25

COMPOUNDS OF CARBON CONTAINING HALOGENS

- The replacement of hydrogen atom(s) in hydrocarbon, aliphatic or aromatic, by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.
- Haloalkanes (Alkyl halides) are halogen derivatives of alkanes with general formula
  $[C_nH_{2n+1}X]$. (X = F, Cl, Br or I)
- Haloarenes (Aryl halides) are halogen derivatives of arenes with general formula Ar-X.
- Since halogen is more electronegative than C, hence C ñ X bond is polar.

$$\overset{\delta+}{C}-\overset{\delta-}{X}$$

NOMENCLATURE OF HALOALKANES AND HALOARENES

Nomenclature of Haloalkanes

- Select the longest chain of carbon atoms containing the halogen atom.
- Number the chain to give the minimum number to the carbon carrying halogen atom.

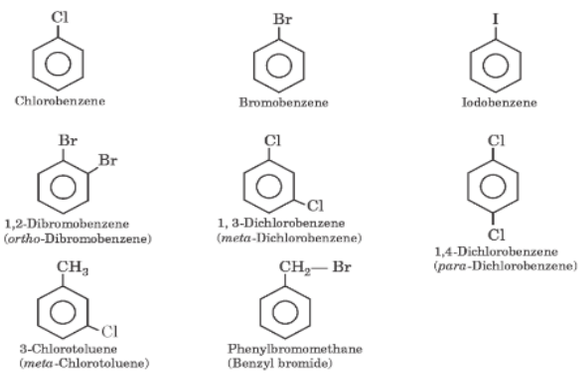
Table 25.1: Names of Some Haloalkanes

Formula	Common name	IUPAC name
CH_3-Cl	Methyl chloride	chloromethane
CH_3-CH_2-Br	Ethyl bromide	bromoethane
$CH_3-CH_2-CH_2-I$	n-propyl iodide	1-iodopropane
$CH_3-\underset{Cl}{CH}-CH_3$	Isopropyl chloride	2-chloropropane
$CH_3-CH_2-CH_2-CH_2-Br$	n-butyl bromide	1-bromobutane
$CH_3-CH_2-\underset{Br}{CH}-CH_3$	sec-butyl bromide	2-bromobutane
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$	tert-butyl bromide	2-bromo-2-methylpropane
$CH_3-CH-CH_2-Br$ (CH₃ branch)	Isobutyl bromide	1-bromo-2-methylpropane
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-Br$	Neopentyl bromide	1-bromo-2,2-dimethylpropane

- If multiple bonds (double or triple bond) is present, then it is given the preference in numbering the carbon chain.
- The IUPAC name of any halogen derivative is always written as one word.

Nomenclature of Haloarenes

- Aryl halides are named by prefixing "halo" to the name of the parent aromatic hydrocarbon.
- If there is more than one substituent on the ring then the relative positions of the substituents are indicated by mathematical numerals.
- In the common system, the relative position of two groups is shown by prefixes ortho, meta or para.



PREPARATION OF HALOALKANES AND HALOARENES

Preparation of Haloalkanes

$$R\text{–}OH + HX \xrightarrow{ZnCl_2} R\text{–}X + H_2O$$

$$R\text{–}OH + NaBr + H_2SO_4 \longrightarrow R\text{–}Br + NaHSO_4 + H_2O$$

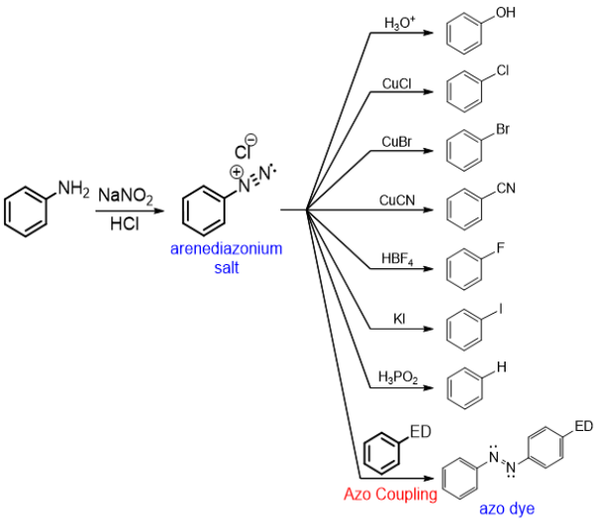
$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3 \quad (X = Cl, Br)$$

$$R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$$

$$R\text{–}OH \xrightarrow[X_2=Br_2,I_2]{\text{red } P/X_2} R\text{–}X$$

$$R\text{–}OH + SOCl_2 \longrightarrow R\text{–}Cl + SO_2 + HCl$$

Preparation of Haloarenes



PROPERTIES OF HALOALKANES AND HALOARENES

Physical Properties of Haloalkanes

1. Boiling point orders

1. $R-I > R-Br > R-Cl > R-F$
2. $CH_3-(CH_2)_2-CH_2Br > (CH_3)_2CHCH_2Br > (CH_3)_3CBr$
3. $CH_3CH_2CH_2 > CH_3CH_2X > CH_3X$

2. Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is:

3. Dipole moment decreases as the electronegativity of the halogen decreases.

4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is

$RI > RBr > RCl > RF$ (For the same alkyl group)

$CH_3I > C_2H_5I > C_3H_7I$

Physical Properties of Aryl Halides

1. Aryl halides are colourless liquids or colourless solids with characteristic odour.

2. Boiling point generally increases with increase in the size of aryl group or halogen atom. Boiling point order is:

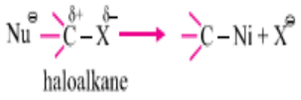
$$Ar-I > Ar-Br > Ar-Cl > Ar-F$$

3. The melting point of p -isomer is more than o- and m- isomer. This is because of more symmetrical nature of p-isomer.

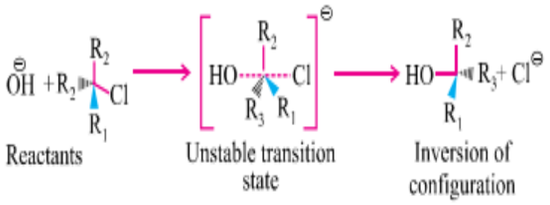
4. Due to resonance in chlorobenzene, C-Cl bond is shorter and hence, its dipole moment is less than that of cyclohexylchloride.

Chemical Properties of Haloalkanes and Haloarenes

Nucleophilic Substitution Reactions

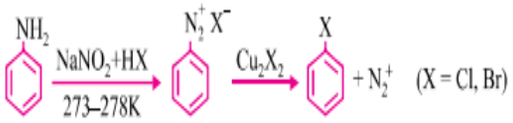


(a) Substitution nucleophilic bimolecular (S_N^2) :



Named Reactions

(a) Sandmeyer Reaction :



(b) Finkelstein Reaction :

$$R-X+NaI \xrightarrow{\text{dry acetone}} R-I+NaX \quad (X = Cl, Br)$$

(c) Swartz Reaction :

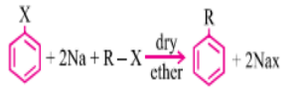
$CH_3 - Br + AgF \rightarrow CH_3 - F + AgBr$

Instead of Ag – F, other metallic fluoride like Hg_2F_2, CoF_2 or SbF_3 can also be used.

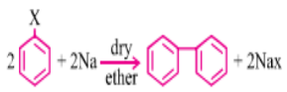
(d) Wurtz Reaction :

$$2R - X + 2Na \xrightarrow{\text{dry ether}} R - R + 2NaX$$

(e) Wurtz-Fittig Reaction :



(f) Fittig Reaction :



biphenyl or diphenyl

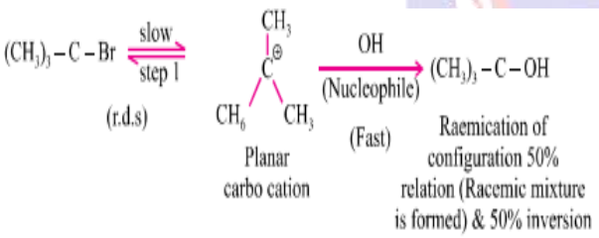
1. 1º haloalkane

2. Bimolecular, 2nd order

3. One step Order of reactivity : 1º > 2º > 3º

4. Deciding factor: Steric hindrance

(a) Substitution nucleophilic unimolecular (SN^1):



1. 3º haloalkane

2. Unimolecular, 1st order

3. Two steps Order of reactivity : 3º > 2º > 1º

4. Deciding factor: Stability of carbocation.

5. Allylic $\left[CH_2 = CH - \overset{\oplus}{C}H_2\right]$ and benzylic $\left[C_6H_5\overset{\oplus}{C}H_2\right]$ halides undergo reaction via SN^1 mechanism as the corresponding carbo cations are resonance stabilized.Aryl halides are much less reactive towards nucleophilic substitution reactions than haloalkanes.

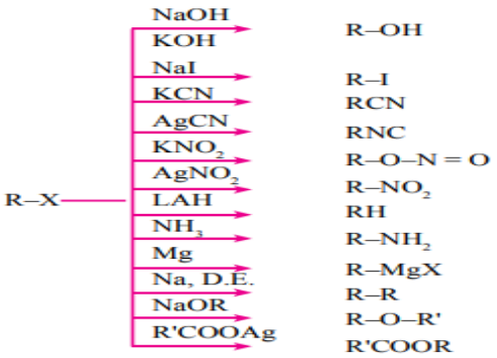
7. Halogen is deactivating but *o*, *p*-directing in electrophilic substitution reaction of haloarenes.

8. $CHCl_3$ is stored in dark bottles upto brim so that formation of poisonous gas phosgene in presence of air and light can be avoided.

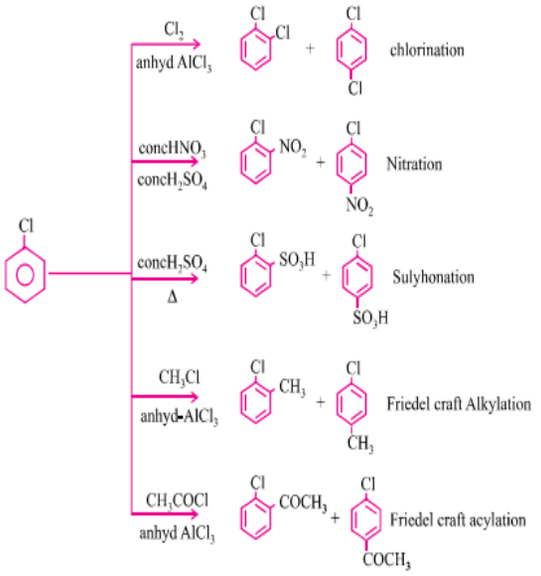
$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$

Chloroform — Carbonyl chloride (phosgene)

Reaction of Haloalkanes



Electrophilic Substitution Reaction of Haloarenes



Distinguishing test for alkyl chlorides, bromides and iodide

- Alkyl chlorides react with $AgNO_3$ to give white precipitate which is soluble in alcoholic ammonium hydroxide. Alkyl bromides react with $AgNO_3$ to give a yellow precipitate which is sparingly soluble in alcoholic ammonium hydroxide. Alkyl iodides react with $AgNO_3$ to give dirty yellow precipitate, which is insoluble in alcoholic ammonium hydroxide.

E.g., $CH_3 - Cl \xrightarrow[AgNO_3]{HNO_3} AgCl\downarrow$ White ppt.

- Vinyl and aryl halides do not yield silver halide under these conditions.

SOME USEFUL POLY HALOGEN COMPOUNDS

Chloroform

- Chlorofom is a derivative of the simplest hydrocarbon, methane. Its IUPAC name is trichloromethane.

Preparation

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[-2HCl]{Cl_2} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[-3HCl]{3Cl_2} \underset{\text{Trichloroethanal (Chloral)}}{Cl_3CCHO}$$

$$Ca(OH)_2 + 2Cl_3C-CHO \longrightarrow \underset{\text{Calcium formate}}{(HCOO)_2Ca} + 2\underset{\text{chloroform}}{CHCl_3}$$

Iodoform

- Iodoform is a pale yellow solid with a distinct smell. Its IUPAC name is triiodomethane.

Preparation

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 3NaI + 3H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3CONa + 3NaI + 3H_2O$$

Dichlorodiphenyltrichloroethane (DDT)

- It is available in several different forms : powder, aerosols, granules, etc.
- **Uses:** It is used mainly to control mosquito-borne malaria. It is also used as an argicultural insecticide. The use of DDT has been banned in many countries because being non-biodegradable, it accumulates in environment. It is toxic to other living organisms such as: mammals, birds, fishes, etc.

Test Yourself

Question: Show the polarization of carbon-magnesium bond in the following structure.

$CH_3 - CH_2 - CH_2 - CH_2 - Mg - X$

Answer:

$CH_3 - CH_2 - CH_2 - \overset{\delta-}{C}H_2 \leftarrow \overset{\delta+}{M}g - X$

Carbon is more electronegative than magnesium.

Check Yourself

1. Which of the following molecules have the highest dipole moment?

(A) CH_3Cl (B) CH_2Cl_2

(C) $CHCl_3$ (D) CCl_4

2. Which of the following have the highest boiling point?

(A) 1-chloropentane

(B) 2-chloropentane

(C) 3-chloropentane

(D) All have equal boiling point

3. Which of the following cannot be prepared by Sandmeyer's reaction?

(A) Chlorobenzene (B) Bromobenzene

(C) Iodobenzene (D) All of these

4. Which of the following reagent is used in the conversion of benzene diazonium chloride to chlorobenzene?

(A) $CuCl_2$ (B) Cu_2Cl_2

(C) $FeCl_2$ (D) $FeCl_3$

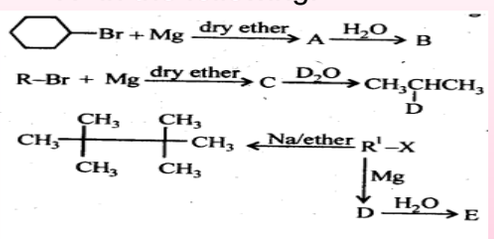
5. At normal temperature iodoform is

(A) Thick viscous liquid (B) Gas

(C) Volatile liquid (D) Solid

Stretch Yourself

1. Why is sulphuric acid not used during the reaction of alcohols with KI?
2. Write structures of different dihalogen derivatives of propane.
3. Identify A, B, C, D, E, R and R^1 in the following:



4. Which one of the following has the highest dipole moment?

(i)CH_3Cl_2 (ii) $CHCl_3$ (iii) CCl_4

5. What are ambident nucleophiles? Explain with an example.

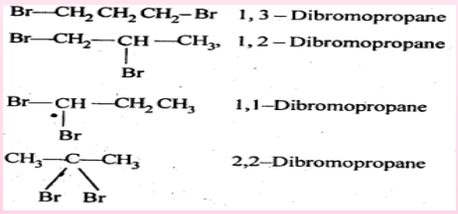
Answers

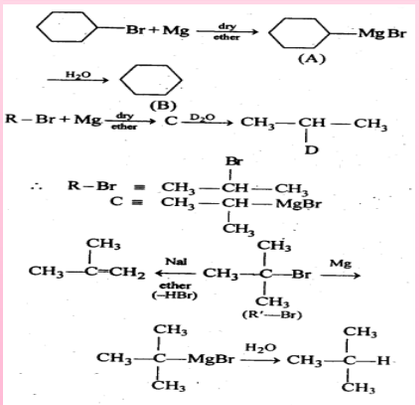
Check Yourself

Answer: 1(B); 2(A); 3(C); 4(B); 5(D)

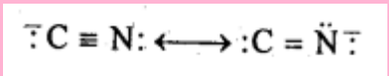
Stretch Yourself

1. Do it by yourself.
2. Four isomers are possible. These are:



3. 

4. Do it by yourself.
5. Nucleophiles which can attack through two different sites are called ambident nucleophiles. For example, cyanide ion is a resonance hybrid of the following two structures:



It can attack through carbon to form cyanide and through N to form is O cyanide.