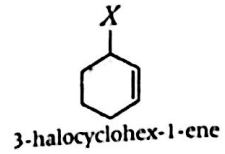


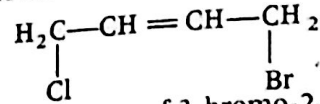
haloalkanes and haloarenes-CBSE(Solutions)

2. In allylic halides, the halogen is bonded to the sp^3 -hybridised carbon atom next to a carbon-carbon double bond. Thus,

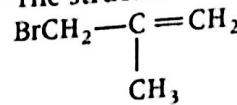


is an allylic halide.

3. The structure of 1-bromo-4-chlorobut-2-ene is (1)



4. The structure of 3-bromo-2-methylprop-1-ene is (1)



5. $\overset{1}{\text{CH}_3}-\overset{2}{\underset{\text{Br}}{\text{CH}}}-\overset{3}{\text{CH}_2}-\overset{4}{\text{CH}_2}-\overset{5}{\text{CH}_3}$
2-bromopentane (1)

6. $\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{H}_3\text{C} \end{array} - \overset{3}{\text{CH}} - \overset{2}{\underset{\text{Cl}}{\text{CH}}} - \overset{1}{\text{CH}_3}$
2-chloro-3-methylbutane (1)

7. $\overset{5}{\text{CH}_3}-\overset{4}{\underset{\text{Cl}}{\text{CH}}}-\overset{3}{\text{CH}_2}-\overset{2}{\text{CH}}=\overset{1}{\text{CH}_2}$
4-chloropent-1-ene
(As double bond have preference over halogen) (1)

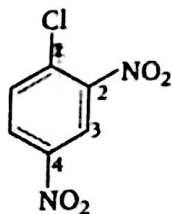
8. $\overset{1}{\text{CH}_3}-\overset{2}{\text{CH}}=\overset{3}{\text{CH}}-\overset{4}{\underset{\text{Br}}{\overset{\text{CH}_3}{\text{C}}}}-\overset{5}{\text{CH}_3}$
4-bromo-4-methylpent-2-ene (1)

9. $\overset{4}{\text{CH}_3}-\overset{3}{\underset{\text{CH}_3}{\text{C}}}-\overset{2}{\underset{\text{Cl}}{\text{CH}}}-\overset{1}{\text{CH}_3}$
2-chloro-3,3-dimethylbutane (1)

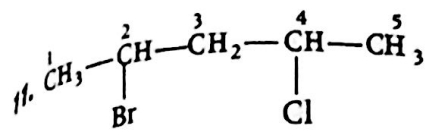
10.
1,4-dichloro-2-methylbenzene (1)

Explanations

1. The structure of 2,4-dinitrochlorobenzene is



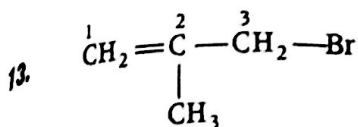
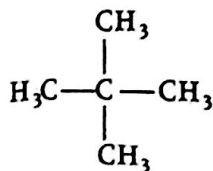
(1)



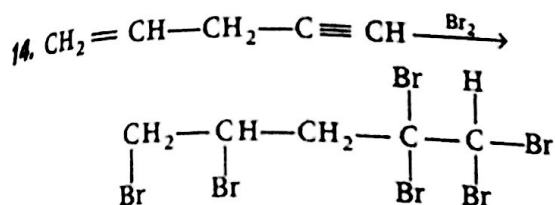
2-bromo-4-chloropentane

Numbering will be done in alphabetically manner

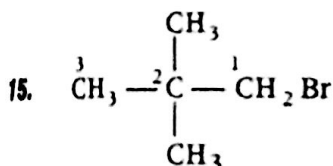
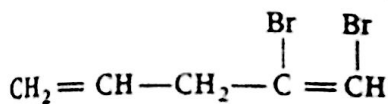
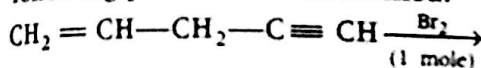
12. Hydrocarbon which gives only one monochlorination product is



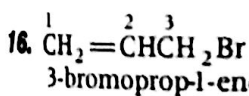
3-bromo-2-methylprop-1-ene.



The above product is formed when Br₂ is used in excess. But, if only one mole of Br₂ is used, the following product will be formed.

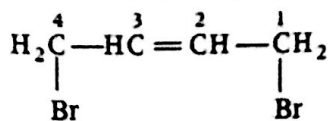


1-bromo-2,2-dimethyl propane

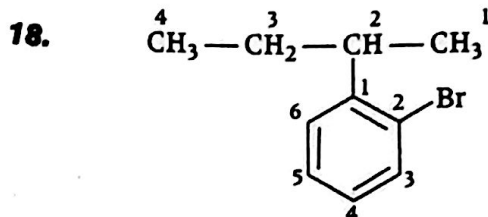


3-bromoprop-1-ene

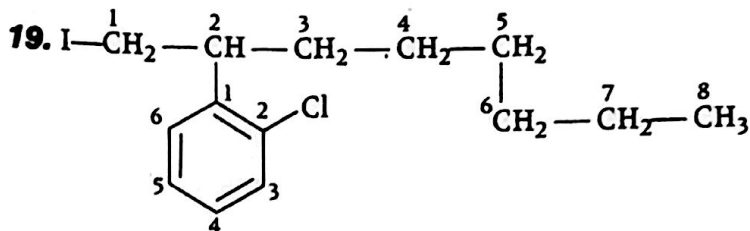
17. C-chain of 4 atoms, —Br at C₁ and C₄, double bond between C₂ and C₃.



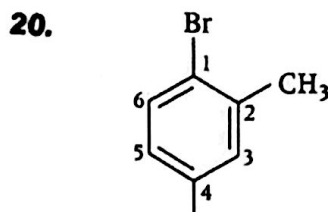
1,4-dibromobut-2-ene



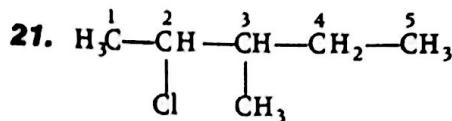
2-(2-bromophenyl) butane



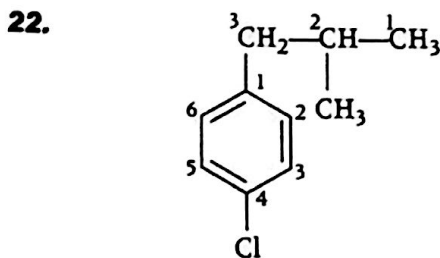
2-(2-chlorophenyl)-1-iodooctane



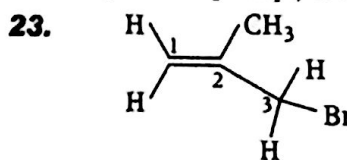
1-bromo-4-sec-butyl-2-methylbenzene



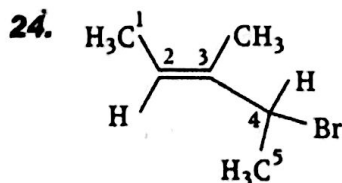
2-chloro-3-methylpentane



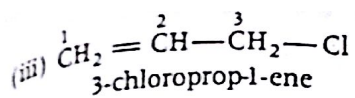
3-(4-chlorophenyl)-2-methylpropane



3-bromo-2-methylprop-1-ene

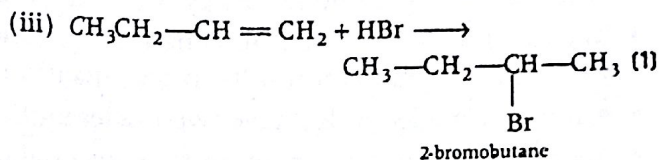
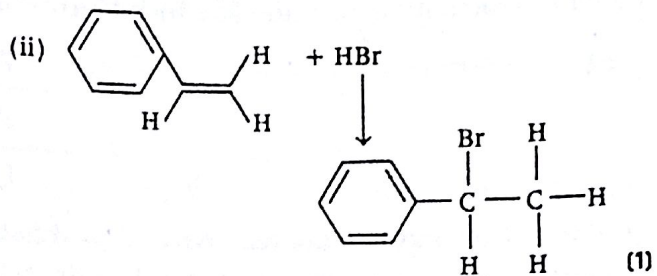
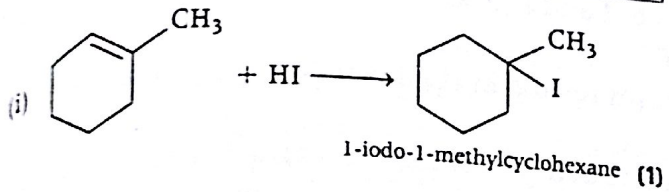


4-bromo-3-methylpent-2-ene



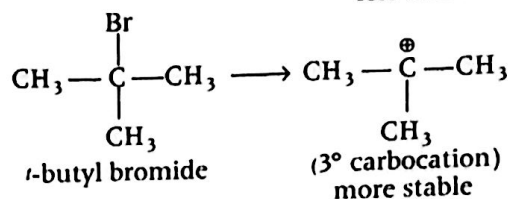
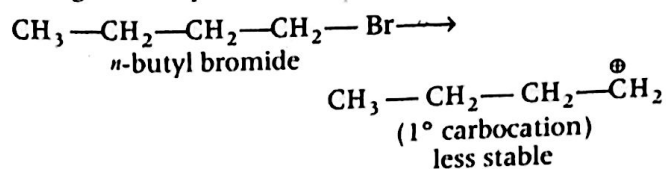
(1)

In case of non-symmetric unsaturated compounds, addition of HI and HBr takes place according to Markownikoff's rule.

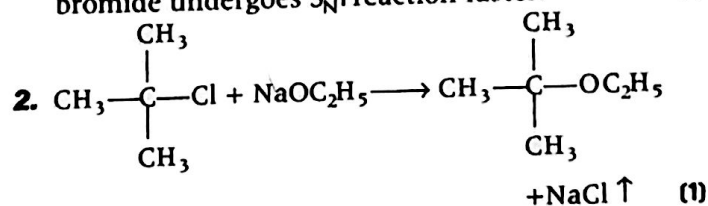


Explanation

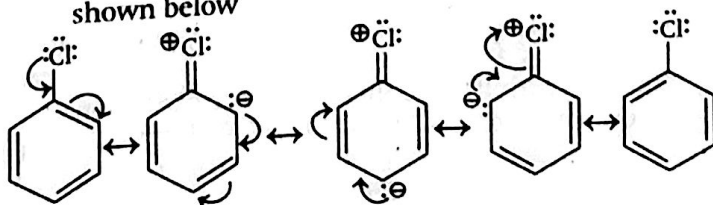
1. In S_N1 reaction, reactivity depends upon the stability of intermediate carbocation formed. Let us consider the formation of carbocation of the two given alkyl halides.



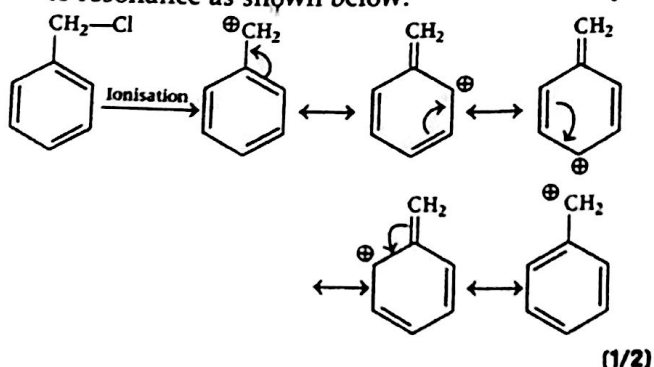
Carbocation formed by ter-butyl bromide being tertiary is more stable than primary, hence *t*-butyl bromide undergoes S_N1 reaction faster. (1)



3. C—Cl bond in chlorobenzene is stronger than C—Cl bond in benzyl chloride. Therefore hydrolysis of benzyl chloride is easy. It is due to the fact that in chlorobenzene the lone pairs of electrons on halogen atom are delocalised as shown below

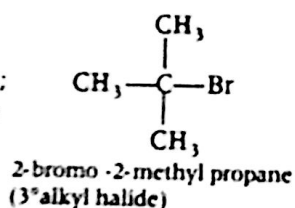
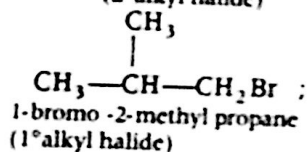
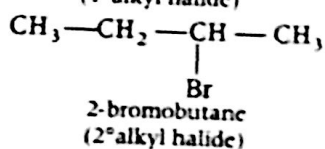
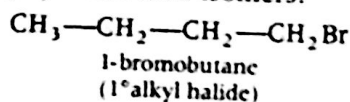


Due to this C—Cl bond have some double bond character. Whereas in benzyl chloride C—Cl bond is weak. Cleavage of C—Cl bond in benzyl chloride forms benzyl cation which is stable due to resonance as shown below: (1/2)

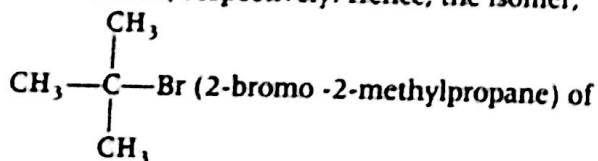


4. Tertiary (3°) alkyl halides are most reactive towards S_N1 reactions followed by secondary (2°) and primary (1°) alkyl halides.

C_4H_9Br has four isomers:



As 3° alkyl halides form a more stable 3° carbocation intermediate than secondary and primary alkyl halides which form 2° and 1° carbocation, respectively. Hence, the isomer,



compound C_4H_9Br is most reactive towards S_N1 reactions. (1)

5. $CH_3-CH_2-CH(CH_3)-Cl$ will undergo

S_N1 reaction faster because it is a secondary alkyl halide and forms a secondary carbocation that can stabilise itself more than primary carbocation formed by $CH_3-CH_2-CH_2Cl$. (1)

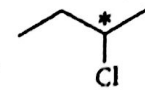


6. Secondary alkyl halides prefer to undergo S_N1 reaction than primary alkyl halides because of formation of more stable 2° carbocation. Hence, out of the given pair, $CH_3-CH(Br)-CH_3$

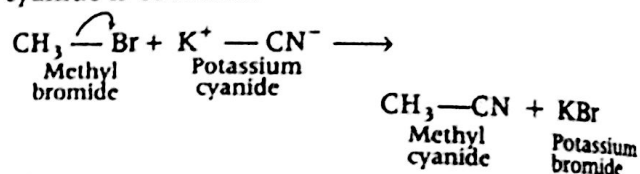
would undergo S_N1 reaction faster. (1)

7. On the basis of steric hindrance, 1° alkyl halides are more reactive than *tert*-alkyl halides towards S_N2 reactions. Thus, CH_3-CH_2-Br would undergo S_N2 reaction faster than $[(CH_3)_3CBr]$ because it is a primary halide, i.e. less hindered. (1)

8. As I^- ion is a better leaving group than Br^- ion, therefore iodides are more reactive than bromides. Therefore, CH_3-CH_2-I is more reactive than CH_3-CH_2-Br towards S_N2 reaction and hence, CH_3-CH_2-I would undergo S_N2 reaction faster than CH_3-CH_2-Br . (1)

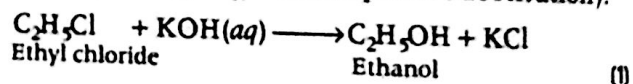
9.  is chiral molecule as it contains an asymmetric carbon atom (which is denoted by *). (1)

10. When CH_3-Br is treated with KCN, methyl cyanide is obtained.

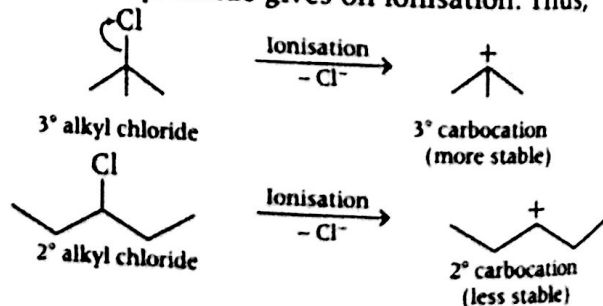


It is a nucleophilic substitution reaction. Nucleophile CN^- substitutes Br^- . (1)


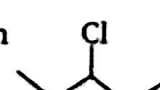
11. Ethyl chloride undergoes hydrolysis to form ethyl alcohol (through S_N2 nucleophilic substitution).



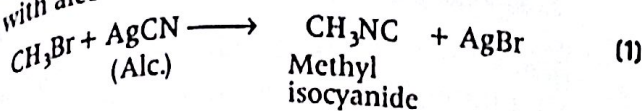
12. The reactivity towards S_N1 reaction depends upon the stability of the intermediate carbocation which an alkyl halide gives on ionisation. Thus,



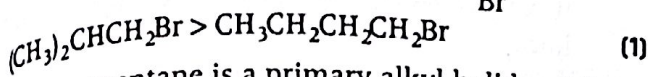
As 3° carbocations are more stable than

2° carbocations, therefore,  will react faster than  in S_N1 reaction. (1)

(13) It can be done by treating the methyl bromide with alcoholic silver cyanide.



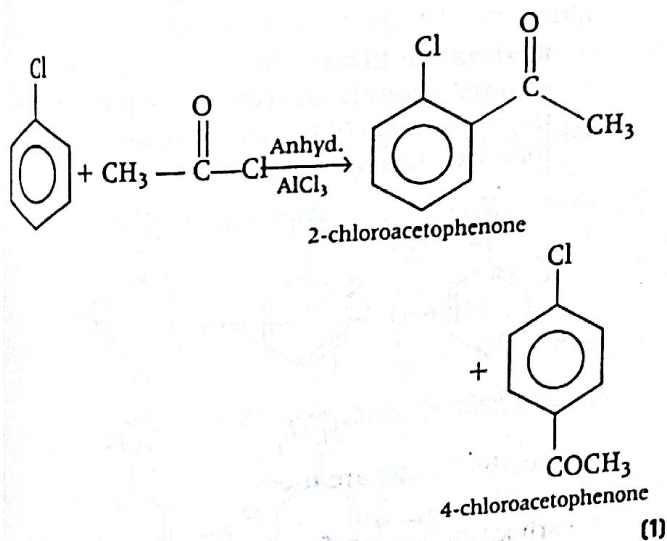
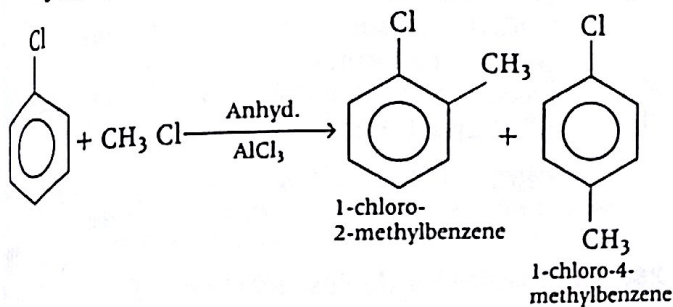
(14) Order of reactivity of four isomeric bromobutanes in S_N1 reaction is $(\text{CH}_3)_3\text{CBr} > \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Br} >$



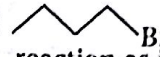
15. 1-bromopentane is a primary alkyl halide while 2-bromopentane is a secondary alkyl halide. Since, primary alkyl halides are sterically less hindered therefore, 1-bromopentane reacts faster towards S_N2 reaction. (1)

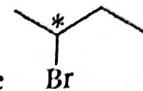
16. The hydrolysis of alkyl halide with aqueous KOH occurs by S_N1 mechanism. Further, the reactivity in S_N1 depends upon the stability of carbocation. Since, $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ forms more stable 2° carbocation on ionisation than $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$, therefore, $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ hydrolyses faster than $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$. (1)

17. Haloarenes in presence of Lewis acid react with alkyl halide or acid chloride to give a mixture of *o*- and *p*-haloalkylbenzene (or haloacylbenzene)



18. In S_N2 reactions, reactivity depends upon the steric hindrance. $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CH}_3$ is secondary alkyl halide while $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ is a primary alkyl halide. Since, primary alkyl halides are sterically less hindered, therefore, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ reacts faster towards S_N2 reaction. (2)

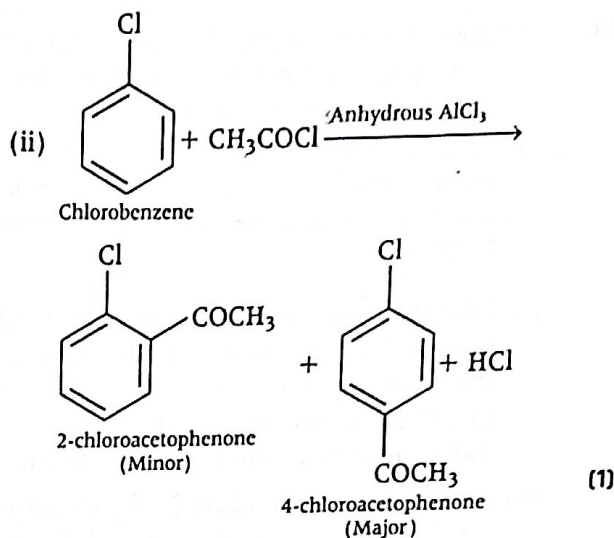
19. (i) (a)  undergoes faster towards S_N2 reaction as it is a primary halide. (1/2)

(b) The alkyl halide  is chiral as it contains asymmetric carbon (*) atom. (1/2)

(ii) (a) S_N2 reaction occurs with inversion of configuration. (1/2)

(b) S_N1 reaction proceeds with racemisation. (1/2)

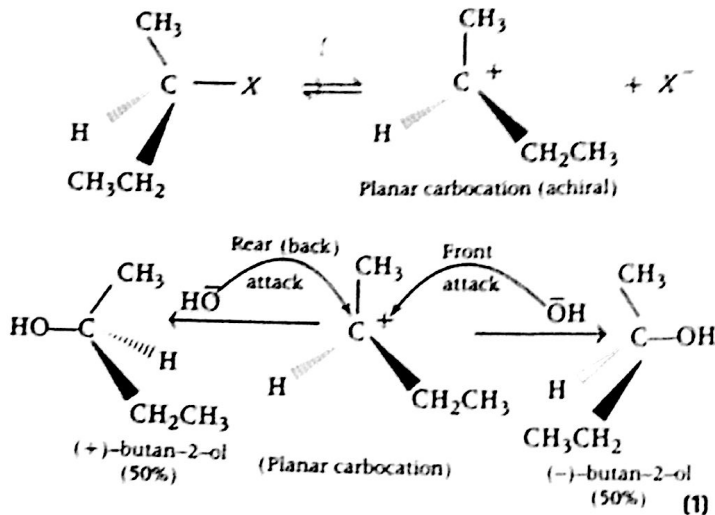
20. (i) Refer to solution 11 (1)



21. (i) In S_N2 reactions, reactivity depends upon the steric hindrance. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ is a primary alkyl halide while $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$ is a secondary alkyl halide. Since, primary alkyl halides are sterically less hindered therefore, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ reacts faster towards S_N2 reaction. (1)

(ii) In S_N1 reactions, if the alkyl halide is optically active, the product obtained is a racemic mixture. The intermediate carbocation formed in slowest step being sp^2 -hybridised is planar (achiral) species. Therefore, the attack of the nucleophile on it, can occur from both the faces (front and back) with equal ease, forming a 50:50 mixture of two enantiomers, i.e. the products with opposite configuration.

Thus, S_N1 reaction of optically active alkyl halides are accompanied by racemisation. e.g.

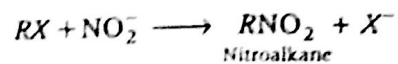
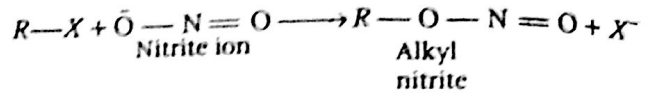


24. Define ambident nucleophile, then draw resonating structures of the example and explain.

Ambident nucleophiles have two nucleophilic sites through which they can attack, e.g. nitrite ion is an ambident nucleophile.

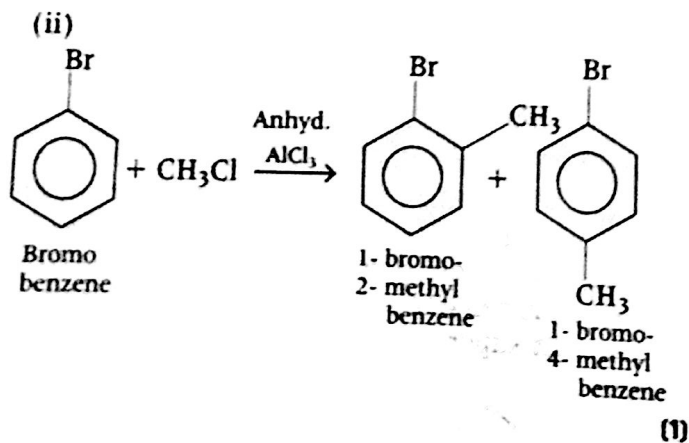
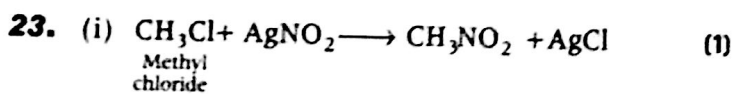
$$[\text{O}=\ddot{\text{N}}=\text{O}]$$

It can attack through oxygen resulting in the formation of alkyl nitrites. Also, it can attack through nitrogen resulting in the formation of nitroalkanes.

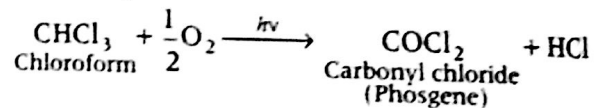


22. (i) Lesser the bond dissociation energy, faster is the reaction so, find the molecule in which bond dissociation enthalpy is less
- (ii) If both halide groups are same, steric hindrance will be considered in case of S_N2 reaction. More the steric hindrance, lesser the reactivity towards S_N2 reaction.

- (i) CH_3I will react faster as compared to CH_3Br because CH_3I has lower bond dissociation energy and I^- is a better leaving group than Br^- . Thus, in the presence of nucleophile, iodide ion will be released at a faster rate. (1)
- (ii) In S_N2 reactions, reactivity depends upon the steric hindrance CH_3Cl being a 1° halide will react faster as compared to $(\text{CH}_3)_3\text{CCl}$ which is a 3° halide because 1° halides undergo S_N2 mechanism faster than 3° halides. (1)

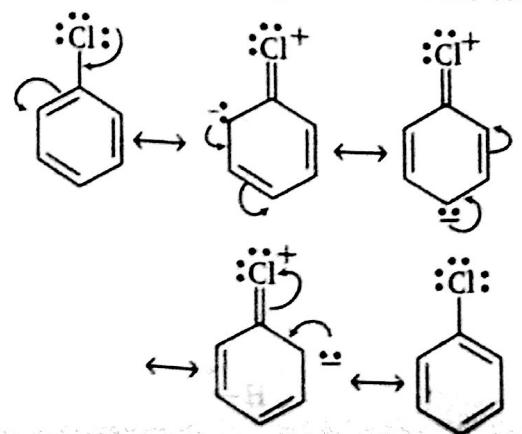


25. (i) Due to delocalisation of lone pairs of electrons of the X atom over the benzene ring, C—X bond in halobenzene acquires some double bond character while in $\text{CH}_3\text{—X}$, C—X bond is a pure single bond. Therefore, C—X bond in halobenzene is shorter than in $\text{CH}_3\text{—X}$. (1)
- (ii) In the presence of air and sunlight, chloroform gets oxidised to phosgene (carbonyl chloride, COCl_2), a poisonous compound. Thus, to prevent the formation of phosgene, chloroform is stored in dark brown bottles filled upto brim.



26. Two reasons for the less reactivity of chlorobenzene towards a nucleophilic substitution reaction are as follows:

- (i) **Resonance Effect** The electron pair of chlorine atom is involved in conjugation with the π -electrons of the benzene ring and the following resonating structures are obtained:

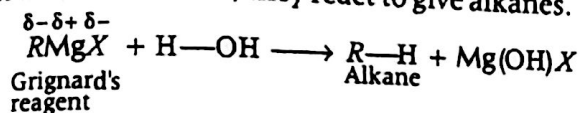


As a result, electrons of C—Cl bond get delocalised and a partial double bond character develops in the bond and hence, it becomes difficult for the nucleophile to cleave the C—Cl bond.

(ii) **Increased Electron Density** A repulsion is suffered by the nucleophile due to increased electron density on the benzene ring which prohibits the nucleophile to make a close access for the attack on the molecule. (1)

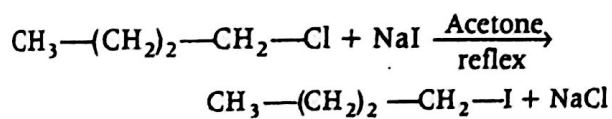
27. (i) To be miscible with (or soluble in water) water, the solute-water force of attraction must be stronger than the solute-solute and water-water forces of attraction. Alkyl halides are polar molecules and so held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new force of attraction between the alkyl halides and water molecules is weaker than the forces of attraction already existing between alkyl halide-alkyl halide and water-water molecules. Hence, alkyl halides (though polar) are immiscible with (or insoluble in) water. (1)

(ii) Grignard's reagent are very reactive. In the presence of moisture, they react to give alkanes.

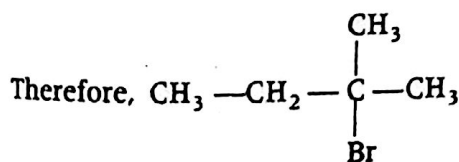


Therefore, Grignard's reagents should be prepared under anhydrous conditions. (1)

28. (a) **1-iodobutane from 1-chlorobutane** As iodine can replace chlorine from alkyl halide (due to more reactive nature), it gives 1-iodobutane from 1-chlorobutane *via* Finkelstein reaction :

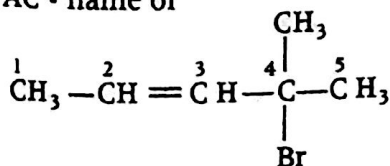


(b) As all the given species have same number of carbon atoms, the 3° carbocation is most stable, thus has most reactive halide molecule.



(2-bromo-2-methylbutane) is most reactive.

(c) IUPAC - name of

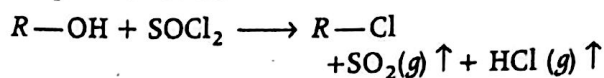


4-bromo 4-methyl pent-2-ene.

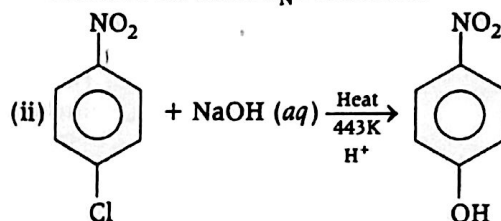
29. (a) —NO₂ shows -I and -M effect when present at *ortho* and *para* position w.r.t. halogens. It has tendency to attract the electrons towards itself, thus they decreases the electron density between C—X (X = halogens) bond. Therefore —NO₂ at *ortho* and *para* positions w.r.t. halogens in haloarenes increases the reactivity.

(b) *p*-dichlorobenzene has higher melting point than that of *ortho* or *meta*-isomers due to its symmetrical structure, which make more compact compound and increases the melting point.

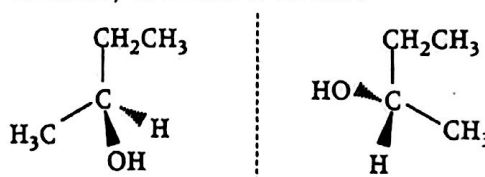
(c) Thionyl chloride (SOCl₂) is preferred for preparation of alkyl chloride from alcohol, because the by-products we get in this reaction are escapable gases, thus we get good yield of alkyl-chloride i.e.



30. (i) Both (CH₃)₃C—Br and (CH₃)₃C—I forms 3° carbocation which is highly stable, but the size of I is larger than Br. Thus, it is a better leaving group and hence (CH₃)₃C—I is more reactive towards S_N1 reaction.



(iii) The dextro and laevo rotatory isomers (optical isomers) of butan-2-ol are :

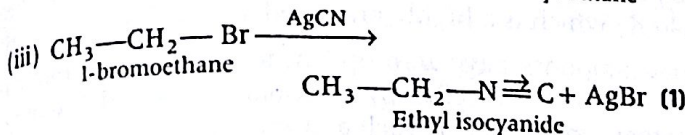
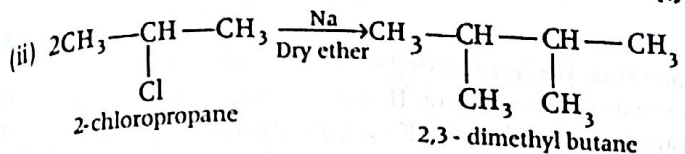
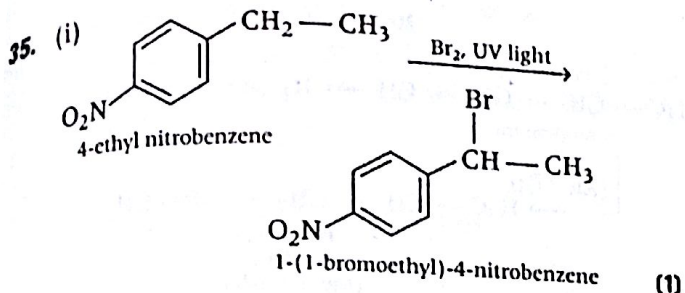


These are enantiomers (mirror images which give opposite rotation) and thus will have almost same boiling point which will make their separation difficult by fractional distillation.

31. (i) A molecule which completely lacks symmetry is called chiral. The mirror images of such molecules are non-superimposable. Molecule (i) is chiral as its mirror image is non-superimposable.

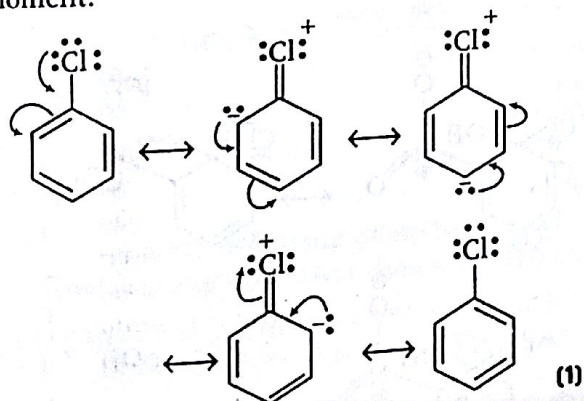


(1)

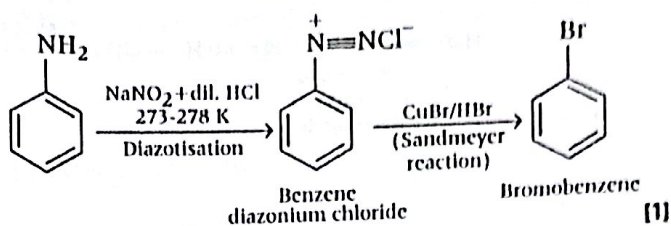


36. (i) In chlorobenzene, the lone pair of electrons present on Cl-atom are in conjugation with π -electrons of the benzene ring. As a result, C—Cl bond acquires some double bond character while in $\text{CH}_3\text{—Cl}$, bond is a pure single bond. Since, bond length of C—Cl single bond is greater than C—Cl partial double bond. Therefore, C—Cl bond in halobenzene is shorter than that in $\text{CH}_3\text{—Cl}$.

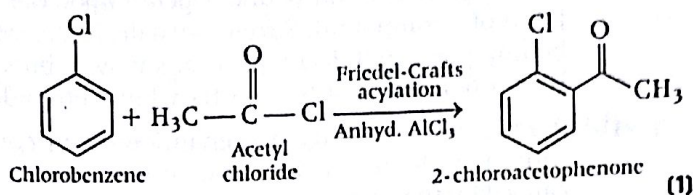
(ii) In chlorobenzene, the Cl-atom is linked to a sp^2 -hybridised carbon atom whereas in cyclohexyl chloride, the Cl-atom is linked to a sp^3 -hybridised carbon atom. As, sp^2 -hybridised carbon has more s-character so, it is more electronegative, thus the density of electrons of C—Cl bond near the Cl-atom is less in chlorobenzene than in cyclohexyl chloride. Hence, the C—Cl bond of cyclohexyl chloride is more polar, i.e. it has higher dipole moment.



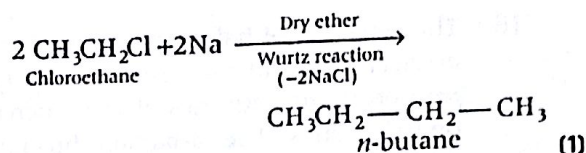
37. (i) Aniline to bromobenzene



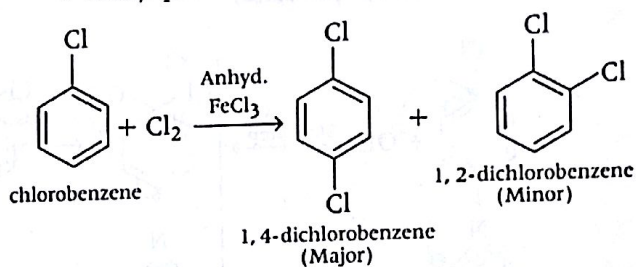
(ii) Chlorobenzene to 2-chloroacetophenone



(iii) Chloroethane to butane

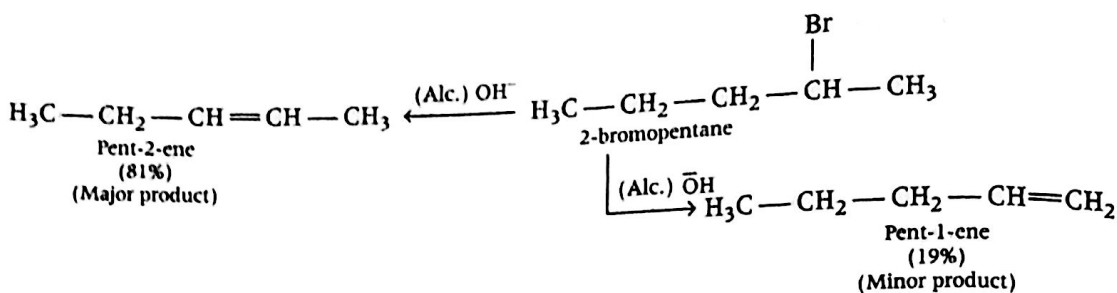


38. (i) When chlorobenzene is treated with $\text{Cl}_2 / \text{FeCl}_3$, o- and p-products are formed as:



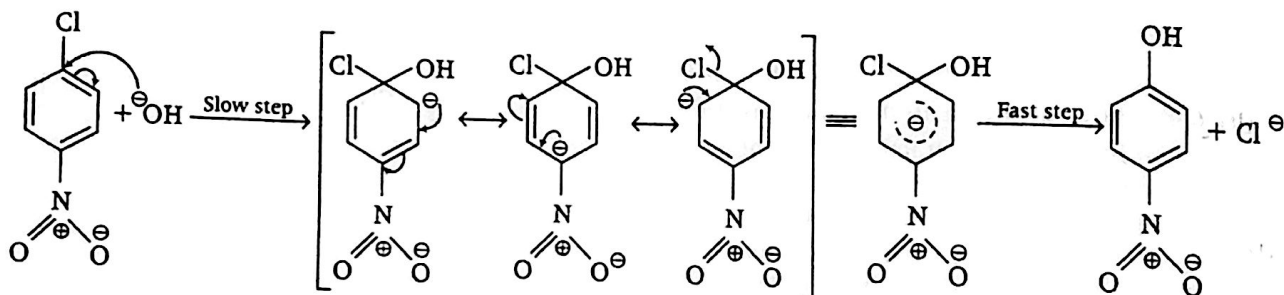
(ii) When ethyl chloride is treated with AgNO_2 , nitroethane is formed.
 $\text{CH}_3\text{CH}_2\text{Cl} + \text{AgNO}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{NO}_2 + \text{AgCl}$ (1)

(iii) When 2-bromopentane is treated with alcoholic KOH, it undergoes dehydrohalogenation leading to the formation of two or more different products depending upon the number of different types of β -hydrogen available. The more highly substituted alkene (i.e. having lesser number of hydrogen atoms on the doubly bonded carbon atoms) is the major product of dehydrohalogenation. This is in accordance to Saytzeff rule.

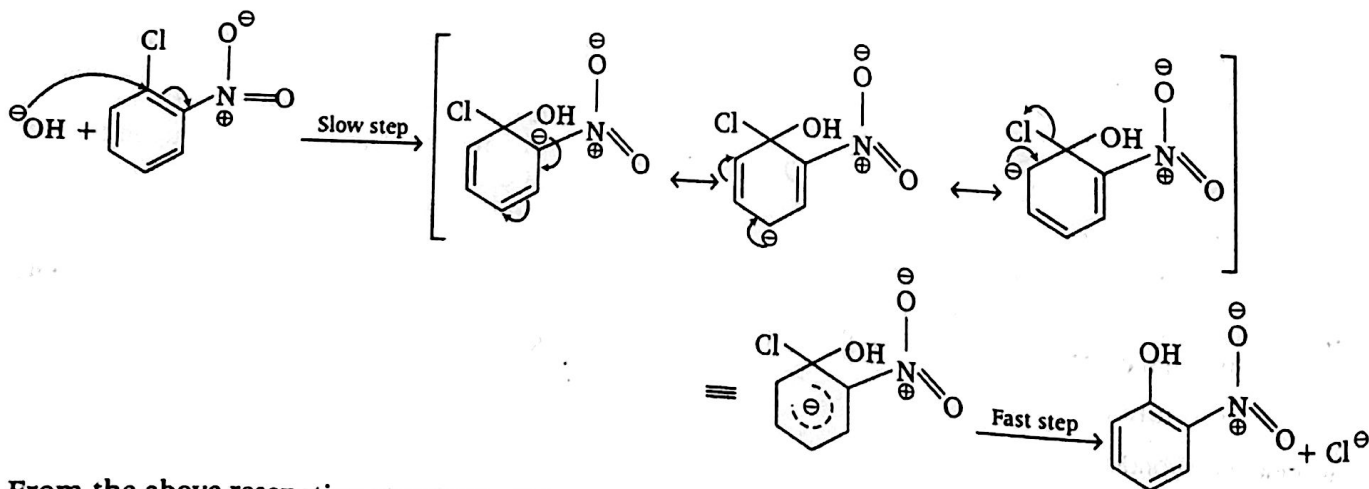


39. (i) Boiling point of a compound depends upon the surface area. Higher the surface area, higher will be the boiling point of a compound. Surface area decreases with increase in branching. If the compound has branching, its boiling point will decrease. That's why, *n*-butyl bromide being (bp 375 K) a straight chain alkyl halide has higher boiling point than tertiary butyl bromide (346 K) which is a highly branched alkyl halide. (1)
- (ii) A mixture containing two enantiomers in equimolar amounts have zero optical rotation, as the rotation caused by the molecules of one isomer (enantiomer) is exactly cancelled by an equal and opposite rotation caused by the same number of molecules of other isomer (enantiomer). Such a mixture is known as racemic mixture. Since, enantiomers have equal and opposite specific rotations, a racemic mixture exhibits no optical activity. (1)
- (iii) The reactivity of haloarenes towards nucleophilic substitution reactions can be increased by the presence of an electron withdrawing group ($-\text{NO}_2$) at *ortho* and *para*-positions. This is because, $-\text{NO}_2$ group at *ortho* and *para*-positions withdraw electron density from the benzene ring and thus, facilitates the nucleophilic attack on haloarenes. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho* and *para* position with respect to the halogen substituent is stabilised by $-\text{NO}_2$ group. The mechanism can be shown as:

Attack at *p*-position

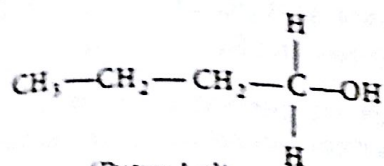


Attack at *o*-position



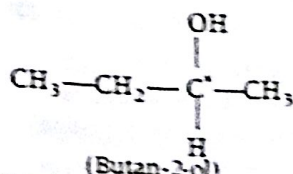
From the above resonating structures, it is very clear that electron density is rich at *ortho* and *para*-positions. So, presence of EWG will facilitate nucleophilic attack at *ortho* and *para*-positions. (1)

- (i) Refer to solution 27 (i).
 (ii) Butan-1-ol is optically inactive compound due to the absence of asymmetric C-atom (or chiral C-atom) whereas butan-2-ol is optically active compound due to the presence of asymmetric C-atom (or chiral C-atom). (1)



(Butan-1-ol)

Achiral compound due to the presence of similar groups on C-atoms, thus, optically inactive

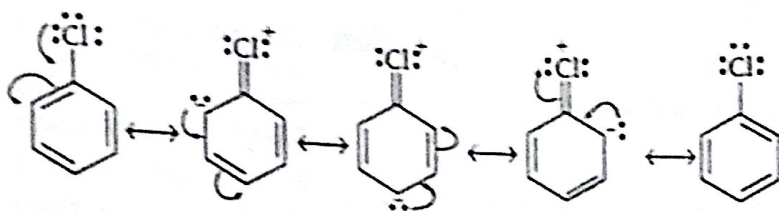


(Butan-2-ol)

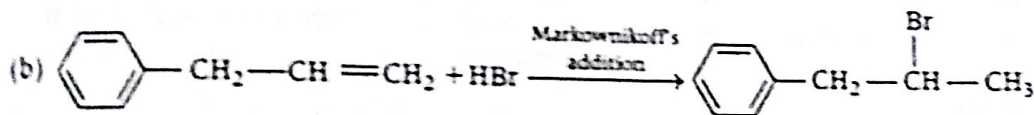
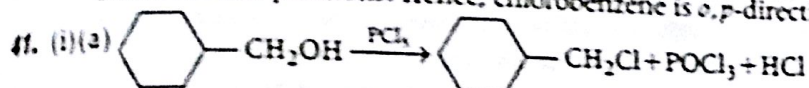
Chiral compound due to the presence of different atoms on C-atom, thus, optically active

NOTE If \pm butan-2-ol is present as equimolar mixture (in a given mixture), then the mixture is optically inactive due to racemisation. (1)

- (iii) In chlorobenzene, one of the lone pair on chlorine atom conjugates with the ring. It is the resonance hybrid of the following structures:

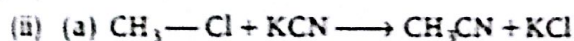


Since, electron density is maximum at *o*- and *p*-positions due to +R-effect, therefore an electrophile can easily attack at such positions. Hence, chlorobenzene is *o,p*-directing in electrophilic aromatic substitution reactions. (1)

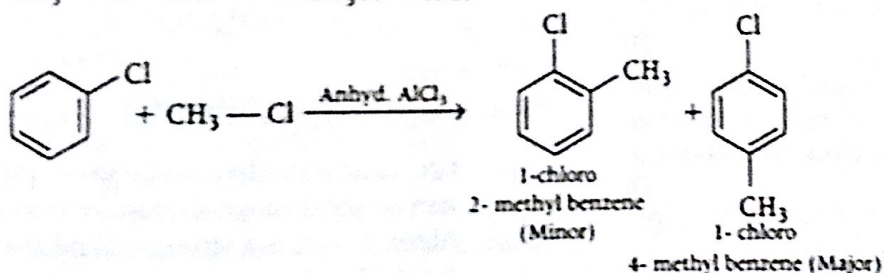


(ii) Refer to solution 22. (1)

42. (i) Refer to solution 22. (1)



(b)



43. (i) Iodide ion is a better leaving group because of its larger size than bromide ion, therefore ethyl iodide undergoes $\text{S}_{\text{N}}2$ reaction faster than ethyl bromide. (1)

(ii) (\pm) 2-butanol is a racemic mixture. It is a mixture which contains two enantiomers in equal proportion and thus, have zero optical rotation. Therefore, it is optically inactive. (1)

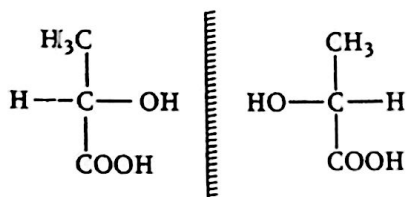
(iii) Refer to solution 25 (i).

44. (i) Find the hybridisation of C-atoms in chlorobenzene and cyclohexyl chloride and electronegativity to find the bond polarity and thus, dipole moment.
 (ii) Strong intermolecular H-bonding among water molecules.
 (iii) Consider reactive nature of Grignard's reagent with water.

- (i) Refer to solution 36 (ii). (1)
 (ii) Refer to solution 27 (i). (1)
 (iii) Refer to solution 27 (ii). (1)

45. Refer to solution 40 (iii). (3)

46. (i) An object or molecule which is non-superimposable on its mirror image is called **chiral** and the property of being chiral is known as **chirality**, e.g. lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$



Mirror

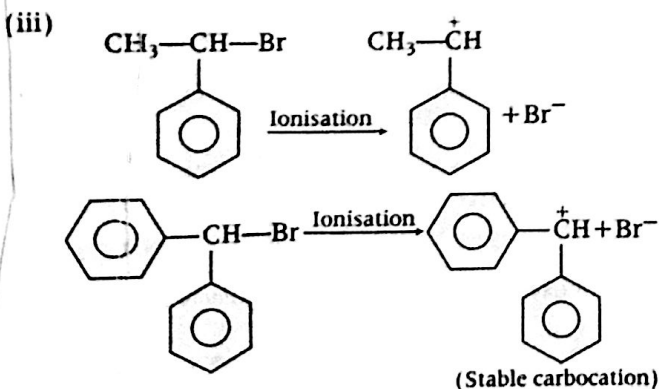
- (ii) $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{CH}_2\text{CH}_3$ is more easily

hydrolysed by KOH because this hydrolysis occurs through $\text{S}_{\text{N}}1$ mechanism and this alkyl halide forms a more stable 2° carbocation than $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{Cl}$ which forms a less stable 1° carbocation as $\text{S}_{\text{N}}1$ depends on stability of carbocation. (1)

- (iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$, as iodide ion is a better leaving group because of its larger size, therefore, it undergoes faster $\text{S}_{\text{N}}2$ reaction. (1)

47. (i) Haloalkanes easily dissolve in organic solvents because both are covalent in nature (like dissolves like). Also, the steric effect in haloalkanes is not more as seen in the case of haloarenes. (1)

- (ii) A mixture containing two enantiomers in equal proportions will have zero optical rotation. Such mixtures are called **racemic mixtures**, e.g. (\pm) butan-2-ol. (1)



The carbocation intermediate formed from $(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ is more stable because it is stabilised by two phenyl groups due to resonance, so $(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_5)\text{Br}$ is more reactive towards $\text{S}_{\text{N}}1$ reaction. (1)

48. $\text{S}_{\text{N}}2$ reactions depend upon steric hindrance. More the steric hindrance, slower is the reaction. So, order of reactivity is $1^\circ > 2^\circ > 3^\circ$.

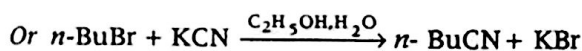
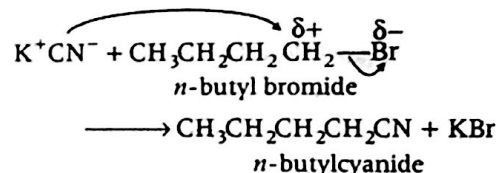
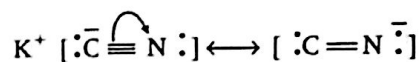
- (i) 1-bromopentane > 2-bromopentane > 2-bromo-2-methylbutane (1)
 (ii) 1-bromo-3-methylbutane > 3-bromo-2-methylbutane > 2-bromo-2-methylbutane (1)

NOTE 3-bromo-2-methylbutane is incorrect IUPAC name as bromo is a functional group it should be given priority over methyl group. Thus, the correct name should be 2-bromo-3-methylbutane.

- (iii) 1-bromobutane > 1-bromo-3-methylbutane > 1-bromo-2-methylbutane > 1-bromo-2, 2-dimethylpropane (1)

49. (i) KCN is a reagent that gives CN^- ion as nucleophile in aqueous medium.

Resonating forms of KCN It is a resonance hybrid of the following two contributing structures.

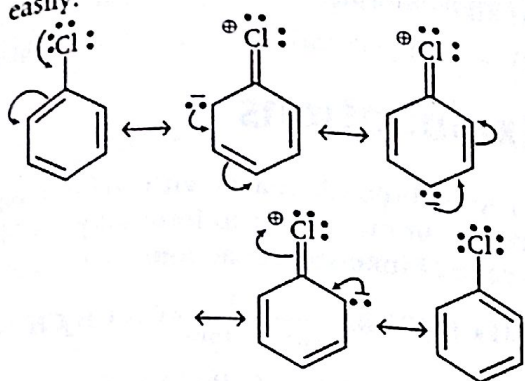


CN^- is an ambident nucleophile therefore, it can attack through C-atom or through N-atom. Since, C—C is a stronger bond than C—N bond, therefore, attack occurs through C to C of *n*-butyl bromides to form *n*-butyl cyanide. (1)

- (ii) Refer to solution 36 (ii). (1)

50. (i) (a) Benzyl chloride when treated with AgNO_3 solution, will give a white ppt. while chlorobenzene will not. (1/2)
 (b) Chloroform when treated with 1° amine and KOH, gives offensive smell of isocyanides while CCl_4 does not give this test. (1/2)
 (ii) Chlorobenzene is stabilised by resonance, so, it has a double bond character between C and Cl.

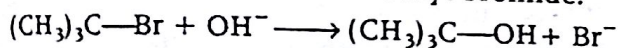
Secondly, C is sp^2 -hybridised so more electronegative, thus Cl atom is not replaced easily.



While in methyl chloride, C—Cl has a single bond character which can be cleaved easily and hence, it is hydrolysed more easily than chlorobenzene. (1)

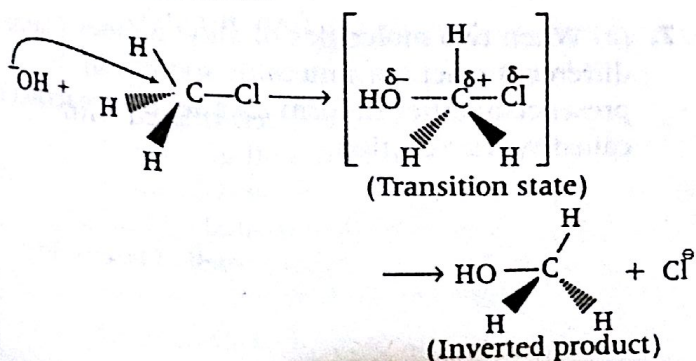
51. (i) DDT is used as an insecticide and iodoform is used as a mild antiseptic. (1)
- (ii) Reactivity of S_N2 reactions depends on steric hindrance. Therefore, (1)
- (a) 1-bromopentane will react faster because it is a primary alkylhalide and hence less sterically hindered. (1)
- (b) 1-bromo-2-methyl butane, as it is a primary alkyl halide and less sterically hindered. (1)

52. In S_N1 mechanism of substitution reaction, the rate of reaction depends upon the concentration of only one reactant, e.g. in the reaction between *tert*-butyl bromide and hydroxide ion to form *tert*-butyl alcohol, rate of reaction depends only on the concentration of *tert*-butyl bromide.



It involves the formation of carbocation intermediate and racemisation takes place. (1½)

In S_N2 mechanism of substitution reaction, the rate of reaction depends upon the concentration of both the reactants i.e. on both haloalkane and nucleophile, e.g. in the reaction between methyl chloride and hydroxide ion to form methanol, rate of reaction depends on the concentration of both the reactants.

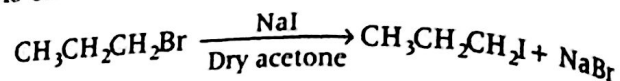


It involves the formation of transition state and inversion (Walden inversion) of configuration take place. (1½)

53. (i) Refer to solution 36 (ii). (1)
- (ii) Refer to solution 27 (i). (1)
- (iii) Refer to solution 22. (1)

☑ Explanations (objectives)

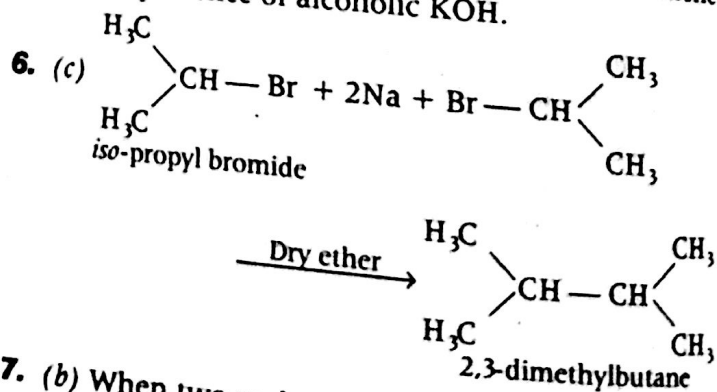
1. (c) Alkyl bromide reacts with sodium iodide (in acetone or methanol) to form alkyl iodides. This is called Finkelstein reaction.



The high reactivity of alkyl halide is due to highly polarised covalent C—X bond.

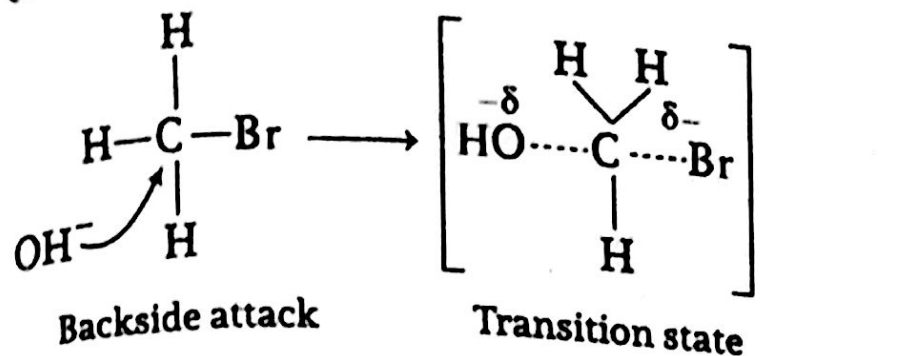
In nucleophilic substitution C^{δ+} site is susceptible to attack by nucleophiles.

2. (c) CH₃Cl is used as methylating agent. The methylating agent is one which is used for the introduction of methyl groups.
3. (b) $2\text{CH}_3\text{CH}_2\text{I} + \text{Ag}_2\text{O} \xrightarrow{\Delta} (\text{CH}_3\text{CH}_2)_2\text{O} + 2\text{AgI}$
Diethyl ether
4. (b) S_N2 mechanism involves the back side attack and formation of a transition state, thus less hindered alkyl halide readily undergoes S_N2 mechanism. Among the given, CH₃Br (methyl bromide) is less hindered, thus hydrolysed by S_N2 mechanism.
5. (b) The given reaction is an example of elimination reaction, in which one molecule of HBr is eliminated from alkyl halide to give alkene in the presence of alcoholic KOH.

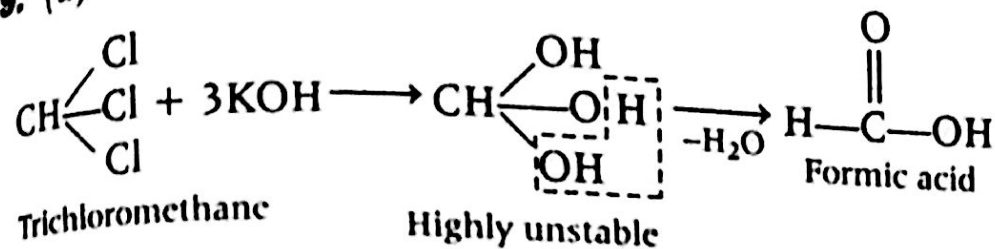


7. (b) When two molecules of alkyl halides (same or different) react with metallic sodium in the presence of ether to form alkane, this reaction is called Wurtz reaction.

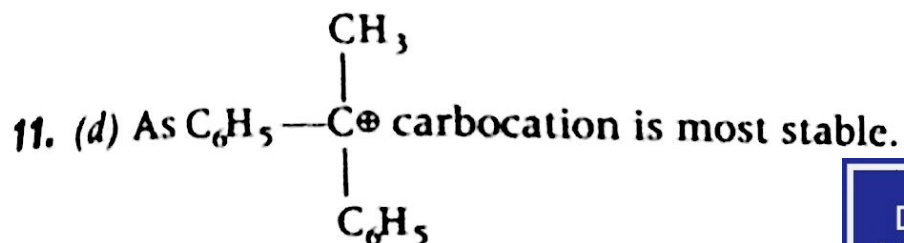
8. (d) Since, the reaction rate depends upon the concentration of both reactant and nucleophile, it is an S_N2 reaction. It involves inversion of configuration.



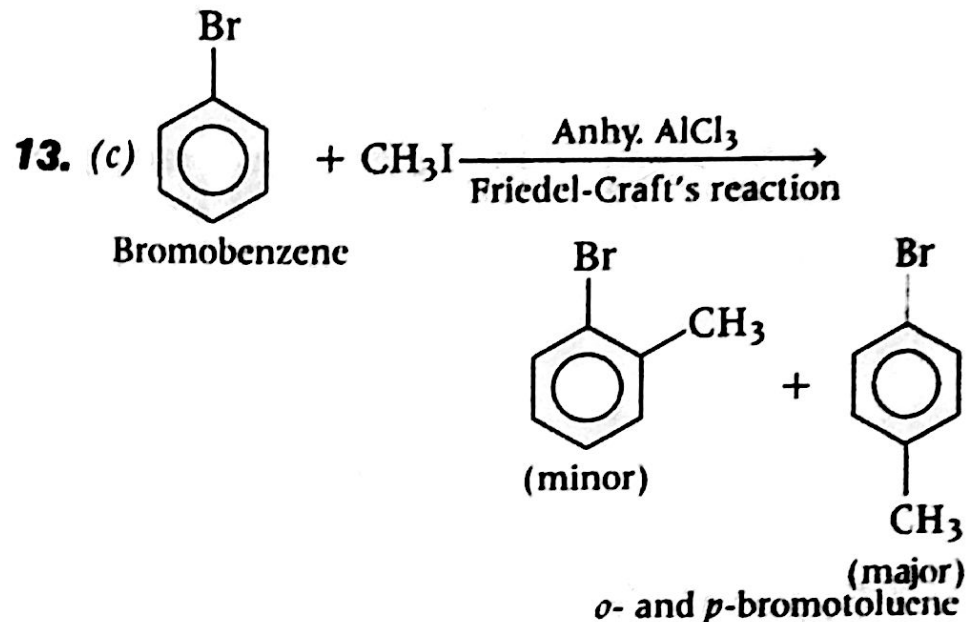
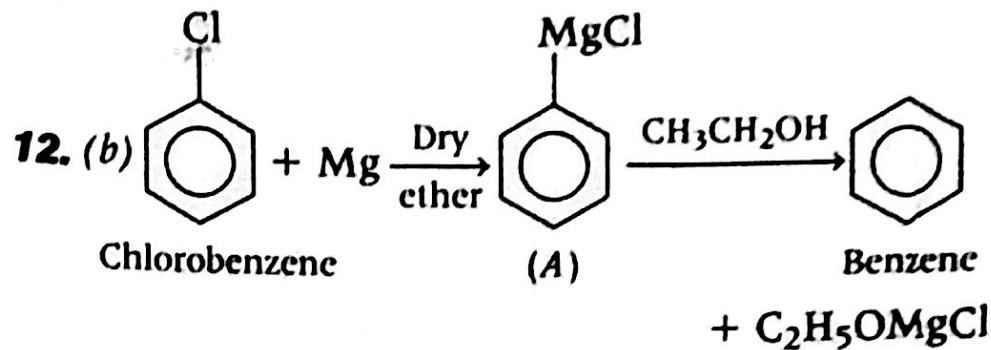
9. (d)



10. (a) Reaction of aryl halides with sodium in ether to form diaryl is known as Fittig reaction.



$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$ readily undergoes S_N1 reaction.



14. (d) Hydrolysis of alkyl halides depends on the stability of carbocation and stability order is $\text{Benzyl} > \text{Allyl} > 2^\circ > 1^\circ$