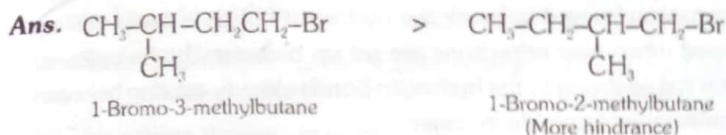
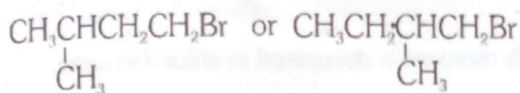


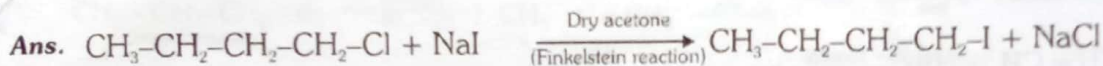
7. Why chloroform is stored in dark coloured bottles away from sunlight.
Ans. Chloroform is slowly oxidised by air in presence of light to form an extremely poisonous gas phosgene (carbonyl chloride)



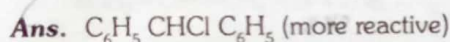
8. Which alkyl halide from the following pairs would you expect to react more rapidly by an $\text{S}_\text{N}2$ mechanism?



9. Write the equation for the preparation of 1-iodobutane from 1-chlorobutane.



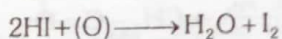
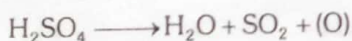
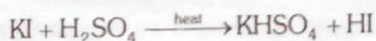
10. Out of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$, which is more easily hydrolysed by aqueous KOH?



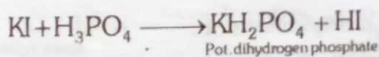
Short Answer Type Questions (2 mark)

11. Why is sulphuric acid not used during the reaction of alcohols with KI?

Ans. KI is expected to give HI on reacting with H_2SO_4 which will convert alcohols (R---OH) to alkyl iodides (R---I). However, H_2SO_4 is a strong oxidising agent and it oxidises HI formed during the reaction to I_2 which does not react with alcohol.



To solve the problem, H_2SO_4 is replaced by phosphoric acid (H_3PO_4) which provides HI for the reaction and does not give I_2 as is done by H_2SO_4 .



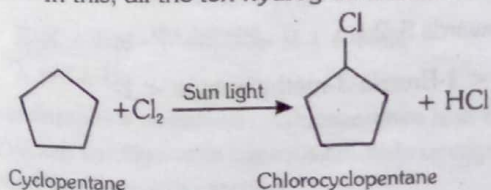
12. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monobromo compound in bright sun light. Identify the hydrocarbon.

Ans. (i) The hydrocarbon with molecular formula C_5H_{10} is either an alkene or cycloalkane.

(ii) Since the hydrocarbon does not react with chlorine (Cl_2) in the dark, it is not an alkene.

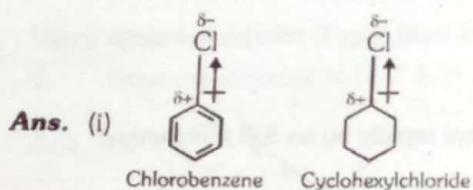
(iii) As it forms only single monochloroderivative in bright sun light, it is cyclopentane which is symmetrical.

In this, all the ten hydrogen atoms are identical.



13. Explain why

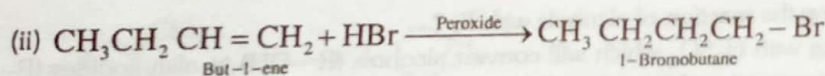
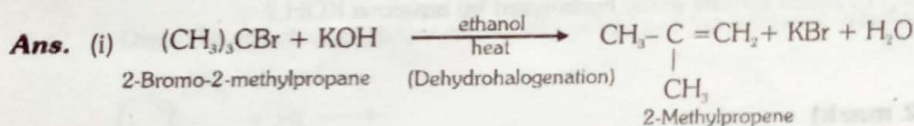
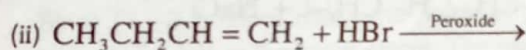
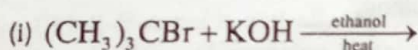
- (i) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
 (ii) Alkyl halides, though polar, are immiscible with water?



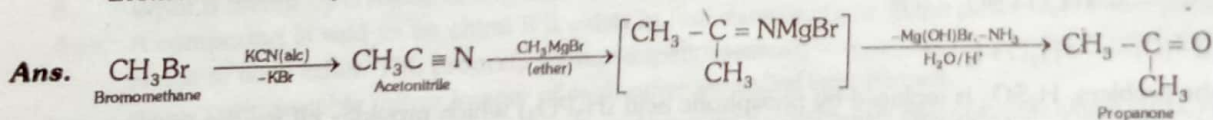
+M of -Cl and -I of -Cl are in opposite direction so dipole moment is decreased in chlorobenzene.

- (ii) If a haloalkane/haloarene is to dissolve in water, energy is required to overcome the forces of attraction already existing between haloalkane/haloarene molecules and to break the hydrogen bonds already existing between water molecules. Less energy is released when new attractions are set up between the haloalkane/haloarene and water molecules because these are not as strong as the hydrogen bonds already existing between H₂O molecules. As a result, haloalkanes and haloarenes insoluble in water.

14. Write the structure of the major organic product in each of the following reactions.]



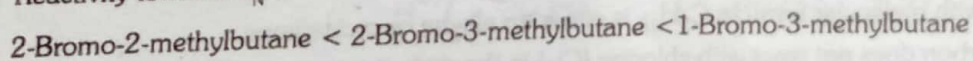
15. How will you bring about the following conversions?
 "Bromomethane to propanone"



16. Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

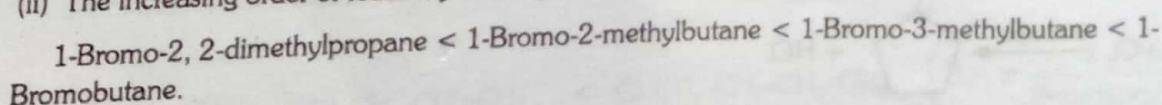
- (i) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane
 (ii) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo 3-methylbutane.

Ans. (i) Reactivity towards S_N2 is



(Reactivity of S_N2 displacement $\propto \frac{1}{\text{Steric hindrance}}$)

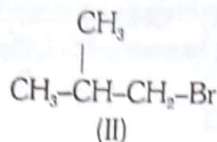
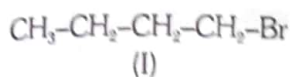
(ii) The increasing order of reactivity of the given compounds towards S_N2 is:



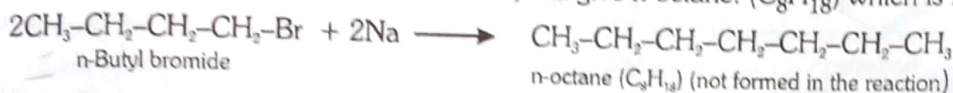
Short Answer Type Questions (3 mark)

17. Primary alkyl halide (a) C_4H_9Br was reacted with alcoholic KOH to give compound (b). Compound (b) was reacted with HBr to give (c) which was an isomer of (a). When (a) was reacted with sodium metal, it gave a compound (d) C_8H_{18} that was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

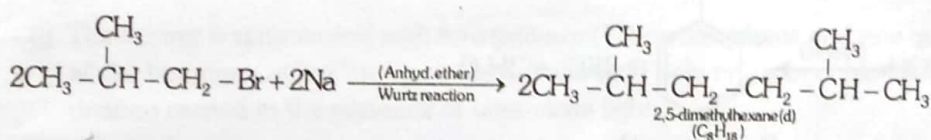
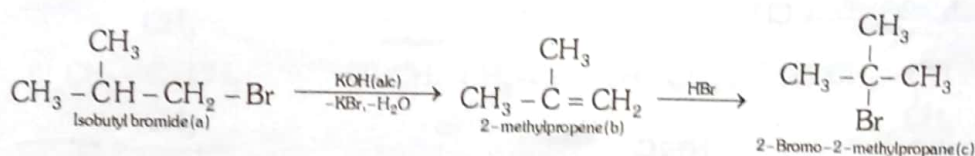
Ans. The two primary alkyl bromides are possible from the molecular formula (a) C_4H_9Br . These are



According to the available information, the isomer (I) does not represent the correct compound because this on reacting with sodium metal (Wurtz reaction) will give n-octane. (C_8H_{18}) which is not actually formed.

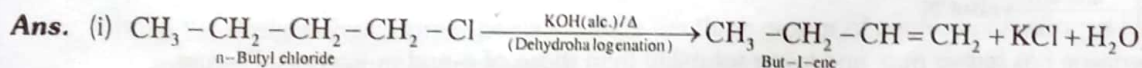


This means that structure (II) is the correct isomer. It gives the desired reactions which are listed.

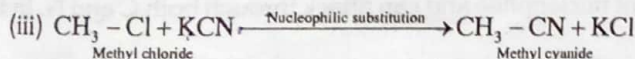
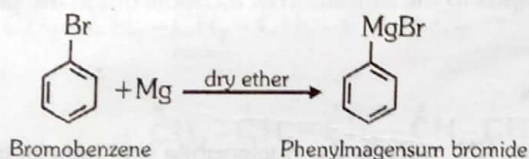


18. What happens when

- (i) n-butyl chloride is treated with alcoholic KOH,
- (ii) bromobenzene is treated with Mg in the presence of dry ether,
- (iii) methyl chloride is treated with KCN



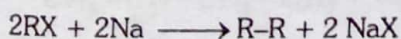
- (ii) Phenylmagnesium bromide is formed.



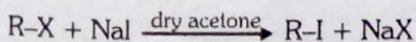
19. Write a short note on:

- (i) Wurtz reaction
- (ii) Finkelstein reaction
- (iii) Sandmeyer reaction

Ans. **Wurtz reaction**- Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide this reaction is known as wurtz reaction.

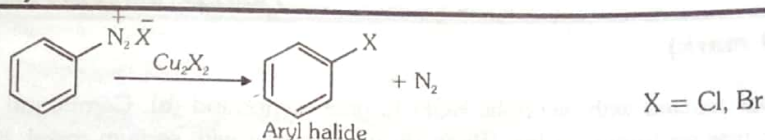


Finkelstein reaction- Alkyl iodides are prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.



X = Cl, Br

Sandmeyer's reaction- Chloroarenes and bromoarenes can be obtained by treating freshly prepared diazonium salt solution with cuprous chloride or cuprous bromide dissolved in HCl and HBr respectively. The reaction called Sandmeyer's reaction.



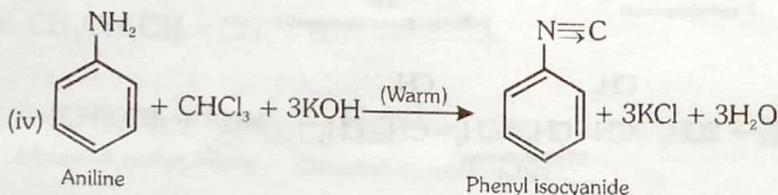
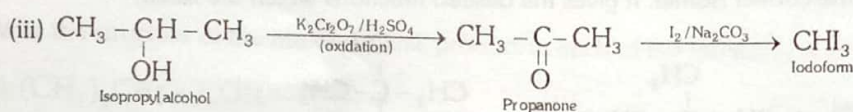
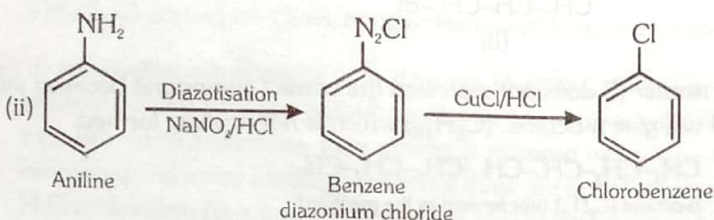
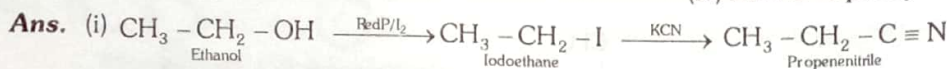
20. How the following conversions can be carried out ?

(i) Ethanol to propanenitrile

(ii) Aniline to chlorobenzene

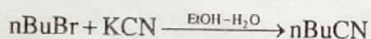
(iii) Isopropyl alcohol to iodoform

(iv) Aniline to phenyl isocyanide.



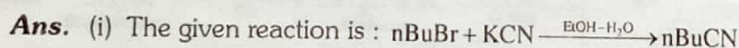
The reaction is known as carbyl amine reaction / Isocyanide test

21. (i) Write the mechanism of the following reaction :

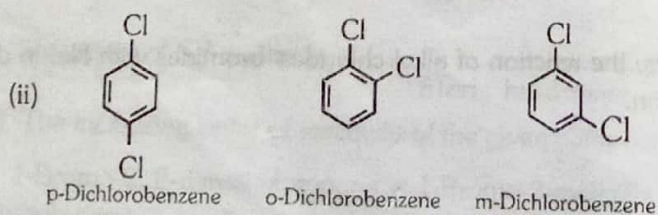
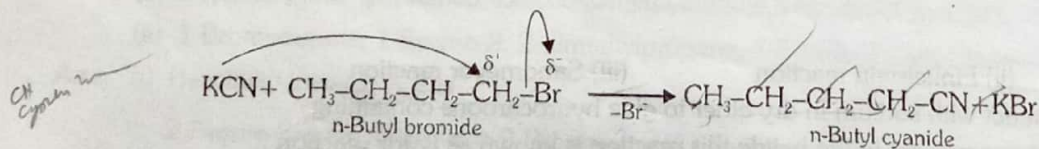


(ii) p-Dichlorobenzene has higher m.p. and lower solubility than those of o- and m-isomers. Discuss.

(iii) The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.



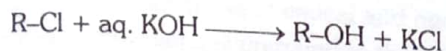
The given reaction is an $\text{S}_{\text{N}}2$ reaction. In this reaction, CN^- acts as the nucleophile and attacks the carbon atom to which Br is attached. CN^- ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.



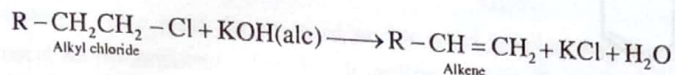
p-Dichlorobenzene is more symmetrical than o- and m-isomers. For this reason, molecules of p-dichlorobenzene

are more closely packed than o- and m-isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of p-dichlorobenzene.

- (iii) OH⁻ ion is highly solvated in an aqueous solution and as a result, the basic character of OH⁻ ion decreases. Therefore, it cannot abstract a hydrogen from the β-carbon. So substitution takes place forming alcohols.

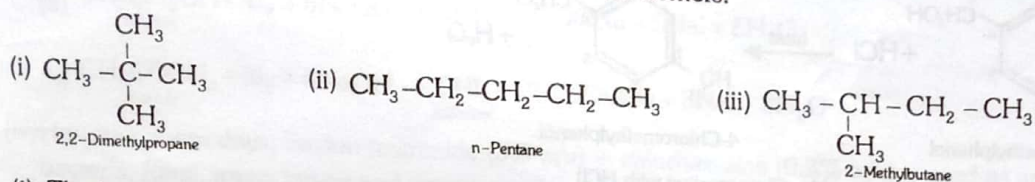


On the other hand, an alcoholic solution of KOH contains alkoxide (RO⁻) ion, which is a strong base. Thus, it can abstract hydrogen from the β-carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.

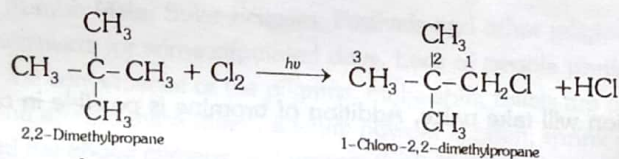


- 22.** Among the isomeric alkanes of molecular formula C₅H₁₂, identify the one which on photochemical chlorination yields (i) A single monochloride (ii) Three isomeric monochlorides (iii) Four isomeric monochlorides.

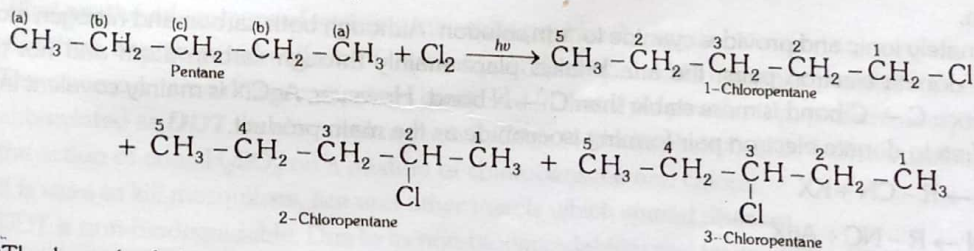
Ans. The molecular formula C₅H₁₂ represents three structural isomers.



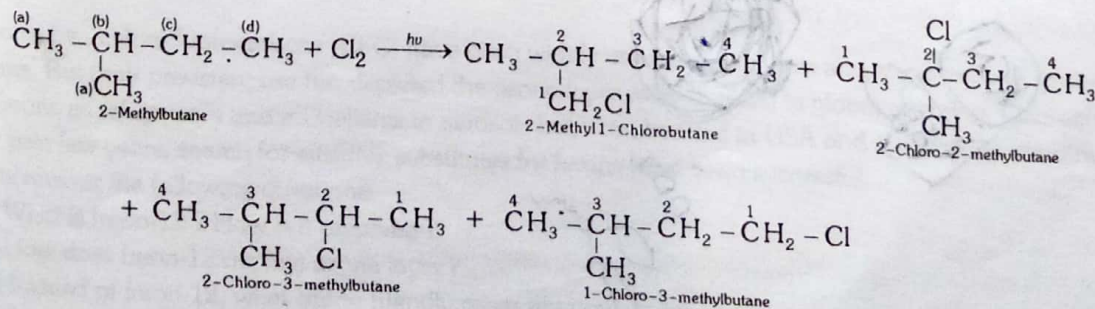
- (i) The isomer is symmetrical with four primary (1°) carbon atoms and one quaternary (4°) carbon atom. Since all the hydrogen atoms are equivalent, it will yield only one monochloride upon photochlorination i.e., chlorination carried in the presence of ultra-violet light.



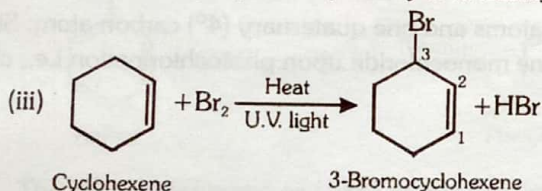
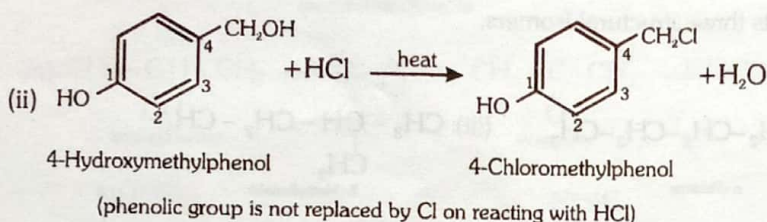
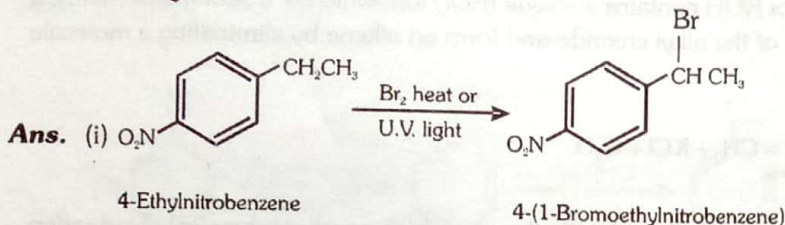
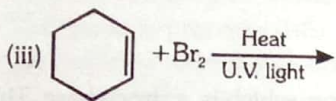
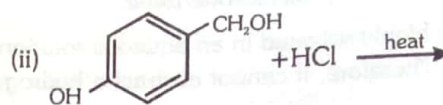
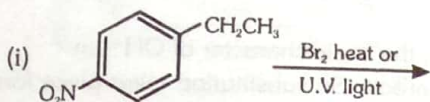
- (ii) In the straight chain isomer pentane, there are three groups of equivalent hydrogen atoms. As a result, three isomeric monochlorides are possible.



- (iii) The branched chain isomer has four types of equivalent hydrogen atoms present. It will give four isomeric monochlorides upon chlorination.



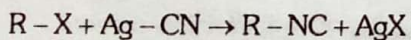
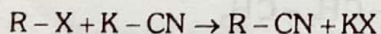
23. Draw the structures of the major monohalo products in each of the following reactions-



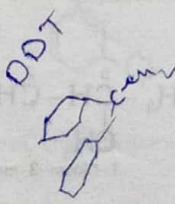
Under the reaction conditions allylic halogenation will take place. Addition of bromine is possible in case the reaction is carried at room temperature.

24. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

Ans. KCN is predominately ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C — C bond is more stable than C — N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.



KX

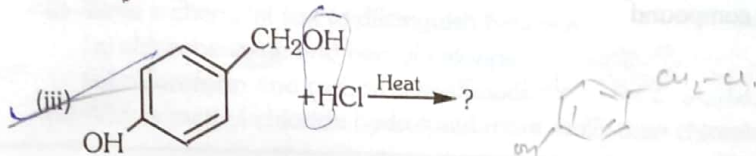
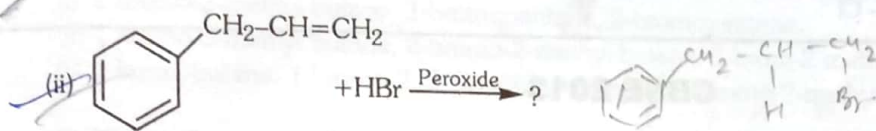
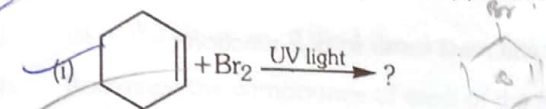


EXERCISE-1

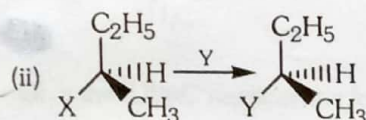
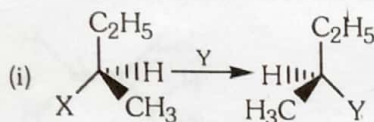
PREVIOUS YEARS BOARD PROBLEMS

CBSE 2016

1. Write the major monohalo product(s) in each of the following reactions:

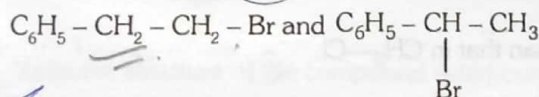


2. Which of the following two reactions is S_N2 and why?



CBSE 2015

1. Which would undergo S_N2 reaction faster in the following pair:



2. How do you convert the following:

(i) Prop-1-ene to Propan-2-ol C=CC >> C(O)CC $\xrightarrow{\text{H}_2\text{O}/\text{H}^+}$

(ii) Bromobenzene to 2-bromoacetophenone c1ccccc1Br >> c1ccccc1C(=O)CBr $\xrightarrow{\text{CH}_3\text{COCl}/\text{AlCl}_3}$

(iii) 2-bromobutane to But-2-ene CC(Br)CC >> CC=CC $\xrightarrow{\text{alkon}}$

3. What happens when

(i) ethyl chloride is treated with NaI in the presence of acetone, CCCl + NaI >> CCI + NaI

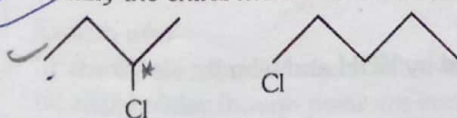
(ii) chlorobenzene is treated with Na metal in the presence of dry ether, c1ccccc1Cl + Na >> c1ccccc1[Na]

(iii) methyl chloride is treated with KNO₂? CCl + KNO2 >> CNO2 + KCl

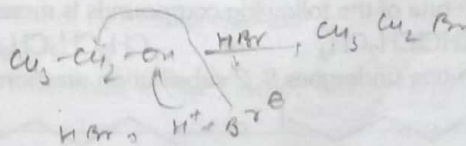
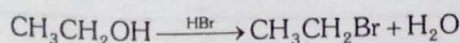
Write chemical equations in support of your answer.

CBSE 2014

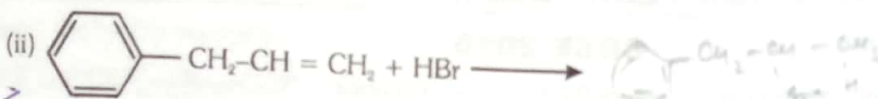
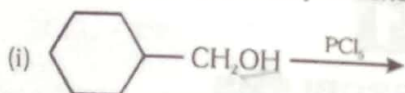
1. Identify the chiral molecule in the following pair: (1)



2. Write the mechanism of the following reaction:



8. (a) Draw the structures of major monohalo products in each of the following reactions:

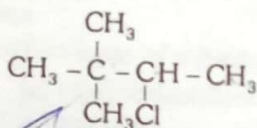


(b) Which halogen compound in each of the following pairs will react faster in S_N2 reaction:

- (i) CH_3Br or CH_3I
 (ii) $(\text{CH}_3)_3\text{C}-\text{Cl}$ or CH_3-Cl

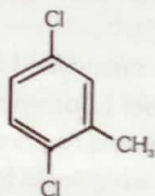
CBSE 2013

1. Write the IUPAC name of the following compound



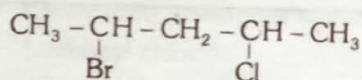
2-chloro-2,3-dimethylbutane

2. Write the IUPAC name of the following compound.



1,4-dichloro-2-methylbenzene

3. Write the IUPAC name of the following compound



2-bromo-3-chloropentane

4. Account for the following-

- (i) The C—C bond length in chloro-benzene is shorter than that in CH_3-Cl .
 (ii) Chloroform is stored in closed dark brown bottles.

5. Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same.

6. Give reasons for the following-

- (i) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.
 (ii) (\pm) 2-Butanol is optically inactive.
 (iii) C—X bond length in halobenzene is smaller than C—X bond length in CH_3-X .

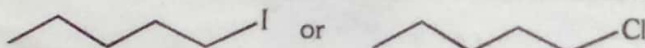
CBSE 2012

1. What happens when bromine attacks $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{C} \equiv \text{CH}$?

2. Answer the following questions.

- (i) What is meant by chirality of a compound?
 (ii) Which one of the following compounds is more easily hydrolyzed by KOH and why?
 $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

(iii) Which one undergoes S_N2 substitution reaction faster and why?

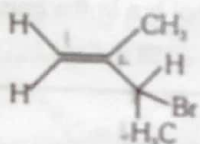


CBSE 2011

- Write the IUPAC name of the following compound $\text{CH}_2 = \text{CHCH}_2\text{Br}$.
- Write the structure of 2-(2-chlorophenyl)-1-iodooctane.
- Write the structure of the following compound: 1-bromo-4-sec butyl-2-methyl benzene.
- Write the structure of the following organic compound: 2-chloro-3-methylpentane.
- Rearrange the compounds of each of the following sets in order of reactivity towards $\text{S}_{\text{N}}2$ displacement.
 - 2-bromo-2-methyl butane, 1-bromopentane, 2-bromopentane.
 - 1-bromo-3-methyl butane, 2-bromo-2-methyl butane, 3-brom-2-methyl butane
 - 1-bromobutane, 1-bromo-2, 2-dimethyl propane, 1-bromo-2-methyl butane, 1-bromo-3-methyl butane
- Write a chemical test to distinguish between
 - chlorobenzene and benzyl chloride
 - chloroform and carbon tetrachloride
 - Why is methyl chloride hydrolysed more easily than chlorobenzene?

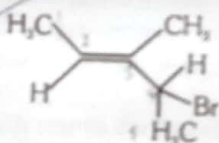
CBSE 2010

- Write the IUPAC name of the following.



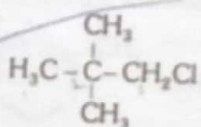
3-bromo-2-methylbut-2-ene

- Give the IUPAC name of the following.



2-bromo-2,3-dimethylbut-2-ene

- Write the structure of the compound 4-tert-butyl-3-iodoheptane.
- Write the IUPAC name of the following compound.



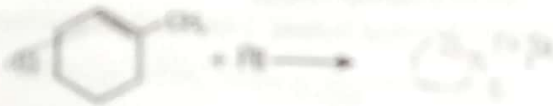
2,2-dimethylpropane

- Write the structure of the compound 1-chloro-4-ethylcyclohexane.
- Which compound in each of the following pairs will react faster in $\text{S}_{\text{N}}2$ reaction with OH^- ? Why?
 - CH_3Br or CH_3I
 - $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl
- How would you differentiate between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanism of substitution reactions? Give one example of each.
- Explain why
 - the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
 - alkyl halides though polar are immiscible with water?
 - in the pair, $(\text{CH}_3)_3\text{C}-\text{Cl}$ and CH_3Cl , CH_3Cl will react faster in $\text{S}_{\text{N}}2$ reaction with OH^- ?

1. Which one in the following pairs undergoes S_N1 substitution reaction faster and why?



2. Complete the following reaction equations



3. Give reasons for the following observations

- (i) p-dichlorobenzene has higher melting point than those of o and m isomers.
- (ii) Fluoromethane is less reactive than iodomethane towards nucleophilic substitution reaction.
- (iii) The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product.

70
Que: 1/2/21

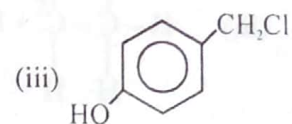
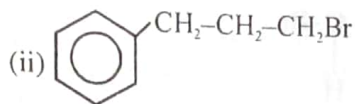
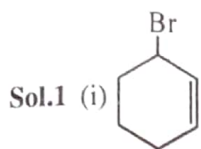
TREATMENT OF REACTANT

EXERCISE-1

SOLUTION PREVIOUS YEARS BOARD PROBLEMS

HALOALKANE AND HALOARENE

CBSE 2016

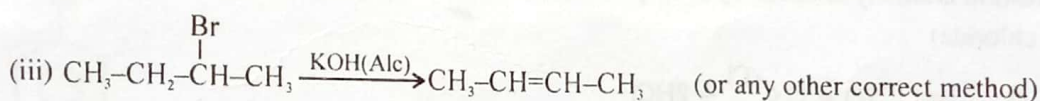
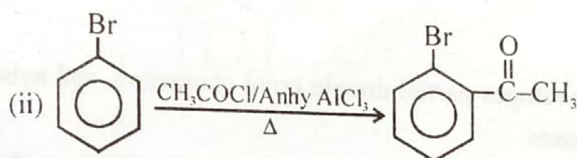


Sol.2 (i) Inversion of configuration

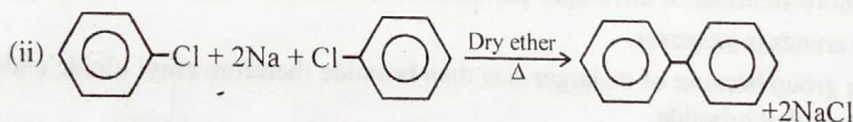
CBSE 2015

Sol.1 $C_6H_5-CH_2CH_2-Br$

Sol.2 (i) $CH_3-CH=CH_2 \xrightarrow{H_2O/H^+} CH_3-CH(OH)-CH_3$

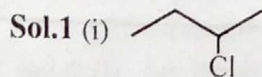


Sol.3 (i) $C_2H_5Cl + NaI \xrightarrow{Acetone} C_2H_5I + NaCl$

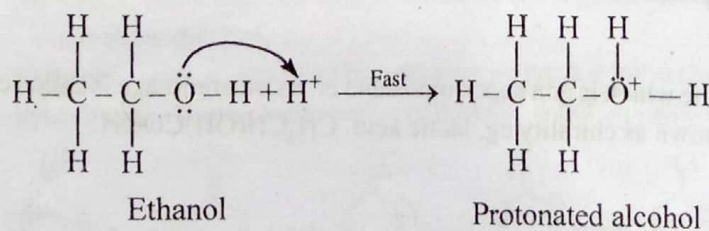


(iii) $CH_3Cl + KNO_2 \xrightarrow{\Delta} CH_3-ONO + KCl$

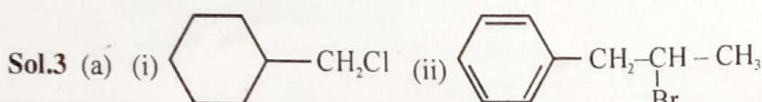
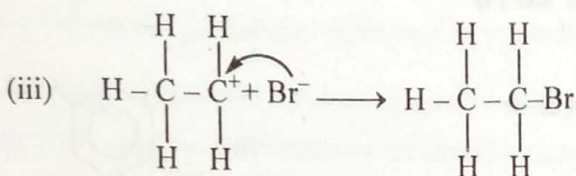
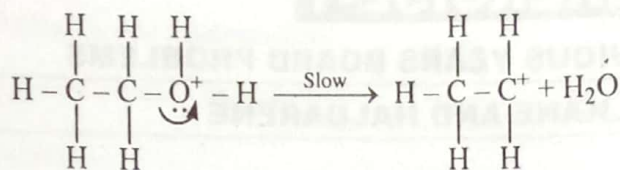
CBSE 2014



Sol.2 (i) Formation of protonated alcohol :



(ii) Formation of carbocation :



(b) (i) CH_3Br (ii) $\text{CH}_3\text{-Cl}$

CBSE 2013

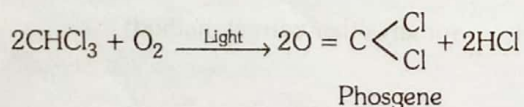
Sol.1 2-Chloro-3,3-dimethylbutane

Sol.2 1,4-dichloro-2-methylbenzene

Sol.3 2-bromo-4-chloropentane

Sol.4 (i) Because of resonance in chloro Benzene. It develops partial double bond characters, sp^2 hybridized Thus C-Cl Bond length in halo arenes is increases.

(ii) Chloroform is slowly oxidised by air in presence of light to form an extremely poisonous gas phosgene (carbonyl chloride)



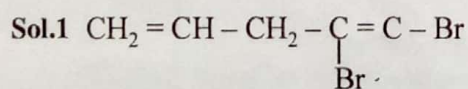
Sol.5 Because of resonance in chloro Benzene. It develops partial double bond characters, sp^2 hybridized Thus C-Cl Bond length in halo arenes is increases.

Sol.6 (i) Iodide is better leaving group because of its larger size than bromide therefore ethyl iodide under goes SN^2 reaction faster than ethyl bromide.

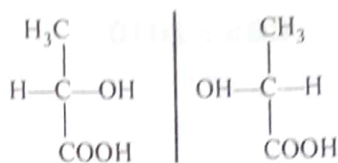
(ii) +2 butanol is a racemic mixture it is a mixture which contains two enantiomers in equal proportion and thus have zero optical rotation so it is optically inactive.

(iii) Due to delocalisation of lone pairs of electron of X atom over the benzene ring. C-X bond in halogenzen acquire some = bond character while in $\text{CH}_3\text{-X}$, C-X bond is a single bond.

CBSE 2012

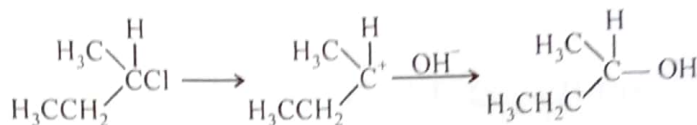


Sol.2 (i) Chirality An object or molecule which is non superimposable on its mirror image is called chiral and the property of being chiral is known as chirality eg. lactic acid. $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$.



Mirror

- (ii) $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ is more reactive than $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ as the former one gives more stable carbocation intermediate.

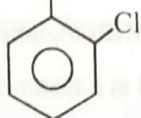


- (iii) Iodide is a better leaving group because of its larger size therefore it undergoes SN^2 reaction faster.

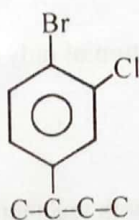
CBSE 2011

Sol.1 3-Bromo prop-1-ene

Sol.2 C-C-C-C-C-C-C-C-I



Sol.3



Sol.4 C-C-C-C-C
 | |
 CH₃ Cl

Sol.5 (I) SN^2 reaction depends upon steric hinderance. More is steric hinderance slower the reaction, so order of reactivity is $1^\circ > 2^\circ > 3^\circ$

1-bromopentane > 2-bromopentane > 2-bromo-2-methyl butane

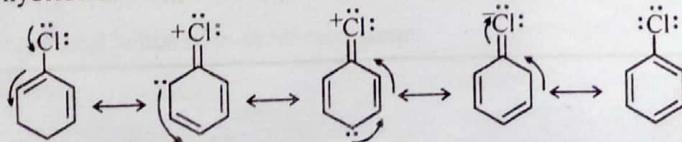
(II) 1-bromo-3-methyl butane > 3-bromo-2-methyl butane > 2-bromo-2-methyl butane.

(III) 1-bromo butane > 1-bromo-3-methyl butane > 1-bromo-2-methyl butane > 1-bromo-2-dimethyl propane

Sol.6 (I) (a) Benzyl chloride when treated with AgNO_3 solution will give a white ppt. while chlorobenzene will not.

(b) CHCl_3 when treated with 1° amine & KOH gives offensive smelling isocyanides while CCl_4 does not show this test.

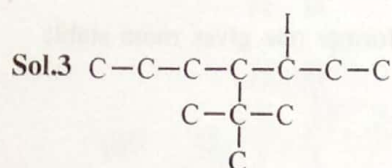
(II) Chlorobenzene is stabilised by reanance so has a π bond character between C & Cl, C is sp^2 hybridised so more electronegative thus Cl^- is not replaced easily



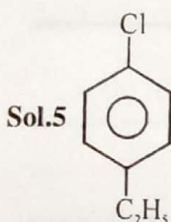
CBSE 2010

Sol.1 3-bromo-2-methyl prop-1-ene

Sol.2 4-Bromo-3-Methyl pent-2-ene



Sol.4 1-Chloro-2,2-dimethyl, propane



Sol.6 (i) CH_3I will react faster as compared to CH_3Br because CH_3I has lower bond dissociation energy & iodide is better leaving group. In the presence of nucleophile it will be released at a faster rate.

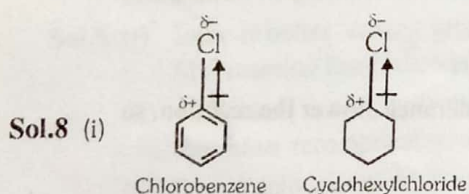
(ii) CH_3Cl will react faster as compared to $(\text{CH}_3)_3\text{CCl}$ because 1° halide undergo SN^2 mechanism faster than 3° halides to minimize steric hindrance

Sol.7 In $\text{S}_{\text{N}}1$ mechanism of substitution reaction the rate of reaction depends upon the concentration of only one reactant which is tert. butyl bromide.

It involves the formation of carbocation intermediate.

In SN^2 mechanism of substitution reaction, the rate of reaction depends upon the conc. of both reactants

It involves the formation of transition state and inversion of configuration.




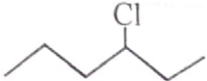
+M of $-\text{Cl}$ and $-\text{I}$ of $-\text{Cl}$ are in opposite direction so dipole moment is decreased in chlorobenzene.

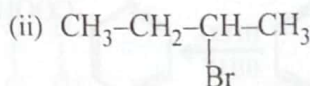
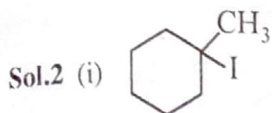
(ii) If a haloalkane/haloarene is to dissolve in water, energy is required to overcome the forces of attraction already existing between haloalkane/haloarene molecules and to break the hydrogen bonds already existing between water molecules. Less energy is released when new attractions are set up between the haloalkane/haloarene and water molecules because these are not as strong as the hydrogen bonds already existing between H_2O molecules. As a result, haloalkanes and haloarenes insoluble in water.

(iii) due to less steric hindrance.

CBSE 2009

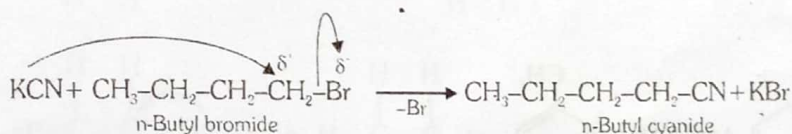
Sol.1 (i)  tertiary halide reacts faster than sec. halide tertiary carbocation intermediate.

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

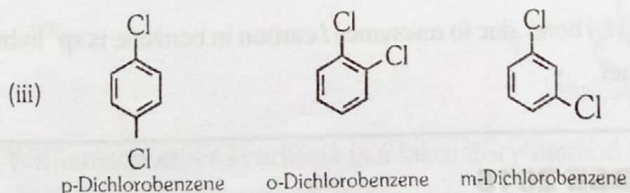


Sol.3 (i) The given reaction is : $n\text{BuBr} + \text{KCN} \xrightarrow{\text{EtOH-H}_2\text{O}} n\text{BuCN}$

The given reaction is an $\text{S}_{\text{N}}2$ reaction. In this reaction, CN^- acts as the nucleophile and attacks the carbon atom to which Br is attached. CN^- ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.



(ii) Because of resonance in chloro Benzene. It develops partial double bond characters, sp^2 hybridized. Thus C-Cl Bond length in halo arenes is increases.



p-Dichlorobenzene is more symmetrical than o- and m-isomers. For this reason, molecules of p-dichlorobenzene are more closely packed than o- and m-isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of p-dichlorobenzene.