

Experiment 3:

Simple distillation

Purpose:

The purpose of this laboratory exercise is to identify and assess the purity of an unknown solid organic compound by determining its melting point and comparing this number to a list of possible compounds.

Introduction:

Distillation is the most common method used to separate and purify liquids. The process consists of heating a liquid to its boiling point and conducting the vapors to a cooling device where they are condensed. The condensate is then collected.

There are four types of distillation processes:

1. *Simple distillation:* Separating liquids that boil below 150°C at one atmosphere (1 atm) from non-volatile impurities or another liquid boiling at least 50°C higher than the first liquid.

Note: the liquids to be distilled must be mixable with each other. If they are not then they would form separable layers, which you separate much more easily with a separating funnel.

2. *Fractional distillation:* Separating mixable liquid mixtures that boil at less than 50°C from each other at 1 atm.

3. *Steam distillations:* Separating or isolating tars, oils, and other liquid compounds insoluble or slightly soluble, in water at all temperatures.

4. *Vacuum distillation:* is a technique for the distillation of high boiling liquids, and for compounds that decompose at atmospheric pressure. At the low pressures employed, those compounds distil at much lower temperatures.

The Simple distillation is the most common method because:

- 1- It is a technique used for the purification of liquids.
- 2- Separation of liquid mixtures.

3- Detection the real boiling point.

Procedure:

A typical set-up for simple distillation is given in **Figure 4** :

When carrying out a distillation, the following practical points should be observed:

- a.* The boiling flask should not be more than half full.
- b.* Boiling stones are added to the liquid to prevent bumping.
- c.* Each ground joint should be greased to ensure a completely sealed system.
- d.* Cooling water in the condenser should enter at the lower end and exit at the upper end. This ensures that the condenser jacket is always full of water.
- e.* The bulb of the thermometer should be below the opening of the side arm so as to measure the temperature at which liquid and vapor are in equilibrium.
- f.* Heat sources used depend on the nature of the liquid. A water bath is used to distil low-boiling and flammable liquids, while a burner with a wire gauze is used for higher boiling and less flammable liquids.

Figure : Simple distillation apparatus.

Apparatus:

Thermometer

clamp

Bunsen burner

Tripod

stand

condenser

Conical flask

Round bottom flask

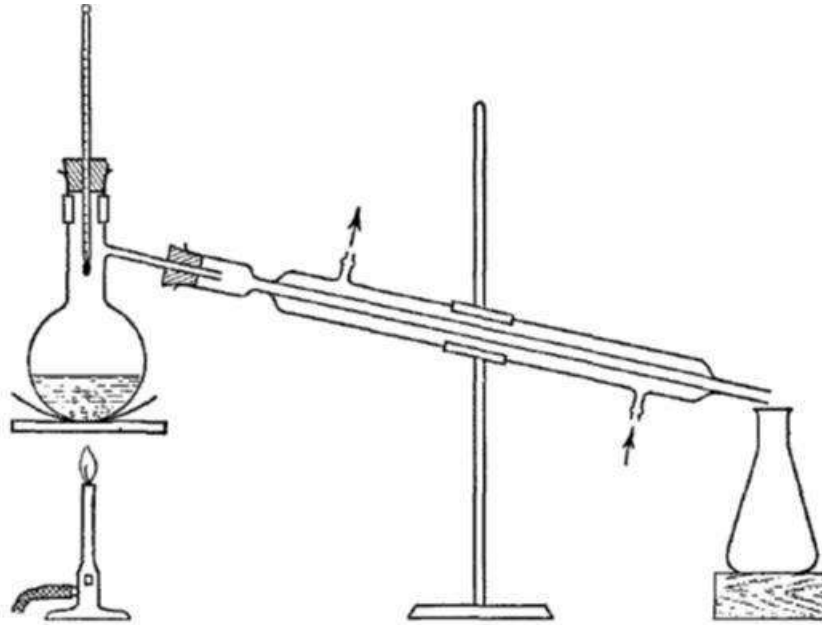
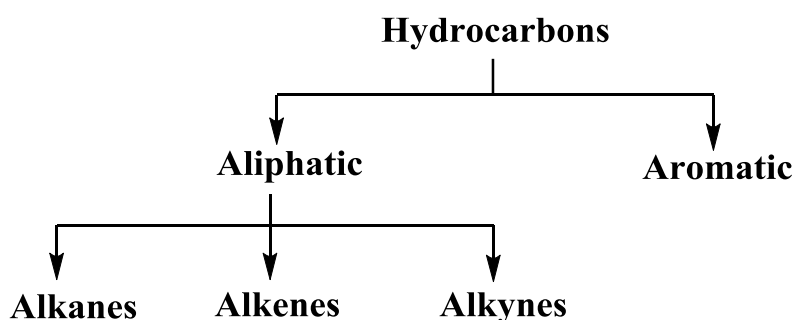


Figure 6: Simple distillation apparatus

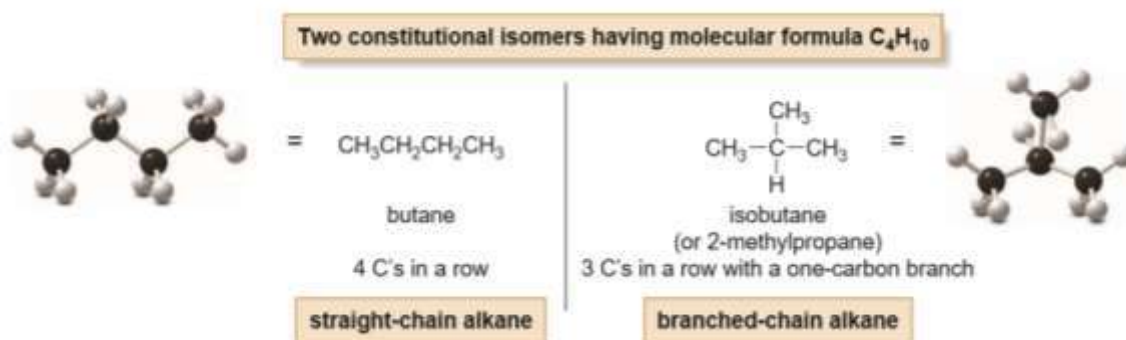
Hydrocarbons: are Compounds that contain only carbon and hydrogen atoms.



Alkanes

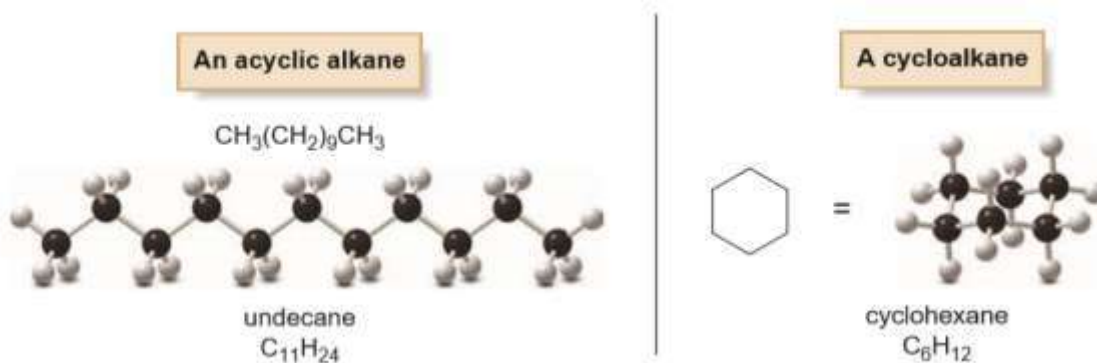
Alkanes: are aliphatic hydrocarbons having only C–C and C–H σ bonds. Alkanes can be subdivided into the following two groups:

- A **cyclic alkanes** have the molecular formula $C_nH_{2n} + 2$ and contain only linear and branched chains of carbon atoms. They are also called saturated hydrocarbons because they have the maximum number of hydrogen atoms per carbon.



- **Cycloalkanes** contain carbons joined in one or more rings, the general formula is C_nH_{2n} , they have two fewer H atoms than an acyclic alkane with the same number of carbons.

Alkanes are the simplest and least reactive hydrocarbon species containing only carbons and hydrogens and lack any other functional groups.

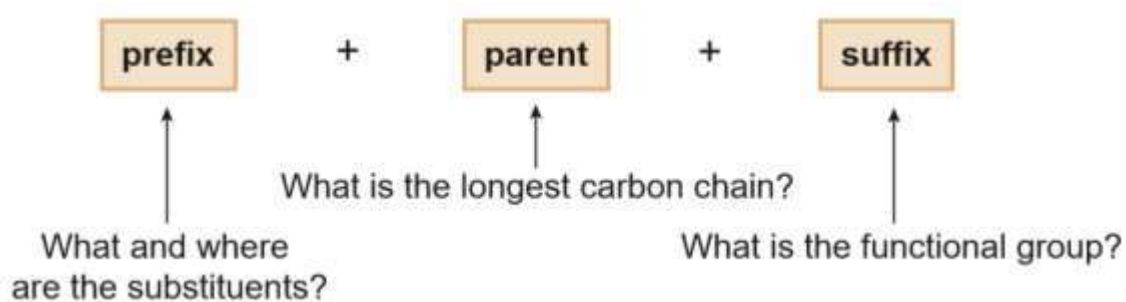


Nomenclature

A systematic method of naming compounds was developed by the International Union of Pure and Applied Chemistry. It is referred to as the **IUPAC** system of nomenclature.

The name of every organic molecule has three parts.

- The **parent** name indicates the number of carbons in the longest continuous carbon chain in the molecule.
- The **suffix** indicates what functional group is present.
- The **prefix** reveals the identity, location, and number of substituents attached to the carbon chain.

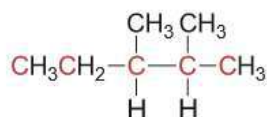


Number of C atoms	Molecular formula	Name (<i>n</i> -alkane)	Number of constitutional isomers
1	CH ₄	methane	—
2	C ₂ H ₆	ethane	—
3	C ₃ H ₈	propane	—
4	C ₄ H ₁₀	butane	2
5	C ₅ H ₁₂	pentane	3
6	C ₆ H ₁₄	hexane	5
7	C ₇ H ₁₆	heptane	9
8	C ₈ H ₁₈	octane	18
9	C ₉ H ₂₀	nonane	35
10	C ₁₀ H ₂₂	decane	75
20	C ₂₀ H ₄₂	eicosane	366,319

The simple **n-alkanes** consist of the **parent** name, which indicates the number of carbon atoms in the longest carbon chain, and the **suffix** -ane, which indicates that the compounds are alkanes. The parent name for one carbon is meth-, for two carbons is eth-, and so on. We are already familiar with two parts of the name of an organic compound.

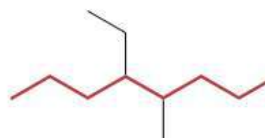
Prefix, name the carbon groups (called alkyl groups) or substituents that are bonded to the longest carbon chain.

- **An alkyl group** is formed by removing one hydrogen from an alkane, to name an alkyl group, change the **-ane** ending of the parent alkane to **-yl**. Thus, methane (CH₄) becomes methyl (CH₃-) and ethane (CH₃CH₃) becomes ethyl (CH₃CH₂-).



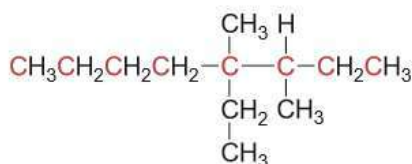
2,3-dimethylpentane

[Number to give the 1st methyl group the lower number.]



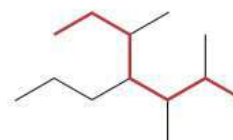
4-ethyl-5-methyloctane

[Assign the lower number to the 1st substituent alphabetically: the e of ethyl before the m of methyl.]



4-ethyl-3,4-dimethyloctane

[Alphabetize the e of ethyl before the m of methyl.]

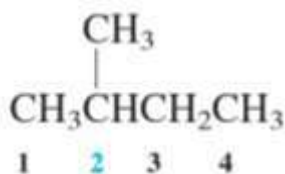


2,3,5-trimethyl-4-propylheptane

[Pick the long chain with more substituents.]

IN SUMMARY when naming a branched alkane:

(1) Find the longest chain; (2) find the names of all the alkyl groups attached to the chain; (3) number the chain; (4) name the alkane, with substituent names in alphabetical order. Haloalkanes are named in accord with the rules that apply to naming the alkanes, the halo substituent being treated the same as alkyl groups.



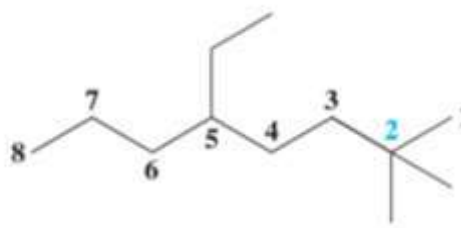
er.

not 4

3

2

1



not 1

2

3

4

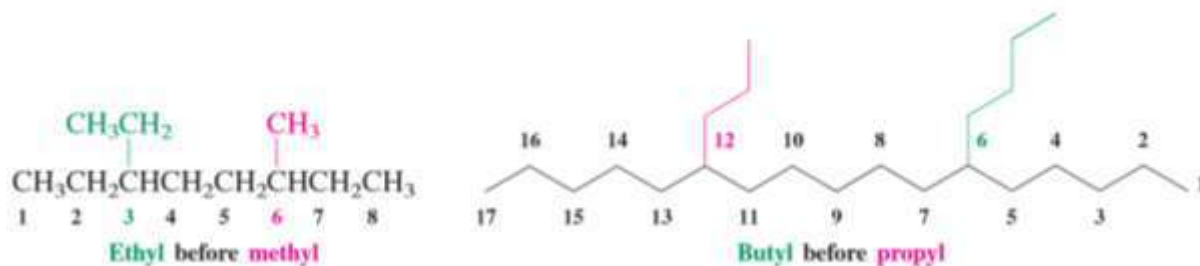
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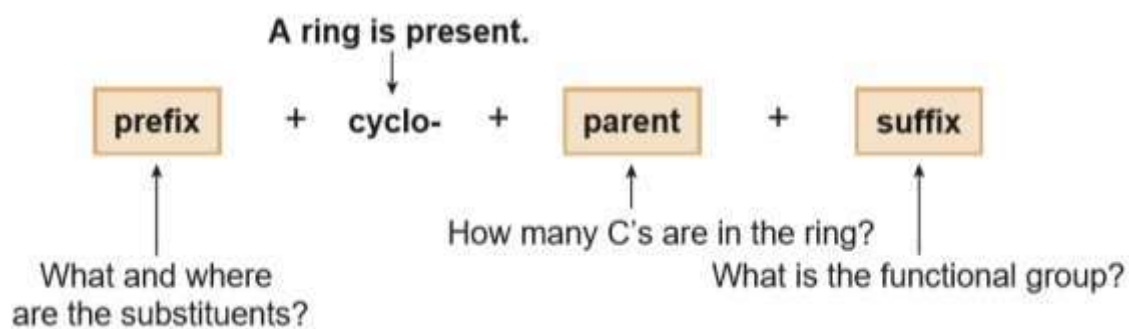
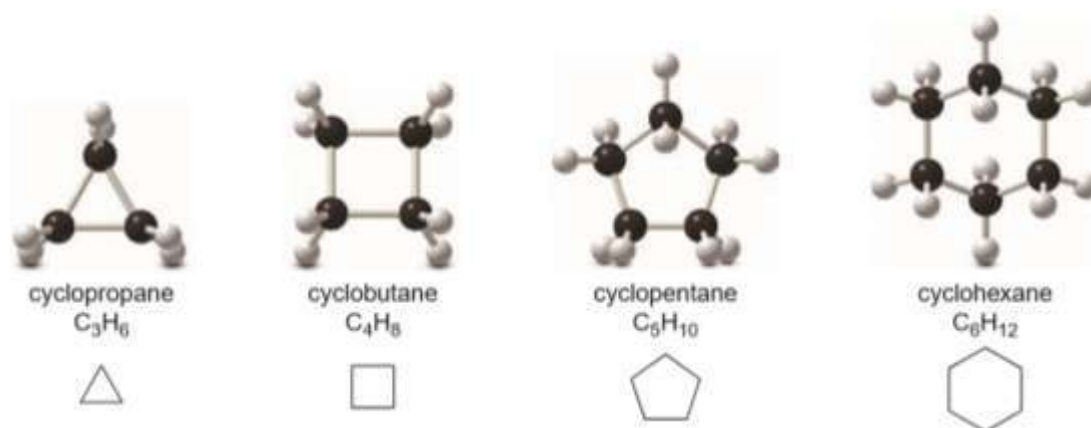
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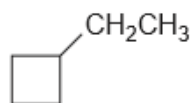
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If there are two substituents at equal distance from the two ends of the chain, use the alphabet to decide how to number. The substituent to come first in alphabetical order is attached to the carbon with the lower number.



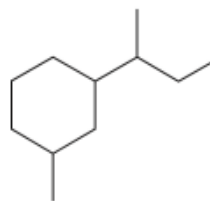
Cycloalkanes are named by adding the prefix cyclo- to the name of the acyclic alkane having the same number of carbons.





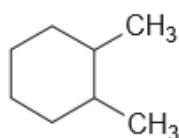
ethylcyclobutane

[No number is needed with only one substituent.]



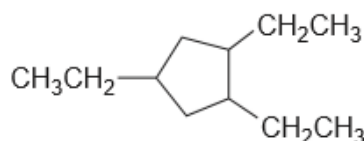
1-sec-butyl-3-methylcyclohexane

[Assign the lower number to the 1st substituent alphabetically: the **b** of **butyl** before the **m** of **methyl**.]



1,2-dimethylcyclohexane

[Number to give the 2nd CH₃ group the lower number: 1,2- not 1,6-.]



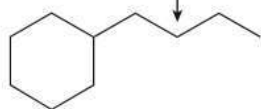
1,2,4-triethylcyclopentane

[Number to give the 2nd CH₃CH₂ group the lower number: 1,2,4- not 1,3,4- or 1,3,5-.]

Naming compounds containing both a ring and a long chain of carbon atoms:

More carbons in the ring

4 C's in the chain —
a **butyl** group



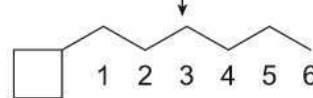
6 C's in the ring — **cyclohexane**

Name as a **cyclohexane** with a substituent.

Answer: butylcyclohexane

More carbons in the chain

6 C's in the chain —
a **hexane**



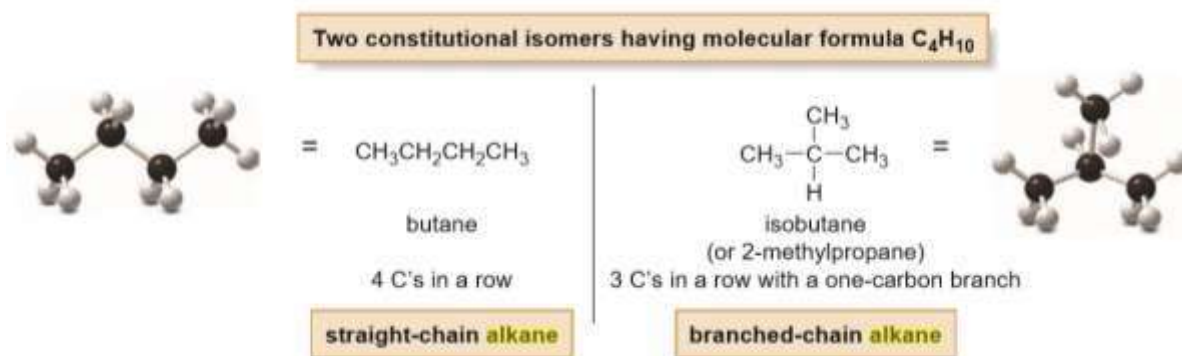
4 C's in the ring — a **cyclobutyl** group

Name as a **hexane** with a substituent.

Answer: 1-cyclobutylhexane

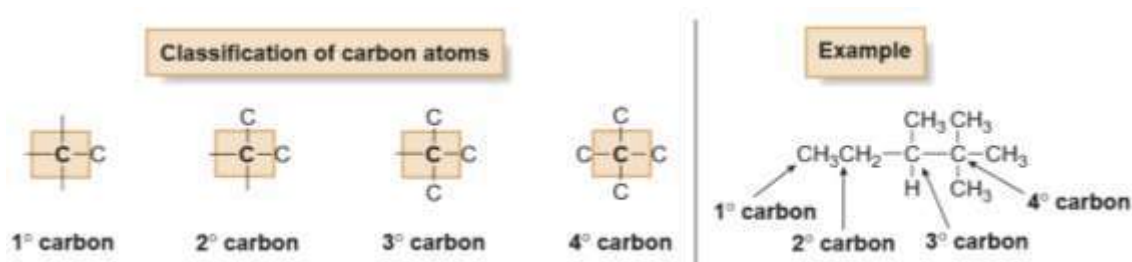
Structural isomers:

There are two different ways to arrange four carbons, giving two compounds with molecular formula C_4H_{10} , named butane and isobutane.



Carbon atoms in alkanes and other organic compounds are classified by the number of other carbons directly bonded to them.

- A **primary carbon** (1° carbon) is bonded to one other C atom.
- A **secondary carbon** (2° carbon) is bonded to two other C atoms.
- A **tertiary carbon** (3° carbon) is bonded to three other C atoms.
- A **quaternary carbon** (4° carbon) is bonded to four other C atoms.



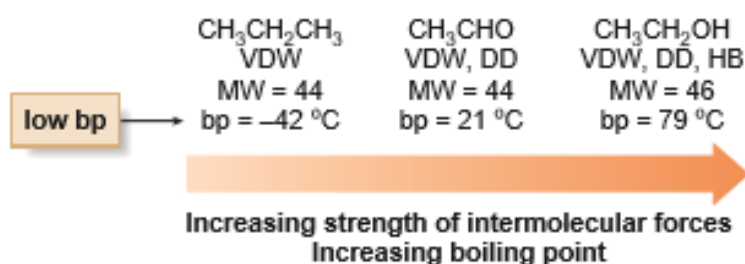
Hydrogen atoms are classified as primary (1°), secondary (2°), or tertiary (3°) depending on the type of carbon atom to which they are bonded.

Physical properties of alkanes:

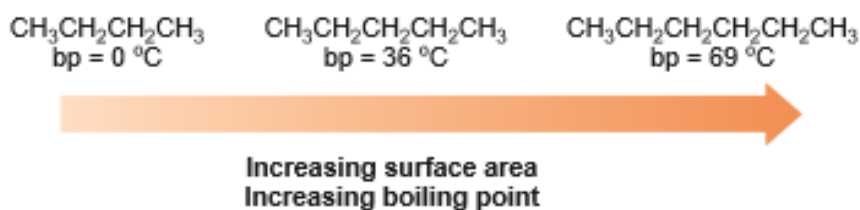
Alkanes contain only nonpolar C–C and C–H bonds, and as a result they exhibit only **weak van der Waals forces**.

Alkanes are soluble in organic solvents, insoluble in water, have low bp's and mp's compared to more polar compounds of comparable size.

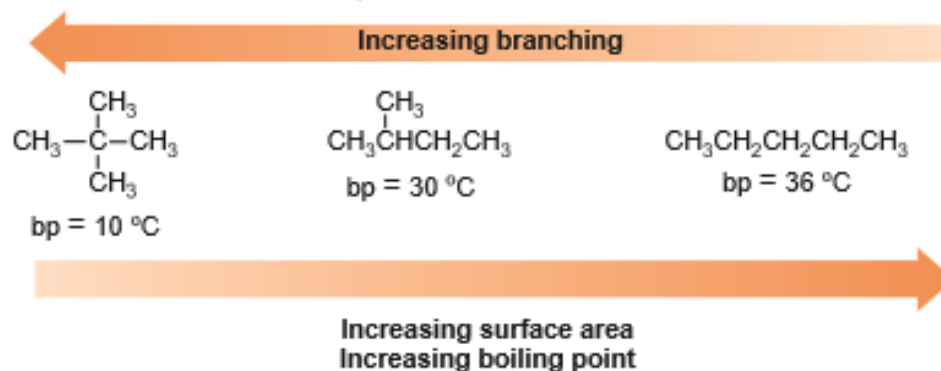
- Alkanes have low bp's compared to more polar compounds of comparable size.



- Bp increases as the number of carbons increases because of increased surface area.



- The bp of isomers decreases with branching because of decreased surface area.

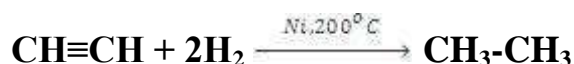
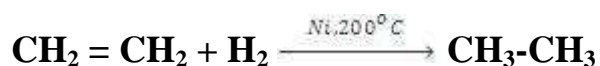


Preparation of Alkanes

- 1- Hydrogenation of Alkenes and alkynes.
- 2- Reduction of Alkyl Halides.
- 3- Reduction of Carbonyl Compounds.
- 4- Decarboxylation.
- 5- Grignard Reagents.
- 6- Wurtz Reaction.
- 7- Corey- House Synthesis.

Hydrogenation of Alkenes and alkynes:

Alkenes and alkynes on catalytic hydrogenation give alkanes

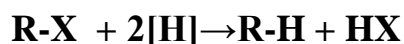


If **Pt** or **Pd** are used as catalyst, reaction occurs at normal temperature.

Also some times Raney nickel is used as catalyst.

Reduction of Alkyl Halides

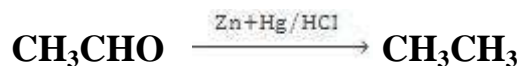
Alkyl halides on reduction with hydrogen form alkanes.

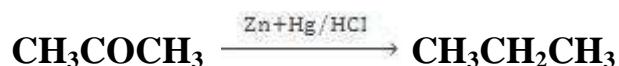


Alkyl halides can also be reduced to alkane by **H₂/Pd** or **LiAlH₄** or by **H₂/Ni**. The yields are generally high and the hydrocarbons formed are pure.

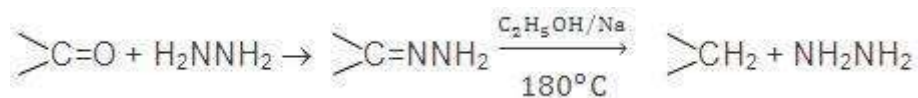
Reduction of Carbonyl Compounds

The reduction of carbonyl compounds by **amalgamated zinc** and **conc. HCl** also yields alkanes. This is **Clemmensen reduction**.



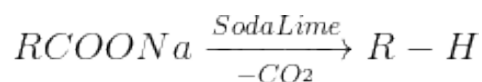


Carbonyl compounds may also be reduced to alkanes by **Wolf Kishner reaction**.



Decarboxylation

Decarboxylation refers to the process of removal of CO_2 from the molecules having **-COOH** group. Saturated monocarboxylic acid salt of sodium or potassium on dry distillation with soda lime ($\text{CaO} + \text{NaOH}$) gives alkane.



The alkane formed by decarboxylation process always contains one carbon atom less than the original acid. The yield is good in case of lower members but poor for higher members.

The decarboxylation of sodium formate yields H_2 .

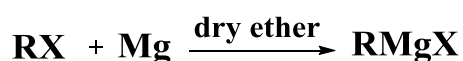


Grignard Reagents

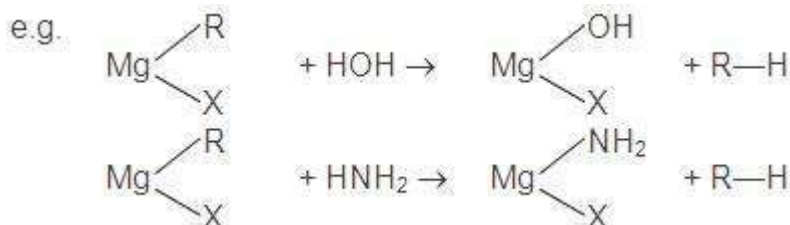
Organic compounds in which a metal atom is directly linked to carbon atom are known as organometallic compound. e.g. $\text{HC}\equiv\text{CNa}$, $(\text{C}_2\text{H}_5)_4\text{Pb}$, $(\text{C}_2\text{H}_5)_2\text{Zn}$.

Alkyl or aryl magnesium halide (**R-MgX**) are called Grignard reagents or organometallic compounds.

Grignard reagents form via the reaction of an alkyl or aryl halide with magnesium metal:



Grignard reagent decomposition with **water** or with other compounds having active **H**(the hydrogen attached on **O, N, F** or triple bonded carbon atom are known as **active hydrogen**) give alkane.



Wurtz Reaction

In wurtz reaction a solution of alkyl halide in ether on heating with sodium gives alkane.



An alkyl halide on Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms. Two different alkyl halides, on Wurtz reaction give all possible alkanes.



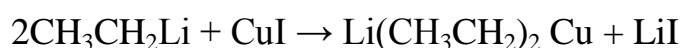
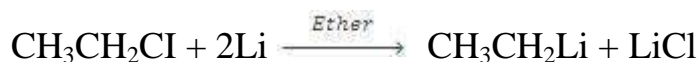
The separation of mixture into individual members is not easy because their boiling points are near to each other and thus Wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atoms.

Limitations of Wurtz reaction :

- a. Methane cannot be obtained by this method
- b. The reaction fails in case of tertiary halides

Corey- House Synthesis

Alkyl chloride say chloroethane reacts with lithium in presence of ether to give lithium alkyl then reacts with CuI to give lithium dialkylcuprate. This lithium dialkylcuprate now again reacts with alkyl chloride to give alkane.



The **Corey–House synthesis** is a powerful for the synthesis of a large alkane from two smaller alkyl halides.

Reactions of alkanes

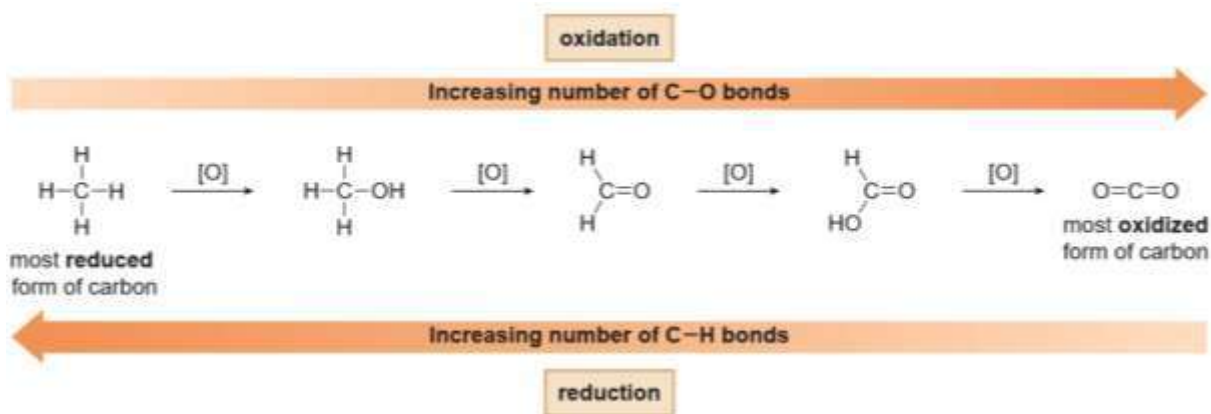
Alkanes are the only family of organic molecules that have no functional group, and therefore, alkanes undergo few reactions. In fact, alkanes are inert to reaction unless forcing conditions are used.

Oxidation and Reduction Reactions

- Oxidation is the loss of electrons.
- Reduction is the gain of electrons.

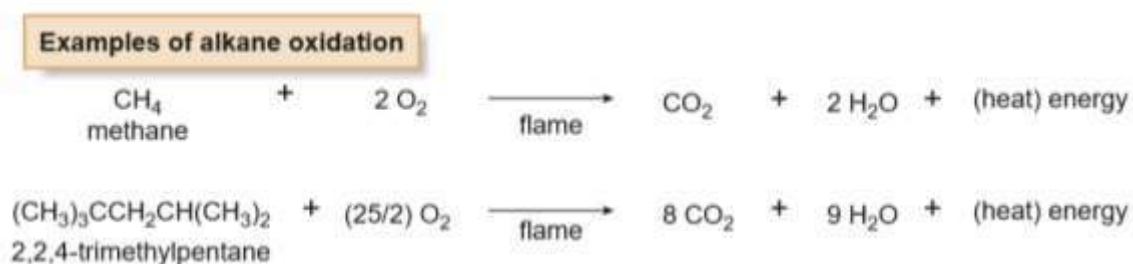
Oxidation and reduction are opposite processes.

- Oxidation results in a decrease in the number of **C-H** bonds.
- Reduction results in an increase in the number of **C-H** bonds.



Combustion of Alkanes

Alkanes undergo combustion that is, they burn in the presence of oxygen to form carbon dioxide and water. This is a practical example of oxidation.



Halogenation: is the replacement of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine or iodine).

Halogenation of Alkanes:

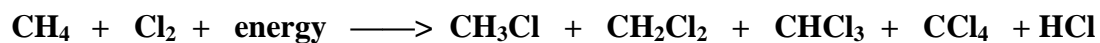
The reaction of a halogen with an alkane in the presence of ultraviolet (UV) light or heat leads to the formation of a **haloalkane (alkyl halide)**. An example is the chlorination of methane.

The chlorination of methane, provides a simple example of this reaction.



The relative amounts of the various products depend on the proportion of the two reactants used. In the case of methane, a large excess of the

hydrocarbon favors formation of methyl chloride as the chief product; whereas, an excess of chlorine favors formation of chloroform and carbon tetrachloride.

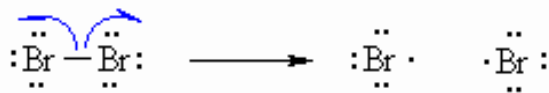


- When treated with Br_2 or Cl_2 , radical substitution of R-H generates the alkyl halide and HX.
- Alkane R-H relative reactivity order : tertiary > secondary > primary > methyl.
- Halogen reactivity $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- Only chlorination and bromination are useful in the laboratory.
- Bromination is selective for the R-H that gives the most stable radical.
- Chlorination is less selective
- Reaction proceeds via an radical chain mechanism which involves radical intermediates.

Radical chain mechanism for reaction of methane with Br_2

Step 1 (Initiation)

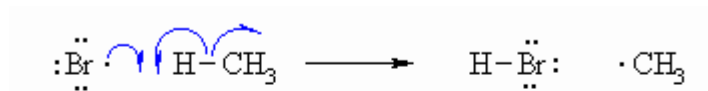
Heat or uv light cause the weak halogen bond to undergo homolytic cleavage to generate two bromine radicals and starting the chain process.



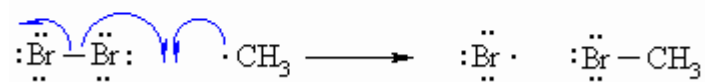
Step 2

(Propagation)

(a) A bromine radical abstracts a hydrogen to form HBr and a methyl radical, then

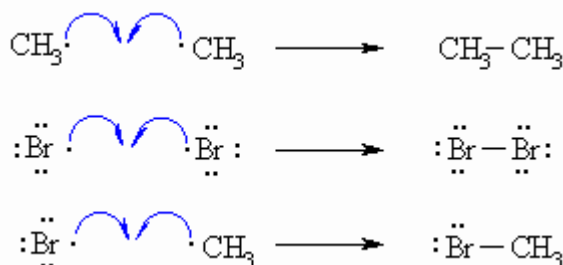


(b) The methyl radical abstracts a bromine atom from another molecule of Br_2 to form the methyl bromide product



Step3 (Termination)

Various reactions between the possible pairs of radicals allow for the formation of ethane, Br_2 or the product, methyl bromide. These reactions remove radicals and do not perpetuate the cycle.



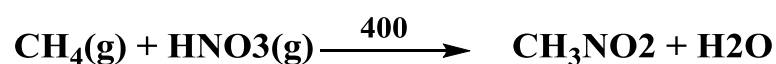
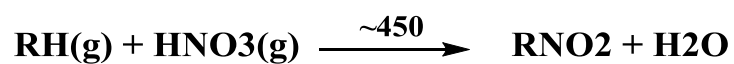
When alkanes larger than ethane are halogenated, isomeric products are formed. Thus chlorination of propane gives both 1-chloropropane and 2-chloropropane as mono-chlorinated products.



Nitration of Alkanes

Nitration: A nitro group substitutes for a hydrogen.

Replacement of **H** atom of alkane by **-NO₂** group is known as nitration, the nitration of alkanes gives nitroalkanes. Such reactions usually are carried out in the vapor phase at high temperatures using nitric acid (HNO₃) or nitrogen tetroxide (N₂O₄) as the nitrating agent:



Experiment 3:

Simple distillation

Purpose:

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Introduction:

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Note: the liquids to be distilled must be mixable with each other. If they are not then they would form separable layers, which you separate much more easily with a separating funnel.

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The Simple distillation is the most common method because:

- 1-** It is a technique used for the purification of liquids.
- 2-** Separation of liquid mixtures.

3- Detection the real boiling point.

Procedure:

A typical set-up for simple distillation is given in **Figure 4** :

When carrying out a distillation, the following practical points should be observed:

- a.* The boiling flask should not be more than half full.
- b.* Boiling stones are added to the liquid to prevent bumping.
- c.* Each ground joint should be greased to ensure a completely sealed system.
- d.* Cooling water in the condenser should enter at the lower end and exit at the upper end. This ensures that the condenser jacket is always full of water.
- e.* The bulb of the thermometer should be below the opening of the side arm so as to measure the temperature at which liquid and vapor are in equilibrium.
- f.* Heat sources used depend on the nature of the liquid. A water bath is used to distil low-boiling and flammable liquids, while a burner with a wire gauze is used for higher boiling and less flammable liquids.

Figure : Simple distillation apparatus.

Apparatus:

Thermometer

clamp

Bunsen burner

Tripod

stand

condenser

Conical flask

Round bottom flask

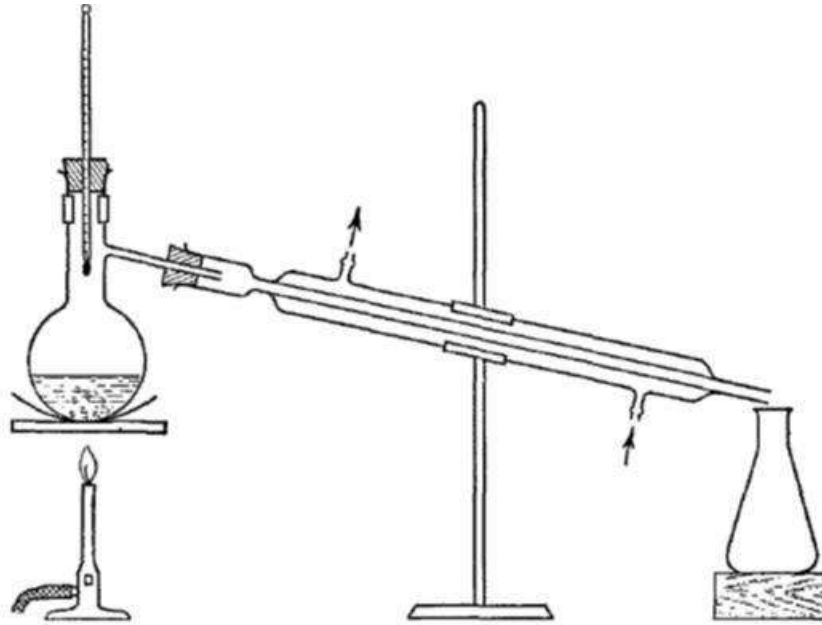


Figure 6: Simple distillation apparatus