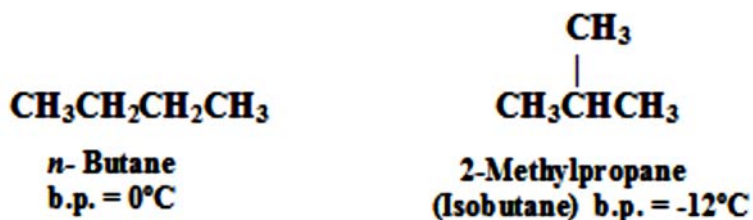### *Alkanes*

Introduction

The atoms of the alkane hydrocarbons are joined to one another only through single bonds. The carbon-carbon single bond is of low reactivity. The general formula is C_nH_{2n+2}, where n is the number of carbon atoms. For example, if the molecule contains three carbon atoms, $n = 3$ and $(2n + 2) = 8$, the formula is C_3H_8. If the molecule contains ten carbon atoms, $n = 10$ and $(2n + 2) = 22$, the formula is $C_{10}H_{22}$. Each member of the alkanes series differs from the preceding and the succeeding members by CH_2 atoms, and each carbon atom of an alkane molecule is covalently bonded to for other atoms. The first ten members of this series are listed in Table 3.1.

Table 3.1 The first ten member of the alkanes

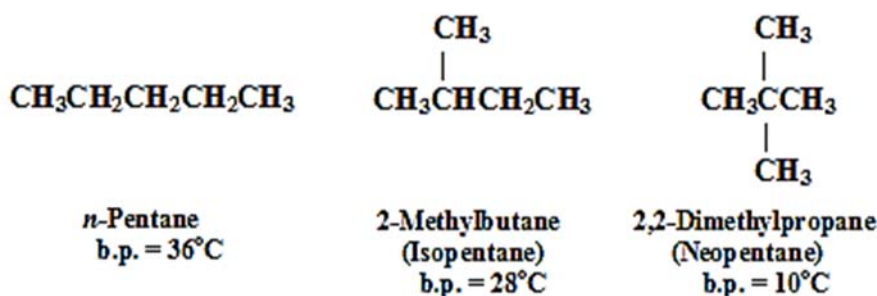| General formula	Structure	Name
CH_4	CH_4	Methane
C_2H_6	CH_3CH_3	Ethane
C_3H_8	$CH_3CH_2CH_3$	Propane
C_4H_{10}	$CH_3(CH_2)_2CH_3$	Butane
C_5H_{12}	$CH_3(CH_2)_3CH_3$	Pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	Hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	Heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	Octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	Nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	Decane

Isomerism in Alkanes

Compounds that have the same molecular formula but different structural formulas were defined as isomers. Isomeric compounds are not possible in the alkanes series until we reach the molecular formula C_4H_{10}. There are two arrangements for the formula C_4H_{10}, and two isomers are known as shown:

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$$CH_3CH_2CH_2CH_3$$

n- Butane
b.p. = 0°C

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

2-Methylpropane
(Isobutane) b.p. = -12°C

(C₄H₁₀ isomers)

They differ both chemically and physically from one another. Experimentally, they can be identified by differences in their melting points, boiling points, densities, solubilities and some other features.

For the formula C_5H_{12}, three isomers have been found, as shown:

$$CH_3CH_2CH_2CH_2CH_3$$

n-Pentane
b.p. = 36°C

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

2-Methylbutane
(Isopentane)
b.p. = 28°C

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3$$

2,2-Dimethylpropane
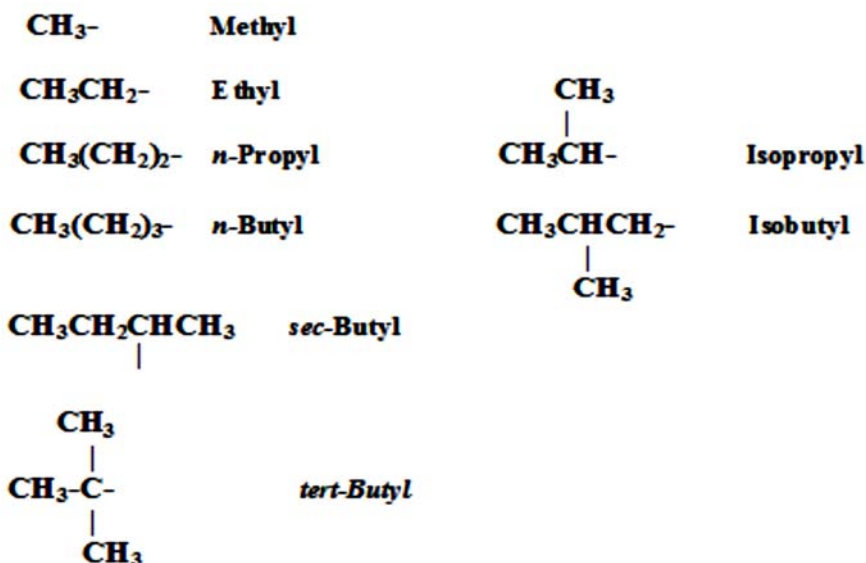**(Neopentane)**
b.p. = 10°C

(C₅H₁₂ isomers)

The difference in the structure is due to different arrangements of the carbon atoms.
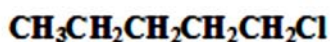
Alkyl Groups

Any branch consisting of only carbon and hydrogen and only single bond is called **alkyl group**. The general formula for an alkyl group is C_nH_{2n+1}, since it contains one less hydrogen than the parent alkane, C_nH_{2n+2}.

CH_3- **Methyl**

CH_3CH_2- **E thyl**

$CH_3(CH_2)_2-$ **n-Propyl**
$$CH_3CH- \quad \text{Isopropyl}$$
with CH_3 branch above.

$CH_3(CH_2)_3-$ **n-Butyl**
$$CH_3CHCH_2- \quad \text{Isobutyl}$$
with CH_3 branch below.

$CH_3CH_2CHCH_3$ **sec-Butyl**

$$CH_3-C- \quad \text{tert-Butyl}$$
with CH_3 branches above and below.

Beyond butyl the number of groups becomes so great that it is impracticable to designate them all by various prefixes. Even though limited, this system is so useful for the small groups just described.

However large the group concerned, the prefix *n-* is used to designate any alkyl group in which all carbons form a single continuous chain and in which the point of attachment is the very end carbon.
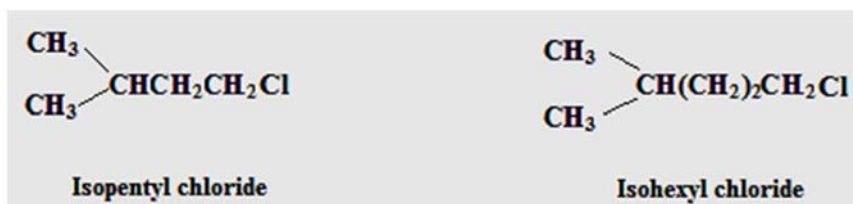
$$CH_3CH_2CH_2CH_2CH_2Cl \qquad\qquad CH_3(CH_2)_4CH_2Cl$$
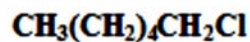
n-Pentyl chloride   **n-Hexyl chloride**

The prefix *iso-* is used to designate any alkyl group (of six carbons or fewer) that has a single one-carbon branch on the next-to-last carbon of a chain and has the point of attachment at the opposite end of the chain.

$$\begin{aligned}CH_3 \\ CH_3\end{aligned}\!\!>\!CHCH_2CH_2Cl \qquad\qquad \begin{aligned}CH_3 \\ CH_3\end{aligned}\!\!>\!CH(CH_2)_2CH_2Cl$$

Isopentyl chloride   **Isohexyl chloride**

If the branching occurs at any other position, or if the point of attachment is at any other position, this name does not apply.
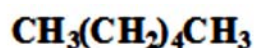
Nomenclature

Common names:

The prefixes *n-*, *iso-*, and *neo-* are adequate to differentiate the various butanes and pentanes, but beyond this point an impracticable number of prefixes would be required. However, the prefix *n-* has been retained for any alkane, no matter how large, in which all carbon forms a continuous chain with no branching:

$$CH_3CH_2CH_2CH_2CH_3 \qquad\qquad CH_3(CH_2)_4CH_3$$
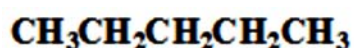
n-Pentane   *n*-Hexane

An *isoalkane* is a compound of six carbons or fewer in which all carbons except one from a continuous chain and that one carbon is attached to the next-to-end carbon:

$$CH_3\!\!\diagdown\!\!\underset{CH_3\diagup}{}CHCH_2CH_3 \qquad\qquad CH_3\!\!\diagdown\!\!\underset{CH_3\diagup}{}CH(CH_2)_2CH_3$$
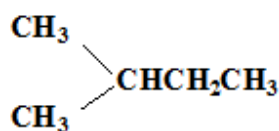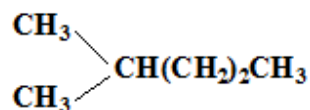
Isopentane   Isohexane

In naming any other of the higher alkanes, we make use of the IUPAC system.

IUPAC system:

Essentially the rules of the IUPAC system (International Union of Pure and Applied Chemistry) are:

1- Use the ending (**–ane**) for all alkanes.

2- Attach a prefix to this, to specify the number of carbon atoms in the longest continuous chain in the molecule. The prefixes through C-10 are:

Meth- 1C	Hex- 6
Eth- 2C	Hept- 7C
Prop- 3C	Oct- 8C
But- 4C	Non- 9C
Pent- 5C	Dec- 10C

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3- Pick the longest continuous chain in a branched chain alkane as the basis for the name.

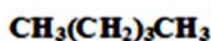4- To specify which carbon atom of the parent chain holds a branch, number the parent chain from whichever end of its chain reaches the first branch with the lower number.

5- Determine the correct name for each branch or any other group or atom such as a halogen atom.

6- If the same group occurs more than ones as a side chain, indicate this by the prefix di-, tri-, tetra-, etc., to show how many of these groups are, and indicate by various numbers the positions of each group.

7- If there are several different groups attached to the parent chain, name them in alphabetical order.

$CH_3(CH_2)_3CH_3$

Pentane
(*n*-Pentane)

CH_3
$CH(CH_2)_2CH_3$
CH_3
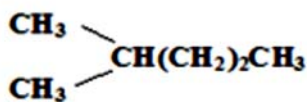
2-Methylpentane
(Isohexane)
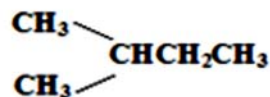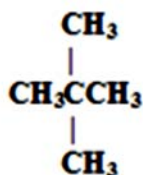
CH_3
$CHCH_2CH_3$
CH_3

(Isopentane)

CH_3
$|$
CH_3CCH_3
$|$
CH_3

Dimethylpropane
(Neopentane)

CH_3
$|$
$CH_3CHCHCH_2CH_3$
$|$
CH_3

2,3-Dimethylpentane

CH_3CHCH_3
$|$
CH_3

Methylpropane
(Isobutane)

CH_3
$|$
$CH_3CHCH_2CCH_3$
$||$
CH_3CH_3

2,2,4-Trimethylpentane

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$$CH_3 \quad CH_2CH_3$$
$$CH_3-CH-C-CH_2-CH_2-CH_3$$
$$CH_3$$

3-Ethyl-2,3-dimethylhexane

$$CH_3$$
$$CH_2$$
$$CH_3-CH_2-CH_2-CH-CH-C-CH_2-CH_3$$
$$CH \quad CH_3 \quad CH_2$$
$$CH_3 \quad CH_3 \quad CH_3$$
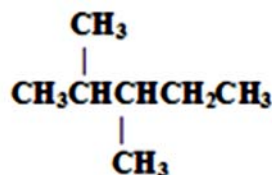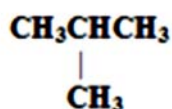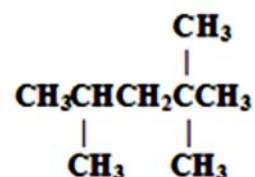
3,3-Diethyl-5-isopropyl-4-methyloctane
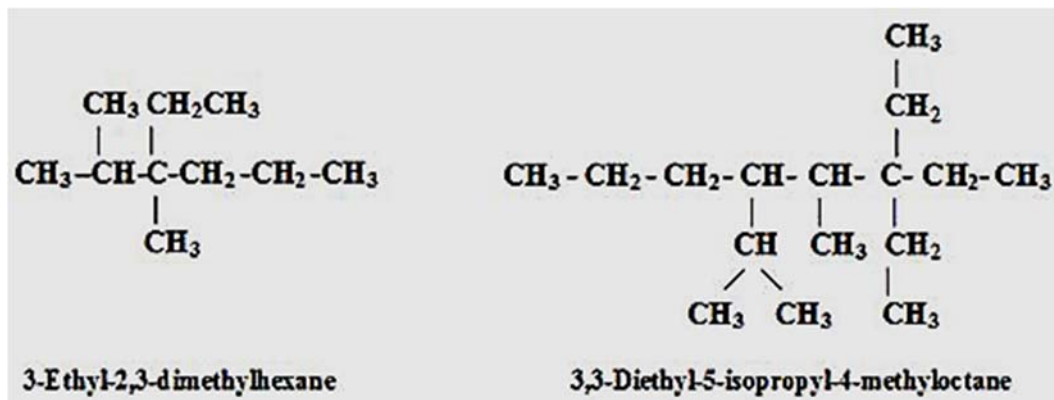
The alkyl halides which appear so often in the alkane chemistry are named *haloalkanes*; that is, halogen is simply treated as a side chain. We first name the alkane as though no halogen were present, and then add *fluoro, chloro, bromo,* or *iodo,* together with any needed number and prefixes.

CH_3Cl

Chloromethane
(Methyl chloride)

CH_3CH_2Br

Bromoethane
(Ethyl bromide)

$$CH_3CHCH_3$$
$$Cl$$

2-Chloropropane
(Isopropyl chloride)

$CH_3CH_2CH_2CH_2Cl$

1-Chlorobutane
(Butyl chloride)

$$CH_3CH_2CHCH_3$$
$$Br$$

2-Bromobutane

$$CH_3$$
$$CH_3-C-Cl$$
$$CH_3$$

2-Chloro-2-methylpropane

$$CH_3$$
$$CH_3CH_2CCHCH_3$$
$$Cl \; Cl$$

2,3-Dichloro-3-methylpentane

$Cl_2CH - CHCl_2$

1,1,2,2-Tetrachloroethane

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$$CH_3$$
$$|$$
$$CH_3CHCH_2I$$

1-Iodo-2-methylpropane

$$CH_3$$
$$|$$
$$CH_3- C- CH_3$$
$$|$$
$$F$$

2-Fluro-2-methylpropane

$$Br \quad NO_2$$
$$| \quad |$$
$$CH_3CHCHCH_3$$

2-Bromo-3-nitrobutane

$$NO_2$$
$$|$$
$$BrCH_2CH_2CHCH_3$$

1-Bromo-3-nitrobutane

The names shown beneath the structural formulas are systematic names. Those shown in parentheses are common names.

Physical Properties of Alkanes

The alkane molecule is held together entirely by covalent bonds, which either join two atoms of the same kind and hence are non-polar, or join atoms that differ very little in electronegativity and hence are only slightly polar. Furthermore, these bonds are directed in a very symmetrical way, so that the slight bond polarities tend to cancel out. As a result, an alkane molecule is either non-polar or very weakly polar. The forces holding non-polar molecules are limited to van der Waals forces, they are weak and of very short range. They act only between the portions of different molecules that are in close contact, that is, between the surfaces of molecules. Within a family, therefore, we would expect that the larger the molecule and hence the larger its surface area the stronger the intermolecular forces.

The boiling points and the melting points of the alkanes rise as the number of the carbons increases. That is because boiling and melting require overcoming the intermolecular forces of liquid and a solid; the boiling point and melting points rise because these intermolecular forces increase as the molecules get larger.

The branching, lower the boiling points because with branching the shape of the molecule tends to approach that of a sphere; and as this happens the surface area

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decreases, with the result that the intermolecular forces become weaker and are overcome at a lower temperature.

The first four n-alkanes are gases, the next 13 (C_5-C_{17}) are liquids, and those-containing 18 carbons or more are solids.

In agreement with the rule of thumb, "like dissolves like", alkanes are soluble in non-polar solvents such as benzene, ether, and chloroform, and are insoluble in water and other highly polar solvents. Considered themselves as a solvent, the liquid alkanes dissolves compounds of low polarity and do not dissolve compounds of high polarity. The relative density increases with size of the alkanes, and all alkanes are less dense than water. In general, to be denser than water a compound must contain a heavy atom like Br or I, or several atoms like Cl.

Preparation of Alkanes

In some of these equations, the symbol R is used to represent any alkyl group.

1- Hydrogenation of alkenes

Hydrogenation is the most useful method for preparing alkanes. It is the addition of H_2 to a multiple bond.
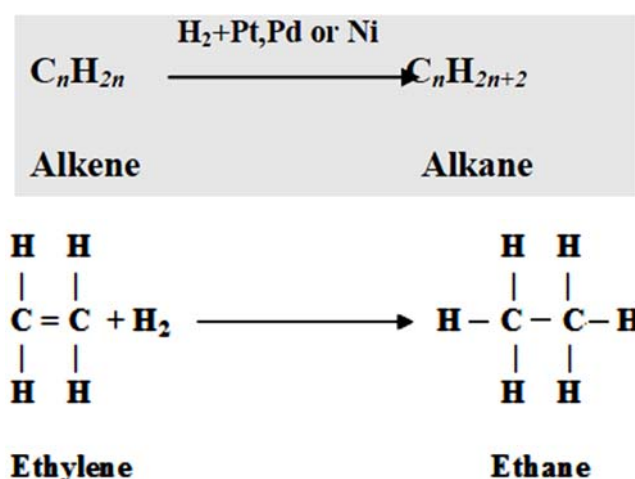
the most important of these methods is the hydrogenation of alkenes. When shaken under a slight pressure of hydrogen gas in the presence of a small amount of catalyst, alkenes are converted smoothly and quantitatively into alkanes of the same carbon skeleton.

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2- Reduction of alkyl halides

(a) Hydrolysis of Grignard reagent

When a solution of an alkyl halide in dry ethyl ether, is allowed to stand over turnings of metallic magnesium, the resulting solution is known as a Grignard reagent. The reaction with water gives an alkane.

$$RX + Mg \longrightarrow \underset{\substack{\text{Grignard} \\ \text{reagent}}}{RMgX} \xrightarrow{H_2O} RH$$

Example:

$$\underset{\substack{| \\ Br \\ \textit{sec-}\text{Butyl bromide}}}{CH_3CH_2CHCH_3} \xrightarrow{Mg} \underset{\substack{| \\ MgBr \\ \textit{sec-}\text{Butylmagnesium} \\ \text{bromide}}}{CH_3CH_2CHCH_3} \xrightarrow{H_2O} \underset{\substack{| \\ H \\ \textit{n-}\text{Butane}}}{CH_3CH_2CHCH_3} + Mg(OH)Br$$
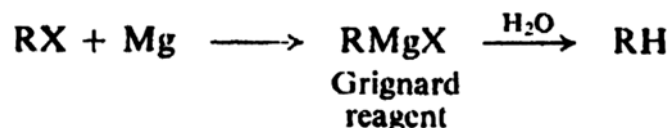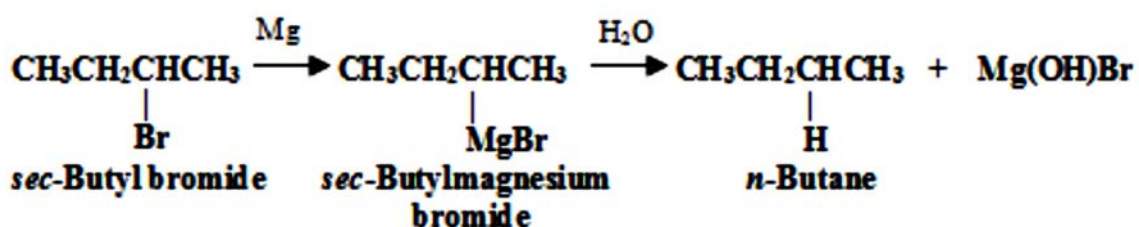
(b) Reduction by metal and acid

Reduction of an alkyl halide with metal and acid, involves the replacement of a halogen atom by a hydrogen atom. The product is an alkane.

$$RX + Zn + H^+ \longrightarrow RH + Zn^{++} + X^-$$

Example:

$$\underset{\substack{| \\ Br \\ \textit{sec-}\text{Butyl bromide}}}{CH_3CH_2CHCH_3} \xrightarrow{Zn, \ H^+} \underset{\substack{| \\ H \\ \textit{n-}\text{Butane}}}{CH_3CH_2CHCH_3}$$
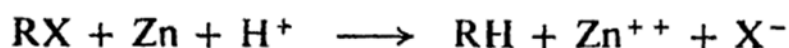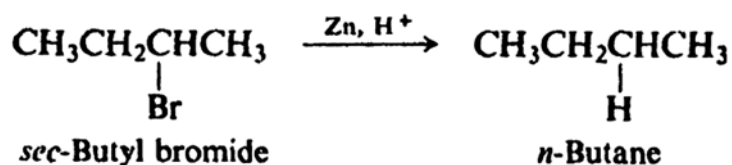
The Grignard reagent: an organometallic compound:

When a solution of an alkyl halide in dry ethyl ether, $(C_2H_5)_2O$, is allowed to stand over turnings of metallic magnesium, a vigorous reaction takes place. The resulting solution is known as a Grignard reagent, It is one of the most useful and versatile reagents known to the organic chemist.

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$$CH_3I + Mg \xrightarrow{ether} CH_3MgI$$

Methyl iodide   Methylmagnesium iodide

$$CH_3CH_2Br + Mg \xrightarrow{ether} CH_3CH_2MgBr$$

Ethyl bromide   Ethylmagnesium bromide
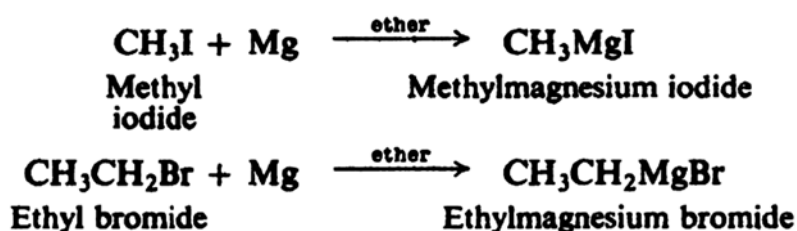
The Grignard reagent has the general formula RMgX, and the general name alkylmagnesium halide. The magnesium becomes bonded to the same carbon that previously held halogen, the n-propyl chloride yields n-propylmagnesium chloride, and isopropyl chloride yields isopropylmagnesium chloride.

$$CH_3CH_2CH_2Cl + Mg \xrightarrow{ether} CH_3CH_2CH_2MgCl$$

n-Propyl chloride   n-Propylmagnesium chloride

$$CH_3CHClCH_3 + Mg \xrightarrow{ether} CH_3CHMgClCH_3$$

Isopropyl chloride   Isopropylmagnesium chloride
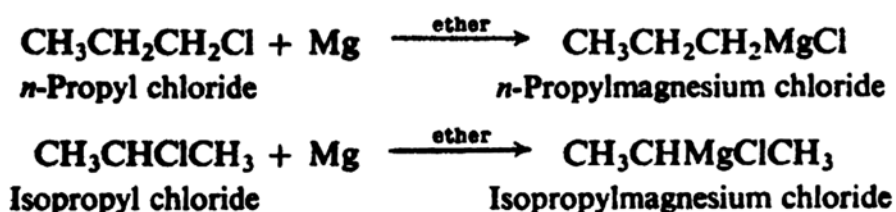
The Grignard reagent is the best-known member of a broad class of substances, called organometallic compounds, in which carbon is bonded to a metal: lithium, potassium, sodium, zinc, mercury, lead, thallium almost any metal known. The carbon-metal bond like the one in the Grignard reagent is highly polar.

$$\overset{\delta_-}{R}\!-\!\overset{\delta_+}{M}$$
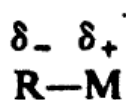
The Grignard reagent is highly reactive. In view of the marked carbanion character of the alkyl group, we may consider the Grignard reagent to be the magnesium salt, RMgX, of the extremely weak acid, R H.

$$RMgX + HOH \longrightarrow R-H + Mg(OH)X$$

Stronger acid   Weaker acid
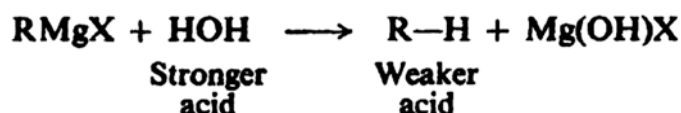
For the preparation of an alkane, one acid is as good as another, so we naturally choose water as the most available and convenient.

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3- Coupling of alkyl halides with organometallic compounds:

To make an alkane of higher carbon number than the starting material requires formation of carbon-carbon bonds, most directly by the coupling together of two alkyl groups. Coupling takes place in the reaction between a lithium dialkylcopper R_2CuLi, and an alkyl halide, R'X. (R' stands for an alkyl group that may be the same as, or different from, R.)

$$R_2CuLi \; + \; R'X \; \longrightarrow \; R\text{--}R' + RCu + LiX$$

| Lithium dialkylcopper | Alkyl halide | Alkane |

An alkyllithium, RLi, is prepared from an alkyl halide, RX, in much the same way as a Grignard reagent. To it is added cuprous halide, CuX, and then, finally, the second alkyl halide, R'X. Ultimately, the alkane is synthesized from the two alkyl halides, RX and R'X.

$$RX \xrightarrow{\;Li\;} RLi \xrightarrow{\;CuX\;} R_2CuLi$$

Alkyl lithium ; Lithium dialkylcopper

$$R'X \longrightarrow R\text{--}R'$$

For good yields, R'X should be a primary halide; the alkyl group R in the organometallic may be primary, secondary, or tertiary. For example:

$$CH_3Br \xrightarrow{\;Li\;} CH_3Li \xrightarrow{\;CuI\;} (CH_3)_2CuLi$$

Methyl bromide ; Methyllithium ; Lithium dialkylcopper

$$CH_3(CH_2)_6CH_2I \longrightarrow CH_3(CH_2)_7CH_3$$

n-Octyl iodide ; n-Nonane

$$CH_3CH_2CHCH_3 \xrightarrow{\;Li\;} \xrightarrow{\;CuI\;} (CH_3CH_2CH\text{--})_2CuLi$$

(with $|$ Cl)

sec-Butyl chloride

$$CH_3CH_2CH_2CH_2CH_2Br \longrightarrow CH_3CH_2CH(CH_2)_4CH_3$$

n-Pentyl bromide ; 3-Methyloctane

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Although the mechanism is not understood, evidence strongly suggests this much: the alkyl group R is transferred from copper, taking a pair of electrons with it, and attaches itself to the alkyl group R' by pushing out halide ion (nucleophilic aliphatic substitution).

Reactions of Alkanes

Alkanes are generally not considered to be very reactive substance. However, under suitable conditions they are do react.

1- Halogenation

Alkanes react with the halogens (except iodine) to form substitution products.

$$-\overset{|}{\underset{|}{C}}-H + X_2 \xrightarrow{\text{250–400°, or light}} -\overset{|}{\underset{|}{C}}-X + HX$$

Usually a mixture

Reactivity X_2: $Cl_2 > Br_2$

H: $3° > 2° > 1° > CH_3{-}H$
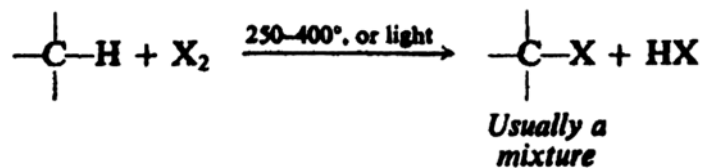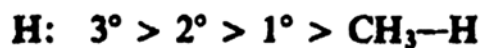
Experiment has shown that on halogenation an alkane yields a mixture of all possible isomeric products, indicating that all hydrogen atoms are susceptible to replacement. For example, for chlorination:

$$CH_3CH_3 \xrightarrow[\text{light, 25°}]{Cl_2} CH_3CH_2{-}Cl$$

Ethane

b.p. 13°
Chloroethane
Ethyl chloride

$$CH_3CH_2CH_3 \xrightarrow[\text{light, 25°}]{Cl_2} CH_3CH_2CH_2{-}Cl \quad \text{and} \quad CH_3\overset{|}{\underset{|}{C}}HCH_3$$

Propane

b.p. 47°
1-Chloropropane
n-Propyl chloride
45%

Cl
b.p. 36°
2-Chloropropane
Isopropyl chloride
55%

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{light, 25°}]{Cl_2} CH_3CH_2CH_2CH_2{-}Cl \quad \text{and} \quad CH_3CH_2\overset{|}{\underset{|}{C}}HCH_3$$

n-Butane

b.p. 78.5°
1-Chlorobutane
n-Butyl chloride
28%

Cl
b.p. 68°
2-Chlorobutane
sec-Butyl chloride

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{|}{C}}HCH_3 \xrightarrow[\text{light, 25°}]{Cl_2} CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{|}{C}}HCH_2{-}Cl \quad \text{and} \quad CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}CH_3$$

Isobutane

b.p. 69°
1-Chloro-2-methylpropane
Isobutyl chloride
64%

b.p. 51°
2-Chloro-2-methylpropane
tert-Butyl chloride
36%

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Bromination gives the corresponding bromides but in different proportions:

$$CH_3CH_3 \xrightarrow[\text{light, } 127°]{Br_2} CH_3CH_2Br$$

Ethane

$$CH_3CH_2CH_3 \xrightarrow[\text{light, } 127°]{Br_2} CH_3CH_2CH_2Br \quad \text{and} \quad CH_3CHCH_3$$

Propane, 3%, Br, 97%

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{light, } 127°]{Br_2} CH_3CH_2CH_2CH_2Br \quad \text{and} \quad CH_3CH_2CHCH_3$$

n-Butane, 2%, Br, 98%

$$\underset{CH_3CHCH_3}{\overset{CH_3}{|}} \xrightarrow[\text{light, } 127°]{Br_2} \underset{CH_3CHCH_2Br}{\overset{CH_3}{|}} \quad \text{and} \quad \underset{CH_3CCH_3}{\overset{CH_3}{|}}$$

Isobutane, trace, Br, over 99%
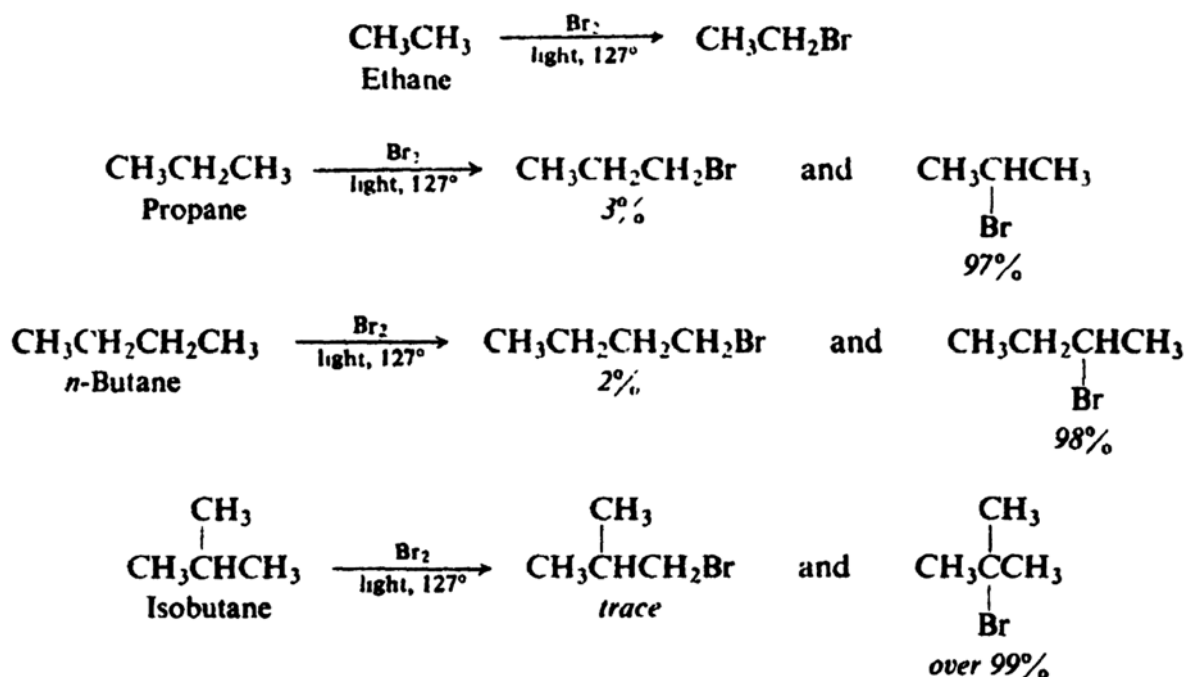
Although both chlorination and bromination yield mixtures of isomers, the results given above show that the relative amounts of the various isomers differ markedly depending upon the halogen used. Chlorination gives mixtures in which no isomer greatly predominates; in bromination, by contrast, one isomer may predominate to such an extent as to be almost the only product, making up 97- 99% of the total mixture. In bromination, there is a high degree of selectivity as to which hydrogen atoms are to be replaced.

Mechanism of halogenation:

Halogenation of alkanes proceeds by the following mechanism:

(1) $\quad X_2 \xrightarrow[\substack{\text{or} \\ \text{ultraviolet} \\ \text{light}}]{250\text{–}400°} 2X\cdot$ **Chain-initiating step**

(2) $\quad X\cdot + RH \longrightarrow HX + R\cdot$

(3) $\quad R\cdot + X_2 \longrightarrow RX + X\cdot$ } **Chain-propagating steps**
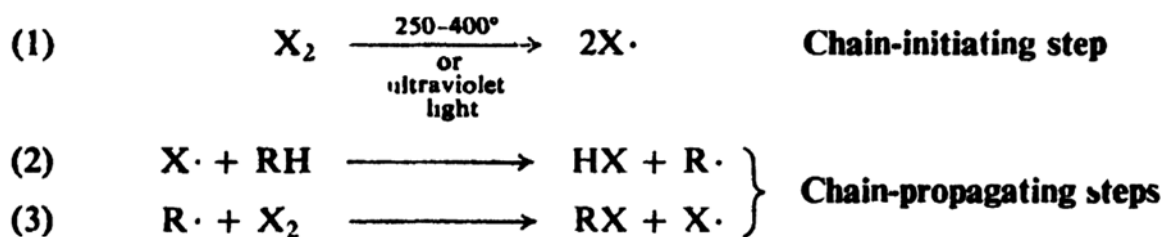
then (2), (3), (2), (3), etc., until finally a chain is terminated.

A halogen atom abstracts hydrogen from the alkane (RH) to form an alkyl radical

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(R·). The radical in turn abstracts a halogen atom from a halogen molecule to yield the alkyl halide (RX).

Which alkyl halide is obtained depends upon which alkyl radical is formed.

$$CH_4 \xrightarrow{X·} CH_3· \xrightarrow{X_2} CH_3X$$

Methane — Methyl radical — Methyl halide

$$CH_3CH_3 \xrightarrow{X·} CH_3CH_2· \xrightarrow{X_2} CH_3CH_2X$$

Ethane — Ethyl radical — Ethyl halide

$$CH_3CH_2CH_3 \xrightarrow{X·}$$

Propane

abstraction of 1° H → $CH_3CH_2CH_2·$ (n-Propyl radical) $\xrightarrow{X_2}$ $CH_3CH_2CH_2X$ (n-Propyl halide)

abstraction of 2° H → CH_3CHCH_3 (Isopropyl radical) $\xrightarrow{X_2}$ $CH_3\overset{|}{C}HCH_3$ with X (Isopropyl halide)

2- Oxidation (Combustion)

Although alkanes are resistant to attack by oxidizing agents generally, they all undergo combustion in air or oxygen, the products of complete oxidation being carbon dioxide and water.

$$C_nH_{2n+2} + \text{excess } O_2 \xrightarrow{\text{flame}} nCO_2 + (n+1) H_2O$$

$$CH_4 + 2O_2 \xrightarrow{\text{flame}} CO_2 + 2H_2O$$

$$C_5H_{12} + 8O_2 \xrightarrow{\text{flame}} 5CO_2 + 6H_2O$$

3- Pyrolysis: cracking

Decomposition of a compound by the action of heat alone is known as pyrolysis. This word is taken from the Greek pyr, fire, and lysis, a losing, and hence to chemists means "cleavage by heat"; compare hydro-lysis, "cleavage by water."

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The pyrolysis of alkanes, particularly when petroleum is concerned, is known as cracking. In thermal cracking alkanes are simply passed through a chamber heated to a high temperature. Large alkanes are converted into smaller alkanes, alkenes, and some hydrogen. This process yields predominantly ethylene (C_2H_4) together with other small molecules.

$$alkane \xrightarrow{\text{400-600:; with or without catalysts}} H_2 + \text{smaller alkanes} + \text{alkenes}$$