

ALKYL HALIDE AND ARYL HALIDE

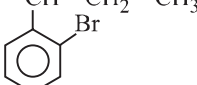
Detailed Solutions

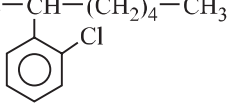
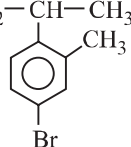
- $$\text{H}_3\text{C}-\underset{\text{Br}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$$
- 4-Chloropent-1-ene
- 4-Bromo-4-methylpent-2-ene
- 2-Chloro-3-methyl butane
- 3-Chloro-2,2-dimethyl butane
- 2-Bromo-4-chloropentane
- $$\text{CH}_3-\overset{4}{\text{C}}=\overset{3}{\underset{\text{CH}_3}{\text{C}}}-\overset{2}{\underset{\text{Br}}{\text{C}}}-\overset{1}{\text{CH}_2}\text{OH}$$

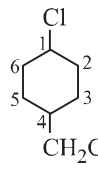
2-Bromo-3-methylbut-2-en-1-ol
- $$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{CH}_2\text{Br}$$

3-Bromo-2-methylpropene
- $$\text{H}_3\text{C}-\overset{2}{\underset{\text{CH}_3}{\text{C}}}-\overset{1}{\text{CH}_2}-\text{Br}$$

1-Bromo-2,2-dimethylpropane
- $$\text{CH}_2=\text{CHCH}_2\text{Br}$$

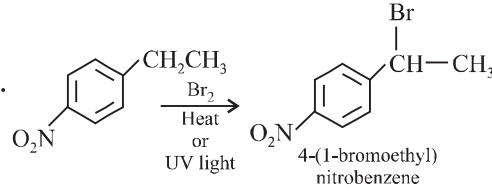
3-Bromoprop-1-ene
- $$\text{H}_2\text{C}-\underset{\text{Br}}{\text{CH}}=\text{CH}-\underset{\text{Br}}{\text{CH}_2}$$
- $$\text{CH}_3-\underset{\text{Br}}{\text{CH}}-\text{CH}_2-\text{CH}_3$$

- $$\text{CH}_3\text{CH}=\overset{3}{\underset{\text{CH}_3}{\text{C}}}-\overset{4}{\underset{\text{Br}}{\text{CH}}}-\overset{5}{\text{CH}_3}$$

4-Bromo-3-methylpent-2-ene
- $$\text{H}_2\text{C}-\underset{\text{Cl}}{\text{CH}}-(\text{CH}_2)_4-\text{CH}_3$$

- $$\text{CH}_3-\text{CH}_2-\underset{\text{Br}}{\text{CH}}-\overset{\text{CH}_3}{\text{C}}-\text{CH}_3$$

- $$\text{H}_3\text{C}-\text{CH}_2-\underset{\text{I}}{\text{CH}}-\underset{\text{C}(\text{CH}_3)_3}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$$
- $$\text{H}_3\text{C}-\overset{3}{\text{C}}-\overset{2}{\underset{\text{CH}_3}{\text{C}}}-\overset{1}{\text{CH}_2}\text{Cl}$$

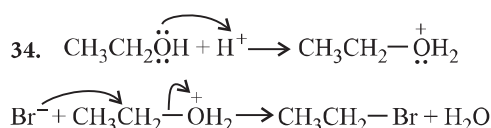
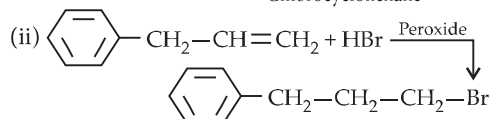
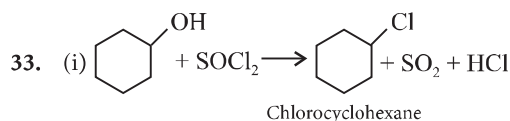
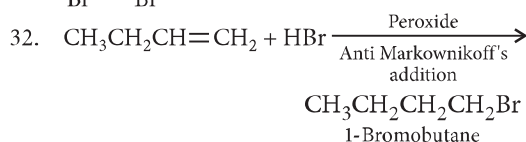
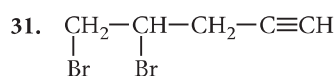
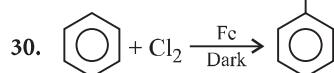
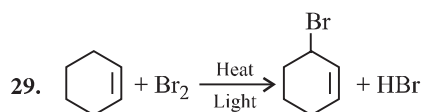
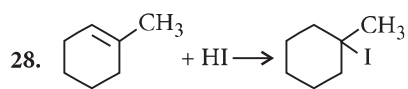
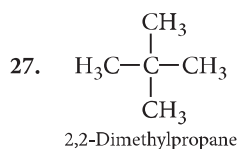
1-Chloro-2,2-dimethylpropane
- 
- $$\text{CH}_3-\overset{3}{\underset{\text{Cl}}{\text{CH}}}-\overset{2}{\underset{\text{Br}}{\text{CH}}}-\overset{1}{\text{CH}_3}$$

2-Bromo-3-chlorobutane
- 1-Bromobut-2-ene
- $$\text{ClCH}_2-\overset{3}{\text{C}}\equiv\overset{2}{\text{C}}-\overset{1}{\text{CH}_2}-\text{Br}$$

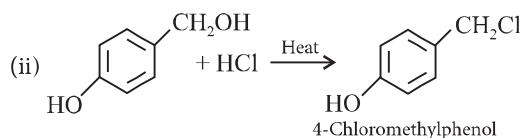
1-Bromo-4-chlorobut-2-yne
- (i) Refer to answer 10.
(ii) 2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane
- (i) 2-Bromobutane
(ii) 1,3-Dibromobenzene
(iii) 3-Chloropropene
- $$\text{CH}_3\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow[\text{Propene}]{\text{Peroxide}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$$
- $$\xrightarrow[\text{Acetone}]{\text{NaI}} \text{CH}_3-\text{CH}_2-\text{CH}_2\text{I}$$

1-Iodopropane
- 
- $$\text{CH}_3-\text{CH}_2-\overset{\text{Br}}{\text{C}}-\text{CH}_3$$

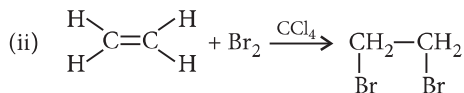
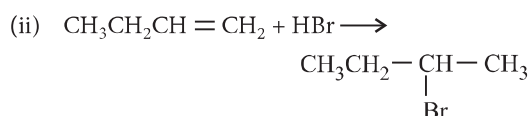
2-Bromo-2-methylbutane (Markownikov's addition)



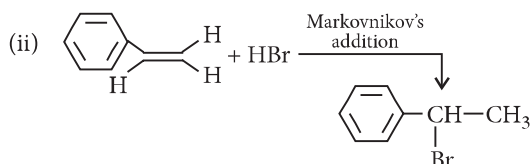
35. (i) Refer to answer 33 (i).



36. (i) Refer to answer 28.



38. (i) Refer to answer 28.



(iii) Refer to answer 36 (ii).

39. (i) Refer to answer 38(ii).

(ii) Refer to answer 28.

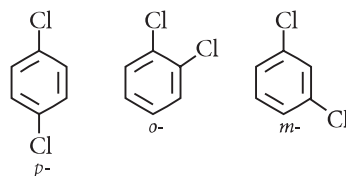
(iii) Refer to answer 33(i).

40. *n*-Butyl bromide, being a straight chain molecule have strong intermolecular forces whereas *t*-butyl bromide being a branched chain molecule have weaker intermolecular forces due to smaller surface area.

Hence, boiling point of *n*-butyl bromide is higher than that of *t*-butyl bromide.

41. Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H - bond among water molecules is much higher than energy released by water halide interaction.

42. *p*-Dichlorobenzene has higher melting point than those of *o*- and *m*-isomers because it is more symmetrical and packing is better in solid form. Hence, it has stronger intermolecular force of attraction than *o*- and *m*-isomers.



43. Refer to answer 41.

44. Haloalkanes dissolve in organic solvents because the intermolecular attractions between haloalkanes and organic solvent molecules have the same strength as in the separate haloalkanes and solvent molecules.

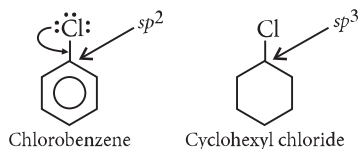
45. The boiling point of ethyl bromide is higher due to the greater magnitude of the van der Waals forces which depend upon molecular size and mass.

46. (i) There are two reasons :

(a) In case of chlorobenzene, carbon to which chlorine is attached is sp^2 hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3 hybridised. So the net dipole moment is lower in chlorobenzene.

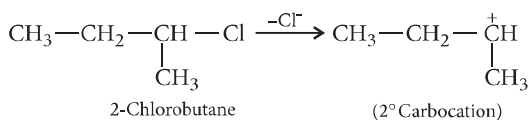
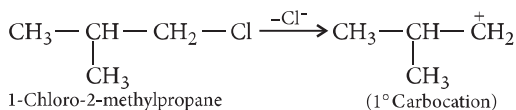
(b) In chlorobenzene C—Cl bond has some double bond character so its bond length is smaller.

Hence dipole moment is smaller than cyclohexyl chloride which has a longer C—Cl single bond.

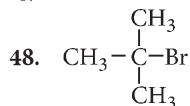


(ii) Refer to answer 41.

47. The S_N1 reaction proceeds through carbocation formation thus, the compound which forms more stable carbocation will be more reactive.

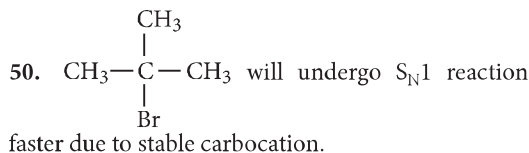


As, 2° carbocation is more stable than 1° carbocation thus, 2-chlorobutane is more reactive towards S_N1 reaction.



Tertiary butyl bromide
or 2-Bromo-2-methylpropane

49. $\text{CH}_3-\text{CH}_2-\text{Br}$ would undergo S_N2 reaction faster due to forming of less steric hindrance.



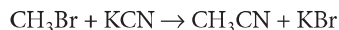
51. Since I^- is a better leaving group than Br^- , thus, $\text{CH}_3\text{CH}_2\text{I}$ undergoes S_N2 reaction faster than $\text{CH}_3\text{CH}_2\text{Br}$.

52. is a chiral molecule.

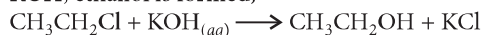
53. (i) CH_3I will give faster S_N2 reaction.

(ii) CH_3Cl will give faster S_N2 reaction.

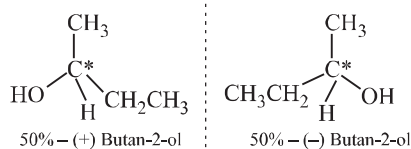
54. CH_3CN is formed by nucleophilic substitution reaction.



55. When ethyl chloride is treated with aqueous KOH, ethanol is formed,

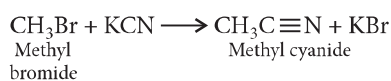


56. The (\pm)-Butan-2-ol is optically inactive because it exist in two enantiomeric forms which are non-superimposable mirror images of each other. Both the isomers are present in equal amounts therefore, it does not rotate the plane of polarized light and is optically inactive.

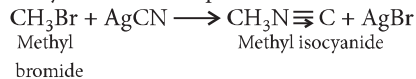


57. Tertiary halide reacts faster than the secondary halide because of the greater stability of *tert*-carbocation.

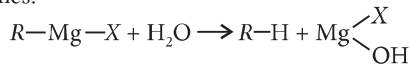
58. KCN is predominantly ionic and provides cyanide ions in solution



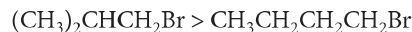
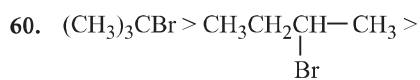
AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as main product.

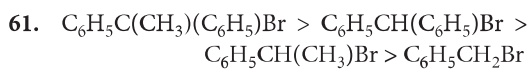


59. Grignard reagents react with water to form alkanes.



So, they must be prepared under anhydrous conditions.





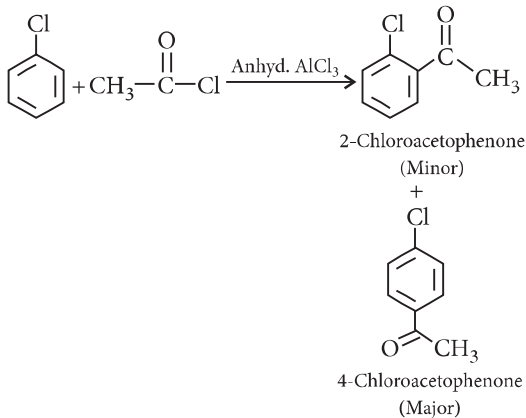
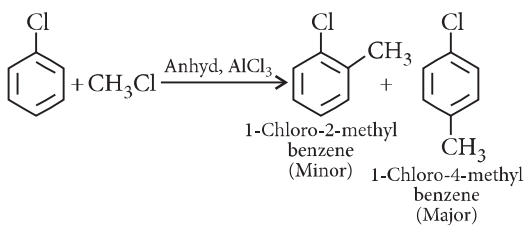
62. C_2H_5Br reacts with $AgNO_3$ to give yellow precipitate of $AgBr$ while C_6H_5Br will not.

63. 1-Bromopentane is a primary alkyl halide, hence reacts faster in S_N2 displacement than secondary halide 2-bromopentane.

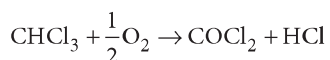
64. 2-Bromobutane will react faster in S_N1 displacement reaction because it will form more stable secondary carbocation intermediate.

65. $CH_3CH_2CH(Cl)CH_3$ hydrolyses easily with KOH because it is secondary halide.

66. Haloarenes can undergo both freidal craft alkylation (with alkyl halide) or freidal craft acylation (with acid halide) in presence of Lewis acid catalyst to give a mixture of *o*- and *p*-haloalkyl benzene or *o*- and *p*-haloacylbenzene.



67. Chloroform when exposed to air and sunlight changes to phosgene which is a poisonous gas.

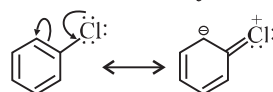


It is kept in dark coloured bottles to prevent the oxidation.

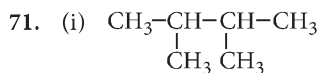
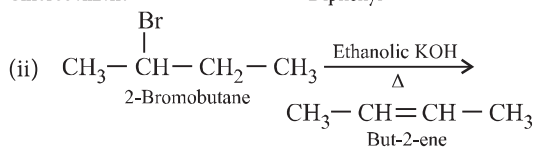
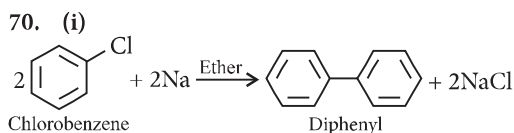
68. CH_3Cl will react faster in S_N2 reaction with OH^- .

69. (i) In halobenzene $C-X$ bond has partial double bond character due to resonance while CH_3-X bond is single bond.

Thus bond length of $C-X$ bond in halobenzene is smaller than that in CH_3-X .

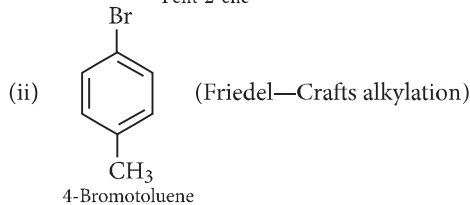
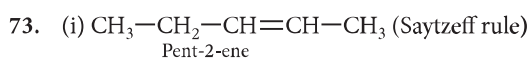


(iii) In S_N1 reaction carbocation intermediate is formed which is a planar molecule so, an incoming nucleophile can attack from either side and a equimolar mixture of two components are formed and resulting mixture is optically inactive.

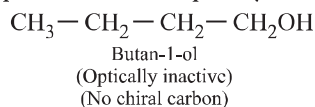


72. (i) Racemic mixture contains equal amount of *d* and *l* forms, hence rotation due to one enantiomer is cancelled by another.

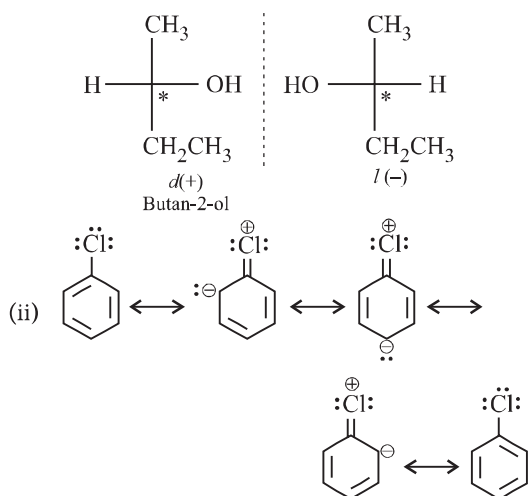
(ii) The presence of nitro group at *o*- and *p*-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by resonance.



74. (i) Butan-1-ol is achiral, *i.e.*, does not have chiral 'C' atom which is attached to four different groups, therefore, it is optically inactive.



Butan-2-ol is chiral, *i.e.*, has chiral 'C' atom, attached to four different groups.



Although Cl is electron withdrawing (*I* effect) but still *o*- and *p*-directing as due to *+R* effect, electrons density is maximum at *o*- and *p*-positions.

75. (i) (a) Br undergoes faster S_N2 reaction.

(b) is chiral.

(ii) (a) S_N2 reaction occurs with inversion of configuration.

(b) S_N1 reaction occurs with racemisation.

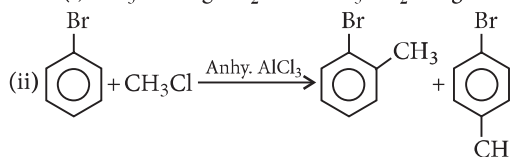
76. (i) Refer to answer 55.

(ii) Refer to answer 66.

77. (i) 1-Bromobutane is 1° alkyl halide while 2-bromobutane is 2° alkyl halide. Due to steric hindrance in 2° alkyl halides, 1° alkyl halide will react faster than 2° alkyl halide in S_N2 reaction.

(ii) Carbocations are formed in S_N1 reaction which are planar species, thus, racemisation occurs.

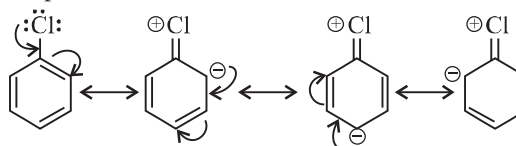
78. (i) $\text{CH}_3\text{Cl} + \text{AgNO}_2 \longrightarrow \text{CH}_3\text{NO}_2 + \text{AgCl}$



79. A nucleophile which can attack from more than one centres, is known as ambident nucleophile.
e.g., $\text{C}\equiv\text{N}^-$: Cyanide ion

80. Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons.

(i) Resonance effect : In haloarenes the electron pairs on halogen atom are in conjugation with π -electrons of the ring and the following resonating structures are possible.



C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation of carbon atom in C—X bond.

81. (i) Refer to answer 69(i).

(ii) Refer to answer 67.

82. (i) Refer to answer 51.

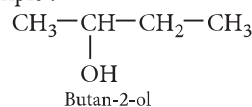
(ii) Refer to answer 69(i).

83. In haloarenes $-ve$ charge gets localised on arenes using resonance, therefore they undergo electrophilic substitution.

Haloalkanes have electrophilic carbon centre due to polarity of $\text{C}\rightarrow\text{X}$ bond.

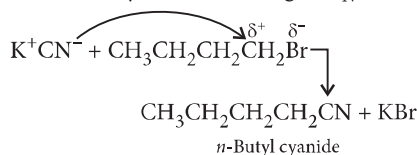
84. (i) An equimolar mixture of a pair of enantiomers is called racemic mixture. A racemic mixture is optically inactive due to external compensation.

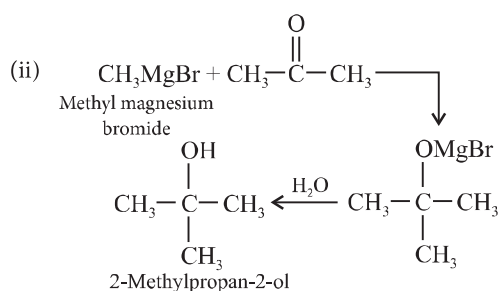
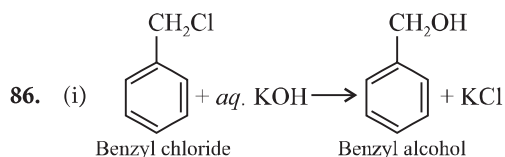
Example :



(ii) Of the two bromo derivatives, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ and $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$, the $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ is more reactive than $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ for S_N1 reaction because its carbocation is resonance stabilised by two phenyl groups.

85. Normal butyl bromide will give S_N2 reaction :

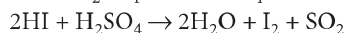
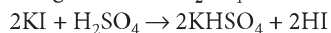




87. (i) 1-Bromopentane, as it is a primary alkyl halide.

(ii) 1-Bromo-2-methylbutane, as it is a primary alkyl halide.

88. (i) H_2SO_4 is an oxidant. KI reacts with H_2SO_4 and give HI and H_2SO_4 oxidises HI to I_2 .

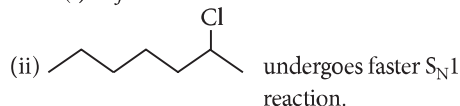


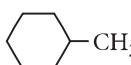
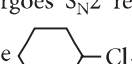
Thus HI will not be available for reaction with alcohol to form alkyl iodide.

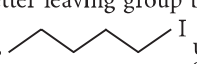
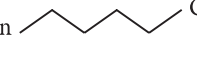
This is why sulphuric acid is not used during the reaction of alcohols with KI.


(ii) Refer to answer 80.

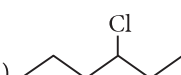
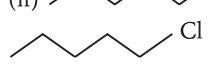
89. (i) Refer to answer 59.



90. (i)  is primary halide and therefore, undergoes $\text{S}_{\text{N}}2$ reaction faster than the secondary halide .

(ii) As iodide is a better leaving group because of its large size, therefore,  undergoes $\text{S}_{\text{N}}2$ reaction faster than .

91. (i)  : Tertiary halide reacts faster than secondary halide because of the greater stability of *tert.* carbocation.

(ii)  reacts faster than  because of greater stability of secondary carbocation than primary.

92. (i) Among the various halides with same alkyl group the order of reactivity is $\text{RI} > \text{RBr} > \text{RCl}$.

Due to increasing bond strength of C-I , C-Br and C-Cl the reactivity decreases.

(ii) Neopentyl chloride being a primary halide reacts slowly through $\text{S}_{\text{N}}1$ and the carbon carrying halogen is sterically more hindered. Hence it does not follow $\text{S}_{\text{N}}2$ mechanism.

93. (i) Refer to answer 80.

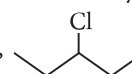
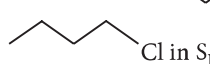
(ii) In aqueous solution, KOH is almost completely involved to give OH^- ion which being a better nucleophile gives a substitution reaction on alkyl halides to form alcohol. But an alcoholic solution of KOH containing alkoxide (RO^-) ions which being a much stronger base than OH^- ion preferentially snatches a H^+ ion from an alkyl chloride to form alkenes.

94. (i) Refer to answer 80.

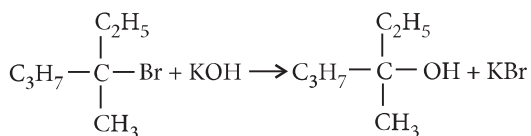
(ii) Refer to answer 57.

95. (i) Refer to answer 80.

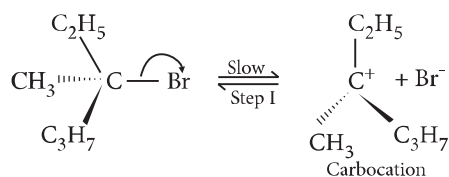
(ii) Due to greater stability of 2° carbocation over

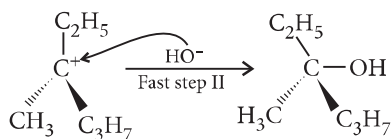
1° carbocation,  will react faster than  in $\text{S}_{\text{N}}1$ reaction.

96. In $\text{S}_{\text{N}}1$ mechanism of substitution reaction, the rate of reaction depends upon the concentration of only one reactant. It is two steps.

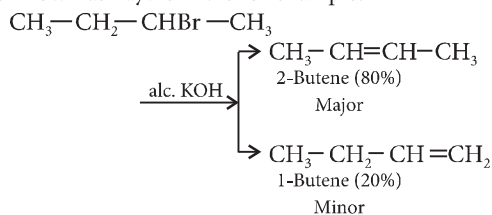


Mechanism :

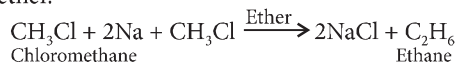




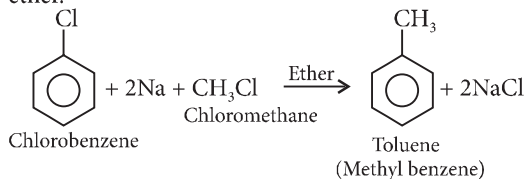
97. Saytzeff rule : In elimination reaction alkene having the lesser number of hydrogen on the double bonded carbon atom is formed. This generalisation is known as Saytzeff rule for example.



98. (i) Wurtz reaction : It converts alkyl halide into higher alkane in presence of sodium metal and dry ether.



(ii) **Wurtz-Fittig reaction :** It converts aryl halide into alkyl arenes in presence of sodium metal and ether.



99. (i) Chiral object : An object which has no plane of symmetry (cannot be divided into two identical halves) is called chiral (Greek; Chiral-Hand) or dissymmetric or asymmetric. A Chiral object is not superimposable on its mirror image.

e.g., left and right hand of a person are mirror images of each other and are not superimposable.



(ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$ hydrolyses easily with KOH

because it is secondary halide.

(iii) As iodide is a better leaving group because of its large size, therefore, I undergoes $\text{S}_{\text{N}}2$ reaction faster than Cl.

100. (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane.

- (ii) 1-Bromo-3-methylbutane > 3-Bromo-2-methylbutane > 2-Bromo-2-methylbutane
 (iii) 1-Bromobutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane

101. (a) (i) Benzyl chloride gives white precipitate with AgNO_3 solution while chlorobenzene does not. (ii) CHCl_3 with aniline in presence of alc. KOH gives foul smelling isocyanides whereas CCl_4 does not. (b) CH_3Cl is hydrolysed easily than $\text{C}_6\text{H}_5\text{Cl}$ as chlorobenzene has partial double bond character between C—Cl bond which is difficult to break.

102.

	$\text{S}_{\text{N}}1$ mechanism	$\text{S}_{\text{N}}2$ mechanism
1.	It is two step process, carbocation intermediate is formed.	It is single step process. No intermediate is formed.
2.	It obeys 1 st order kinetics. Rate = k [Reactant]	It obeys 2 nd order kinetics. Rate = k [Reactant] [Nucleophile]
3.	Order of reactivity $3^\circ > 2^\circ > 1^\circ$.	Order of reactivity $1^\circ > 2^\circ > 3^\circ$.
4.	Optically inactive product is formed (racemic mixture).	Inversion of configuration takes place.
5.	e.g., $(\text{CH}_3)_3\text{CBr} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$ 2-Bromo-2-methylpropane ↓ $(\text{CH}_3)_3\text{COH} + \text{Br}^-$ 2-Methylpropan-2-ol	e.g.,

103. (ii) DDT is used as an insecticide and iodoform is used as a mild antiseptic.

