HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

1. $2A(g) \longrightarrow B(g) + 3C(g)$ (elementary reaction)

$$\text{Rate} = -\frac{1}{2}\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt}$$

2. $A + 2B \xrightarrow{K} 3C$ (elementary reaction)

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k[A][B]^2$$

5. Order of reaction $= \frac{3}{2} + (-1) = 0.5$.

6. $A + B \xrightarrow{\text{Slow}} C + D$

$A + B \xrightarrow{\text{fest}}$

$R = k[A][B]$ (slow step is determining step).

9. $AlCl_3$ is electron deficient species thus it is a Lewis acid.

10. Nucleophilicity $\propto$ size (in a group).

11. The nucleophilicity order is $R^{\ominus} > \overset{\ominus}{N}H_2 > CH_3O^{\ominus} > OH^{\ominus}$

14. Weaker bases are better leaving group.

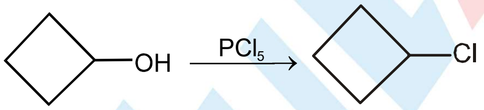
17. S_N1 reactions occur through the intermediate formation of carbocations.

22. Reactivity towards H_2O is proportional to stability of carbocation.

24. $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{HBr} CH_3-CH_2-CH_2-CH_2-Br$

Unbranched 1° alcohol give S_N2 reaction with HX.

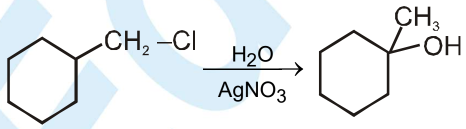
25.



It is S_N2 reaction

26. $CH_3-C\equiv CH \xrightarrow{Na} CH_3-C\equiv C^{-}Na^{+} \xrightarrow[S_N2]{CH_3-CH_2-I} CH_3-C\equiv C-CH_2-CH_3$

27.



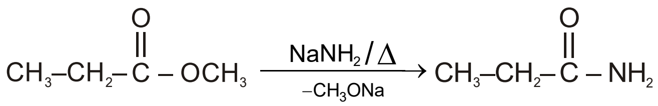
28. S_N2 mechanism is a single step concerted process and proceed through transition state is formed.

29. Rate of $S_N2 \propto [R-X][Nu^-]$

$$\frac{r_2}{r_1} = \frac{[3RX]\left[\frac{1}{2}OH^-\right]}{[RX][OH^-]}$$

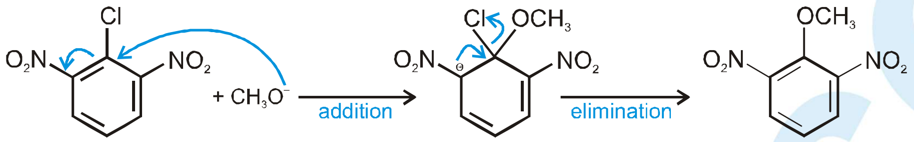
$r_2 = 1.5\, r_1$

31.



$$CH_3-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-OCH_3 \xrightarrow[-CH_3ONa]{NaNH_2/\Delta} CH_3-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-NH_2$$

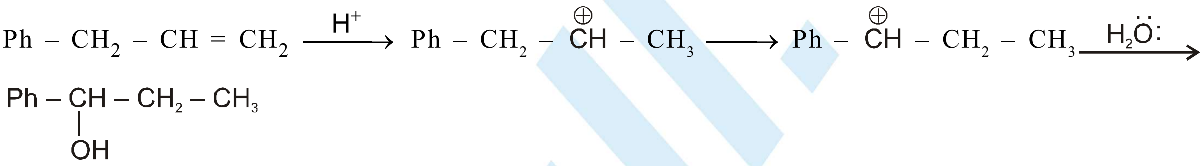
33.



36. Because rate of S_N2 Ar is Ar–F > Ar–Cl > Ar–Br > Ar–I.

41. Electron releasing group and stability of carbocation will increase rate of an electrophilic addition reaction.

45.



$$Ph-CH_2-CH=CH_2 \xrightarrow{H^+} Ph-CH_2-\overset{\oplus}{C}H-CH_3 \longrightarrow Ph-\overset{\oplus}{C}H-CH_2-CH_3 \xrightarrow{H_2\ddot{O}:} Ph-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-CH_3$$

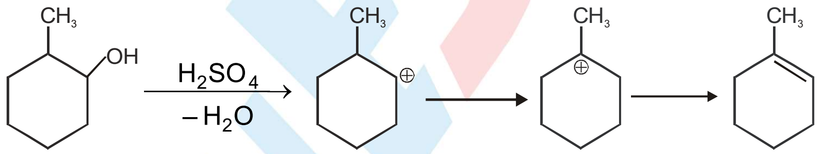
52. As steric hinderance increases on carbonyl group the rate of nucleophilic addition reaction decreases.

55. According to stability of carbocation.

56. It is E2 reaction (anti elimination).

$$CH_3-\underset{\displaystyle Cl}{\underset{|}{C}H}-CH_2-CH_3 \xrightarrow{Alc.KOH} CH_3-CH{=}CH-CH_3$$

59.



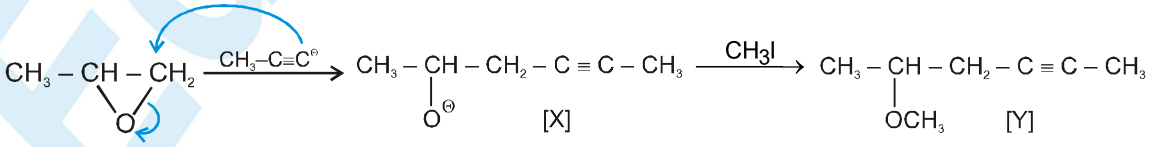
60. β-Hydrogen is absent.

EXERCISE - 2

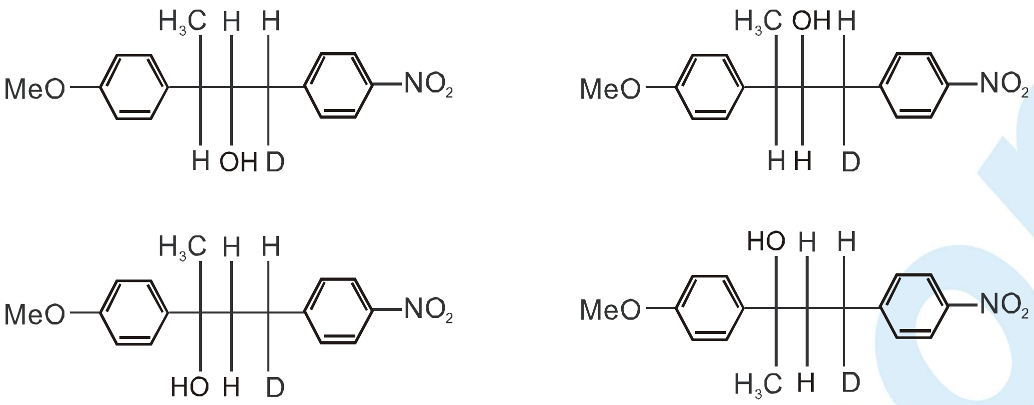
Part # I : Multiple Choice

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

2.

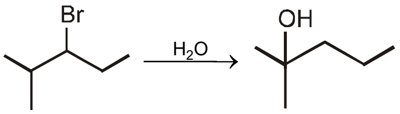


3. Product mixture

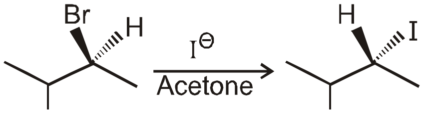


Product mixture react with PCl_5 by S_N2 mechanism and four products are formed. They are positional isomers and diastereomers so after fractional distillation four fraction are obtained.

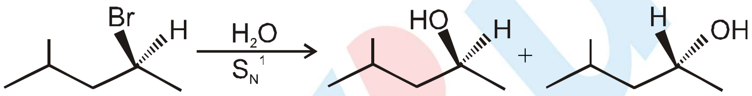
4. Correct product for (3) option.



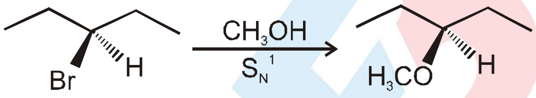
5.



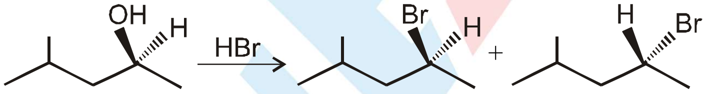
[Only one product]



[Enantiomeric pair]



[Only one product]

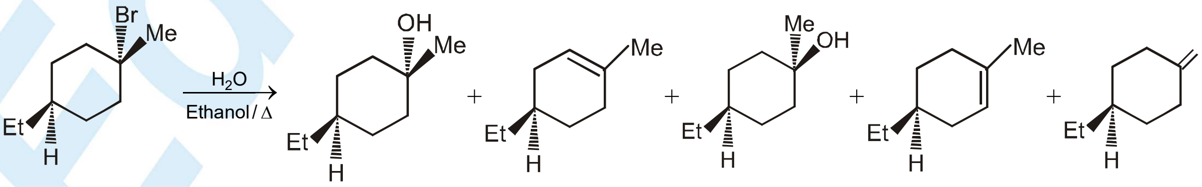


[Enantiomeric pair]

6. If concentration of nucleophile increased S_N2 is affected, but not S_N1 because S_N1 does not depend upon concentration of nucleophile.

7. [C] is incorrect because more than one isomer gives a single alkene on E2 elimination.

8.

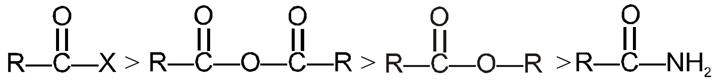


Answer is A, B and C.

9. – As increases the alkyl group rate of reaction decreases in S_N2 reaction so first two can explain by S_N2 mechanism.
– 3° Alkyl halides is favourable for S_N1 mech.
– Alkyl halide is insoluble in water so small amount of alcohol is added to dissolve the alkyl halide in water.

12. Anionic nucleophiles are better nucleophile than their neutral nucleophiles.

13. Hydrolysis of acid derivative is S_N2Th reaction and the reactivity of acid derivatives toward S_N2Th is

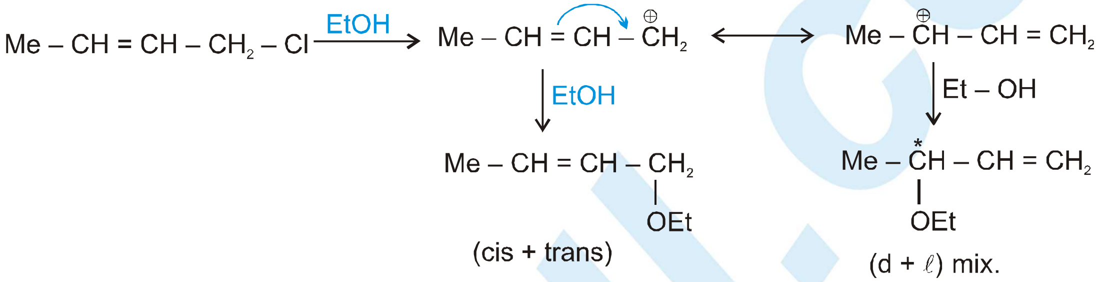


$$R-\overset{O}{\overset{\|}{C}}-X > R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R > R-\overset{O}{\overset{\|}{C}}-O-R > R-\overset{O}{\overset{\|}{C}}-NH_2$$

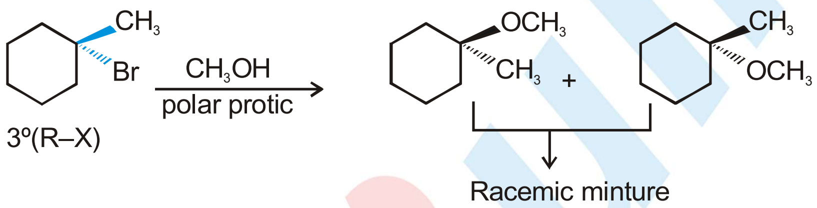
17. In both S_N1 and E_1 rearrangement is possible due to formation of carbocation.

18. All the three have more acdic β–Hydrogen so in presence of strong base gives product through E_{1cB} reaction.

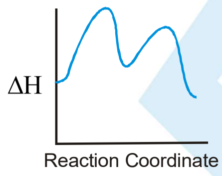
22.



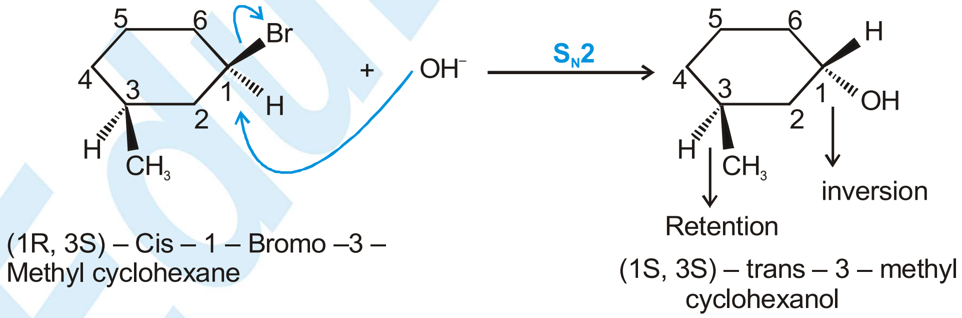
23.



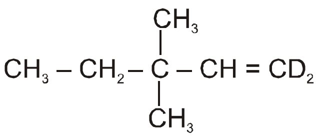
Two transition states are formed and one stable carbocation is formed in the reaction.

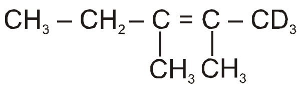


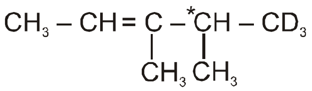
24.

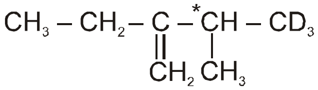


25. Strong anionic Nucleophile so mechanism is S_N2.

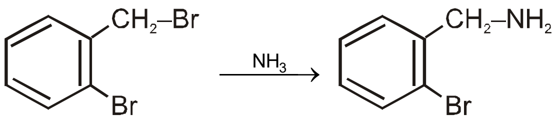
26. X can be 
$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH=CD_2$


$CH_3-CH_2-\underset{CH_3}{C}=\underset{CH_3}{C}-CD_3$ (cis/trans)


$CH_3-CH=\underset{CH_3}{C}-\underset{CH_3}{\overset{*}{C}H}-CD_3$ cis (d,●) & trans (d,●)

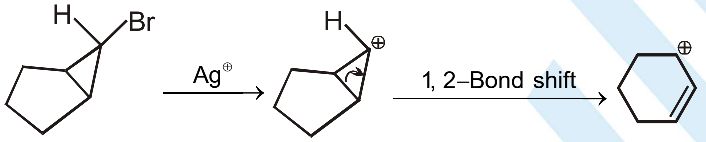

$CH_3-CH_2-\underset{\overset{\|}{CH_2}}{C}-\underset{CH_3}{\overset{*}{C}H}-CD_3$ (d + ●)

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

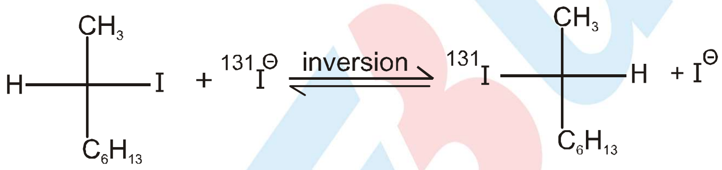
27. 

Because aromatic halides do not give S_N reaction in normal condition.

28. Polar aprotic solvent favours S_N2 mechanism.

29. 

(rearranged carbocation)

30. 

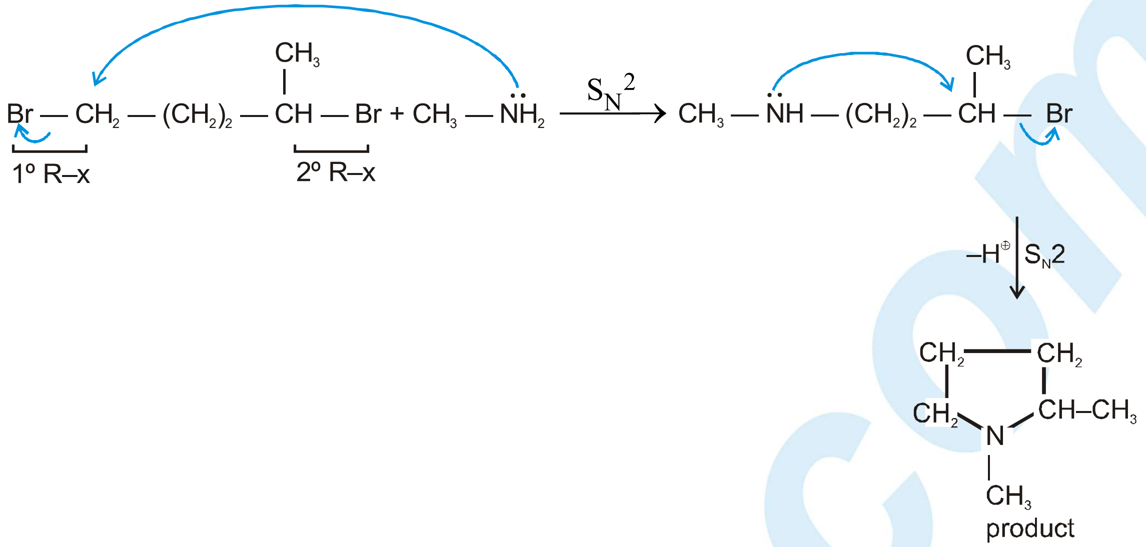
2°(R – X)

The reaction is an equilibrium reaction and at equilibrium both reactant and product are present in equal amount so racemic mixture is formed.

31. Nucleophilic substitution of alcohol is acid catalysed reaction.

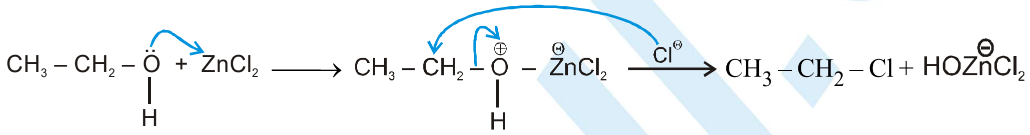
32. $K_1 > K_2$ due to steric hinderance of Nucleophile.

33.



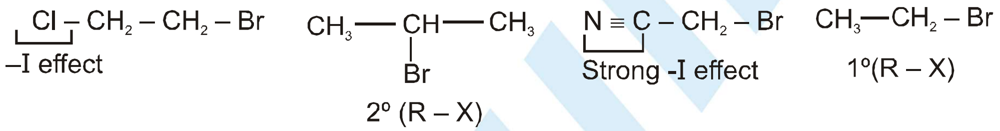
$$\underbrace{Br-CH_2}_{1^\circ\ R-x}-(CH_2)_2-\underbrace{\overset{CH_3}{\overset{|}{CH}}-Br}_{2^\circ\ R-x}+CH_3-\ddot{N}H_2 \xrightarrow{S_N2} CH_3-\ddot{N}H-(CH_2)_2-\overset{CH_3}{\overset{|}{CH}}-Br \xrightarrow[S_N2]{-H^{\oplus}} \text{product}$$

34.



$$CH_3-CH_2-\underset{H}{\underset{|}{\ddot{O}}}+ZnCl_2 \longrightarrow CH_3-CH_2-\underset{H}{\underset{|}{\overset{\oplus}{O}}}-\overset{\ominus}{Z}nCl_2 \xrightarrow{Cl^{\ominus}} CH_3-CH_2-Cl+HO\overset{\ominus}{Z}nCl_2$$

35.



$$\underbrace{Cl-}_{}CH_2-CH_2-Br \qquad CH_3-\underset{Br}{\underset{|}{CH}}-CH_3 \qquad \underbrace{N\equiv C-}_{}CH_2-Br \qquad CH_3-CH_2-Br$$

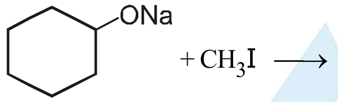
–I effect

2° (R – X)

Strong -I effect

1°(R – X)

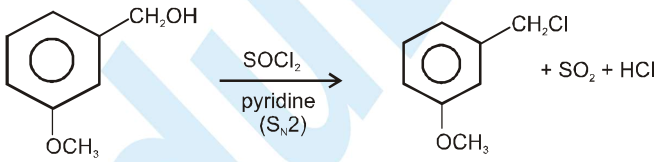
36.



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

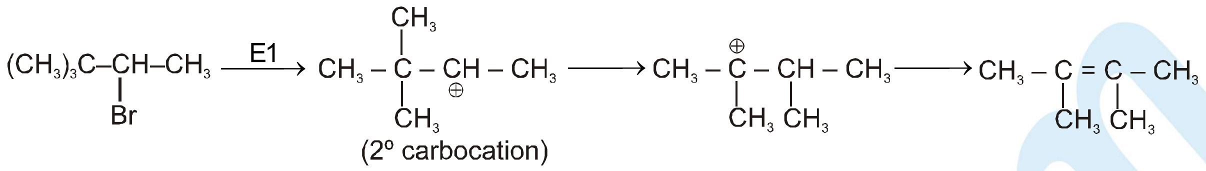
37. Not any alkyl halide can give exclusively 2-Methylbut-2-ene.

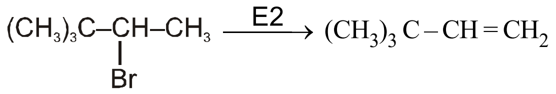
38.



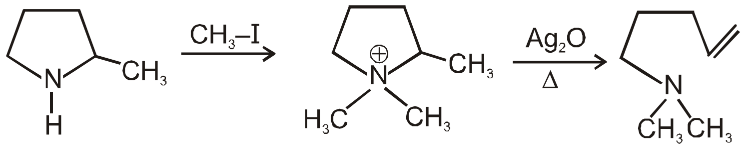
39. I ⇒ Only one T.S. So it is for S_N2 and $\Delta H = -ve$.
II ⇒ Only one T.S. So it is for S_N2 and $\Delta H = +ve$.
III ⇒ More than one T.S. so it is for S_N1 and 1st step is rds.

40.

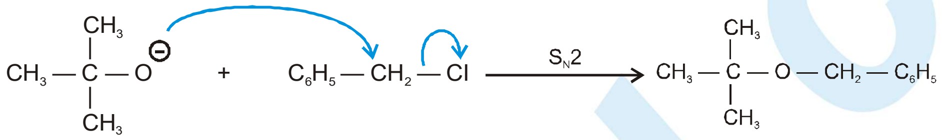




41.



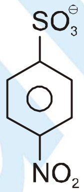
42.



EXERCISE - 4

Subjective Type

1. **(a)** H_2O; **(b)** $F^{\ominus}$; **(c)** $Br^{\ominus}$; **(d)**



2. Protic solvent (c, f, h) ; Aprotic solvent (a, b, d, e,g)

3. (b, g)

4. CN^- and NH_3 are nucleophile.

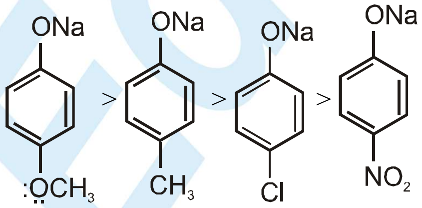
b, c, d, e, f, h

5. a, c, d

6. **(a)** Nucleophilicity $\propto$ Size.

$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > H_2O$

(b) +I and +M group increases nucleophilicity.



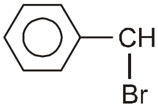
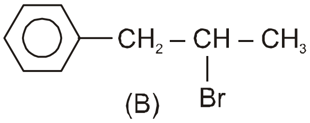
7. **(a)** 2-Bromopentane ; **(b)** 2-Bromo-2-methylbutane

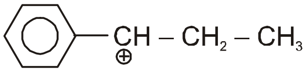
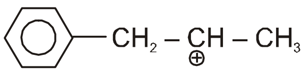
Reason : Carbocation stability order is 3° > 2°> 1°.

8. **(a)** Rate of S_N1 reaction $\propto$ $[(CH_3)_3CBr]$

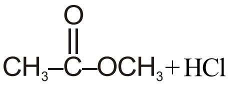
(b) Rate of S_N1 reaction $\propto$ $[(CH_3)_3CBr]$

(a) Rate - doubled ; **(b)** Rate - tripled

9.  (A) &  (B)

(A) is predominant since intermediate  (benzylic carbocation) is more stable due to conjugation than  (secondary carbocation).

10. As the size of the substituents on the α C increases, the tetrahedrally bonded intermediate becomes more crowded. The greater the crowding, the larger is ΔH of the TS and the slower is the reaction.

11. **(a)** 

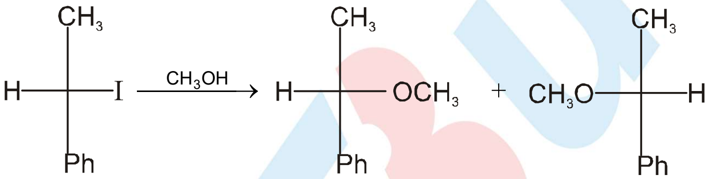
$CH_3-\overset{\overset{O}{||}}{C}-OCH_3 + HCl$

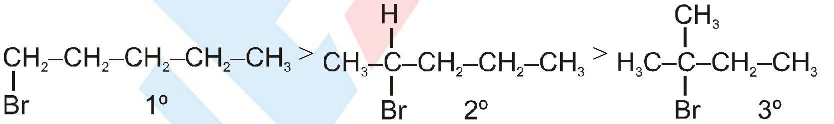
(b) 

$CH_3-\overset{\overset{O}{||}}{C}-OH + CH_3CH_2OH$

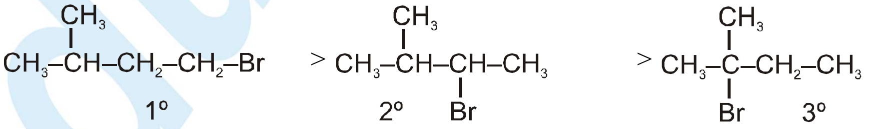
12. NO_2 group at ortho & para position to Cl group facilitate the nucleophilic attack for substitution reaction.

II > III > I

13. 

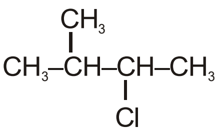
14. **(a)** 

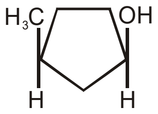
1-Bromopentane 2-Bromopentane 2-Bromo-2-methylbutane

(b) 

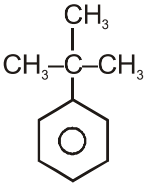
1-Bromo-3-methylbutane 2-Bromo-3-methylbutane 2-Bromo-2-methylbutane

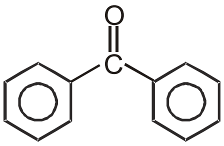
Steric factors are controlling. The usual S_N2 order is 1° > 2° > 3°.

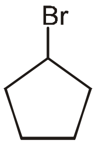
15. **(a)** 
$CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{\underset{Cl}{|}}{CH}-CH_3$

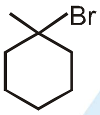
(b) 

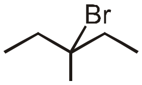
16. (II) > (III) > (IV) > (I)

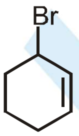
17. **(a)** 

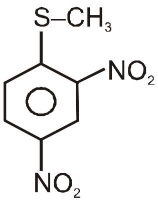
(b) 

18. **(a)** 

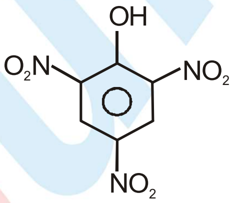
(b) 

(c) 

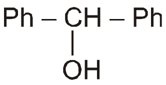
(d) 

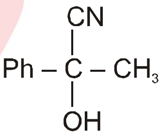
19. **(a)** 

+ NaCl

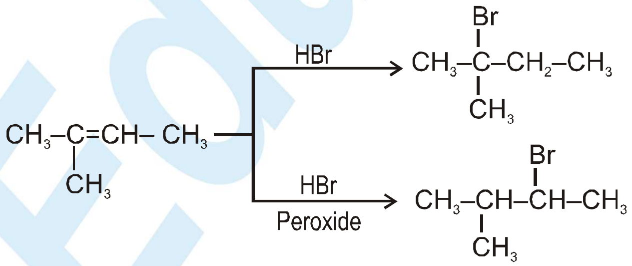
(b) 

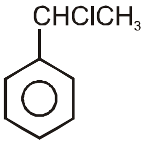
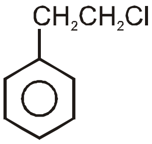
+ NaCl

20. **(a)** 
$Ph-\underset{\underset{OH}{|}}{CH}-Ph$

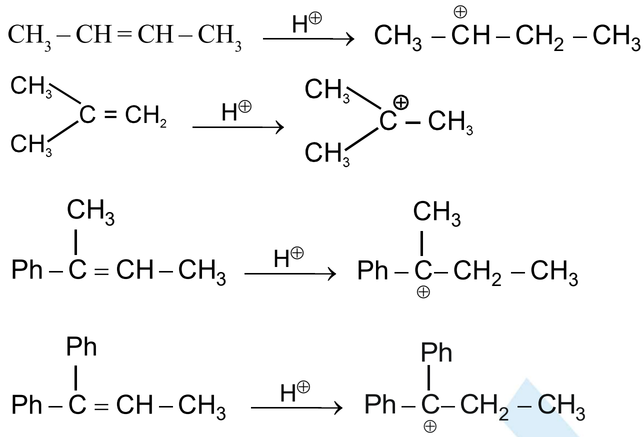
(b) 
$Ph-\overset{CN}{\overset{|}{\underset{\underset{OH}{|}}{C}}}-CH_3$

21. 2 (b & d)

22. 

23. (X) =  ; (Y) = 

24. Since the reactivity towards ionic addition ∝ stability of carbocation intermediate.



I $CH_3-CH=CH-CH_3 \xrightarrow{H^{\oplus}} CH_3-\overset{\oplus}{C}H-CH_2-CH_3$

II $(CH_3)_2C=CH_2 \xrightarrow{H^{\oplus}} (CH_3)_2\overset{\oplus}{C}-CH_3$

III $Ph-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow{H^{\oplus}} Ph-\underset{\oplus}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_3$

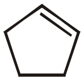
IV $Ph-\overset{Ph}{\overset{|}{C}}=CH-CH_3 \xrightarrow{H^{\oplus}} Ph-\underset{\oplus}{\overset{Ph}{\overset{|}{C}}}-CH_2-CH_3$

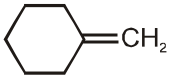
Stability of carbocation intermediate : IV > III > II > I. reactivity of alkene : IV > III > II > I.

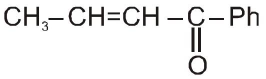
25. $CH_3CH_2CBr_2CHBr_2$

26. $CH_3CH_2CH_2CHBr_2$

27. III < I < II

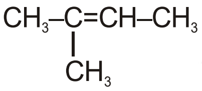
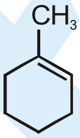
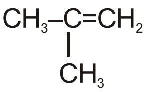
28. **(a)**  **(b)** 

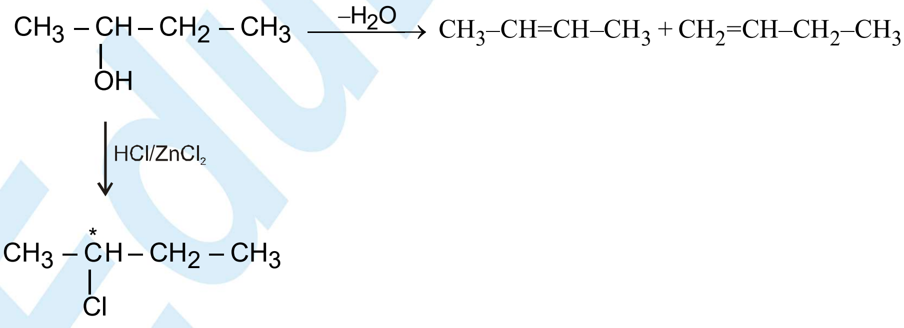
29. 

30. **(a)** $CH_3-CH=CH-CH_3$; E2 **(b)** $CH_3-CH=CH-Ph$; E1 **(c)**  $CH_3-CH=CH-\underset{\|}{\overset{}{C}}-Ph$; E1cB

$\underset{O}{}$

31. I < III < II.

32. **(a)**  $CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH_3$ **(b)**  **(c)**  $CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$

33. 

$$CH_3-\underset{OH}{\underset{|}{C}H}-CH_2-CH_3 \xrightarrow{-H_2O} CH_3-CH=CH-CH_3 + CH_2=CH-CH_2-CH_3$$

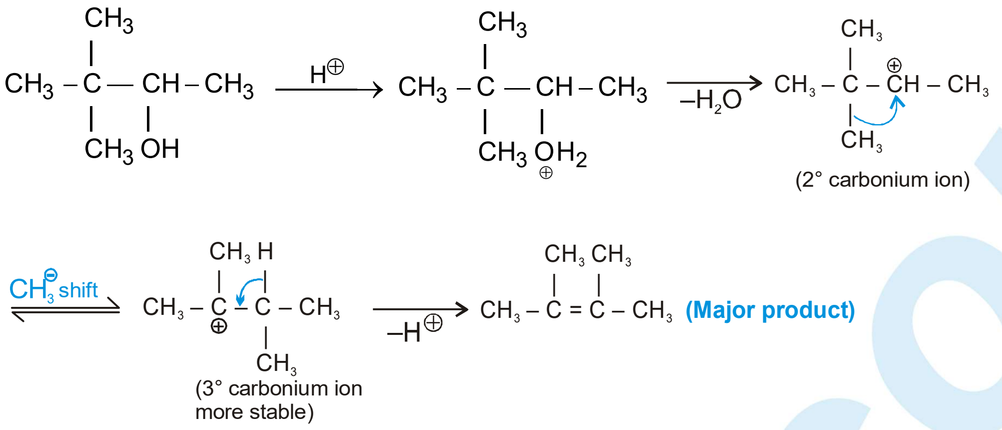
$$\big\downarrow HCl/ZnCl_2$$

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

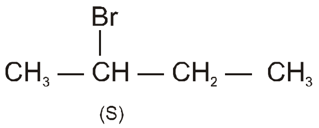
(d + ●)

Y = 3, Z = 2

34. **Mechanism**

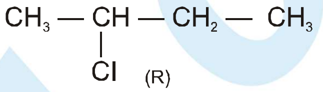


35. **(a)**



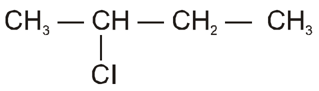
$CH_3 - \underset{(S)}{\overset{Br}{CH}} - CH_2 - CH_3$

(b)



$CH_3 - \underset{Cl\ (R)}{CH} - CH_2 - CH_3$

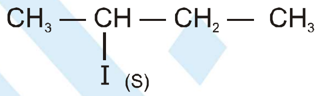
(c)



$CH_3 - \underset{Cl}{CH} - CH_2 - CH_3$

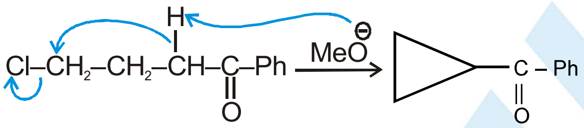
(Racemic mixture)

(d)



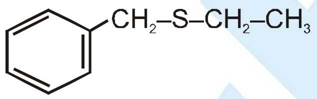
$CH_3 - \underset{I\ (S)}{CH} - CH_2 - CH_3$

36.



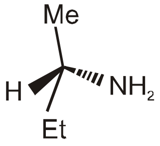
37. In a period nucleophilicity depends upon electronegativity but not on size since there is no such large difference in atomic radius. In polar aprotic solvent anions are not solvated therefore in a group smaller anions / atoms being less stable react faster. But in polar protic solvents smaller atoms/anions are highly solvated herefore larger size nucleophiles react faster.

38. **(a)**

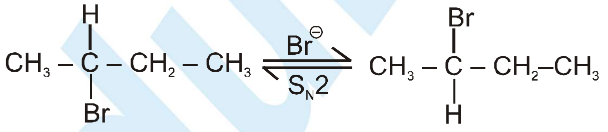


(b) $CH_3–CH_2–CH_2–CH_2–C{\equiv}C–CH_3$

(c)



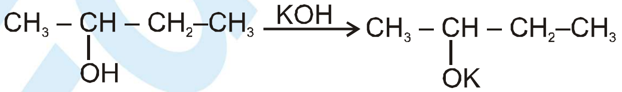
39. **(a)**



$CH_3 - \underset{Br}{\overset{H}{C}} - CH_2 - CH_3 \underset{S_N2}{\overset{Br^{\ominus}}{\rightleftharpoons}} CH_3 - \underset{H}{\overset{Br}{C}} - CH_2–CH_3$

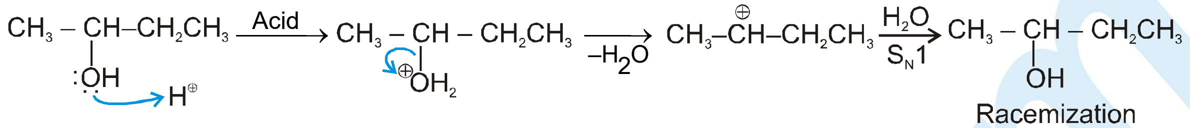
At equilibrium, reactant and product will be in equal amount i.e. reacmic mixture.

(b)

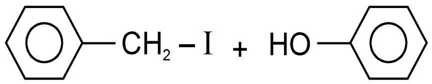


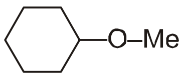
$CH_3 - \underset{OH}{CH} - CH_2–CH_3 \xrightarrow{KOH} CH_3 - \underset{OK}{CH} - CH_2–CH_3$

It is an acid base reaction so no change at chiral center.

(c) 

$$CH_3-\underset{\ddot{O}H}{CH}-CH_2CH_3 \xrightarrow{Acid} CH_3-\underset{\overset{\oplus}{O}H_2}{CH}-CH_2CH_3 \xrightarrow[-H_2O]{} CH_3-\overset{\oplus}{C}H-CH_2CH_3 \xrightarrow[S_N1]{H_2O} CH_3-\underset{OH}{CH}-CH_2CH_3$$

40. **(a)** $(P+Q) = PhCH_2OH + PhCH_2I$ **(b)** $(X+Y) =$ 

(c) $(W) =$  **(d)** $(Z) = (CH_3)_2CHOCH_2CH_2CH_3$

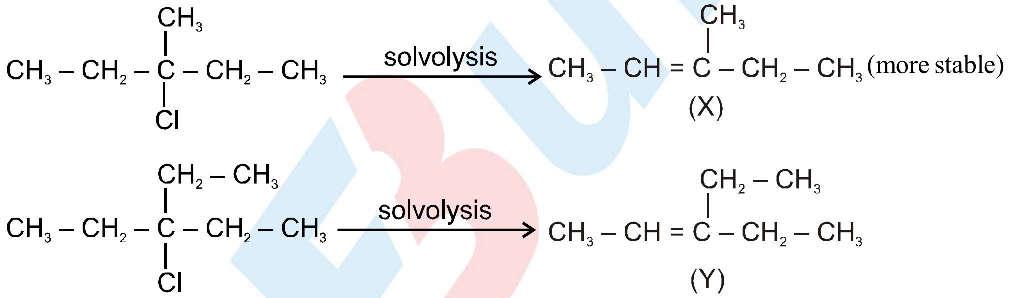
41. **(a)** Rate will be doubled
(b) Rate will be increased to six times
(c) Elimination product dominates

42. Say after completion (100%) of reaction, there will be 66.66% S_N1 product (Racemic mixture) and 33.33% S_N2 product (inverted product)
So enantiomeric excess = 33.33 %
Pure (S) -2-butanol has + 13.5° sp.rotation

So observed rotation $= \dfrac{33.33\times 13.5^{\circ}}{100} = 4.5^{\circ}$

43. $$\% S_N1 = \frac{S_N1}{S_N2+S_N1}\times 100 = \frac{0.24\times 10^{-5}[RX]}{4.7\times 10^{-5}[RX][5]+0.24\times 10^{-5}[RX]}\times 100$$

$$= \frac{0.24}{4.7\times 5+0.24}\times 100 = 1.01\%$$

44. 

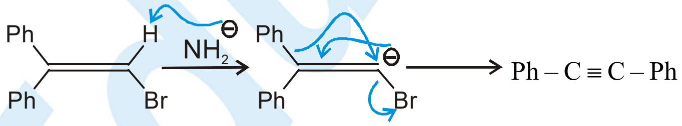
$$CH_3-CH_2-\underset{Cl}{\overset{CH_3}{C}}-CH_2-CH_3 \xrightarrow{solvolysis} \underset{(X)}{CH_3-CH=\overset{CH_3}{C}-CH_2-CH_3}\ \text{(more stable)}$$

$$CH_3-CH_2-\underset{Cl}{\overset{CH_2-CH_3}{C}}-CH_2-CH_3 \xrightarrow{solvolysis} \underset{(Y)}{CH_3-CH=\overset{CH_2-CH_3}{C}-CH_2-CH_3}$$

Greater product stability accounts for an increases in elimination.

45. **(a)** $Ph\,CMe_2\,Br$ **(b)** $Ph\,CH_2-CH_2\,Br$ **(c)** $Ph\,CMe_2\,Br$

46. For reaction **(a)** the transition state is more polar than the reactant therefore the activation energy decreases. While for the reaction **(b)** the transition state is less polar than the reactants therefore activation energy increases.

47. 

(α = Elimination)

EXERCISE - 5

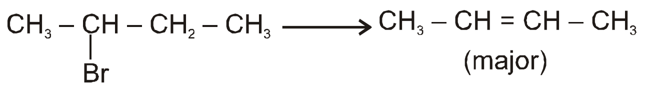
Part # I : AIEEE/JEE-MAIN

1. Among the given option Cl^- is the best leaving group hence the rate of reaction will be fastest in case of RCOCl.

2. According to stability of carbocation.

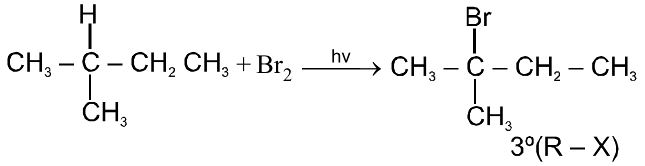
3. Steric hinderence.

4.



$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3 \longrightarrow \underset{(major)}{CH_3-CH=CH-CH_3}$$

5.



$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2\,CH_3+Br_2 \xrightarrow{hv} CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3 \quad 3^o(R-X)$$

2-Bromo-2-methyl butane

6. Generally, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation. Thus, a reaction involving two different reactants can never be unimolecular.

7. For endothermic reaction, $\Delta H =$ ve $\quad \Delta H = E_f - E_b$, it means $E_b < E_f$.

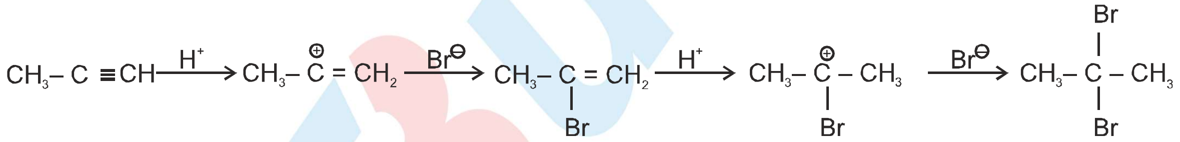
8. As steric hinderance increases around carbonyl group, rate of nucleophilic addition reaction decreases.

9. Since this reaction will follow S_N2 pathway so stronger the base better its nucleophilicity.
The correct order of nucleophiles would be :
$CH_3O^- > OH^- > PhO^- > AcO^-$

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

11. The reactivity of a compound towards S_N2 reaction decreases as the crowding at the C-atom containing leaving group increases.

12.



$$CH_3-C\equiv CH \xrightarrow{H^+} CH_3-\overset{\oplus}{C}=CH_2 \xrightarrow{Br^\ominus} CH_3-\underset{\underset{Br}{|}}{C}=CH_2 \xrightarrow{H^+} CH_3-\underset{\underset{Br}{|}}{\overset{\oplus}{C}}-CH_3 \xrightarrow{Br^\ominus} CH_3-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$$

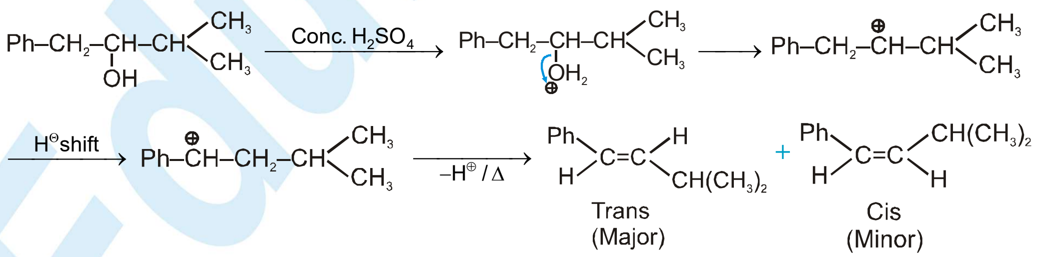
13. CH_3Cl show complete stereochemical inversion during an S_N2 reaction.

14. $$\frac{1}{2}A \longrightarrow 2B \Rightarrow -\frac{1}{1/2}\frac{d(A)}{dt}=\frac{1}{2}\frac{d(B)}{dt} \Rightarrow \boxed{-\frac{d(A)}{dt}=\frac{1}{4}\frac{d(B)}{dt}}$$

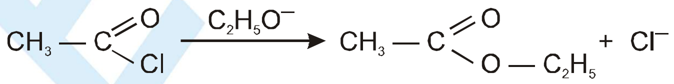
15. Reaction of alcohol with HCl and anhydrous $ZnCl_2$ is an S_N reaction.
3° alcohol react faster with HCl and anhydrous $ZnCl_2$ since it forms more stable carbocation intermediate.

16. Rate of S_N1 reaction $\propto$ stability of carbocation

17.

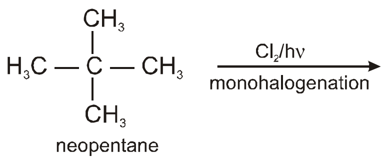


18.



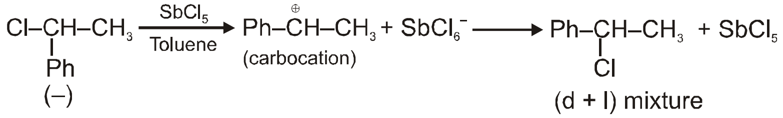
19. $RS^{\ominus}$ is more nucleophilic than $R–O^{\ominus}$ due to larger size of orbitals and polarization but $RS^{\ominus}$ is less basic than $R–O^{\ominus}$ as the negative charge get stabilized due to larger size of sulphur atom.

20.



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\text{monohalogenation}]{Cl_2/h\nu} \text{single product.}$$

21.



$$Cl–\underset{Ph}{CH}–CH_3 \xrightarrow[\text{Toluene}]{SbCl_5} Ph–\overset{\oplus}{C}H–CH_3 + SbCl_6^- \longrightarrow Ph–\underset{Cl}{CH}–CH_3 + SbCl_5$$

22. 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.

23. Rate of S_N2 reaction $\propto \dfrac{1}{\text{steric over crowding in transition state}}$

24. For any S_N1 reaction activity is decided by ease of dissociation of alkyl halide

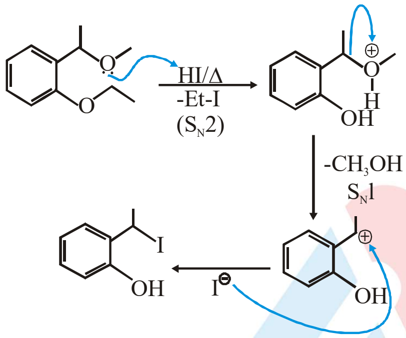
$$R-X \rightleftharpoons R^{\oplus} + X^-$$

Higher the stability of $R^{\oplus}$ (carbocation) higher would be reactivity of S_N1 reaction.

$$CH_3-CH_2-\overset{\oplus}{C}H_2 < CH_3-\overset{\oplus}{C}H-CH_2-CH_3 < p-H_3CO-C_6H_4-\overset{\oplus}{C}H_2$$

Hence correct order is : [II < I < III]

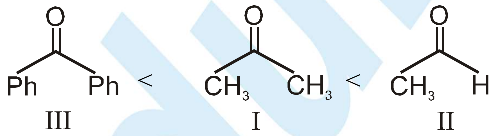
25.



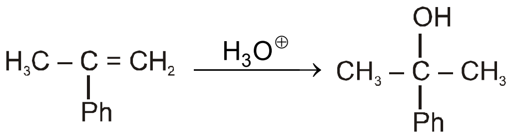
It is nucleophilic substitution reaction.

Part # II : IIT-JEE ADVANCED

1.



2.



$$H_3C-\underset{Ph}{C}=CH_2 \xrightarrow{H_3O^{\oplus}} CH_3-\underset{Ph}{\overset{OH}{C}}-CH_3$$

3. Concentrated H_3PO_4 is a dehydrating agent.

4. $Ph_3C—CO \xrightarrow[H_2O]{H^+} Ph_3C—OH + ROH$

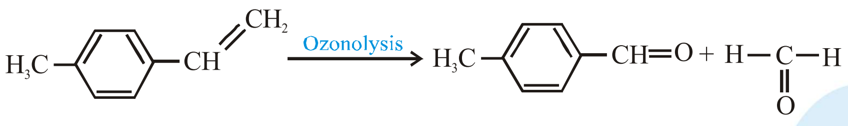
The reaction proceeds by S_N1 Mechanism :

$$Ph_3C–OR + H^{\oplus} \rightleftharpoons Ph_3CO^{\oplus}HR \rightleftharpoons Ph_3C^{\oplus} \xrightleftharpoons{H_2O} Ph_3C–O^{\oplus}H_2 \xrightarrow{-H^{\oplus}} Ph_3C–OH$$

Greater the electron releasing effect of the attached groups greater is the stability of intermediate carbocation, & faster is the rate of reaction.

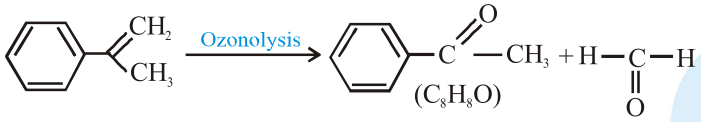
If two ph – groups are replaced by MeO··· grops, strong +M effect of MeO– groups stablize, the carbocation better there by making the reaction faster.

5. **(B)**



(C_8H_8O)

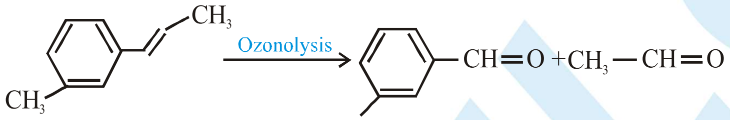
It gives Cannizaro rxn but not haloform rxn



(C_8H_8O)

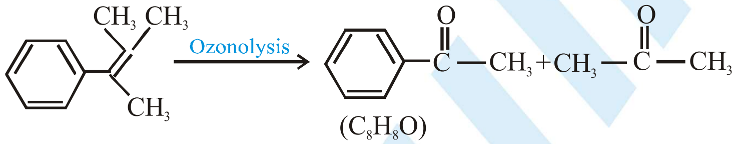
It gives haloform but not Cannizaro rxn.

(C)



(C_8H_8O)

It gives Cannizaro rxn but not haloform rxn.

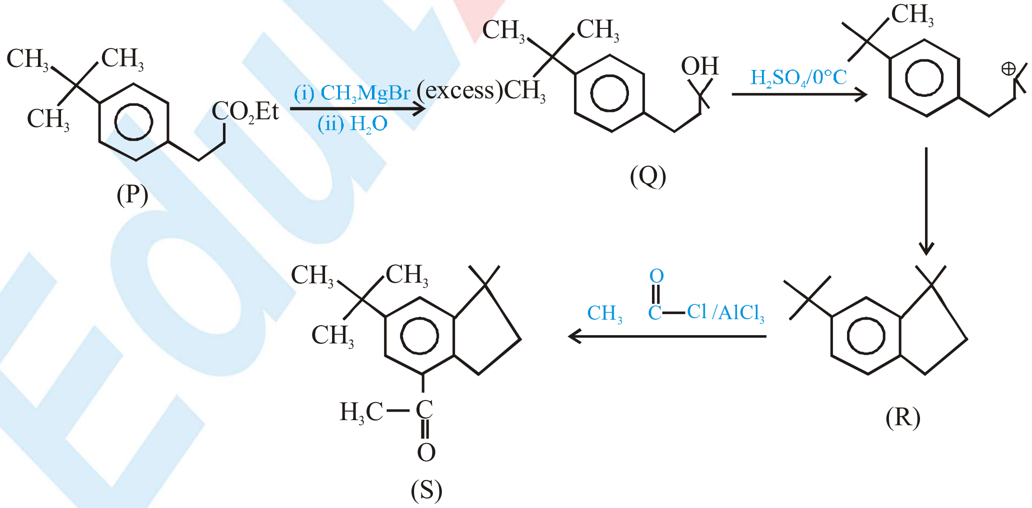


(C_8H_8O)

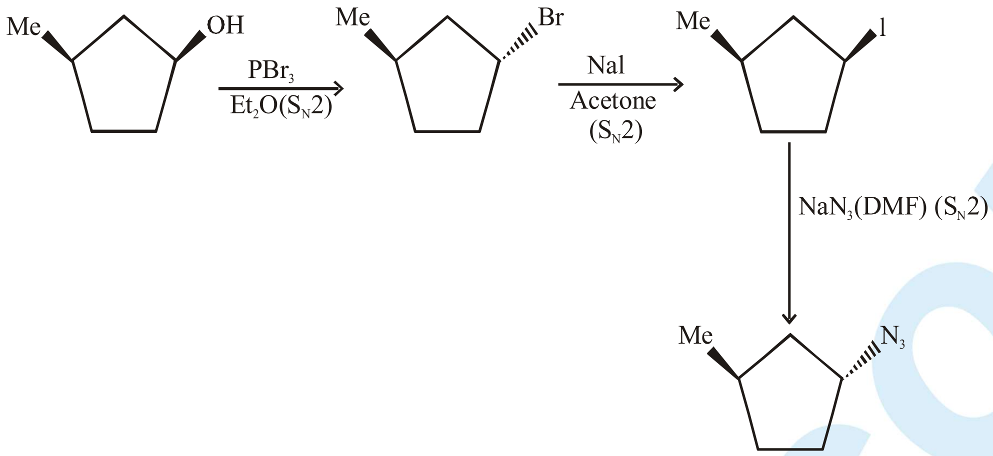
It gives haloform rxn but not Cannizaro rxn

6. **(A)** Benzylic acid and 1° halides both follow S_N2 mechanism.
(B) Benzylic 2° halides can undergo inversion of configuration.
(C) The order of reactivity would be IV > I > III if both S_N1 and S_N2 are considered suitably for substates.
(D) Benzylic and 3° halides both follow S_N1 mechanism.

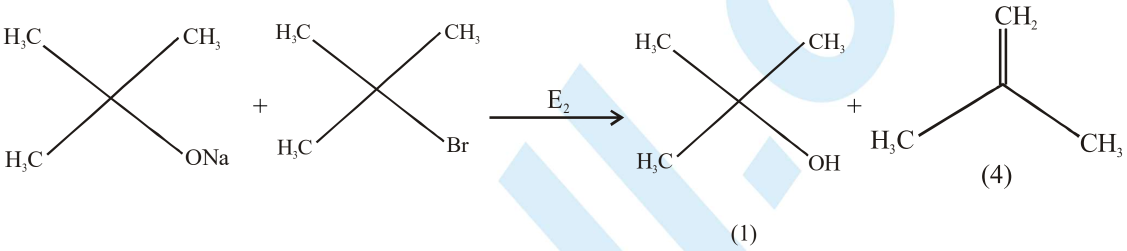
7.



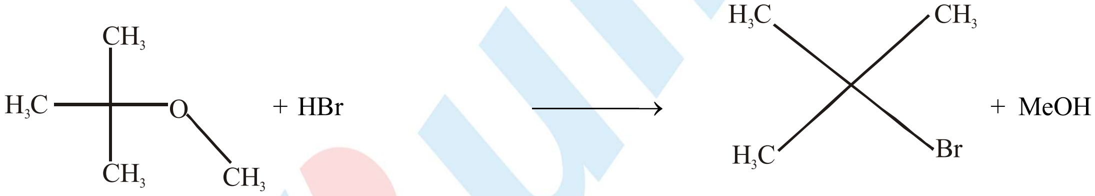
9.


Me
OH
PBr_3
$Et_2O(S_N2)$
Me
Br
NaI
Acetone
(S_N2)
Me
I
$NaN_3(DMF)\ (S_N2)$
Me
N_3

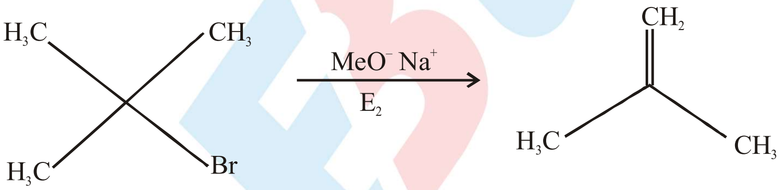
10. **P :**


H_3C
CH_3
H_3C
ONa
+
H_3C
CH_3
H_3C
Br
E_2
H_3C
CH_3
H_3C
OH
(1)
+
CH_2
H_3C
CH_3
(4)

Q :


CH_3
H_3C
O
CH_3
CH_3
+ HBr
H_3C
CH_3
H_3C
Br
+ MeOH

R :

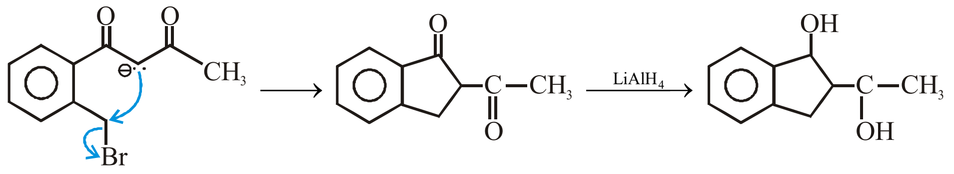

H_3C
CH_3
H_3C
Br
$MeO^- Na^+$
E_2
CH_2
H_3C
CH_3

S :


H_3C
CH_3
H_3C
ONa
+ MeBr
SN^2
H_3C
CH_3
H_3C
OMe

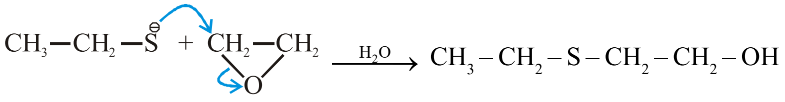
MOCK TEST

1

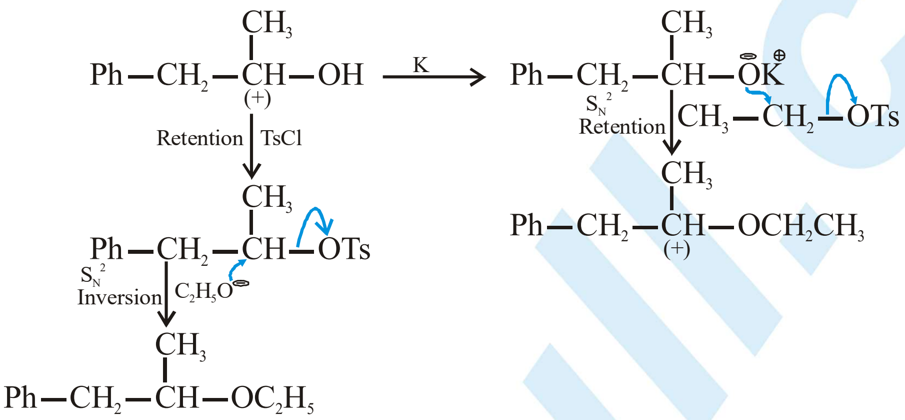


2 S_N2' mechanism

3



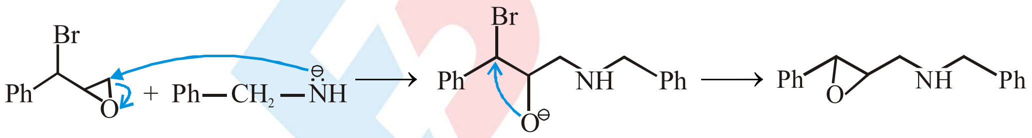
4



5 By the question **(B)** is correct answer.

6 $Ph-OH \xrightarrow{\overset{\ominus}{O}H} Ph\overset{\ominus}{O} \xrightarrow{Me_2SO_4} PhOMe$

7

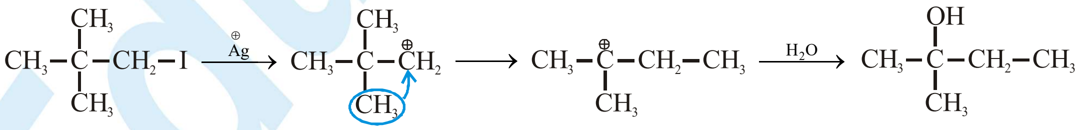


8 Example of pinacol-pinacolone rearrangement.

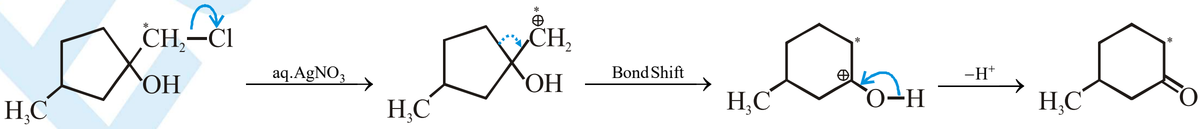
9 Given compound is 'S' in configuration due to Walden inversion on attack by $I^{\ominus}$ we get 'R' configuration.

10 Sterically hindered base leads to elimination product.

11

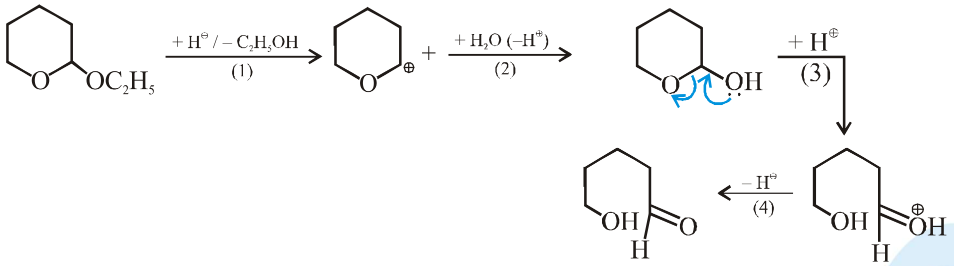


12

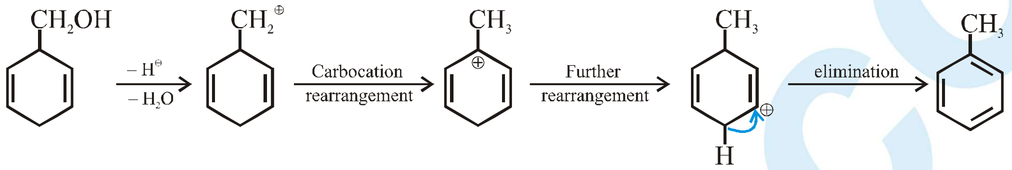


13 Example of pinacol pinacolone rearrangement.

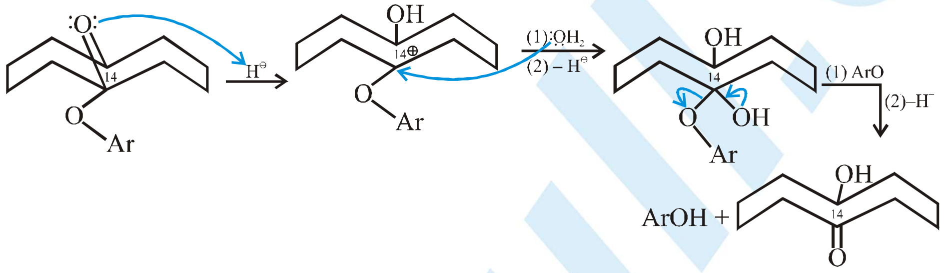
14



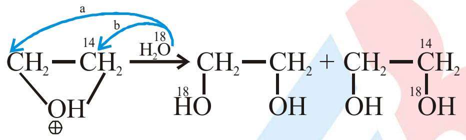
15



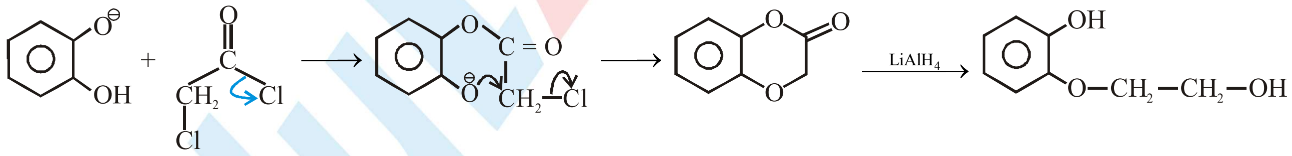
17



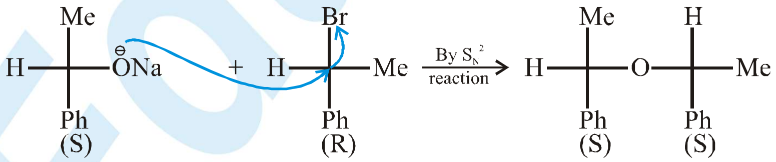
18



20



23 **(A)**

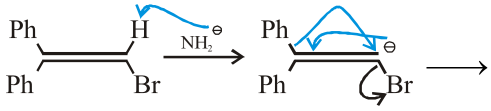


24 Solvent effect.

29 $X \longrightarrow R, \quad Y \longrightarrow S, \quad Z \longrightarrow Q, \quad W \longrightarrow P$

30 A → q, B → r, C → q, D → s

31



$\longrightarrow$ Ph – C ≡ C – Ph (α = Elimination)

32

A =


B =

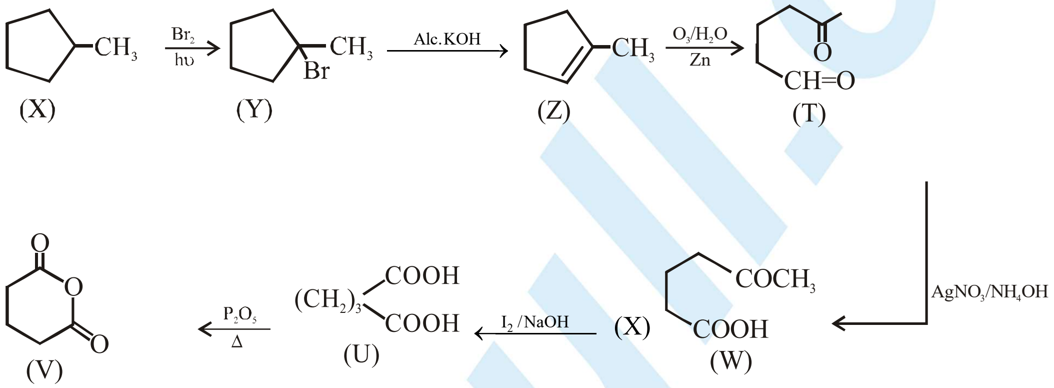

C =


D =


E =


F =


35



38 **(B)**