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Organic chemistry

Hydrocarbons

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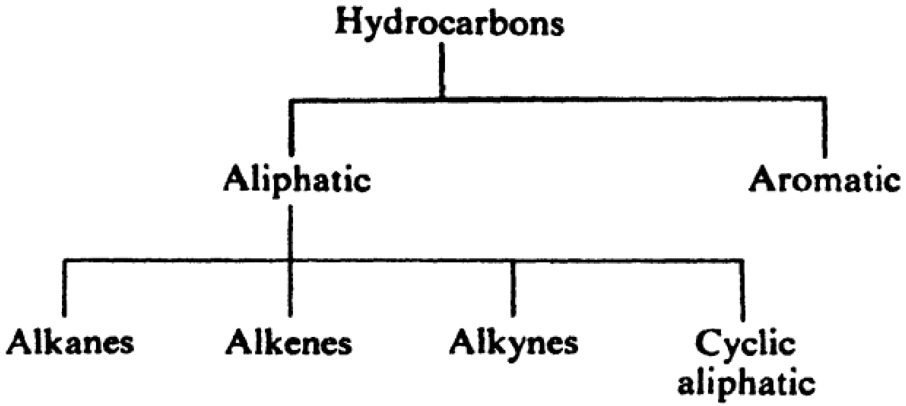
Hydrocarbons

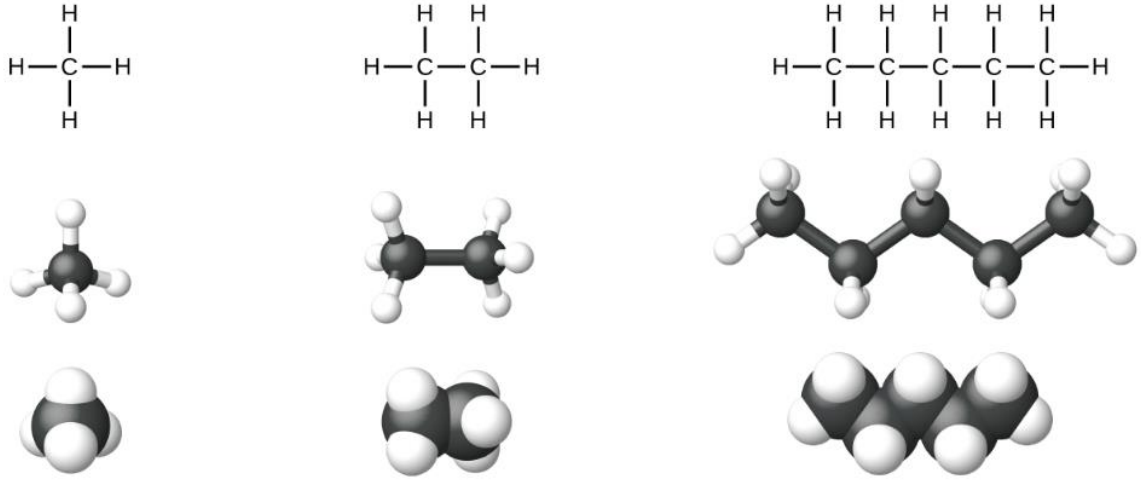
Certain organic compounds contain only two elements, hydrogen and carbon, and hence are known as **hydrocarbons**. On the basis of structure, hydrocarbons are divided into two main classes, **aliphatic** and **aromatic**. Aliphatic hydrocarbons are further divided into families: alkanes, alkenes, alkynes, and their cyclic analogs (cycloalkanes, etc.). We shall take up these families in the order given.



The simplest member of the alkane family and, indeed, one of the simplest of all organic compounds is **methane**, CH_4. We shall study this single compound at some length, since most of what we learn about it can be carried over with minor modifications to any alkane.

Alkanes

Alkanes, or saturated hydrocarbons, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has sp3 hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen. The Lewis structures and models of methane, ethane, and pentane.



methane CH_4 | ethane CH_3CH_3 or C_2H_6 | pentane $CH_3CH_2CH_2CH_2CH_3$ or C_5H_{12}

Properties of Some Alkanes[3]

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP[4]	Number of Structural Isomers
methane	CH_4	–182.5	–161.5	gas	1
ethane	C_2H_6	–183.3	–88.6	gas	1
propane	C_3H_8	–187.7	–42.1	gas	1
butane	C_4H_{10}	–138.3	–0.5	gas	2
pentane	C_5H_{12}	–129.7	36.1	liquid	3
hexane	C_6H_{14}	–95.3	68.7	liquid	5
heptane	C_7H_{16}	–90.6	98.4	liquid	9
octane	C_8H_{18}	–56.8	125.7	liquid	18
nonane	C_9H_{20}	–53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	–29.7	174.0	liquid	75
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

The Basics of Organic Nomenclature: Naming Alkanes

The International Union of Pure and Applied Chemistry (**IUPAC**) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

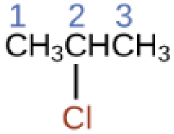
1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10). These prefixes can be seen in the names of the alkanes described in [link].
2. Add prefixes to the name of the longest chain to indicate the positions and names of **substituents**. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.

This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

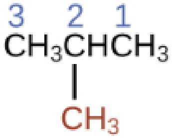
Alkyl Group	Structure
methyl	$CH_3—$
ethyl	$CH_3CH_2—$
n-propyl	$CH_3CH_2CH_2—$
isopropyl	$CH_3\overset{\vert}{C}HCH_3$
n-butyl	$CH_3CH_2CH_2CH_2—$
sec-butyl	$CH_3CH_2\overset{\vert}{C}HCH_3$
isobutyl	$CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2—$
tert-butyl	$CH_3\overset{\vert}{\underset{\underset{CH_3}{\vert}}{C}}CH_3$

Common names of alkanes

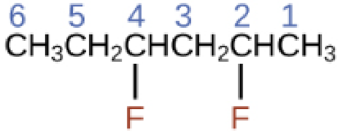
propane



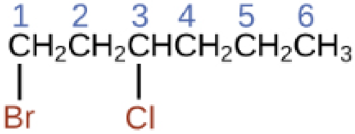
2-chloropropane



2-methylpropane



2,4-difluorohexane



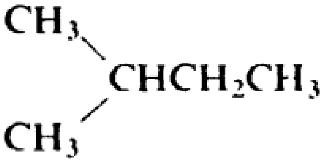
1-bromo-3-chlorohexane

$$CH_3CH_2CH_2CH_2CH_3$$

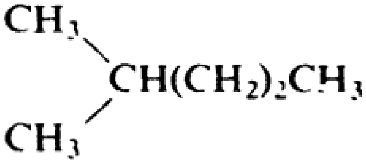
n-Pentane

$$CH_3(CH_2)_4CH_3$$

n-Hexane

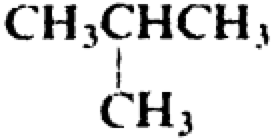


Isopentane



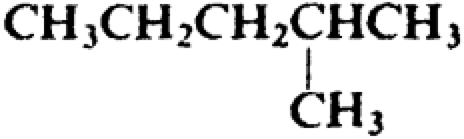
Isohexane

IUPAC names of alkanes



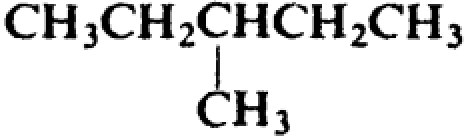
I

Methylpropane
(Isobutane)



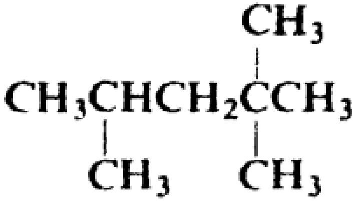
II

2-Methylpentane



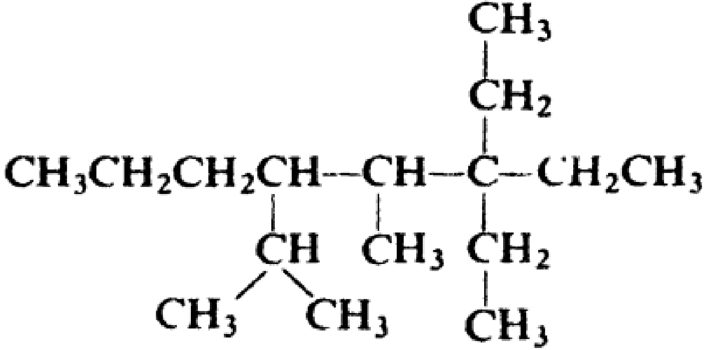
III

3-Methylpentane



IV

2,2,4-Trimethylpentane



V

4-Methyl-3,3-diethyl-5-isopropyloctane

Structures Alkanes

Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule

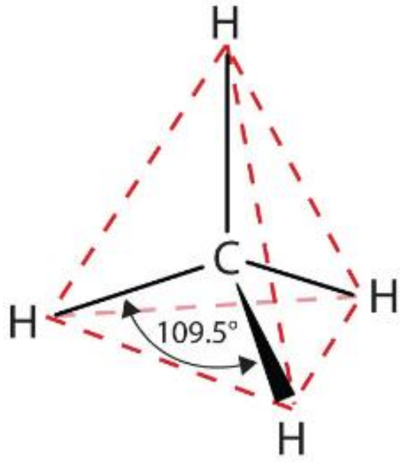


Figure : The Tetrahedral Methane Molecule

Preparation of Alkanes

✓ Preparation of Alkanes from Unsaturated Hydrocarbons

Unsaturated hydrocarbons (alkenes and alkynes) react with H_2 in the presence of finely divided catalysts such as platinum, palladium or nickel to form alkanes. This process is called **hydrogenation.**

$$CH_2{=}CH_2 + H_2 \xrightarrow{Pt/Pd/Ni} CH_3{-}CH_3$$

$$CH_3{-}C{\equiv}CH + 2H_2 \xrightarrow{Pt/Pd/Ni} CH_3{-}CH_2{-}CH_3$$

Preparation of Alkanes from Alkyl Halides

The following methods are used to prepare alkanes from alkyl halides (R–X) :

- Alkyl halides (except alkyl fluorides) on reduction with zinc and dilute hydrochloric acid produce alkanes.

$$CH_3Cl + H_2 \xrightarrow{Zn,\ H^+} CH_4 + HCl$$

$$C_3H_7Cl + H_2 \xrightarrow{Zn,\ H^+} C_3H_8 + HCl$$

- Haloalkanes (Alkyl halides) react with metallic sodium in dry ether to form symmetrical alkanes with double the number of carbon atoms present in the alkyl halide. This reaction is known as **Wurtz reaction**. Limitations of Wurtz reaction are discussed in reactions of haloalkanes.

$$CH_3-Br + 2Na + Br-CH_3 \xrightarrow{\text{dry ether}} CH_3CH_3 + 2NaBr$$

Preparation of Alkanes from Carboxylic Acids

- **Decarboxylation :** Sodium salts of carboxylic acids (RCOONa) on heating with soda lime (NaOH + CaO) form alkanes containing one carbon atom less than the salt.

$$\underset{\text{Sodium ethanoate}}{CH_3COONa} + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Note: CaO is used to keep NaOH dry as NaOH tends to absorb moisture from air.

- **Kolbe's electrolytic method :** A concentrated aqueous solution of sodium or potassium salt of carboxylic acid on electrolysis forms alkane containing even number of carbon atoms at the anode.

$$2CH_3COO^-Na^+ + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

Alkane Physical Properties:

- Alkanes have no color
- Alkanes are lighter than water and have a lower density
- Alkanes dissolve more readily in non-polar than polar solvents because they are nonpolar molecules
- Alkanes do not dissolve in water
- The melting and boiling temperatures of shorter chain alkanes are low, but as the number of carbon atoms in the carbon chain rises, the melting and boiling values of alkanes rise

Alkane Chemical Properties:

- Alkanes have low reactivity
- Strong acids, bases, oxidizing agents and reducing agents do not react with alkanes
- Alkanes are valuable as fuels because they burn and release energy
- In the presence of ultraviolet light, alkanes will react with halogens such as chlorine gas and bromine water

Reactions of Alkanes

Alkanes contain only C–C and C–H σ-bonds. Since σ-bonds are quite strong bonds, alkanes are generally inert towards acids, bases, oxidising and reducing agents. However, they undergo the following reactions under certain conditions :

Substitution reactions

In substitution reactions, a hydrogen of a hydrocarbon is replaced by an atom or a group of atoms. For example, hydrogen is replaced by a halogen in **halogenation**.

Halogenation

When the mixture of hydrocarbon and halogen is heated at 520-670 K in dark or is subjected to ultraviolet light at room temperature, the free radical substitution reaction takes place.

$$CH_3{-}CH_3 + Cl_2 \xrightarrow[\text{or } h\nu]{520\text{-}670K} CH_3{-}CH_2{-}Cl$$

The reactivity of hydrogen towards free radical substitution is 3° > 2° > 1°. For example, when butane is used in free radical substitution reaction, the products we get are 1-Chlorobutane and 2-Chlorobutane. 2-Chlorobutane being 2° is the major product.

Oxidation of Alkanes

Some important oxidation reactions of alkanes are given below :

Combustion of Alkanes

Alkanes on heating in the presence of air or O_2 produce CO_2 and H_2O with the evolution of large amount of heat.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad \Delta_cH^\circ = -890\ KJ/mol$$

The general formula for combustion is :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

Combustion of ethane :

$$C_2H_6 + (7/2)O_2 \longrightarrow 2CO_2 + 3H_2O \quad \Delta_cH^\circ = -2875.84\ KJ/mol$$

Isomerisation of Alkanes

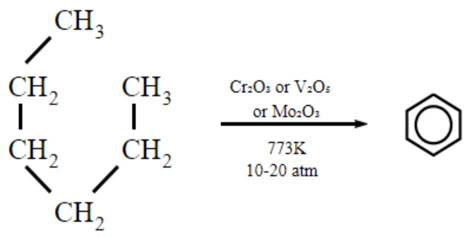
Straight chain alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas are converted to their branched chain isomers.

$$\text{n-Hexane} \xrightarrow{\text{Anh. } AlCl_3/HCl} \text{2-Methylpentane} + \text{3-Methylpentane}$$

+ minor products

Aromatization of Alkanes

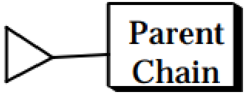
Straight chain alkanes containing six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of a catalyst consisting of oxides of chromium, vanadium and molybdenum supported over alumina get dehydrogenated and converted into benzene and its homologues.



Cycloalkanes

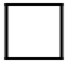
Propane

Cyclopropane

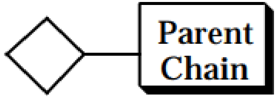


cyclopropyl

Butane

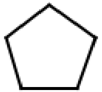


Cyclobutane

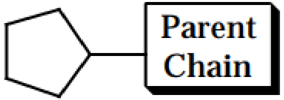


Cyclobutyl

Pentane

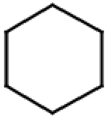


Cyclopentane

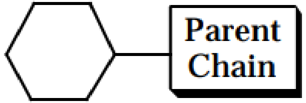


Cyclopentyl

Hexane



Cyclohexane



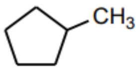
Cyclohexyl

Naming Cycloalkanes General Formula: $C_nH_{(2n)}$

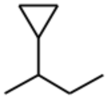
1. *Parent Chain*

a. Use the cycloalkane as the parent chain if it has a greater number of carbons than any alkyl substituent.

b If an alkyl chain off the cycloalkane has a greater number of carbons, then use the alkyl chain as the parent and the cycloalkane as a **cycloalkyl-** substituent.



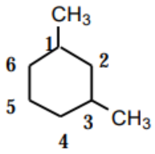
Methylcyclopentane



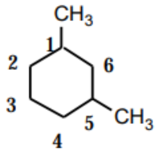
2-Cyclopropylbutane

2. *Numbering the Cycloalkane*

a When numbering the carbons of a cycloalkane, start with a substituted carbon so that the substituted carbons have the lowest numbers (sum).



1,3-Dimethylcyclohexane



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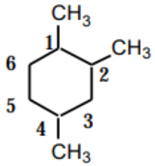
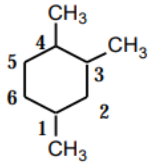
1,5-Dimethylcyclohexane



1,2,4-Trimethylcyclohexane



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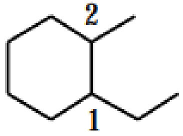
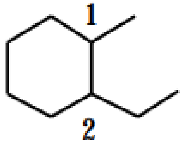
1,3,4-Trimethylcyclohexane

b. When two or more different substituents are present, number according to alphabetical order.



1-Ethyl-2-methylcyclohexane

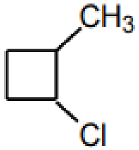


-not-
2-Ethyl-1-methylcyclohexane

3. *Halogen Substituents*

Halogen substituents are treated exactly like alkyl groups:

-F	fluoro-
-Cl	chloro-
-Br	bromo-
-I	iodo-



1-Chloro-2-methylcyclobutane