Alcohols, Phenols and Ethers-solutions

SUBJECTIVE PROBLEMS:

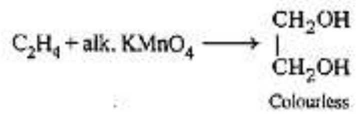
Sol 1.

'A' is C_2H_5OH and 'B' is C_2H_4

$C_2H_5OH \xrightarrow[-H_2O]{Conc.H_2SO_4} C_2H_4$

(A) (B)

(Ethyl alcohol) (Ethane)



$C_2H_4 + alk.\ KMnO_4 \longrightarrow \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$

Colourless

$C_2H_4 + H_2 \xrightarrow{Ni} C_2H_6$

Ethane ethane

Sol 2.

The unreactivity of the compound (X) towards sodium indicates that it is neither an acid nor and 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.

$R - O - R \xrightarrow[excess\ \ of\ \ HI]{Re\ flux\ \ with} 2RI \xrightarrow{hydrolysis} 2ROH$

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

(Z)

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

$C_2H_5 - O - C_2H_5 + 2HI \xrightarrow{reflux} 2C_2H_5I$

Diethyl ether (X) Ethyl iodide (Y)

$\xrightarrow{OH^-} 2C_2H_5OH \xrightarrow{KMnO_4} CH_3COOH$

Ethyl alcohol (Z) Acetic acid

(Eq. wt. = 60)

Sol 3.

(i) $C_2H_5OH \xrightarrow[(O)]{I_2} CH_3CHO$

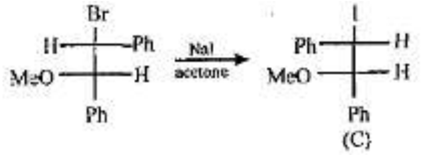
$CH_3CHO + 3I_2 + 4NaOH$

$\xrightarrow[reaction]{Haloform} HCOONa + CHI_3 + 3H_2O + 3NaI$

(ii)

The reaction takes place by S_N2 reaction mechanism.

Solution: Br is replaced by I following S_N2 mechanism. There will be Walden inversion at the place of replacement.



Sol 4.

(i) $CH_3CH(OH)CH_3 \xrightarrow[-H_2O]{Conc.H_2SO_4} Ch_3.CH = CH_2$

2-propanol

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

1-propanol

(ii) $Ch_3CH_2OH \xrightarrow[350°C]{Al_2O_4} CH_2\ CH_2$

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

$\xrightarrow{CH_3COOH} CH_2 = CHOCOCH_3$

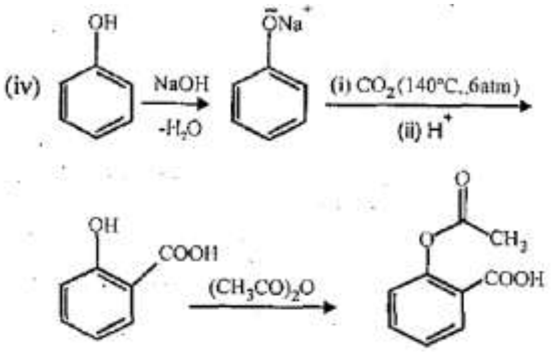
Vinyl acetate

Or $CH_3CH_2OH \xrightarrow{oxi} CH_3CHO$

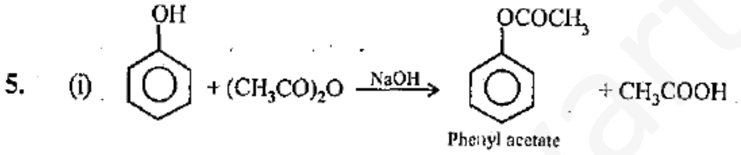
$\rightarrow CH_3COOH \xrightarrow{CH \equiv CH} CH_2 = CHOCOCH_3$

Vinyl acetate

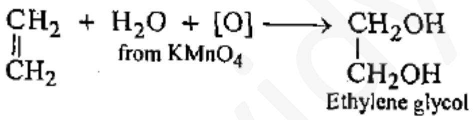
(iii) $C_6H_5OH \xrightarrow[distillation]{Zn} C_6H_6 \xrightarrow[(anhy \quad AlCl_3)]{CH_3COCl}$



Sol 5.



(ii)



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

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 NaHCO base 3 (a weaker base) to form peroxide ion (a stronger base) and carbonic acid (a stronger acid).

C base 6H base 5OH + NaHCO base 3 ⇌ C base 6H base 5ONa + H base 2CO base 3

Weaker acid weaker base stronger base stronger acid

Since acid-base equilibrium lie towards the weaker acid and weaker base, phenol does not

decompose NaHCO base 3 (difference from carboxylic acids).

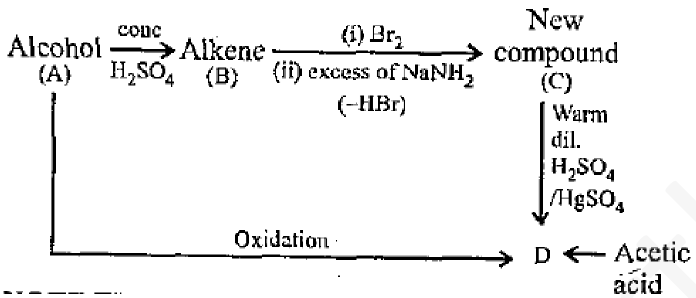
RCOOH + NaHCO ⇌ RCOONa + H base 2CO base 3

Stronger acid stronger base weaker base weaker acid

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

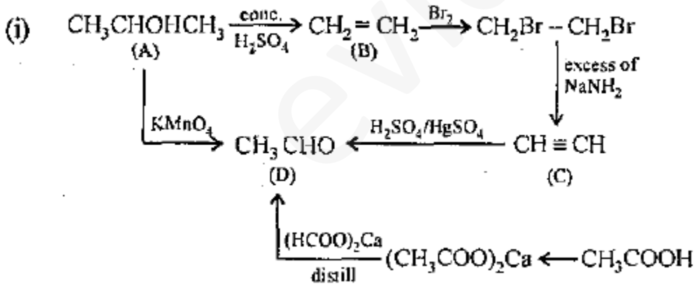
Sol 7.

The given problem can be sketached as below.



NOTE THIS STEP:

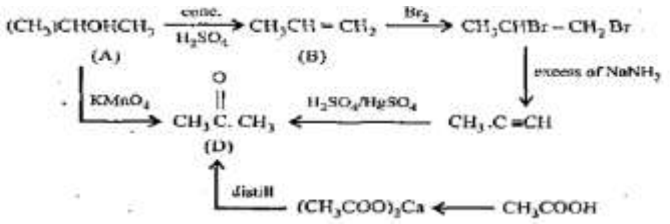
From the problem it appears that the compound C is an alkyne, hence D must be an aldehyde or ketone. Further since D can be obtained from acetic acid through its calcium salt it may be either ethyl alcohol or iso-propanol both of which explains the given set of reactions.



Hence

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

(ii) ALTERNATIVE SOLUTION:



Hence

A is isopropyl alcohol, $CH_3.CHOH.CH_3$

B is propene, $CH_3.CH = CH_2$

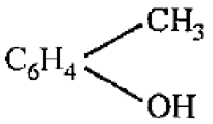
C is propane, $CH_3C \equiv CH$

D is acetone, $CH_3.CO.CH_3$

Sol 8.

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

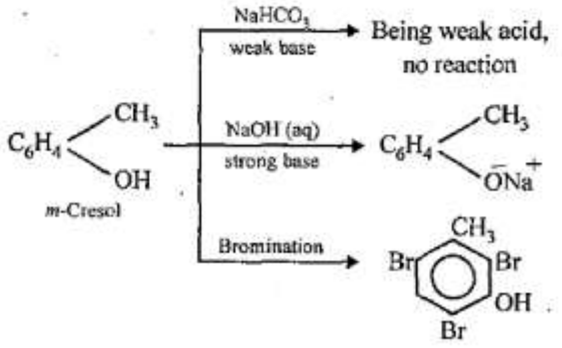
(ii) The compound, on treatment with Br_2 water, gives $C_7H_5OBr_3$. Taking into account of molecular formulae of the two compounds, the parent compound seems to be cresol.



Cresols

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

(iv) The reaction are



Sol 9.

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

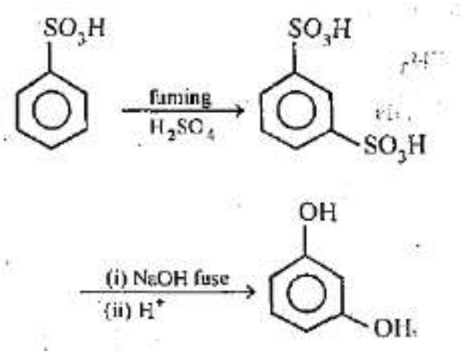
C base 2H base 5OH + 4I base 2 + 6NaOH

→ CHI base 3 ↓ + 5NaI + HCOONa + 5H base 2O

Sol 10.

(i) $CHCl_3$ + NaOH

(ii)



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., ≡ C – H grouping is present.

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

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

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

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

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

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

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

∴ Eq. wt. of the compound X = 42

Reactions of the compound X :

(i) $HC \equiv C.CH_2.CH_2OH$

(X)

$\xrightarrow[NH_4OH]{AgNO_3} AgC \equiv C.CH_2CH_2CH_2OH \downarrow$

(ii) $HC \equiv C.CH_2\ CH_2.CH_2OH$

(X)

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

(iii) $HC \equiv C.CH_2\ CH_2.CH_2OH$

(X)

$\xrightarrow{H_2/Pt} CH_3CH_2CH_2\ CH_2.CH_2OH$

$\xrightarrow{HI} CH_3CH_2CH_2\ CH_{2CH}3$

N-Pentane

Sol 12.

N-Butanol gives the following reaction in which the purple colour of $KMnO_4$ changes to brown. *Tert*-Alcohol are not oxidisable easily, hence purple colour of $KMnO_4$ remains same.

$CH_3CH_2CH_2CH_2OH + KMnO_4$

N-Butanol purple

$\rightarrow Ch_3CH_2CH_2COOK + MnO_2 \downarrow + KOH$

Soluble in H_2O Brown

The brown precipitate is of MnO_2.

Sol 13.

(I, iv)

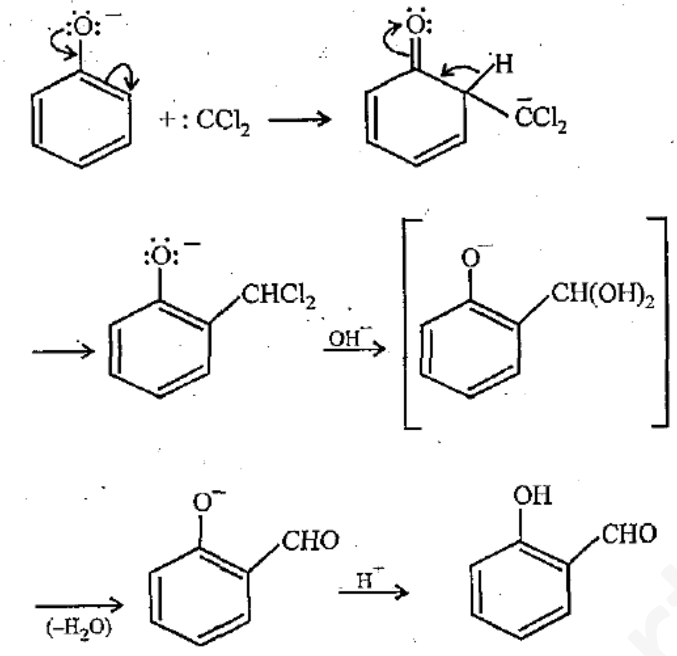
The reaction involves electrophilic substitution on the highly reactive peroxide ion.

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

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

$CCI_3^- \rightleftharpoons :CCI_2 + CI^-$

Dichlorocarbene

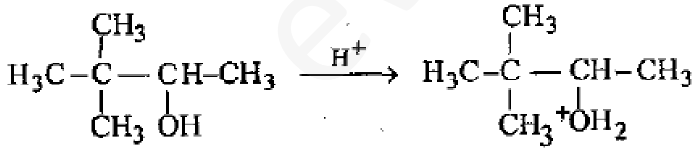


Salicylaldehyde
(o-Hydroxybenzaldehyde)

Sol 14.

The steps involved in the suggested mechanism are as follows.

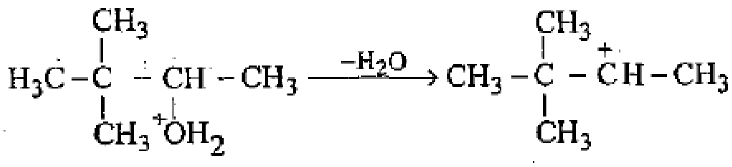
(a) The protonation of hydroxyl group.



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

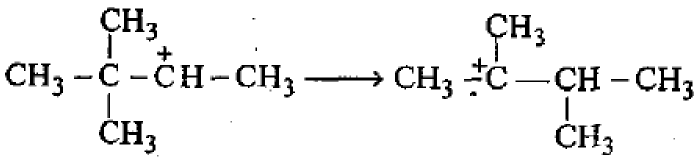
3, 3–Dimethylbutan–2–ol

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

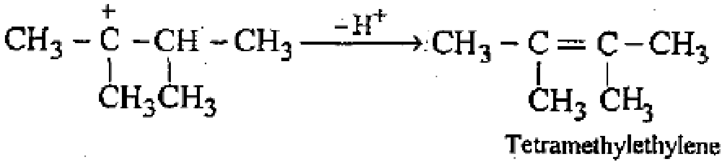


$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\underset{^+OH_2}{CH}-CH_3 \xrightarrow{-H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{C}H-CH_3$$

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

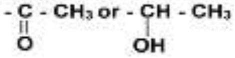


(d) The removal of H^+ to form a double bond

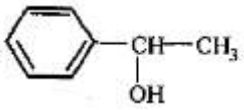


Sol 15.

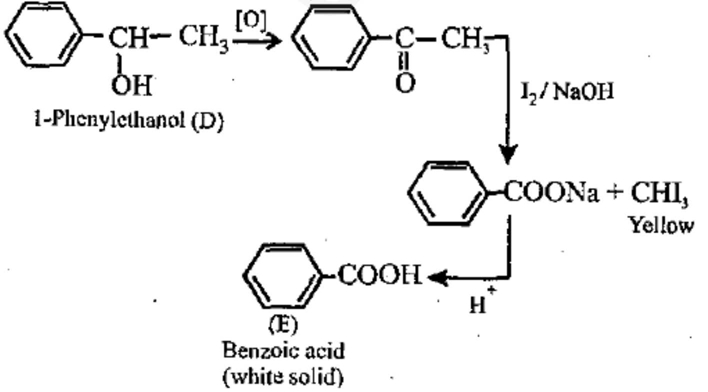
NOTE:

The reaction of D ($C_8H_{10}O$) with alkaline soluble of iodine is an iodoform reaction. This reaction is possible if the D has  $-\underset{\underset{O}{\|}}{C}-CH_3$ or $-\underset{\underset{OH}{|}}{CH}-CH_3$ 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 $C_6H_5CH(OH)CH_3$,

i.e,



The given reactions are



Sol 16.

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

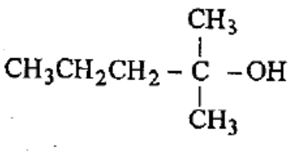
(b) Since (B) is optically inactive, it must have at least two alkyl groups similar

$C_6H_{10}O \xrightarrow{2H_2} C_6H_{14}O$

(A) (B)

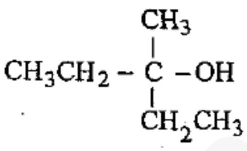
Thus the five carbon atoms can be adjusted into three alkyl groups (of which two are similar) either as $-CH_3$, $-CH_3$, and $-C_3H_7$, or as $-C_2H_5$, $-C_2H_5$ and CH_3,

Thus the possible structure of alcohol (B) is either



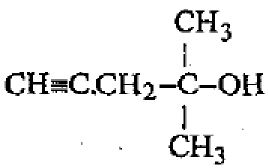
$CH_3CH_2CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

or



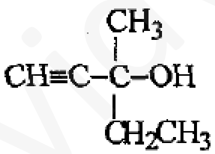
$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-OH$

Hence the corresponding compound (A) is either



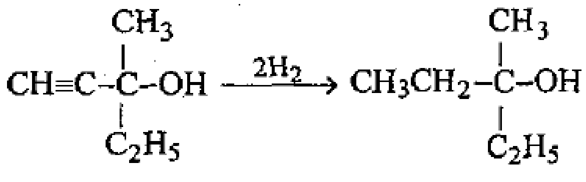
$CH{\equiv}C.CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

or



$CH{\equiv}C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-OH$

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

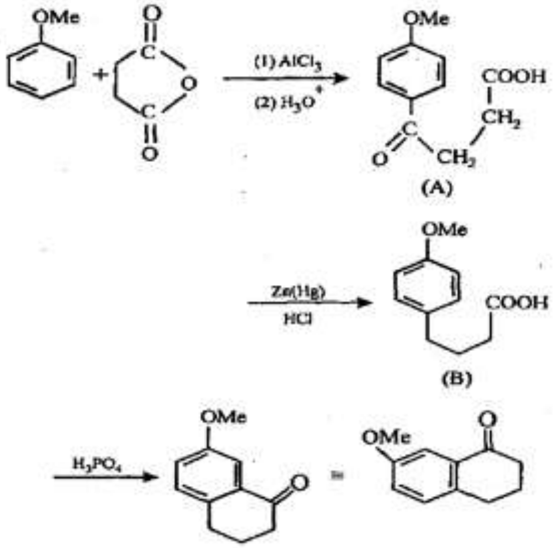


$CH{\equiv}C-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-OH \xrightarrow{2H_2} CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-OH$

(A) (B)

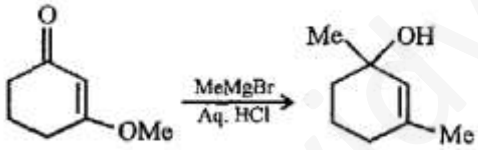
Sol 17.

17.



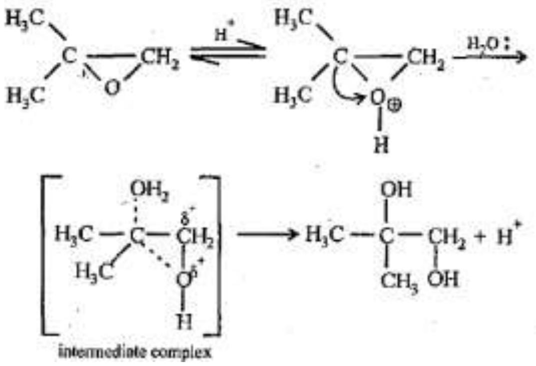
Sol 18.

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.

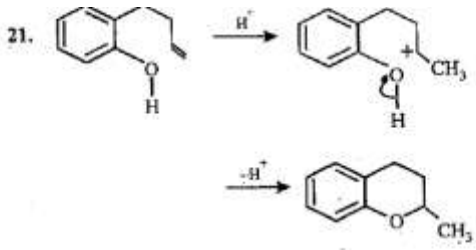
(i) $(CH_3)_3\,CBr \xrightarrow{CH_3ONa} (CH_3)_2\,C = CH_2$

Alkene

(ii) $CH_3Br + NaOC(CH_3)_3 \rightarrow CH_3 - O - C(CH_3)_3$

Either

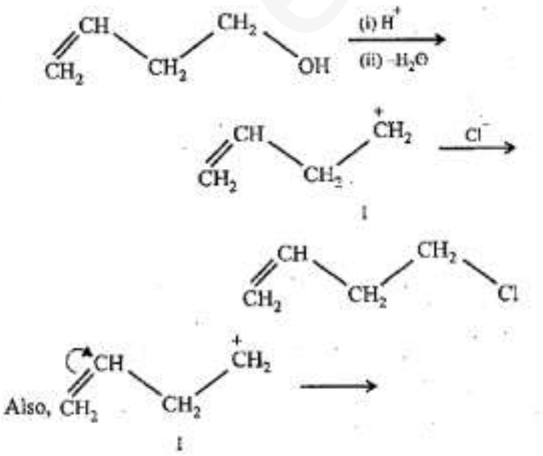
Sol 21.

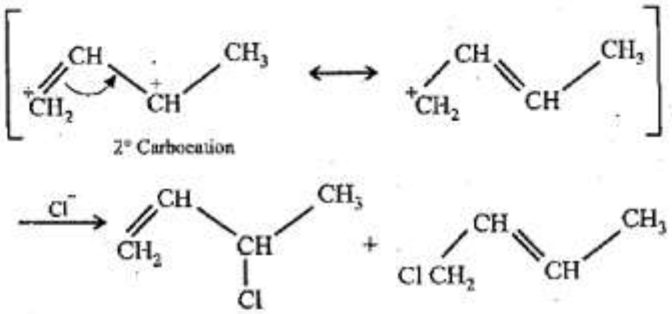


Sol 22.

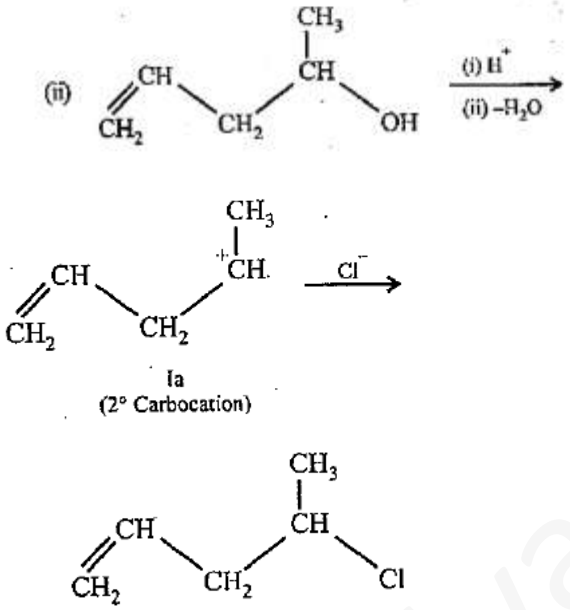
(i) NOTE:

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.





(ii)

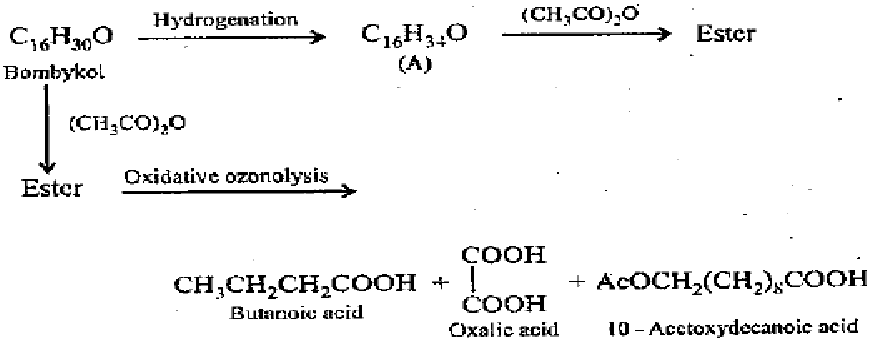


NOTE:

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

Sol 23.

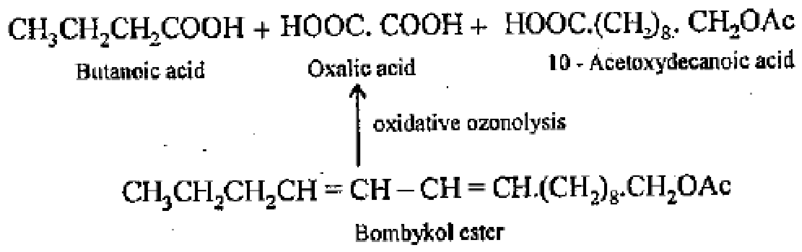
Let us summarise the given facts.



(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.

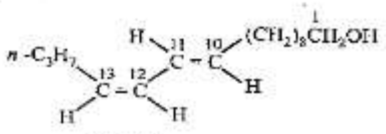


The structure of the bombykol ester suggests that bombykol has the following structure :

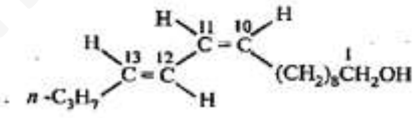
$CH_3CH_2CH_2CH = CH - CH = CH.(CH_2)_8.CH_2OH$ (Bombykol) and the structure of A is

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

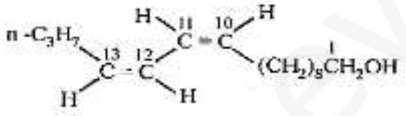
Four geometrical isomers are possible for the above bombykol structure (as it has two double bonds).



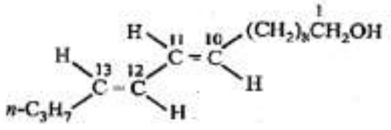
10 E, 12 Z



10 Z, 12 E



10 Z, 12 Z



10E, 12E

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

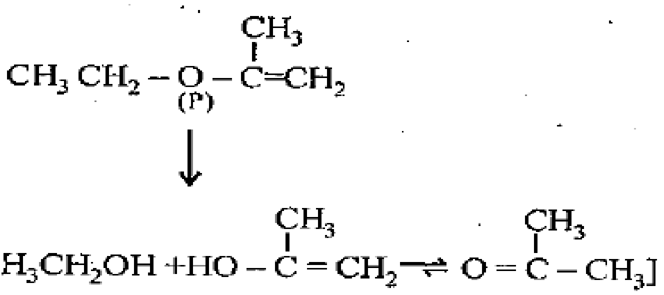
The only possible linkage that can explain such hydrolysis is ether. Hence P should have following type of structure. C_2 – component – O – C_3 – component should have double bond, thus the possible structure for P should 'be either of the following two structures which explains all the given reactions.

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

$$\downarrow$$

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

(Q and R), Both responds iodoform test



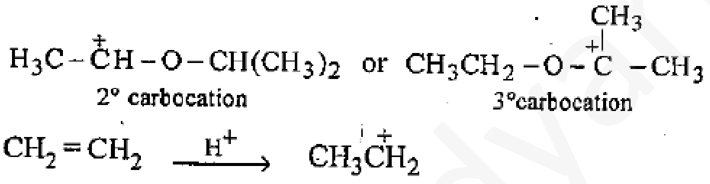
$$\text{or}\quad CH_3CH_2-\underset{(P)}{O}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

$$\downarrow$$

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

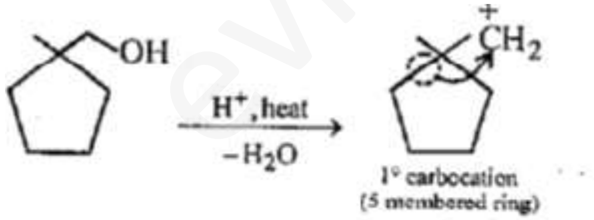
(Q and R), Both responds iodoform test

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



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

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



Sol 25.