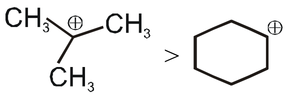
HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

26. Leaving group ability ∝ Stability of anion.

27. Carbocation Stability

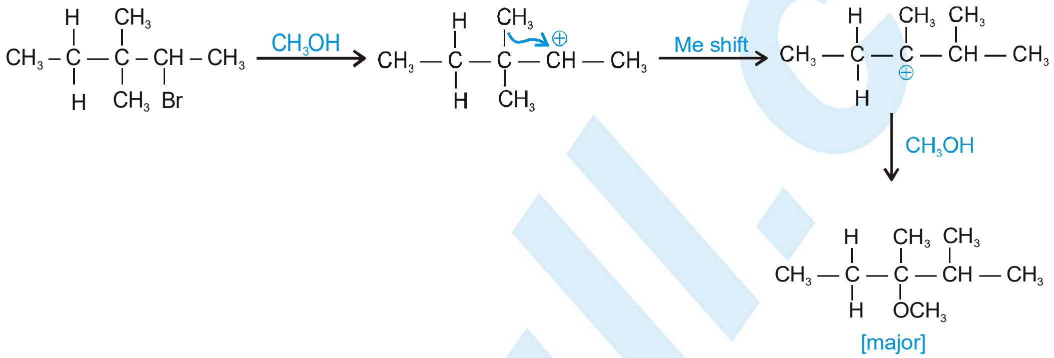


leaving group ability is $Br^{\ominus} > Cl^{\ominus}$

over all reaction order $r_1 > r_3 > r_2$

28. On the basis of carbocation stability.

29.



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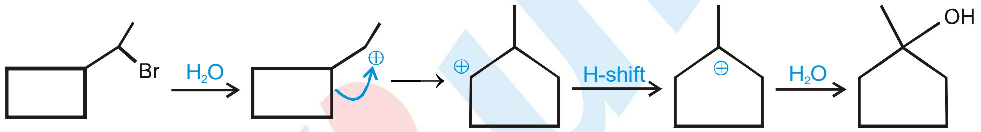
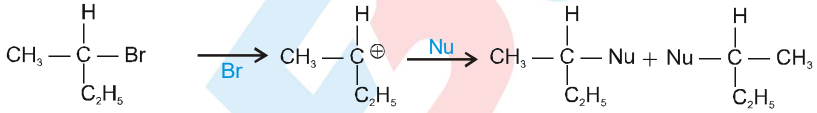


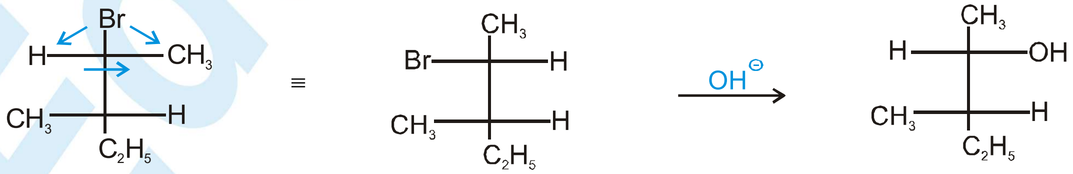
31.



32.

In aryl halides the C–X bond has partial double bond character due to resonance so it will not give S_N reaction.

33.

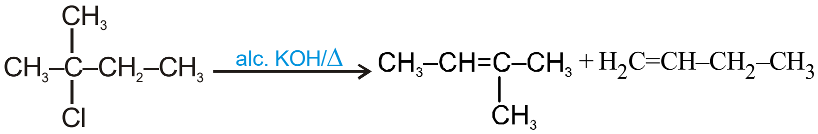


34. According to stability of carbocation and leaving ability of leaving group.

35. According to stability of carbocation

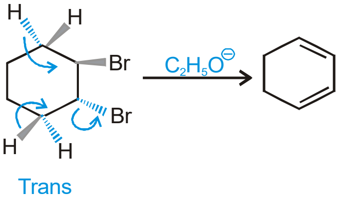
36. β-Hydrogen is absent.

38.



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

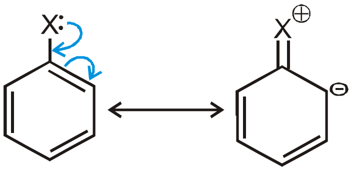
39.



41. Rate of E2 reaction ∝ Stability of alkene

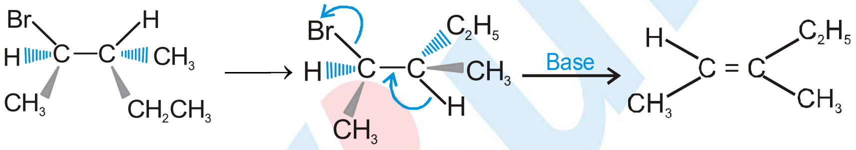
42. 1° R-X gives S_N2 reaction fastest and 3° R-X gives S_N1 reaction fastest.

43. In aryl halides the C – X bond has partial double bond character due to resonance so the cleavage of C – X bond becomes difficult.



44. $I^{\ominus}$ is not a strong base so it do not gives E2 reaction.

45.

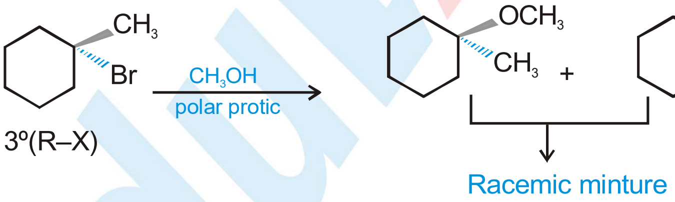


46. Rate of S_N2 reaction : 1° > 2° > 3°, as β-branching increases steric crowding increases in transition state so it makes less stable T.S.

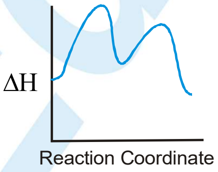
47. Strong anionic Nucleophile so mechanism is S_N2.

48. According to stability of carbocation because mechanism is S_N1.

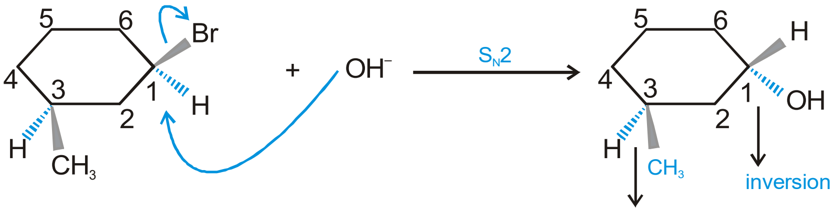
49.



Two transition states are formed and one stable carbocation is formed in the reaction.



50.

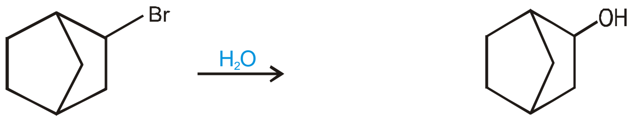


(1R, 3S) – Cis – 1 – Bromo –3 – Methyl cyclohexane

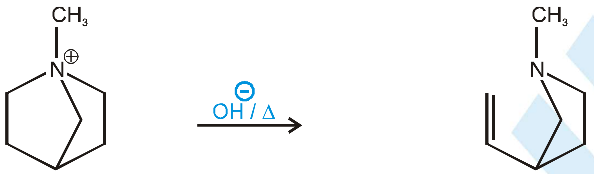
Retention

(1S, 3S) – trans – 3 – methyl cyclohexanol

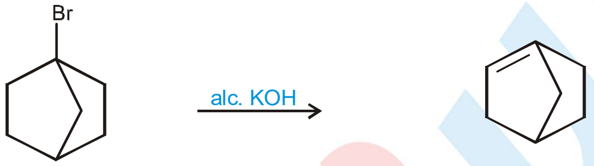
51.



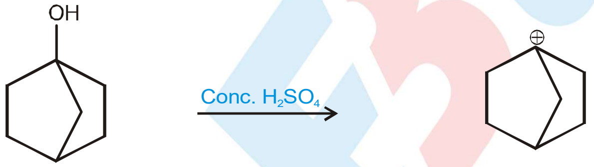
Substitution product is formed.



product is possible



Double bond at bridge head not possible



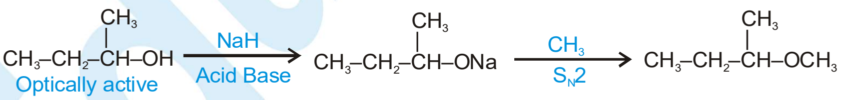
Carbocation is not possible

52. I ⇒ Only one T.S. So it is for S_N2 and ΔH = –ve.

II ⇒ Only one T.S. So it is for S_N2 and ΔH = +ve.

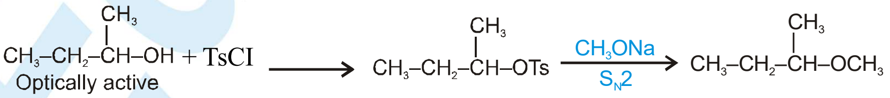
III ⇒ More than one T.S. so it is for S_N1 and 1st step is rds.

53.



$$\underset{\text{Optically active}}{CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-OH} \xrightarrow[\text{Acid Base}]{NaH} CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-ONa \xrightarrow[S_N2]{CH_3} CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-OCH_3$$

Retention of product.

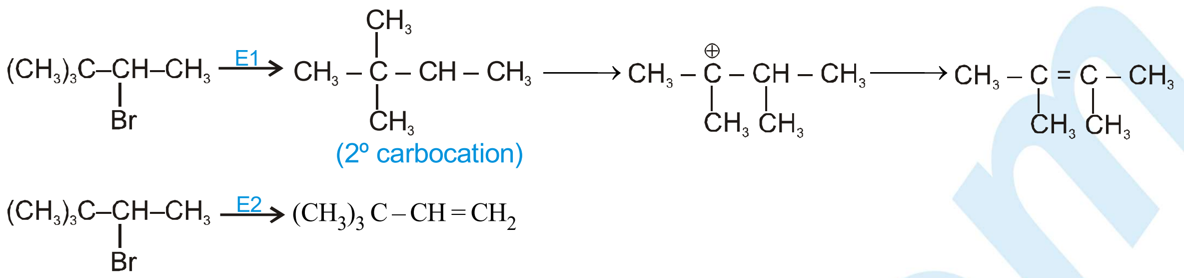


$$\underset{\text{Optically active}}{CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-OH} + TsCl \longrightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-OTs \xrightarrow[S_N2]{CH_3ONa} CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-OCH_3$$

inversion take place.

M = Retention product and M′ = inversion product, so they are enantiomers.

54.

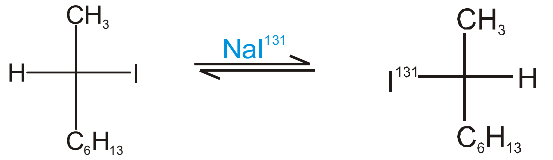


$$(CH_3)_3C\text{–}\underset{\underset{Br}{|}}{CH}\text{–}CH_3 \xrightarrow{E1} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH-CH_3 \longrightarrow CH_3-\overset{\oplus}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3$$

(2° carbocation)

$$(CH_3)_3C\text{–}\underset{\underset{Br}{|}}{CH}\text{–}CH_3 \xrightarrow{E2} (CH_3)_3\,C-CH=CH_2$$

55.



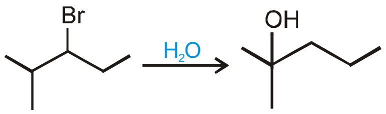
2-Iodooctane
(+)

(A) It is S_N2 reaction so rate of reaction depends on [R – I] and [I^-]
(B) Racemisation is exactly twice the rate of reaction
(C) In S_N2 inversion takes place
(D) Final solution has both type of I^{127} and I^{131} .

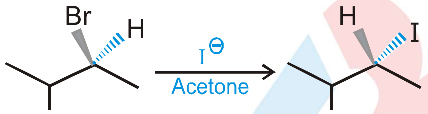
EXERCISE - 2

Part # I : Multiple Choice

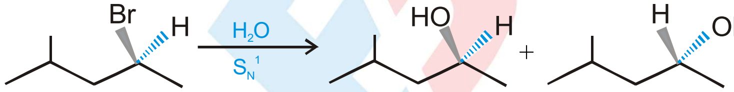
21. Correct product for (C) option.



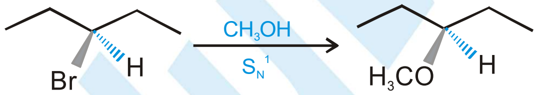
22.



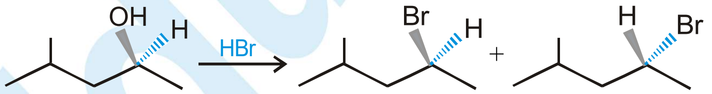
[Only one product]



[Enantiomeric pair]

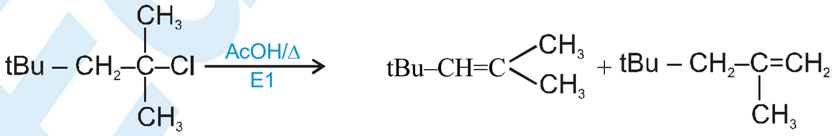


[Only one product]



[Enantiomeric pair]

23.

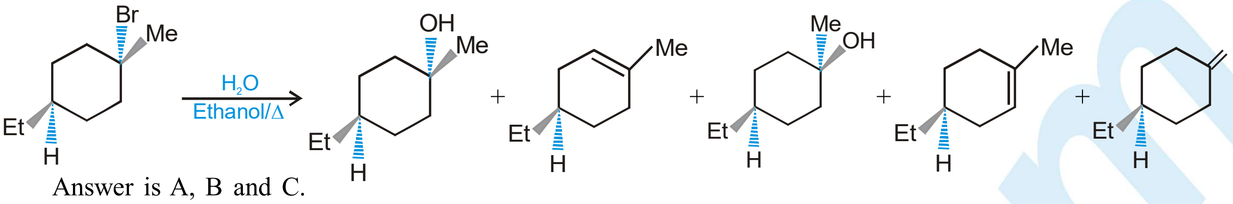


$$tBu-CH_2\text{–}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{–}Cl \xrightarrow[E1]{AcOH/\Delta} tBu\text{–}CH{=}C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} + tBu-CH_2\text{–}\underset{\underset{CH_3}{|}}{C}{=}CH_2$$

(minor) (major)

Less substituted product is formed as major product because of steric hindrance of t-Butyl group.

24.



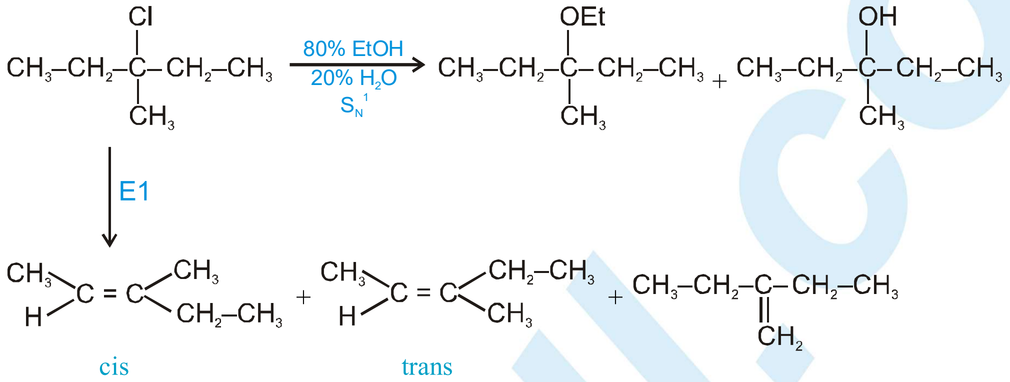
Answer is A, B and C.

25. Rate of solvolysis ∝ Stability of carbocation.

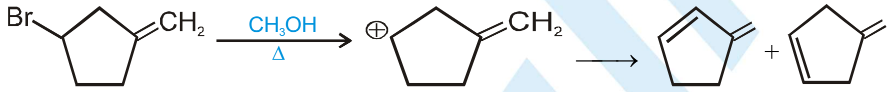
26. Due to steric effect.

27. It is an example of S_N2 reaction.

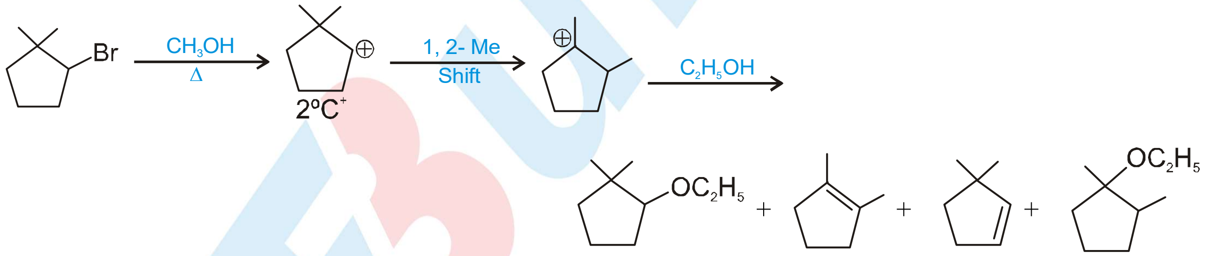
28.



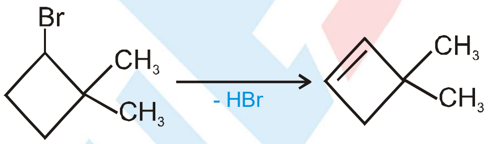
29.



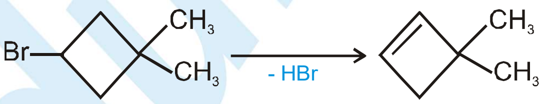
30.



31. (A)



(B)



32. (C) (X) Stabilises the carbanion due to electron withdrawing nature.

EXERCISE - 4

Subjective Type

1. **(a)** F **(b)** T **(c)** F **(d)** T **(e)** T **(f)** F **(g)** F **(h)** T

2. 1° > 2° > 3° Anion of acetic acid is more stabilised by resonance than phenoxide ion.

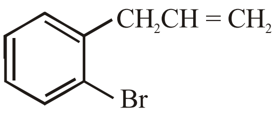
3. 1-chlorohexane
Because it follows Sn2 path.

4. IV > I > II > III

5. **(a)** I **(b)** II **(c)** I **(d)** I

6. **(a)** T **(b)** F **(c)** T **(d)** F **(e)** T **(f)** T **(g)** T **(h)** T

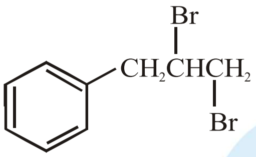
7. **(a)**



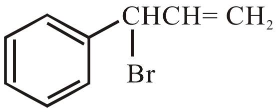
Ortho

and para

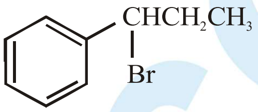
(b)



(c)

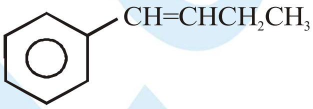


(d)

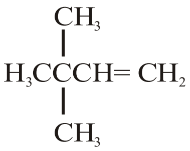


(1, 2-H^- shift gives more stable benzylic carbocation)

8. **(a)** $CH_3CH=CHCH_3$ **(b)** $CH_3CH=CHCH_3$ **(c)**

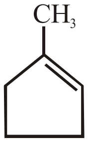


(d)

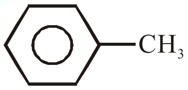


$H_3C\overset{CH_3}{\underset{CH_3}{C}}CH=CH_2$

(e)

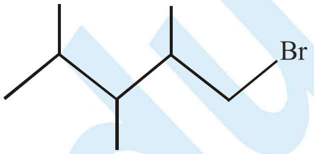


9. Ease of backside attack (less steric hindrance) decides which undergoes S_N2 faster (except in **(b)** in which iodide is better leaving group). In all cases first one is fater than the other for S_N2 reaction.

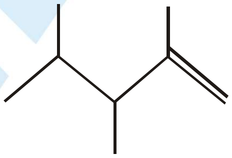
10. Gas B is CH_4, hence A is CH_3MgBr. CH_3Br forms  on reaction with benzene.

11. Only II can be used for successful synthesis of Grignard reagent, rest all contain acidic proton and will react with R^- (from Grignard reagent) forming alkane.

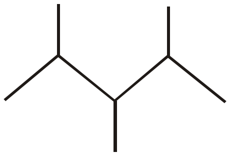
12.



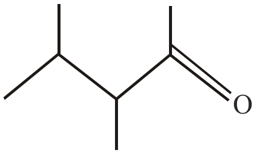
A



B

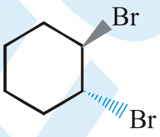


C

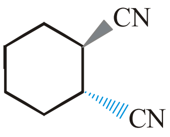


D

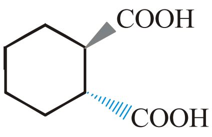
13. **(A)**

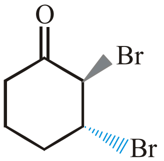


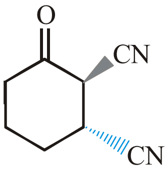
(B)

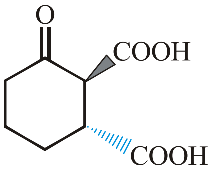


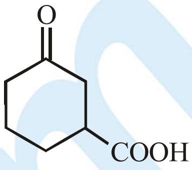
(C)



(D) 

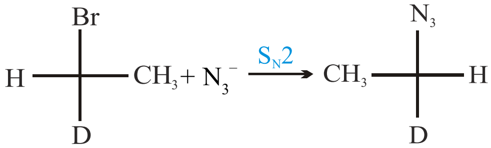
(E) 

(F) 

(G) 

(decarboxylation takes place on heating when there is a keto group at β- position)

14. **(a)** Though neopentylbromide is primary, bulky tertiary butyl group possess very large steric hindrance to the attack of bulky nucleophile N_3^-.

(b) 

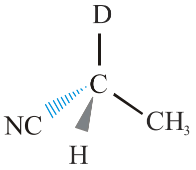
$$H-\overset{Br}{\underset{D}{C}}-CH_3 + N_3^- \xrightarrow{S_N2} CH_3-\overset{N_3}{\underset{D}{C}}-H$$

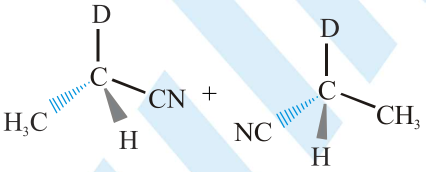
(c) Rate will double

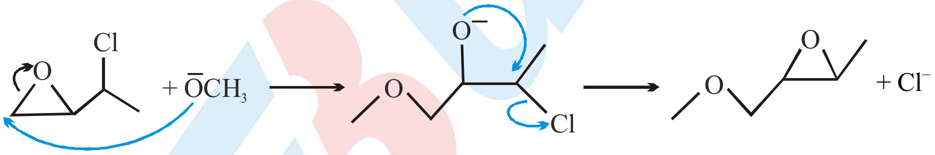
(d) Rate will double

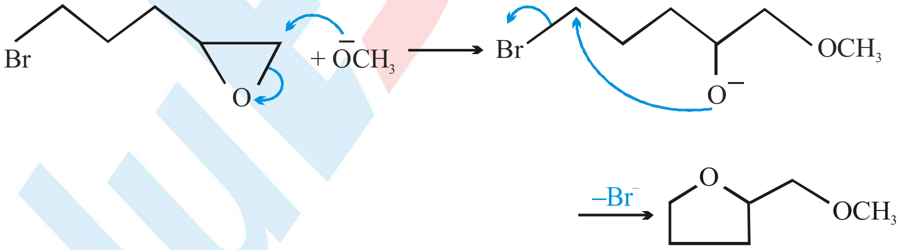
(e) not related

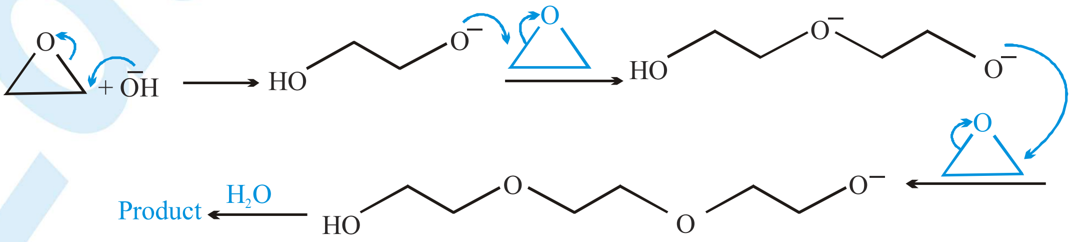
(f) Recemization occur through carbocation intermediate

15. **(a)** 

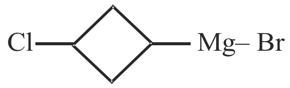
(b) 

16. **(a)** 

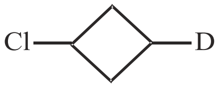
(b) 

(c) 

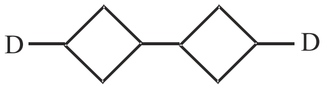
17. **(B)**



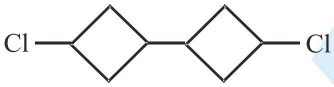
(C)



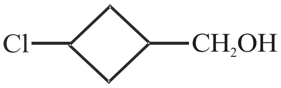
(D)



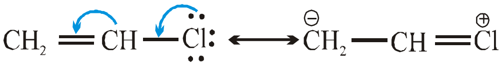
(E)



(F)

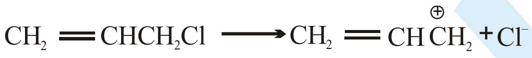


18. In Vinyl chloride, C – Cl bond is stable due to resonance (as in chlorobenzene)



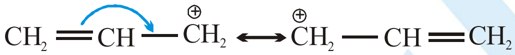
Hence S_N reaction in which Cl is replaced by nucleophile is not possible. In addition to this, sp^2- hybridised carbon is more acidic than sp^3- carbon, hence removal of proton (H^+) is easier than removal of halide (Cl^-)

In allyl chloride, S_N reaction is easier since allyl carbocation formed after removal of Cl^- is stabilised by resonance.



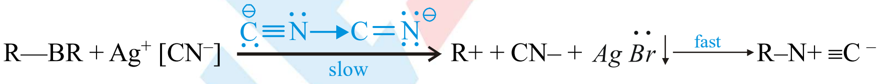
$$CH_2=CHCH_2Cl \longrightarrow CH_2=CH\overset{\oplus}{C}H_2 + Cl^-$$

Allyl carbocation



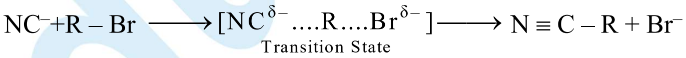
19. **(a)** $CF_3^- < CH_3O^- < CH_3S^-$; **(b)** $CH_3COO^- < CH_3SO_3^- < CF_3SO_3^-$

20. As $[CN]^-$ is an ambident nuicleophile which ahve two nucleophile which have two nucleophilic sites and can attack from either side. In a highly polar solvent, AgCN promotes the formation of carbocation R^+, precipitation of AgBr.



$$R—BR + Ag^+[CN^-] \xrightarrow[\text{slow}]{\overset{\ominus}{C}\equiv\ddot{N}\rightarrow C=\ddot{N}^{\ominus}} R+ + CN- + Ag\ddot{B}r\downarrow \xrightarrow{\text{fast}} R–N+\equiv C^-$$

In the absence of such promotion by Ag^+, with $Na+[CN]^-$, the resulting S_N2 reaction is found to proceed with preferential attack on the atom in the nucleophile which is more polarisable i.e. C.

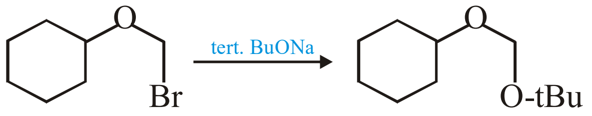


$$NC^- + R - Br \longrightarrow \underset{\text{Transition State}}{[NC^{\delta-}....R....Br^{\delta-}]} \longrightarrow N\equiv C - R + Br^-$$

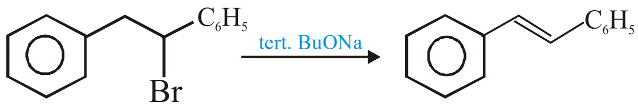
EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

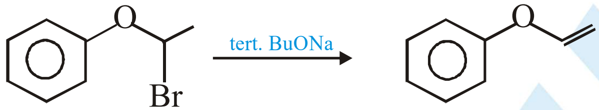
9.



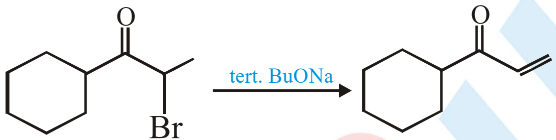
(fails to decolorise the
colour of bromine)



(it decolorise
bromine solution)

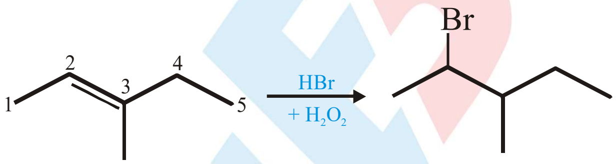


(it decolorise bromine
solution due to unsaturation)



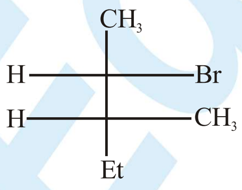
(it decolorise bromine
solution due to unsaturation)

10.

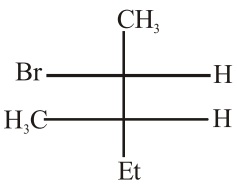


3-methyl pent-2-ene

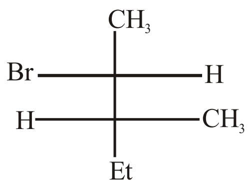
Anti markownikov product
(4 stereo isomers possible
due to 2 chiral centre as
molecule is nonsymmetric)



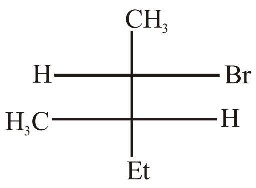
(I)



(II)



(III)



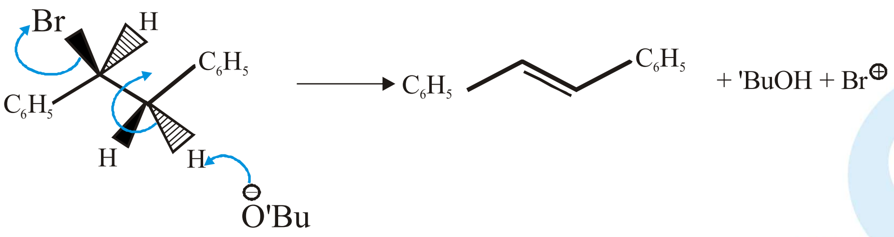
(IV)

11. Elimination reaction is highly favoured if

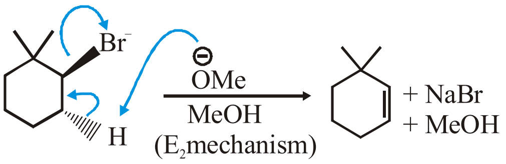
(a) Bulkier base is used

(b) Higher temperature is used

Hence in given reaction biomolecular elimination reaction provides major product.



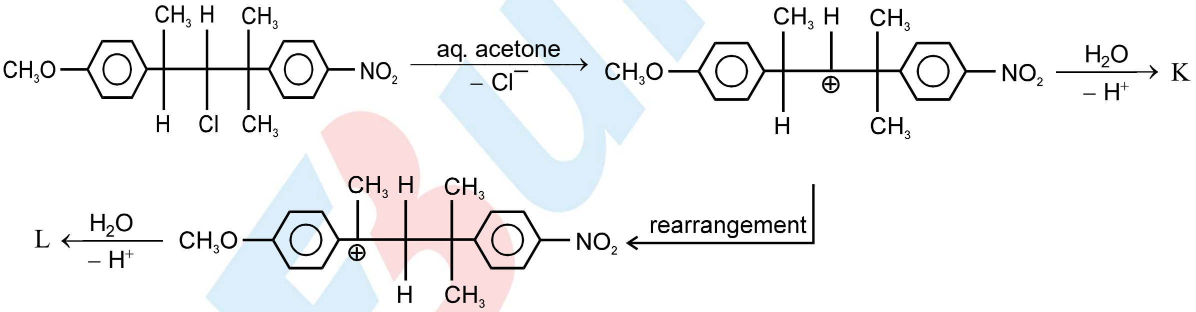
12.



Reaction is dehydrohalogenation E^2 - elimination reaction. Elimination takes place in single step and proceed by formation of transition state from anti position.

Part # II : IIT-JEE ADVANCED

1.



7. **A.** $CH_3-CHBr-CD_3 \xrightarrow[E2]{\text{Alc. KOH}} CH_2=CH-CD_3$

E2 reaction is a single-step reaction in which both deprotonation from β-C and loss of leaving group from α-C occur simultaneously in the rate-determining step.

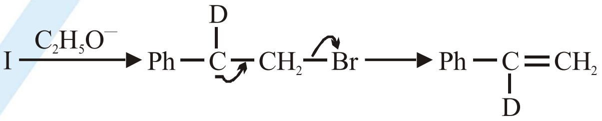
C-D bond is stronger than C—H bond, C—H, is preferably broken in elimination.

B. Ph—CHBr—CH_3 reacts faster than Ph—CHBr—CD_3 in E2 reaction because in latter case, stronger C—D bond is to be broken in the rate determining step.

C. $Ph-CH_2-CH_2Br \xrightarrow[C_2H_5O^-]{C_2H_5OD} Ph-CD=CH_2$

Deuterium incorporation in the product indicates E_1CB mechanism

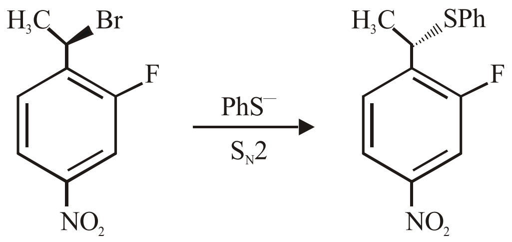
$$Ph-CH_2-CH_2Br \underset{}{\overset{C_2H_5O^-}{\rightleftharpoons}} Ph-\underset{\text{carbanion}}{\bar{C}H-CH_2Br} \overset{C_2H_5OD}{\rightleftharpoons} \underset{I}{Ph-CHD-CH_2Br}$$

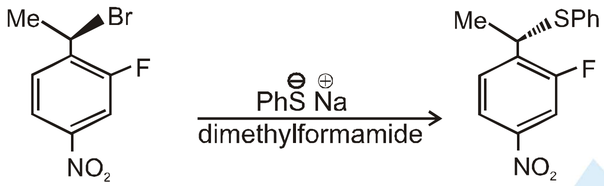


$$I \xrightarrow{C_2H_5O^-} Ph-\overset{D}{\bar{C}}-CH_2-Br \longrightarrow Ph-\underset{D}{C}=CH_2$$

D. Both $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ will react at same rate in E1 reaction because C—H bond is broken in fast non rate determining step. Also E1 reaction follow first order kinetics.

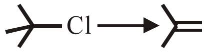
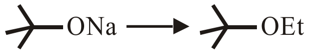
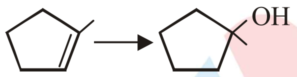
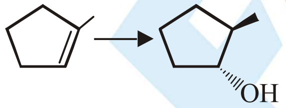
8. Nucleophile PhS^- substitute the Br^- through S_N2 mechanism with inversion of configuration at α-C.



11. 

It is S_N2 reaction so back side attack is possible.

12.

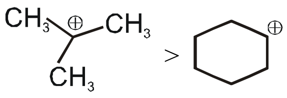
	Column I	Column II	Explanation
P.		NaOEt(2)	$\overline{\text{O}}$ Et (strong nucleophile) causes dehydrohalogenation of 3° alkyl halide
Q.		EtBr (3)	3° butoxide undergoes S_N reaction with 1° alkyl halide
R.		(i) $Hg(OAC)_2$ (ii) NaBH4 (I)	Mercuration-demercuration adds H_2O by Markownikoff's rule without rearrangement
S.		(i) BH_3 (ii) H_2O_2/OH^- (4)	Hydroboro-oxidation adds H_2O by. anti-Markownikoff's rule

Thus, P — (2), Q — (3), R — (1), S — (4)

MOCK TEST

1. **B** **2.** **D** **3.** **D** **4.** **B** **5.** **D**

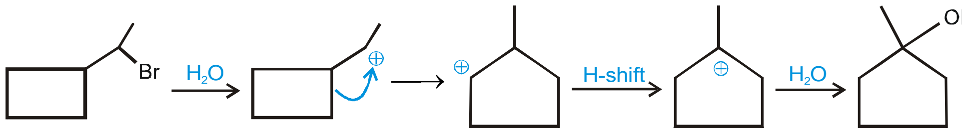
6. Leaving group ability ∝ Stability of anion.

7. Carbocation Stability 

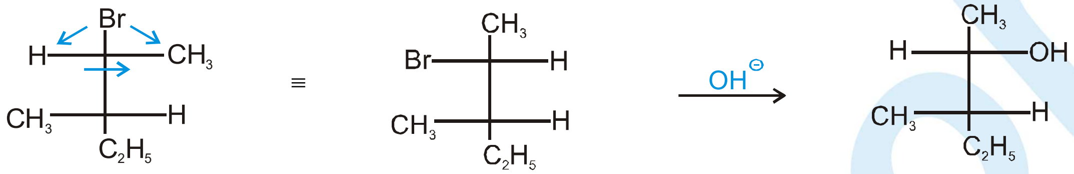
leaving group ability is $Br^{\ominus} > Cl^{\ominus}$

over all reaction order $r_1 > r_3 > r_2$

8.



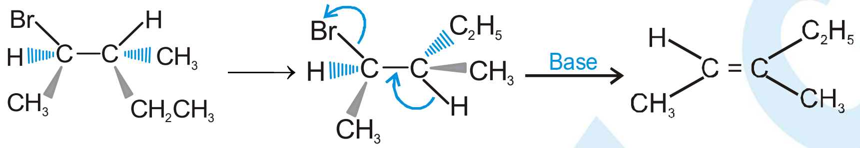
9.



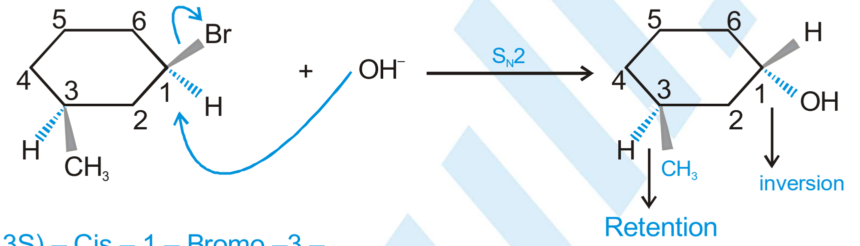
10. According to stability of carbocation

11. **B**

12.



13.



(1R, 3S) – Cis – 1 – Bromo –3 – Methyl cyclohexane

(1S, 3S) – trans – 3 – methyl cyclohexanol

14.

2-Iodooctane
(+)

(A) It is S_N2 reaction so rate of reaction depends on [R – I] and [I^-]

(B) Racemisation is exactly twice the rate of reaction

(C) In S_N2 inversion takes place

(D) Final solution has both type of I^{127} and I^{131} .

15. **A,B,C** **16.** **A,B** **17.** **B,C,D**

18. Correct product for (C) option.