CHAPTER 19

Alcohols, Phenols and Ethers

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is ..... . *(1983 - 1 Mark)*
2. The acidity of phenol is due to the ..... of its anion. *(1984 - 1 Mark)*
3. Formation of phenol from chlorobenzene is an example of ..... aromatic substitution. *(1989 - 1 Mark)*
4. Phenol is acidic because of resonance stabilization of its conjugate base, namely ..... . *(1990 - 1 Mark)*
5. 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. Glycerine contains one ..... hydroxy group. *(1997 - 1 Mark)*

B True / False

1. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. *(1986 - 1 Mark)*

C MCQs with One Correct Answer

1. 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. 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) $H_3C-\overset{\overset{O}{\|}}{C}-OH$

3. 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

4. A compound that gives a positive iodoform test is *(1982 - 1 Mark)*

(a) 1-pentanol (b) 2-pentanone

(c) 3-pentanone (d) pentanal

5. Diethyl ether on heating with conc. HI gives two moles of *(1983 - 1 Mark)*

(a) ethanol (b) iodoform

(c) ethyl iodide (d) methyl iodide

6. 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

7. 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

8. 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

9. 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

10. Phenol reacts with bromine in carbon disulphide at low temperature to give *(1988 - 1 Mark)*

(a) *m*-bromophenol (b) *o*- and *p*-bromophenol

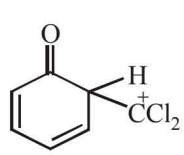
(c) *p*-bromophenol (d) 2, 4, 6-tribromophenol

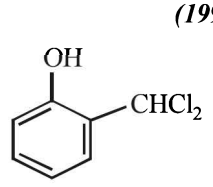
11. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives *(1990 - 1 Mark)*

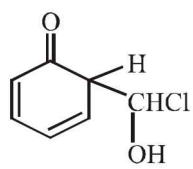
(a) *o*-Cresol (b) *p*-Cresol

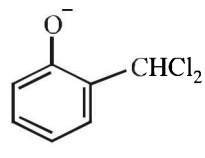
(c) 2, 4-Dihydroxytoluene (d) Benzoic acid

12. 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) 

13. 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) $(CH_3)_3CCl$

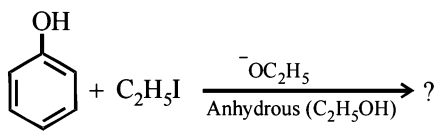
14. 1–Propanol and 2–propanol can be best distinguished by *(2001S)*

(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

15.  *(2003S)*

(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$

(c) $C_6H_5OC_6H_5$ (d) C_6H_5I

16. 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

17. 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

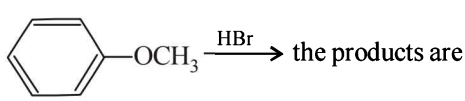
18. The increasing order of boiling points of the below mentioned alcohols is *(2006 - 3M, –1)*

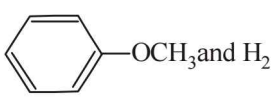
(I) 1,2-dihydroxybenzene (II) 1,3-dihydroxybenzene

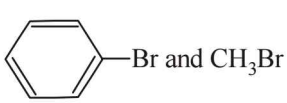
(III) 1,4-dihydroxybenzene (IV) Hydroxybenzene

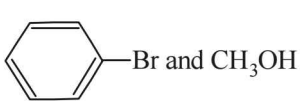
(a) I < II < IV < III (b) I < II < III < IV

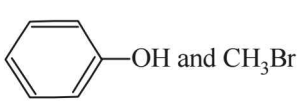
(c) IV < II < I < III (d) IV < I < II < III

19. In the reaction  the products are *(2010)*

(a) 

(b) 

(c) 

(d) 

20. For the identification of β-naphthol using dye test, it is necessary to use *(JEE Adv. 2014)*

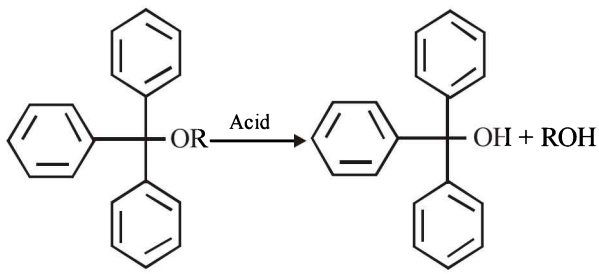
(a) Dichloromethane solution of β-naphthol

(b) Acidic solution of β-naphthol

(c) Neutral solution of β-naphthol

(d) Alkaline solution of β-naphthol

21. The acidic hydrolysis of ether (X) shown below is fastest when *(JEE Adv. 2014)*



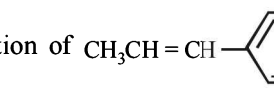
(a) One phenyl group is replaced by a methyl group

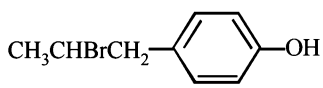
(b) One phenyl group is replaced by a *para*-methoxyphenyl group

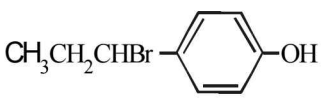
(c) Two phenyl groups are replaced by two *para*-methoxyphenyl groups

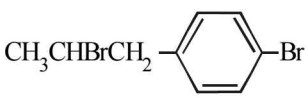
(d) No structural change is made to *X*

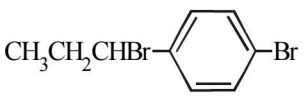
D MCQs with One or More Than One Correct

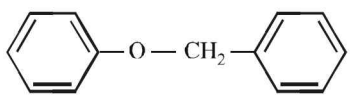
1. The reaction of  with HBr gives *(1998 - 2 Marks)*

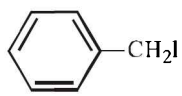
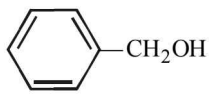
(a) 

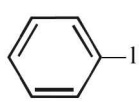
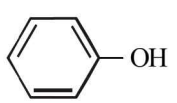
(b) 

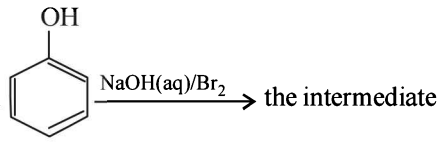
(c) 

(d) 

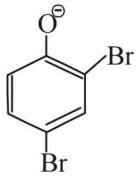
2. The ether  when treated with HI produces *(1999 - 3 Marks)*

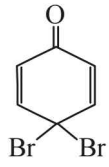
(a)  (b) 

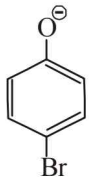
(c)  (d) 

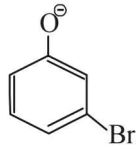
3. In the reaction 

the intermediate (s) is (are) ***(2010)***

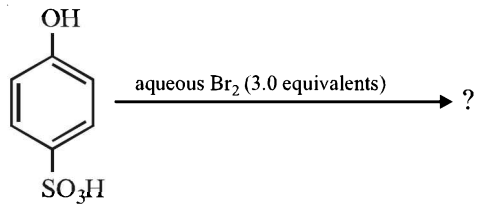
(a) 

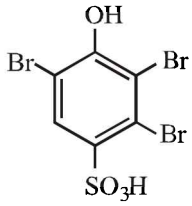
(b) 

(c) 

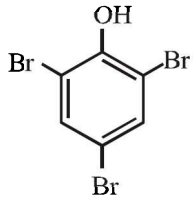
(d) 

4. The major product(s) of the following reaction is(are) ***(JEE Adv. 2013)***

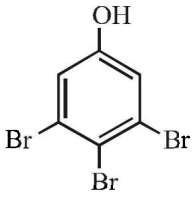




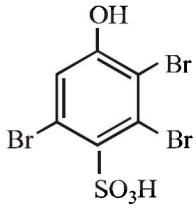
P



Q



R

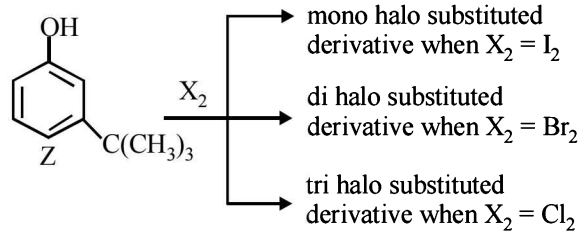


S

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

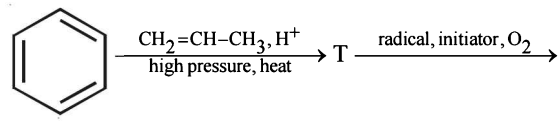
5. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are ***(JEE Adv. 2014)***
(a) Tert-butanol and 2-methylpropan-2-ol
(b) Tert-butanol and 1, 1-dimethylethan-1-ol
(c) n-butanol and butan-1-ol
(d) Isobutyl alcohol and 2-methylpropan-1-ol

6. The reactivity of compound Z with different halogens under appropriate conditions is given below: ***(JEE Adv. 2014)***

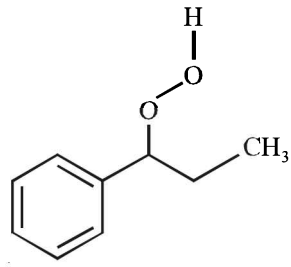


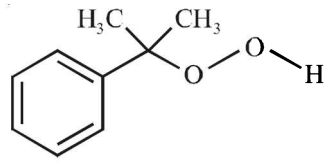
The observed pattern of electrophilic substitution can be explained by
(a) The steric effect of the halogen
(b) The steric effect of the *tert*-butyl group
(c) The electronic effect of the phenolic group
(d) The electronic effect of the *tert*-butyl group

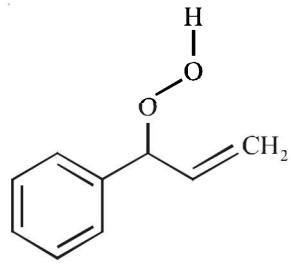
7. The major product U in the following reactions is

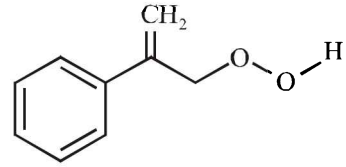


(JEE Adv. 2015)

(a) 

(b) 

(c) 

(d) 

E Subjective Problems

1. 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)***

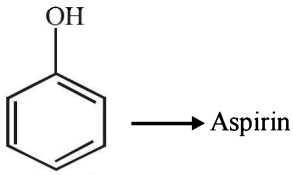
2. A compound (X) containing C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff's reagent. On refluxing with an excess of hydriodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (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)***

3. Outline the reaction sequence for the conversion of

(i) 1-propanol from 2-propanol (in three steps) ***(1982 - 1 Mark)***

(ii) ethyl alcohol to vinyl acetate. (in not more than 6 steps) ***(1986 - 3 Marks)***

(iii) phenol to acetophenone ***(1989 - 1½ Marks)***

(iv) 

(2003 - 2 Marks)

4. State with balanced equations what happens when :

(i) acetic anhydride reacts with phenol in presence of a base. ***(1982 - 1 Mark)***

(ii) Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate. ***(1991 - 1 Mark)***

5. Give reasons for the following :

(i) Sodium metal can be used for drying diethyl ether but not ethanol. ***(1982 - 1 Mark)***

(ii) Phenol is an acid but it does not react with sodium bicarbonate. ***(1987 - 1 Mark)***

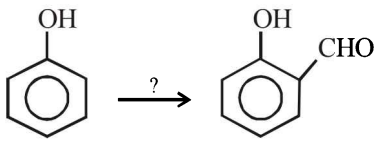
(iii) Acid catalysed dehydration of t-butanol is faster than that of *n*-butanol. ***(1998 - 2 Marks)***

6. 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)***

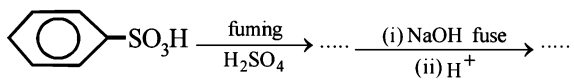
7. A compound of molecular formula C_7H_8O is insoluble in water and dilute sodium bicarbonate but dissolves in dilute aqueous sodium hydroxide. On treatment with bromine water, it readily gives a precipitate of $C_7H_5OBr_3$. Write down the structure of the compound. ***(1985 - 2 Marks)***

8. Give a chemical test/suggest a reagent to distinguish between methanol and ethanol. ***(1985 - 1 Mark)***

9. Complete the following with appropriate structures :

(i) 

(1986 - 1 Mark)

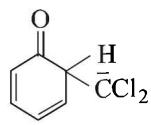
(ii) 

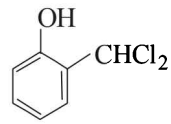
(1992 - 1 Mark)

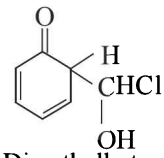
10. Compound 'X' (molecular formula, C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammonical silver nitrate. With excess of MeMgBr, 0.42 g of 'X' gives 224 ml of CH_4 at STP. Treatment of 'X' with H_2 in presence of Pt catalyst followed by boiling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

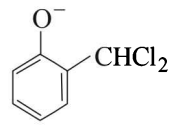
11. When *t*-butanol and *n*-butanol are separately treated with a few drops of dilute $KMnO_4$, in one case only the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? ***(1994 - 2 Marks)***

12. 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)***

(i) 

(ii) 

(iii) 

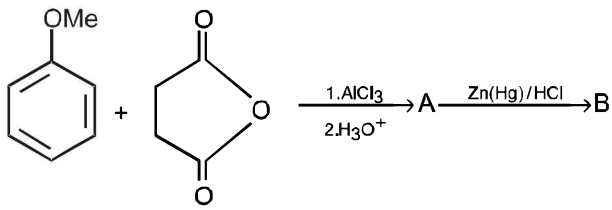
(iv) 

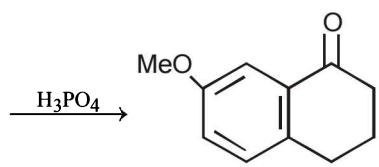
13. 3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. ***(1996 - 2 Marks)***

14. 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)***

15. 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)***

16. Predict the structures of the intermediates/products in the following reaction sequence :





(1996 - 2 Marks)

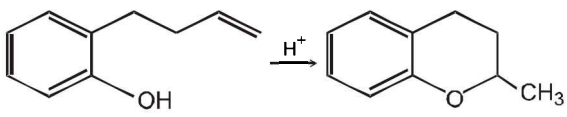
17. 2, 2-Dimethyloxirane can be cleaved by acid (H^+). Write mechanism. ***(1997 - 2 Marks)***

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

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

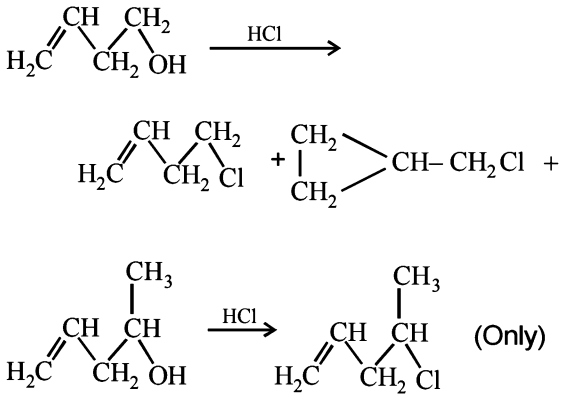
(ii) $CH_3Br + NaO\text{-}t\text{-}Bu \rightarrow$ ***(1997 - 2 Marks)***

19. Write the intermediate steps for each of the following reaction.



(1998 - 1 Mark)

20. Explain briefly the formation of the products giving the structures of the intermediates. ***(1999 - 3 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.

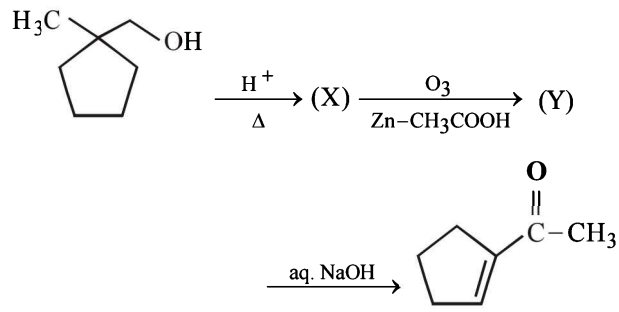
Determine the number of double bonds in bombykol. Write the structures of compound **A** and bombykol. How many geometrical isomers are possible for bombykol?

22. 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)

23. Identify (X) and (Y) in the following reaction sequence.

(2005 - 2 Marks)

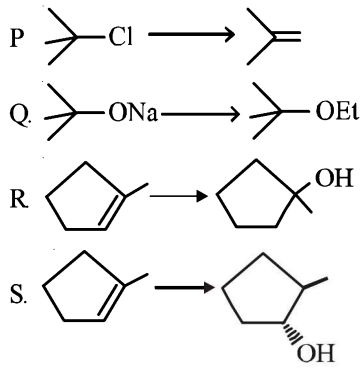


F Match the Following

Following question has matching lists. The codes for the lists have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

1. 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 : ***(JEE Adv. 2013)***

List I **List II**



1. (i) $Hg(OAc)_2$; (ii) $NaBH_4$
2. NaOEt
3. Et-Br
4. (i) BH_3; (ii) H_2O_2/NaOH

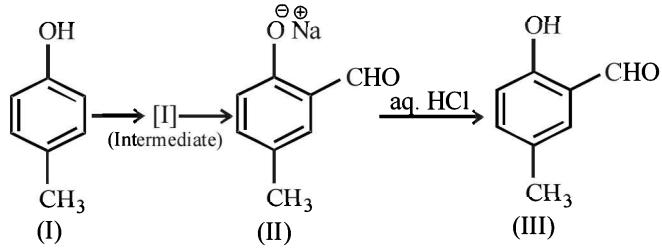
Codes :

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

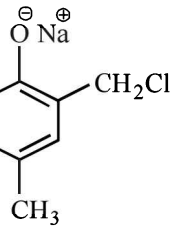
G Comprehension Based Questions

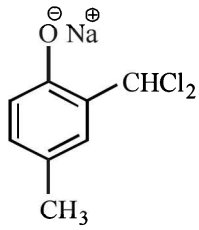
PASSAGE-I

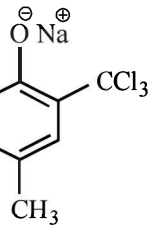
Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehyde as depicted below.

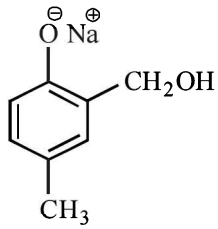


1. Which one of the following reagents is used in the above reaction ? *(2007)*
   (a) aq.NaOH + CH_3Cl (b) aq.NaOH + CH_2Cl_2
   (c) aq.NaOH + $CHCl_3$ (d) aq.NaOH + CCl_4
2. The electrophile in the reaction is *(2007)*
   (a) $:CHCl$ (b) $^+CHCl_2$
   (c) $:CCl_2$ (d) CCl_3
3. The structure of the intermediate I is *(2007)*

(a) 

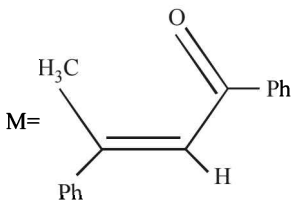
(b) 

(c) 

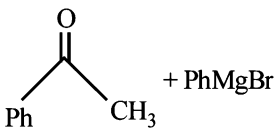
(d) 

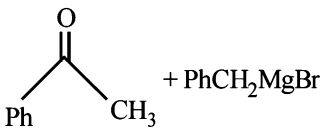
PASSAGE-2

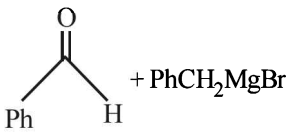
A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and compound L, whereas K on reaction with KOH gives only M.

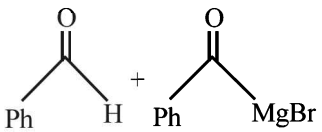
M= 

4. Compound H is formed by the reaction of *(2008)*

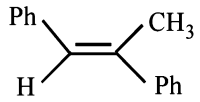
(a) 

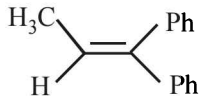
(B) 

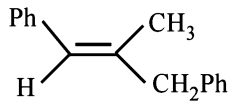
(c) 

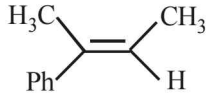
(d) 

5. The structure of compound I is *(2008)*

(a) 

(b) 

(c) 

(d) 

6. The structure of compounds J, K and L respecitvely, are – *(2008)*
   (a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$
   (b) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$
   (c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$
   (d) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$

H Assertion & Reason Type Questions

1. Read the following statement and explanation and answer as per the options given below : *(1988 - 2 Marks)*

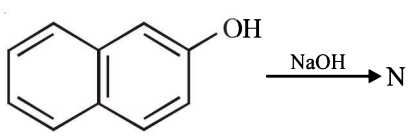
   Statement (S) : Solubility of *n*-alcohols in water decreases with increase in molecular weight.

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

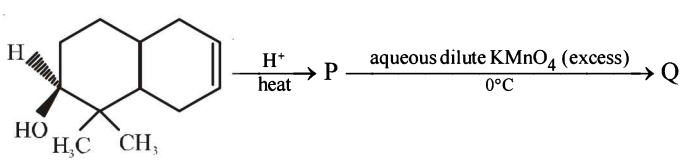
   (a) Both (S) and (E) are correct and (E) is the correct explanation of (S).
   (b) Both (S) and (E) are correct but (E) is not the correct explanation of (S).
   (c) (S) is correct but (E) is wrong.
   (d) (S) is wrong but (E) is correct.

I Integer Value Correct Type

1. The number of resonance structures for N is *(JEE Adv. 2015)*



2. The number of hydroxyl group(s) in Q is *(JEE Adv. 2015)*



Section-B JEE Main / AIEEE

1. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is **[2003]**

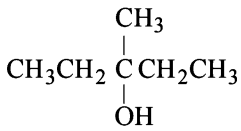
(a) formation of carbocation

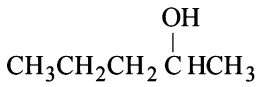
(b) elimination of water

(c) formation of an ester

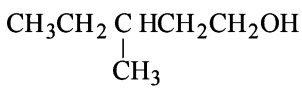
(d) protonation of alcohol molecule

2. Among the following compounds which can be dehydrated very easily is **[2004]**

(a) 

(b) 

(c) $CH_3CH_2CH_2CH_2CH_2OH$

(d) 

3. The best reagent to convert pent-3-en-2-ol into pent-3-in-2-one is **[2005]**

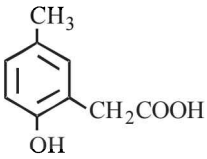
(a) Pyridinium chloro-chromate

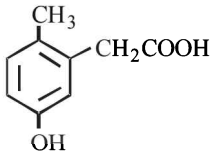
(b) Chromic anhydride in glacial acetic acid

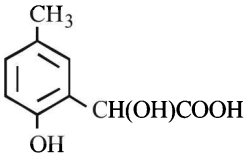
(c) A acidic dichromate

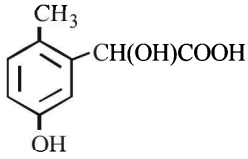
(d) Acidic permanganate

4. p -cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is **[2005]**

(a) 

(b) 

(c) 

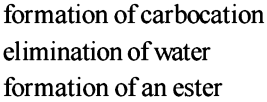
(d) 

5. HBr reacts with $CH_2 = CH - OCH_3$ under anhydrous conditions at room temperature to give **[2006]**

(a) $BrCH_2 - CH_2 - OCH_3$ (b) $H_3C - CHBr - OCH_3$

(c) CH_3CHO and CH_3Br (d) $BrCH_2CHO$ and CH_3OH

6. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is **[2006]**

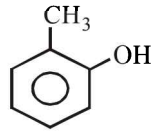
(a) 

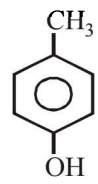
(b) $PhCHOHCH_3$

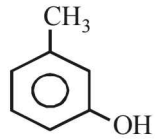
(c) $CH_3CH_2CH(OH)CH_2CH_3$

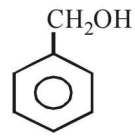
(d) $C_6H_5CH_2CH_2OH$

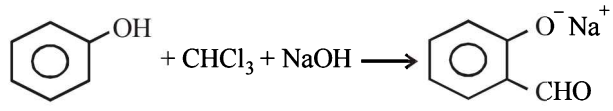
7. The structure of the compound that gives a tribromo derivative on treatment with bromine water is **[2006]**

(a) 

(b) 

(c) 

(d) 

8. 

The electrophile involved in the above reaction is

(a) trichloromethyl anion $(\overset{\ominus}{C}Cl_3)$ **[2006]**

(b) formyl cation $(\overset{\oplus}{C}HO)$

(c) dichloromethyl cation $(\overset{\oplus}{C}HCl_2)$

(d) dichlorocarbene $(:CCl_2)$

9. In the following sequence of reactions,

$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

the compound D is **[2007]**

(a) propanal (b) butanal

(c) *n*-butyl alcohol (d) *n*-propyl alcohol.

10. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives **[2008]**

(a) 2, 4, 6-trinitrobenzene

(b) *o*-nitrophenol

(c) *p*-nitrophenol

(d) nitrobenzene

11. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is **[2009]**

(a) salicylaldehyde (b) salicylic acid
(c) phthalic acid (d) benzoic acid

12. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is **[2010]**

(a) 2-Butanol (b) 2- Methylpropan-2-ol
(c) 2-Methylpropanol (d) 1- Butanol

13. The main product of the following reaction is **[2010]**

$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{conc.H_2SO_4} ?$$

(a) H_5C_6, H, C = C, H, $CH(CH_3)_2$

(b) $C_6H_5CH_2$, H, C = C, CH_3, CH_3

(c) $H_5C_6CH_2CH_2$, H_3C, C = CH_2

(d) C_6H_5, H, C = C, $CH(CH_3)_2$, H

14. Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is : **[2011]**

(a) 2-Bromophenol (b) 3-Bromophenol
(c) 4-Bromophenol (d) 2, 4, 6-Tribromophenol

15. Arrange the following compounds in order of decreasing acidity : **[JEE M 2013]**

OH, Cl (I); OH, CH_3 (II); OH, NO_2 (III); OH, OCH_3 (IV)

(a) II > IV > I > III (b) I > II > III > IV
(c) III > I > II > IV (d) IV > III > I > II

16. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism : **[JEE M 2013]**

(a) secondary alcohol by S_N1
(b) tertiary alcohol by S_N1
(c) secondary alcohol by S_N2
(d) tertiary alcohol by S_N2

17. Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces C.

ONa $+CO_2 \xrightarrow[5\ Atm]{125°C}$ B $\xrightarrow[Ac_2O]{H^+}$ C

The major product C would be **[JEE M 2014]**

(a) $OCOCH_3$, $COOH$ (b) OH, $COCH_3$, $COCH_3$

(c) OH, $COOCH_3$ (d) $OCOCH_3$, $COOH$

18. Thiol group is present in : **[JEE M 2016]**

(a) Cysteine (b) Methionine
(c) Cytosine (d) Cystine

19. The product of the reaction given below is: **[JEE M 2016]**

$\xrightarrow[2.\ H_2O/K_2CO_3]{1.\ NBS/hv}$ X

(a) O (b) CO_2H

(c) (d) OH

20. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields: **[JEE M 2016]**

(1) $C_2H_5CH_2C(CH_3)_2OCH_3$ (2) $C_2H_5CH_2C(CH_3)=CH_2$

(3) $C_2H_5CH=C(CH_3)-CH_3$

(a) (3) only (b) (a) and (b)
(c) All of these (d) (a) and (c)

19 Alcohols, Phenols and Ethers

Section-A : JEE Advanced/ IIT-JEE

A **1.** aldol (β-hydroxybutanal) **2.** resonance stabilization **3.** nucleophilic **4.** phenoxide ion
5. peroxides **6.** secondary

B **1.** F

C

1.	(c)	**2.**	(a)	**3.**	(d)	**4.**	(b)	**5.**	(c)	**6.**	(a)	**7.**	(d)
8.	(a)	**9.**	(c)	**10.**	(b)	**11.**	(d)	**12.**	(d)	**13.**	(a)	**14.**	(c)
15.	(b)	**16.**	(c)	**17.**	(b)	**18.**	(d)	**19.**	(d)	**20.**	(d)	**21.**	(c)

D **1.** (b) **2.** (a, d) **3.** (a, c) **4.** (b) **5.** (a, c, d) **6.** (a, b, c) **7.** (b)

E **1.** A is C_2H_5OH and B is C_2H_4

X Y Z A

2. $C_2H_5OC_2H_5$, C_2H_5I, C_2H_5OH

7. *m*-cresol

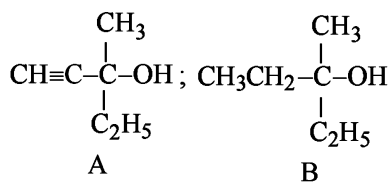
10. $HC \equiv C.CH_2.CH_2.CH_2OH$

11. *n*-butanol, MnO_2

14. $C_6H_5CH(OH)CH_3$, C_6H_5COOH

D E

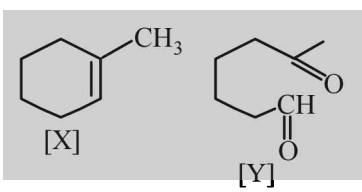
15.



A B

21. $CH_3CH_2CH_2CH = CH - CH = CH.(CH_2)_8.CH_2OH$ (Bombykol)

23.



F **1.** (a)

G **1.** (c) **2.** (c) **3.** (b) **4.** (b) **5.** (a) **6.** (d)

H **1.** (c)

I **1.** 9 **2.** 4

Section-B : JEE Main/ AIEEE

1.	(d)	**2.**	(a)	**3.**	(a)	**4.**	(c)	**5**	(b)	**6.**	(b)
7.	(c)	**8.**	(d)	**9.**	(d)	**10.**	(b)	**11.**	(b)	**12.**	(b)
13.	(a)	**14.**	(d)	**15.**	(c)	**16.**	(b)	**17.**	(a)	**18.**	(a)
19.	(d)	**20.**	(a)								

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **aldol (β-hydroxybutanal);**

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

2. **resonance stabilization**
3. **nucleophilic**
4. **phenoxide ion**
5. **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)
6. **Secondary.**

B. True / False

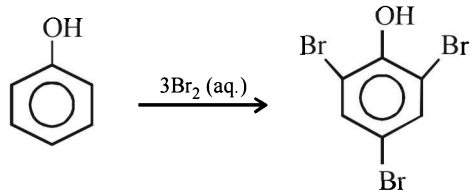
1. **False :** Ethanol is not acidic enough to react with aq. NaOH. Thus sod. ethoxide (C_2H_5ONa) is prepared by the reaction of Na metal with ethyl alcohol.
$2\,C_2H_5OH + 2Na \rightarrow 2\,C_2H_5ONa + H_2\uparrow$

C. MCQs with ONE Correct Answer

1. **(c)** $2C_2H_5OH \xrightarrow[\Delta]{H_2SO_4} C_2H_4 + H_2O$
2. **(a)**
3. **(d)** **TIPS/Formulae :**
The order of reactivity of alcohol with Lucas reagent is *tert.* > *sec.* > *pri.*
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.
Hence 2-methylpropan-2-ol (a 3° alcohol) reacts fastest.
4. **(b)** **TIPS/Formulae :**
Compounds having $-\overset{\overset{O}{\|}}{C}-CH_3$ groups show positive iodoform test.
Hence, $CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ (pentanone-2) gives this test.
5. **(c)** $C_2H_5OC_2H_5 + 2\,HI \xrightarrow{\Delta} 2\,C_2H_5I + H_2O$
6. **(a)** $\underbrace{CO + H_2}_{\text{water gas}} + H_2 \xrightarrow[300°C]{Cr_2O_3 - ZnO} \underset{\text{Methanol}}{CH_3OH}$
7. **(d)**

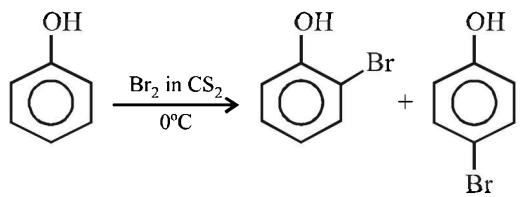


2, 4,6-Tribromophenol

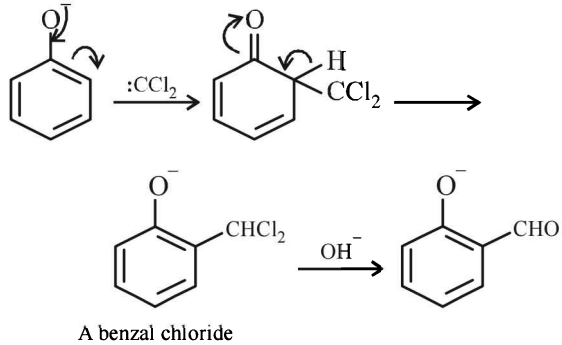
NOTE :
The –OH group in phenol, being activating group, facilitates substitution in the *o*- and *p*-positions.
8. **(a)** Reactions involving cleavage of carbon-oxygen bond, (C – OH) follows the following order :
Tertiary > Secondary > Primary
9. **(c)** **TIPS/Formulae :**
Secondary alcohols oxidise to produce kenone.

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

10. **(b)**

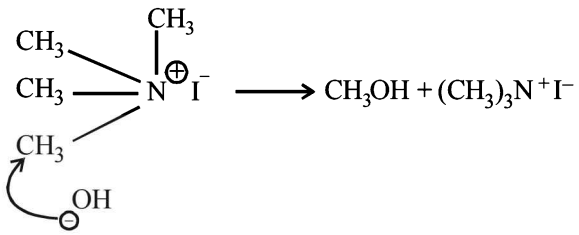


NOTE : In absence of CS_2, polyhalogenation in *o*- and *p*-positions takes place.
11. **(d)** $C_6H_5CH_3 + Cl_2(\text{exc.}) \xrightarrow{\text{light, heat}} C_6H_5CCl_3$
$\xrightarrow{\text{aq. NaOH}} C_6H_5C(OH)_3 \xrightarrow{-H_2O} C_6H_5COOH$
12. **(d)** **TIPS/Formulae :**
Riemer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring.
$HCCl_3 + OH^- \longrightarrow H_2O + {}^-:CCl_3$
$:\bar{C}Cl_3 \longrightarrow Cl^- + \underset{\substack{\text{Note the C has only a}\\ \text{sextet of electrons}}}{:CCl_2}$



A benzal chloride

13. (a) **TIPS/Formulae :**
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^-



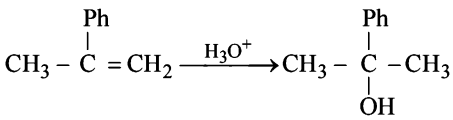
14. (c) **NOTE :**
Fehling solution is a weak oxidising agent which can oxidise aldehyde but not ketone.
Primary alcohols undergoes oxidation with alkaline $KMnO_4$, acidic dichromate and conc. H_2SO_4 to give acids, whereas with Cu they give aldehydes.

$$\underset{\text{Propalol-1}}{CH_3CH_2CH_2OH} \xrightarrow[\text{heat}]{Cu} \underset{\substack{\text{Propanal}\\ \textbf{(responds Fehling solution)}}}{CH_3CH_2CHO}$$

$$\underset{\text{Propalol-2}}{CH_3CHOHCH_3} \longrightarrow \underset{\substack{\text{Propanon}\\ \text{(negative to Fehling solution)}}}{CH_3COCH_3}$$

15. (b) **NOTE :** This reaction is an example of Williamson's synthesis.
$C_2H_5O^-$ will abstract proton from phenol converting the latter into phenoxide ion. This would then make nucleophilic attack on the methylene carbon of alkyl iodide forming $C_6H_5OC_2H_5$. But if $C_2H_5O^-$ is in excess, $C_2H_5OC_2H_5$ will be formed. $C_2H_5O^-$ is a better nucleophile than $C_6H_5O^-$ (phenoxide) ion because in the former the negative charge is localised over oxygen, while in the latter it is delocalised over the whole molecular framework. So, it is $C_2H_5O^-$ ion that would make nucleophilic attack at ethyl iodide to give diethyl ether (Williamson's synthesis).

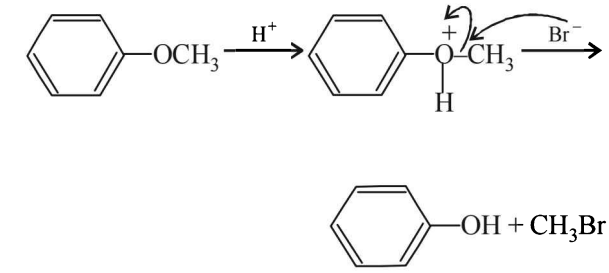
16. (c) **NOTE :** Addition of water to 2-phenylpropene follows Markownikov's rule.



17. (b) **TIPS/Formulae :**
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.

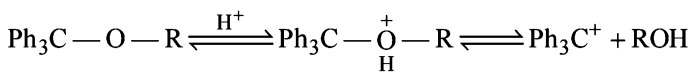
18. (d) Among the given compounds, hydroxybenzene (IV) has least molar mass and therefore possess least boiling point. Among the three isomeric dihydroxybenzenes, 1,2-dihydroxybenzene (I) forms intramolecular H-bonding with the result it will not form intermolecular H-bonding leading to lowest boiling point. On the other hand 1,3-dihydroxybenzene (II) and 1, 4-dihydroxybenzene (III) do not undergo chelation, hence they will involve extensive intermolecular H-bonding leading to higher boiling point. Further intermolecular hydrogen bonding is stronger in the *p*-isomer than the m-isomer hence former has highest b.p. Thus the decreasing order of boiling points is III > II > I > IV.

19. (d)



20. (d) In dye test, phenolic — OH group is converted to $-O^-$ which activates the ring towards electrophilic aromatic substitution

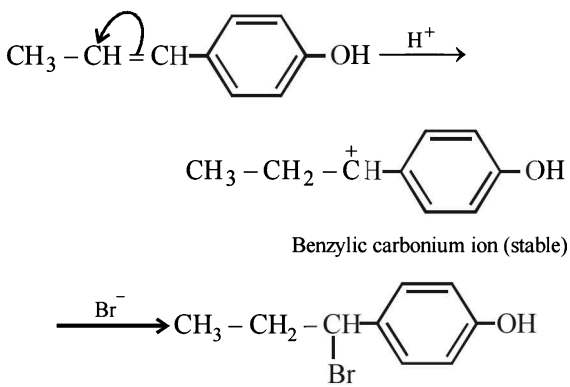
21. (c) The given reaction proceeds through S_N1 mechanism which involves carbocation as intermediate.



Thus, higher the stability of the carbocation, greater will be reactivity. Presence of electron releasing group (e.g., $-OCH_3$) in *p*-position of the phenyl group will disperse the positive charge of the carbocation by +M effect, hence stabilizes the carbocation.

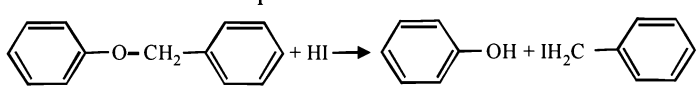
D. MCQs with ONE or More Than One Correct

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

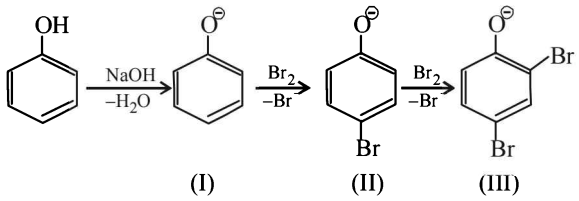


Benzylic carbonium ion (stable)

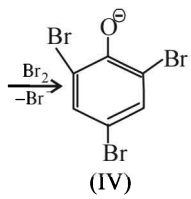
2. (a, d) **TIPS/Formulae :**
The aromatic ethers are cleaved to give phenol as one of the products.



3. **(a, c)**



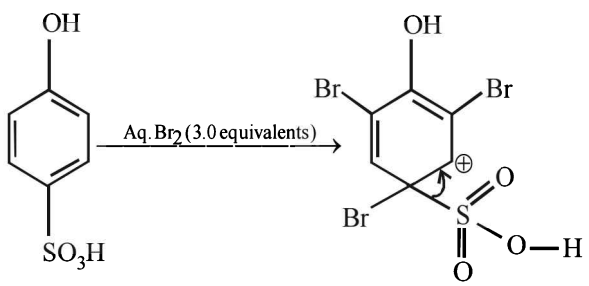
(I) (II) (III)

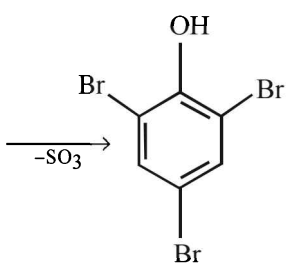


(IV)

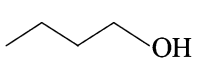
Product of reaction of phenol with $NaOH/Br_2$ is sodium salt of 2,4,6-tribromophenol. Hence, species (I), (II), (III) are formed as intermediate.

4. **(b)**

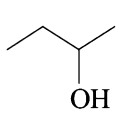




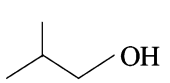
5. **(a, c, d)** Isomeric alcohols with molecular formula $C_4H_{10}O$ are



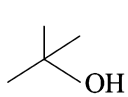
n-Butanol
(Buta-1-ol)



Butan-2-ol

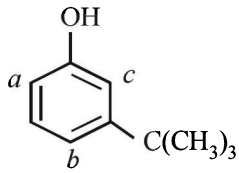


Isobutyl alcohol
(2-methylpropan-1-ol)

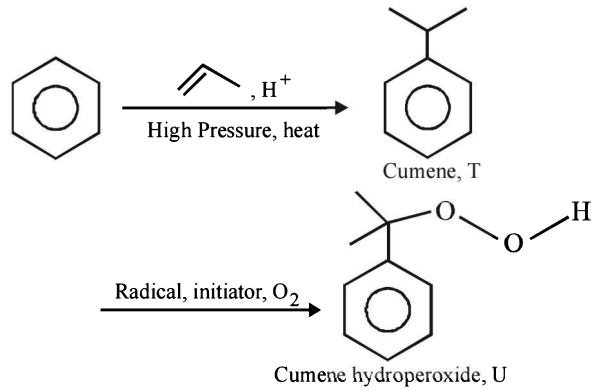


tert-Butanol
(2-methylpropan-2-ol)

6. **(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).



7. **(b)**



Cumene hydroperoxide, U

E. Subjective Problems

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

$$\underset{\text{(A) (ethyl alcohol)}}{C_2H_5OH} \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} \underset{\text{(B) (ethene)}}{C_2H_4}$$

$$C_2H_4 + \text{alk. } KMnO_4 \longrightarrow \underset{\text{Colourless}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}}; \quad \underset{\text{ethene}}{C_2H_4} + H_2 \xrightarrow{Ni} \underset{\text{ethane}}{C_2H_6}$$

2. **TIPS/Formulae :**

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 an ether.

Hence its other reactions are sketched as below.

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

$$\underset{\text{(Y)}}{RI} \xrightarrow{P + I_2} \underset{\text{(Z)}}{ROH}$$

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

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.

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

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

3. (i) $\underset{\text{2-propanol}}{CH_3CH(OH)CH_3} \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} CH_3.CH=CH_2$

$$CH_3.CH_2.CH_2Br \xrightarrow[\text{peroxide}]{HBr} \xrightarrow{\text{aq NaOH}} CH_3.CH_2.CH_2OH$$

1-propanol

(ii) $CH_3CH_2OH \xrightarrow[350^\circ C]{Al_2O_3} CH_2=CH_2$

Ethanol

$$\xrightarrow{Br_2} BrCH_2.CH_2Br \xrightarrow[KOH]{\text{alc.}} CH\equiv CH$$

$$\xrightarrow{CH_3COOH} CH_2=CHOCOCH_3$$

Vinyl acetate

or $CH_3CH_2OH \xrightarrow{\text{Oxi.}} CH_3CHO$

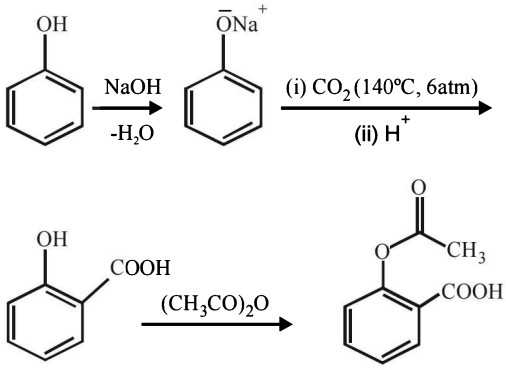
Ethanol

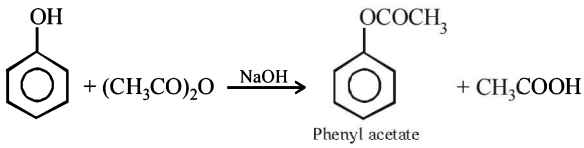
$$\longrightarrow CH_3COOH \xrightarrow{CH\equiv CH} CH_2=CHOCOCH_3$$

Vinyl acetate

(iii) $C_6H_5OH \xrightarrow[\text{distillation}]{Zn} C_6H_6 \xrightarrow[(\text{anhy. } AlCl_3)]{CH_3COCl} C_6H_5COCH_3$

Phenol — Acetophenone

(iv) 

4. (i) 

Phenyl acetate

(ii) $\underset{\|}{CH_2}{}_{CH_2} + H_2O + [O] \xrightarrow{\text{from } KMnO_4} \underset{|}{CH_2OH}{}_{CH_2OH}$

Ethylene glycol

5. (*i*) Ethanol (due to the presence of active hydrogen atom, $C_2H_5 - O - H$) reacts with sodium metal, while ether and benzene have no such hydrogen atom and hence do not react with sodium and thus can be dried by metallic sodium.

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

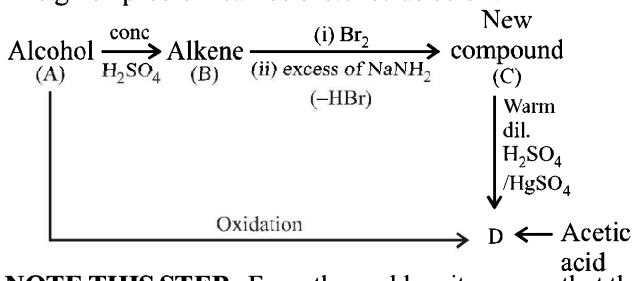
$$\underset{\text{Weaker acid}}{C_6H_5OH} + \underset{\text{Weaker base}}{NaHCO_3} \rightleftharpoons \underset{\text{Stronger base}}{C_6H_5ONa} + \underset{\text{Stronger acid}}{H_2CO_3}$$

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

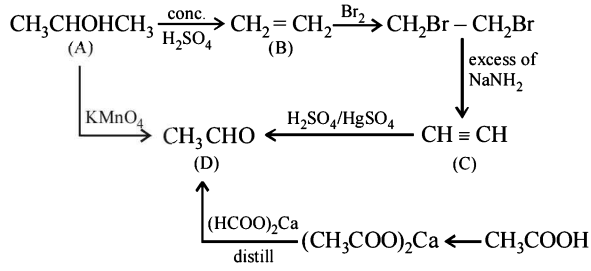
$$\underset{\text{Stronger acid}}{RCOOH} + \underset{\text{Stronger base}}{NaHCO_3} \rightleftharpoons \underset{\text{Weaker base}}{RCOONa} + \underset{\text{Weaker acid}}{H_2CO_3}$$

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

6. The given problem can be sketched as below.



NOTE THIS STEP : 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 may be either ethyl alcohol or *iso*-propanol both of which explains the given set of reactions.



Hence

A is ethyl alcohol, CH_3CH_2OH

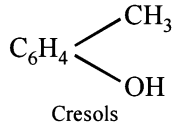
B is ethylene, $CH_2=CH_2$

C is acetylene, $CH\equiv CH$

D is acetaldehyde, $CH_3.CHO$

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

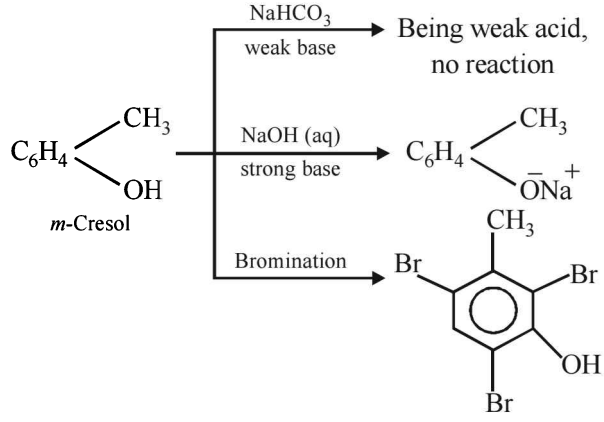
(ii) The compound, on treatment with Br_2 water, gives $C_7H_5OBr_3$. Taking into account of molecular formulae of the two compounds, the parent compound seems to be cresol.



Cresols

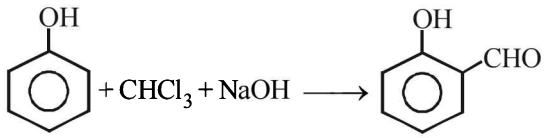
(iii) Bromination of the compound reveals that it is *m*-cresol as it forms tribromo derivative.

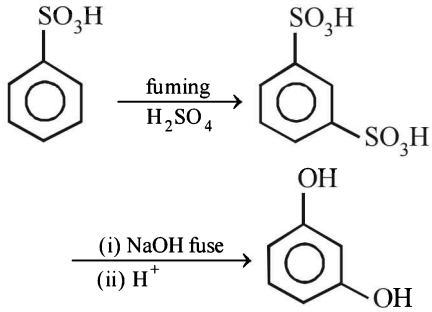
(iv) The reactions are



8. **TIPS/Formulae :**
Iodoform test is used to distinguish methanol and ethanol. Ethanol gives iodoform test while methanol does not respond.

$$C_2H_5OH + 4I_2 + 6NaOH \rightarrow CHI_3\downarrow + 5NaI + HCOONa + 5H_2O$$

9. (*i*) 

(*ii*) 

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

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

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

11. *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.

$$\underset{n\text{–butanol}}{CH_3CH_2CH_2CH_2OH} + \underset{\text{Purple}}{KMnO_4} \longrightarrow CH_3CH_2CH_2COOK + \underset{\text{Brown}}{MnO_2}\downarrow + KOH$$

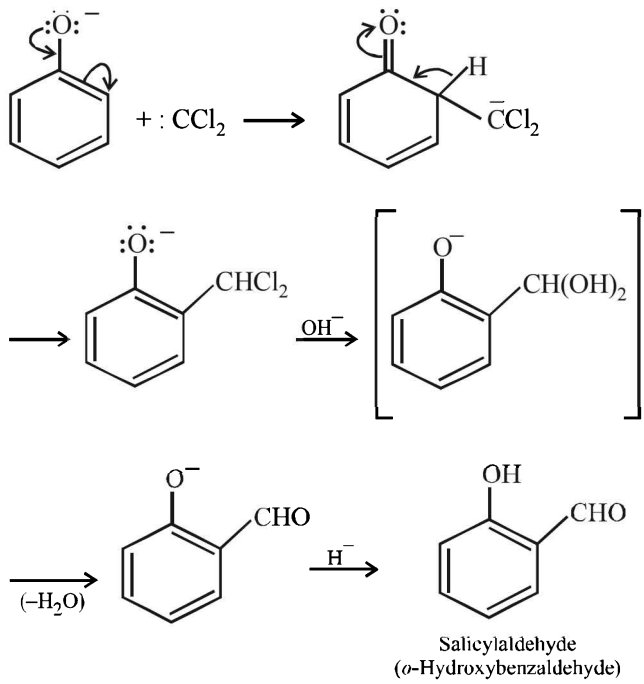
(soluble in H_2O)

The brown precipitate is of MnO_2.

12. **(i, iv) TIPS/Formulae :**
The reaction involves electrophilic substitution on the highly reactive phenoxide ion.
Here the electrophile is dichlorocarbene formed by the action of strong alkali on chloroform.

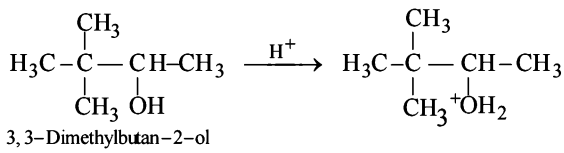
$$CHCl_3 + OH^- \rightleftharpoons CCl_3^- + H_2O$$

$$:CCl_3^- \rightleftharpoons \underset{\text{Dichlorocarbene}}{:CCl_2} + Cl^-$$



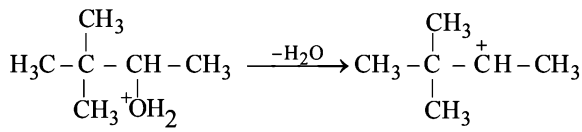
13. The steps involved in the suggested mechanism are as follows.

(a) The protonation of hydroxyl group.

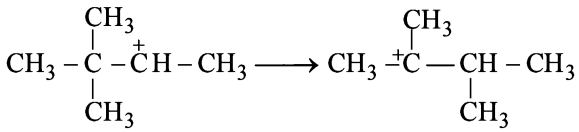


3, 3–Dimethylbutan–2–ol

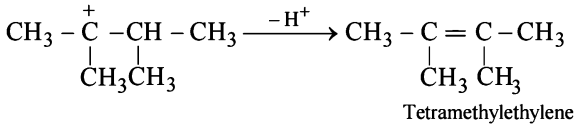
(b) The removal of H_2O to form a secondary (2°) carbonium ion



(c) The conversion of 2° carbonium to the more stable 3° carbonium ion by the shift of CH_3 group



(d) The removal of H^+ to form a double bond

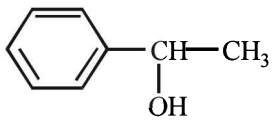


Tetramethylethylene

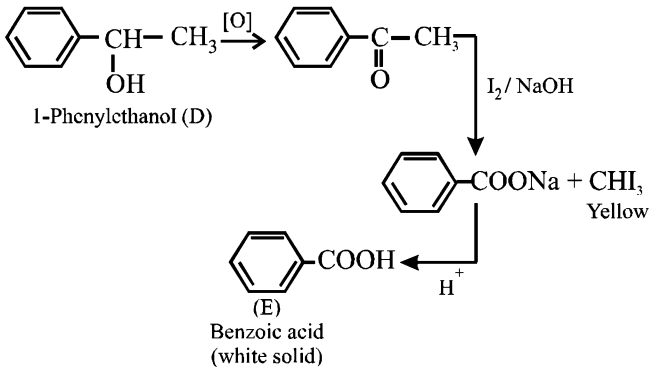
14. NOTE:

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 $C_6H_5CH(OH)CH_3$,

i.e, 

The given reactions are



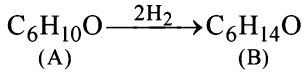
1-Phenylethanol (D)

(E) Benzoic acid (white solid)

15. TIPS/Formulae :

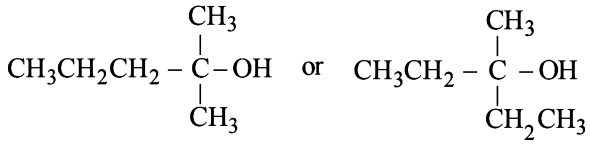
(a) Since (B) is resistant to oxidation, it must be *ter*-alcohol.

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

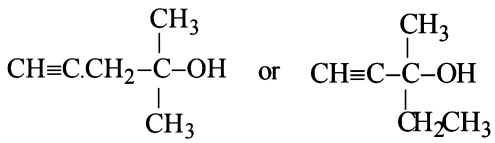


Thus the five carbon atoms can be adjusted into three alkyl groups (of which two are similar) either as $-CH_3$, $-CH_3$, and $-C_3H_7$, or as $-C_2H_5$, $-C_2H_5$ and $-CH_3$,

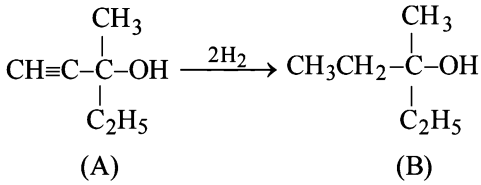
Thus the possible structure of alcohol (B) is either



Hence the corresponding compound (A) is either

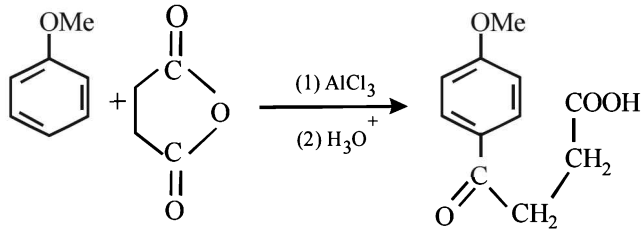


However, the compound (A) is optically active, so (A) and hence also (B) should have right side structure.

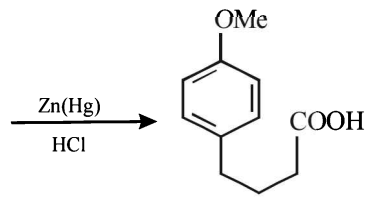


(A) (B)

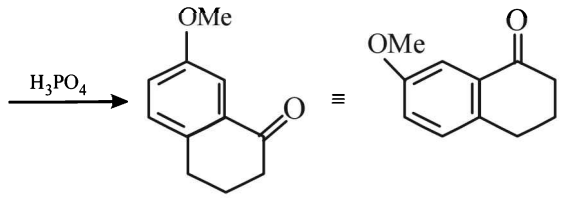
16.



(A)

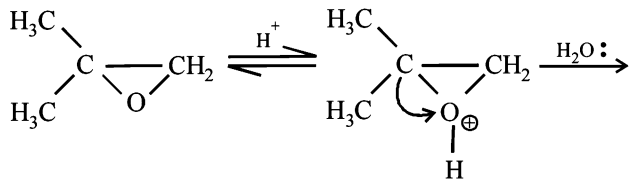


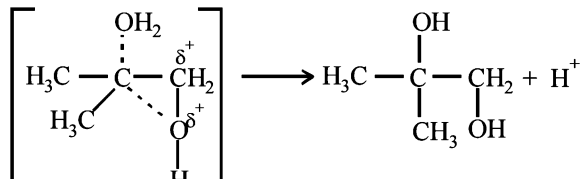
(B)



17. TIPS/Formulae :

The oxirane ring is cleaved via S_N2 mechanism





intermediate complex

18. The method given in (ii) is the correct method for the formation of ether because method (i) leads alkene as the main product.

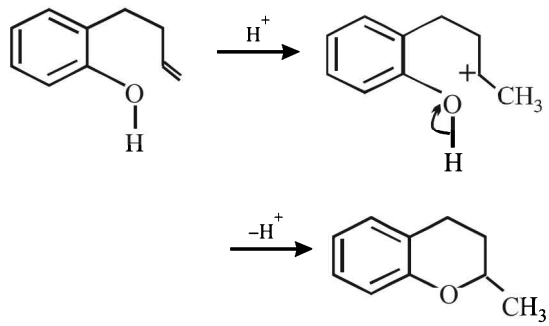
NOTE:

3° alkyl halides are easily dehydrohalogenated by base.

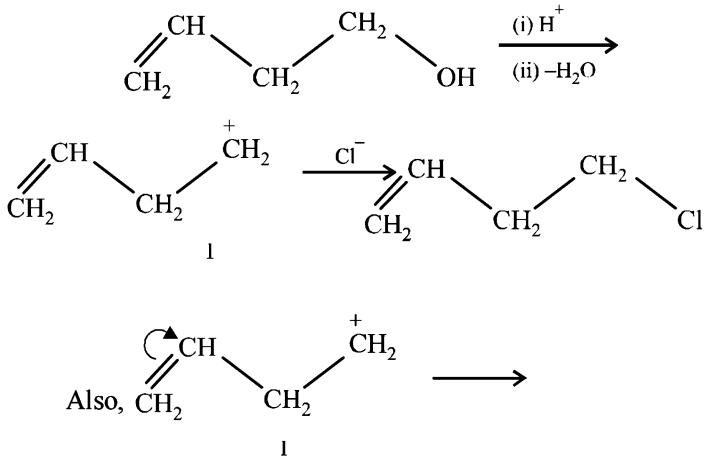
(i) $(CH_3)_3CBr \xrightarrow{CH_3ONa} \underset{\text{alkene}}{(CH_3)_2C=CH_2}$

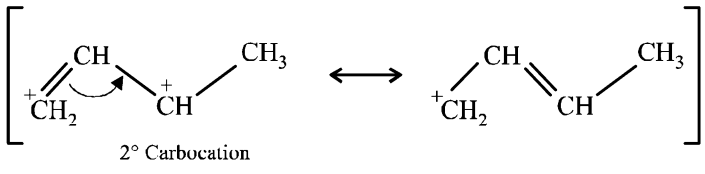
(ii) $CH_3Br + NaOC(CH_3)_3 \longrightarrow \underset{\text{ether}}{CH_3-O-C(CH_3)_3}$

19.

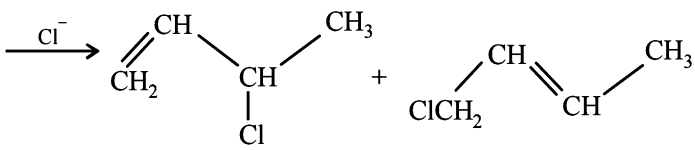


20. (i) **NOTE:**
Since the large propenyl group is attached to the carbon atom bearing the hydroxyl group, so the reaction is likely to occur via S_N1 mechanism.

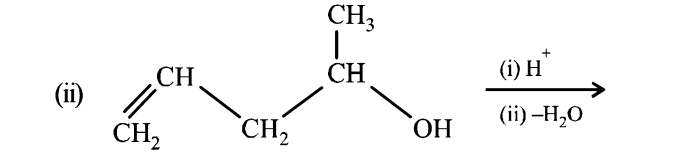




2° Carbocation



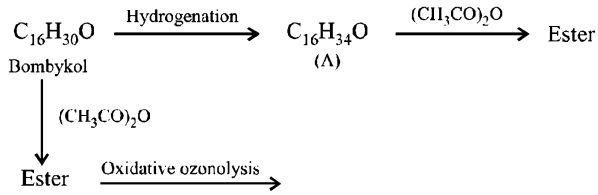
(ii)

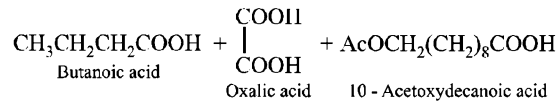


I
(2° Carbocation)

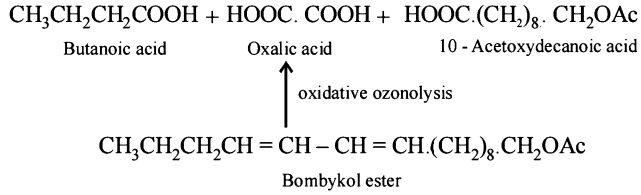
NOTE:
In the intermediate carbocation, Ia carbon bearing positive charge has CH_3 group which decreases the positive charge and hence prevents cyclisation of the compound.

21. TIPS/Formulae:
Let us summarise the given facts.

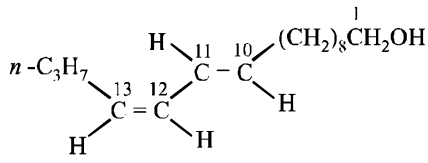




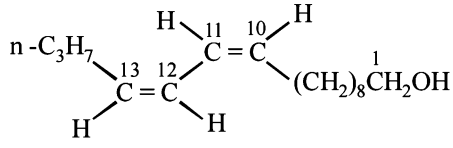
(i) Hydrogenation of bombykol ($C_{16}H_{30}O$) to $C_{16}H_{34}O$ (A) indicates the presence of two double bonds in bombykol.
(ii) Reaction of A with acetic anhydride to form ester indicates the presence of an alcoholic group in A and hence also in bombykol.
(iii) Products of oxidative ozonolysis of bombykol ester suggests the structure of bombykol.



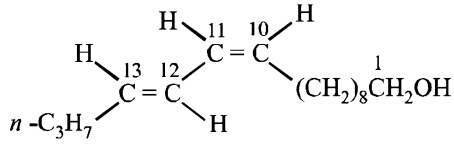
The structure of the bombykol ester suggests that bombykol has the following structure :
$CH_3CH_2CH_2CH=CH-CH=CH.(CH_2)_8.CH_2OH$ (Bombykol)
and the structure of A is
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2(CH_2)_8.CH_2OH$ or $C_{16}H_{33}OH$.
Four geometrical isomers are possible for the above bombykol structure (as it has two double bonds).



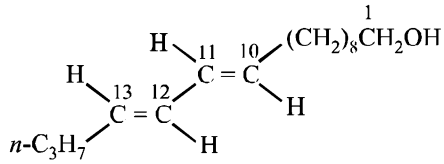
10 E, 12 Z



10 Z, 12 Z



10 Z, 12 E



10E, 12E

22. (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.

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

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

(Q and R), Both responds iodoform test

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

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

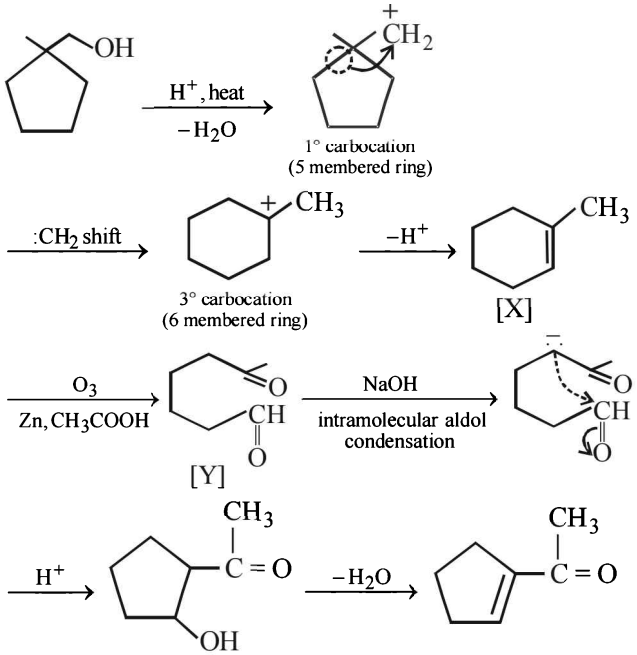
(Q and R), Both responds iodoform test

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

$\underset{2° \text{ carbocation}}{H_3C-\overset{+}{C}H-O-CH(CH_3)_2}$ or $\underset{3° \text{carbocation}}{CH_3CH_2-O-\overset{CH_3}{\overset{+|}{C}}-CH_3}$

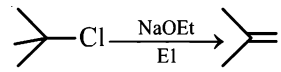
$$CH_2=CH_2 \xrightarrow{H^+} \underset{1° \text{ carbocation}}{CH_3\overset{+}{C}H_2}$$

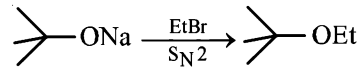
23.

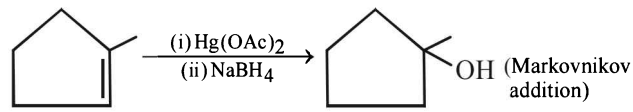


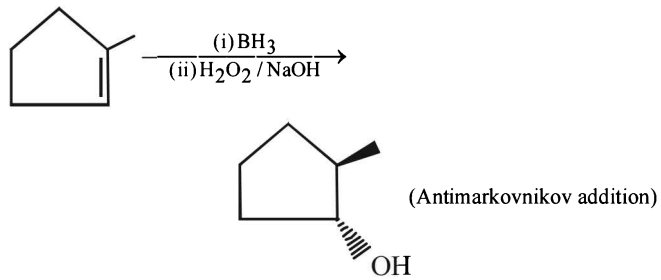
F. Match the Following

1. (a)

(P) 

(Q) 

(R) 

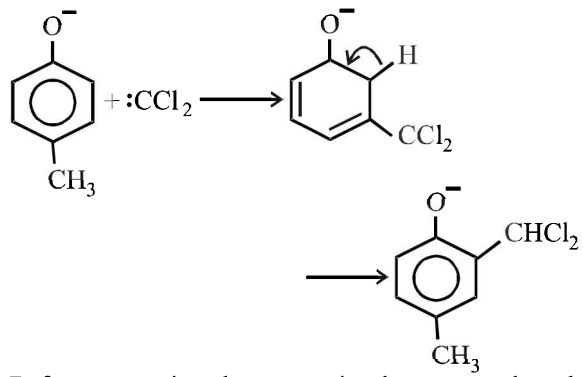
(S) 

G. Comprehension Based Questions

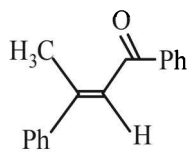
1. (c) Reagents for Reimer - Tiemann reaction are aq. $NaOH + CHCl_3$.

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

$CCl_3 \longrightarrow Cl^- + :CCl_2$ (Dichlorocarbene)

3. (b) 

For 4-6. Before answering these question let us complete the sequence of reactions given in data.

The given compound (M) i.e. 

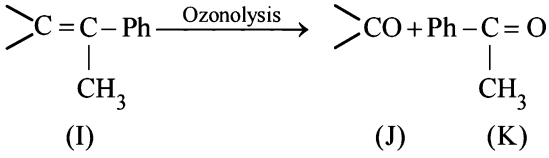
is the only product formed by the action of KOH on compound K.

The compound K is $Ph-\underset{\underset{CH_3}{|}}{C}=O$

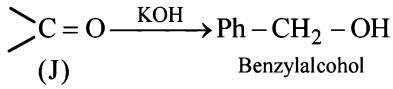
$$2Ph-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow[\text{(Aldol conden.)}]{KOH} Ph-\underset{\underset{CH_3}{|}}{C}=CH-\overset{\overset{O}{||}}{C}-Ph$$

Compound K (i.e. $Ph-\underset{\underset{CH_3}{|}}{C}=O$) is one of the products

of ozonolysis of compound I. Therefore the compound I may be

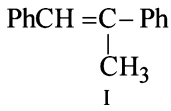


(I) (J) (K)



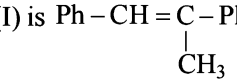
(J) Benzylalcohol

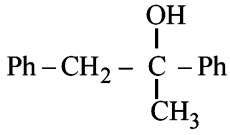
Thus J seems to be C_6H_5CHO and hence I is

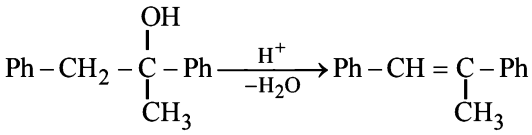


I

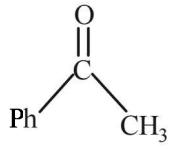
Now we will try to answer the questions.

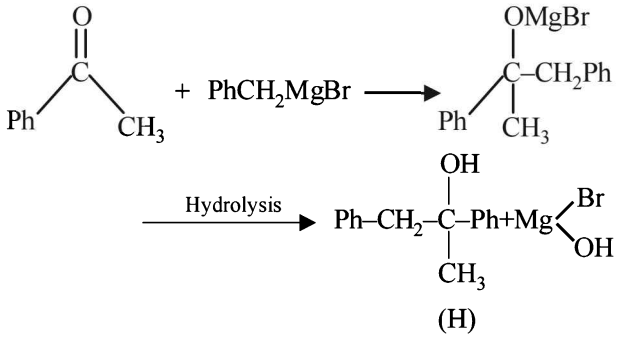
4. (b) As can be seen from above reaction sequence compound (I) is  and it is formed by catalytic dehydration (acid catalysed) of a tertiary alcohol (compound H). Therefore compound H is





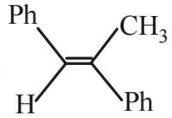
(H) (I)

(H) can be formed by the action of  with $PhCH_2MgBr$ as follows



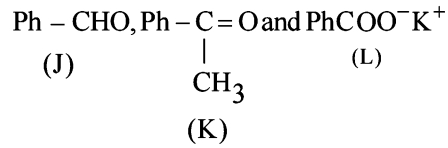
(H)

Therefore the correct answer is option (b)

5. (a) As can be seen form the above sequence of reactions the structure of compound (I) is 

Therefore the correct answer is option (a).

6. (d) As can be seen from the above sequence of reactions the structures of compounds J, K and L respectively are



(J) (K) (L)

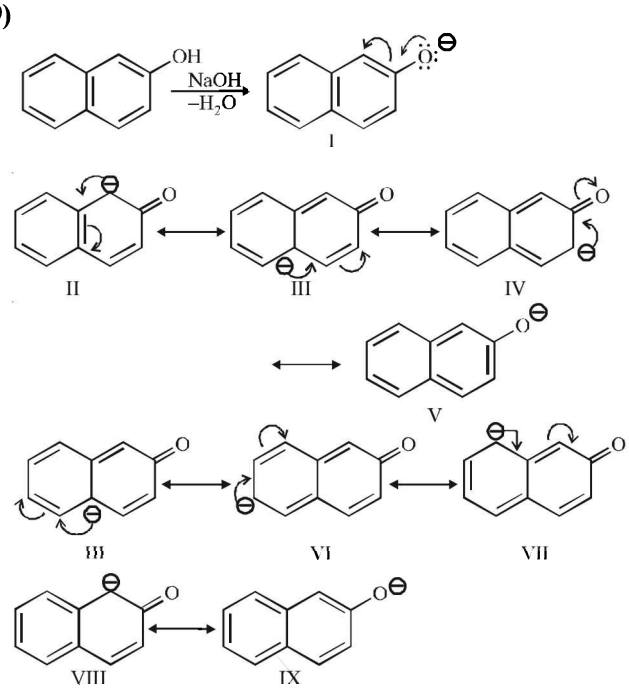
Thus the correct answer is option (d)

H. Assertion & Reason Type Questions

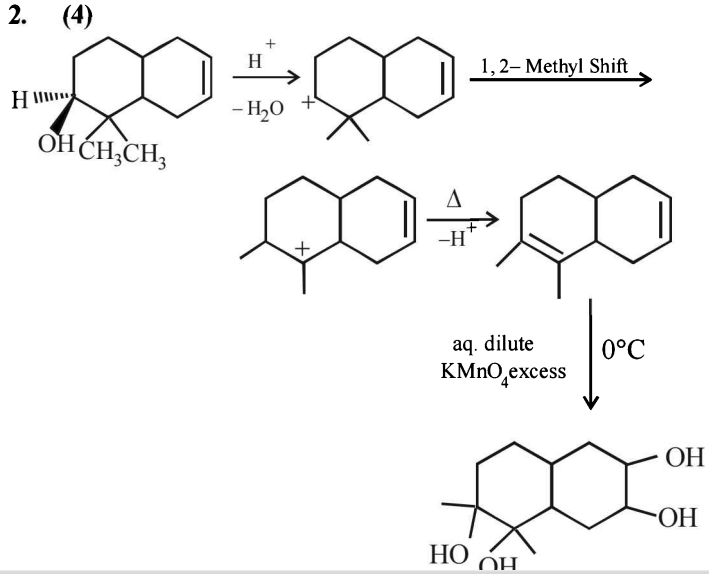
1. (c) The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised –OH groups present both in alcohol and water. However, in higher alcohols the hydrocarbon character (alkyl chain) of the molecule increases and thus alcohols tend to resemble 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.

I. Integer Value Correct Type

1. (9)



2. (4)



Section-B JEE Main/ AIEEE

1. (d) The dehydration of alcohol to form alkene occurs in following three step. Step (1) is initiation step.

Step (1) Formation of protonated alcohol.

$$CH_3-CH_2-\ddot{O}-H + H^+ \rightleftharpoons CH_3CH_2-\overset{+}{O}\begin{matrix}H\\H\end{matrix}$$

(Protonated ethanol)

Step (2) Formation of carbocation

$$CH_3-CH_2-\overset{+}{O}\begin{matrix}H\\H\end{matrix} \xrightarrow{\text{Slow}} CH_3-\overset{+}{C}H_2 + H_2O$$

Ethyl carbocation

Step (3) Elimination of a proton to form ethene

$$H-CH_2-\overset{+}{C}H_2 \xrightarrow{\text{Fast}} CH_2=CH_2 + H^+$$

ethene

2. (a) 3-methyl pentanol-3 will be dehydrated most readily since it produces tertiary carbonium ion as intermediate.

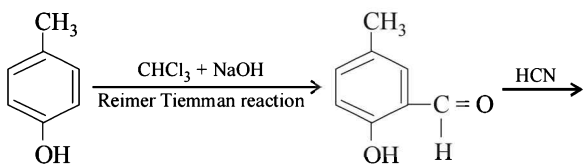
$$CH_3-CH_2-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-CH_3 \xrightarrow{H^+} CH_3-CH_3-\underset{\oplus}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-CH_3$$

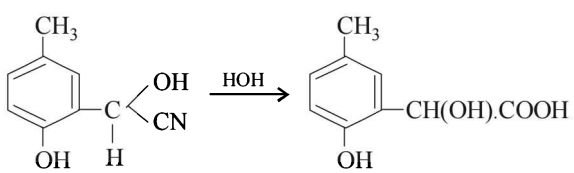
3. (a)

$$CH_3-\underset{OH}{CH}-CH=CH-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH=CH-CH_3$$

Pyridiminum chloro-chromate (PCC) is specific for the conversion.

4. (c)





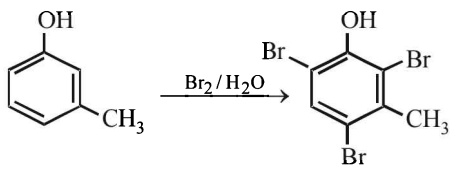
Cyanohydrin

5. (b) Methyl vinyl ether under anhydrous condition at room temperature undergoes addition reaction.

$$CH_2=CH-OCH_3 \xrightarrow{HBr} CH_3-\underset{Br}{CH}-O-CH_3$$

6. (b) Only those alcohols which contain $-CHOHCH_3$ group undergo haloform reaction. Among the given options only (b) contain this group, hence undergo haloform reaction.

7. (c) **NOTE :** OH group activates the benzene nucleus and



8. (d) **NOTE :** This is Riemer-Tiemann reaction and the electrophile is dichlorocarbene.

$$H-\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-Cl + NaOH \longrightarrow Cl-\ddot{C}-Cl + NaCl + H_2O$$

dichlorocarbene

α-elimination

9. (d)

$$CH_3CH_2OH \xrightarrow{P+I_2} \underset{A}{CH_3CH_2I}$$

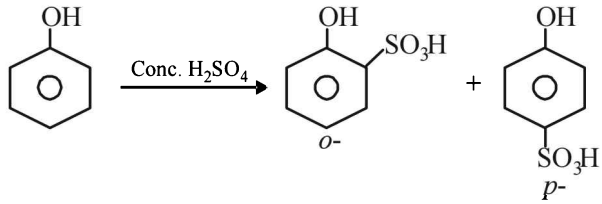
$$\xrightarrow[\text{Ether}]{Mg} \underset{(B)}{CH_3CH_2MgI} \xrightarrow{HCHO} H-\underset{H}{\overset{CH_2CH_3}{\underset{|}{\overset{|}{C}}}}-OMgI$$

$$\xrightarrow{H_2O} H-\underset{H}{\overset{CH_2CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

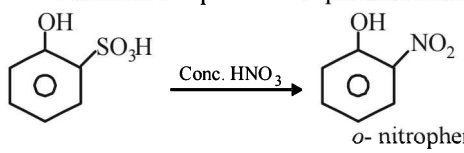
(D)

n–propyl alcohol

10. (b) Phenol on reaction with conc. H_2SO_4 gives a mixture of *o-* and *p-* products (i.e., $-SO_3H$ group, occupies *o-*, *p-* position). At room temperature *o*-product is more stable, which on treatment with conc. HNO_3 will yield *o*-nitrophenol.

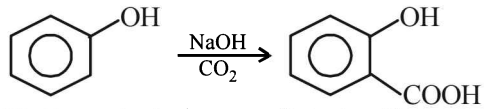


At room temperature *o-* product is more stable



Hence (b) is the correct answer.

11. (b)



12. (b) Tertiary alcohols react fastest with conc. HCl and anhydrous $ZnCl_2$ (lucas reagent) as its mechanism proceeds through the formation of stable tertiary carbocation.

Mechanism

$$\text{Step 1 : } CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH + H-Cl$$

2 Methyl Propan-2-ol

$$\rightleftharpoons (CH_3)_3C-\overset{+}{O}H_2 + Cl^-$$

Step 2 : $(CH_3)_3C-\overset{+}{O}H_2 \rightleftharpoons \underset{3^\circ\text{ Carbocation}}{(CH_3)C^+} + H_2O$

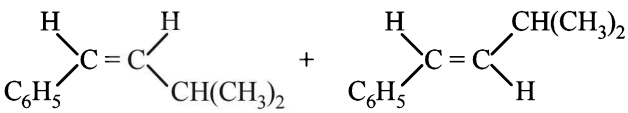
Step 3 : $(CH_3)_3C^+ + Cl^- \rightleftharpoons \underset{\text{t–Butyl chloride}}{(CH_3)_3C-Cl}$

13. (a) Whenever dehydration can produce two different alkenes, major product is formed according to **Saytzeff rule** *i.e.* more substituted alkene (alkene having lesser number of hydrogen atoms on the two doubly bonded carbon atoms) is the major product.

Such reactions which can produce two or more structural isomers but one of them in greater amounts than the other are called **regioselective** *;* in case a reaction is 100% regioselective, it is termed as **regiospecific.**

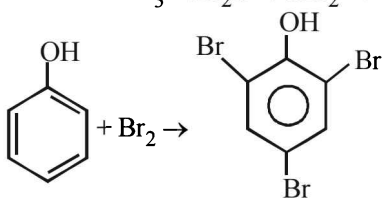
In addition to being regioselective, alcohol dehydrations are **stereoselective** (*a reaction in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amount than any other).*

$$C_6H_5-CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{\text{Conc. } H_2SO_4}$$

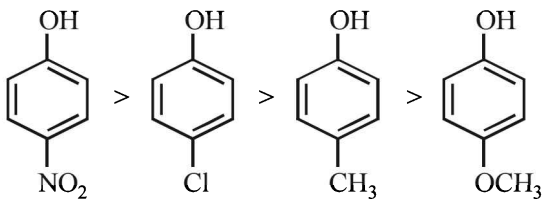


cis (minor) *trans* (major)

14. (d) $5KBr + KBrO_3 + 3H_2O \rightarrow 3Br_2 + 6KOH$



15. (c) Electron withdrawing substituents like $-NO_2$, Cl increase the acidity of phenol while electron releasing substituents like $-CH_3$, $-OCH_3$ decreases acidity. hence the correct order of acidity will be



Further $(-I)\,NO_2 > (-I)\,Cl$ and $(+I)\,CH_3 > (+I)\,OCH_3$

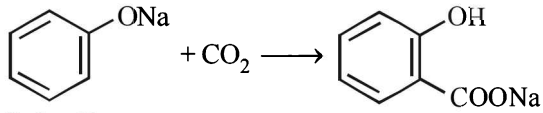
16. (b) Tertiary alchols reacts fastest with lucas reagnet as the rate of reaction is directly proportional to the stability of carbocation formed in the reaction. Since most stable 3° carbocation is formed in the reaction hence it will react fastest further tetriary alcohols appears to react by S_N1 mechanism.

Step 1. $(CH_3)_3C-OH + H-Cl \rightleftharpoons (CH_3)_3-\overset{+}{O}H_2 + Cl^-$

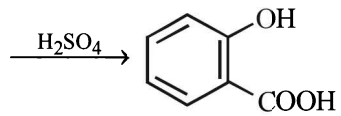
Step 2. $(CH_3)_3C-\overset{+}{O}H_2 \rightleftharpoons (CH_3)_3C^+ + H_2O$

Setp 3. $(CH_3)_3C^+ + Cl^- \longrightarrow \underset{\textit{tert}\text{-Butyl chloride}}{(CH_3)_3C-Cl}$

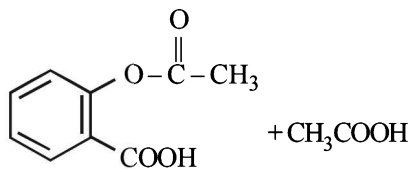
17. (a)



Sodium Phenoxide



Salicylic acid



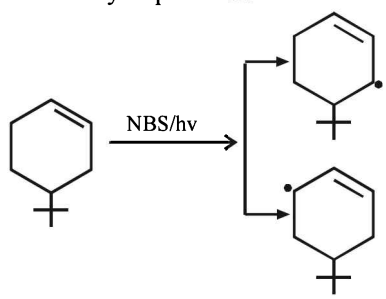
Aspirin (Acetyl Salicylate)

18. (a) Among 20 naturally occuring amino acids "Cysteine" has '– SH' or thiol functional group.

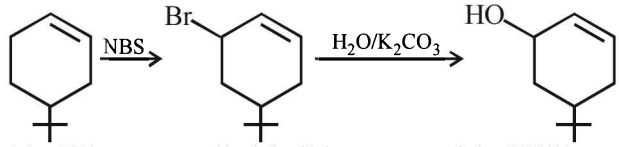
⇒ General formula of amino acid → $R-\underset{\underset{NH_2}{|}}{CH}-COOH$

⇒ Value of R = $-CH_2-SH$ in Cysteine.

19. (d) N – bromosuccinimide results into bromination at allylic and benzylic positions



More *stable*



20. (a) When *tert* -alkyl halides are used in Williamson synthesis elimination occurs rather than substitution resulting into formation of alkene. Here alkoxide ion abstract one of the β-hydrogen atom along with acting as a nucleophile.

$$CH_3-CH_2-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + Na^+\bar{O}CH_3 \xrightarrow{CH_3OH}$$

2-Chloro-2-methylpentane

$$CH_3CH_2-\underset{}{\overset{H}{\overset{|}{C}}}=\underset{}{\overset{CH_3}{\overset{|}{C}}}-CH_3 + CH_3OH + NaBr$$

2-Methyl-pent-2-ene