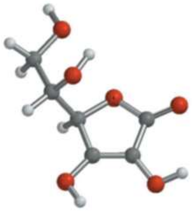
CHEM 240

PRINCIPLES OF ORGANIC CHEMISTRY I

FOR CHEMISTRY' STUDENTS, COLLEGE OF SCIENCE

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 2 (2+0)



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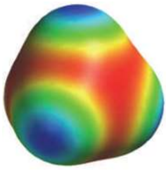
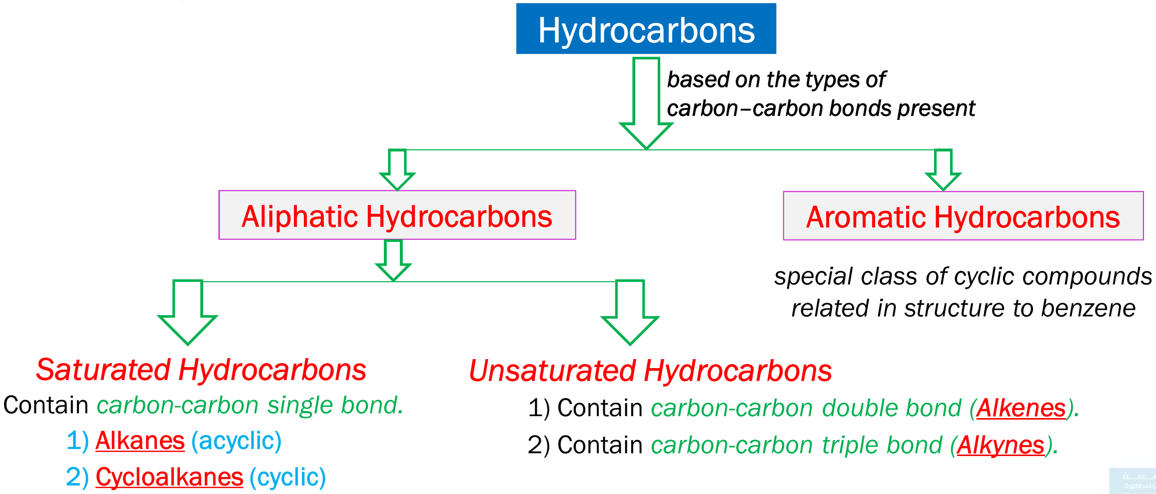
HYDROCARBONES



HYDROCARBONS

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



Hydrocarbons

based on the types of carbon–carbon bonds present

Aliphatic Hydrocarbons

Aromatic Hydrocarbons

special class of cyclic compounds related in structure to benzene

Saturated Hydrocarbons

Contain *carbon-carbon single bond.*

1) Alkanes (acyclic)

2) Cycloalkanes (cyclic)

Unsaturated Hydrocarbons

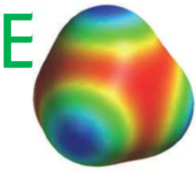
1) Contain *carbon-carbon double bond (Alkenes).*

2) Contain *carbon-carbon triple bond (Alkynes).*

CHAPTER 2

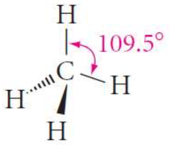
SATURATED HYDROCARBONES

ALKANES AND CYCLOALKANE

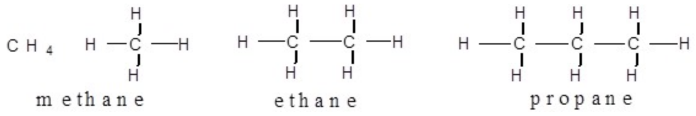


THE STRUCTURES OF ALKANES

- 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.



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_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

- *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_2- 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.*

THE STRUCTURES OF ALKANES

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

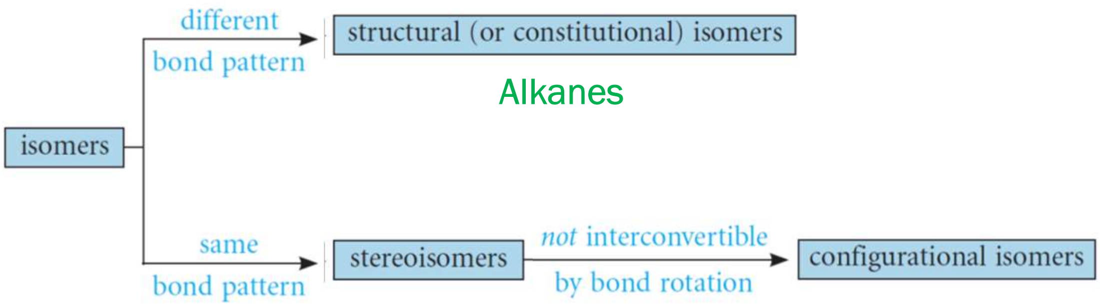
PROBLEM 2.2 What is the molecular formula of an alkane with 12 carbon atoms?

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



Alkanes

Cycloalkanes
& Alkenes

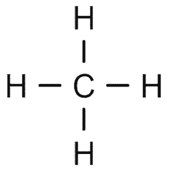
THE STRUCTURES OF ALKANES

ISOMERISM

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

CH_4

Methane



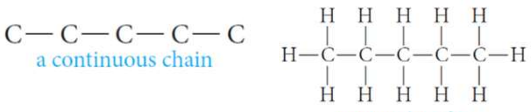
- Isomers are molecules with the same number and kinds of atoms but different arrangements of the atoms.
- Structural (or constitutional) isomers are compounds that have the same molecular formula, but different structural formulas.

THE STRUCTURES OF ALKANES

ISOMERISM

Writing Structural Formulas

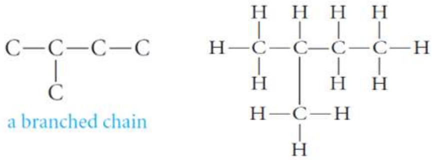
- Suppose we want to write out all possible structural formulas that correspond to the molecular formula C_5H_{12}.
  - We begin by writing all five carbons in a continuous chain.



a continuous chain

pentane, bp 36°C

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



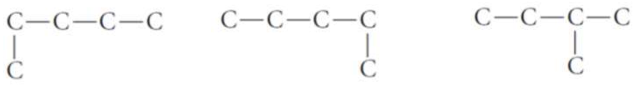
a branched chain

2-methylbutane, bp 28°C
(isopentane)

THE STRUCTURES OF ALKANES

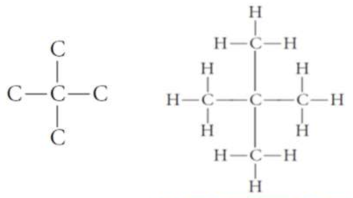
ISOMERISM

- 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 C_5H_{12}.

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

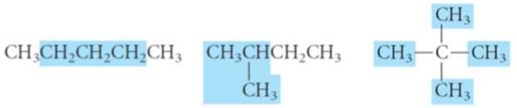


2,2-dimethylpropane, bp 10°C
(neopentane)

THE STRUCTURES OF ALKANES

ISOMERISM

- Three (and only three) different structural formulas that correspond to the molecular formula C_5H_{12},
  - n-pentane (n for normal, with an unbranched carbon chain),
  - Isopentane
  - neopentane.



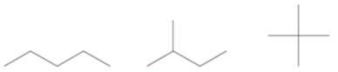
$CH_3CH_2CH_2CH_2CH_3$ n-pentane

$CH_3CHCH_2CH_3$ with CH_3 below: isopentane

$CH_3\text{—}C\text{—}CH_3$ with CH_3 above and below: neopentane

a single line formula $CH_3(CH_2)_3CH_3$ n-pentane $(CH_3)_2CHCH_2CH_3$ isopentane $(CH_3)_4C$ neopentane

a line-segment formula

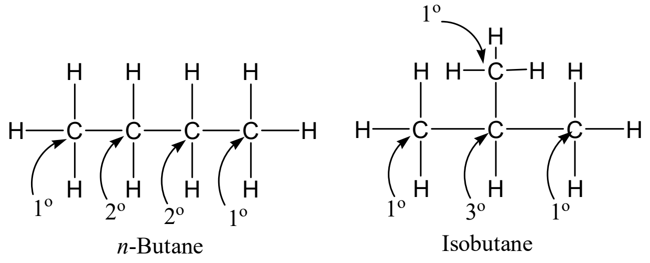


n-pentane isopentane neopentane

THE STRUCTURES OF ALKANES

CLASSES OF CARBONS AND HYDROGEN

- 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.



n-Butane Isobutane

- Hydrogens are also referred to as 1°, 2°, or 3° 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.

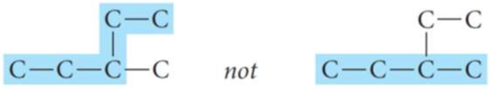
9. If two or more different types of substituents are present, they are listed alphabetically, except that prefixes such as *di-* and *tri-* are not considered when alphabetizing.

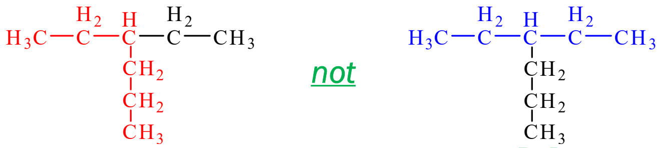
10. Punctuation is important when writing IUPAC names.
    - IUPAC names for hydrocarbons are written as one word.
    - Numbers are separated from each other by commas and are separated from letters by hyphens.
    - There is no space between the last named substituent and the name of the parent alkane that follows it.

IUPAC RULES FOR NAMING ALKANES

1. Locate the longest continuous carbon chain.

   This gives the name of the *parent hydrocarbon*.





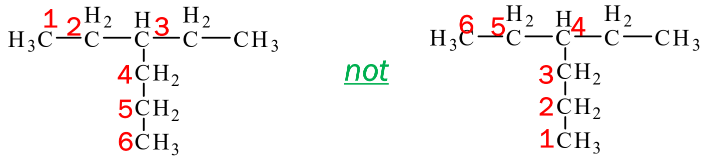
Ethylhexane

Propylpentane

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.

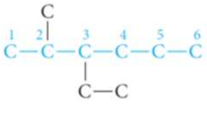


3-Ethyl hexane

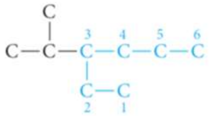
4-Ethyl hexane

IUPAC RULES FOR NAMING ALKANES

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

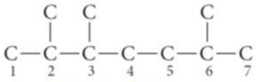


two branches

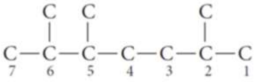


one branch

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

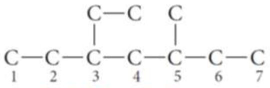


2,3,6-trimethylheptane

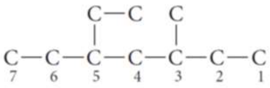


2,5,6-trimethylheptane

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



3-ethyl-5-methylheptane



5-ethyl-3-methylheptane

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 (-).

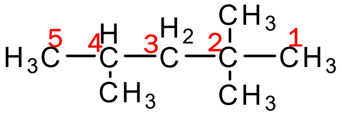
3) The combined name of the substituent (ethyl).

4) The parent carbon chain (hexane)

3 -Ethylhexane

IUPAC RULES FOR NAMING ALKANES

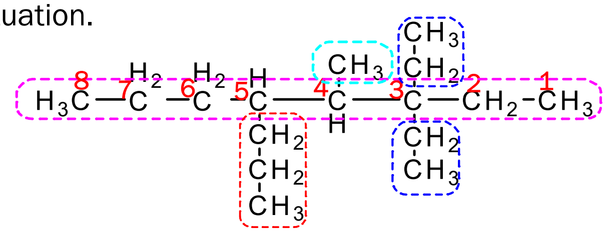
3. If the same alkyl substituent occurs more than once on the parent carbon chain, the prefixes di-, tri-, tetra-, penta-, and so on are used to indicate two, three, four, five, and so on.



$H_3C-CH(CH_3)-CH_2-C(CH_3)_2-CH_3$

2,2,4-Tri methylpentane

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



$H_3C-CH_2-CH_2-CH(CH_2CH_2CH_3)-CH(CH_3)-C(CH_2CH_3)_2-CH_2-CH_3$

3,3- diethyl

4- methyl

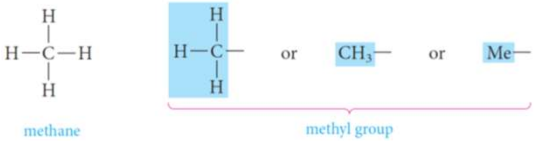
5- propyl

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.

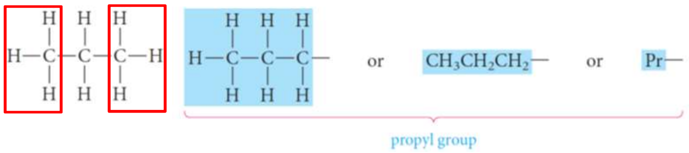
CH_3CH_3 CH_3CH_2— or C_2H_5— or Et—

ethane ethyl group

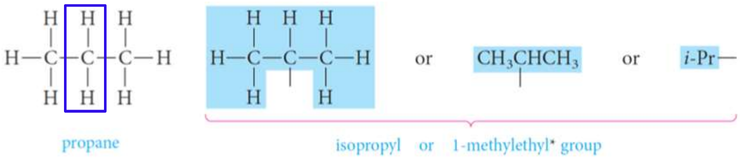
IUPAC RULES FOR NAMING ALKANES

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**.



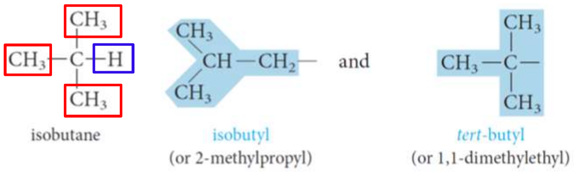
IUPAC RULES FOR NAMING ALKANES

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.



IUPAC RULES FOR NAMING ALKANES

ALKYL AND HALOGEN SUBSTITUENTS

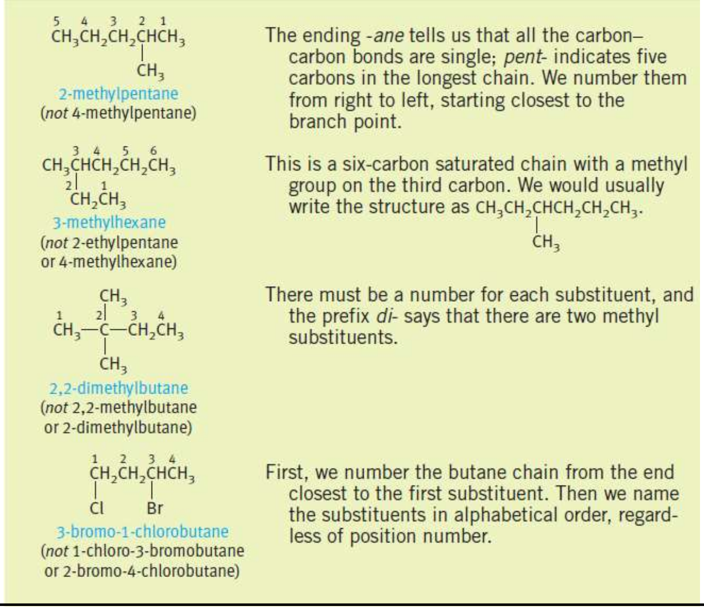
○ The formula R - Cl stands for any alkyl chloride (methyl chloride, ethyl chloride, and so on).

○ Halogen substituents are named by changing the *-ine* ending of the element to *-o*.

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

IUPAC RULES FOR NAMING ALKANES

EXAMPLES



$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H\overset{1}{C}H_3$ (with CH_3 on C-2)

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.

$CH_3\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$ (with $\overset{2}{C}H_2\overset{1}{C}H_3$ on C-3)

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 $CH_3CH_2CHCH_2CH_2CH_3$ (with CH_3 below CH).

$\overset{1}{C}H_3—\overset{2}{C}(CH_3)_2—\overset{3}{C}H_2\overset{4}{C}H_3$

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.

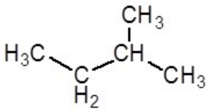
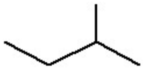
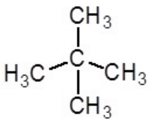
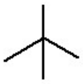
$\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H\overset{4}{C}H_3$ (with Cl on C-1 and Br on C-3)

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

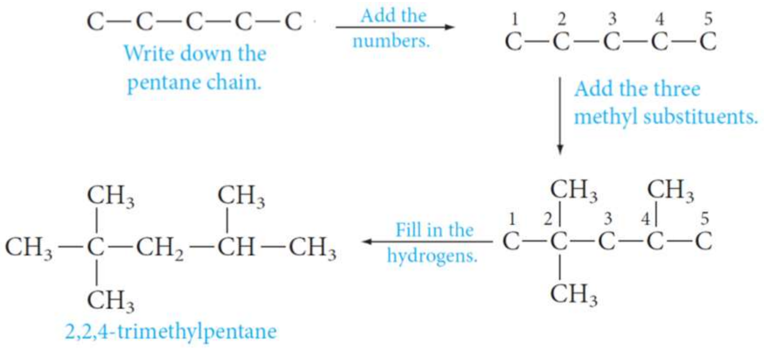
EXAMPLES

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

IUPAC RULES FOR NAMING ALKANES

EXAMPLES

Write the formula for 2,2,4-trimethylpentane



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;

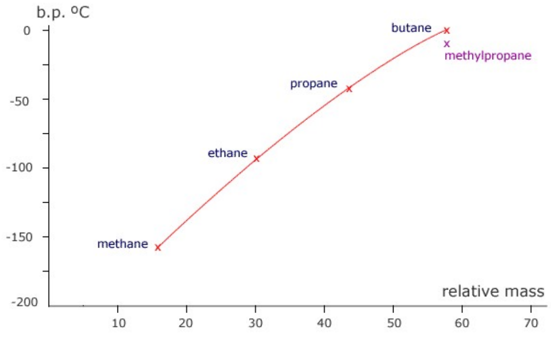
      carbon tetrachloride, CCl_4 and benzene,
    - Alkanes are insoluble in polar solvents like water.

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.



Graph showing boiling point of the alkanes against relative mass

- 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.

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

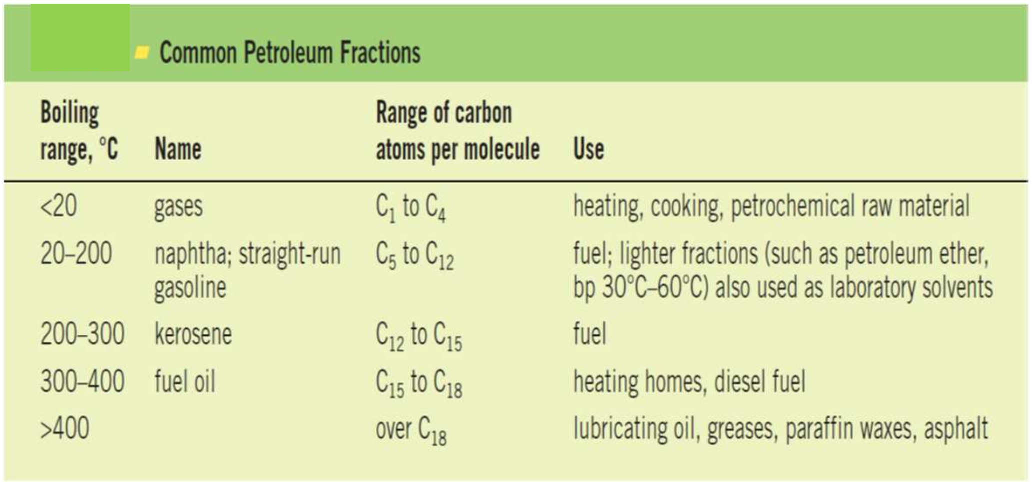
- Refining is a process done by distilling the petroleum into fractions of different boiling and then treating the distilled petroleum in various ways to remove the undesirable components.
- The most volatile components come out first

  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_1 to C_4	heating, cooking, petrochemical raw material
20–200	naphtha; straight-run gasoline	C_5 to C_{12}	fuel; lighter fractions (such as petroleum ether, bp 30°C–60°C) also used as laboratory solvents
200–300	kerosene	C_{12} to C_{15}	fuel
300–400	fuel oil	C_{15} to C_{18}	heating homes, diesel fuel
>400		over C_{18}	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).

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, $(C_2H_5)_4$ 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.

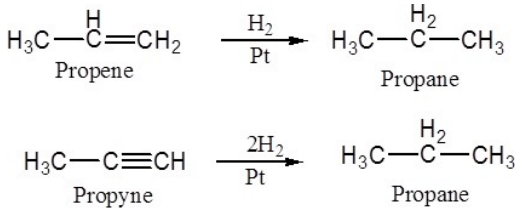
SOURCES OF ALKANES

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^3) of liquefied gas is equivalent to about 600 m^3 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.

PREPARATION OF ALKANES

1. Hydrogenation of unsaturated hydrocarbon:



$$H_3C-\overset{H}{C}=CH_2 \xrightarrow[Pt]{H_2} H_3C-\overset{H_2}{C}-CH_3$$

Propene Propane

$$H_3C-C\equiv CH \xrightarrow[Pt]{2H_2} H_3C-\overset{H_2}{C}-CH_3$$

Propyne Propane

2. Hydrolysis of Grignard reagent

$$CH_3CH_2Br + Mg^{2+} \xrightarrow{\text{Dry ether}} CH_3CH_2MgBr$$

Grignard reagent

$$CH_3CH_2MgBr \xrightarrow{H_3O^+} CH_3CH_3 + Mg(OH)Br$$

PREPARATION OF ALKANES

3. Reduction of Alkyl halides By lithium dialkyl cuprate

$$(CH_3CH_2)_2CuLi + CH_3Br \longrightarrow CH_3CH_2CH_3$$

4. The Wurtz reaction

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

$$2R\text{-}X + 2Na \longrightarrow R\text{-}R + 2Na^+X^-$$

$$2\ H_3C\text{—}Br + 2\ Na \longrightarrow H_3C\text{—}CH_3 + 2\ NaBr$$

PREPARATION OF ALKANES

5. From carboxylic acids

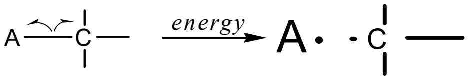
- ○ Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid.

$$\underset{\text{Sodium ethanoate}}{CH_3COO^-Na^+} + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

- ○ Decarboxylation; This process of elimination of carbon dioxide from a carboxylic acid.

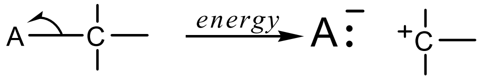
NOTATIONS FOR BOND BREAKING AND BOND MAKING

- **A covalent bond can be broken in either two ways,**
  - Homolytic cleavage.

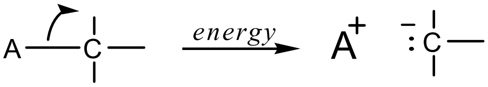


Free radicals

  - Heterolytic cleavage.



Carbocation

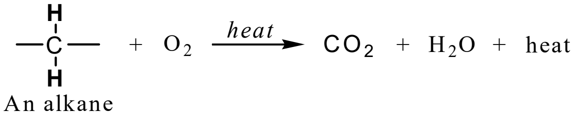


Carboanion

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.

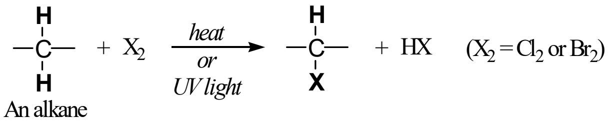
Combustion



$$-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}- + O_2 \xrightarrow{heat} CO_2 + H_2O + \text{heat}$$

An alkane

Halogenation



$$-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}- + X_2 \xrightarrow[UV\ light]{heat\ or} -\overset{\text{H}}{\underset{\text{X}}{\text{C}}}- + HX \quad (X_2 = Cl_2 \text{ or } Br_2)$$

An alkane

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

$$C_nH_{2n+2} + \frac{3n+1}{2} O_2 \longrightarrow n\,CO_2 + (n+1)\,H_2O + \textbf{\textit{heat}}$$

- Examples

$$\underset{\text{Methane}}{CH_4} + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + \textbf{\textit{213}}\text{ kcal/mole}$$

$$\underset{\text{Ethane}}{C_2H_6} + 7/_2\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O + \textbf{\textit{373}}\text{ kcal/mole}$$

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

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.

$$\underset{\text{Methane}}{CH_4} + 3\,O_2 \longrightarrow 2\,CO + 4\,H_2O$$

$$\underset{\text{Methane}}{CH_4} + O_2 \longrightarrow C + 2H_2O$$

$$\underset{\text{Methane}}{CH_4} + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + \textbf{\textit{213}}\text{ kcal/mole}$$

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,

$$R{-}H + Cl{-}Cl \xrightarrow[\text{heat}]{\text{light or}} R{-}Cl + H{-}Cl$$ chlorination.

$$R{-}H + Br{-}Br \xrightarrow[\text{heat}]{\text{light or}} R{-}Br + HBr$$ bromination

- Flourine reacts explosively with alkanes

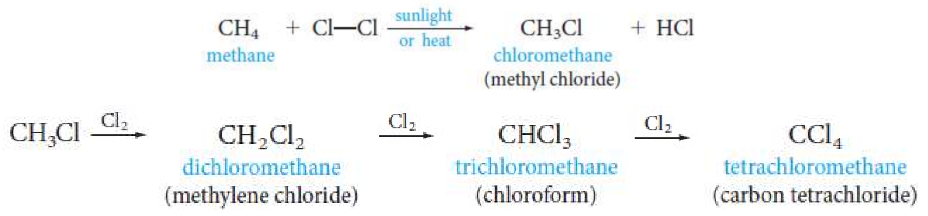
  It is unsuitable reagent for the preparation of the alkyl fluorides.
- Iodine is too unreactive

  It is not used in the halogenation of alkanes.

REACTIONS OF ALKANES

2) HALOGENATION OF ALKANES

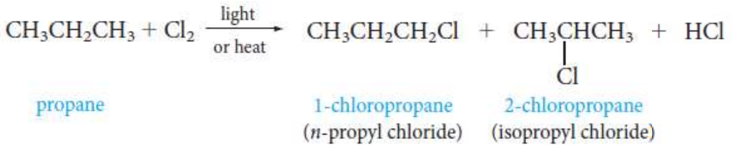
- If excess halogen is present, the reaction can continue further to give polyhalogenated products.



$$CH_4 + Cl{-}Cl \xrightarrow[\text{or heat}]{\text{sunlight}} CH_3Cl + HCl$$

$$CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

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



$$CH_3CH_2CH_3 + Cl_2 \xrightarrow[\text{or heat}]{\text{light}} CH_3CH_2CH_2Cl + CH_3CH(Cl)CH_3 + HCl$$

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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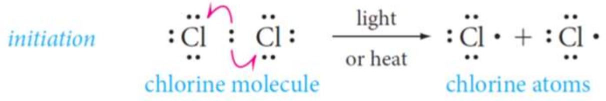
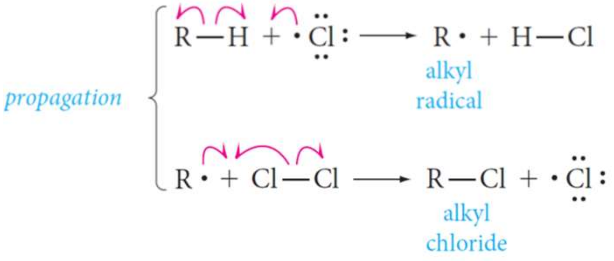
2) HALOGENATION OF ALKANES

The Free-Radical Chain Mechanism of Halogenation

1) Chain-initiation step;



2) Chain-propagating step;

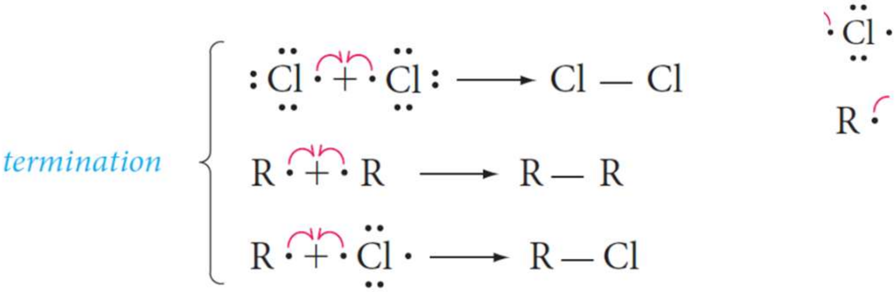


REACTIONS OF ALKANES

2) HALOGENATION OF ALKANES

The Free-Radical Chain Mechanism of Halogenation

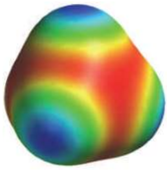
3) Chain-termination step;



CHAPTER 2

SATURATED HYDROCARBONES

CYCLOALKANES



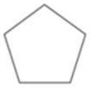
CYCLOALKANES

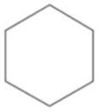
CYCLOALKANE NOMENCLATURE

- 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.


cyclopropane
bp −32.7°C


cyclobutane
bp 12°C


cyclopentane
bp 49.3°C


cyclohexane
bp 80.7°C

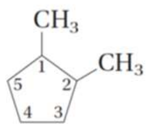
CYCLOALKANES

CYCLOALKANE NOMENCLATURE

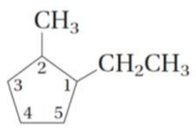
- Alkyl or halogen substituents attached to the rings are named in the usual way.
- If only one substituent is present, no number is needed to locate it.
- If there are several substituents, numbers are required.

  With different substituents, the one with highest alphabetic priority is located at carbon 1.

methylcyclopentane
(*not* 1-methylcyclopentane)



1,2-dimethylcyclopentane
(*not* 1,5-dimethylcyclopentane)

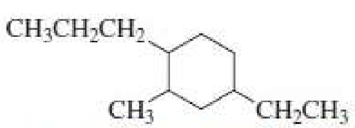


1-ethyl-2-methylcyclopentane
(*not* 2-ethyl-1-methylcyclopentane)

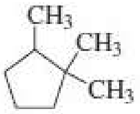
CYCLOALKANES

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.



4-ethyl-2-methyl-1-propylcyclohexane
not
1-ethyl-3-methyl-4-propylcyclohexane
because 2 < 3
not
5-ethyl-1-methyl-2-propylcyclohexane
because 4 < 5

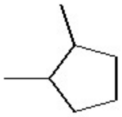


1,1,2-trimethylcyclopentane
not
1,2,2-trimethylcyclopentane
because 1 < 2
not
1,1,5-trimethylcyclopentane
because 2 < 5

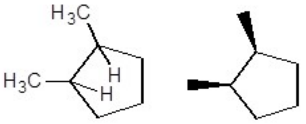
CYCLOALKANES

cis-trans ISOMERISM IN CYCLOALKANES

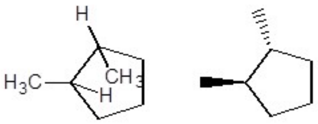
cis–trans isomerism (sometimes called **geometric isomerism**) is one kind of stereoisomerism.



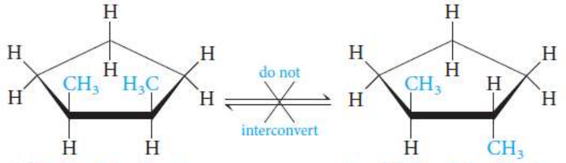
1,2-Dimethylcyclopentane



cis-1,2-Dimethylcyclopentane



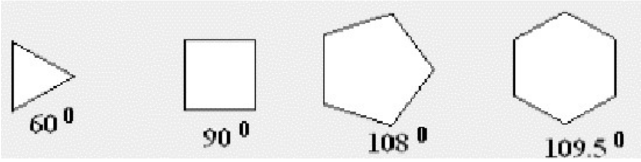
trans-1,2-Dimethylcyclopentane



cis-1,2-dimethylcyclopentane *trans*-1,2-dimethylcyclopentane

RING STRAIN

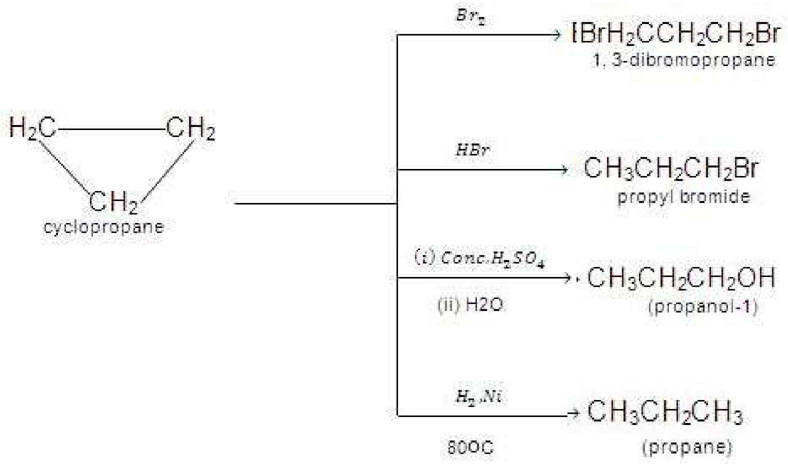
- Ring Strain is a type of instability that exists when bonds in a molecule form angles that are abnormal.
- Baeyer suggested that the stability of a cycloalkane could be predicted by determining how close the bond angle of a planar cycloalkane is to the ideal tetrahedral bond angle of 109.5°.



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

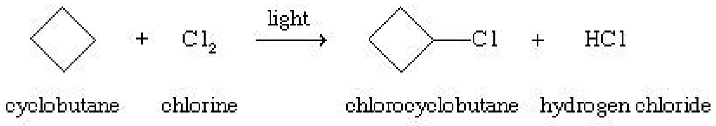
REACTIONS OF CYCLOALKANES

- **Less stable rings; ring opening due to ring strain**



REACTIONS OF CYCLOALKANES

- **Less stable rings;** ring opening due to ring strain



- **More stable 5 and 6 rings**