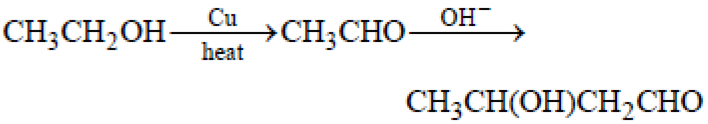
Fill Ups & True False of Alcohols, Phenols and Ethers

Fill in the Blanks

1. Ethanol vapour is passed over heated copper and the product is treated with aqueous NaOH. The final product is .... (1983 - 1 Mark)

Ans: aldol (β-hydroxybutanal)

Solution:



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

2. The acidity of phenol is due to the .... of its anion. (1984 - 1 Mark)

Ans: resonance stabilization

3. Formation of phenol from chlorobenzene is an example of .... aromatic substitution. (1989 - 1 Mark)

Ans: nucleophilic

4. Phenol is acidic because of resonance stabilization of its conjugate base, namely .... (1990 - 1 Mark)

Ans: phenoxideion

5. Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove .... which are formed on prolonged standing in contact with air. (1992 - 1 Mark)

Ans: peroxides

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

6. Glycerine contains one .... hydroxyl group. (1997 - 1 Mark)

Ans: secondary

True / False

1. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide.

Ans: False

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

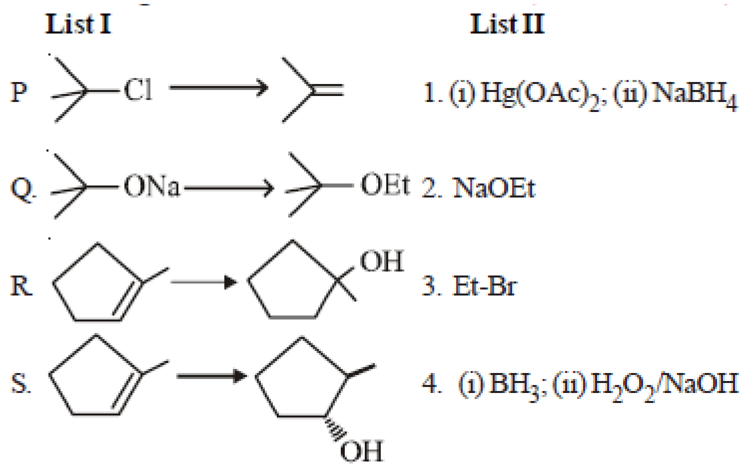
$$2\,C_2H_5OH + 2Na \rightarrow 2\,C_2H_5ONa + H_2\uparrow$$

Matching & Integer Type question of Alcohols, Phenols & Ethers

<u>Match the Following :</u>

Direction : The codes for the lists have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

Q. 1. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists : (JEE Adv. 2013)



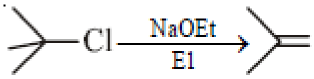
1. (i) $Hg(OAc)_2$; (ii) $NaBH_4$
2. NaOEt
3. Et-Br
4. (i) BH_3; (ii) H_2O_2/NaOH

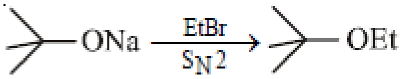
Codes:

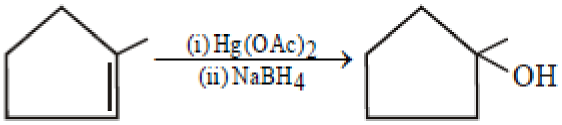
	P	Q	R	S
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

Ans: a

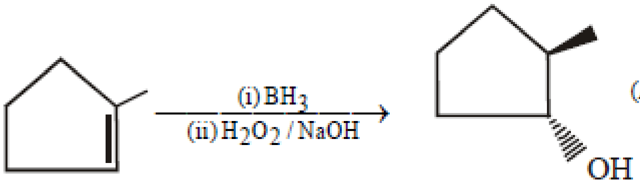
Solution:

(P) 

(Q) 

(R) 

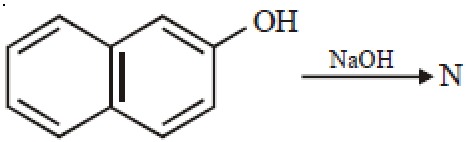
(Markovnikov addition)

(S) 

(Antimarkovnikov addition)

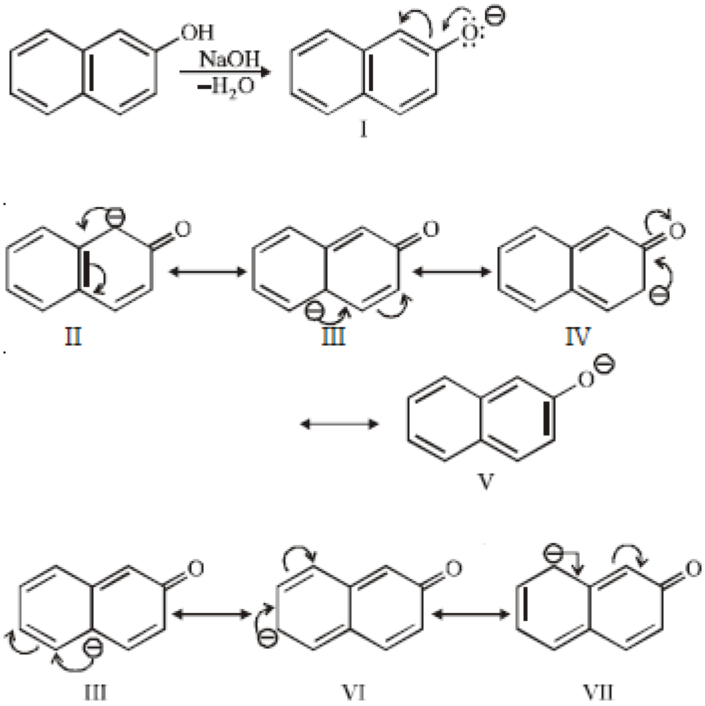
Integer Value Type

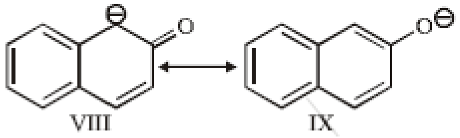
1. The number of resonance structures for N is (JEE Adv. 2015)



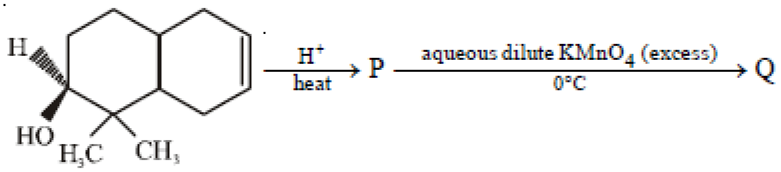
Ans: 9

Solution:



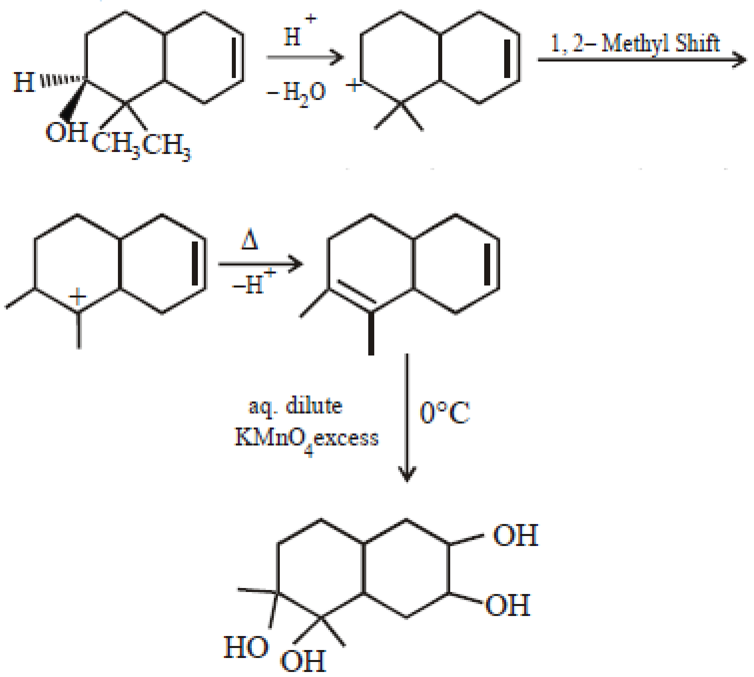


2. The number of hydroxyl group(s) in Q is (JEE Adv. 2015)



Ans: 4

Solution:

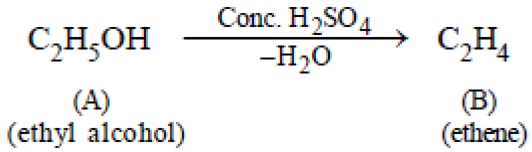


Subjective Qn. of Alcohols, Phenols & Ethers, Past year Questions (Part - 1)

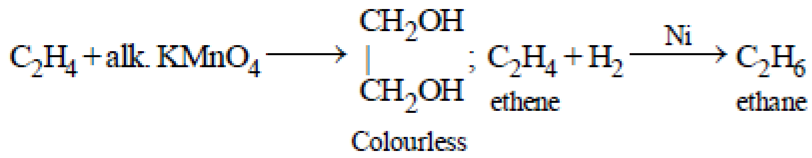
1. An organic liquid (A), containing C, H and O with boiling point : 78°C, and possessing a rather pleasant odour, on heating with concentrated sulphuric acid gives a gaseous product (B) – with the empirical formula, CH_2. 'B' decolourises bromine water as well as alkaline $KMnO_4$ solution and takes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

Solution:

'A' is C_2H_5OH and 'B' is C_2H_4



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



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

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

Solution:

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

$$\begin{tikzcd}[column sep=huge] \underset{(X)}{R-O-R} \arrow[r, "\text{Reflux with}", "\text{excess of HI}"'] & \underset{(Y)}{2RI} \arrow[r, "\text{hydrolysis}"] & \underset{(Z)}{2ROH} \arrow[l, bend left, "P + I_2"] \end{tikzcd}$$

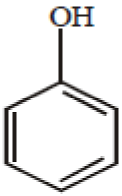
$$\underset{(Z)}{ROH} \xrightarrow[(O)]{KMnO_4} -COOH$$

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

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

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

3. Outline the reaction sequence for the conversion of
(i) 1-propanol from 2-propanol (in three steps) (1982 - 1 Mark)
(ii) ethyl alcohol to vinyl acetate. (in not more than 6 steps) (1986 - 3 Marks)
(iii) phenol to acetophenone (1989 - 1½ Marks)

(iv)  $\longrightarrow$ Aspirin **(2003 - 2 Marks)**

Solution :

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

$$\xrightarrow[\text{peroxide}]{HBr} CH_3.CH_2.CH_2Br \xrightarrow{\text{aq NaOH}} \underset{\text{1-propanol}}{CH_3.CH_2.CH_2OH}$$

(ii)

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[350^\circ C]{Al_2O_3} CH_2=CH_2$$

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

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

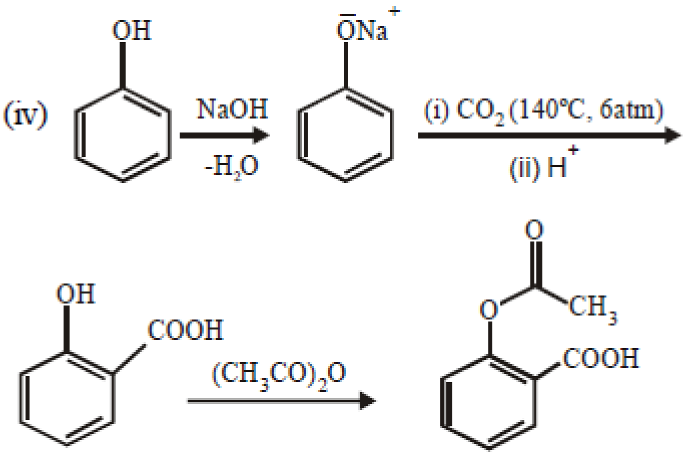
$$\text{or } \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{Oxi.} CH_3CHO$$

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

(iii)

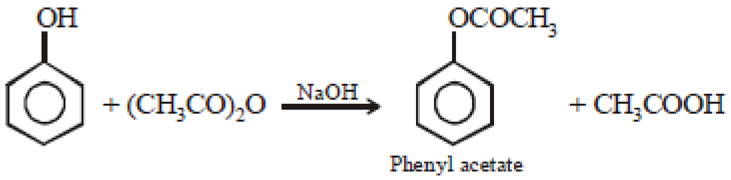
$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[\text{distillati on}]{Zn} C_6H_6 \xrightarrow[(\text{anhy. }AlCl_3)]{CH_3COCl} \underset{\text{Acetophenone}}{C_6H_5COCH_3}$$

(iv)

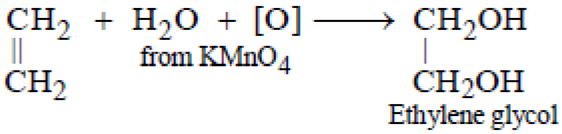


4. State with balanced equations what happens when :
(i) acetic anhydride reacts with phenol in presence of a base. (1982 - 1 Mark)
(ii) Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate. (1991 - 1 Mark)

Solution : (i)



(ii)



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O + \underset{\text{from } KMnO_4}{[O]} \longrightarrow \underset{\text{Ethylene glycol}}{\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}}$$

5. Give reasons for the following :
(i) Sodium metal can be used for drying diethyl ether but not ethanol.
(1982 - 1 Mark)
(ii) Phenol is an acid but it does not react with sodium bicarbonate.
(1987 - 1 Mark)
(iii) Acid catalysed dehydration of t-butanol is faster than that of n-butanol.
(1998 - 2 Marks)

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

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

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

Since acid-base equilibria lie towards the weaker acid and weaker base, phenol does not decompose $NaHCO_3$

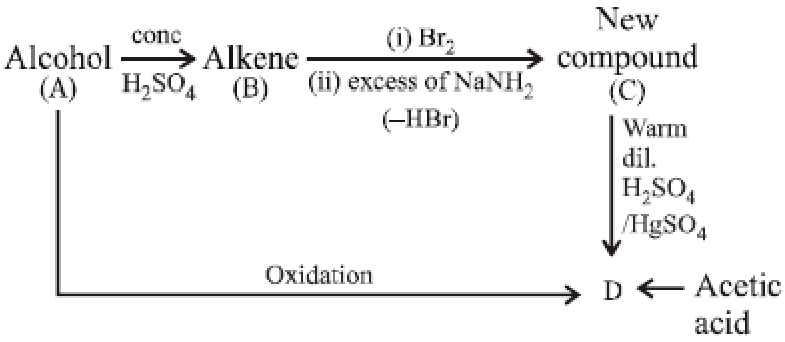
(difference from carboxylic acids).

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

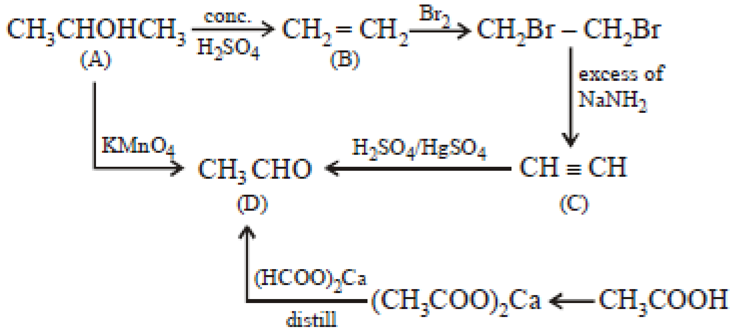
(iii) Since 3° carbocation (formed in case of t-butanol) is more stable than 1° (formed in n-butanol), the dehydration in the former proceeds faster than in the latter.

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

Solution : The given problem can be sketched as below.



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



Hence

A is ethyl alcohol, CH_3CH_2OH

B is ethylene, $CH_2 = CH_2$

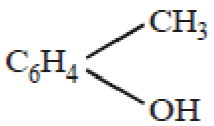
C is acetylene, $CH \equiv CH$

D is acetaldehyde, $CH_3 . CHO$

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

Solution: (i) The compound (C_7H_8O) is soluble in aq. NaOH but insoluble in NaHCO3, indicating it to have a phenolic group.

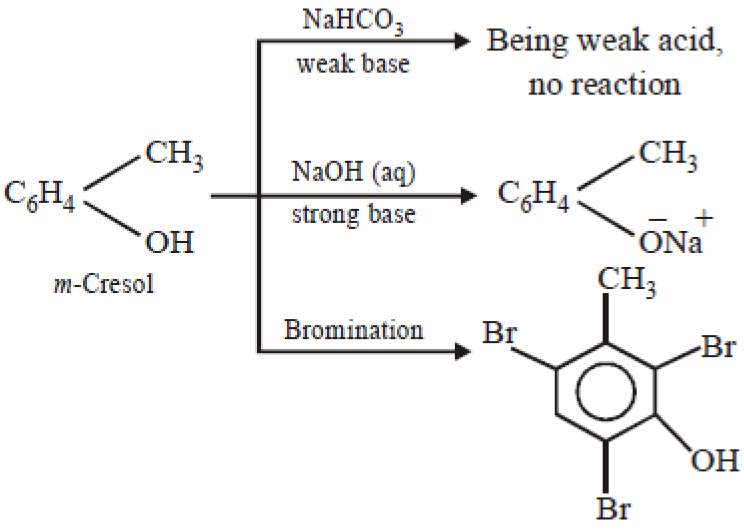
(ii) The compound, on treatment with Br_2 water, gives $C_7H_5OBr_3$. Taking into account of molecular formulae of the two compounds, the parent compound seems to be cresol.



Cresols

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

(iv) The reactions are



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

ethanol. (1985 - 1 Mark)

Solution :

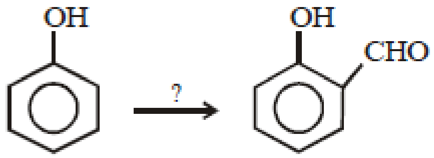
TIPS/Formulae : Iodoform test is used to distinguish methanol and ethanol. Ethanol gives iodoform test while methanol does not respond.

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

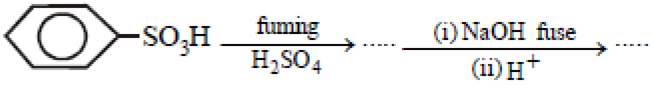
9. Complete the following with appropriate structures :

Solution.

(i)

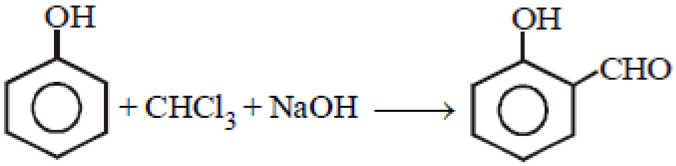


(ii)



Solution:

(i)



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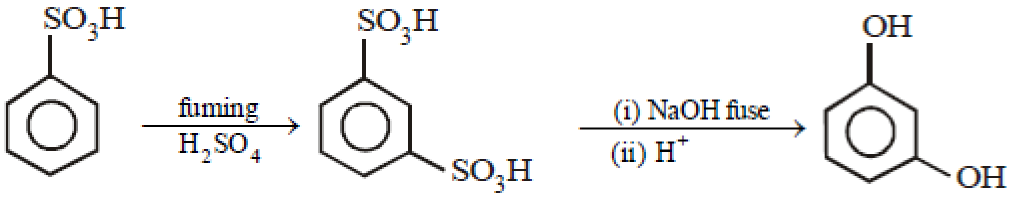


10. Compound ‘X’ (molecular formula, C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammonical silver nitrate. With excess of MeMgBr, 0.42 g of ‘X’ gives 224 ml of CH_4 at STP. Treatment of ‘X’ with H2 in presence of Pt catalyst followed by boiling with excess HI, gives n-pentane. Suggest structure for ‘X’ and write the equation involved. (1992 - 5 Marks)

Solution : (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 H2/Pt followed by boiling with excess of HI gives n-pentane. It indicates that the compound does not have any branch.
On the basis of the above points, compound X (C_5H_8O) may be assigned following structure.

$HC \equiv C – CH_2 – CH_2 – CH_2OH$

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

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

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

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

∴ Eq. wt. of the compound X = 42

Reactions of the compound X :

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

(ii)

$$\underset{(X)}{HC \equiv C.CH_2\,CH_2.CH_2OH}$$

$$\xrightarrow{2CH_3MgBr} MgBrC \equiv C.CH_2CH_2CH_2OMgBr + 2CH_4$$

(iii)

$$\underset{(X)}{HC \equiv C.CH_2\,CH_2.CH_2OH}$$

$$\xrightarrow{H_2/Pt} CH_3CH_2CH_2CH_2CH_2OH$$

$$\xrightarrow{HI} \underset{n-\text{Pentane}}{CH_3CH_2CH_2CH_2CH_3}$$

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

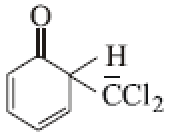
Solution : n-Butanol gives the following reaction in which the purple colour of $KMnO_4$ changes to brown. tert-Alcohols are not oxidisable easily, hence purple colour of KMnO4 remains same.

$$\underset{n-\text{butanol}}{CH_3CH_2CH_2CH_2OH} + \underset{\text{Purple}}{KMnO_4} \longrightarrow \underset{\text{soluble in } H_2O}{CH_3CH_2CH_2COOK} + \underset{\text{Brown}}{MnO_2\downarrow} + KOH$$

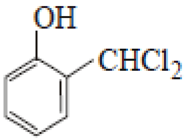
The brown precipitate is of MnO_2

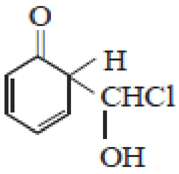
12. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates? (1995 - 2 Marks)

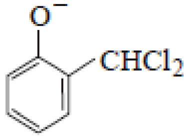
(i)



(ii)



(iii) 

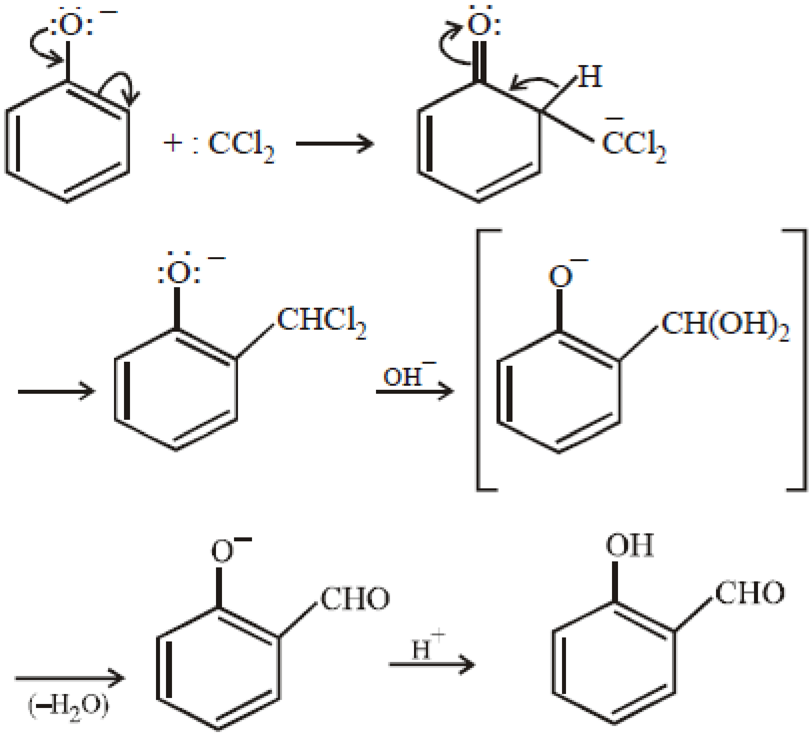
(iv) 

Solution :

TIPS/Formulae : The reaction involves electrophilic substitution on the highly reactive phenoxideion.
Here the electrophile is dichlorocarbene formed by the action of strong alkali on chloroform.

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

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

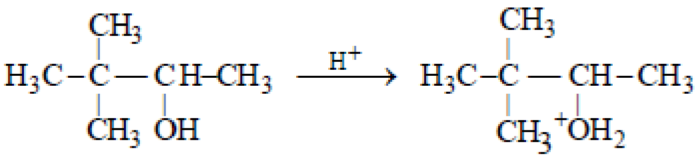


Salicylaldehyde
(*o*-Hydroxybenzaldehyde)

Subjective Qn. of Alcohols, Phenols & Ethers, Past year Questions (Part - 2)

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

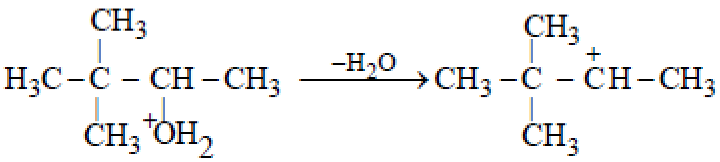
Solution : The steps involved in the suggested mechanism are as follows.
(a) The protonation of hydroxyl group.



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow{H^+} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\underset{{}^+OH_2}{CH}-CH_3$$

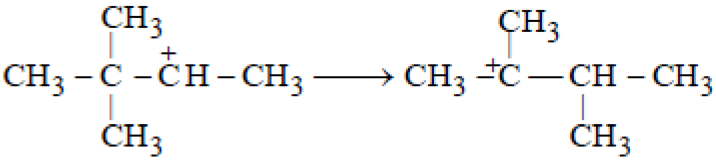
3, 3–Dimethylbutan–2–ol

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



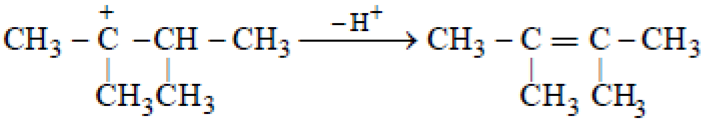
$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\underset{{}^+OH_2}{CH}-CH_3 \xrightarrow{-H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{C}H-CH_3$$

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



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{C}H-CH_3 \longrightarrow CH_3-{}^+\overset{CH_3}{C}-\underset{CH_3}{CH}-CH_3$$

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

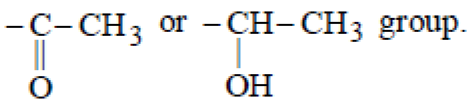


$$CH_3-\underset{CH_3}{\overset{+}{C}}-\underset{CH_3}{CH}-CH_3 \xrightarrow{-H^+} CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-CH_3$$

Tetramethylethylene

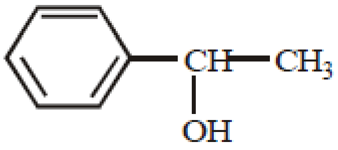
14. A compound D ($C_8H_{10}O$) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E ($C_7H_6O_2$). Write the structures of D and E and explain the formation of E. (1996 - 2 Marks)

Solution : NOTE : The reaction of D ($C_8H_{10}O$) with alkaline solution of iodine is an iodoform reaction. This reaction is possible if the compound D

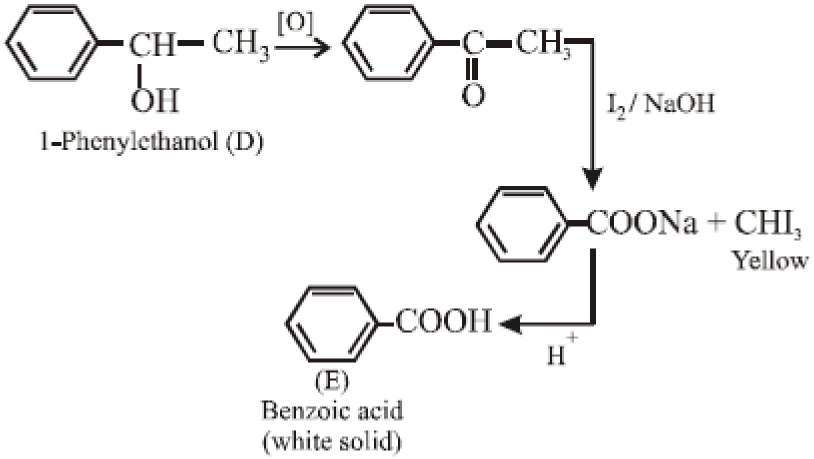
has 

$-\underset{\underset{O}{\|}}{C}-CH_3$ or $-\underset{\underset{OH}{|}}{CH}-CH_3$ group.

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

i.e, 

The given reactions are



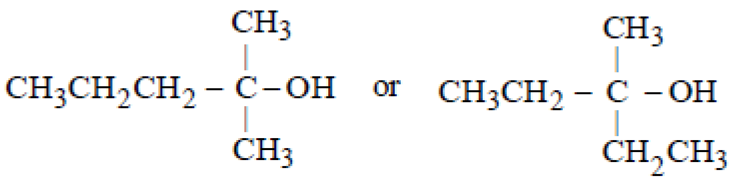
15. An optically active alcohol A ($C_6H_{10}O$) absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B. The compound B is resistant to oxidation by CrO_3 and does not show any optical activity. Deduce the structures of A and B. (1996 - 2 Marks)

Solution :

TIPS/Formulae : (a) Since (B) is resistant to oxidation, it must be ter-alcohol.
(b) Since (B) is optically inactive, it must have at least two alkyl groups similar.

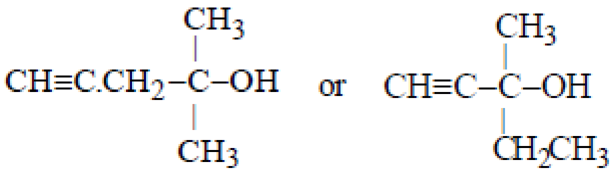
$$\underset{(A)}{C_6H_{10}O} \xrightarrow{2H_2} \underset{(B)}{C_6H_{14}O}$$

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



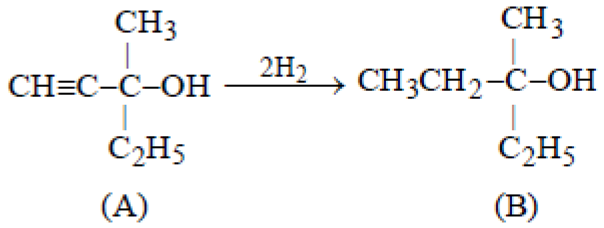
$$CH_3CH_2CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \quad \text{or} \quad CH_3CH_2-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

Hence the corresponding compound (A) is either



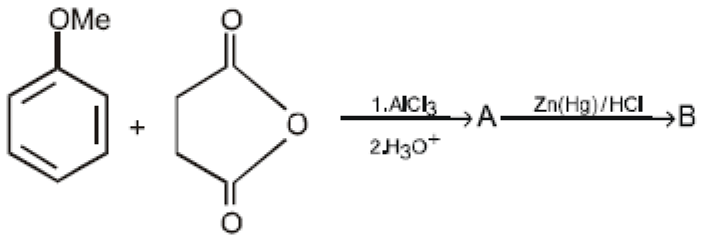
$$CH{\equiv}C.CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \quad \text{or} \quad CH{\equiv}C-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

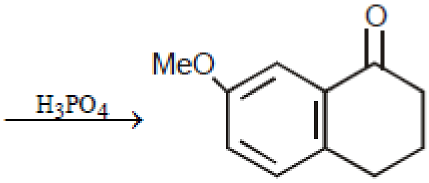
However, the compound (A) is optically active, so (A) and hence also (B) should have right side structure.



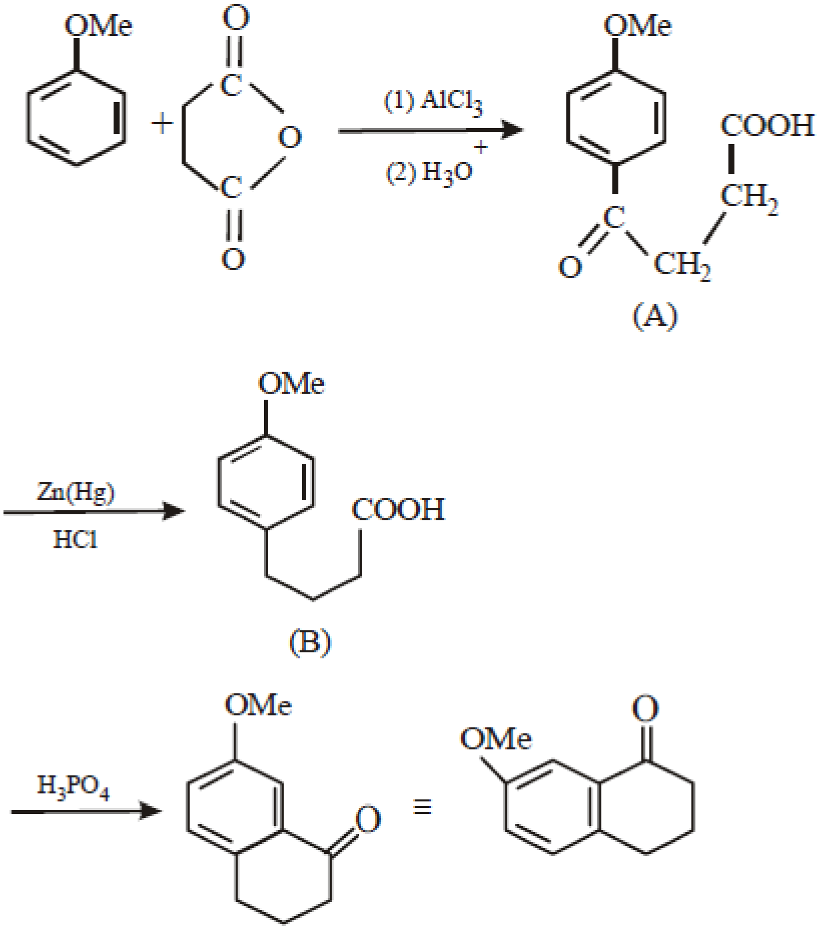
$$\underset{(A)}{CH{\equiv}C-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH} \xrightarrow{2H_2} \underset{(B)}{CH_3CH_2-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH}$$

16. Predict the structures of the intermediates/products in the following reaction sequence : (1996 - 2 Marks)





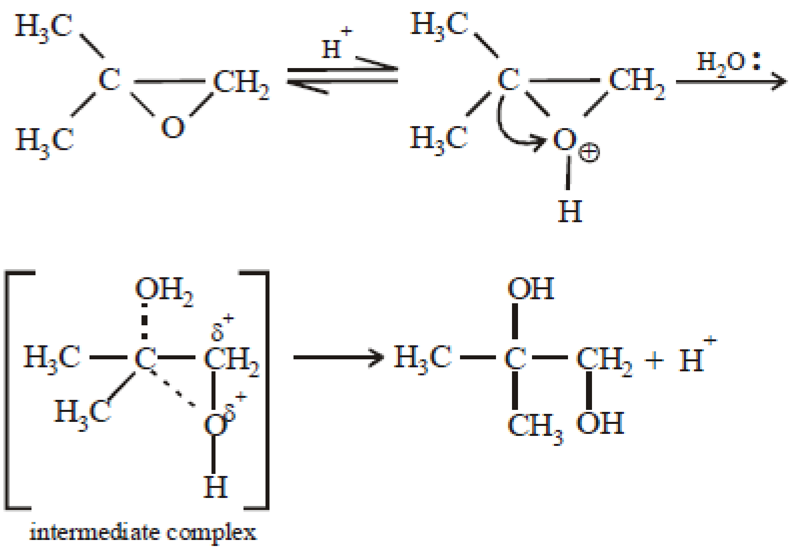
Solution :



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

Solution :

TIPS/Formulae : The oxirane ring is cleaved via S_N2 mechanism



18. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?
(i) $(CH_3)_3CBr$ + NaOMe →
(ii) CH_3Br + NaO-t-Bu → **(1997 - 2 Marks)**

Solution :

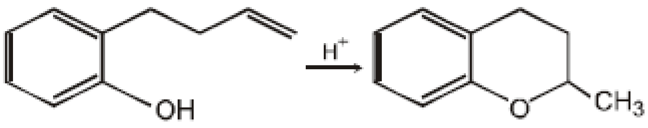
The method given in (ii) is the correct method for the formation of ether because method (i) leads alkene as the main product.

NOTE : 3° alkyl halides are easily dehydrohalogenated by base.

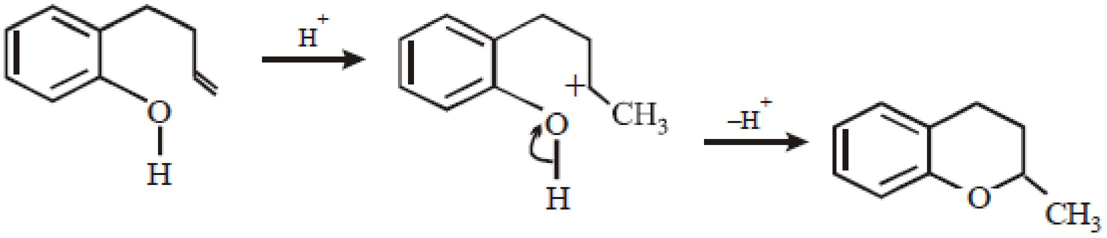
(i) $(CH_3)_3CBr \xrightarrow{CH_3ONa} \underset{\text{alkene}}{(CH_3)_2C=CH_2}$

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

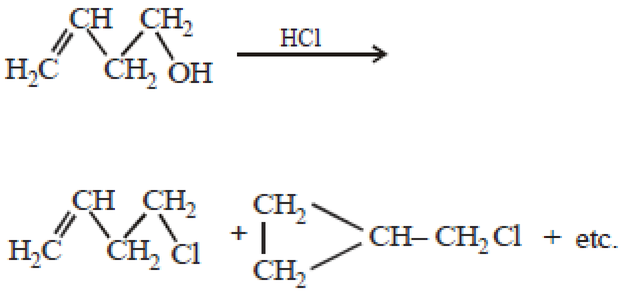
19. Write the intermediate steps for each of the following reaction.

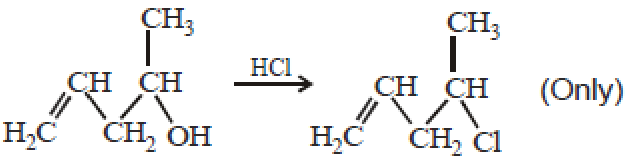


Solution :



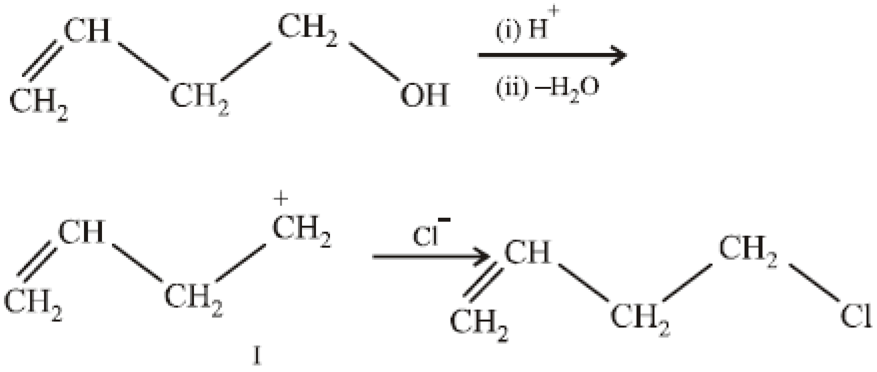
20. Explain briefly the formation of the products giving the structures of the intermediates. (1999 - 3 Marks)



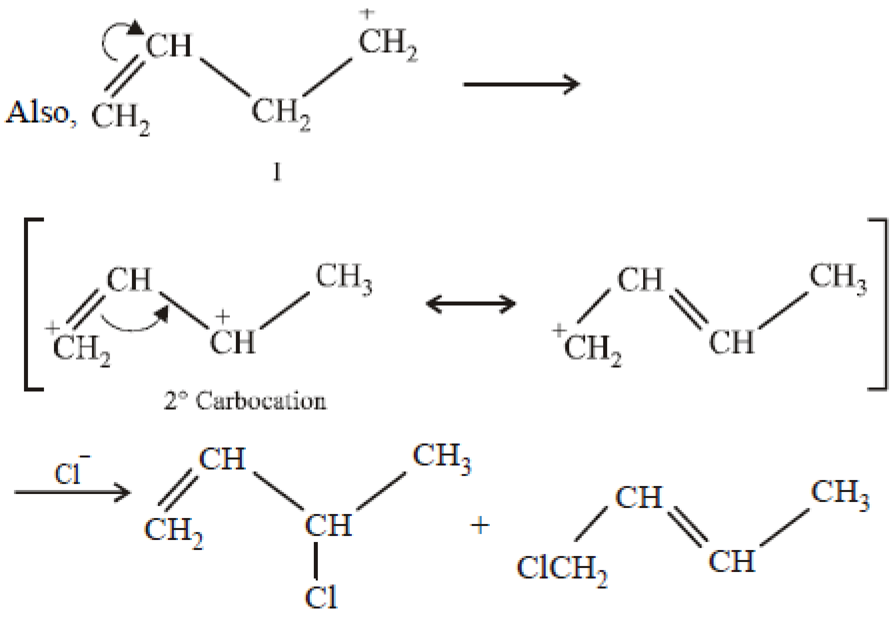


Solution:

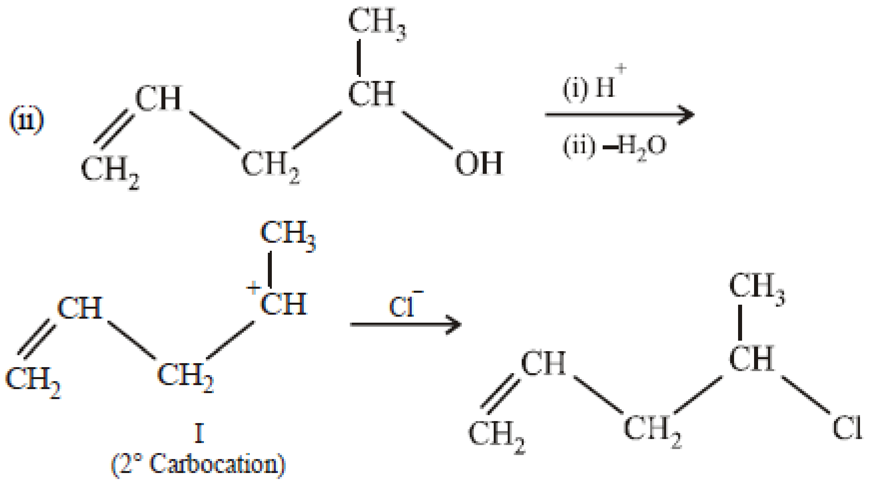
(i) NOTE: Since the large propenyl group is attached to the carbon atom bearing the hydroxyl group, so the reaction is likely to occur via S_N1 mechanism.



Also,



(ii)



NOTE : In the intermediate carbocation, Ia carbon bearing positive charge has CH3 group which decreases the positive charge and hence prevents cyclisation of the compound.

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

(a) On hydrogenation, bombykol gives a compound A, $C_{16}H_{34}O$, which reacts with acetic anhydride to give an ester;

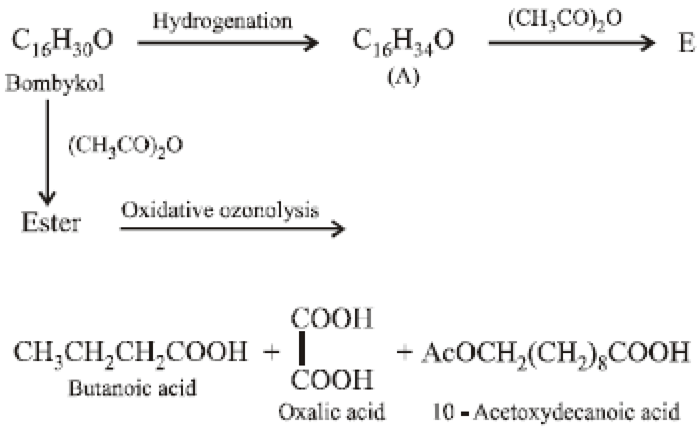
(b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O_3/H_2O_2) gives a mixture of butanoic acid, oxalic acid and 10-

acetoxydecanoic acid.

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

Solution :

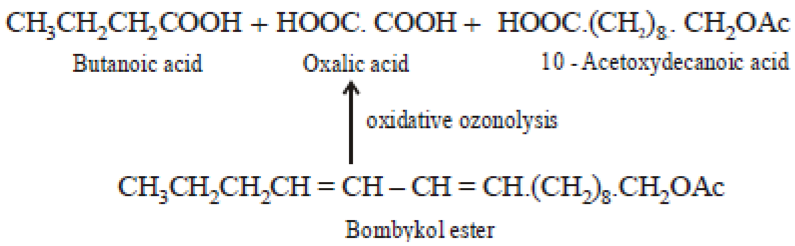
TIPS/Formulae : Let us summarise the given facts.



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

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

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

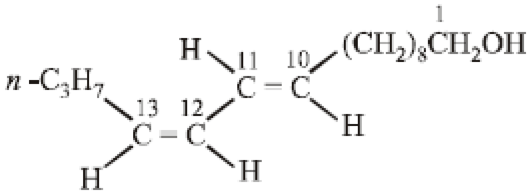


The structure of the bombykol ester suggests that bombykol has the following structure:

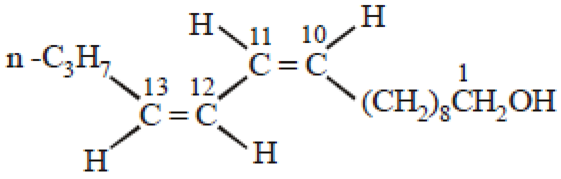
$CH_3CH_2CH_2CH = CH – CH = CH.(CH_2)_8.CH_2OH$ (Bombykol) and the structure of A is

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

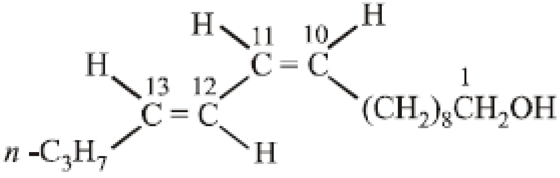
Four geometrical isomers are possible for the above bombykol structure (as it has two double bonds).



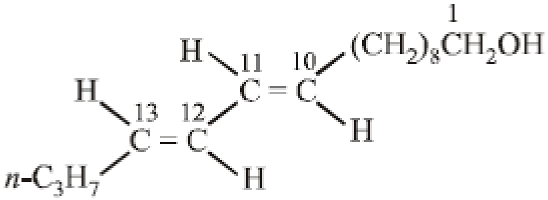
10 E, 12 Z



10 Z, 12 Z



10 Z, 12 E



10E, 12E

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

Solution:

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

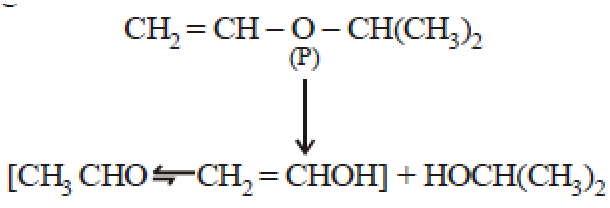
(ii) Acidic hydrolysis of P to Q and R, both of which responds iodoform test, indicates that Q and R should have following structure.

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

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

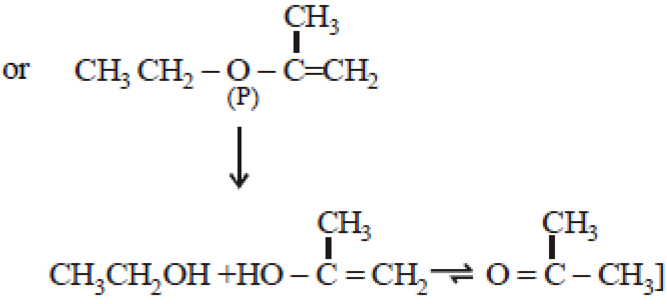
C_2 – Component – O – C_3 – Component

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



$$\underset{(P)}{CH_2=CH-O-CH(CH_3)_2} \longrightarrow [CH_3CHO \leftrightharpoons CH_2=CHOH] + HOCH(CH_3)_2$$

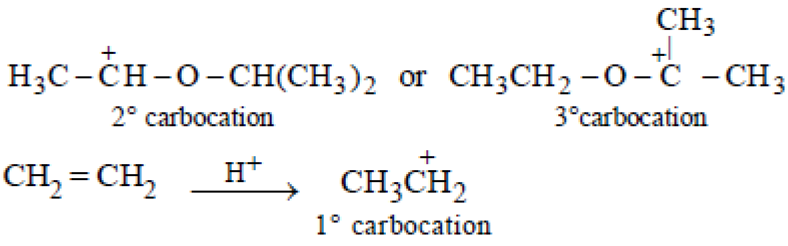
(Q and R), Both responds iodoform test



$$\text{or}\quad \underset{(P)}{CH_3CH_2-O-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2} \longrightarrow CH_3CH_2OH + HO-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \rightleftharpoons O=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3]$$

(Q and R), Both responds iodoform test

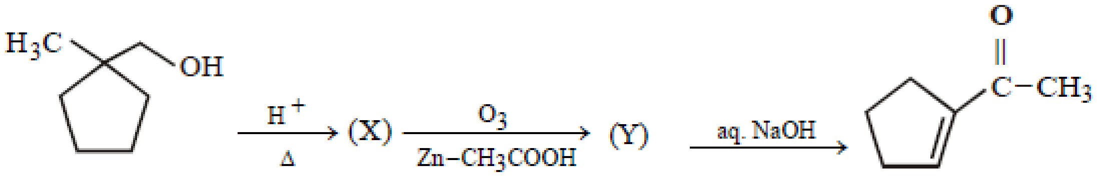
Extra reactivity of P toward dil. H_2SO_4 than ethylene is due to formation of highly stable carbocation



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

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

23. Identify (X) and (Y) in the following reaction sequence. (2005 - 2 Marks)



Solution :