Organic Chemistry
CHEM 145

2 Credit hrs

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HYDROCARBONS

Hydrocarbons

- **Hydrocarbons** are Organic Compounds, which contain only the two elements **carbon** and **hydrogen**.

Hydrocarbons

- **Aliphatic Hydrocarbons**
  - *Saturated*
    - **Alkanes**
      Contain *carbon-carbon single bond.*
  - *Unsaturated*
    1. **Alkenes**
       Contain *carbon-carbon double bond.*
    2. **Alkynes**
       Contain *carbon-carbon triple bond.*
- **Aromatic Hydrocarbons**
  benzene-like in its properties

Saturated Hydrocarbons
Alkanes

- General formula is C_nH_{2n+2}
- Names and Molecular formulas of the first ten Alkanes

Name	Molecular Formula
Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}
Heptane	C_7H_{16}
Octane	C_8H_{18}
Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$

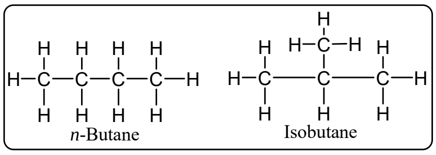
Structural Isomerism

- Isomers are different compounds with identical molecular formulas.

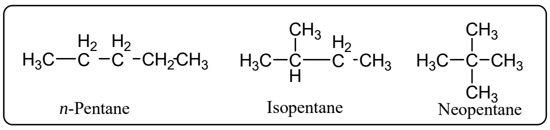
  The phenomenon is called *isomerism*.

- Structural or constitutional isomers are isomers which differ in the sequence of atoms bonded to each other.

- Examples:
  - Butanes, C_4H_{10}.



  - Pentanes, C_5H_{12}.



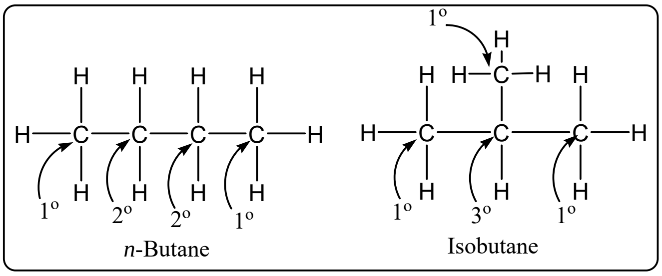
Structural Isomerism

- Number of Possible Structural Isomers of Alkanes.

Name	Molecular Formula	Number of isomers
Methane	CH_4	1
Ethane	C_2H_6	1
Propane	C_3H_8	1
Butane	C_4H_{10}	2
Pentane	C_5H_{12}	3
Hexane	C_6H_{14}	5
Heptane	C_7H_{16}	9
Octane	C_8H_{18}	18
Nonane	C_9H_{20}	35
Decane	$C_{10}H_{22}$	75

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.

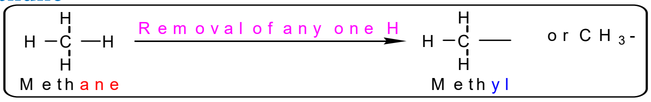


- Hydrogens are also referred to as 1°, 2°, or 3° according to the type of carbon they are bonded to.

Alkyl Groups

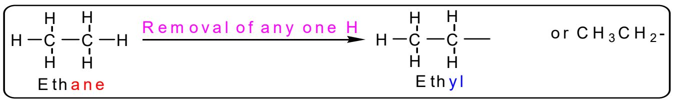
- An alkyl group is an alkane from which a hydrogen has been removed.
- General formula C_nH_{2n+1}.
- Alky group is represented by R.
- Nomenclature of alkyl groups by replacing the suffix *–ane* of the parent alkane by *–yl*.
  i.e. Alkane – ane + yl = Alkyl
- Examples:

Methane



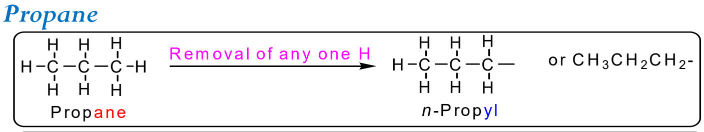
CH_3- (Methane – ane + yl) = methyl

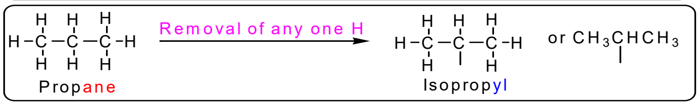
Ethane



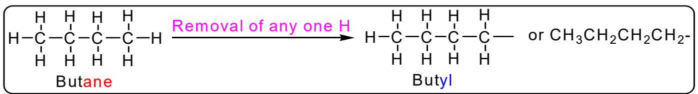
CH_3CH_2- (Ethane – ane + yl) = ethyl

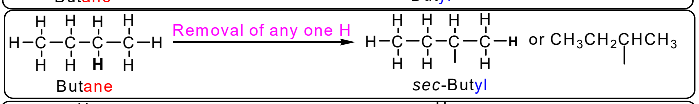
Propane

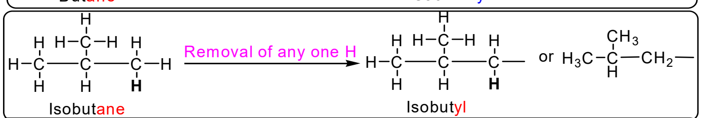


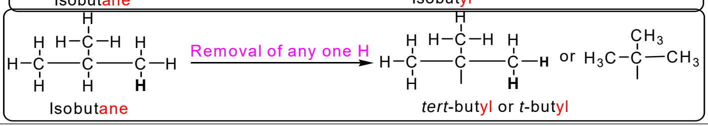


Butane







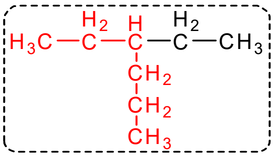


The IUPAC System of Nomenclature

- Most organic compounds are known by two or more names:
  - The older unsystematic names, (*Common names*).
  - The IUPAC names.
- IUPAC: International Union of Pure & Applied Chemistry

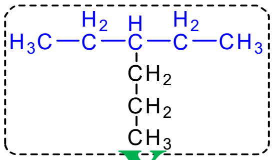
The IUPAC Rules

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



Ethylhexane

not



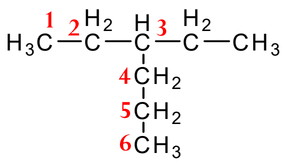
Propylpentane X

the longest continuous chain is not necessarily straight.

The IUPAC Rules

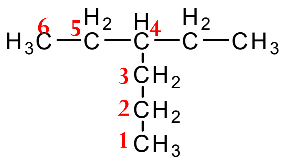
2) Number the carbons in the parent chain

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



3-Ethyl hexane

not



4-Ethyl hexane X

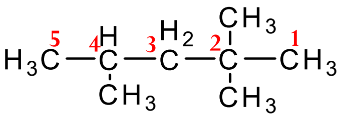
To name the compound;

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

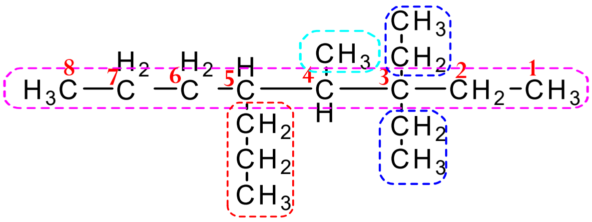
The IUPAC Rules

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

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



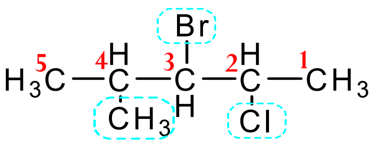
3,3-diethyl
4-methyl
5-*n*-propyl

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

The IUPAC Rules

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

-F fluoro	$-NO_2$ nitro
-Cl chloro	NH_2 amino
-Br bromo	-CN cyano
-I iodo	



2- chloro
3- bromo
4- methyl

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

Physical Properties of Alkanes

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

A. Physical States

- 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.

B. Solubility

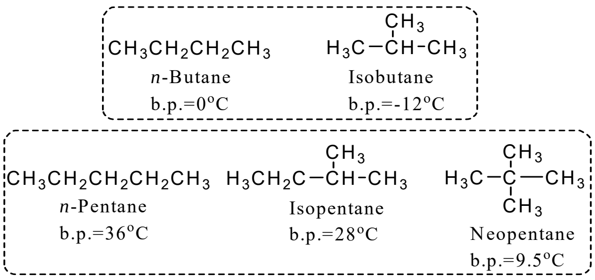
- Alkanes are nonpolar compounds.
- Their solubility " Like dissolve like"
- Alkanes are soluble in the nonpolar solvents;
  - carbon tetrachloride, CCl_4 and benzene,
- Alkanes are insoluble in polar solvents like water.

C. Melting Points

- Melting point increase with increasing molecular weight.

D. Boiling Points

- The boiling 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.
- For the very small alkanes, the boiling point rises 20-30°C for each addition of a carbon atom to the chain.
- 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 and natural gas constitute the chief sources of
    - Alkanes up to 40 Carbons
    - Aromatic,
    - Alicyclic (Cyclic aliphtic hydrocarbons)
    - Heterocyclic

Preparation of Alkanes

1. Hydrogenation of unsaturated hydrocarbon:

$$H_2C{=}CH_2 \xrightarrow[200,\ 300]{\text{Ni or Pd or Pt / } H_2} H_3C{-}CH_3$$

2. Reduction of Alkyl halides By lithium dialkyl cuprate

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

3. The Wurtz reaction

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

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

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

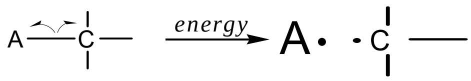
4. Hydrolysis of Grignard reagent

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

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

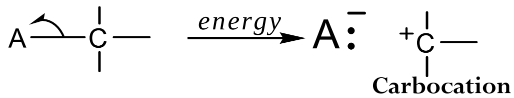
Notations for Bond Breaking and Bond Making

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

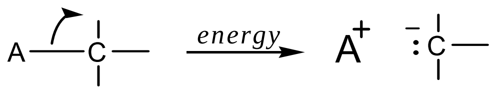


Free radicals

  - **Heterolytic cleavage.**



Carbocation

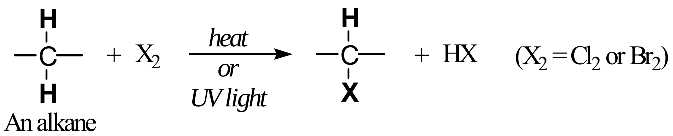


Carboanion

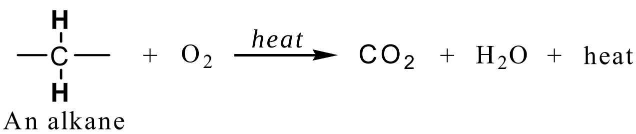
Reactions of Alkanes

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

Halogenation



Combustion

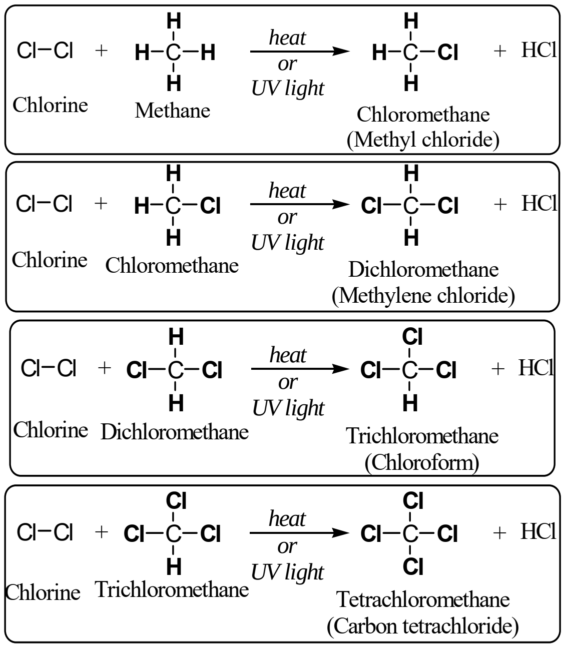


Reactions of Alkanes

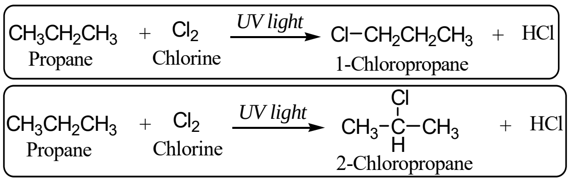
A. Halogenation

- **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

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



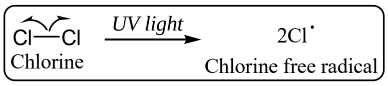
- Both methane and ethane give only one monochlorinated product because in each compound all hydrogen atoms are equivalent.
- When propane is chlorinated,
  two monochlorinated products;
  1-chloropropane and 2-chloropropane.



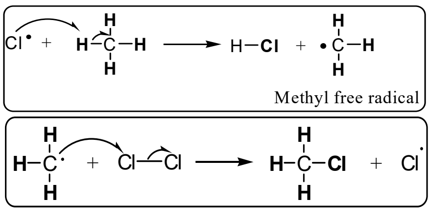
Mechanism of Halogenation of Alkanes

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

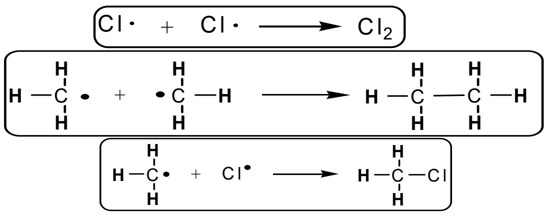
1) Chain-initiation step;



2) Chain-propagating step;



3) Chain-termination step;



B. Combustion of Alkanes

- When ignited in the presence of excess oxygen,
  Alkanes are oxidized to
  Carbon dioxide and Water and heat is liberated.
- General equation

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

- Examples

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

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

$$\underset{\text{Propane}}{C_3H_8} + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O + 531 \text{ kcal/mole}$$

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

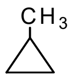
- The incomplete combustion of alkanes.
  liberates poisons carbon monoxide (CO) or carbon.
  both are major contributors to air pollution.

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

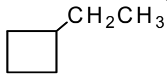
$$\underset{\text{Methane}}{CH_4} + O_2 \longrightarrow C + 2H_2O$$

Cycloalkanes: Nomenclature

- Cycloalkanes are saturated hydrocarbons that exist in the form of a ring.
- Cycloalkanes are named by adding the prefix *cyclo-* to the name of the open-chain hydrocarbon.
- For example;
  three-carbon cycloalkane is called cyclopropane.
  four-carbon cycloalkane called cyclobutane.
- When only one substituent is attached to the ring,
  the substituent first and then name the ring.

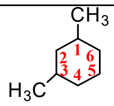


Methylcyclopropane

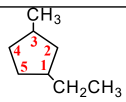


Ethylcyclobutane

- If two or more substituents are attached to the ring.
  their positions are specified by numbers.



1,3-Dimethylcyclohexane



1-Ethyl-3-methylcyclopentane

Ring Strain

- Compounds with five- and six-membered rings were more stable than compounds with three- or four-membered rings.
- In 1885, the German chemist Adolf von Baeyer proposed that the instability of three- and four-membered rings was due to angle strain.
- We know that, ideally, an hybridized carbon has bond angles of 109.5°.

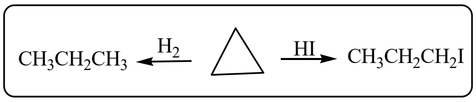
  Baeyer suggested that the stability of a cycloalkane could be predicted by determining how close the bond angle of a planar cycloalkane is to the ideal tetrahedral bond angle of 109.5°.

  The angles in an equilateral triangle are 60°. The bond angles in cyclopropane, therefore, are compressed from the ideal bond angle of 109.5° to 60°, a 49.5° deviation.

  This deviation of the bond angle from the ideal bond angle causes strain called angle strain.

Reactions of Cycloalkanes

- **Less stable rings**



- **More stable 5 and 6 rings**