

# Introduction to Organic Chemistry

## CHEM 108

Credit hrs.: (3+1)

King Saud University

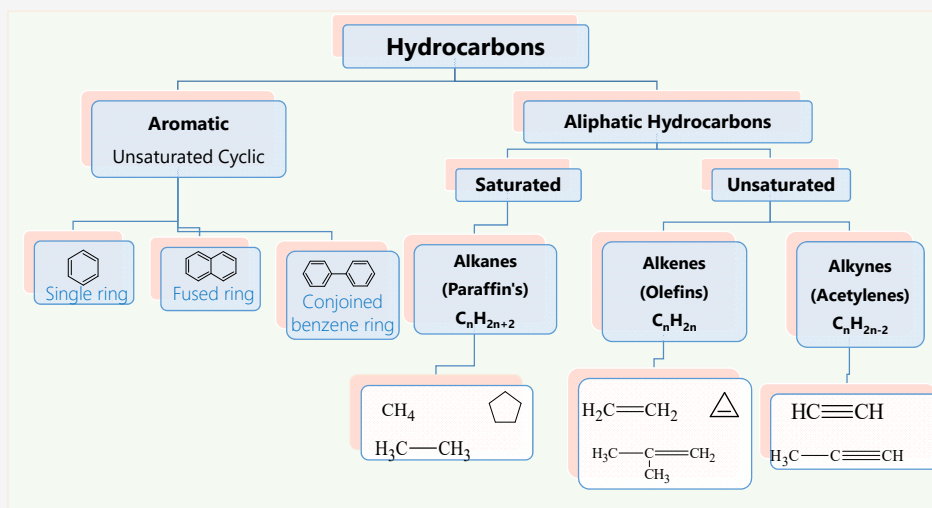
College of Science, Chemistry Department

### CHAPTER 2: Aliphatic Hydrocarbon

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## Hydrocarbons

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



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# Aliphatic Hydrocarbons

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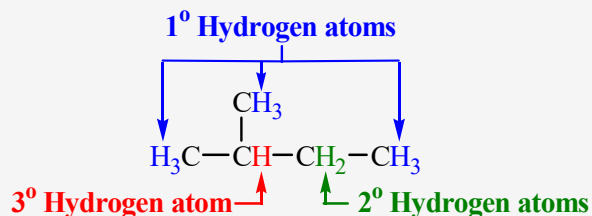
## Names and Molecular Formulas of the First Ten Alkanes

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH <sub>4</sub>	CH <sub>4</sub>	1
ethane	2	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>3</sub>	1
propane	3	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	1
butane	4	C <sub>4</sub> H <sub>10</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	2
pentane	5	C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	3
hexane	6	C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	5
heptane	7	C <sub>7</sub> H <sub>16</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	9
octane	8	C <sub>8</sub> H <sub>18</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	18
nonane	9	C <sub>9</sub> H <sub>20</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	35
decane	10	C <sub>10</sub> H <sub>22</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	75

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## Classes of Carbons and Hydrogen

- A primary ( $1^\circ$ ) carbon is one that is bonded to only one other carbon.
- A secondary ( $2^\circ$ ) carbon is one that is bonded to two other carbons.
- A tertiary ( $3^\circ$ ) carbon is one that is bonded to three other carbons.



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

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## Alkyl Group

## Nomenclature

- An alkyl group is formed by loss of a hydrogen atom from the corresponding alkane.
- General formula  $\text{C}_n\text{H}_{2n+1}$ .
- The letter **R** is used as a general symbol for an alkyl group.
- An alkyl group is named by replacing the suffix *-ane* of the parent alkane by *-yl*.

i.e. Alkane – ane + yl = Alkyl

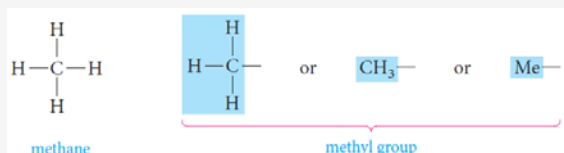
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## Alkyl Group

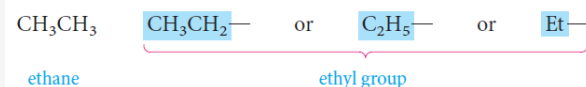
## Nomenclature

### Examples:

- Derived from **methane** by removing one of the hydrogens, a **one-carbon substituent** is called a **methyl group**.



- Thus the **two-carbon alkyl group** is called the **ethyl group**, from **ethane**.

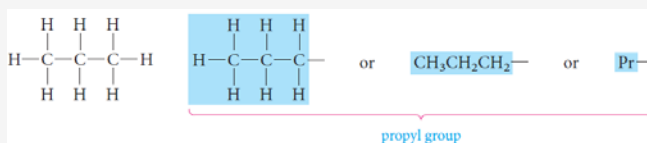


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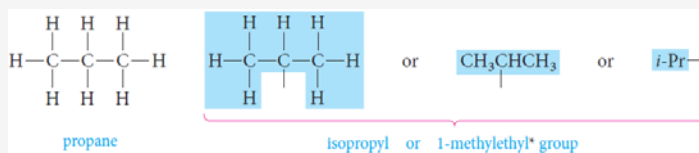
## Alkyl Group

## Nomenclature

- When we come to **propane**, there are **two possible alkyl groups**, depending on which type of hydrogen is removed.
  - If a **terminal hydrogen is removed**, the group is called a **propyl group**.



- If a **hydrogen is removed from the central carbon atom**, we get a different isomeric propyl group, called the **isopropyl group**.

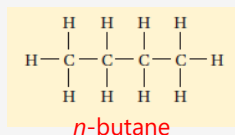


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## Alkyl Group

## Nomenclature

- For **four-carbon alkyl group**, there are **four different butyl groups**.
  - The **butyl** and **sec-butyl** groups are based on ***n*-butane**.
  - The **isobutyl** and **tert-butyl** groups come from **isobutane**.



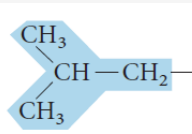
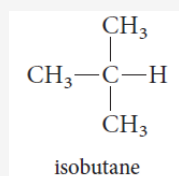
butyl

and



sec-butyl

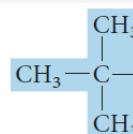
(or 1-methylpropyl)



isobutyl

(or 2-methylpropyl)

and



tert-butyl

(or 1,1-dimethylethyl)

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## Nomenclature of Alkanes

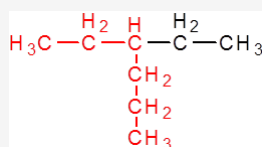
## Nomenclature of Saturated Hydrocarbons

- The older unsystematic names, (*Common names*).
- The **IUPAC names**.

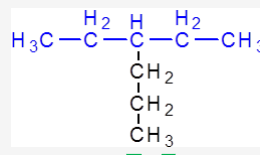
IUPAC: International Union of Pure & Appplied Chemistry

### The IUPAC Rules

- Select the parent structure; **the longest continuous chain**



Ethylhexane

**not**

Propylpentane

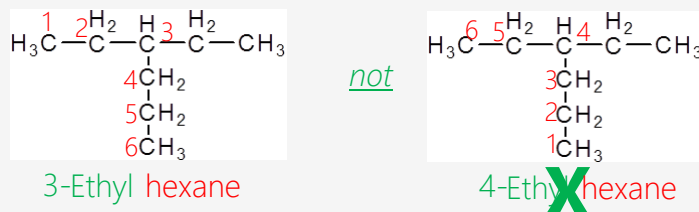
The **longest continuous chain** is **not necessarily straight**.

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## Nomenclature of Alkanes

## Nomenclature of Saturated Hydrocarbons

- 2) **Number** the carbons in the parent chain  
*starting from the end which gives the lowest number for the substituent*



To name the compound;

- 1) The position of the substituent on the parent carbon chain by a number.
- 2) The number is followed by a hyphen (-).
- 3) The combined name of the substituent (ethyl).
- 4) The parent carbon chain (hexane).

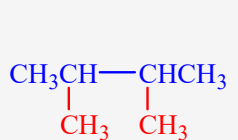
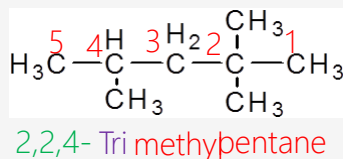
3-Ethylhexane

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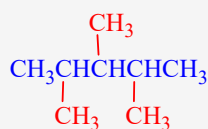
## Nomenclature of Alkanes

## Nomenclature of Saturated Hydrocarbons

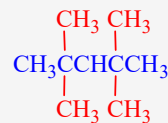
- 3) If the **same alkyl substituent** occurs more than once on the parent carbon chain, the prefixes **di-**, **tri-**, **tetra-**, **penta-**, and so on are used to indicate **two**, **three**, **four**, **five**, and so on.



2,3-Dimethylbutane



2,3,4-Trimethylpentane



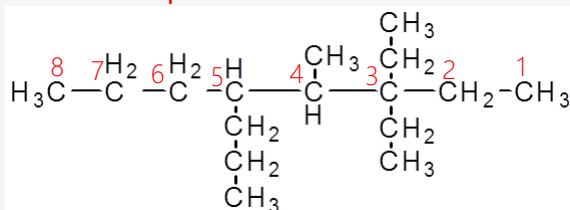
2,2,4,4-Tetramethylpentane

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## Nomenclature of Alkanes

## Nomenclature of Saturated Hydrocarbons

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

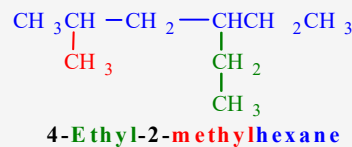


3,3-Diethyl -4-methyl-5 -propyl octane

3,3-diethyl  
4-methyl  
5-propyl

### Note that

- Each substituent is given a number corresponding to its location on the longest chain.
- The substituent groups are listed alphabetically.



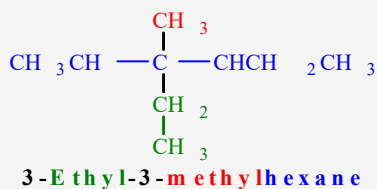
4-Ethyl-2-methylhexane

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## Nomenclature of Alkanes

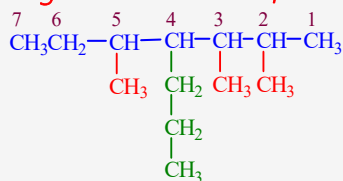
## Nomenclature of Saturated Hydrocarbons

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



3-Ethyl-3-methylhexane

- 6) When two chains of equal length compete for selection as the parent chain, choose **the chain with the greater number of substituents**.



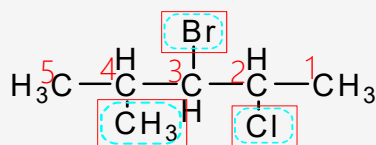
2,3,5-Trimethyl-4-n-propylheptane

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## Nomenclature of Alkanes

## Nomenclature of Saturated Hydrocarbons

7) If substituents other than alkyl groups are also present on the parent carbon chain; all substituents are named alphabetically.



2-chloro  
3-bromo  
4-methyl

3-bromo-2-chloro-4-methylpentane

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## Nomenclature of Alkanes

## Nomenclature of Saturated Hydrocarbons

### Examples

		Common name:	IUPAC name:
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>		n-Pentane	Pentane
$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{H}_3\text{C}-\text{C}-\text{CH}-\text{CH}_3 \\    \\  \text{H}_2  \end{array}  $		Isopentane	2-Methylbutane
$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $		Neopentane	2,2-Dimethylpropane

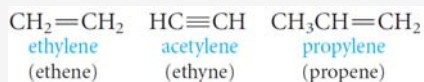
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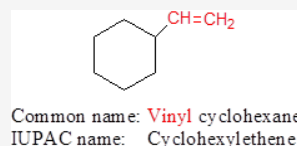
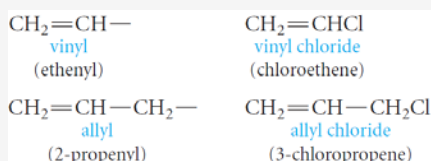
## Common Names

## Nomenclature of Unsaturated Hydrocarbons

- The simplest members of the **alkene and alkyne** series are frequently referred to by their older common names, ethylene, acetylene, and propylene.



- Two important groups also have common names; They are the **vinyl** and **allyl** groups and are used in common names.



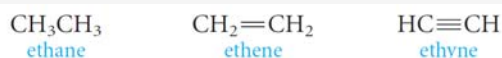
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## The IUPAC Rules

## Nomenclature of Unsaturated Hydrocarbons

The IUPAC rules for naming alkenes and alkynes are similar to those for alkanes, but a few rules must be added for naming and locating the multiple bonds.

- The ending **-ene** is used to designate a carbon-carbon double bond.  
The ending **-yne** is used to designate a carbon-carbon triple bond.



- Select the **longest chain that includes both carbons of the double (triple) bond**.

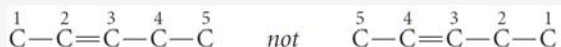


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## The IUPAC Rules

## Nomenclature of Unsaturated Hydrocarbons

3. Number the chain from the end nearest the double (triple) bond so that the carbon atoms in that bond have the lowest possible numbers.



If the multiple bond is equidistant from both ends of the chain, number the chain from the end nearest the first branch point.



4. Indicate the position of the multiple bond using the lower numbered carbon atom of that bond.



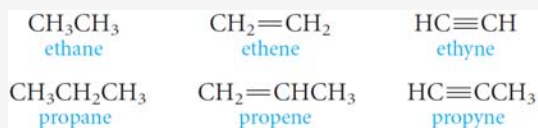
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## The IUPAC Rules

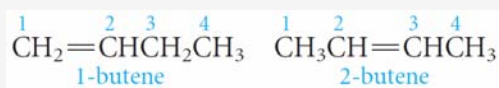
## Nomenclature of Unsaturated Hydrocarbons

### NOTES

- o The root of the name (*eth-* or *prop-*) tells us the number of carbons, and the ending (*-ane*, *-ene*, or *-yne*) tells us whether the bonds are single, double, or triple.
- o *No number is necessary in these cases, because in each instance, only one structure is possible.*



- o *With four carbons, a number is necessary to locate the double bond.*

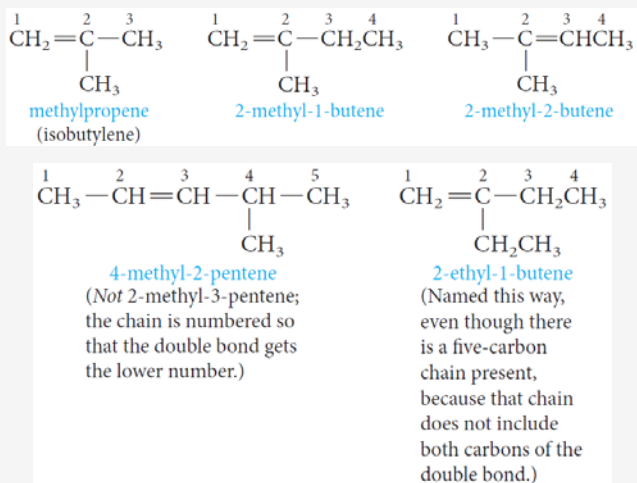


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## The IUPAC Rules

## Nomenclature of Unsaturated Hydrocarbons

- o **Branches** are named in the usual way.



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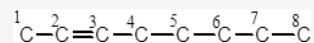
## The IUPAC Rules

## Nomenclature of Unsaturated Hydrocarbons

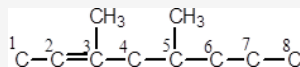
**Example:** Write the structural formula of **4-Isopropyl-3,5-dimethyl-2-octene**.

- 1) The parent carbon chain is an **Octene**.

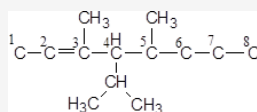
The double bond is located between the 2<sup>nd</sup> and 3<sup>rd</sup> carbons.



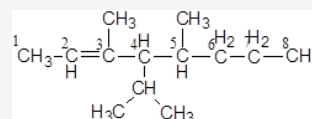
- 2) Two **methyl groups** are attached on the parent carbon chain, one on **carbon 3** and the other on **carbon 5**.



- 3) An **isopropyl group** is attached on **carbon 4**.



- 4) Put the missing hydrogens to get the correct structure.

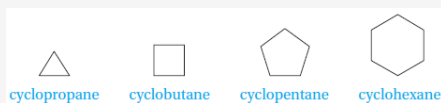


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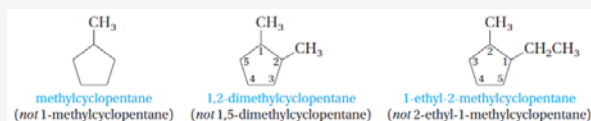
## Nomenclature of Cycloalkanes

## Nomenclature of Cycloalkanes and Cycloalkenes

- **Cycloalkanes** are saturated hydrocarbons that have at least one ring of carbon atoms.
- **Cycloalkanes** are named by placing the prefix *cyclo-* before the **alkane name** that corresponds to the number of carbon atoms in the ring.



- If only one substituent is present, no number is needed to locate it.
- **If there are several substituents, numbers are required.**  
*With different substituents, the one with highest alphabetic priority is located at carbon 1.*

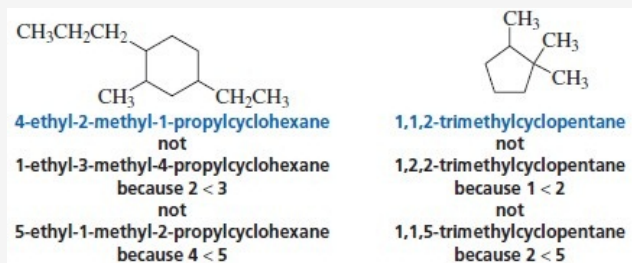


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## Nomenclature of Cycloalkanes

## Nomenclature of Cycloalkanes and Cycloalkenes

- If there are more than two substituents on the ring, they are cited in alphabetical order.
- The substituent given the number 1 position is the one that results in a second substituent getting as low a number as possible.
- If two substituents have the same low number, the ring is numbered in the direction that gives the third substituent the lowest possible number.
- **Examples,**

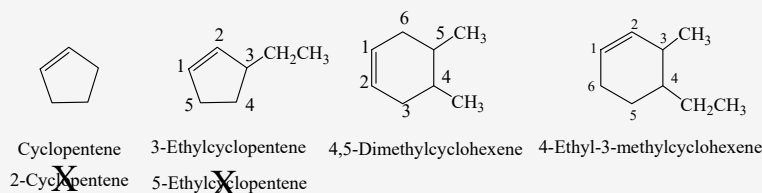


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## Nomenclature of Cycloalkenes

## Nomenclature of Cycloalkanes and Cycloalkenes

- We start numbering the ring with the carbons of the double bond.
- A number is not needed to denote the position of the functional group, because the ring is always numbered so that the double bond is between carbons 1 and 2.
- Put the lowest substituent number into the name not in the direction that gives the lowest sum of the substituent numbers.



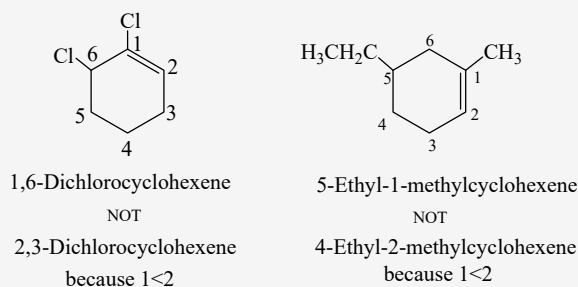
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## Nomenclature of Cycloalkenes

## Nomenclature of Cycloalkanes and Cycloalkenes

### ○ Example

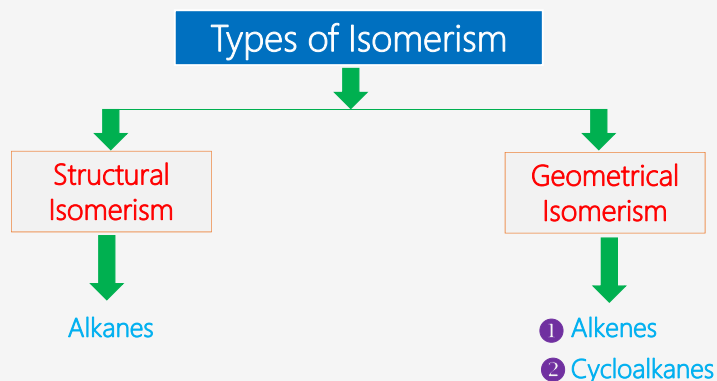
1,6-dichlorocyclohexene is not called 2,3-dichlorocyclohexene because 1,6-dichlorocyclohexene has the lowest substituent number (1), even though it does not have the lowest sum of the substituent numbers ( $1+6=7$  versus  $2+3=5$ ).



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## Isomerism

- **Isomers** are different compounds with identical molecular formulas.
- The phenomenon is called *isomerism*.



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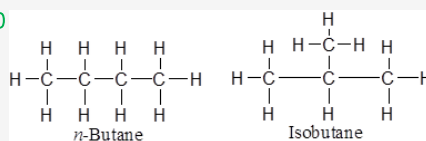
## Structural Isomerism in Alkanes

## Isomerism

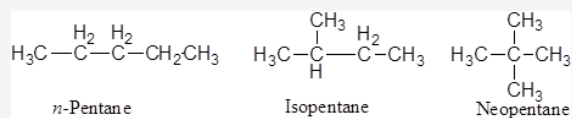
- **Structural** or **constitutional isomers** are isomers which differ in the sequence of atoms bonded to each other.

- **Examples:**

- **Butanes,  $C_4H_{10}$**



- **Pentanes,  $C_5H_{12}$**

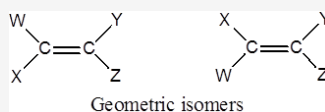


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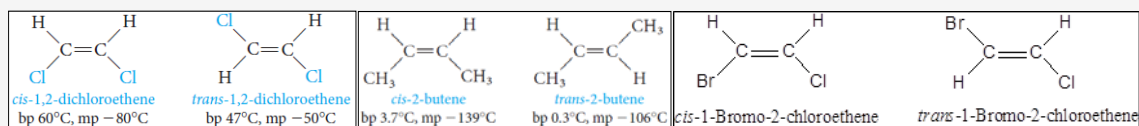
## Geometric Isomerism in Alkenes

## Isomerism

- In **alkenes**, **geometric isomerism** is due to **restricted rotation** about the **carbon - carbon double bond**.



A) when **W** differs from **X** and **Y** from **Z**, Alkenes exist as **geometric isomers**



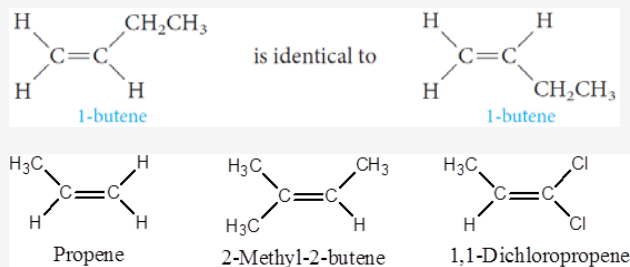
- cis* isomer**; when two similar groups are on the **same side** of the double bond.
- trans* isomer**; when two similar groups are on the **opposite sides** of the double bond.
- They have **different physical properties** and can be separated by **fractional crystallization or distillation**.

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## Geometric Isomerism in Alkenes

## Isomerism

B) If (**W = X** or **Y = Z**), geometric isomerism is not possible.

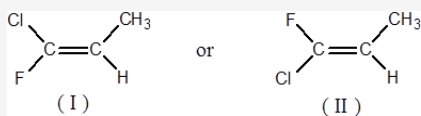


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## Geometric Isomerism in Alkenes

## Isomerism

- For alkenes with four different substituents such as



Another system, the *E, Z* system,

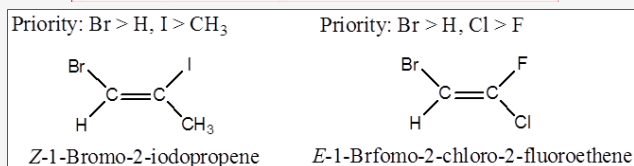
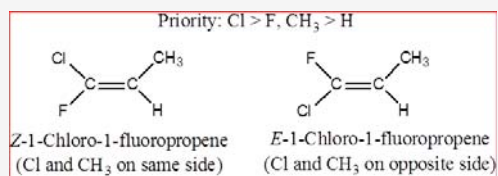
- Basically, the *E, Z* system works as follows;  
*Arrange the groups on each carbon of the C=C bond in order of priority*
- The priority depends on atomic number:  
*The higher the atomic number of the atom directly attached to the double-bonded carbon, the higher the priority.*
- Thus, in structure (I),  
 $\text{Cl} > \text{F}$ , and  $\text{CH}_3 > \text{H}$ .

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## Geometric Isomerism in Alkenes

## Isomerism

- If the two groups of higher priority are on the **same side** of the C=C plane,  
*The isomer is labeled Z:* (from the German *zusammen*, together).
- If the two groups of higher priority are on **opposite sides** of the C=C plane,  
*The isomer is labeled E:* (from the German *entgegen*, opposite).



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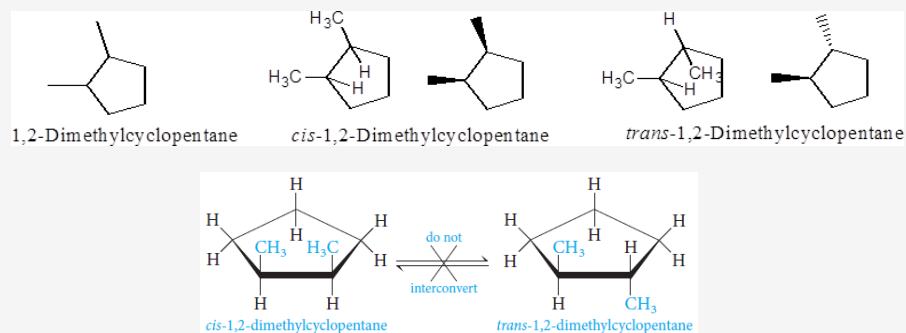


## Geometric Isomerism in Cycloalkanes

## Isomerism

### *cis-trans* Isomerism in Cycloalkanes

*cis-trans* isomerism (sometimes called geometric isomerism) is one kind of stereoisomerism.



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## Physical Properties of Aliphatic Hydrocarbons

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

### o Physical State

*Alkanes occur at room temperature are gases, liquids, and solids.*

- C1 (C2) to C4 are gases,
- C5 to C17 are liquids,
- C18 and larger are wax -like solids.

### o Solubility

- Aliphatic hydrocarbons are **nonpolar** compounds.
- Their solubility " **Like dissolve like**"
- Aliphatic hydrocarbons are soluble in the nonpolar solvents;
  - carbon tetrachloride,  $\text{CCl}_4$  and benzene,
- Aliphatic hydrocarbons are insoluble in polar solvents like water.

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## Physical Properties of Aliphatic Hydrocarbons

### Boiling Points & Melting Points

#### Effect of Molecular Weight

The boiling points and melting 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.*

#### Effect of Branching

- Among **isomers**, straight chain compound has the highest boiling point.

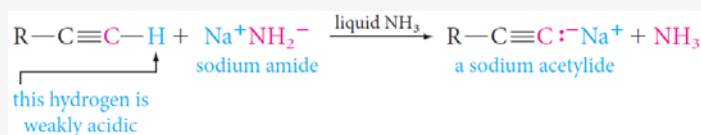
- The greater the number of branches, the lower the boiling point.

Name	Formula	Boiling point, °C
pentane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	36
2-methylbutane (isopentane)	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	28
2,2-dimethylpropane (neopentane)	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	10

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## Acidity of Alkynes

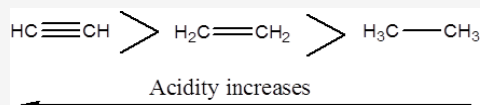
- A hydrogen atom on a triply bonded carbon (**Terminal Alkyne**) is weakly acidic and can be removed by a very strong base (as Sodium amide).



- Internal alkynes (**Non-Terminal Alkyne**) have no exceptionally acidic hydrogens.

#### Relative Acidity of the Hydrocarbon.

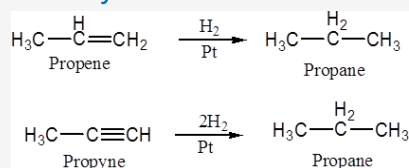
Terminal alkynes, are more acidic than other hydrocarbons



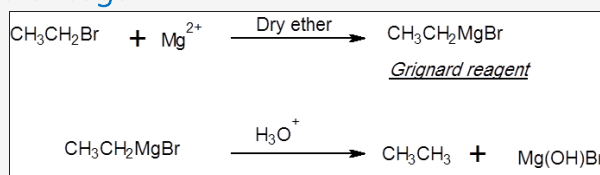
36

## Preparation of Alkanes

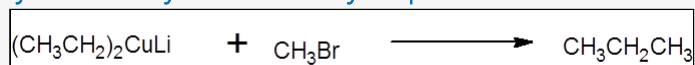
### 1. Hydrogenation of unsaturated hydrocarbon:



### 2. Hydrolysis of Grignard reagent



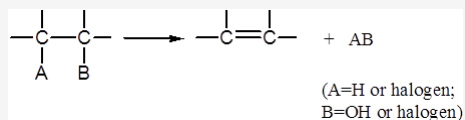
### 3. Reduction of Alkyl halides By lithium dialkyl cuprate



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## Preparation of Unsaturated hydrocarbons

- Unsaturated hydrocarbons are prepared by *Elimination* of an atom or group of atoms from adjacent carbons to form *carbon-carbon double or triple bond*.



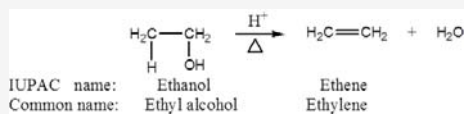
38

## Preparation of Alkenes

## Preparation of Unsaturated Hydrocarbons

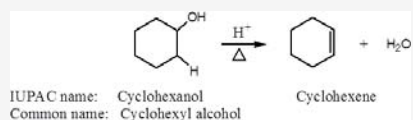
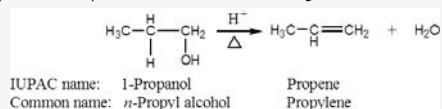
### 1) Dehydration of Alcohols

- When an alcohol is heated in the presence of a mineral acid catalyst, it readily loses a molecule of water to give an *alkene*.



The acid catalysts most commonly used are mineral acids as *sulfuric acid, H<sub>2</sub>SO<sub>4</sub>* and *phosphoric acid, H<sub>3</sub>PO<sub>4</sub>*.

- Removal of OH group and a proton from two adjacent carbon atoms using mineral acids.



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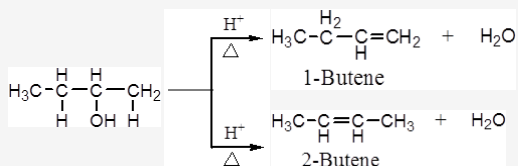
## Preparation of Alkenes

## Preparation of Unsaturated Hydrocarbons

### Which Alkene Predominates?; Saytzeff's Rule

The loss of water from adjacent carbon atoms, can give rise to *more than one alkene*.

*Example: the dehydration of 2-butanol.*



2-butene is the major (with two alkyl substituents attached to C=C)

### Saytzeff's Rule applies

In every instance in which more than one *Alkene* can be formed

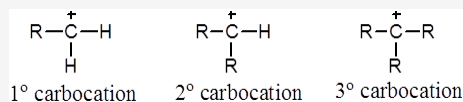
The major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.

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## Preparation of Alkenes

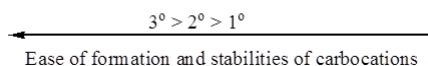
## Preparation of Unsaturated Hydrocarbons

### Classes of Carbocations



according to the number of carbon atoms attached to the positively charged carbon.

The ease of formation and the stabilities of carbocations follow the order



### Generally

1. The dehydration of alcohols requires an **acid catalyst**.
2. The predominant alkene formed follows **Saytzeff's rule**.
3. The reaction proceeds *via* a **carbocation intermediate**.
4. The stabilities of carbocations and the ease of dehydration of alcohols follows the order  $3^\circ > 2^\circ > 1^\circ$ .

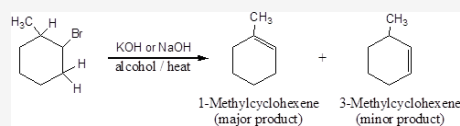
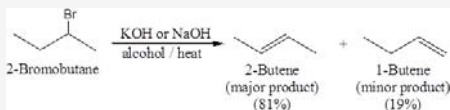
41

## Preparation of Alkenes

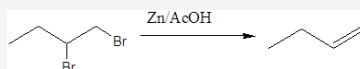
## Preparation of Unsaturated Hydrocarbons

### 2) Dehydrohalogenation of Alkyl Halides

- Alkenes can also be prepared under alkaline conditions.  
*heating an alkyl halide with a solution of KOH or NaOH in alcohol, yields an alkene.*



### 3) Dehalogenation of Vicinal Dibromides



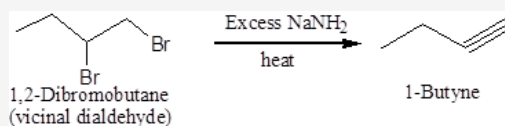
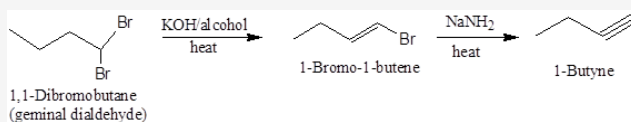
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## Preparation of Alkynes

## Preparation of Unsaturated Hydrocarbons

### 1) Dehydrohalogenation of Alkyl dihalides

Alkynes can be prepared under alkaline conditions via dehydrohalogenation of alkyl dihalides.



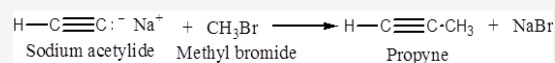
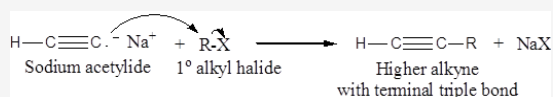
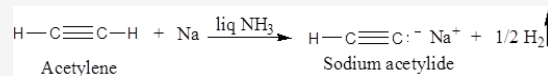
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## Preparation of Alkynes

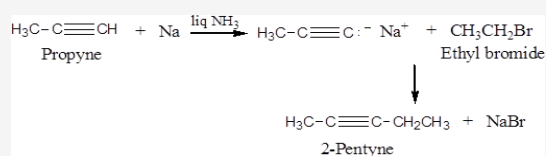
## Preparation of Unsaturated Hydrocarbons

### 2) Reaction of Sodium Acetylide with Primary Alkyl Halides

#### o Acetylene



#### o Monosubstituted Acetylenes

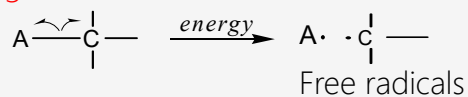


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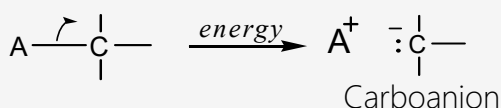
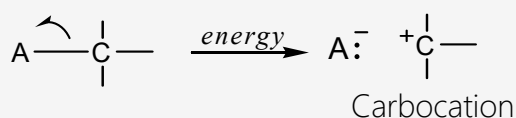
## Notations for bond breaking and bond making

o A covalent bond can be broken in either two ways,

- Homolytic cleavage.



- Heterolytic cleavage.



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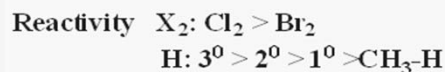
## Reactions of Alkanes

## Reactions of Saturated Hydrocarbons

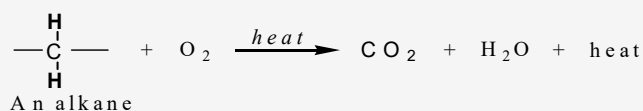
Saturated hydrocarbons undergo very few reactions, so they are called **Paraffinic hydrocarbons**. (Latin *parum*, little; *affinis*, affinity)

### Halogenation

The halogenation of an alkane appears to be a simple free radical substitution in which a C-H bond is broken and a new C-X bond is formed



### Combustion



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## Reactions of Alkanes

## Reactions of Saturated Hydrocarbons

### A) Halogenation

- o Substitution reaction of alkanes, i.e. replacement of hydrogen by halogen, usually chlorine or bromine, giving alkyl chloride or alkyl bromide.
- o Fluorine reacts explosively with alkanes  
It is unsuitable reagent for the preparation of the alkyl fluorides.
- o Iodine is too unreactive  
It is not used in the halogenation of alkanes.
- o Halogenation of alkanes take place at high temperatures or under the influence of ultraviolet light

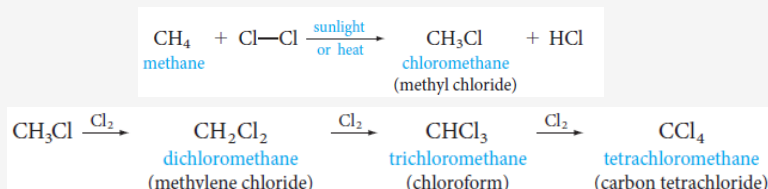
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## Reactions of Alkanes

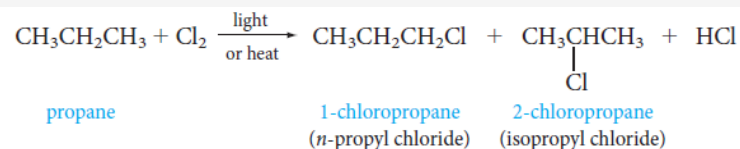
## Reactions of Saturated Hydrocarbons

### A) Halogenation

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



- o With longer chain alkanes, mixtures of products may be obtained even at the first step. For example, with propane,

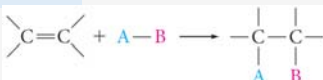


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## Reactions of Unsaturated Hydrocarbons

### (1) Electrophilic Addition Reactions



Addition of *Symmetric and Unsymmetric Reagents to symmetric Alkenes.*

1. Addition of Hydrogen: Catalytic Hydrogenation
2. Addition of Halogens: Halogenation

Addition of *Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule.*

1. Addition of Hydrogen Halides
2. Addition of Sulfuric Acid
3. Addition of Water: Hydration
4. Addition of HOX: Halohydrin Formation

### (2) Oxidation Reactions

1. Ozonolysis
2. Oxidation Using  $\text{KMnO}_4$

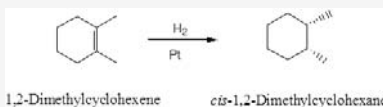
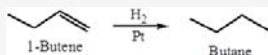
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## Electrophilic Addition Reactions

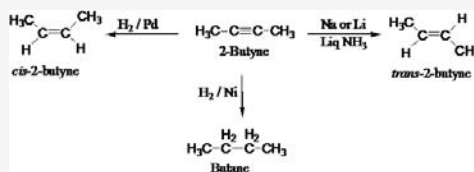
## Reactions of Unsaturated Hydrocarbons

### 1. Addition of Hydrogen: Hydrogenation

- o Addition of a mole of hydrogen to carbon-carbon double bond of *Alkenes* in the presence of suitable catalysts to give an *Alkane*.



- o With an ordinary nickel or platinum catalyst, *Alkynes* are hydrogenated all the way to alkanes.



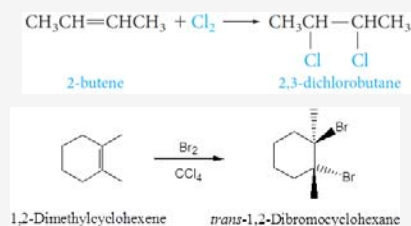
50

## Electrophilic Addition Reactions

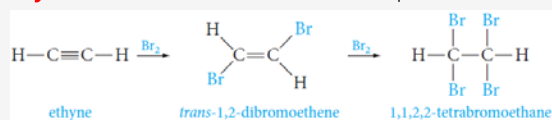
## Reactions of Unsaturated Hydrocarbons

### 2. Addition of Halogen: Halogenation

- When an **alkene** is treated at room temperature with a solution of **bromine** or **chlorine** in carbon tetrachloride to give the corresponding **vicinal dihalide** (two halogens attached to adjacent carbons)



- Bromine adds to **alkynes** as follows; In the first step, the addition occurs mainly *trans*.



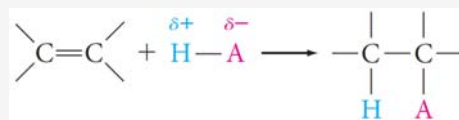
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## Electrophilic Addition Reactions

## Reactions of Unsaturated Hydrocarbons

### 3. Addition of Acids

- A variety of acids add to the double bond of alkenes.  
*The hydrogen ion (or proton) adds to one carbon of the double bond, and the remainder of the acid becomes connected to the other carbon.*



- Acids that add in this way are the **hydrogen halides** (H-F, H-Cl, H-Br, H-I), and **water** (H-OH).

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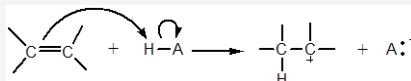
## Electrophilic Addition Reactions

## Reactions of Unsaturated Hydrocarbons

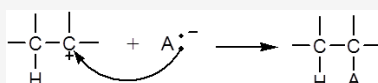
### 3. Addition of Acids

- The addition of H—A to an alkene is believed to be a **two-step process**.

**Step 1.** The hydrogen ion (the **electrophile**) attacks the  $\pi$ -electrons of the alkene, forming a C—H bond and a **carbocation**.



**Step 2.** The negatively charged species A: - (a **nucleophile**) attacks the carbocation and forms a new C—A bond.



- The attack by an electrophilic reagent on the  $\pi$ -electrons, falls in a general category called **electrophilic addition reactions**.

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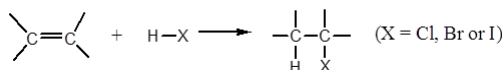
## Electrophilic Addition Reactions

## Reactions of Unsaturated Hydrocarbons

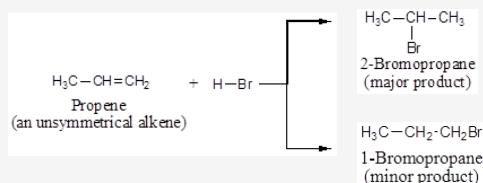
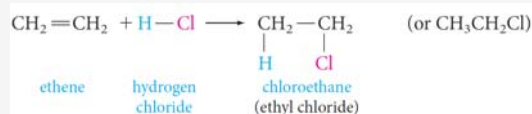
### 3.1. Addition of Hydrogen Halide

Alkenes react with hydrogen chloride, HCl, hydrogen bromide, HBr and hydrogen iodide, HI, to form alkyl halides, RX.

General equation



- Examples;



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## Electrophilic Addition Reactions

## Reactions of Unsaturated Hydrocarbons

- Reagents and alkenes can be classified as either **symmetric** or **unsymmetric** with respect to addition reactions.
  - If a reagent and/or an alkene is symmetric, only one addition product is possible.
  - But if *both* the reagent *and* the alkene are *unsymmetric*, two products are, in principle, possible.

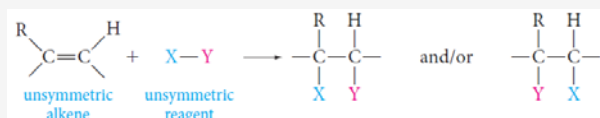




Table 3.2 Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

	Symmetric	Unsymmetric
Reagents	$\text{Br}-\text{Br}$ $\text{Cl}-\text{Cl}$ $\text{H}-\text{H}$	$\text{H}-\text{Br}$ $\text{H}-\text{OH}$ $\text{H}-\text{OSO}_3\text{H}$
Alkenes	$\text{CH}_2=\text{CH}_2$  mirror plane	$\text{CH}_3\text{CH}=\text{CH}_2$  not a mirror plane

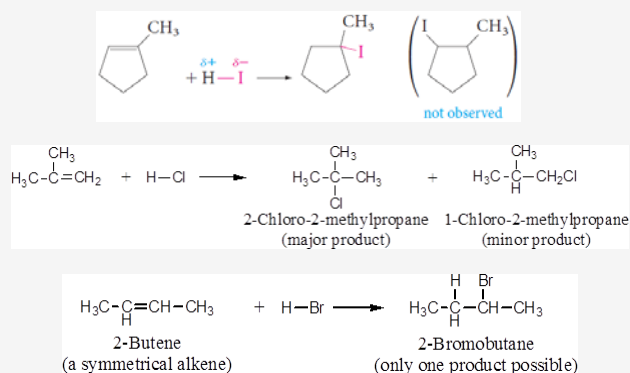
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## Electrophilic Addition Reactions

## Reactions of Unsaturated Hydrocarbons

### Markovnikov's Rule

In electrophilic addition of  $\text{H}-\text{X}$  to *Unsymmetrical Alkenes* the hydrogen of the hydrogen halide adds to the double-bonded carbon that bears the greater number of hydrogen atoms and the negative halide ion adds to the other double-bonded carbon.



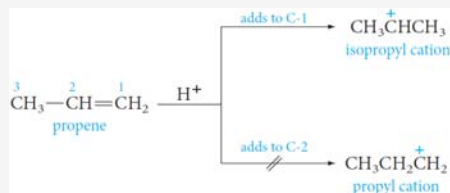
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## Electrophilic Addition Reactions

## Reactions of Unsaturated Hydrocarbons

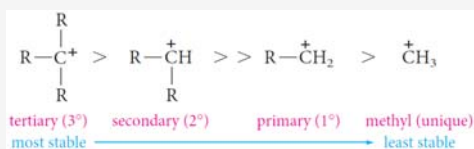
### Explanation for Markovnikov's Rule

Example; the addition of HBr to propene



- In modern terms Markovnikov's rule can be restated:

The addition of an unsymmetrical reagent HX to an unsymmetrical alkene proceeds in such a direction as to produce *the more stable carbocation*.



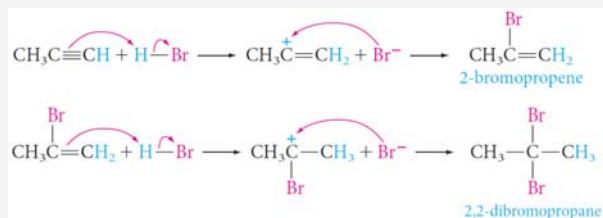
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## Electrophilic Addition Reactions

## Reactions of Unsaturated Hydrocarbons

### 3.1. Addition of Hydrogen Halide

With unsymmetric triple bonds and unsymmetric reagents, Markovnikov's Rule is followed in each step, as shown in the following example:



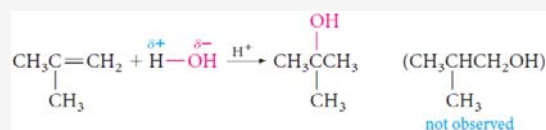
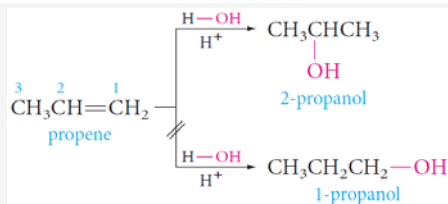
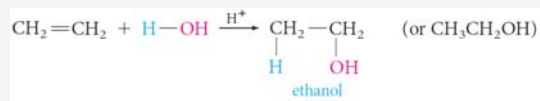
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## Electrophilic Addition Reactions

## Reactions of Unsaturated Hydrocarbons

### 3.2. Addition of Water: Hydration

If an acid catalyst is present, water (as H-OH) adds to *alkenes* and the product is alcohol.



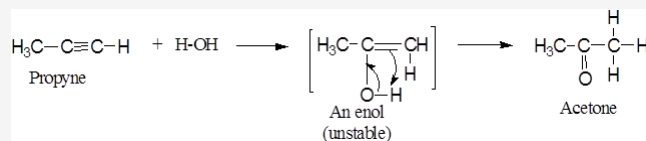
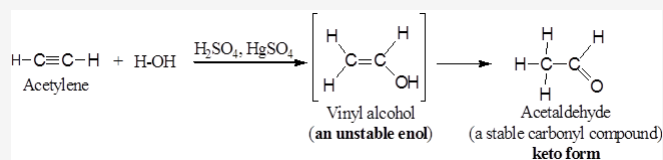
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## Electrophilic Addition Reactions

## Reactions of Unsaturated Hydrocarbons

### 3.2. Addition of Water: Hydration

- o Addition of water to *alkynes* requires not only an acid catalyst but mercuric ion as well.
- o The mercuric ion forms a complex with the triple bond and activates it for addition.
- o Although the reaction is similar to that of alkenes, the initial product—a **vinyl alcohol** or **enol**—rearranges to a carbonyl compound.



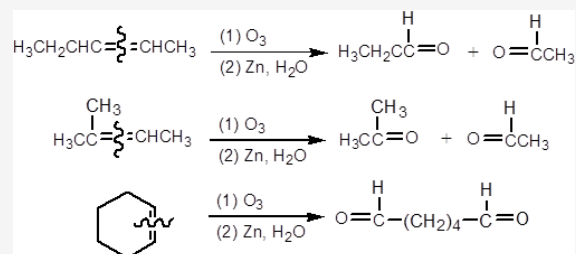
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## Oxidation Reactions

## Reactions of Unsaturated Hydrocarbons

### 1. Ozonolysis

- Ozonolysis can be used to locate the position of a double bond.
- Example**, ozonolysis of 1-butene gives two different aldehydes, whereas 2-butene gives a single aldehyde.



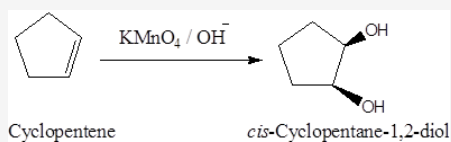
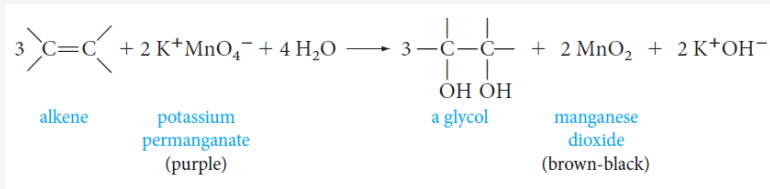
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## Oxidation Reactions

## Reactions of Unsaturated Hydrocarbons

### 2. Oxidation Using $\text{KMnO}_4$

Alkenes react with alkaline potassium permanganate to form glycols (compounds with two adjacent hydroxyl groups).



Hexane does not react with purple  $\text{KMnO}_4$  (left), cyclohexene (right) reacts, producing a brown-black precipitate of  $\text{MnO}_2$ .

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