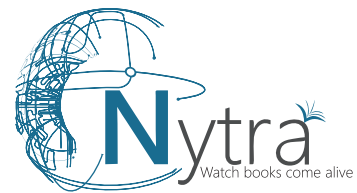


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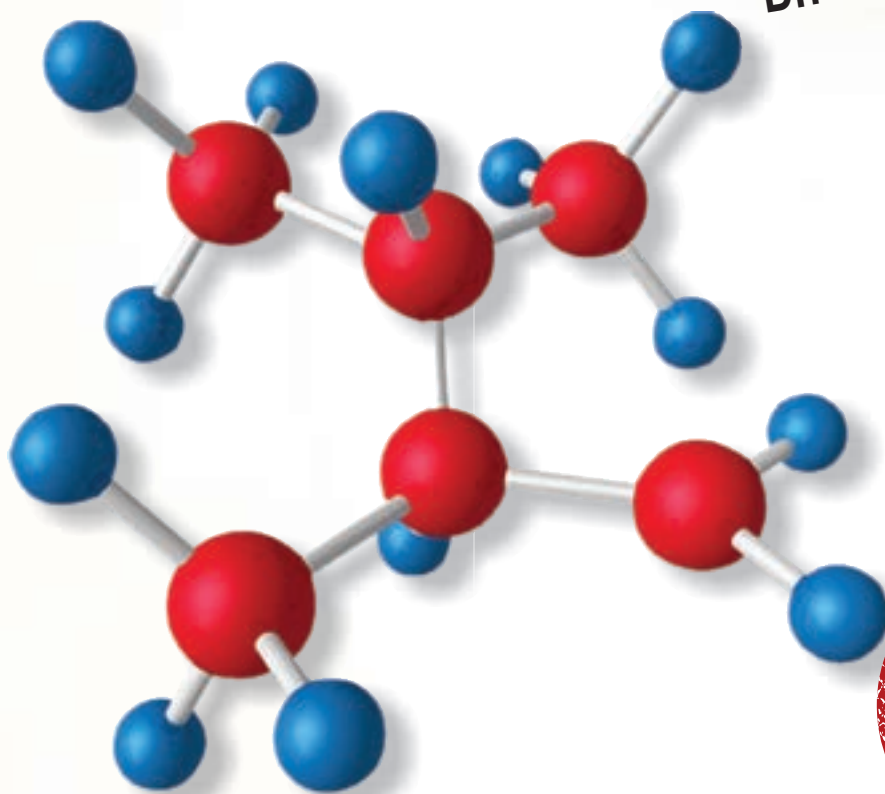
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CLASS-XII

PART-II



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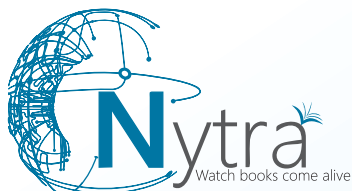
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Strictly
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Guidelines and Syllabus
Including
Value Based Questions
issued by
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By

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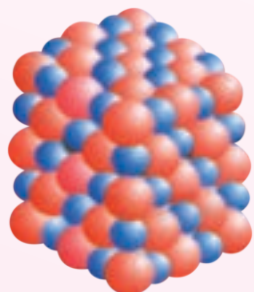
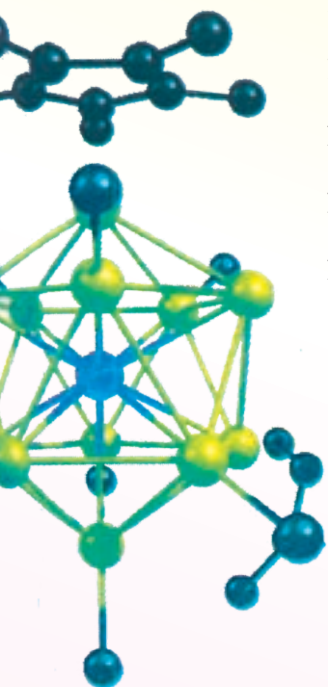
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UNIT 10

HALOALKANES AND HALOARENES

The replacement of one or more hydrogen atoms of a hydrocarbon, aliphatic or aromatic, by an equal number of halogen atoms results in the formation of **haloalkanes** (or **alkyl halides**) and **haloarenes** (or **aryl halides**) respectively.

Haloalkane : RX where R is *alkyl group*

Haloarene : ArX where Ar is *arene*.

X is halogen atom (F, Cl, Br, I)

Thus, haloalkanes and haloarenes are **halogen derivatives of aliphatic and aromatic hydrocarbons**.

Haloalkanes contain halogen atom (s) attached to the sp^3 hybridised carbon atom(s) of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of aryl group.

These classes of compounds find wide applications in industry as well as in our day-to-day life. Some naturally occurring halogen containing organic compounds are important in **health care** and **medicine**. For example, chlorine containing antibiotic, *chloramphenicol*, produced by soil micro-organisms is very effective in the treatment of typhoid fever. An iodine containing hormone, known as *thyroxine* is produced in our body. The deficiency of this hormone causes a disease called *goitre*. Some synthetic organic halogen compounds are also clinically useful. For example, *chloroquine* is used for the treatment of malaria and *halothane* ($CF_3CHClBr$) is used in surgery as an anaesthetic. In modern electronics industry, halogenated solvents such as trichloroethylene are used for cleaning semiconductors, chips and other components.

Above all, these organic halogen compounds are regarded as **synthetic tools in the hands of a chemist** because these serve as important starting materials for the synthesis of a wide range of other substances.

CLASSIFICATION OF HALOGEN DERIVATIVES OF HYDROCARBONS

The halogen derivatives of hydrocarbons are broadly classified into two simple types :

1. *Aliphatic halogen compounds*
2. *Aromatic halogen compounds*

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1. Aliphatic halogen compounds

These are the compounds which are obtained by the replacement of one or more hydrogen atoms of an aliphatic hydrocarbon by an equal number of halogen atoms. These can be further classified on the basis of the nature of aliphatic hydrocarbon, whether alkanes, alkenes or alkynes as haloalkanes, haloalkenes or haloalkynes, respectively.

(i) **Haloalkanes : The halogen derivatives of alkanes are called haloalkanes.** These are also called **alkyl halides**. These are formed by replacing one hydrogen atom in alkane by a halogen.



The general formula of haloalkanes or alkyl halides is $\text{C}_n\text{H}_{2n+1}\text{X}$ or commonly written as RX where R is an alkyl group and X is a halogen atom (F, Cl, Br or I) and $n = 1, 2, 3 \dots$.

Some common examples are :

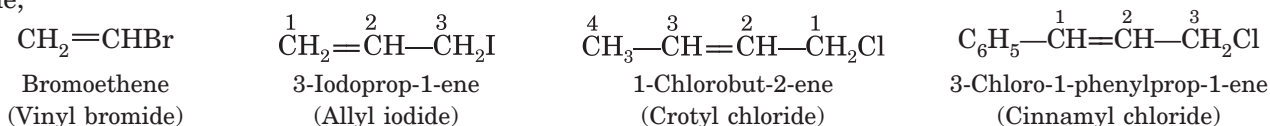
CH_3Cl	$\text{CH}_3\text{CH}_2\text{Br}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{I}$
Chloromethane	Bromoethane	Chloropropane	Iodoethane
(Methyl chloride)	(Ethyl bromide)	(<i>n</i> -Propyl chloride)	(Ethyl iodide)

NOTE

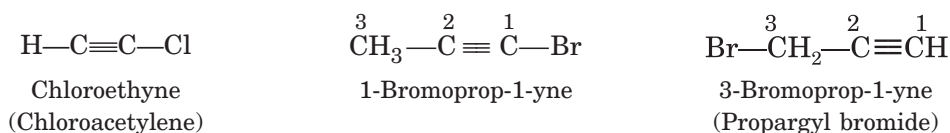
Whenever, two names are given under the formula, the name outside the brackets refers to IUPAC name and the name given in the brackets refers to the common name.

The compounds are also known in which more than one hydrogen atoms of the alkane molecule have been replaced by halogen atoms. These compounds are called polyhalogen derivatives of alkanes or **polyhaloalkanes**.

(ii) **Haloalkenes or alkenyl halides.** *The halogen derivatives of alkenes are called haloalkenes or alkenyl halides.* The monohalogen derivatives of alkenes have the general formula $\text{C}_n\text{H}_{2n-1}\text{X}$ where X = F, Cl, Br or I. For example,



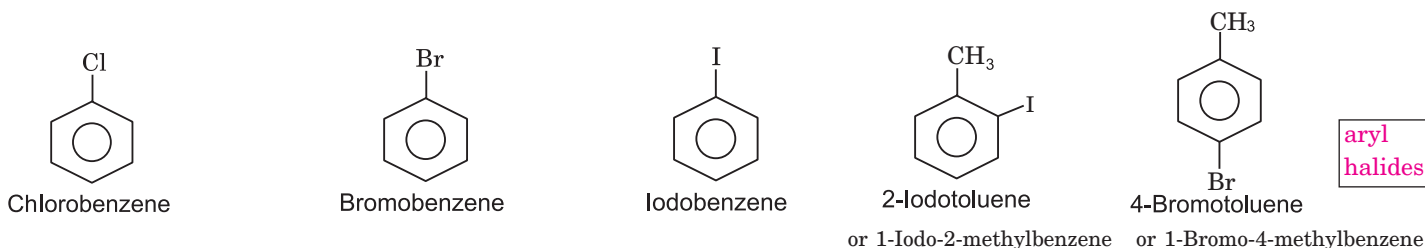
(iii) **Haloalkynes or alkynyl halides.** *These are the halogen derivatives of alkynes.* The monohalogen derivatives of alkynes have the general formula $\text{C}_n\text{H}_{2n-3}\text{X}$, where X = F, Cl, Br or I. For example,



2. Aromatic halogen compounds

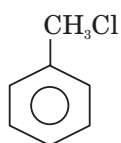
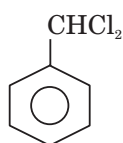
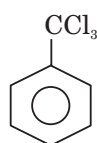
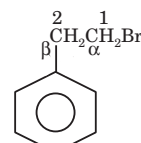
These are the compounds which are obtained by the replacement of one or more hydrogen atoms of aromatic hydrocarbons by an equal number of halogen atoms. These are of two types :

(i) **Nuclear halogen derivatives.** *These are the halogen derivatives of aromatic hydrocarbons which are derived by replacing hydrogen atom attached to the benzene ring by a halogen atom.* These are also called **haloarenes** or **aryl halides**. Therefore, in **haloarenes, the halogen atom (F, Cl, Br or I) is directly bonded to the aromatic (benzene) ring.** For example,



The aryl halides are commonly written as Ar-X , where Ar (short name for aryl) represents a phenyl group.

(ii) **Side chain halogen derivatives.** These are the derivatives of aromatic hydrocarbons in which one or more atoms of the alkyl side chain of a benzene are replaced by the halogen atoms. These compounds are not regarded as aryl halides because halogen is not directly attached to the benzene ring. These are called **side chain substituted aryl halides or aralkyl halides**. For example,

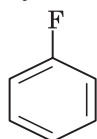
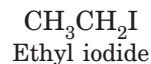
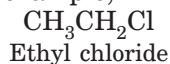
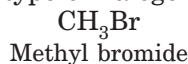
1-Chloro-1-phenylmethane
(Benzyl chloride)1, 1-Dichloro-1-phenylmethane
(Benzal dichloride)1, 1, 1-Trichloro-1-phenylmethane
(Benzo trichloride)1-Bromo-2-phenylethane
(β -phenylethyl bromide)

aralkyl
halides

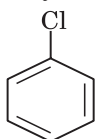
These **haloalkanes or haloarenes may be simply classified on** the basis of the type of halogen atom present, the number of halogen atoms and the nature of carbon atom to which the halogen is attached.

A. Type of halogen atom

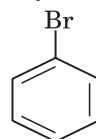
The halogen derivatives of hydrocarbons may be classified as fluoro, chloro, bromo and iodo compounds depending upon the type of halogen present. For example,



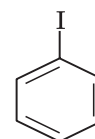
Fluorobenzene



Chlorobenzene



Bromobenzene

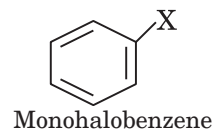
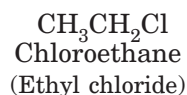
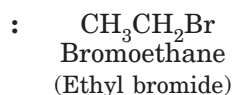


Iodobenzene

B. Number of halogen atoms

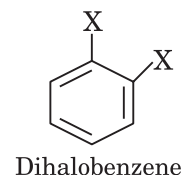
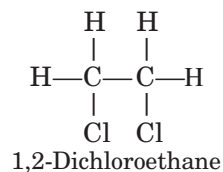
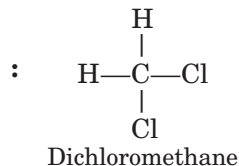
The halogen derivatives of hydrocarbons may be classified as mono, di, tri ... halo compounds depending upon whether they contain one, two, three... halogen atoms in their molecules. For example,

Monohalo compounds



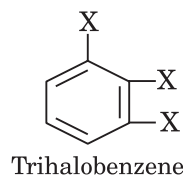
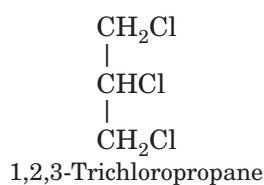
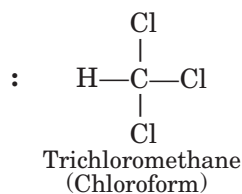
Monohalobenzene

Dihalo compounds



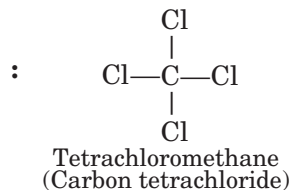
Dihalobenzene

Trihalo compounds



Trihalobenzene

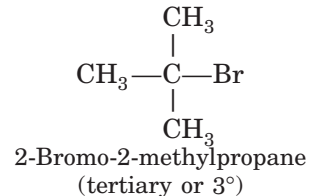
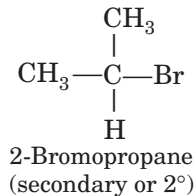
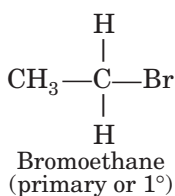
Tetrahalo compounds



C. Nature of carbon atom

Haloalkanes are classified as *primary* (1°), *secondary* (2°) or *tertiary* (3°) depending upon the nature of carbon atom to which the halogen is attached.

- Primary haloalkanes** are those which have *one or none alkyl group* on the carbon bonded to the halogen atom.
- Secondary haloalkanes** are those which have *two alkyl groups* on the carbon bonded to the halogen atom.
- Tertiary haloalkanes** are those which have *three alkyl groups* on the carbon bonded to the halogen atom.



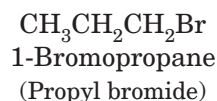
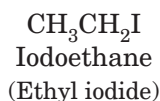
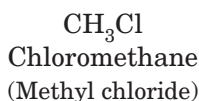
Classification on the basis of type of hybridization of carbon bonded to the halogen atom

The monohalo compounds may further be classified according to the type of hybridization of the carbon atom bonded to the halogen atom.

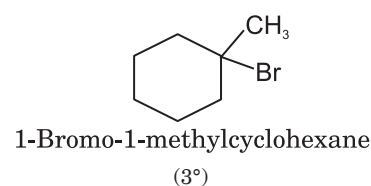
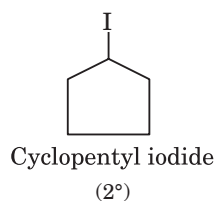
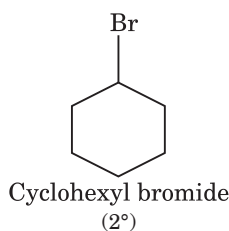
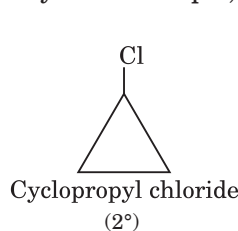
1. Compounds containing sp^3 hybridised carbon [$C(sp^3) - X$]

These compounds contain sp^3 hybridised carbon atom bonded to a halogen atom ($X = F, Cl, Br, I$). These are of the following types :

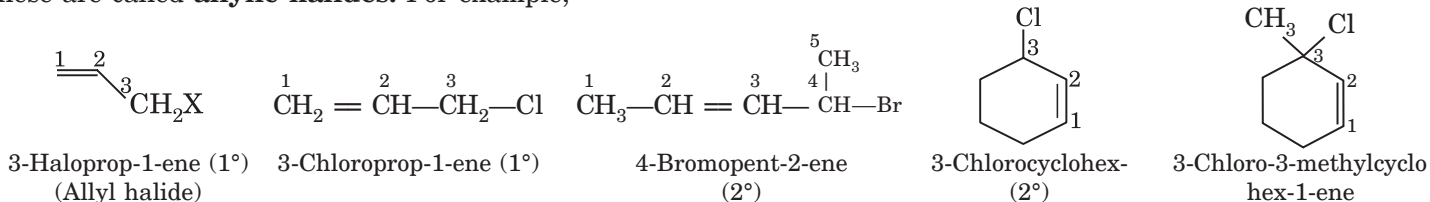
(a) **Haloalkanes or alkyl halides (RX).** In these halides, the halogen atom (X) is bonded to an alkyl group (R). These form homologous series of compounds represented by $C_nH_{2n+1}X$. For example,



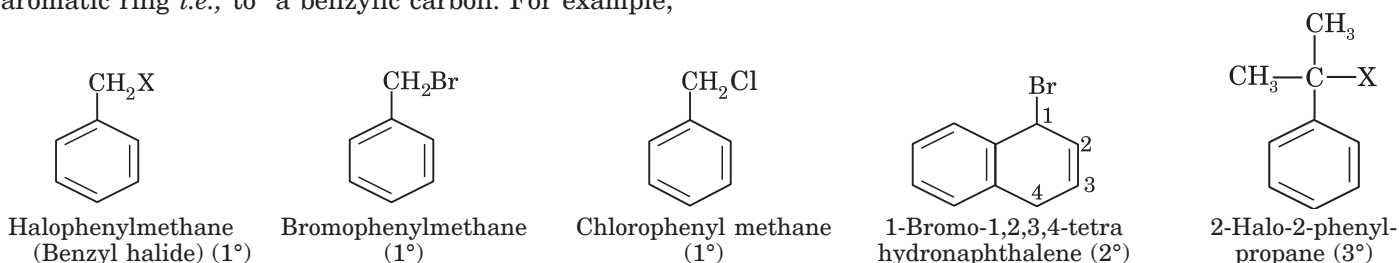
If R is alicyclic in $R-X$, the halide is called cyclo alkyl halide or halocyclo alkane, which may be secondary or tertiary. For example,



(b) **Allylic halides.** In these halides, the halogen is bonded to an sp^3 hybridized carbon atom next to a carbon-carbon double bond. The carbon atom next to carbon-carbon double bond is called allylic carbon and therefore, these are called **allylic halides**. For example,

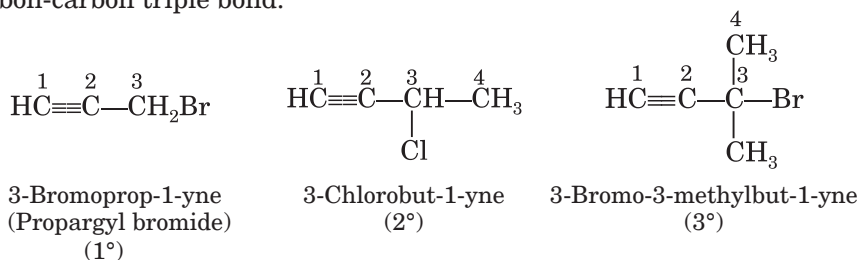


(c) **Benzylic halides.** In these halides the halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring *i.e.*, to a benzylic carbon. For example,



It may be noted that allylic and benzylic halides may be primary (1°), secondary (2°) or tertiary (3°).

(d) **Propargyl halides.** In these halides, the halogen atom is bonded to a sp^3 hybridised carbon atom next to a carbon-carbon triple bond.

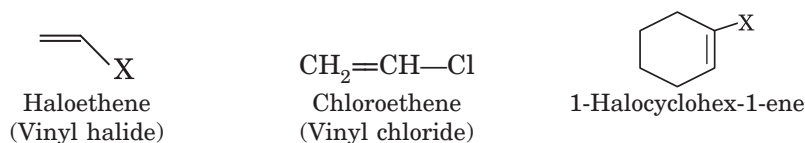


2. Compounds containing sp^2 hybridised carbon [$C(sp^2)-X$]

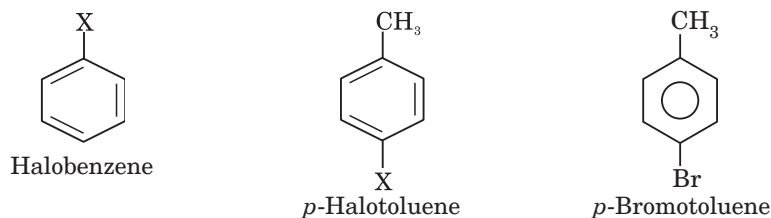
These halogen derivatives of hydrocarbons contain sp^2 hybridised carbon. In these compounds, halogen is directly

bonded to one of the carbon atoms of a double bond ($-C=C-X$). These include :

(a) **Vinyl halides.** In these halides the halogen atom is bonded to an sp^2 hybridised carbon of one of the carbon atoms of a double bond *i.e.* vinylic carbon. For example,



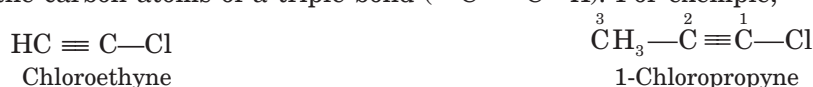
(b) **Aryl halides.** In these halides, the halogen atom is bonded to a sp^2 hybridised carbon of an aromatic ring. For example,



These aromatic halogen compounds are also called **haloarenes**.

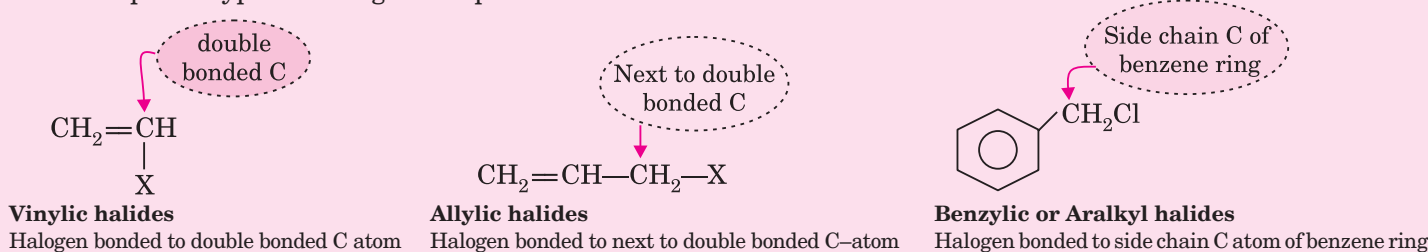
3. Compounds containing sp hybridised carbon [$C(sp) - X$]

These halogen derivatives of hydrocarbons contain sp hybridised carbon. In these halogen derivatives, halogen is directly bonded to one of the carbon atoms of a triple bond ($-\text{C} \equiv \text{C}-\text{X}$). For example,



REMEMBER

Some special types of halogen compounds are :



Let us discuss the chemistry of **alkyl halides and aryl halides**.

NOMENCLATURE OF HALOALKANES AND HALOARENES

Naming haloalkanes (or alkyl halides)

Monohalogen derivatives

Common Names : In the **common** or **trivial system** the monohalogen derivatives of alkanes are called **alkyl halides**. These are named by naming *the alkyl group attached to halogen and adding the name of the halide*. For example,

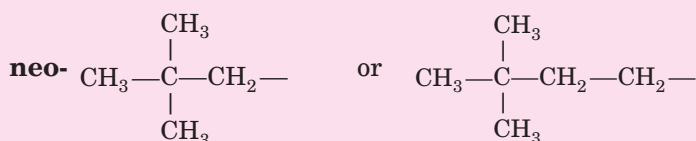
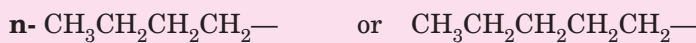


The name of the alkyl and halide is always written as two separate words. The prefixes *n*-, *iso*-, *sec*-, *tert*-, etc. used for the alkyl group are also written.

► It may be noted that *sec*- or *tert*- compounds are written with a dash between *sec*- or *tert*- and the name of the alkyl group. For example, *tert*-butyl, etc. However, the *iso*- or *neo*-compounds are written as one word. For example, isobutane, neopentane, etc.

REMEMBER

The prefixes **n**-, **iso**-, **neo**- are used for the following alkyl groups :



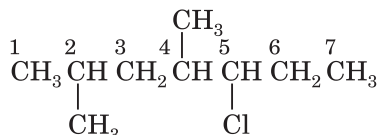
The prefix *n*- is used for alkyl group having continuous chain of C-atoms with no branching.

The prefix *iso*- is used for those alkyl groups in which one methyl group is attached to the next to end C-atom.

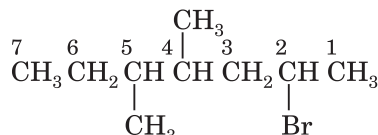
The prefix *neo*- is used for those alkyl groups which have two methyl groups attached to the next to end C-atom.

IUPAC names : In the **IUPAC system**, the monohalogen derivatives of alkanes are named as **haloalkanes**. The names are written by *prefixing the word halo to the name of the alkane corresponding to longest continuous carbon chain holding the halogen atom*. In case of branched chain alkanes, the following **rules** are followed :

- Select the longest continuous chain containing the carbon attached to the halogen group and name it as the **parent chain**. If a double or triple bond is present, the parent chain must contain it.
- Number the carbon atoms of the parent chain, beginning from the end nearer to the first substituent, **regardless of whether it is alkyl or halo group**.
- If two or more substituents are present on the parent chain, these are named in the alphabetical order alongwith their appropriate positions.
 - It may be noted that di, tri, tetra etc. are not considered while comparing the substituents for alphabetizing purpose. For example,

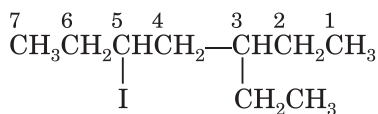


5-Chloro-2, 4-dimethylheptane



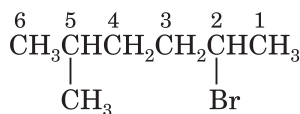
2-Bromo-4, 5-dimethylheptane

- If two different substituents are present at **equivalent positions** from the two ends of the chain, then numbering the chain is done in such a way that the substituent which comes first in the alphabetical order (written first in the name) gets lower number. For example,



3-Ethyl-5-iodoheptane

(Not 5-Ethyl-3-iodoheptane)

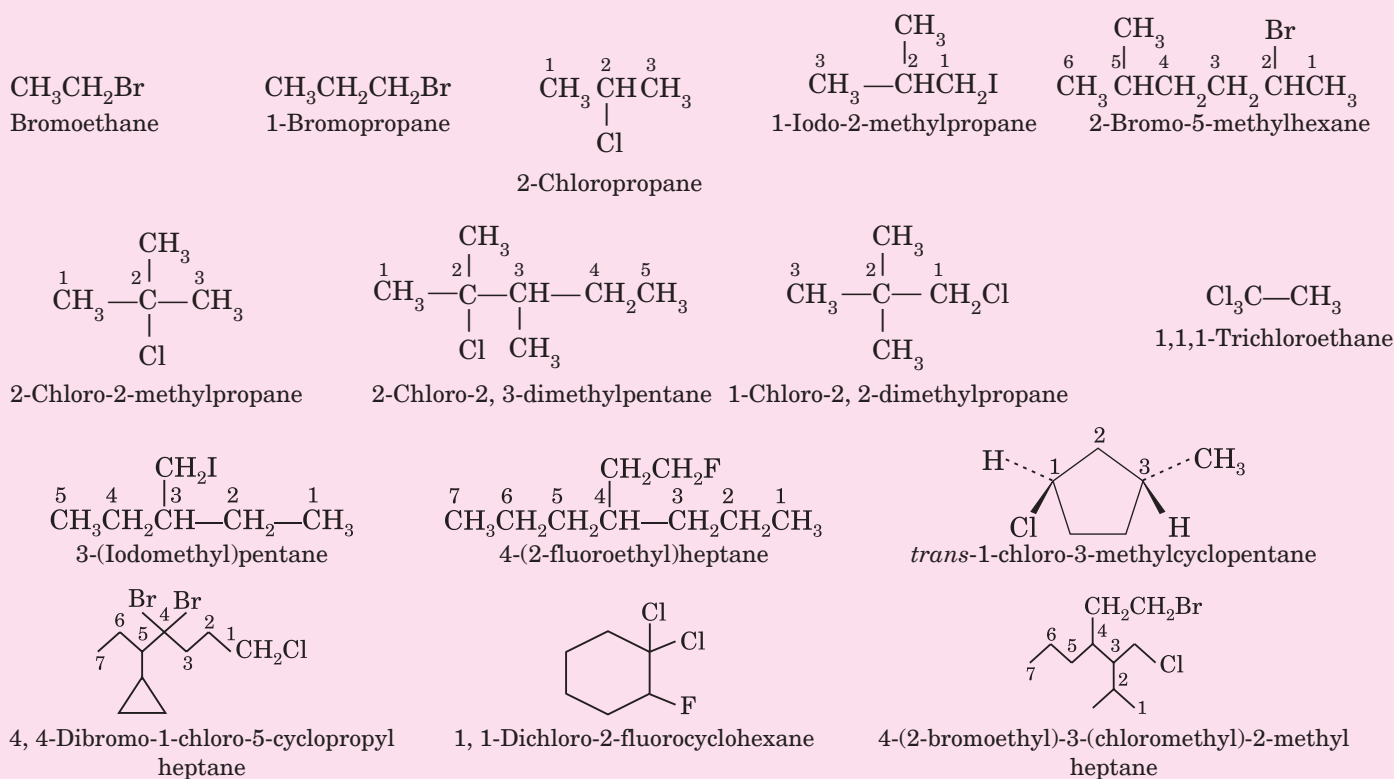


2-Bromo-5-methylhexane

(Not 5-Bromo-2-methylhexane)

[For more rules see Appendix A]

To illustrate the rules, some examples are given below:



The common and IUPAC names of a few alkyl halides are given below :

Alkyl halide	Common name	IUPAC name
CH_3Cl	Methyl chloride	Chloromethane
$\text{CH}_3\text{CH}_2\text{Br}$	Ethyl bromide	Bromoethane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$	<i>n</i> -Propyl fluoride	1-Fluoropropane
$\begin{array}{c} \text{CH}_3\text{CHI} \\ \\ \text{CH}_3 \end{array}$	Isopropyl iodide	2-Iodopropane
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	<i>n</i> -Butyl chloride	1-Chlorobutane
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	<i>sec</i> -Butyl chloride	2-Chlorobutane
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	Isobutyl chloride	1-Chloro-2-methylpropane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{Cl} \end{array}$	<i>tert</i> -Butyl chloride	2-Chloro-2-methylpropane
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{Cl}$	<i>n</i> -Pentyl chloride or <i>n</i> -Amyl chloride	1-Chloropentane
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2\text{CH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	Isopentyl chloride or Isoamyl chloride	1-Chloro-3-methylbutane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2\text{CH}_3 \\ \\ \text{Cl} \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Pentyl chloride or <i>tert</i> -Amyl chloride	2-Chloro-2-methylbutane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	Neopentyl chloride or Neoamyl chloride	1-Chloro-2,2-dimethylpropane

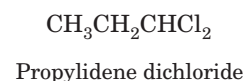
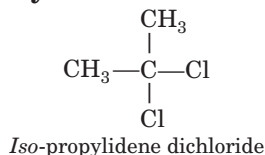
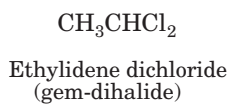
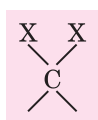
NOTE

Amyl is commonly used for C_5H_{11} -group. The prefixes *iso*, *neo*, *cyclo* are written as non-hyphenated prefixes while *n*-, *sec*- or *tert*- are written as hyphenated prefixes.

Dihalo and polyhalo derivatives

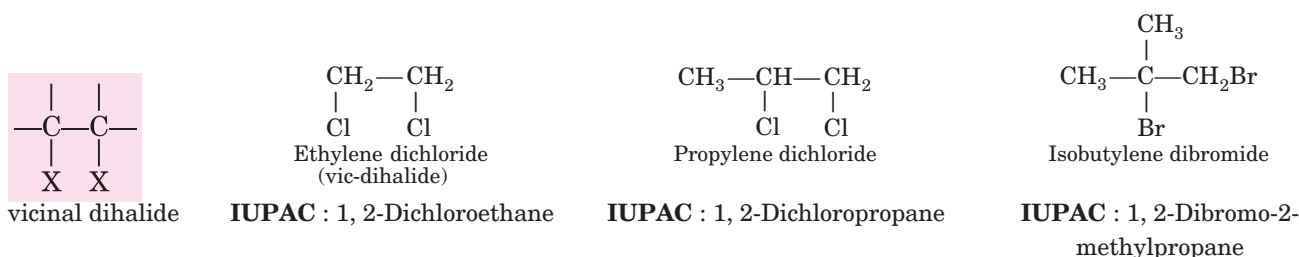
The dihalo derivatives have special common names depending upon whether the halogen atoms are present on the same or different carbon atoms. These are commonly named according to IUPAC system.

- (i) When both the halogen atoms are attached to the same C-atom, these are called **gem-dihalides**. These are also called **alkylidene dihalides** or simply **alkylidene halides**. For example,

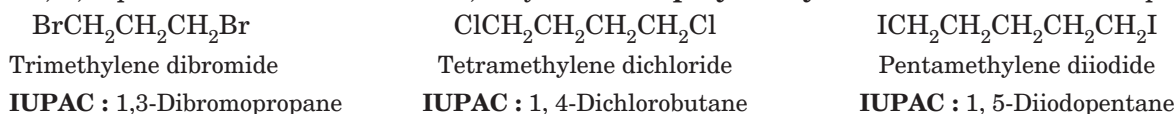


gem dihalide IUPAC : 1, 1-Dichloroethane IUPAC : 2, 2-Dichloropropane IUPAC : 1, 1-Dichloropropane

- (ii) When the two halogen atoms are in adjacent C-atoms, they are called **vicinal dihalides** or simply **vic-dihalides**. These are named as the dihalide of alkene from which they may be prepared by the addition of halogen atoms *i.e.*, **alkylene dihalide** or simply **alkylene halide**. For example,

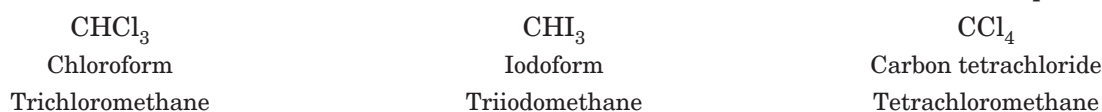


(iii) **Polymethylene dihalides.** When the same two halogen atoms are present on the terminal carbon atoms *i.e.*, α , ω positions of the carbon chain, they are called **polymethylene dihalides**. For example,



Polyhalogen derivatives are named according to IUPAC system.

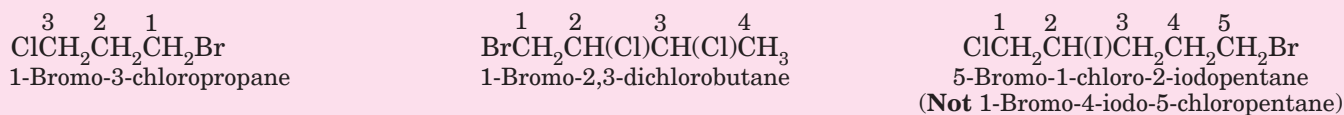
Trihalomethanes and tetrahalomethanes are named as haloforms and tetrahalomethanes respectively.



Fully halogenated hydrocarbons are also called **perhalohydrocarbons** (per means that all the hydrogens of the hydrocarbons are replaced by halogen atoms). It may be noted that polyhaloalkanes and other complex halogen compounds are named according to IUPAC system.



It may be noted that the name of di- and polyhaloalkanes containing different halogen atoms are written by prefixing the name of each halogen atom (in alphabetical order) alongwith its locant to the name of the parent alkane. The lowest locant being given to that halogen atom which comes first in alphabetical order *provided it does not violate the lowest locant sum rule*. For example,

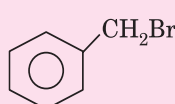


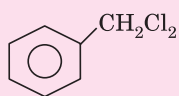
HELP

The compound $\text{ClCH}_2\text{CH}(\text{I})\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ cannot be named 1-Bromo-4-iodo-5-chloropentane because it violates lowest set of locants rule.

Some of these are given in Table 1.

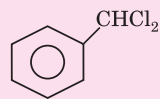
Table 1. Common names and IUPAC names of polyhaloalkanes and complex halogen compounds.

Structure	Common name	IUPAC name
CH_2Cl_2	Methylene chloride	Dichloromethane
$\text{CH}_2 = \text{CHCl}$	Vinyl chloride	Chloroethene
$\text{CH}_2 = \text{CHCH}_2\text{Br}$	Allyl bromide	1-Bromopropane
$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	Ethylene chloride	1,2-Dichloroethane
CH_3CHCl_2	Ethylidene chloride	1,1-Dichloroethane
CHCl_3	Chloroform	Trichloromethane
CHI_3	Iodoform	Triiodomethane
CHBr_3	Bromoform	Tribromomethane
	Benzyl bromide	1-Bromo-1-phenylmethane



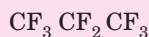
Benzylic chloride

1,1-Dichloro-1-phenylmethane



Benzochloride

1,1,1-Trichlorophenylmethane

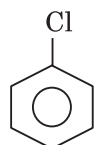


Perfluoropropane

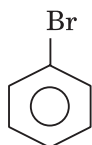
Octafluoropropane

Naming haloarenes (or aryl halides)

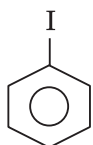
Haloarenes or aryl halides are named by adding the prefix *halo* (fluoro, chloro, bromo, iodo) *before the name of the aromatic hydrocarbon*. In case of disubstituted compounds, the relative positions of the substituents 1, 2 ; 1, 3 and 1, 4 are indicated by the prefixes *ortho* (*o*-), *meta* (*m*-) and *para* (*p*-) respectively. For example,



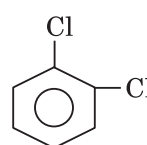
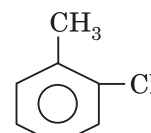
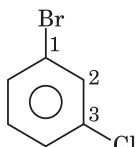
Chlorobenzene



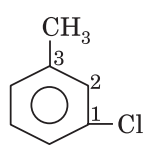
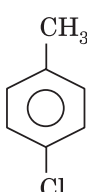
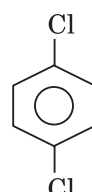
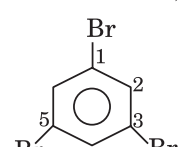
Bromobenzene



Iodobenzene

1,2-Dichlorobenzene
(*o*-Dichlorobenzene)1-Chloro-2-methylbenzene
2-Chlorotoluene
(*o*-Chlorotoluene)

1-Bromo-3-chlorobenzene

3-Chlorotoluene
1-Chloro-3-methylbenzene
(*m*-Chlorotoluene)1-Chloro-4-methylbenzene
4-Chlorotoluene
(*p*-Chlorotoluene)1,4-Dichlorobenzene
(*p*-Dichlorobenzene)1,3,5-Tribromobenzene
(*sym*-Tribromobenzene)

REMEMBER

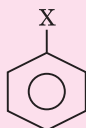
Special names



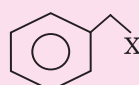
Vinyl



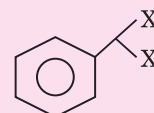
Allyl



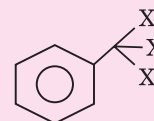
Phenyl



Benzyl



Benzal

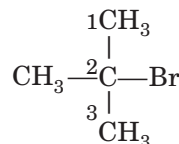
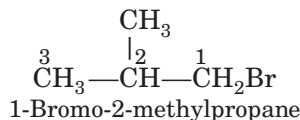
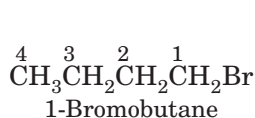


Benzo

ISOMERISM IN HALOALKANES AND HALOARENES

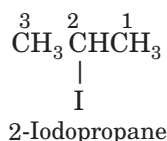
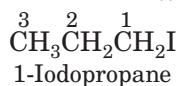
Haloalkanes show two types of isomerisms :

1. Chain isomerism. The haloalkanes containing four or more carbon atoms exhibit chain isomerism in which the *isomers differ in the chain of carbon atoms*. For example, $\text{C}_4\text{H}_9\text{Br}$ has three chain isomers as :

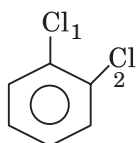


2-Bromo-2-methylpropane

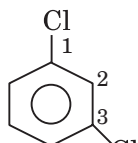
2. Position isomerism. The haloalkanes containing three or more carbon atoms exhibit position isomerism in which the *isomers differ in the position of halogen atom*. For example, $\text{C}_3\text{H}_7\text{I}$ has two position isomers :



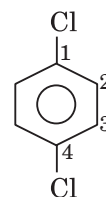
Haloarenes also show position isomerism as :



1,2-Dichlorobenzene
(*o*-Dichlorobenzene)



1,3-Dichlorobenzene
(*m*-Dichlorobenzene)

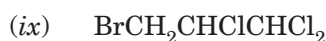
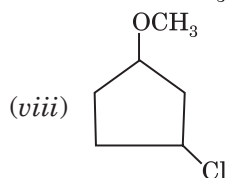
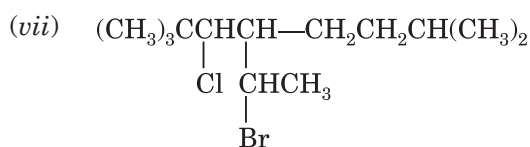
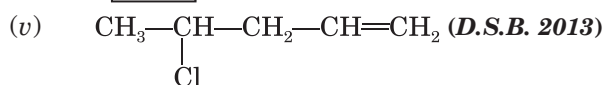
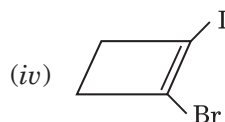
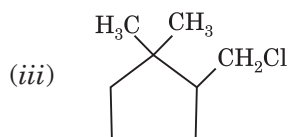
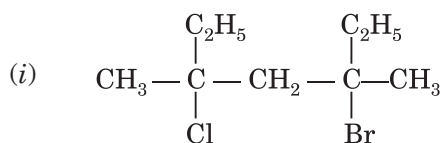


1,4-Dichlorobenzene
(*p*-Dichlorobenzene)

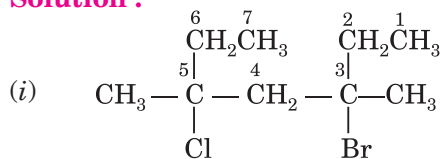
SOLVED EXAMPLES

Example 1.

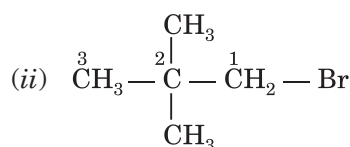
Write IUPAC names of the following compounds :



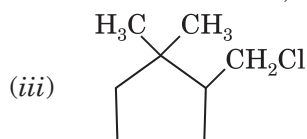
Solution :



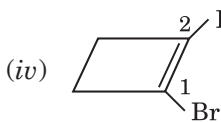
3-Bromo-5-chloro-3, 5-dimethylheptane



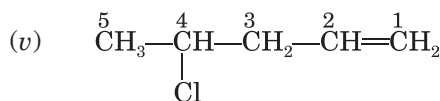
1-Bromo-2,2-dimethylpropane



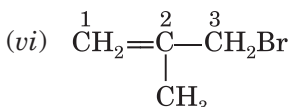
2-Chloromethyl-1, 1-dimethylcyclopentane



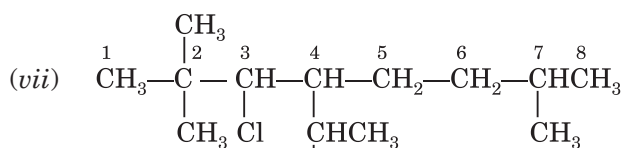
1-Bromo-2-iodocyclobutene



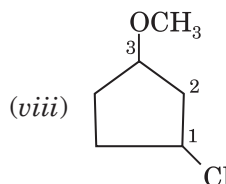
4-Chloropent-1-ene



3-Bromo-2-methylpropene

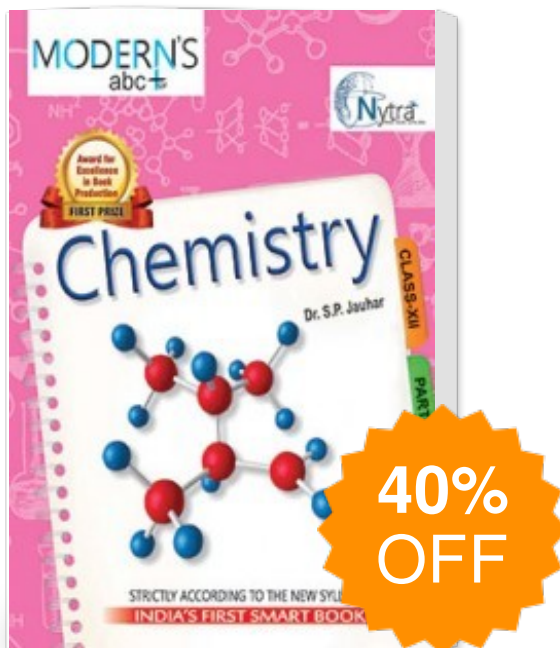


4-(1-Bromoethyl)-3-chloro-2, 2, 7-trimethyloctane



1-Chloro-3-methoxycyclopentane

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