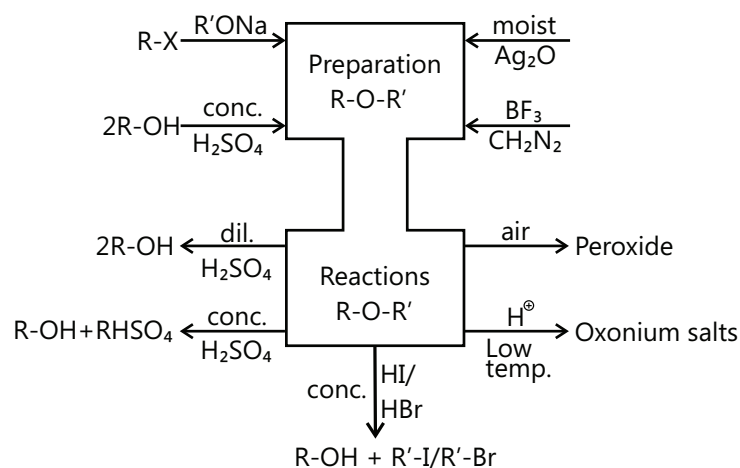


## POINTS TO REMEMBER



## Solved Examples

## JEE Main/Boards

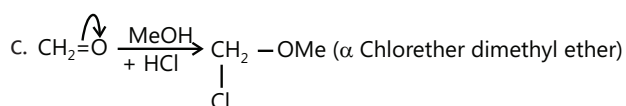
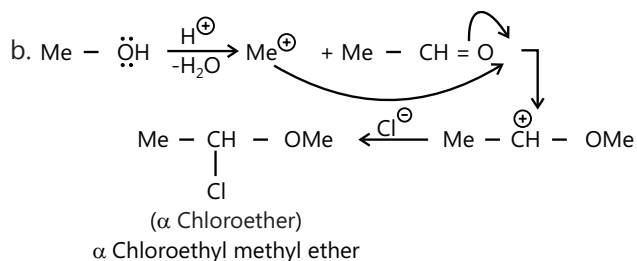
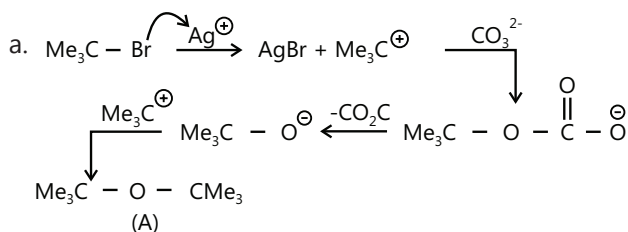
**Example 1:** Complete the following reactions:

- $2\text{Me}_3\text{C}-\text{Br} \xrightarrow[\Delta]{\text{Ag}_2\text{CO}_3} \text{(A)}$
- $2\text{MeOH} + \text{MeCH}=\text{O} + \text{HCl (g)} \rightarrow \text{(B)}$
- $\text{MeOH} + \text{H}_2\text{C}=\text{O} + \text{HCl (g)} \rightarrow \text{(C)}$

**Sol:** A = Me<sub>3</sub>C - O - Me<sub>3</sub> (Di-t-butyl ether)

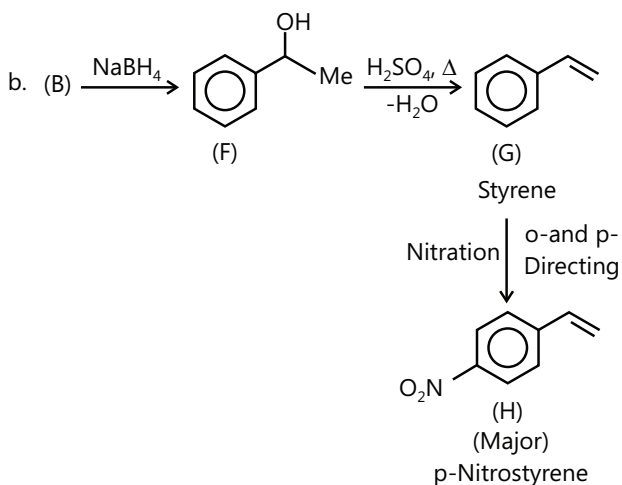
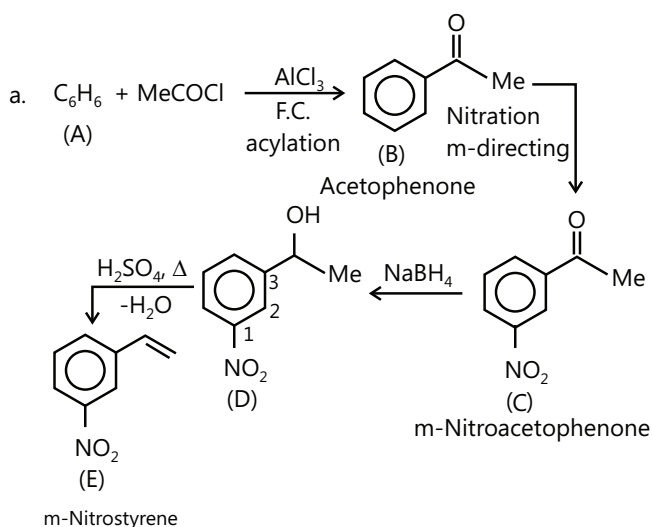
Ag<sup>+</sup> reacts with Br<sup>-</sup> leaving Me<sub>3</sub>C<sup>⊕</sup>, which reacts with CO<sub>3</sub><sup>2-</sup> to give Me<sub>3</sub>C - OCO<sub>2</sub><sup>⊖</sup>. The latter loses CO<sub>2</sub> leaving Me<sub>3</sub>COO which reacts with Me<sub>3</sub>C<sup>⊕</sup> to give the product. Due to steric hindrance, the yield is less.

**Mechanism:**



**Example 2:** Complete the following reactions:

- $\text{C}_6\text{H}_6 + \text{MeCOCl} \xrightarrow{\text{AlCl}_3} \text{B} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \text{C} \xrightarrow{\text{NaBH}_4} \text{D} \xrightarrow[\Delta]{\text{H}_2\text{SO}_4} \text{E}$   
Benzene (A)
- (B)  $\xrightarrow{\text{NaBH}_4} \text{F} \xrightarrow[\Delta]{\text{H}_2\text{SO}_4} \text{G} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \text{H}$

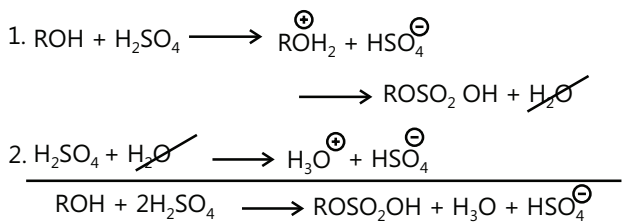
**Sol:**

**Example 3:** (a) Calculate the depression in freezing point ( $DT_f$ ) of 0.1 m solution of ROH in cold conc.

$H_2SO_4$ ,  $K_f = K \text{ kg mol}^{-1}$ .

(b) Calculate the  $DT_f$  of 0.2 m soln of  $Ph_3C-OH$  in cold conc.  $H_2SO_4$ .  $K_f = K \text{ kg mol}^{-1}$ .

**Sol:** (a) ROH reacts with cold conc.  $H_2SO_4$  as follows:

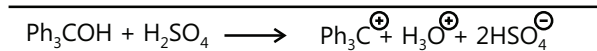
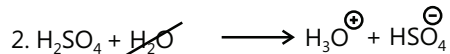
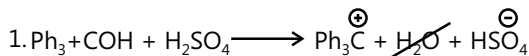


Number of moles of particles formed per mole of solute

(i) (van't Hoff factor) = 3 The reaction does not produce  $R^+$ , because  $R^+$  ion or even  $R_3C^+$  ion is not stable enough to persist.

$$\therefore \Delta T_f = i K_f \times M ; \quad 3x \times 0.1 = 0.3x K$$

(b)  $Ph_3C-OH + H_2SO_4$  reacts with cold, conc.  $H_2SO_4$  as follows:



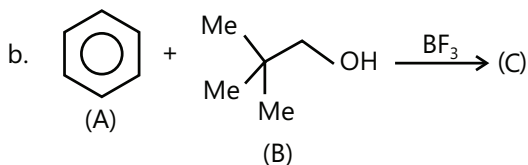
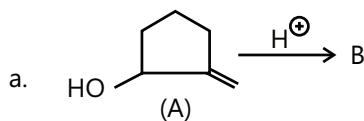
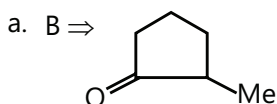
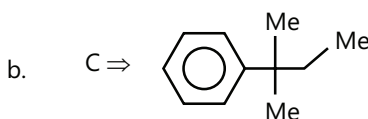
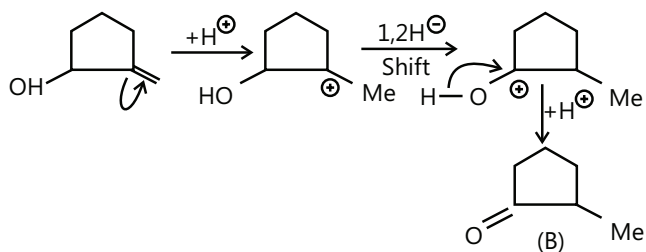
Number of moles of particles formed per mole solute

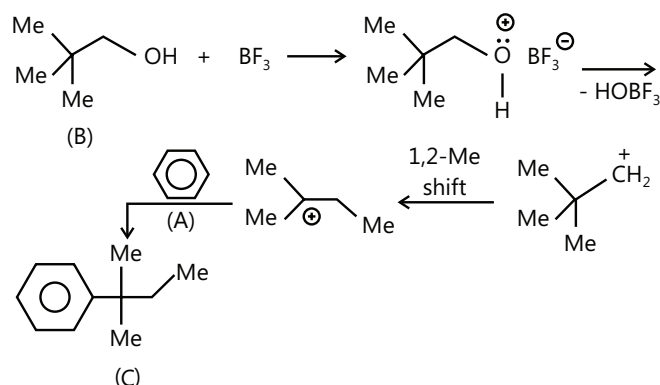
(i) (Van't Hoff factor) = 4

(The reaction produces stable  $Ph_3C^+$  ion due to resonance stabilization, and  $Ph_3C^+$  ion, and  $Ph_3C^+$  persists in the solution.)

$$\therefore \Delta T_f = i K_f \times M ; \quad = 4x \times 0.2 = 0.8x K$$

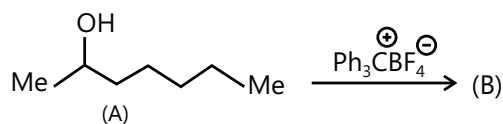
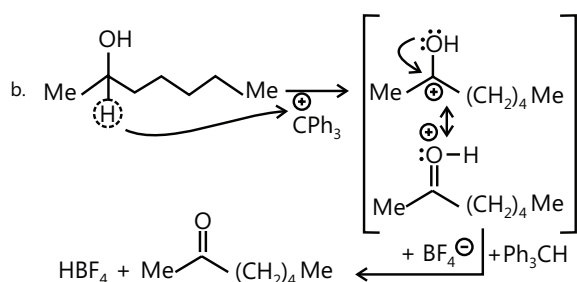
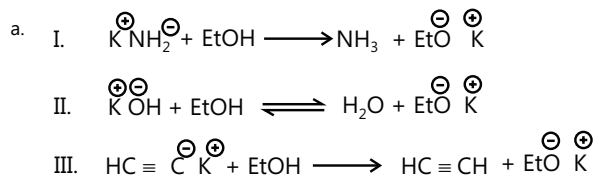
**Example 4:** Complete the following reactions:

**Sol:****Mechanism:**

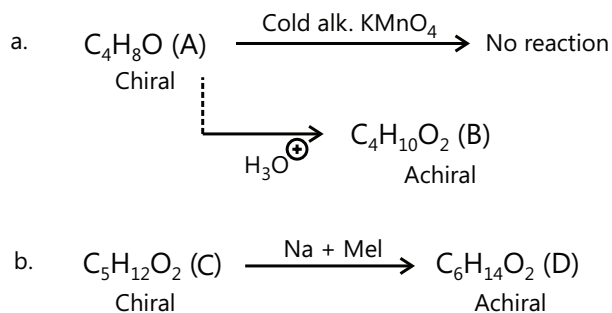
**Mechanism:**

**Example 5:** (a) Write the reaction of EtOH with (i)  $\text{KNH}_2$  (ii) aq. KOH (iii) Potassium ethynide.

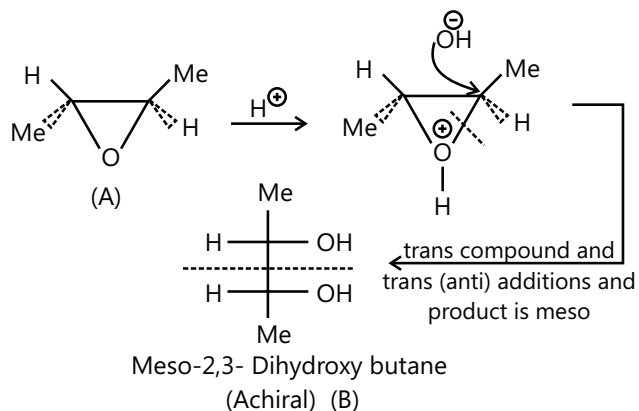
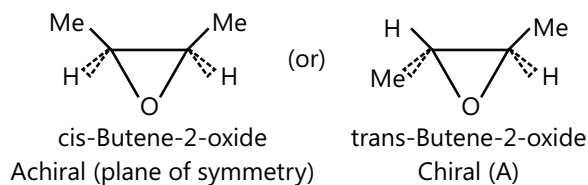
(b) Complete the following reaction:

**Sol:**

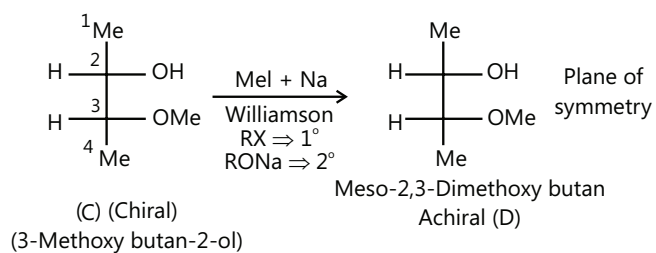
**Example 6:** Identify the following compounds:



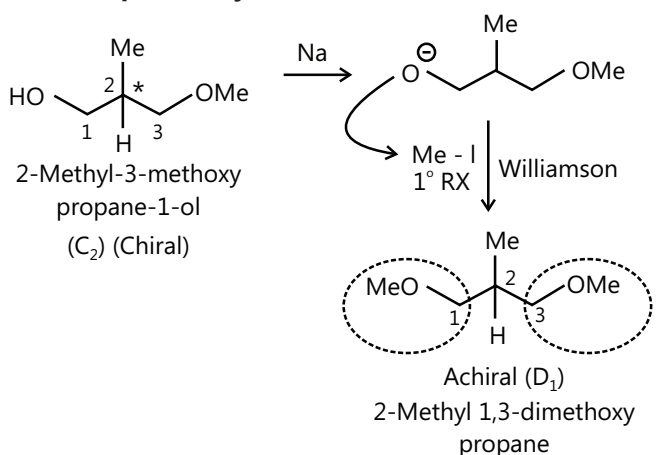
**Sol:** (a) One DU in (A) and unreactivity with cold alk.  $\text{KMnO}_4$  (Baeyer's reagent) suggest (A) to be a ring compound. (A) is optically active, suggesting a trans epoxide.



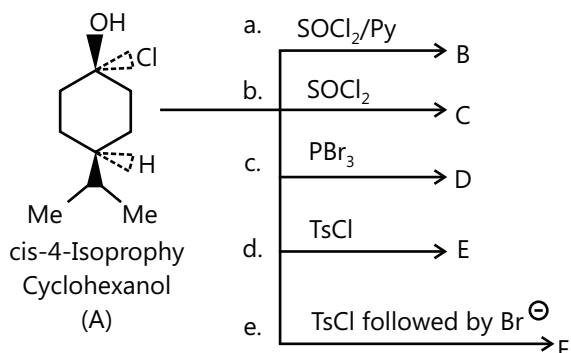
(b) Zero DU is (C) and (D) suggests that both are saturated compounds; (C) can be either diol or containing one (OH) and one (OMe) group since only one mole MeI reacts with (C) (five C atoms) to give (D) (six C atoms). Compound (C) contains one (OH) and one (OMe) given at adjacent positions to make (C) chiral.



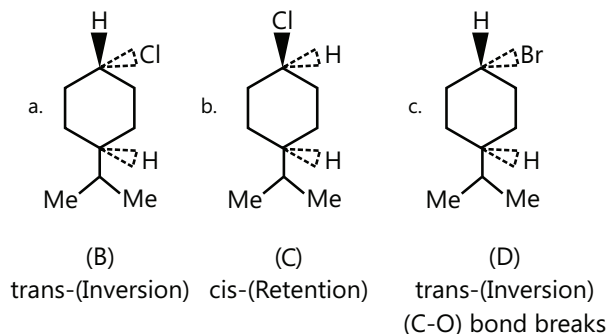
**Another possibility is;**



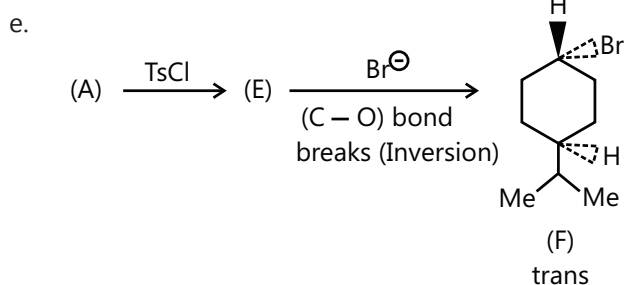
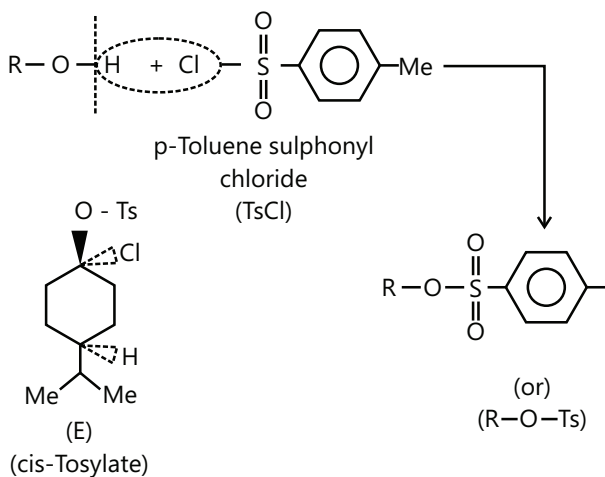
**Example 7:** Give the stereochemical product of following reactions:



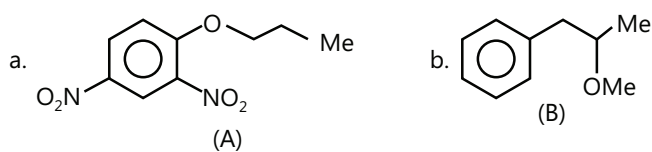
**Sol:** ROH with  $\text{SOCl}_2$  gives RCl (with retention configuration) but with  $\text{SOCl}_2/\text{pyridine}$ , RCl is found with inversion of configuration ( $\text{S}_{\text{N}}1$  reaction)



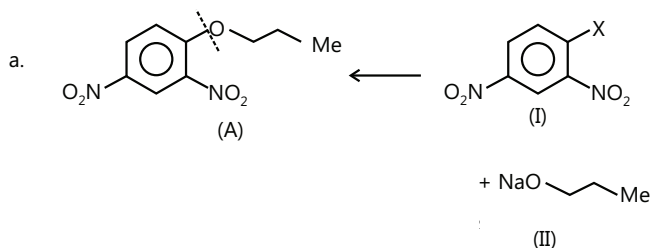
d. cis-Tosylate, no change in configuration because none of the (C-O) bonds breaks.



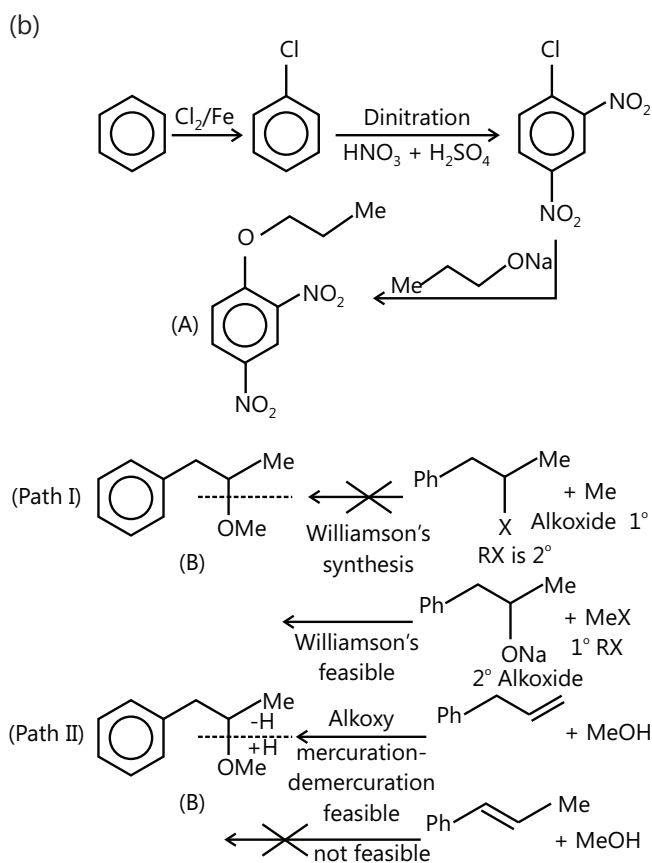
**Example 8:** Convert benzene to the following compounds:



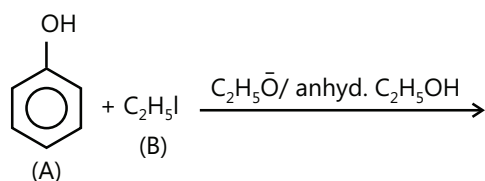
**Sol:** Williamson's synthesis of (I) and (II) would take place since ArSN is feasible in (I) because (I) is activated by two ( $-\text{NO}_2$ ) groups. Synthesis (I) from benzene and then react with (II) to obtain the product.



Williamson's synthesis of (I) and (II) would take place since ArSN is feasible in (I) because (I) is activated by two ( $-\text{NO}_2$ ) groups. Synthesis (I) from benzene and then react with (II) to obtain the product.



**Example 9:** Complete the reaction:

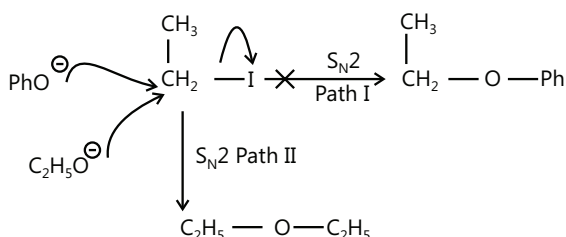


**Sol:**  $\text{C}_2\text{H}_5\text{O}^-$  acts as a base. It abstracts  $\text{H}^+$  from phenol to form  $\text{PhO}^-$  ion.

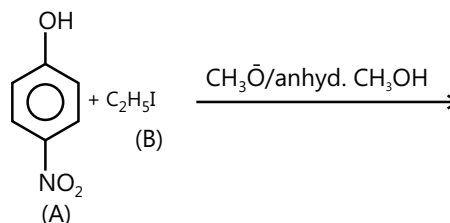
$\text{C}_2\text{H}_5\text{O}^-$  is a stronger nucleophile than  $\text{PhO}^-$ . Hence, the product is obtained by path II.

(acidic character:  $\text{PhOH} > \text{C}_2\text{H}_5\text{OH}$ )

(Basic and nucleophilic character :  $\text{PhO}^- < \text{C}_2\text{H}_5\text{O}^-$ )



**Example 10:**



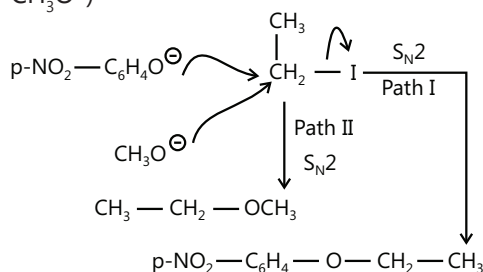
- $\text{P-NO}_2\text{-C}_6\text{H}_4\text{-OC}_2\text{H}_5$
- $\text{P-NO}_2\text{-C}_6\text{H}_4\text{-O-NO}_2\text{-P}$
- $\text{C}_2\text{H}_5\text{-O-CH}_3$
- $\text{P-NO}_2\text{-C}_2\text{H}_5\text{-I}$

**Sol:** (iii)  $\text{CH}_3\text{O}^-$  acts as a base. It abstracts  $\text{H}^+$  from p-nitrophenol to form  $\text{p-NO}_2\text{-C}_6\text{H}_4\text{O}^-$

$\text{CH}_3\text{O}^-$  is a stronger nucleophile than

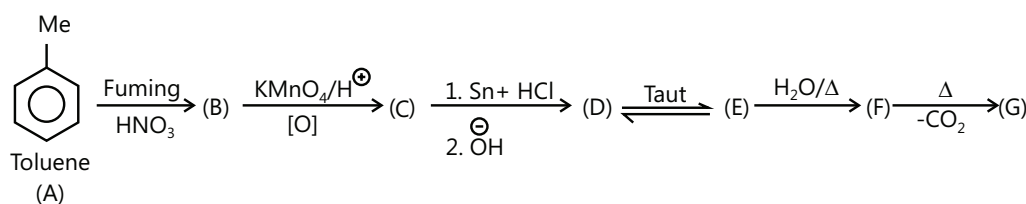
$\text{p-NO}_2\text{-C}_6\text{H}_4\text{O}^-$ , hence the product is obtained by path II.

(Basic and nucleophilic character :  $\text{p-NO}_2\text{-C}_6\text{H}_4\text{O}^- < \text{CH}_3\text{O}^-$ )

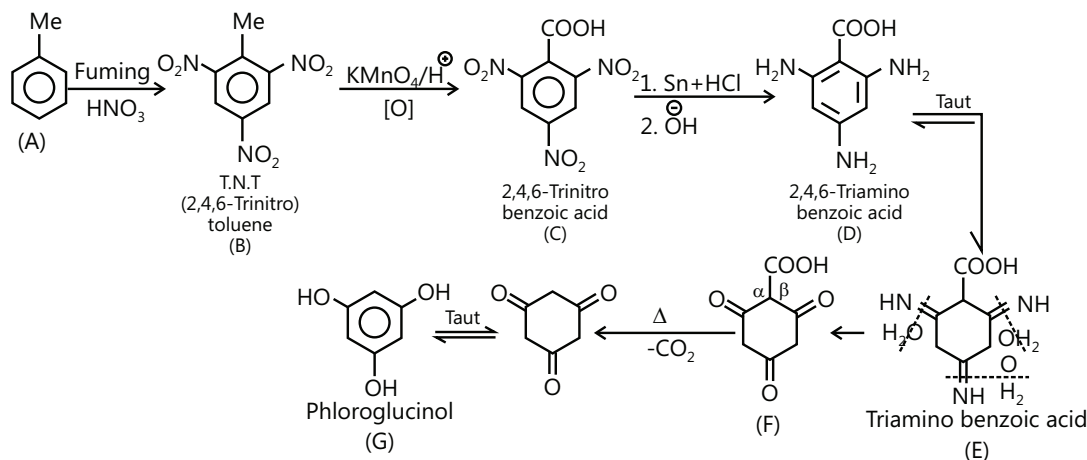


## JEE Advanced/Boards

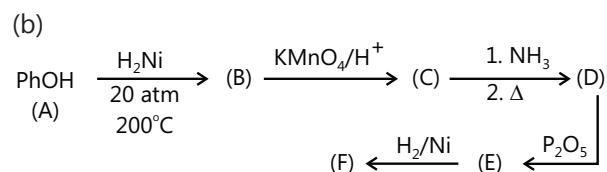
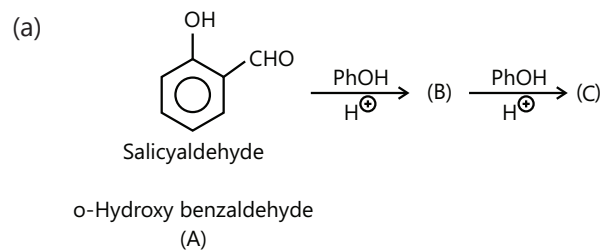
**Example 1:** Complete the following reactions:



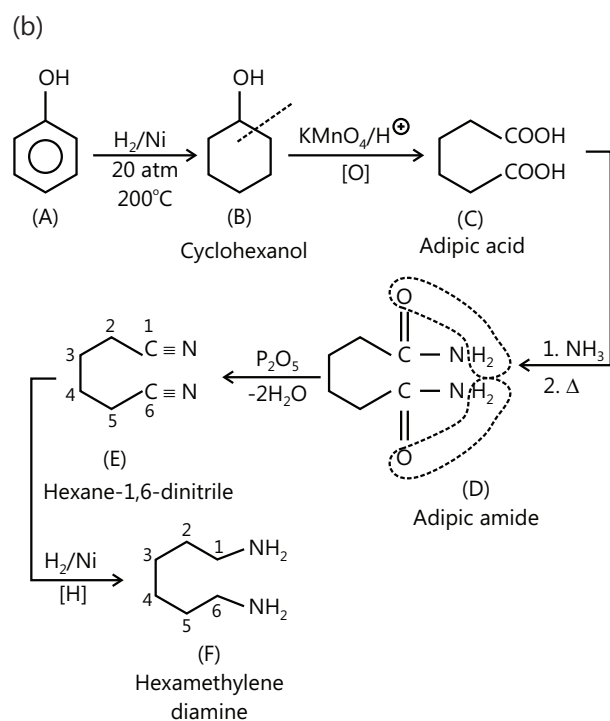
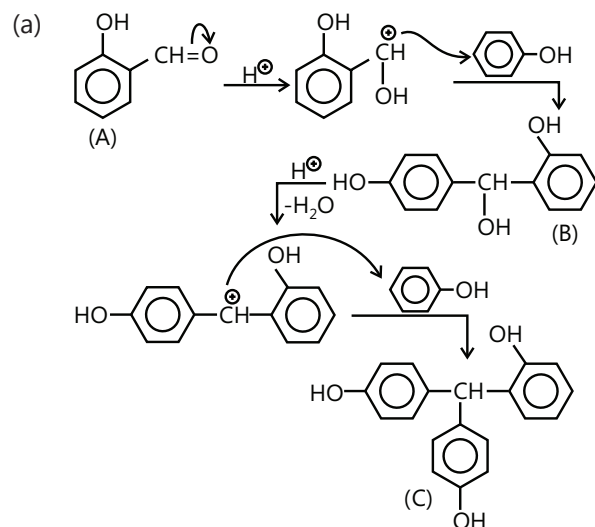
**Sol:**



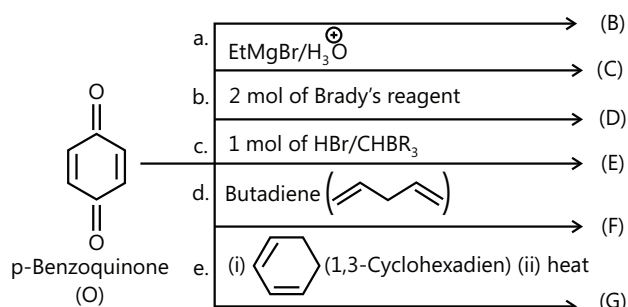
**Example 2:** Complete the following reactions:



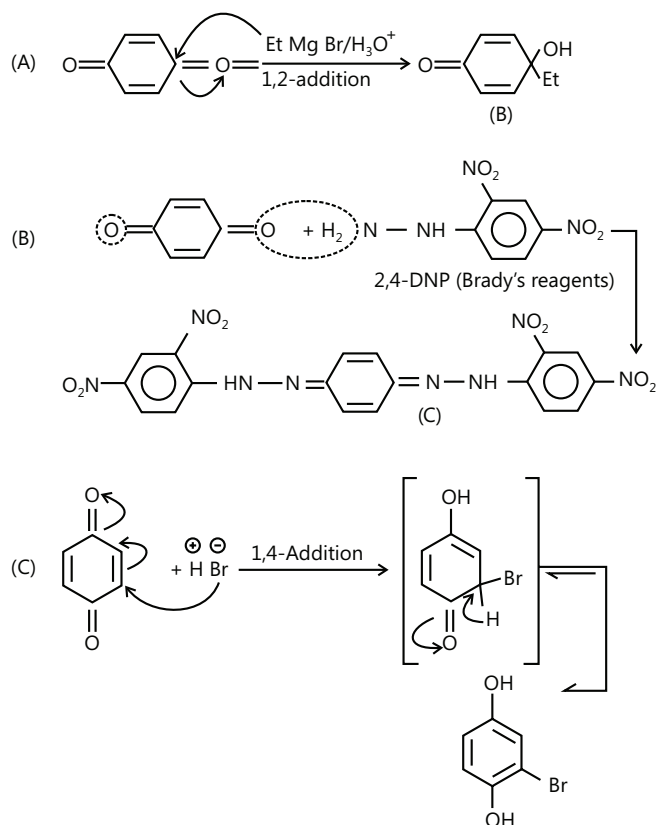
**Sol:**



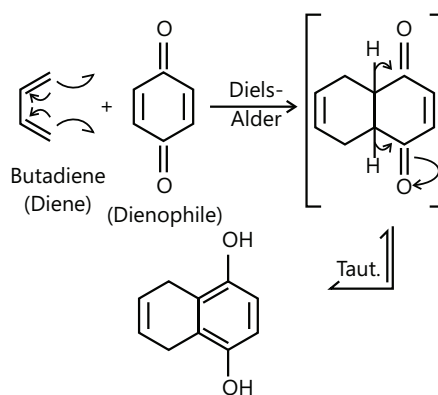
**Example 3:** Complete the following reactions:

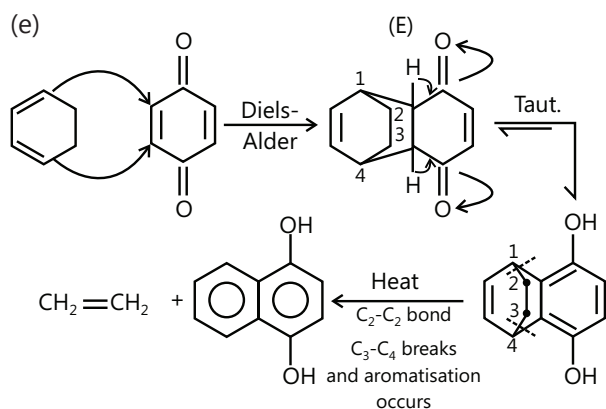


**Sol:** The reaction of quinones is that of  $\alpha,\beta$ -unsaturated ketone.

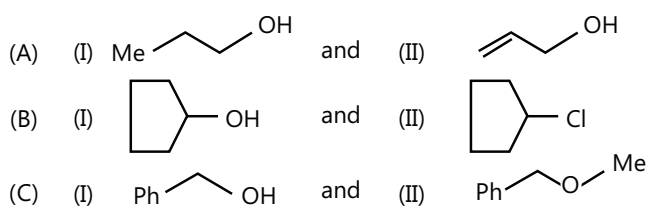


(d) It is an example of Diels-Alder reaction.





**Example 4:** Distinguish between the following pairs:

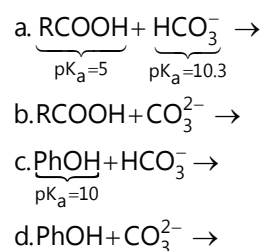


**Sol:** (a) (II) is unsaturated alcohols (allyl alcohol). When  $\text{Br}_2/\text{CCl}_4$  solution is added to it, orange colour of  $\text{Br}_2/\text{CCl}_4$  disappears. However, (I) (propyl alcohol) does not react with  $\text{Br}_2/\text{CCl}_4$  and orange colour persists.

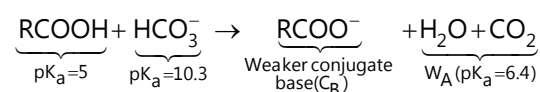
(b) (I) (cyclopentanol) dissolves in conc.  $\text{H}_2\text{SO}_4$  and forms one layer, while (II) (cyclopentyl chloride) does not dissolve in conc.  $\text{H}_2\text{SO}_4$  and two distinct layers appear.

(c) (I) (benzyl alcohol) ( $1^\circ$  ROH) is oxidized by acid  $\text{Cr}_2\text{O}_7^{2-}$  and orange colour of  $\text{Cr}_2\text{O}_7^{2-}$  changes to green ( $\text{Cr}^{3+}$ ), whereas (II) (benzyl methyl ether) does not react.

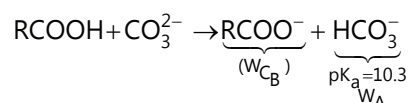
**Example 5:** Explain which of the following reactions will occur.



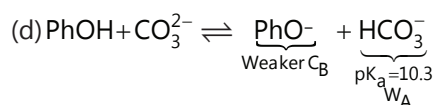
**Sol:** (a) The reaction is ;



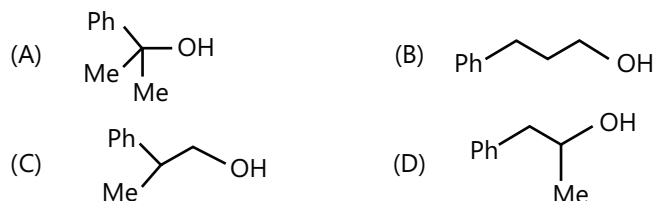
(b) Reaction occurs



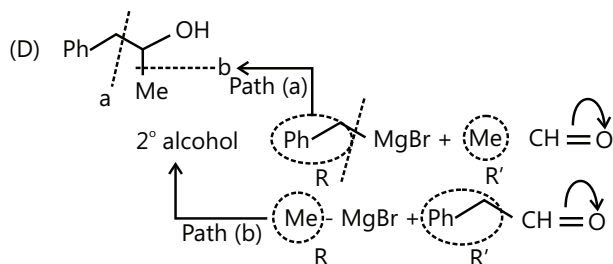
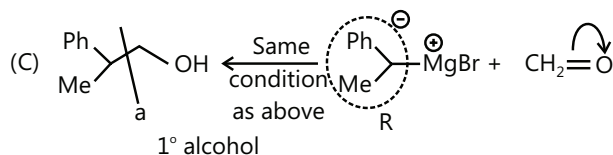
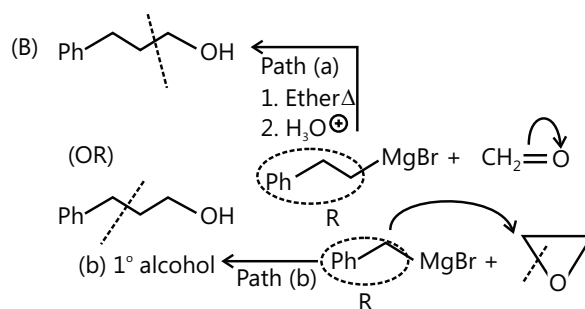
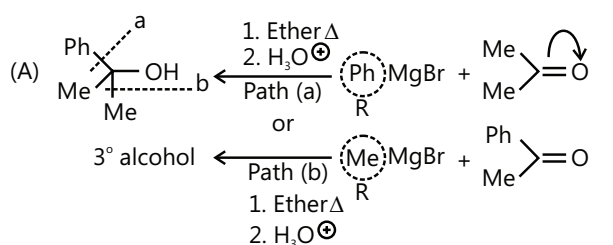
(c) Reverse reaction occurs.



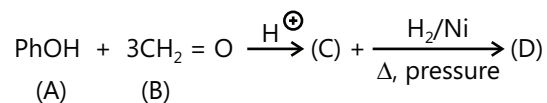
**Example 6:** How will you synthesize the following alcohol using grignard reagent



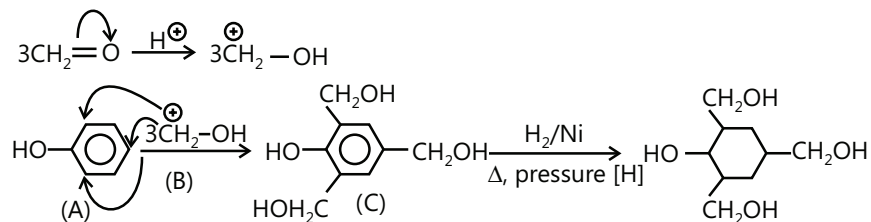
**Sol:**



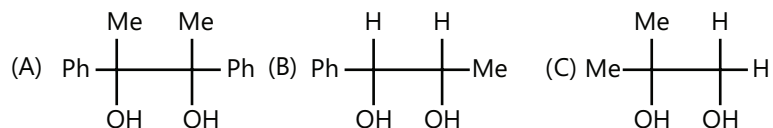
**Example 7:** Complete the following reaction



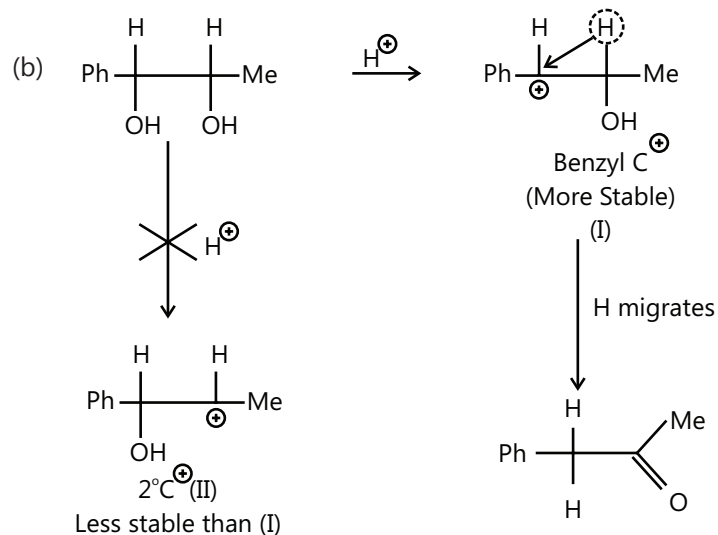
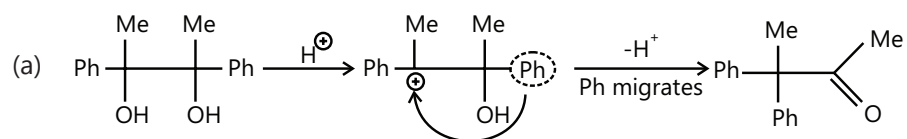
**Sol:**



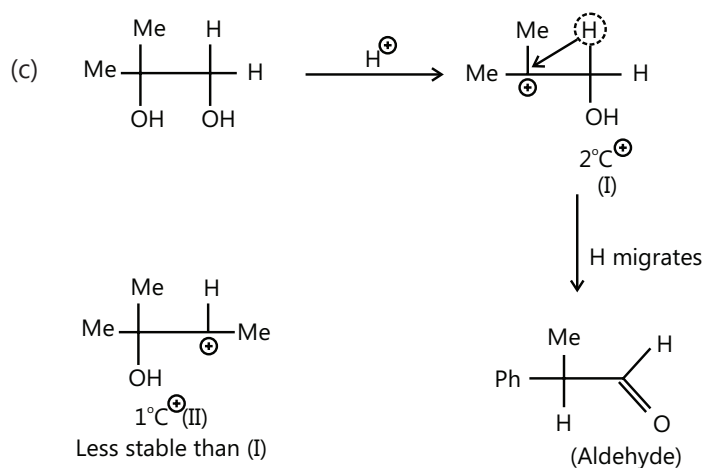
**Example 8:** Give the products of the pinacol rearrangement of the following glycols in acids.



**Sol:**



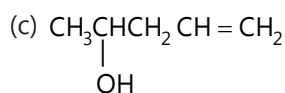
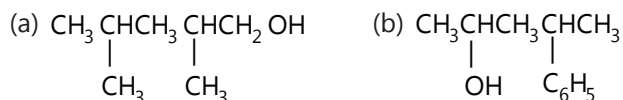




## JEE Main/Boards

### Exercise 1

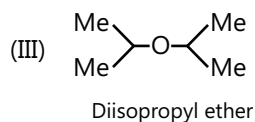
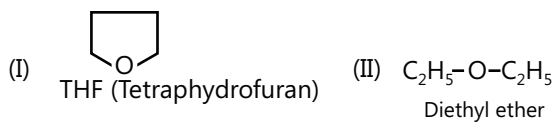
**Q.1** Give IUPAC substitutive names for the following alcohols:



**Q.2** How will you convert ethanol into the following compounds?

(i) Butane-1, 3-diol      (ii) But-2-enal      (iii) But-2-enoic acid

**Q.3** Write all the stereoisomers of 2-isopropyl-5-methylcyclohexanol and give the decreasing order of their stabilities.



**Q.4** How will you prepare the following:

(1) 3-phenyl but-1-ene to 2-phenyl butan-2-ol

(2) =  $\text{CH}_2$  to cyclopentyl methanol

**Q.5** Arrange the following compounds in the decreasing order of their boiling points and solubility in  $\text{H}_2\text{O}$ .

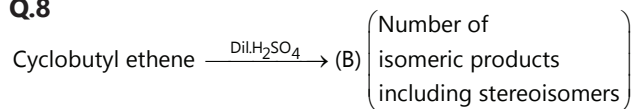
- a. (I) Methanol      (II) Ethanol  
(III) Propan-1-ol      (IV) Butane-1-ol  
(V) Butane-2-ol      (VI) Pentan-1-ol
- b. (I) Pentanol      (II) n-Butane  
(III) Pentanal      (IV) Ethoxy ethane
- c. (I) Pentane      (II) Pentane-1, 2, 3-triol  
(III) Butanol

**Q.6** Explain the less solubility and lower boiling point of:

- (I) o-Nitrophenol  
(II) o-Hydroxy benzaldehyde  
(III) o-Hydroxybenzoic acid (salicylic acid) compared with their p- and m-isomers.

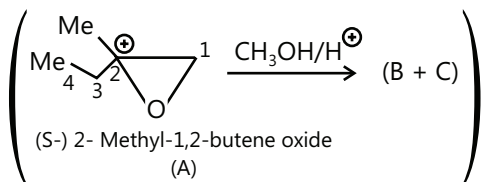
**Q.7** Which isomer (o, m, or p) of hydroxy acetophenone is steam volatile?

**Q.8**



**Q.9** Give the decreasing order of Lewis basicities of the following:

**Q.10** Explain the formation of B and C, optically pure different isomers from (A) with little racemisation.



**Q.11** Show how will you synthesize

- 1-phenylethanol from a suitable alkene,
- Cyclohexylemethanol using an alkyl halide by an  $\text{S}_{\text{N}}2$  reaction,
- Pentan-1-ol using a suitable alkyl halide?

**Q.12** Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

**Q.13** Compound (D), an isomer of (A) in Problem 4, reacts with  $\text{BH}_3 \cdot \text{THF}$  and then  $\text{H}_2\text{O}_2 / \text{OH}^-$  to give chiral (E). Oxidation of (E) with  $\text{KMnO}_4$  or acid dichromate affords a chiral carboxylic acid, (F). Ozonolysis of (D) after reduction with Zn gives the same compound (G) obtained by oxidation of 2-methyl pentan-3-ol with  $\text{KMnO}_4$ . Identify (D), (E), (F), and (G).

**Q.14** An organic compound (A) ( $\text{C}_8\text{H}_8\text{O}_3$ ) was insoluble in water, dilute HCl, and  $\text{NaHCO}_3$ . It was soluble in NaOH. A solution of (A) in dilute NaOH was boiled and steam distilled and distillate was reacted with NaOH to give a yellow precipitate was reacted with NaOH to give a yellow precipitate. The alkaline residue is acidified to give a solid (B) ( $\text{C}_7\text{H}_6\text{O}_3$ ). (B) dissolved in aqueous  $\text{NaHCO}_3$  with the evolution of gas. Identify (A) and (B).

**Q.15** Neutralisation of 30 gm of a mixture of acetic acid and phenol solutions required 100 ml of 2M sodium hydroxide solution. When the same mixture was treated with bromine water, 33.1 gm of precipitate was

formed. Determine the mass percentage of acetic acid and phenol in the given solution.

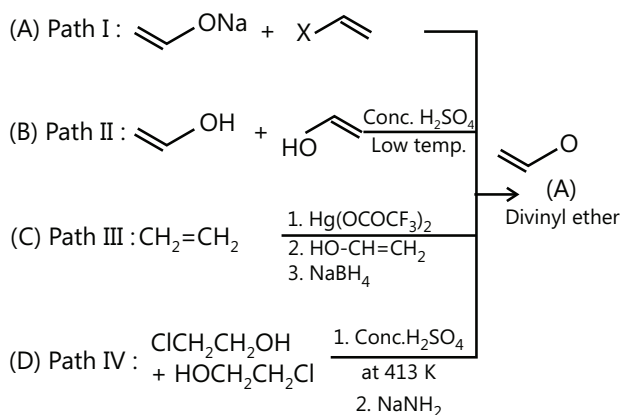
**Q.16** Find the structure of (A),  $\text{C}_{10}\text{H}_{10}\text{O}_2$ , a sweet-smelling liquid that has the following properties. It does not dissolve in NaOH or give a colour with  $\text{FeCl}_3$ ; it adds one equivalent of  $\text{H}_2$  on catalytic hydrogenation. Reductive ozonolysis affords  $\text{H}_2\text{C}=\text{O}$  and  $\text{C}_9\text{H}_8\text{O}_3$  (B) that gives a positive Tollens test. Oxidation of (A) with  $\text{KMnO}_4$  gives an acid (C) (MW=166) which gives no colour with  $\text{FeCl}_3$ . When (C) is refluxed with concentrated HI,  $\text{H}_2\text{C}=\text{O}$  and 3,4-dihydroxybenzoic acid are isolated and identified.

## Exercise 2

**Q.1** An organic compound (A) with molecular formula  $\text{C}_7\text{H}_8\text{O}$  dissolves in NaOH and gives characteristic colour with  $\text{FeCl}_3$ . On treatment with  $\text{Br}_2$ , it gives a tribromo product  $\text{C}_7\text{H}_5\text{OBr}_3$ . The compound is:

- p-Hydroxybenzene
- 2-Methoxy-2-phenyl propane
- m-Cresol
- p-Cresol

**Q.2** Which of the following paths is/are feasible for the preparation of ether (A)?



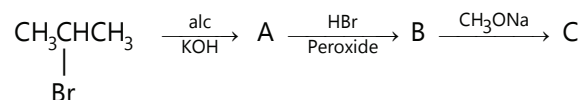
**Q.3** Which of the following statement is correct?

- Glycerol on reaction with oxalic acid at  $110^\circ\text{C}$  (383 K) and followed by heating and hydrolysis gives formic acid and glycerol.
- Glycerol on reaction with oxalic acid at  $230^\circ\text{C}$  (503 K) and followed by heating gives allyl alcohol.
- Glycerol on oxidation with dil.  $\text{HNO}_3$  gives a mixture of glyceric and tartaric acid.

iv. Glycerol on oxidation with conc.  $\text{HNO}_3$  gives glycerol acid.

- (A) i and ii                      (B) i and iii  
(C) iii and iv                    (D) i, ii, iii, iv

**Q.4** In the reaction



- (A) Diethyl ether                      (B) 1-Methoxypropane  
(C) Isopropyl alcohol                (D) Propylene glycol.

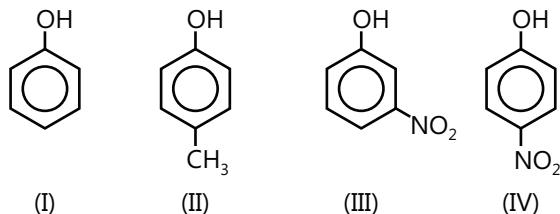
**Q.5** The compound which is not isomeric with diethyl ether is:

- (A) n-propyl methyl ether            (B) 2-methyl propan-2-ol  
(C) Butanone                          (D) Butan-1-ol

**Q.6** Phenol reacts with bromine water in  $\text{CS}_2$  at low temperature to give:

- (A) o-Bromophenol                    (B) o- and p-Bromophenol  
(C) p-Bromophenol                    (D) 2,4, 6-Tribromophenol

**Q.7** In the following compounds:



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)

**Q.8** The reaction of  $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$  with HBr gives

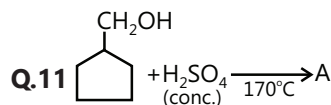
- (A)  $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_4-\text{OH}$   
(B)  $\text{CH}_3\text{CHBr}-\text{C}_6\text{H}_4-\text{OH}$   
(C)  $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_3(\text{Br})-\text{OH}$   
(D)  $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4-\text{OH}$

**Q.9** Reaction involving anti addition is:

- (A)  $\text{CH}_2=\text{CH}_2 \xrightarrow{\text{H}^+/\text{H}_2\text{O}}$   
(B)  $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{HX}}$   
(C)  $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow[\text{NaBH}_4]{\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}}$   
(D)  $\text{CH}_2=\text{CH}_2 \xrightarrow[\text{H}_2\text{O}_2/\text{OH}^-]{\text{B}_2\text{H}_6/\text{THF}}$

**Q.10**  $\xrightarrow{\text{H}_2\text{O}/\text{H}^+}$  ? Product/(s) will be:

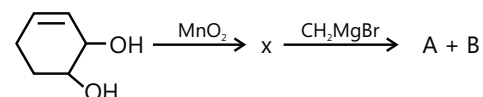
- (A)   
(B)   
(C)   
(D)



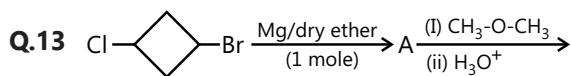
What is the major product A?

- (A)      (B)   
(C)      (D)

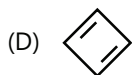
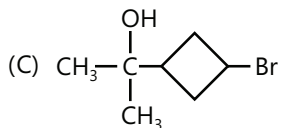
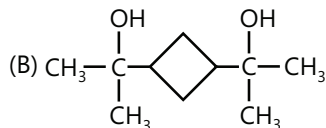
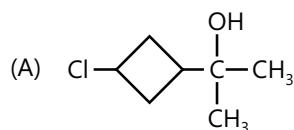
**Q.12**



- (A)      (B) &  $\text{CH}_4$   
(C)      (D)



What is B?

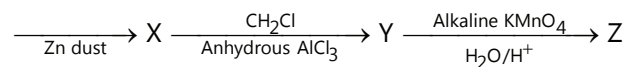


**Q.14** When 3, 3-dimethyl 2-butanol is heated with  $\text{H}_2\text{SO}_4$ , the major product obtained is

- (A) 2, 3-dimethyl 2-butene  
 (B) cis and trans isomers of 2, 3-dimethyl 2-butene  
 (C) 2, 3-dimethyl 1-butene  
 (D) 3, 3-dimethyl 1-butene

**Q.15** Consider the following reaction

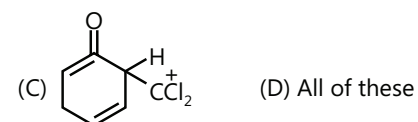
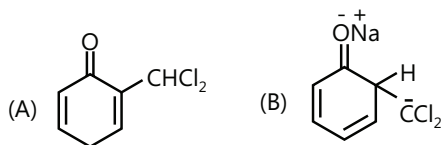
Phenol



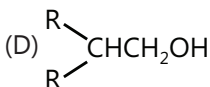
The product Z is

- (A) Benzene (B) Toluene  
 (C) Benzaldehyde (D) Benzoic acid

**Q.16** In Reimer-Tiemann reaction, the intermediate which does not form is



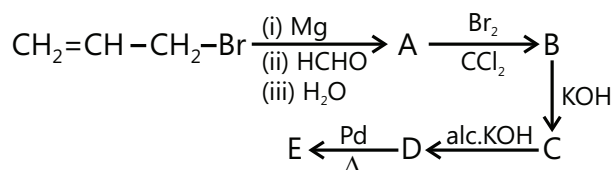
**Q.17** Reaction of  $\text{CH}_2=\text{CH}_2$  with  $\text{RMgX}$  leads to formation of

- (A)  $\text{RCH}_2\text{CH}_2\text{OH}$  (B)  $\text{RCHOHCH}_3$   
 (C)  $\text{RCHOHR}$  (D) 

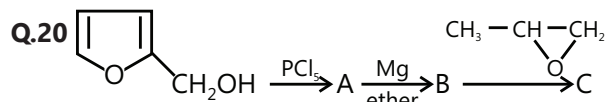
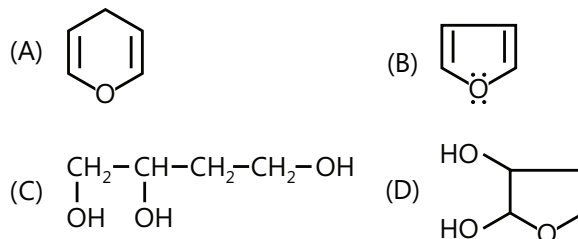
**Q.18** Ethyl chloride is converted into diethyl ether by

- (A) Perkin's reaction (B) Grignard reaction  
 (C) Wurtz synthesis (D) Williamson's synthesis

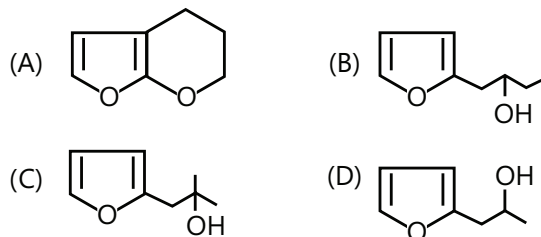
**Q.19**



Product (E) is



Product (C) is



## Previous Years Questions

**Q.1** Hydrogen bonding is maximum in

(1987)

- (A) Ethanol (B) Diethyl ether  
 (C) Ethyl chloride (D) Triethyl amine

**Q.2** Hydrogen bonding is maximum in (1987)

- (A) Ethanol (B) Diethyl ether  
(C) Ethyl chloride (D) Triethyl amine

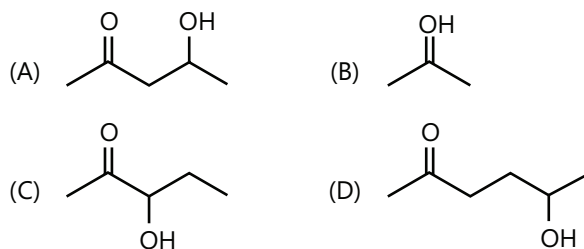
**Q.3** In  $\text{CH}_3\text{CH}_2\text{OH}$ , the bond that undergoes heterolytic cleavage most readily is (1988)

- (A) C – C (B) C – O (C) C – H (D) O – H

**Q.4** The products of combustion of an aliphatic thiol (RSH) at 298 K are (1992)

- (A)  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$  and  $\text{SO}_2(\text{g})$   
(B)  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and  $\text{SO}_2(\text{g})$   
(C)  $\text{CO}_2(\text{l})$ ,  $\text{H}_2\text{O}(\text{l})$  and  $\text{SO}_2(\text{g})$   
(D)  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and  $\text{SO}_2(\text{l})$

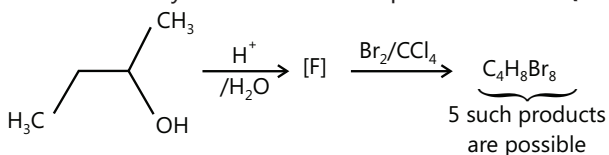
**Q.5** Which one of the following will most readily be dehydrated in acidic condition? (2000)



**Q.6** Compound 'A' (molecular formula  $\text{C}_3\text{H}_8\text{O}$ ) is treated with acidified potassium dichromate to form a product 'B' (molecular formula  $\text{C}_3\text{H}_6\text{O}$ ) 'B' forms a shining silver mirror on warming with ammonical silver nitrate. 'B' when treated with an aqueous solution of  $\text{H}_2\text{NCONHNH}_2$  and sodium acetate gives a product 'C'. Identify the structure of 'C' (2002)

- (A)  $\text{CH}_3\text{CH}_2\text{CH} = \text{NNHCONH}_2$   
(B)  $\text{H}_3\text{C} - \underset{\text{CH}_3}{\text{C}} = \text{NNHCONH}_2$   
(C)  $\text{H}_3\text{C} - \underset{\text{CH}_3}{\text{C}} = \text{NCONHNH}_2$   
(D)  $\text{CH}_3\text{CH}_2\text{OH} + \text{NCONHNH}_2$

**Q.7** How many structures of F is possible? (2003)



- (A) 2 (B) 5 (C) 6 (D) 3

**Q.8** Read the following question and answer as per the direction given below:

(A) Statement-I is true ; statement-II is true; statement-II is a correct explanation of statement-I.

(B) Statement is true; statement-II is true; statement-I is not the correct explanation of statement-I.

(C) Statement-I is true; statement-II is false.

(D) Statement-I is false ; statement-II is true.

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

**Statement-II:** The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permit enhanced hydrogen bonding with water (1988)

**Q.9** The yield of a ketone when a secondary alcohol is oxidized is more than the yield of aldehyde when a primary alcohol is oxidized. (1983)

**Q.10** Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. (1985)

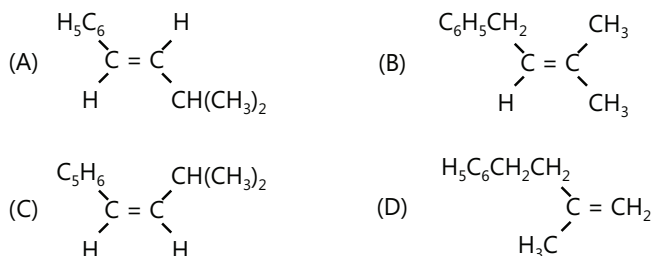
**Q.11** A liquid was mixed with ethanol and a drop of concentrated  $\text{H}_2\text{SO}_4$  was added. A compound with a fruity smell was formed. The liquid was: (2009)

- (A)  $\text{CH}_3\text{OH}$  (B)  $\text{HCHO}$   
(C)  $\text{CH}_3\text{COCH}_3$  (D)  $\text{CH}_3\text{COOH}$

**Q.12** The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is: (2009)

- (A) Benzoic acid (B) Salicylaldehyde  
(C) Salicylic acid (D) Phthalic acid

**Q.13** The main product of the following reaction is  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{CH}_3)_2 \xrightarrow{\text{conc. H}_2\text{SO}_4} ?$  (2010)



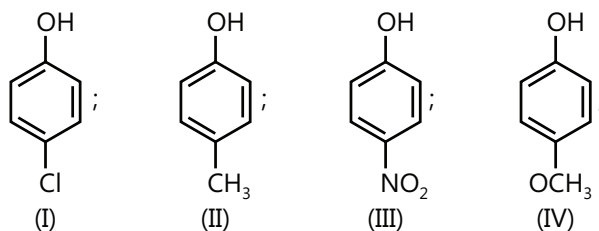
**Q.14** Ortho-Nitrophenol is less soluble in water than p- and m- Nitrophenols because: **(2012)**

- (A) o-Nitrophenol is more volatile in steam than those of m- and p-isomers  
 (B) o-Nitrophenol shows Intramolecular H-bonding  
 (C) o-Nitrophenol shows Intermolecular H-bonding  
 (D) Melting point of o-Nitrophenol is lower than those of m- and p-isomers.

**Q.15** Iodoform can be prepared from all except: **(2012)**

- (A) Ethyl methyl ketone  
 (B) Isopropyl alcohol  
 (C) 3-Methyl - 2- butanone  
 (D) Isobutyl alcohol

**Q.16** Arrange the following compounds in order of decreasing acidity: **(2013)**



- (A) II > IV > I > III      (B) I > II > III > IV  
 (C) III > I > II > IV      (D) IV > III > I > II

**Q.17** 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: **(2013)**

- (A) Secondary alcohol by  $S_N1$   
 (B) Tertiary alcohol by  $S_N1$   
 (C) Secondary alcohol by  $S_N2$   
 (D) Tertiary alcohol by  $S_N2$

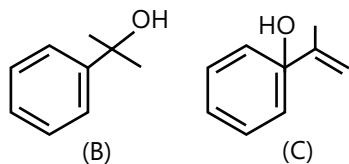
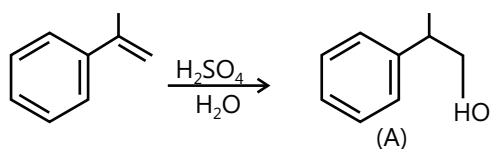
## JEE Advanced/Boards

### Exercise 1

**Q.1** Calculate the depression in freezing point ( $\Delta T_f$ ) of 0.1 m solution of ROH in cold conc.  $H_2SO_4$ .  $K_f = x \text{ K kg mol}^{-1}$

**Q.2** 0.218 gm of the acetyl derivative of a polyhydric alcohol (molecular mass = 92) requires 0.168 gm of KOH for hydrolysis. Calculate the number of (-OH) groups in the alcohol.

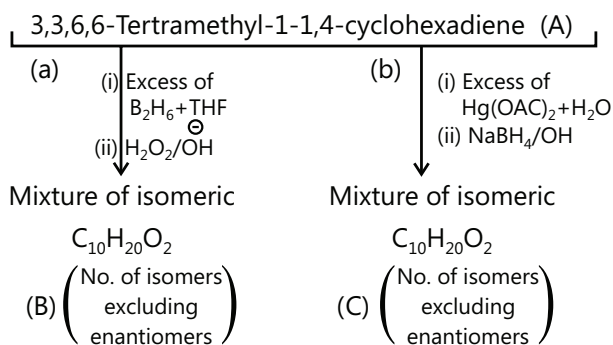
**Q.3** Consider the following reaction:



(i) Provide a complete mechanism for the formation of the major product

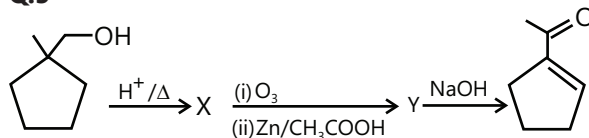
(ii) Briefly explain the choice of major product.

**Q.4**



What are the numerical values of (B) and (C)?

**Q.5**



**Q.6** Compound X (molecular formula,  $C_5H_8O$ ) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal 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.

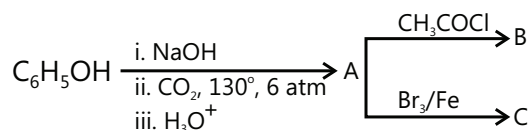
**Q.7** An organic compound (A) gives positive Liebermann reaction and on treatment with  $CHCl_3 / KOH$  followed by hydrolysis gives (B) and (C). Compound (B) gives colour with Schiff's reagent but not (C), which is steam volatile. (C) on treatment with  $LiAlH_4$  gives (D),  $C_7H_8O_2$ , which on oxidation gives (E). Compound (E) reacts with  $(CH_3CO)_2O / CH_3COOH$  to give a pain reliever (F). Give the structures of (A) to (F) with proper reasoning.

**Q.8** Two isomeric compound, (A) and (B), have the same formula  $C_{11}H_{13}OCl$ . Both are unsaturated, yield the same compound (C) on catalytic hydrogenation, and produce 4-chloro-3-ethoxybenzoic acid on vigorous oxidation. (A) exists in geometrical isomers, (D) and (E), but not (B). Give structures of (A) to (E) with proper reasoning.

**Q.9** 15 Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon: 42.86%, hydrogen: 2.40%, nitrogen: 16.67%, and oxygen: 38.07%.  
(i) Calculate the empirical formula of the minor product.  
(ii) When 5.5 gm of the minor product is dissolved in 45 gm of benzene, the boiling point of the solution is  $1.84^\circ C$  higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula.

(Molal boiling point elevation constant of benzene is  $2.53 K kg mol^{-1}$ .)

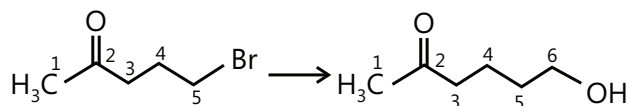
**Q.10** Identify A, B and C in the following reaction.



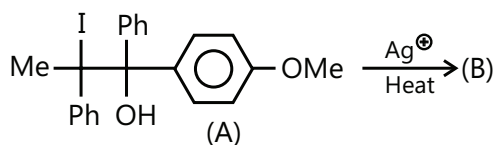
**Q.11** 20 If  $Me-\overset{OH}{\underset{|}{CH}}-CCl_3$  is treated with alkaline  $NaN_3$  and followed by reduction with  $H_2 / Pd$  it gives an

$\alpha$ -amino acid alanine  $\left( \begin{array}{c} Me-CH-COOH \\ | \\ NH_2 \end{array} \right)$ . Explain the reaction.

**Q.12** Convert

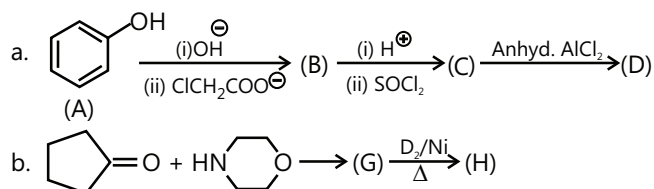


**Q.13** Assign the structure of (B), the principal organic product of the following reaction:



**Q.14** When a mixture of t-butyl alcohol and ethyl alcohol is heated with conc.  $H_2SO_4$ , a single ether product is obtained. Identify the product giving proper reasons.

**Q.15** Identify the major products (B) to (H).



**Q.16** When pent-4-en-1-ol is treated with aqueous  $Br_2 / OH^-$ , a cyclic bromo ether is formed rather than the expected bromohydrin. Propose a suitable mechanism for the above.

## Exercise 2

### Single Correct Choice Type

**Q.1** Select the correct statement.

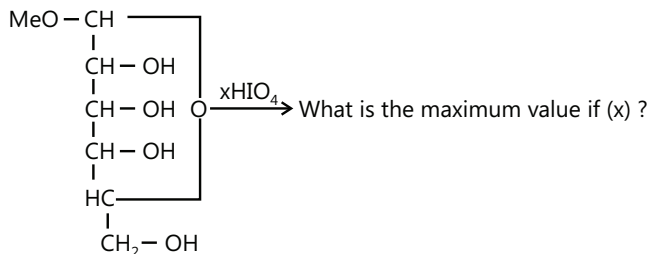
(A) Solvolysis of  $(CH_3)_2C=CH-CH_2Cl$  in ethanol is over 6000 times than alkyl chloride ( $25^\circ C$ )

(B)  $CH_3-CH=CH-CH_2-OH$  when reacts with  $HBr$  give a mixture of 1-bromo-2-butene and 3-bromo 1-butene

(C) When solution of 3-buten-2-ol in aqueous sulphuric acid is allowed to stand for one week, it was found to contain both 3-buten-2-ol and 2-buten-1-ol

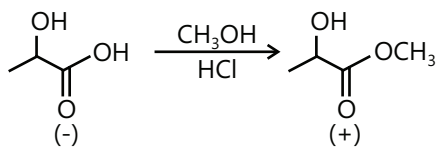
(D) All of these

### Q.2

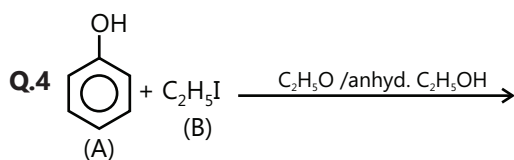


- (A) 1      (B) 2      (C) 3      (D) 4

**Q.3** Esterification (shown below) is a reaction converting a carboxylic acid to its ester. It involves only the carbonyl carbon. Esterification of (-) lactic acid with methanol yields (+) methyl lactate. Assuming that there are no side reactions, what is true about this reaction?

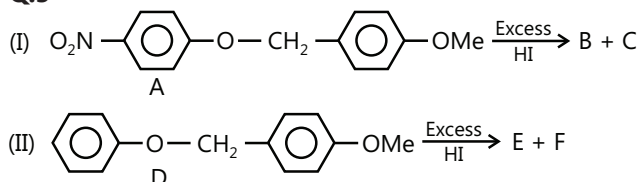


- (A) An  $S_N2$  process has occurred, inverting the absolute configuration of the chiral center.
- (B) An  $S_N1$  reaction at the chiral center has inverted the optical rotation.
- (C) A diastereomer has been produced; diastereomers have different physical properties including optical rotation
- (D) Optical rotation is not directly related to absolute configuration, so the change in sign of rotation is merely a coincidence



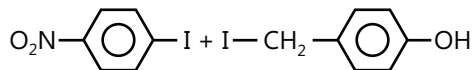
- (A)  $\text{PhOC}_2\text{H}_5$       (B)  $\text{Ph}-\text{O}-\text{Ph}$   
 (C)  $\text{PhI}$       (D)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$

### Q.5

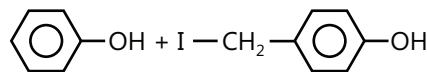


Which of the following statements is/are correct about the above reaction?

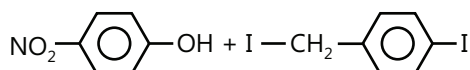
(A) The compounds (B) and (C), respectively, are:



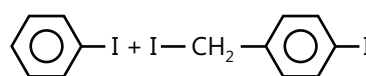
(B) The compound (D) and (E), respectively, are:



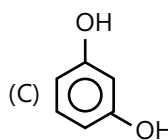
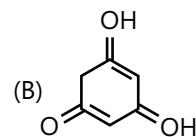
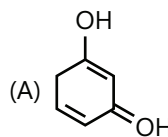
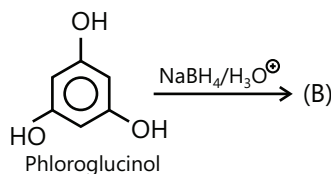
(C) The compound (B) and (C), respectively, are:



(D) The compounds (E) and (F), respectively, are:



**Q.6** Phenols are generally not changed with  $\text{NaBH}_4/\text{H}_3\text{O}^\oplus$  1, 3- and 1, 4-benzenediols and 1, 3, 5-benzenetriols are unchanged under these conditions. However, 1, 3, 5-benzenetriol (phloroglucinol) gives a high yield of product (B).



**Q.7** Diethyl ether on heating with conc. HI gives two moles of

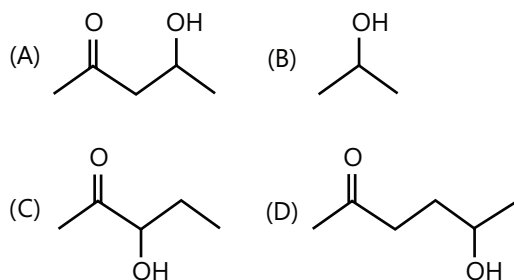
- (A) Ethanol      (B) Iodoform  
 (C) Ethyl iodide      (D) Methyl iodide

**Q.8** An industrial method of preparation of methanol is

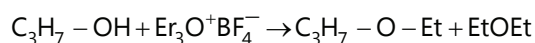
- (A) catalytic reduction of carbon monoxide in presence of  $\text{ZnO}-\text{Cr}_2\text{O}_3$   
 (B) by reacting methane with steam at  $900^\circ\text{C}$  with nickel catalyst  
 (C) by reducing formaldehyde with  $\text{LiAlH}_4$   
 (D) by reacting formaldehyde with aqueous sodium hydroxide solution



**Q.9** Which one of the following will most readily be dehydrated in acidic condition?



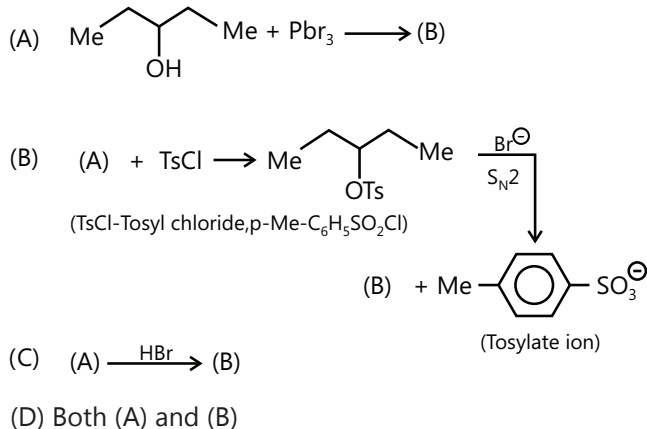
**Q.10**



Which of the following statements is wrong?

- (A) The nucleophile in the reaction is  $\text{C}_3\text{H}_7\text{OH}$ .  
 (B) The nucleophile in the reaction is  $\text{BF}_4^-$ .  
 (C) The leaving group is  $\text{Et}_2\text{O}$ .  
 (D)  $\text{S}_{\text{N}}2$  reaction occurs

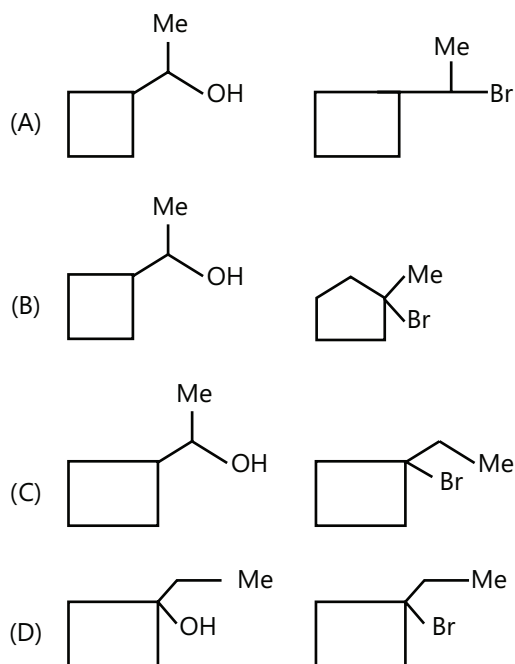
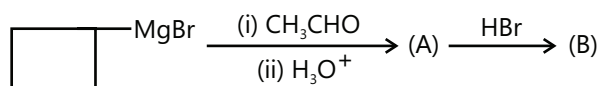
**Q.11** Which of the best method for the conversion of (A) pentan-3-ol to 3-bromopentane (B)?



**Q.12** In Zeisel's method for the determination of methoxyl groups, a sample of 2.68 gm of a compound (A) gave 14.08 gm of AgI. If the molecular weight of compound (A) is 134, the number of (-OCH<sub>3</sub>) group(s) in the compound (A) is:

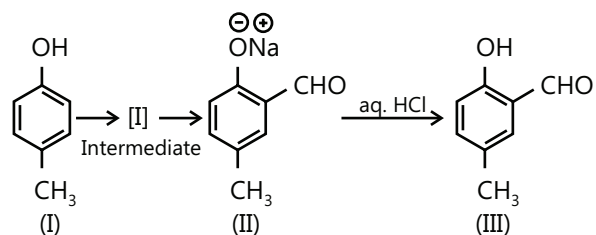
- (A) 1 (B) 2 (C) 3 (D) 4

**Q.13**



**Comprehension Type**

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



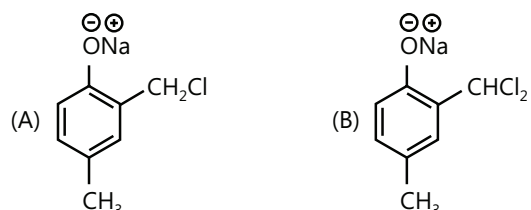
**Q.14** Which one of the following reagents is used in the above reaction?

- (a) aq. NaOH + CH<sub>3</sub>Cl (b) aq. NaOH + CH<sub>2</sub>Cl<sub>2</sub>  
 (c) aq. NaOH + CHCl<sub>3</sub> (d) aq. NaOH + CCl<sub>4</sub>

**Q.15** The electrophile in this reaction is:

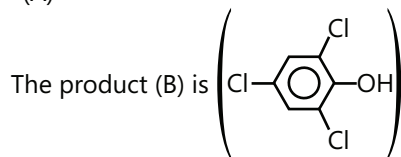
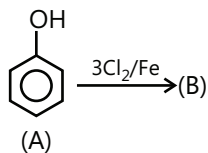
- (A) :CHCl (B)  $\oplus\text{CHCl}_2$  (C) :CCl<sub>2</sub> (D)  $\cdot\text{CCl}_3$

**Q.16** The structure of the intermediate (I) is:



## Assertion Reasoning Type

## Q.17 Assertion:

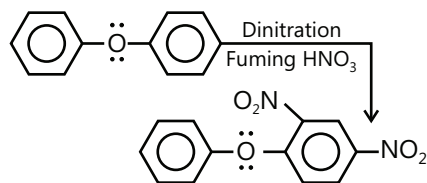


Reason (R): Phenol cannot be chlorinated because the ring is susceptible to oxidation by  $\text{Cl}_2$ .

**Q.18 Assertion:** 2, 6-Dimethyl-4-nitrophenol (I) is more acidic than 3, 5-dimethyl-4-nitrophenol (II).

**Reason:** It is due to steric inhibition of the resonance of  $(-\text{NO}_2)$  group with two (Me) groups in (II).

**Q.19 Assertion:** Diphenyl ether (I) on dinitration gives the product (II).



**Reason:** The ring with first nitro group is deactivated by  $\bar{e}$  withdrawing  $\text{NO}_2$  group, so the second nitro group enters the other ring.

## Match the Columns

**Q.20** Match the reactions of column I with the Mechanism of column II.

	Column I		Column II
	Reactions		Mechanism
(A)		(p)	Carbocation intermediate
(B)		(q)	Bromochloro carbene intermediate
(C)		(r)	SE reaction
(D)		(s)	Rearrangement of carbocation intermediate
(E)		(t)	$\text{S}_{\text{N}}1$ mechanism
(F)		(u)	No rearrangement

## Previous Years' Questions

**Q.1** When phenyl magnesium bromide reacts with tert-butanol, which of the following is formed? **(2005)**

- (A) Tert-butyl methyl ether      (B) Benzene  
(C) Tert-butyl benzene          (D) Phenol

**Q.2** The best method to prepare cyclohexene from cyclohexanol is by using **(2005)**

- (A) conc. HCl + ZnCl<sub>2</sub>    (B) conc. H<sub>3</sub>PO<sub>4</sub>  
(C) HBr                      (D) conc. HCl

**Q.3** (I) 1, 2-dihydroxy benzene

(II) 1, 3-dihydroxy benzene

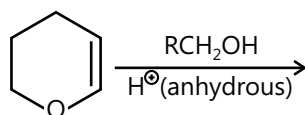
(III) 1, 4-dihydroxy benzene

(IV) Hydroxy benzene

The increasing order of boiling points of above mentioned alcohols is **(2006)**

- (A) I < II < III < IV      (B) I < II < IV < III  
(C) IV < I < II < III      (D) IV < II < I < III

**Q.4** The major product of the following reaction is **(2011)**

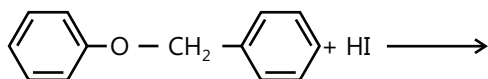


- (A) A hemiacetal      (B) An acetal  
(C) An ether          (D) An ester

**Q.5** The products of reaction of alcoholic silver nitrate with ethyl bromide are **(1998)**

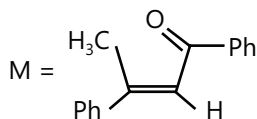
- (A) Ethane              (B) Ethene  
(C) Nitroethane      (D) Ethyl alcohol

**Q.6** The following ether, when treated with HI produces **(1999)**

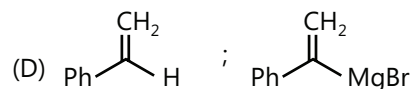
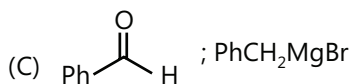
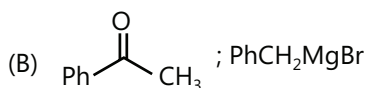
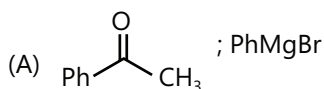


- (A)      (B)   
(C)      (D)

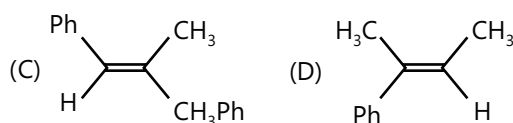
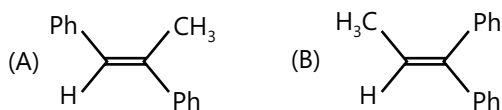
**Paragraph 1:** A tertiary alcohol H upon acid catalysed dehydration gives product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound L, whereas K on reaction with KOH gives only M. **(2008)**



**Q.7** Compound H is formed by the reaction of



**Q.8** The structure of compound I is

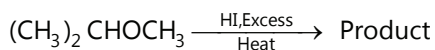


**Q.9** The structures of compound J, K and L respectively, are

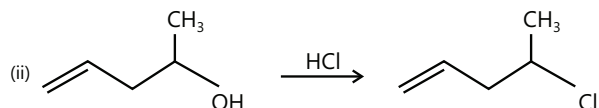
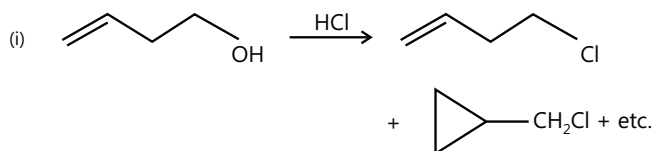
- (A) PhCOCH<sub>3</sub>, PhCH<sub>2</sub>COCH<sub>3</sub> and PhCH<sub>2</sub>COO<sup>-</sup> K<sup>+</sup>  
(B) PhCHO, PhCH<sub>2</sub>CHO and PhCOO<sup>-</sup> K<sup>+</sup>  
(C) PhCOCH<sub>3</sub>, PhCH<sub>2</sub>CHO and CH<sub>3</sub>COO<sup>-</sup> K<sup>+</sup>  
(D) PhCHO, PhCOCH<sub>3</sub> and PhCOO<sup>-</sup> K<sup>+</sup>

**Q.10** Give reasons for the following in one or two sentences. "Acid catalysed dehydration of t-butanol is faster than that of n-butanol." **(1998)**

**Q.11** Write the structures of the products: **(1998)**

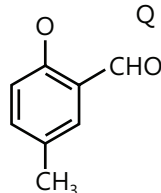
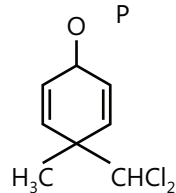
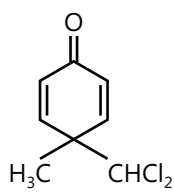
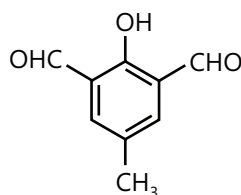
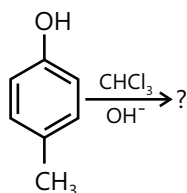


**Q.12** Explain briefly the formation of products giving the structures of the intermediates. **(1999)**



**Q.13** Cyclobutylbromide on treatment with magnesium in dry ether forms an organometallic compound (A). The organometallic reacts with ethanol to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B). **(2001)**

**Q.14.** In the following reaction, the product(s) formed is (are) **(2013)**



(A) P(major)

(B) Q(minor)

(C) R(minor)

(D) S(major)

**Q.15** The correct statement(s) about  $\text{O}_3$  is (are) **(2013)**

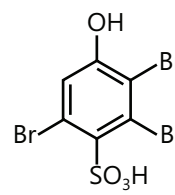
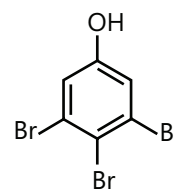
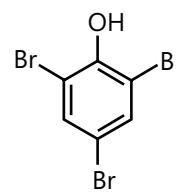
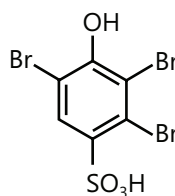
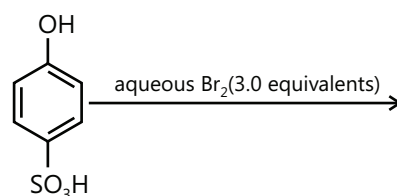
(A) O–O bond lengths are equal

(B) Thermal decomposition of  $\text{O}_3$  is endothermic

(C)  $\text{O}_3$  is diamagnetic in nature

(D)  $\text{O}_3$  has a bent structure

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



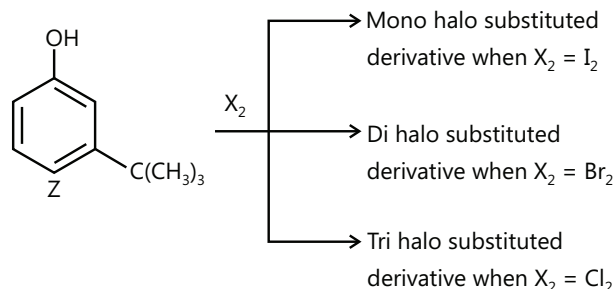
(A) P

(B) Q

(C) R

(D) S

**Q.17** The reactivity of compound Z with different halogens under appropriate conditions is given below: **(2014)**



The observed pattern of electrophilic substitution can be explained by

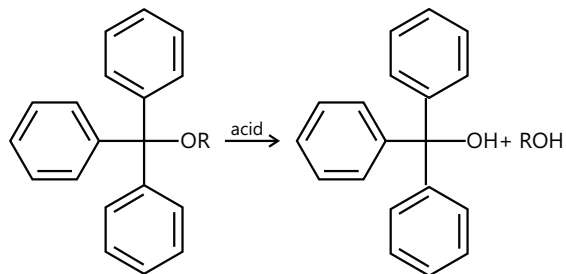
(A) The steric effect of the halogen

(B) The steric effect of the tert-butyl group

(C) The electronic effect of the phenolic group

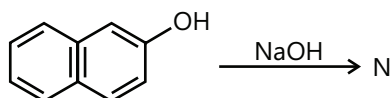
(D) The electronic effect of the tert-butyl group

**Q.18** The acidic hydrolysis of ether (X) shown below is fastest when (2014)

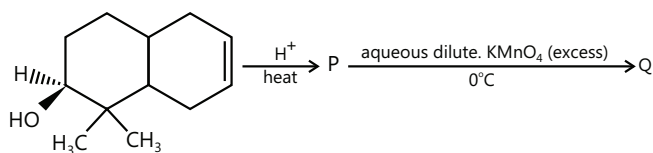


- (A) One phenyl group is replaced by a methyl group.  
 (B) One phenyl group is replaced by a para-methoxyphenyl group.  
 (C) Two phenyl groups are replaced by two para-methoxyphenyl groups.  
 (D) No structural change is made to X.

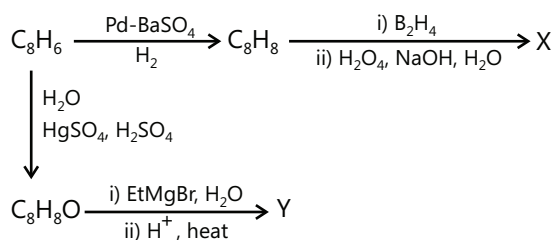
**Q.19** The number of resonance structures for N is (2015)



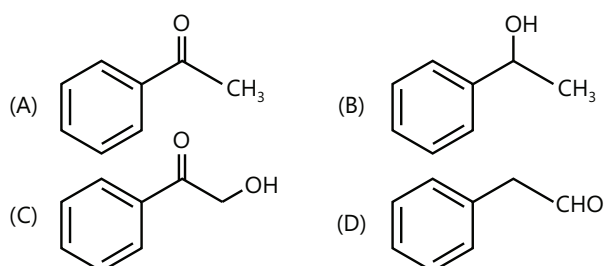
**Q.20** The number of hydroxyl group(s) in Q is (2015)



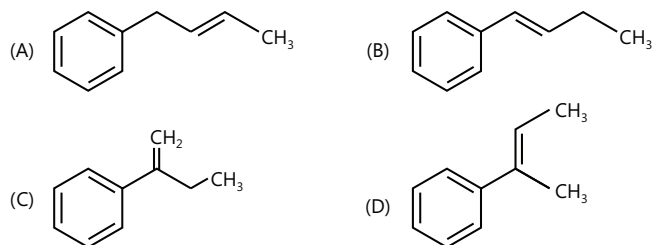
**Paragraph 2:** In the following reactions



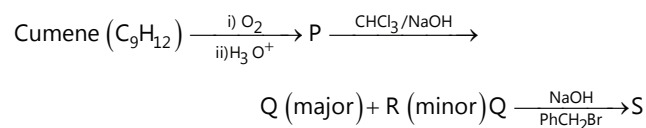
**Q.21** Compound X is (2015)



**Q.22** The major compound Y is (2015)



**Q.23** The correct statement(s) about the following reaction sequence is(are) (2016)



- (A) R is steam volatile  
 (B) Q gives dark violet coloration with 1% aqueous  $\text{FeCl}_3$  solution  
 (C) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine  
 (D) S gives dark violet coloration with 1% aqueous  $\text{FeCl}_3$  solution

# MASTERJEE Essential Questions

## JEE Main/Boards

### Exercise 1

Q.1      Q.5      Q.8  
Q.10

### Exercise 2

Q.2      Q.3      Q.7  
Q.14    Q.15    Q.16

### Previous Years' Questions

Q.3      Q.4      Q.6

## JEE Advanced/Boards

### Exercise 1

Q.1      Q.8      Q.11  
Q.15

### Exercise 2

Q.2      Q.5      Q.7  
Q.10    Q.12    Q.15  
Q.18

### Previous Years' Questions

Q.3      Q.6      Q.8  
Q.12

## Answer Key

## JEE Main/Boards

### Exercise 2

#### Single Correct Choice Type

Q.1 C	Q.2 D	Q.3 D	Q.4 B	Q.5 B	Q.6 B
Q.7 D	Q.8 B	Q.9 C	Q.10 A	Q.11 C	Q.12 B
Q.13 A	Q.14 A	Q.15 D	Q.16 D	Q.17 A	Q.18 D
Q.19 B	Q.20 C				

### Previous Years' Questions

Q.1 A	Q.2 A	Q.3 D	Q.4 B	Q.5 A	Q.6 A
Q.7 D	Q.8 C	Q.9 F	Q.10 F	Q.11 D	Q.12 D
Q.13 A	Q.14 B	Q.15 D	Q.16 C	Q.17 B	

## JEE Advanced/Boards

### Exercise 2

#### Single Correct Choice Type

Q.1 D	Q.2 B	Q.3 D	Q.4 A	Q.5 A	Q.6 C
Q.7 C	Q.8 A	Q.9 A	Q.10 B	Q.11 B	Q.12 C
Q.13 B					

#### Comprehension Type

Q.14 C	Q.15 C	Q.16 B
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#### Assertion Reasoning Type

Q.17 D	Q.18 A	Q.19 D
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#### Match the Columns

Q.20 A → q, r; B → p, s; C → u; D → p, t; E → p, r, s; F → p, s

### Previous Years' Questions

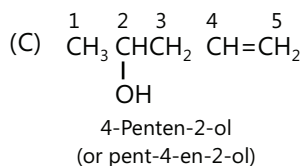
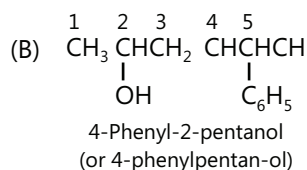
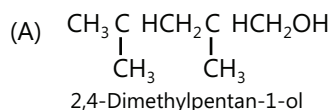
Q.1 B	Q.2 B	Q.3 C	Q.4 A	Q.5 C, E	Q.6 A, D
Q.7 B	Q.8 A	Q.9 D	Q.14 B, D	Q.15 A, C, D	Q.16 B
Q.17 A, B, C	Q.18 C	Q.19 9	Q.20 D	Q.21 C	Q.22 D
Q.23 B, C					

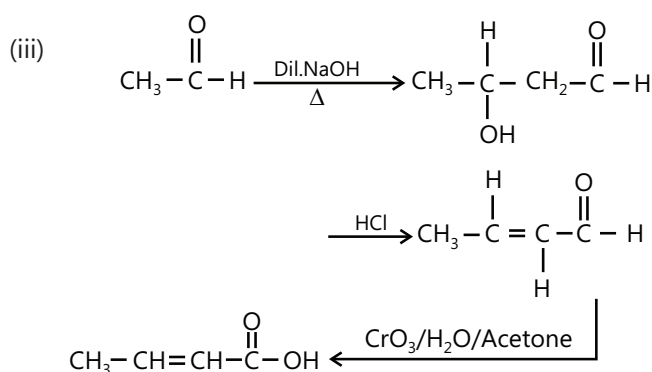
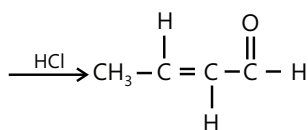
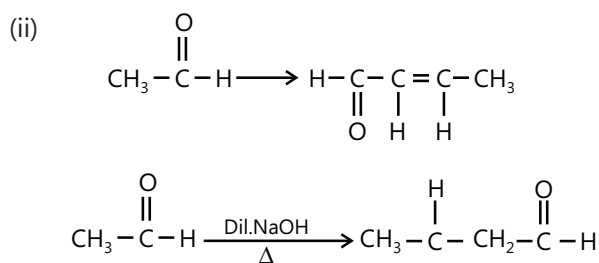
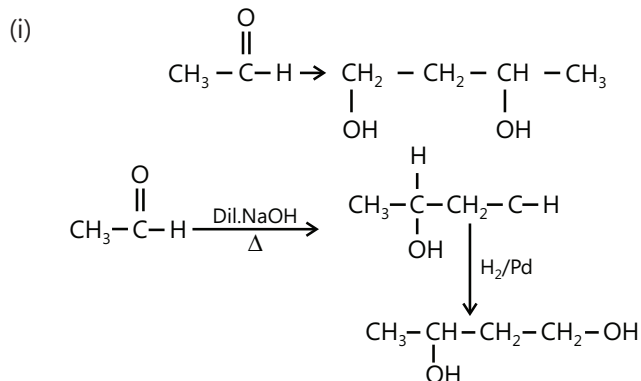
## Solutions

### JEE Main/Boards

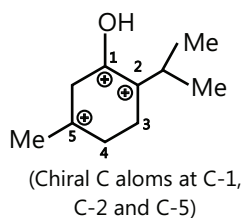
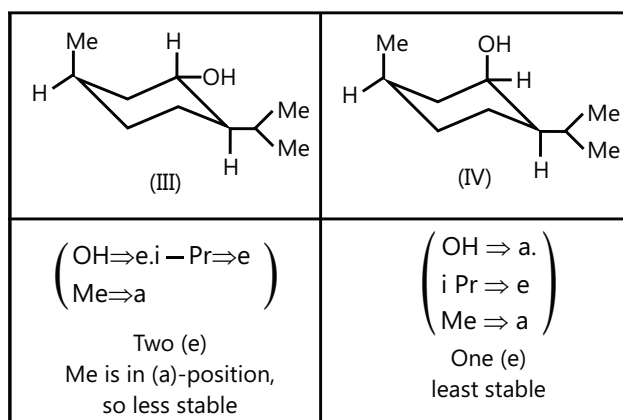
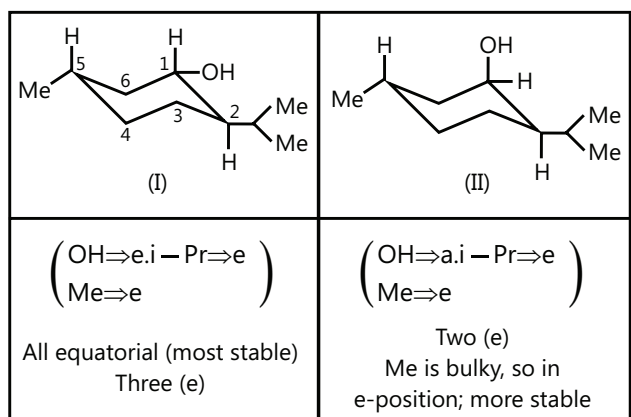
#### Exercise 1

**Sol 1:** The longest chain to which the hydroxyl group is attached gives us the base name. The ending is ol. We then number the longest chain from the end that gives the carbon bearing the hydroxyl group the lower number. Thus, the names, in both of the accepted IUPAC formats, are

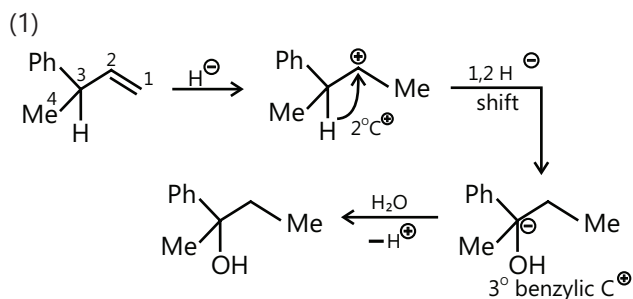


**Sol 2:**

**Sol 3:** There are three chiral C atoms and there are four diastereomers, each with a pair of enantiomers. Thus total stereoisomers are 8.



Stability order is: I > II > III > IV

**Sol 4:**

**Sol 5:** a. Boiling point order: VI > IV > V > III > II > I

Solubility order: I > II > III > V > IV > VI

Explanation: All of them are alcohols, so all have H-bonding. As the molecular mass and surface area increases, the boiling point increases and solubility decreases.

Out of (IV) and (V), there is branching in (V) and has less surface area than (IV), so the boiling point of (IV) > (V), but solubility of (V) > (IV).

b. Boiling point order: I > III > IV > II

Solubility order: I > III > IV > II



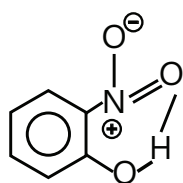
In (I), there is H-bonding in (II) (aldehyde), dipole-dipole interaction, in (III) (ether), slightly polar due to EN of O, and in (IV) (alkane), van der Waals interaction (non-polar).

c. Boiling point order: II > III > I

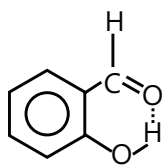
Solubility order: II > III > I

In (II), three (-OH) groups, more H-bonding; in (III), one (-OH) group, less H-bonding; in (I) (alkane), van der Waals interaction.

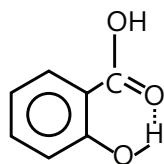
**Sol 6:** In ortho-isomers of (I), (II), and III, intramolecular H-bonding (chelation) occurs which inhibits the intermolecular attraction between these molecules and thus lowers the boiling point and also reduces H-bonding of these molecules with H<sub>2</sub>O, thereby, decreases water solubility. Intramolecular chelation does not occur on p- and m-isomers.



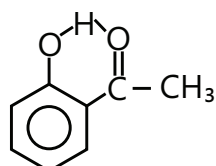
o-Nitrophenol



o-Hydroxybenzaldehyde  
(Salicylaldehyde)



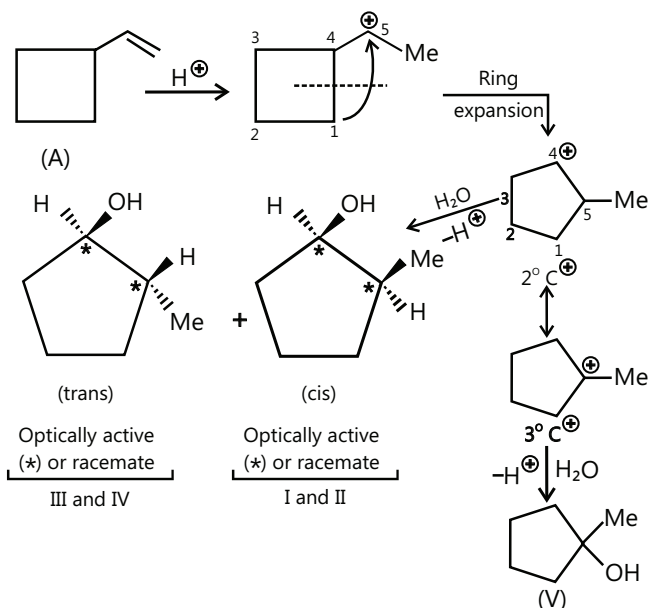
o-Hydroxybenzoic acid  
(Salicylic acid)



o-Hydroxyacetophenone

**Sol 7:** Chelated o-isomers have a minimum attraction with H<sub>2</sub>O, and they are steam volatile or steam distills. Steam volatile or steam distills are the compounds which are mixed with boiling H<sub>2</sub>O but not dissolved. On passing steam to such boiling mixture, steam carries the compound with it.

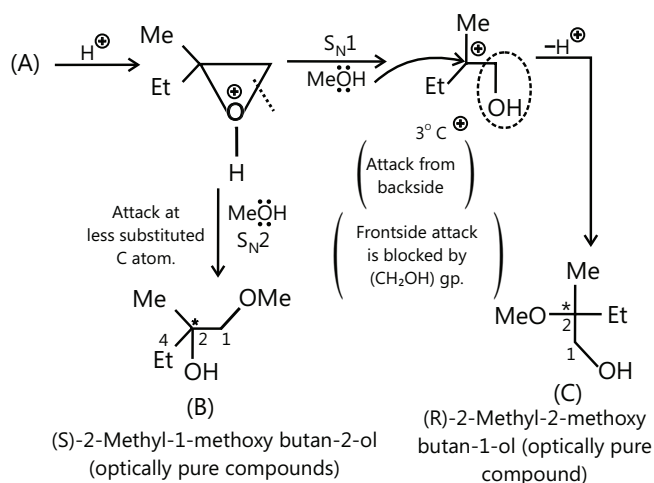
**Sol 8:**



The total number of isomeric products including stereoisomers is 5.

**Sol 9:** Greater the steric hindrance in the ether molecule encountered in the formation of the coordinate bond, weaker is the Lewis basicity. In (i), R groups (the side of the ring) are 'tied back' leaving a very exposed O atom free to serve as basic site. In other words, more compact the molecule (due to ring), more easily O atom can donate its LP e<sup>-</sup>s to the Lewis acid, and therefore, stronger the Lewis base.

**Sol 10:**

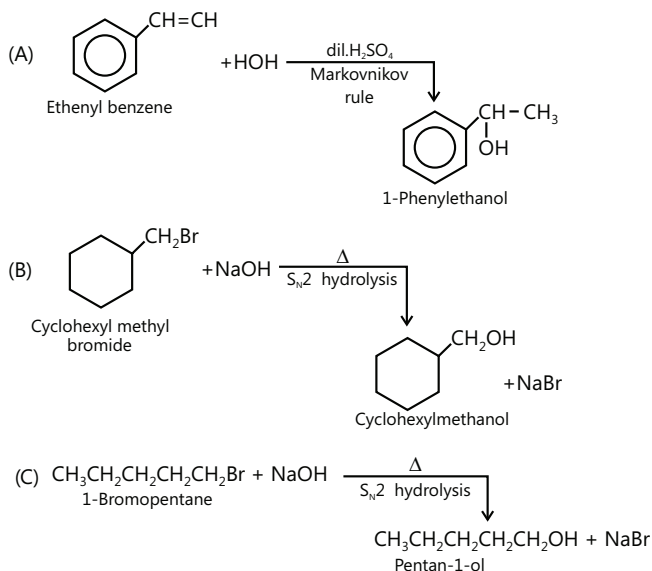


(B) is obtained by S<sub>N</sub>2 by the attack of nucleophile

$\left( \begin{array}{c} \cdot\cdot \\ MeOH \\ \cdot\cdot \end{array} \right)$  at less substituted C, without changing the

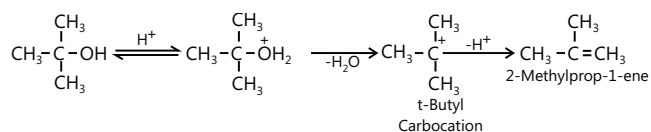
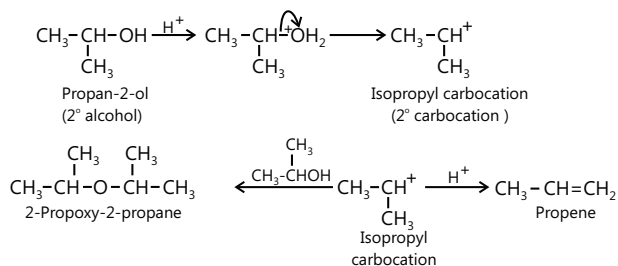
configuration or groups priorities and the product is S-stereoisomer.

(C) is obtained by  $S_N1$  ring opening to give stable  $3^\circ C^\oplus$ . The nucleophile  $\left(\text{MeOH}\right)$  attacks from the backside because front side attack is blocked by the  $(-\text{CH}_2\text{OH})$  group.

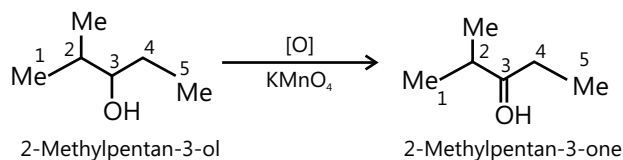
**Sol 11:**

**Sol 12:** Acid-catalyzed dehydration of  $1^\circ$  alcohols to ethers takes place by  $S_N2$  reaction involving nucleophilic attack by the alcohol molecule on the protonated alcohol molecule as.

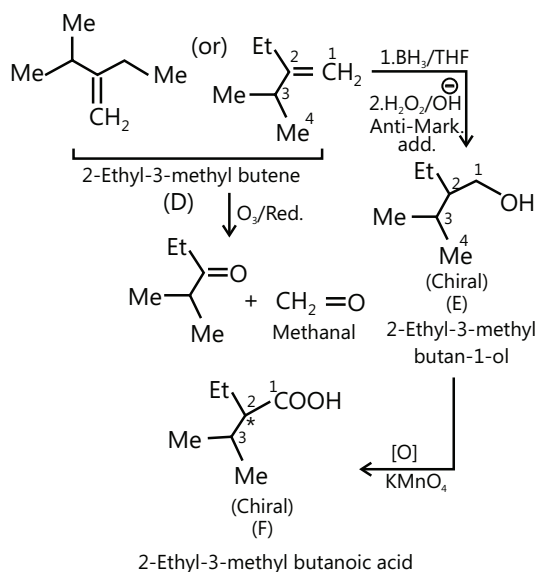
However, under these conditions,  $2^\circ$  alcohols give alkenes rather than ethers. This is because of the steric hindrance, nucleophilic attack by the alcohol on the protonated alcohol molecule does not take place. Instead of this, the protonated  $2^\circ$  and  $3^\circ$  alcohols lose a molecule of water to form stable  $2^\circ$  and  $3^\circ$  carbocations. These carbocations then prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.



**Sol 13:** Proceed reverse from the oxidation of 2-methylpentan-3-ol.



The possible structure of (D) is:

**Sol 14:**

i. DU in (A) =  $\frac{(2n_C + 2) - n_H}{2} = \frac{(8 \times 2 + 2) - 8}{2} = 5^\circ$

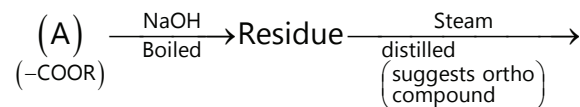
ii. Five DU and (C:H  $\approx$  1:1) suggest benzene ring (4 DU) and 1 DU has to be accounted.

iii. It does not contain  $(-\text{COOH})$  group, since it is not soluble in  $\text{NaHCO}_3$ .

iv. It is soluble in NaOH, which suggests phenolic (OH) group.

v. (A) contains three O atoms, which suggests an ester group  $(-\text{COOR})$  and one phenolic (OH) group.

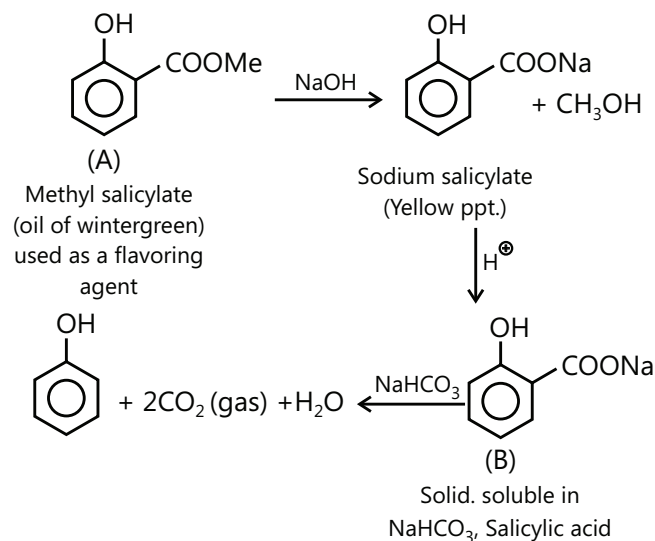
The presence of an ester group is also indicated by the reaction of (B) with  $\text{NaHCO}_3$ .



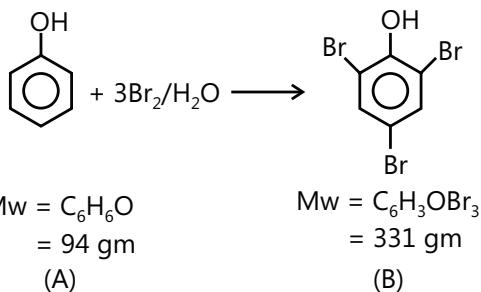
Distillate  $\xrightarrow{\text{NaOH}}$  Yellow ppt.  $\xrightarrow{\text{H}^{\oplus}}$

(B) (-COOH group)  $\left( \begin{array}{l} \text{Dissolves} \\ \text{in NaHCO}_3 \end{array} \right)$

vi. Yellow precipitate with NaOH is a characteristic test for methyl salicylate.



**Sol 15:**



331 gm of (B) is obtained from 94 gm of (A).

33.1 gm (B) is obtained from =  $\frac{94}{331} \times 33.1$

= 9.4 gm of phenol

Weight of phenol = 9.4 gm

$$= \frac{9.4}{94} = 0.1 \text{ mol}$$

ii. NaOH will react with both  $\text{CH}_3\text{COOH}$  and phenol.

Total molar equivalent of NaOH =  $100 \times 2$

$$= 200 \text{ mEq}$$

$$= \frac{200}{1000} = 0.2 \text{ Eq. of NaOH}$$

$$= 0.2 \text{ mol of NaOH}$$

Acid + Phenol = 0.2 mol

Acid + 0.1 mol = 0.2 mol

$$\therefore \text{Acid} = 0.2 - 0.1 = 0.1 \text{ mol} \\ = 0.1 \text{ Eq.}$$

1 Eq. of  $\text{CH}_3\text{COOH}$  = 60 gm

0.1 Eq. of  $\text{CH}_3\text{COOH}$  = 6 gm

Weight of acid = 6 gm

Weight of phenol = 9.4 gm

$$\text{Mass percentage of acid} = \frac{6}{30} \times 100 = 20 \%$$

$$\text{Mass percentage of phenol} = \frac{9.4}{30} \times 100 = 31.3 \%$$

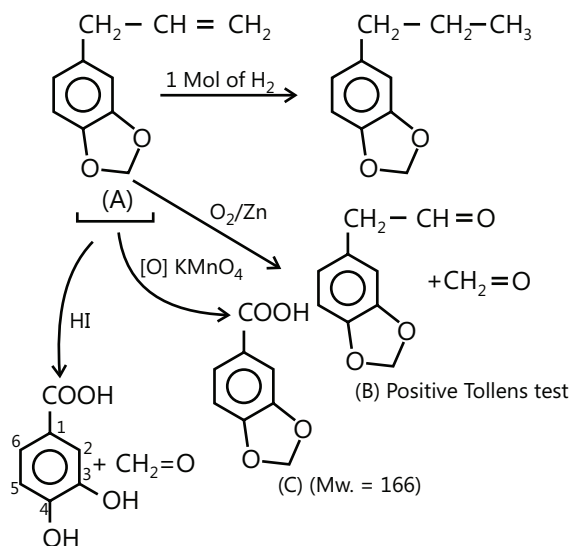
**Sol 16:** i. Six DU in (A) and ( $\text{C}:\text{H} \approx 1:1$ ) suggest benzene ring (4 DU).

ii. (A) does not contain phenolic group since it does not dissolve in NaOH and does not colour with  $\text{FeCl}_3$ .

iii. (A) reacts with 1 Eq. of  $\text{H}_2$ , which suggests one ( $\text{C}=\text{C}$ ) bond. Ozonolysis also suggests one ( $\text{C}=\text{C}$ ) bond. It also counts one more DU.

iv. Remaining two oxygen atoms must be present in fused ring (which is conformed by the formation of 3,4-dihydroxybenzoic acid with HI) (Acetal ring).

Reactions:



## Exercise 2

### Single Correct Choice Type

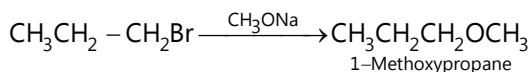
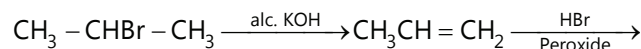
**Sol 1: (C)** Four DU in A and (C: H  $\approx$  1: 1) suggest benzene ring with one extra C atom. Reactivity with NaOH and FeCl<sub>3</sub> suggest (A) to be a phenol. The formation of a tribromo product suggests that o-positions are vacant. Hence, (A) is m-cresol.

**Sol 2: (D)** The ether preparation follows the following steps-

1. Protonation
2. Nucleophilic substitution(S<sub>N</sub>2)
3. Deprotonation by the base and release of HCl by shifting of bonds due to the presence of a good leaving group to give stability.

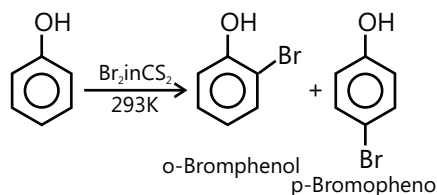
**Sol 3: (D)** All of the given statements regarding glycerol are correct.

**Sol.4: (B)**



**Sol 5: (B)** Ethers on exposure to sunlight slowly react with oxygen from air to form peroxide. These peroxide are unstable and decompose on distillation resulting violent reaction.

**Sol 6: (B)**



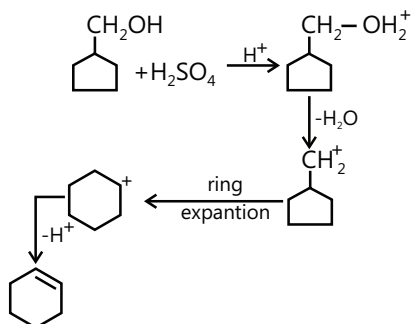
**Sol 7: (D)** Phenol is more acidic than cresol but less acidic than nitrophenol. P-nitrophenol is more acidic than m-nitrophenol. Thus, the correct order is p-nitrophenol > m-nitrophenol > phenol > cresol.

**Sol 8: (B)** The addition of a proton at  $\beta$ -carbon gives a carbocation (I) which is resonance stabilized because of electron donating effect of -OH group. The addition of Br<sup>-</sup> ion to the carbocation gives the main product.

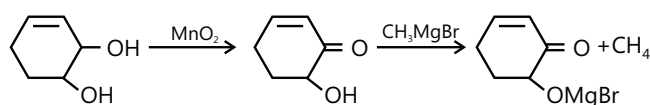
**Sol 9: (C)** Oxymercuration demercuration is anti Markovnikov addition of water molecule to alkenes.

**Sol.10: (A)** Ethers on hydrolysis gives alcohol.

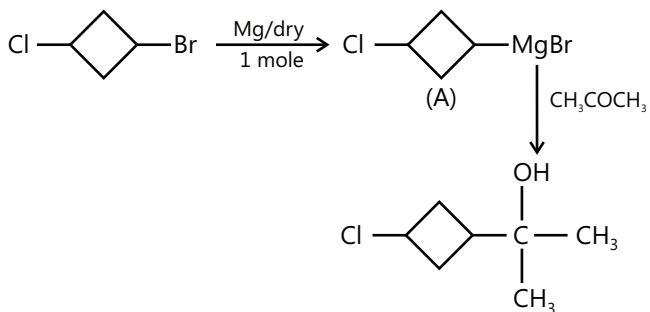
**Sol 11: (C)**



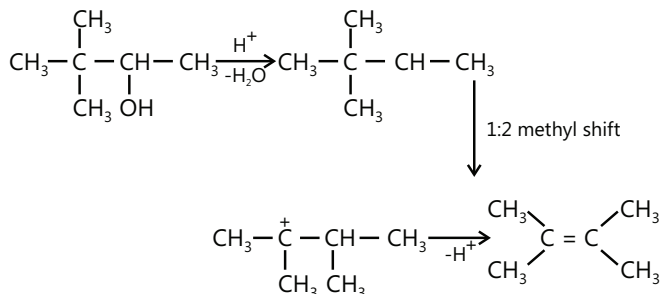
**Sol 12: (B)**

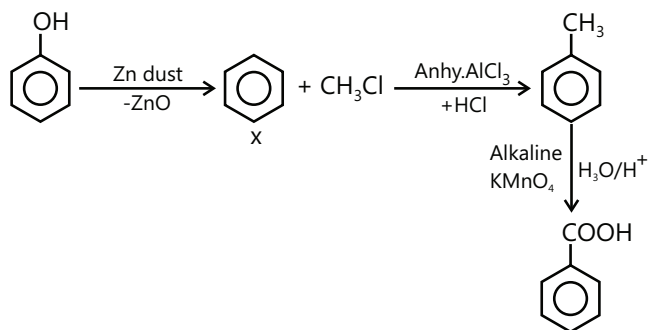
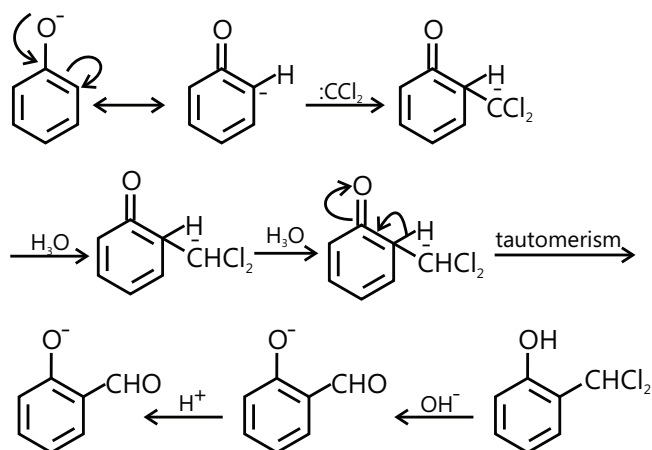
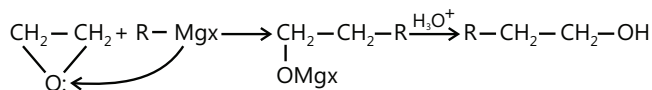


**Sol 13: (A)**

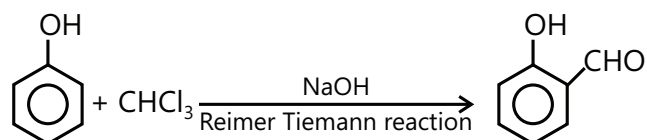
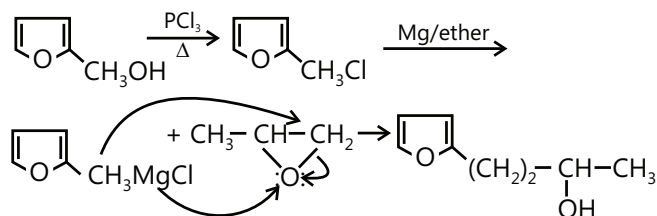
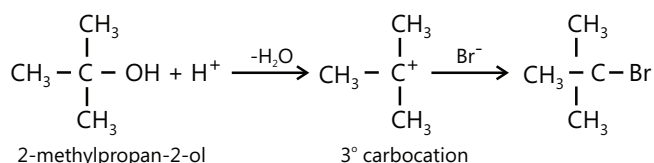


**Sol 14: (A)**

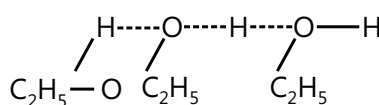


**Sol 15: (D)****Sol 16: (D)****Sol 17: (A)**

**Sol 18: (D)** Heating of alkyl halide with sodium or potassium alkoxide gives ether. This is a good method for preparation of simple as well as mixed ether known as Williamson's synthesis.

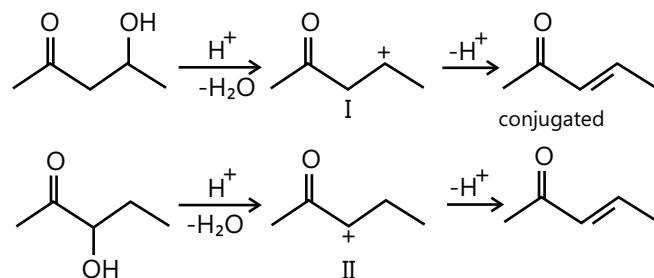
**Sol 19: (B)****Sol 20: (C)****Previous Years' Questions****Sol 1: (A)**

**Sol 2: (A)** Ethanol is capable in forming intermolecular H-bonds:



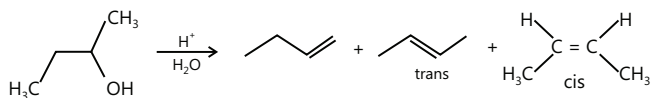
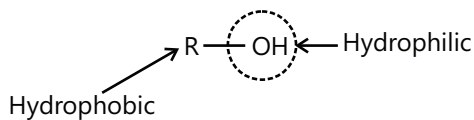
**Sol 3: (D)**  $\text{OH} \rightarrow \text{O}^- + \text{H}^+$  (has maximum electronegativity difference)

**Sol 4: (B)** Thiol,  $\text{RSH}$ , on combustion produces  $\text{CO}_2(\text{g})$ ,  $\text{SO}_2(\text{g})$  and  $\text{H}_2\text{O}$ . At 298 K,  $\text{H}_2\text{O}$  will be liquid phase.

**Sol 5: (A)**

Although both reactions are giving the same product, carbocation I is more stable than II.

**Sol 6: (A)** A is an alcohol and its oxidation product gives Tollen's test i.e., B must be an aldehyde ( $\text{CH}_3\text{CH}_2\text{CHO}$ )

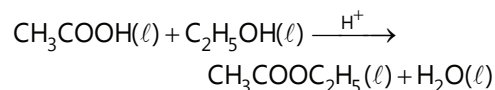
**Sol 7: (D)****Sol 8: (C)**

Increasing molecular weight increases hydrocarbon (R) proportion that lowers the solubility in water.

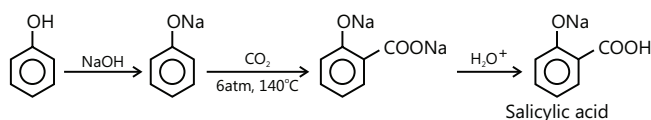
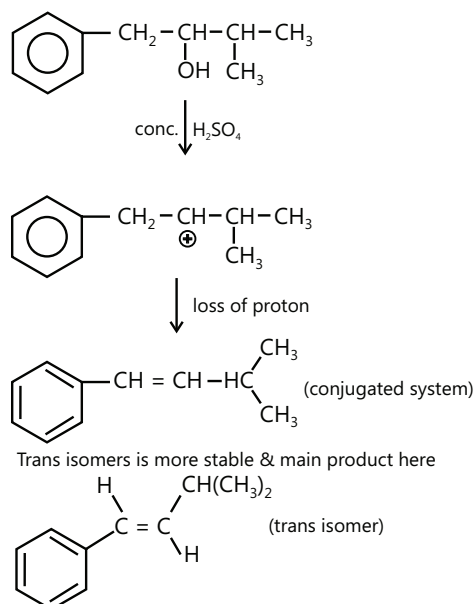
**Sol 9: (F)**  $2^\circ$  - alcohol on oxidation yields ketone while  $1^\circ$  alcohol on oxidation produces aldehyde which can further be oxidized to acid.

**Sol 10: (F)** Ethanol is weaker acid than water, not neutralized with NaOH.

**Sol 11: (D)** Esterification reaction is involved

**Sol 12: (D)**

Kolbe – Schmidt reaction is

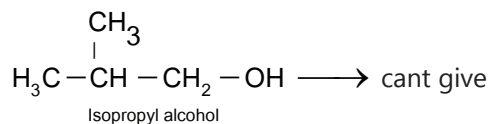
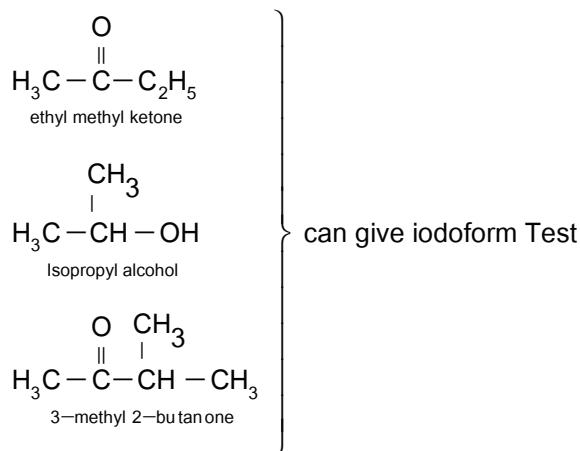
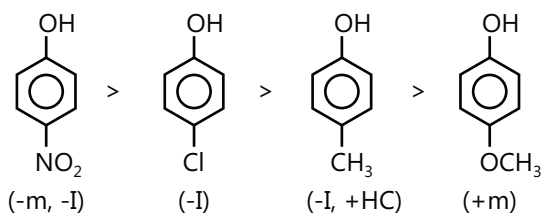
**Sol 13: (A)**

**Sol 14: (B)** Ortho-Nitrophenol is less soluble in water than p- and m- Nitrophenols because o-Nitrophenol shows Intramolecular H-bonding.

**Sol 15: (D)** Iodoform is given by

- 1) methyl ketones  $\text{R}-\text{CO}-\text{CH}_3$
- 2) alcohols of the type  $\text{R}-\text{CH}(\text{OH})\text{CH}_3$

Where R can be hydrogen also

**Sol 16: (C)**

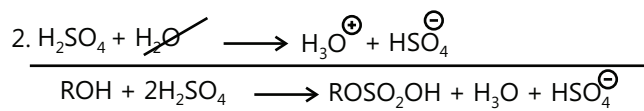
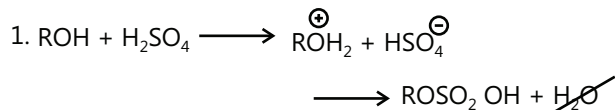
Electron releasing group decreases and electron withdrawing group increases acidic strength.

**Sol 17: (B)** The reaction of alcohol with Lucas reagent is mostly an  $\text{S}_{\text{N}}1$  reaction and the rate of reaction is directly proportional to the carbocation stability formed in the reaction, since  $3^\circ \text{R}-\text{OH}$  forms  $3^\circ$  carbocation hence it will react fastest.

## JEE Advanced/Boards

### Exercise 1

**Sol 1:** ROH reacts with cold conc.  $\text{H}_2\text{SO}_4$  as follows:



Number of moles of particles formed per mole of solute (i) (van't Hoff factor) = 3 (The reaction does not produce  $\text{R}^{\oplus}$ , because  $\text{R}^{\oplus}$  ion or even  $\text{R}_3\text{C}^{\oplus}$  ion is not stable enough to persist)

$$\therefore \Delta T_f = iK_f \times M$$

$$= 3 \times 0.1 = 0.3 \times K$$

**Sol 2:** Let the formula of alcohol is  $\text{R}(\text{OH})_n$ , and the formula of its acetyl derivative is  $\text{R}(\text{OCOCH}_3)_n$ .

Molecular mass of  $\text{R}(\text{OCOCH}_3) = (M + 42n)$

M is the molecular mass of alcohol.

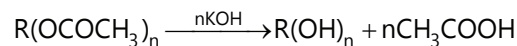
Molecular mass of  $(\text{CH}_3 - \text{CO} -)$  group = 43

One H atom is replaced by (OH) group of  $\text{CH}_3\text{COOH}$  group

Therefore, molecular mass of  $\text{R}(\text{OCOCH}_3)$

$$= [M + (43 - 1)n]$$

$$= (M + 42n)$$



Molecular mass of  $n\text{KOH} = 56n$

0.218 gm of acetyl derivative requires 0.168 gm of KOH for hydrolysis.

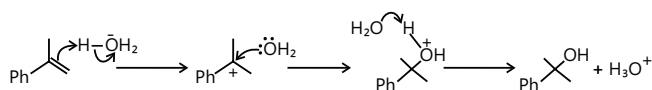
$\therefore (M + 42n)$  gm of acetyl derivative requires

$$= \frac{0.168(M + 42n)}{0.218} = 56n$$

On solving, we get  $n = 3$

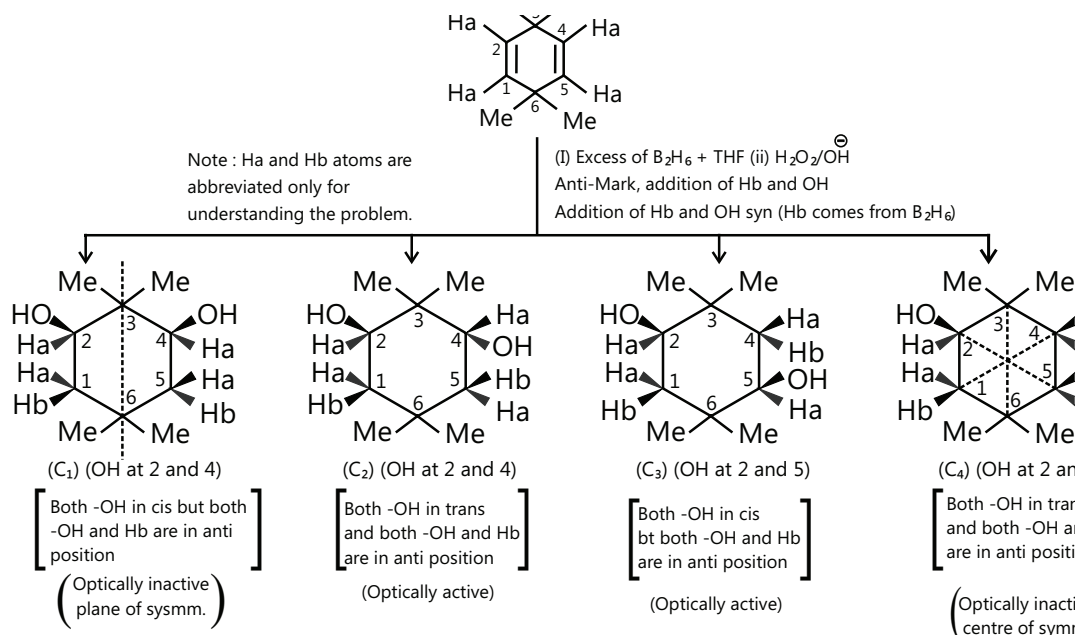
$$\left[ \begin{array}{l} \text{Use the formula: } \frac{w(M + 42n)}{W} = 56n \\ w = \text{Weight of KOH, } W = \text{weight of acetyl derivative,} \\ M = \text{Molecular mass of alcohol; } n = \text{Number of} \\ \text{(-OH) groups} \end{array} \right]$$

**Sol 3:**

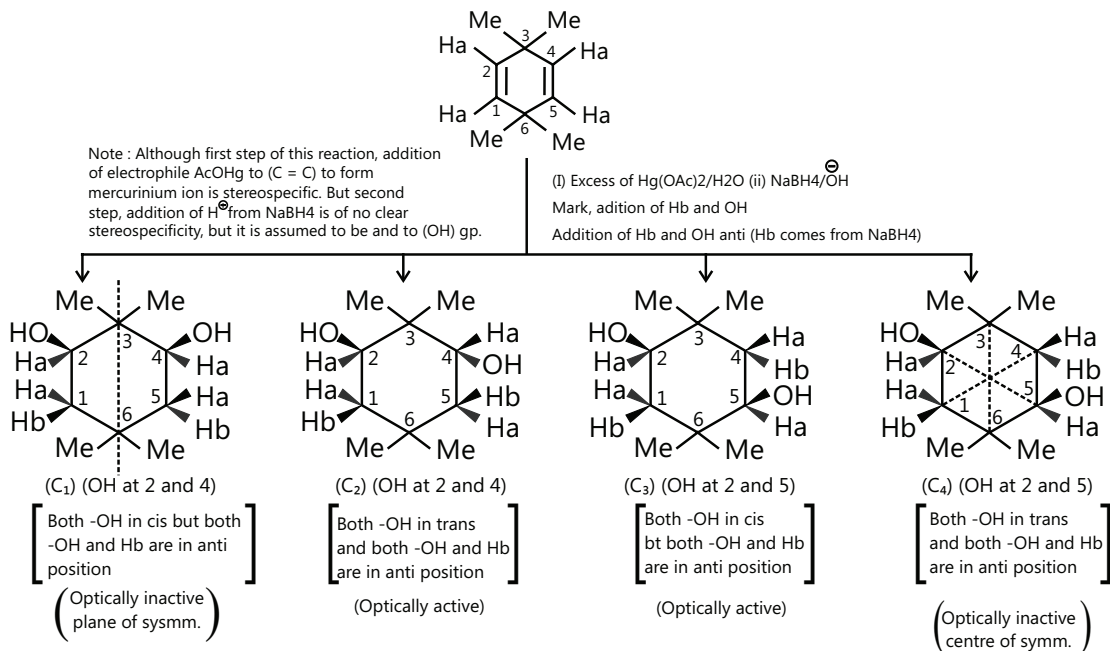


(b) Initial reaction of the alkene with  $\text{H}_3\text{O}^+$  can form two carbocations. The more stable benzylic tertiary carbocation (shown in the above mechanism) is formed in preference to the less stable primary carbocation. This is the rate determining step, and thus controls the product distribution. Formation of the more stable carbocation is the mechanistic basis for Markovnikov's rule.

**Sol 4:**



Thus, the number of isomers excluding enantiomers is 4.

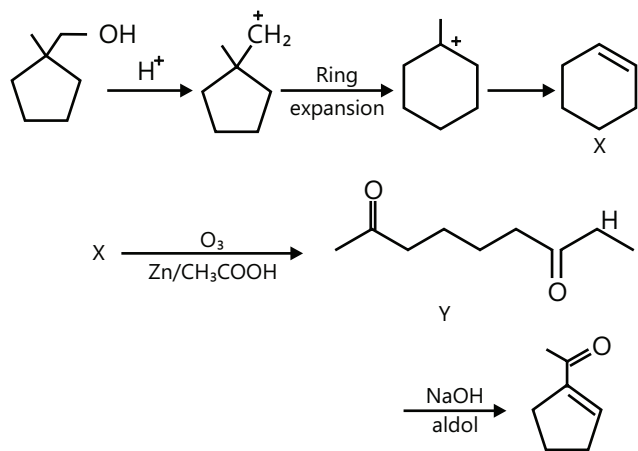


Thus, the number of isomers excluding enantiomers is 4.

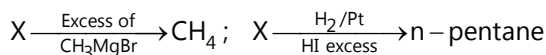
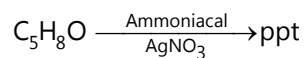
Note: The products  $\text{B}_1$  and  $\text{C}_1$ ,  $\text{B}_2$  and  $\text{C}_2$ ,  $\text{B}_3$  and  $\text{C}_3$ ,  $\text{B}_4$  and  $\text{C}_4$  are same.

If the reaction (a) is carried out with excess of  $\text{B}_2\text{D}_6 + \text{THF} + \text{H}_2\text{O}_2/\text{OH}^-$  and (b) is carried out with excess of  $\text{Hg}(\text{OAc})_2 + \text{H}_2\text{O} + \text{NaBD}_4$ , then in place of  $\text{H}_b$ ,  $\text{D}$  will come in all product, and the product, and the products  $\text{B}_1$  and  $\text{C}_1$ ,  $\text{B}_2$  and  $\text{C}_2$ ,  $\text{B}_3$  and  $\text{C}_3$ , and  $\text{B}_4$  and  $\text{C}_4$  would be different.

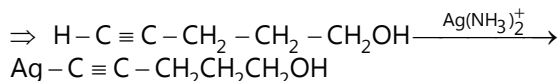
**Sol 5:**



**Sol 6:** Compound 'X'  $\xrightarrow{\text{Lucas reagent}}$  No reaction at room temperature.

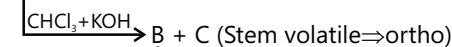


Above information suggest that X has a terminal triple bond and it contain primary  $-\text{OH}$  group.

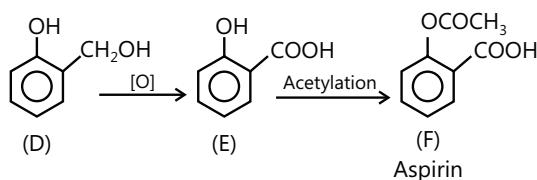
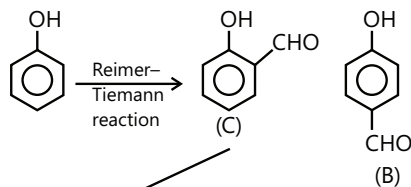
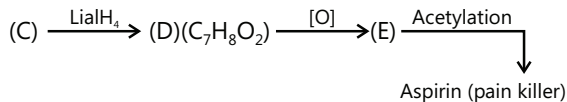


**Sol 7:**

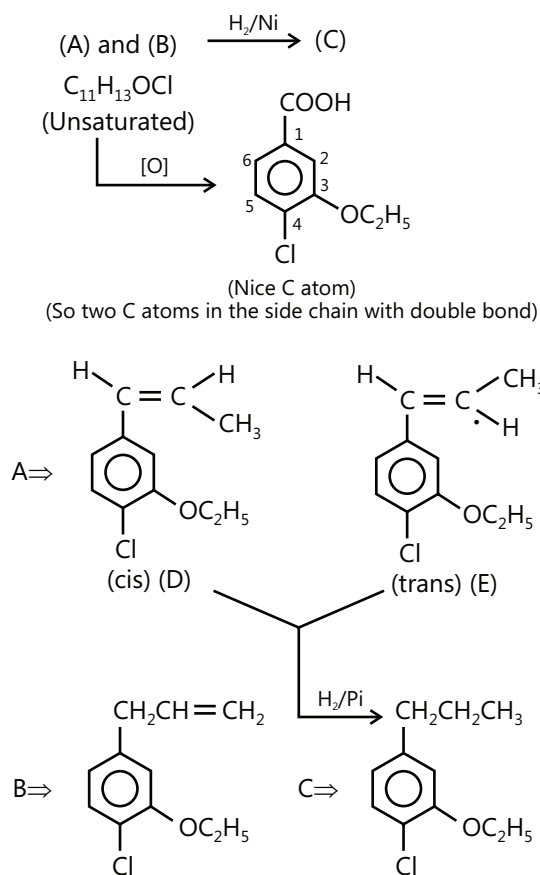
(A)  $\longrightarrow$  Positive Liebermann's test (test for phenol)



Positive Schiff's test (test for  $(-\text{CHO})$  group)





**Sol 8:**

**Sol 9:** The ratios of atoms in the minor products are:

$$C : H : N : O :: \frac{42.86}{12} : \frac{2.40}{1} : \frac{16.67}{14} : \frac{38.07}{16}$$

$$:: 3.57 : 2.40 : 1.19 : 2.38$$

$$:: 3 : 2 : 1 : 2$$

Empirical formula of the minor product:  $C_3H_2NO_2$

Molar empirical formula mass of the minor product is  
 $(3 \times 12 + 2 \times 1 + 1 \times 14 + 2 \times 16) \text{ gm mol}^{-1} = 84 \text{ gm mol}^{-1}$

Let  $M$  be the molar mass of the minor product. For 5.5 gm of the minor product dissolved in 45 gm benzene, the molality of solution is given by

$$m = \frac{55 \text{ gm} / M}{0.045 \text{ kg}}$$

Substituting this in the expression of elevation of boiling point, we get

$$\Delta T_a = K_b m$$

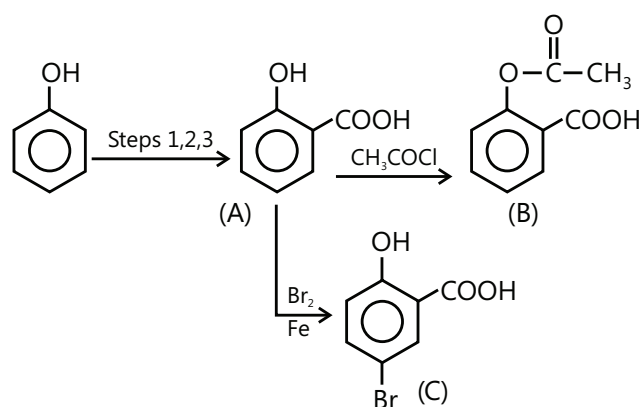
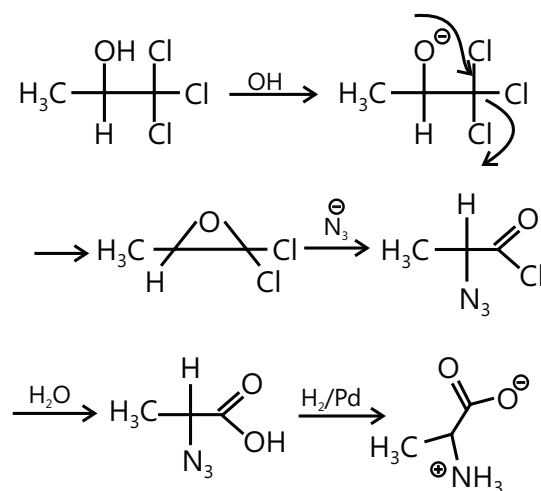
$$1.84 \text{ K} = \left( 2.53 \text{ K kg mol}^{-1} \right) \left( \frac{55 \text{ gm} / M}{0.045 \text{ kg}} \right)$$

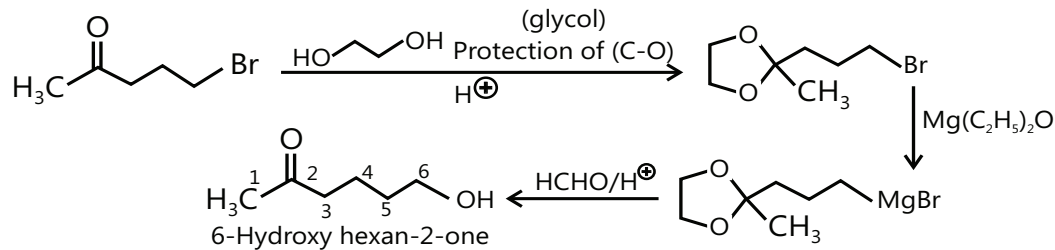
$$M = \left( \frac{2.53 \times 55}{1.84 \times 0.045} \right) \text{ gm mol}^{-1} = 168 \text{ gm mol}^{-1}$$

Number of unit of empirical formula in the molecular formula

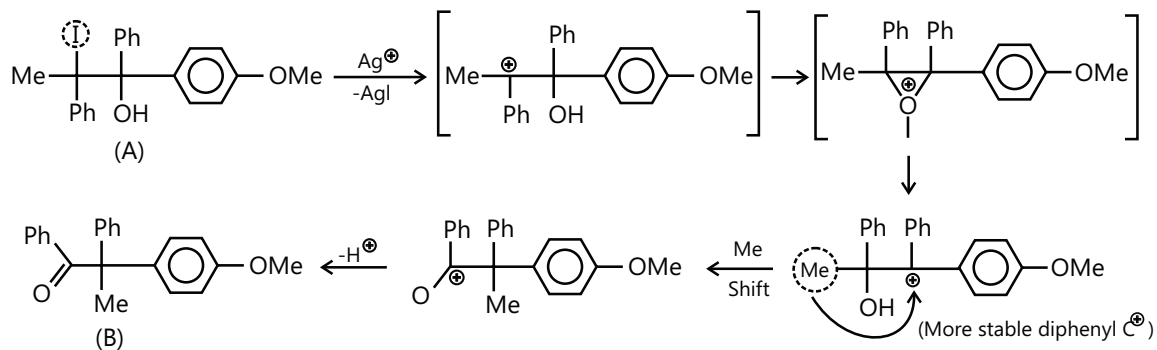
$$= \frac{168 \text{ gm mol}^{-1}}{84 \text{ gm mol}^{-1}} = 2$$

Hence, the molecular formula of the minor product is  $2(C_3H_2NO_2)$ , i.e.,  $C_6H_4(NO_2)_2$ . The product is m-dinitrobenzene.

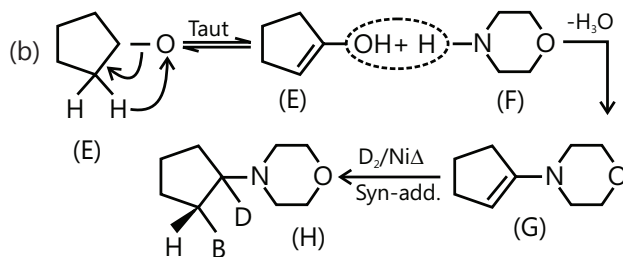
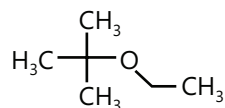
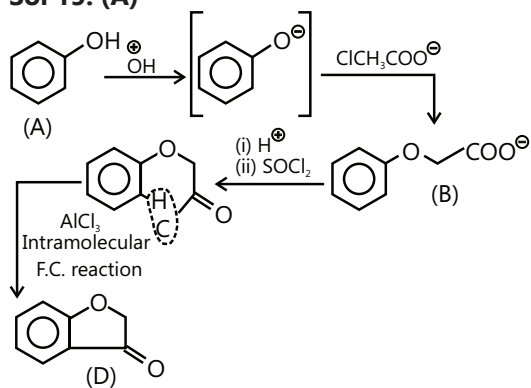
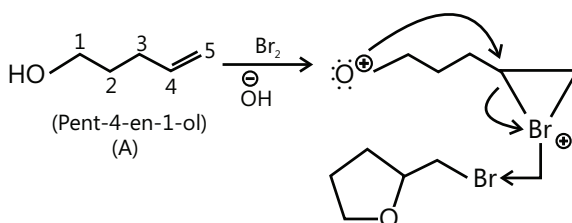
**Sol 10:****Sol 11:**

**Sol 12:**

**Sol 13:** It is an intramolecular  $\text{S}_{\text{N}}2$ -type reaction that proceeds through an intermediate epoxide.



**Sol 14:** t-Butylalcohol on heating in the presence conc.  $\text{H}_2\text{SO}_4$  forms a stable  $3^\circ$  carbocation which then reacts with  $\text{C}_2\text{H}_5\text{OH}$  (nucleophile) to give the product.

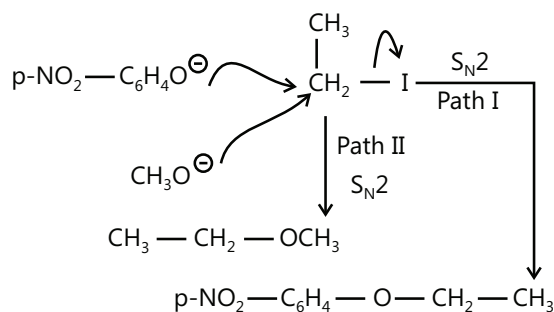
**Sol 15: (A)****Sol 16:****Exercise 2****Single Correct Choice Type**

**Sol 1: (D)** All of the above given statements are correct.

**Sol 2: (B)** vicinal diol sites are only two, thus only 2 equivalents of  $\text{HIO}_4$  will be consumed

**Sol 3: (D)** Refer mechanism of esterification in the theory.

**Sol 4: (A)** iv.  $C_2H_5O^-$  acts as a base. It abstracts  $H^+$  from phenol to form  $PhO^-$  ion.  $C_2H_5O^-$  is a stronger nucleophile than  $PhO^-$ . Hence the product is obtained by path II.



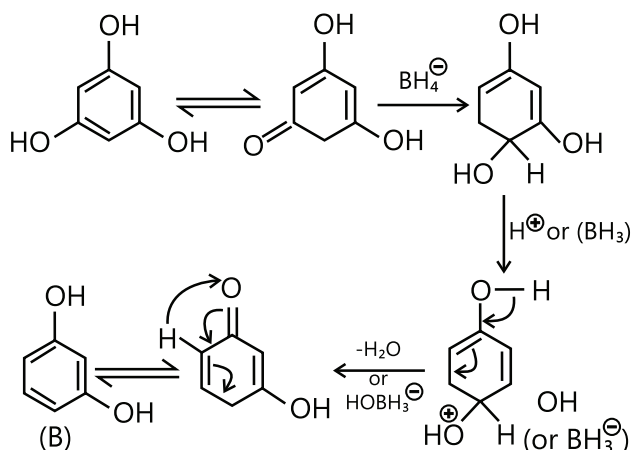
(Acidic character:  $PhOH > C_2H_5OH$ )

(Basic and nucleophilic character:  $PhO^- < C_2H_5O^-$ )

**Sol 5: (A)** 1. Presence of electron-donating or electron-withdrawing group on the respective rings.

2.  $S_N2$  reaction mechanism is followed in which protonation is followed by attack of halo group.

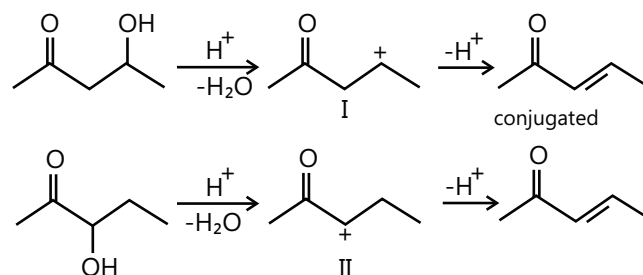
**Sol 6: (C)**



**Sol 7: (C)**  $CH_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3 + HI \rightarrow 2C_2H_5I$

**Sol 8: (A)**  $CO + H_2 \xrightarrow[\text{heat}]{ZnO-Cr_2O_3} CH_3OH$

**Sol 9: (A)** Although both reactions are giving the same product, carbocation I is more stable than II.



**Sol 10: (B)**  $BF_3$ , being a good Lewis acid accepts a pair of electrons to give us a good conjugate acid, and not a nucleophile.

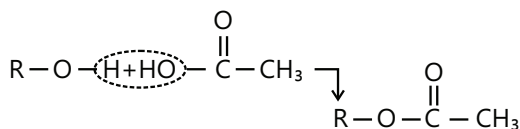
**Sol 11: (B)** Method (c) would give rearranged product also. It would give a mixture of 2-bromo and 3-bromo pentane. In methods (a) and (b), no rearrangement occurs and it gives (B) exclusively. The tosyl group a good leaving group, is then easily displaced by reaction with  $Br^-$  in an  $S_N2$  reaction.

**Sol 12: (C)** c. 2.68 gm of (A) gives 14.08 gm of AgI

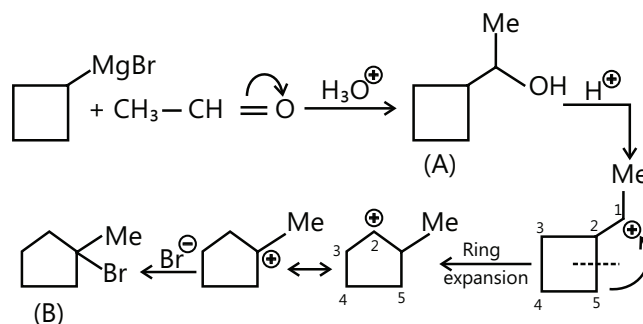
134 gm of (A) gives  $\frac{14.08 \times 134}{2.68} = 704$  gm of AgI

=  $\frac{704}{235}$  mol of AgI

= 3 (OMe) groups



**Sol 13: (B)**



**Comprehension Type:**

**Sol 14 to 16: (C, C, B)** Refer Reimer-Tiemann reaction from the theory part.

**Assertion Reasoning Type**

**Sol 17: (D)** Phenols can be chlorinated. Moreover, presence of  $-OH$  on the benzene ring, is an electron-donating group which makes the attachment of the Cl electrophile on the o- and p-position possible.

**Sol 18: (A)** self-explanatory. Remember,  $-NO_2$  is an electron-withdrawing and  $-CH_3$  is an electron-donating group.

**Sol 19: (D)** Electron-withdrawing nature of  $-NO_2$  and electron-donating nature of  $-O-Ar$  makes the reaction possible.

**Match the Columns**

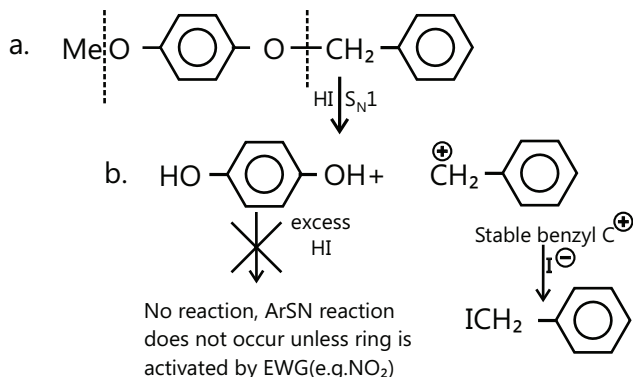
**Sol 20:** A  $\rightarrow$  q, r; B  $\rightarrow$  p, s; C  $\rightarrow$  u; D  $\rightarrow$  p, t; E  $\rightarrow$  p, r, s; F  $\rightarrow$  p, s

A. Reimer-Tiemann reaction proceeds by  $(CBrCl)$  (bromochlorocarbene), which acts as an electrophile. So, it is an SE reaction.

B. The reaction proceeds by the formation of carbocation with rearrangement.

C. No reaction proceeds by the formation of carbocation with rearrangement.

D.



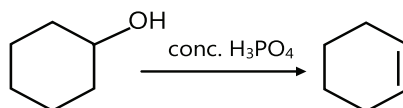
E. It is Friedel-Crafts alkylation which proceeds by the formation of a carbocation followed by rearrangement. So, it is an SE reaction.

F. It is hydration of alkene and proceeds by the formation of a carbocation with rearrangement.

**Previous Years' Questions**

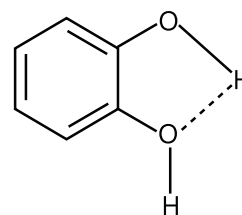
**Sol 1: (B)**  $C_6H_5MeBr + (CH_3)_3COH \rightarrow C_6H_6 + Mg[(CH_3)_3CO]Br$

**Sol 2: (B)**



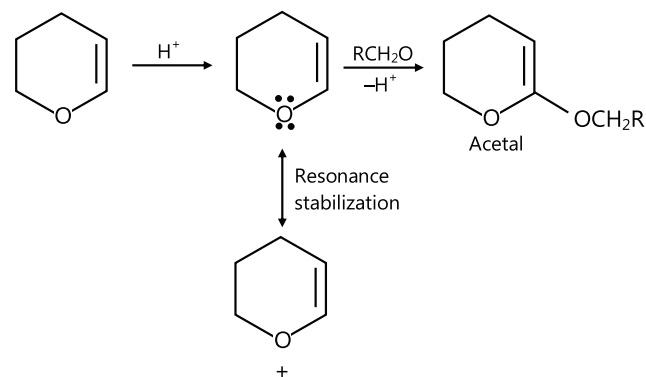
Concentrated  $H_3PO_4$  solution does not involve any substitution product while with others, substitution products are also formed.

**Sol 3: (C)** All dihydroxy benzene will have higher boiling points, than monohydroxy benzene. Also among dihydroxy benzenes, 1,2-di-hydroxy benzene has lowest boiling point due to intra-molecular H-bonding.

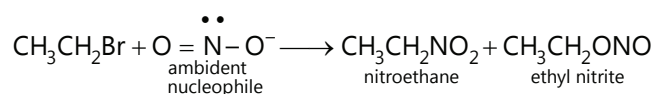


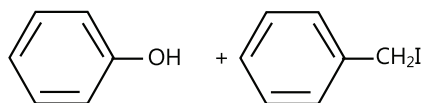
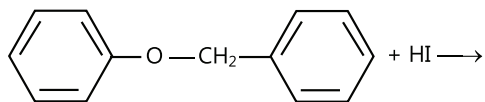
Intramolecular H-bonding in 1,2-dihydroxy benzene

**Sol 4:**



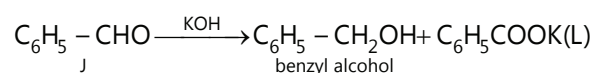
**Sol 5: (C, E)**



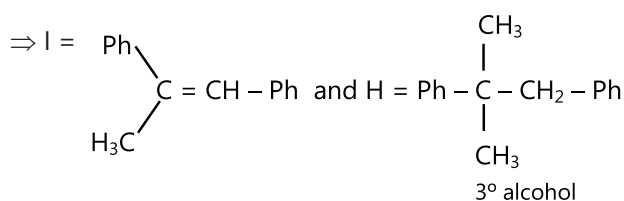
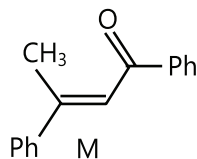
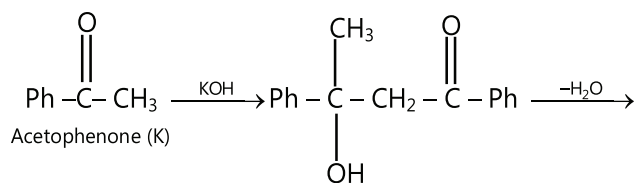
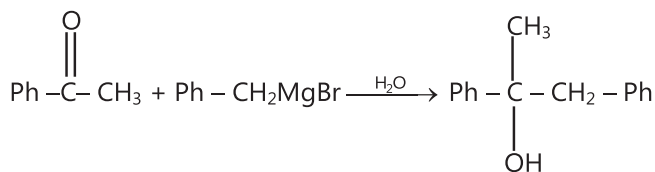
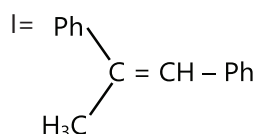
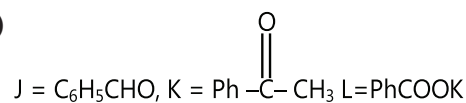
**Sol 6: (A, D)**

Phenol does not react further with HI.

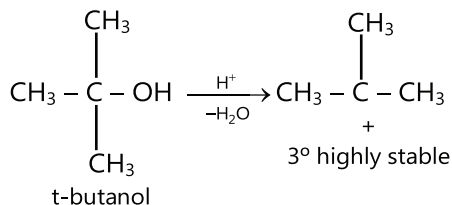
**Paragraph 1:** Compound J must be benzaldehyde because it one treatment with KOH undergoing Cannizaro's reaction producing benzyl alcohol and potassium-benzoate (L).



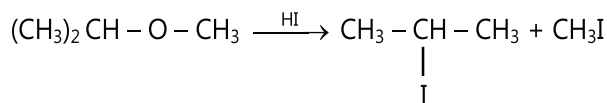
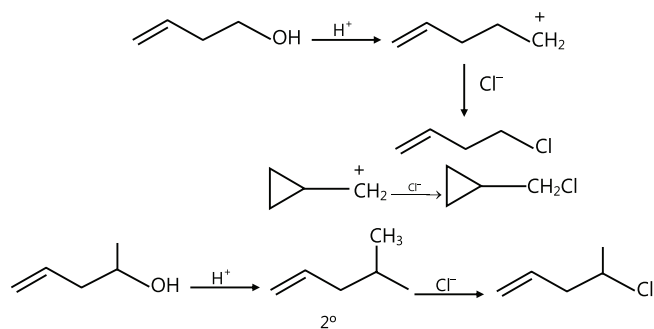
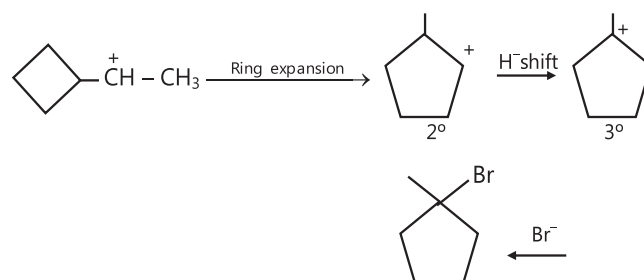
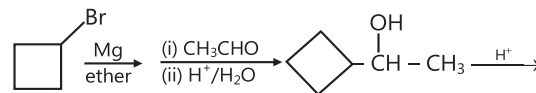
Also M is aldol condensation product formed from acetophenone

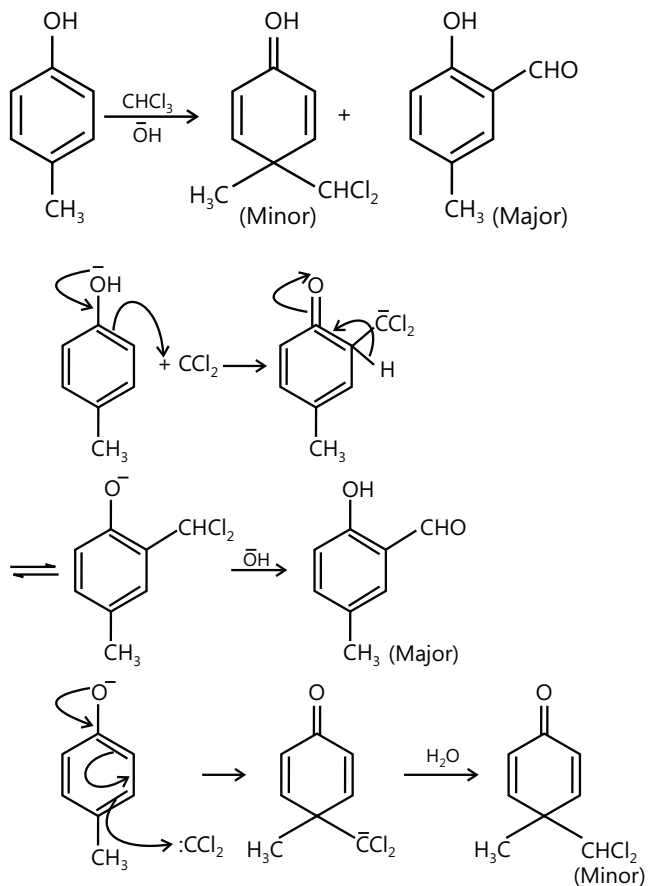
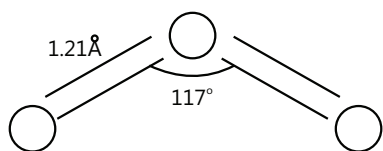
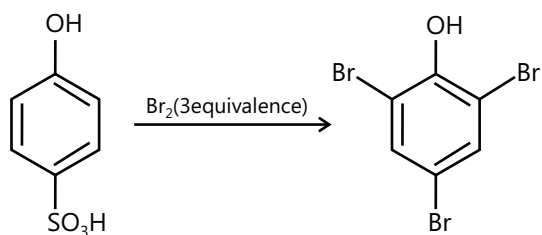
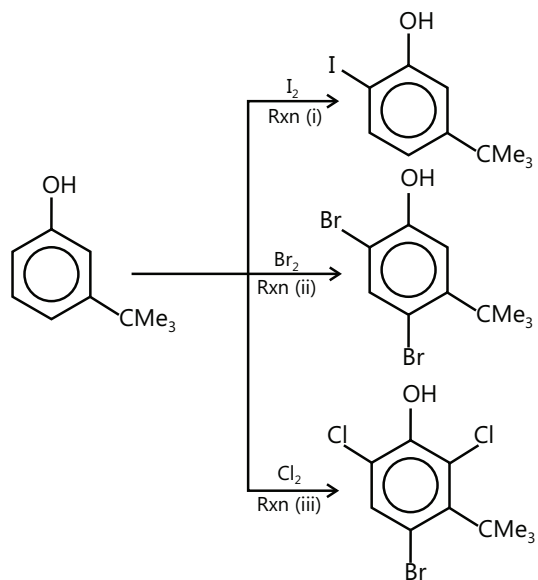
**Sol 7: (B)****Sol 8: (A)****Sol 9: (D)**

**Sol 10:** Acid catalysed dehydration proceeds via carbocation intermediate. Also, greater the stability of reactive intermediate, faster the reaction :

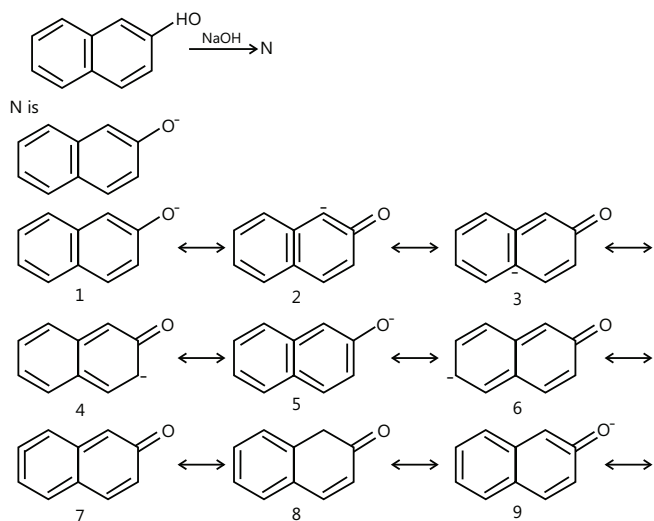
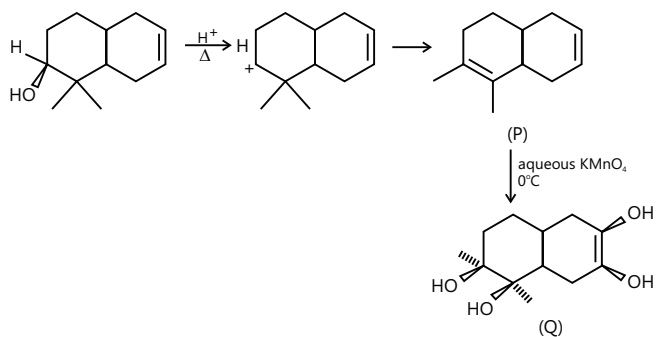


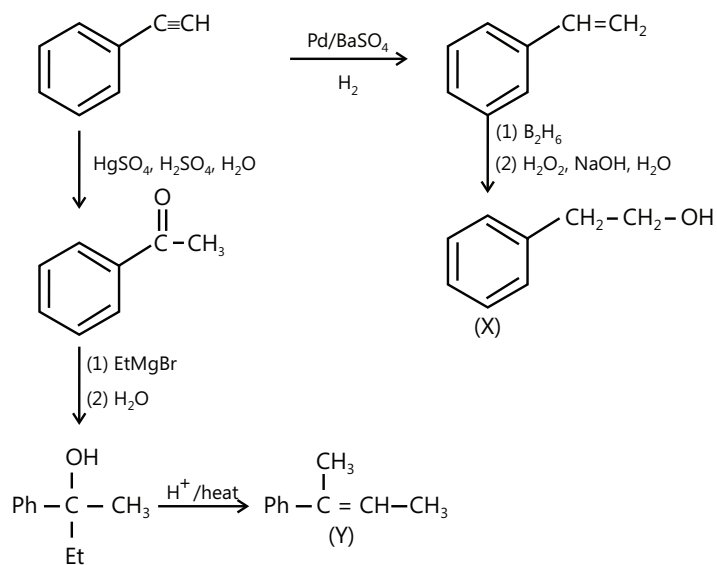
n-butanol forms less stable (1°) carbocation.

**Sol 11:****Sol 12:****Sol 13:**

**Sol:14 (B, D)****Sol 15: (A, C, D)****Sol16: (B)****Sol 17: (A, B, C)**

**Sol 18: (C)** When two phenyl groups are replaced by two para methoxy group, carbocation formed will be more stable.

**Sol 19: (9)****Sol 20: (D)**

**Sol 21 (C) and 22 (D):****Sol 23: (B,C)**