Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

College of Science, Chemistry Department

CHEM 109

CHAPTER 2. ALIPHATIC HYDROCARBON

Learning Objectives

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At the end of this chapter, students will able to:

- Identify the different types of aliphatic hydrocarbons (alkanes, cycloalkanes, alkenes, cycloalkenes and alkynes).
- Recognize the basic properties (structure, physical and chemical properties) of alkanes, alkenes and alkynes.
- Identify the structure of a hydrocarbon from its IUPAC and common name.
- Identify the name from the structure of hydrocarbons
- Explain the type of isomer in organic compounds and draw the different isomer structures of the compound.
- Know the different methods for the synthesis of aliphatic hydrocarbons.
- Identify the general reactions of aliphatic hydrocarbons.

Hydrocarbons

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- **Hydrocarbons** are Organic Compounds, which contain only the two elements **carbon** and **hydrogen**.
- **Aliphatic hydrocarbons** are subdivided into:
  - ***Saturated hydrocarbons***
    - Alkanes; C_nH_{2n+2} (*contain carbon-carbon single bond*)
    - Cycloalkanes: C_nH_{2n} (*contain carbon-carbon single bond in a single ring*)

    Alkanes and cycloalkanes are so similar that many of their properties can be considered side by side.
  - ***Unsaturated hydrocarbons***
    - Alkenes : C_nH_{2n} (contain *carbon-carbon double bond*)
    - Alkynes : $C_n H_{2n-2}$ (contain *carbon-carbon triple bond*)

Hydrocarbons

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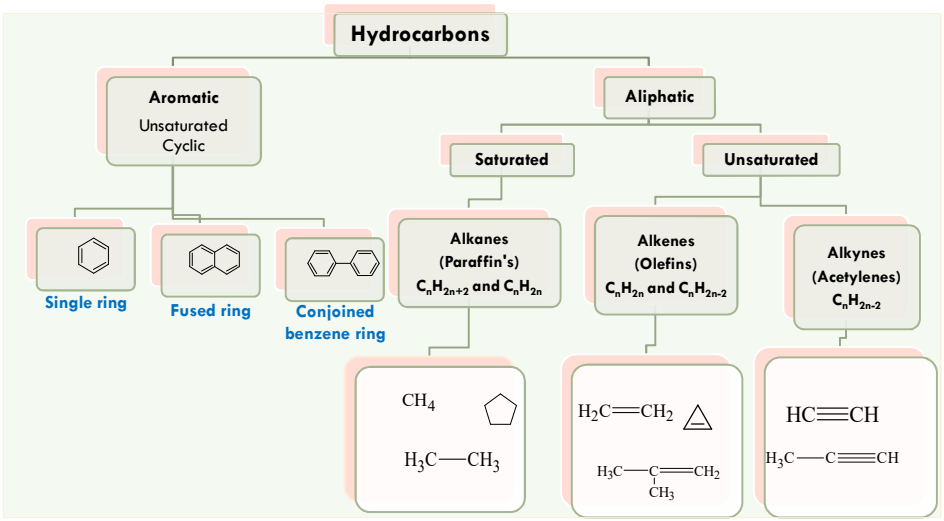

Saturated Hydrocarbons
1. Alkanes

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- **General formula is C_nH_{2n+2}**
- In **alkanes**, the four sp^3 orbitals of carbon repel each other into a tetrahedral arrangement with bond angles of 109.5° like in CH_4.
- Each sp^3 orbital in carbon overlaps with the 1s orbital of a hydrogen atom to form a C-H bond.

Names, Molecular formulas and Number of Isomers of the first ten Alkanes

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

Saturated Hydrocarbons
1. Alkanes

Classes of Carbons and Hydrogen

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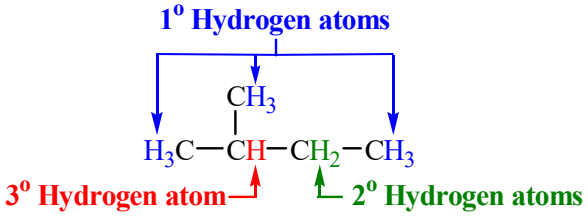
- **A primary (1°) carbon** is one that is bonded to only one other carbon.
- **A secondary (2°) carbon** is one that is bonded to two other carbons.
- **A tertiary (3°) carbon** is one that is bonded to three other carbons.



- **Hydrogens** are also referred to as 1°, 2°, or 3° according to the type of carbon they are bonded to.

Alkyl Group

Nomenclature

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- An alkyl group is formed by loss of a hydrogen atom from the corresponding alkane.
- General formula C_nH_{2n+1}.
- The letter **R** is used as a general symbol for an **alkyl group**.
- An alkyl group is named by replacing the suffix ***–ane*** of the parent alkane by *–yl*.

i.e. Alkane – ane + yl = Alkyl

Alkyl Group

Nomenclature

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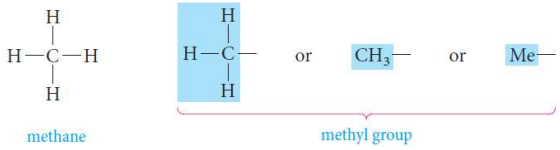
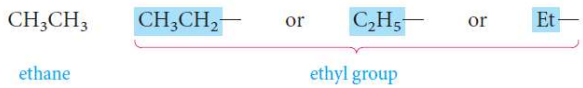
- **Examples:**
  - **Derived from methane** by removing one of the hydrogens, a one-carbon substituent is called a **methyl group**.



  - Thus the two-carbon alkyl group is called the **ethyl group**, **from ethane**.



Alkyl Group

Nomenclature

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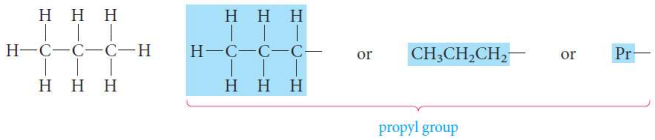
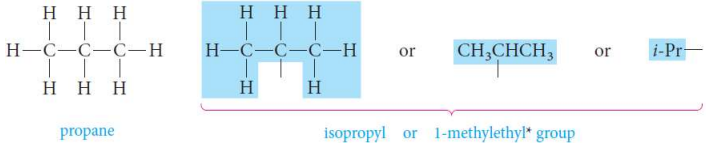
- When we come to **propane**, there are two possible alkyl groups, depending on which type of hydrogen is removed.
  - If a *terminal* hydrogen is removed, the group is called a **propyl group**.



  - If a hydrogen is removed from the *central* carbon atom, we get a different isomeric propyl group, called the **isopropyl group**.



Alkyl Group

Nomenclature

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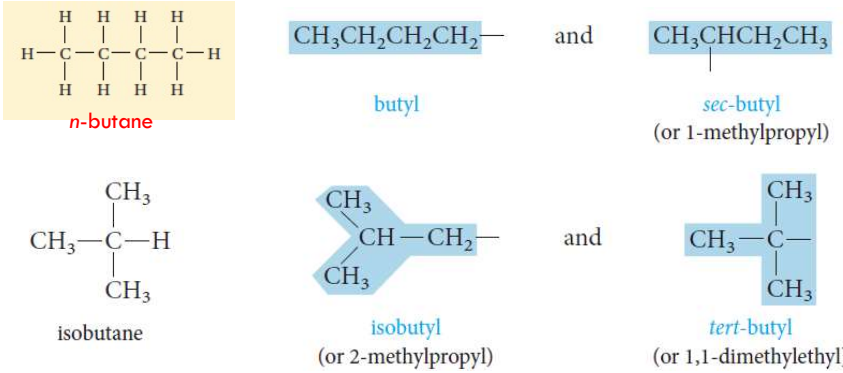
- For four-carbon alkyl group, there are four different butyl groups.
  - The butyl and *sec*-butyl groups are based on ***n*-butane**.
  - The isobutyl and *tert*-butyl groups come from **isobutane**.



Saturated Hydrocarbons
1. Alkanes

Nomenclature; IUPAC Rules

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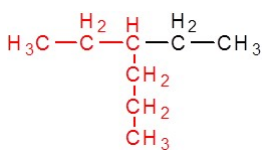
- The older unsystematic names, (***Common names***).
- The **IUPAC names**.

International Union of Pure & Applied Chemistry

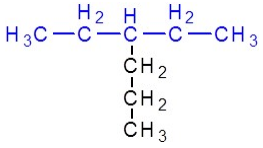
The IUPAC Rules

1) Select the parent structure; ***the longest continuous chain***



Ethylhexane

not



Propylpentane

The longest continuous chain is not necessarily straight.

Saturated Hydrocarbons
1. Alkanes

Nomenclature; IUPAC Rules

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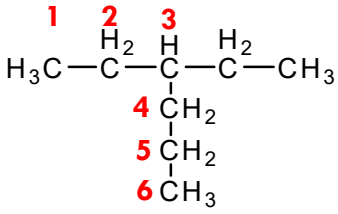
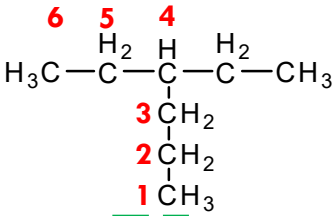
2) Number the carbons in the parent chain

starting from the end which gives the lowest number for the substituent



3-Ethyl hexane

not



4-Ethyl hexane

Saturated Hydrocarbons
1. Alkanes

Nomenclature; IUPAC Rules

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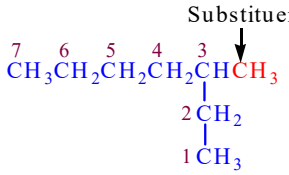
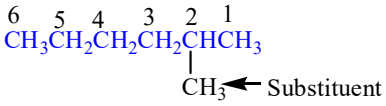
2) Number the carbons in the parent chain



3-Methylheptane



2-Methylhexane

To name the compound;

1) Determine The position of the substituent on the parent carbon chain by a number.
2) The number is followed by a hyphen (-)
3) The combined name of the substituent (ethyl).
4) The parent carbon chain (hexane), So the full name will be: **3 - Ethyl hexane**

Saturated Hydrocarbons
1. Alkanes

Nomenclature; IUPAC Rules

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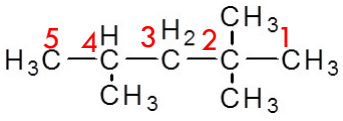
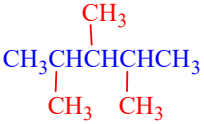
3) If the **same alkyl substituent** occurs more than once on the parent carbon chain, the prefixes **di-**, **tri-**, **tetra-**, **penta-**, and so on are used to indicate **two**, **three**, **four**, **five**, and so on.

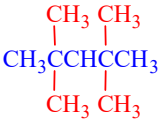


2,2,4- Trimethylpentane

2,3-Dimethylbutane



2,3,4-Trimethylpentane



2,2,4,4-Tetramethylpentane

Saturated Hydrocarbons
1. Alkanes

Nomenclature; IUPAC Rules

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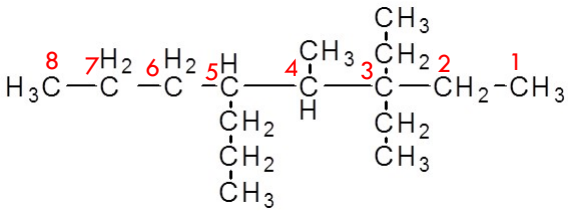
4) If **different alkyl substituents** are attached on the parent carbon chain, they are named in order of **alphabetical order**.

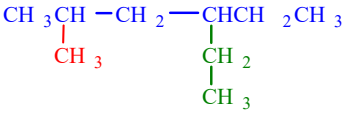


3,3-diethyl
4-methyl
5-propyl

3,3-Diethyl - 4-methyl - 5 - propyl octane

Note that

- Each substituent is given a number corresponding to its location on the longest chain.
- The substituent groups are listed alphabetically.



4-Ethyl-2-methylhexane

Saturated Hydrocarbons
1. Alkanes

Nomenclature; IUPAC Rules

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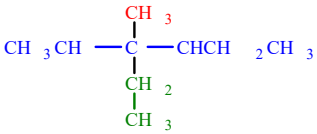
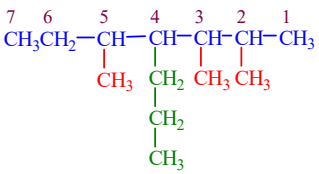
5) When two substituent are present on the same carbon, use the number twice.



3-Ethyl-3-methylhexane

6) When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.



2,3,5-Trimethyl-4-*n*-propylheptane

Saturated Hydrocarbons
1. Alkanes

Nomenclature; IUPAC Rules

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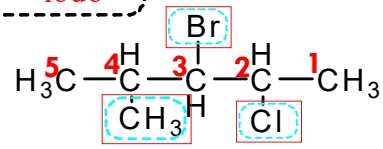
7) If substituents other than alky groups are also presents on the parent carbon chain;
all substituents are named alphabetically.

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

$-NO_2$ nitro
$-NH_2$ amino
-CN cyano



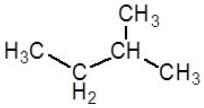
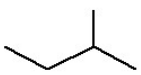
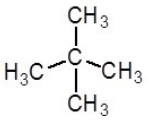
2-chloro
3-bromo
4- methyl

3-bromo -2-chloro -4-methyl pentane

Saturated Hydrocarbons
1. Alkanes

Nomenclature; IUPAC Rules

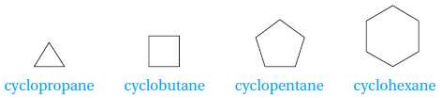
Examples

		Common name:	IUPAC name:
$CH_3CH_2CH_2CH_2CH_3$		n-Pentane	Pentane
		Isopentane	2-Methylbutane
		Neopentane	2,2-Dimethylpropane

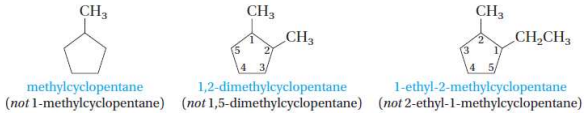
Saturated Hydrocarbons
1. Alkanes

Nomenclature of Cycloalkanes

- **Cycloalkanes** are saturated hydrocarbons that have at least one ring of carbon atoms.
- **Cycloalkanes** are named by placing the prefix *cyclo-* before the alkane name that corresponds to the number of carbon atoms in the rina.



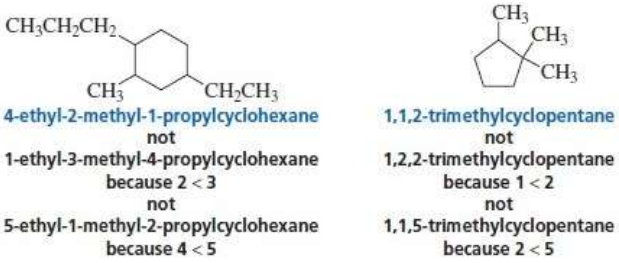
- If only one substituent is present, no number is needed to locate it.
- **If there are several substituents, numbers are required.**
  With different substituents, the one with highest alphabetic priority is located at carbon 1.



Saturated Hydrocarbons
1. Alkanes

Nomenclature of Cycloalkanes

- If there are more than two substituents on the ring, they are cited in alphabetical order.
- The substituent given the number 1 position is the one that results in a second substituent getting as low a number as possible.
- If two substituents have the same low number, the ring is numbered in the direction that gives the third substituent the lowest possible number.
- **Examples,**



Aliphatic Hydrocarbons

Physical Properties of Alkanes, Alkenes and Alkynes

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Those properties that can be observed without the compound undergoing a chemical reaction such as its physical states, density, color, Boiling and melting points and solubility.

A. Physical States

C1 (C2) to C4 are gases,
C5 to C17 are liquids,
C18 and larger alkanes are wax –like solids.

B. Solubility

- Alkanes, Alkenes and Alkynes are nonpolar compounds.
- Their solubility " Like dissolve like"
- Alkanes, Alkenes and Alkynes are soluble in the nonpolar solvents;
  carbon tetrachloride, CCl_4 and benzene,
- Alkanes, Alkenes and Alkynes are insoluble in polar solvents like water.

Aliphatic Hydrocarbons

Physical Properties of Alkanes, Alkenes and Alkynes

- **Boiling Points & Melting Points**
  - **Effect of Molecular Weight**

    The boiling points and melting points of normal hydrocarbons increase with increasing molecular weight.

    As the molecules become larger, there are more forces of attraction between them, and more energy is needed.

  - **Effect of Branching**
    - Among isomers, straight chain compound has the highest boiling point.
    - The greater the number of branches, the lower the boiling point.

Name	Formula	Boiling point, °C
pentane	$CH_3CH_2CH_2CH_2CH_3$	36
2-methylbutane (isopentane)	$CH_3CHCH_2CH_3$ (CH$_3$ branch)	28
2,2-dimethyl-propane (neopentane)	$CH_3-C(CH_3)_2-CH_3$	10

Saturated Hydrocarbons
1. Alkanes

Preparation of Alkanes

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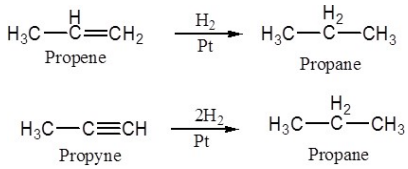
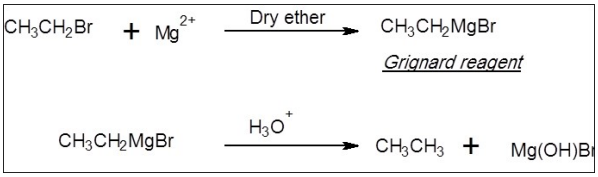
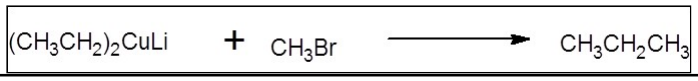
1. Hydrogenation of unsaturated hydrocarbon:



2. Hydrolysis of Grignard reagent



3. Reduction of Alkyl halides By lithium dialkyl cuprate



Saturated Hydrocarbons
1. Alkanes

Reactions of Alkanes

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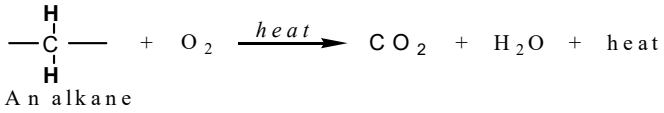
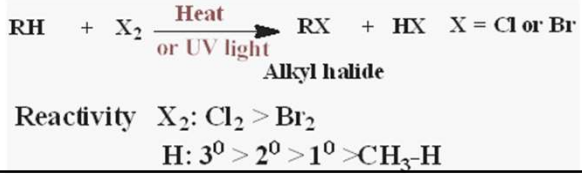
Saturated hydrocarbons undergo very few reactions, so they are called Paraffinic hydrocarbons. (Latin *parum*, little; *affinis*, affinity)

Combustion



Halogenation

The halogenation of an alkane appears to be a simple free radical substitution in which a C-H bond is broken and a new C-X bond is formed



Saturated Hydrocarbons
1. Alkanes

Reactions of Alkanes

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A. Halogenation

- **Substitution reaction of alkanes,**
  i.e. replacement of hydrogen by halogen,
  usually chlorine or bromine, giving alkyl chloride or alkyl bromide.
- **Flourine reacts explosively with alkanes**
  It is unsuitable reagent for the preparation of the alkyl flourides.
- **Iodine is too unreactive**
  It is not used in the halogentaion of alkanes.
- **Halogenation of alkanes take place at**
  high temperatures or under the influence of ultraviolet light

Saturated Hydrocarbons
1. Alkanes

Reactions of Alkanes

A) Halogenation

- **Chlorination of an alkane usually gives a mixture of products**

$$\underset{\text{methane}}{CH_4} + Cl{-}Cl \xrightarrow[\text{or heat}]{\text{sunlight}} \underset{\substack{\text{chloromethane}\\(\text{methyl chloride})}}{CH_3Cl} + HCl$$

$$CH_3Cl \xrightarrow{Cl_2} \underset{\substack{\text{dichloromethane}\\(\text{methylene chloride})}}{CH_2Cl_2} \xrightarrow{Cl_2} \underset{\substack{\text{trichloromethane}\\(\text{chloroform})}}{CHCl_3} \xrightarrow{Cl_2} \underset{\substack{\text{tetrachloromethane}\\(\text{carbon tetrachloride})}}{CCl_4}$$

- With longer chain alkanes, mixtures of products may be obtained even at the first step. For example, with propane,

$$\underset{\text{propane}}{CH_3CH_2CH_3} + Cl_2 \xrightarrow[\text{or heat}]{\text{light}} \underset{\substack{\text{1-chloropropane}\\(n\text{-propyl chloride})}}{CH_3CH_2CH_2Cl} + \underset{\substack{\text{2-chloropropane}\\(\text{isopropyl chloride})}}{CH_3\overset{\overset{Cl}{|}}{C}HCH_3} + HCl$$

Uses of Alkanes

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- **Alkanes** are unreactive compounds and mainly used as a source of energy;

  Examples:

  - Natural gas is composed mostly of methane, but it also contains small amounts of ethane, propane, butane, and pentane.
  - Diesel itself is a mixture of hydrocarbons, ranging from $C_{10}H_{20}$, (decane) to $C_{15}H_{28}$.
- **Petroleum jelly (Vaseline)** is petrolatum, a hydrocarbon, $C_{15}H_{15}N$ (1,1,2 Trimethylbenzeindole).
- Most petroleum jelly today is used as an ingredient in skin lotions and cosmetics.
- **Paraffin wax (or petroleum wax)** is a soft colorless solid, derived from petroleum, that consists of a mixture of hydrocarbon molecules containing between twenty and forty carbon atoms.
- Common applications for paraffin wax include lubrication, electrical insulation, and candles
- **Cyclopropane** is used as an anaesthetic
- **General uses;**

- Making organic compounds and used as Organic solvents

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2. ALKENES

Unsaturated Hydrocarbons
1. Alkenes

The Structure of Alkenes

29

- **Alkenes** are hydrocarbons that contain a ***carbon–carbon double bond***.
- **Alkenes are also *Olefins*.**
- **General formula is C_nH_{2n}**
- The simplest members of the **Alkenes** series are **C_2 & C_3**

	$CH_2{=}CH_2$	$H_3C{-}CH{=}CH_2$
Common name:	Ethylene	Propylene
IUPAC name:	Ethene	Propene

- Hybridization; ***sp^2*-hybridized orbitals**
- The angle between them is 120° and bond length C=C (1.34 Å).
- A **trigonal planar.**

Unsaturated Hydrocarbons
1. Alkenes

Nomenclature; Common Names

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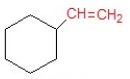
- The simplest members of the alkene and alkyne series are frequently referred to by their older common names, ethylene, acetylene, and propylene.

$CH_2{=}CH_2$	$HC{\equiv}CH$	$CH_3CH{=}CH_2$
ethylene	acetylene	propylene
(ethene)	(ethyne)	(propene)

- Two important groups also have common names; They are the **vinyl** and **allyl** groups.
- These groups are used in common names.

$CH_2{=}CH{-}$ vinyl (ethenyl)	$CH_2{=}CHCl$ vinyl chloride (chloroethene)
$CH_2{=}CH{-}CH_2{-}$ allyl (2-propenyl)	$CH_2{=}CH{-}CH_2Cl$ allyl chloride (3-chloropropene)



Common name: Vinyl cyclohexane
IUPAC name: Cyclohexylethene

Unsaturated Hydrocarbons
1. Alkenes

Nomenclature; IUPAC Rules

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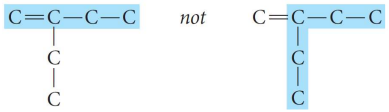
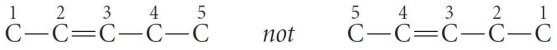
The IUPAC rules for naming alkenes are similar to those for alkanes, but a few rules must be added for naming and locating the multiple bonds.

1. The ending **-ene** is used to designate a carbon–carbon double bond.
2. Select the **longest chain that includes *both carbons of the double bond***.



3. **Number the chain from the end nearest the double bond** so that the carbon atoms in that bond have the lowest possible numbers.



Unsaturated Hydrocarbons
1. Alkenes

Nomenclature; IUPAC Rules

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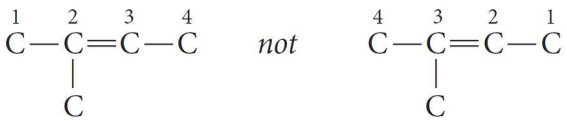
If the multiple bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.



4. Indicate the **position of the multiple bond using the *lower numbered carbon atom*** of that bond.

Unsaturated Hydrocarbons
1. Alkenes

Nomenclature; IUPAC Rules

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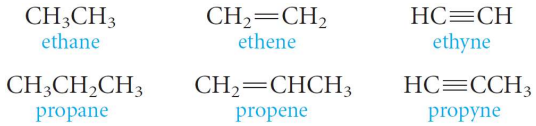
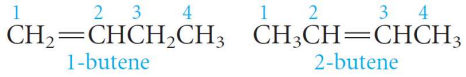
NOTES

The root of the name (*eth-* or *prop-*) tells us the number of carbons, and the ending (*-ane, -ene,* or *-yne*) tells us whether the bonds are single, double, or triple.

No number is necessary in these cases, because in each instance, only one structure is possible.



With four carbons, a number is necessary to locate the double bond.



Unsaturated Hydrocarbons
1. Alkenes

Nomenclature; IUPAC Rules

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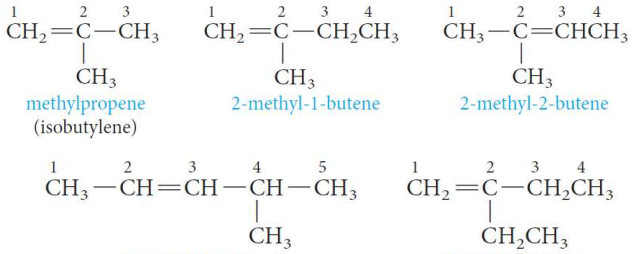
- Branches are named in the usual way.



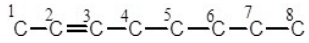
Unsaturated Hydrocarbons
1. Alkenes

Nomenclature; IUPAC Rules

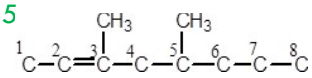
Example: Write the structural formula of 4-Isopropyl-3,5-dimethyl-2-octene.

1) The parent carbon chain is an **Octene**.

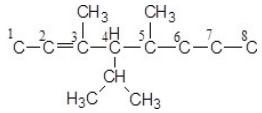
The double bond is located between the 2nd and 3rd carbons.



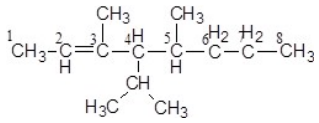
2) Two methyl groups are attached on the parent carbon chain, one on carbon 3 and the other on carbon 5



3) An isopropyl group is attached on carbon 4.



4) Put the missing hydrogens to get the correct structure.



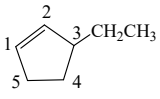
Unsaturated Hydrocarbons
1. Alkenes

Nomenclature of Cycloalkenes

- We start numbering the ring with the carbons of the double bond.
- A number is not needed to denote the position of the functional group, because the ring is always numbered so that the double bond is between carbons 1 and 2.
- Put the lowest substituent number into the name not in the direction that gives the lowest sum of the substituent numbers.

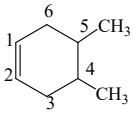
Cyclopentene

2-Cyclopentene ✗

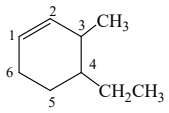


3-Ethylcyclopentene

5-Ethylcyclopentene ✗



4,5-Dimethylcyclohexene



4-Ethyl-3-methylcyclohexene