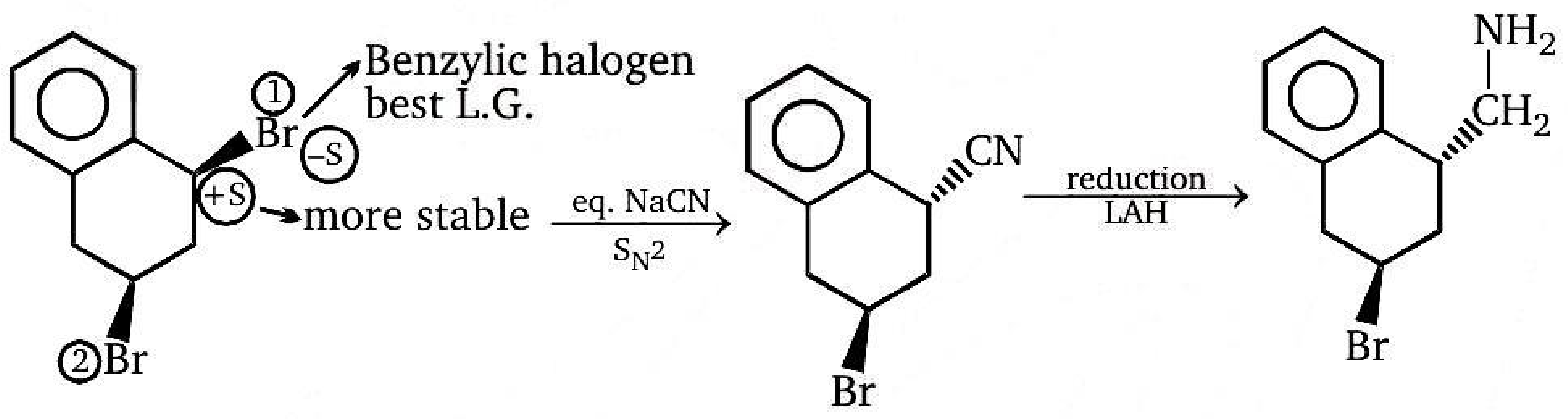
5c Alkyl Halides

Level - 1

1. (c)

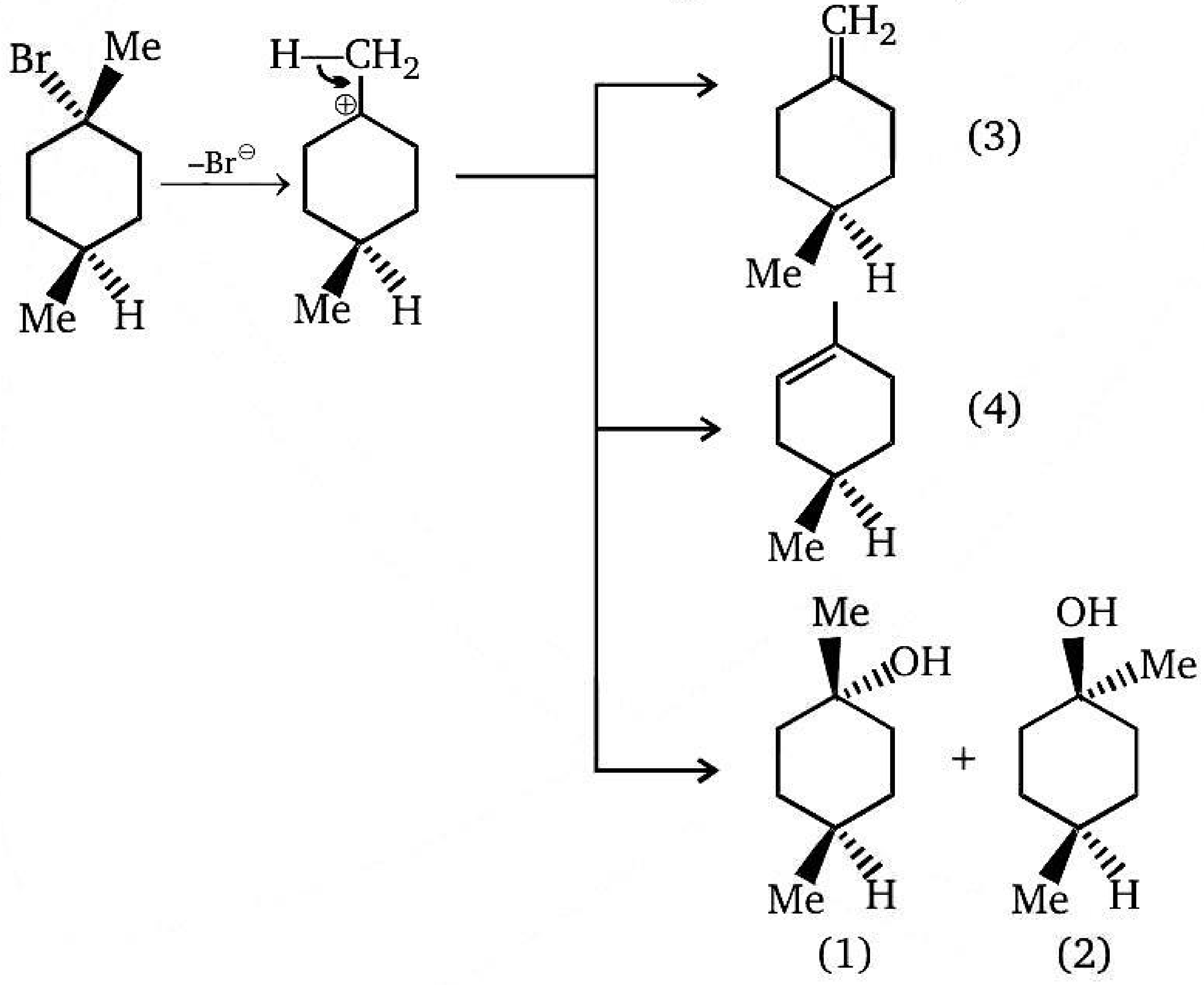


2. (c) $R-Cl \xrightarrow{(1)\ KCN} R-CN \xrightarrow{LAH} \underset{(1°)}{R-CH_2-NH_2} \rightarrow$ (functional group isomers)

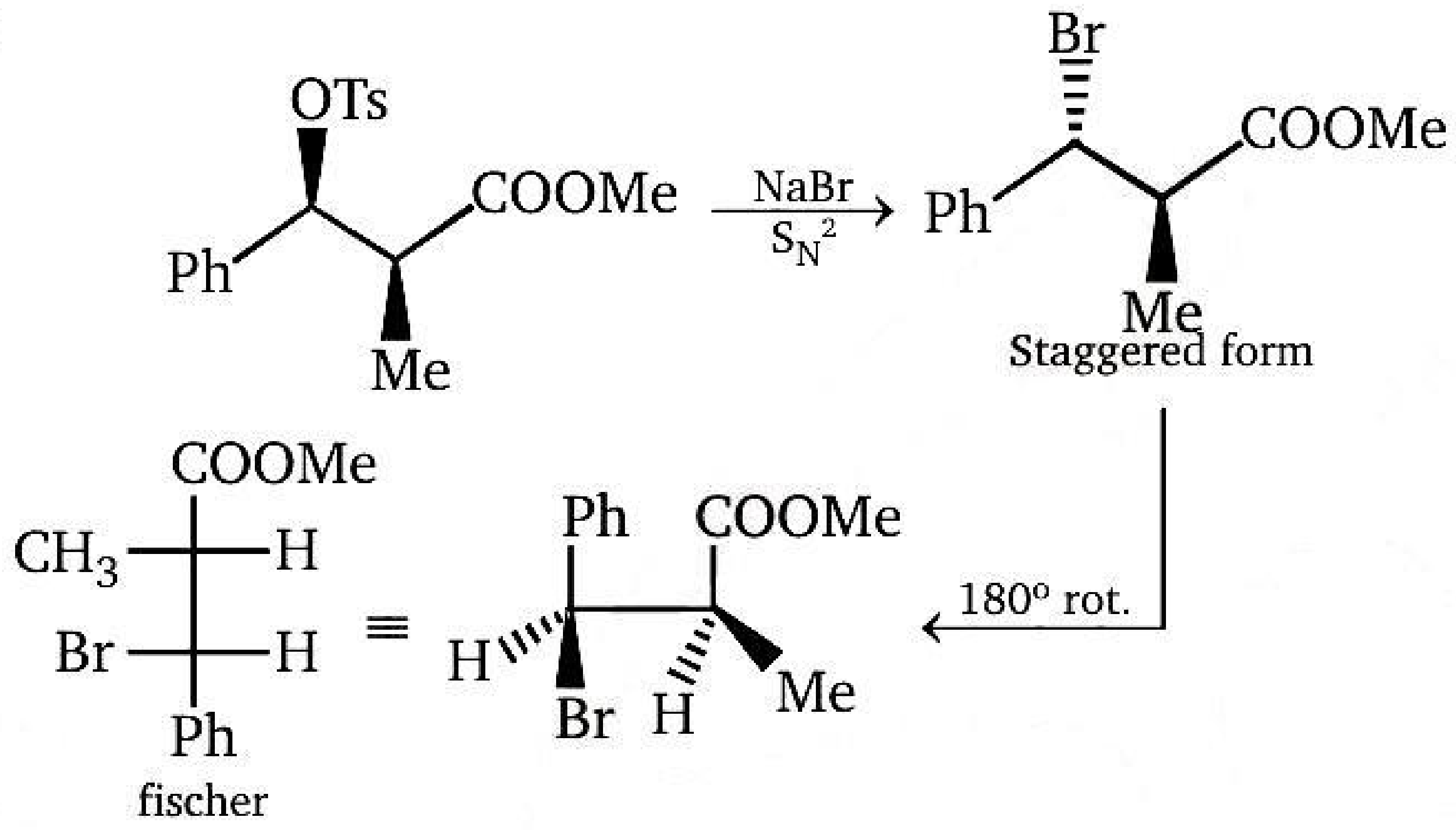
$R-Cl \xrightarrow{(1)AgCN} R-NC \xrightarrow{LAH} \underset{(2°)}{R-NH-CH_3}$

3. (b) 'Cl' is best L.G. & inversion of configuration takes place.

4. (a)

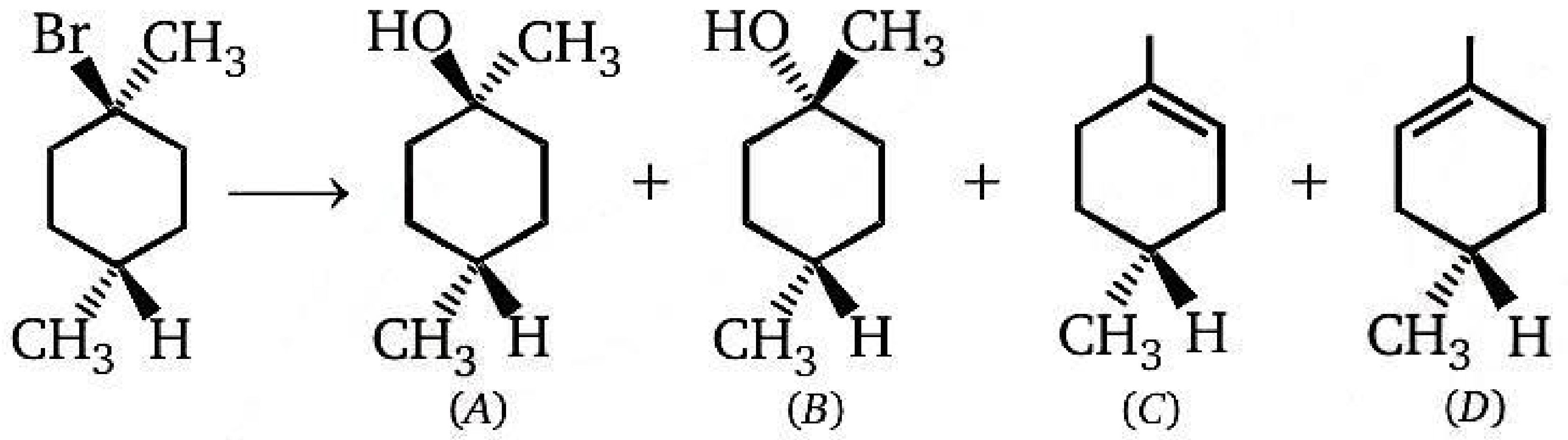


5. (a)



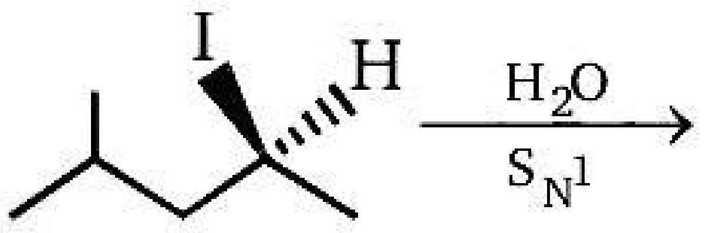
6. (a) Nucleophilicity $\propto \dfrac{1}{\text{size of Nu}^{\ominus}}$

7. (c)



8. (b)

9. (b)



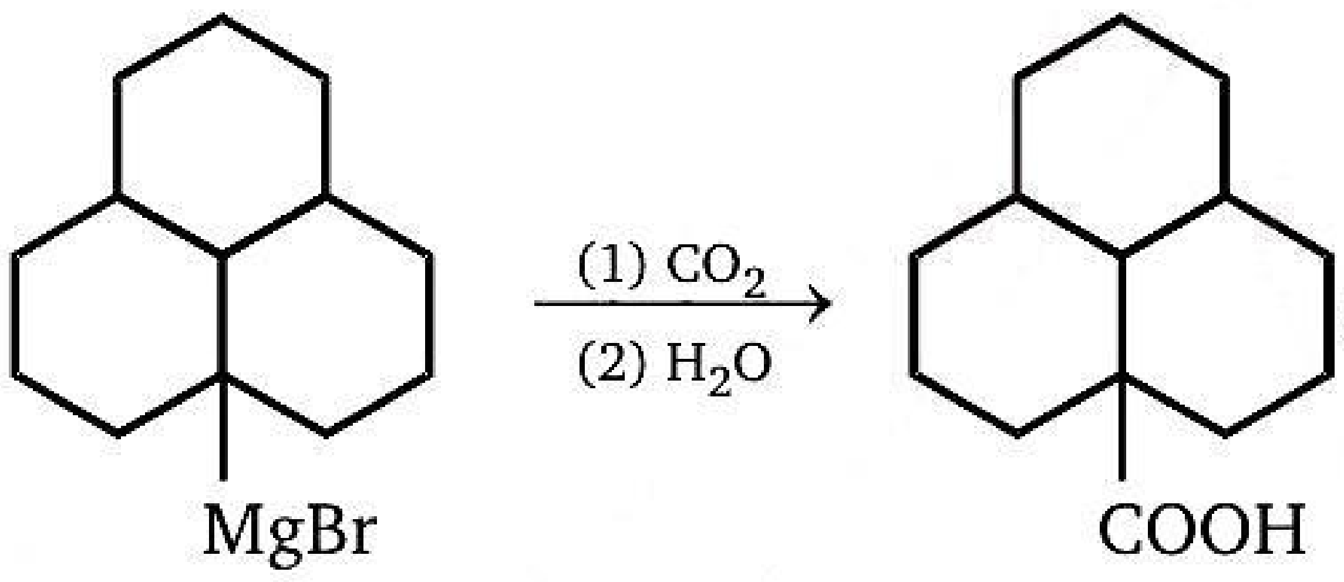
(*dl*) Racemic mixture.

10. (d) Informative question [All are correct]

11. (c) At bridge head S_N2 doesn't take place. According to bredt's rule bridge head carbon can't be sp^2-hybridized.

(NaI + Acetone) + R–X reaction S_N2 depends on

(1) Leaving group tendency ∴

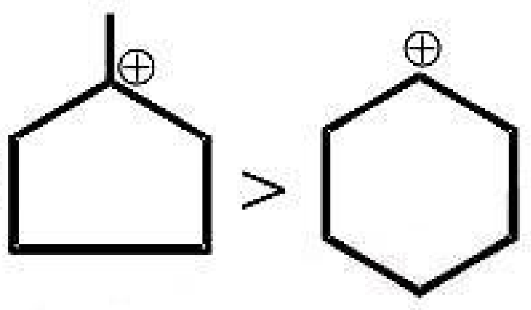


is suitable preparation.

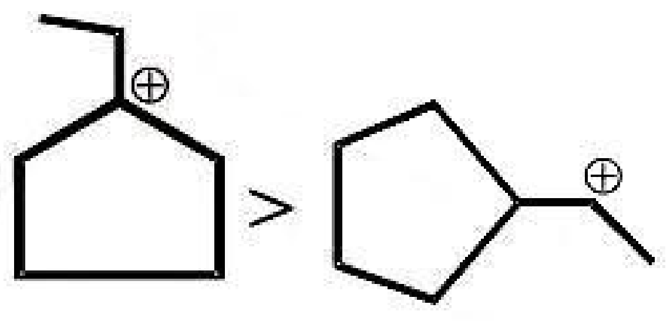
(2) Steric crowding.

12. (c) $EtS^{\ominus}$ is weak base than $EtO^{\ominus}$ but more $Nu^{\ominus}$ than $EtO^{\ominus}$ due to less solvation and more polarizability of donar 'S' atom.

13. (d) (a)

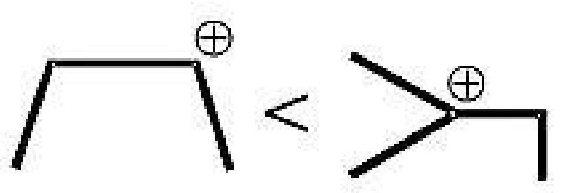


(b)



(c)

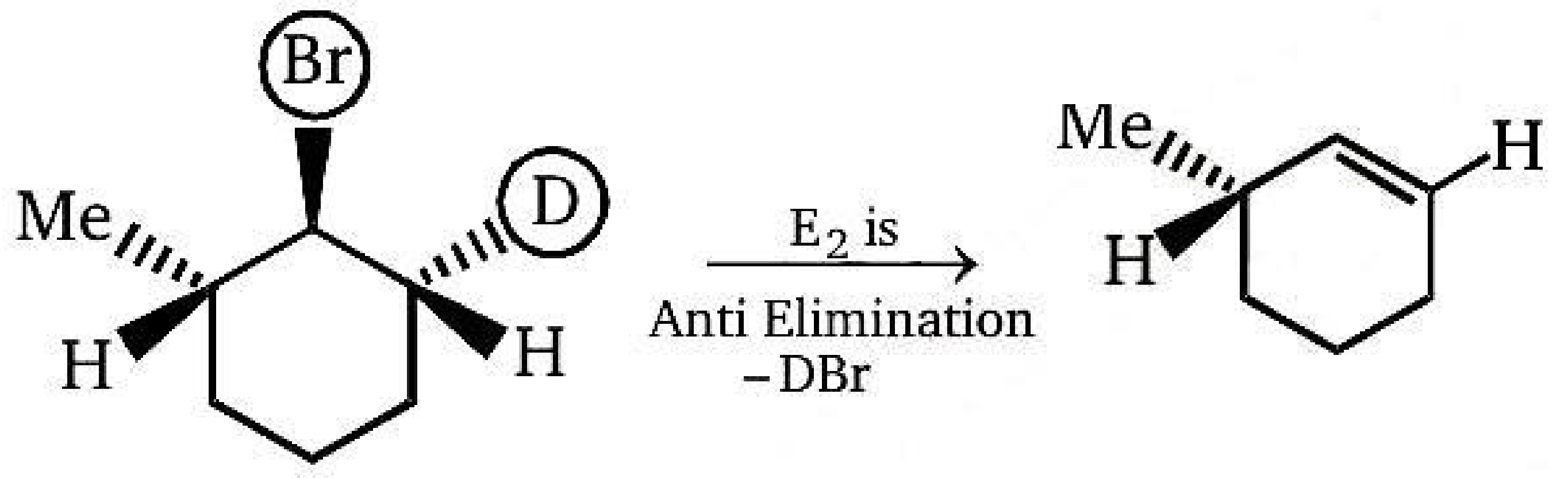
(d)



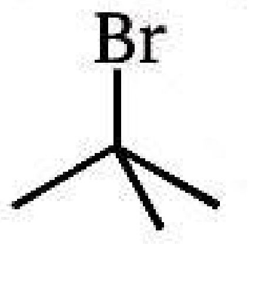
14. (a) S_{N^1} reaction.

15. (c) Hydrolysis of –CN & substitution of –Br group takes place in given reaction.

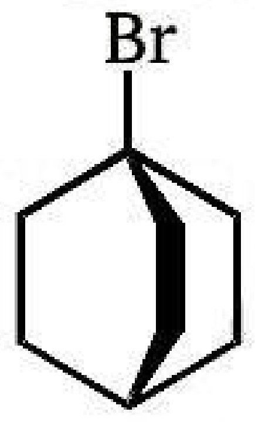
16. (c)



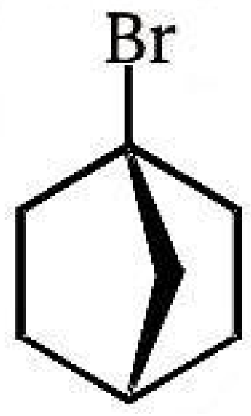
17. (c) The effect of structure on relative reactivity may be seen particularly clearly when a halogen atom is located at the bridgehead of a bicyclic system. Thus the following rates were observed for solvolysis in 80% aqueous ethanol at 25°:



(8)
1



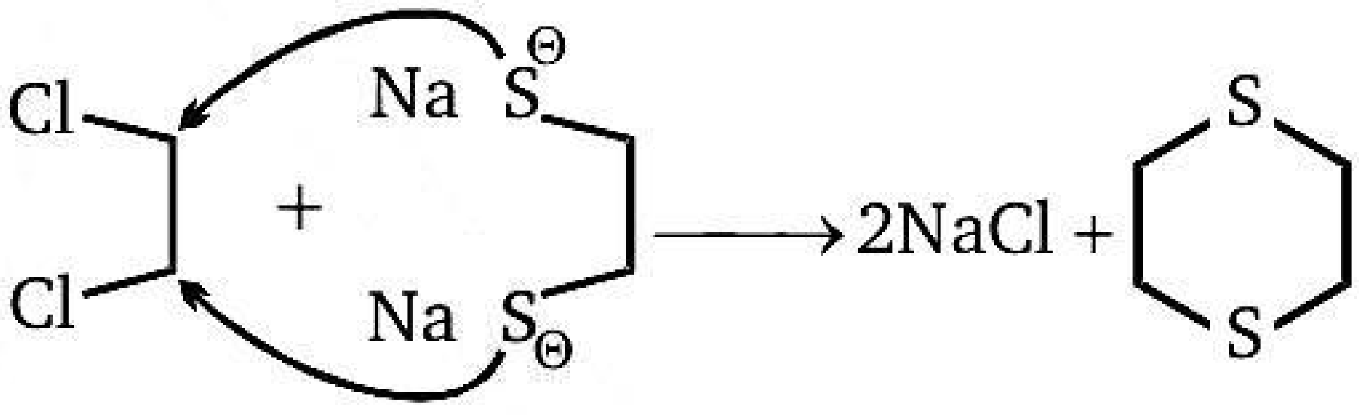
(16)
$\approx 10^{-6}$



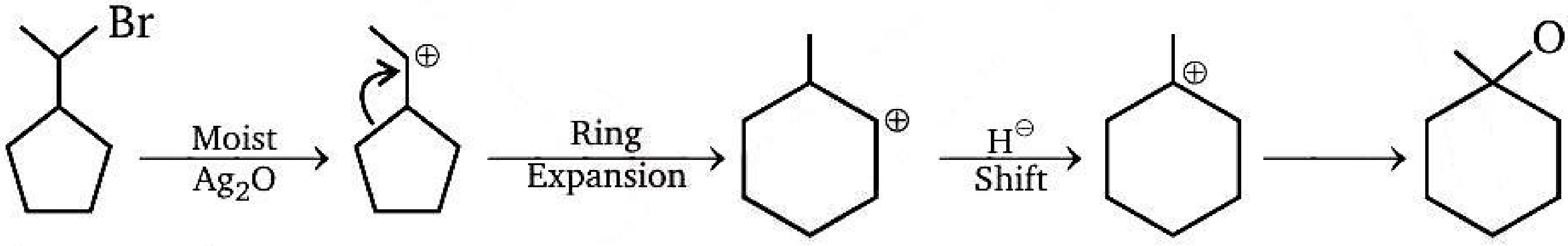
(17)
$\approx 10^{-14}$

All are tertiary halides so that attack by the S_{N^2} mode would not be expected to occur on (16) or (17) any more than it did on (8). S_{N^2} attack 'from the back' on the carbon atom carrying Br would in any case be prevented in (16) and (17) both sterically by their cagelike structure, and also by the impossibility of forcing their fairly rigid framework through transition states with the required planar distribution of bonds to the bridgehead carbon atom. Solvolysis via rate- limiting formation of the ion pair (S_{N^1}), as happens with (8) is also inhibited because the resultant carbocations from (16) and (17) would be unable, because of their rigid frameworks, to stabilise themselves by collapsing to the stable planar state. These carbocation intermediates are thus of very much higher energy level than usual, and therefore are formed only slowly and with reluctance. The very greatly reduced solvolysis rate of (17) compared with (16) reflects the greater rigidity about the bridgehead (cationic) carbon with a one carbon (17), than with a two- carbon (16), bridge.

18. (a)

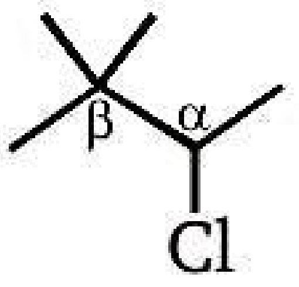


19. (c) Ring expansion.

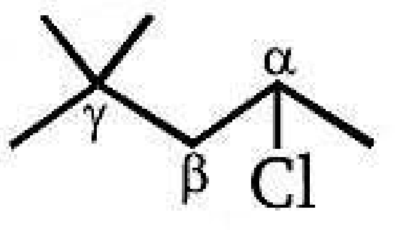


20. (b) S_{N^2} reaction.

21. (d)



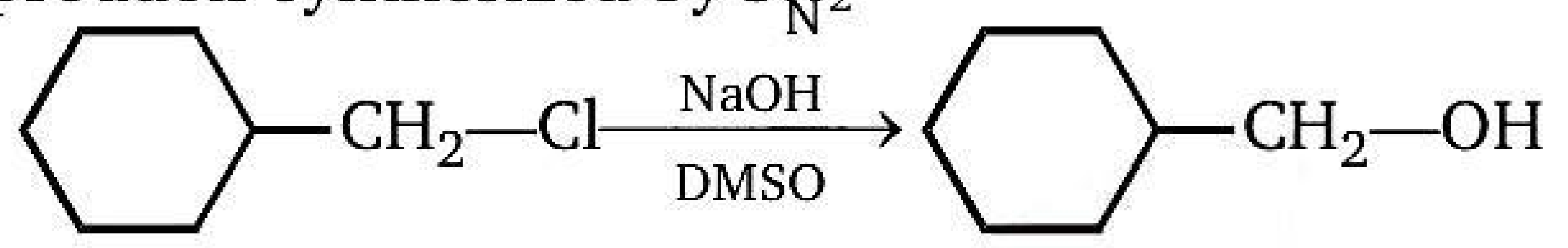
Branching
β-position



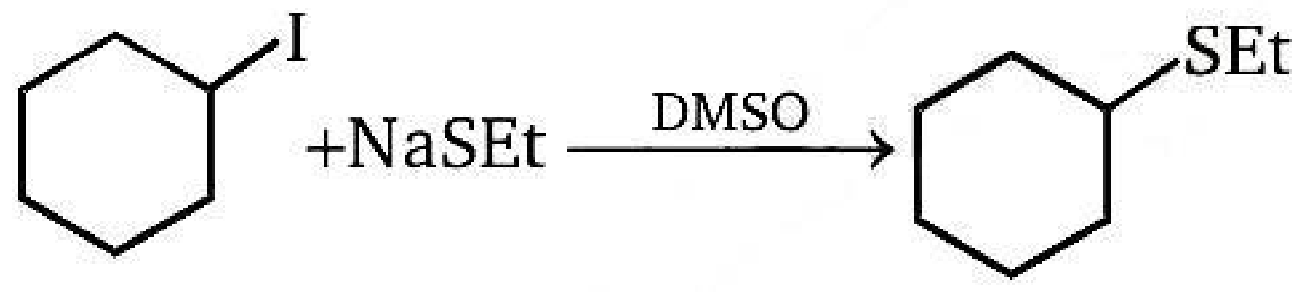
Branching at
γ-position so it
more reactive for S_{N^2}

22. (d) All products synthesized by S_N2

(1)

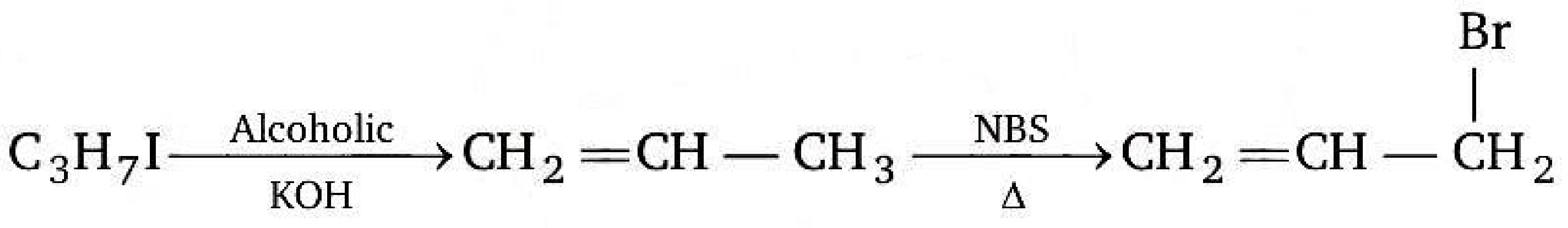


(2)



(3) $Me_3C-O^{\ominus}Na + Me-I \longrightarrow Me_3C-O-Me$

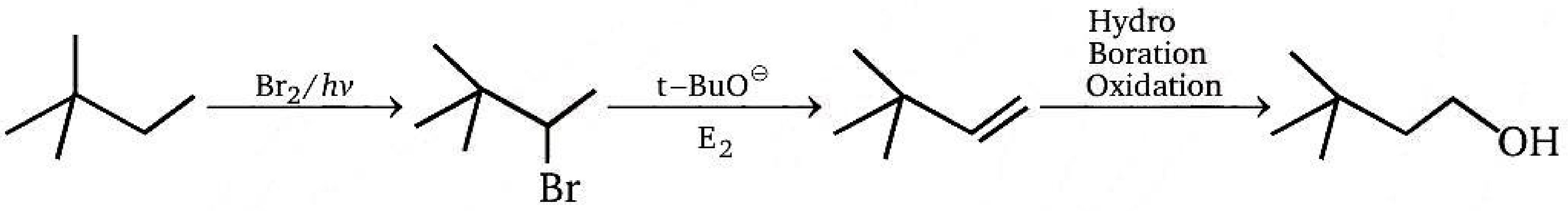
23. (b)



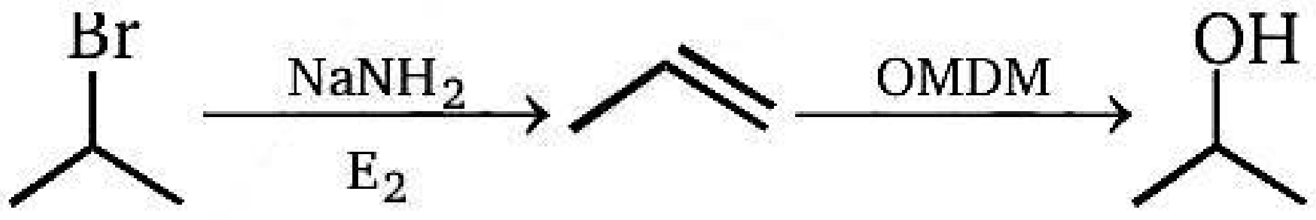
$C_3H_7I \xrightarrow[KOH]{Alcoholic} CH_2=CH-CH_3 \xrightarrow[\Delta]{NBS} CH_2=CH-\overset{Br}{\overset{|}{CH_2}}$

$\xrightarrow{\substack{NaCN\\Alcoholic}} CH_2=CH-CH_2-CN$

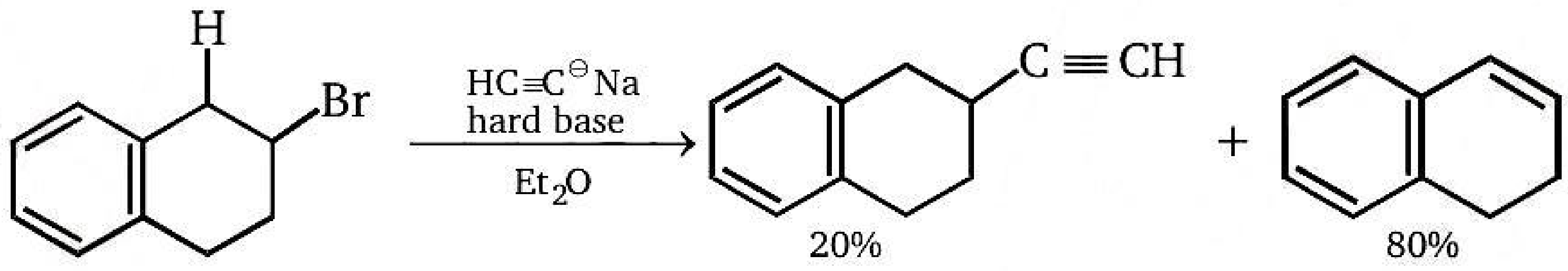
24. (d)



25. (d)

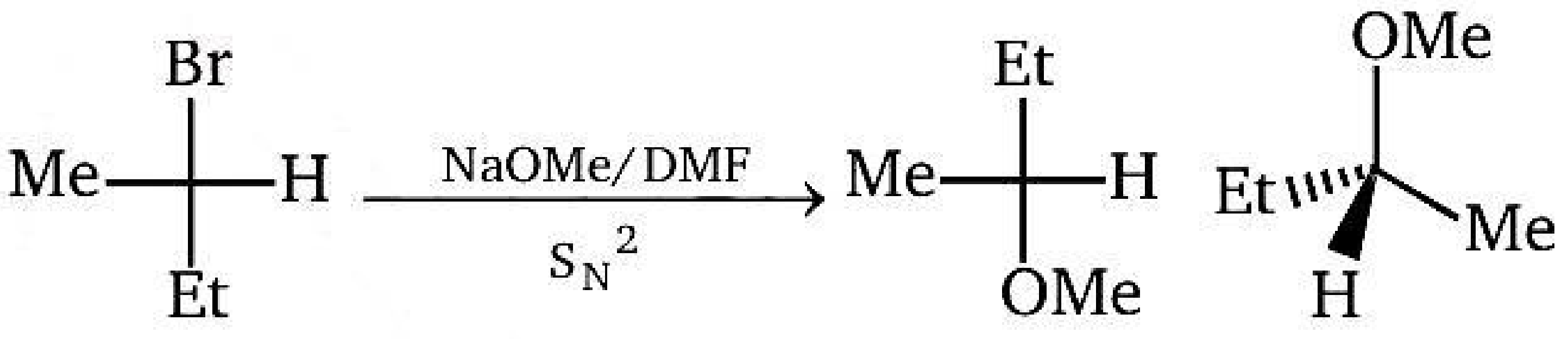


26. (b)



Elimination is more favourable.

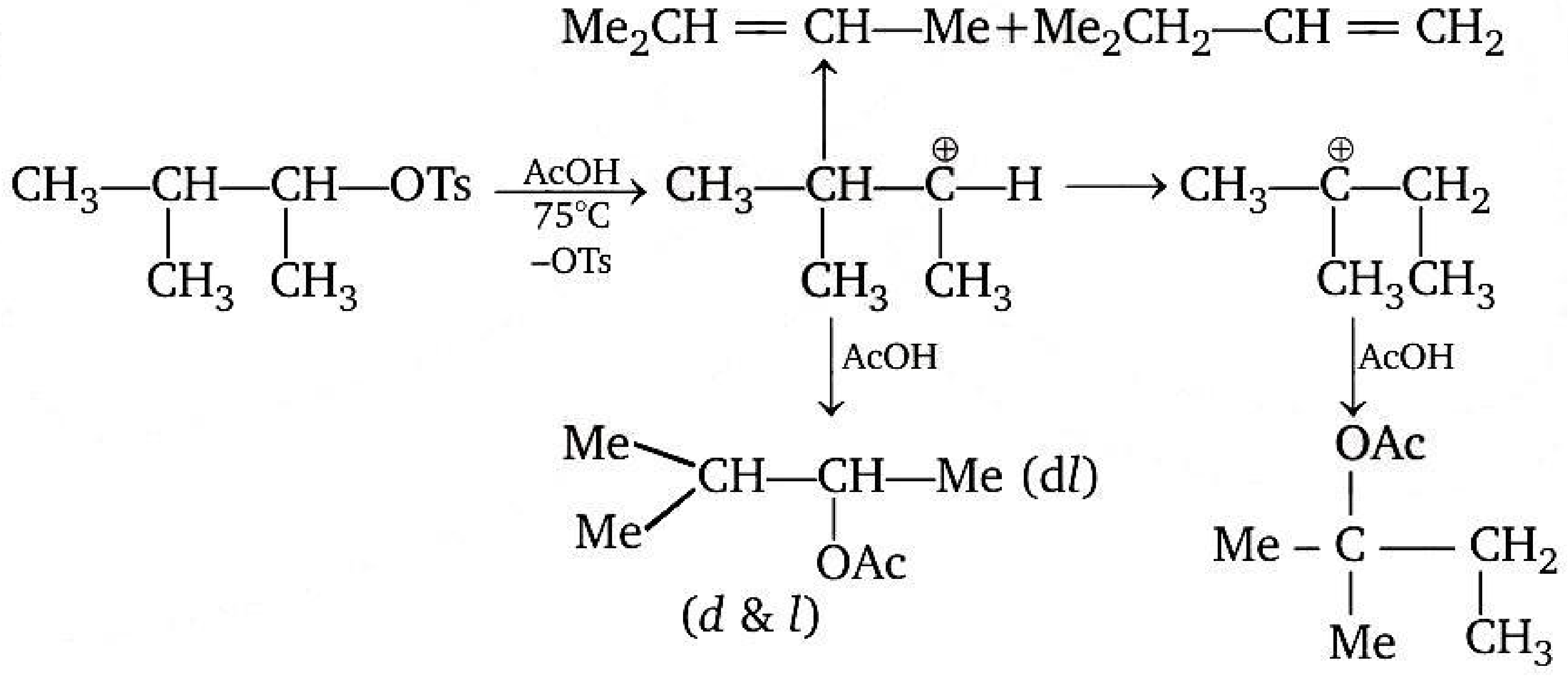
27. (d)



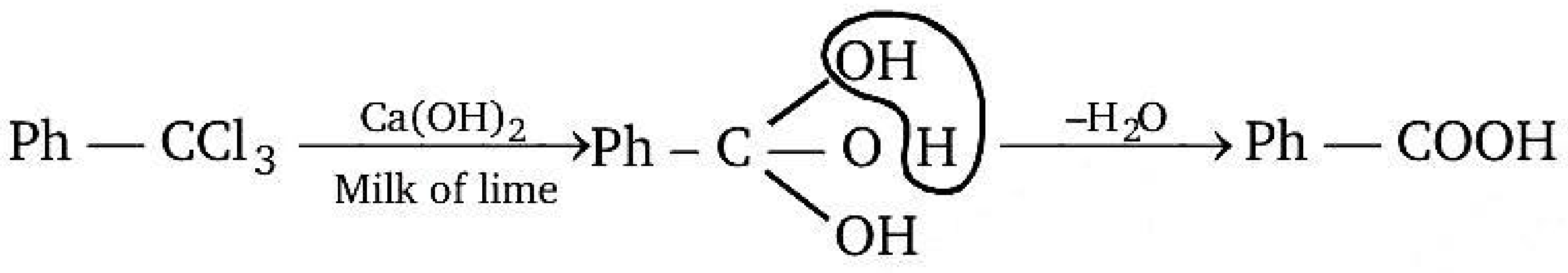
28. (a) Informative question.

29. (a) Rate of reaction of alcohol with H—Br ∝ Stability of $C^{\oplus}$ formed in R.D.S.

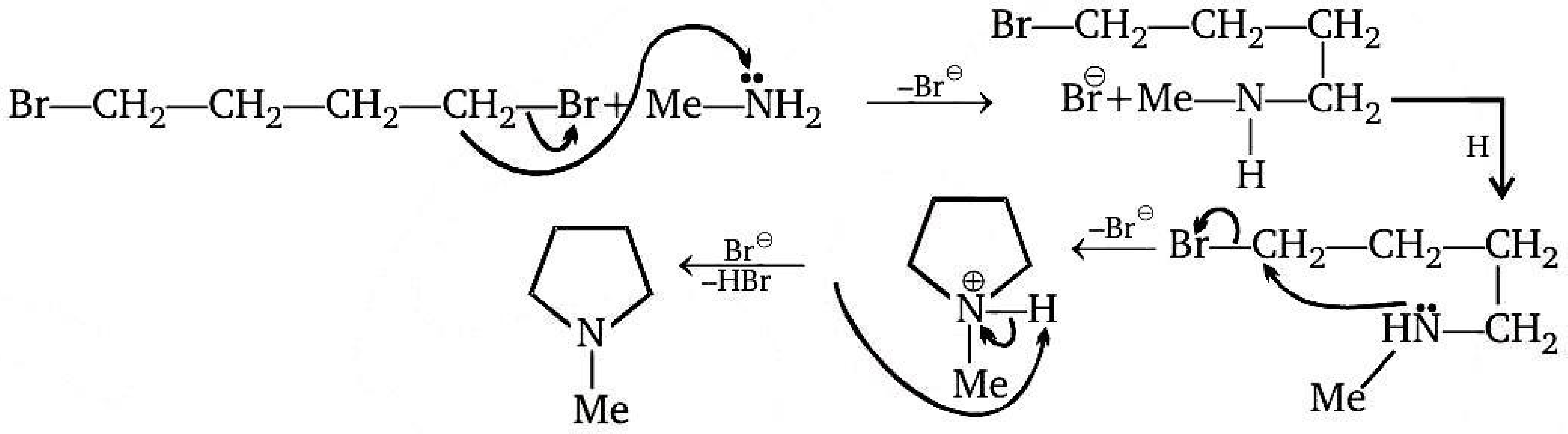
30. (d)



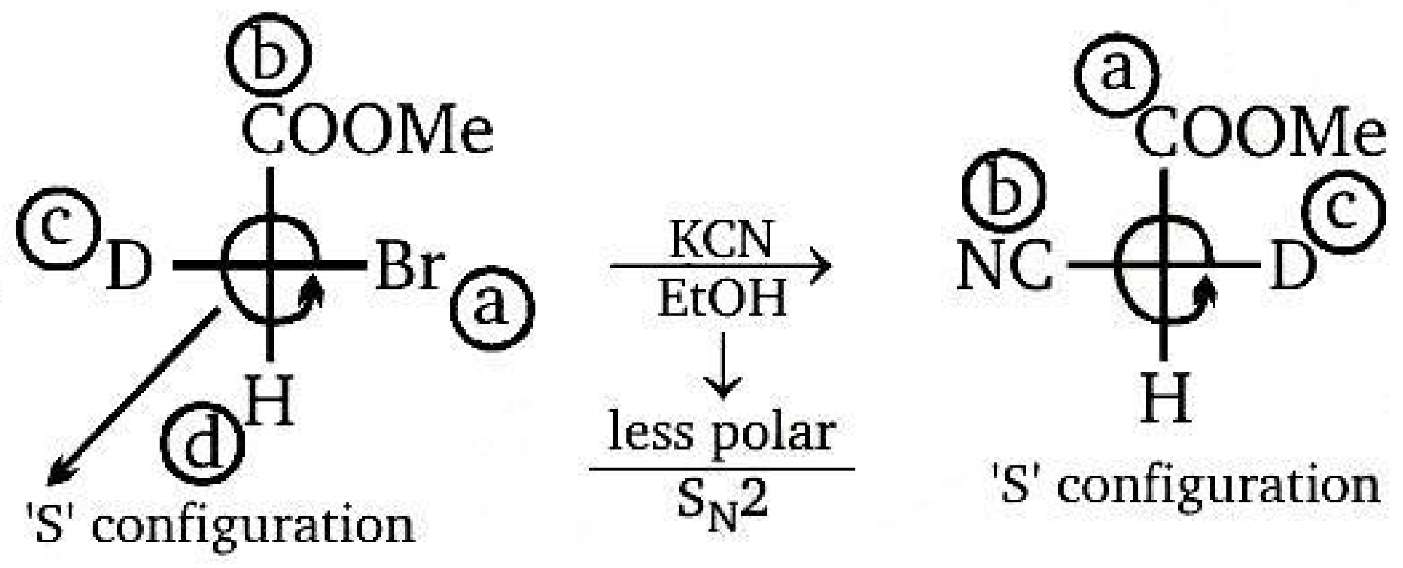
31. (b)



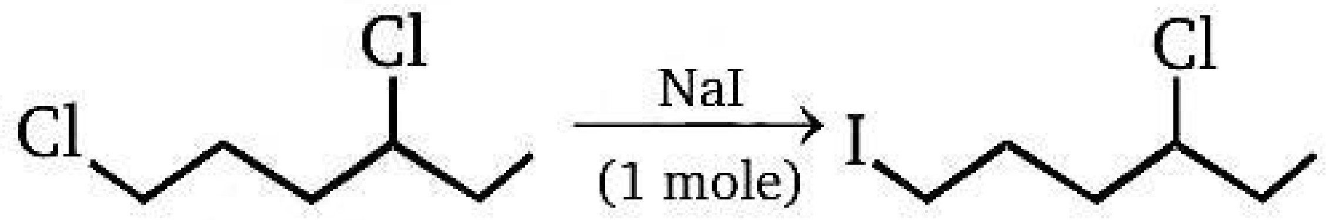
32. (b)



33. (d)



34. (d)

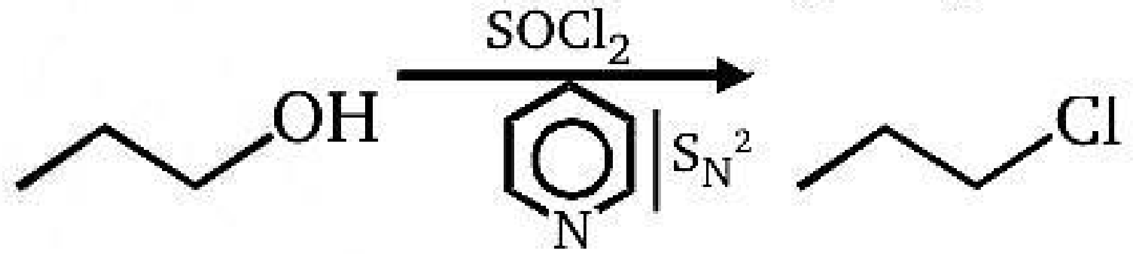


rate of S_N2 faster at 1° than 2°

35. (c) $C_2H_5OH + NaCl \not\longrightarrow C_2H_5Cl + NaOH$

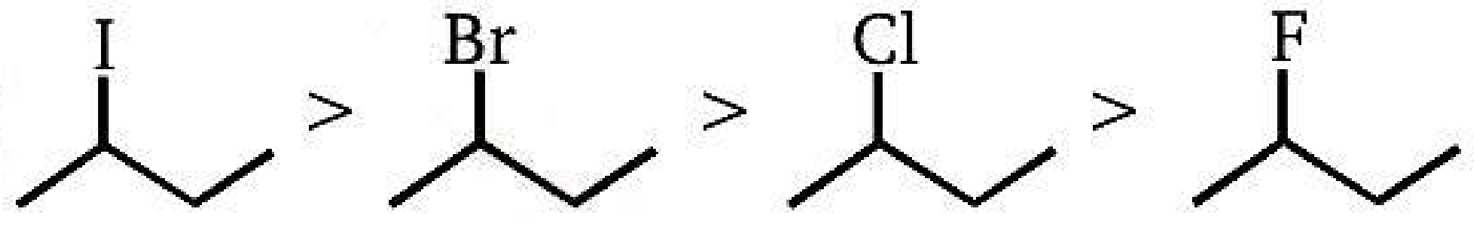
$Cl^{\ominus}$ can not replace OH group because 'Cl' is best L.G.

36. (c)



37. (a) Density ∝ molecular mass.

38. (d)



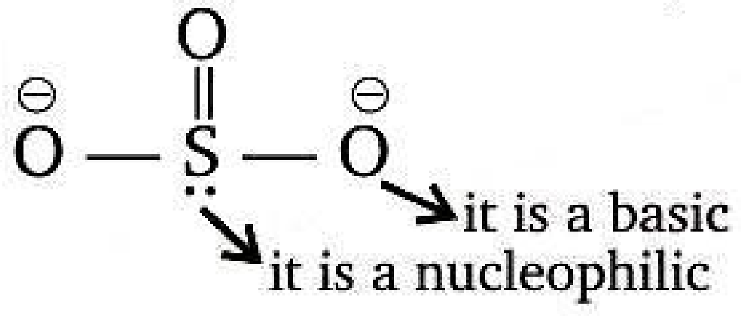
Decreasing order of rate of S_N2 reaction.

39. (c) $Ph — CH_2 — Cl + KCN \xrightarrow{EtOH} Ph — CH_2 — CN$

40. (d) Rate of $S_N2 \propto$ L.G. tendency $\propto \dfrac{1}{\text{Partial D.B. characters in C – X bond}}$

41. (b) Williamson's ether synthesis is S_N2 not possible in 3° alkyl halide.

42. (b)



$\overset{\ominus}{O} — \overset{\overset{O}{\|}}{\underset{\cdot\cdot}{S}} — \overset{\ominus}{O}$

(Sulphur is better nucleophile than oxygen.) (But oxygen is better base than sulphur)

(*A*) is formed by acid-base reaction therefore oxygen will react.

(*B*) is formed by electrophile and nucleophile reaction therefore sulphur will react.

43. (a)

44. (b)

Level - 2

1. Vinyl and aryl halide do not show substitution and elimination.

2. (a) 1° resonance stabilized transition state will be more reactive.

(b) 1° resonance stabilized transition state will be more reactive.

(c) Good leaving group.

3. Basic information of organic reaction.

Subjective Problems

1.