# Unsaturated Hydrocarbons
# 1. Alkenes

## Nomenclature; IUPAC Rules

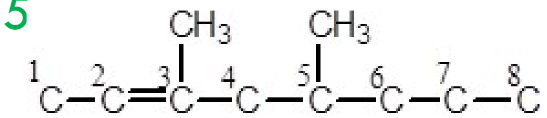
**Example**: Write the structural formula of 4-Isopropyl-3,5-dimethyl-2-octene.

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

*The double bond is located between the 2nd and 3rd carbons.*

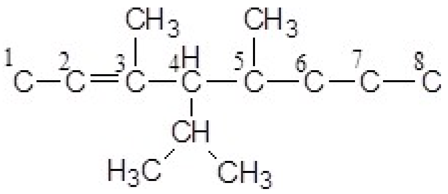
$$^{1}C-^{2}C=^{3}C-^{4}C-^{5}C-^{6}C-^{7}C-^{8}C$$

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

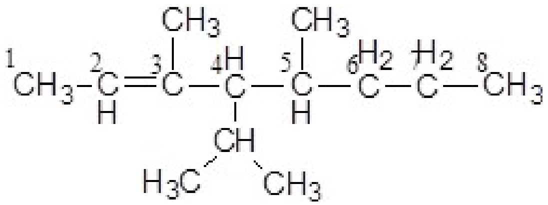


$$^{1}C-^{2}C=^{3}\overset{CH_3}{\overset{|}{C}}-^{4}C-^{5}\overset{CH_3}{\overset{|}{C}}-^{6}C-^{7}C-^{8}C$$

3) An isopropyl group is attached on carbon 4.

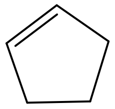


4) Put the missing hydrogens to get the correct structure.



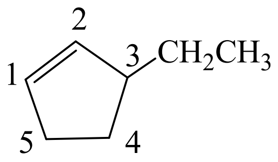
## Nomenclature of Cycloalkenes

- 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.



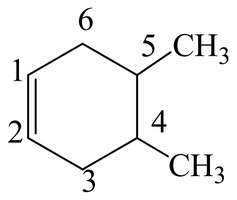
Cyclopentene

~~2-Cyclopentene~~

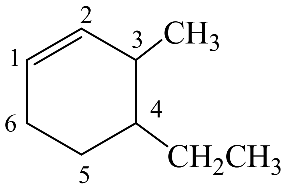


3-Ethylcyclopentene

~~5-Ethylcyclopentene~~



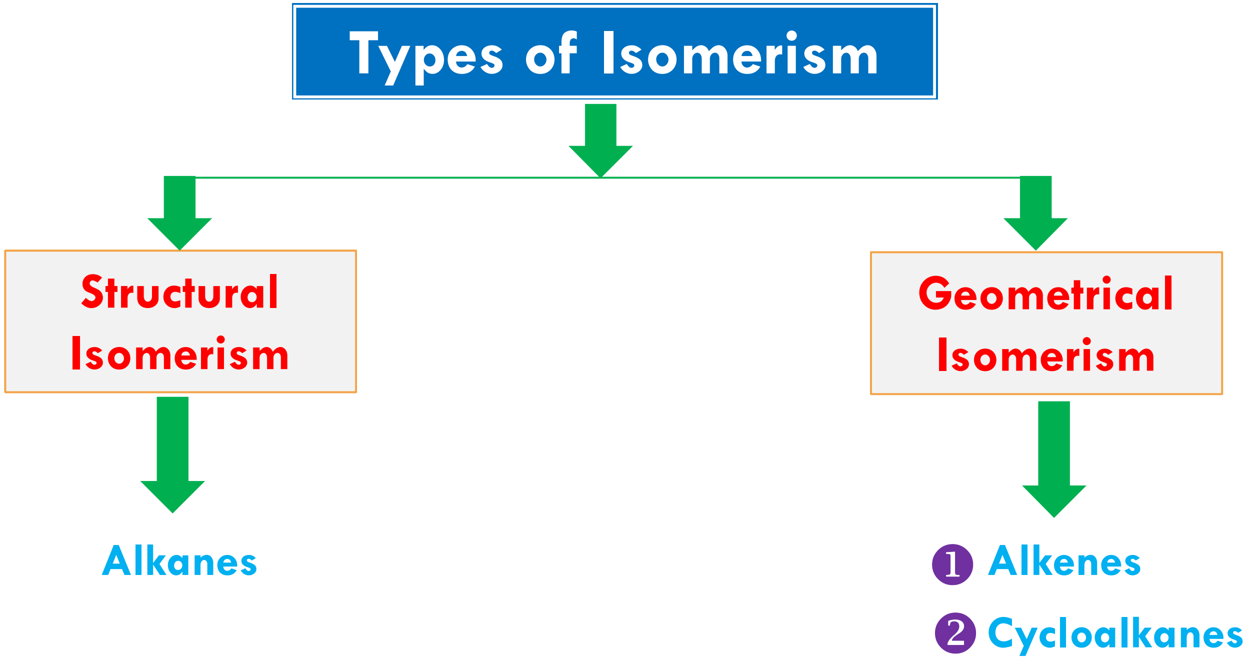
4,5-Dimethylcyclohexene



4-Ethyl-3-methylcyclohexene

# Isomerism

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



**Types of Isomerism**

**Structural Isomerism**

Alkanes

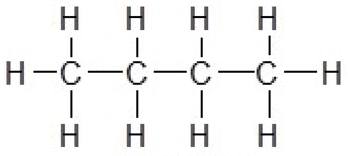
**Geometrical Isomerism**

❶ Alkenes

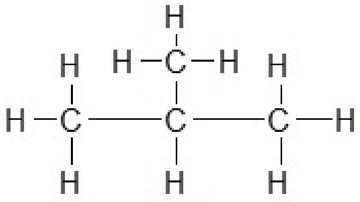
❷ Cycloalkanes

## Structural Isomerism in Alkanes

- **Structural** or **constitutional isomers** are isomers which differ in the sequence of atoms bonded to each other.
  - **Examples:**
    - **Butanes, $C_4H_{10}$**

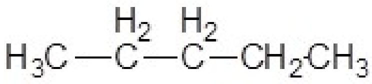


*n*-Butane



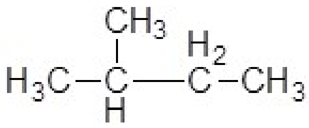
Isobutane

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



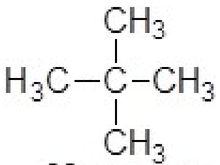
$H_3C-\overset{H_2}{C}-\overset{H_2}{C}-CH_2CH_3$

*n*-Pentane



$H_3C-\underset{H}{\overset{CH_3}{C}}-\overset{H_2}{C}-CH_3$

Isopentane



$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

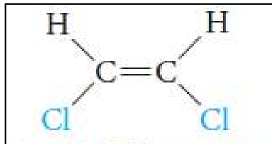
Neopentane

## Geometric Isomerism in Alkenes

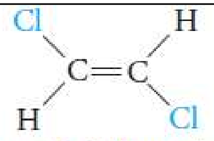
- In alkenes, geometric isomerism is due to restricted rotation about the carbon - carbon double bond.

Geometric isomers

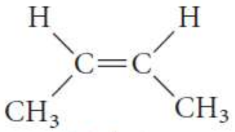
**A) when W differs from X and Y from Z, Alkenes exist as geometric isomers**



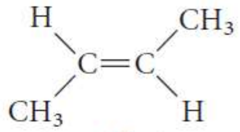
*cis*-1,2-dichloroethene
bp 60°C, mp −80°C



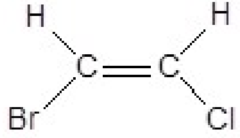
*trans*-1,2-dichloroethene
bp 47°C, mp −50°C



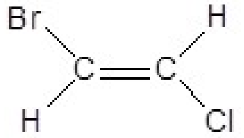
*cis*-2-butene
bp 3.7°C, mp −139°C



*trans*-2-butene
bp 0.3°C, mp −106°C



*cis*-1-Bromo-2-chloroethene



*trans*-1-Bromo-2-chloroethene

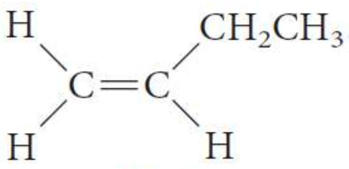
- ***cis* isomer;** when two similar groups are on the same side or same side of the double bond.
- ***trans* isomer;** when two similar groups are on the opposite direction or opposite sides of the double bond.

- *They have different physical properties and can be separated by fractional crystallization or distillation.*

## Geometric Isomerism in Alkenes

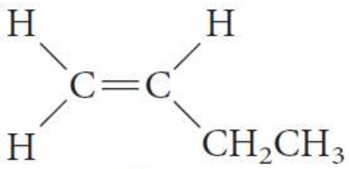
B) If (W = X or Y = Z), geometric isomerism is not possible.

Geometric isomers

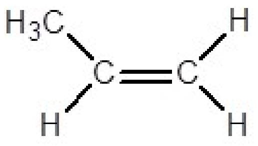


1-butene

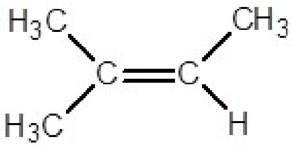
is identical to



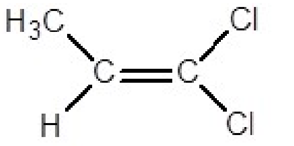
1-butene



Propene



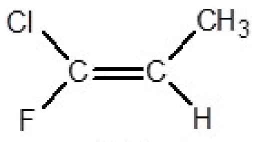
2-Methyl-2-butene



1,1-Dichloropropene

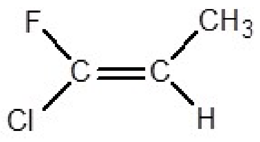
## Geometric Isomerism in Alkenes

- For alkenes with four different substituent such as



( I )

or



( II )

**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),

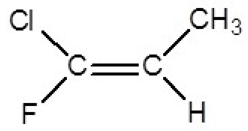
Cl > F, and $CH_3$ > H.

## Geometric Isomerism in Alkenes

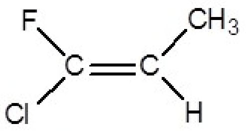
- If the two groups of **higher priority** are on the **same side** of the C=C plane, *The isomer is labeled Z;* (from the German *zusammen*, together).

- **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).*

Priority: Cl > F, $CH_3$ > H

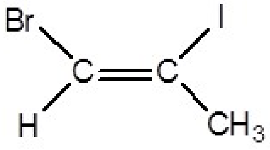


*Z*-1-Chloro-1-fluoropropene
(Cl and $CH_3$ on same side)



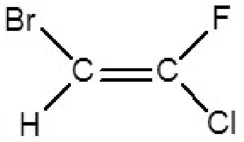
*E*-1-Chloro-1-fluoropropene
(Cl and $CH_3$ on opposite side)

Priority: Br > H, I > $CH_3$



*Z*-1-Bromo-2-iodopropene

Priority: Br > H, Cl > F

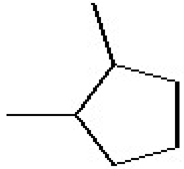


*E*-1-Brfomo-2-chloro-2-fluoroethene

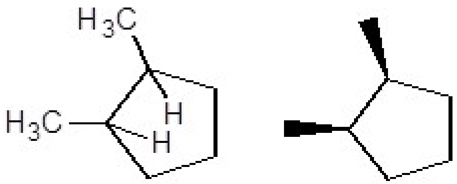
## Geometric Isomerism in Cycloalkanes

### *cis-trans* Isomerism in Cycloalkanes

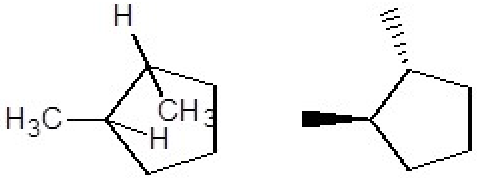
***cis–trans*** **isomerism (sometimes called geometric isomerism) is one kind of stereoisomerism.**



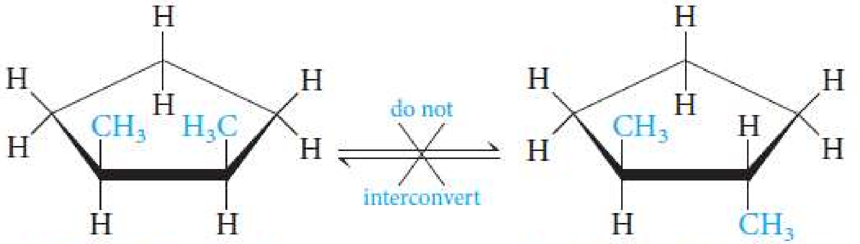
1,2-Dimethylcyclopentane



*cis*-1,2-Dimethylcyclopentane



*trans*-1,2-Dimethylcyclopentane

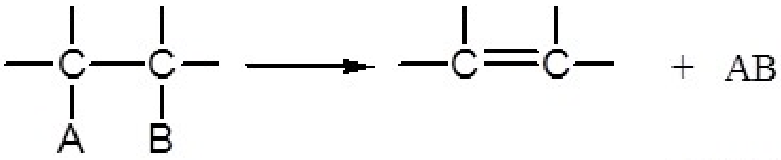


*cis*-1,2-dimethylcyclopentane

*trans*-1,2-dimethylcyclopentane

# 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.*

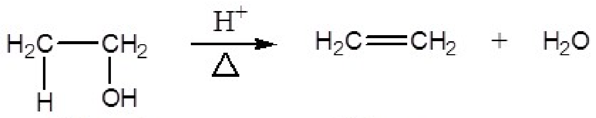


(A=H or halogen;
B=OH or halogen)

## 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.*

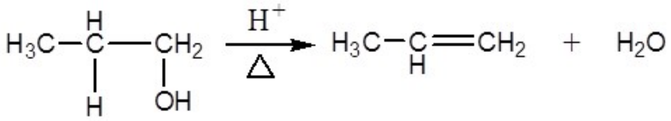
# Preparation of Unsaturated hydrocarbons (Alkenes)



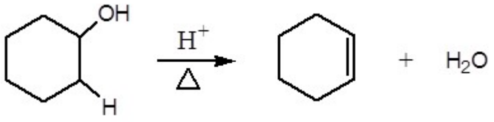
IUPAC name: Ethanol Ethene
Common name: Ethyl alcohol Ethylene

*The acid catalysts most commonly used are mineral acids as **sulfuric acid, $H_2SO_4$, and phosphoric acid, $H_3PO_4$.***

- Removal of OH group and a proton from two adjacent carbon atoms using mineral acids such as HCl, $H_2SO_4$ and H3PO4



IUPAC name: 1-Propanol Propene
Common name: *n*-Propyl alcohol Propylene



IUPAC name: Cyclohexanol Cyclohexene
Common name: Cyclohexyl alcohol

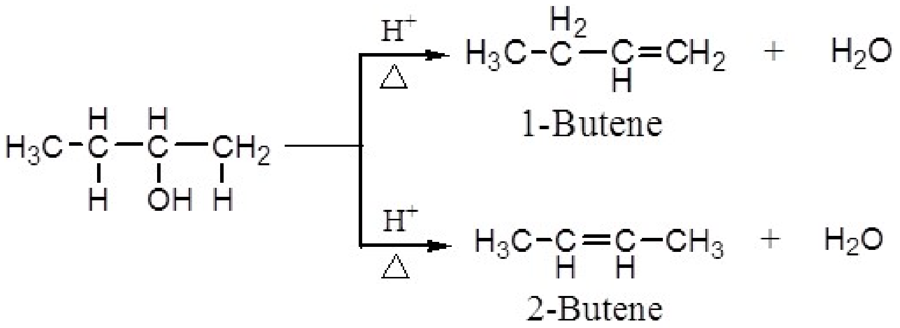
# Preparation of Unsaturated hydrocarbons (Alkenes)

## 1) Dehydration of Alcohols

### **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.*



$$H_3C-CH_2-CH(OH)-CH_3 \xrightarrow[\triangle]{H^+} H_3C-CH_2-CH=CH_2 + H_2O$$

$$H_3C-CH_2-CH(OH)-CH_3 \xrightarrow[\triangle]{H^+} H_3C-CH=CH-CH_3 + H_2O$$

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

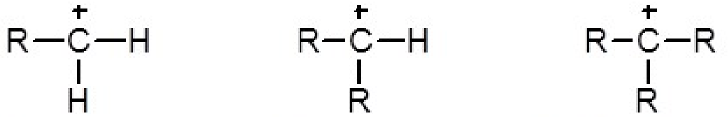
***Saytzeff's Rule applies***

*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.*

## 1) Dehydration of Alcohols

- **Classes of Carbocations**



1° carbocation 2° carbocation 3° carbocation

*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

3° > 2° > 1°
←
Ease of formation and stabilities of carbocations

- **Generally**

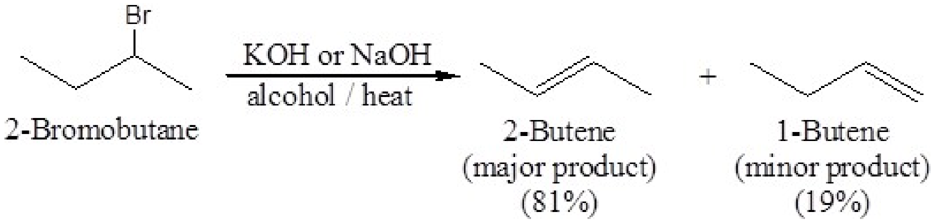
1. The dehydration of alcohols requires an acid catalyst.
2. The predominant alkene formed follows Saytzeffs rule.
3. The reaction proceeds *via* a carbocation intermediate.
4. The stabilities of carbocations and the ease of dehydration of alcohols follows the order 3° > 2° > 1°.

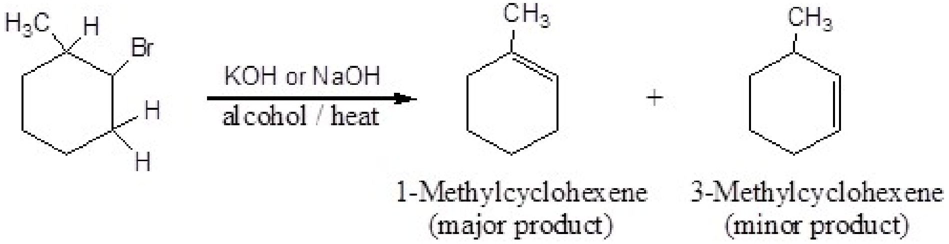
# Preparation of Unsaturated hydrocarbons (Alkenes)

## 2) Dehydrohalogenation of Alkyl Halides

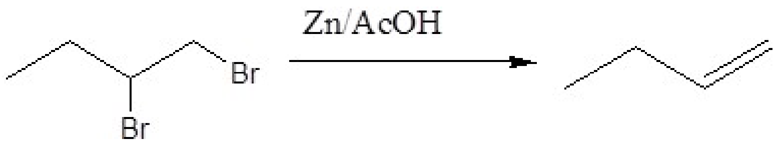
- Alkenes can also be prepared under alkaline conditions.

*heating an alkyl halide with a solution of KOH or NaOH in alcohol, yields an alkene.*



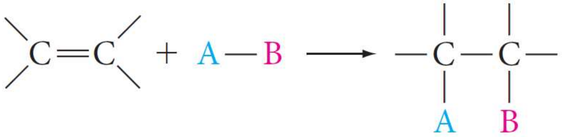


## 3) Dehalogenation of Vicinal Dibromides



# 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

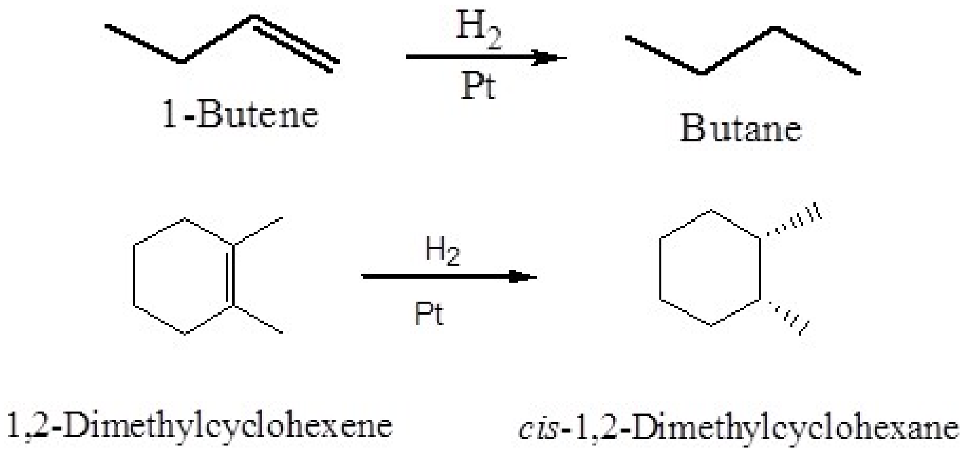
1. Ozonolysis
2. Oxidation Using $KMnO_4$

# Reactions of Unsaturated hydrocarbons (Alkenes)

## Electrophilic Addition Reactions

### 1. Addition of Hydrogen: Hydrogenation

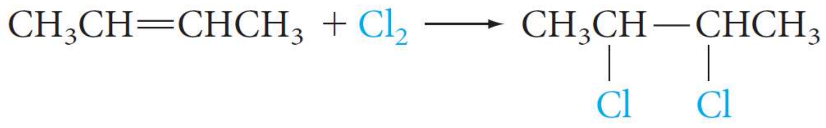
*Addition of a mole of hydrogen to carbon-carbon double bond of Alkenes in the presence of suitable catalysts to give an* Alkane.



## Electrophilic Addition Reactions

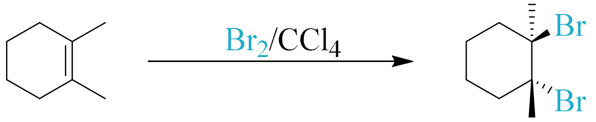
### 2. Addition of Halogen: Halogenation

*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)*



$$CH_3CH{=}CHCH_3 + Cl_2 \longrightarrow CH_3\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH}}CH_3$$

2-butene 2,3-dichlorobutane



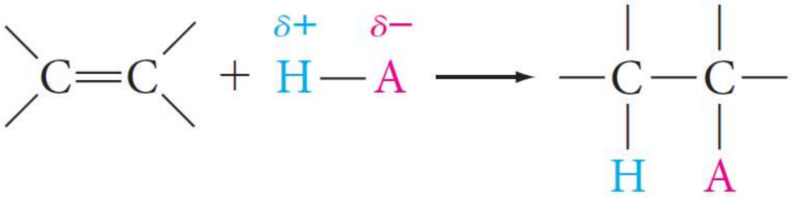
1,2-Dimethyl-cyclohexene *trans*-1,2-Dibromo-1,2-dimethyl-cyclohexane

## Electrophilic Addition Reactions

### 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).

# Electrophilic Addition Reactions

- Any electron-deficient species is called an electrophile.
- Any electron-rich species is called a nucleophile.

**Examples of Electrophile:**

i) Positive reagents: protons ($H^+$), alkyl group $R^+$ , nitronium ion ($NO_2^{\ +}$), etc….

ii) Neutral reagents having positively polarized centers: HCl, bromine (because it can be polarized so that one end is positive).

iii) Lewis acids: molecules or ions that can accept an electron pair ⇒ $BF_3$ and $AlCl_3$.

**Examples of Nucleophile:**

a)Negative ions

e.g. $H\underset{\cdot\cdot}{\ddot{O}}\colon^{-}$ Hydroxide ion, $H\underset{\cdot\cdot}{\ddot{S}}\colon^{-}$ Hydrosulphide ion, $R\underset{\cdot\cdot}{\ddot{O}}\colon^{-}$ Alkoxide ions,

$\colon N{\equiv}C\colon^{-}$ Cyanide ion, $\colon\underset{\cdot\cdot}{\ddot{X}}\colon^{-}$ Halide ions, ...etc.

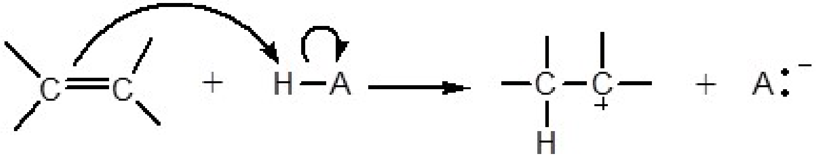
b) Neutral molecules

e.g. $H_2\underset{\cdot\cdot}{\ddot{O}}$ , $R-\underset{\cdot\cdot}{\ddot{O}}-H$ , $R-\underset{\cdot\cdot}{\ddot{O}}-R$ , $H_3\ddot{N}$ , $R_3\ddot{N}$ , ...etc.

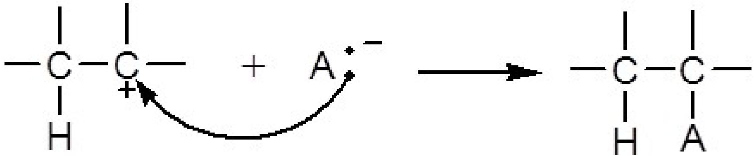
## 3. Addition of Acids

- 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 ∏-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 ∏-electrons, falls in a general category called **electrophilic addition reactions**.

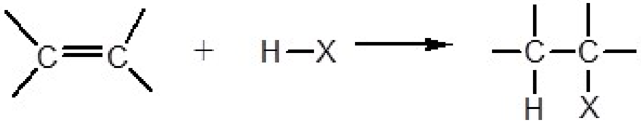
# Reactions of Unsaturated hydrocarbons (Alkenes)

## Electrophilic Addition Reactions

### 3.1. Addition of Hydrogen Halide

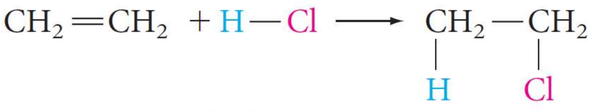
*Alkenes react with hydrogen chloride, HC1, hydrogen bromide, HBr and hydrogen iodide, HI, to form alkyl halides, RX.*

*General equation*



(X = Cl, Br or I)

**Examples;**



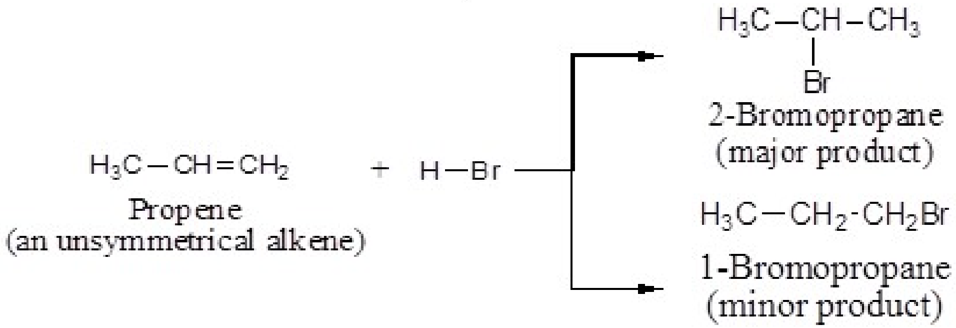
$$CH_2{=}CH_2 + H{-}Cl \longrightarrow \underset{H}{CH_2}{-}\underset{Cl}{CH_2}$$

(or $CH_3CH_2Cl$)

ethene

hydrogen chloride

chloroethane
(ethyl chloride)



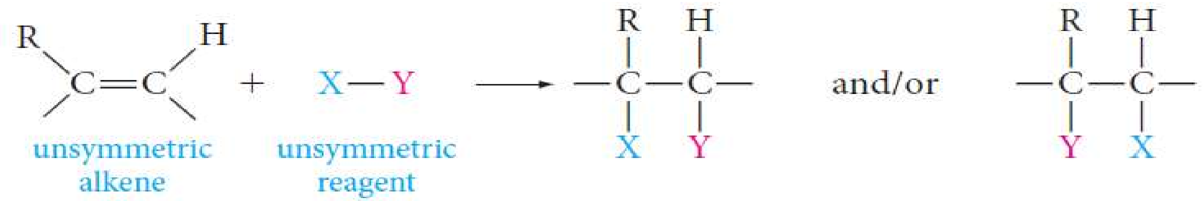
Propene
(an unsymmetrical alkene)

2-Bromopropane
(major product)

1-Bromopropane
(minor product)

# Electrophilic Addition Reactions

- **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.



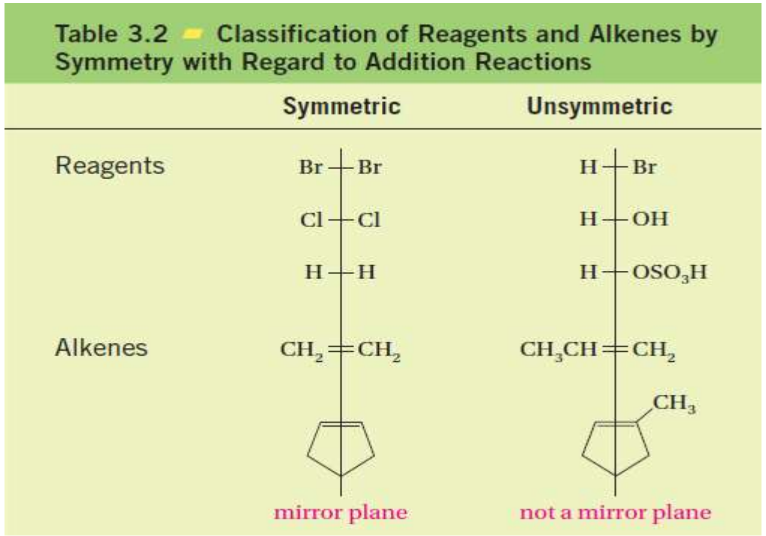


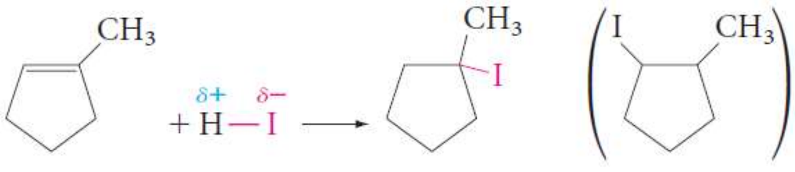
Table 3.2 ▬ Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

| | Symmetric | Unsymmetric |
|---|---|---|
| Reagents | Br–Br<br>Cl–Cl<br>H–H | H–Br<br>H–OH<br>H–$OSO_3H$ |
| Alkenes | $CH_2{=}CH_2$<br>mirror plane | $CH_3CH{=}CH_2$<br>$CH_3$<br>not a mirror plane |

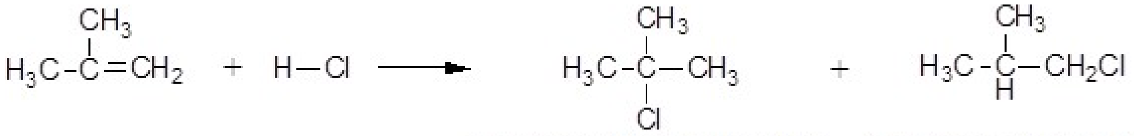
## Electrophilic Addition Reactions

### Markovnikov's Rule

*In electrophilic addition of H—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.*



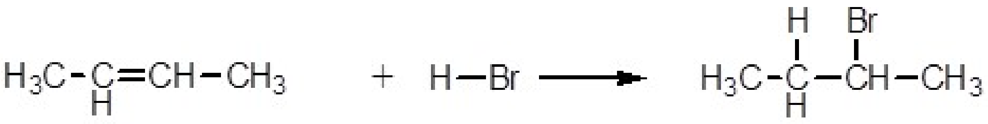
not observed



$$H_3C-\overset{CH_3}{C}=CH_2 + H-Cl \longrightarrow H_3C-\overset{CH_3}{\underset{Cl}{C}}-CH_3 + H_3C-\overset{CH_3}{\underset{H}{C}}-CH_2Cl$$

2-Chloro-2-methylpropane (major product)

1-Chloro-2-methylpropane (minor product)



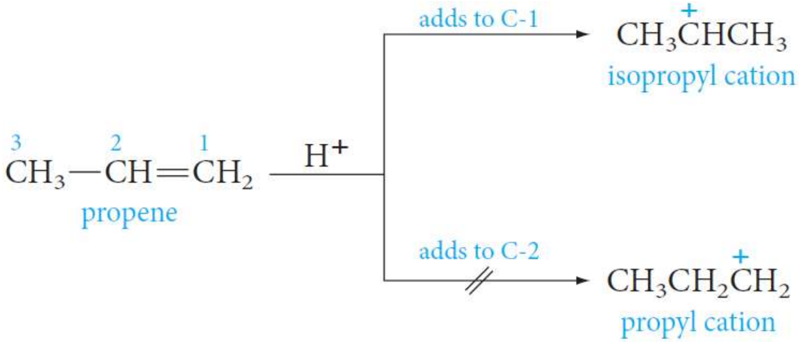
$$H_3C-\underset{H}{C}=CH-CH_3 + H-Br \longrightarrow H_3C-\overset{H}{\underset{H}{C}}-\overset{Br}{CH}-CH_3$$

2-Butene
(a symmetrical alkene)

2-Bromobutane
(only one product possible)

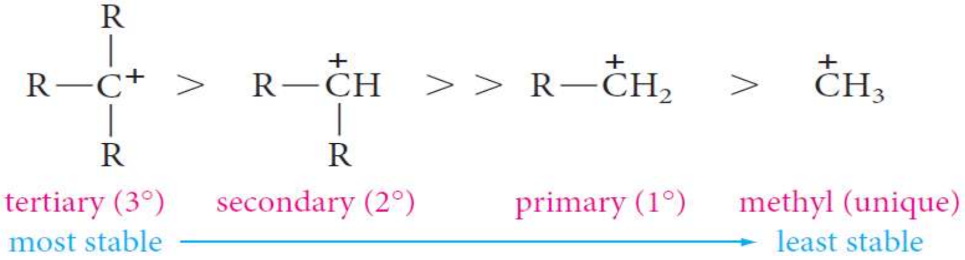
## Explanation for Markovnikov’s Rule

**Example;** *Addition of HBr to propene*



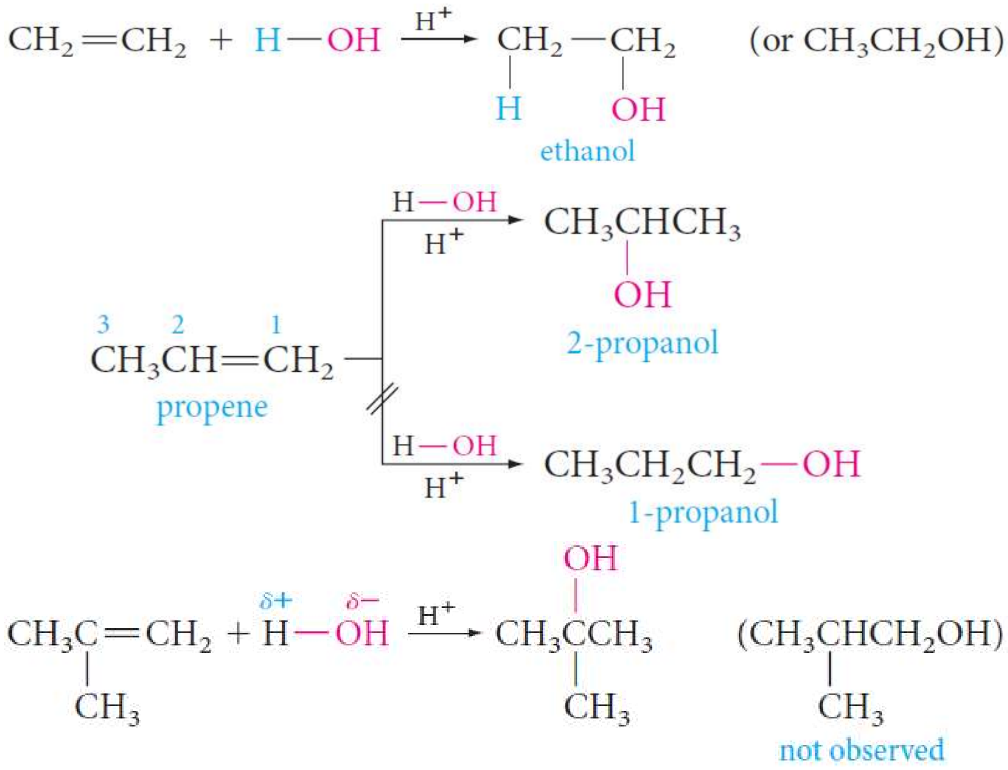
- **In modern terms Markovnikov’s rule can be restated:**

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



## 3.2. Addition of Water: Hydration

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



$$CH_2{=}CH_2 + H{-}OH \xrightarrow{H^+} \underset{H}{CH_2}{-}\underset{OH}{CH_2} \quad (\text{or } CH_3CH_2OH)$$

ethanol

$$\overset{3}{C}H_3\overset{2}{C}H{=}\overset{1}{C}H_2 \xrightarrow[H^+]{H-OH} CH_3\underset{OH}{C}HCH_3$$

propene

2-propanol

$$CH_3CH{=}CH_2 \xrightarrow[H^+]{H-OH} CH_3CH_2CH_2{-}OH$$

1-propanol

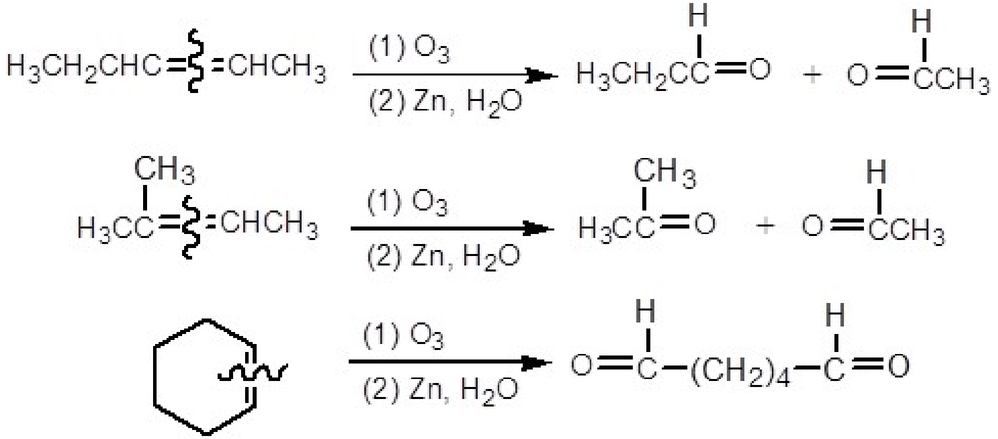
$$CH_3\underset{CH_3}{C}{=}CH_2 + \overset{\delta+}{H}{-}\overset{\delta-}{OH} \xrightarrow{H^+} CH_3\overset{OH}{\underset{CH_3}{C}}CH_3 \quad (CH_3\underset{CH_3}{C}HCH_2OH)$$

not observed

# Oxidation Reactions

## 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.

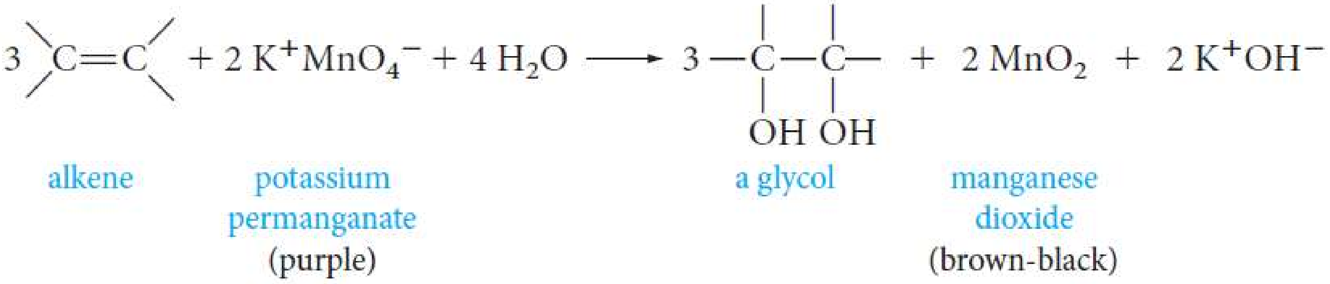


# Reactions of Unsaturated hydrocarbons (Alkenes)

## Oxidation Reactions

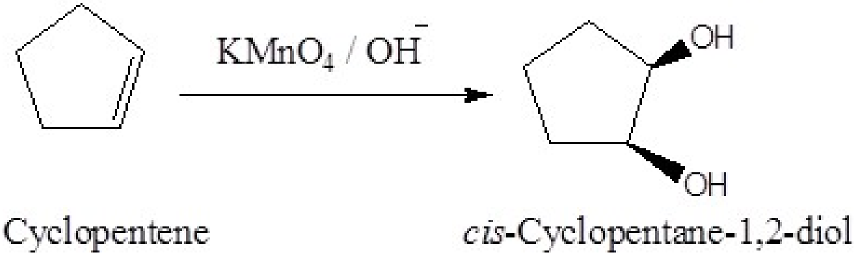
### 2. Oxidation Using $KMnO_4$

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



$$3\ \mathrm{C{=}C} + 2\,K^+MnO_4^- + 4\,H_2O \longrightarrow 3\ \mathrm{-\overset{|}{\underset{OH}{C}}-\overset{|}{\underset{OH}{C}}-} + 2\,MnO_2 + 2\,K^+OH^-$$

Hexane does not react with purple $KMnO_4$ (left); cyclohexene (right) reacts, producing a brown-black precipitate of $MnO_2$.



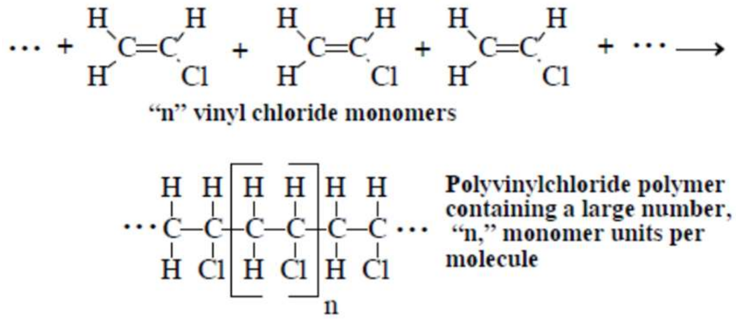
# Uses of Alkenes

## SYNTHETIC POLYMERS

Synthetic polymers are produced when small molecules called monomers bond together to form a much smaller number of very large molecules.

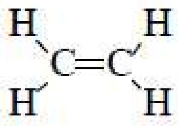
An important example:

- Polyvinylchloride; manufacture of water and sewer pipe.
- Polyethylene (plastic bags, milk cartons),
- Polypropylene, (impact-resistant plastics, indoor-outdoor carpeting),
- Polyacrylonitrile (Orlon, carpets),
- Polystyrene (foam insulation)

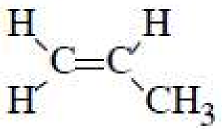


"n" vinyl chloride monomers

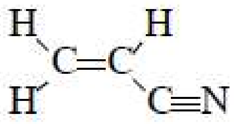
Polyvinylchloride polymer containing a large number, "n," monomer units per molecule



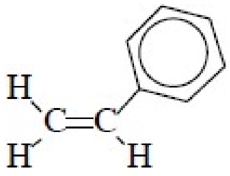
Ethylene



Propylene



Acrylonitrile

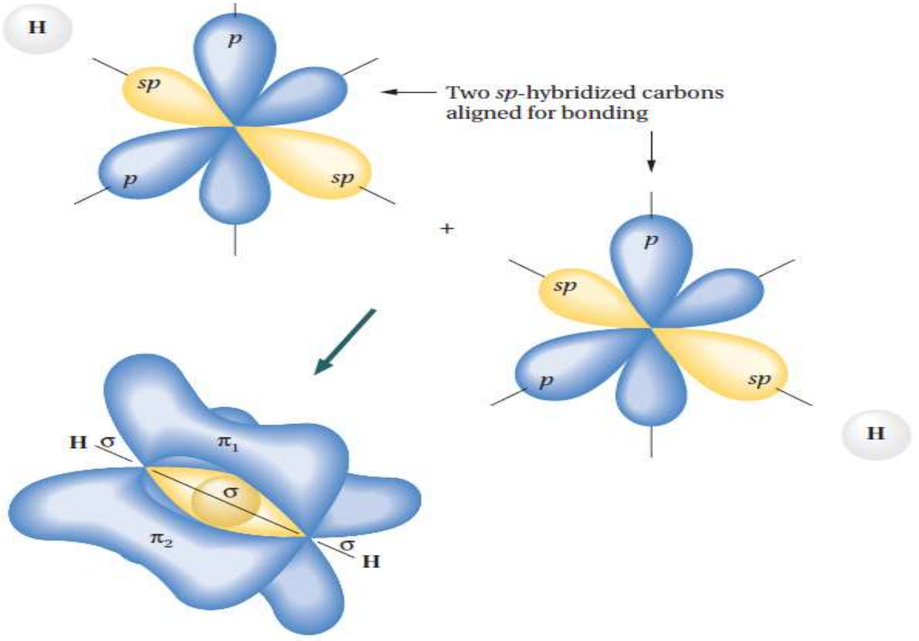


Styrene

# 3. ALKYNES

## The Structure of Alkynes

- **Alkynes** are hydrocarbons that contain a ***carbon–carbon triple bond*.**
- **Alkynes** are also known as *Acetylenes*.
- General formula is $C_nH_{2n-2}$
- Hybridization; ***sp*-hybridized orbitals**
- The angle between them is **180°** and the bond length **1.20 A°**
- The geometry is **Linear.**



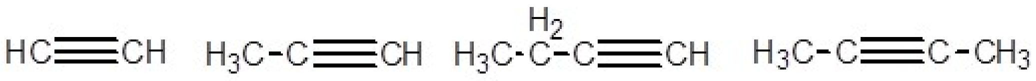
Two *sp*-hybridized carbons aligned for bonding

The resulting carbon–carbon triple bond, with a hydrogen atom attached to each remaining *sp* bond. (The orbitals involved in the C—H bonds are omitted for clarity.)

# Unsaturated hydrocarbons
# 2. Alkynes

## The Structure of Alkynes

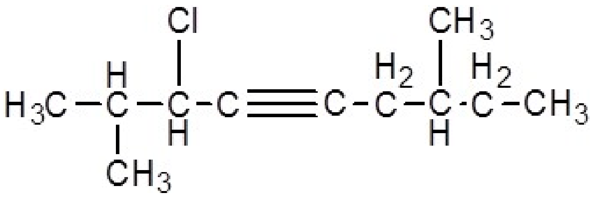
- The simplest members of the Alkynes series are $C_2$ & $C_3$
- The IUPAC names are derived from the corresponding alkanes by replacing the –ane ending by –yne.
- IUPAC rules as discussed for Alkenes .



$HC\equiv CH \quad H_3C-C\equiv CH \quad H_3C-\overset{H_2}{C}-C\equiv CH \quad H_3C-C\equiv C-CH_3$

| | | | | |
|---|---|---|---|---|
| IUPAC name: | Ethyne | Propyne | 1-Butyne | 2-Butyne |
| Common name: | Acetylene | | | |

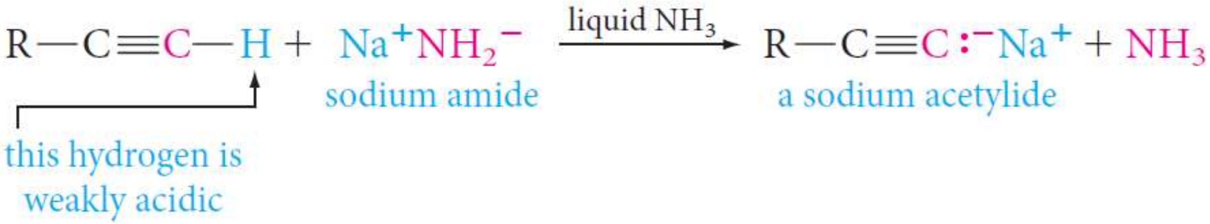
- **Example:**



**3-Chloro-2,7-dimethyl-4-nonyne**

# 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).



$$R{-}C{\equiv}C{-}H + Na^{+}NH_2^{-} \xrightarrow{\text{liquid } NH_3} R{-}C{\equiv}C{:}^{-}Na^{+} + NH_3$$

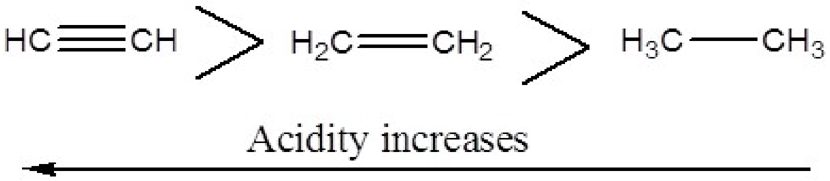
sodium amide

a sodium acetylide

this hydrogen is weakly acidic

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

  - Relative Acidity of the Hydrocarbon.
    Terminal alkynes, are more acidic than other hydrocarbons



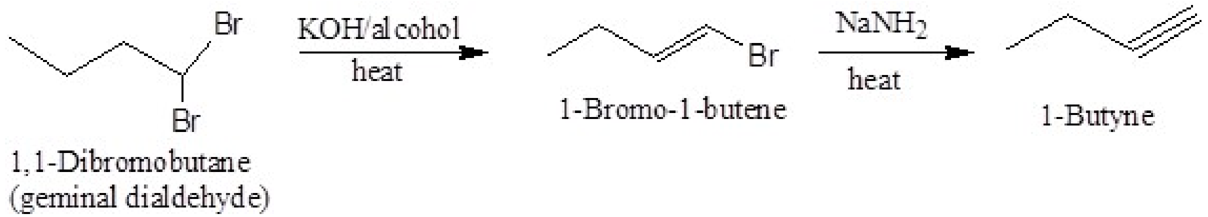
$$HC{\equiv}CH > H_2C{=}CH_2 > H_3C{-}CH_3$$

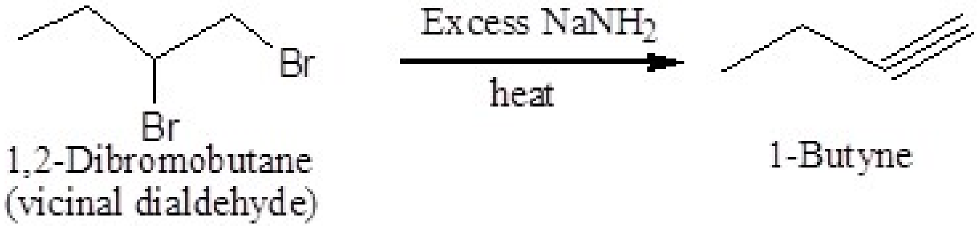
Acidity increases

# Preparation of Unsaturated hydrocarbons (Alkynes)

## 1) Dehydrohalogenation of Alkyl dihalides

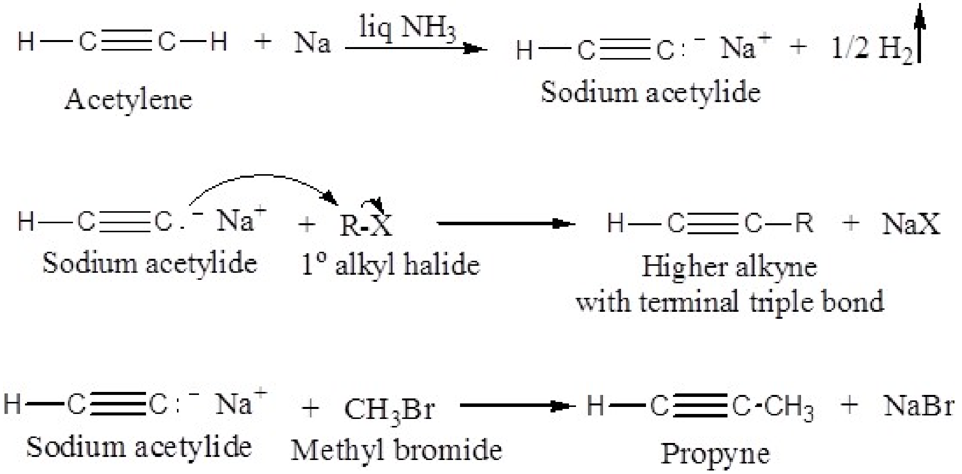
**Alkynes** can be prepared under alkaline conditions via deydrohalogenation of alkyl dihalides



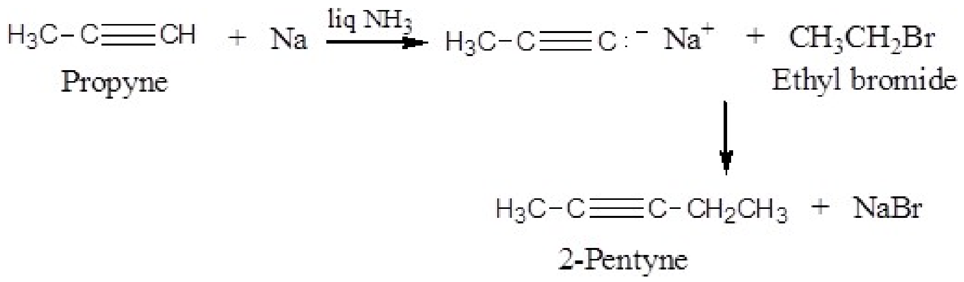


# 2) Reaction of Sodium Acetylide with Primary Alkyl Halides

- **Acetylene**



- **Monosubstituted Acetylenes**

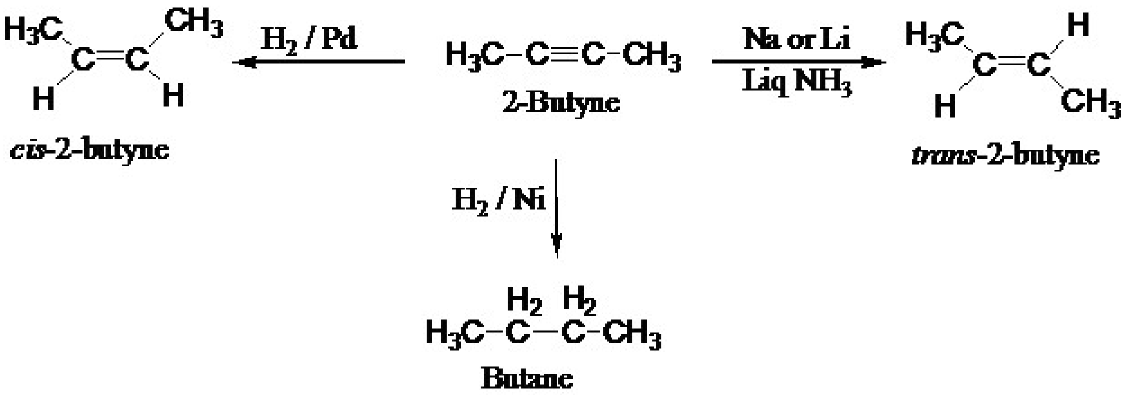


# Reactions of Unsaturated hydrocarbons (Alkynes)

## Electrophilic Addition Reactions

### 1. Addition of Hydrogen: Hydrogenation

- With an ordinary nickel or platinum catalyst, alkynes are hydrogenated all the way to alkanes.
- However, a special palladium catalyst (called Lindlar's catalyst) can control hydrogen addition so that only one mole of hydrogen adds. In this case, the product is a *cis* alkene.
- On the other hand, reduction using metals such a s sodium or lithium in liquid ammonia results in formation of trans alkenes.

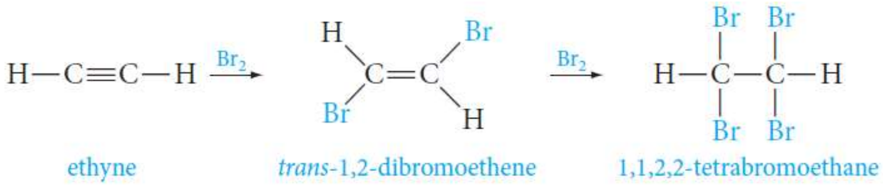


# Reactions of Unsaturated hydrocarbons (Alkynes)

## Electrophilic Addition Reactions

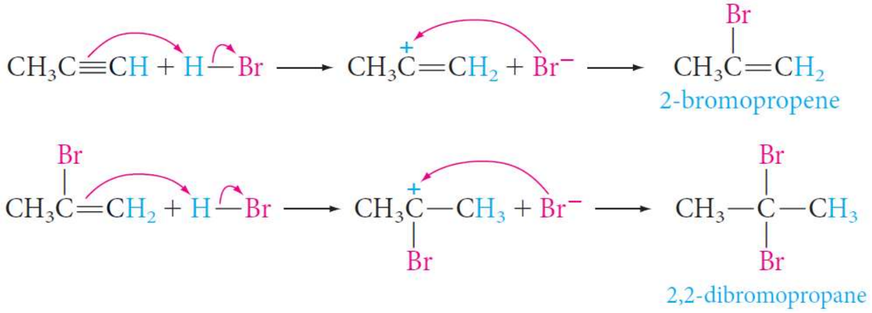
### 2. Addition of Halogen: Halogenation

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



### 3. Addition of Hydrogen Halide

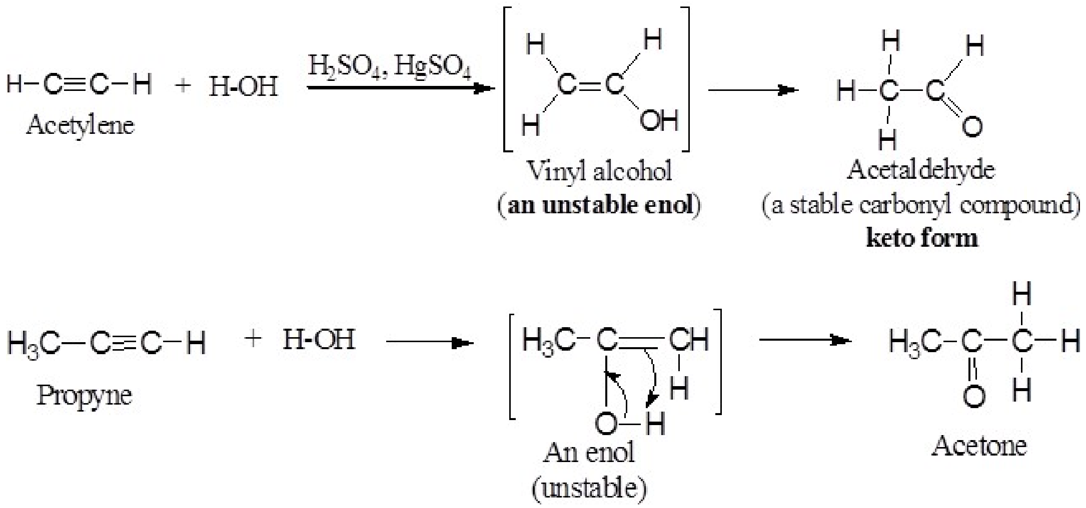
With unsymmetrical triple bonds and unsymmetrical reagents, Markovnikov's Rule is followed in each step, as shown in the following example:



# Reactions of Unsaturated hydrocarbons (Alkynes)

## 4. Addition of Water: Hydration

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



# Uses of Alkynes

**Alkynes;**

- Ethyne or acetylene reacts with oxygen to produce enough heat to weld metals.
- Anti-tumor agent

  Many alkynes are dangerous for humans when used in pharmaceuticals. However, specific alkynes, known as ene-diynes, hold a very strong and aggressive anti-tumor compound. Calicheamicin is an example of an anti-tumor working agent
- Drug production

  Alkynes are used in the manufacture of many drugs on the market, such as antiretroviral efavirenz and the antifungal terbinafine.

**- General uses;**

  - Making organic compounds
  - Organic solvents