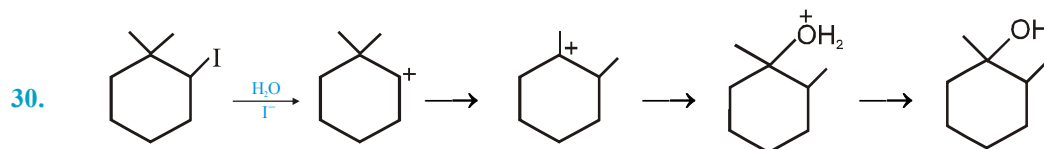


HINTS & SOLUTIONS

EXERCISE - 1

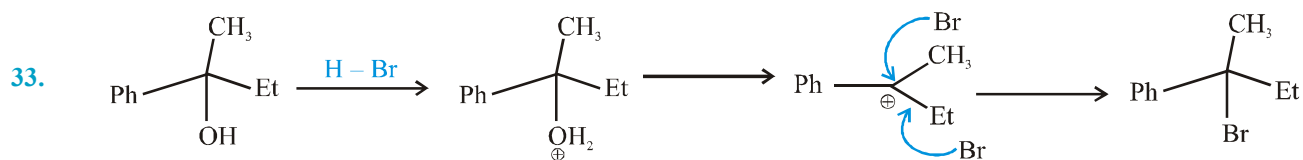
Single Choice

26. Nucleophilicity
- \propto
- Size (in group)



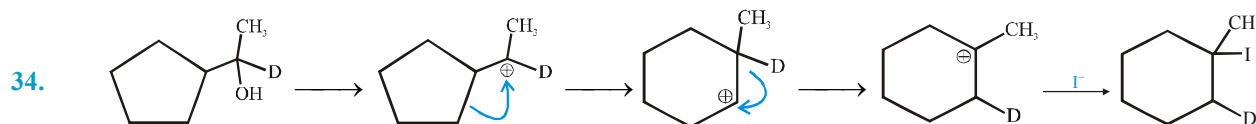
31. According to carbocation stability
-
- IV > III > II > I

32. According to carbocation stability

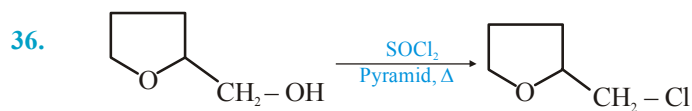
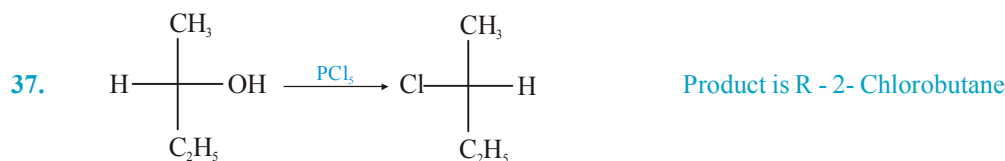


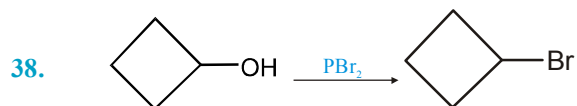
(Chiral carbon atom)

(±) Racemic Mixture

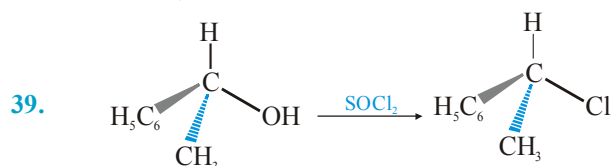


- 35.
- $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH} \xrightarrow[\text{S}_\text{N}2]{\text{NaBr, H}_2\text{SO}_4} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Br}$
-
- unbranched 1° alcohol give
- $\text{S}_\text{N}2$
- reaction with HX.

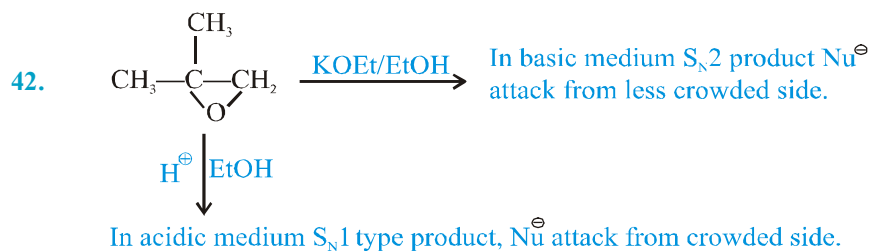
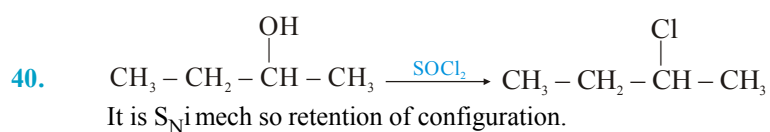
It is $\text{S}_\text{N}2$ reaction.



It is S_N2 reaction

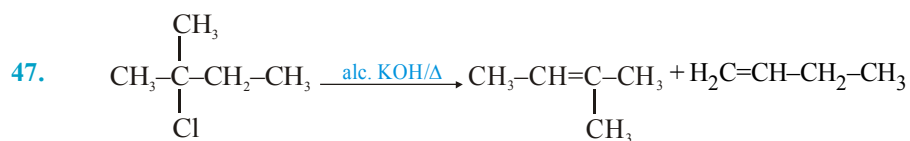
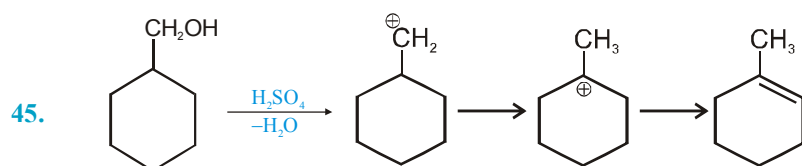


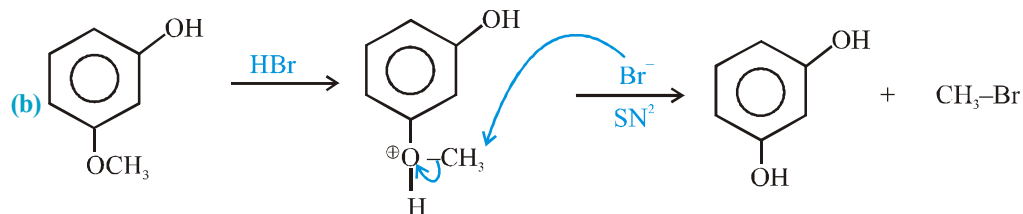
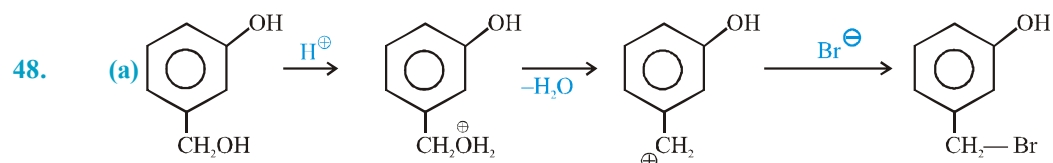
It is S_Ni mech so retention of configuration



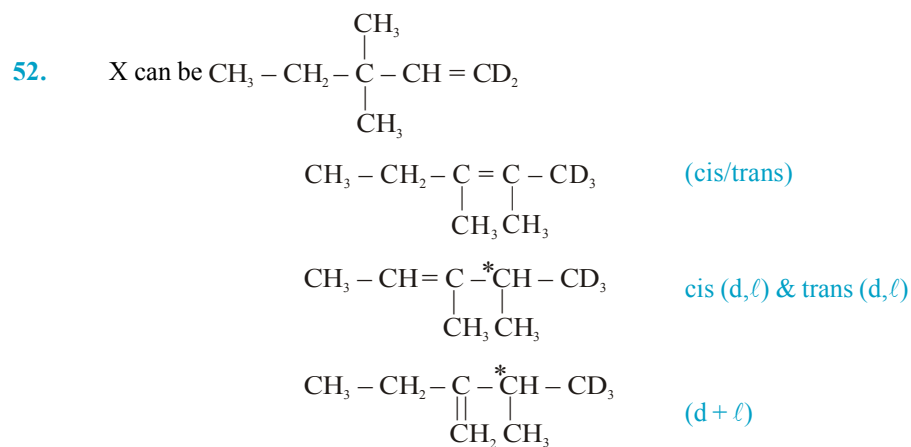
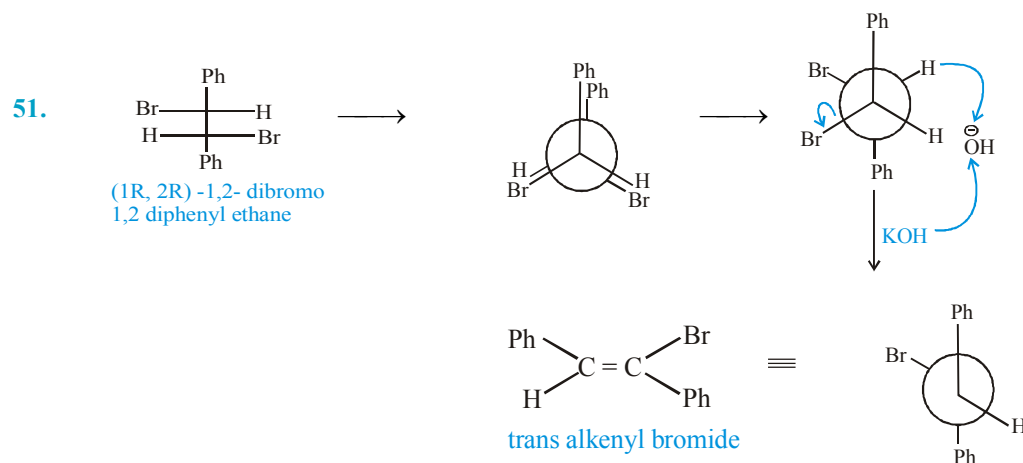
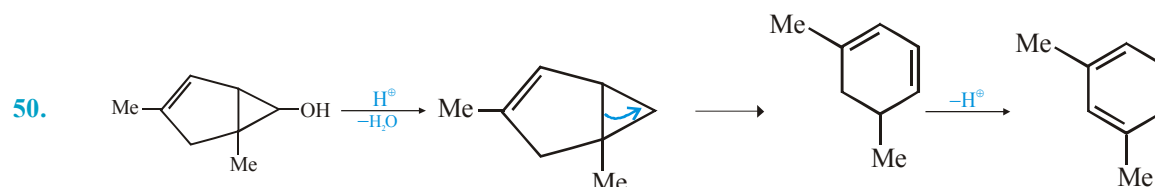
43. According to stability of carbocation.

44. Ring expansion so q will migrate.

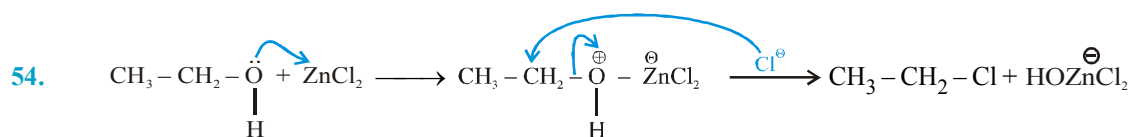
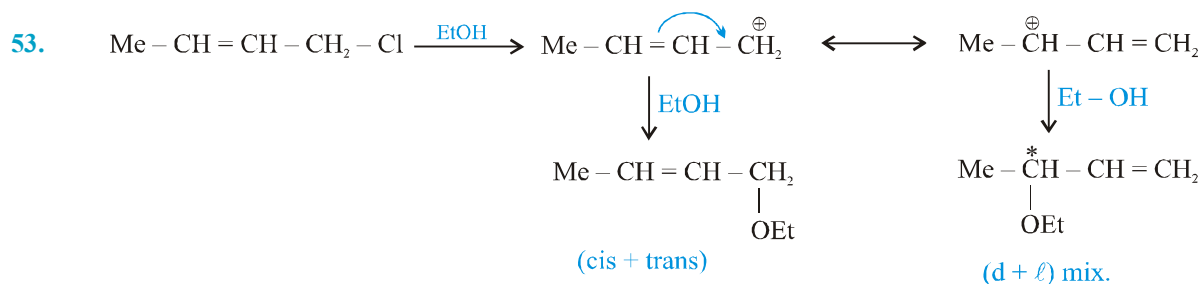




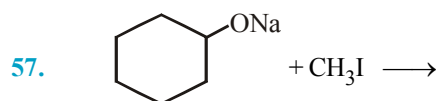
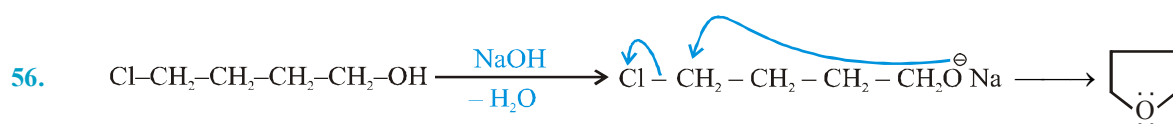
49. In case of S_N1 no inversion occurs but in presence of pyridine S_N2 reaction takes place and configuration is inverted.



Total 9 alkenes are formed and after fractional distillation 6 are separated.



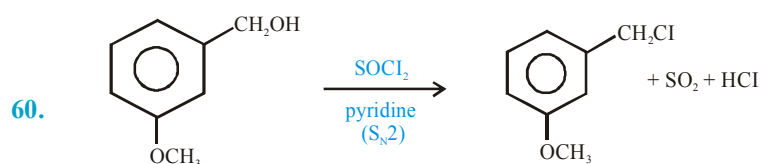
55. Strength of Nucleophile generally increases on going down a group in the periodic table, so (D) is not true.



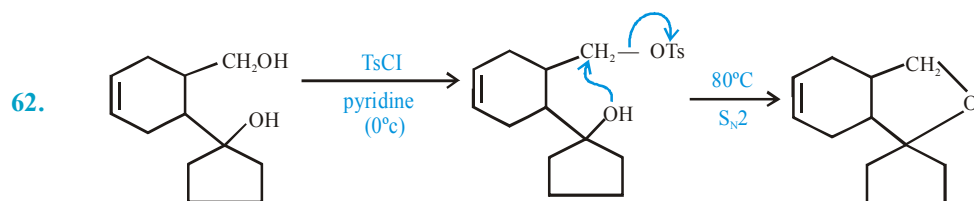
strong anionic nucleophile and 1° alkyl halide favours $\text{S}_{\text{N}}2$ mechanism.

58. Nucleophilic substitution of alcohol is acid catalysed reaction.

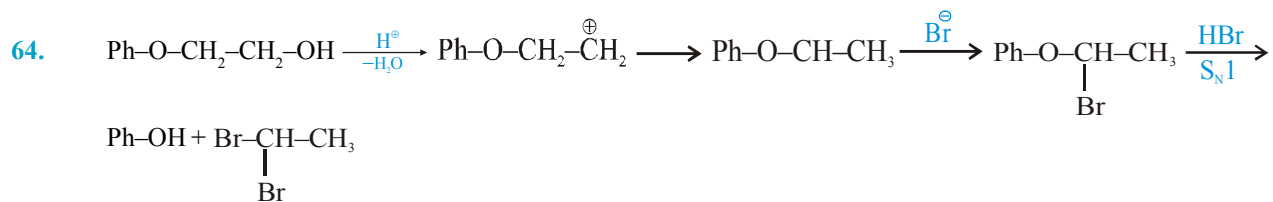
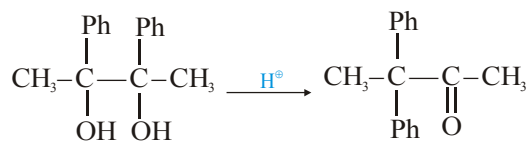
59. Bridge head carbocation is not formed.



61. I \Rightarrow Only one T.S. So it is for $\text{S}_{\text{N}}2$ and $\Delta H = -ve$.
 II \Rightarrow Only one T.S. So it is for $\text{S}_{\text{N}}2$ and $\Delta H = +ve$.
 III \Rightarrow More than one T.S. so it is for $\text{S}_{\text{N}}1$ and 1st step is rds.



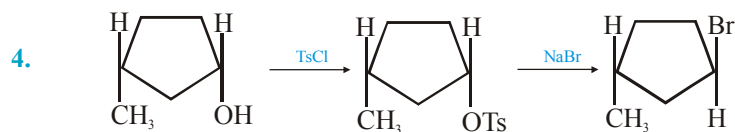
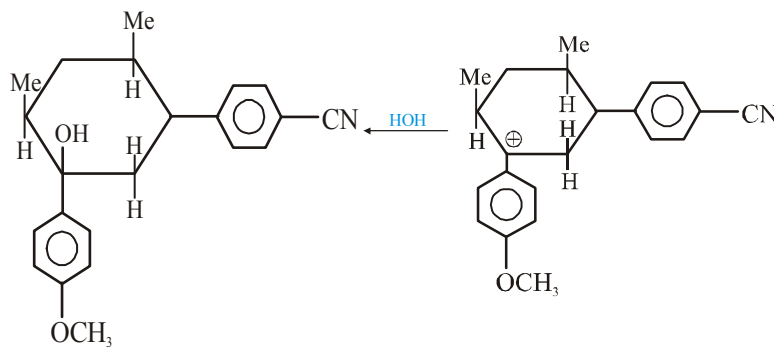
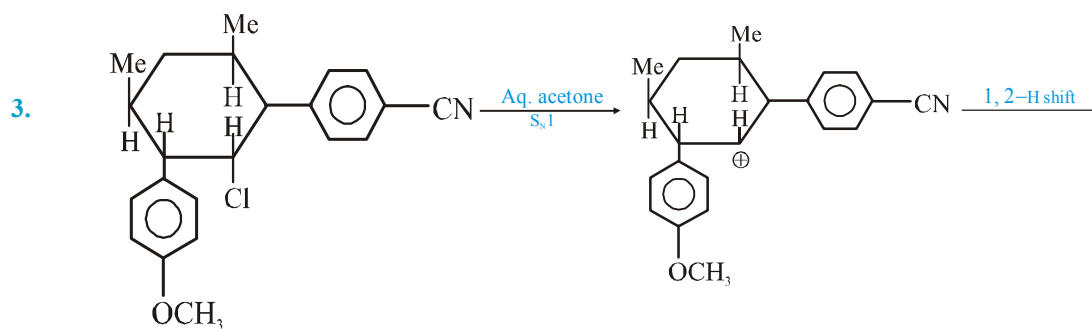
63. Correct Product for (C) option.

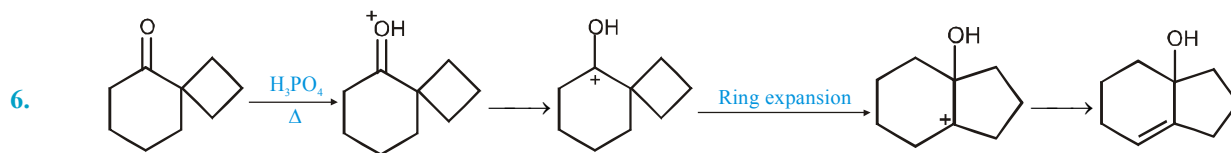
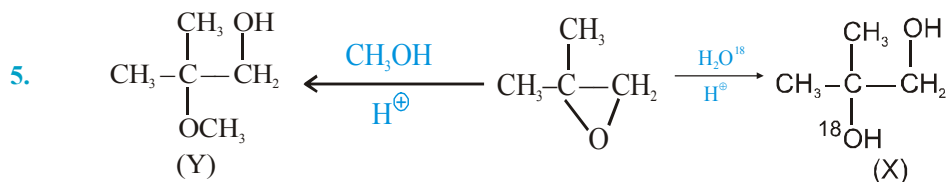


EXERCISE - 2

Part # I : Multiple Choice

1. Nucleophiles are electron rich species.
2. Anionic nucleophiles are better than their neutral nucleophiles.

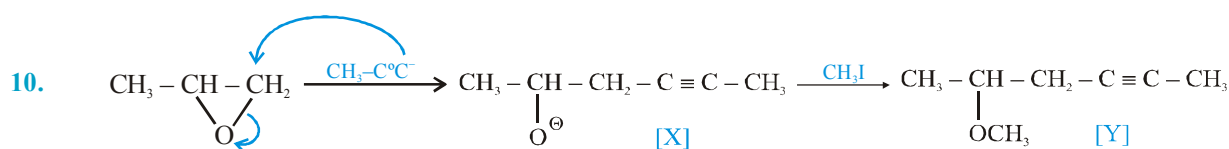




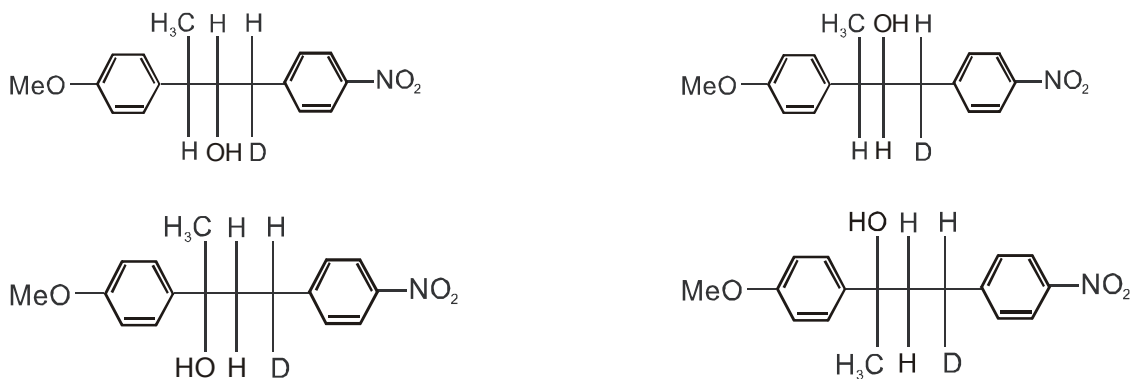
7. Rate of E² reaction ∝ Stability of alkene

8. All statement are correct.

9. 1° alkyl halide is more reactive than 2° alkyl halide. So transition state in II reaction is more stable than I reaction.

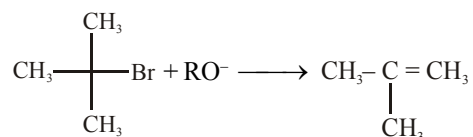


11. Product mixture

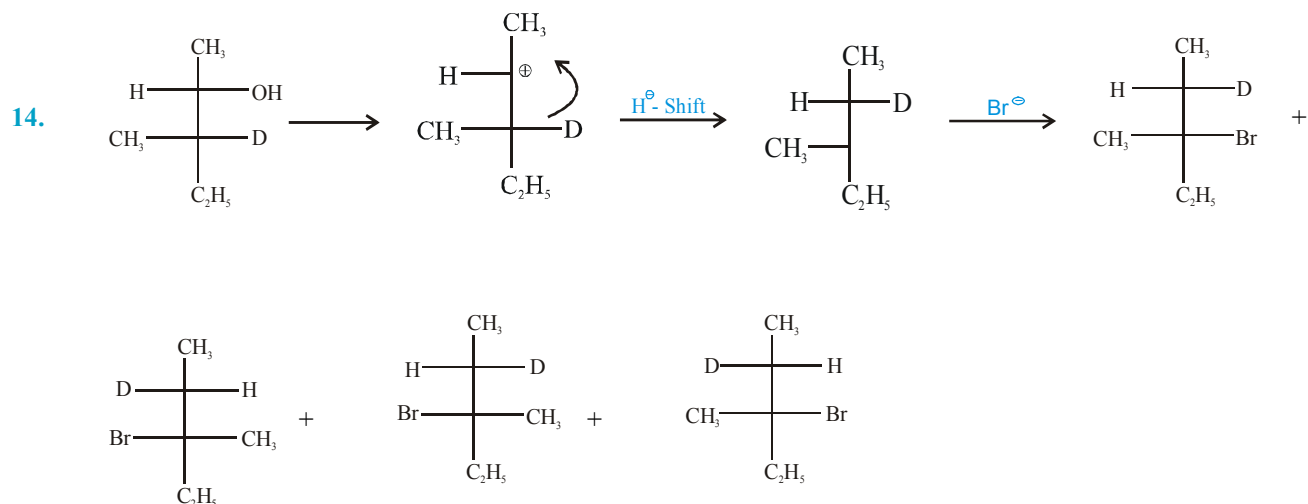
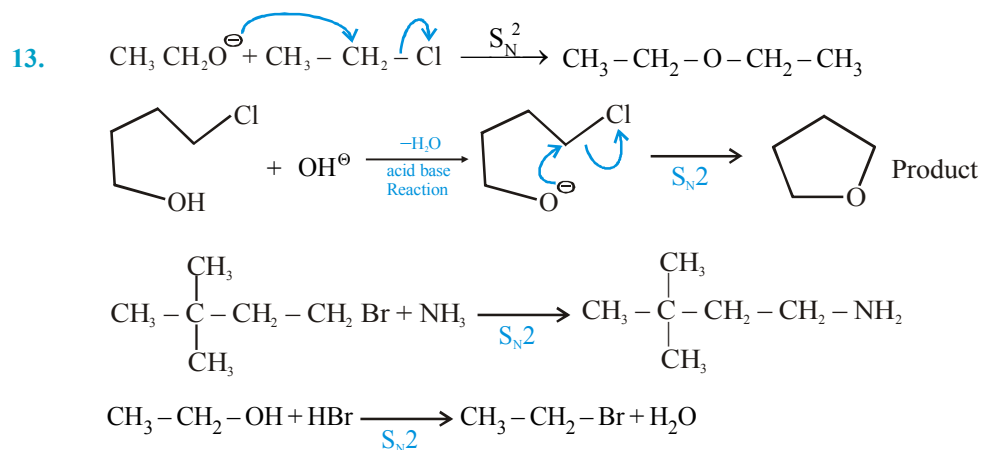


Product mixture react with PCl₅ by S_N2 mechanism and four products are formed. They are positional isomers and diastereomers so after fractional distillation four fraction are obtained.

12. Correct product for (B) option.



Option (D) is also not feasible because aromatic halide do not given SN reaction in normal condition.



Part # II : Assertion & Reason

- S-1 and S-2 is correct and S-2 is correct explanation of S-1.
- S-1 is true and S-2 is false.
The transition state for the anti-periplanar arrangement is a staggered conformation, with the base far away from the leaving group. In most cases, this transition state is lower in energy than that for the syn-periplanar elimination.
- $\text{S}_\text{N}2$ is not possible at 3° alkyl halide by strong base.
- Alcohol give S_N reaction only in acidic medium.
- Polar aprotic solvent is used for $\text{S}_\text{N}2$ reaction because they do not solvate the anion appreciable
- By going top to bottom in periodic table nucleophilicity increases (in protic solvent) because polarisability increases and Iodide is weakly solvated in a protic solvent.

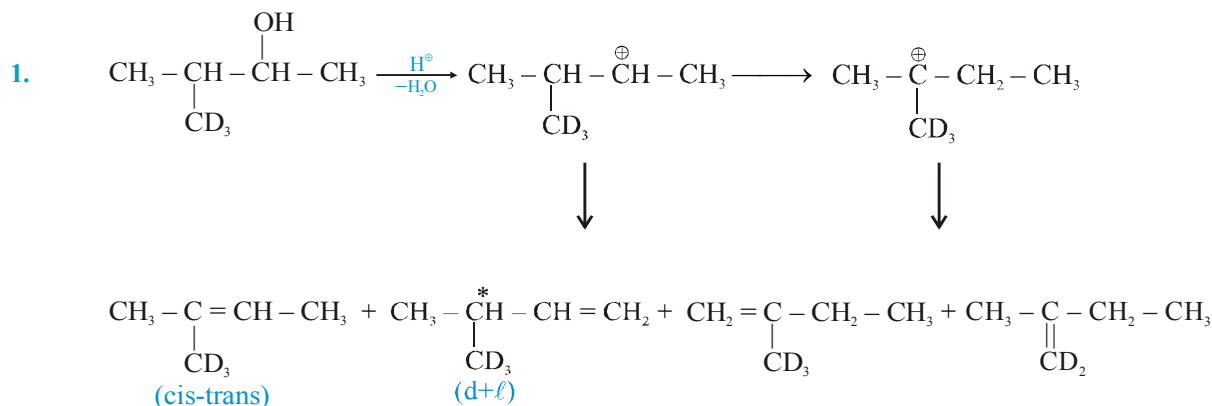
EXERCISE - 3

Part # I : Matrix Match Type

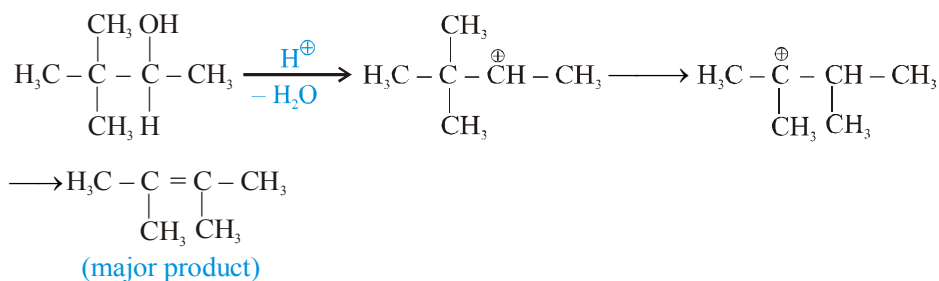
3. Weak neutral nucleophile $\Rightarrow S_N1$, so rearrangement is possible.
 Strong anionic nucleophile $\Rightarrow S_N2$, walden inversion is possible.
 Strong anionic nucleophile $\Rightarrow S_N2$ but α carbon is not stereogenic.
 Aq. NaOH $\Rightarrow S_N1$, carbocation is already stable so no rearrangement.
4. 1° Alkyl halide and anionic strong nucleophile $\Rightarrow S_N2$
 2° Alkyl halide and anionic strong base $\Rightarrow E^2$
 3° Alcohol and acidic medium $\Rightarrow E^1$
 3° Alkyl halide and weak neutral nucleophile $\Rightarrow S_N1$

Part # II : Comprehension

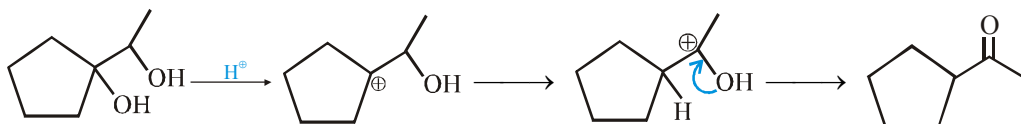
Comprehension # 1 :



2. Most stable alkene (saytzeff alkene) is major product.



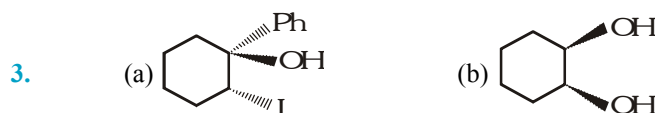
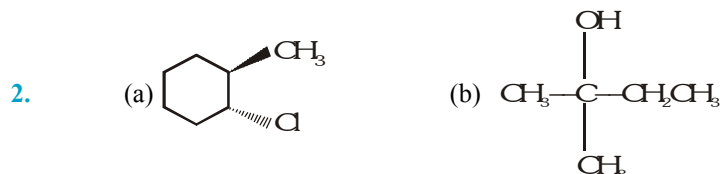
3. In this reaction pinacol pinacolone rearrangement takes place



EXERCISE - 4

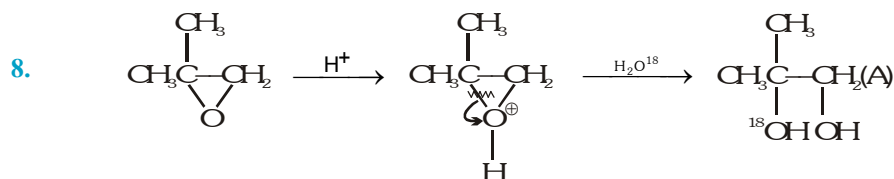
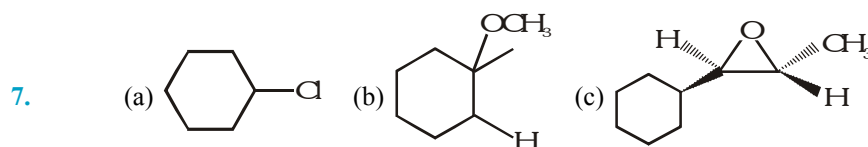
Subjective Type

1. S_N2 attack on a carbon of benzene ring does not occur nor does the high energy $C_6H_5^+$ form by an S_N1 reaction. Hence ArI cannot be a product even in an excess of conc. HI .

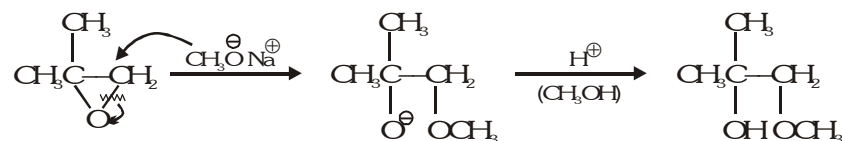


4. (A) C_2H_5Cl ; (B) C_2H_5CN ; (C) C_2H_5COOH ; (D) $C_2H_5COONH_4$; (E) $C_2H_5CONH_2$
 5. (A) C_3H_7Br ; (B) $CH_3CH=CH_2$; (C) $CH_3CHBrCH_3$; (D) $CH_3CHNH_2CH_3$

6. The +I.E. of three methyl groups on central C-atom of tert-butyl alcohol makes it partially negative with the result that it pushes the electron pair of $-OH$ bond towards H-atom and thus H-atom is not replaced easily.



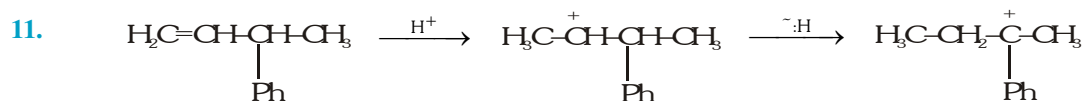
(nucleophile attacks the more substituted carbon in acid-catalysed reaction)

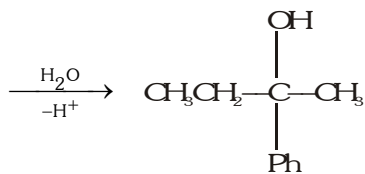


(nucleophile attacks the less substituted carbon in base-catalysed reaction)

9. I : bond b ; II : bond a

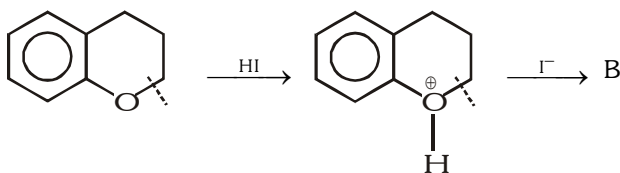
10. A is laevo - isomer



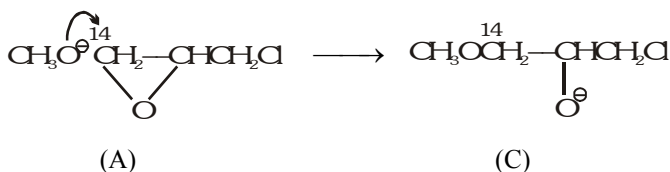


(Hydration gives an intermediate 2^o C⁺, which undergoes a hydride shift. Although phenyl is a better migrator than H, migration of H occurs leading to a more stable 3^o benzylic carbocation.)

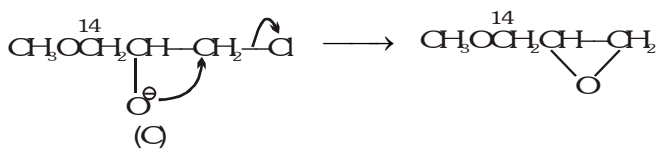
12. Bond energy of C (vinylic)—O bond (α) is greater than that of C(alkylic)—O bond (β). Hence, when A reacts with HI, bond β breaks forming B.



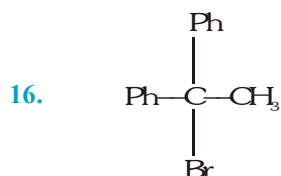
13. CH₃O⁻ (nucleophile) attacks less substituted carbon (which is C-14 in this case) forming intermediate (C).



(C) will displace Cl⁻ forming (B)

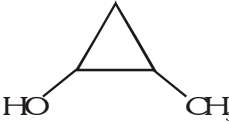
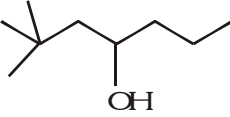
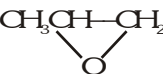


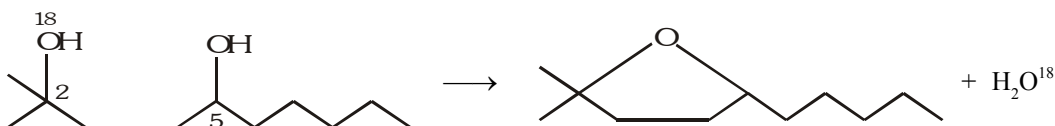
14. C_2H_5OH C_2H_5Cl
Ethyl alcohol Ethyl chloride
(X) (Y)
15. $(CH_3)_2CHCH_2OH$; $(CH_3)_2C=CH_2$; $(CH_3)_3COH$
(A) (B) (C)



Synchronous migration of Ph provides greater assistance in the removal of H₂O from the protonated alcohol

17.
$$\begin{array}{c} CH_2 \\ / \quad \backslash \\ O \end{array} - CH_2 \xleftarrow{C_6H_5CO_3H} CH_2=CH_2 \xrightarrow[2. Mg]{1. HBr} CH_3CH_2MgBr$$

- (B) $A + B \xrightarrow{H_2O} CH_3CH_2CH_2CH_2OH$
- (C)
18. (A)  (B)  (C) 
19. 3 alcohol at C₂ is more basic than 2 alcohol at C₅. Hence, intramolecular dehydration takes place such that H of 2 alcoholic group at C₅ eliminates OH of 3 alcoholic groups at C₂ (with isotopic ¹⁸O) to form cyclic ether

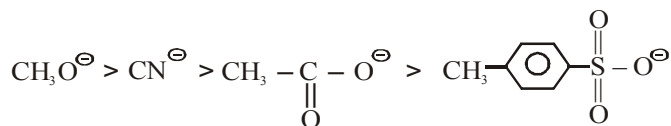


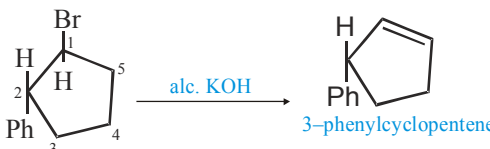
20. A is a mixture of d- and l- and thus racemic mixture.

EXERCISE - 5

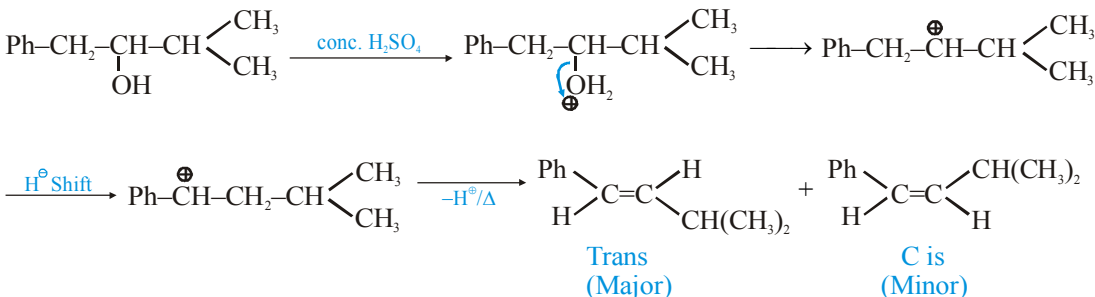
Part # I : AIEEE/JEE-MAIN

- $R-OH \xrightarrow{H^+} R-OH_2^+$ this step is initiation step.
- According to stability of carbocation.
- Nucleophilicity order



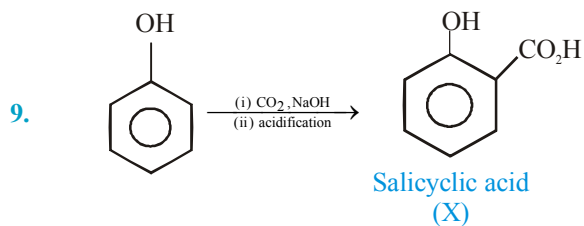
4. 

It is anti elimination reaction so hydrogen atom from second carbon will not eliminated as it is in syn-position rather hydrogen atom from 5th carbon will be eliminated.

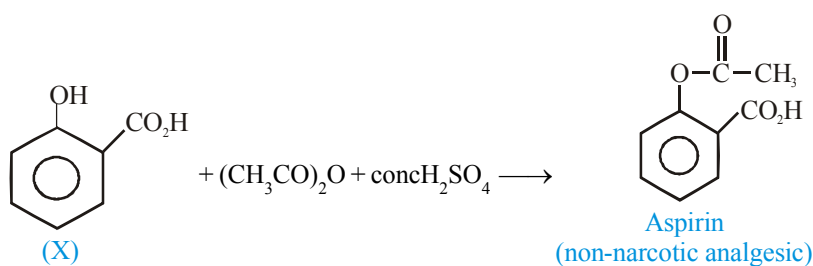
5. 
- Trans (Major)
Cis (Minor)

CHEMISTRY FOR JEE MAIN & ADVANCED

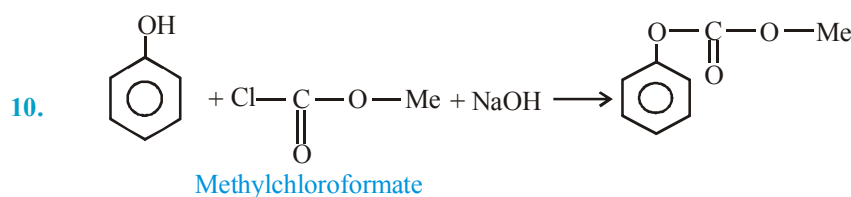
6. Reaction of alcohol with HCl and anhydrous ZnCl_2 is an $\text{S}_{\text{N}}1$ reaction. 3° alcohol react faster with HCl and anhydrous ZnCl_2 since it forms more stable carbocation intermediate.
7. RS^\ominus is more nucleophilic than R-O^\ominus due to larger size of orbitals and polarization but RS^\ominus is less basic than R-O^\ominus as the negative charge get stabilized due to larger size of sulphur atom.
8. The reaction of alcohol with lucas reagent is mostly an $\text{S}_{\text{N}}1$ reaction and the rate of reaction is directly proportional to the carbocation stability formed in the reaction, since 3° R-OH forms 3° carbocation hence it will react fastest.



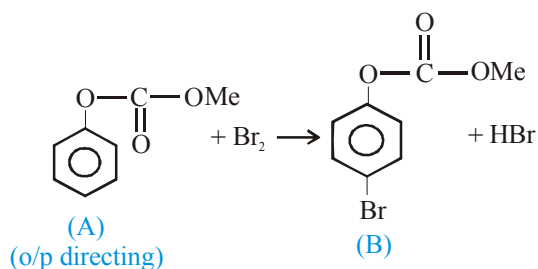
This is called Kolbe reactions.



This step is called acylation reaction.

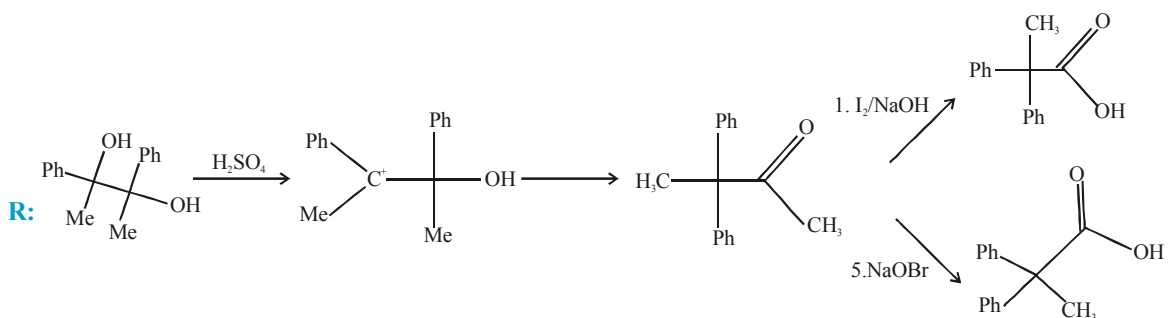
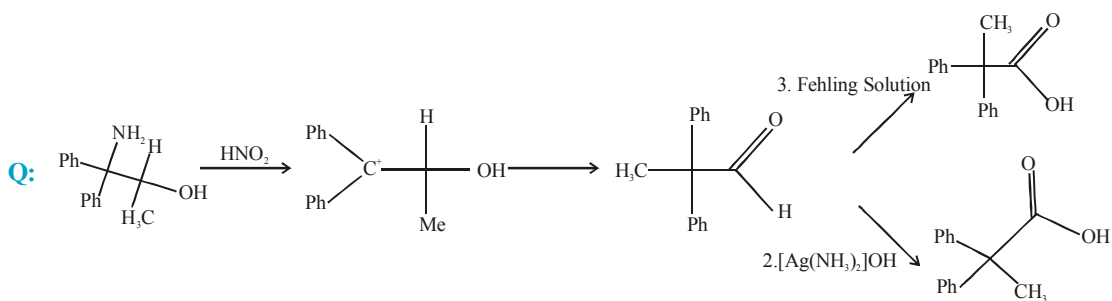
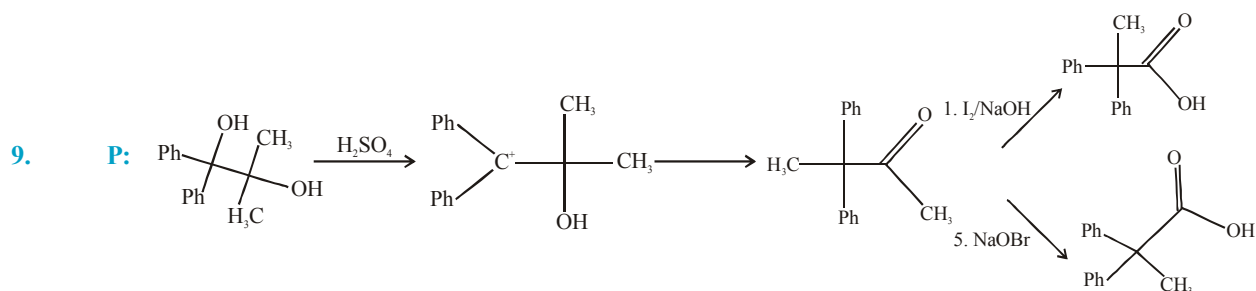
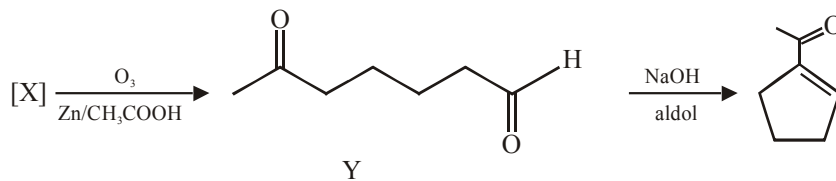
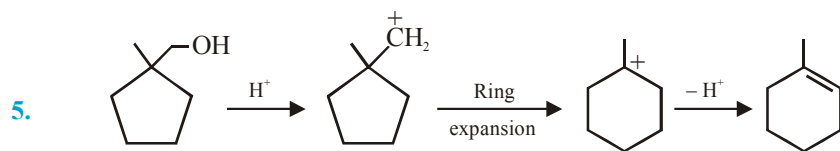


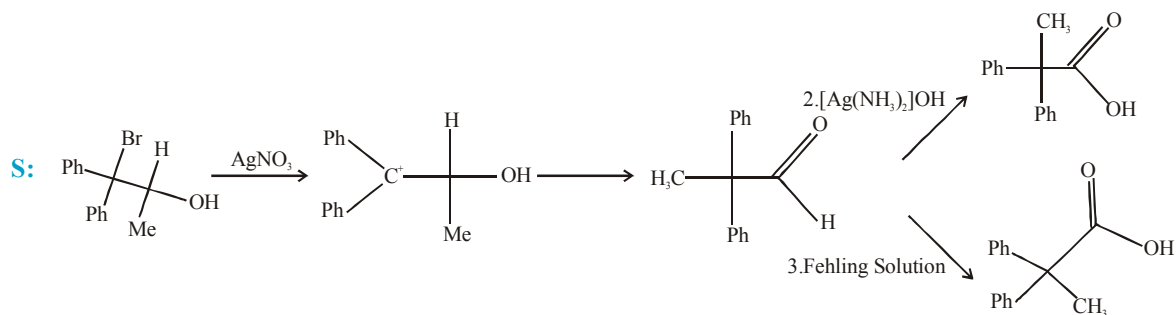
This step involves acid base reaction at first followed by $\text{S}_{\text{N}}\text{AE}$ reactions.



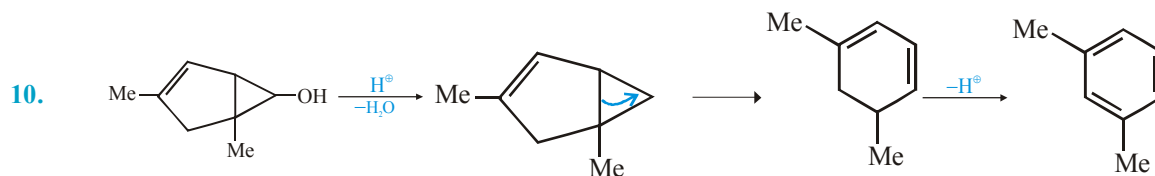
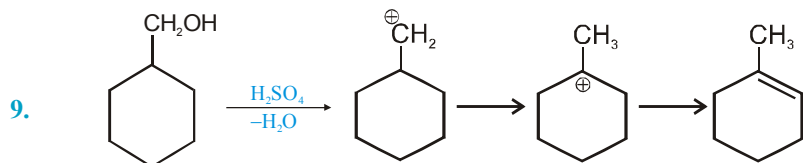
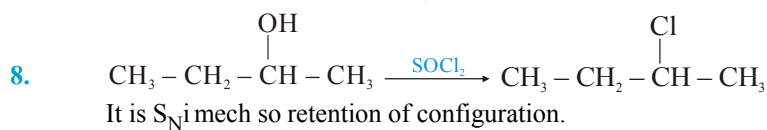
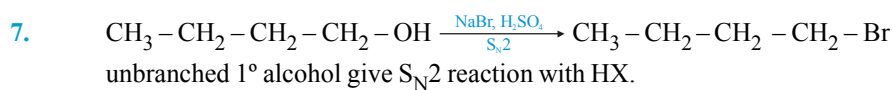
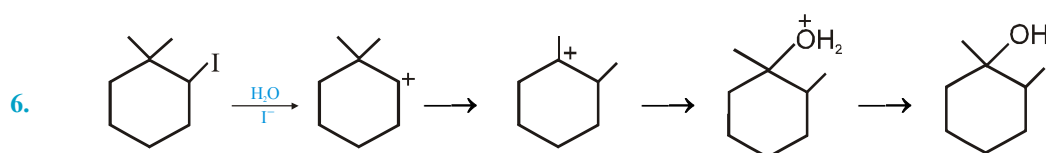
This step is called bromination.

Part # II : IIT-JEE ADVANCED

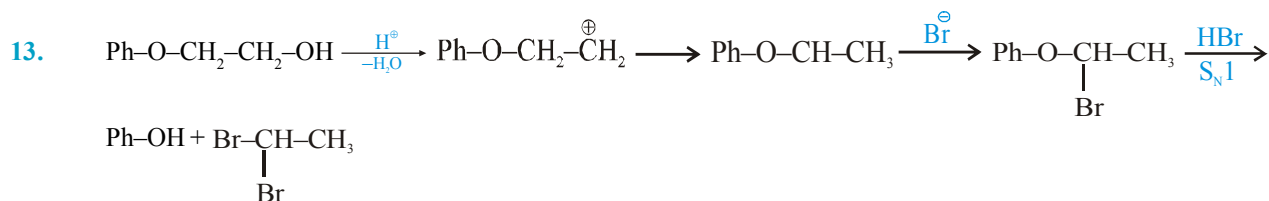
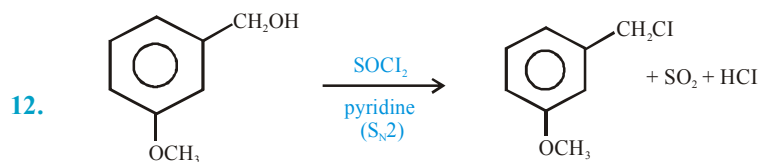




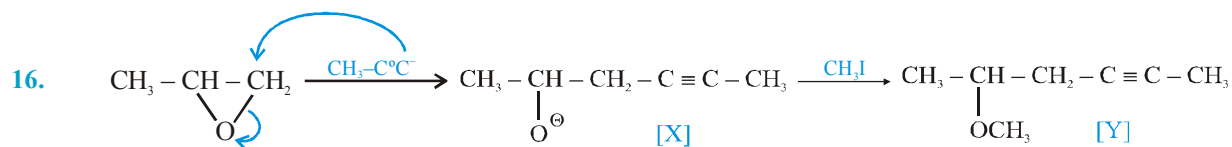
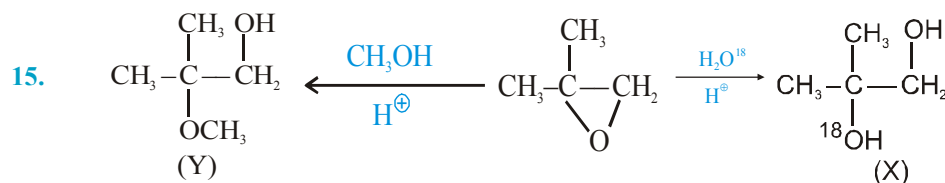
MOCK TEST



11. Strength of Nucleophile generally increases on going down a group in the periodic table, so (D) is not true.



14. Nucleophiles are electron rich species.



22. S-1 is true and S-2 is **false**.

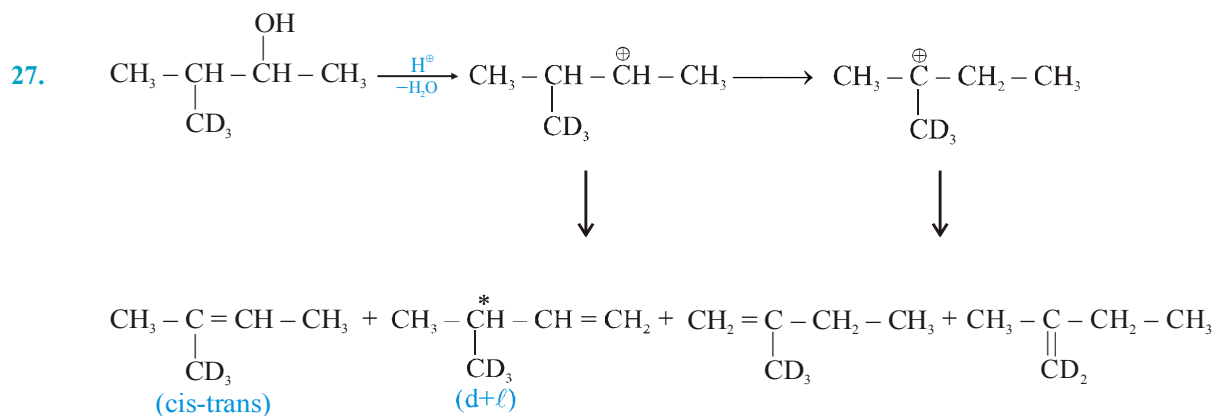
The transition state for the anti-periplanar arrangement is a staggered conformation, with the base far away from the leaving group. In most cases, this transition state is **lower** in energy than that for the syn-periplanar elimination.

23. $\text{S}_{\text{N}}2$ is not possible at 3° alkyl halide by strong base.

24. Alcohol give S_{N} reaction only in acidic medium.

25. Polar aprotic solvent is used for $\text{S}_{\text{N}}2$ reaction because they do not solvate the anion appreciable

26. By going top to bottom in periodic table nucleophilicity increases (in protic solvent) because polarisability increases and Iodide is weakly solvated in a protic solvent.



30. – 1° Alkyl halide and anionic strong nucleophile $\Rightarrow \text{S}_{\text{N}}2$

– 2° Alkyl halide and anionic strong base $\Rightarrow \text{E}^2$

– 3° Alcohol and acidic medium $\Rightarrow \text{E}^1$

– 3° Alkyl halide and weak neutral nucleophile $\Rightarrow \text{S}_{\text{N}}1$