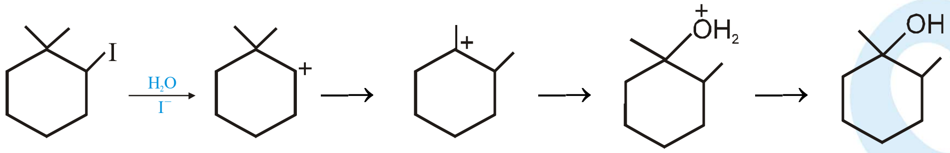
HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

26. Nucleophilicity ∝ Size (in group)

30.

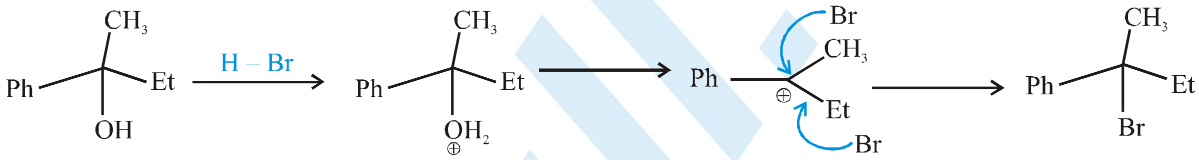


31. According to carboction stability

IV > III > II > I

32. According to carbocation stability

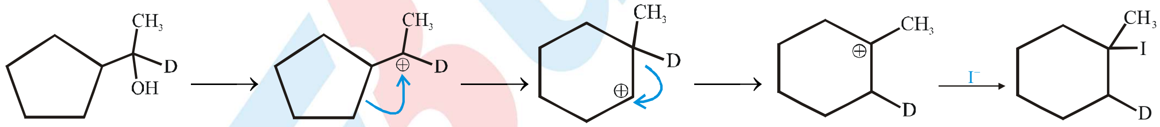
33.



(Chiral carbon atom)

(±) Racemic Mixture

34.



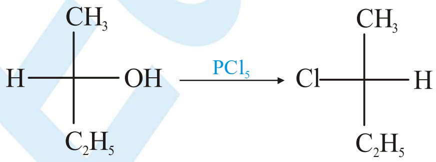
35. $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[S_N2]{NaBr,\ H_2SO_4} CH_3-CH_2-CH_2-CH_2-Br$

unbranched 1° alcohol give S_N2 reaction with HX.

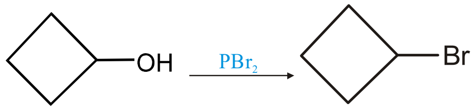
36.

It is S_N2 reaction.

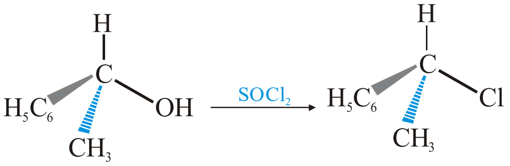
37.



Product is R - 2- Chlorobutane

38. 

It is S_N2 reaction

39. 

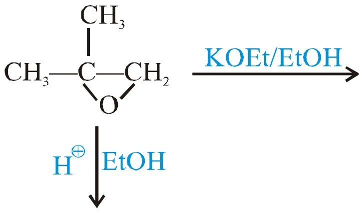
It is S_Ni mech so retention of configuration

40. 

$$CH_3-CH_2-\underset{}{\overset{OH}{\overset{|}{C}H}}-CH_3 \xrightarrow{SOCl_2} CH_3-CH_2-\overset{Cl}{\overset{|}{C}H}-CH_3$$

It is S_Ni mech so retention of configuration.

41. $CH_3-CH_2-CH_2-O-CH_2-CH_3 \xrightarrow{HCl/\Delta} CH_3-CH_2-CH_2-OH + CH_3-CH_2-Cl$

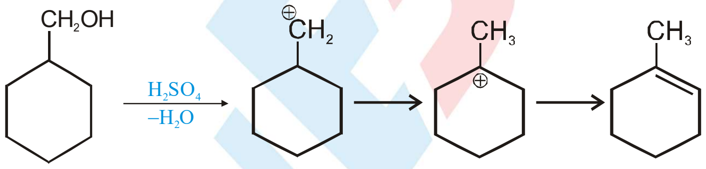
42. 

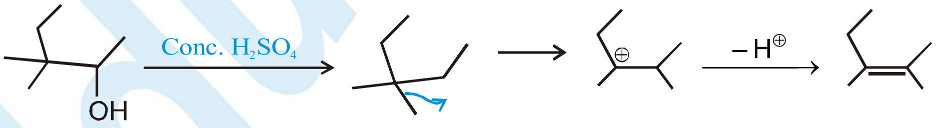
In basic medium S_N2 product $Nu^\ominus$ attack from less crowded side.

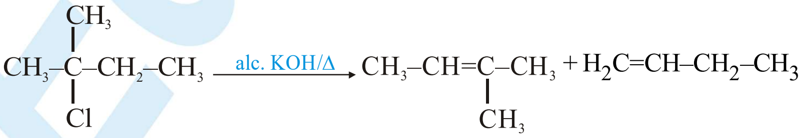
In acidic medium S_N1 type product, $\overset{\ominus}{Nu}$ attack from crowded side.

43. According to stability of carbocation.

44. Ring expansion so q will migrate.

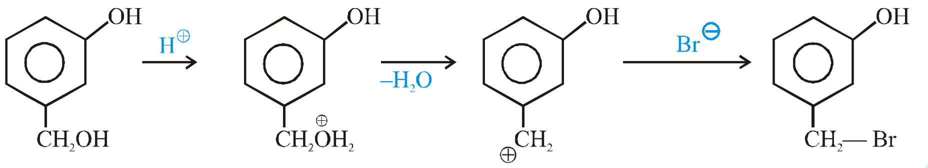
45. 

46. 

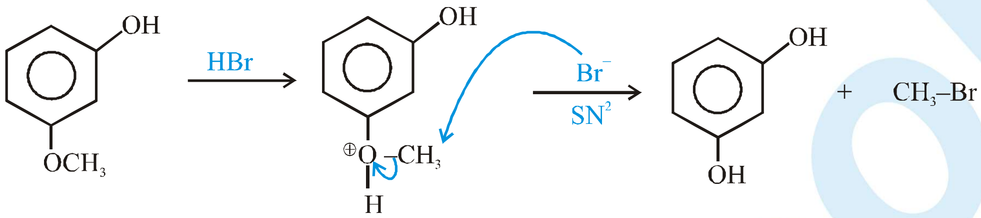
47. 

$$CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH_3 \xrightarrow{alc.\ KOH/\Delta} CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CH_3 + H_2C=CH-CH_2-CH_3$$

48. **(a)**

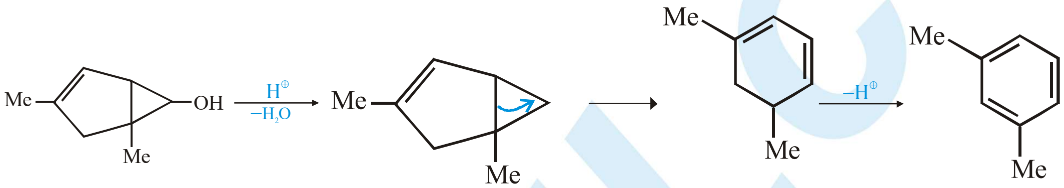


(b)

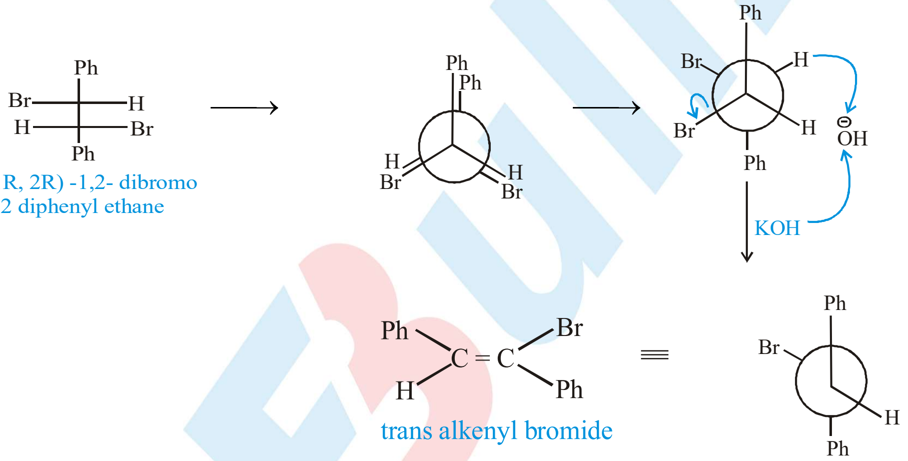


49. In case of S_Ni no inverson occurs but in presence of pyridine S_N2 reaction takes place and configuration is inverted.

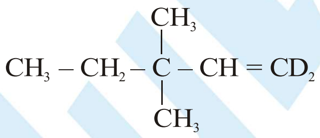
50.



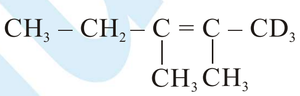
51.



52. X can be

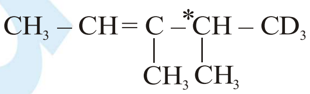


$$CH_3 - CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH = CD_2$$



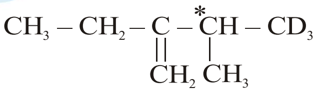
$$CH_3 - CH_2 - \underset{\underset{CH_3}{|}}{C} = \underset{\underset{CH_3}{|}}{C} - CD_3$$

(cis/trans)



$$CH_3 - CH = \underset{\underset{CH_3}{|}}{C} - \underset{\underset{CH_3}{|}}{\overset{*}{C}H} - CD_3$$

cis (d,●) & trans (d,●)

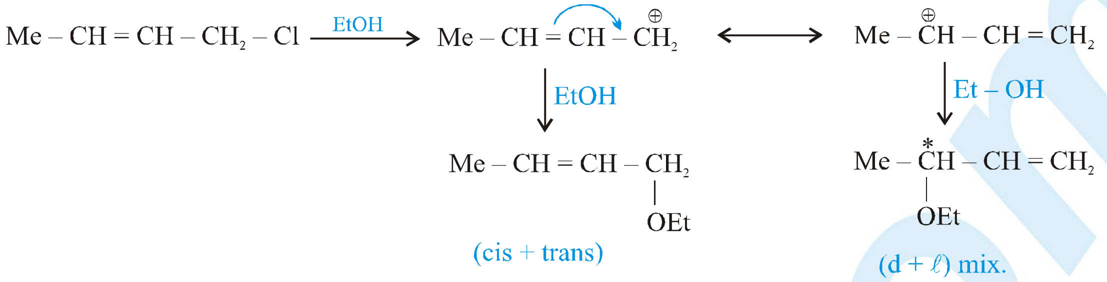


$$CH_3 - CH_2 - \underset{\underset{CH_2}{||}}{C} - \underset{\underset{CH_3}{|}}{\overset{*}{C}H} - CD_3$$

(d + ●)

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

53.

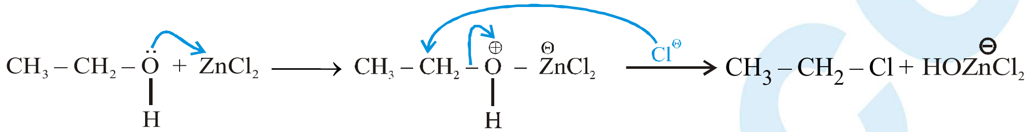


$$\mathrm{Me-CH=CH-CH_2-Cl} \xrightarrow{EtOH} \mathrm{Me-CH=CH-\overset{\oplus}{C}H_2} \longleftrightarrow \mathrm{Me-\overset{\oplus}{C}H-CH=CH_2}$$

$\xrightarrow{EtOH}$ $\mathrm{Me-CH=CH-CH_2-OEt}$ (cis + trans)

$\xrightarrow{Et-OH}$ $\mathrm{Me-\overset{*}{C}H(OEt)-CH=CH_2}$ (d + ℓ) mix.

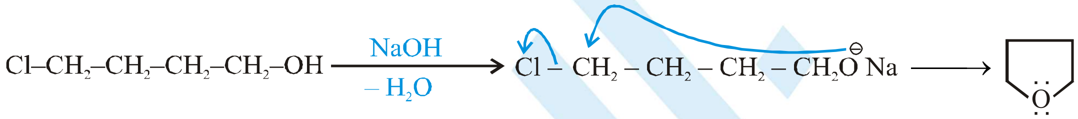
54.



$$\mathrm{CH_3-CH_2-\ddot{O}H + ZnCl_2 \longrightarrow CH_3-CH_2-\overset{\oplus}{O}(H)-\overset{\ominus}{Zn}Cl_2 \xrightarrow{Cl^{\ominus}} CH_3-CH_2-Cl + HO\overset{\ominus}{Zn}Cl_2}$$

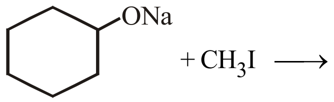
55. Strength of Nucleophile generally increases on going down a group in the periodic table, so (D) is not true.

56.



$\mathrm{Cl{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}OH} \xrightarrow[-H_2O]{NaOH} \mathrm{Cl-CH_2-CH_2-CH_2-CH_2\overset{\ominus}{O}\,Na} \longrightarrow$

57.

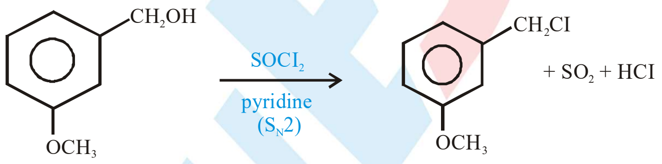


strong anionic nucleophile and 1° alkyl halide favours S_N2 mechanism.

58. Nucleophilic substitution of alcohol is acid catalysed reaction.

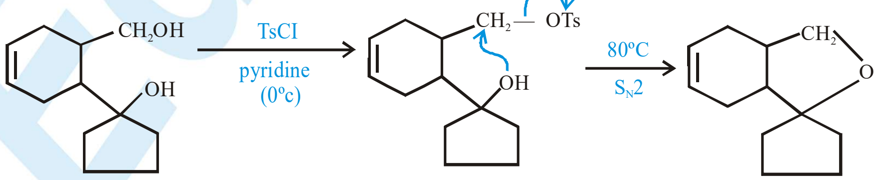
59. Bridge head carbocation is not formed.

60.

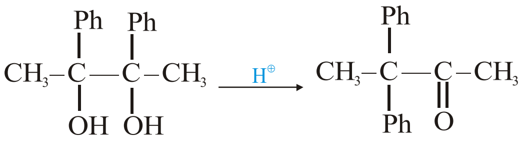


61. I ⇒ Only one T.S. So it is for S_N2 and $\Delta H = -ve$.
II ⇒ Only one T.S. So it is for S_N2 and $\Delta H = +ve$.
III ⇒ More than one T.S. so it is for S_N1 and 1st step is rds.

62.

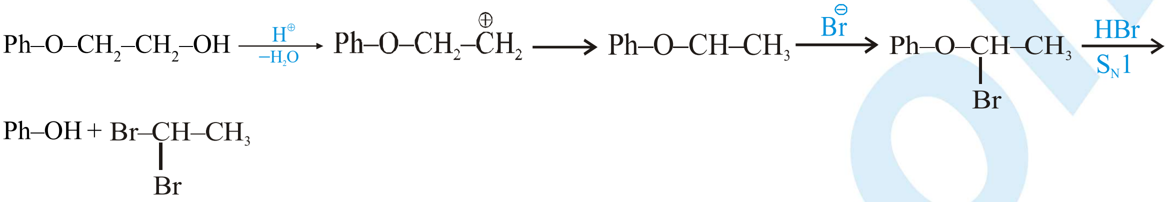


63. Correct Product for (C) option.



$$CH_3-\underset{OH}{\overset{Ph}{C}}-\underset{OH}{\overset{Ph}{C}}-CH_3 \xrightarrow{H^{\oplus}} CH_3-\underset{Ph}{\overset{Ph}{C}}-\underset{\overset{\|}{O}}{C}-CH_3$$

64.



$$Ph-O-CH_2-CH_2-OH \xrightarrow[-H_2O]{H^{\oplus}} Ph-O-CH_2-\overset{\oplus}{C}H_2 \longrightarrow Ph-O-CH-CH_3 \xrightarrow{\overset{\ominus}{Br}} Ph-O-\underset{Br}{CH}-CH_3 \xrightarrow[S_N1]{HBr}$$

$$Ph-OH + Br-\underset{Br}{CH}-CH_3$$

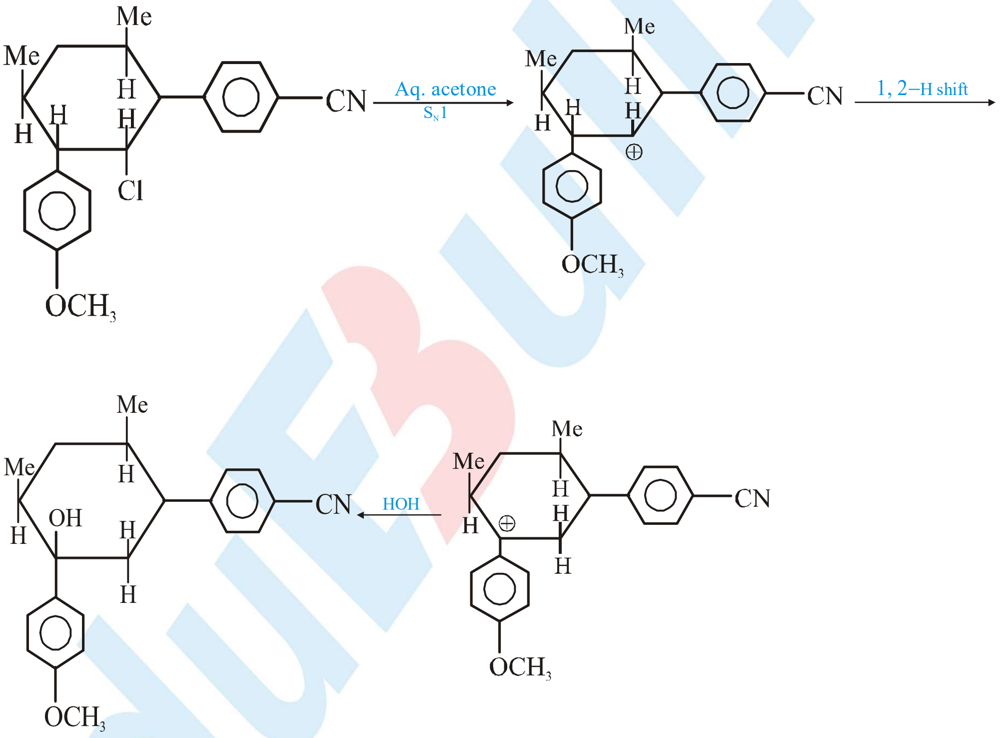
EXERCISE - 2

Part # I : Multiple Choice

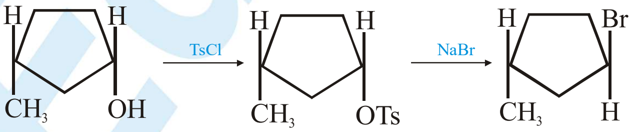
1. Nucleophiles are electron rich species.

2. Anionic nucleophiles are better than their neutral nucleophiles.

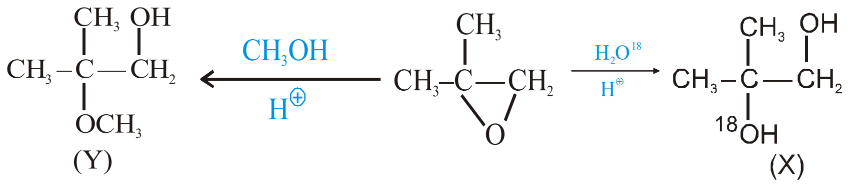
3.



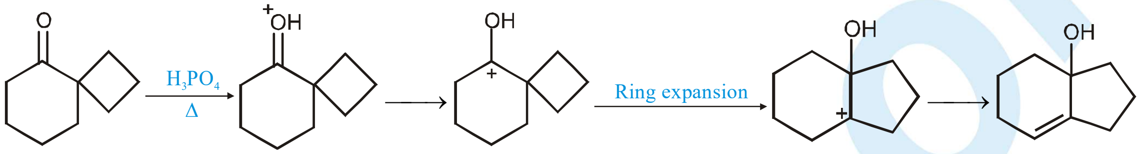
4.



5.



6.

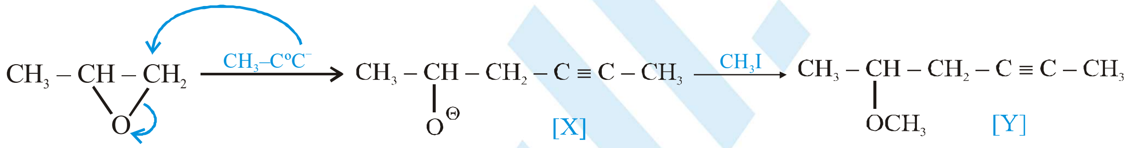


7. Rate of E^2 reaction ∝ Stability of alkene

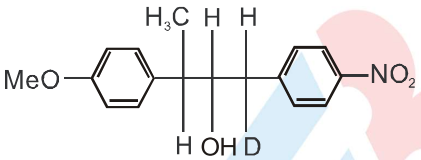
8. All statement are correct.

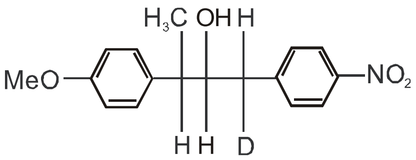
9. 1° alkyl halide is more reactive than 2° alkyl halide. So transition state in II reaction is more stable than I reaction.

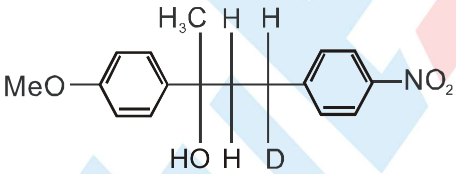
10.

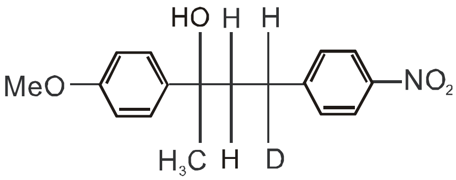


11. Product mixture



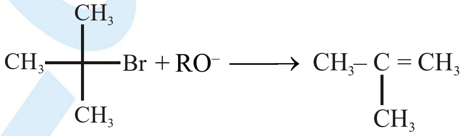






Product mixture react with PCl$_5$ by S$_N$2 mechanism and four products are formed. They are positional isomers and diastereomers so after fractional distillation four fraction are obtained.

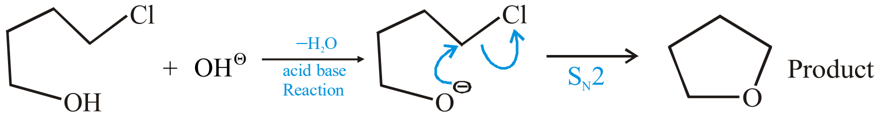
12. Correct product for (B) option.

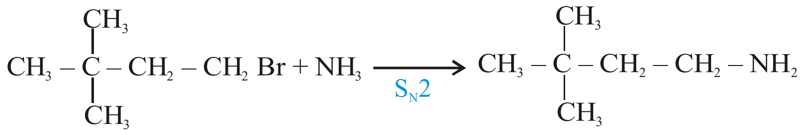


$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + RO^- \longrightarrow CH_3-\underset{CH_3}{C}=CH_3$$

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

13. $CH_3CH_2O^{\ominus} + CH_3-CH_2-Cl \xrightarrow{S_N2} CH_3-CH_2-O-CH_2-CH_3$

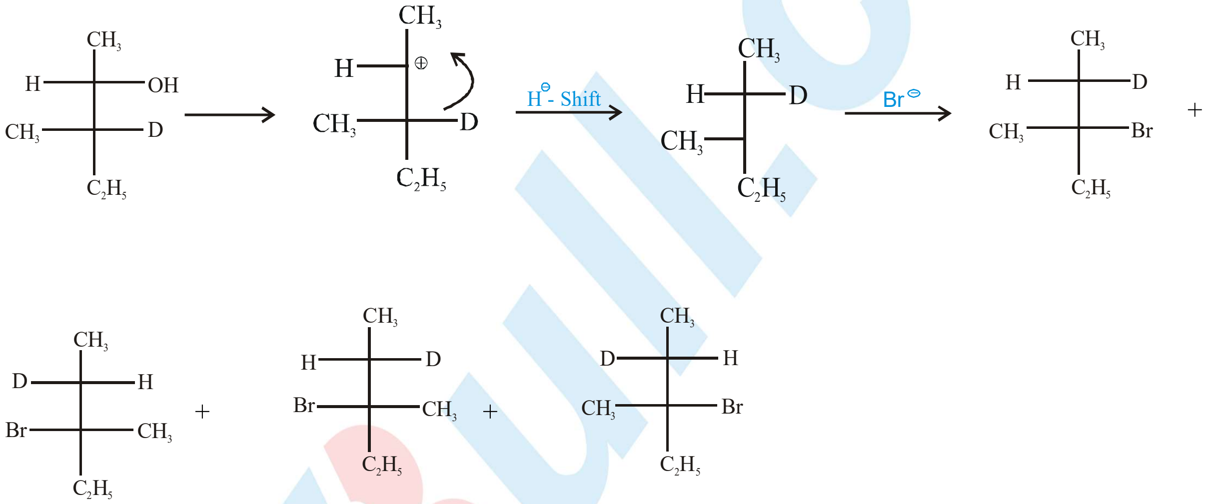




$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2Br + NH_3 \xrightarrow[S_N2]{} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-NH_2$$

$$CH_3-CH_2-OH + HBr \xrightarrow[S_N2]{} CH_3-CH_2-Br + H_2O$$

14.



Part # II : Assertion & Reason

6. S-1 and S-2 is correct and S-2 is correct explanation of S-1.

7. 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.

8. S_N2 is not possible at 3° alkyl halide by strong base.

9. Alcohol give S_N reaction only in acidic medium.

10. Polar aprotic solvent is used for S_N2 reaction because they do not solvate the anion appreciable

11. 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 ⇒ S_N1, so rearrangement is possible.

Strong anionic nucleophile ⇒ S_N2, walden inversion is possible.

Strong anionic nucleophile ⇒ S_N2 but α carbon is not stereogenic.

Aq. NaOH ⇒ S_N1, carbocation is already stable so no rearrangement.

4. 1° Alkyl halide and anionic strong nucleophile ⇒ S_N2

2° Alkyl halide and anionic strong base ⇒ E^2

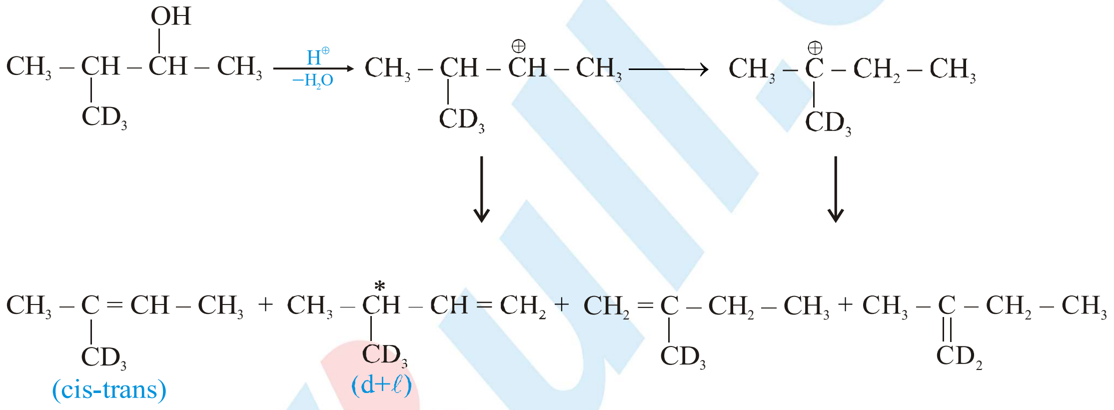
3° Alcohol and acidic medium ⇒ E^1

3° Alkyl halide and weak neutral nucleophile ⇒ S_N1

Part # II : Comprehension

Comprehension # 1 :

1.

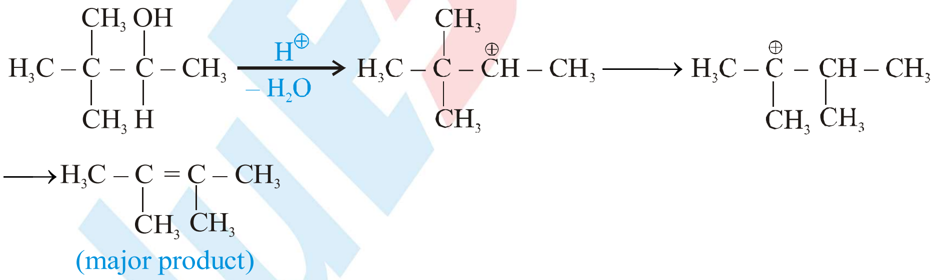


$$CH_3-\underset{\underset{CD_3}{|}}{CH}-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[-H_2O]{H^{\oplus}} CH_3-\underset{\underset{CD_3}{|}}{CH}-\overset{\oplus}{CH}-CH_3 \longrightarrow CH_3-\underset{\underset{CD_3}{|}}{\overset{\oplus}{C}}-CH_2-CH_3$$

$$CH_3-\underset{\underset{CD_3}{|}}{C}=CH-CH_3 + CH_3-\underset{\underset{CD_3}{|}}{\overset{*}{C}H}-CH=CH_2 + CH_2=\underset{\underset{CD_3}{|}}{C}-CH_2-CH_3 + CH_3-\underset{\underset{CD_2}{||}}{C}-CH_2-CH_3$$

(cis-trans) (d+ℓ)

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

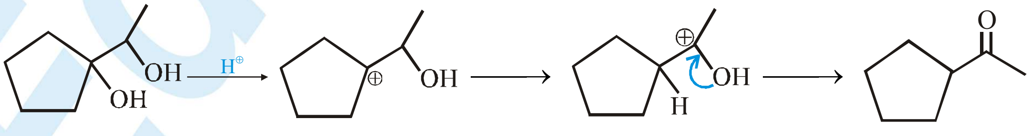


$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow[-H_2O]{H^{\oplus}} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\oplus}{CH}-CH_3 \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

$$\longrightarrow H_3C-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3$$

(major product)

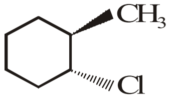
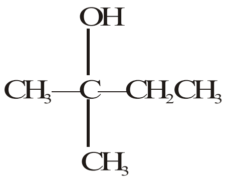
3. In this reaction pinacol pinacolone rearrangement takes place

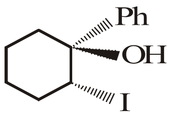


EXERCISE - 4

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.

2. (a)

(b)

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

3. (a)

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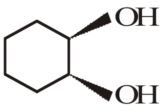
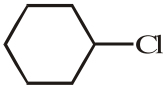


4. (A) C_2H_5Cl; (B) C_2H_5CN; (C) C_2H_5COOH; (D) $C_2H_5COONH_4$; (E) $C_2H_5CONH_2$

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 is 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.

7. (a)

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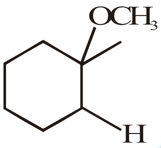
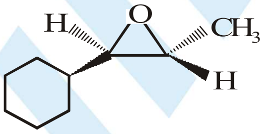
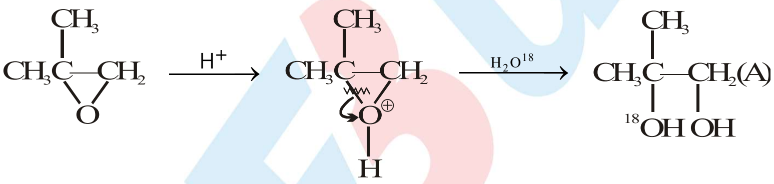
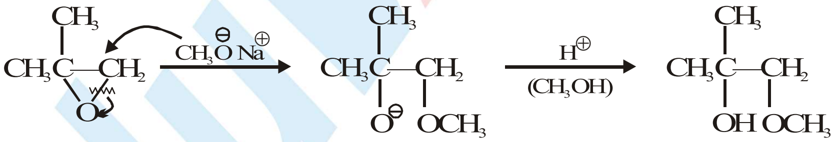

(c)


8.


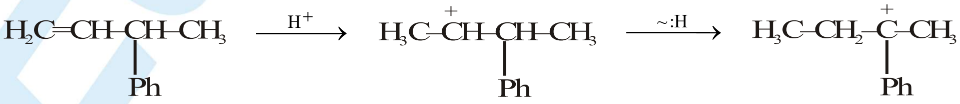
(nucleophile attacks the more substituted carbon in acid-catalysed reaction)

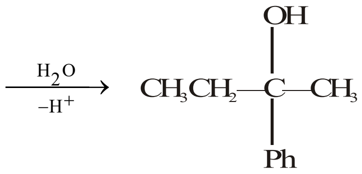


(nucleophile attacks the less substituted carbon in base-catalysed reaction)

9. I : bond b ; II : bond a

10. A is laevo - isomer

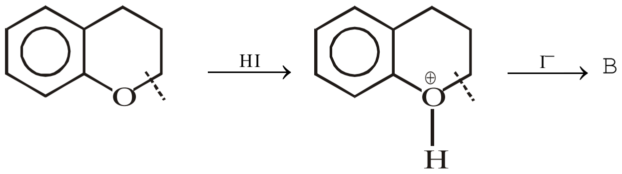
11.

$H_2C=CH-\underset{Ph}{CH}-CH_3 \xrightarrow{H^+} H_3C-\overset{+}{C}H-\underset{Ph}{CH}-CH_3 \xrightarrow{\sim:H} H_3C-CH_2-\underset{Ph}{\overset{+}{C}}-CH_3$



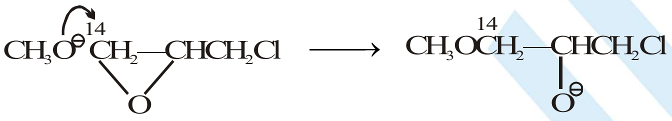
$$\xrightarrow[-H^+]{H_2O} CH_3CH_2-\overset{\overset{\large OH}{|}}{\underset{\underset{\large Ph}{|}}{C}}-CH_3$$

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

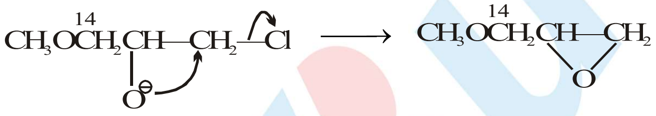


13. CH_3O^- (nucleophile) attacks less submituted carbon (which is C-14 in this case) forming intermediate (C).



(A) (C)

(C) will displace Cl^- forming (B)



(C)

14. C_2H_5OH C_2H_5Cl

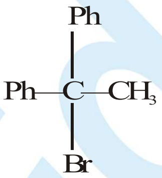
Ethyl alcohol Ethyl chloride

(X) (Y)

15. $(CH_3)_2CHCH_2OH$; $(CH_3)_2C{=}CH_2$; $(CH_3)_3COH$

(A) (B) (C)

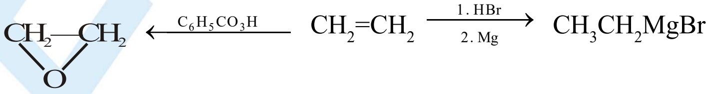
16.



$$Ph-\overset{\overset{\large Ph}{|}}{\underset{\underset{\large Br}{|}}{C}}-CH_3$$

Synchronous migration of Ph provides greater assistance in the removal of H_2O form the protonated alcohol

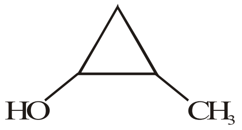
17.

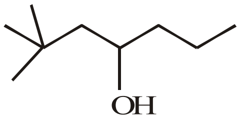


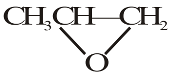
(B) (A)

$$A + B \xrightarrow{H_2O} CH_3CH_2CH_2CH_2OH$$

(C)

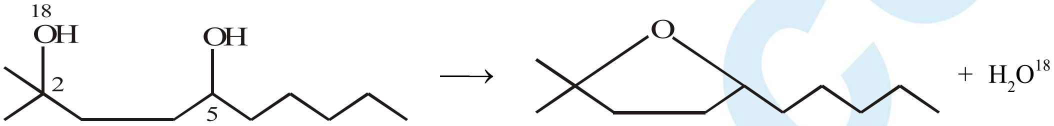
18. (A) 

(B) 

(C) 

CH_3CH-CH_2 with O bridging CH and CH_2

19. 3° alcohol at C_2 is more basic than 2° alcohol at C_5. Hence, intramolecular dehydration takes place such that H of 2° alcoholic group at C_5 eliminates OH of 3° alcoholic groups at C_2 (with isotopic ^{18}O) to form cyclic ether



20. A is a mixture of d- and 1- and thus racemic mixture.

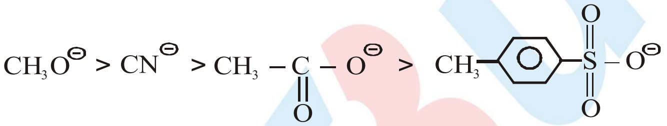
EXERCISE - 5

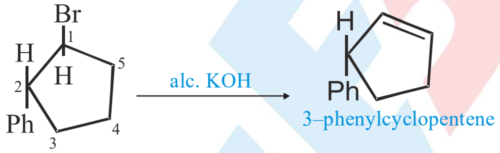
Part # I : AIEEE/JEE-MAIN

1. $R-OH \xrightarrow{H^{\oplus}} R-\overset{\oplus}{O}H_2$ this step is initiation step.

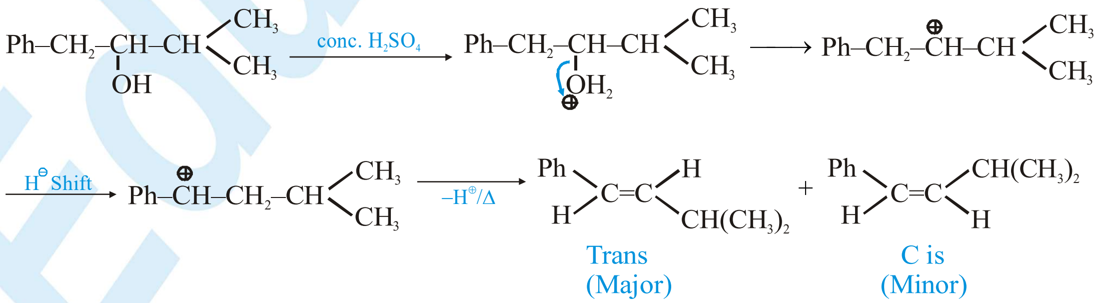
2. According to stability of carbocation.

3. 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.

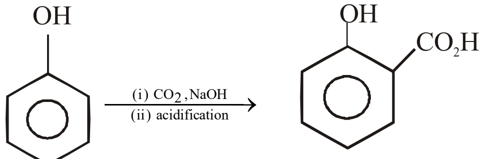
5. 

6. Reaction of alcohol with HCl and anhydrous $ZnCl_2$ is an S_N 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.

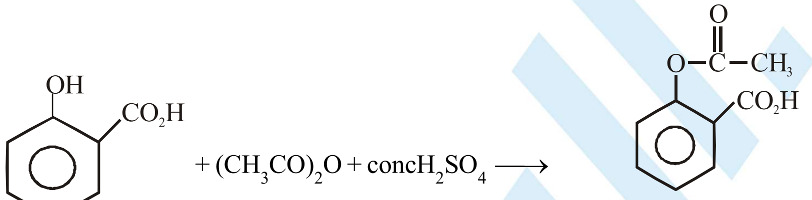
8. The reaction of alcohol with lucas reagent is mostly an S_N1 reaction and the rate of reaction is directly proportional to the carbocation stability formed in the reaction, since 3° R–OH forms 3° carbocation hence it will react fastest.

9.



Salicyclic acid
(X)

This is called Kolbe reactions.

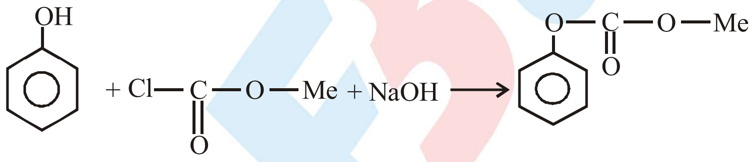


(X)

Aspirin
(non-narcotic analgesic)

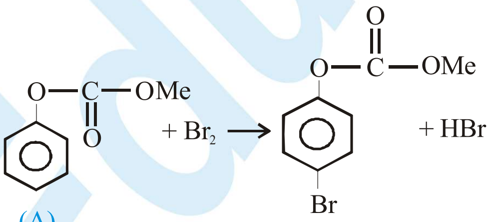
This step is called acylation reaction.

10.



Methylchloroformate

This step involves acid base reaction at first followed by S_NAE reactions.



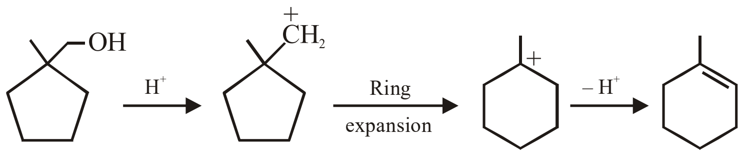
(A)
(o/p directing)

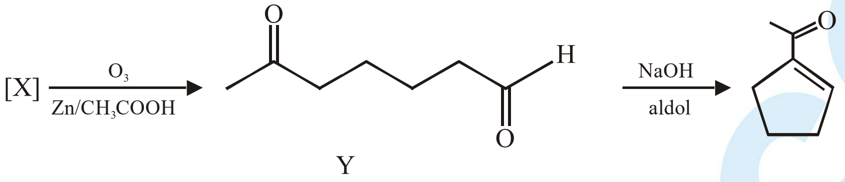
(B)

This step is called bromination.

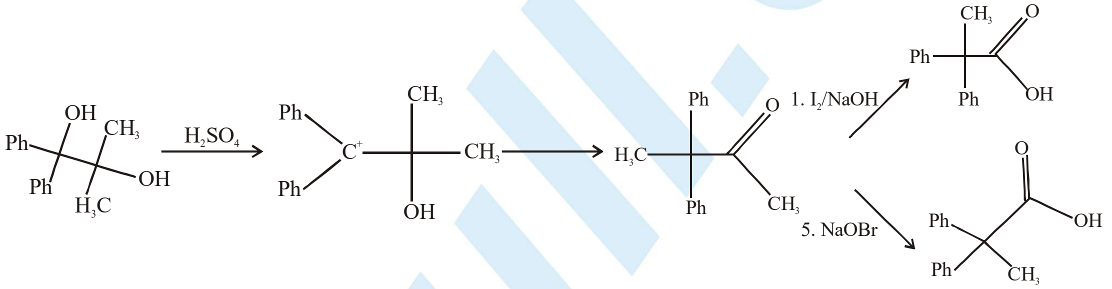
Part # II : IIT-JEE ADVANCED

5.

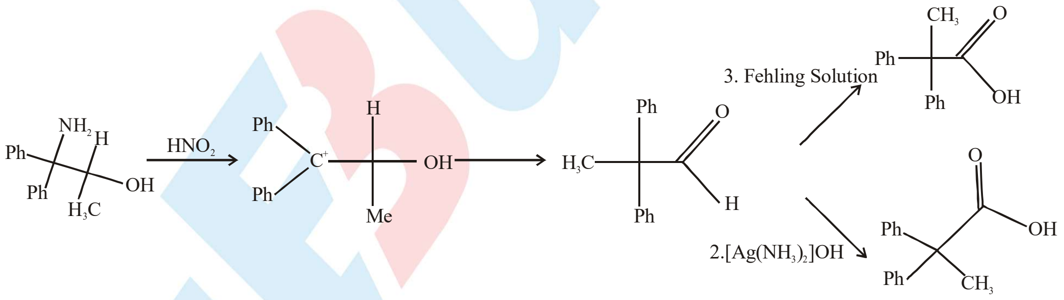




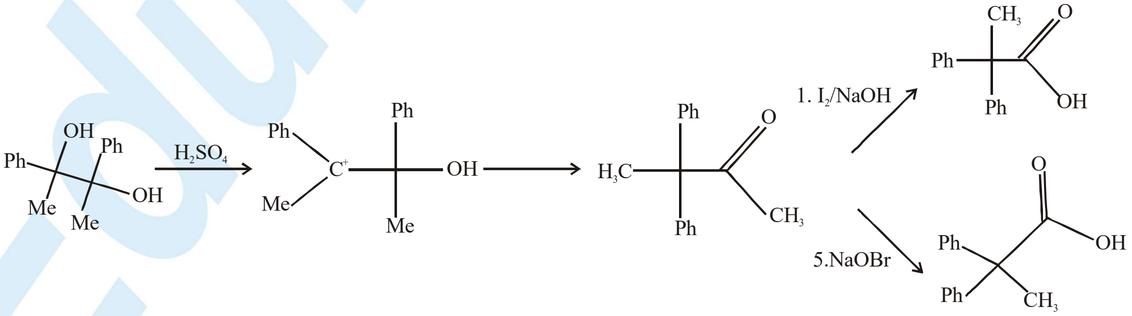
9. **P:**



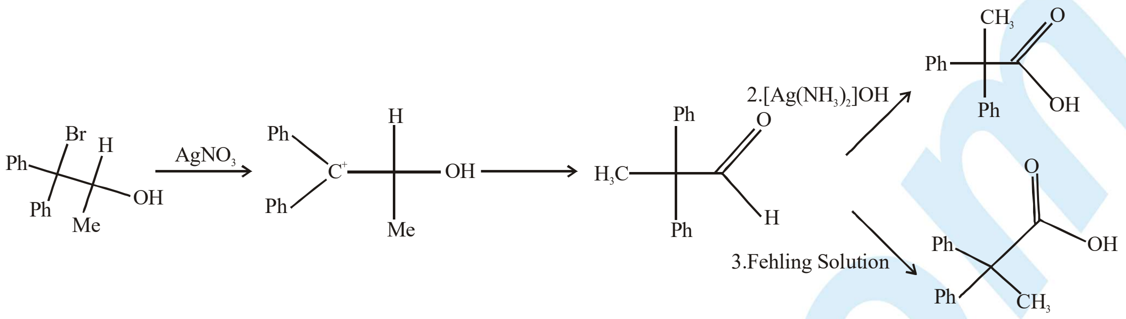
Q:



R:

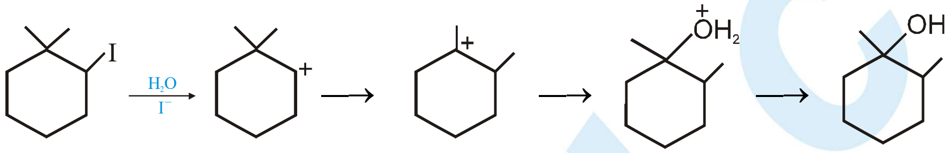


S:



MOCK TEST

6.



7. $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[S_N2]{NaBr,\ H_2SO_4} CH_3-CH_2-CH_2-CH_2-Br$

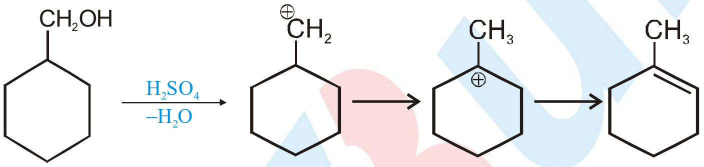
unbranched 1° alcohol give S_N2 reaction with HX.

8.

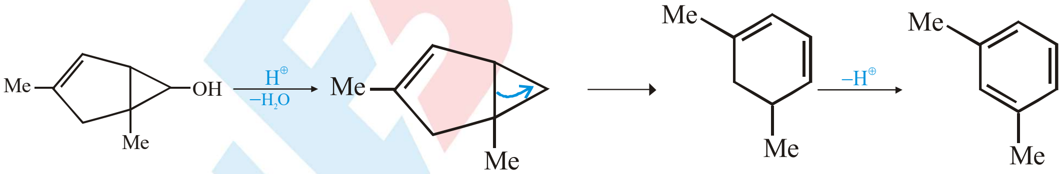
$$CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow{SOCl_2} CH_3-CH_2-\overset{Cl}{\overset{|}{CH}}-CH_3$$

It is S_Ni mech so retention of configuration.

9.

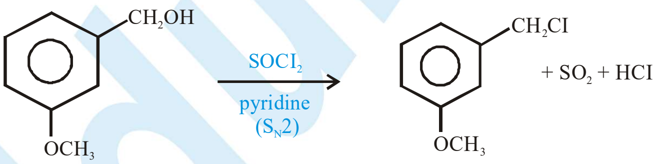


10.

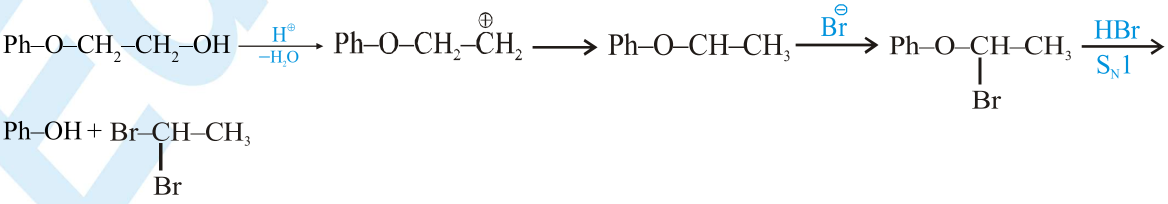


11. Strength of Nucleophile generally increases on going down a group in the periodic table, so (D) is not true.

12.



13.

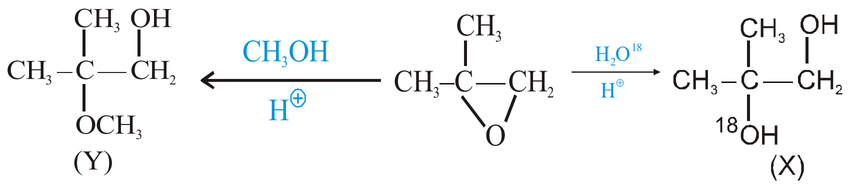


$$Ph–O–CH_2–CH_2–OH \xrightarrow[-H_2O]{H^{\oplus}} Ph–O–CH_2–\overset{\oplus}{C}H_2 \longrightarrow Ph–O–CH–CH_3 \xrightarrow{\overset{\ominus}{Br}} Ph–O–\underset{Br}{\underset{|}{CH}}–CH_3 \xrightarrow[S_N1]{HBr}$$

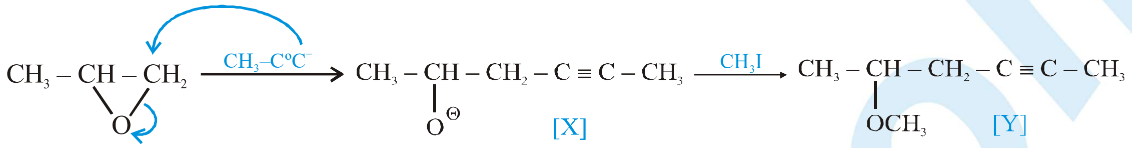
$$Ph–OH + Br–\underset{Br}{\underset{|}{CH}}–CH_3$$

14. Nucleophiles are electron rich species.

15.



16.



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.

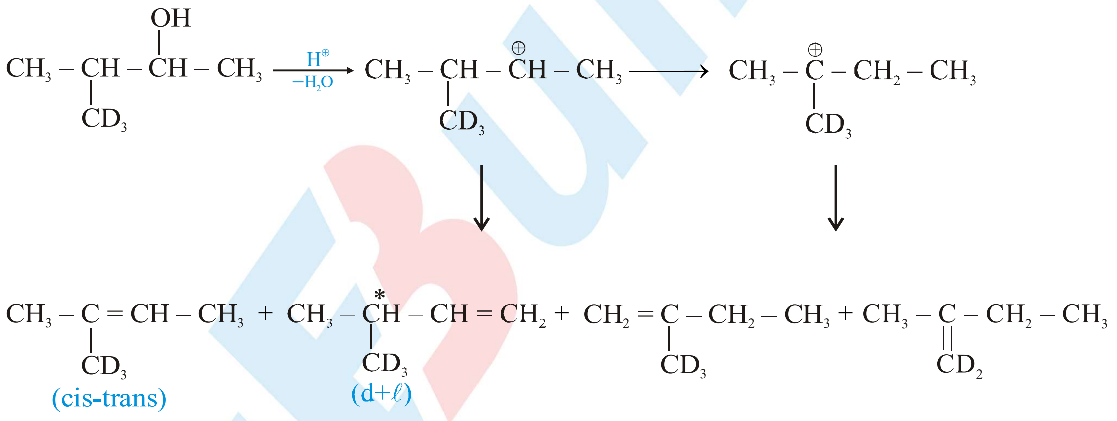
23. S_N2 is not possible at 3° alkyl halide by strong base.

24. Alcohol give S_N reaction only in acidic medium.

25. Polar aprotic solvent is used for S_N2 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.

27.



30.
- 1° Alkyl halide and anionic strong nucleophile ⇒ S_N2
- 2° Alkyl halide and anionic strong base ⇒ E^2
- 3° Alcohol and acidic medium ⇒ E^1
- 3° Alkyl halide and weak neutral nucleophile ⇒ S_N1