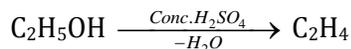


Alcohols, Phenols and Ethers-solutions

SUBJECTIVE PROBLEMS:

Sol 1.

'A' is C₂H₅OH and 'B' is C₂H₄

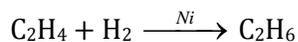
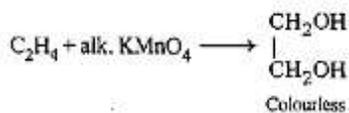


(A)

(B)

(Ethyl alcohol)

(Ethane)



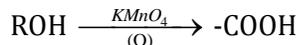
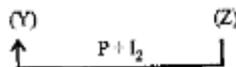
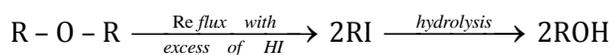
Ethane

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.

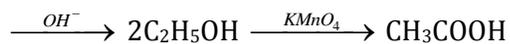


(Z)

Since the carboxylic acid has equivalent weight of 60, it must be acetic acid (CH₃COOH), hence Z must be ethyl alcohol, (Y) ethyl iodide and (X) diethyl ether.



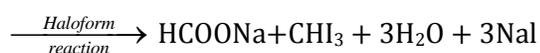
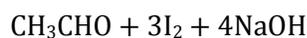
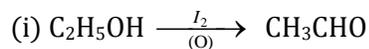
Diethyl ether (X) Ethyl iodide (Y)



Ethyl alcohol (Z) Acetic acid

(Eq. wt. = 60)

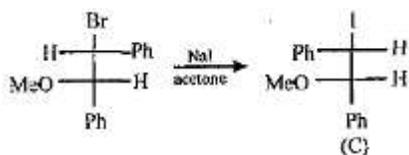
Sol 3.



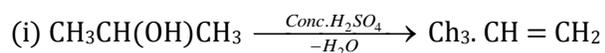
(ii)

The reaction takes place by S_N2 reaction mechanism.

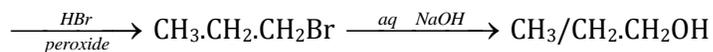
Solution: Br is replaced by I following S_N2 mechanism. There will be Walden inversion at the place of replacement.



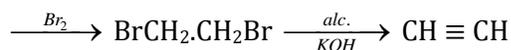
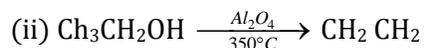
Sol 4.



2-propanol



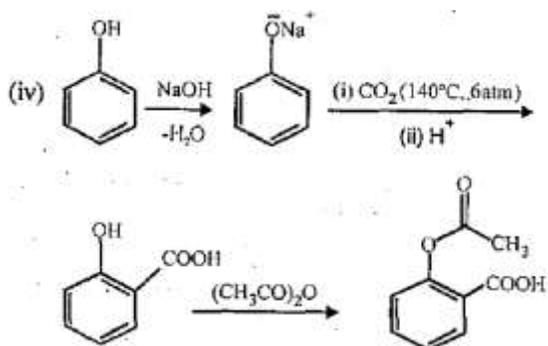
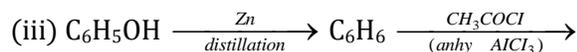
1-propanol



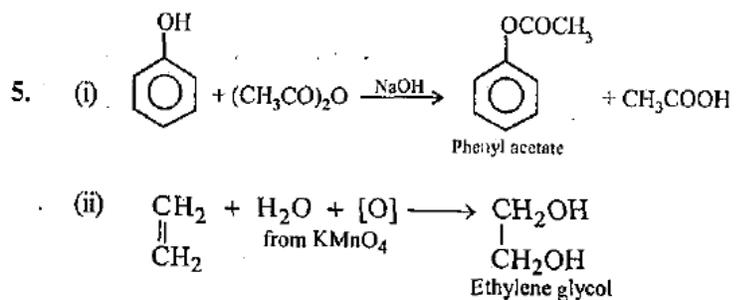
Vinyl acetate



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 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 NaHCO_3 (difference from carboxylic acids).

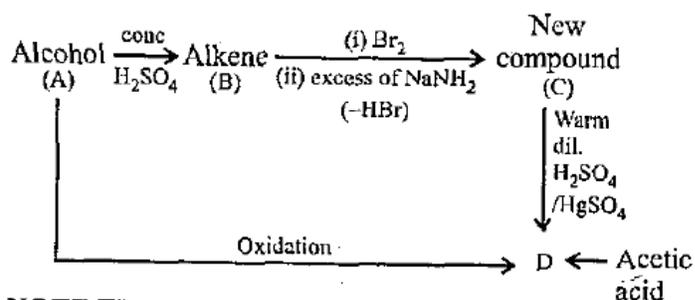


Stronger acid stronger base weaker base weaker acid

(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.

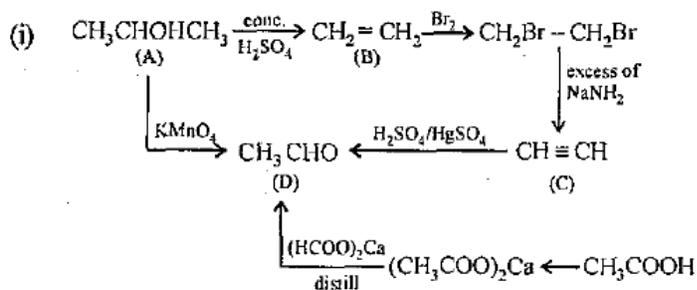
Sol 7.

The given problem can be 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, $\text{CH}_3 \cdot \text{CHO}$

Sol 9.

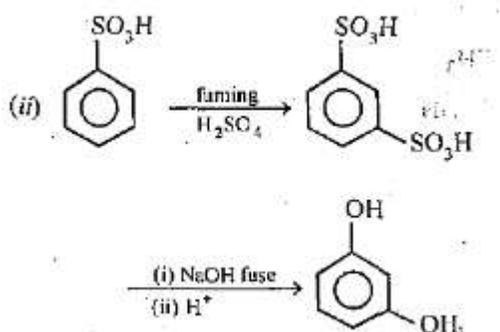
Iodoform test is used to distinguish methanol and ethanol. Ethanol gives iodoform test white methanol does not respond.

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

→ CHI base 3 ↓ + 5NaI + HCOONa + 5H base 20

Sol 10.

(i) $\text{CHCl}_3 + \text{NaOH}$



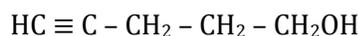
Sol 11.

(i) Since the compound X ($\text{C}_5\text{H}_8\text{O}$) does not react appreciably with Lucas reagent, it indicates that the compound has a primary alcoholic group ($-\text{CH}_2\text{OH}$).

(ii) Reaction of the compound X with ammoniacal silver nitrate to give a precipitate indicates that it has an acetylenic hydrogen atom, i.e., $\equiv \text{C} - \text{H}$ 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 ($\text{C}_5\text{H}_8\text{O}$) 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

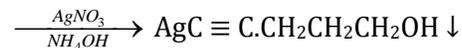
22400 ml. of CH_4 at STP = $0.42/224 * 22400 = 42$ g

∴ Eq. wt. of the compound X = 42

Reactions of the compound X :



(X)



(X)



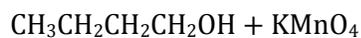
(X)



N-Pentane

Sol 12.

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



N-Butanol purple



Soluble in H_2O Brown

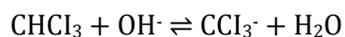
The brown precipitate is of MnO_2 .

Sol 13.

(I, iv)

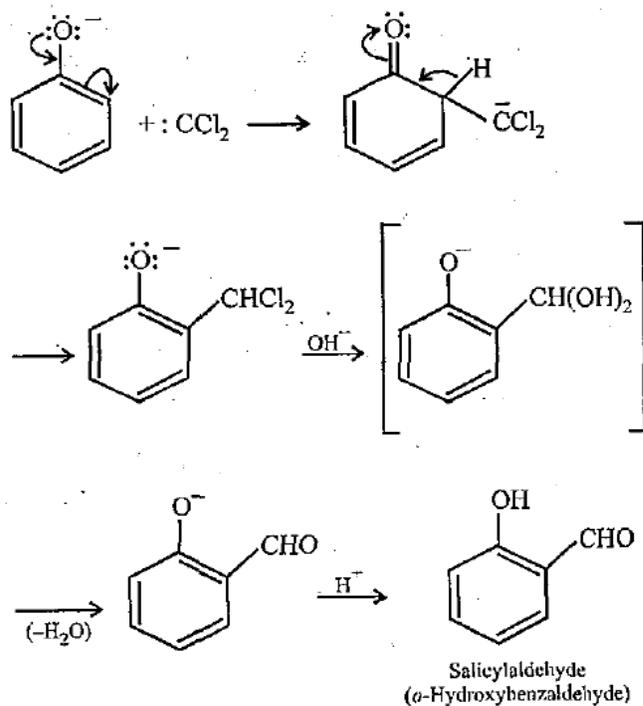
The reaction involves electrophilic substitution on the highly reactive peroxide ion.

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





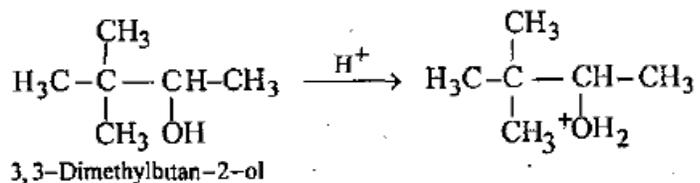
Dichlorocarbene



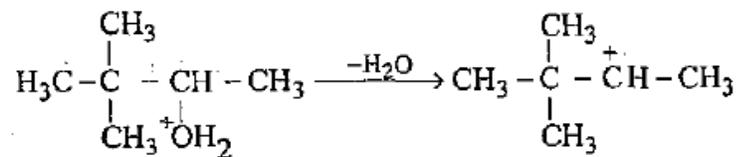
Sol 14.

The steps involved in the suggested mechanism are as follows.

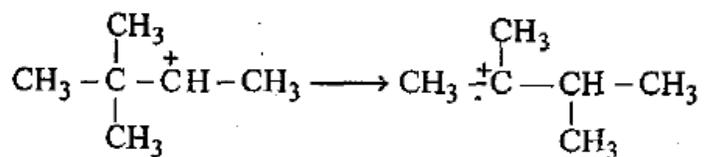
(a) The protonation of hydroxyl group.



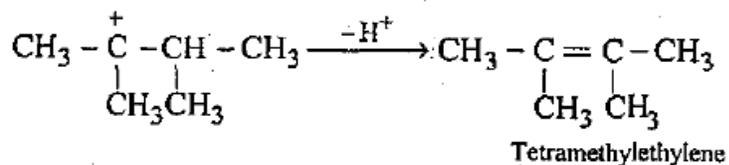
(b) The removal of H_2O to form a secondary (2°) carbonium ion



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



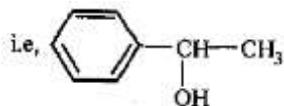
(d) The removal of H⁺ to form a double bond



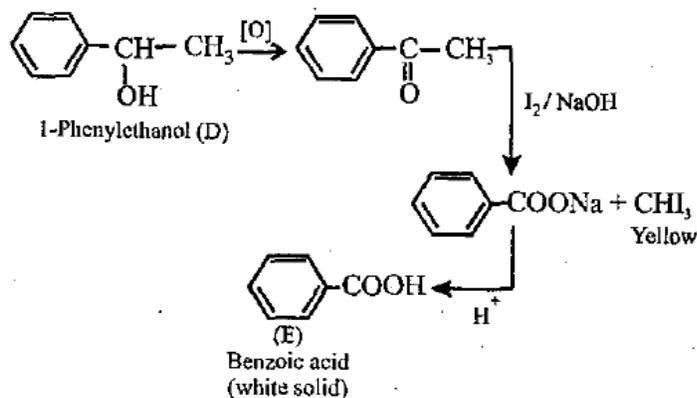
Sol 15.

NOTE:

The reaction of D (C₈H₁₀O) with alkaline soluble of iodine is an iodoform reaction. This reaction is possible if the D has $\begin{matrix} -\text{C}-\text{CH}_3 \\ \parallel \\ \text{O} \end{matrix}$ 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 C₆H₅CH(OH)CH₃,



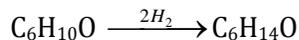
The given reactions are



Sol 16.

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

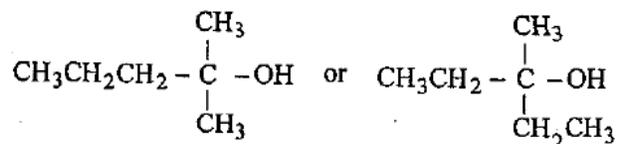
(b) Since (B) is optically inactive, it must have at least two alkyl groups similar



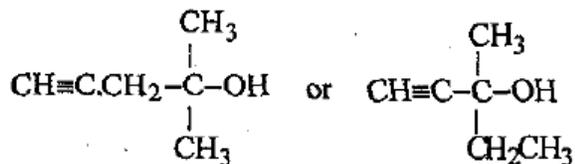
(A) (B)

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 CH_3 ,

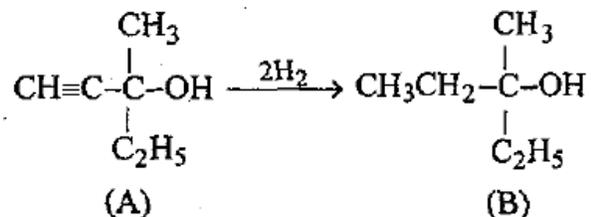
Thus the possible structure of alcohol (B) is either



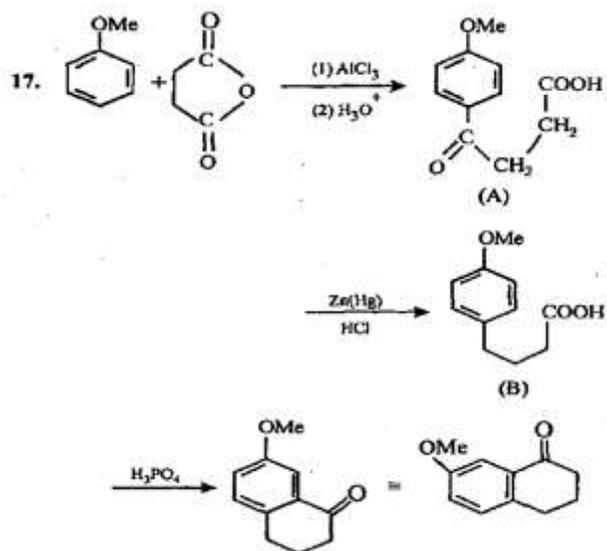
Hence the corresponding compound (A) is either



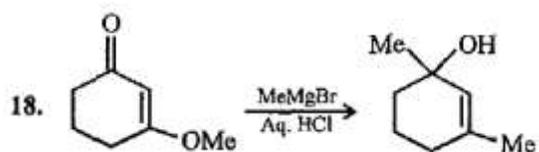
However, the compound (A) is optically active, so (A) and hence also (B) should have right side structure.



Sol 17.

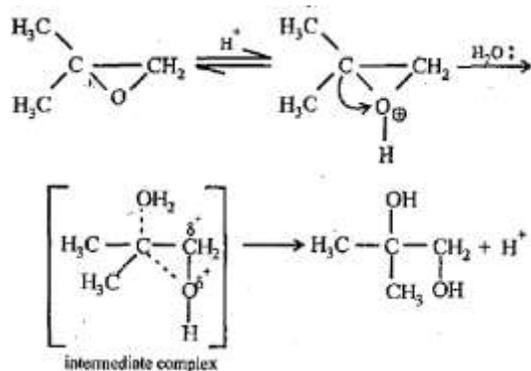


Sol 18.



Sol 19.

The oxirane ring is cleaved via $\text{S}_{\text{N}}2$ mechanism

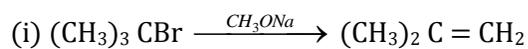


Sol 20.

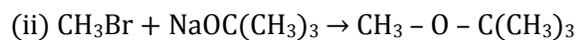
The method given in (ii) is the correct method for the formation of ether because method (i) leads alkene as the main product.

NOTE:

3° alkyl halides are easily dehydrohalogenated by base.

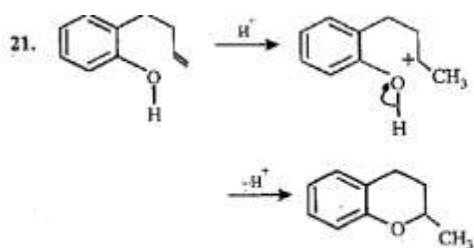


Alkene



Either

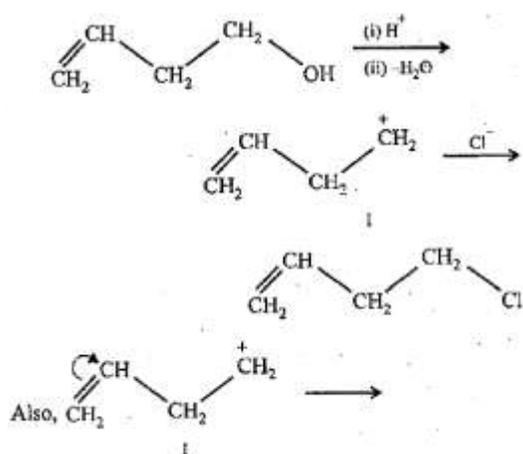
Sol 21.

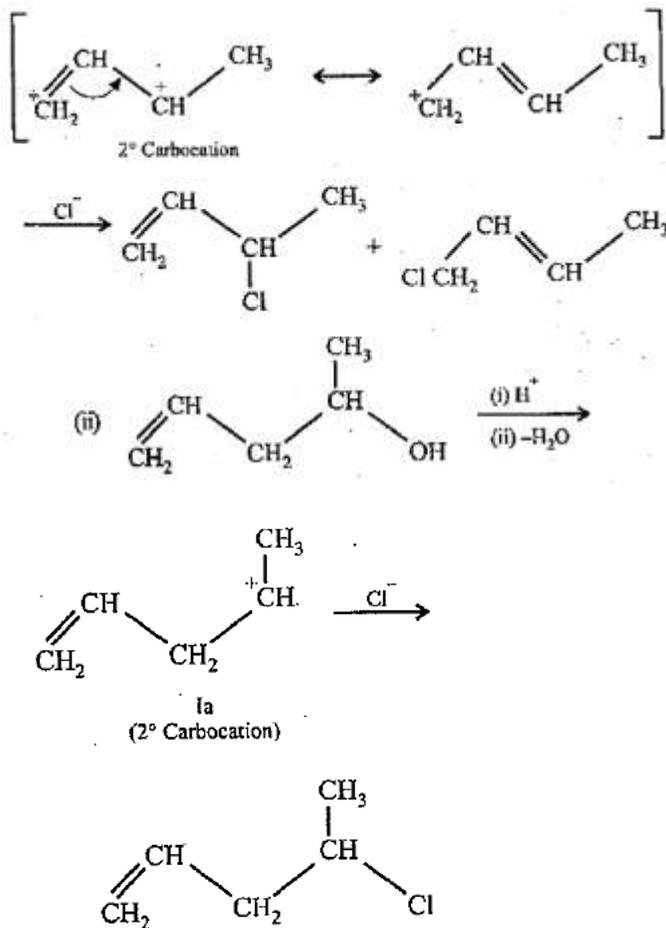


Sol 22.

(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.



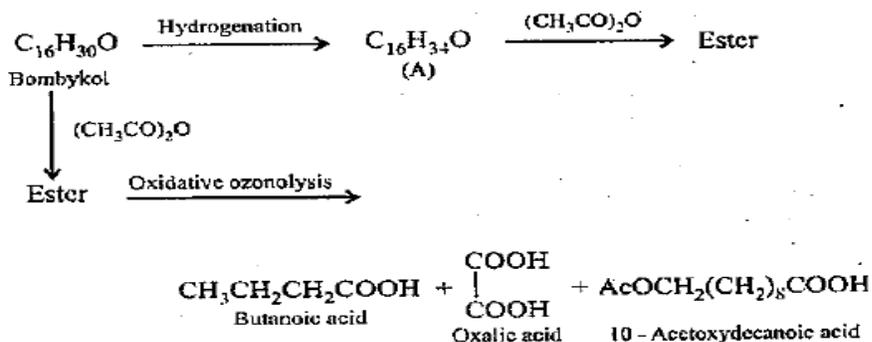


NOTE:

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

Sol 23.

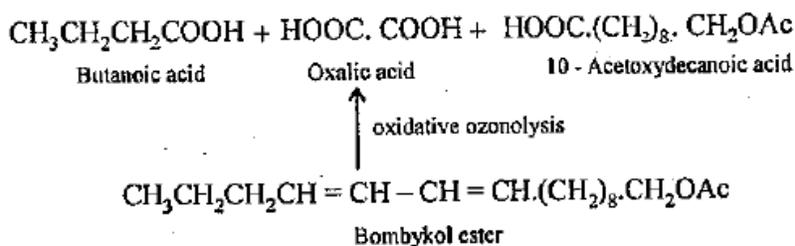
Let us summarise the given facts.



(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.

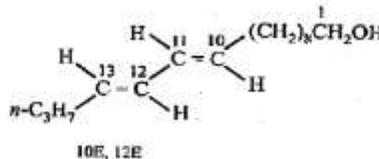
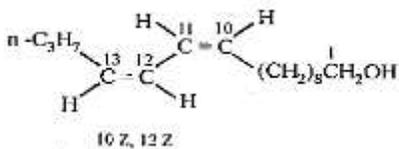
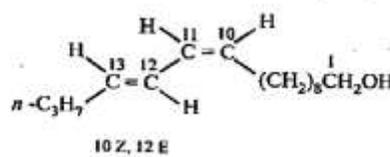
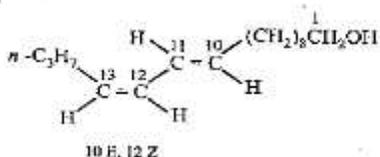


The structure of the bombykol ester suggests that bombykol has the following structure :

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-\text{CH}=\text{CH}\cdot(\text{CH}_2)_8\cdot\text{CH}_2\text{OH}$ (Bombykol) and the structure of A is

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_8\cdot\text{CH}_2\text{OH}$ or $C_{16}H_{33}OH$ /

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



Sol 24.

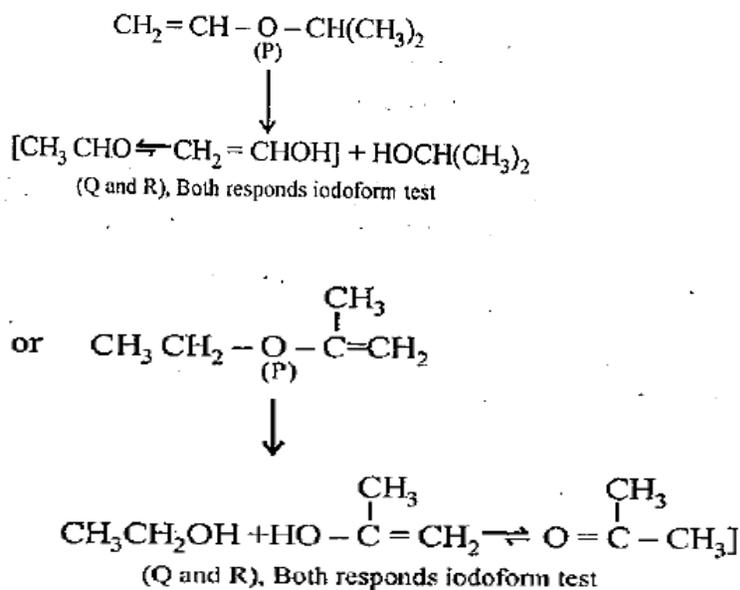
(i) Molecular formula of P, $C_5H_{10}O$ indicates 1° of unsaturation. So it should have double bond.

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

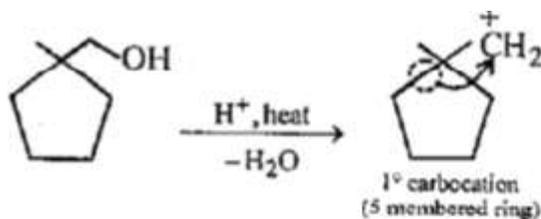
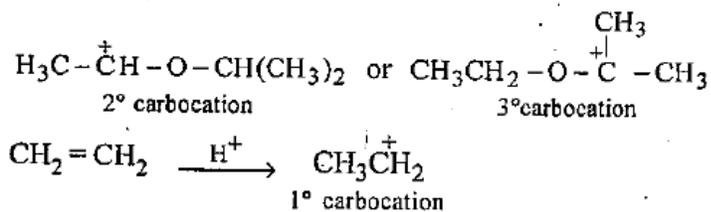
$\text{CH}_3\text{CH}_2\text{OH}$, $(\text{CH}_3)_2\text{CHOH}$, CH_3CHO or CH_3COR

The only possible linkage that can explain such hydrolysis is ether. Hence P should have following type of structure. C₂ - component - O - C₃ - 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. H_2SO_4 than ethylene is due to formation of highly stable carbonation



Sol 25.

