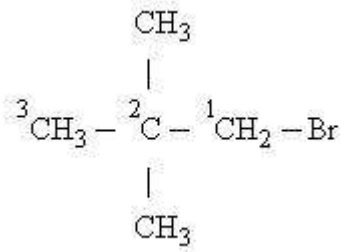
Chapter: Haloalkanes and Haloarenes

Characteristics of halo compounds.

Question 1

Write the IUPAC name of the following compound:$(CH_3)_3CCH_2Br$

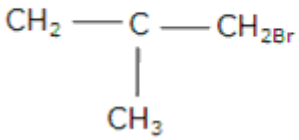
Ans.



The IUPAC name of the given structure is 2, 2-Dimethylbromopropane.

Question 2

Give the IUPAC name of the following compound.



Ans.

3-Bromo-2-methylpro-1-ene

Question 3

Give the common name of the following.

(i) 1- Bromopropane

(ii) 2-chloro propane

(iii) 1-chloro-2-methylpropane

Ans.

(i) Common name of 1- Bromopropane is n-propylbromide

(ii) Common name of 2-chloro propane is Isopropyl chloride

(iii) Common name of 1-chloro-2-methylpropane Isobutyl chloride

Question 4

Classify the following as alkyl, allyl, benzyl, vinyl or aryl halides:

(i) $(CH_3)_2CHCH(Cl)CH_3$
(ii) $(CH_3)_3CCH_2CH(Br)C_6H_5$
(iii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$
(iv) $CH_3CH=CHC(Br)(CH_3)_2$
(v) *p*-$ClC_6H_4CH_2CH(CH_3)_2$

Ans.

(i) Alkyl halide: $(CH_3)_2CHCH\ (Cl)\ CH_3$
(ii) Allyl halide: $CH_3CH=CHC\ (Br)\ (CH_3)_2$
(iii) Benzyl halide: $(CH3)_3CCH_2CH\ (Br)\ C_6H_5$
(iv) Vinyl halide: $CH_3CH=C\ (Cl)\ CH_2CH\ (CH_3)_2$
(v) Aryl halide: *p*-$ClC_6H_4CH_2CH\ (CH_3)_2$

Question 5

Write the isomers of the compound having formula C_4H_9Br.

Ans.

i. $CH_3CH_2CH_2\ CH_2Br$
ii. $CH_3CH_2\ CH\ (Br)CH_3$
iii. $CH_3CH(CH_3)\ CH_2Br$
iv. $CH_3CBr(CH_3)\ CH_3$

Question 6

Define racemisation?

Ans.

A mixture containing two enantiomers in equal proportions is known as **racemic mixture** and the process of conversion of enantiomers into a racemic mixture is known as **racemisation.**

Question 7

What are enantiomers? Give example.

Ans.

The stereoisomers related to each other as nonsuperimposable mirror images are called **enantiomers.**

For example –

2-chloro butane ($CH_3CH_2\ C^*H\ (Cl)\ CH_3$).

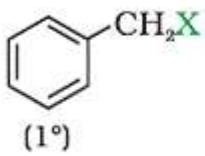
Here the carbon atom marked is the chiral centre and posses four different group.

Question 8

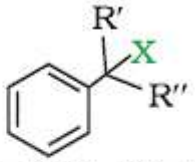
What is benzylic halide? Give the structure.

Ans.

The compounds in which the halogen atom is bonded to an sp^3-hybridised carbon atom next to an aromatic ring is called benzylic halide.



(1°)



$R' = CH_3, R'' = H$ (2°)

$R' = R'' = CH_3$ (3°)

Question 9

What is the common name of 1, 3-Dibromobenzene?

Ans.

***m*-** Dibromobenzene.

Question 10

What is the general formula for alkyl halide?

Ans.

$C_nH_{2n+1}X$, where X is halogen atom and n is the number of carbon atom.

Question 11

Write the structures of the following organic halogen compound.

2-Chloro-3-methylpentane.

Ans.

$CH_3CH\ (Cl)\ CH\ (CH_3)\ CH_2CH_3$

Question 12

Give the IUPAC name of the compound $CH_3CH\ (Cl)\ CH\ (Br)\ CH_3$.

Ans.

2-bromo-3-chloro-Butane

General methods of preparation

Question 1

Write the structure of the major organic product in each of the following reactions:

(i) $CH_3CH_2CH_2OH + SOCl_2 \rightarrow$

(ii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{peroxide}}$

(iii) $CH_3CH = C(CH_3)_2 + HBr \rightarrow$

Ans.

(i) $CH_3CH_2CH_2Cl$

(ii) $CH_3CH_2CH_2CH_2Br$

(iii) $CH_3CH_2\ CBr(CH_3)_2$

Question 2

Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol
(ii) 1-chlorobutane
(iii) But-1-ene.

Ans.

(i) $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{red}P/I_2} CH_3CH_2CH_2CH_2I$
1-butanol 1-iodobutane

(ii) $CH_3CH_2CH_2CH_2Cl + NaI \rightarrow CH_3CH_2CH_2CH_2I + NaCl$
1-chlorobutane 1-iodobutane

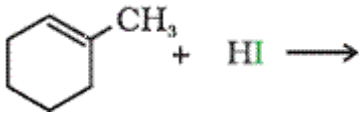
(iii) $CH_3CH_2CH = CH_2 + HI \rightarrow CH_3CH_2CH_2CH_2I$
But-1-ene. 1-iodobutane

Question 3

Complete the following reactions:

(i)

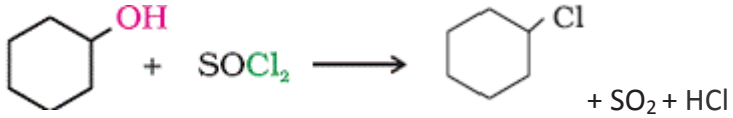
(ii)



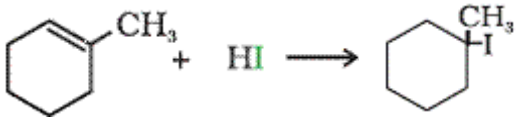
(iii) $CH_3CH_2Br + NaI \rightarrow$

Ans.

(i)



(ii)



(iii) $CH_3CH_2Br + NaI \rightarrow CH_3CH_2I + NaBr$

Question 4

***p*-Dichlorobenzene has higher melting point and solubility than those of *ortho*- and *meta*-isomers. Discuss.**

Ans.

Due to its symmetry p-Dichlorobenzene fits in crystal lattice better as compared to *o*- and *m*-isomers. As a result the melting point and solubility of *p*-Dichlorobenzene is higher than ortho- and meta-isomers.

Question 5

Explain the statement "Alkyl halides, though polar, are immiscible with water".

Ans.

Energy is required to overcome the attractions between the haloalkane molecules and to break the hydrogen bonds between water molecules. The energy released during the formation of new attractive force between Haloalkane and the water molecule is very less as the attractions between the haloalkane and the water molecule is not as strong as the original hydrogen bonds in water. Thus Alkyl halides, though polar, are immiscible with water.

Question 6

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

Ans.

H_2SO_4 converts KI to corresponding HI and then oxidizes it to I_2. Hence it cannot be used during the reaction of alcohols with KI.

Question 7

Name the aromatic salt formed as intermediate during the Sandmeyer's Reaction.

Ans.

Benzene diazonium halide also known as diazonium salt is formed as intermediate during the Sandmeyer's Reaction.

Question 8

Which alkyl halides show colour on exposure to light?

Ans.

Alkyl Bromide and Alky iodide.

Question 9

Give the Swarts reaction for the synthesis of fluoromethane.

Ans.

Question 10

Give the order of reactivity of alcohols with a given haloacid.

Ans.

The order of reactivity of alcohols with a given haloacid is 3°>2°>1°.

Chemical properties

Question 1

Answer the following:

(i) Haloalkanes easily dissolve in organic solvents, why?

(ii) What is known as a racemic mixture? Give an example.

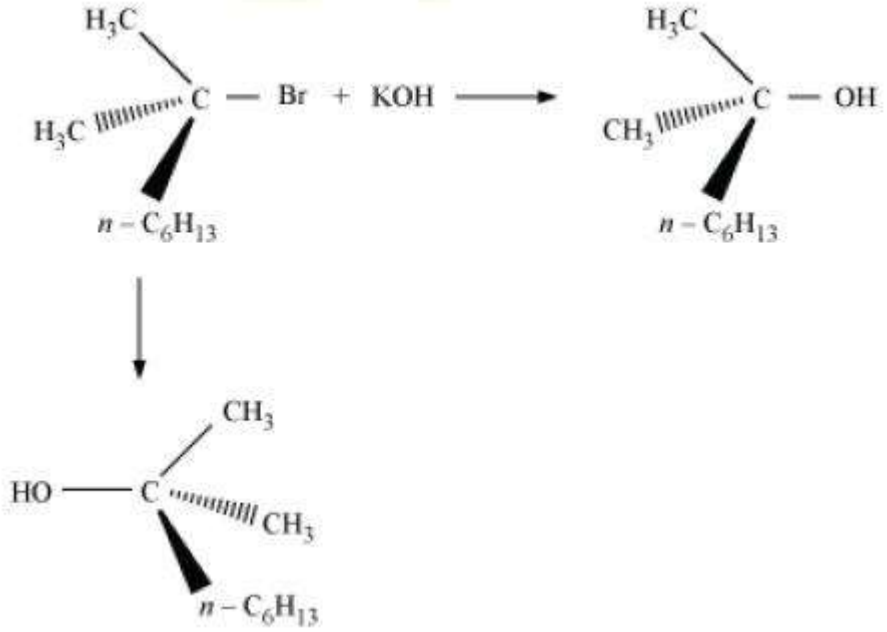
(iii) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N1 substitution reaction and why?

Ans.

(i) Haloalkanes can easily dissolve in organic solvents of low polarity because the new forces of attraction set up between haloalkanes and the solvent molecules are of same strength as the forces of attraction being broken.

(ii) A mixture of equal amounts of two enantiomers is known as racemic mixture.

For example: When a 3^{o} halide undergoes substitution with KOH, the reaction proceeds through S_N1 mechanism forming the racemic mixture in which one of the products has the same configuration as a reactant, while the product has an inverted configuration.



(iii) The S_N1 substitution reaction involves the formation of carbocation, which is not affected by the presence of bulky groups.

Thus, $C_6H_5CH(C_6H_5)Br$ will be more reactive towards S_N1 substitution reaction forming racemic mixture.

Question 2

A solution of KOH hydrolyses CH_3 $CHClCH_2CH_3$ and $CH_2CH_2CH_2CH_2Cl$.Which one of these is more easily hydrolysed?

Ans.

$CH_3CH_2CH_2CH_2Cl$ undergoes hydrolysis more easily than $CH_3CHClCH_2CH_3$.

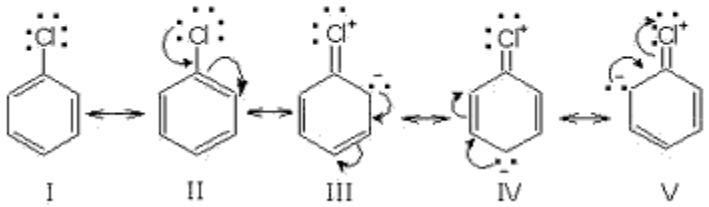
$CH_3CH_2CH_2CH_2Cl$ being a primary alkyl halide has less steric hindrance than $CH_3CHClCH_2CH_3$ which is secondary alkyl halide.

Question 3

Although chlorine is an electron withdrawing group, yet it is ortho-, para-directing in electrophilic aromatic substitution reaction. Explain why it is so?

Ans.

In aromatic compound chlorine attached to the ring acts as the electrons donor group because the lone pair of chlorine becomes involved in process of resonance and is responsible to create the negative charge at ortho and para positions so acts as ortho-para director.



Question 4

Give reasons for the following:

(i) Grignard reagent should be prepared under anhydrous conditions.

(ii) Neo-pentyl bromide undergoes nucleophilic substituting reactions very slowly.

(iii) p-Methoxybenzyl bromide reacts faster than p-nitrobenzyl bromide with ethanol to form an ether product.

Ans.

(i) Grignard reagent reacts with water and gets decomposed, so it is produced in anhydrous conditions.

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

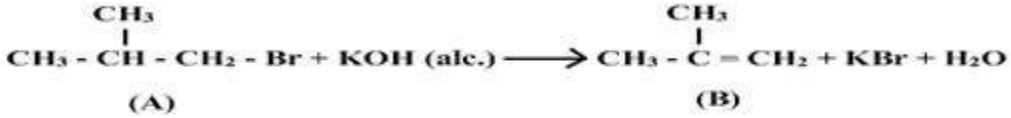
(ii) Neo-pentyl bromide being a primary halide reacts slowly through SN_1, and being a sterically hindered halide reacts slowly even through SN_2 mechanism.
(iii) Methoxy ($-OCH_3$) group being an electron releasing group stabilizes the intermediate carbocation. On the other hand nitro group ($-NO_2$) is an electron withdrawing group and hence it destabalises the intermediate carbocation. Thus p-methoxy benzyl bromide reacts faster than p-nitrobenzyl bromide because in its case the reaction proceeds via more stable intermediate carbocation.

Question 5

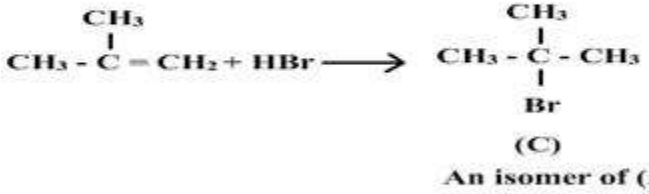
A primary alkyl halide (A) C_4H_9 reacts with alcoholic KOH to give a compound (B). The compound (B) reacts with HBr to give the compound C which is an isomer of A. When A reacts with sodium metal it give a compound (D) whose molecular formula is C_8H_{18}. The compound D is different from the compound formed when n-butyl bromide reacts with sodium. Give the structural formula of A and write all the equations involved in the reaction.

Ans.

For C_4H_9Br, two primary halides are possible $CH_3CH_2CH_2CH_2Br$ (n-butyl bromide) and $(CH_3)_2CHCH_2Br$ (iso-butyl bromide). Since A is not normal –butyl bromide, it must be iso-butyl bromide.



(A) (B)



(C)

An isomer of (A)

2, 5- Dimethylhexane (C_8H_{18})

Question 6

Give reasons for the following:

i) Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanide as the chief products.

ii) Alcohols do not react with NaBr, but when H_2SO_4 is added, they form alkyl bromides.

Ans.

i) KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms of CN can donate electron pairs but the attack takes place mainly through carbon atom and not through nitrogen atom because 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.

ii) Br^- is a weak base. So it cannot displace the strong base OH^- when H_2SO_4 is added, it leads to protonation of alcohol, as a result of which water molecule is formed. Since water molecule is a very weak base it is easily replaced by Br^-.

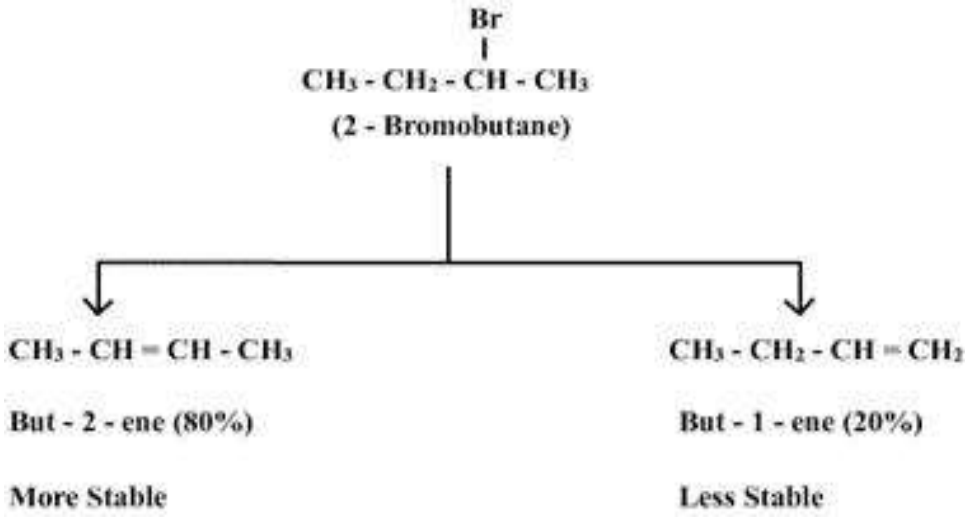
Question 7

What is Saytzeff rule? Illustrate with suitable example.

Ans.

According to Saytzeff rule in dehydrohalogenation reactions the Haloalkane can form more than one alkene due to the availability of more than one alpha hydrogen atoms. In such a case the preferred alkene is that alkene which has greater number of alkyl groups attached to the doubly bonded carbon atoms.

For example: the dehydrohalogenation of 2-bromobutane yields two products 1 butene and 2 butene. Out of these 2 butene is the major product (80%) as it is more highly substituted and it is more stable

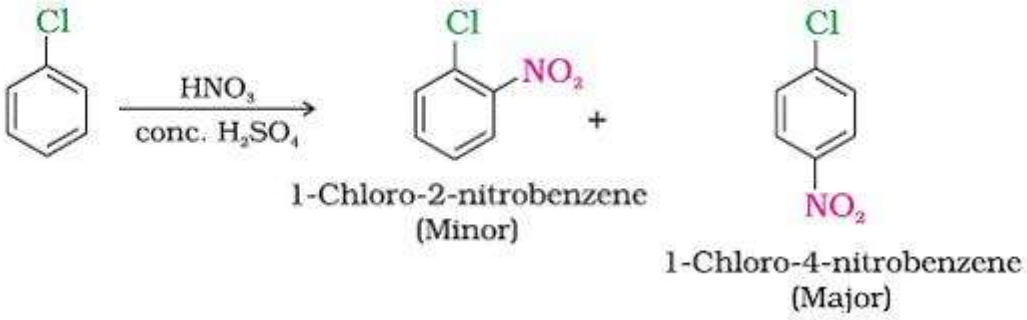


Question 8

Give the nitration and sulphonation reaction of chlorobenzene.

Ans.

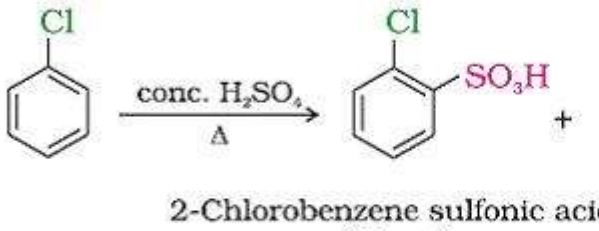
(i) Nitration:



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

(ii) Sulphonation:



2-Chlorobenzene sulfonic acid (Minor)

4-Chlorobenzene sulfonic acid (Major)

Question 9

Which compound in each of the following pairs will react faster in S_N2 reaction with -OH?

(i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

Ans.

(i) CH3I will react faster than CH3Br because the order of reactivity is as follows

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

(ii) CH_3Cl will react faster than $(CH_3)_3CCl$ because the order of reactivity is as follows in SN_2 reaction.

Question 10

What is the directive influence of chlorine in chlorobenzene?

Ans.

The -Cl group is ortho and para directing in chlorobenzene.

Question 11

What is Grignard reagent?

Ans.

It is an organometallic compound having formula RMgX also called alkyl magnesium halide.

Question 12

Give the order of reactivity for S_N1 reaction in methyl, primary, secondary and tertiary halide.

Ans.

Methyl halide >Primary halide > secondary halide> Tertiary halide

order of reactivity →

Question 13

What are ambident nucleophiles?

Ans.

Nucleophiles that possess two nucleophilic centres are called ambident nucleophiles.
Example cyanide

$[^{\ominus}C{\equiv}N \leftrightarrow :C{=}N^{\ominus}]$

Polyhalogen compounds

uestion 1

(i) State one use each of DDT and iodoform.

(ii) Which compound in the following couples will react faster in S_N2

displacement and why?

(a) 1-Bromopentane or 2-bromopentane

(b) 1-Bromo-2-methylbutane or 2-bromo-2methylbutane.

Ans.

(i) Use of DDT: It is used as an insecticide.
Use of iodoform: It is used as an antiseptic.
(ii) (a) 1 – Bromopentane will undergo faster S_N2 displacement reaction than 2-bromopentane because 1- bromopentane has less steric hindrance than 2 – bromopentane. This is because 1- bromopentane is a primary alkyl halide whereas 2-bromopentane is a secondary alkyl halide.
(b) 1- Bromo-2-methylbutane will undergo S_N2 reaction faster than 2- Bromo-2-methylbutane because 1- Bromo-2-methylbutane has less steric hindrance than 2-Bromo-2-methylbutane. This is because 1- Bromo-2-methylbutane is a primary alkyl halide whereas 2- Bromo-2-methylbutane is a tertiary alkyl halide.

Question 2

What is DDT and why its use is banned in United States?

Ans.

DDT is p, p'-Dichlorodiphenyltrichloroethane and is used as insecticide. It is banned for the following reason

(i) Its high toxicity towards fish.

(ii) DDT is not metabolized very rapidly by animals but get deposited and stored in the fatty tissues.

Question 3

Give the three uses of each of the following:

(i) Dichloromethane

(ii) Tetrachloromethane

Ans.

Dichloromethane: It can be used

(i) As solvent

(ii) As paint remover

(iii) As aerosol propellant

Tetrachloro methane: It can be used

(i) As a solvent

(ii) As a fire extinguisher

(iii) As a degreasing agent

Question 4

What is the reason that Haloarenes are less reactive than haloalkane towards nucleophilic substitution reaction?

Ans.

In haloalkane, the halogen is attached to sp^2 hybridised carbon atom while in case of haloarene it is attached to sp^2 hybridised carbon atom. The sp^2 hybridized carbon have greater *s*-character than sp^3-hybridised carbon and thus more electronegative and can hold the electron pair of C—X bond more tightly than in haloalkane . The, C—Cl bond length in haloalkane is greater than in haloarene. Since it is difficult to break a shorter bond than a longer bond, therefore, Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

Question 5

Why chloroform is kept closed in dark colored bottles?

Ans.

Chloroform is oxidized slowly by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as Phosgene

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

Hence it is kept closed in dark colored bottles.

Question 6

Give the role of carbon tetrachloride and Freon on environmental degradation.

Ans.

Both the carbon tetrachloride and Freon causes depletion of ozone layer when released in air because they remain unchanged and diffuses into stratosphere. The depletion of ozone layer increases the exposure of UV rays to human being which results in skin cancer, eye disorder and immune system diseases.

Question 7

Why the use of chloroform as anesthetic is decreasing?

Ans.

Inhaling chloroform vapors depresses the central nervous system and its chronic exposure may cause damage to the liver and kidneys due to metabolism of chloroform to phosgene gas. Hence the use of chloroform as anesthetic is decreasing.

Question 8

Give two hazardous effects of methylene dichloride.

Ans.

i) It harms the central nervous system.

(ii) On direct contact with skin causes severe burning.

Question 9

What is iodoform? Give one use of it.

Ans.

Triodomethane is called iodoform and can be used as antiseptic due to liberation of free iodine.

Question 10

What are freons? Give one example.

Ans.

Freons are chloro fluoro carbons used as refrigerants. Example CCl_2F_2.

Give the full name of DDT.

Ans.

p,p'-Dichlorodiphenyltrichloroethane

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