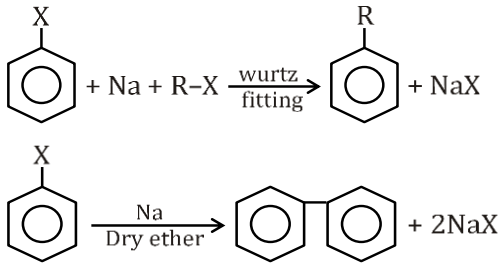
Haloalkanes and Haloarenes

SOLUTIONS

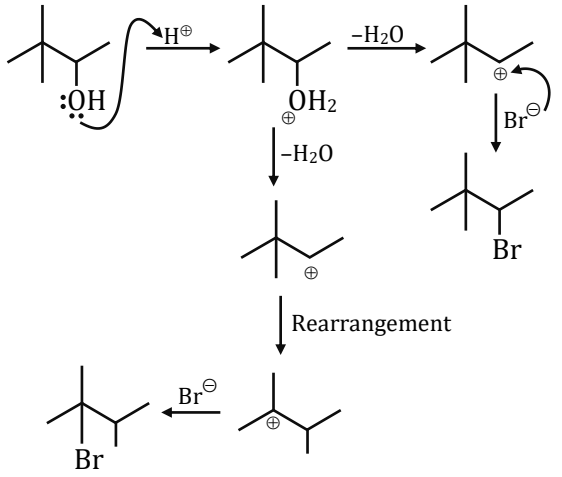
Exercise-I (Conceptual Questions)

1. Ans. (4)

$$R{-}X \xrightarrow[\text{Dry ether}]{Na} R{-}R + 2NaX$$



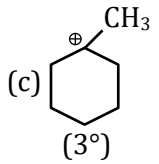
2. Ans. (1)



3. Ans. (4)

(a) $Ph{-}\overset{\oplus}{C}H_2$ Resonance

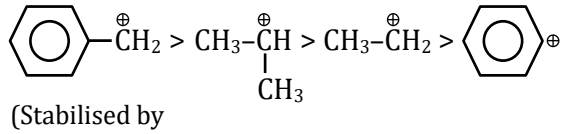
(b)  Aromatic

(c)  (3°)

(d) $CH_3{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}\overset{\oplus}{C}H_2$ (1°)

b > a > c > d

4. Ans. (3)



(Stabilised by Resonance)

5. Ans. (3)

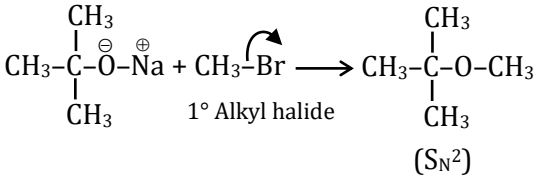
Chloroform is slowly oxidised by air is the presence of light to an extremely poisonous gas, carbonyl chloride also known as phosgene.

6. Ans. (3)

$$CH_3{-}CH_2{-}CH_2{-}Cl + \overset{\oplus}{K}\overset{\ominus}{SH} \xrightarrow{DMSO} CH_3{-}CH_2{-}CH_2{-}SH + KCl$$

This reaction follow S_N2 mechanism, involve one step reaction.

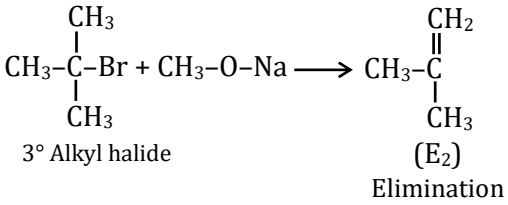
7. Ans. (4)



(S_N2)

$CH_3{-}CH_2{-}Br + NaCN \xrightarrow{DMSO} CH_3{-}CH_2{-}CN$ (S_N2)

$CH_3{-}CH_2{-}Br + NaI \xrightarrow{\text{Dry acetone}} CH_3{-}CH_2{-}I$ (S_N2)



(E_2) Elimination

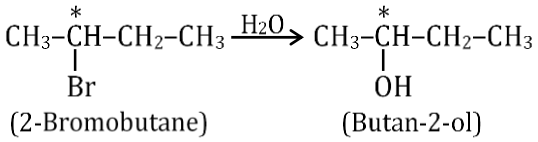
8. Ans. (4)

$$R{-}\overset{\beta}{C}H_2{-}\overset{\alpha}{C}H_2{-}X \xrightarrow{\text{Alc. KOH}} R{-}CH{=}CH_2$$

(Alkene)

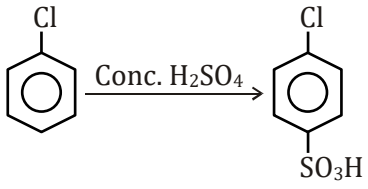
[β-elimination]

9. Ans. (3)



(2-Bromobutane) (Butan-2-ol)

10. Ans. (3)

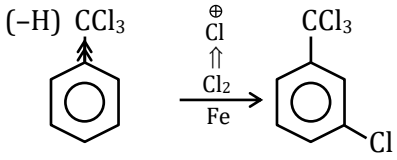


{$E^{\oplus} \Rightarrow SO_3$}

+M of Cl ∴ ortho/para directing

–I of Cl ∴ deactivating in nature

11. Ans. (1)

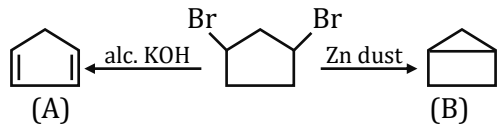


12. Ans. (1)

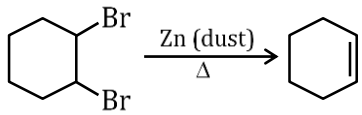
$CH_3—CH_2—CH_2—Cl + NaI \xrightarrow[\text{acetone}]{\text{dry}} CH_3—CH_2—CH_2—I$

Finkelstein reaction is a type of S_N2 reaction that involves the exchange of halide ion.

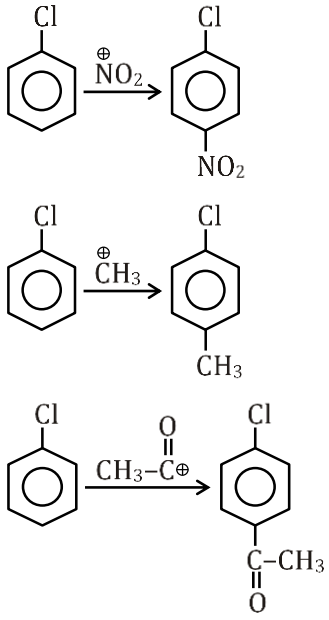
13. Ans. (4)



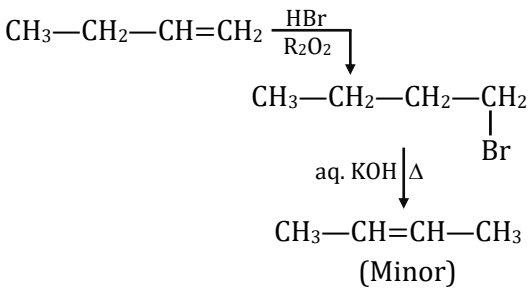
14. Ans. (1)



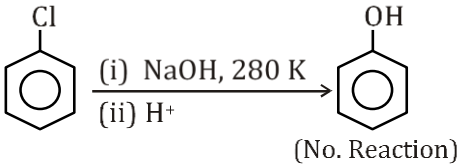
15. Ans. (4)



16. Ans. (3)

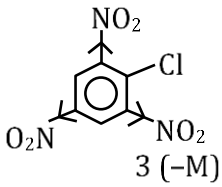


17. Ans. (1)



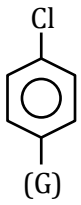
$\therefore$ High temperature required

18. Ans. (4)



$SnAr \propto \frac{-M}{+M} \propto \frac{-H}{+H} \propto \frac{-I}{+I}$

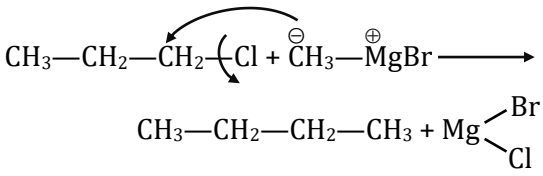
19. Ans. (3)



$SnAr \propto \frac{-M/-H/-I}{+M/+H/+I}$

Here ; G must be electron withdrawing group i.e. $-NO_2$

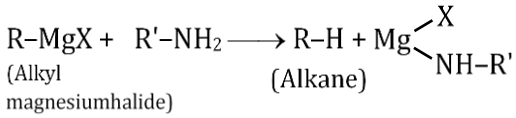
20. Ans. (1)



21. Ans. (2)

C–Mg bond is polar covalent.

22. Ans. (2)



It is a reaction of active-H.

23. Ans. (1)

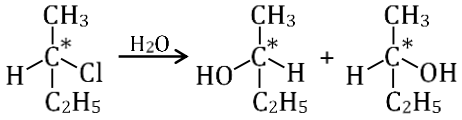
DDT is used as Insecticide

24. Ans. (4)

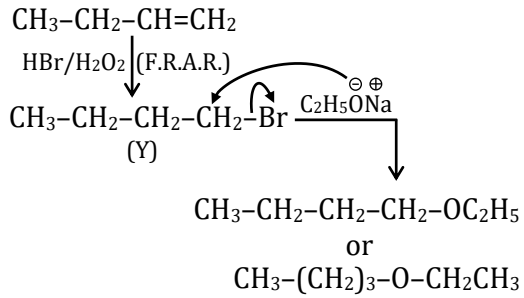
D.D.T. $\Rightarrow$ fat soluble in nature

Exercise-II (Previous Year Questions)

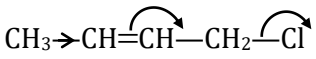
1. Ans. (4)



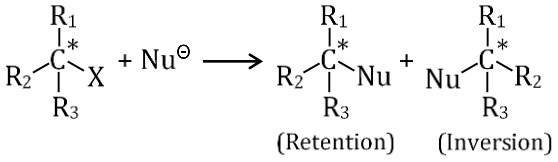
2. Ans. (1)



3. Ans. (2)

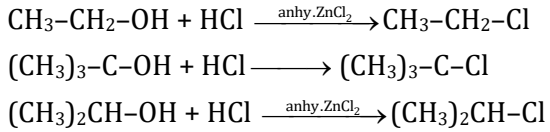


4. Ans. (4)

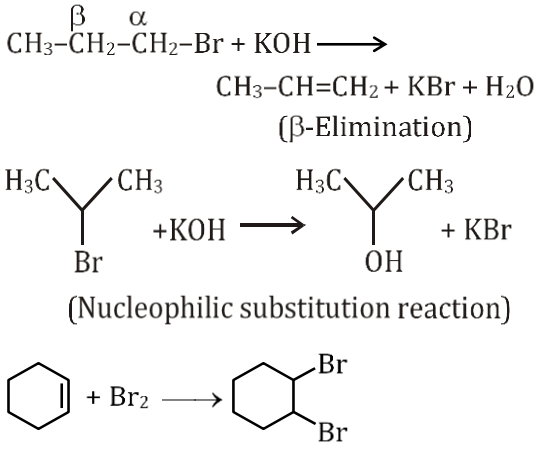


Both inversion and retention take place. But, inversion is more than retention leading to partial racemization.

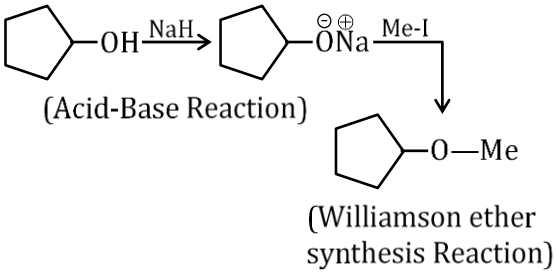
5. Ans. (3)



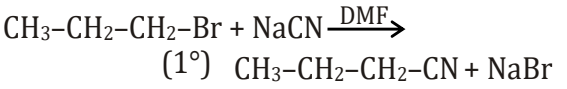
6. Ans. (2)



7. Ans. (1)

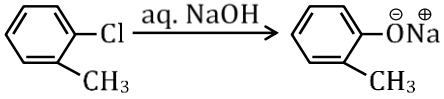


8. Ans. (1)



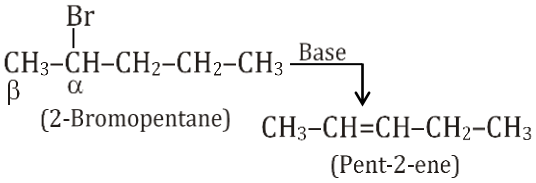
Path is S_N2. Hence, this reaction will be fastest in D.M.F.

9. Ans. (1)



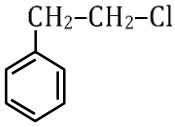
Because aryl halides are less reactive than alkyl halides.

10. Ans. (2)



It is β-elimination.
It follows Zaitsev (saytzeff's) rule.
It is Dehydrohalogenation reaction.

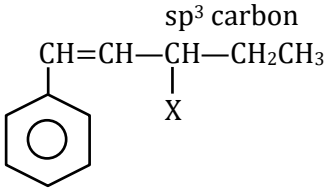
11. Ans. (3)

Amongst the given options  is 1° alkyl halide where S_N1 does not take place.

12. Ans. (2)

$CH_3–F > CH_3–Cl > CH_3–Br > CH_3–I$
[C–X bond enthalpy]
The size of halogen atom increases from F to I i.e. F < Cl < Br < I hence; bond length from C–F to C–I increases. That's why bond enthalpy from CH_3–F to CH_3–I decreases.

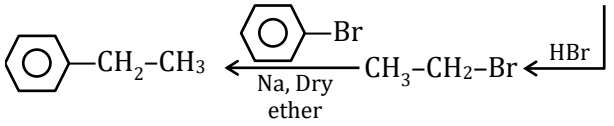
13. Ans. (2)



Allylic halide → Halogen attached to sp^3 carbon which is next to C=C

14. Ans. (4)

$CH_3-CH=O \xrightarrow[H_3O^+]{LiAlH_4} CH_3-CH_2-OH \xrightarrow[\Delta]{H^+} CH_2=CH_2$



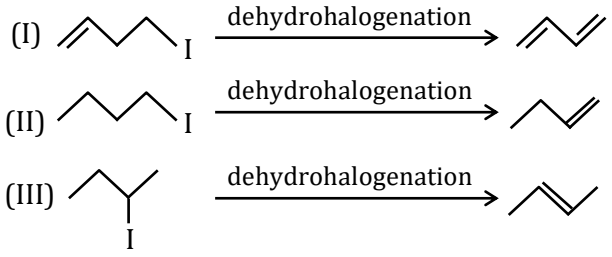
(Wurtz – Fitting reaction)

15. Ans. (3)

$R-X + Ag-C\equiv N \rightarrow R-NC$

Isonitrile

16. Ans. (4)



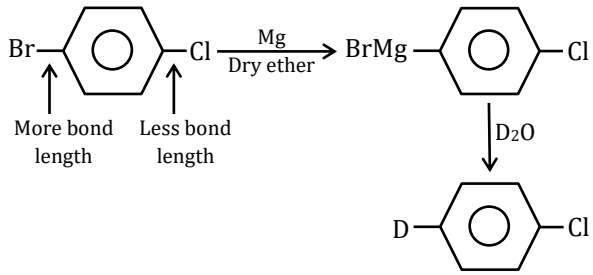
Rate of Dehydrohalogenation :

II < III < I

↓ ↓ ↓

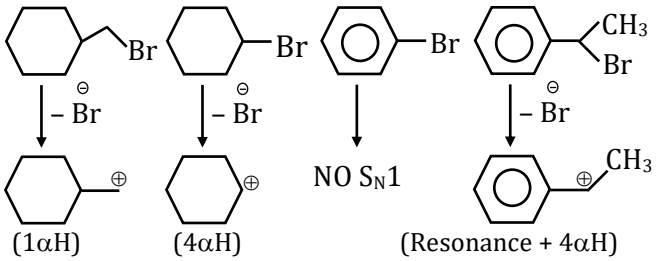
2αH 6αH Resonance

17. Ans. (1)



18. Ans. (4)

Reactivity towards S_N1 ∝ stability of carbocation



19. Ans. (4)

$3R-OH + PCl_3 \rightarrow 3RCl + H_3PO_3$

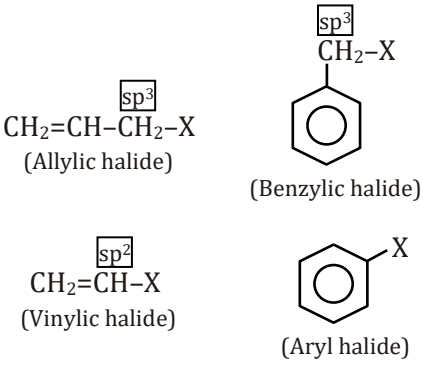
$R-OH + PCl_5 \rightarrow R-Cl + HCl + POCl_3$

$A \rightarrow H_3PO_3$

$B \rightarrow POCl_3$

Exercise-III (Analytical Questions)

1. Ans. (4)



2. Ans. (2)

Nucleophilicity ⇒ $CH_3-O^{\ominus}$

If e^- donor is same atom then

$$\left\{N.S. \propto \frac{1}{\text{stablity of anion}}\right\}$$

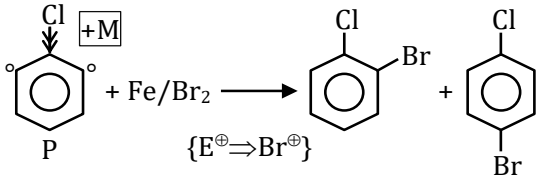
3. Ans. (1)

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

Polar aprotic solvent DMF is given

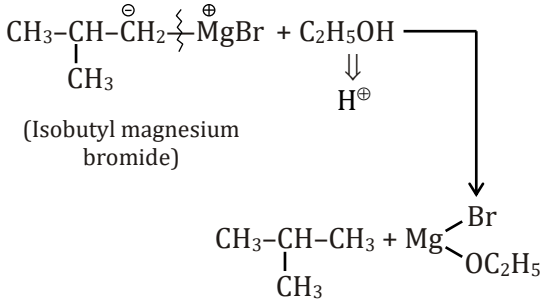
$$\left[\text{Nucleophilicity} \propto \frac{1}{\text{size}}\right]$$

4. Ans. (3)

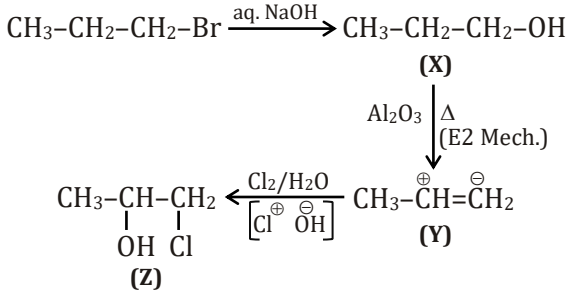


5. Ans. (4)

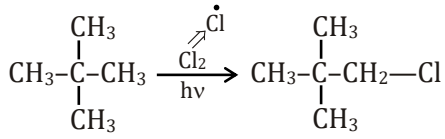
Reaction of active –H



6. Ans. (2)



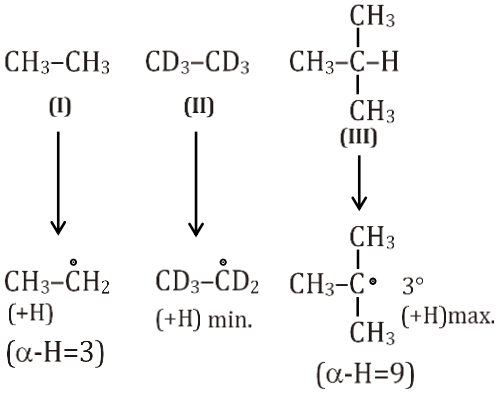
7. Ans. (3)



(Neopentane) (1-Chloro-2,2-dimethyl propane)

8. Ans. (1)

{Rate of photo bromination (i.e. towards FRSR) ∝ stability of formed free radical}

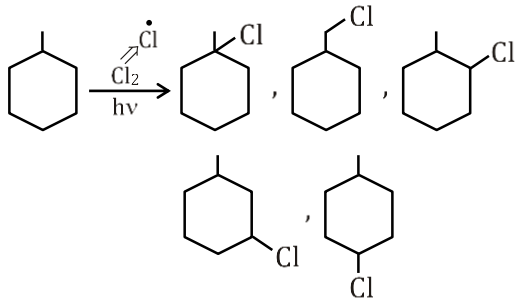


(+H) (α-H=3) (+H) min. 3° (+H)max. (α-H=9)

III > (I, II)

III > I > II

9. Ans. (2)



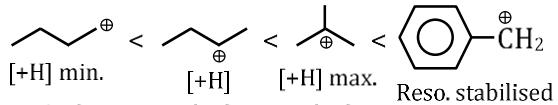
(5 Possible product)

10. Ans. (3)

In S_N1, the first step involves the formation of carbocation.

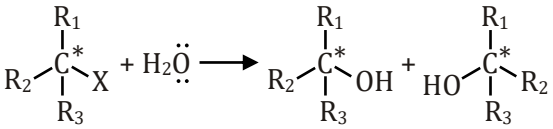
11. Ans. (2)

{Reactivity towards S_N1 reaction ∝ Stability of carbocation}



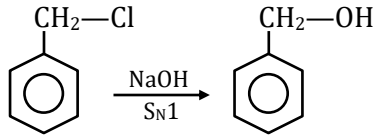
[+H] min. (1°) [+H] (2°) [+H] max. (3°) Reso. stabilised

12. Ans. (3)



(Partially Racemised Product)

13. Ans. (4)



(Benzyl Chloride)

14. Ans. (3)

$$\left[\text{Stability of carbocation} \propto \frac{+M}{-M} \propto \frac{+H}{-H} \propto \frac{+I}{-I}\right]$$

$C_6H_5-\overset{\oplus}{C}(C_6H_5)-C_6H_5 > C_6H_5-\overset{\oplus}{C}H-C_6H_5 > C_6H_5-\overset{\oplus}{C}H_2 > CH_3-\overset{\oplus}{C}(CH_3)-CH_3$

[+H] only

15. Ans. (4)

$R—X + NaOH \longrightarrow R—OH$ [N.S.R.]

(Alkyl halide)

16. Ans. (4)

F is weaker base

For 2° alky halide, steric hindrance is more than 1° alkyl halide

$\therefore$ slowest S_N2 reaction.

17. Ans. (4)

S_N2 reaction requires polar aprotic solvent (PAS) i.e. DMSO

18. Ans. (4)

$$\left\{\text{Rectivity towards } S_{N^2} \propto \frac{1}{\text{Steric Hindrance}}\right\}$$

$C_6H_5CH_2-Br$ is 1° alkyl halide.

19. Ans. (2)

$CH_3-Br + \overset{\ominus}{O}H \longrightarrow CH_3-OH + Br^{\ominus}$

1° Alkyl Halide

It follows S_N2 mechanism.

20. Ans. (4)

$CH_3-CH_2-CH_2-Cl + KCN \longrightarrow$

(Propyl chloride) $CH_3-CH_2-CH_2-CN + KCl$ (Butanenitrile)

21. Ans. (2)

$C_2H_5-Br + KCN_{(aq.)} \longrightarrow C_2H_5-CN + KBr$

22. Ans. (4)

$CH_2=CH-\ddot{Cl}:$ [Stabilised by Resonance]

(Vinyl chloride)

23. Ans. (1)

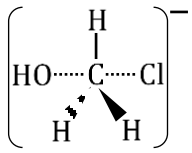
$$CH_3{-}X > CH_3{-}CH_2{-}X > CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{CH}}{-}X > CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}X$$

24. Ans. (3)

$$\underset{(1°)}{R{-}X} + R{-}\overset{\ominus}{O}\overset{\oplus}{Na} \longrightarrow R{-}O{-}R \quad [S_N2]$$

(Williamson synthesis)

25. Ans. (2)



Transition state

It is sp^2 hybrid.

26. Ans. (4)

$$CH_3(CH_2)_5\underset{\displaystyle H_3C}{\overset{\displaystyle H}{C}}{-}Br \xrightarrow{\overset{\ominus}{O}H} HO{-}\underset{\displaystyle CH_3}{\overset{\displaystyle H}{C}}{-}(CH_2)_5CH_3$$

(2°)

$\overset{\ominus}{O}H$ is strong nucleophile and it is 2° alkyl halide hence inversion taking place, so it follows S_N2 path.

27. Ans. (3)

$$CH_3{-}\underset{\displaystyle CH_3}{CH}{-}CH_2{-}Cl \xrightarrow[[S_N2]]{\text{aq. KOH}} CH_3{-}\underset{\displaystyle CH_3}{CH}{-}CH_2{-}OH$$

(1°)

On the rear side of Cl of C_1 carbon.

28. Ans. (1)

$$CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}O{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}CH_3$$

(Di tert. butyl ether)

bulky group

$\therefore$ more steric hindrance

29. Ans. (1)

$$C_2H_5\{O{-}Ph \xrightarrow[[S_N2]]{\overset{\oplus}{H}\overset{\ominus}{Br}} Ph{-}OH + C_2H_5{-}Br$$

30. Ans. (1)

$$\underset{\text{(Sodium ethoxide)}}{C_2H_5{-}ONa} + C_2H_5{-}I \longrightarrow \underset{\text{(Ether)}}{C_2H_5{-}O{-}C_2H_5} + NaI$$

31. Ans. (3)

$$\underset{\text{(ethyl iodide)}}{C_2H_5{-}I} + \underset{\text{(Sodium ethoxide)}}{C_2H_5ONa} \longrightarrow C_2H_5{-}O{-}C_2H_5 + NaI$$

It is a Nucleophile substitution Reaction.

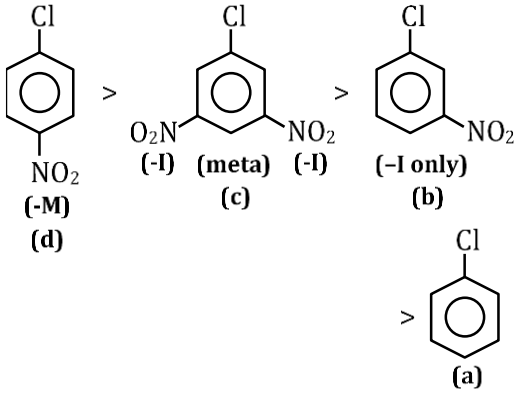
32. Ans. (1)

$R{-}X + R'{-}ONa \longrightarrow R{-}O{-}R'$

$\{R{-}X \Rightarrow CH_3{-}X > 1° > 2° > 3°\}$

33. Ans. (3)

$$\left\{\text{Reactivity towards SnAr} \propto \frac{-M}{+M} \propto \frac{-H}{+H} \propto \frac{-I}{+I}\right\}$$



34. Ans. (2)

$R{-}X + AgCN \longrightarrow R{-}NC + AgX$

35. Ans. (2)

$R{-}Cl + Hg_2F_2 \longrightarrow R{-}F + Hg_2Cl_2$

[Swartz reaction]

36. Ans. (4)

$C_2H_5{-}Br + AgNO_2 \longrightarrow C_2H_5{-}NO_2 + AgBr\downarrow$

37. Ans. (3)

E_1 elimination involves formation of carbocation.

$$CH_3{-}CH_2{-}OH \xrightarrow[\Delta]{\overset{\oplus}{H}} CH_3{-}\overset{\oplus}{C}H_2 \longrightarrow CH_2{=}CH_2$$

38. Ans. (3)

Though it is a 3° alkyl halide hence S_N2 not possible.

$$\underset{\text{(3°)}}{CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}{-}Cl} + C_2H_5ONa \longrightarrow CH_3{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2}{C}} \quad \text{or} \quad (CH_3)_2C{=}CH_2$$

39. Ans. (1)

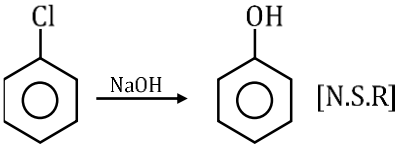
$CH_3-CH_2-Br + HS^{\ominus} \longrightarrow CH_3-CH_2-SH + Br^{\ominus}$ [N.S.R.]

$(CH_3)_2-C=CH_2 + HOCl \longrightarrow$

$(CH_3)_2-\underset{OH}{\underset{|}{C}}-CH_2-Cl$ [E.A.R]

$CH_3-CH_2-Br + \overset{\ominus}{O}H \rightarrow CH_2=CH_2 + Br^{\ominus} + H_2O$ [Elimination]

$(CH_3)_3CCH_2-OH + HBr \longrightarrow (CH_3)_3CBrCH_2CH_3 + H_2O$ [N.S.R.]



[N.S.R]

40. Ans. (4)

$CH_2=CH-CH_2-CH_3 \xrightarrow[\text{Aq. KOH}]{HBr} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$

$CH_2=CH-CH_2-CH_3 \xrightarrow[\text{Aq. KOH}]{HBr/H_2O_2}$

$CH_2(OH)-CH_2-CH_2-CH_3$

$CH_2=CH-CH_3 \xrightarrow[\text{(ii) } CH_3COOH]{\text{(i) } BH_3/THF} CH_3-CH_2-CH_3$

$CH_3-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow[HBr/R_2O_2]{\text{Alc. KOH}} \underset{Br}{\underset{|}{CH_2}}-CH_2-CH_3$

41. Ans. (2)

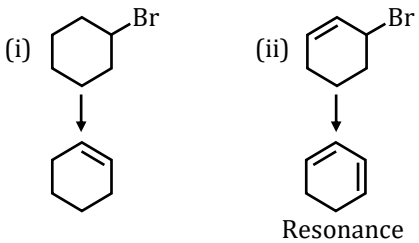
Reactivity order $\Rightarrow$ R–I > R–Br > R–Cl > R–F

42. Ans. (3)

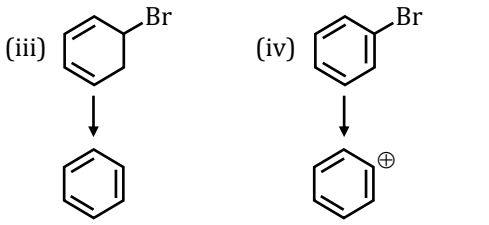
$CH_3-\underset{\beta_1}{CH}(Br)-\underset{\alpha}{CH_2}-\underset{\beta_2}{CH_3} \xrightarrow[(-HBr)]{\Delta} CH_2=CH-CH_2-CH_3 + CH_3-CH=CH-CH_3$

(Sec. butyl bromide)

43. Ans. (2)



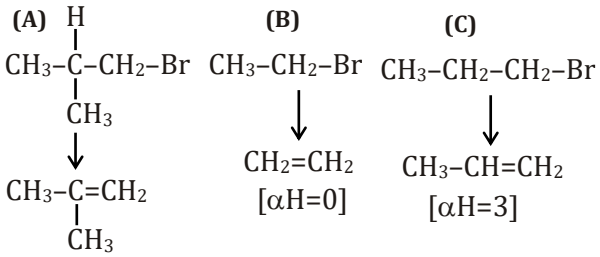
Resonance



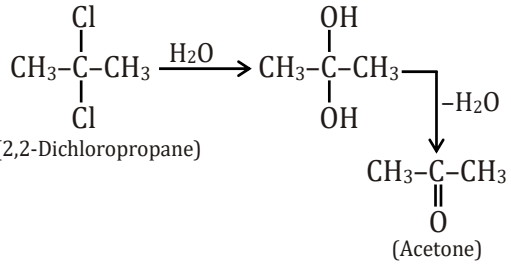
(Aromatic) (Highly unstable)

(iii) > (ii) > (i) > (iv)

44. Ans. (4)

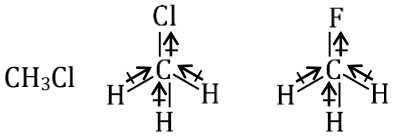


45. Ans. (1)



(2,2-Dichloropropane) (Acetone)

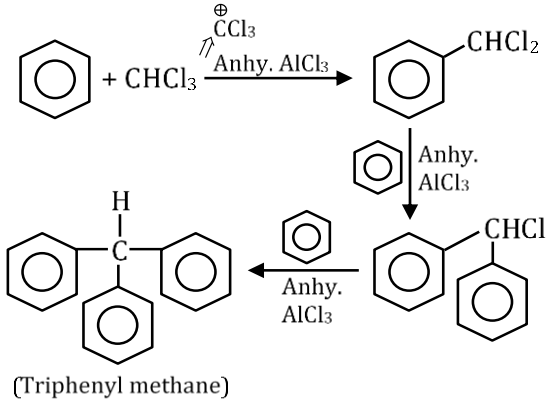
46. Ans. (1)



(μ=1.94D) (μ=1.82D)

The charge separation is larger in CH_3Cl as compared to CH_3-F.

47. Ans. (4)



(Triphenyl methane)