A) 8. (A) 9. (B) 10. (A)

IV ONE WORD TYPE QUESTIONS

1. PCC
2. *ortho*-Nitrophenol
3. *para*-bromoanisole
4. Reimer-Tiemann reaction
5. Picric acid
6. $NaBH_4$
7. $B_2H_6/H_2O_2, OH^-$
8. Primary
9. 2,4,6-Trinitrophenol (Picric Acid)
10. $H_3\overset{1}{C}=\overset{2}{C}H-\overset{3}{C}H(OH)-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$
11. Iodoform Test
12. Intermolecular H-bond
13. Benzoquinone
14. 2-Acetoxybenzoic acid

CASE STUDY BASED QUESTIONS

1 : (A) b (B) b (C) a (D) c

2: (A) CH_3COCH_3, C_2H_5MgCl

(B) $C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-CH_2\text{-}CH=CH_2$ IUPAC (i) 1-Methyl-1-phenyl but -3-ene-1-ol

(D) It react with water to form alkane R-Mgx+H-OH→R-H+Mg-X-OH

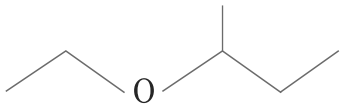
3: (A) d (B) d (C) a (D) 3-Ethyl-5-chlorophenol

UNIT TEST

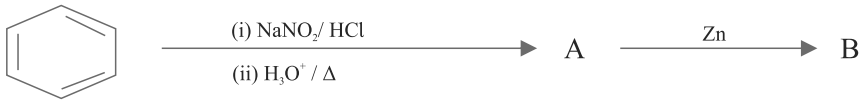
Alcohols, phenols and ethers

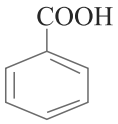
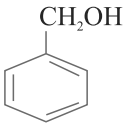
Maximum Marks : 20 **Time : 1 Hour**

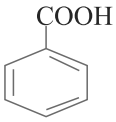
1. Write the IUPAC name of:

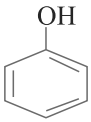


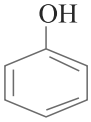
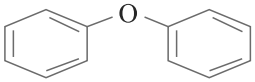
2. A and B in the following reaction are :



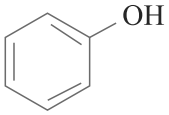
(a) A.  B. 

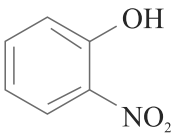
(b) A.  B. 

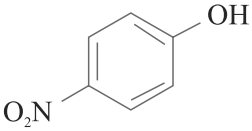
(c) A.  B. 

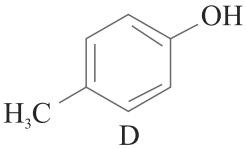
(d) A.  B. 

3. The correct order of acidic strength of following phenols is–


A


B


C


D

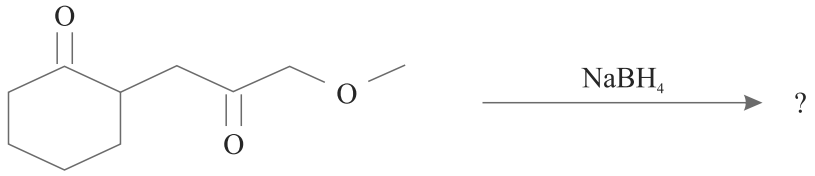
(a) A<B<C<D

(b) B<A<C<D

(c) D<A<B<C

(d) D<C<B<A

4. Identity the product: a



5. $(CH_3)_3C\text{-}OCH_3 + HI \rightarrow ?$

6. Give an example of following name reactions:

(I) Kolbe's reaction

(ii) Williamsons synthesis

7. Write the products formed by nitration of phenol . Which of the product has higher boiling point and why ?

8. Identify the product formed when ethanol is heated at 413 K. Write the mechanism of the reaction.

9. How will you convert ?

(i) Ethanol into propan-2-ol

(ii) Aniline into phenol

(iii) Methanol into methoxyethane

10. Explain the following:

(i) Alcohols are more soluble in water than ethers of comparable molar masses.

(ii) t-Butyl chloride on heating with sodium methoxide gives 2- Methylpropene instead of t-Butylmethly ether.

(iii) Reaction of phenol with bromine leads to formation of 2,4,6- tribromophenol

11. An Ether 'A' ($C_5H_{12}O$) when treated with excess of hot conc HI, produced two alkyl halides which on hydrolysis form 'B' and 'C'. Oxidation of 'B' forms an acid 'D', whereas oxidation of 'C' give a ketone 'E'. Identify A, B and C and reactions involved.

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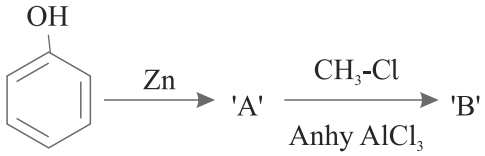
UNIT TEST-2

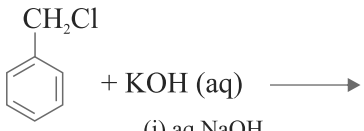
Alcohols, phenols and ethers

Maximum Marks : 20 **Time : 1 Hour**

1. Write the IUPAC name of C_6H_5-CH_2-CH_2-OH
2. Out of t-Butyl alcohol and n-Butanol, which undergoes acid catalysed dehydration faster and why?
3. Write 'A' and 'B' in following reaction.



4. Name the reagent used for conversion of primary alcohol to an aldehyde.
5. Out of phenol and methanol, which one has smaller dipole moment
6. Write the mechanism of conversion of propan-1-ol into propene.
7. Explain Williamson synthesis and Reimer–Tiemann Reaction
8. Complete the reaction.

(a) 

(b) C_6H_5-OH $\xrightarrow[\text{(ii) } CO_2,\ H^+]{\text{(i) aq.NaOH}}$

9. Convert the following
   (i) Phenol to picric acid
   (ii) Propan -2-ol to 2-methyl propan-2-ol
   (iii) Phenol to aspirin
10. Write the reason of following observations:
    (a) alcohols are generally soluble in water but alkyl halides are not.
    (b) Phenol exhibits acidic character.
    (c) *o*-nitrophenol is more steam volatile than *p*-nitrophenol
11. An ether 'A' ($C_5H_{12}O$) when heated with excess of hot conc HI produces two alkyl halides which on hydrolysis form compound 'B' and 'C'. Oxidation of 'B' gives an acid 'D' whereas oxidation of 'C' gives ketone 'E'. Write structures of A, B, C, D, E .