Unit 9

HYDROCARBON DERIVATIVES AND THEIR REACTIONS

Section 1: Alkyl halides and aryl halides

Section 2: Alcohols, ethers, and amines

Section 3: Carbonyl Compounds

Section 1: Alkyl halides and aryl halides

Remember: in hydrocarbons, carbon atoms are bonded to hydrogen atoms, And the carbon atom can form strong covalent bonds with the atoms of other elements such as: S, O, N, P, F, Cl, Br, I

These elements are present as part of the functional group.

Functional group: An atom or group of atoms that enter the composition of the organic compound molecule, and they **always react in the same way.**

Note: **1** - When adding a functional group to the hydrocarbon compound it always produces a new substance that has different chemical and physical properties than the original hydrocarbon compound**.**

2 - By knowing the properties of the functional group, it is possible to predict the properties of the organic compounds in which it is present even if you have not previously studied it**.**

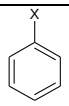
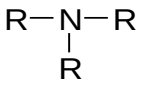
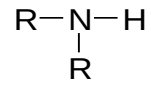
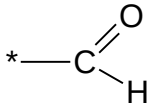
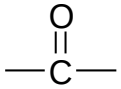
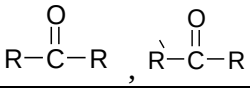
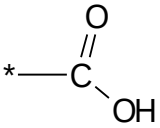
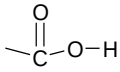
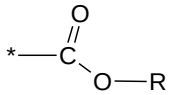
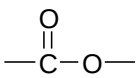
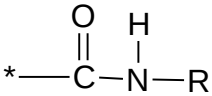
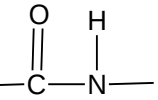
Compound type		general formula	functional group
Halocarbons	Alkyl halides	R—X , (X = F - Cl - Br - I)	Halogen —X
	aryl halides	 , (X = F - Cl - Br - I)	
alcohol		R—OH	Hrdroxyl —OH
Ether		R—O—R , R—O—R	ether —O—
Amine		$R-NH_2$	Amine (Amino) —NH_2 Primary amine $R-NH_2$ Tertiary amine  Secretary amine 
Aldehyde		 Or *-CHO	Carbonyl 
Ketone			
Carboxylic acid			 or —COOH Carboxyl
Ester			Ester 
Amide			Amide 

Figure 22.1 All of these items contain at least one of the functional groups that you will study in this chapter. For example, the fruit and flowers have sweet-smelling aromas that are due to ester molecules.

Important note: The bonds (~~—~~), (=), and (≡) that formed between carbon atoms are functional groups although they are present in a compound consisting of only carbon and hydrogen atoms. **Why?**

Section 1 : alkyl halides and aryl halides

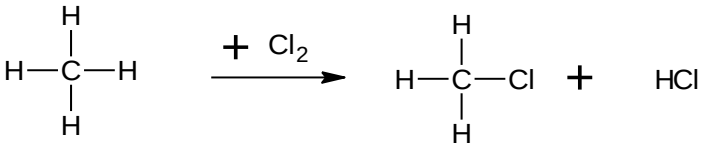
Halogens are the simplest of the compensatory functional groups that can replace hydrogen atoms in hydrocarbons (compensatory = they are a branch of the main carbon chain of the organic compound)

Alkyl halides: is an organic compound containing a halogen atom covalently bonded to an aliphatic carbon atom.(It has the simplest functional group)

General formula: R - X (X = F – Cl - Br – I)

How to get it: From alkane by replacing a hydrogen atom.

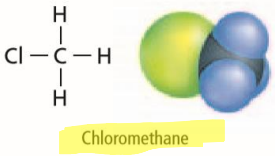
Example**:**



Alkane
methane

Alkyl Halide
Chloro methane

Note: The first four halogens (fluorine-chlorine-bromine-iodine) are included in the synthesis of many organic compounds**.**



■ **Figure 22.2** Chloromethane is an alkyl halide that is used in the manufacturing process for silicone products, such as window and door sealants.

IUPAC Nomenclature :

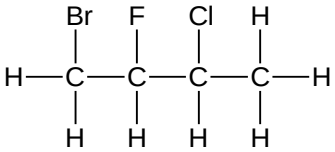
1 - Halo + Alkan (the main parent alkan name) (Halo: Chloro-Floro-Promo-Iodo).

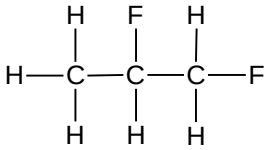
2 - If there are more than two halogens, the atoms are arranged in English alphabetical order.

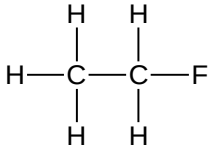
3 - The series is numbered so that the lowest position number for the atom related to the halogen atom is given in alphabetical order.

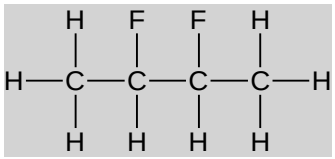
4 - Note that when halogen is repeated, we use (di - tri - ..... preceded by the numbers as before

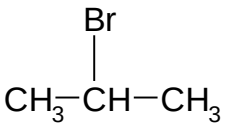
Q: Type the name of the following compounds using IUPAC system:

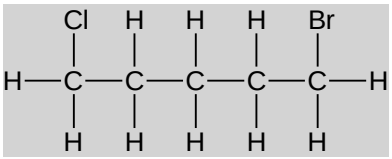


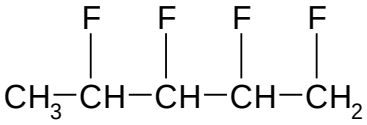


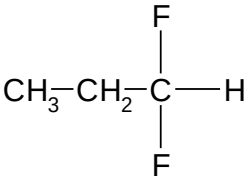


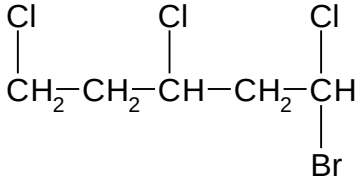


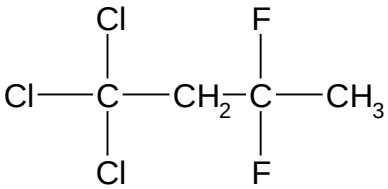












Q: Draw structural formulas for each of the following:

2- Iodo Propane

1, 1, 1, 2- tetra Bromo Propane

1 – fluorohexane

1- Promo - 1,1,3,3,3-penta Iodo Propane

1- Pormo-3,4- Dichlorohexane

2,3,4 - Trichloropentane

1,1-diIodopropane

2,2- dichloro -1,1-difluoro propane

Connection to Earth Science Alkyl halides are widely used as refrigerants. Until the late 1980s, alkyl halides called chlorofluorocarbons (CFCs) were widely used in refrigerators and air-conditioning systems. Recall from Chapter 1 how CFCs affect the ozone layer. CFCs have been replaced by HFCs (hydrofluorocarbons), which contain only hydrogen and fluorine atoms bonded to carbon. One of the more common HFCs is 1,1,2-trifluoroethane, also called R134a.

Properties of alkyl halides:

Table 22.2 A Comparison of Alkyl Halides and Their Parent Alkanes

Structure	Name	Boiling Point (°C)	Density (g/mL) in Liquid State
CH_4	methane	−162	0.423 at −162°C (boiling point)
CH_3Cl	chloromethane	−24	0.911 at 25°C (under pressure)
$CH_3CH_2CH_2CH_2CH_3$	pentane	36	0.626
$CH_3CH_2CH_2CH_2CH_2F$	1-fluoropentane	62.8	0.791
$CH_3CH_2CH_2CH_2CH_2Cl$	1-chloropentane	108 *Increases*	0.882 *Increases*
$CH_3CH_2CH_2CH_2CH_2Br$	1-bromopentane	130	1.218
$CH_3CH_2CH_2CH_2CH_2I$	1-iodopentane	155	1.516

ماذا قرأت؟ **اشرح** العلاقة بين عدد الإلكترونات في الهالوجين ودرجة الغليان.

علل : **تزداد درجة الغليان والكثافة عند الانتقال عبر الهالوجينات من الفلور ← اليود** (أي بزيادة حجم ذرة الهالوجين)

لأنه عند الانتقال من الفلور إلى اليود يزداد بُعد الإلكترونات الخارجية عن النواة ، وتميل هذه الإلكترونات إلى تغيير مكانها بسهولة ، فيزداد ميل هاليدات الألكيل لتكوين مركبات ثنائية القطب مؤقتة ، وبالتالي تتجاذب الأقطاب معاً ، فتزداد الطاقة اللازمة لفصل الجزيئات عن بعضها ، وبذلك تزداد درجة غليان هاليدات الألكيل بزيادة حجم ذرة الهالوجين .

Explain : Boiling point and density increase when moving across halogens from fluorine → iodine (i.e. by increasing the size of the halogen atom)

Because when moving from fluorine to iodine, the **distance** of the **outer electrons** from the nucleus **increases**, and these electrons tend to **change their position easily**, so the tendency of alkyl halides to form **temporary dipole compounds increases**, and thus the **polars attract together**, so the energy needed to separate the molecules from each other increases, **thus increasing the boiling point of the halides Alkyl increased the size of the halogen atom**.

Explain: the boiling point and density of alkyl chloride are higher than the boiling point and density of alkanes containing the same number of carbon atoms

Compound:	**CH_4**	**CH_3Cl**
Boiling point:	-162°C	-24°C
Density:	0.423 g/mL	0.911 g/mL

In chloromethane: the presence of a chlorine atom works as a dipolar compound, so the dipoles of molecules attract together, the bonding between particles increases, and the boiling point and density increase.

In methane: a non-polar molecule whose molecules are bonded by the weak forces of London's dispersion force, so the boiling point and the density decrease.

Note: **Human thyroid hormones** contain organic iodide (it is rare to obtain organic halide in nature) (explain) because halogen atoms that bond to carbon atoms are more active than the hydrogen atoms that have replaced them.

Uses of alkyl halides:

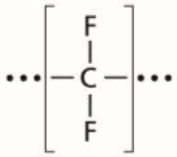
1 - A **raw material** in many **chemical industries(as a** starting materials in the chemical industry**)**

2 - Solvents and Cleaning agents **explain**: because they dissolve non-polar molecules easily, such as oils and fats.

3 - **polytetrafluoroethene** (**PTFE**), a plastic made from gaseous tetrafluoroethylene. A plastic is a polymer that can be **heated** and **molded** while relatively soft

4 - Another plastic commonly called **vinyl** is **polyvinyl chloride** (PVC). It can be manufactured soft or hard, as thin sheets, or molded into objects.

Figure 22.4 Polytetrafluoroethene (PTFE) is made up of hundreds of units. PTFE provides a nonstick surface for many kitchen items, including bakeware.



PTFE

PTFE Application

Substitution reaction: is the substitution of atom or atomic group by another atom or atomic group in the compound

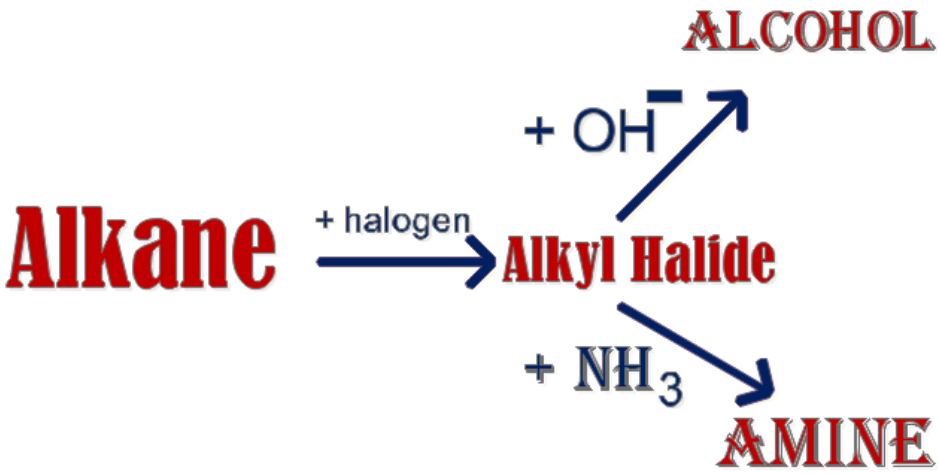
Table 22.3 Substitution Reactions

Generic Substitution Reaction	Example of General Substitution Reaction (Halogenation)
$R{-}CH_3 + X_2 \rightarrow R{-}CH_2X + HX$ where X is fluorine, chlorine, or bromine	$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$ Ethane Chloroethane
General Alkyl Halide-Alcohol Reaction $R{-}X + OH^- \rightarrow R{-}OH + X^-$ Alkyl halide Alcohol	**Example of an Alkyl Halide-Alcohol Reaction** $CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$ Chloroethane Ethanol
General Alkyl Halide-Ammonia Reaction $R{-}X + NH_3 \rightarrow R{-}NH_2 + HX$ Alkyl halide Amine	**Example of an Alkyl Halide-Ammonia Reaction** $CH_3(CH_2)_6CH_2Br + NH_3 \rightarrow CH_3(CH_2)_6CH_2NH_2 + HBr$ 1-Bromooctane Octaneamine

Halogenation: It is the substitution of a halogen atom with a hydrogen atom.

►**In the case of alkanes**: A halogen atom such as Cl or Br can replace a hydrogen atom in the halogenation process.

►**With substitution reactions**, alkanes can be converted into different compounds such as:



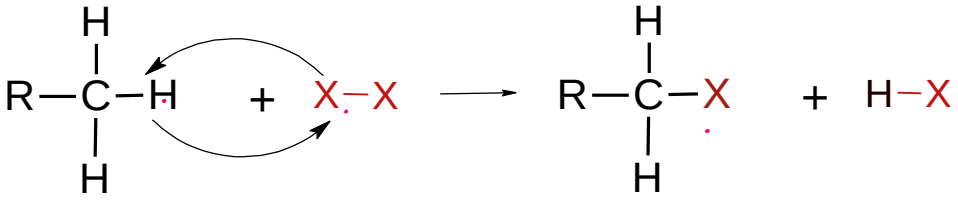
Remember: 1- Oil is the **primary source** of all industrial organic compounds.
2 - Oil is considered a form of fossil fuel, which consists of almost all hydrocarbons, especially alkanes.
3 - **Alkanes** may be **converted** to **other compounds** such as **alkyl halides, alcohols and amines.**

1 - General substitution reactions for the formation of alkyl halides:

(Where X represents a fluorine, chlorine, or bromine atom)

$$R - CH_3 + X_2 \rightarrow R - CH_2X + HX$$

Clarification:



Alkane Alkyl halide

Complete:

$$C_2H_6 + Cl_2 \rightarrow \quad +$$

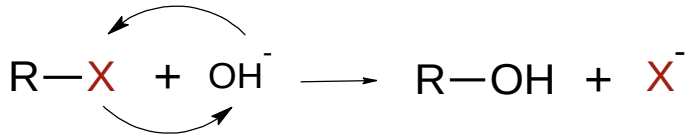
☺ When alkanes are halogenated, the alkyl halide becomes permeable to another substitution reaction. Where one atom or group of atoms replaces a hydrogen atom.

Example: Complete the halogenation in four stages with chlorine, bromine, fluorine, and chlorine

$$CH_4 + Cl_2 \rightarrow \quad +$$

2 - General substitution reactions for alcohol formation:

Alkyl halide reacts with basic solutions, where the OH^- group replaces the halogen atom to produce alcohol.



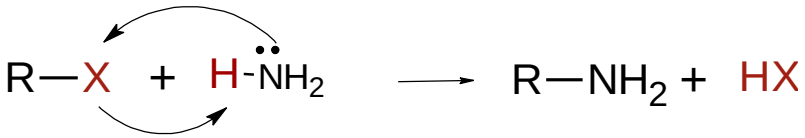
alkyl halide basic solution alcohol

Ex : $CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$

chloro ethane ethanol

3 - General substitution reactions for amines formation:

Alkyl halide reacts with the NH_3 ammonia, where the amine $-NH_2$ group replaces the halogen atom to produce the alkyl amine



$CH_3(CH_2)_6CH_2Br + NH_3 \rightarrow CH_3(CH_2)_6CH_2NH_2 + HBr$

1-bromooctane Octyl amine

Example: Halothane: (2-bromo--2-chloro-1,1,1-trifluoroethane):

It was first used in anesthesia in the 1950s for the first time

Figure 22.6 Halothane was introduced into medicine in the 1950s as a general anesthetic for patients undergoing surgery.

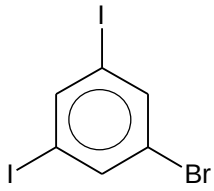
Note: In the halogenation process, we use the halogens X = F, Cl, Br, but I (I) is not? because: Iodine does not interact well with alkanes.

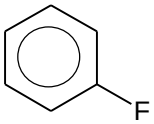
Aryl halides: An organic compound containing a halogen atom bonded with a benzene ring or other aromatic group.

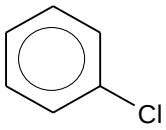
Writing the structural formula for aryl halides:

1 - Draw the structural formula of the aromatic compound

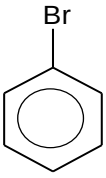
2- Replace the hydrogen atoms with the halogen atoms

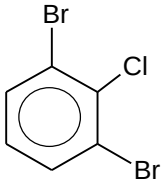






$CH_3-CH_2-CH_2-CH_2-CH_2-Br$





Section 22.1 Assessment

Section Summary

- The substitution of functional groups for hydrogen in hydrocarbons creates a wide variety of organic compounds.
- An alkyl halide is an organic compound that has one or more halogen atoms bonded to a carbon atom in an aliphatic compound.

4. MAIN Idea **Compare and contrast** alkyl halides and aryl halides.
5. **Draw** structures for the following molecules.
   - **a.** 2-chlorobutane
   - **b.** 1,3-difluorohexane
   - **c.** 1,1,1-trichloroethane
   - **d.** 4-bromo-1-chlorobenzene
6. **Define** *functional group* and name the group present in each of the following structures. Name the type of organic compound each substance represents.
   - **a.** $CH_3CH_2CH_2OH$
   - **b.** CH_3CH_2F
   - **c.** $CH_3CH_2NH_2$
   - **d.** $CH_3C(=O)-OH$
7. **Evaluate** How would you expect the boiling points of propane and 1-chloropropane to compare? Explain your answer.
8. **Interpret Scientific Illustrations** Examine the pair of substituted hydrocarbons illustrated at right, and decide whether it represents a pair of optical isomers. Explain your answer.

Mastering Concepts

26. What is a functional group?

27. Describe and compare the structures of alkyl halides and aryl halides.

28. What reactant would you use to convert methane to bromomethane?

29. Name the amines represented by each of the condensed formulas.

a. $CH_3(CH_2)_3CH_2NH_2$

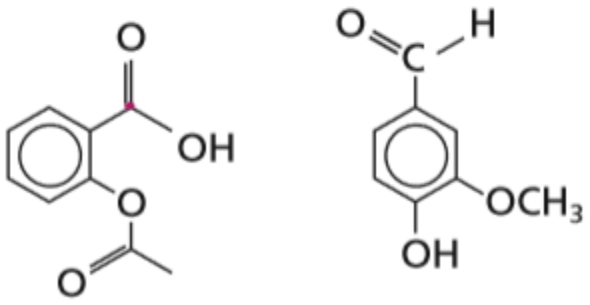
b. $CH_3(CH_2)_5CH_2NH_2$

c. $CH_3(CH_2)_2CH(NH_2)CH_3$

d. $CH_3(CH_2)_8CH_2NH_2$

30. Explain why the boiling points of alkyl halides increase in order going down the column of halides in the periodic table, from fluorine through iodine.

Mastering Problems



a Acetylsalicylic acid **b** Vanillin

■ **Figure 22.22**

31. Circle and name each of the functional groups circled in the structures shown in **Figure 22.22**.

32. Draw structures for these alkyl and aryl halides.

a. chlorobenzene
b. 1-bromo-4-chlorohexane
c. 1,2-difluoro-3-iodocyclohexane
d. 1,3-dibromobenzene
e. 1,1,2,2-tetrafluoroethane

33. For 1-bromo-2-chloropropane:

a. Draw the structure.
b. Does the compound have optical isomers?
c. If the compound has optical isomers, identify the chiral carbon atom.

34. Draw and name all of the structural isomers possible for an alkyl halide with no branches and the molecular formula $C_5H_{10}Br_2$.

35. Name one structural isomer created by changing the position of one or more halogen atoms in each alkyl halide.

a. 2-chloropentane
b. 1,1-difluropropane
c. 1,3-dibromocyclopentane
d. 1-bromo-2-chloroethane