

## Alcohols, Phenols and Ethers

### SUBJECTIVE PROBLEMS:

#### Q1.

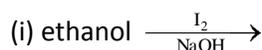
An organic liquid (A), containing C, H and O with boiling point: 78°C, and possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product (B) – with the empirical formula, CH<sub>2</sub>. 'B' decolorizes bromine water as well as alkaline KMnO<sub>4</sub> solution and takes up one mole of H<sub>2</sub> (per mole of 'B') in the presence of finely divided nickel at high temperature. Identify the substances 'A' and 'B'.  
(IIT JEE 1997 – 4 Marks)

#### Q2.

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

#### Q3.

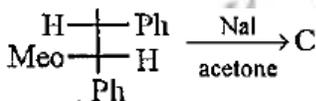
Write the structural formula of the main organic product formed when :



(IIT JEE 1985 – 1 Marks)

(ii) Predict the structure of the product in the following reaction.

(IIT JEE 1996 – 1 Marks)



#### Q4.

Outline the reaction sequence for the conversion of

(i) 1-Propanol from 2-Propanol (in three steps)

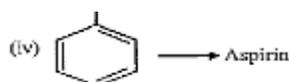
(IIT JEE 1982 – 1 Marks)

(ii) Ethyl alcohol to vinyl acetate. (in not more than 6 steps)

(IIT JEE 1986 – 3 Marks)

(iii) Phenol to acetophenone

(IIT JEE 1989 – 1 ½ Marks)



(IIT JEE 2003 – 2 Marks)

**Q5.**

State with balanced equations what happens when:

(i) Acetic anhydride reacts with phenol in presence of a base.

**(IIT JEE 1982 – 1 Marks)**

(ii) Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate.

**(IIT JEE 1991 – 1 Marks)**

**Q6.**

Give reasons for the following:

A. Sodium metal can be used for drying diethyl ether but not ethanol.

B. phenol is an acid but it does not react with sodium bicarbonate.

C. Acid catalyzed dehydration of t-butanol is faster than that of *n*-butanol.

**Q7.**

An alcohol A, when heated with conc.  $\text{H}_2\text{SO}_4$  gives an alkene B. When B is bubble through bromine water and the product obtained is dehydrohalogenated with excess of sod amide, a new compound C is obtained. The compound C gives D when treated with warm dilute  $\text{H}_2\text{SO}_4$  in presence of  $\text{HgSO}_4$ . D can also be obtained either by oxidizing A with  $\text{KmnO}_4$  or from acetic acid through its calcium salt. Identify A, B, C and D.

**(IIT JEE 1983 – 4 Marks)**

**Q8.**

A compound of molecular formula  $\text{C}_7\text{H}_8\text{O}$  is insoluble in water and dilute sodium bicarbonate but dissolves in dilute aqueous sodium hydroxide. On treatment with bromine water, it readily gives a precipitate of  $\text{C}_7\text{H}_5\text{OBr}_3$ . Write down the structure of the compound.

**(IIT JEE 1985 – 2 Marks)**

**Q9.**

Give a chemical test/suggest a reagent to distinguish between methanol and ethanol.

**(IIT JEE 1985 – 2 Marks)**

**Q10.**

Complete the following with appropriate structures :

**Q11.**

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.

(IIT JEE 1992 – 5 Marks)

**Q12.**

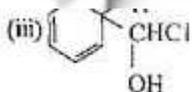
When *t*-butanol and *n*-butanol are separately treated with a few drops of dilute  $KMnO_4$  in one case only the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate?

(IIT JEE 1994 – 2 Marks)

**Q13.**

When phenol is reacted with  $CHCl_3$  and  $NaOH$  followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates?

(IIT JEE 1995 – 2 Marks)



**Q14.**

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

**Q15.**

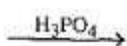
A compound D ( $C_8H_{10}O$ ) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E ( $C_7H_6O_2$ ). Write the structures of D and E and explain the formation of E. (IIT JEE 1996 – 2 Marks)

**Q16.**

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

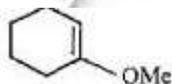
**Q17.**

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



**Q18.**

Predict the major product in the following reactions

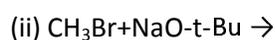
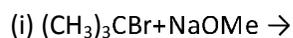


**Q19.**

2, 2-Dimethyloxirane can be cleaved by acid ( $H^+$ ). Write mechanism (IIT JEE 1997 – 2 Marks)

**Q20.**

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



(IIT JEE 1997 – 2 Marks)

**Q21.**

Write the intermediate steps for each of the following reaction.

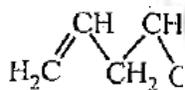


(IIT JEE 1998 – 1 Marks)

**Q22.**

Explain briefly the formation of the products giving the structures of the intermediates.

(IIT JEE 1999 – 3 Marks)

**Q23.**

A biologically active compound, bombykol ( $\text{C}_{16}\text{H}_{30}\text{O}$ ) is obtained from a natural source. The structure of the compound is determined by the following reactions.

(IIT JEE 2002 – 5 Marks)

(A). on hydrogenation, bombykol gives a compound A,  $\text{C}_{16}\text{H}_{34}\text{O}$ , which reacts with acetic anhydride to give as ester,

(B). Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis ( $\text{O}_3/\text{H}_2\text{O}_2$ ) gives a mixture of botanic acid, oxalic acid and 10-acetoxydecanoic acid.

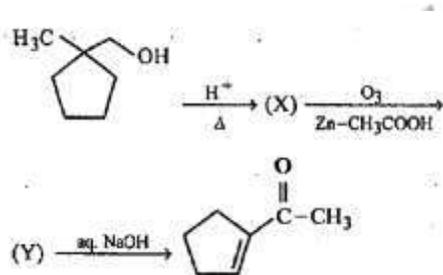
Determine the number of double bonds in bombykol. Write the structures of compound A and bombykol. How many geometrical isomers are possible for bombykol?

**Q24.**

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

**Q25.**

Identify (X) and (Y) in the following reaction sequence. **(IIT JEE 2005 – 2 Marks)**

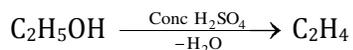


## Alcohols, Phenols and Ethers-solutions

### SUBJECTIVE PROBLEMS:

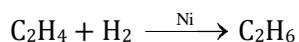
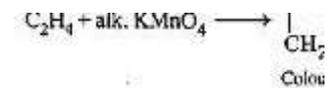
#### Sol 1.

'A' is  $C_2H_5OH$  and 'B' is  $C_2H_4$



(A) (B)

(Ethyl alcohol) (Ethane)

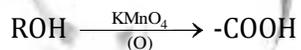
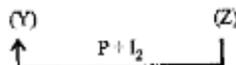


Ethane ethane

#### Sol 2.

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

Hence its other reactions are sketched as below.



(Z)

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



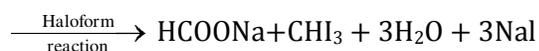
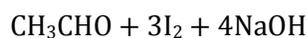
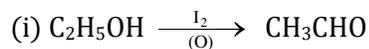
Diethyl ether (X)                      Ethyl iodide (Y)



Ethyl alcohol (Z)                      Acetic acid

(Eq. wt. = 60)

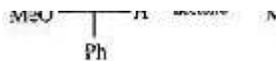
### Sol 3.



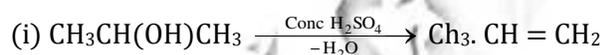
(ii)

The reaction takes place by  $\text{S}_{\text{N}}2$  reaction mechanism.

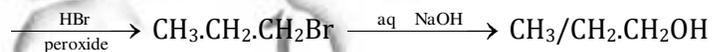
Solution: Br is replaced by I following  $\text{S}_{\text{N}}2$  mechanism. There will be Walden inversion at the place of replacement.



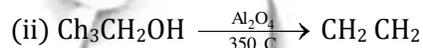
### Sol 4.



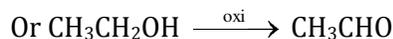
2-propanol



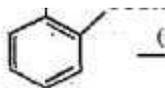
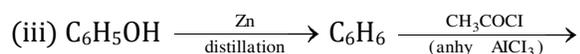
1-propanol



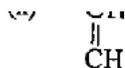
Vinyl acetate



Vinyl acetate



**Sol 5.**



**Sol 6.**

(i) Ethanol (due to the presence of active hydrogen atom, C base 2H base 5 - O - H) reacts with sodium metal, while ether and benzene have no such hydrogen atom and hence do not react with sodium and thus can be dried by metallic sodium.

(ii) Phenol (a weaker acid) reacts with  $\text{NaHCO}_3$  (a weaker base) to form phenoxide ion (a stronger base) and carbonic acid (a stronger acid).



Weaker acid                      weaker base      stronger base                      stronger acid

Since acid-base equilibrium lie towards the weaker acid and weaker base, phenol does not decompose  $\text{NaHCO}_3$  (difference from carboxylic acids).



Stronger acid stronger base weaker base weaker acid

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

### Sol 7.

The given problem can be sketched as below.



#### **NOTE THIS STEP:**

From the problem it appears that the compound C is an alkyne, hence D must be an aldehyde or ketone. Further since D can be obtained from acetic acid through its calcium salt it may be either ethyl alcohol or iso-propanol both of which explains the given set of reactions.

Hence

A is ethyl alcohol,	$\text{CH}_3\text{CH}_2\text{OH}$
B is ethylene,	$\text{CH}_2 = \text{CH}_2$
C is acetylene,	$\text{CH} \equiv \text{CH}$
D is acetaldehyde,	$\text{CH}_3 \cdot \text{CHO}$

**(ii) ALTERNATIVE SOLUTION:**

**Hence**

A is isopropyl alcohol,  $\text{CH}_3\text{CHOH}\cdot\text{CH}_3$

B is propene,  $\text{CH}_3\text{CH}=\text{CH}_2$

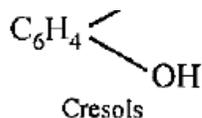
C is propane,  $\text{CH}_3\text{C}\equiv\text{CH}$

D is acetone,  $\text{CH}_3\text{CO}\cdot\text{CH}_3$

**Sol 8.**

(i) The compound ( $\text{C}_7\text{H}_8\text{O}$ ) is soluble in aq.  $\text{NaOH}$  but insoluble in  $\text{NaHCO}_3$ , indicating it to have a phenolic group.

(ii) The compound, on treatment with  $\text{Br}_2$  water, gives  $\text{C}_7\text{H}_5\text{OBr}_3$ . Taking into account of molecular formulae of the two compounds, the parent compound seems to be cresol.

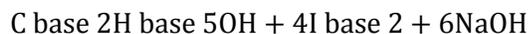


(iii) Bromination of the compound reveals that it is m-cresol as it forms tribromo derivative.

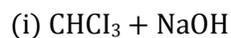
(iv) The reaction are

### Sol 9.

Iodoform test is used to distinguish methanol and ethanol. Ethanol gives iodoform test white methanol does not respond.



### Sol 10.



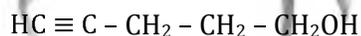
### Sol 11.

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

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

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

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



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

The above structure for the compound X is in accordance with its equivalent weight obtained from the given data.

224 ml. of  $CH_4$  at STP is obtained from 0.42 g

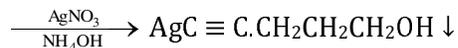
22400 ml. of  $CH_4$  at STP =  $0.42/224 * 22400 = 42$  g

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

Reactions of the compound X :



(X)



(X)



(X)



N-Pentane

### Sol 12.

*N*-Butanol gives the following reaction in which the purple colour of  $\text{KMnO}_4$  changes to brown. *Tert*-Alcohol are not oxidisable easily, hence purple colour of  $\text{KMnO}_4$  remains same.



N-Butanol                      purple



Soluble in  $\text{H}_2\text{O}$                       Brown

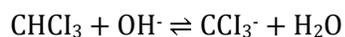
The brown precipitate is of  $\text{MnO}_2$ .

### Sol 13.

(I, iv)

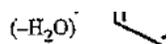
The reaction involves electrophilic substitution on the highly reactive peroxide ion.

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





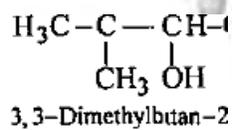
Dichlorocarbene



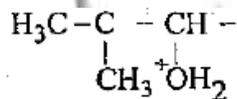
### Sol 14.

The steps involved in the suggested mechanism are as follows.

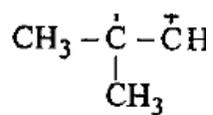
(a) The protonation of hydroxyl group.



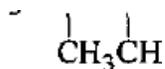
(b) The removal of  $\text{H}_2\text{O}$  to form a secondary ( $2^\circ$ ) carbonium ion



(c) The conversion of  $2^\circ$  carbonium to the more stable  $3^\circ$  carbonium ion by the shift of  $\text{CH}_3$  group



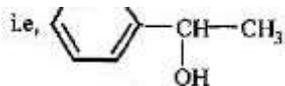
(d) The removal of H<sup>+</sup> to form a double bond



### Sol 15.

NOTE:

The reaction of D (C<sub>8</sub>H<sub>10</sub>O) with alkaline soluble of iodine is an iodoform reaction. This reaction is possible if the D has  $\begin{matrix} -\text{C}-\text{CH}_3 \\ \text{O} \end{matrix}$  or  $\begin{matrix} -\text{CH}-\text{CH}_3 \\ \text{OH} \end{matrix}$  group. The high carbon in D indicates that D is an aromatic compound containing a benzene ring. To account for the given formula, the compound D may be C<sub>6</sub>H<sub>5</sub>CH(OH)CH<sub>3</sub>,

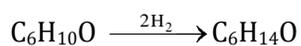


The given reactions are

**Sol 16.**

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

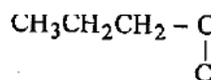
(b) Since (B) is optically inactive, it must have at least two alkyl groups similar



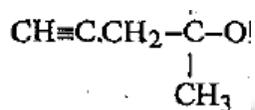
(A)                      (B)

Thus the five carbon atoms can be adjusted into three alkyl groups (of which two are similar) either as  $-\text{CH}_3$ ,  $-\text{CH}_3$ , and  $-\text{C}_3\text{H}_7$ , or as  $-\text{C}_2\text{H}_5$ ,  $-\text{C}_2\text{H}_5$  and  $\text{CH}_3$ ,

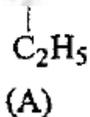
Thus the possible structure of alcohol (B) is either



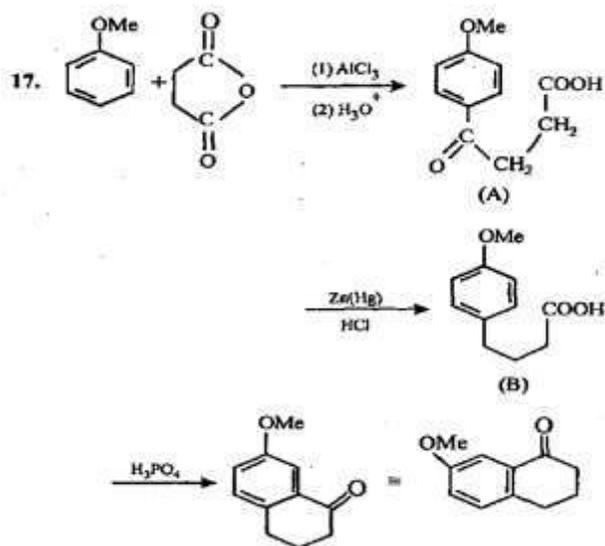
Hence the corresponding compound (A) is either



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



**Sol 17.**

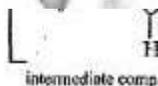


**Sol 18.**



**Sol 19.**

The oxirane ring is cleaved via  $S_N2$  mechanism

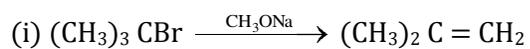


### Sol 20.

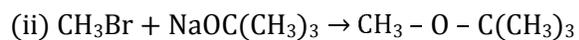
The method given in (ii) is the correct method for the formation of ether because method (i) leads alkene as the main product.

#### NOTE:

3° alkyl halides are easily dehydrohalogenated by base.



Alkene



Either

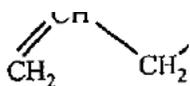
### Sol 21.

### Sol 22.

(i) NOTE:

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

Also,  $CH_2 =$



**NOTE:**

In the intermediate carbocation, the carbon bearing positive charge has a  $\text{CH}_3$  group which decreases the positive charge and hence prevents cyclisation of the compound.

**Sol 23.**

Let us summarise the given facts.

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

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

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

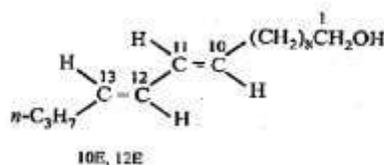
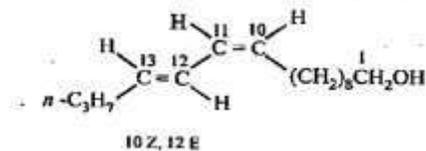


The structure of the bombykol ester suggests that bombykol has the following structure :

$CH_3CH_2CH_2CH = CH - CH = CH.(CH_2)_8.CH_2OH$  (Bombykol) and the structure of A is

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

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



### Sol 24.

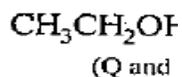
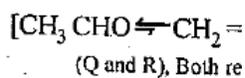
(i) Molecular formula of P,  $C_5H_{10}O$  indicates 1° of unsaturation. So it should have double bond.

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

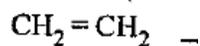
$CH_3CH_2OH$ ,  $(CH_3)_2CHOH$ ,  $CH_3CHO$  or  $CH_3COR$

The only possible linkage that can explain such hydrolysis is ether. Hence P should have following type of structure.  $C_2$  - component - O -  $C_3$  - component should have double bond, thus the possible

structure for P should be either of the following two structures which explains all the given reactions.



Extra reactivity of P toward dil.  $\text{H}_2\text{SO}_4$  than ethylene is due to formation of highly stable carbonation



Sol 25.

