4. *When ethylene glycol is heated with a mixture of concentrated* HNO_3 *and concentrated* H_2SO_4*, it produces*

(A) $\begin{array}{l}COOH\\|\\COOH\end{array}$ **(B)** $CO_2 + H_2$ **(C)** $\begin{array}{l}CH_2ONO_2\\|\\CH_2ONO_2\end{array}$ **(D)** $\begin{array}{l}CH_2ONO_2\\|\\CH_2OH\end{array}$

5. *When glycerol is heated with an excess of HI, it produces :*

(A) *allyl iodide* **(B)** *propene* **(C)** *glycerol tri-iodide* **(D)** *2-iodopropane*

6. *When glycerol is heated with oxalic acid at 533 K, it produces :*

(A) *formic acid* **(B)** *allyl alcohol* **(C)** *acrolein* **(D)** *glyceric acid*

7. *Ethylene glycol is used in car radiators to :*

(A) *facilitate evaporation*
(B) *increase the temperature of the water in the radiator*
(C) *lower the freezing point of the water in the radiator*
(D) *lower the viscosity of the water in the radiator*

ILLUSTRATIONS Section - 5

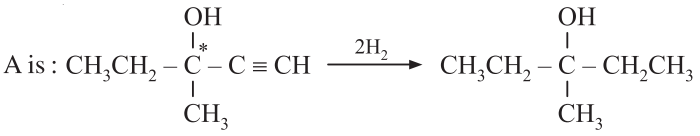
Illustration - 1 *An optically active alcohol* $A(C_6H_{10}O)$ *absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B. The compound B is resistant to oxidation by* CrO_3 *and does not show any optical activity. Deduce the structures of A and B.*

SOLUTION :

$$\underset{\text{(Optically active)}}{C_6H_{10}O(A)} \xrightarrow{2H_2} B \xrightarrow[CrO_3]{(O)} \text{resists oxidation}$$

Clearly, A has a – C ≡ C – bond and B should be a 3° alcohol as they resist oxidation.

Now visualise the structure of A keeping in mind a chiral centre (optically active).



$$\text{A is : } CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|*}}{C}}-C\equiv CH \xrightarrow{2H_2} CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2CH_3$$

Optically inactive

(* : Chiral Centre)

Illustration - 2 3, 3-*Dimethylbutan*-2-ol *loses a molecule of water in the presence of hot conc.* H_2SO_4 *to give tetramethyl ethylene as the major product. Suggest a proper mechanism. Also identify the minor product.*

SOLUTION :

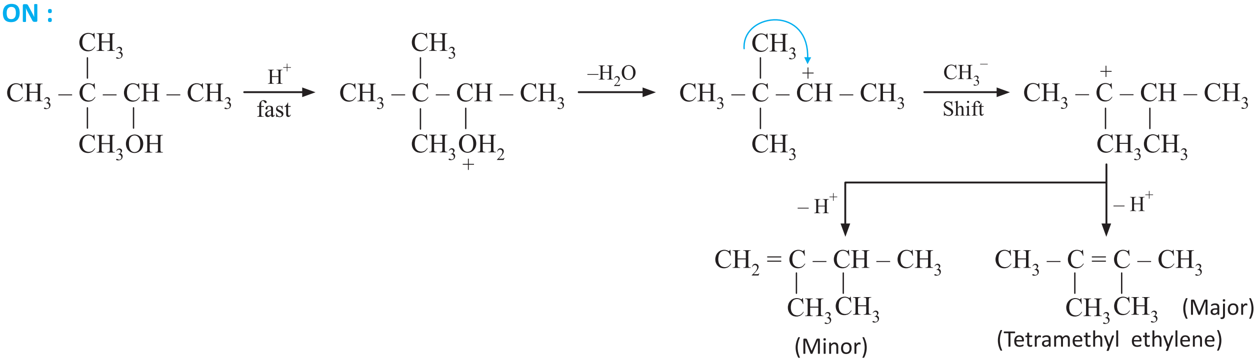
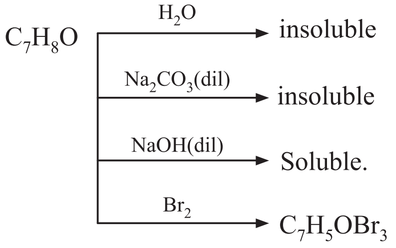


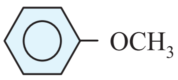
Illustration - 3 *A compound of molecular formula C_7H_8O is insoluble in water and dil. Na_2CO_3 but dissolves in dil. NaOH solution. On treatment with Br_2/H_2O, it readily gives a precipitate of $C_7H_5OBr_3$. What is the structure of compound ?*

SOLUTION :

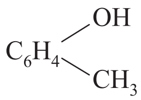


The possible structures of compounds having molecular formula as C_7H_8O are :

Benzyl alcohol

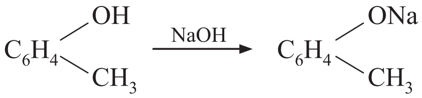


Anisole

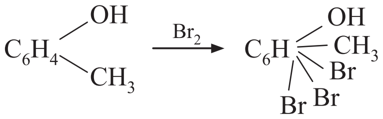


Cresol

It can not be benzyl alcohol or anisole as alcohols and ether (o, p, m) are insoluble in NaOH. It can be only be cresol. Note that phenols are soluble in dil. NaOH forming phenoxides.

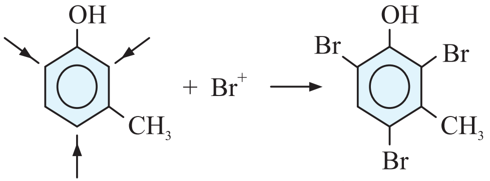


Now cresol can be o, p or m. How to identify it ?



$(C_7H_5OBr_3)$

Observe that it is S_E (electrophilic substitution) giving a tri-substituted product as –OH is a strongly activating group (+M effect). The only possible isomer giving a trisubtituted derivative can be m-cresol.



$(C_7H_5OBr_3)$

Note that both – OH and – CH_3 activate same positions (i.e. o and p). Though, due to steric factor, bromination at the position between –OH and –Me group is quite difficult.

Illustration - 4 *A compound X(C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammonical $AgNO_3$. With excess of MeMgBr, 0.42 gm 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 the structure of X and give all reactions involved.*

SOLUTION :

C_5H_8O (0.42 gm) $\xrightarrow{\text{Lucas Reagent}}$ No appreciable reaction

C_5H_8O (0.42 gm) $\xrightarrow{AgNO_3\ (amm)}$ a precipitate

C_5H_8O (0.42 gm) $\xrightarrow{MeMgBr}$ 224 mL CH_4 (STP)

$$X \xrightarrow{AgNO_3} \text{precipitate}$$

⇒ X contains $-C \equiv C-H$ group, which is confirmed by action of MeMgBr to give CH_4.

$$\frac{0.42}{84} \text{ mol of } X \equiv 0.005 \text{ mol.}$$

$$224 \text{ mL } CH_4 \text{ (STP)} \equiv \frac{224}{22400} \text{ mol} = 0.01 \text{ mol of X}$$

⇒ $1 \text{ mol X} \equiv 2 \text{ mol } CH_4$

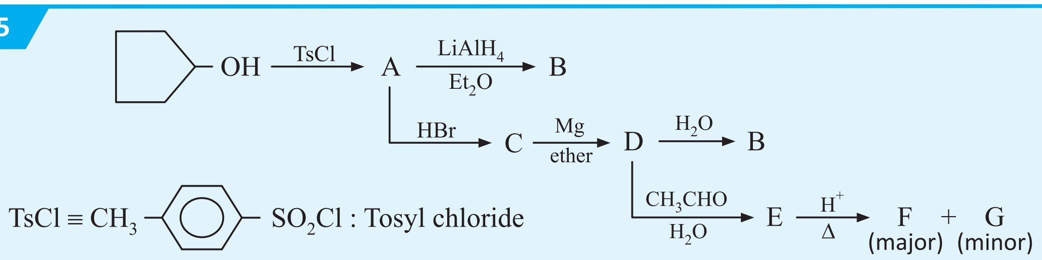
Hence X contains two acidic H-atoms.

The structure of X should be : $\overset{\delta+}{H}C \equiv C - CH_2CH_2CH_2\,O\overset{\delta+}{H}$

Note that 'X' has to be 1° alcohol as it does not give Lucas test. Also note that 2° alcohol react with Grignard Reagent to give alkanes, hence Lucas test is very important here.

<u>Finally checking</u> : $HC \equiv C - CH_2CH_2CH_2OH \xrightarrow[Pt]{H_2} \xrightarrow{HI} \underset{\text{(n − Pentane)}}{H_3C - CH_2 - CH_2CH_2CH_3}$

Illustration - 5



SOLUTION :

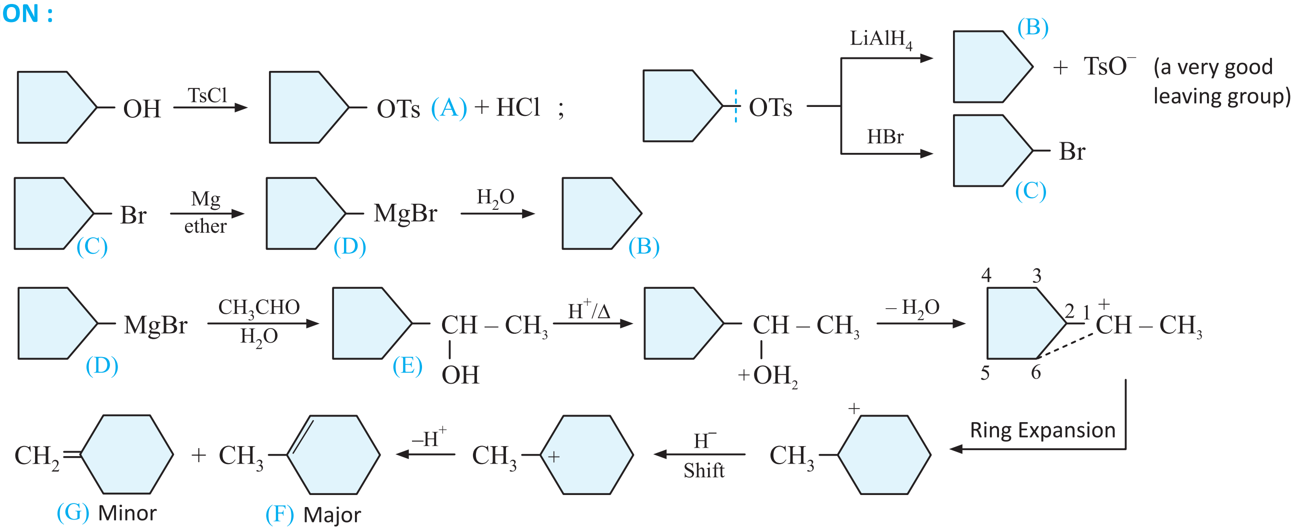
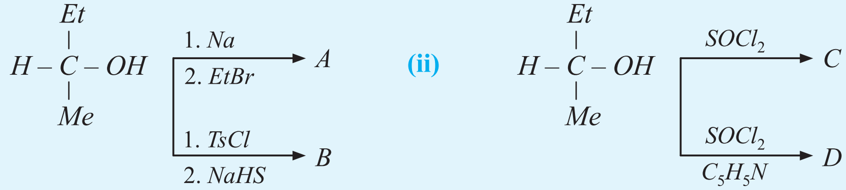


Illustration - 6 *Identify the products in the following reactions and comment on the stereochemistry of the products.*

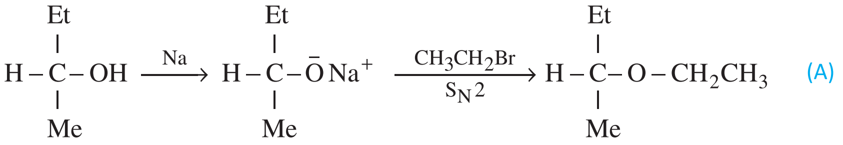


(i) $H-\overset{Et}{\underset{Me}{C}}-OH \xrightarrow{1.\ Na,\ 2.\ EtBr} A$; $H-\overset{Et}{\underset{Me}{C}}-OH \xrightarrow{1.\ TsCl,\ 2.\ NaHS} B$

(ii) $H-\overset{Et}{\underset{Me}{C}}-OH \xrightarrow{SOCl_2} C$; $H-\overset{Et}{\underset{Me}{C}}-OH \xrightarrow[C_5H_5N]{SOCl_2} D$

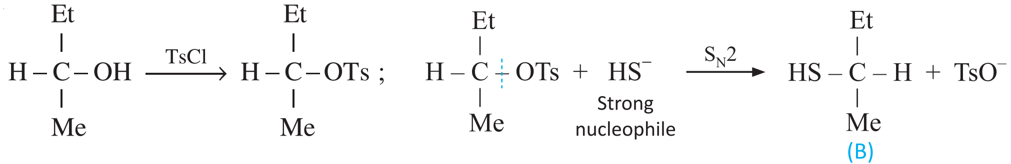
SOLUTION :

(i) Observe that alcohol has a chiral centre.



$$H-\overset{Et}{\underset{Me}{C}}-OH \xrightarrow{Na} H-\overset{Et}{\underset{Me}{C}}-\bar{O}Na^+ \xrightarrow[S_N2]{CH_3CH_2Br} H-\overset{Et}{\underset{Me}{C}}-O-CH_2CH_3 \quad (A)$$

Note that here O – H bond breaks to give alkoxide and in S_N2 reaction ether is formed retaining the configuration of alcohol.

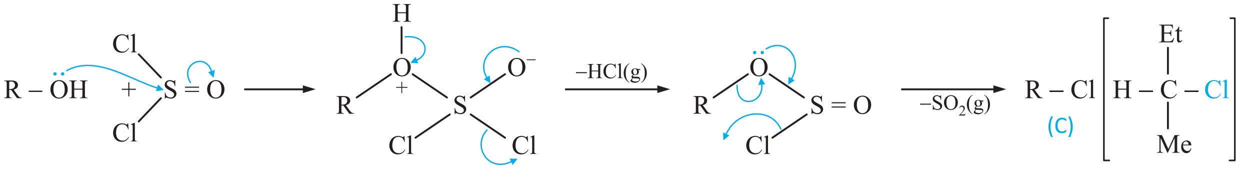


$$H-\overset{Et}{\underset{Me}{C}}-OH \xrightarrow{TsCl} H-\overset{Et}{\underset{Me}{C}}-OTs\ ;\quad H-\overset{Et}{\underset{Me}{C}}-OTs + \underset{\text{Strong nucleophile}}{HS^-} \xrightarrow{S_N2} HS-\overset{Et}{\underset{Me}{C}}-H + TsO^- \quad (B)$$

HS^- will make an S_N2 attack from the back at α-carbon (chiral) to give an inverted configuration.

Note that TsO^- is a very good leaving group assisting S_N2 reaction.

(ii) Reaction of alcohol with $SOCl_2$ proceed by intramolecular nucleophilic substitution reaction (S_Ni) mechanism, hence there is retention in configuration.



In second reaction product B is formed by S_N2 reaction mechanism of nucleophilic substitution reaction hence there is inversion in configuration of chiral carbon atom.

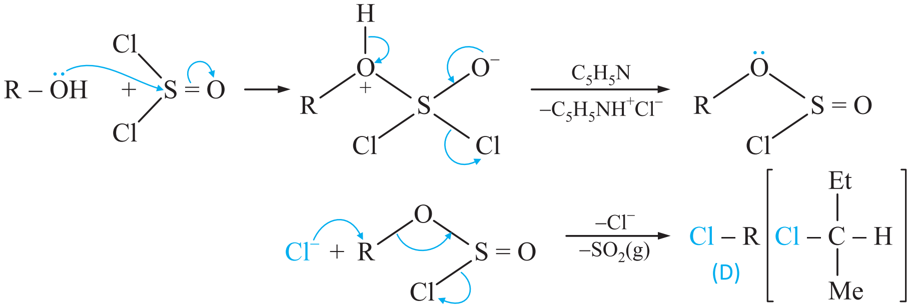


Illustration - 7 *Give the possible products in the following reactions. Also comment upon the type of pathways.*

(a) $CH_3CH_2OH + CH_3CH_2CH_2OH \xrightarrow[T\sim 140^\circ C]{H_2SO_4} ???$ **(b)** $CH_3CH_2OH + (CH_3)_3-C-OH \xrightarrow[T\sim 140^\circ C]{H_2SO_4} ???$

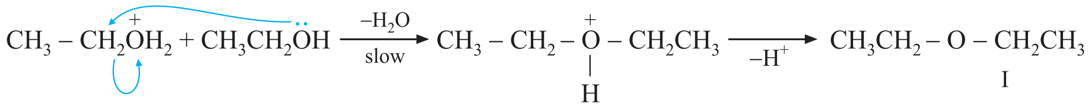
SOLUTION :

(*a*) $CH_3CH_2OH + CH_3CH_2CH_2OH \xrightarrow[T\sim 140°C]{H_2SO_4}$

Note that both alcohols are 1° alcohols, so none of these is capable of carbocation formation (1° carbocations being poorly stable). So here, ethers will be formed via S_N2 pathway as temperature is around 140°C.

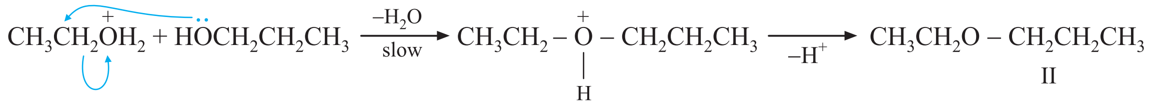
In the first step, either or both of two alcohols can form oxonium ion $(R\overset{+}{O}H_2)$ and then the second step, the other one will make an S_N2 attack on α-carbon to give a protonated ether which eventually will give ether as final product.

Due to absence of steric factors in two alcohols, possible products are : $CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2\overset{+}{O}H_2$



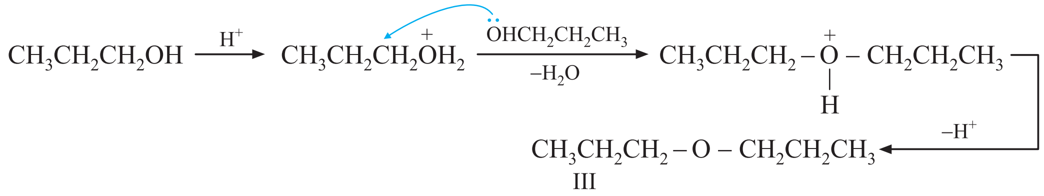
$$CH_3-CH_2\overset{+}{O}H_2 + CH_3CH_2\ddot{O}H \xrightarrow[\text{slow}]{-H_2O} CH_3-CH_2-\underset{\substack{|\\ H}}{\overset{+}{O}}-CH_2CH_3 \xrightarrow[-H^+]{} \underset{\text{I}}{CH_3CH_2-O-CH_2CH_3}$$

or



$$CH_3CH_2\overset{+}{O}H_2 + \ddot{H}OCH_2CH_2CH_3 \xrightarrow[\text{slow}]{-H_2O} CH_3CH_2-\underset{\substack{|\\ H}}{\overset{+}{O}}-CH_2CH_2CH_3 \xrightarrow[-H^+]{} \underset{\text{II}}{CH_3CH_2O-CH_2CH_2CH_3}$$

Also

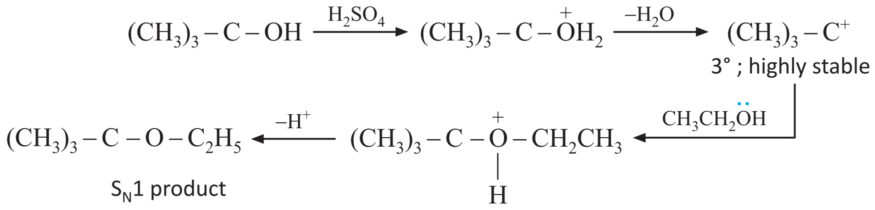


$$CH_3CH_2CH_2OH \xrightarrow{H^+} CH_3CH_2CH_2\overset{+}{O}H_2 \xrightarrow[-H_2O]{\ddot{O}HCH_2CH_2CH_3} CH_3CH_2CH_2-\underset{\substack{|\\ H}}{\overset{+}{O}}-CH_2CH_2CH_3 \xrightarrow{-H^+} \underset{\text{III}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3}$$

Hence the products (I, II, III) are formed via S_N2 path.

(*b*) $CH_3CH_2OH + (CH_3)_3-C-OH \xrightarrow{H_2SO_4} ?$

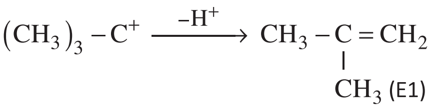
Note that one of these is tertiary butyl alcohol (3°), so it will form stable carbocation which will finally give ether as the main product via S_N1 path.



$$(CH_3)_3-C-OH \xrightarrow{H_2SO_4} (CH_3)_3-C-\overset{+}{O}H_2 \xrightarrow{-H_2O} \underset{\text{3° ; highly stable}}{(CH_3)_3-C^+}$$

$$(CH_3)_3-C^+ \xrightarrow{CH_3CH_2\ddot{O}H} (CH_3)_3-C-\underset{\substack{|\\ H}}{\overset{+}{O}}-CH_2CH_3 \xrightarrow{-H^+} \underset{S_N1\text{ product}}{(CH_3)_3-C-O-C_2H_5}$$

Note :
- A stable carbocation also give alkenes as minor product via E1 path.



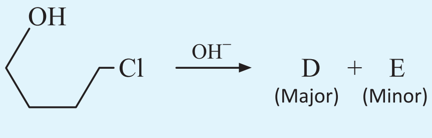
$$(CH_3)_3-C^+ \xrightarrow{-H^+} CH_3-\underset{\substack{|\\ CH_3}}{C}=CH_2 \text{ (E1)}$$

- If T ~ 160 – 170°C, E1 will be the major product.

Illustration - 8 *Identify the products in the following :*

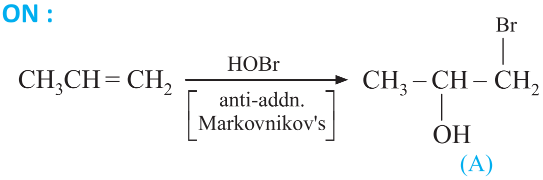
(*a*) $CH_3CH=CH_2 \xrightarrow{HOBr} A$; $A \xrightarrow{OH^-} B$; $A \xrightarrow{aq.\ KOH} C$

(*b*)

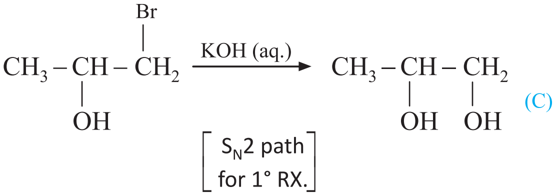


SOLUTION :

(*a*)



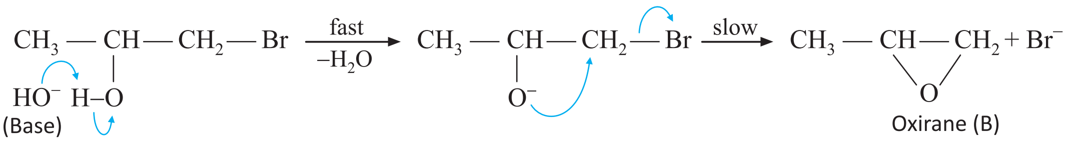
$$CH_3CH=CH_2 \xrightarrow[\text{anti-addn. Markovnikov's}]{HOBr} CH_3-\underset{\underset{OH}{|}}{CH}-\overset{\overset{Br}{|}}{CH_2}\ \ (A)$$



$$CH_3-\underset{\underset{OH}{|}}{CH}-\overset{\overset{Br}{|}}{CH_2} \xrightarrow[\left[\substack{S_N2\text{ path}\\ \text{for } 1^\circ\ RX.}\right]]{KOH\ (aq.)} CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}\ \ (C)$$

Note that if reagent is OH^-, then visualise its action as a base.

(usually alcoholic KOH is visualised as : OH^- as a base)



(*b*)

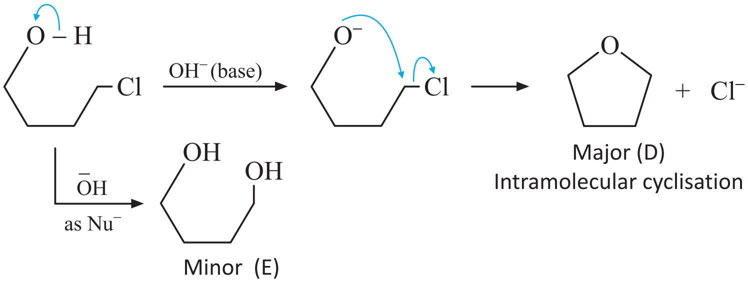
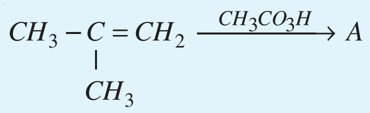


Illustration - 9 *Identify compounds A, B, C . . . . in the following reaction setup.*



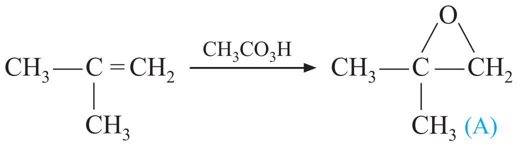
$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 \xrightarrow{CH_3CO_3H} A$$

$$A \xrightarrow[H_2O^{18}]{H^+} B$$

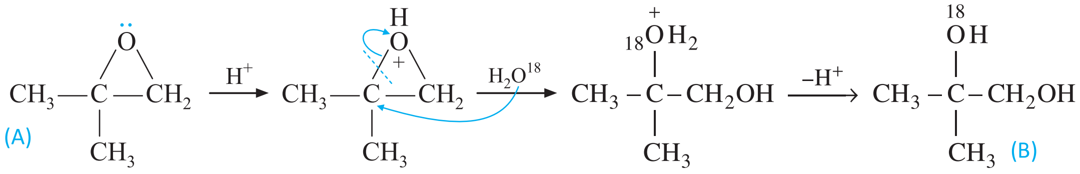
$$A \xrightarrow[CH_3OH]{CH_3ONa} C$$

$$B \xrightarrow{H_2SO_4\ conc.} D$$

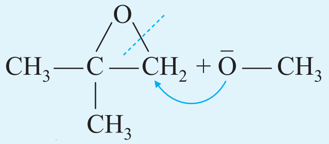
SOLUTION :



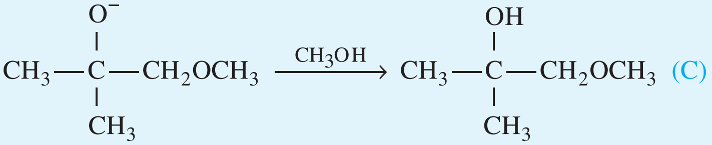
2, 2-Dimethyl oxirane



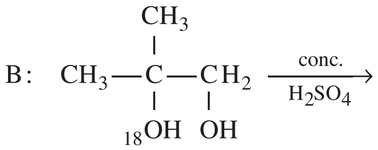
Note : ➤ Observe that Nu^- (i.e., H_2O^{18}) attaches to more alkylated carbon in an acid catalysed ring opening. It is S_N1 type ring opening.



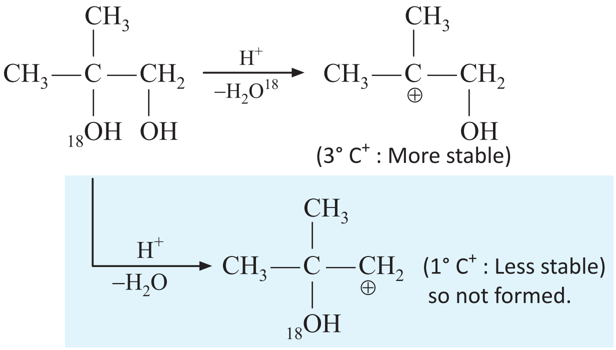
→ [CH_3O^- will attack at least steric hindered carbon atom in an S_N2 type attack].

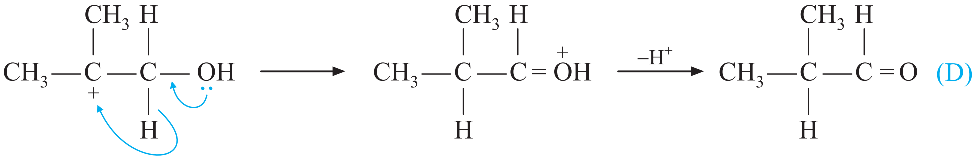


➤ Observe that Nu^- (CH_3O^-) attaches to less alkylated carbon in a base catalysed ring opening.

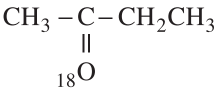


Visualise Pinnacol - Pinnacolone Rearrangement in glycols.



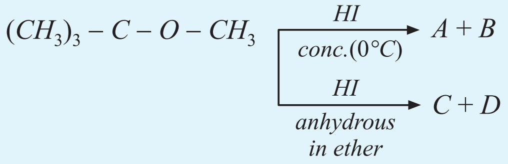


Note that the wrong answer is :



$$CH_3-\underset{\underset{^{18}O}{\|}}{C}-CH_2CH_3$$

Illustration - 10 *Identify the products A, B, C and D and describe the pathways.*

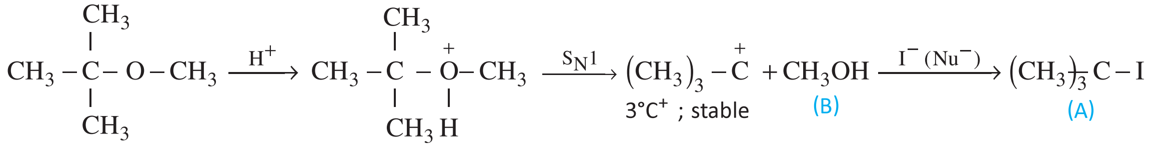


$(CH_3)_3-C-O-CH_3 \xrightarrow[conc.(0°C)]{HI} A+B$

$(CH_3)_3-C-O-CH_3 \xrightarrow[\text{anhydrous in ether}]{HI} C+D$

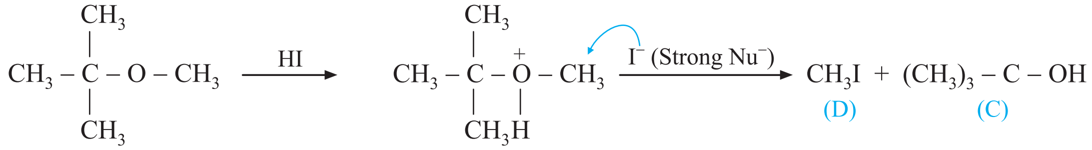
SOLUTION :

conc. HI ≡ solvent is H_2O.



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 \xrightarrow{H^+} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{+}{O}}-CH_3 \xrightarrow{S_N1} \underset{3°C^+\ ;\ stable}{(CH_3)_3-\overset{+}{C}} + \underset{(B)}{CH_3OH} \xrightarrow{I^-\ (Nu^-)} \underset{(A)}{(CH_3)_3C-I}$

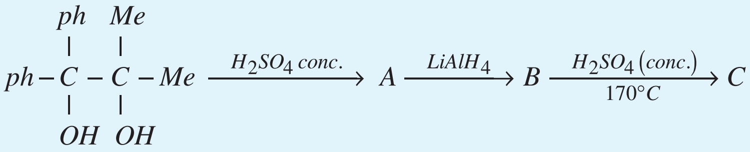
When solvent is ether, it being less polar favours S_N2 path with I^- as a strong nucleophile will make an S_N2 attack at $-CH_3$ group (no steric hindrance).



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 \xrightarrow{HI} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{+}{O}}-CH_3 \xrightarrow{I^-\ \text{(Strong Nu}^-)} \underset{(D)}{CH_3I} + \underset{(C)}{(CH_3)_3-C-OH}$

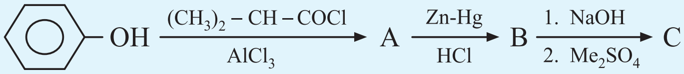
Illustration - 11 *Identify A, B, C, ... in the following reactions :*

(*a*)



$ph-\underset{OH}{\overset{ph}{C}}-\underset{OH}{\overset{Me}{C}}-Me \xrightarrow{H_2SO_4\ conc.} A \xrightarrow{LiAlH_4} B \xrightarrow[170°C]{H_2SO_4\ (conc.)} C$

(*b*)

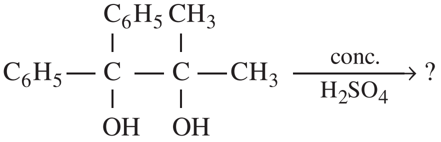


$C_6H_5OH \xrightarrow[AlCl_3]{(CH_3)_2-CH-COCl} A \xrightarrow[HCl]{Zn\text{-}Hg} B \xrightarrow[2.\ Me_2SO_4]{1.\ NaOH} C$

(*c*) $CH_3CH=CH_2 \xrightarrow[CCl_4]{NBS} A \xrightarrow{KOH\ (aq.)} B \xrightarrow[2.\ MeBr]{1.\ Na} C \xrightarrow[\Delta]{HI\ (conc.)} D+E$

SOLUTION :

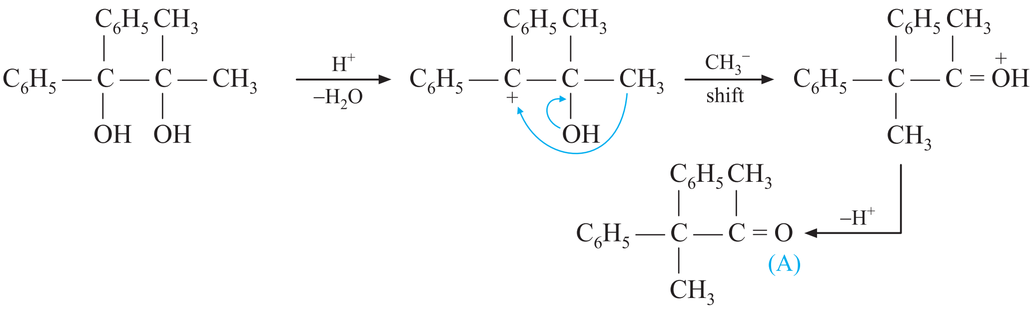
(*a*)



$C_6H_5-\underset{OH}{\overset{C_6H_5}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[H_2SO_4]{conc.} ?$

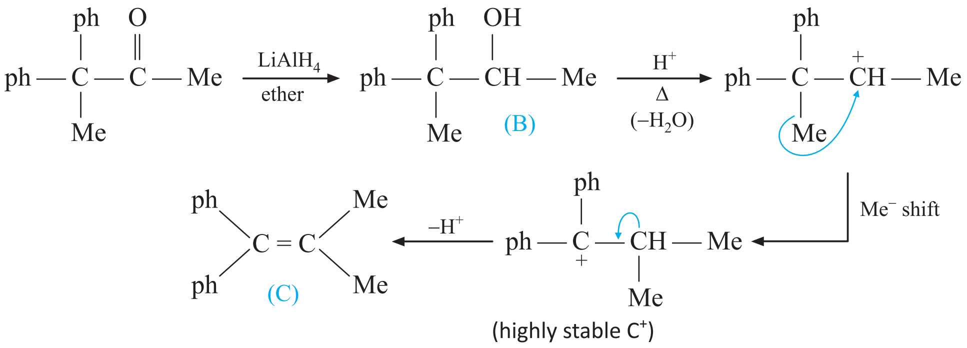
It is a case of Pinnacol-Pinnacolone type of rearrangement.

Observe that first visualise the most stable carbocation and then follow migration in order : H → ph → R.

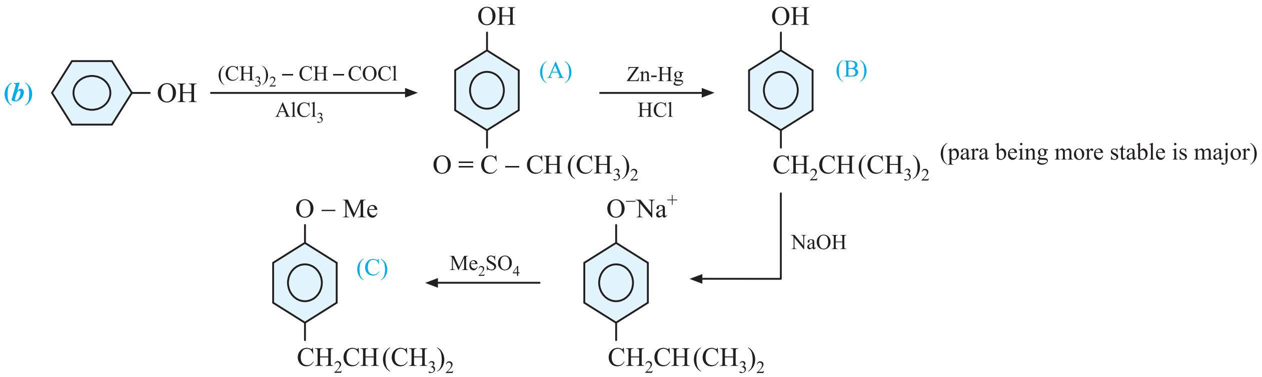


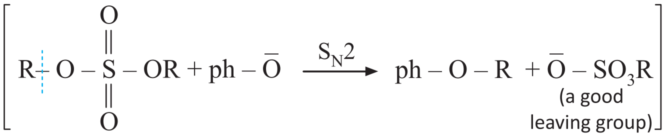
$C_6H_5-\underset{OH}{\overset{C_6H_5}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[-H_2O]{H^+} C_6H_5-\underset{+}{\overset{C_6H_5}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[shift]{CH_3^-} C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-\overset{CH_3}{C}=\overset{+}{O}H \xrightarrow{-H^+} \underset{(A)}{C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-\overset{CH_3}{C}=O}$

Rewriting (A) as :



(highly stable C⁺)





$$\left[R - O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - OR + ph - \bar{O} \xrightarrow{S_N2} ph - O - R + \bar{O} - SO_3R \right]$$

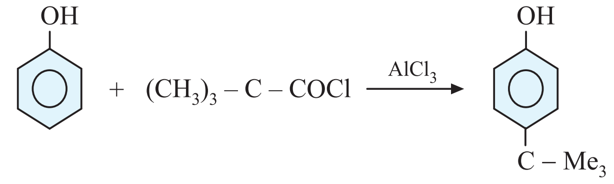
(a good leaving group)

Note : In general, $R\overset{+}{C}O$ does not undergo rearrangement but if R is 3° then it breaks as mentioned below :

$$\begin{tikzcd}
(CH_3)_3 - C - COCl \arrow[r, "AlCl_3"] & (CH_3)_3 - C - \overset{+}{C}O \arrow[r, leftrightarrow] \arrow[d] & (CH_3)_3 - C - C \equiv \overset{+}{O} \ \text{(Resonance)} \\
\text{As an electrophile} & \boxed{(CH_3)_3 - \overset{+}{C}} + CO \arrow[l] &
\end{tikzcd}$$

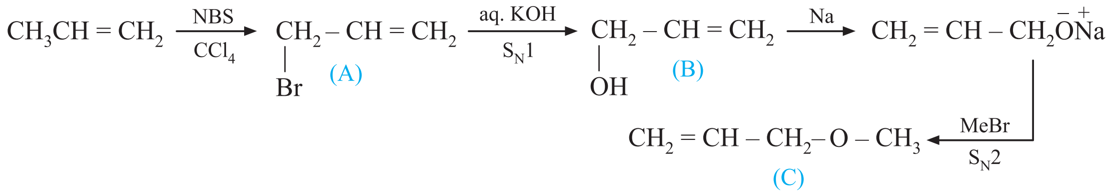
3°C⁺ : highly stable

For Example :



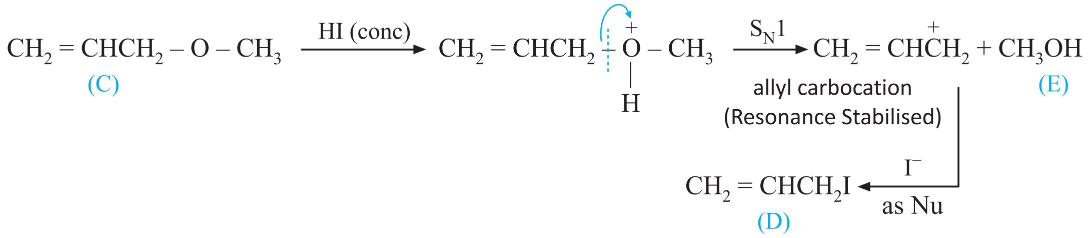
Note : If R is 1° or 2° (RCOCl) ; it will be simply Friedal craft acylation.

(c)



$$CH_3CH=CH_2 \xrightarrow[CCl_4]{NBS} \underset{(A)}{\underset{Br}{\underset{|}{CH_2}}-CH=CH_2} \xrightarrow[S_N1]{aq.\ KOH} \underset{(B)}{\underset{OH}{\underset{|}{CH_2}}-CH=CH_2} \xrightarrow{Na} CH_2=CH-CH_2\overset{-}{O}\overset{+}{Na}$$

$$\xrightarrow[S_N2]{MeBr} \underset{(C)}{CH_2=CH-CH_2-O-CH_3}$$



$$\underset{(C)}{CH_2=CHCH_2-O-CH_3} \xrightarrow{HI\ (conc)} CH_2=CHCH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_3 \xrightarrow{S_N1} \underset{\text{allyl carbocation (Resonance Stabilised)}}{CH_2=CH\overset{+}{C}H_2} + \underset{(E)}{CH_3OH}$$

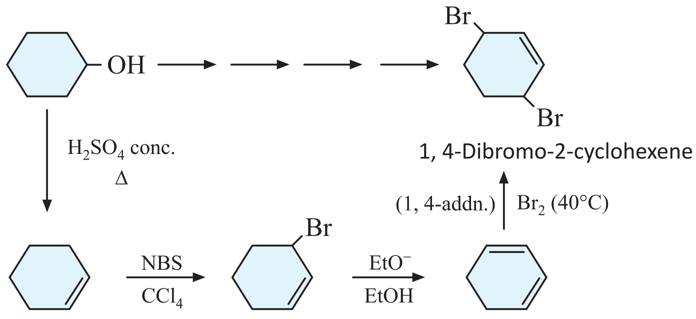
$$\xrightarrow[\text{as Nu}]{I^-} \underset{(D)}{CH_2=CHCH_2I}$$

Illustration - 12 *(a)* *How will you convert cyclohexanol to* 1, 4-*Dibromo-2-cyclohexene in not more than* 4-*steps* ?

(b) *How will you prepare* 2, 3-*Dimethyl-2-butanol from* 2-*Propanol as the only starting organic material* ?

SOLUTION :

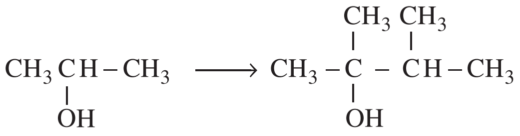
(a)



1, 4-Dibromo-2-cyclohexene

allylic substitution

(b)

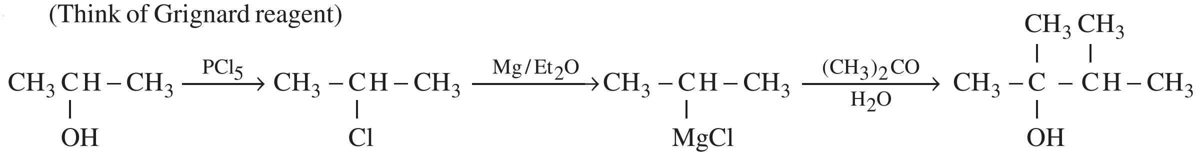


$$CH_3\underset{OH}{\underset{|}{CH}}-CH_3 \longrightarrow CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

2, 3-Dimethyl-2-butanol

2° alcohol ⟶ 3° alcohol

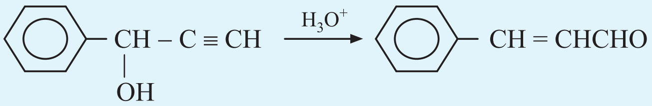
(Think of Grignard reagent)



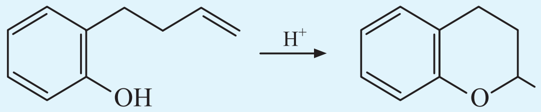
$$CH_3\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{PCl_5} CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3 \xrightarrow{Mg/Et_2O} CH_3-\underset{MgCl}{\underset{|}{CH}}-CH_3 \xrightarrow[H_2O]{(CH_3)_2CO} CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

Illustration - 13 *Propose mechanism for the following reactions.*

(a)

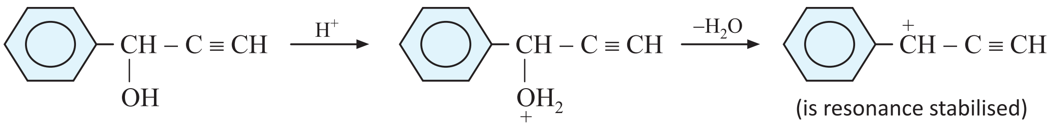


(b)

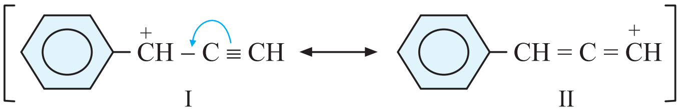


SOLUTION :

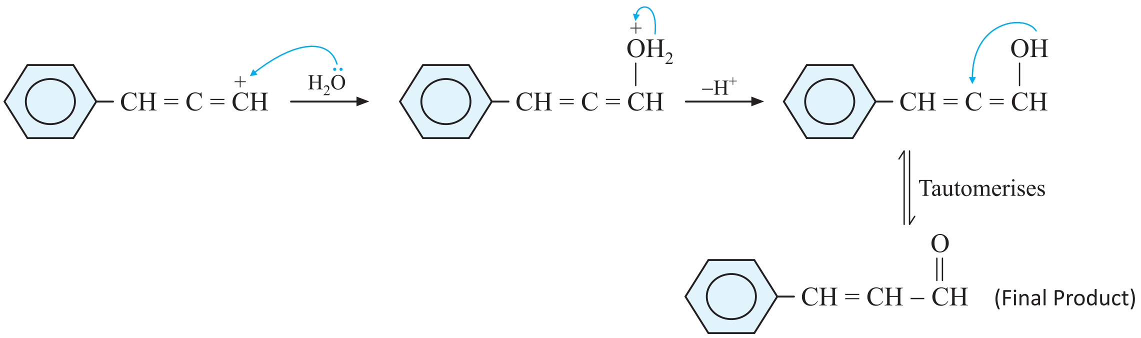
(a)



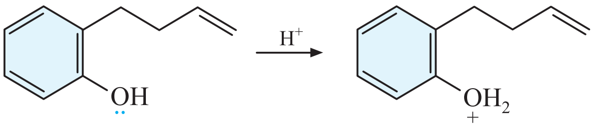
(is resonance stabilised)



Looking at the product . . . . . . Pick the structure II.



(b)



Observe carefully that this step will lead to nowhere as $\overset{+}{O}H_2$ is attached to phenyl ring. So think of alternative path.

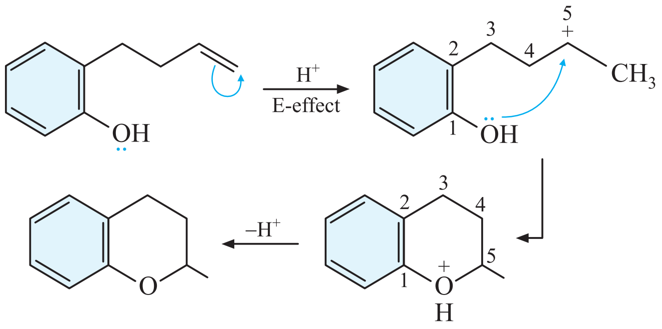
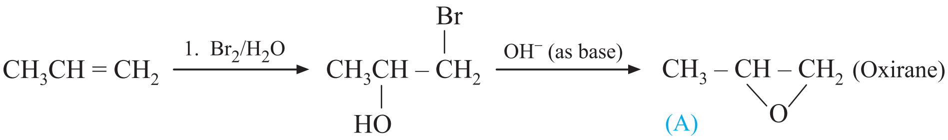
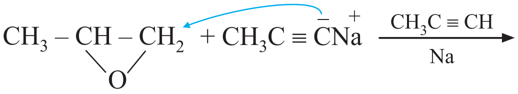


Illustration - 14

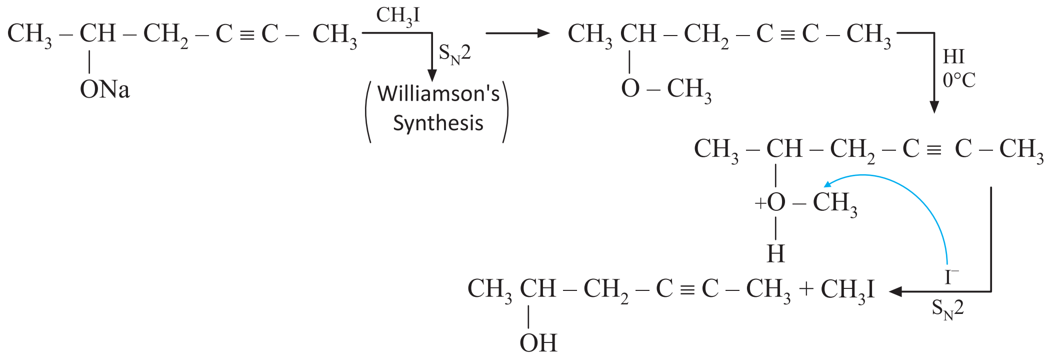
$$CH_3CH=CH_2 \xrightarrow[2.\ OH^-]{1.\ Br_2/H_2O} A \xrightarrow[Na]{CH_3C\equiv CH} B \xrightarrow{CH_3I} C \xrightarrow[\Delta]{HI\,(conc.)} D+E$$

SOLUTION :





Visualise base catalysed (S_N2) ring opening (consider steric factors).



Note : I^- as strong Nu^- will attack at the least hindered CH_3 group.

ANSWERS - IN-CHAPTER EXERCISES

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