CHAPTER

Haloalkanes and Haloarenes

10.4 Methods of Preparation of Haloalkanes

 The reaction of C₆H₅CH CHCH₃ with HBr produces

 (a) C₆H₅CH₂CH₂CH₂Br



(c)
$$C_6H_5CHCH_2CH_3$$

|
Br

(2015, Cancelled)

(d) C₆H₅CH₂CHCH₃ | Br

2. In the replacement reaction

$$\rightarrow$$
CI + MF $\longrightarrow \rightarrow$ CF + M

The reaction will be most favourable if M happens to be

- (a) Na (b) K (c) Rb (d) Li (*Mains* 2012)
- **3.** When chlorine is passed through propene at 400°C, which of the following is formed?
 - (a) PVC
 - (b) Allyl chloride
 - (c) Propyl chloride
 - (*d*) 1, 2-Dichloroethane (1993)

10.7 Chemical Reactions

- **4.** Elimination reaction of 2-bromopentane to form pent-2-ene is
 - (A) β -Elimination reaction
 - (B) Follows Zaitsev rule
 - (C) Dehydrohalogenation reaction
 - (D) Dehydration reaction

(a)
$$(A), (B), (C)$$
 (b) $(A), (C), (D)$

(c)
$$(B), (C), (D)$$
 (d) $(A), (B), (D)$

(NEET 2020)

5. The hydrolysis reaction that takes place at the slowest rate, among the following is

(a)
$$(H_3 \cap CH_3 \cap CH_3 \cap CH_3)$$

(b) $H_3 \cap CH_2 - CH_2 \cap CH_3 \cap CH_3$
(c) $H_2 \cap CH_2 - CH_2 \cap C$

- 6. The compound *A* on treatment with Na gives *B*, and with PCl₅ gives *C*. *B* and *C* react together to give diethyl ether. *A*, *B* and *C* are in the order
 - (a) C_2H_5OH , C_2H_6 , C_2H_5Cl
 - (b) C_2H_5OH , C_2H_5Cl , C_2H_5ONa
 - (c) $C_2H_5Cl, C_2H_6, C_2H_5OH$
 - (d) C_2H_5OH , C_2H_5ONa , C_2H_5Cl (NEET 2018)
- 7. The compound C_7H_8 undergoes the following reactions :

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

The product C is

- (a) *m*-bromotoluene
- (b) *o*-bromotoluene
- (c) 3-bromo-2,4,6-trichlorotoluene
- (d) p-bromotoluene. (NEET 2018)
- 8. Identify *A* and predict the type of reaction.

(a)
$$NaNH_2 \rightarrow A$$

 $NaNH_2 \rightarrow A$
 NH_2 and elimination addition reaction



This reaction will be the fastest in

- (a) ethanol
- (b) methanol
- (c) N, N'-dimethylformamide (DMF)
- (*d*) water. (*NEET-II 2016*)
- **10.** Which of the following biphenyls is optically active?



11. For the following reactions: (A) CH CH CH Br + KOH \longrightarrow $_{3}$ $_{2}$ $_{2}$ CH₃CH = CH₂ + KBr + H₂O





Which of the following statements is correct?

- (a) (A) is elimination, (B) and (C) are substitution reactions.
- (b) (A) is substitution, (B) and (C) are addition reactions.
- (c) (A) and (B) are elimination reactions and (C) is addition reaction.
- (d) (A) is elimination, (B) is substitution and (C) is addition reaction. (*NEET-I 2016*)
- **12.** Twopossiblestereo-structures of CH₃CHOHCOOH, which are optically active, are called
 - (a) atropisomers (b) enantiomers
 - (c) mesomers (d) diastereomers. (2015)
- **13.** In an S_N 1 reaction on chiral centres, there is
 - (a) inversion more than retention leading to partial racemisation
 - (b) 100% retention
 - (c) 100% inversion
 - (d) 100% racemisation. (2015)
- **14.** Which of the following compounds will undergo racemisation when solution of KOHhydrolyses?

(i)
$$CH_2Cl$$

(ii) $CH_3CH_2CH_2Cl$
(iii) $H_3C-CH-CH_2Cl$ (iv) $H \xrightarrow{CH_3}{I}$
(iv) $H_3C-CH-CH_2Cl$ (iv) $H \xrightarrow{C}{I}$
(a) (i) and (ii) (b) (ii) and (iv)
(c) (iii) and (iv) (d) (i) and (iv)

15. Given:



I and II are

- (a) identical
- (b) a pair of conformers
- (c) a pair of geometrical isomers
- (d) a pair of optical isomers.

(Karnataka NEET 2013)

(2014)

- **16.** Which of the following acids does not exhibit optical isomerism?
 - (a) Maleic acid
 (b) α-Amino acids
 (c) Lactic acid
 (d) Tartaric acid
 (2012)

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17. Consider the reactions : (i) $(CH_3)_2CH - CH_2Br \xrightarrow{C_2H_5OH}$ $(CH_3)_2CH - CH_2OC_2H_5 + HBr$ (ii) $(CH_3)_2CH - CH_2Br \xrightarrow{}$ $(CH_3)_2CH - CH_2OC_2H_5 + Br^-$ The mechanisms of reactions (i) and (ii) are respectively (a) S_N1 and S_N2 (b) S_N1 and S_N1 (c) S_N2 and S_N2 (d) S_N2 and S_N1 (Mains 2011)

18. Which of the following compounds undergoes nucleophilic substitution reaction most easily?



- **19.** Which one is most reactive towards S_N1 reaction?
 - (a) $C_6H_5CH(C_6H_5)Br$
 - (b) C₆H₅CH(CH₃)Br
 - (c) $C_6H_5C(CH_3)(C_6H_5)Br$
 - (d) $C_6H_5CH_2Br$
- 20. The correct order of increasing reactivity of



C—X bond towards nucleophile in the following compounds is

(a) $I < II < IV < III$	(b) $II < III < I < IV$
(c) $IV < III < I < II$	(d) $III < II < I < IV$

21. In the following reaction,

 $\begin{array}{c} C H CH Br \xrightarrow{1. Mg, Ether} X, \\ 6 5 2 & 2 \end{array} \xrightarrow{2. H_3O^+} X, \\ the product 'X' is \\ (a) C_6H_5CH_2OCH_2C_6H_5 \\ (b) C_6H_5CH_2OH \\ (c) C_6H_5CH_3 \end{array}$

(d) $C_6H_5CH_2CH_2C_6H_5$ (Mains 2010)

22. Which of the following reactions is an example of nucleophilic substitution reaction?

(a)
$$2RX + 2Na \longrightarrow R - R + 2NaX$$

(b) $RX + H_2 \longrightarrow RH + HX$
(c) $RX + Mg > RMgX$
(d) $RX + KOH \longrightarrow ROH + KX$ (2009)

23. How many stereoisomers does this molecule have? CH₃CH = CHCH₂CHBrCH₃

24. In a $S_N 2$ substitution reaction of the type

$$R$$
—Br + Cl⁻ \longrightarrow R —Cl + Br⁻

which one of the following has the highest relative rate?

(a)
$$CH_3 - C - CH_2Br$$
 (b) CH_3CH_2Br
 CH_3
(c) $CH_3CH_2CH_2Br$ (d) $CH_3 - CH - CH_2Br$
 CH_3

- **25.** If there is no rotation of plane polarised light by a compound in a specific solvent, though to be chiral, it may mean that
 - (a) the compound is certainly meso
 - (b) there is no compound in the solvent
 - (c) the compound may be a racemic mixture
 - (d) the compound is certainly a chiral. (2007)
- **26.** $CH_3 CHCl CH_2 CH_3$ has a chiral centre. Which one of the following represents its *R*-configuration?

(a)
$$H - C - CH_3$$

(b) $CI - C - CH_3$
(c) $H - C - CI$
(c) H

- **27.** Which of the following is not chiral?
 - (a) 2-Hydroxypropanoic acid
 - (b) 2-Butanol

(2010)

(2010)

- (c) 2,3-Dibromopentane
- (d) 3-Bromopentane (2006)
- **28.** Which of the following undergoes nucleophilic substitution exclusively by S_N1 mechanism?
 - (a) Ethyl chloride
 - (b) Isopropyl chloride
 - (c) Chlorobenzene
 - (d) Benzyl chloride

(2005)

(2008)

29. The chirality of the compound

- **30.** Which of the following is least reactive in a nucleophilic substitution reaction?
 - (a) $(CH_3)_3C Cl$
 - (b) $CH_2 = CHCl$
 - (c) CH₃CH₂Cl
 - (2004)(d) $CH_2 = CHCH_2Cl$
- **31.** Which of the following pairs of compounds are enantiomers?



32. Reactivity order of halides for dehydrohalogenation is

(a) R - F > R - Cl > R - Br > R - I

- (b) R I > R Br > R Cl > R F(c) R - I > R - Cl > R - Br > R - F
- (d) R F > R I > R Br > R Cl(2002)

(d) K = 1 ... 33. $CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} \chi \xrightarrow{acetic anhydride} Z$

Z in the above reaction sequence is

- (a) CH₃CH₂CH₂NHCOCH₃
- (b) CH₃CH₂CH₂NH₂
- (c) CH₃CH₂CH₂CONHCH₃
- (d) CH₃CH₂CH₂CONHCOCH₃ (2002)

- 34. $CH_3 CH_2 CH CH_3$ obtained by chlorination of Cl *n*-butane will be (a) meso form (b) racemic mixture (c) *d*-form (d) *l*-form. (2001)
- **35.** An organic compound $A(C_4H_9Cl)$ on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative then, A is
 - (a) *t*-butyl chloride (b) *s*-butyl chloride
 - (c) *iso*-butyl chloride (d) *n*-butyl chloride.

(2001)

- **36.** A compound of molecular formula C_7H_{16} shows optical isomerism, compound will be
 - (a) 2,3-dimethylpentane
 - (b) 2,2-dimethylbutane
 - (c) 2-methylhexane
 - (d) none of these. (2001)
- **37.** Which of the following compounds is notchiral? (a) CH₃CHDCH₂Cl (b) CH₃CH₂CHDCl (c) DCH₂CH₂CH₂Cl (d) CH₃CHClCH₂D

(1998)

- 38. Replacement of Cl of chlorobenzene to give phenol requires drastic conditions. But chlorine of 2,4-dinitrochlorobenzene is readily replaced because
 - (a) NO₂ donates e^- at meta position
 - (b) NO₂ withdraws *e*⁻ from *ortho/para* positions
 - (c) NO_2 makes ring electron rich at ortho and para
 - (d) NO₂ withdraws e^{-} from meta position.

(1997)

- **39.** The alkyl halide is converted into an alcohol by
 - (a) elimination
 - (b) dehydrohalogenation
 - (c) addition
 - (d) substitution. (1997)
- **40.** The following reaction is described as

$$\begin{array}{c} H_{3}C(CH_{2})_{5} \\ C - Br \xrightarrow{OH^{-}} HO - C \\ H_{3}C \xrightarrow{I} H \\ H \\ CH_{3} \\ (a) S_{N}2 \\ (b) S_{N}0 \\ (c) S_{E}2 \\ (d) S_{N}1 \\ (1997) \end{array}$$

- **41.** Reaction of *t*-butyl bromide with sodium methoxide produces
 - (a) sodium *t*-butoxide
 - (b) *t*-butyl methyl ether
 - (c) isobutane
 - (d) isobutylene.

(1994)

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- **42.** Grignard reagent is prepared by the reaction between
 - (a) magnesium and alkane
 - (b) magnesium and aromatic hydrocarbon
 - (c) zinc and alkyl halide
 - (d) magnesium and alkyl halide. (1994)
- **43.** Chlorobenzene reacts with Mg in dry ether to give a compound (*A*) which further reacts with ethanol to yield
 - (a) phenol (b) benzene
 - (c) ethyl benzene (d) phenyl ether. (1993)
- **44.** Benzene reacts with *n*-propyl chloride in the presence of anhydrous AlCl₃ to give
 - (a) 3-propyl-1-chlorobenzene
 - (b) *n*-propylbenzene
 - (c) no reaction
 - (d) isopropylbenzene. (1993)
- **45.** Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

(a)
$$O_2 N \longrightarrow Cl$$
 (b) $O_2 N \longrightarrow Cl$
NO2
(c) $Me_2 N \longrightarrow Cl$ (d) $C_6 H_5 Cl$ (1989)

- **46.** Which of the following is an optically active compound?
 - (a) 1-Butanol
 - (c) 2-Chlorobutane

(d) 4-Hydroxyheptane

(b) 1-Propanol

(1989)

10.8 Polyhalogen Compounds

47. Trichloroacetaldehyde, CCl₃CHO reacts with chlorobenzene in presence of sulphuric acid and produces



- **48.** Industrial preparation of chloroform employs acetone and
 - (a) phosgene
 - (b) calcium hypochlorite
 - (c) chlorine gas
 - (d) sodium chloride. (1993)
- **49.** Phosgene is a common name for
 - (a) phosphoryl chloride
 - (b) thionyl chloride
 - (c) carbon dioxide and phosphine
 - (d) carbonyl chloride. (1988)

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1.	(c)	2.	(c)	3.	(b)	4.	(a)	5.	(a)	6.	(d)	7.	(a)	8.	(d)	9.	(c)	10.	(d)
11.	(d)	12.	(b)	13.	(a)	14.	(None)	15.	(b)	16.	(a)	17.	(c)	18.	(a)	19.	(c)	20.	(a)
21.	(c)	22.	(d)	23.	(c)	24.	(b)	25.	(a)	26.	(b)	27.	(d)	28.	(d)	29.	(a)	30.	(b)
31.	(a)	32.	(b)	33.	(a)	34.	(b)	35.	(a)	36.	(a)	37.	(c)	38.	(b)	39.	(d)	40.	(a)
41.	(d)	42.	(d)	43.	(b)	44.	(d)	45.	(a)	46.	(c)	47.	(c)	48.	(b)	49.	(d)		

(2009)

Hints & Explanations

1. (c) :
- CH=CH
$$\in$$
H₃ $\xrightarrow{\text{HBr}}$
- CH $-$ CH $-$ CH₂ $-$ CH₃
More stable
(Benzyl carbocation)
- CH \in H₂ $-$ CH₃
Br

2. (c) : Tertiary halide shows $S_N 1$ mechanism *i.e.*, ionic mechanism. In the given reaction negative ion will attack on carbocation. Thus greater the tendency of ionisation (greater ionic character in M - F bond) more favourable will be reaction. The most ionic bond is Rb – F in the given examples thus most favourable reaction will be with Rb–F.

3. (b):
$$CH_3CH = CH_2 \xrightarrow{Cl_2, 400^{\circ}C} CICH_2CH = CH_2$$

At 400°C temperature, substitution occurs instead of addition.

4. (a):
$$CH_3 - CH_2 - CH_2 - CH - CH_3 - CH_2 - CH = CH - CH_3$$

Pent-2-ene (More substituted alkene is formed, Zaitsev's rule)

5. (a) : Arylhalidesarelessreactiveascomparedtoalkyl halides as the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles such as OH⁻, NH⁻₂ etc. In chlorobenzene, the electron pair of chlorine atom is in conjugation with π -electrons of benzene ring. Thus C—Cl bond acquires double bond character and is difficult to break.

8. (d): *m*-Bromoanisole gives only the respective *meta* substituted aniline. This is a substitution reaction which goes by an elimination-addition pathway.

9. (c) : The reaction,

 $CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$

follows $S_N 2$ mechanism which is favoured by polar aprotic solvent *i.e.*, N, N' dimethylformamide (DMF),

$$H = C = N(CH_3)_2$$

10. (d) : *o*-Substituted biphenyls are optically active as both the rings are not in one plane and their mirror images are non-superimposable.

11. (d) :
$$CH_3CH_2CH_2Br + KOH CH_3CH CH_2 = + KBr + H_2O$$

Saturated compound is converted into unsaturated compound by removal of group of atoms hence, it is an elimination reaction.

$$H_3C \xrightarrow{CH_3} + KOH \xrightarrow{H_3C} \xrightarrow{CH_3} + KBr$$

—Br group is replaced by — OH group hence, it is a substitution reaction.

Addition of Br₂ converts an unsaturated compound into a saturated compound hence, it is an addition reaction.

12. (b) :
$$H - C - OH$$

 $H - C - OH$
 $H - C - OH$
 $H - C - H$
 $H -$

13. (a) : In case of optically active alkyl halides,

 S_N1 reaction is accompanied by racemisation. The carbocation formed in the slow step being sp^2 hybridised is planar and attack of nucleophile may take place from either side resulting in a mixture of products, one having the same configuration and other having inverted configuration.

The isomer corresponding to inversion is present in slight excess because $S_N 1$ also depends upon the degree of shielding of the front side of the reacting carbon.

14. (None) : Due to chirality
$$\begin{pmatrix} CH_3 \\ I_* \\ H \\ C \\ C_2H_5 \end{pmatrix}$$
, only

compound (iv) will undergo racemisation. Hence, all the given options are incorrect.

15. (b): I and II are staggered and eclipsed conformers.

16. (a) : Maleic acid shows geometrical isomerism and not optical isomerism.

$$HOOC$$
 $H C = C H COOH$

17. (c) : If reaction is $S_N 1$, there will be the formation of carbocation and the rearrangement takes place. In these reactions there is no rearrangement hence both are $S_N 2$ mechanism.

18. (a) : Electron withdrawing groups like — NO_2 facilitates nucleophilic substitution reaction in chlorobenzene.

19. (c) : $S_N 1$ reactions proceed *via* the formation of a carbocation intermediate.

More stable is the carbocation more reactive is the alkyl/ aryl halide towards $S_N 1$.

In $C_6H_5C^+(CH_3)(C_6H_5)$ carbocation, the two phenyl rings by their +*R* effect and —CH₃ by its +*I* effect diminish the positive charge and make it stable.

20. (a) : I < II < IV < III

The order of reactivity is dependent on the stability of the intermediate carbocation formed by cleavage of C-X bond. The 3° carbocation (formed from III) will be more stable than its 2° counter part (formed from IV) which in turn will be more stable than the arenium ion (formed from I). Also, the aryl halide has a double bond character in the C-X bond which makes the cleavage more difficult. However, inspite of all the stated factors, II will be more reactive than I due to the presence of the electron withdrawing $-NO_2$ group. C-X bond becomes weak and undergoes nucleophilic substitution reaction.

21. (c) :
$$C_6H_5CH_2Br \xrightarrow{Mg, ether} C_6H_5CH_2MgBr$$

 $\downarrow H_3O^+$
 $C_6H_5CH_3 + Mg \xrightarrow{Br} OH$

22. (d)

23. (c) : The given compound may be written as

$$CH_{3} = C = C H H_{CH_{2}-C-CH_{3}}$$

Both geometrical isomerism (*cis-trans* form) and optical isomerism is possible in the given compound.

No. of optical isomer $= 2^n = 2^1 = 2$

(where n = no. of asymmetric carbon)

Hence total no. of stereoisomers = 2 + 2 = 4

24. (b) : $S_N 2$ mechanism is followed in case of primary and secondary alkyl halides *i.e.* $S_N 2$ reaction is favoured by small groups on the carbon atoms attached to halogen so, $CH_3 - X > R - CH_2 - X > R_2CH - X > R_3C - X$. Primary is more reactive than secondary and tertiary alkyl halides.

25. (a) : Meso compound does not rotate plane polarised light. Compound which contains tetrahedral atoms with four different groups but the whole molecule is achiral, is known as meso compound. It possesses a plane of symmetry and is optically inactive. One of the asymmetric carbon atoms turns the plane of polarised light to the right and other to the left and to the same extent so that the rotation due to upper half is compensated by the lower half, *i.e.*, internally compensated, and finally there is no rotation of plane polarised light.

26. (b) : C1
$$\xrightarrow{c}_{1} \xrightarrow{c}_{c}_{1}$$
 CH₃
 $\stackrel{H}{\xrightarrow{d}}_{r}$ R-configuration

h

27. (d) :
$$H_3C - CH_2 - CH_2 - CH_3$$

Due to absence of asymmetric carbon atom.

28. (d) : S_N1 reaction is favoured by heavy (bulky) groups on the carbon atom attached to halogens and nature of carbonium ion in substrate is Benzyl > Allyl > Tertiary > Secondary > Primary > Methyl halides.

Lowest priority atom is always away from the viewer. Priority is seen on the basis of atomic no. and if atomic no. are same then on the basis of atomic mass.

If clockwise then it is R, if anticlockwise then it is S. Name of the molecule is, (R) 1-bromo-1-chloroethane.

30. (b) : The non-reactivity of the chlorine atom in vinyl chloride can be explained from the molecular orbital point of view as follows. If the chlorine atom has sp^2 hybridisation, the C – Cl bond will be a σ -bond and the two lone pairs of electrons would occupy the other two sp^2 orbitals. This would leave a *p* orbital containing a lone pair, and this orbital could now conjugate with the π -bond of the ethylenic link. Thus two M.O's will be required to accommodate these four π -electrons. Furthermore, since

chlorine is more electronegative than carbon, the electrons will tend to be found in the vicinity of the chlorine atom. Nevertheless, the chlorine atom has now lost full control of the lone pair and so, is less negative than it would have been had there been no conjugation. Since two carbon atoms have acquired a share in the lone pair, each carbon atom acquires a small negative charge. Hence, owing to delocalisation of bonds (through conjugation), the vinyl chloride molecule has an increased stability. Before the chlorine atom can be displaced by some other group, the lone pair must be localised again on the chlorine atom. This requires energy, and so the chlorine is more firmly bound.

31. (a) : These two are non-superimposable mirror images of each other, so they are enantiomers.

32. (b) : I > Br > Cl > F-atomic radii

F, Cl, Br, I belong to the same group orderly. Atomic radii go on increasing as the nuclear charge increases in preceding downwards in a group. The decreasing order of bond length

C - I > C - Br > C - Cl > C - F. The order of bond dissociation energy R - F > R - Cl > R - Br > R - I. During dehydrohalogenation C - I bond breaks more easily than C - F bond. So reactivity order of halides is,

$$R - I > R - Br > R - Cl > R - F.$$

33. (a) :
$$CH_3CH_2Cl \xrightarrow{NaCN} CH_3CH_2CN$$

 $\xrightarrow{Ni/H_2} CH_3CH_2CH_2NH_2 \xrightarrow{acetic} anhydride$
 (Y)
 $CH_3CH_2CH_2NHCOCH_3$
 (Z)

34. (b) : Chlorination of *n*-butane takes place *via* free radical formation. *i.e.* $Cl_2 \rightarrow Cl + Cl$

$$CH_3CH_2CH_2CH_3 \xrightarrow{CI} CH_3CHCH_2CH_3 + HCl$$

 $sp^{2}\text{-}$ hybrid planar shape intermediate and $^{*}\!\mathrm{Cl}$ may attack from either side to give

$$\begin{array}{c} \mathrm{CH}_{3}\dot{\mathrm{C}}\mathrm{H}\mathrm{CH}_{2}\mathrm{CH}_{3} + \dot{\mathrm{Cl}} \longrightarrow \\ & \overset{\mathrm{H}}{\overset{\mathrm{I}}{\operatorname{CH}_{3}}} - \overset{\mathrm{Cl}}{\underset{\mathrm{C}}{\operatorname{CH}_{2}}} - \overset{\mathrm{Cl}}{\operatorname{CH}_{2}} + \overset{\mathrm{Cl}}{\underset{\mathrm{H}}{\operatorname{CH}_{3}}} + \overset{\mathrm{Cl}}{\underset{\mathrm{H}}{\operatorname{CH}_{3}}} - \overset{\mathrm{Cl}}{\underset{\mathrm{H}}{\operatorname{CH}_{2}}} - \overset{\mathrm{Cl}}{\underset{\mathrm{H}}{\operatorname{CH}_{2}}} - \overset{\mathrm{Cl}}{\underset{\mathrm{H}}{\operatorname{CH}_{2}}} + \overset{\mathrm{Cl}}{\underset{\mathrm{H}}{\operatorname{CH}_{3}}} + \overset{\mathrm{CL}}{\underset{\mathrm{H}}{\operatorname{CH}_{3}} + \overset{\mathrm{CL}}{\underset{\mathrm{H}}{\operatorname{CH}_{3}}} + \overset{\mathrm{CL}}{\underset{\mathrm{H}}{}} + \overset{\mathrm{CL}}{\underset{\mathrm{H}}}{$$

35. (a) : Wurtz reaction : It involves the reaction of alkyl halides with Na in ether to form higher alkanes. $2R - X + 2Na \longrightarrow R - R + 2NaX$

In the given problem
$$C H \cdot C H + 2NaCl$$

 $49 \qquad 49 \qquad 49 \qquad 49$

Compound A is t-butyl chloride, in this compound all - CH₃ groups have primary hydrogen only and able to give only, one chloro derivative.

$$(CH_3)_3CC(CH_3)_3 \xrightarrow{Cl_2} CH_2Cl(CH_3)_2C - C(CH_3)_3$$

36. (a) : Organic compounds exhibit the property of enantiomerism (optical isomerism) only when their molecules are chiral. Most chiral compounds have a chiral centre, which is an atom bonded to four different atoms or groups.

$$CH_3 > CH - C - CH_2CH_3$$

 $CH_3 > CH - C - CH_2CH_3$

2,3-Dimethylpentane has one chiral C-atom and does not have any symmetric element.

37. (c):
$$D_{-}$$
 $\begin{pmatrix} H & H & H \\ | & | & | \\ C_{-} & C & C_{-}Cl \\ | & | & | \\ H & H & H \end{pmatrix}$

The above compound has no chiral 'C'-atom. All the 'C' atoms are attached to two identical 'H' atoms, so they are not asymmetrical.

38. (b) :
$$\bigcup_{NO_2}^{Cl} NO_2$$

Withdrawal of electrons by - NO₂ groups from *ortho/* para positions cause easier removal of - Cl atom due to the development of positive charge on *o*- and *p*- positions.

39. (d) : $C_2H_5Br + KOH C_2H_3OH + KBr$

Ethyl bromide (aqueous) Ethyl alcohol

40. (a): $S_N 2$ reaction are bimolecular reactions where rate of reaction depends on the concentration of both substrate and nucleophile. When OH⁻ attacks the substrate from the opposite side of the leaving group *i.e.*, Br⁻ a transition state results, to which both OH and Br are partially bonded to carbon atom.

41. (d) : Isobutylene is obtained.

$$H_{3}C - C - CH_{3} + CH_{3}ONa \longrightarrow$$

$$CH_{3} - C + CH_{3}CH_{3} - CH_{3}CH_{3}$$

$$CH_{3} - C = CH_{2} + CH_{3}OH + NaBr$$

Thus, the reaction produces isobutylene.

42. (d) : Grignard reagent is prepared by heating an alkyl halide with dry magnesium powder in dry ether.

 $R \longrightarrow X + Mg \xrightarrow{\text{Dry ether}} R \longrightarrow Mg \longrightarrow X$ Grignard reagent

43. (b):
$$C_6H_5Cl \xrightarrow{Mg} C_6H_5MgCl$$

 $\xrightarrow{CH_3CH_2OH} C_6H_6 + CH_3CH_2OMgCl$
44. (d): $C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow{Anhy.}_{AlCl_3}$
 $C_6H_5 \xrightarrow{CH_3}_{l}$

Isopropylbenzene

45. (a) : Cl in 2, 4, 6-trinitrochlorobenzene is activated by three $-NO_2$ groups at *o*-and *p*-positions and hence undergoes hydrolysis most readily.

46. (c):
$$CH_3 - CH_2 - \overset{*}{CH} - CH_3$$

2-Chlorobutane contains a chiral carbon atom andhence it is optically active compound.

47. (c) : It gives D.D.T

(*p*,*p*- dichlorodiphenyltrichloroethane)

$$2C_{6}H_{5}Cl + CCl_{3}CHO \xrightarrow{H_{2}SO_{4}} Cl_{3}CCH \xrightarrow{-Cl} -Cl$$

$$48. (b) : CaOCl_{2} + H_{2}O \longrightarrow Ca(OH)_{2} + Cl_{2}$$

$$CH_{3}COCH_{3} + 3Cl_{2} \longrightarrow CCl_{3}COCH_{3} + 3HCl$$

$$Ca(OH)_{2} + 2CCl_{3}COCH_{3} \longrightarrow 2CHCl_{3}$$

$$+ \begin{array}{c} CH_{3}COO \\ CH_{3}COO \end{array} \xrightarrow{-Cl} Ca$$

