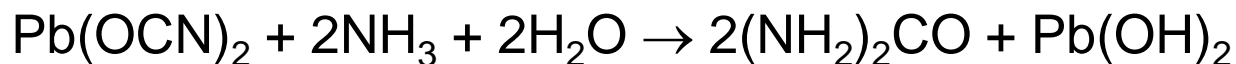


# Introduction

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## ■ What is Organic Chemistry?

→ Organic chemistry is the study of carbon compounds. The word “organic” was originally used by eighteenth-century chemists to describe substances obtained from living sources—plants and animals. These chemists believed that nature possessed a certain vital force and that only living things could produce organic compounds. This romantic notion was disproved in 1828 by Friedrich Wohler, a German chemist who prepared urea, an organic compound, from the reaction between inorganic compounds lead cyanate and aqueous ammonia:



→ Today, well over 20 million synthetic and natural organic compounds are known.

# Introduction

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## ■ Classes of Organic Compounds:

→ Carbon can form more compounds than any other element because carbon atoms are able not only to form single, double, and triple carbon-carbon bonds, but also to link up with each other in chains and ring structures.

→ **The branch of chemistry that deals with carbon compounds is organic chemistry.**

→ Classes of organic compounds can be distinguished according to functional groups they contain.

→ **A functional group is a group of atoms that is largely responsible for the chemical behavior of the parent molecule.**

Different molecules containing the same kind of functional group or

# Introduction

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## ■ Classes of Organic Compounds:

→ Different molecules containing the same kind of functional group or groups undergo similar reactions. Thus, by learning the characteristic properties of a few functional groups, we can study and understand the properties of many organic compounds.

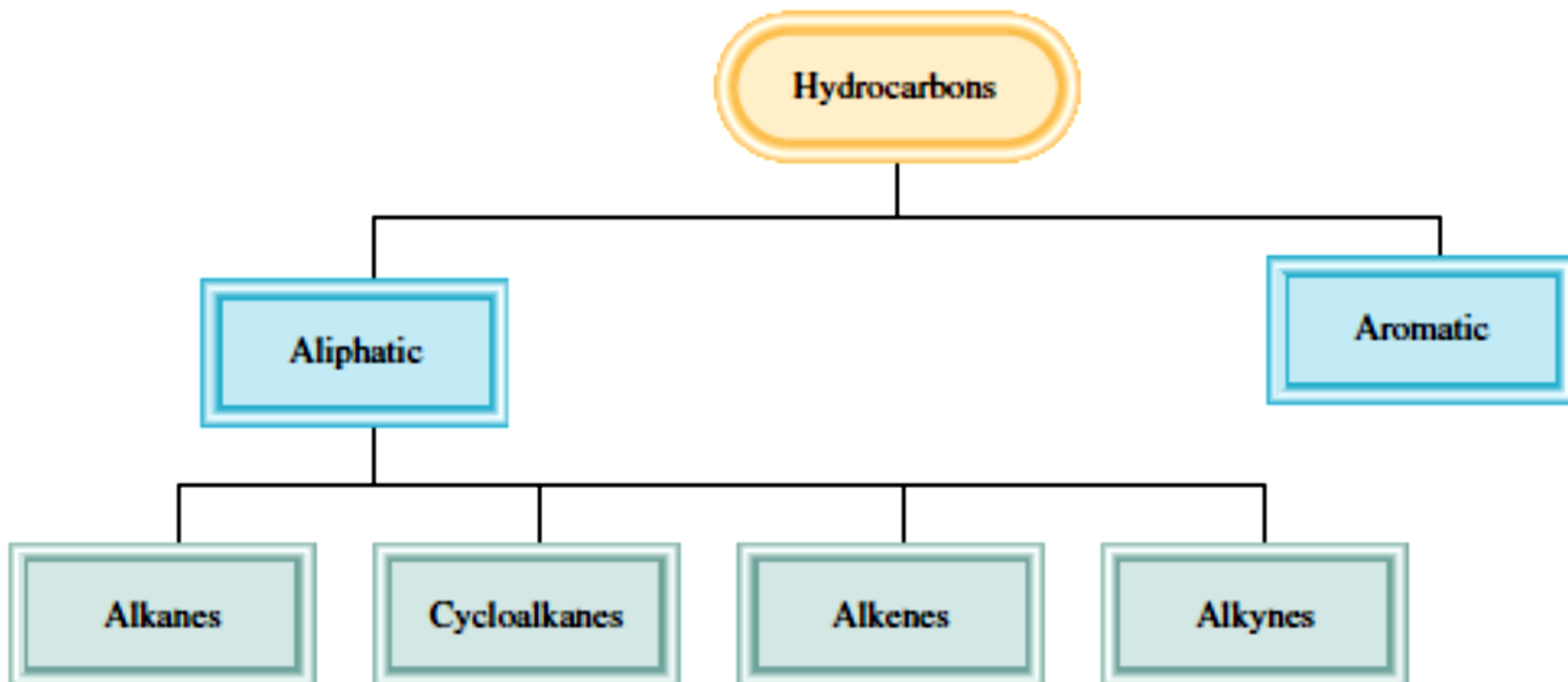
→ The functional groups known as **alcohols**, **ethers**, **aldehydes** and **ketones**, **carboxylic acids**, and **amines**, **ester**.

→ Most organic compounds are derived from a group of compounds known as **hydrocarbons** because they are made up of only hydrogen and carbon. On the basis of structure, hydrocarbons are divided into **two main classes—aliphatic and aromatic**. Aliphatic hydrocarbons do not contain the benzene group, or the benzene ring, whereas aromatic hydrocarbons contain one or more benzene rings.

# Introduction

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## ■ Classes of Organic Compounds:

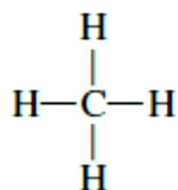


# Organic Chemistry

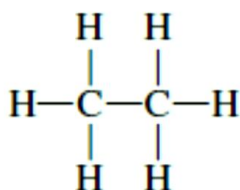
## ■ Aliphatic Hydrocarbons:

### → Alkanes:

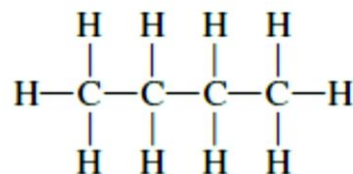
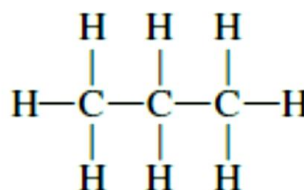
→ Alkanes have the general formula  $C_nH_{2n+2}$ , where  $n = 1, 2, \dots$ . The essential characteristic of alkane hydrocarbon molecules is that only single covalent bonds are present. The alkanes are known as saturated hydrocarbons because they contain the maximum number of hydrogen atoms that can bond with the number of carbon atoms present.



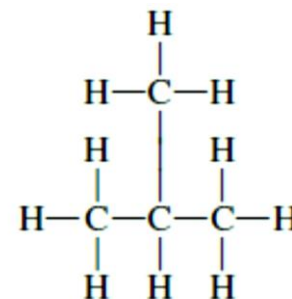
Methane



Ethane



*n*-Butane



Isobutane

# Organic Chemistry

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## → Alkanes:

→ The carbon atoms in all the alkanes can be assumed to be  $sp^3$ -hybridized. The structures of ethane and propane are straightforward, for there is only one way to join the carbon atoms in these molecules. Butane, however, has two possible bonding schemes resulting in the **structural isomers** n-butane (n stands for normal) and isobutane, *molecules that have the same molecular formula, but different structures.*

→ In the alkane series, as the number of carbon atoms increases, the number of structural isomers increases rapidly.

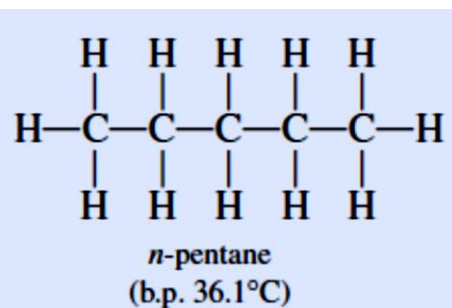
For example, butane,  $C_4H_{10}$ , has two isomers; decane,  $C_{10}H_{22}$ , has 75 isomers; and the alkane  $C_{30}H_{62}$  has over 400 million, or  $4 \times 10^8$ , possible isomers!

# Organic Chemistry

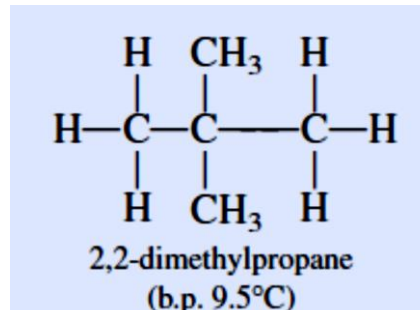
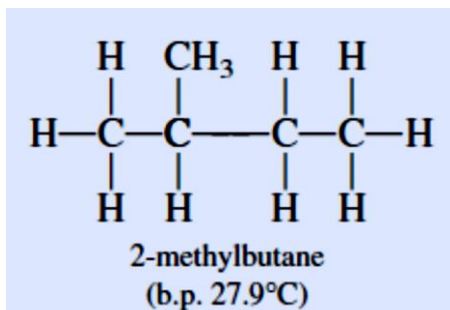
→ How many structural isomers can be identified for pentane,  $C_5H_{12}$ ?

→ For small hydrocarbon molecules (eight or fewer C atoms), it is relatively easy to determine the number of structural isomers by trial and error.

→ The first step is to write the straight-chain structure.



The second structure, by necessity, must be a branched chain:

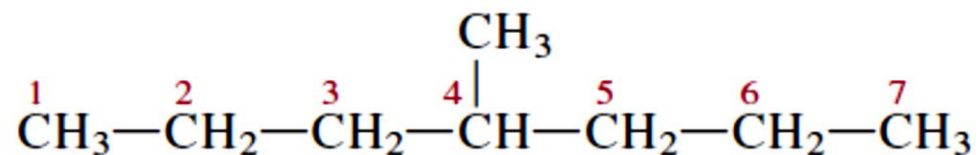


# Organic Chemistry

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## ■ Alkane Nomenclature:

1. The parent name of the hydrocarbon is that given to the longest continuous chain of carbon atoms in the molecule. Thus, the parent name of the following compound is heptane because there are seven carbon atoms in the longest chain.

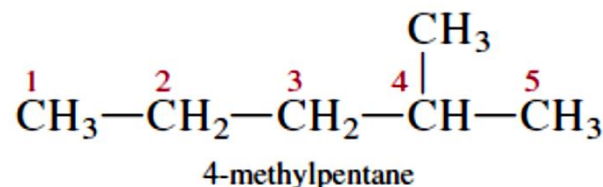
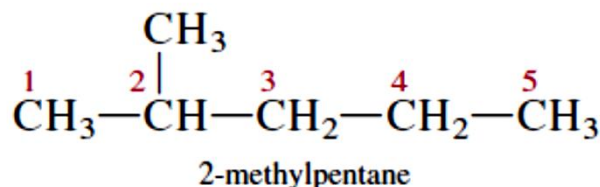


2. An alkane less one hydrogen atom is an alkyl group. For example, when a hydrogen atom is removed from methane, we are left with the  $\text{CH}_3$  fragment, which is called a methyl group. Similarly, removing a hydrogen atom from the ethane molecule gives an ethyl group, or  $\text{C}_2\text{H}_5$ . Any chain branching off the longest chain is named as an alkyl group.

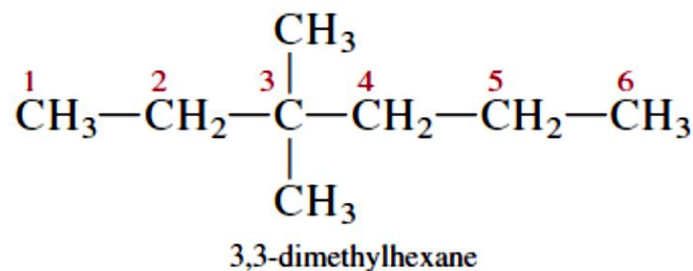
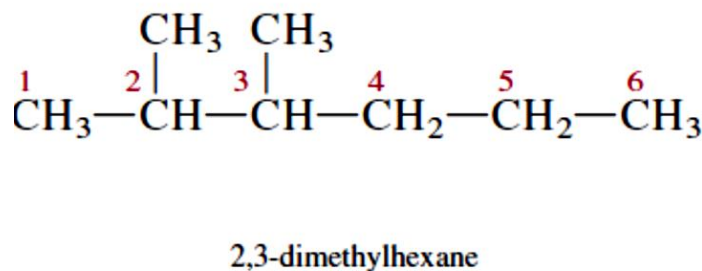


# Organic Chemistry

3. When one or more hydrogen atoms are replaced by other groups, the name of the compound must indicate the locations of carbon atoms where replacements are made. The procedure is to number each carbon atom on the longest chain in the direction that gives the smaller numbers for the locations of all branches.

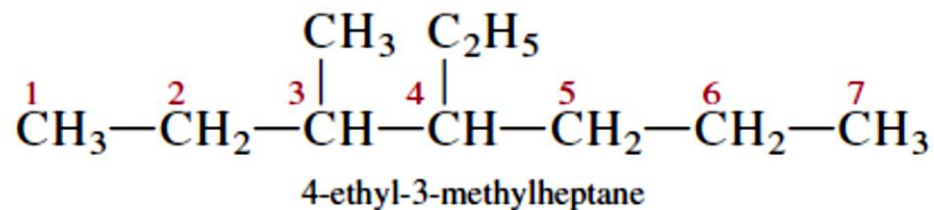


4. When there is more than one alkyl branch of the same kind present, we use a prefix such as di-, tri-, or tetra- with the name of the alkyl group. Consider the following examples:

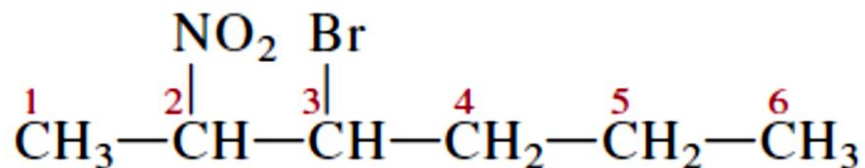


# Organic Chemistry

When there are two or more different alkyl groups, the names of the groups are listed alphabetically. For example,



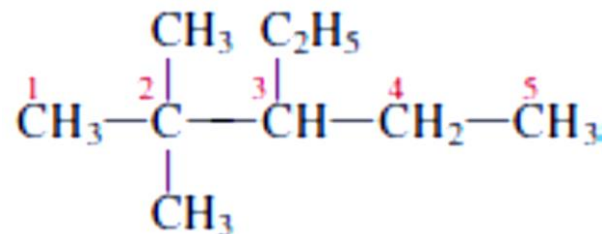
5. Of course, alkanes can have many different types of substituents. The names of some substituents, including nitro and bromo. Thus, the compound is called 3-bromo-2-nitrohexane. Note that the substituent groups are listed alphabetically in the name, and the chain is numbered in the direction that gives the lowest number to the first substituted carbon atom.



# Organic Chemistry

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- Give the IUPAC name of the following compound:



- Write the structural formula of 5-ethyl-2,4,6-trimethyloctane.

# Organic Chemistry

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## ■ Optical Isomerism of Substituted Alkanes:

Optical isomers are compounds that are non-superimposable mirror images of each other.

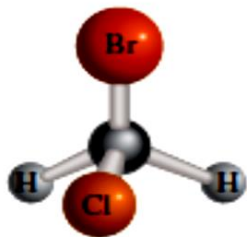
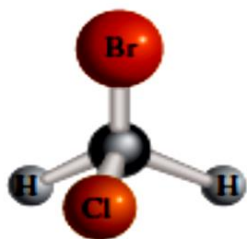
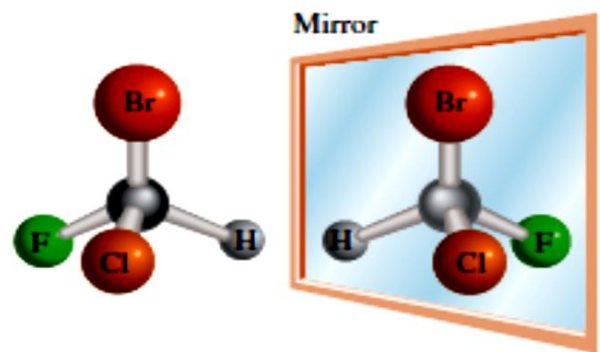
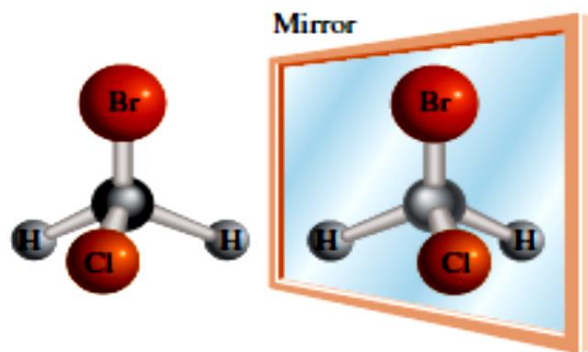
The mirror images of  $\text{CH}_2\text{ClBr}$  are superimposable but those of  $\text{CHFCIBr}$  are not, no matter how we rotate the molecules. Thus, the  $\text{CHFCIBr}$  molecule is chiral.

Most simple chiral molecules contain at least one asymmetric carbon atom—that is, ***a carbon atom bonded to four different atoms or groups of atoms.***

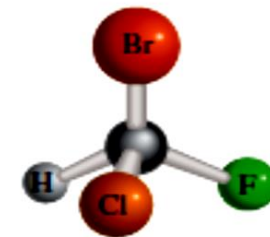
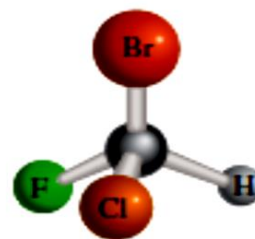
# Organic Chemistry

## ■ Optical Isomerism of Substituted Alkanes:

Perspective drawings of the substituted methanes  $\text{CH}_2\text{ClBr}$  and  $\text{CHFClBr}$  and their mirror images.



(a)



(b)

# Organic Chemistry

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## ■ Cycloalkanes:

Alkanes whose carbon atoms are joined in rings are known as cycloalkanes. They have the general formula  $C_nH_{2n}$ , where  $n = 3, 4, \dots$ . The simplest cycloalkane is cyclopropane,  $C_3H_6$ .

Many biologically significant substances such as cholesterol, testosterone, and progesterone contain one or more such ring systems.

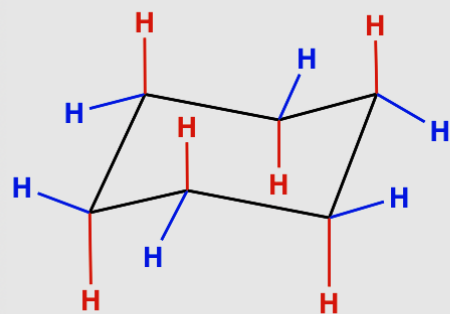
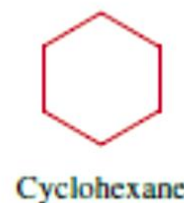
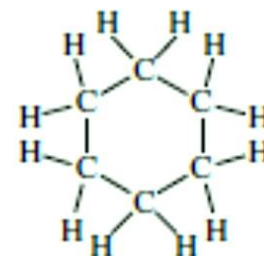
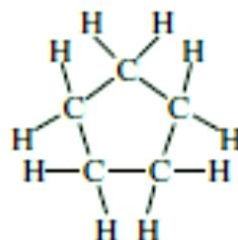
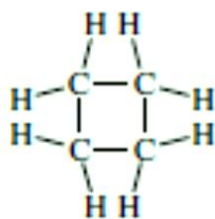
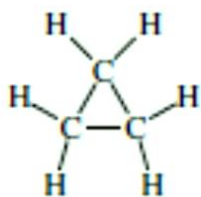
Theoretical analysis shows that cyclohexane can assume two different geometries that are relatively free of strain. By “strain” we mean that bonds are compressed, stretched, or twisted out of normal geometric shapes as predicted by  $sp^3$  hybridization.

The most stable geometry is the chair form.

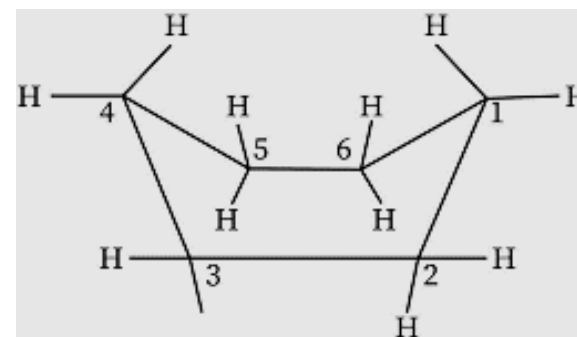
# Organic Chemistry

## ■ Cycloalkanes:

*Structures of the first four cycloalkanes and their simplified forms.*



Chair conformation of cyclohexane



Boat conformation of cyclohexane

# Organic Chemistry

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## ■ Alkenes:

The alkenes (also called olefins) contain at least one carbon-carbon double bond.

Alkenes have the general formula  $C_nH_{2n}$ , where  $n = 2, 3, \dots$ . The simplest alkene is  $C_2H_4$ , ethylene, in which both carbon atoms are  $sp^2$ -hybridized and the double bond is made up of a sigma bond and a pi bond.

## ■ Alkenes Nomenclature:

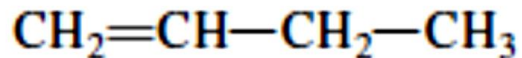
In naming alkenes we indicate the positions of the carbon-carbon double bonds. The names of compounds containing  $C=C$  bonds end with *-ene*. As with the alkanes, the name of the parent compound is determined by the number of carbon atoms in the longest chain.



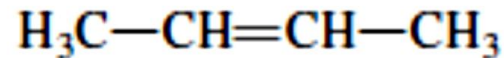
# Organic Chemistry

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## ■ Alkenes Nomenclature:



1-butene



2-butene

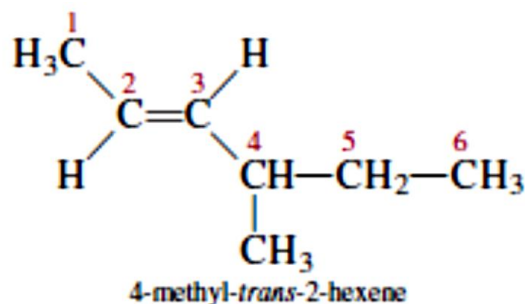
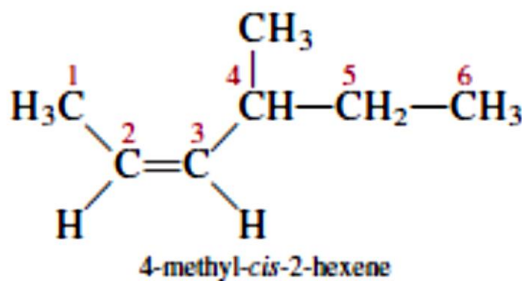
→ The numbers in the names of alkenes refer to the lowest numbered carbon atom in the chain that is part of the C=C bond of the alkene. The name “butene” means that there are four carbon atoms in the longest chain.

→ Alkene nomenclature must specify whether a given molecule is *cis* or *trans* if it is a geometric isomer.

→ In the *cis isomer*, the two H atoms are on the same side of the C=C bond; in the *trans isomer*, the two H atoms are across from each other.

# Organic Chemistry

## ■ Geometric isomerism:



→ The numbers in the names of alkenes refer to the lowest numbered carbon atom in the chain that is part of the C=C bond of the alkene. The name “butene” means that there are four carbon atoms in the longest chain.

→ Alkene nomenclature must specify whether a given molecule is *cis* or *trans* if it is a geometric isomer.

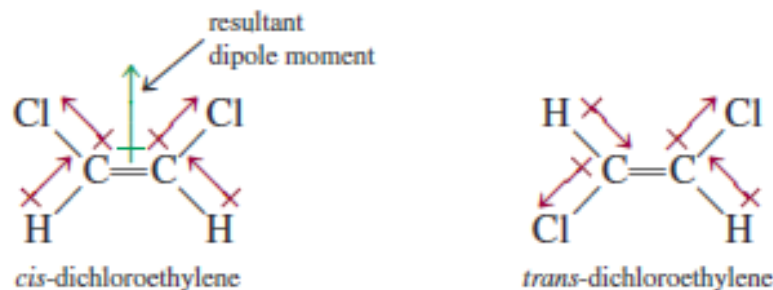
→ The term **cis** means that two particular atoms (or groups of atoms) are adjacent to each other, and **trans** means that the two atoms (or groups of atoms) are across from each other.

# Organic Chemistry

## ■ Geometric isomerism:

Geometric isomers, which cannot be interconverted without breaking a chemical bond.

■ The molecule dichloroethylene,  $\text{ClHC}=\text{CHCl}$ , can exist as one of the two geometric isomers called cis-dichloroethylene and trans-dichloroethylene:



Generally, *cis* and *trans* isomers have distinctly different physical and chemical properties. Heat or irradiation with light is commonly used to bring about the conversion of one geometric isomer to another, a process called *cis-trans* isomerization, or geometric isomerization. As the above data show, dipole moment measurements can be used to distinguish between geometric isomers. In general, *cis* isomers possess a dipole moment, whereas *trans* isomers do not.

# Organic Chemistry

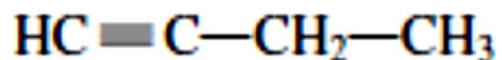
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## ■ Alkynes:

Alkynes contain at least one carbon-carbon triple bond. They have the general formula  $C_nH_{2n-2}$ , where  $n = 2, 3, \dots$

## ■ Alkyne Nomenclature:

Names of compounds containing carbon-carbon triple bonds end with *-yne*. Again, the name of the parent compound is determined by the number of carbon atoms in the longest chain for names of alkane counterparts. As in the case of alkenes, the names of alkynes indicate the position of the carbon-carbon triple bond, as, for example,



1-butyne



2-butyne

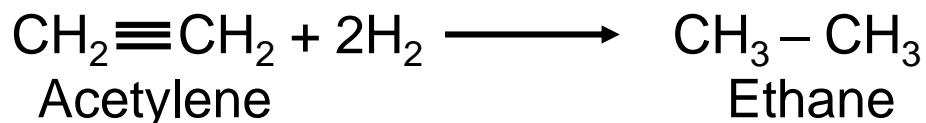
# Organic Chemistry

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## ■ Preparation of Alkanes:

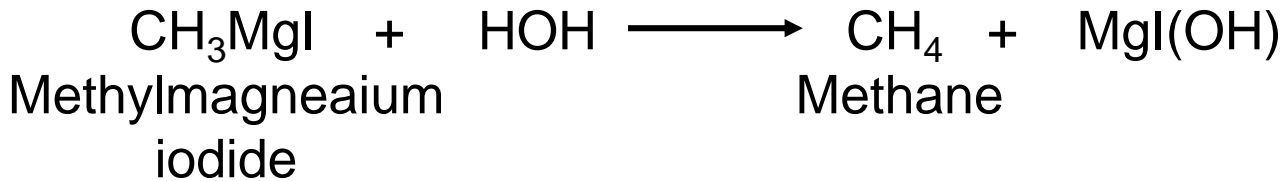
### 1) Hydrogenation of unsaturated hydrocarbons.

Alkanes are formed by passing a mixture of an unsaturated hydrocarbon and hydrogen over finely divided nickel ((or platinum) at 250° to 300° C. (Sabatier and Senderens Reaction).



### 2) From Grignard Reagents:

Alkylmagnesium halides (Grignard reagents) when decomposed with water yield pure alkanes.



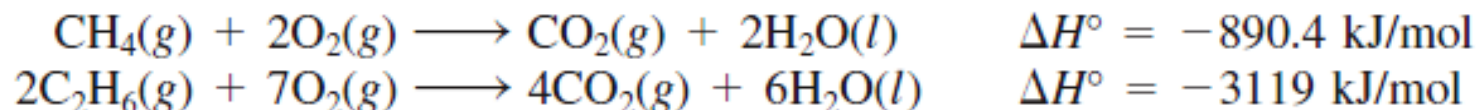
# Organic Chemistry

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## ■ The general reactions of alkanes:

→ Alkanes are generally not considered to be very reactive substances.

→ However, under suitable conditions they do react. For example, natural gas, gasoline, and fuel oil are alkanes that undergo highly exothermic combustion reactions:



### (1) Halogenation:

Chlorine and bromine can substitute the hydrogen atoms of alkanes with considerable ease, chlorine being more reactive than bromine. Thus by the action of chlorine at ordinary temperature in diffused daylight all the four hydrogen atoms of methane can be successively replaced by chlorine atoms.

# Organic Chemistry

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→ If an excess of chlorine gas is present, the reaction can proceed further:



→ A great deal of experimental evidence suggests that the initial step of the first halogenation reaction occurs as follows:



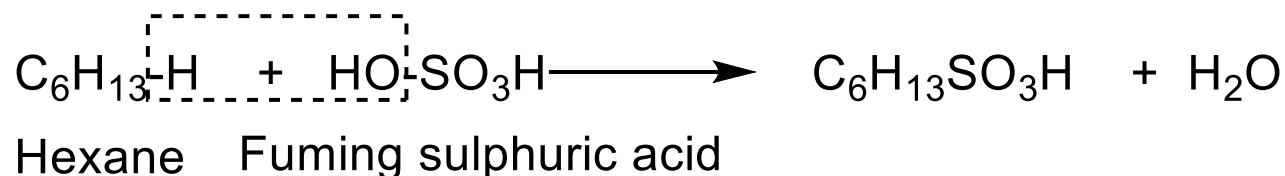
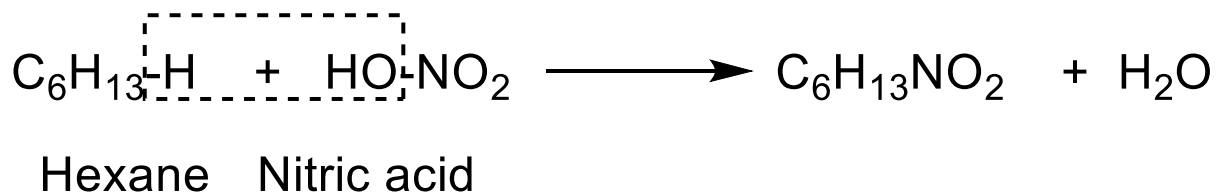
# Organic Chemistry

## (2) Reaction with acids (HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>):

→ Nitric acid has no action on lower alkanes but by its long, continued action on higher hydrocarbons one of their hydrogen atoms may be replaced by a nitro-group, NO<sub>2</sub> (**Nitration**).

→ Alkanes react with fuming sulphuric acid at elevated temperatures to produce alkanesulphonic acids.

The process involves the replacement of one H of the alkane by sulphonic acid group, -SO<sub>3</sub>H and is known as **Sulphonation**.





# Organic Chemistry

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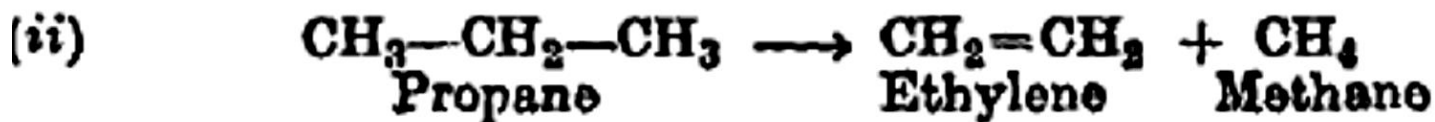
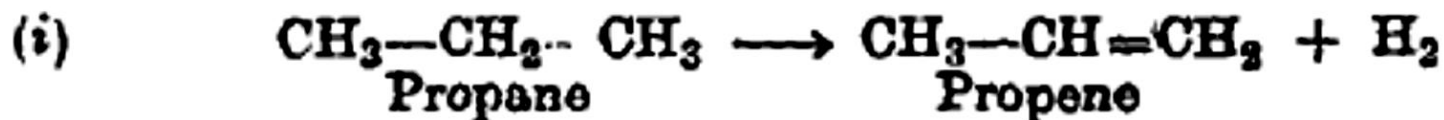
## (3) Pyrolysis:

By the term pyrolysis (Gr., pyr=fire ; *lysis*= loosing) is meant the conversion of an organic substance to one or more new substances by the action of heat alone. **(In absence of air)**

→ chemical decomposition occurs in two ways:

(i) by fission of C-H linkages to form an unsaturated hydro carbon and hydrogen gas ; and (ii) by fission of C-C linkages to give simpler hydrocarbons - one alkane and one alkene.

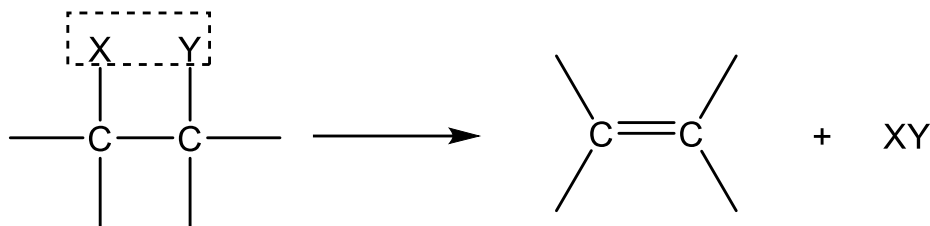
→ Thus propane when pyrolysed at about 600°C , is decomposed as follows:



# Organic Chemistry

## ■ Methods of Formation of Alkene:

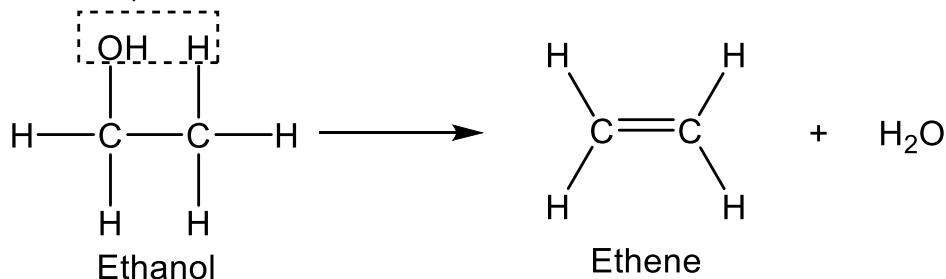
→ Most of the methods of preparation of alkenes depend upon the principle that the removal of atoms or groups from adjacent carbon atoms of n-chain, results in the creation of a double bond.



Where X and Y may be same or different

### 1) By dehydration of alcohols:

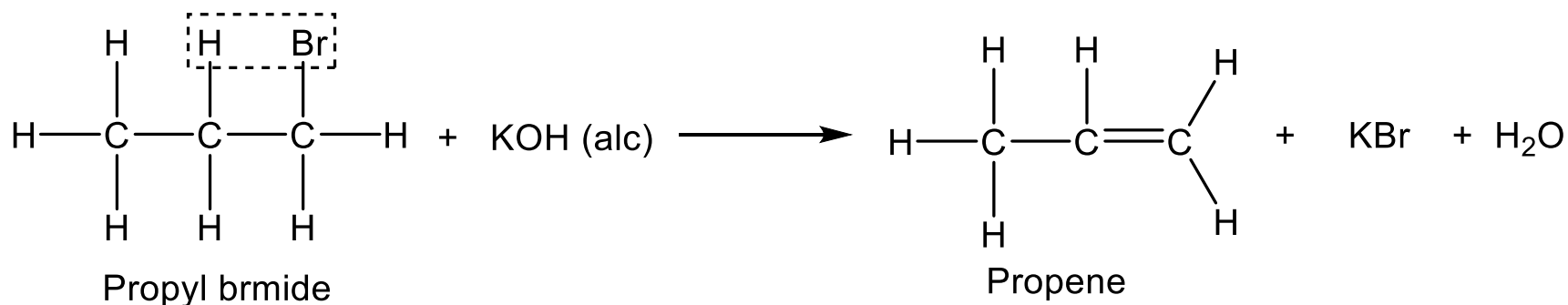
When heated with a dehydrating agent; like concentrated sulphuric acid or phosphoric acid, alcohols lose a molecule of water forming alkenes.



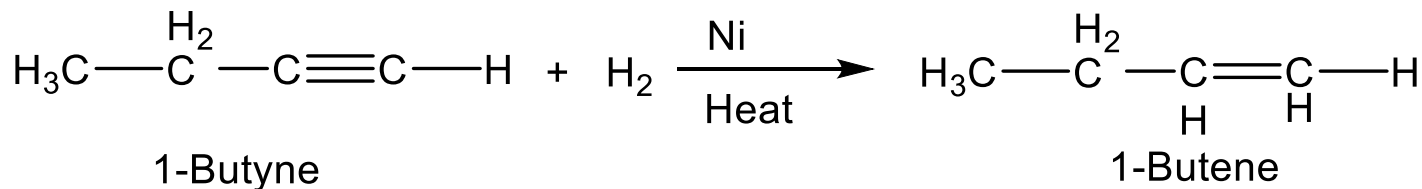
# Organic Chemistry

## (2) By dehydrohalogenation of alkyl halides:

When heated with alcoholic solution of potassium hydroxide (alcoholic potash), alkyl halides eliminate a Hydrogen and halogen atom from adjacent carbon atoms to form an alkene:



**(2) By partial hydrogenation of alkynes:** The alkyne mixed with hydrogen gas is passed over finely divided platinum or palladium, or heated nickel, when it adds only two H atoms to give alkene.



# Organic Chemistry

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## ■ Reactions of Alkene:

→ In general, alkenes give the following types of reactions:

### **(i) Addition Reaction:**

In these reactions, the reagent adds along the double bond, which is then converted to a single bond.

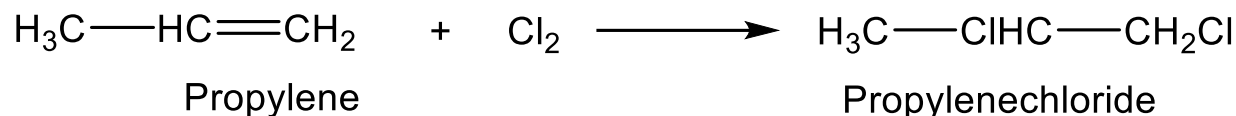
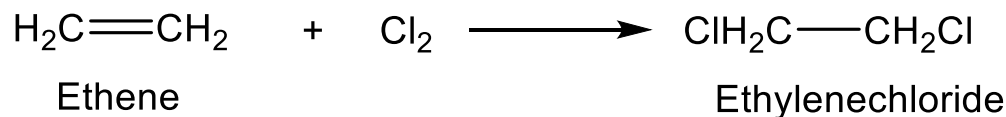
### **(ii) Polymerisation:**

The valenc bonds constituting the double bond are not in a stable condition. They become more labile at high temperature. Thus many molecules of an alkene may join together to form compound of higher molecular weights.

# Organic Chemistry

## (i) Addition of Halogens:

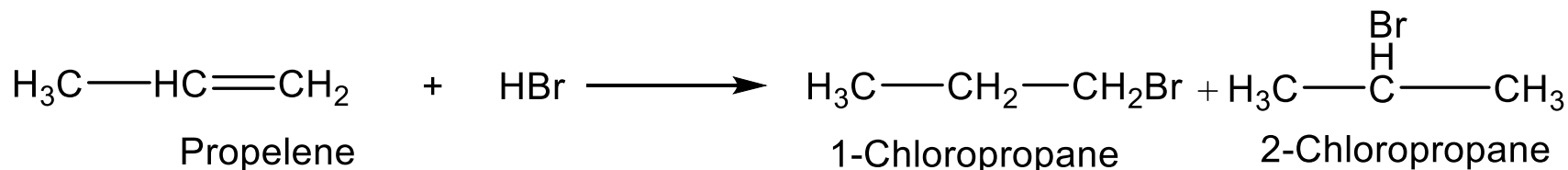
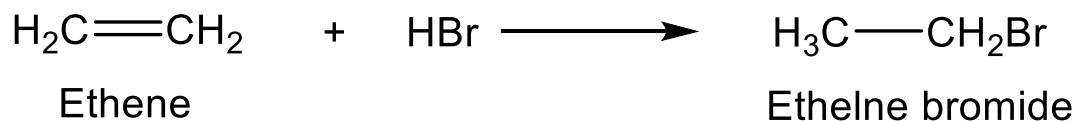
Alkenes react readily with halogens by addition, forming dihalogen derivatives:



## (iii) Addition of Halogen acids:

The addition reactions to the C=C bond includes;

The addition of a hydrogen halide to an unsymmetrical alkene such as propene is more complicated because two products are possible

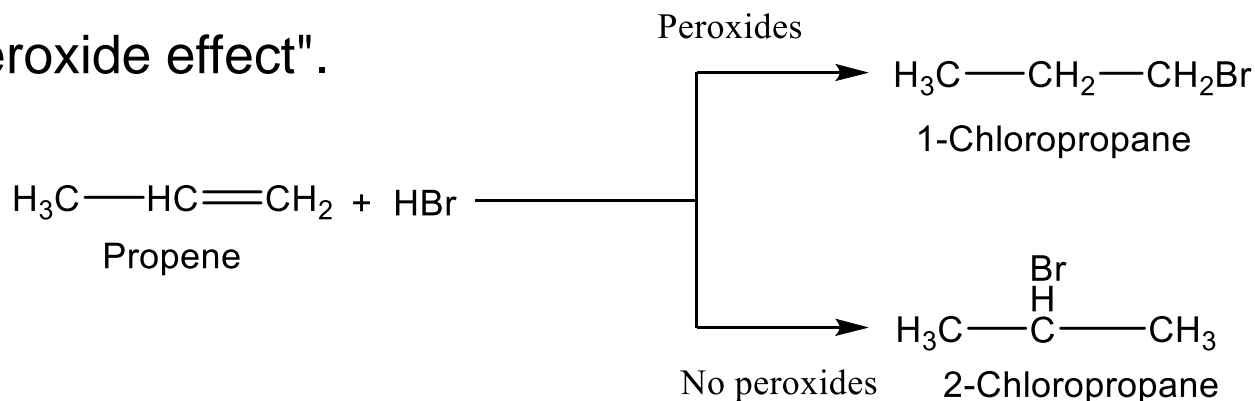


# Organic Chemistry

■ In 1871, Vladimir Markovnikov<sup>†</sup> postulated a generalization that enables us to predict the outcome of such an addition reaction.

■ This generalization, now known as Markovnikov's rule, states that in the addition of unsymmetrical (that is, polar) reagents to alkenes, the positive portion of the reagent (usually hydrogen) adds to the carbon atom that already has the most hydrogen atoms.

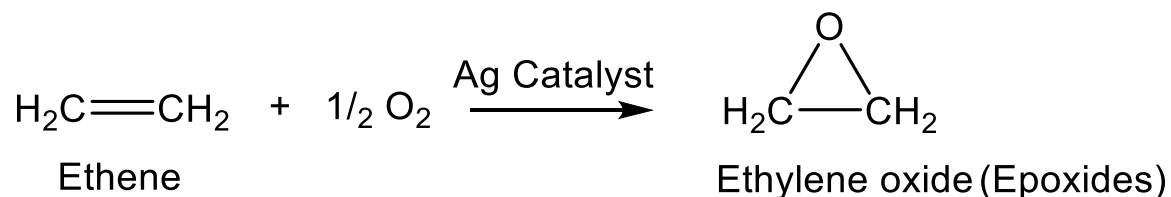
■ In the presence of oxygen or peroxides as catalysts, the addition of HBr to propene takes a course opposite to that predicted by Markovnikov's rule. This effect caused by the presence of peroxide is called "peroxide effect".



# Organic Chemistry

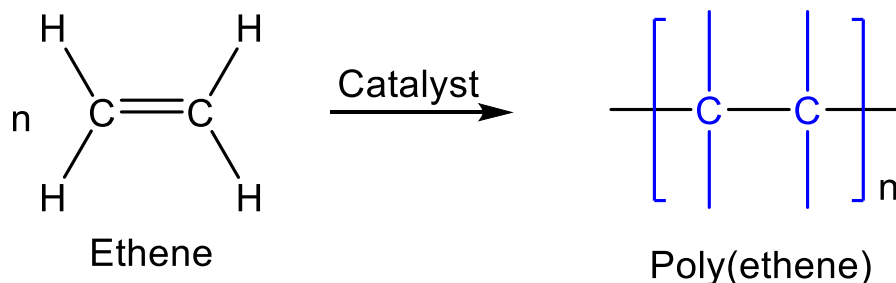
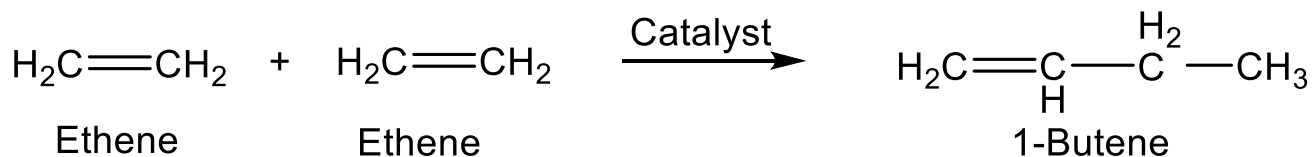
## (iii) Addition of oxygen:

Lower alkenes react with oxygen by addition in the presence of If special catalyst to form epoxides.



## (iv) Polymerisation:

At high temperature and in the presence of acid catalyst alkene molecules add to one another to form **polymers**.



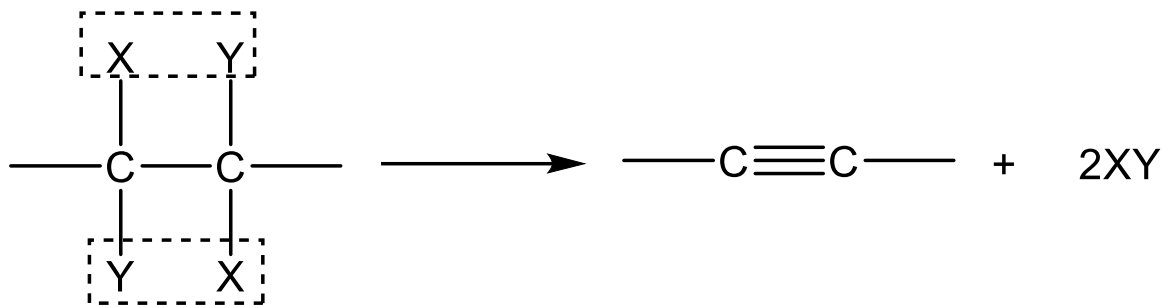
# Organic Chemistry

## ■ Methods of Formation of Alkyne:

→ The methods of formation of alkynes are essentially of two types:

(i) Those in which a triple bond is created in a 'more saturated' molecule by the elimination of sufficient atoms from adjacent carbon atoms.

(if) Those in which a compound already containing a triple bond is taken as the starting material from which is built the length of the carbon chain.



Where X and Y may be same or different

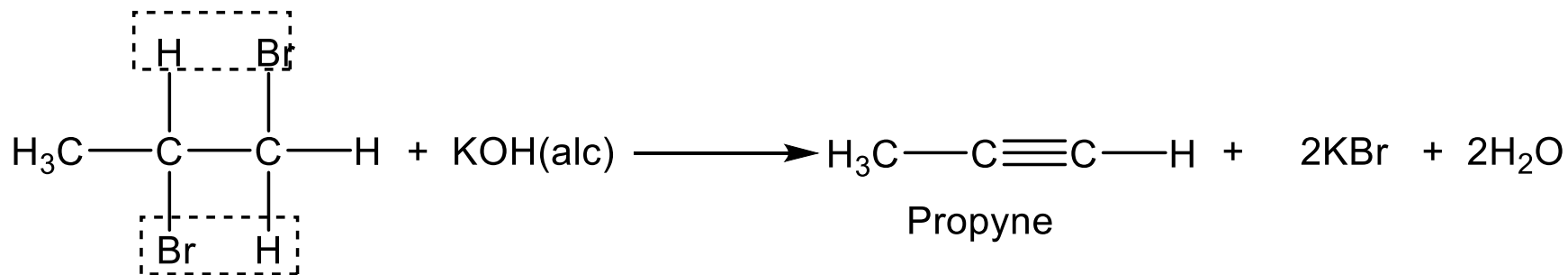


# Organic Chemistry

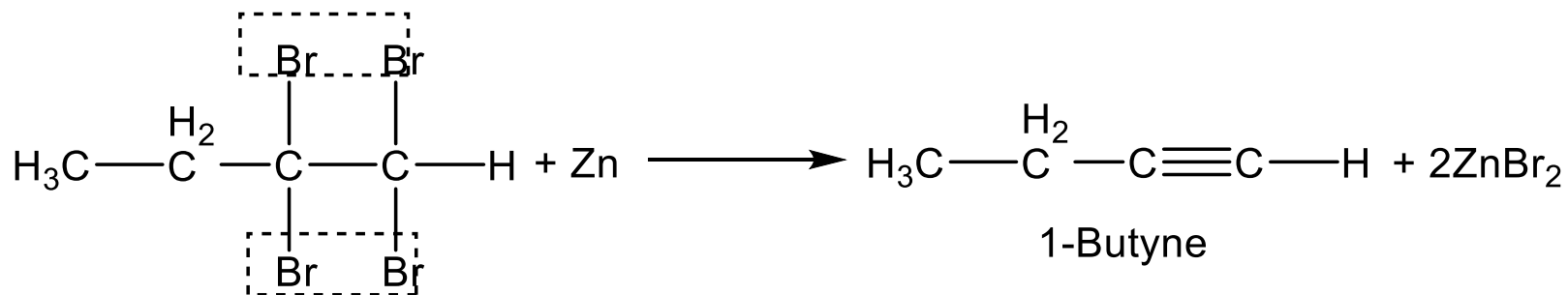
## ■ Methods of Formation of Alkyne:

### (1) Dehydrohalogenation of dihaloalkanes:

Dihaloalkane substituted alkanes with alcoholic potash eliminate two atoms of hydrogen and two atoms of halogen from the adjacent carbon atoms resulting in the formation of alkynes.



1, 2-dibromopropane



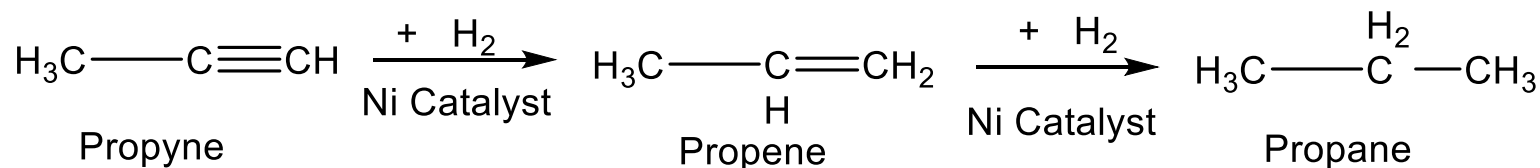
1,1, 2,2-Tetraibromopropane

# Organic Chemistry

## ■ Reactions of Alkyne:

### (i) Addition of hydrogen:

In the presence of suitable catalyst alkynes add two molecule of hydrogen first forming corresponding alkenes and finally the alkanes.



### (ii) Polymerisation:

Alkyne which passed through a red hot quartz or iron tube polymerize to give benzene.

