Organic Chemistry
244 CHEM

Hydrocarbons

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Hydrocarbons

- **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} (saturated)

    Contain *carbon-carbon single bond.*

    Cycloalkanes: C_nH_{2n} (saturated)

    (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.

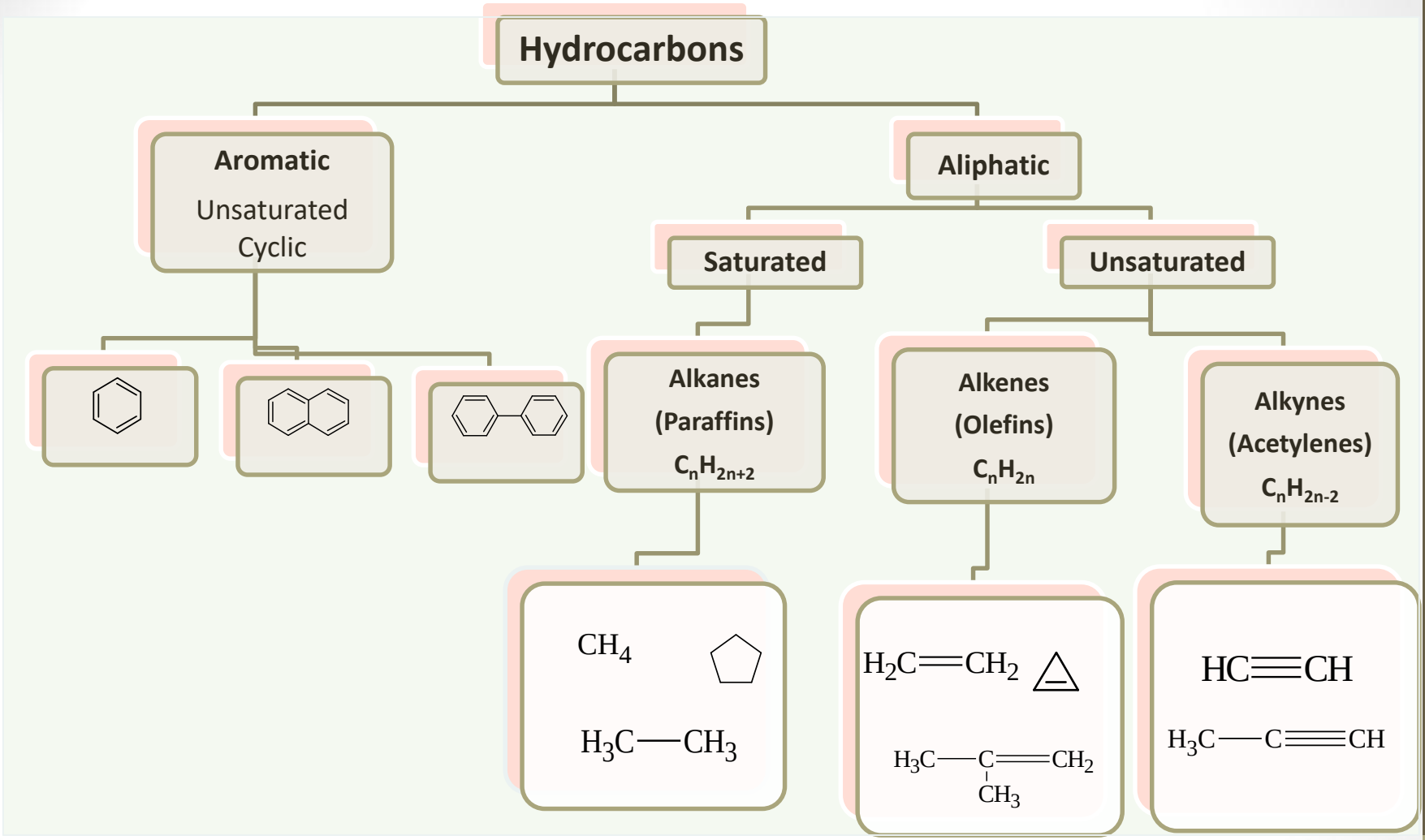
Unsaturated hydrocarbons

1. **Alkenes : C_nH_{2n}**

   Contain *carbon-carbon double bond.*

2. **Alkynes : $C_n\ H_{2n-2}$**

   Contain *carbon-carbon triple bond.*


Hydrocarbons
Aromatic
Unsaturated
Cyclic
Aliphatic
Saturated
Unsaturated
Alkanes
(Paraffins)
C_nH_{2n+2}
Alkenes
(Olefins)
C_nH_{2n}
Alkynes
(Acetylenes)
C_nH_{2n-2}
CH_4
$H_3C—CH_3$
$H_2C=CH_2$
$H_3C—C(CH_3)=CH_2$
$HC\equiv CH$
$H_3C—C\equiv CH$

Saturated Hydrocarbons
Alkanes

General formula is C_nH_{2n+2}

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	$C_{10}H_{22}$

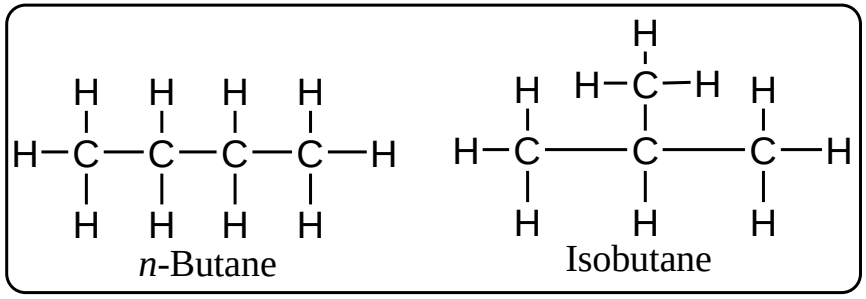
Structural Isomerism

- **Isomers** are different compounds with identical molecular formulas.

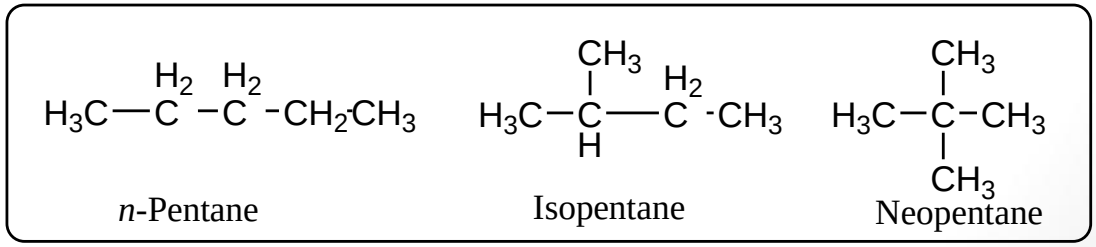
  The phenomenon is called *isomerism*.

- **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

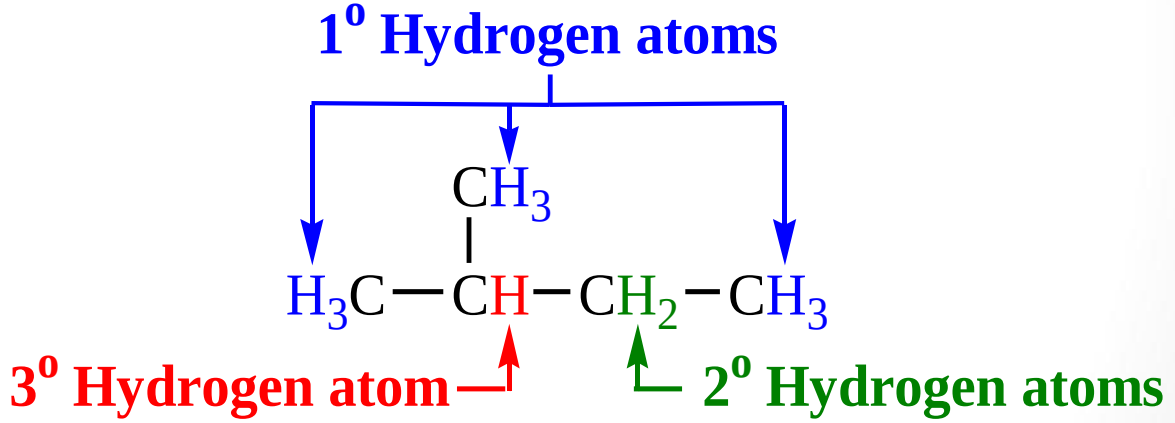
Number of Possible Structural Isomers of Alkanes.

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.

Primary (1°),
Secondary (2°),
Tertiary (3°):



- **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**

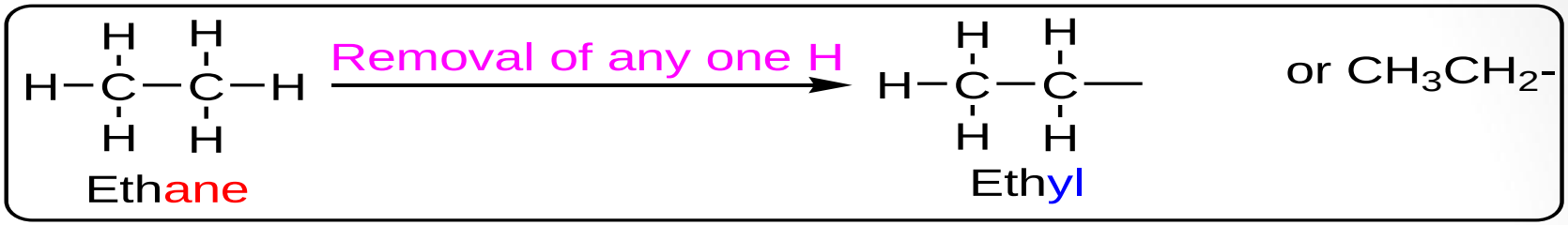
  replacing the suffix *–ane* of the parent alkane by *–yl*.

  i.e. Alkane – ane + yl = Alkyl
- **Examples:**
  - *Methane*

CH_3- (Methane – ane + yl) = methyl

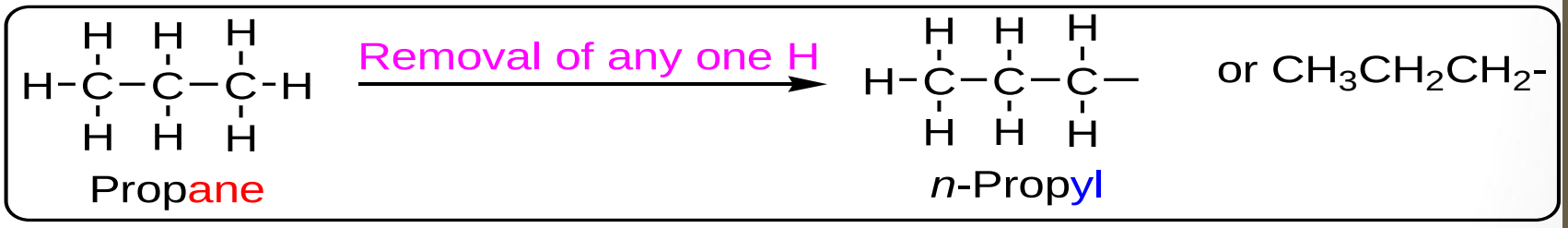
Alkyl Groups

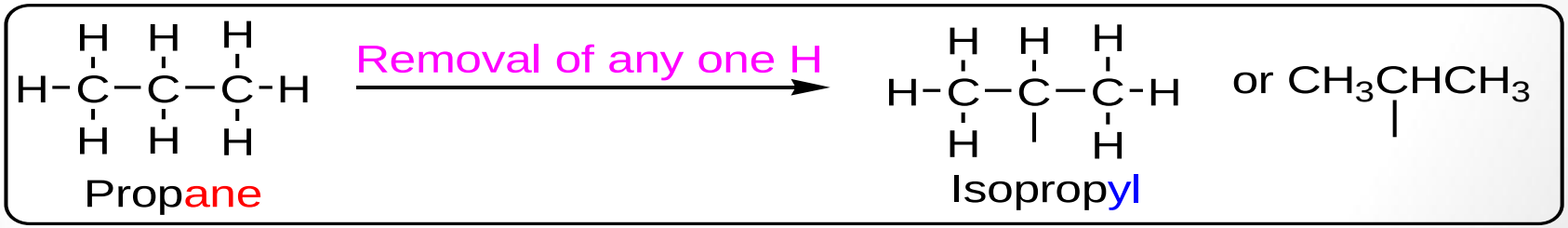
Ethane



CH_3CH_2- (Ethane – ane + yl) = ethyl

Propane

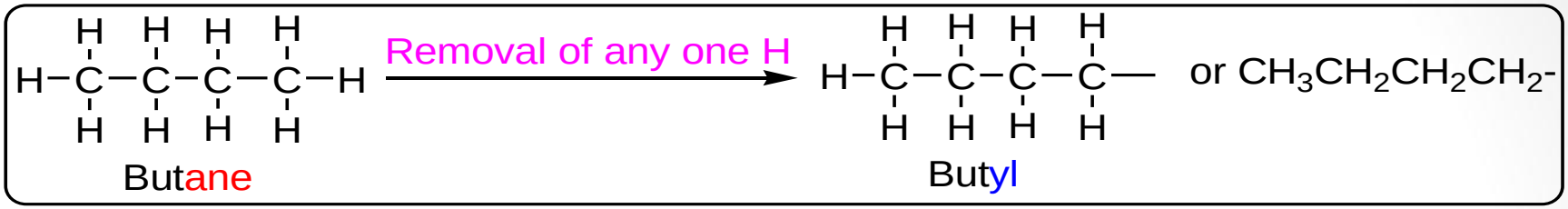


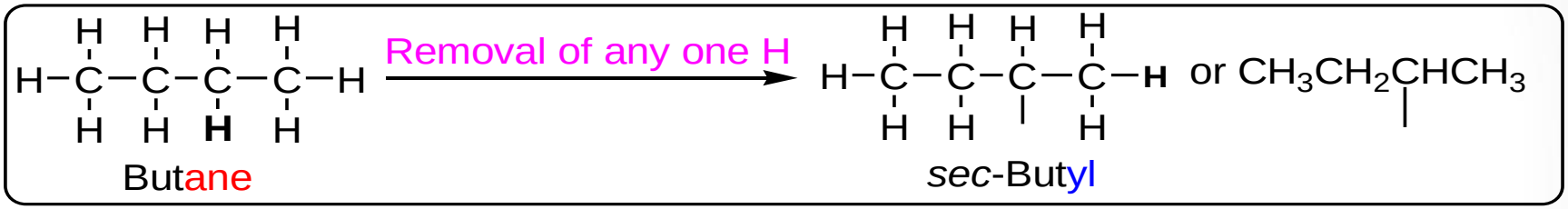


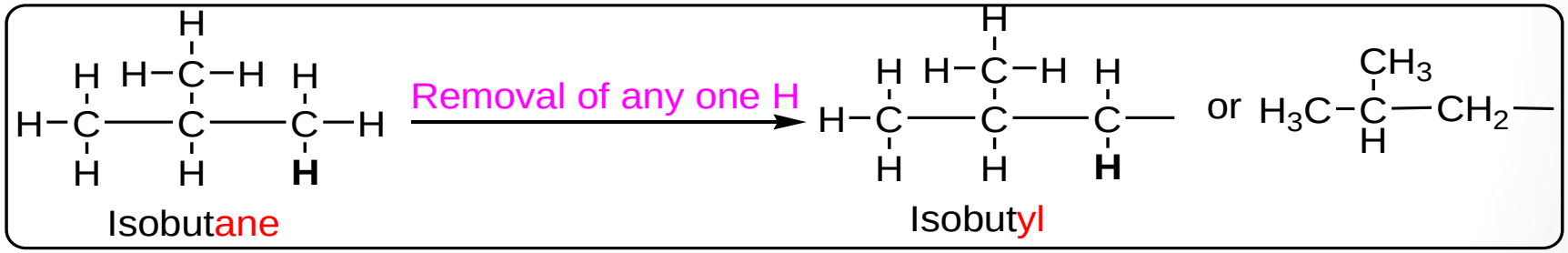
Propane – ane + yl = *n*-propyl or isopropyl

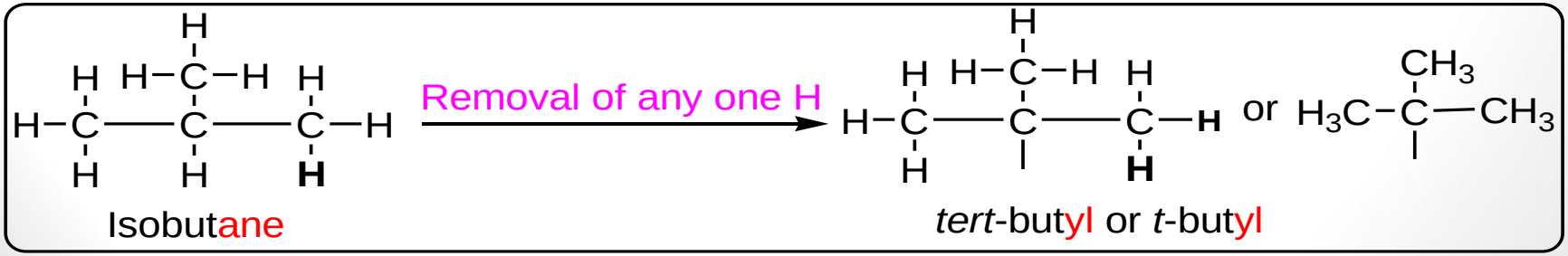
Alkyl Groups

Butane









Alkane		Alkyl Group	Abbreviation
$CH_3—H$ **Methane**	becomes	$CH_3—$ **Methyl**	Me–
$CH_3CH_2—H$ **Ethane**	becomes	$CH_3CH_2—$ **Ethyl**	Et–
$CH_3CH_2CH_2—H$ **Propane**	becomes	$CH_3CH_2CH_2—$ **Propyl**	Pr–
$CH_3CH_2CH_2CH_2—H$ **Butane**	becomes	$CH_3CH_2CH_2CH_2—$ **Butyl**	Bu–

The IUPAC System of Nomenclature

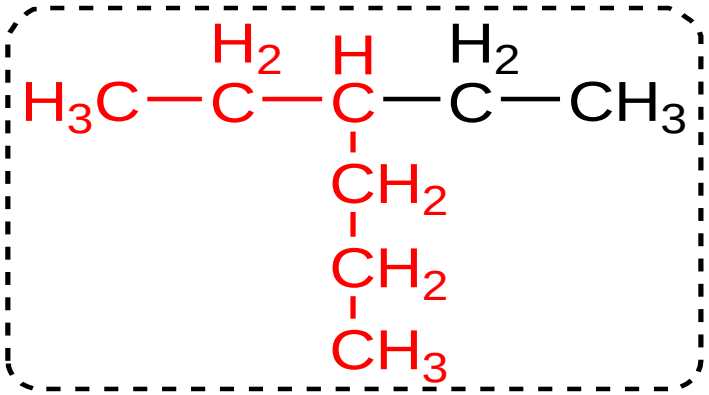
- Most organic compounds are known by two or more names:
  - The older unsystematic names, (*Common names*).
  - The IUPAC names.
- **IUPAC**

  International Union of Pure & Applied Chemistry

The IUPAC Rules

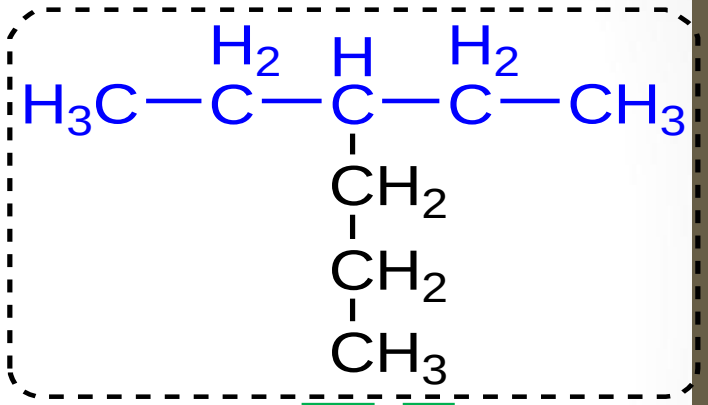
1) Select the parent structure .

the longest continuous chain



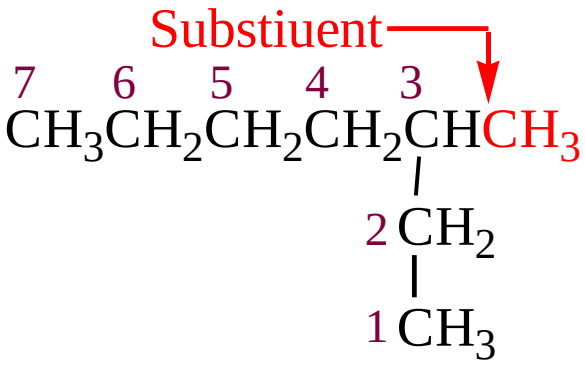
Ethylhexane

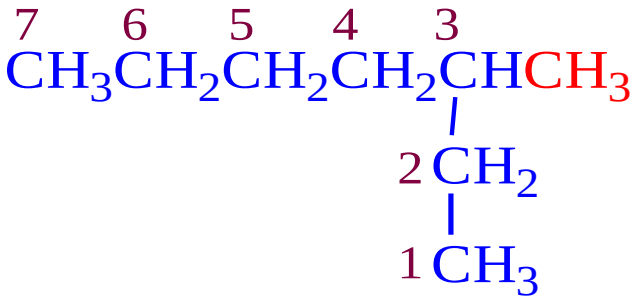
not



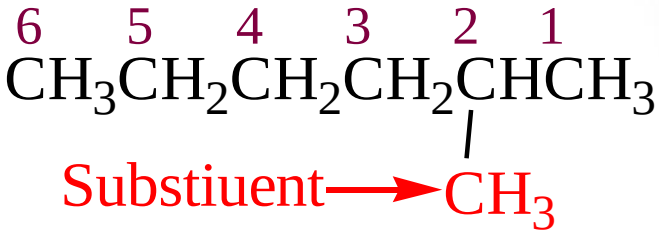
Propylpentane

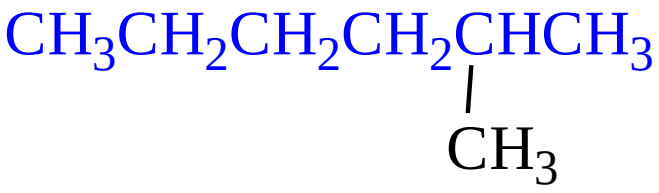
the longest continuous chain is not necessarily straight.





3-Methylheptane



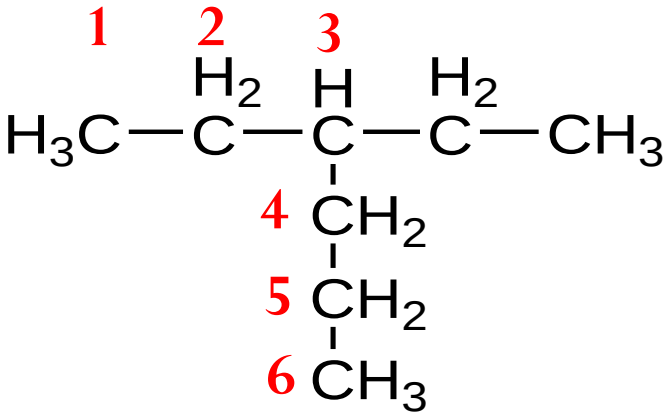


2-Methylpentane

The IUPAC Rules

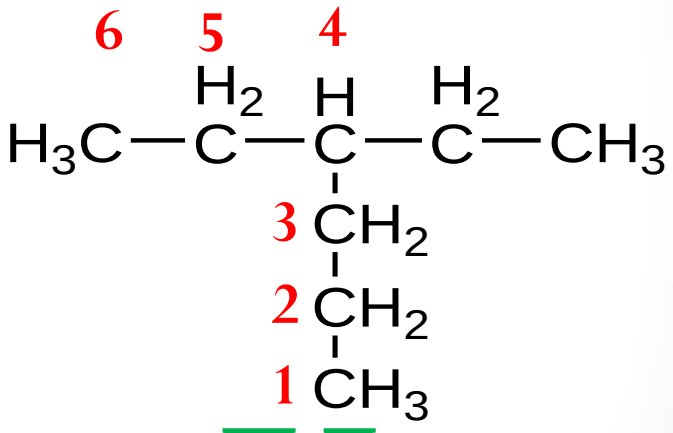
2) Number the carbons in the parent chain

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



3-Ethyl hexane

not



4-Ethyl hexane

X

The IUPAC Rules

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)

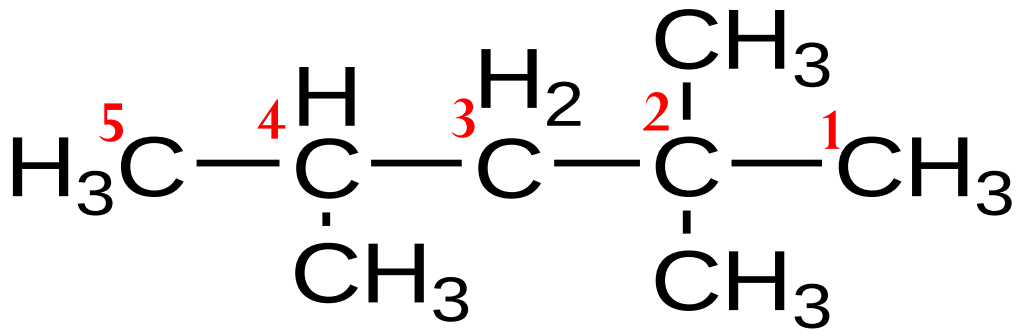
3 - Ethyl hexane

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.

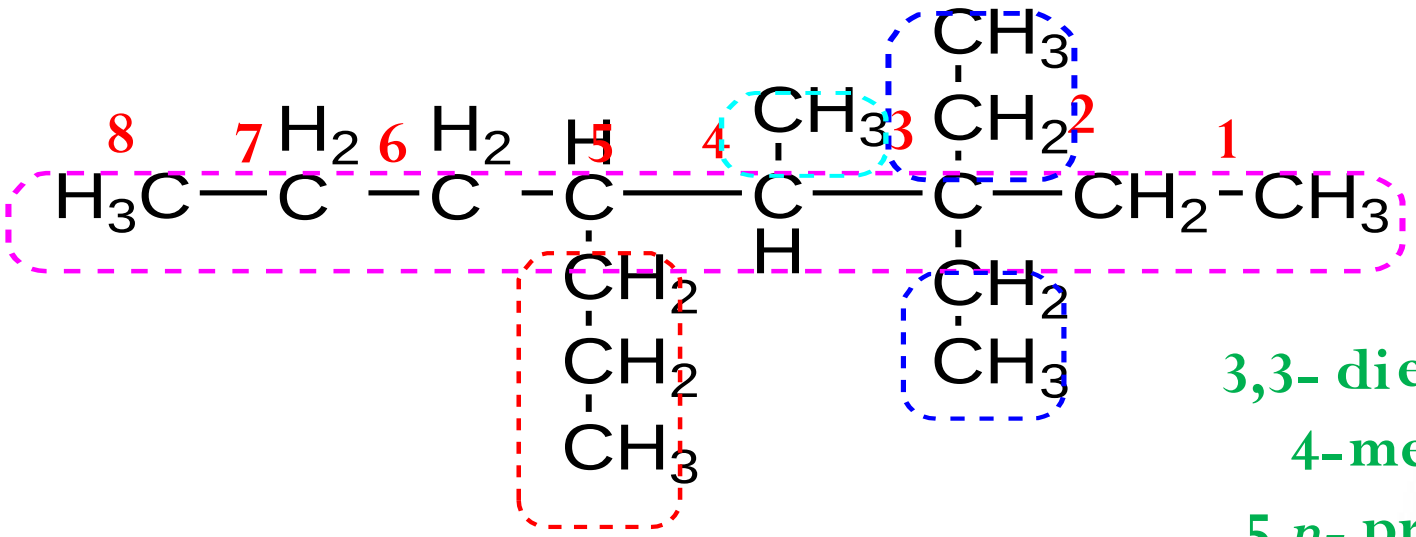


2,2,4-Tri methyl pentane

The IUPAC Rules

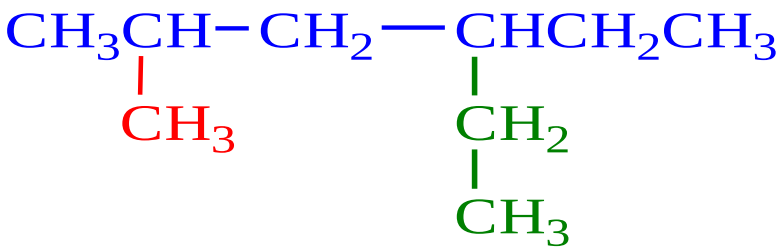
4) If **different alkyl substituents** are attached on the parent carbon chain,

they are named in order of **alphabetical order**.



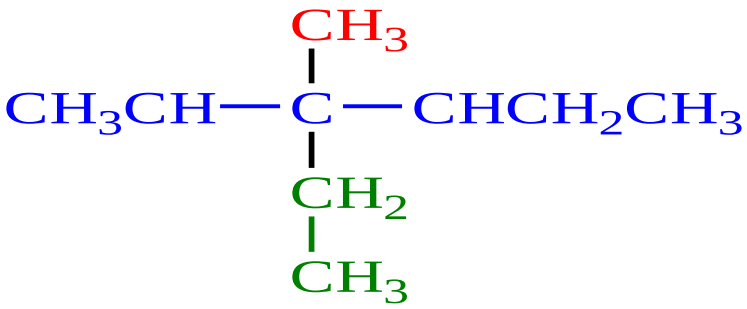
3,3-Diethyl-4-methyl-5-*n*-propyloctane

Note that each **each substituent is given a number corresponding to its location** on the longest chain. The **substituent groups** are listed **alphabetically**.



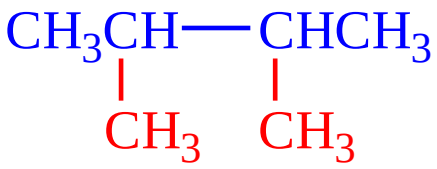
4-Ethyl-2-methylhexane

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

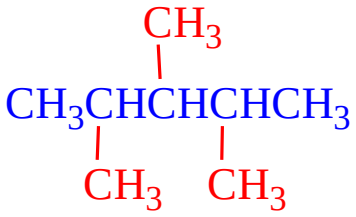


3-Ethyl-3-methylhexane

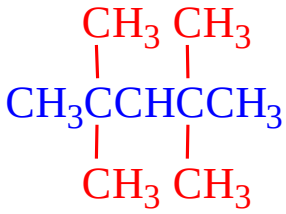
6) When two or more substituents are identical, indicate this by the use of the prefixes **di-**, **tri-**, **tetra-**, and so on.



2,3-Dimethylbutane

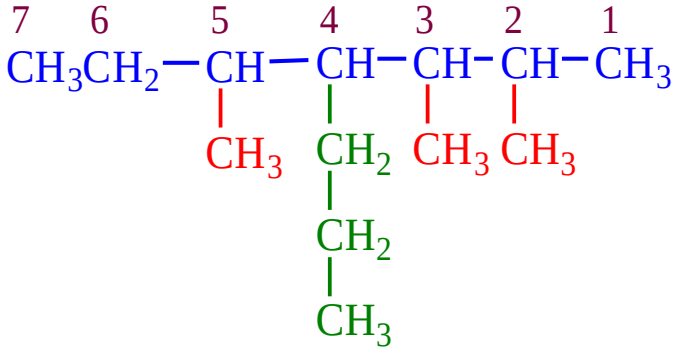


2,3,4-Trimethylpentane



2,2,4,4-Tetramethylpentane

7) 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

The IUPAC Rules

8) If **substituents other than alky groups** are also presents on the parent carbon chain;

all substituents are named alphabetically.

-F fluoro

-Cl chloro

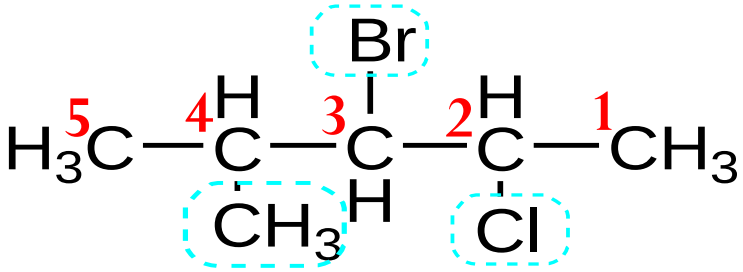
-Br bromo

-I iodo

$-NO_2$ nitro

$-NH_2$ amino

-CN cyano

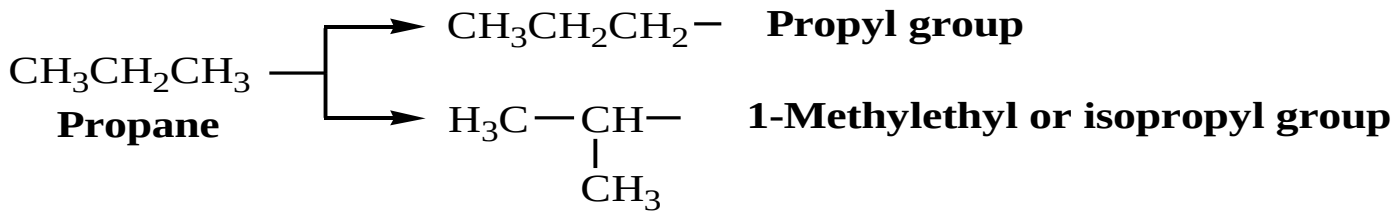


2-chloro
3-bromo
4- methyl

3-bromo -2-chloro-4-methylpentane

NOMENCLATURE OF BRANCHED ALKYL GROUPS

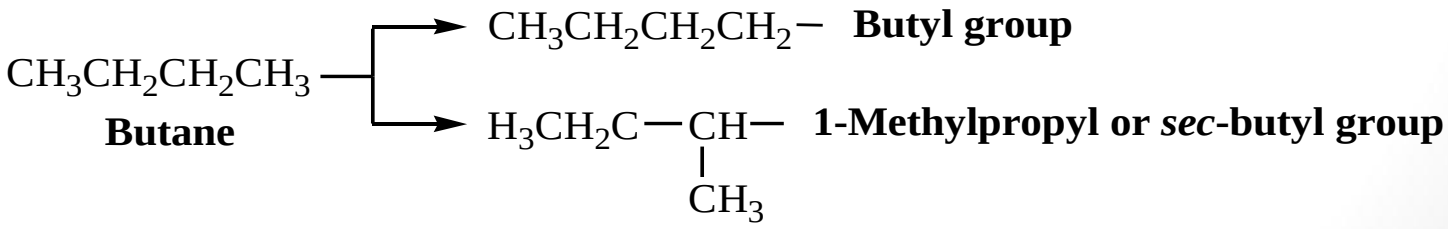
a) Three-Carbon Groups

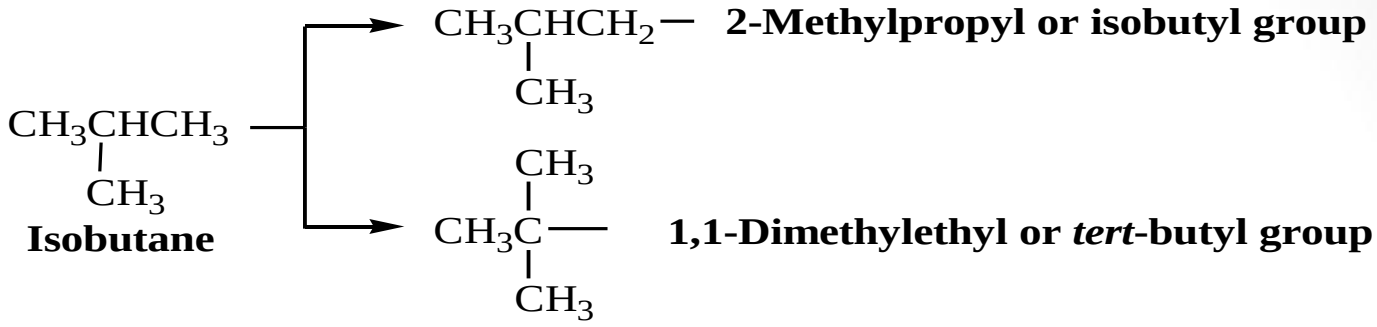


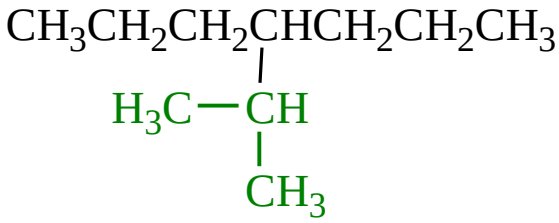
i- 1-Methylethyl is the **systematic name**; **isopropyl** is a **common name**.

ii- *Numbering always begins at the point where the group is attached to the main chain.*

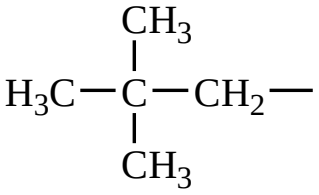
b) *Four-Carbon Groups*



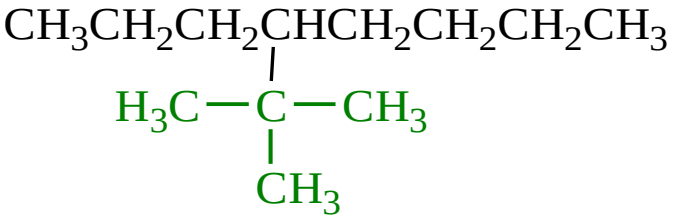




4-(1-Methylethyl)heptane or 4-isopropylheptane



2,2-Dimethylpropyl or neopentyl group



4-(1,1-Dimethylethyl)octane or 4-*tert*-butyloctane

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

Sources of Alkanes

- **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.

Petroleum Cracking

Catalytic cracking: When a mixture of alkanes from the gas oil fraction (C_{12} and higher) is heated at very high temperature (~500 °C) in the presence of a variety of catalysts, the molecules break apart and rearrange to smaller, more highly branched alkanes containing 5-10 carbon atoms.

Thermal cracking: tend to produce unbranched chains which have very low "octane rating".

Octane rating

Octane Number: It represents the knocking power of a gasoline (fuel mixture) determined by the percentage of isooctane (2,2.4-trimethylpentane) that must be mixed with *n*-heptane to produce the knocking quality of the fuel being tested.

Sources of Alkanes

Petroleum Refining

Some components of refined petroleum

Fraction	Boiling range (°C)	Caron content
Gas	Below 20	C1 – C4
Petroleum ether	20 – 60	C5 – C6
Naphtha	60 – 100	C6 – C7
Gasoline	40 – 200	C5 – C10
Kerosine	175 – 325	C11 – C18
Gas oil	300 – 500	C15 – C40
Lubricating oil, asphalt, petroleum coke and paraffins	Above 400	C15 – C40

Sources of Alkanes

Octane Number

- The higher octane number assigned to a fuel, the better its performance and the lower incidence of "knock" in the engine.
- Knocking is caused by the premature ignition of the fuel-air mixture before completion of the compression stroke.
- In setting up the octane number scale,
  n-heptane, a poor fuel that causes severe Knocking,
  So it was assigned an octane rating of zero.

  2,2,4-trimethylpentane (known as isooctane by the petroleum industry) was assigned an octane rating of 100
- 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.

Sources of Alkanes

Octane Number

Octane numbers of some hydrocarbons

Hydrocarbon	Octane number
n-Hexane	26
n-Heptane	0
n-Octane	-20
n-Nonane	-35
2-methylpentane	73
2-methylhexane	45
2-methylheptane	24
2,2-dimethylhexane	77
2,3-dimethylbutane	93

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.

Methyl t-butyl ether (MTBE) a colorless liquid has been used in gasoline at low levels since 1979 to replace tetraethyl lead and to increase its octane rating helping prevent engine knocking, and reduce emissions of some other pollutants.

Sources of Alkanes

Natural Gas

- Natural gas consists of the low molecular weight alkanes from C1 to C5.
  - 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.
  - Natural gas is also converted into many other important organic compounds such as alcohols, aldehydes, ketones, carboxylic acids, and alkyl halides.

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.

Physical Properties of Alkanes

C. 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.

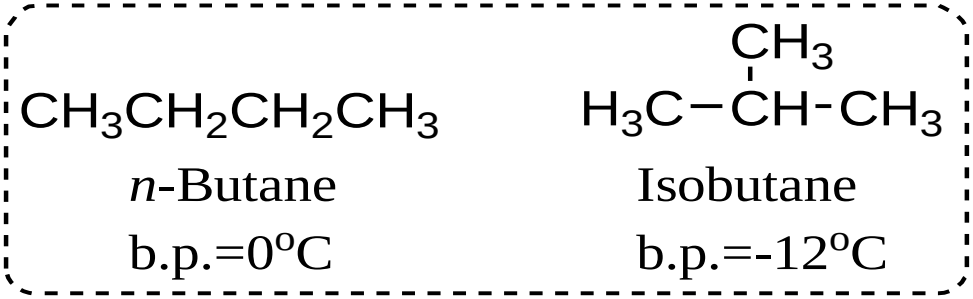
- For the **very small alkanes**, the boiling point rises 20-30°C for each addition of a carbon atom to the chain.

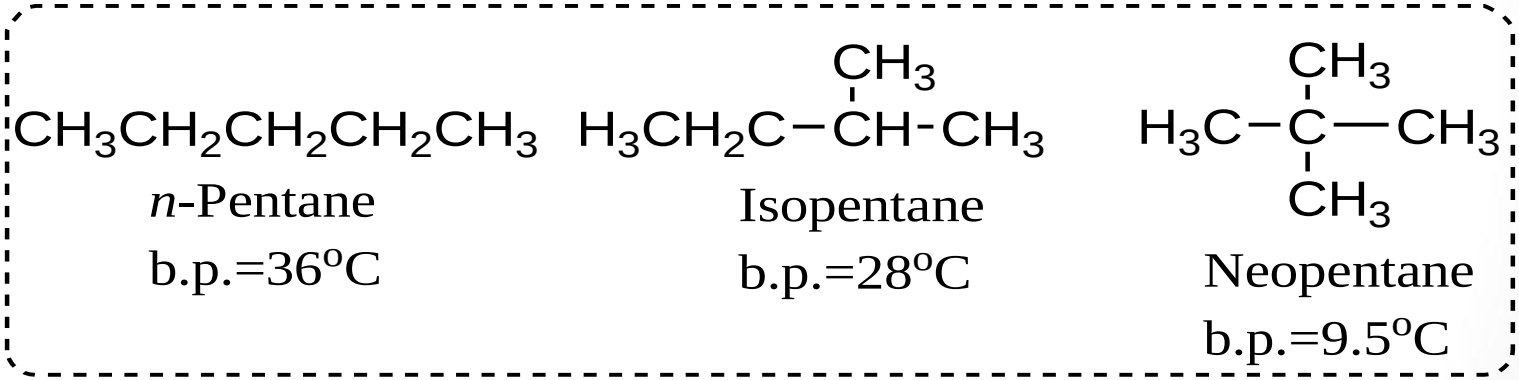
- **Among isomeric alkanes**, straight chain compound has the highest boiling point

- The greater the number of branches, the lower the boiling point

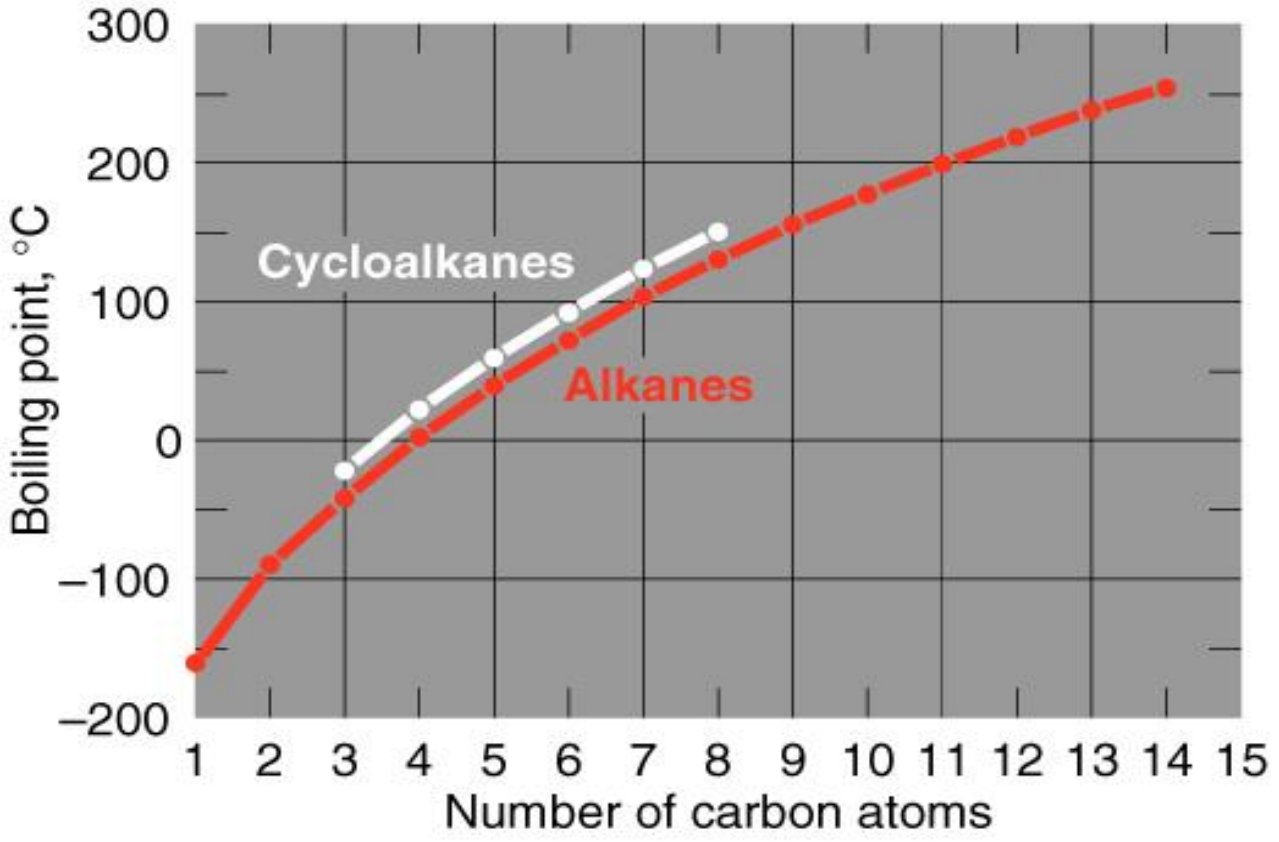
Physical Properties of Alkanes

C. Boiling Points



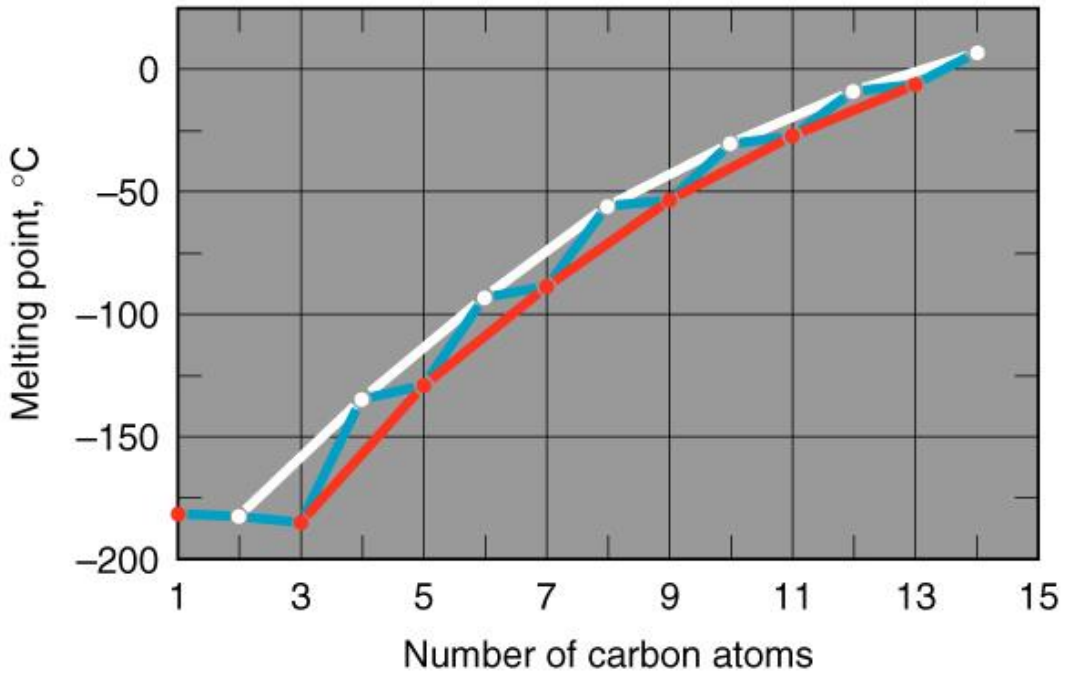


The boiling points of the unbranched alkanes show a regular increase with increasing molecular weight. **Branching** of the alkane chain **lowers** the **boiling point**



D. Melting Points

- Melting point increase with increasing molecular weight.



Preparation of Alkanes

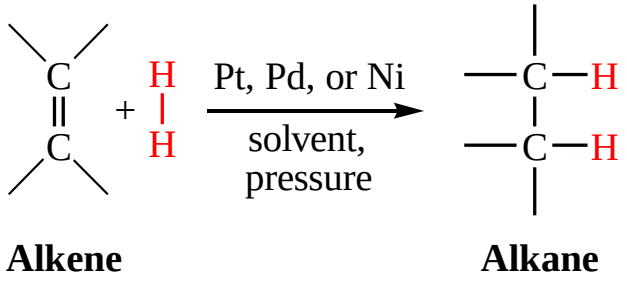
- A great number of alkanes can be obtained by fractional distillation of crude petroleum and subsequent reactions as follows:

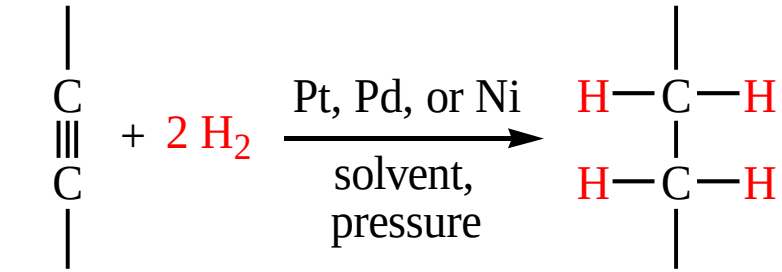
Hydrogenation of Alkenes and Alkynes

1.**Catalytic hydrogenation:**

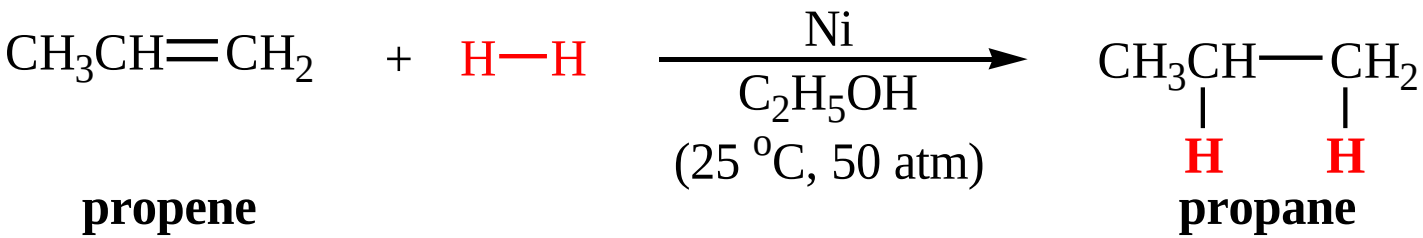
a)Alkenes and alkynes react with hydrogen in the presence of metal catalysts such as nickel, palladium, and platinum to produce alkanes.

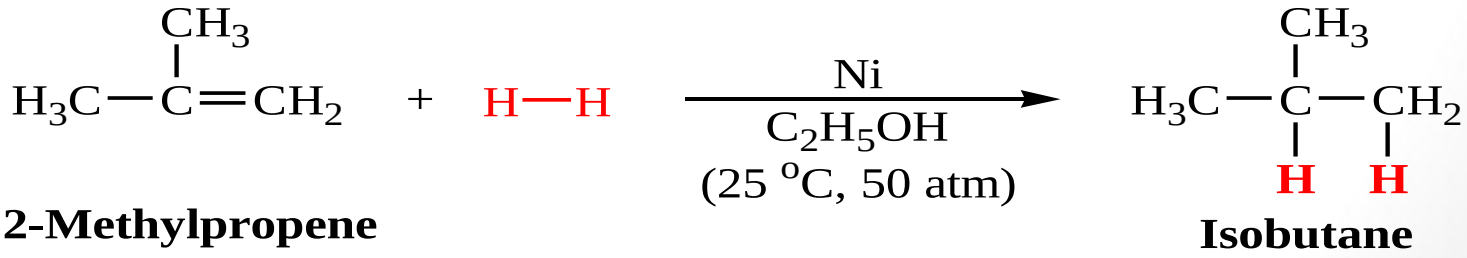
General Reaction





Specific Examples

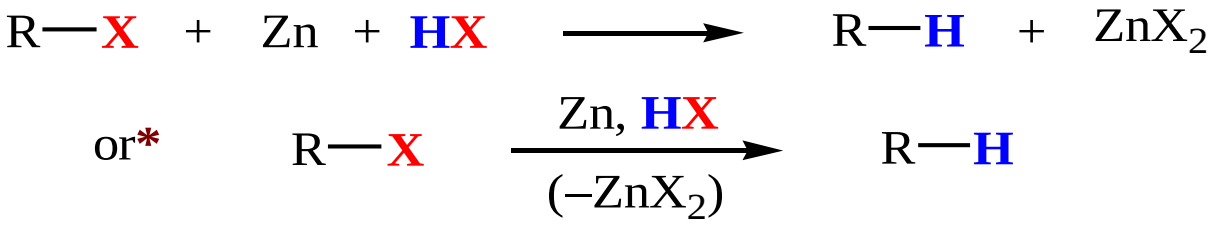




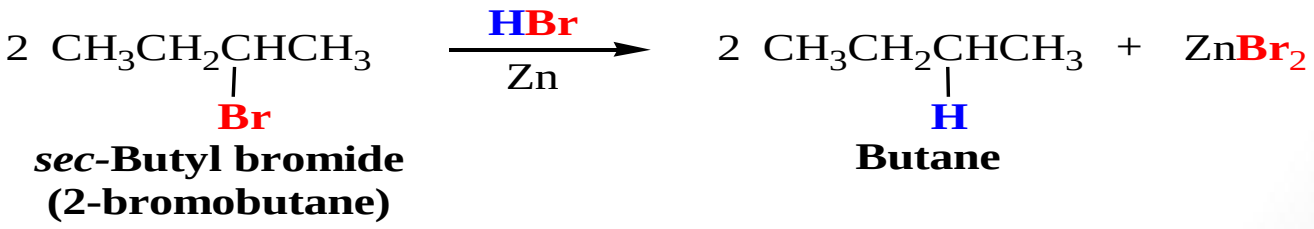
2) Reduction of Alkyl Halides

Most alkyl halides react with zinc and aqueous acid to produce an alkane

General Reaction



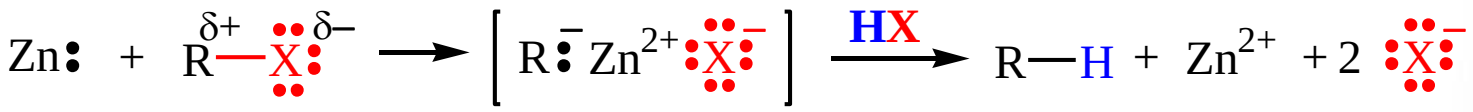
Specific Examples



Isopentyl bromide
(1-bromo-3-methylbutane)

Isopentane
(2-methylbutane)

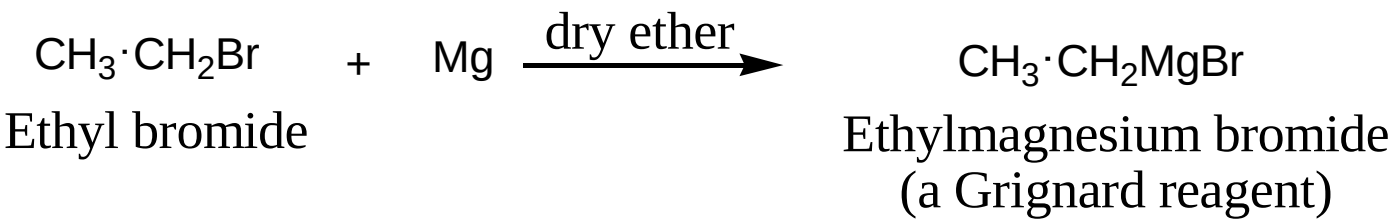
The possible mechanism for the reaction is that an alkylzinc halide forms first and then reacts with the acid to produce the alkane:



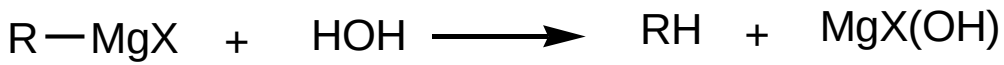
Reducing agent **Alkylzinc halide** **Alkane**

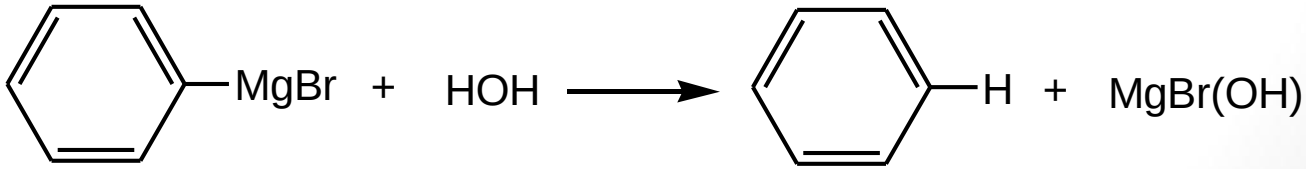
Formation Uses of Organometallic Compounds

Grignard reagent



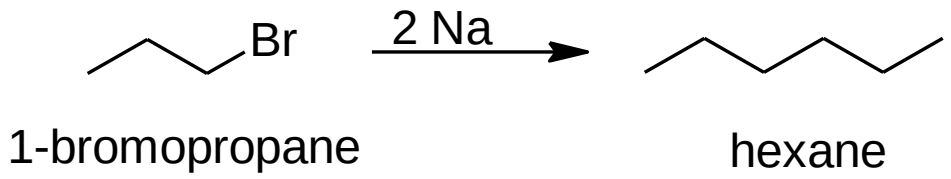
➡ ***Grignard reagents*** **react readily with any source of protons to give hydrocarbons.**





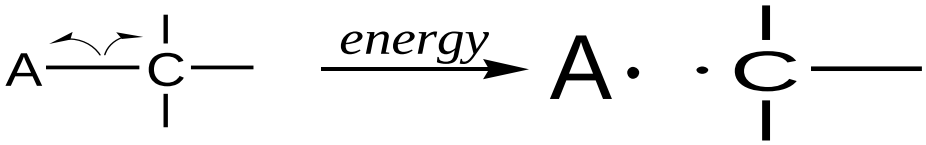
Wurtz Reaction

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



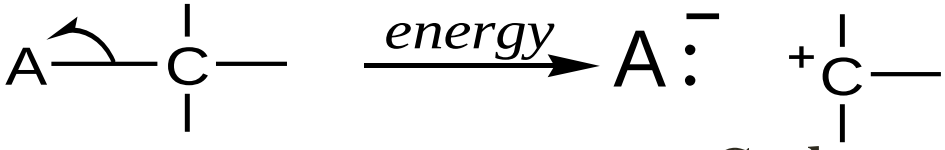
Notations for bond breaking and bond making

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

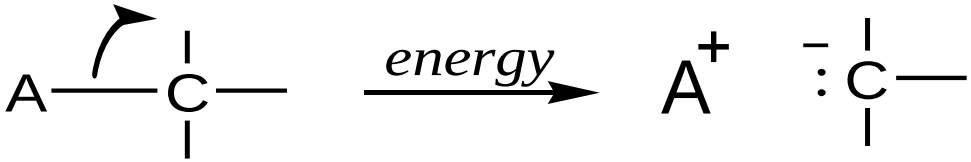


Free radicals

  - **Heterolytic cleavage.**

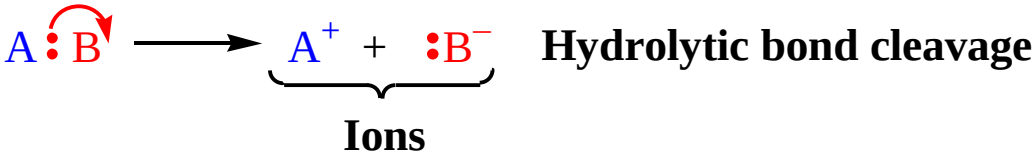


Carbocation



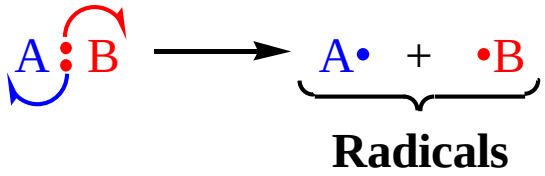
Carboanion

1. **Heterolytic** bond dissociation (**heterolysis**): electronically *unsymmetrical* bond breaking ⇒ produces **ions**.



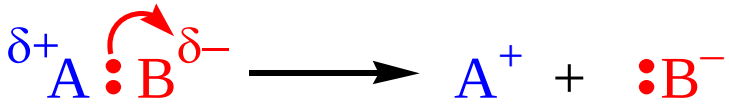
Hydrolytic bond cleavage

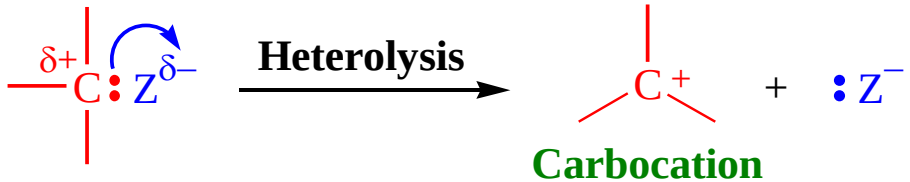
2. **Homolytic** bond dissociation (**homolysis**): electronically *symmetrical* bond breaking ⇒ produces **radicals**.

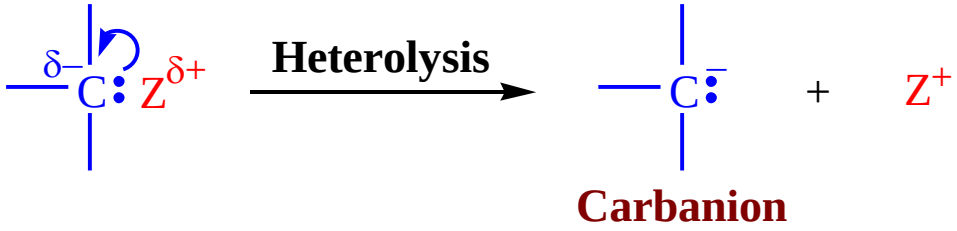


Homolytic bond cleavage

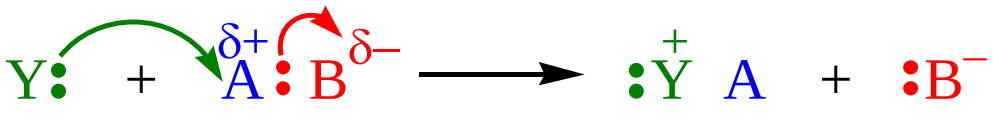
3. **Heterolysis** requires the bond to be **polarized**. ***Heterolysis requires separation of oppositely charged ions***.

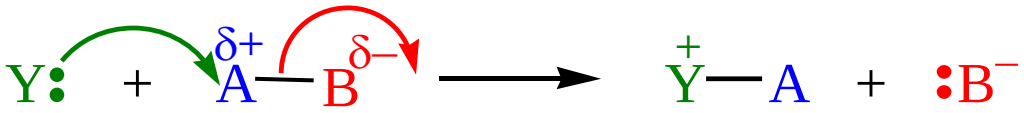






4. **Heterolysis** is assisted by a molecule with an **unshared pair**:

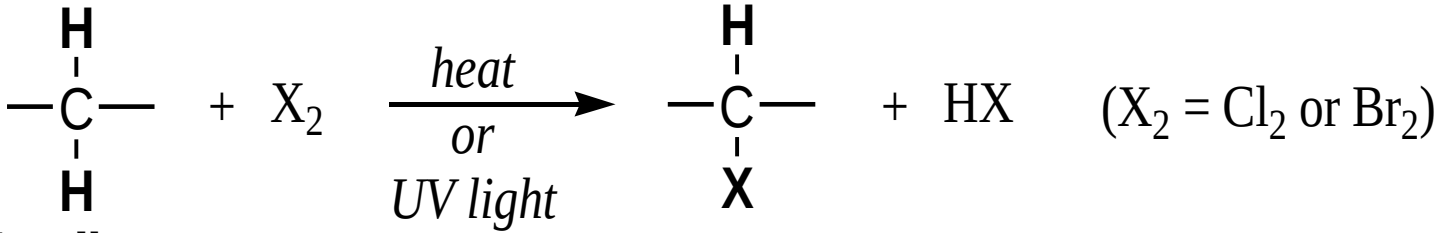




Reactions of Alkanes

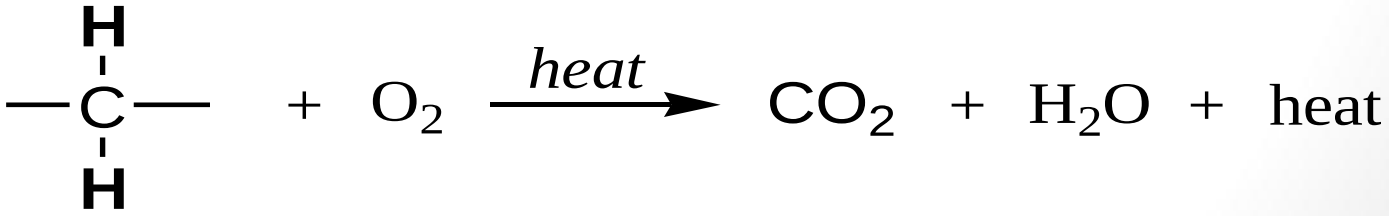
- Saturated hydrocarbons undergo very few reactions, so they are called **Paraffinic hydrocarbons**. (Latin *parum*, little; *affinis*, affinity)

Halogenation



An alkane

Combustion



An alkane

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.

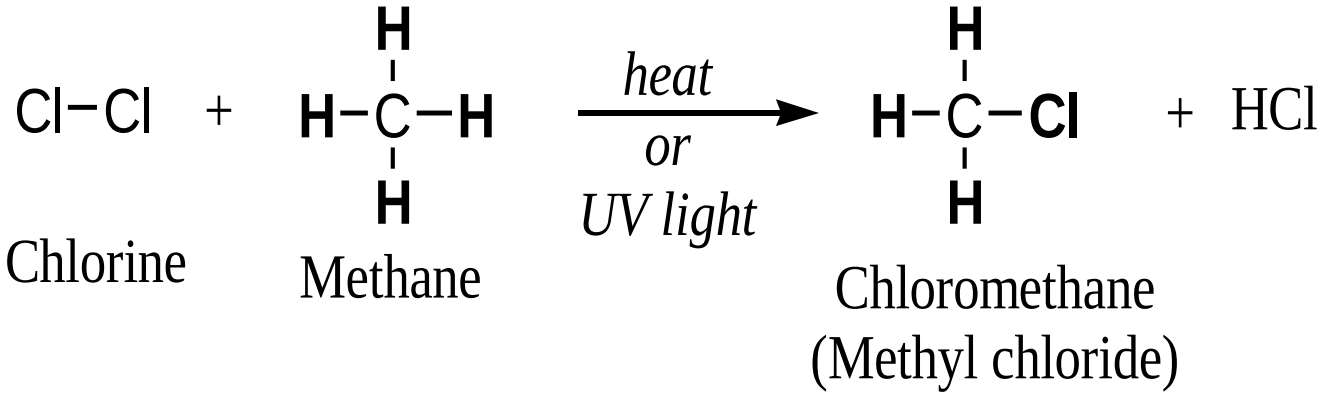
- **Iodine is too unreactive**
  It is not used in the halogentaion of alkanes.

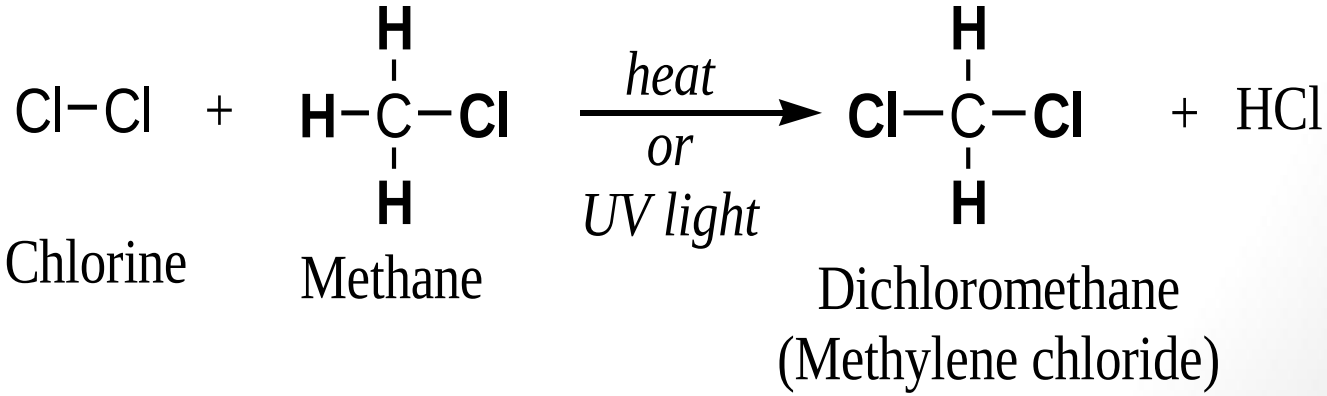
- Halogenation of alkanes take place at
  high temperatures or under the influence of **ultraviolet light**

Reactions of Alkanes

A. Halogenation

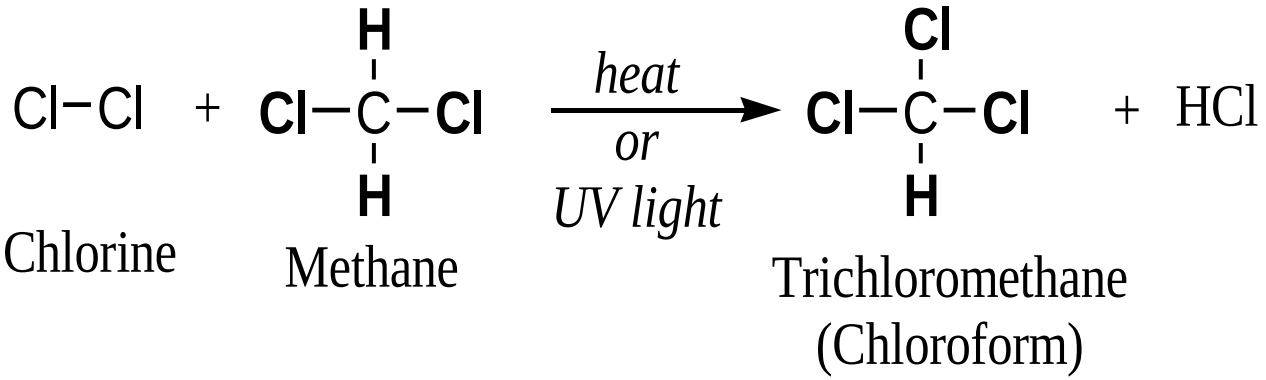
- **Chlorination of an alkane usually gives a mixture of products**

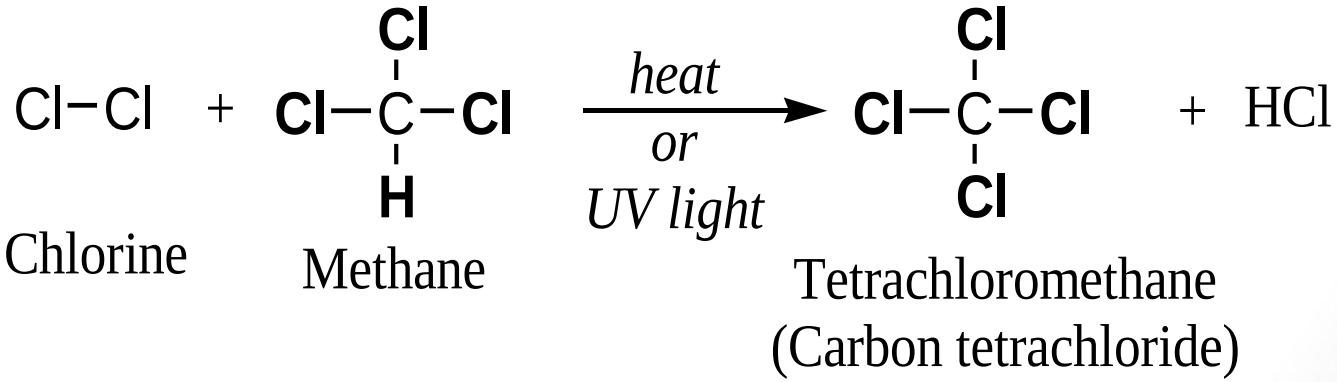




Reactions of Alkanes

A. Halogenation





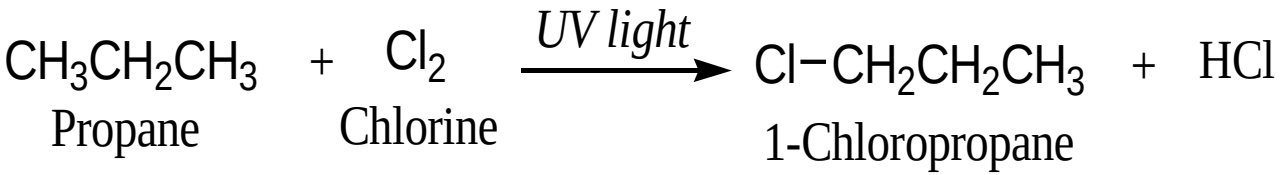
Reactions of Alkanes

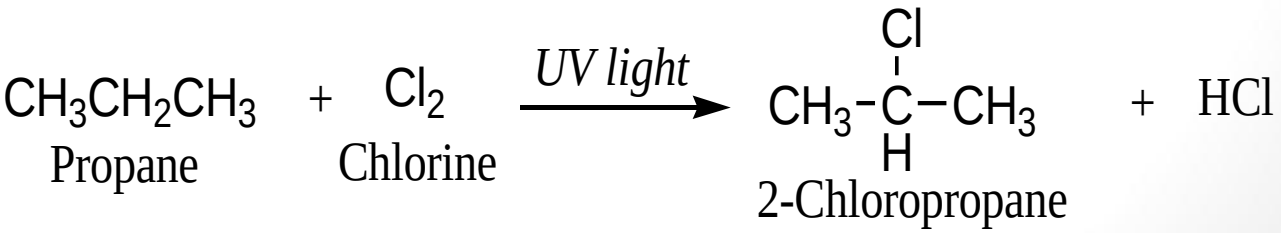
A. Halogenation

- 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.





Reactions of Alkanes

A. Halogenation

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;

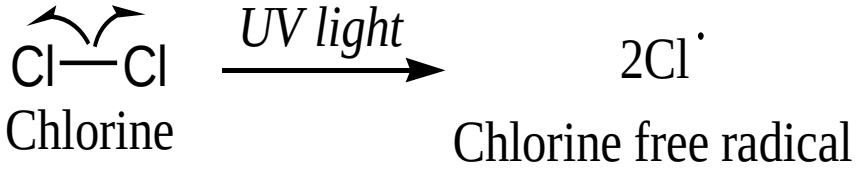
3) Chain-termination step;

Reactions of Alkanes

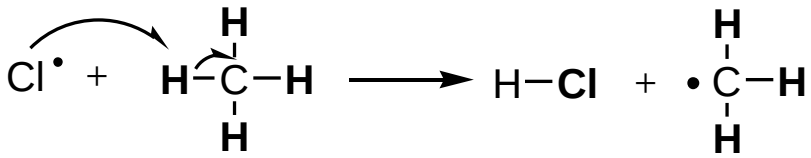
A. Halogenation

Mechanism of Halogenation of Alkanes

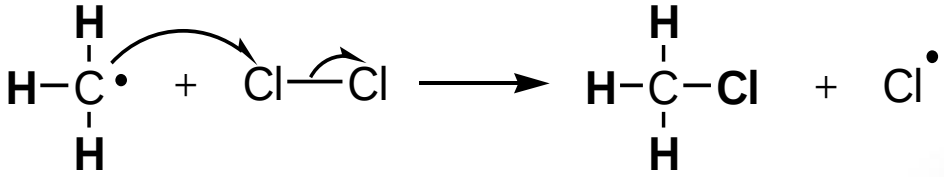
1) Chain-initiation step; formation of free radicals



2) Chain-propagating step;



Methyl free radical

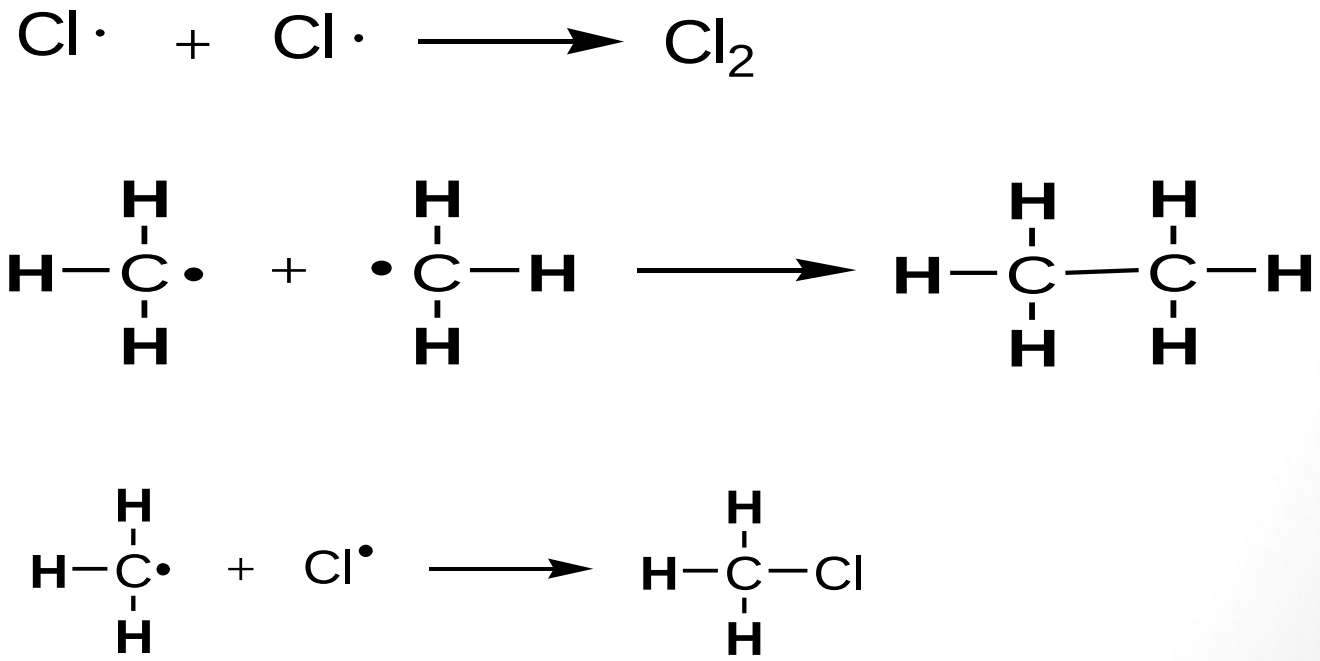


Reactions of Alkanes

A. Halogenation

Mechanism of Halogenation of Alkanes

3) Chain-termination step;



Reactions of Alkanes

B. Combustion of Alkanes

- When ignited in the presence of excess oxygen,

  Alkanes are oxidized to

  Carbon dioxide and Water.

  A large quantity of heat is liberated.

- It is the source of power used to warm our homes and run our machines.

- General equation

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

Reactions of Alkanes

B. Combustion of Alkanes

Examples

$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O +$ ***213*** kcal/mole

Methane

$C_2H_6 + 7/_2\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O +$ ***373*** kcal/mole

Ethane

$C_3H_8 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O +$ ***531*** kcal/mole

Propane

160 Kcal of heat is liberated for each methylene group.

Reactions of Alkanes

B. Combustion of Alkanes

☛ **The incomplete combustion of alkanes.**

liberates poisons carbon monoxide (CO) or carbon.

both are major contributors to air pollution.

$$CH_4 + 3\,O_2 \longrightarrow 2\,CO + 4\,H_2O$$

Methane

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

Methane

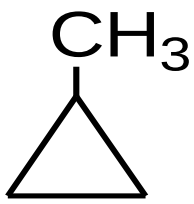
Cycloalkanes: Nomenclature

- **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;

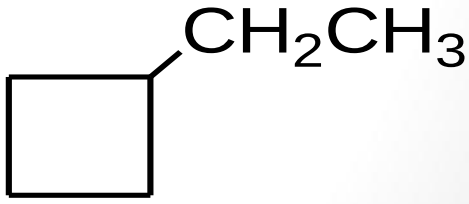
  three-carbon cycloalkane is called **cyclopropane**.

  four-carbon cycloalkane called **cyclobutane**.
- When only one substituent is attached to the ring,

  the substituent first and then name the ring.



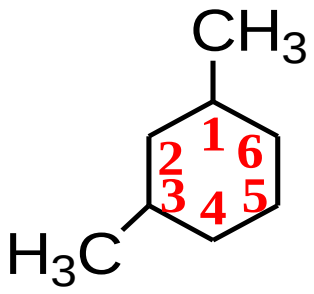
Methylcyclopropane



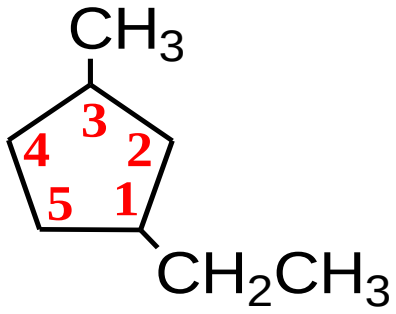
Ethylcyclobutane

Cycloalkanes: Nomenclature

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



1,3-Dimethylcyclohexane



1-Ethyl-3-methylcyclopentane