Chapter
Alcohols Phenols & Ethers

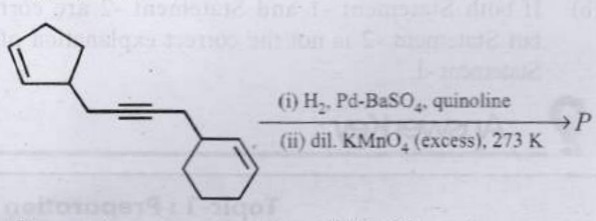
Topic-1: Preparation and Properties of Alcohols

1 MCQs with One Correct Answer

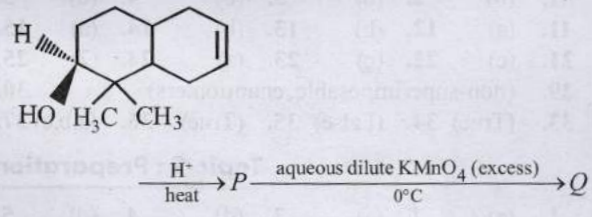
1. The best method to prepare cyclohexene from cyclohexanol is by using **[2005S]**
   (a) Conc. $HCl + ZnCl_2$ (b) Conc. H_3PO_4
   (c) HBr (d) Conc. HCl
2. The product of acid catalyzed hydration of 2-phenylpropene is **[2004S]**
   (a) 3-phenyl-2-propanol (b) 1-phenyl-2-propanol
   (c) 2-phenyl-2-propanol (d) 2-phenyl-1-propanol
3. 1–propanol and 2–propanol can be best distinguished by **[2001S]**
   (a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution
   (b) oxidation with acidic dichromate followed by reaction with Fehling solution
   (c) oxidation by heating with copper followed by reaction with Fehling solution
   (d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution
4. The compound that will react most readily with NaOH to form methanol is **[2001S]**
   (a) $(CH_3)_4N^+I^-$ (b) CH_3OCH_3
   (c) $(CH_3)_3S^+I^-$ (d) $(CH_3)_3CCl$
5. Which of the following compounds is oxidised to prepare methyl ethyl ketone? **[1987 - 1 Mark]**
   (a) 2-Propanol (b) l-Butanol
   (c) 2-Butanol (d) t-Butyl alcohol
6. HBr reacts fastest with : **[1986 - 1 Mark]**
   (a) 2-methylpropan-2-ol (b) propan-1-ol
   (c) propan-2-ol (d) 2-methylpropan-1-ol
7. An industrial method of preparation of methanol is : **[1984 - 1 Mark]**
   (a) catalytic reduction of carbon monoxide in presence of $ZnO–Cr_2O_3$
   (b) by reacting methane with steam at 900°C with a nickel catalyst
   (c) by reducing formaldehyde with lithium aluminium hydride
   (d) by reacting formaldehyde with aqueous sodium hydroxide solution
8. The compound which reacts fastest with Lucas reagent at room temperature is **[1981 - 1 Mark]**
   (a) butan-1-ol (b) butan-2-ol
   (c) 2-methylpropan-1-ol (d) 2-methylpropan-2-ol
9. Which of the following is basic **[1980]**
   (a) CH_3-CH_2-OH (b) $OH-CH_2-CH_2-OH$
   (c) $H-O-O-H$ (d) $H_3C-\overset{\overset{O}{\|}}{C}-OH$
10. Ethyl alcohol is heated with conc H_2SO_4 the product formed is **[1980]**
    (a) $H_3C-\overset{\overset{O}{\|}}{C}-OC_2H_5$ (b) C_2H_6
    (c) C_2H_4 (d) C_2H_2

2 Integer Value Answer

11. Total number of hydroxyl groups present in a molecule of major product P is ___ **[Adv. 2019]**

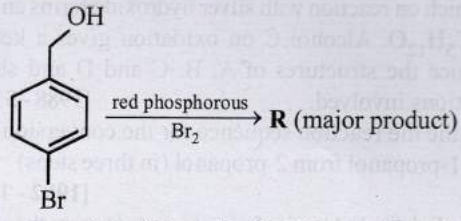


12. The number of hydroxyl group(s) in Q is **[Adv. 2015]**



3 Numeric / New Stem Based Questions

13. Consider the following reaction. **[Adv. 2022]**



On estimation of bromine in 1.00 g of **R** using Carius method, the amount of AgBr formed (in g) is _____. [Given: Atomic mass of H = 1, C = 12, O = 16, P = 31, Br = 80, Ag = 108]

4 Fill in the Blanks

14. Glycerine contains one ..... hydroxy group. **[1997 - 1 Mark]**

15. Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is ..... . **[1983 - 1 Mark]**

5 True / False

16. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. **[1986 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

17. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are **[Adv. 2014]**

(a) tert-butanol and 2-methylpropan-2-ol
(b) tert-butanol and 1, 1-dimethylethan-1-ol
(c) *n*-butanol and butan-1-ol
(d) isobutyl alcohol and 2-methylpropan-1-ol

18. The reaction of $CH_3CH=CH-C_6H_4-OH$ with HBr gives **[1998 - 2 Marks]**

(a) $CH_3CHBrCH_2-C_6H_4-OH$
(b) $CH_3CH_2CHBr-C_6H_4-OH$
(c) $CH_3CHBrCH_2-C_6H_4-Br$
(d) $CH_3CH_2CHBr-C_6H_4-Br$

9 Assertion and Reason /Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

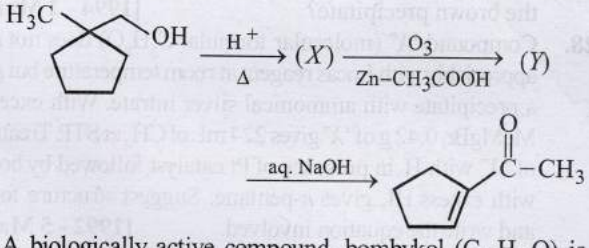
19. Read the following statement and explanation and answer as per the options given below : **[1988 - 2 Marks]**

Statement : Solubility of *n*-alcohols in water decreases with increase in molecular weight.

Explanation : The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permits enhanced hydrogen bonding with water.

10 Subjective Problems

20. Identify (*X*) and (*Y*) in the following reaction sequence. **[2005 - 2 Marks]**

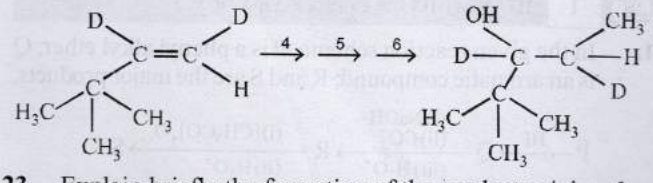


21. A biologically active compound, bombykol ($C_{16}H_{30}O$) is obtained from a natural source. The structure of the compound is determined by the following reactions. **[2002 - 5 Marks]**

(a) On hydrogenation, bombykol gives a compound **A**, $C_{16}H_{34}O$, which reacts with acetic anhydride to give an ester;
(b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O_3/H_2O_2) gives a mixture of butanoic acid, oxalic acid and 10-acetoxydecanoic acid.

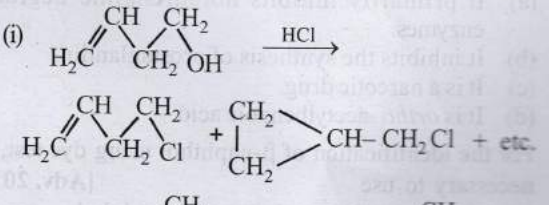
Determine the number of double bonds in bombykol. Write the structures of compound *A* and bombykol. How many geometrical isomers are possible for bombykol?

22. Complete the following reaction with appropriate reagents : **[1999 - 3 Marks]**

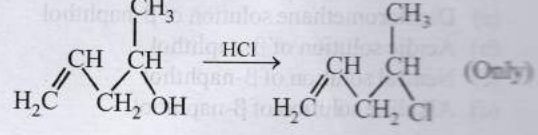


23. Explain briefly the formation of the products giving the structures of the intermediates. **[1999 - 3 Marks]**

(i)



(ii)



24. Give reasons for the following :
Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol. **[1998 - 2 Marks]**

25. An optically active alcohol *A* ($C_6H_{10}O$) absorbs two moles of hydrogen per mole of *A* upon catalytic hydrogenation and gives a product *B*. The compound *B* is resistant to oxidation by CrO_3 and does not show any optical activity. Deduce the structures of *A* and *B*. **[1996 - 2 Marks]**

26. 3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. **[1996 - 2 Marks]**

27. When *t*-butanol and *n*-butanol are separately treated with a few drops of dilute $KMnO_4$, in one case only the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? **[1994 - 2 Marks]**

28. Compound '*X*' (molecular formula, C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammonical silver nitrate. With excess of MeMgBr, 0.42 g of '*X*' gives 224 mL of CH_4 at STP. Treatment of '*X*' with H_2 in presence of Pt catalyst followed by boiling with excess HI, gives *n*-pentane. Suggest structure for '*X*' and write the equation involved. **[1992 - 5 Marks]**

29. State with balanced equations what happens when :
Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate. **[1991 - 1 Mark]**

30. A ketone 'A' which undergoes haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives compound C, which forms monoozonide D, D on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify A, B and C. Write down the reactions involved. **[1989 - 4 Marks]**

31. A hydrocarbon A (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. A adds HBr (in accordance with Markownikoff's rule) to form a compound B which on reaction with silver hydroxide forms an alcohol C, $C_5H_{12}O$. Alcohol C on oxidation gives a ketone D. Deduce the structures of A, B, C and D and show the reactions involved. **[1988 - 5 Marks]**

32. Outline the reaction sequence for the conversion of
(ii) 1-propanol from 2-propanol (in three steps) **[1982 - 1 Mark]**
(i) ethyl alcohol to vinyl acetate. (in not more than 6 steps) **[1986 - 3 Marks]**

33. Give a chemical test/suggest a reagent to distinguish between methanol and ethanol. **[1985 - 1 Mark]**

34. An alcohol *A*, when heated with conc. H_2SO_4 gives an alkene *B*. When *B* is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound *C* is obtained. The compound *C* gives *D* when treated with warm dilute H_2SO_4 in presence of $HgSO_4$. *D* can also be obtained either by oxidizing *A* with $KMnO_4$ or from acetic acid through its calcium salt. Identify *A*, *B*, *C* and *D*. **[1983 - 4 Marks]**

35. An organic liquid (A), containing C, H and O with boiling point : 78°C, and possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product (B) – with the empirical formula, CH_2. 'B' decolourises bromine water as well as alkaline $KMnO_4$ solution and takes up one mole of H_2 (per mole of 'B') in the presence of finely divided nickel at high temperature. Identify the substances 'A' and 'B'. **[1979]**

Topic-2: Preparation and Properties of Phenols

1 MCQs with One Correct Answer

1. In the given reaction scheme, P is a phenyl alkyl ether, Q is an aromatic compound; R and S are the major products.

$$P \xrightarrow{HI} Q \xrightarrow[(iii)\,H_3O^+]{(i)\,NaOH\ (ii)\,CO_2} R \xrightarrow[(ii)\,H_3O^+]{(i)\,(CH_3CO)_2O} S$$

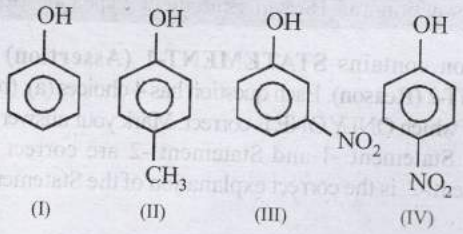
The correct statement about S is **[Adv. 2023]**
(a) It primarily inhibits noradrenaline degrading enzymes.
(b) It inhibits the synthesis of prostaglandin.
(c) It is a narcotic drug.
(d) It is *ortho*–acetylbenzoic acid.

2. For the identification of β-naphthol using dye test, it is necessary to use **[Adv. 2014]**
(a) Dichloromethane solution of β-naphthol
(b) Acidic solution of β-naphthol
(c) Neutral solution of β-naphthol
(d) Alkaline solution of β-naphthol

3. The increasing order of boiling points of the below mentioned alcohols is **[2006 - 3M, –1]**
(I) 1,2-dihydroxybenzene (II) 1,3-dihydroxybenzene
(III) 1,4-dihydroxybenzene (IV) Hydroxybenzene
(a) I < II < IV < III (b) I < II < III < IV
(c) IV < II < I < III (d) IV < I < II < III

4. Which of the following acids has the smallest dissociation constant ? **[2002S]**
(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH
(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

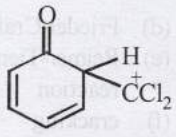
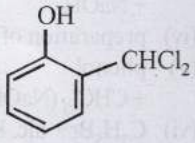
5. In the following compounds, **[1996]**

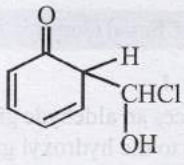
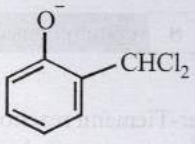


(I) (II) (III) (IV)

The order of acidity is :
(a) III > IV > I > II (b) I > IV > III > II
(c) II > I > III > IV (d) IV > III > I > II

6. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicyladehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate? **[1995S]**

(a)  (b) 

(c)  (d) 

7. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives **[1990 - 1 Mark]**
(a) *o*-Cresol (b) *p*-Cresol
(c) 2, 4-Dihydroxytoluene (d) Benzoic acid

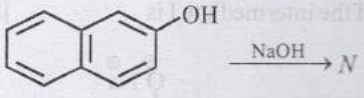
8. Phenol reacts with bromine in carbon disulphide at low temperature to give **[1988 - 1 Mark]**
(a) *m*-bromophenol (b) *o*- and *p*-bromophenol
(c) *p*-bromophenol (d) 2, 4, 6-tribromophenol

9. When phenol is treated with excess bromine water, it gives: **[1984 - 1 Mark]**
(a) *m*-Bromophenol (b) *o*- and *p*-Bromophenol
(c) 2, 4-Dibromophenol (d) 2, 4, 6-Tribromophenol

2 Integer Value Answer

10. An organic compound ($C_8H_{10}O_2$) rotates plane-polarized light. It produces pink color with neutral $FeCl_3$ solution. What is the total number of all the possible isomers for this compound? **[Adv. 2020]**

11. The number of resonance structures for *N* is **[Adv. 2015]**



4 Fill in the Blanks

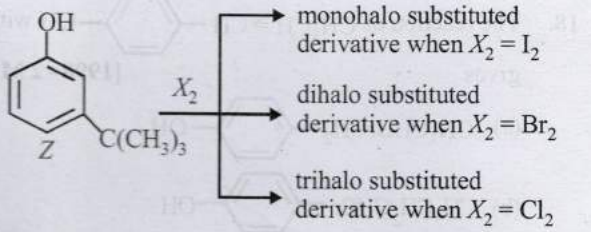
12. Phenol is acidic because of resonance stabilization of its conjugate base, namely ..... . **[1990 - 1 Mark]**

13. Formation of phenol from chlorobenzene is an example of ..... aromatic substitution. **[1989 - 1 Mark]**

14. The acidity of phenol is due to the ..... of its anion. **[1984 - 1 Mark]**

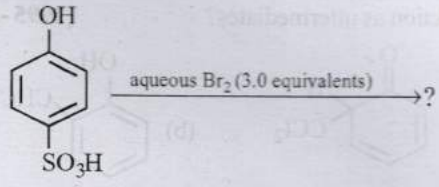
6 MCQs with One or More than One Correct Answer

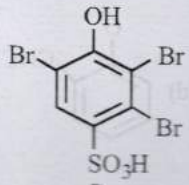
15. The reactivity of compound *Z* with different halogens under appropriate conditions is given below: **[Adv. 2014]**

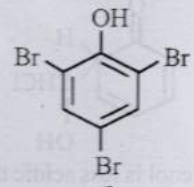


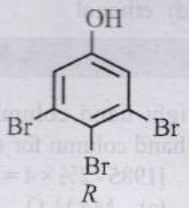
The observed pattern of electrophilic substitution can be explained by
(a) The steric effect of the halogen
(b) The steric effect of the *tert*-butyl group
(c) The electronic effect of the phenolic group
(d) The electronic effect of the *tert*-butyl group

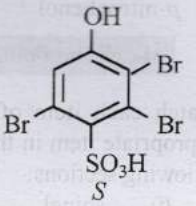
16. The major product(s) of the following reaction is(are) **[Adv. 2013]**



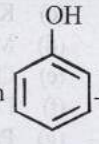


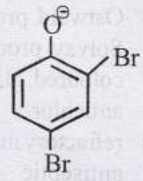


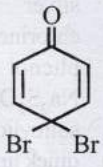


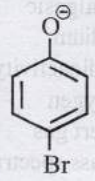


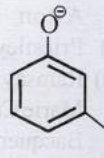
(a) *P* (b) *Q* (c) *R* (d) *S*

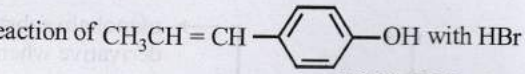
17. In the reaction  the intermediate (s) is (are) **[2010]**

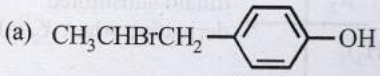
(a) 

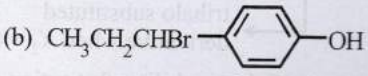
(b) 

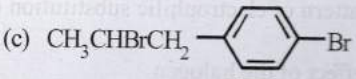
(c) 

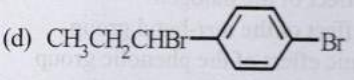
(d) 

18. The reaction of  with HBr gives **[1998 - 2 Marks]**

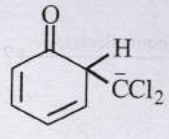
(a) 

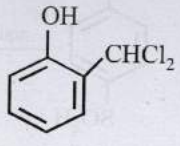
(b) 

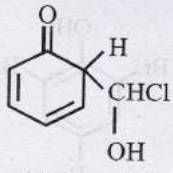
(c) 

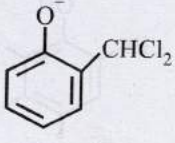
(d) 

19. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates? **[1995 - 2 Marks]**

(a) 

(b) 

(c) 

(d) 

20. Phenol is less acidic than : **[1986]**

(a) acetic acid (b) *p*-methoxyphenol
(c) *p*-nitrophenol (d) ethanol

7 Match the Following

21. Match each item of the right hand column with an appropriate item in the left hand column for each of the following sections: **[1985 - 2½ × 4 = 10 Marks]**

A.	(i)	spinel	(a)	$MgAl_2O_4$
	(ii)	feldspar	(b)	PbCO
	(iii)	cerussite	(c)	$KAlSi_3O_8$
	(iv)	malachite	(d)	$MgSO_4.H_2O$
	(v)	kisserite	(e)	$Cu(OH)_2.CuCO_3$
B.	(vi)	liquid air	(f)	Deacon process
	(vii)	Na_2CO_3	(g)	Parke process
	(viii)	nitric oxide	(h)	Claude process
	(ix)	silver	(i)	Ostwald process
	(x)	chlorine	(j)	Solvay process
C.	(xi)	phenol	(k)	coloured glass
	(xii)	$Na_2S_2O_3$	(l)	antichlor
	(xiii)	salicylic acid	(m)	refractory material
	(xiv)	quick lime	(n)	antiseptic
	(xv)	CuO	(o)	analgesic
D.	(xvi)	Aston	(p)	radium
	(xvii)	Priestley	(q)	radioactivity
	(xviii)	Ramsay	(r)	oxygen
	(xix)	Marie Curie	(s)	inert gas
	(xx)	Bacquerel	(t)	mass spectrum

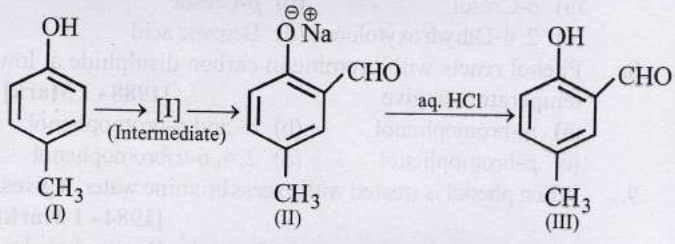
22. Match the following, choosing one item from column **X** and one from column **Y**. **[1982 - 3 Marks]**

X	**Y**
(i) pyrolysis of alkanes	(a) elimination reaction
(ii) benzene+chloroethane (+anhydrous $AlCl_3$)	(b) saponification
(iii) $CH_3COOC_2H_5$ + NaOH	(c) Wurtz reaction
(iv) preparation of alkanes	(d) Friedel-Crafts reaction
(v) phenol + $CHCl_3$ (NaOH)	(e) Reimer-Tiemann reaction
(vi) C_2H_5Br + alc. KOH	(f) cracking

8 Comprehension Passage Based Questions

Passage -I

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehyde as depicted below.



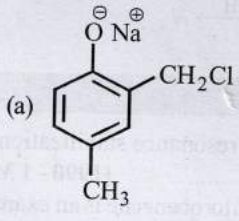
23. Which one of the following reagents is used in the above reaction ? **[2007]**

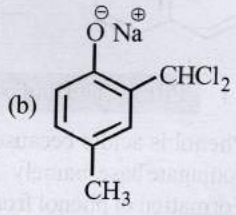
(a) aq.NaOH + CH_3Cl
(b) aq.NaOH + CH_2Cl_2
(c) aq.NaOH + $CHCl_3$
(d) aq.NaOH + CCl_4

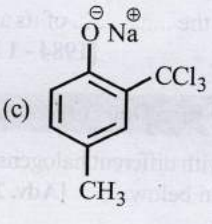
24. The electrophile in the reaction is **[2007]**

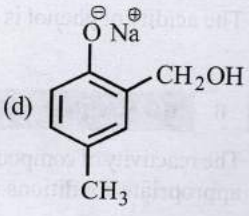
(a) :CHCl (b) $^+CHCl_2$
(c) $:CCl_2$ (d) CCl_3

25. The structure of the intermediate I is **[2007]**

(a) 

(b) 

(c) 

(d) 

9 Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.

(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.

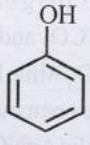
(c) If Statement -1 is correct but Statement -2 is incorrect.

(d) If Statement -1 is incorrect but Statement -2 is correct.

26. **Statement - 1 :** Phenol is more reactive than benzene towards electrophilic substitution reactions.
Statement - 2 : In the case of phenol, the intermediate carbocation is more resonance stabilized. **[2000S]**

10 Subjective Problems

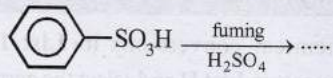
27. Outline the reaction sequence for the conversion of

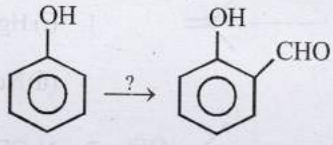
(i)  ⟶ Aspirin **[2003 - 2 Marks]**

(ii) phenol to acetophenone **[1989 - 1½ Marks]**

28. A compound *D* ($C_8H_{10}O$) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid *E* ($C_7H_6O_2$). Write the structures of *D* and *E* and explain the formation of *E*. **[1996 - 2 Marks]**

29. Complete the following with appropriate structures :

(i)  **[1992 - 1 Mark]**

(ii)  **[1986 - 1 Mark]**

30. Give reasons for the following :
Phenol is an acid but it does not react with sodium bicarbonate. **[1987 - 1 Mark]**

31. A compound of molecular formula C_7H_8O is insoluble in water and dilute sodium bicarbonate but dissolves in dilute aqueous sodium hydroxide. On treatment with bromine water, it readily gives a precipitate of $C_7H_5OBr_3$. Write down the structure of the compound. **[1985 - 2 Marks]**

32. What happens when *p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH. **[1984 - 2 Marks]**

33. State with balanced equations what happens when :
acetic anhydride reacts with phenol in presence of a base. **[1982 - 1 Mark]**

Topic-3: Preparation and Properties of Ethers

1 MCQs with One Correct Answer

1. The reaction products of $C_6H_5OCH_3 + HI \xrightarrow{\Delta}$ is : **[1995S]**

(a) $C_6H_5OH + CH_3I$

(b) $C_6H_5I + CH_3OH$

(c) $C_6H_5CH_3 + HOI$

(d) $C_6H_6 + CH_3OH$

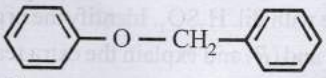
2 Integer Value Answer

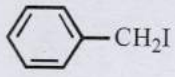
2. Total number of isomers, considering both structural and stereoisomers of cyclic ethers with the molecular formula C_4H_8O is____ **[Adv. 2019]**

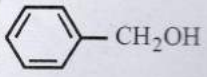
4 Fill in the Blanks

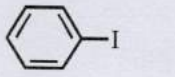
3. Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove ..... which are formed on prolonged standing in contact with air. **[1992 - 1 Mark]**

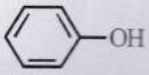
6 MCQs with One or More than One Correct Answer

4. The ether  when treated with HI produces **[1999 - 3 Marks]**

(a) 

(b) 

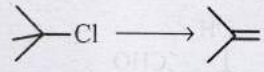
(c) 

(d) 

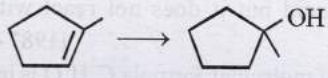
7 Match the Following

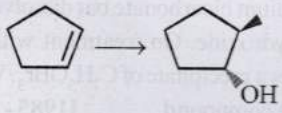
5. Match the chemical conversions in **List I** with the appropriate reagents in **List II** and select the correct answer using the code given below the lists : **[Adv. 2013]**

List I **List II**

P  1. (i) $Hg(OAc)_2$; (ii) $NaBH_4$

Q.  2. NaOEt

R.  3. Et-Br

S.  4. (i) BH_3; (ii) $H_2O_2/NaOH$

Codes :

	P	Q	R	S
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

6. Match the following, choosing one item from column **X** and the appropriate item from column **Y**. **[1983 - 2 Marks]**

X	Y
(i) Decarboxylation	(a) Addition reaction
(ii) Ozonolysis	(b) Soda lime
(iii) Williamson's synthesis	(c) Structure of alkene
(iv) Dichloroethylene	(d) Ether

10 Subjective Problems

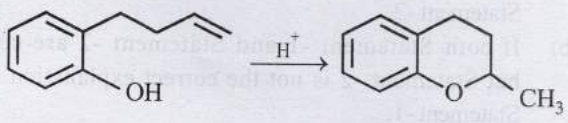
7. An organic compound (*P*) of molecular formula $C_5H_{10}O$ is treated with dil. H_2SO_4 to give two compounds (*Q*) and (*R*) both of which respond iodoform test. The rate of reaction of (*P*) with dil. H_2SO_4 is 10^{10} faster than the reaction of ethylene with dil. H_2SO_4. Identify the organic compounds, (*P*), (*Q*) and (*R*) and explain the extra reactivity of (*P*). **[2004 - 4 Marks]**

8. Write the structural formula of the main organic product formed when :

$$(CH_3)_2CHOCH_3 \xrightarrow{HI\,(excess),\ heat} 2\ Products.$$

[1998 - 2 Marks]

9. Write the intermediate steps for the following reaction.



[1998 - 1 Mark]

10. 2, 2-Dimethyloxirane can be cleaved by acid (H^+). Write mechanism. **[1997 - 2 Marks]**

11. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?

(i) $(CH_3)_3CBr + NaOMe \rightarrow$

(ii) $CH_3Br + NaO\text{-}t\text{-}Bu \rightarrow$ **[1997 - 2 Marks]**

12. An organic compound containing C, H and O exists in two isomeric forms A and B. An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O. A is insoluble in NaOH and $NaHCO_3$ while B is soluble in NaOH. A reacts with conc. HI to give compounds C and D. C can be separated from D by ethanolic $AgNO_3$ solution and D is soluble in NaOH. B reacts readily with bromine water to give compound E of molecular formula, $C_7H_5OBr_3$. Identify, A, B, C, D and E with justification and give their structures. **[1991 - 6 Marks]**

13. Give reasons for the following :

Sodium metal can be used for drying diethyl ether but not ethanol. **[1982 - 1 Mark]**

14. A compound (X) containing C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff's reagent. On refluxing with an excess of hydriodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorus and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compounds (X), (Y) and (Z)? Write chemical equations leading to the conversion of (X) to (Y). **[1981 - 3 Marks]**

Answer Key

Topic-1 : Preparation and Properties of Alcohols

1.	(b)	**2.**	(c)	**3.**	(c)	**4.**	(a)	**5.**	(c)	**6.**	(a)	**7.**	(a)	**8.**	(d)	**9.** (a)
10.	(c)	**11.**	(6)	**12.**	(4)	**13.**	(1.50)	**14.**	(Secondary)			**15.**	(aldol (β-hydroxybutanal))			**16.** (False)
17.	(a, c, d)			**18.**	(b)	**19.**	(c)									

Topic-2 : Preparation and Properties of Phenols

1.	(b)	**2.**	(d)	**3.**	(d)	**4.**	(c)	**5.**	(d)	**6.**	(d)	**7.**	(d)	**8.**	(b)	**9.** (d) **10.** (6)
11.	(9)	**12.**	(phenoxide ion)			**13.**	(nucleophilic)			**14.**	(resonance stabilization)					**15.** (a, b, c)
16.	(b)	**17.**	(a, c)	**18.**	(b)	**19.**	(a, d)	**20.**	(a, c)	**23.**	(c)	**24.**	(c)	**25.**	(b)	**26.** (a)

Topic-3 : Preparation and Properties of Ethers

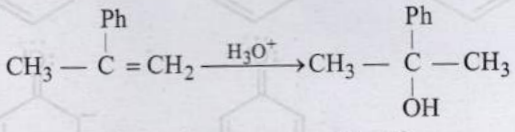
1.	(a)	**2.**	(10)	**3.**	(peroxides)	**4.**	(a, d)	**5.**	(a)	**6.**	(i)-(b); (ii)-(c); (iii)-(d); (iv)-(a)

Hints & Solutions

Topic-1: Preparation and Properties of Alcohols

1. **(b)**
Conc. HCl, HBr and conc. HCl + $ZnCl_2$ all are nucleophiles, thus convert alcohols to alkyl halides. However, conc. H_3PO_4 is a good dehydrating agent which converts an alcohol to an alkene.

2. **(c)** Addition of water to 2-phenylpropene follows Markovnikov's rule.

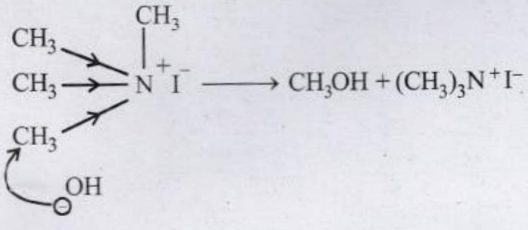


2-Phenyl-2-propanol

3. **(c)** $CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{Cu} CH_3CH_2CHO$
Propanol-1 → Propanal
(responds Fehling solution)

$CH_3CHOHCH_3 \longrightarrow CH_3COCH_3$
Propanol-2 → Propanone
(negative to Fehling solution)

4. **(a)**
Compound $(CH_3)_4N^+I^-$ is most reactive due to (i) better leaving group, I^- and (ii) due to the fact that the methyl group, with positive N, is more electron deficient.
Hence this group is more reactive towards nucleophile, OH^-



5. **(c)**
Secondary alcohols oxidise to produce kenone.

$CH_3CHOHCH_2CH_3 \xrightarrow{(O)} CH_3COCH_2CH_3$
2-Butanol → Ethyl methyl ketone

6. **(a)** Reactions involving cleavage of carbon-oxygen bond, (C – OH) follows the following order :
Tertiary > Secondary > Primary

7. **(a)** $\underbrace{CO + H_2}_{\text{Water gas}} + H_2 \xrightarrow[300°C]{Cr_2O_3 - ZnO} CH_3OH$
Methanol

8. **(d)** **Lucas test** is based on the difference in the three types of alcohols (having 6 or less carbon) towads **Lucas reagent** (a mixture of conc. hydrochloric acid and anhydrous zinc chloride) at room temperature.

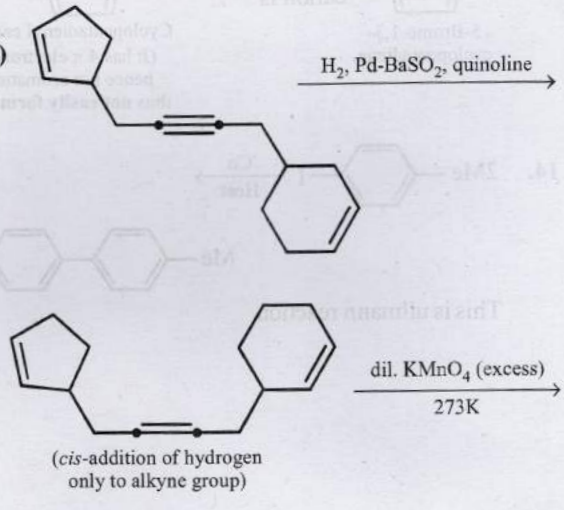
$ROH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$

The tertiary alcohols produce turbidity immediately, the secondary alcohols give turbidity within 5 – 10 minutes, and the primary alcohols do not give turbidity at all, at room temperature. Thus, the order of reactivity of alcohol with Lucas reagent is *tert.* > *sec.* > *pri.*
Hence, 2-methylpropan-2-ol (a 3° alcohol) reacts fastest.

9. **(a)** Among the given options, ethyl alcohol is most basic.

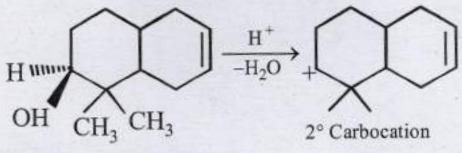
10. **(c)** $C_2H_5OH \xrightarrow[\Delta]{H_2SO_4} C_2H_4 + H_2O$

11. **(6)**

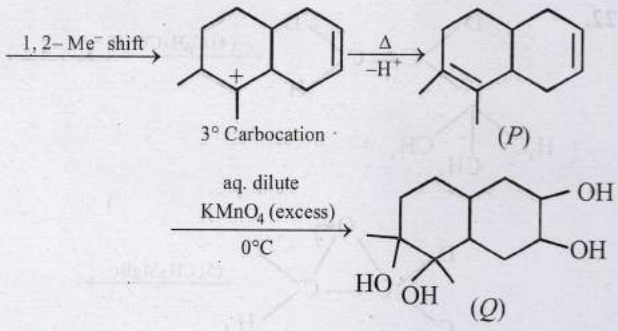


(*cis*-addition of hydrogen only to alkyne group)

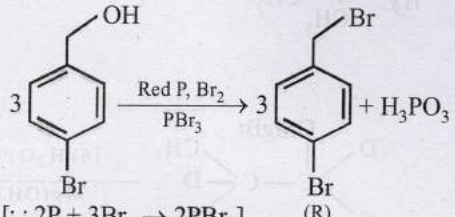
12. **(4)**



2° Carbocation



13. **(1.50)**



$[\because 2P + 3Br_2 \rightarrow 2PBr_3]$

M.W. = 250 g/mol

In Carius method, the halogen present in the organic compound completely forms the silver halide.

$$\text{No. of moles of (R)} = \frac{1\text{ g}}{250\text{ g/mol}} = \frac{1}{250}\text{ mol}$$

1 mol of (R) ≡ 2 mol of Br ≡ 2 mol of AgBr

$$\therefore \frac{1}{250}\text{ mol of (R)} \equiv \frac{2}{250}\text{ mol of Br} \equiv \frac{2}{250}\text{ mol of AgBr}$$

M.W. of AgBr = 108 + 80 = 188 g/mol

$$\therefore \text{The amount of AgBr formed} = \frac{2\times188}{250} = 1.50\text{ g}$$

14. **Secondary.**

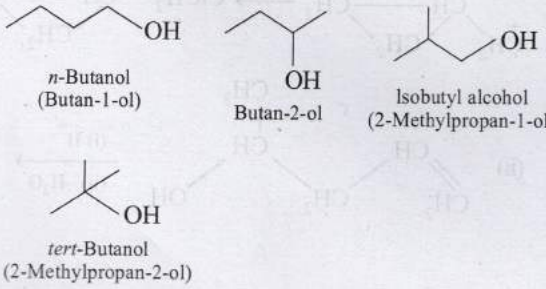
15. **aldol (β-hydroxybutanal);**

$$CH_3CH_2OH \xrightarrow[\text{heat}]{Cu} CH_3CHO \xrightarrow{OH^-} CH_3CH(OH)CH_2CHO$$

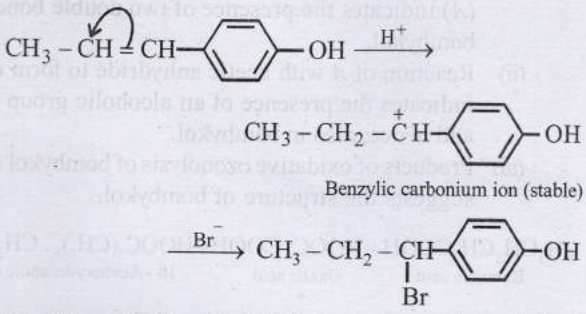
16. **False :** Ethanol is not acidic enough to react with aq. NaOH. Thus, sod. ethoxide (C_2H_5ONa) is prepared by the reaction of Na metal with ethyl alcohol.

$2\,C_2H_5OH + 2Na \rightarrow 2\,C_2H_5ONa + H_2\uparrow$

17. **(a, c, d)** Isomeric alcohols with molecular formula $C_4H_{10}O$ are

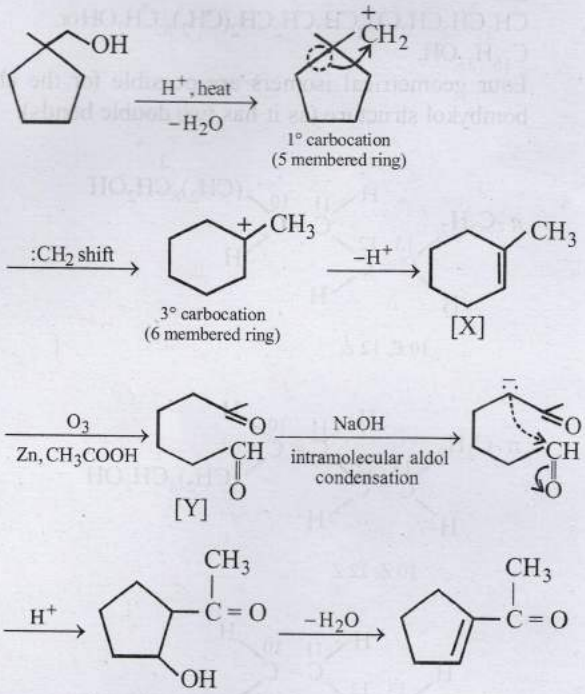


18. **(b)** The mechanism of this reaction is represented as follows.

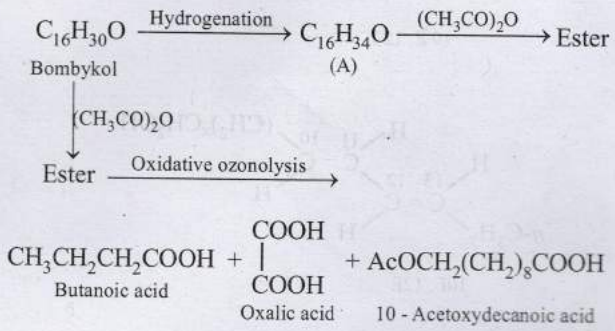


19. **(c)** The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised –OH groups present both in alcohol and water. However, in higher alcohols the hydrocarbon character (alkyl chain) of the molecule increases and thus, alcohols tend to resemble hydrocarbon (which are insoluble in water) and hence, the solubility in water decreases. When the ratio of C to OH is more than 4, alcohols have little solubility in water. So, statement is correct but explanation is not.

20.



21. Let us summarise the given facts.



(i) Hydrogenation of bombykol ($C_{16}H_{30}O$) to $C_{16}H_{34}O$ (*A*) indicates the presence of two double bonds in bombykol.

(ii) Reaction of *A* with acetic anhydride to form ester indicates the presence of an alcoholic group in *A* and hence, also in bombykol.

(iii) Products of oxidative ozonolysis of bombykol ester suggests the structure of bombykol.

$CH_3CH_2CH_2COOH + HOOC.COOH + HOOC.(CH_2)_8.CH_2OAc$

Butanoic acid — Oxalic acid — 10 - Acetoxydecanoic acid

↑ oxidative ozonolysis

$CH_3CH_2CH_2CH=CH-CH=CH.(CH_2)_8.CH_2OAc$

Bombykol ester

The structure of the bombykol ester suggests that bombykol has the following structure :

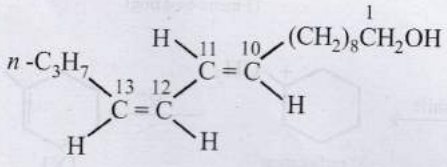
$CH_3CH_2CH_2CH=CH-CH=CH\cdot(CH_2)_8\cdot CH_2OH (C_{16}H_{30}O)$

(Bombykol)

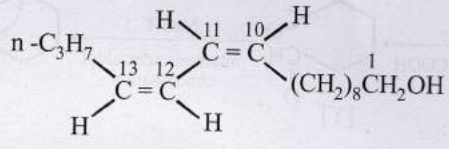
and the structure of *A* is

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2(CH_2)_8.CH_2OH$ or $C_{16}H_{33}OH$.

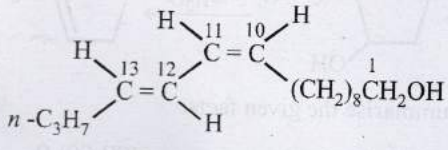
Four geometrical isomers are possible for the above bombykol structure (as it has two double bonds).



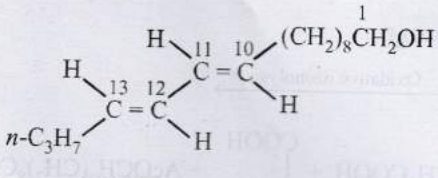
10 E, 12 Z



10 Z, 12 Z

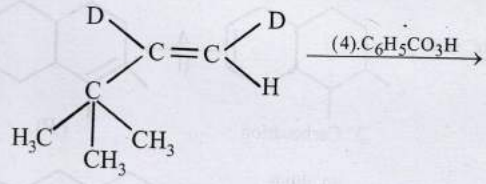


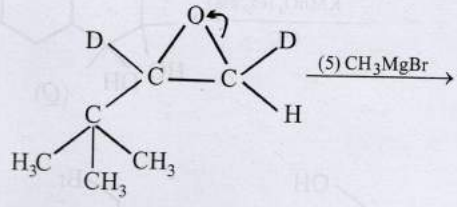
10 Z, 12 E

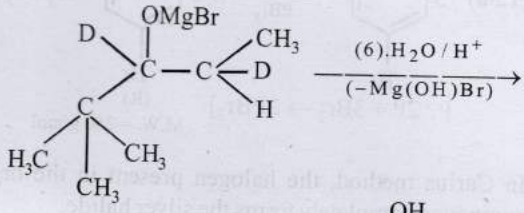


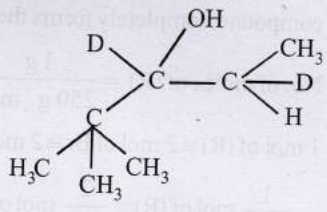
10E, 12E

22.



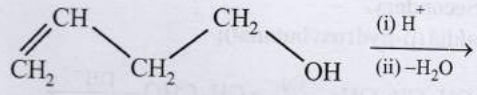


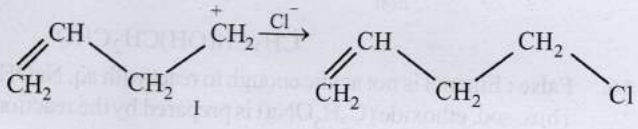


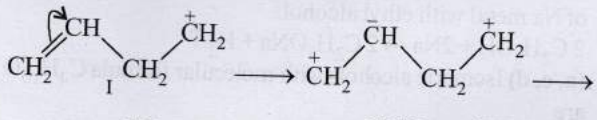


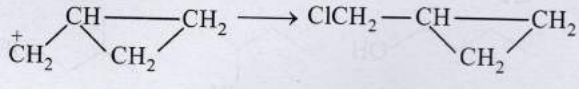
23. (i)

Since the large propenyl group is attached to the carbon atom bearing the hydroxyl group, so the reaction is likely to occur via S_N1 mechanism.

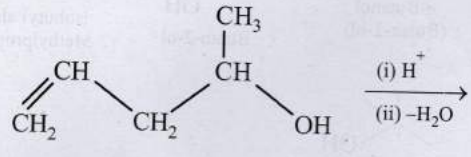


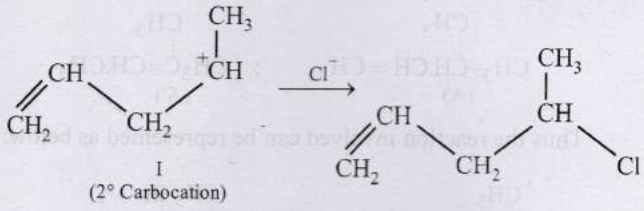






(ii)





I
(2° Carbocation)

In the intermediate carbocation, I, carbon bearing positive charge has CH_3 group which decreases the positive charge and hence prevents cyclisation of the compound.

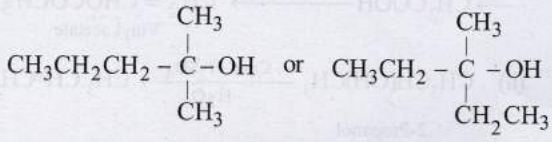
24. Since, 3° carbocation (formed in case of *t*-butanol) is more stable than 1° (formed in *n*-butanol), dehydration in the former proceeds faster than in the latter.

25. (a) Since (B, $C_6H_{14}O$) is resistant to oxidation, it must be *ter*-alcohol.

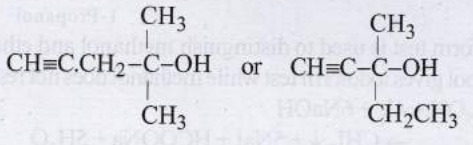
(b) Since (B) is optically inactive, it must have at least two similar alkyl groups.

$$\underset{(A)}{C_6H_{10}O} \xrightarrow{2H_2} \underset{(B)}{C_6H_{14}O}$$

Thus, the five carbon atoms can be adjusted into three alkyl groups (of which two are similar) either as $-CH_3$, $-CH_3$, and $-C_3H_7$, or as $-C_2H_5$, $-C_2H_5$ and $-CH_3$,
Thus the possible structure of alcohol (*B*) is either

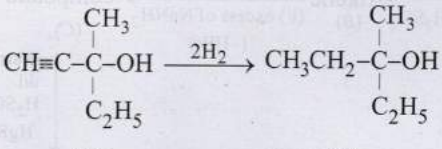


Hence the corresponding compound (*A*) is either



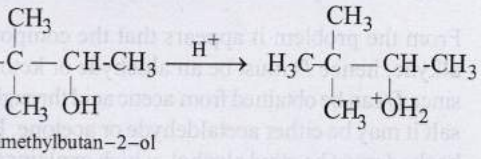
(Option in active) (Optically active)

However, the compound (*A*) is optically active, so (*A*) and hence also (*B*) should have right side structure.

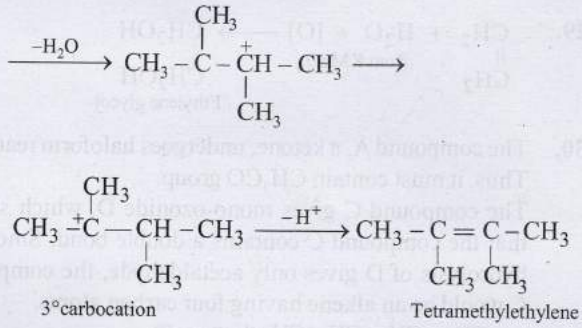


(*A*) (*B*)

26.



3.3–Dimethylbutan–2–ol



3°carbocation Tetramethylethylene

27. *n*-Butanol gives the following reaction in which the purple colour of $KMnO_4$ changes to brown. *tert*-Alcohols are not oxidisable easily, hence purple colour of $KMnO_4$ remains same.

$$\underset{n\text{–Butanol}}{CH_3CH_2CH_2CH_2OH} + \underset{\text{Purple}}{KMnO_4} \longrightarrow$$

$$\underset{(\text{Soluble in } H_2O)}{CH_3CH_2CH_2COOK} + \underset{\text{Brown}}{MnO_2}\downarrow + KOH$$

The brown precipitate is of MnO_2.

28. (i) Since the compound *X* (C_5H_8O) does not react appreciably with Lucas reagent, it indicates that the compound has a primary alcoholic group ($-CH_2OH$).

(ii) Reaction of the compound *X* with ammonical silver nitrate to give a precipitate indicates that it has an acetylenic hydrogen atom, *i.e.*, $\equiv C-H$ grouping is present.

(iii) Treatment of *X* with H_2/Pt followed by boiling with excess of HI gives *n*-pentane. It indicates that the compound does not have any branch.

On the basis of the above points, compound *X* (C_5H_8O) may be assigned following structure.

$$HC \equiv C - CH_2 - CH_2 - CH_2OH$$

(*X*) 4-Pentyn-1-ol (Mol. wt. 84, Eq. wt. = 42)

The above structure for the compound *X* is in accordance with its equivalent weight obtained from the given data.
224 ml. of CH_4 at STP is obtained from 0.42 g

$$22400 \text{ ml. of } CH_4 \text{ at STP} = \frac{0.42}{224} \times 22400 = 42 \text{ g}$$

$\therefore$ Eq. wt. of the compound X = 42

Reactions of the compound X:

(i) $\underset{(X)}{HC \equiv C.CH_2\ CH_2.CH_2OH} \xrightarrow[NH_4OH]{AgNO_3} AgC \equiv C.CH_2CH_2CH_2OH\downarrow$

(ii) $\underset{(X)}{HC \equiv C.CH_2\ CH_2.CH_2OH} \xrightarrow{2CH_3MgBr} MgBrC \equiv C.CH_2CH_2CH_2OMgBr + 2CH_4$

(iii) $\underset{(X)}{HC \equiv C.CH_2\ CH_2.CH_2OH} \xrightarrow{H_2/Pt} CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{HI} \underset{n\text{–Pentane}}{CH_3CH_2CH_2CH_2CH_3}$

29. $CH_2 \parallel CH_2 + H_2O + [O] \xrightarrow[\text{from } KMnO_4]{} CH_2OH | CH_2OH$ (Ethylene glycol)

30. The compound A, a ketone, undergoes haloform reaction. Thus, it must contain CH_3CO group.
The compound C gives mono-ozonide D, which shows that the compound C contains a double bond. Since the hydrolysis of D gives only acetaldehyde, the compound C would be an alkene having four carbon atoms,
i.e. $CH_3-CH=CH-CH_3$ (butene-2).
The compound B is obtained by the reduction of compound A (which contains CH_3CO group). Hence, the compound B would be an alcohol, which on heating with H_2SO_4 gives (C). Hence B and A would be

$CH_3-\underset{\underset{\text{OH}}{|}}{CH}-CH_2-CH_3$ (butan–2–ol (B)) $\qquad CH_3-\overset{\overset{\text{O}}{\|}}{C}-CH_2-CH_3$ (butan–2–one (A))

The reactions involved :

$(A) \xrightarrow{\text{reduction}} (B) \xrightarrow[-H_2O]{\text{conc. } H_2SO_4} CH_3-CH=CH.CH_3$ (C)

$CH_3-CH-O-CH-CH_3 \xrightarrow{O_3} \underset{\text{mono-ozonide (D)}}{\text{O—O}} \xrightarrow{HOH} 2CH_3CHO$

31. For this type of problem, students are advised to summarise the whole problem in the form of reactions.

$H_3C.\underset{\underset{\text{CH}_3}{|}}{CH}.CH_2CH_3 \xleftarrow{H_2} \underset{(C_5H_{10})}{A} \xrightarrow[\text{Markow. addition}]{HBr} \underset{\text{(having Br)}}{B}$
(2–Methylbutane)

$B \xrightarrow{AgOH} \underset{(C_5H_{12}O,\ \text{alcohol})}{C} \xrightarrow{(O)} \underset{\text{(ketone)}}{D}$

Let us draw some conclusions from the above set of reactions.

(i) The molecular formula C_5H_{10} (C_nH_{2n}) for A indicates that it is an alkene having one double bond.

(ii) Since the alcohol C on oxidation gives a ketone D, C must be a secondary alcohol and hence B must be a secondary bromide.

(iii) The structure of 2-methylbutane, the hydrogenated product of A, indicates that the secondary bromide must have following structure.

$CH_3-\underset{\underset{\text{Br}}{|}}{CH}-CH-CH_3$ (B)

(iv) Thus the corresponding olefin A must have structure A which on Markownikoff addition of HBr gives the bromide B, the other possible alkene A' will not give B when HBr is addd on it according to Markownikoff rule.

$CH_3-\underset{\underset{\text{CH}_3}{|}}{CH}.CH=CH_2$ (A) ; $CH_3-\underset{\underset{\text{CH}_3}{|}}{C}=CH.CH_3$ (A')

Thus the reaction involved can be represented as below:

$CH_3-\underset{\underset{\text{CH}_3}{|}}{CH}-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{\underset{\text{Br}}{|}}{\underset{\underset{\text{CH}_3}{|}}{CH}}-CH-CH_3$
(3–Methylbutene–1,A) (2–Bromo–3–methylbutane,B)

$\xrightarrow{AgOH} CH_3-\underset{\underset{\text{CH}_3}{|}}{\underset{\underset{\text{OH}}{|}}{CH}}-CH-CH_3 \xrightarrow{(O)} CH_3-\underset{\underset{\text{CH}_3}{|}}{CH}-\overset{\overset{\text{O}}{\|}}{C}-CH_3$
(3–Methylbutanol–2,C) (3–Methylbutanone–2, D)

32. (i) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[350^\circ C]{Al_2O_3} CH_2=CH_2 \xrightarrow{Br_2} BrCH_2.CH_2Br \xrightarrow[(ii)\ NaNH_2]{(i)\ alc.KOH} CH\equiv CH$

$\xrightarrow{CH_3COOH} \underset{\text{Vinyl acetate}}{CH_2=CHOCOCH_3}$

or $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{[O]} CH_3CHO \longrightarrow CH_3COOH \xrightarrow{CH\equiv CH} \underset{\text{Vinyl acetate}}{CH_2=CHOCOCH_3}$

(ii) $\underset{\text{2-Propanol}}{CH_3CH(OH)CH_3} \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} CH_3.CH=CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3.CH_2.CH_2Br \xrightarrow{\text{aq NaOH}} \underset{\text{1-Propanol}}{CH_3.CH_2.CH_2OH}$

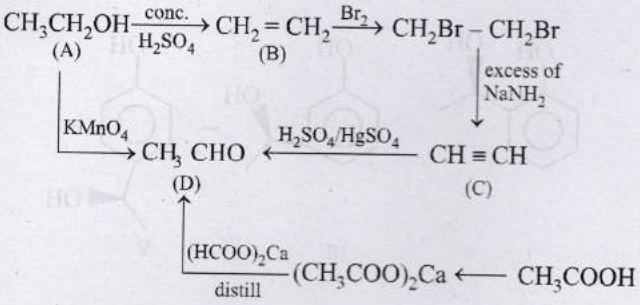
33. Iodoform test is used to distinguish methanol and ethanol. Ethanol gives iodoform test while methanol does not respond.
$C_2H_5OH + 4I_2 + 6NaOH \rightarrow CHI_3\downarrow + 5NaI + HCOONa + 5H_2O$

34. The given problem can be sketched as below.

Alcohol (A) $\xrightarrow[H_2SO_4]{\text{conc}}$ Alkene (B) $\xrightarrow[\text{(ii) excess of } NaNH_2]{\text{(i) } Br_2}$ New compound (C) $\xrightarrow[\text{dil. } H_2SO_4/HgSO_4]{\text{Warm}}$ (D) ← Acetic acid

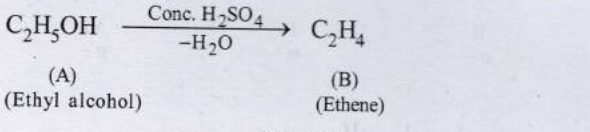
Oxidation

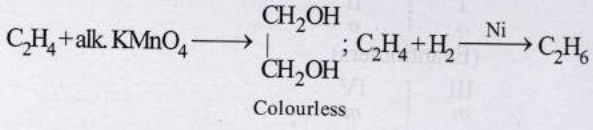
From the problem it appears that the compound *C* is an alkyne, hence *D* must be an aldehyde or ketone. Further, since *D* can be obtained from acetic acid through its calcium salt it may be either acetaldehyde or acetone. Hence going back, *A* must be ethyl alcohol, which explains the given set of reactions.



Hence,
A is ethyl alcohol, CH_3CH_2OH
B is ethylene, $CH_2=CH_2$
C is acetylene, $CH\equiv CH$
D is acetaldehyde, $CH_3.CHO$

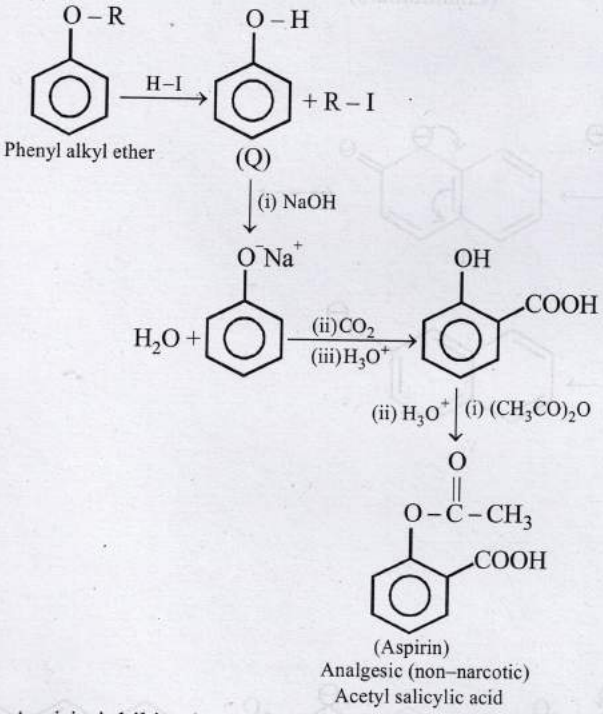
35. 'A' is C_2H_5OH and 'B' is C_2H_4





Topic-2: Preparation and Properties of Phenols

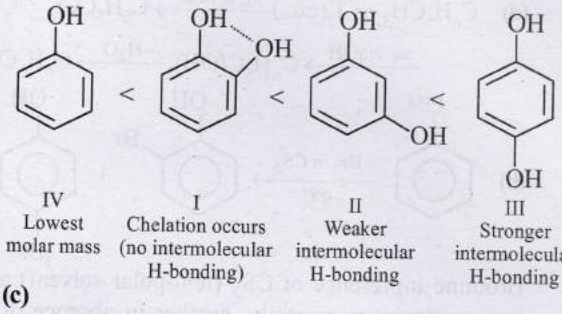
1. **(b)**



Aspirin inhibits the synthesis of prostaglandin.

2. **(d)** In dye test, phenolic — OH group of p-naphthol is converted to — O^- which activates the ring towards electrophilic aromatic substitution.

3. **(d)**



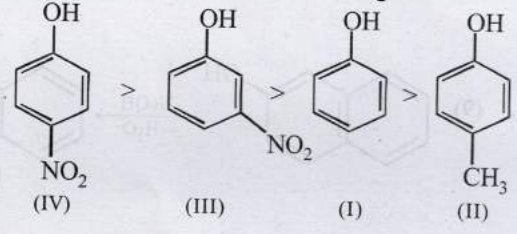
4. **(c)**
(i) The acidity increases with the increase in electronegativity of the halogen present.
(ii) The inductive effect decreases with increase in distance of halogen atom from the carboxylic group and hence, the strength of acid proportionally decreases.

Smallest dissociation constant means weakest acid, which is $BrCH_2CH_2COOH$ because here Br (less electronegative than F) is two carbon atoms away from – COOH

5. **(d)** $-NO_2$ is an electron-attracting group where as $-CH_3$ is an electron-releasing group.

An electron - attracting substituent tends to disperse the negative charge of the phenoxide ion and thus, makes it more stable. This, in turn, **increases the acid strength of phenol.** The substituent in para position is more effective than in the meta position as the former involves a resonating structure bearing negative charge on the carbon attached to the electron - withdrawing substituent.

An **electron - releasing substituent tends to** intensify the negative charge of the phenoxide ion and thus makes it more unstable. This, in turn, **decreases the acid strength of phenol.** Hence, the order of acid strength is



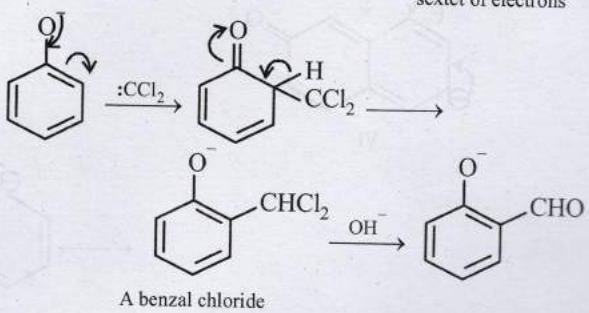
6. **(d)**

Riemer-Tiemann reaction is an electrophilic substitution on the highly reactive phenoxide ring.

$HCCl_3 + OH^- \longrightarrow H_2O + {}^-:CCl_3$

$:\bar{C}Cl_3 \longrightarrow Cl^- + :CCl_2$

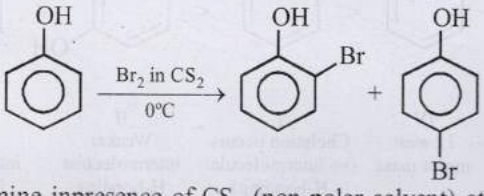
Note the C has only a sextet of electrons



7. **(d)** $C_6H_5CH_3 + Cl_2(exc.) \xrightarrow{\text{light, heat}} C_6H_5CCl_3$

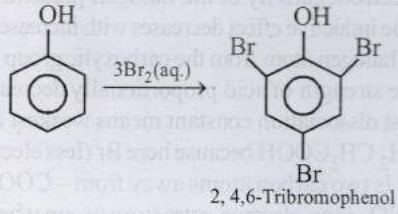
$\xrightarrow{\text{aq. NaOH}} C_6H_5C(OH)_3 \xrightarrow{-H_2O} C_6H_5COOH$

8. **(b)**



Bromine inpresence of CS_2 (non-polar solvent) at low temperature ionises easily. Further in absence of CS_2, polyhalogenation in *o*- and *p*-positions takes place.

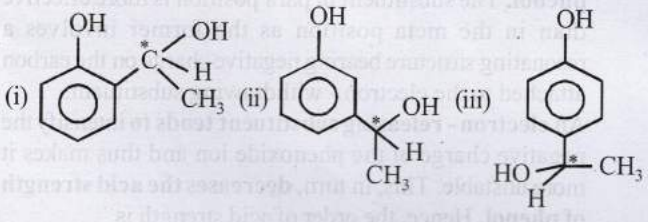
9. **(d)**



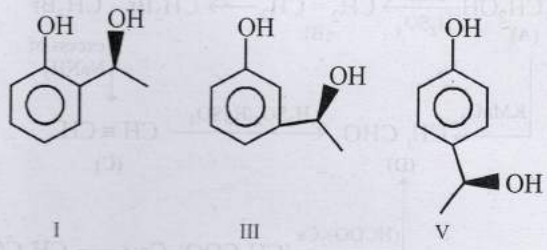
2, 4,6-Tribromophenol

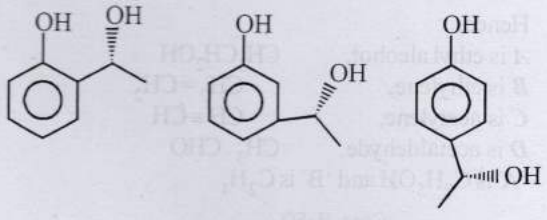
Bromine in water (capalar) solvent ionises earily to give Br^+ ions. Further the –OH group in phenol, being activating group, facilitates substitution in the *o*- and *p*-positions.

10. **(6)** $C_8H_{10}O_2$ gives $FeCl_3$ test means it has phenolic group. It rotates plane polarized light means it is optically active.



(i), (ii), (iii) are optically active and their enantiomers as well.



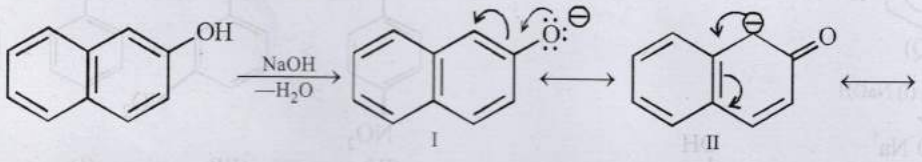


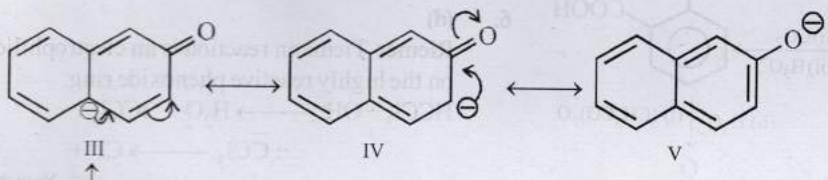
I | II
o | *o*
(Enantiomers)

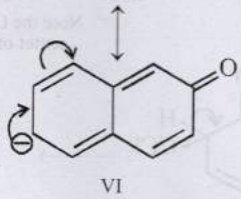
III | IV
m | *m*
(Enantiomers)

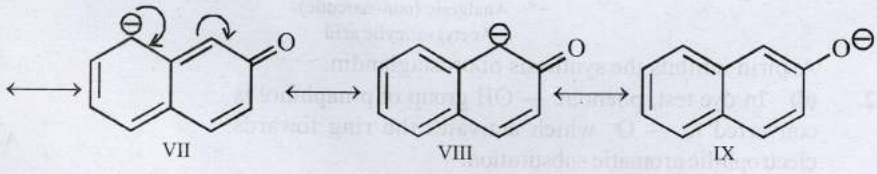
V | VI
p | *p*
(Enantiomers)

11. **(9)**

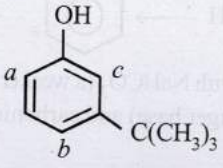




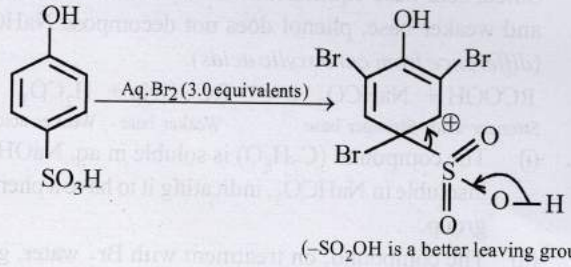




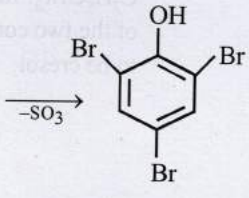
12. **phenoxide ion**
13. **nucleophilic**
14. **resonance stabilization**
15. **(a, b, c)** —OH group is strongly activating and *o*, *p*-directing due to +M effect. Thus positions *a*, *b* and *c* are the sites for attack by an electrophile. However, sites *b* and *c* are not preferred by bulky electrophile due to steric crowding. Thus, more bulky electrophile (like I_2) can attack only site *a*, which is least sterically hindered, a bit smaller electrophile (Br_2) can attack at sites *a* and also *b* (relatively less sterically hindered site) and the smallest electrophile (Cl_2) can attack all the three sites, *viz.*, *a*, *b* and *c* (most sterically hindered site).



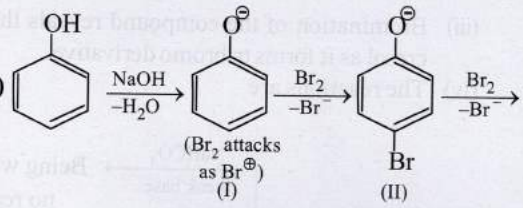
16. **(b)** Phenolic C—OH group is activating and *o*-*p*- directing group.

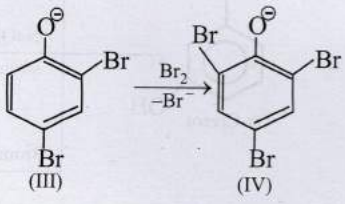


(–SO_2OH is a better leaving group)



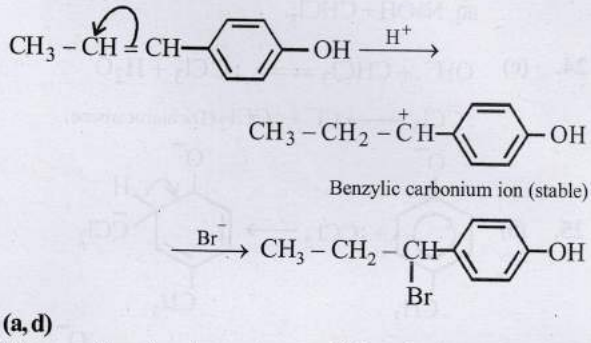
17. **(a, c)**





Product of reaction of phenol with $NaOH/Br_2$ is sodium salt of 2,4,6-tribromophenol. Hence, species (I), (II), (III) are formed as intermediate.

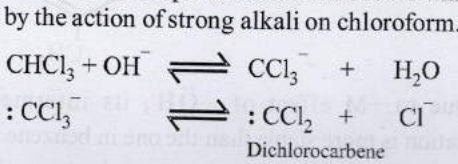
18. **(b)** The mechanism of this reaction is represented as follows.



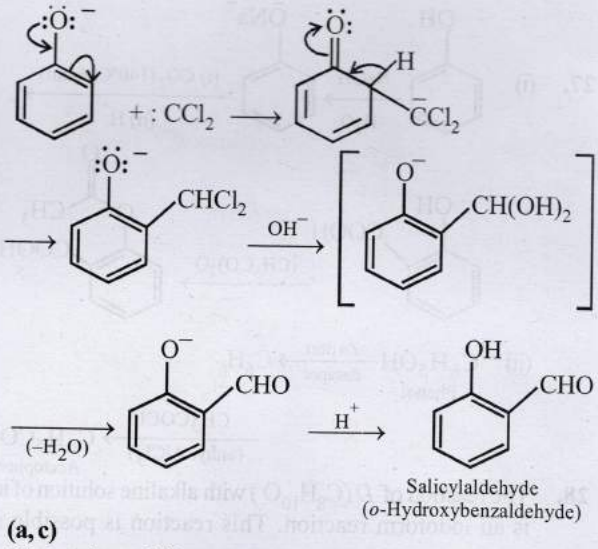
19. **(a, d)**

The reaction involves electrophilic substitution on the highly reactive phenoxide ion.

Here, the electrophile is dichlorocarbene which is formed by the action of strong alkali on chloroform.



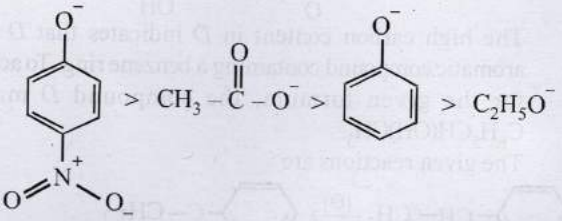
Dichlorocarbene



Salicylaldehyde
(*o*-Hydroxybenzaldehyde)

20. **(a, c)**

Higher the stability of the corresponding anion, more will be the acidic character of the parent compound.



Higher stability of acetate ions than phenoxide ion is due to equivalent resonating structures in the former

21. A. (i) (a) (ii) (c) (iii) (b) (iv) (e) (v) (d)
B. (vi) (h) (vii) (j) (viii) (i) (ix) (g) (x) (f)
C. (xi) (n) (xii) (l) (xiii) (o) (xiv) (m) (xv) (k)
D. (xvi) (t) (xvii) (r) (xviii) (s) (xix) (p) (xx) (q)

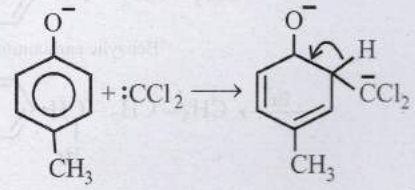
22. (i) (f) (ii) (d) (iii) (b) (iv) (c) (v) (e) (vi) (a)

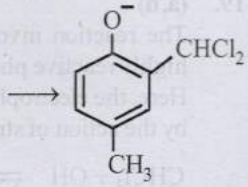
23. **(c)** Reagents for Reimer - Tiemann reaction are aq. $NaOH + CHCl_3$.

24. **(c)** $OH^- + CHCl_3 \rightleftharpoons :\bar{C}Cl_3 + H_2O$

$:\bar{C}Cl_3 \longrightarrow Cl^- + :CCl_2$ (Dichlorocarbene)

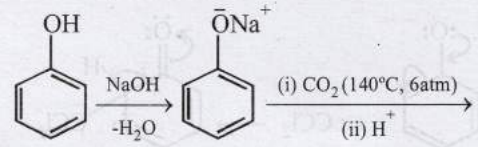
25. **(b)**

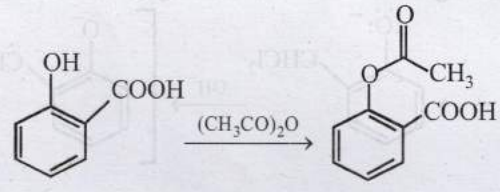




26. **(a)** Due to +M effect of $-\ddot{O}H$, its intermediate carbocation is more stable than the one in benzene.

27. (i)





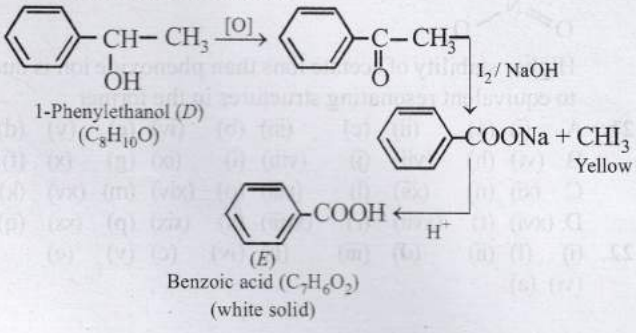
(ii) $C_6H_5OH \xrightarrow[\text{distance}]{\text{Zn dust}} C_6H_6$
Phenol

$\xrightarrow[(\text{anhy. } AlCl_3)]{CH_3COCl} C_6H_5COCH_3$
Acetophenone

28. The reaction of D ($C_8H_{10}O$) with alkaline solution of iodine is an iodoform reaction. This reaction is possible if the compound D has $-\overset{\overset{O}{\|}}{C}-CH_3$ or $-\underset{\underset{OH}{|}}{CH}-CH_3$ group.

The high carbon content in D indicates that D is an aromatic compound containing a benzene ring. To account for the given formula, the compound D may be $C_6H_5CH(OH)CH_3$.

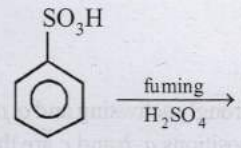
The given reactions are

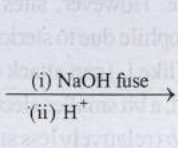


1-Phenylethanol (D) ($C_8H_{10}O$)

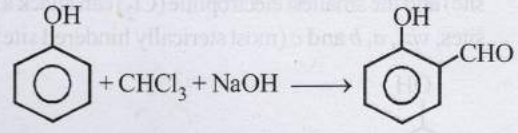
(E) Benzoic acid ($C_7H_6O_2$) (white solid)

29. (i)





(ii)



30. Phenol (a weaker acid) reacts with $NaHCO_3$ (a weaker base) to form phenoxide ion (a stronger base) and carbonic acid (a stronger acid).

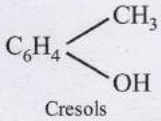
$\underset{\text{Weaker acid}}{C_6H_5OH} + \underset{\text{Weaker base}}{NaHCO_3} \rightleftharpoons \underset{\text{Stronger base}}{C_6H_5ONa} + \underset{\text{Stronger acid}}{H_2CO_3}$

Since, acid-base equilibria lies towards the weaker acid and weaker base, phenol does not decompose $NaHCO_3$ (*difference from carboxylic acids*).

$\underset{\text{Stronger acid}}{RCOOH} + \underset{\text{Stronger base}}{NaHCO_3} \rightleftharpoons \underset{\text{Weaker base}}{RCOONa} + \underset{\text{Weaker acid}}{H_2CO_3}$

31. (i) The compound (C_7H_8O) is soluble in aq. NaOH but insoluble in $NaHCO_3$, indicating it to have a phenolic group.

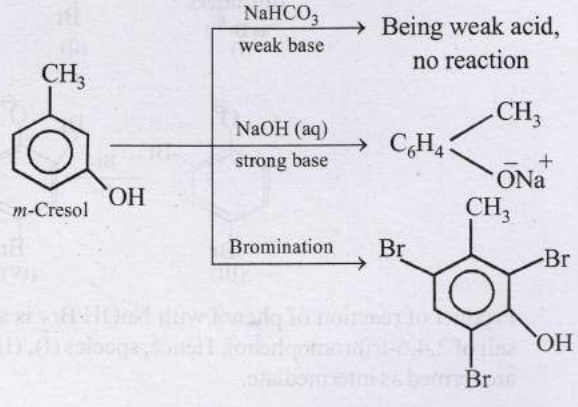
(ii) The compound, on treatment with Br_2 water, gives $C_7H_5OBr_3$. Taking into account of molecular formulae of the two compounds, the parent compound seems to be cresol.



Cresols

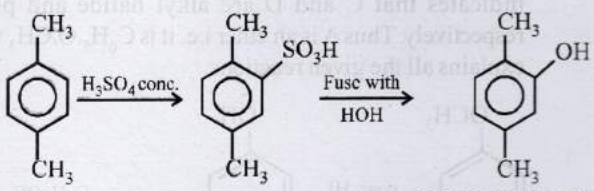
(iii) Bromination of the compound reveals that it is *m*-cresol as it forms tribromo derivative.

(iv) The reactions are



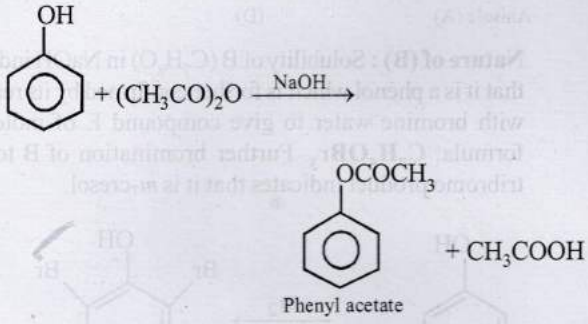
m-Cresol

32.



2, 5- Dimethylphenol

33.

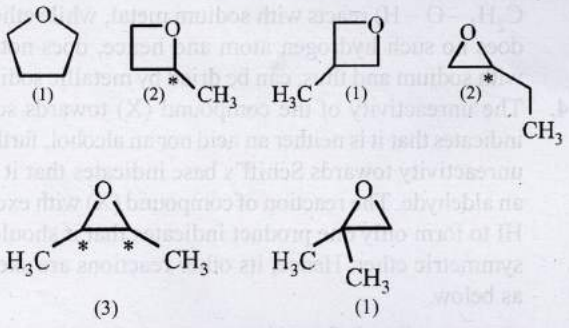


Phenyl acetate

Topic-3: Preparation and Properties of Ethers

1. **(a)** $C_6H_5OCH_3 \xrightarrow{HI} C_6H_5OH + CH_3I$

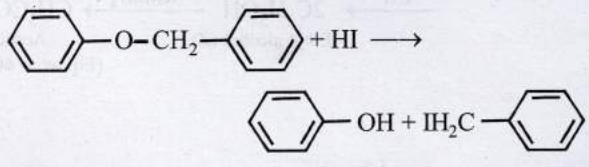
2. **(10)**



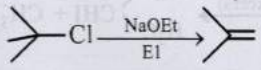
The ether with 2 chiral carbons has a plane of symmetry in *cis*-configuration. Therefore, it will have 3 stereo-isomers.
Total isomers = 1 + 2 + 1 + 2 + 3 + 1 = 10.

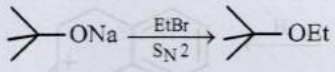
3. **peroxides.** On standing in contact with air, ethers are converted into unstable peroxides ($R_2O \rightarrow O$) *which are highly explosive* even in low concentrations. Hence, *ether is always purified before distillation*. Purification (removal of peroxides) can be done by washing ether with a solution of ferrous salt (which reduces peroxides to alcohols) or by distillation with conc. H_2SO_4 (which oxidises peroxides).

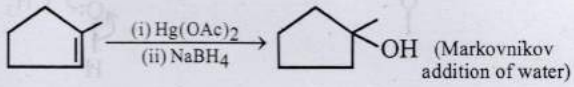
4. **(a, d)**
The given ether is cleaved to give phenol as one of the products because benzyl (a stable carbocations) is formed as an intermediate.

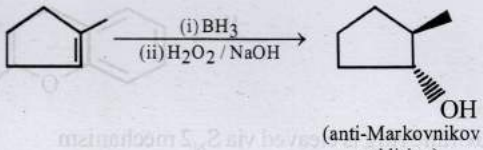


5. **(a)**

(P) 

(Q) 

(R) 

(S) 

(anti-Markovnikov addition)

6. (i)-(b); (ii)-(c); (iii)-(d); (iv)-(a)

7. (i) Molecular formula of *P*, $C_5H_{10}O$ indicates 1° of unsaturation. So, it should have double bond.

(ii) Acidic hydrolysis of *P* to *Q* and *R*, both of which responds iodoform test, indicates that *Q* and *R* should have following structure.

CH_3CH_2OH, $(CH_3)_2CHOH$, CH_3CHO or CH_3COR

The only possible linkage that can explain such hydrolysis is ether. Hence *P* should have following type of structure.

C_2 – Component – O – C_3 – Component

Further either the C_2 – or the C_3 – component should have double bond, thus the possible structure for *P* should be either of the following two structures which explains all the given reactions.

$$CH_2 = CH - \underset{(P)}{O} - CH(CH_3)_2$$

$$\downarrow$$

$$[CH_3CHO \leftrightharpoons CH_2 = CHOH] + HOCH(CH_3)_2$$

(*Q* and *R*), Both responds iodoform test

or

$$CH_3CH_2 - \underset{(P)}{O} - \overset{CH_3}{\overset{|}{C}} = CH_2$$

$$\downarrow$$

$$CH_3CH_2OH + HO - \overset{CH_3}{\overset{|}{C}} = CH_2 \rightleftharpoons O = \overset{CH_3}{\overset{|}{C}} - CH_3]$$

(*Q* and *R*), Both responds iodoform test

Extra reactivity of *P* toward dil. H_2SO_4 than ethylene is due to formation of highly stable carbocation.

$H_3C-\overset{+}{C}H-\ddot{O}-CH(CH_3)_2$ or

2°cabocation

$CH_3CH_2-\ddot{O}-\overset{CH_3}{\overset{+|}{C}}-CH_3$

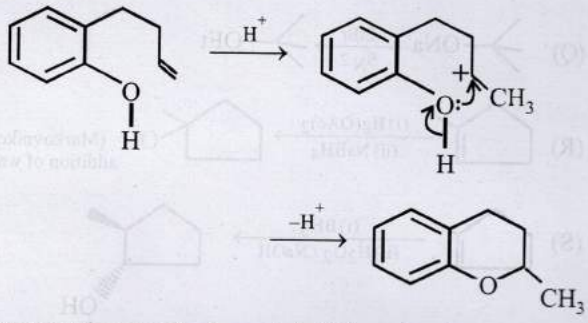
3°carbocation

$CH_2 = CH_2 \xrightarrow{H^+} CH_3\overset{+}{C}H_2$

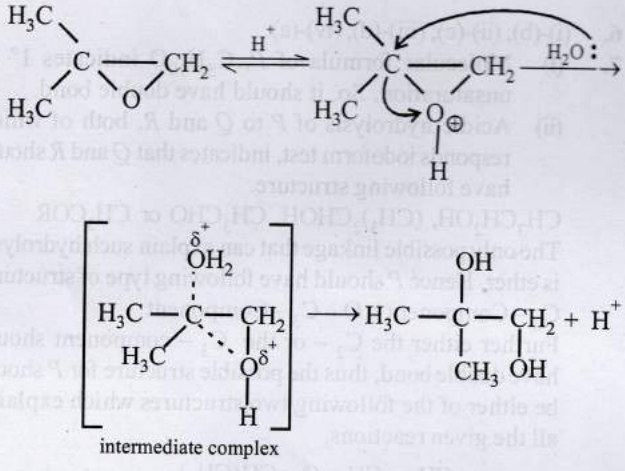
1° carbocation

8. $(H_3C)_2CH-O-CH_3 \xrightarrow{HI\ (Excess)} (H_3C)_2CHI + CH_3I$

9.



10. The oxirane ring is cleaved via S_N2 mechanism



intermediate complex

11. The method given in (ii) is the correct method for the formation of ether because 3° alkyl halides in method (i) leads alkene as the main product.
3° alkyl halides are easily dehydrohalogenated by base.

(i) $(CH_3)_3CBr \xrightarrow[E_2]{CH_3ONa} \underset{\text{Alkene}}{(CH_3)_2C=CH_2}$

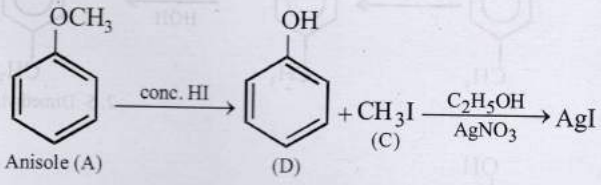
(ii) $CH_3Br + NaOC(CH_3)_3 \xrightarrow[S_N2]{} \underset{\text{Ether}}{CH_3-O-C(CH_3)_3}$

12. Empirical formula of A and B.

	Relative No. of atoms	Simplest ratio
$\%\ of\ C = \frac{12}{44} \times \frac{0.308}{0.108} \times 100 = 77.77$	$\frac{77.77}{12} = 6.48$	$\frac{6.48}{0.92} = 7$
$\%\ of\ H = \frac{2}{18} \times \frac{0.072}{0.108} \times 100 = 7.40$	$\frac{7.40}{1} = 7.40$	$\frac{7.40}{0.92} = 8$
$\therefore \%\ of\ O = 100 - (77.77 + 7.40) = 14.83$	$\frac{14.83}{16} = 0.92$	$\frac{0.92}{0.92} = 1$

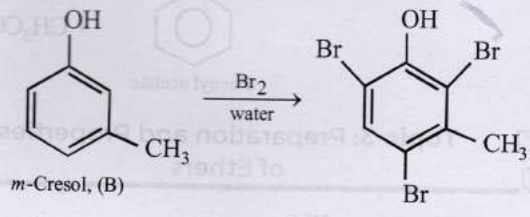
$\therefore$ Empirical formula of A and B = C_7H_8O

Nature of (A) : Since A is insoluble in NaOH and $NaHCO_3$, it can't have –OH and –COOH groups. Further the reaction of A with conc. HI to give compounds C and D separable by means of ammonical $AgNO_3$ and solubility of D in NaOH indicates that C and D are alkyl halide and phenol respectively. Thus A is an ether i.e. it is $C_6H_5.O.CH_3$ which explains all the given reactions.



Anisole (A) (D)

Nature of (B) : Solubility of B (C_7H_8O) in NaOH indicates that it is a phenol which is further confirmed by its reaction with bromine water to give compound E of molecular formula, $C_7H_5OBr_3$. Further bromination of B to give tribromo product indicates that it is *m*-cresol.



m-Cresol, (B) (E), $C_7H_5OBr_3$

13. Ethanol (due to the presence of active hydrogen atom, C_2H_5-O-H) reacts with sodium metal, while ether has does no such hydrogen atom and hence, does not react with sodium and thus, can be dried by metallic sodium.

14. The unreactivity of the compound (X) towards sodium indicates that it is neither an acid nor an alcohol, further its unreactivity towards Schiff's base indicates that it is not an aldehyde. The reaction of compound (X) with excess of HI to form only one product indicates that it should be a symmetric ether. Hence, its other reactions are sketched as below.

$$\underset{(X)}{R-O-R} \xrightarrow[\text{excess of HI}]{\text{Reflux with}} \underset{(Y)}{2RI} \xrightarrow{\text{hydrolysis}} \underset{(Z)}{2ROH}$$

$$\underset{(Z)}{ROH} \xrightarrow[(O)]{KMnO_4} -COOH \quad \text{eq. wt. } 60$$

($P + I_2$ regenerates RI from ROH)

Since, the carboxylic acid has equivalent weight of 60, it must be acetic acid (CH_3COOH). Hence, Z must be ethyl alcohol, (Y) ethyl iodide and (X) diethyl ether.

$$\underset{\text{Diethyl ether (X)}}{C_2H_5-O-C_2H_5} + 2HI \xrightarrow{\text{reflux}} \underset{\text{Ethyl iodide (Y)}}{2C_2H_5I}$$

$$\xrightarrow{OH^-} \underset{\text{Ethyl alcohol (Z)}}{2C_2H_5OH} \xrightarrow{KMnO_4} \underset{\substack{\text{Acetic acid} \\ \text{(Eq. wt. = 60)}}}{CH_3COOH}$$