

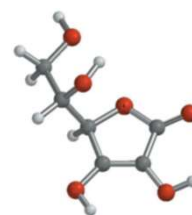
**CHEM 244**

# **PRINCIPLES OF ORGANIC CHEMISTRY I**

FOR CHEMICAL ENGINEERING' STUDENTS, COLLEGE OF ENGINEERING

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 2 (2+0)

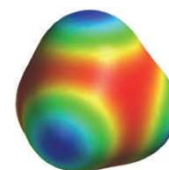


**Dr. Mohamed El-Newehy**

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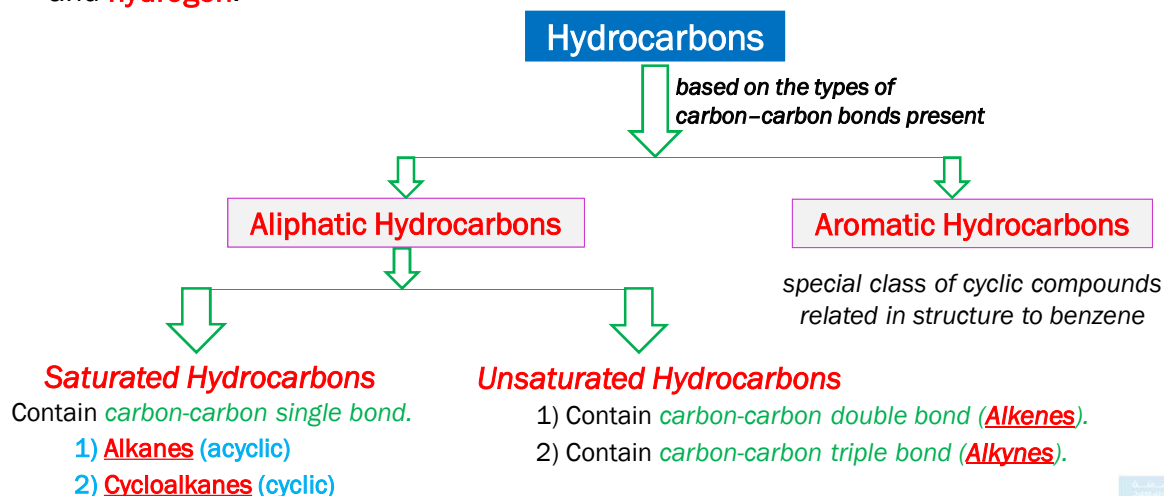
<http://fac.ksu.edu.sa/melnewehy/home>

# **HYDROCARBONES**



## HYDROCARBONS

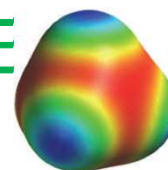
- **Hydrocarbons** are **organic compounds**, which contain only the two elements **carbon** and **hydrogen**.



## CHAPTER 2

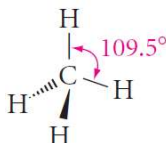
# SATURATED HYDROCARBONES

## ALKANES AND CYCLOALKANE

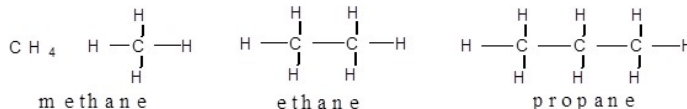


## THE STRUCTURES OF ALKANES

- General formula is  $C_nH_{2n+2}$
- The simplest alkane is **methane**.
- Its **tetrahedral** three-dimensional structure.



- Additional alkanes are constructed by lengthening the carbon chain and adding an appropriate number of hydrogens to complete the carbon valences.



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## THE STRUCTURES OF ALKANES

### Names and Molecular Formulas of the First Ten Alkanes

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH <sub>4</sub>	CH <sub>4</sub>	1
ethane	2	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>3</sub>	1
propane	3	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	1
butane	4	C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	2
pentane	5	C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	3
hexane	6	C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	5
heptane	7	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	9
octane	8	C <sub>8</sub> H <sub>18</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	18
nonane	9	C <sub>9</sub> H <sub>20</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	35
decane	10	C <sub>10</sub> H <sub>22</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	75

- Alkanes with carbon chains that are **unbranched** are called **normal alkanes** or **n-alkanes**.
- Each member of this series differs from the next higher and the next lower member by a **-CH<sub>2</sub>- group** (called a **methylene group**).
- Members of such a series have similar chemical and physical properties, which change gradually as carbon atoms are added to the chain.

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## THE STRUCTURES OF ALKANES

**PROBLEM 2.1** What is the molecular formula of an alkane with six carbon atoms?

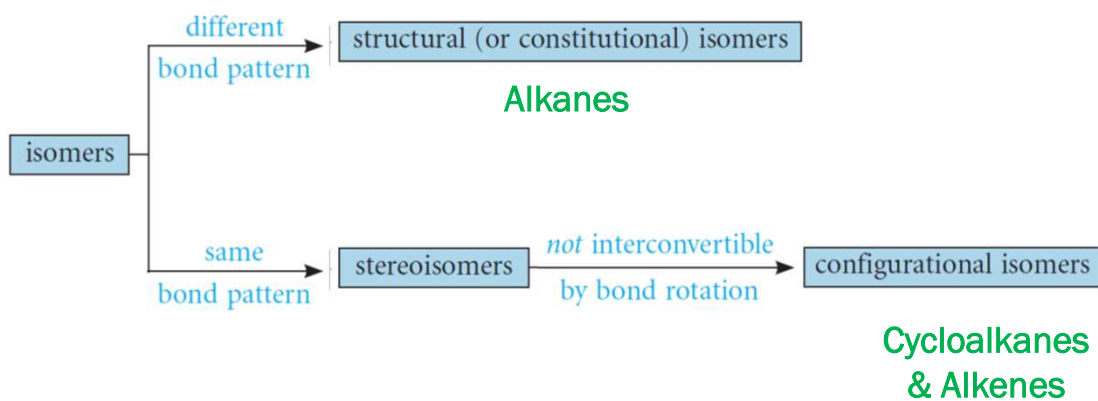
**PROBLEM 2.2** What is the molecular formula of an alkane with 12 carbon atoms?

**PROBLEM 2.3** Which of the following are alkanes?

- a.  $C_7H_{16}$  b.  $C_7H_{12}$  c.  $C_8H_{16}$  d.  $C_{29}H_{60}$

## THE STRUCTURES OF ALKANES

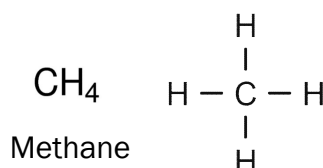
### ISOMERISM



## THE STRUCTURES OF ALKANES

### ISOMERISM

- The **molecular formula** of a substance tells us the numbers of different atoms present.
- Structural formula** tells us how those atoms are arranged.



- Isomers** are molecules with the same number and kinds of atoms but different arrangements of the atoms.
- Structural (or constitutional) isomers** are compounds that have the same molecular formula, but different structural formulas.

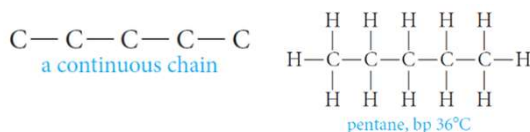
## THE STRUCTURES OF ALKANES

### ISOMERISM

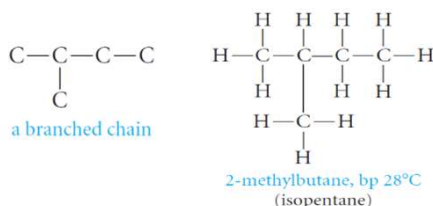
#### Writing Structural Formulas

- Suppose we want to write out all possible structural formulas that correspond to the molecular formula  $\text{C}_5\text{H}_{12}$ .

- We begin by writing all five carbons in a **continuous chain**.



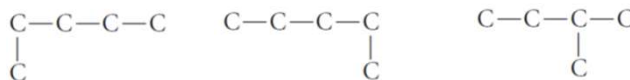
- To find structural formulas for the other isomers, we must consider **branched chains**.



## THE STRUCTURES OF ALKANES

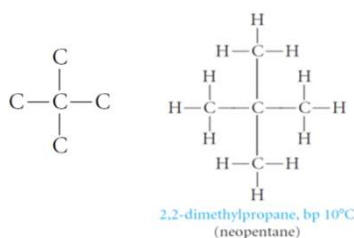
### ISOMERISM

- Suppose we keep the chain of four carbons and try to connect the fifth carbon somewhere else. Consider the following chains:



- But there is a third isomer of  $\text{C}_5\text{H}_{12}$ .

We can find it by reducing the longest chain to only three carbons and connecting two one-carbon branches to the middle carbon



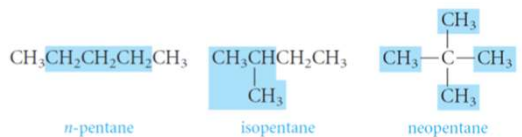
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## THE STRUCTURES OF ALKANES

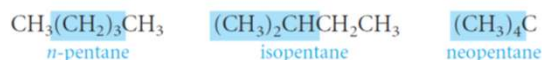
### ISOMERISM

- Three (and only three) different structural formulas that correspond to the molecular formula  $\text{C}_5\text{H}_{12}$ ,

- n-pentane (n for normal, with an unbranched carbon chain),
- Isopentane
- neopentane.



a single line formula



a line-segment formula

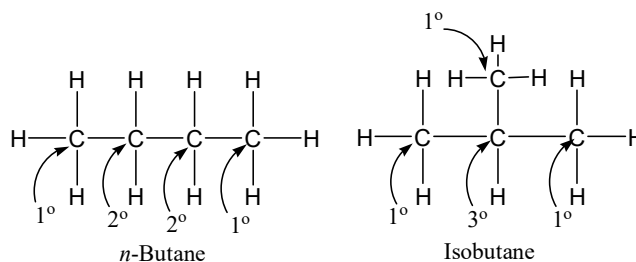


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## THE STRUCTURES OF ALKANES

### CLASSES OF CARBONS AND HYDROGEN

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



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

## IUPAC RULES FOR NAMING ALKANES

### GENERAL NOTES

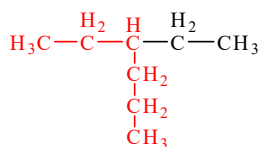
1. The general name for **acyclic saturated hydrocarbons** is **alkanes**.  
The **-ane ending** is used for all saturated hydrocarbons.
2. **Alkanes** without branches are named according to the number of carbon atoms.
3. For **alkanes with branches**, the root name is that of the **longest continuous chain of carbon atoms**.
4. Groups attached to the main chain are called **substituents**.
5. Saturated substituents that contain only carbon and hydrogen are called **alkyl groups**.
6. The main chain is numbered in such a way that the first **substituent** along the chain receives the **lowest possible number**.

## IUPAC RULES FOR NAMING ALKANES

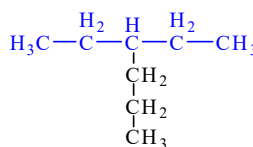
7. Each substituent is then located by its name and by the number of the carbon atom to which it is attached.
8. When two or more identical groups are attached to the main chain, prefixes such as *di-*, *tri-*, and *tetra-* are used.
9. If two or more different types of substituents are present, they are listed **alphabetically**, except that prefixes such as *di-* and *tri-* are not considered when alphabetizing.
10. **Punctuation** is important when writing IUPAC names.
  - IUPAC names for hydrocarbons are written as one word.
  - Numbers are separated from each other by commas and are separated from letters by hyphens.
  - There is no space between the last named substituent and the name of the parent alkane that follows it.

## IUPAC RULES FOR NAMING ALKANES

1. Locate the **longest continuous carbon chain**.  
This gives the name of the *parent hydrocarbon*.



Ethylhexane

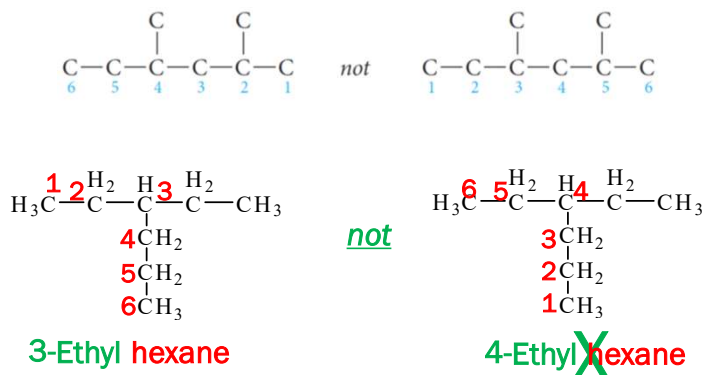
Propyl~~pentane~~

The **longest continuous** chain is **not** necessarily **straight**.



## IUPAC RULES FOR NAMING ALKANES

2. **Number** the longest chain beginning at the end nearest the first branch point.



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## IUPAC RULES FOR NAMING ALKANES

If there are **two equally long continuous chains**, select the one with the most branches.



If there is a **branch equidistant from each end of the longest chain**, begin numbering nearest to a third branch:



If there is **no third branch**, begin numbering nearest the substituent whose name has alphabetic priority:



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## IUPAC RULES FOR NAMING ALKANES

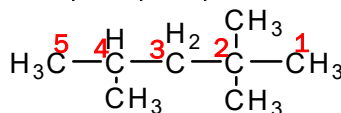
To name the compound;

- 1) 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)

3 -Ethylhexane

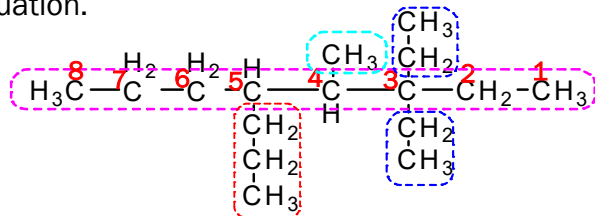
## IUPAC RULES FOR NAMING ALKANES

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-Tri methylpentane

4. Write the name as one word, **placing substituents in alphabetic order** and using proper punctuation.



3,3- diethyl  
4- methyl  
5- propyl

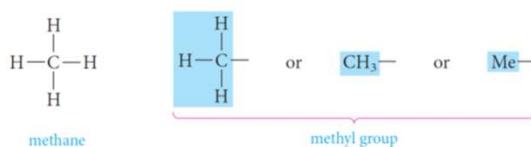
3,3- Diethyl-4- methyl- 5- propyloctane

## IUPAC RULES FOR NAMING ALKANES

### ALKYL AND HALOGEN SUBSTITUENTS

- Alkyl substituents are named by changing the **-ane** ending of alkanes to **-yl**.
- The letter **R** is used as a general symbol for an **alkyl group**.
- The formula **R - H** therefore represents any **alkane**.

➤ A **one-carbon substituent** is called a **methyl group**, from methane



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



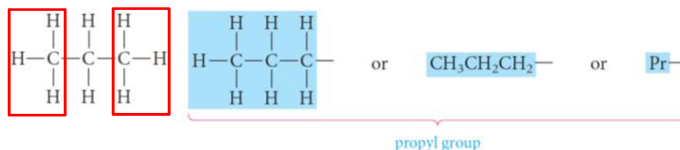
## IUPAC RULES FOR NAMING ALKANES

### ALKYL AND HALOGEN SUBSTITUENTS

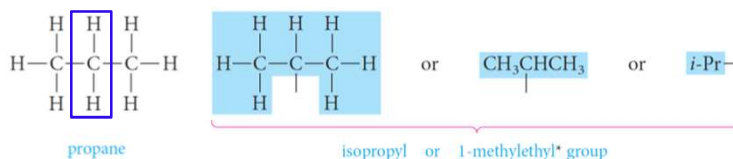
➤ A **three-carbon substituent** from propane.

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** (or 1-methylethyl) **group**.



## IUPAC RULES FOR NAMING ALKANES

### ALKYL AND HALOGEN SUBSTITUENTS

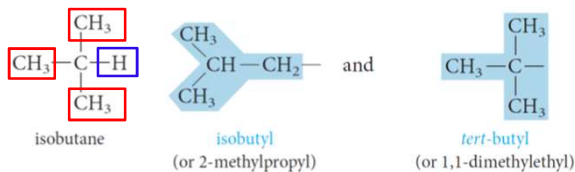
- A **four-carbon substituent** from butane.

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**.

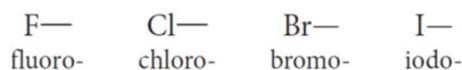


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## IUPAC RULES FOR NAMING ALKANES

### ALKYL AND HALOGEN SUBSTITUENTS

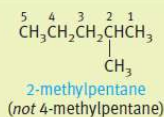
- The formula **R - Cl** stands for any **alkyl chloride** (methyl chloride, ethyl chloride, and so on).
- Halogen substituents** are named by changing the **-ine** ending of the element to **-o**.



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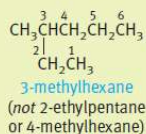
# IUPAC RULES FOR NAMING ALKANES

## EXAMPLES



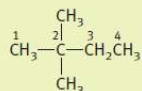
2-methylpentane  
(not 4-methylpentane)

The ending *-ane* tells us that all the carbon-carbon bonds are single; *pent-* indicates five carbons in the longest chain. We number them from right to left, starting closest to the branch point.



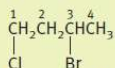
3-methylhexane  
(not 2-ethylpentane or 4-methylhexane)

This is a six-carbon saturated chain with a methyl group on the third carbon. We would usually write the structure as  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ .



2,2-dimethylbutane  
(not 2,2-methylbutane or 2-dimethylbutane)

There must be a number for each substituent, and the prefix *di-* says that there are two methyl substituents.

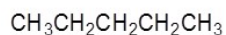


3-bromo-1-chlorobutane  
(not 1-chloro-3-bromobutane or 2-bromo-4-chlorobutane)

First, we number the butane chain from the end closest to the first substituent. Then we name the substituents in alphabetical order, regardless of position number.

# IUPAC RULES FOR NAMING ALKANES

## EXAMPLES

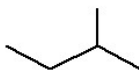
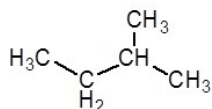


Common name:

n-Pentane

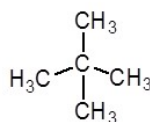
IUPAC name:

Pentane



Isopentane

2-Methylbutane



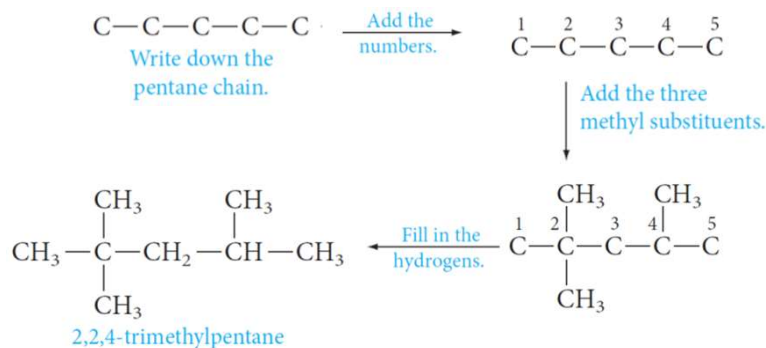
Neopentane

2,2-Dimethylpropane

## IUPAC RULES FOR NAMING ALKANES

### EXAMPLES

Write the formula for 2,2,4-trimethylpentane



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## PHYSICAL PROPERTIES OF ALKANES

- Those properties that can be observed without the compound undergoing a chemical reaction.

### ➤ Physical State

Alkanes occur at room temperature are gases, liquids, and solids.

- C1 to C4 are gases,
- C5 to C17 are liquids,
- C18 and larger alkanes are wax-like solids.

### ➤ Solubility

- Alkanes are nonpolar compounds.
- Their solubility "Like dissolve like"
- Alkanes are soluble in the nonpolar solvents; carbon tetrachloride,  $\text{CCl}_4$  and benzene,
- Alkanes are insoluble in polar solvents like water.

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## PHYSICAL PROPERTIES OF ALKANES

### ➤ Boiling Points & Melting Points

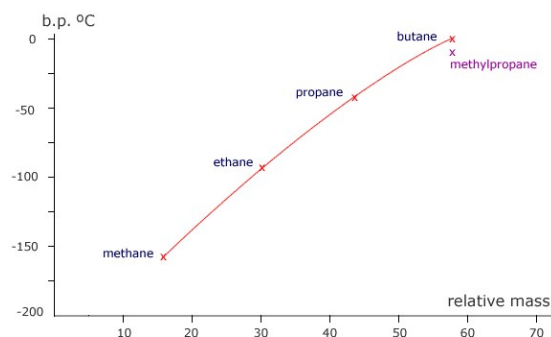
#### ▪ Effect of Molecular Weight

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 **isomeric alkanes**, straight chain compound has the highest boiling point.
- The greater the number of branches, the lower the boiling point.



Graph showing boiling point of the alkanes against relative mass

## SOURCES OF ALKANES

- The two principal sources of alkanes are **petroleum** and **natural gas**.

### Petroleum

- **Petroleum** is at present our most important fossil fuel.
- **Petroleum** is a complex mixture of hydrocarbons formed over eons of time through the gradual decay of buried animal and vegetable matter.
- **Crude oil** is a viscous black liquid that collects in vast underground pockets in sedimentary rock.
- It must be brought to the surface via drilling and pumping. To be most useful, the crude oil must be refined.
- The first step in petroleum refining is usually **distillation**.

## SOURCES OF ALKANES

### Petroleum Refining

- **Refining** is a process done by distilling the petroleum into fractions of **different boiling** and then **treating the distilled petroleum in various ways to remove the undesirable components**.
- The most volatile components come out first  
The less volatile components come out next  
And the highest boiling components (those that boil at temperatures above 400°C) remain behind as residues.
- The **refined products of petroleum**, known as **petrochemicals**,  
They are used as raw materials in the manufacture of many useful finish products.

## SOURCES OF ALKANES

Common Petroleum Fractions			
Boiling range, °C	Name	Range of carbon atoms per molecule	Use
<20	gases	C <sub>1</sub> to C <sub>4</sub>	heating, cooking, petrochemical raw material
20–200	naphtha; straight-run gasoline	C <sub>5</sub> to C <sub>12</sub>	fuel; lighter fractions (such as petroleum ether, bp 30°C–60°C) also used as laboratory solvents
200–300	kerosene	C <sub>12</sub> to C <sub>15</sub>	fuel
300–400	fuel oil	C <sub>15</sub> to C <sub>18</sub>	heating homes, diesel fuel
>400		over C <sub>18</sub>	lubricating oil, greases, paraffin waxes, asphalt



## SOURCES OF ALKANES

### Octane Number

- An **octane rating**, or **octane number**, is a standard measure of the performance of an engine or aviation fuel
- **Octanes** are a family of hydrocarbon that are typical components of gasoline.  
*They are colorless liquids that boil around 125°C.*
- One member of the octane family, **isooctane**, is used as a reference standard to benchmark the tendency of **gasoline** or **LPG** fuels to resist self-ignition.
- The **octane rating of gasoline** is defined by comparison with the **mixture of 2,2,4-trimethylpentane (iso-octane) and heptane**, by volume, of 2,2,4-trimethylpentane in that mixture is the octane number of the fuel.  
**Example;** Regular gasoline with an octane rating of 90 has a knocking characteristic equivalent to that a mixture of **10% n-heptane** and **90% 2,2,4-trimethylpentane**.
- **n-heptane**, a poor fuel that causes severe Knocking (octane number = 0).

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## SOURCES OF ALKANES

### Octane Number

- Octane numbers **decrease** with increasing chain length and **increase** with increasing branching.
- The octane number of a poor fuel can also be improved by blending it with small amounts of **additives**.
- **Tetraethyllead, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> Pb**, is an efficient antiknock agent.  
**but has one disadvantage:**  
its combustion product, **lead oxide**, is reduced to **metallic lead** that clogs the cylinder valves of an engine.
- Other additives such as **TCP (tricresyl phosphate)** and **boron hydrides** have also enhanced the performance of many gasolines.

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## SOURCES OF ALKANES

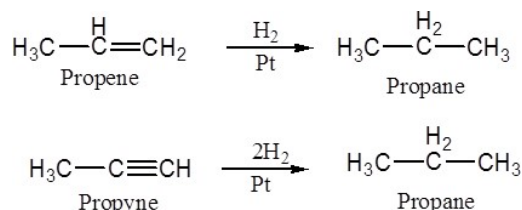
### Natural Gas

- **Natural gas** consists of the low molecular weight alkanes from **C1 to C8**.
  - It is composed of **methane (80%)**; **ethane (13%)**, **propane (3%)**, **butane (1%)**, **C5 through C6 alkanes (0.5%)**, and **nitrogen (2.5%)**.
  - **Natural gas** is a cleaner fuel than petroleum.
  - The **propane** and **butane** can be removed by **liquefaction** and compressed into cylinders to be sold as bottled gas.
    - Propane is the major constituent of liquefied petroleum gas (LPG).
    - To conserve space, the gas is liquefied (2160 °C), because 1 cubic meter (m<sup>3</sup>) of liquefied gas is equivalent to about 600 m<sup>3</sup> of gas at atmospheric pressure.
  - **Natural gas** is also converted into many other important organic compounds such as **alcohols**, **aldehydes**, **ketones**, **carboxylic acids**, and **alkyl halides**.

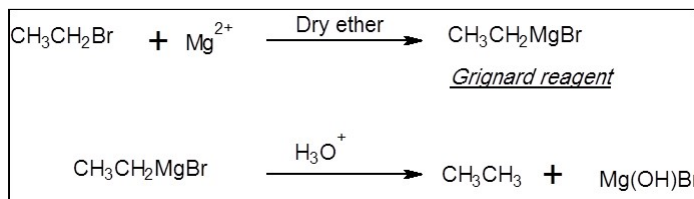
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## PREPARATION OF ALKANES

### 1. Hydrogenation of unsaturated hydrocarbon:



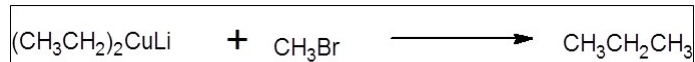
### 2. Hydrolysis of Grignard reagent



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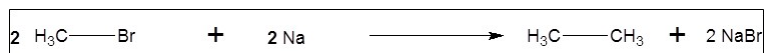
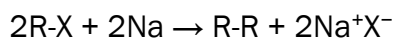
## PREPARATION OF ALKANES

### 3. Reduction of Alkyl halides By lithium dialkyl cuprate



### 4. The Wurtz reaction

*two alkyl halides are reacted with sodium to form a new carbon-carbon bond.*

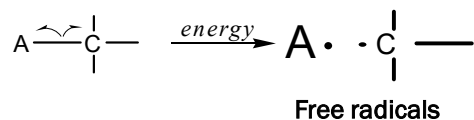


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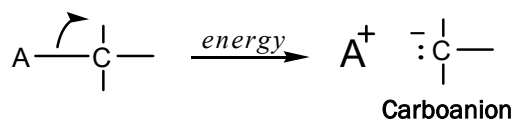
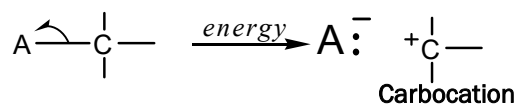
## NOTATIONS FOR BOND BREAKING AND BOND MAKING

- A covalent bond can be broken in either two ways,

- Homolytic cleavage.



- Heterolytic cleavage.

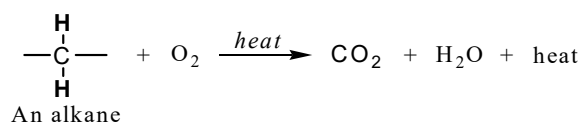


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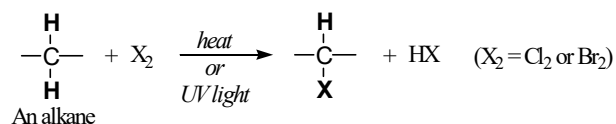
## REACTIONS OF ALKANES

- All of the bonds in **alkanes** are single, covalent, and nonpolar.
- Hence alkanes are relatively inert and they are called **Paraffinic hydrocarbons**. ( Latin *parum*, little; *affinis*, affinity).
- **Alkanes** ordinarily do not react with most common acids, bases, or oxidizing and reducing agents.
- **Alkanes** can be used as solvents.
- **Alkanes** do react with some reagents, such as **molecular oxygen** and the **halogens**.

### Combustion



### Halogenation



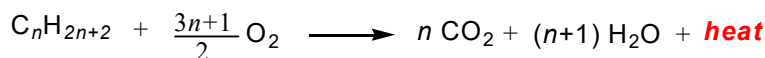
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## REACTIONS OF ALKANES

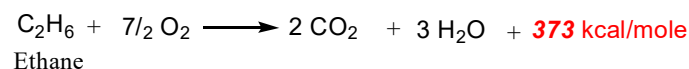
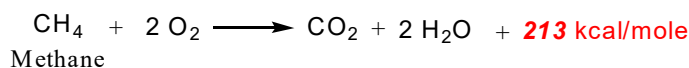
### 1) OXIDATION AND COMBUSTION; ALKANES AS FUELS

- **Combustion** of hydrocarbons is an **oxidation reaction** in which C - H bonds are replaced with C - O bonds.
- When ignited in the presence of excess oxygen,  
Alkanes are oxidized to Carbon dioxide and Water and heat is liberated.

#### General equation



#### Examples



- 160 Kcal of heat is liberated for each **methylene group**.

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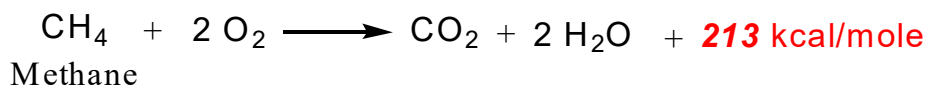
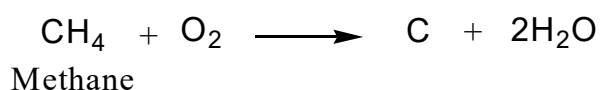
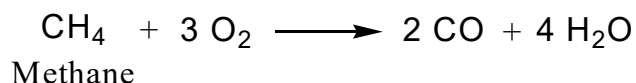
## REACTIONS OF ALKANES

## 1) OXIDATION AND COMBUSTION; ALKANES AS FUELS

- The incomplete combustion of alkanes.

liberates poisons carbon monoxide (CO) or carbon.

both are major contributors to air pollution.

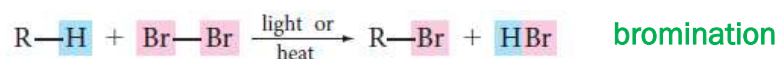
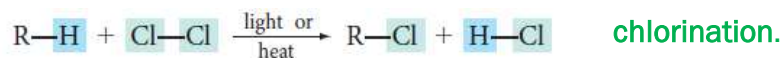


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## REACTIONS OF ALKANES

## 2) HALOGENATION OF ALKANES

- When a mixture of an alkane and chlorine gas is stored at low temperatures in the dark, no reaction occurs.
- In sunlight (ultraviolet light) or at high temperatures, an exothermic reaction occurs.  
One or more hydrogen atoms of the alkane are replaced by chlorine atoms.
- This process is a substitution reaction,



- Flourine reacts explosively with alkanes

It is unsuitable reagent for the preparation of the alkyl fluorides.

- Iodine is too unreactive

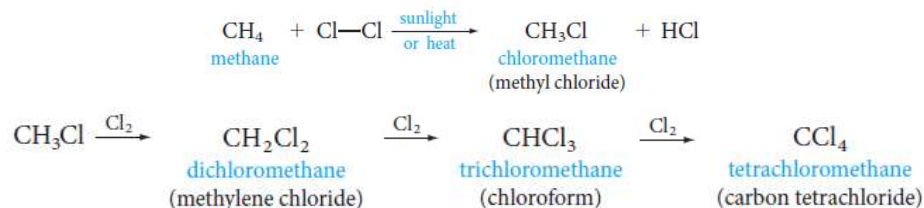
It is not used in the halogenation of alkanes.

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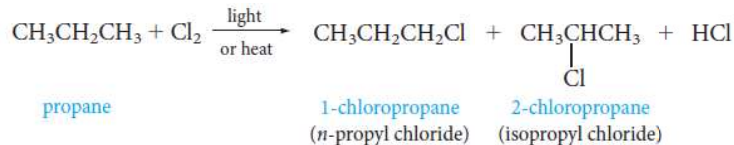
## REACTIONS OF ALKANES

### 2) HALOGENATION OF ALKANES

- If excess halogen is present, the reaction can continue further to give **polyhalogenated products**.



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



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## REACTIONS OF ALKANES

### 2) HALOGENATION OF ALKANES

#### The Free-Radical Chain Mechanism of Halogenation

- Proceeds by a **free-radical chain mechanism**.
- The mechanism involves **three steps**;
  - 1) Chain-initiation step;
  - 2) Chain-propagating step;
  - 3) Chain-termination step;

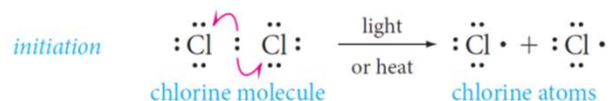
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## REACTIONS OF ALKANES

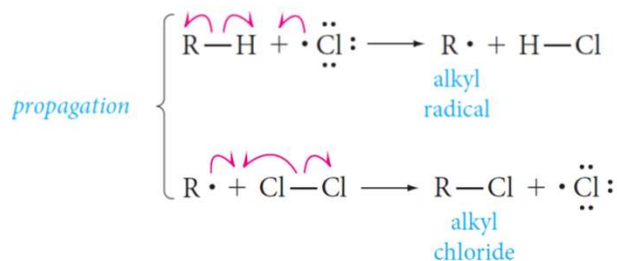
## 2) HALOGENATION OF ALKANES

The Free-Radical Chain Mechanism of Halogenation

## 1) Chain-initiation step;



## 2) Chain-propagating step;

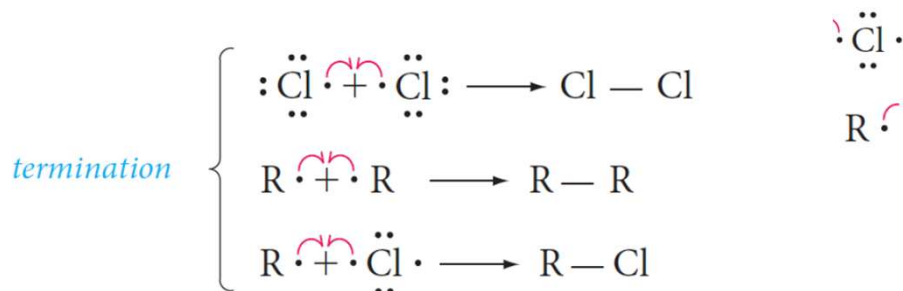
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## REACTIONS OF ALKANES

## 2) HALOGENATION OF ALKANES

The Free-Radical Chain Mechanism of Halogenation

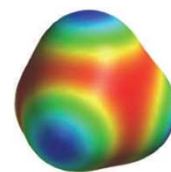
## 3) Chain-termination step;

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## CHAPTER 2

## SATURATED HYDROCARBONES

## CYCLOALKANES

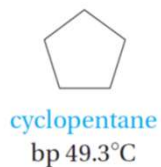
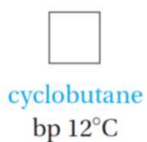
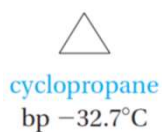


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## CYCLOALKANES

## CYCLOALKANE NOMENCLATURE

- **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 ring.



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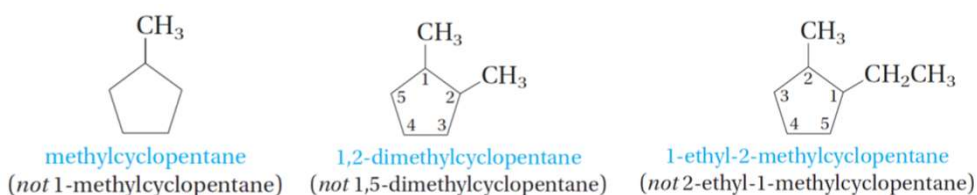


## CYCLOALKANES

## CYCLOALKANE NOMENCLATURE

- Alkyl or halogen substituents attached to the rings are named in the usual way.
- 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.*

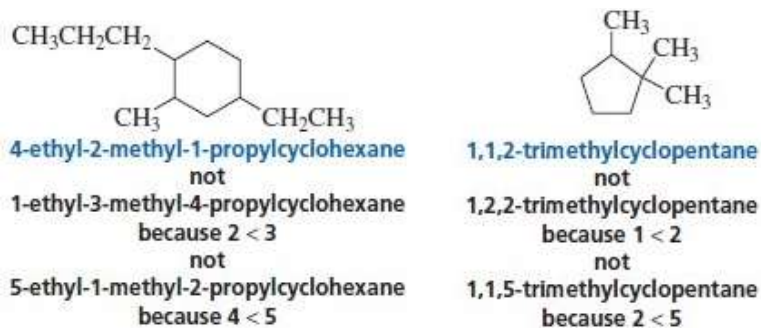


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## CYCLOALKANES

## CYCLOALKANE NOMENCLATURE

- 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.

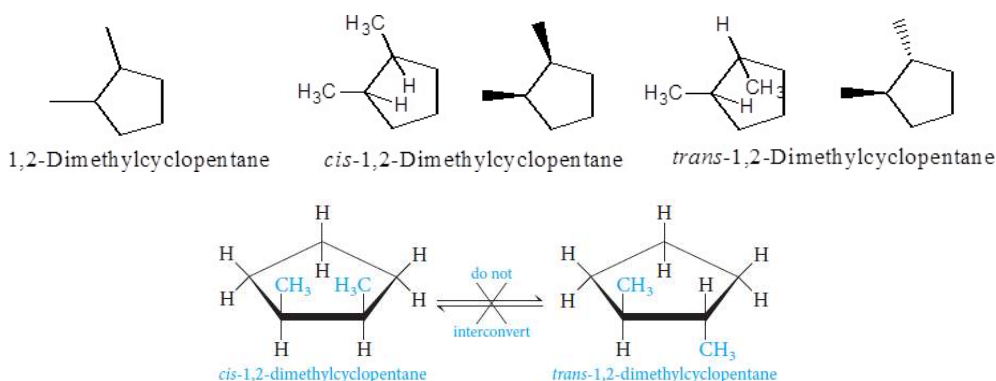


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## CYCLOALKANES

**cis-trans ISOMERISM IN CYCLOALKANES**

**cis-trans isomerism** (sometimes called **geometric isomerism**) is one kind of stereoisomerism.

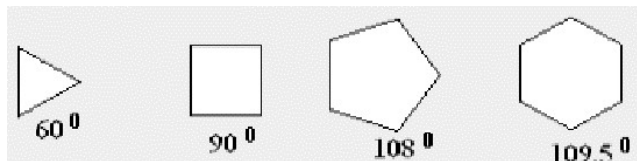


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## CYCLOALKANES

**RING STRAIN**

- **Ring Strain** is a type of instability that exists when bonds in a molecule form angles that are abnormal.
- Baeyer suggested that the stability of a cycloalkane could be predicted by determining how close the bond angle of a planar cycloalkane is to the ideal tetrahedral bond angle of  $109.5^\circ$ .



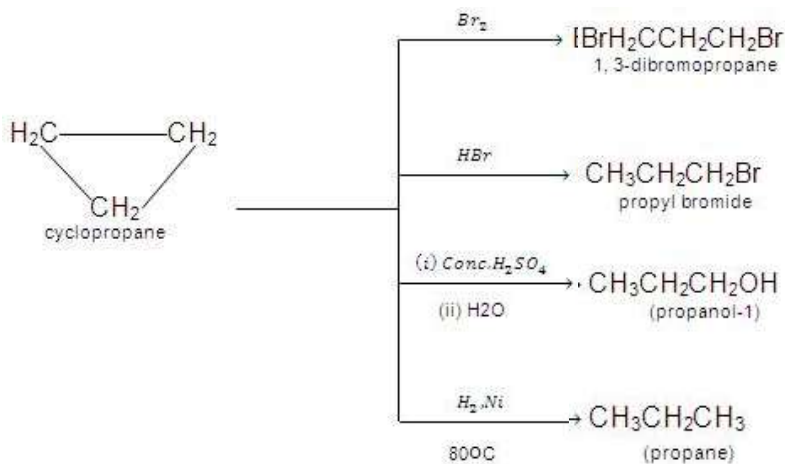
- Strain is most commonly discussed for small rings, such as **cyclopropanes** and **cyclobutanes**.

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## CYCLOALKANES

## REACTIONS OF CYCLOALKANES

- Less stable rings; ring opening due to ring strain

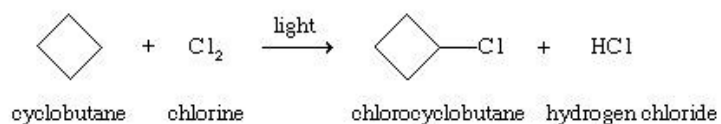


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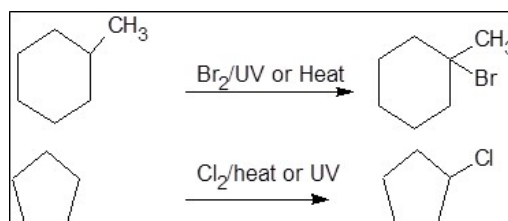
## CYCLOALKANES

## REACTIONS OF CYCLOALKANES

- Less stable rings; ring opening due to ring strain



- More stable 5 and 6 rings



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