

Haloalkanes and Haloarenes

6.

- 1. Arrange the following compounds in order of increasing dipole moment : **Toughnut**
 - (I) Toluene
 - (II) *m*-dichlorobenzene
 - (III) o-dichlorobenzene
 - (IV) p-dichlorobenzene
 - (a) I < IV < II < III (b) IV < I < II < III
 - (c) IV < I < III < II (d) IV < II < III
- 2. Pure chloroform is prepared by
 - (a) distilling chloral hydrate with aqueous sodium hydroxide.
 - (b) heating ethanol with bleaching powder.
 - (c) heating acetone with bleaching powder.
 - (d) reducing carbon tetrachloride.
- 3. The reaction conditions leading to the best yields of C₂H₅Clare:

(a)
$$C_2H_6$$
 (excess) + Cl_2 UV light

(b)
$$C_2H_6 + Cl_2 - \frac{dark}{room temperature}$$

(c)
$$C_2H_6 + Cl_2$$
 (excess) UV light

(d)
$$C_2H_6 + Cl_2 \xrightarrow{UV \text{ light}} \rightarrow$$

- 4. A compound A with molecular formula $C_{10}H_{13}Cl$ gives a white precipitate on adding silver nitrate solution. A on reacting with alcoholic KOH gives compound B as the main product. B on ozonolysis gives C and D. C gives Cannizaro reaction but not aldol condensation. D gives aldol condensation but not Cannizaro reaction. A is :
 - (a) $C_6H_5 CH_2 CH_2 CH_2 CH_2 CH_2$

(b)
$$C_6H_5 - CH_2 - CH_2 - CH - CH_3$$

(c)
$$C_6H_5-CH_2-C$$
 CH_3
 CH_3 CH_3

(d)
$$(H_2 - CH_2 - CH_3 - CH_2 - CH_3)$$

- **5.** The Wurtz-Fittig reaction involves condensation of
 - (a) two molecules of aryl halides.
 - (b) one molecule of each of aryl-halide and alkyl-halide.
 - (c) one molecule of each of aryl-halide and phenol.
 - (d) two molecules of aralkyl-halides.
 - For the compounds CH₃Cl, CH₃Br, CH₃I and CH₃F,

the correct order of increasing C–X bond length is:

- (a) $CH_3F < CH_3Cl < CH_3Br < CH_3I$
- (b) $CH_3F < CH_3Br < CH_3Cl < CH_3I$
- (c) $CH_3F < CH_3I < CH_3Br < CH_3CI$
- (d) $CH_3Cl < CH_3Br < CH_3F < CH_3I$
- 7. The order of reactivity of the given haloalkanes towards nucleophile is :
 - (a) RI > RBr > RCl (b) RCl > RBr > RI
 - (c) RBr > RCl > RI (d) RBr > RI > RCl
- **8.** AgNO₃ does not give precipitate with chloroform because:
 - (a) $CHCl_3$ does not ionise in water.

- (b) $CHCl_3$ is insoluble in water.
- (c) AgNO₃ is insoluble in CHCl₃.
- (d) $CHCl_3$ is an organic compound.
- 9. Consider the following anions.



When attached to sp³-hydridized carbon, their leaving group ability in nucleophilic substitution reaction decreases in the order:

- (a) I > II > III > IV (b) I > II > IV > III
- (c) IV > I > II > III (d) IV > III > II > I

10.
$$C_2H_5Br \xrightarrow{AgCN} X \xrightarrow{Reduction} Y$$
, Here
Zn—Hg/HCl

Yis

- (a) Ethyl methyl amine(b) n-propylamine
- (c) Isopropylamine (d) Ethylamine
- 11. The chief reaction product of reaction between n-butane and bromine at 573K is :
 - (a) CH₃CH₂CH₂CH₂Br
 - (b) CH_3CH_2CHBr \downarrow CH_3
 - (c) $CH_3 CH_2CHBr$ | CH_2Br
 - (d) $CH_3CH_2CBr_2$ $| CH_3$
- **12.** Aryl fluoride may be prepared from arene diazonium chloride using :
 - (a) HBF_4/Δ
 - (b) $HBF_4/NaNO_2, Cu, \Delta$
 - (c) CuF/HF
 - (d) Cu/HF

- **13.** When $CH_3CH_2CHCl_2$ is treated with NaNH₂, the product formed is **Toughnut**
 - (a) $CH_3 CH = CH_2$

(b)
$$CH_3 - C \equiv CH$$

(d)
$$CH_3CH_2CH < Cl_{NH_2}$$

14.
$$CH_3Br Nu^- \longrightarrow CH_3 - Nu Br$$

The decreasing order of the rate of the above reaction with nucleophiles (Nu⁻) A to D is $[Nu^-=(A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O^-]$

Toughnut

(a)
$$A > B > C > D$$
 (b) $B > D > C > A$
(c) $D > C > A > B$ (d) $D > C > B > A$

15. In a nucleophilic substitution reaction:

 $R - Br + Cl^{-} \xrightarrow{DMF} R - Cl Br^{-}$,

Which one of the following undergoes complete inversion of configuration?

- (a) $C_6H_5CHC_6H_5Br$ (b) $C_6H_5CH_2Br$
- (c) $C_6H_5CHCH_3Br$ (d) $C_6H_5CCH_3C_6H_5Br$
- 16. Which of the following statements is wrong?
 - (a) Ethyl chloride on reduction with Zn-Cu couple and alcohol gives ethane.
 - (b) The reaction of methyl magnesium bromide with acetone gives butanol-2.
 - (c) Alkyl halides follow the following reactivity sequence on reaction with alkenes.

R - I > R - Br > R - Cl > R - I

- (d) $C_2H_4Cl_2$ may exist in two isomeric forms.
- 17. Rate of S_N^2 will be negligible in :





18. A major component of Borsch reagent is obtained by reacting hydrazine hydrate with which of the



19. Chlorobenzne reacts with trichloro acetaldehyde in the presence of H_2SO_4 .

NO



The major product formed is:

NO-







(d) Í Cl

- 20. The total number of acyclic isomers including the stereoisomers with the molecular formula C₄H₇Cl Toughnut

- (c) 9 (a) 11 (b) 12 (d) 10 The major product formed when 1, 1, 1-trichloro-21. propane is treated with aqueous potassium hydroxide is:
 - (b) 1-Propanol (a) Propyne
 - (c) 2-Propanol (d) Propionic acid
- 22. Which one of the following reagents is not suitable for the elimination reaction?
 - Br
 - (a) NaI/acetone
 - NaOEt/ EtOH (b)
 - NaOH/H₂O (c)
 - (d) $NaOH/H_2O-EtOH$
- 23. Identify Z in the following serie's

$$C_2H_5I \xrightarrow{Alc. KOH} X \xrightarrow{Br_2} Y \xrightarrow{KCN} Z$$

- (a) CH₃CH₂CN (b) NCCH2-CH2CN
- (c) $BrCH_2-CH_2CN$ (d) BrCH=CHCN
- 24. Among the following, the molecule with the lowest dipole moment is

(a)
$$CHCl_3$$
 (b) CH_3Cl

- (c) CH₂Cl₂ (d) CCl_4
- 25. Which chloride is least reactive with the hydrolysis point of view?
 - (a) CH₃Cl (b) CH₃CH₂Cl
 - (d) $CH_2 = CH Cl$ (c) $(CH_3)_3CCl$
- 26. The reaction is described as

$$(a) \quad S_{E} 2 \quad (b) \quad S_{N} 1 \quad (c) \quad S_{N} 2 \quad (d) \quad S_{N} 0$$

27. Replacement of Cl of chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced. This is because



- (a) NO_2 makes the ring electron rich at ortho and para positions.
- (b) NO_2 withdraws e⁻ from meta-position.
- (c) NO_2 donates e^- at meta-position.
- (d) NO_2 withdraws e⁻ from ortho/para-positions.

28.
$$CH_3 - CH_2 - CH - CH_3$$
 obtained by $CH_3 - CH_2 - CH_3 - CH_3$

chlorination of *n*-butane, will be

- (a) meso-form (b) racemic mixture
- (c) *d*-form (d) *l*-form
- **29.** Which compound in each of the following pairs is most reactive to the conditions indicated ?

(C)
$$\overset{CH_3}{\smile} \overset{Cl}{\sim} \overset{Cl}{\sim} (D) \overset{CH_3}{\smile} \overset{Cl}{\leftarrow} \overset{Cl}{\leftarrow} (NaNH_2 \text{ in } NH_3)$$

- (a) A and C (b) B and C
- (c) A and D (d) B and D
- **30.** 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is
 - (a) 2-Ethoxypentane (b) Pentene-1
 - (c) *cis*-Pentene-2 (d) *trans*-Pentene-2
- 31. In the following reaction, compound (B) is







32. Which of the following is not expected to be intermediate of the following reaction?



33. Among the given halides, which one will give same product in both S_N1 and S_N2 reactions?



Z in the above reaction sequence is

- (a) CH₃CH₂CH₂NHCOCH₃
- (b) CH₃CH₂CH₂NH₂
- (c) CH₃CH₂CH₂CONHCH₃
- (d) CH₃CH₂CH₂CONHCOCH₃

35. Which of the following is most reactive towards S_N^2 reaction?

| ost reactive towards | | (a) $i > ii > iii$ | | | | | | | |
|----------------------|-----|--|--|--|--|--|--|--|--|
| CI | 37. | (c) 1>11>11 Which compound u substitution with NaC | | | | | | | |
| | | | | | | | | | |

Which compound undergoes nucleophilic substitution with NaCN at the fastest rate? Toughnut

(b) ii > iii > i

(d) iii > ii > i





38. Identify correct reactivity order for S_N^{1} reaction

36. Identify correct reactivity order for S_N reaction





39. Which one of the sequences below is the best synthesis of (E)-3-hexene?



(b)
$$^{-}C \equiv CH \xrightarrow{Br} \xrightarrow{I \text{ NaH}} \xrightarrow{I \text{ NaH}} \xrightarrow{Na/NH_3}$$

(c)
$$\xrightarrow{O}_{Me} \xrightarrow{i \quad \overline{CH_2 Li}}_{He} \xrightarrow{HBr} \xrightarrow{-OCH_2CH_3}_{HOCH_2CH_3}$$

(d) $\overline{C} \equiv CH \xrightarrow{Br} \xrightarrow{i \quad NaH}_{ii \quad CH_3Br} \xrightarrow{Na/NH_3}$

40. Which of the following reacts at the fast rate with CH₃OK in CH₃OH ?





41. In the following sequence of reactions

$$\begin{array}{c} CH_{3}CH_{2}I \xrightarrow{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_{2}O} D \\ A \end{array}$$

the compound D is

- (a) propanal (b) butanal
- (c) *n*-butyl alcohol (d) *n*-propyl alcohol
- 42. The correct product obtained in the reaction



43. 2-phenyl-2-hexanol can be prepared by Grignard synthesis. The pair of compounds giving the desired product is



44. In the following reaction sequence :

$$I \xrightarrow{\text{KOH}(aq)} II \xrightarrow{(i)CH_3MgBr} III$$

$$(C_3H_6Cl_2) \xrightarrow{(ii)H_2O/H} III$$
given

(a)
$$CH_2 - CH - CH_3$$

 $I = I = CH_2 - CH_3 - CH_3$
(b) $CH_2 - CH_2 - CH_3 = I = CH_3$
 $CI = CH - CH_2 - CH_3$
(c) $CI - CH - CH_2 - CH_3 = CH_3$
 $CI = CH_3 - C - CH_3 = I = CH_3$
 $CI = CH_3 - C - CH_3 = CH_3$
 $CI = CH_3 - C - CH_3 = CH_3$

45. Compound that on hydrogenation produces optically inactive compound is **Toughnut**

(a)
$$H_{3}C$$

(b) $H_{2}C$
(c) $H_{3}Br$
(c) $H_{3}Br$
(c) $H_{3}Br$
(c) $H_{3}Br$
(c) $H_{3}Br$

(c)
$$H_2C$$
 CH_3 CH_3

(d)
$$H_2C$$

46. Which of the following order is not correct?

- (a) MeBr Me_2CHBr $Me_3CBr Et_3CBr(S_N2)$
- (b) $PhCH_2Br$ PhCHBrMe $PhCBrMe_2$ $PhCBrMePh(S_N1)$
- (c) MeI > MeBr > MeCl > MeF ($S_N 2$)
- (d) All are correct
- 47. The major product of the following reaction is :

(a)
$$C_{6}H_{5}CH_{2} - CH_{2} - CH_{2} - CH_{3}$$

 $\downarrow \\ OC_{2}H_{5}$

(b)
$$C_6H_5CH = C - CH_2 - CH_3$$

 $| CH_3$

(c)
$$C_6H_5CH_2 - C$$
 CHCH₃
 CH_3

(d)
$$C_6H_5CH_2-C_{1}CH_2$$

 H_2CH_3

- **48.** The compound most reactive towards S_N^{1} reaction
 - (a) Me_3COCH_2Cl (b) $MeOCH_2Cl$

(c)
$$C_6H_5CH_2CH_2Cl$$
 (d) $-Cl$

49. Which chloro derivative of benzene among the following would undergo hydrolysis most readily with an aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?



- (d) C₆H₅Cl
- **50.** In the following sequence of reactions, which is incorrect

$$CH_2 \quad CH-CH \quad CH_2 \xrightarrow{HBr} A \xrightarrow{HBr} B$$
$$\xrightarrow{Mg} C$$

- (a) A is $CH_3 CH CH_2Br$
- (b) B is $CH_3CHBr CH_2 CH_2 Br$
- (c) C is cyclopropyl methane
- (d) B on S_N^2 with aqueous NaOH gives CH₃CHOH.CH₂CH₂Br and not

 $\mathrm{CH}_3\mathrm{CHBr}.\mathrm{CH}_2\mathrm{CH}_2\mathrm{OH}$









52. The following reaction proceeds through the intermediate formation of

 $RCOOAg + Br_2 \longrightarrow RBr + CO_2 \quad AgBr$

- (a) $RCOO^{\bullet}$ (b) R^{\bullet}
- (c) Br^{\bullet} (d) All of these

53. The compound

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

Toughnut

(a) *o*-Bromotoluene

The compound C is

- (b) *m*-Bromotoluene
- (c) *p*-Bromotoluene
- (d) 3-Bromo-2, 4, 6-trichlorotoluene
- 54. The product of 1-bromo-3-chloro cyclobutane with Na in presence of dioxane **Tricky**



- (d) None of these
- **55.** Which of the following has the weakest carbon chlorine bond ?





56.
$$Cl_3C.CH = CH_2 \xrightarrow{HCl} A$$
 Toughnut

Which of the following is correct?

- (a) A on reaction with aq. KOH gives HOCH₂CH₂COOK
- (b) B can be resolved into d- and l-forms
- (c) Both (a) and (b)
- (d) Neither (a) nor (b)

- 57. Although hexafluoroethane $(C_2F_6, b.p. -79^{\circ}C)$ and ethane $(C_2H_6, b.p. - 89^{\circ}C)$ differ very much in their molecular weights, their boiling points differ only by 10°C. This is due to
 - (a) low polarizability of F
 - (b) nearly similar size of F and H
 - (c) both (a) and (b)
 - (d) Neither of the two
- **58.** Which of the following is a key intermediate in the reaction shown below ?







59. Which of the following structure is more stable?





- **60.** Which of the following is (are) true concerning the intermediate in the addition-elimination mechanism of the following reaction ?
- 63. Silver benzoate reacts with bromine to form



- (a) PhLi and Ph₃P respectively
- (b) Ph₃P and PhLi respectively
- (c) Ph_3P and C_2H_5ONa respectively
- (d) Either (b) or (c)
- **68.** The reaction of toluene with chlorine in presence of ferric chloride gives predominantly :
 - (a) benzoyl chloride
 - (b) *m*-chlorotoluene
 - (c) benzyl chloride
 - (d) *o* and *p*-chlorotoluene
- 69. Arrange the following in order of decreasing rate of solvolysis with aqueous ethanol (fastest \rightarrow slowest)



(a) 2 > 1 > 3 (b) 1 > 2 > 3

(c) 2 > 3 > 1 (d) 1 > 3 > 2

70. Which of the following alkyl halide undergo rearrangement in S_N^{1} reaction?



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Answer KEYs

| 1 | (b) | 8 | (a) | 15 | (c) | 22 | (a) | 29 | (a) | 36 | (d) | 43 | (a) | 50 | (d) | 57 | (c) | 64 | (b) |
|---|-----|----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|----|-----|
| 2 | (a) | 9 | (b) | 16 | (b) | 23 | (b) | 30 | (d) | 37 | (a) | 44 | (d) | 51 | (c) | 58 | (b) | 65 | (c) |
| 3 | (a) | 10 | (a) | 17 | (c) | 24 | (d) | 31 | (c) | 38 | (d) | 45 | (b) | 52 | (d) | 59 | (b) | 66 | (d) |
| 4 | (c) | 11 | (b) | 18 | (c) | 25 | (d) | 32 | (a) | 39 | (b) | 46 | (b) | 53 | (b) | 60 | (d) | 67 | (d) |
| 5 | (b) | 12 | (a) | 19 | (c) | 26 | (c) | 33 | (c) | 40 | (c) | 47 | (b) | 54 | (c) | 61 | (b) | 68 | (d) |
| 6 | (a) | 13 | (b) | 20 | (b) | 27 | (d) | 34 | (a) | 41 | (d) | 48 | (b) | 55 | (c) | 62 | (d) | 69 | (c) |
| 7 | (a) | 14 | (c) | 21 | (d) | 28 | (b) | 35 | (d) | 42 | (a) | 49 | (a) | 56 | (c) | 63 | (d) | 70 | (d) |



Hints & Solutions



(b) In *p*-dichlorobenzene, the two equal dipoles are in opposite direction, hence the molecule has zero dipole moment. In *o*- and *m*- dichlorobenzenes, the two dipoles are at 60° and 120° apart respectively, and thus according to parallelogram law of forces, the dipole moment of *o*-dichlorobenzene is much higher than that of *m*-isomer. Lastly, toluene with a +I group possesses little dipole moment. Thus the overall order is



- 2. (a) $Cl_3CCH(OH)_2 + NaOH \longrightarrow CHCl_3 HCOONa H_2O$
- 3. (a) C_2H_6 (excess) + $Cl_2 \xrightarrow{UV \text{ light}} C_2H_5Cl$ +HCl
- 4. (c) Compound A reacts with alc. KOH to give compound B which on further ozonolysis gives C (does not contains α H atom) and D (contains α -H atom). This reaction sequence can be achieved by compounds in option (a) and (c). Since compound A gives white ppt. with AgNO₃ preferable option will be (c) as tert alkyl reacts with AgNO₃ more quickly.



5. (b) Reaction between alkyl halide, aryl halide and sodium in presence of ether is known as Wurtz fitting reaction

$$C_6H_5Cl + 2Na + ClCH_3 \longrightarrow C_6H_5CH_3$$
 2NaCl
Toluene

6. (a) The correct order of increasing bond length is $CH_3F < CH_3Cl < CH_3Br < CH_3I$

7. (a) For a given alkyl group, the order of reactivity is $\frac{R-I > R-Br > R-CI > R-F}{\text{increasing bond energy}}$ decreasing halogen

reactivity.

This order depends on the carbon-halogen bond energy; the carbon-fluorine bond energy is maximum and thus fluorides are least reactive while carbon-iodine bond energy is minimum hence iodides are most reactive.

8. (a) Since CHCl₃ is covalent compound it does not produce Cl⁻ ion in H₂O, hence no white ppt is formed during reaction with AgNO₃.

10. (a)
$$C_2H_5Br \xrightarrow{AgCN} C_2H_5NC + AgBr$$

(X)
Reduction
 $Zn - Hg / HCl$
 $C_2H_5NHCH_3$
(Y) ethyl methyl amine

11. (b) The reaction proceeds via free radical mechanism. As 2° free radical is more stable than 1°, so CH₃CH₂CH(Br)CH₃ would be formed.

12. (a)
$$\underset{(Balz-Schiemann's reaction)}{\overset{N}{\longrightarrow}} \stackrel{R}{\longrightarrow} \stackrel{R}{\longrightarrow} \stackrel{F}{\longrightarrow} \stackrel{F}$$

13. (b)
$$CH_3 - CH_2 - CHCl_2 \xrightarrow{NaNH_2} \Delta$$

 $CH_3 - CH = CHCl \xrightarrow{NaNH_2} \Delta$ $CH_3 - C \equiv CH_3$
Final Product

- 14. (c) The acid character follows the order : $CH_3COOH > C_6H_5OH > H_2O > CH_3OH$ The basic character will follow the order $CH_3COO^- < C_6H_5O^- < OH^- < CH_3O^-$ The stronger the acid, the weaker the conjugation of the stronger the acid.
 - The stronger the acid, the weaker the conjugate base formed.
- (c) C₆H₅CHCH₃Br being an optically active secondary alkyl bromide undergoes S_N2 nucleophilic substitution reaction. Hence it undergoes complete inversion of configuration.

$$C_{6}H_{5} \xrightarrow{H}_{C}C \longrightarrow Br + Cl^{-} \xrightarrow{DMF} Cl \longrightarrow Cl \xrightarrow{H}_{C}C_{6}H_{5}$$

16. (b)
$$\begin{array}{c} CH_{3} \\ CH_{2}CH_{3} \\ CH_{3} \\$$

- 17. (c) At bridge head position $S_N 1$ and $S_N 2$ do not takes place.
- 18. (c) The major component of Borsch reagent is 2,4- dinitrophenyl hydrazine which can be obtained by reaction of 2,4-dinitrochloro benzene and hydrazine





2,4 -dinitrophenyl hydrazine

19. (c) Chloral on reaction with chlorobenzene in the presence of a catalytic amount of sulphuric acid forms DDT (dichlorodiphenyl Trichloro ethane).



20. (b) C_4H_7Cl is a monochloro derivative of C_4H_8 which itself exists in three acyclic isomeric forms.

CH₃CH₂CH CH₂ I (Its four C's are different) CH₃CH CHCH₃ II (It has 2 types of carbon)

$$CH_{3}$$

$$CH_{3} - C CH_{2}$$

$$III$$
(It has 2 types of carbon)

Grand total of acyclic isomers = 6+4+2=12

21. (d)
$$Cl_3C - CH_2CH_3 + KOH \xrightarrow{heat}$$

$$(OH)_3C - CH_2CH_3$$
 3KCl
 \downarrow
 O
 $CH_3CH_2C - OH$

22. (a) Alkyl chloride or bromide undergo substitution and get converted to an alkyl iodide on treatment with a solution of sodium iodide in acetone. e.g.

$$CH_3CH_2CH_2Br + Nal \xrightarrow{acetone}$$

 $CH_3CH_2CH_2I + NaBr$ This reaction is also known as Finkelstein Reaction.

23. (b) $C_2H_5I \xrightarrow{\text{alc. KOH}} CH_2 CH_2 \xrightarrow{Br_2}$

$$BrCH_2 - CH_2Br \xrightarrow{KCN} CNCH_2.CH_2CN$$

- 24. (d) CCl_4 has lowest (zero) dipole moment. This is due to its symmetrical tetrahedral structure. Due to which dipole moment of one bond is cancelled by opposite dipole moment of the other three bonds.
- **25.** (d) The non-reactivity of chlorine atom in vinyl chloride is due to resonance stabilisation.

$$\overrightarrow{CH_2} = CH \stackrel{\frown}{=} \stackrel{\frown}{\underline{CH}} \stackrel{\frown}{=} \stackrel{\frown}{\underline{CH}} \stackrel{\frown}{=} \stackrel{\frown}{\underline{CH}} \stackrel{-}{=} \stackrel{-}{\underline{CH}} \stackrel{-}{=} \stackrel{+}{\underline{CH}} \stackrel{-}{=} \stackrel{+}{\underline{CH}} \stackrel{-}{=} \stackrel{-}{\underline{CH}} \stackrel{-}{=} \stackrel{-$$

26. (c) Inversion in configuration occurs in S_N^2 reactions.

- 27. (d) -NO₂ group withdraws electrons from o- and p-positions and hence activates the -Cl present on that position towards 29. nucleophilic substitution.
- **28.** (b) Chlorination of alkanes is a free-radical reaction. Since the intermediate free radical is planar (sp^2 hybridised) it can be attacked

D...

on either side of the face forming racemic mixture.

- (a) In the first case the reaction gives side chain substitution product which is easier in A. In the second case the reaction will proceed by benzyne mechanism for which ortho position w. r. to Cl must have H-atoms.
- **30.** (d) Potassium ethoxide is a strong base, hence causes elimination reaction. The alkene formed is governed by Saytzeff rule "more substituted an alkene, higher will be its stability".

$$\begin{array}{c} \text{Br} \\ \stackrel{|}{\overset{|}{\text{CH}_3}\text{CHCH}_2\text{CH}_2\text{CH}_3 \xrightarrow{-\text{OC}_2\text{H}_5} \text{CH}_2 \\ \stackrel{|}{\underset{\text{Pentene-1}}{\text{CHCH}_2\text{CH}_2\text{CH}_3} \end{array} \xrightarrow{\text{CH}_3\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\ \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \stackrel{|}{\underset{\text{Pentene-2}}{\text{Pentene-2}}} \end{array} \xrightarrow{\text{CH}_3\text{CH$$

Further pentene-2 shows geometrical isomerism, *cis*- and *trans*- in which *trans*-isomer having bulkier groups away from each other is more stable than the *cis*-isomer.

33. (c) S_N^2 and S_N^1 same, if C not rearrange.

34. (a)
$$CH_3CH_2Cl \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow{Ni/H_2}$$

(X) $CH_3CH_2CH_2NH_2 \xrightarrow{(CH_3CO)_2O} CH_3CH_2CH_2NHCOCH_3 + CH_3COOH$
(Y) (Z) (Z)

35. (d) 4-nitrobenzyl chloride is likely to react by the S_N^2 mechanism as the strongly electronwithdrawing nitro group would destabilize the carbocation intermediate of the S_N^1 mechanism, a benzylic chloride that disfavours the S_N^1 mechanism.

36. (d) Stablity



37. (a) Rate of

38.

 S_N^2 Steric crowding near to reaction centre (d)

1



39. (b)
$$-C \equiv CH \xrightarrow{Br} H_5C_2 - C \equiv CH \xrightarrow{(i) \text{ NaH}} H_5C_2 - C \equiv C + C_2H_5 \xrightarrow{(i) \text{ NaH}} H_5C_2 - C \equiv C - C_2H_5 \xrightarrow{Na/NH_3} \underbrace{(E) - 3 - \text{hexene}}_{(E) - 3 - \text{hexene}}$$

40. (c) The electron withdrawing nitro groups weaken the C - F bond by inductive effect and resonance.



42. (a) In 2° halides of this type the product formed has inverted configuration ($S_N 2$ mechanism).



2 - phenyl -2-hexanol



46. (b) The more is the stability of intermediate (carbonium ion), the more is the chance of $S_N 1$ mechanism. The intermediates obtained will be PhCH₂(i), PhCH-Me (ii), PhC-Me₂(iii), PhCMePh (iv). The stability is of the order iv > iii > ii.

47. (b)
More
$$C_{2}H_{5}O^{-}$$

 H CH_{3} H
 $C_{6}H_{5}$ CH CH_{7} CH_{7} CH_{7} CH_{7}
 $C_{6}H_{5}$ CH CH_{7} CH_{7} CH_{7}
 $C_{2}H_{5}ONa$
 $C_{2}H_{5}OH$
 $C_{2}H_{5}OH$
 CH_{3}
 CH_{7}
 $CH_$

48. (b)
$$\operatorname{MeOCH}_2\operatorname{Cl} \xrightarrow{\operatorname{Slow}} \operatorname{Me} \overset{\operatorname{OCH}_2 + \operatorname{Cl}^-}{\underset{(i)}{(i)}} \overset{(i)}{\xrightarrow{}} \operatorname{Me} - \underset{(ii)}{\bigcirc} \operatorname{CH}_2$$

Though (ii) contains +ve charge on oxygen. Since octet around each atom does complete the structure II is more stable than I.

- **49.** (a) Cl in 2, 4, 6-trinitrochlorobenzene is activated by three NO₂ groups at *o*, and *p*-positions and hence undergoes hydrolysis most readily.
- **50.** (d) A is 1, 4-addition product due to conjugation B is obtained by further addition of HBr. (CH₃CHBr.CH₂.CH₂Br). B gives C by cyclisation CH₃ – CH – CH₂. If B reacts by S_N^2 mechanism, CH₂

Br on 1° carbon must be replaced by OH^- to give $CH_3CHBr - CH_2 - CH_2OH$.



52. (d) Mechanism of Hunsdiecker's reaction is

$$R-COO^{-}Ag \xrightarrow[-AgBr]{} RCOOBr \longrightarrow RCOO Br \longrightarrow R^{\bullet} CO_2;$$



54. (c) Bond strength follows the order C-F > C-Cl > C-Br > C-I



- 55. (c) Nuclear substituted halogen has double bond character due to resonance.
- 56. (c) The compound A is

$$Cl_3C.CH_2.CH_2Cl \xrightarrow{aq.KOH} (OH)_3C.CH_2CH_2OH \xrightarrow{-2H_2O} HO CH_2.CH_2COOK.$$

The compounds B is $Cl_3C - CH - CH_2Br$ has chiral centre and can be resolved into d- and *l*- form.

- 57. (c) Small difference in boiling points of C_2F_6 and C_2H_6 is due to the fact that (i) the F atom is slightly larger than H, and (ii) F has low polarizability
- **58.** (b) The benzyne is an intermediate of this type of reaction.
- **59.** (b) Structure (b) is more stable because here negative charge is dispersed to the maximum extent as it is present on the carbon atom bearing an electron-withdrawing $(-NO_2)$ group





61. (b)
$$CH_3CH_2CH_2Br \xrightarrow{aq. NaOH} CH_3CH_2CH_2OH \xrightarrow{Al_2O_3}_{heat}$$

 $CH_3CH \quad CH_2 \xrightarrow{Cl_2/H_2O} CH_3.CHOH.CH_2Cl$

62. (d) Addition product is formed by anti-Markownikoff's rule.



- **68.** (d) The given reaction is an example of electrophilic subsitution. Further, CH_3 group in toluene is o, p-directing
- **69.** (c) Rate of solvolysis stability of C^+ .
- **70.** (d) Unstable C has general tendency to rearrange to more stable C^+ .