CHAPTER

25

Alcohols, Phenols and Ethers

1. **(c)** $CH_2OH-CHOH-CH_2OH \xrightarrow{3HI} CH_2I-CHI-CH_2I \xrightarrow{-I_2}$

$CH_2=CH-CH_2I \xrightarrow{HI(excess)} CH_3-CHI-CH_2I \xrightarrow{-I_2}$

$CH_3-CH=CH_2 \xrightarrow{HI} CH_3-CHI-CH_3$

$\therefore$ All the compounds except (c), $CH_2OH-CHI-CH_2OH$ are formed during reaction of glycerol with excess HI.

2. **(d)** Lucas reagent is anhydrous $ZnCl_2$ and conc. HCl. It is used to distinguish between 1°, 2° and 3° alcohols.

3° alcohols $\rightarrow$ immediate turbidity

2° alcohols $\rightarrow$ turbidity after 5 minutes

1° alcohols $\rightarrow$ No turbidity at room temp.

$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$ is a tertiary alcohol hence it will give fastest reaction with Lucas reagent.

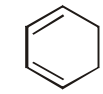
3. **(d)** Among the given compounds only CH_3OH does not give iodoform reaction.

4. **(b)** The ease of dehydration can be determined by seeing the stability of carbocation as intermediate.

$\underset{(I)}{CH_3-CH_2-CH_2-\overset{+}{C}H_2}$

$\underset{(II)}{CH_3-CH_2-\overset{+}{C}H-CH_3}$

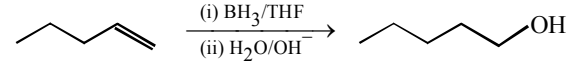
$\underset{(III)}{CH_2=CH-\overset{+}{C}H-CH_3}$



(IV)

(IV) is most stable due to resonance followed by (III) which is allylic carbocation. Next is (II) as it is a secondary carbocation and least stable is (I) as it is a primary carbocation.

5. **(a)** Hydroboration-oxidation leads to *anti*-Markownikoff's hydration, thus



1-Pentanol

6. **(d)**

$CH_3\underset{NH_2}{\underset{|}{C}}HCH_3 \xrightarrow{HNO_2} CH_3\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow{oxi.} CH_3COCH_3$

$\xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgI} CH_3-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_3$

2-Methyl –2 propanol

7. **(c)**

$C_2H_5OH \xrightarrow{PCl_5} \underset{[A]}{C_2H_5Cl} + POCl_3 + HCl$

$\xrightarrow{AgNO_2} \underset{[B]}{C_2H_5NO_2}$

8. **(c)** Higher the stability of the carbocation, more easily it is formed and more will be the ease of its dehydration. Stability of the carbocations of the corresponding alcohols is

$F_3C\overset{+}{C}H_2 < Cl_3C\overset{+}{C}H_2 < H_3C\overset{+}{C}H_2 <$

Least stable due to intensification of charge

$C_6H_5\overset{+}{C}H_2$

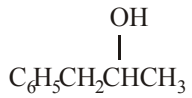
Most stable due to resonance

$F_3CCH_2OH < Cl_3CCH_2OH < H_3CCH_2OH$

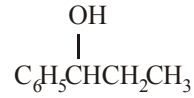
$< C_6H_5CH_2OH$ (Ease of dehydration)

9. **(b)** Hydroboration – oxidation reaction of alkenes leads to anti-Markovnikov's hydration. Further addition of water adds in *syn*-manner, i.e., H and OH are added to the same face of the double bond leading *trans*-product. In short, hydroboration-oxidation of alkenes is regioselective as well as stereoselective.

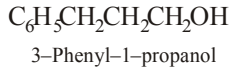
10. **(b)** It is a nucleophilic substitution reaction, 1-phenyl -1-propanol will be most reactive because of formation of more stable benzyl type of carbocation.



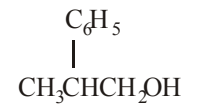
1–Phenyl–2–propanol



1–Phenyl–1–propanol

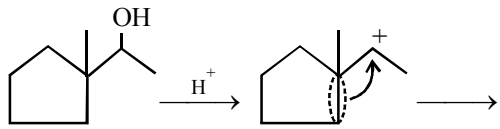


3–Phenyl–1–propanol

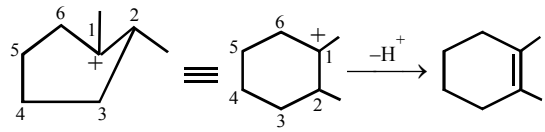


2–Phenyl–1–propanol

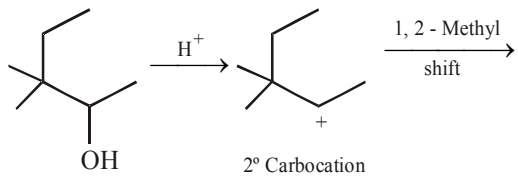
11. **(c)**



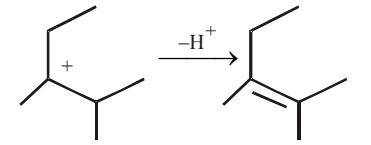
2º Cabocation



12. **(c)** It is an example of dehydration of alcohol. The 2º carbocation formed at first stage rearranges to the more stable 3º.



2º Carbocation



3º Carbocation More stable (alkene)

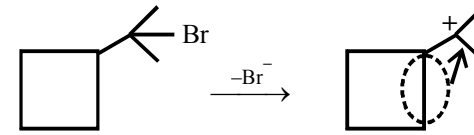
13. **(c)** Although in both cases products are CH_3I and C_6H_5OH; the two reactions follow different mechanism.

$$C_6H_5-O-CH_3 \xrightarrow[S_N2]{HI(g)} CH_3I + C_6H_5OH$$

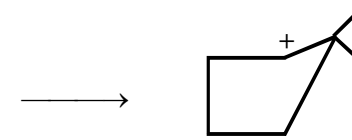
$$C_6H_5-O-CH_3 \xrightarrow[S_N1]{conc.\,HI} CH_3I + C_6H_5OH$$

Remember that during S_N1 reaction, CH_3^+ is formed because it is more stable than $C_6H_5^+$.

14. **(c)**



3° Carbocation (Four membered ring with large strain)



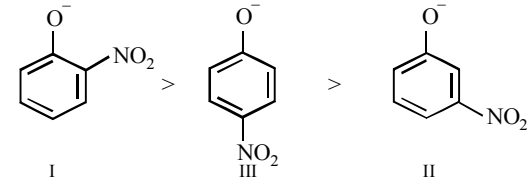
2° Carbocation (Five membered ring with less strain)

15. **(b)** Base catalysed epoxide opening is a typical S_N2 reaction in which attack of the nucleophile takes place at the less hindered expoxide.

16. **(b)**

17. **(c)** In presence of non-protic solvent such as $CHCl_3$ or CCl_4, concentration of electrophile (Br^+) is less, hence reaction stops at the monobromo stage

18. **(c)** Observe the relative stability of their corresponding conjugate bases.

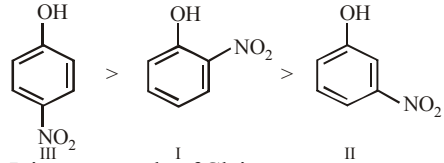


I
Stabilised by both –I and – R effects of the $-NO_2$ group

III
Stabilised by both –I and – R effects, but – I is less than in I

II
Stabilised only by –I effect

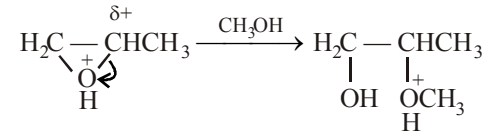
However, the acidity of the corresponding phenols will be different because of H–bonding in the ortho isomer.



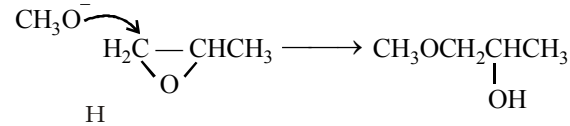
III I II

19. **(d)** It is an example of Claisen rearrangement.

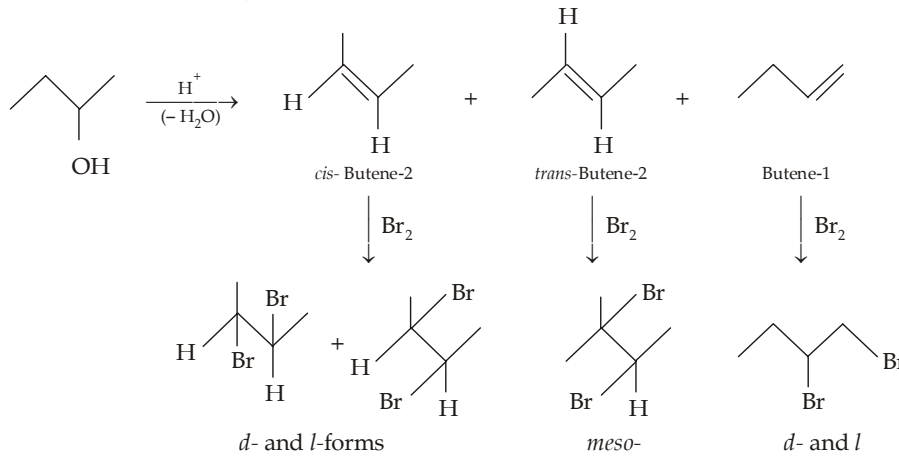
20. **(b)** In the acid-catalysed ring opening of an unsymmetrical ethoxide, the nucleophile attacks primarily at the more substituted carbon atom because such atom of the protonated epoxide acquires a considerable positive charge. This resembles like a more stable 2° or 3° carbocation and hence the reaction is S_N1 like.



In case of CH_3ONa, $^-OCH_3$, being a strong nucleophile, opens the strained epoxide ring in a direct S_N2 reaction, i.e. by attacking at the least hindered carbon atom.

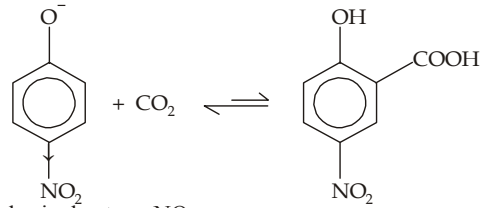


21. **(3)**



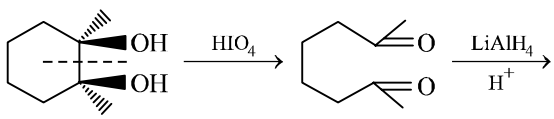
d- and *l*-forms *meso*- *d*- and *l*

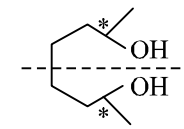
22. **(1)** The corresponding phenoxide ion will be less basic, hence equilibrium will not lie favourably toward carboxylation.



Less basic due to —NO_2 group

23. **(3)**



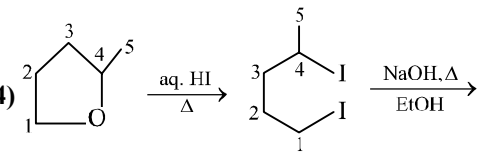


Plane of symmetry

2 chiral carbons and one plane of symmetry

$\Rightarrow$ 3 stereoisomers.

24. **(4)**



25. **(3)** 3 acidic hydrogens will produce, 3 moles of methane gas.