Fundamentals of Organic Chemistry

CHEM 108

King Saud University

College of Science, Chemistry Department

CHEM 108

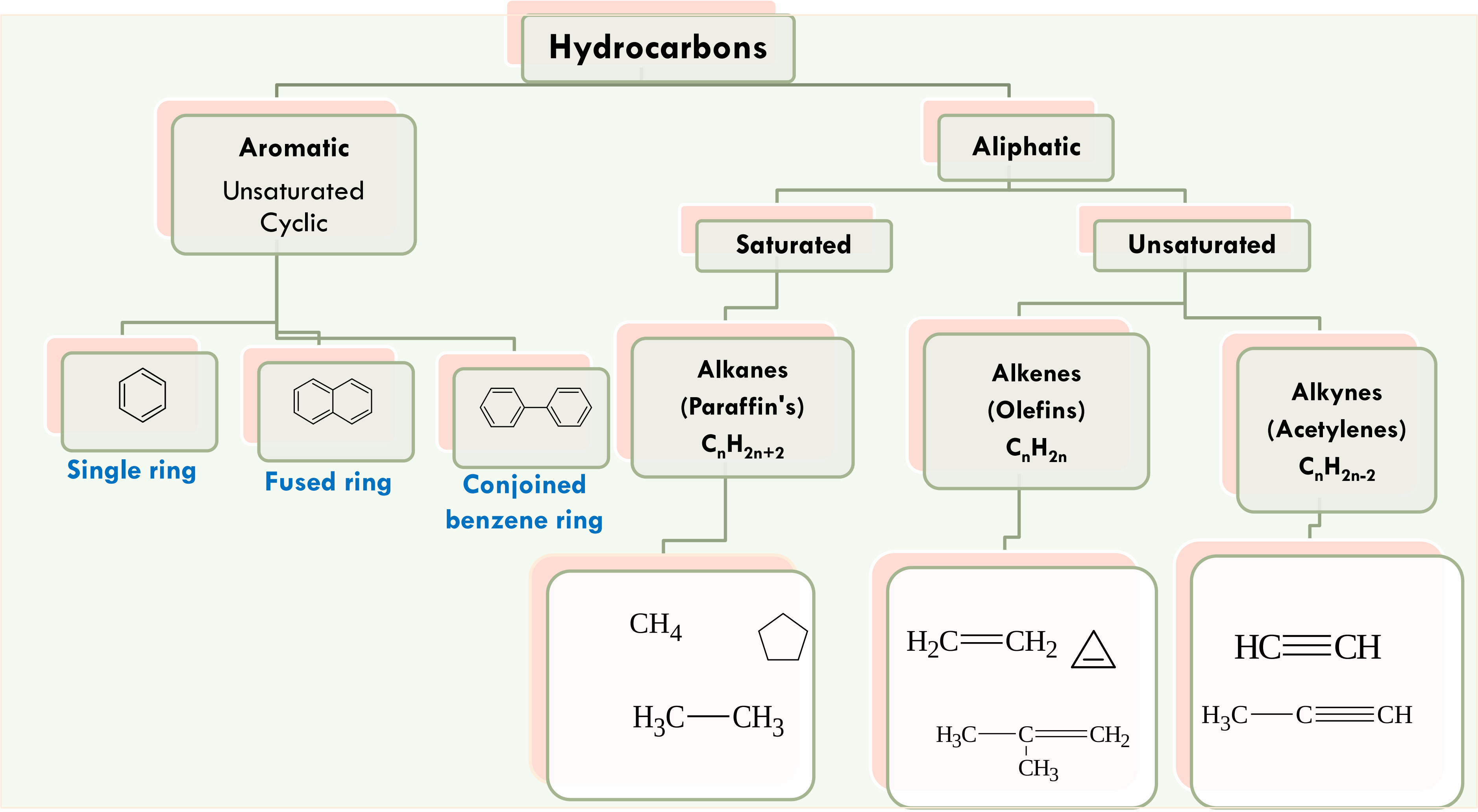
CHAPTER 2. ALIPHATIC HYDROCARBON

Hydrocarbons

- **Hydrocarbons** are Organic Compounds, which contain only the two elements **carbon** and **hydrogen**.
- **Aliphatic hydrocarbons** are subdivided into:
  - ***Saturated hydrocarbons***
    - Alkanes; C_nH_{2n+2} (*contain carbon-carbon single bond*)
    - Cycloalkanes: C_nH_{2n} (*contain carbon-carbon single bond in a single ring*)

    Alkanes and cycloalkanes are so similar that many of their properties can be considered side by side.
  - ***Unsaturated hydrocarbons***
    - Alkenes : C_nH_{2n} (contain *carbon-carbon double bond)*
    - Alkynes : $C_n\ H_{2n-2}$ (contain *carbon-carbon triple bond)*

Hydrocarbons



Hydrocarbons

Aromatic

Unsaturated
Cyclic

Single ring

Fused ring

Conjoined benzene ring

Aliphatic

Saturated

Unsaturated

Alkanes
(Paraffin's)
C_nH_{2n+2}

CH_4

H_3C-CH_3

Alkenes
(Olefins)
C_nH_{2n}

$H_2C=CH_2$

$H_3C-\underset{CH_3}{\underset{|}{C}}=CH_2$

Alkynes
(Acetylenes)
C_nH_{2n-2}

$HC\equiv CH$

$H_3C-C\equiv CH$

Saturated Hydrocarbons
1. Alkanes

- **General formula is C_nH_{2n+2}**
- In **alkanes**, the four *sp*^{3} orbitals of carbon repel each other into a TETRAHEDRAL arrangement with bond angles of 109.5° like in CH_4.
- Each *sp*^{3} orbital in carbon overlaps with the 1s orbital of a hydrogen atom to form a C-H bond.

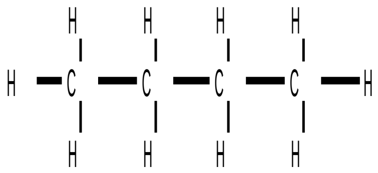
Saturated Hydrocarbons
1. Alkanes

Names, Molecular formulas and Number of Isomers of the first ten Alkanes

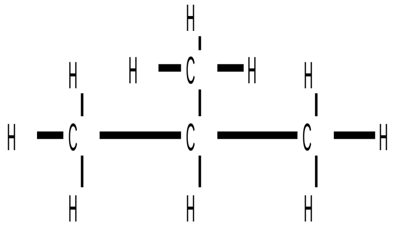
Name	Molecular Formula	Number of isomers
Methane	CH_4	1
Ethane	C_2H_6	1
Propane	C_3H_8	1
Butane	C_4H_{10}	2
Pentane	C_5H_{12}	3
Hexane	C_6H_{14}	5
Heptane	C_7H_{16}	9
Octane	C_8H_{18}	18
Nonane	C_9H_{20}	35
Decane	$C_{10}H_{22}$	75

Structural Isomerism

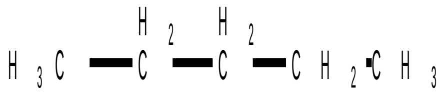
- **Isomers** are different compounds with identical molecular formulas.
  The phenomenon is called ***isomerism***.
- **Structural** or **constitutional isomers** are isomers which differ in the sequence of atoms bonded to each other.
- **Examples:**
  - **Butanes, C_4H_{10}.**
  - **Pentanes, C_5H_{12}.**



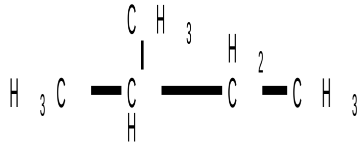
n-Butane



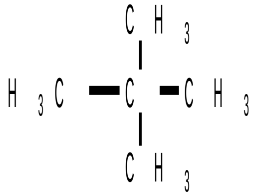
Isobutane



n-Pentane



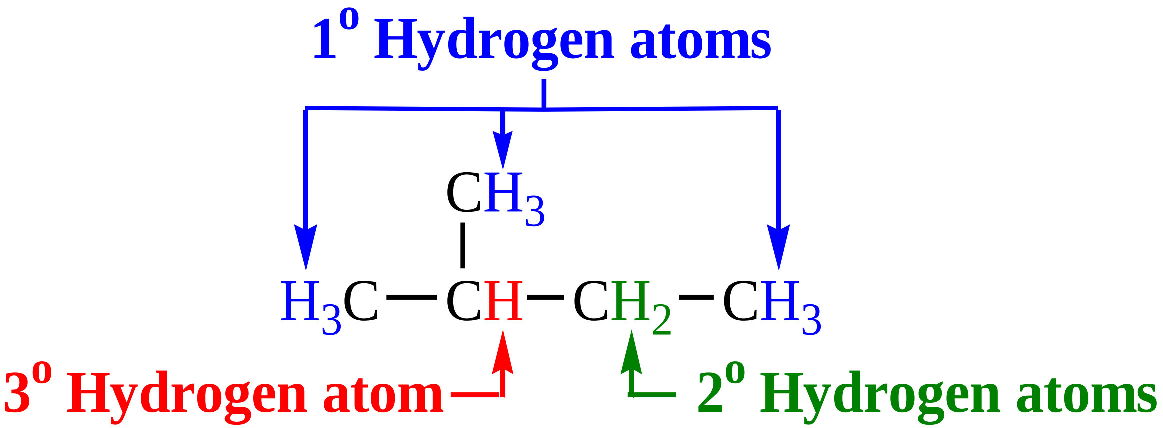
Isopentane



Neopentane

Classes of Carbons and Hydrogen

- **A primary (1°) carbon** is one that is bonded to only one other carbon.
- **A secondary (2°) carbon** is one that is bonded to two other carbons.
- **A tertiary (3°) carbon** is one that is bonded to three other carbons.



$$H_3C-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2-CH_3$$

- **Hydrogens** are also referred to as 1°, 2°, or 3° according to the type of carbon they are bonded to.

Alkyl Groups

- An **alkyl group** is an alkane from which a hydrogen has been removed.
- **General formula C_nH_{2n+1}.**
- **Alky group** is represented by **R**.
- **Nomenclature of alkyl groups by**

  replacing the suffix *– ane* of the parent alkane by *–yl*.

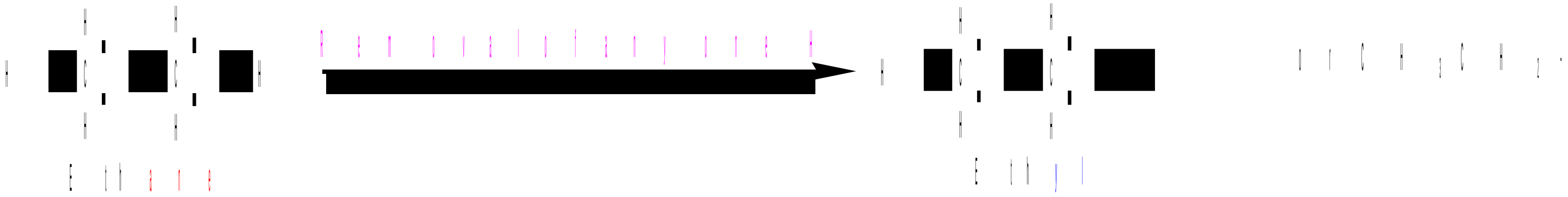
  i.e. Alkane – ane + yl = Alkyl
- **Examples:**
  - *Methane*

CH_3- (Methane – ane + yl) = methyl

Saturated Hydrocarbons
1. Alkanes

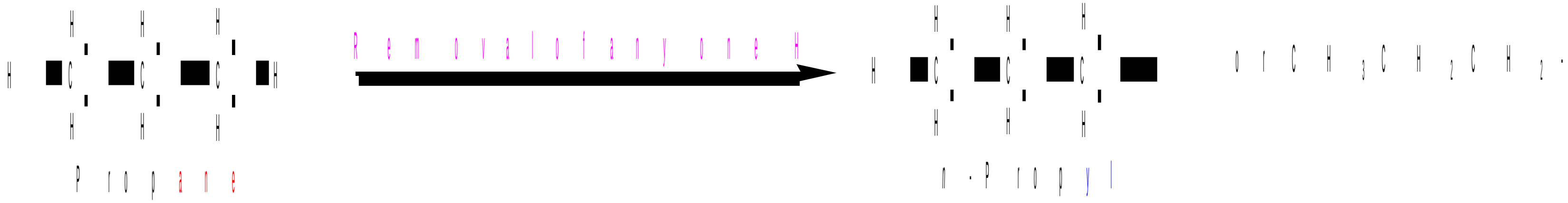
Alkyl Groups

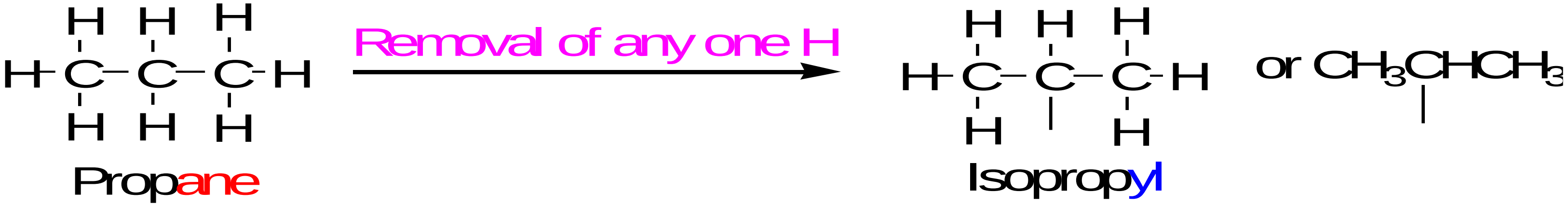
- **Ethane**



CH_3CH_2- (Ethane – ane + yl) = ethyl

- **Propane**



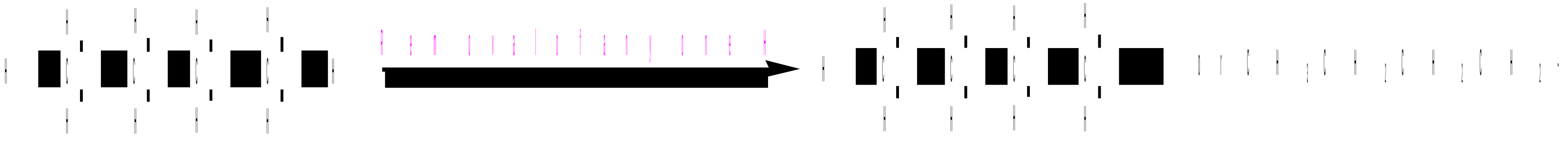


Propane – ane + yl = *n*-propyl or isopropyl

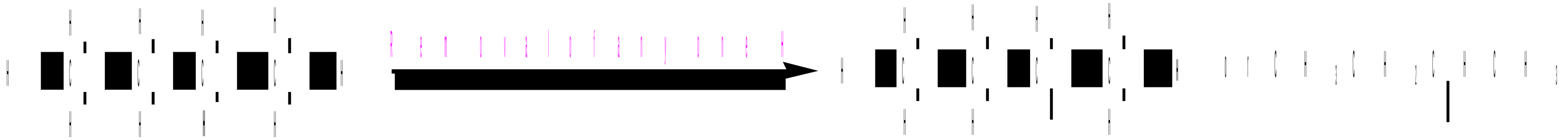
Saturated Hydrocarbons
1. Alkanes

Alkyl Groups

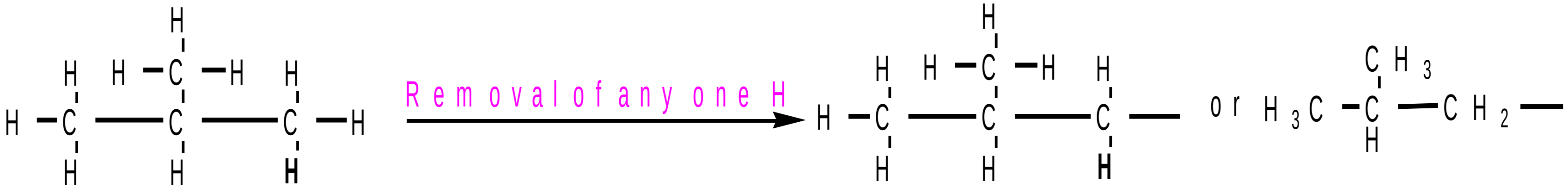
- ***Butane***



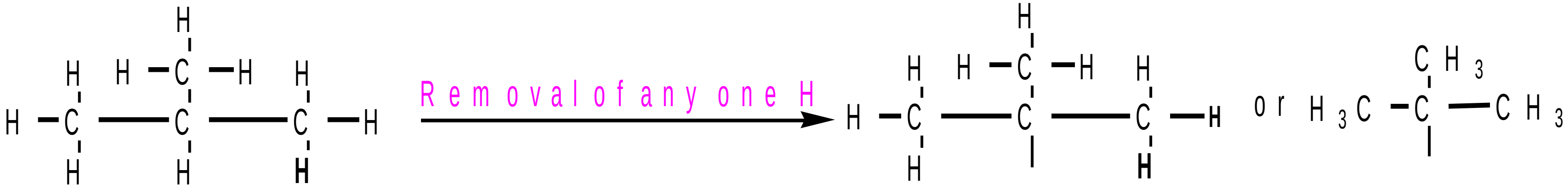
Butane   Butyl



Butane   sec-Butyl



Isobutane   Isobutyl



Isobutane   *tert*-butyl or *t*-butyl

Saturated Hydrocarbons
1. Alkanes

Alkyl Groups

Alkane		Alkyl Group	Abbreviation
CH_3—H **Methane**	becomes	CH_3— **Methyl**	Me–
CH_3CH_2—H **Ethane**	becomes	CH_3CH_2— **Ethyl**	Et–
$CH_3CH_2CH_2$—H **Propane**	becomes	$CH_3CH_2CH_2$— **Propyl**	Pr–
$CH_3CH_2CH_2CH_2$—H **Butane**	becomes	$CH_3CH_2CH_2CH_2$— **Butyl**	Bu–

Saturated Hydrocarbons
1. Alkanes

Nomenclature

- **Most organic compounds are known by two or more names:**
  - **The older unsystematic names, (*Common names*).**
  - **The IUPAC names.**

International Union of Pure & Applied Chemistry

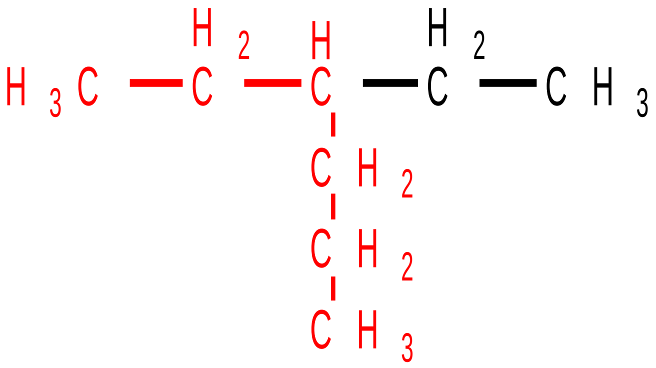
Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

1) **Select the parent structure .**

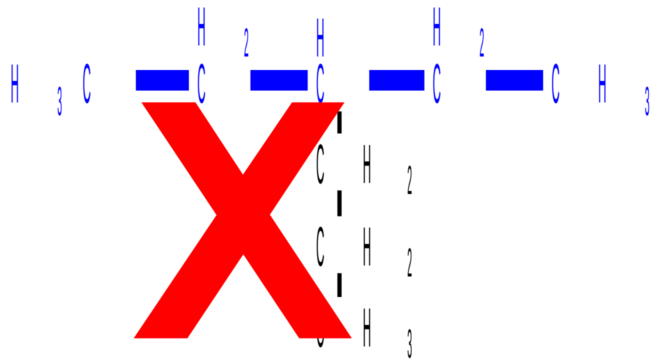
the longest continuous chain



$H_3C-CH_2-CH(CH_2CH_2CH_3)-CH_2-CH_3$

Ethyl hexane

not



$H_3C-CH_2-CH(CH_2CH_2CH_3)-CH_2-CH_3$

Propyl pentane

The longest continuous chain is not necessarily straight.

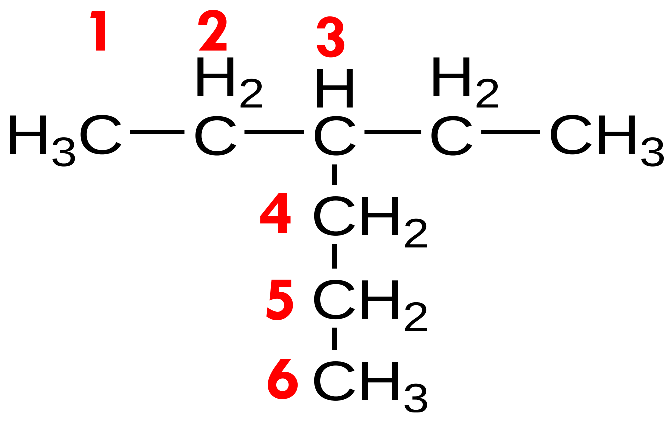
Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

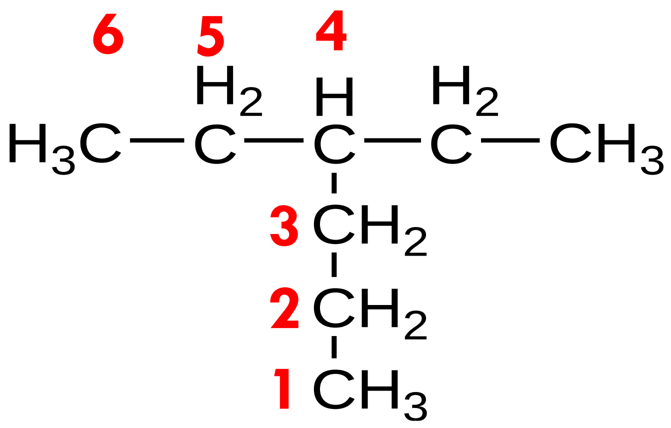
2) **Number the carbons in the parent chain**

starting from the end which gives the lowest number for the substituent



3-Ethyl hexane

not



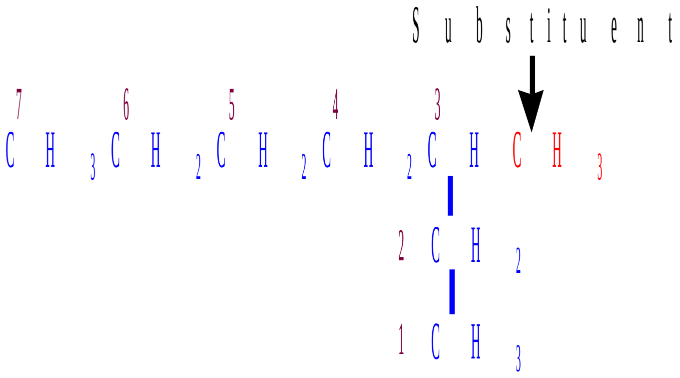
4-Ethyl hexane X

Saturated Hydrocarbons
1. Alkanes

Nomenclature

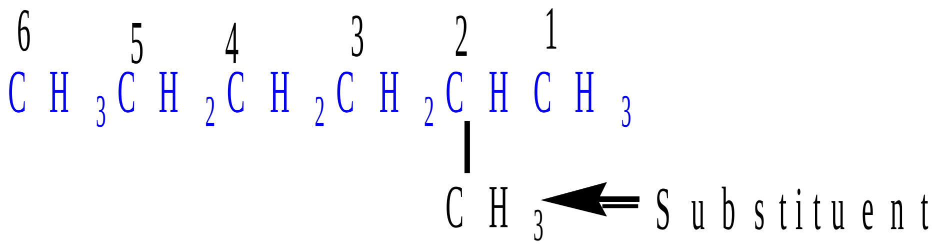
The IUPAC Rules

2) Number the carbons in the parent chain



$\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H(\overset{2}{C}H_2\overset{1}{C}H_3)CH_3$

3-Methylheptane



$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H(CH_3)\overset{1}{C}H_3$

2-Methylpentane

Nomenclature

The IUPAC Rules

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)

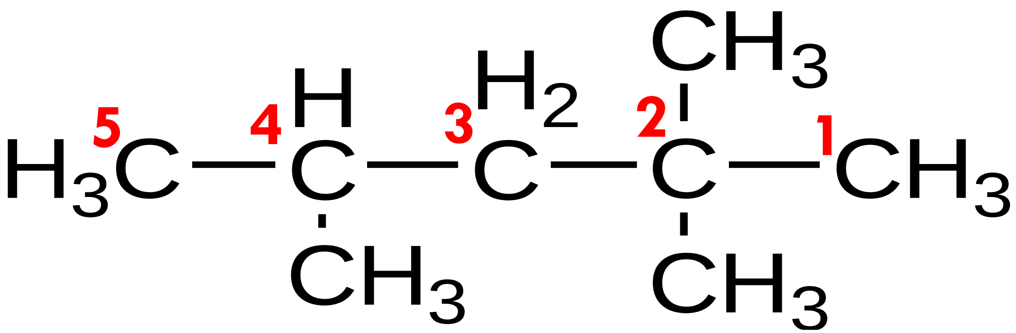
3 - Ethyl hexane

The IUPAC Rules

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.



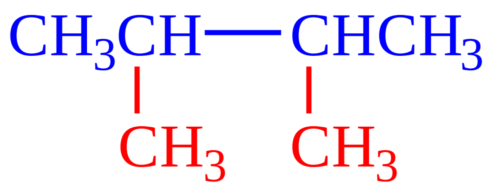
$H_3C{-}CH(CH_3){-}CH_2{-}C(CH_3)_2{-}CH_3$

2,2,4- Tri methyl pentane

Saturated Hydrocarbons
1. Alkanes

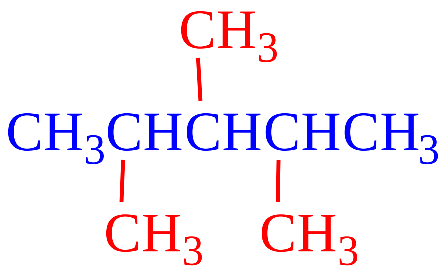
Nomenclature

The IUPAC Rules



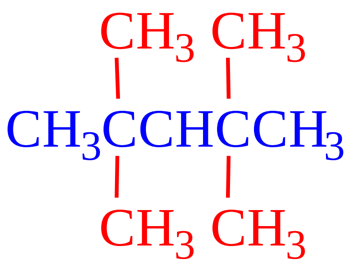
$$CH_3\underset{CH_3}{\underset{|}{C}}H-\underset{CH_3}{\underset{|}{C}}HCH_3$$

2,3-Dimethylbutane



$$CH_3\underset{CH_3}{\underset{|}{C}}H\overset{CH_3}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_3$$

2,3,4-Trimethylpentane



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

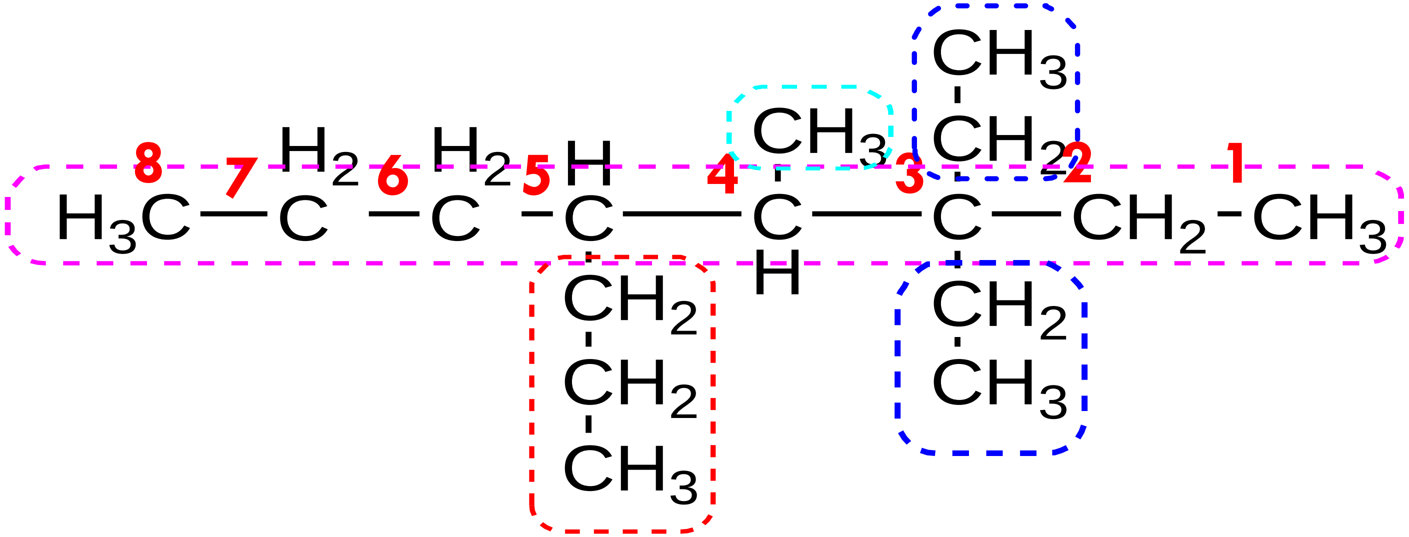
2,2,4,4-Tetramethylpentane

Nomenclature

The IUPAC Rules

4) If **different alkyl substituents** are attached on the parent carbon chain,

they are named in order of alphabetical order.



3,3- di ethyl
4- methyl
5- propyl

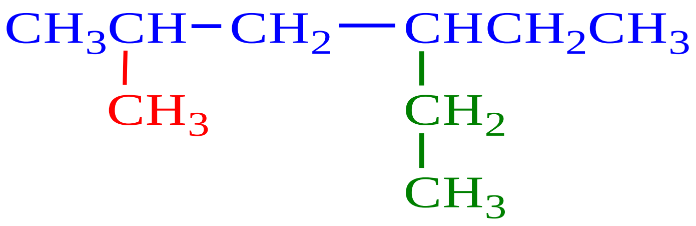
3,3-Diethyl -4-methyl - 5-propyl octane

Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

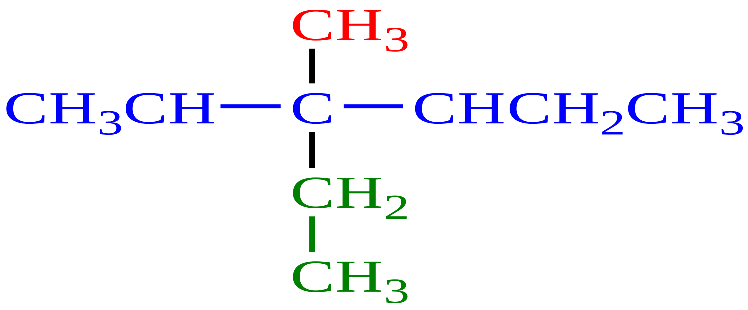
Note that each substituent is given a number corresponding to its location on the longest chain. The substituent groups are listed alphabetically.



$$CH_3\underset{\overset{|}{CH_3}}{CH}-CH_2-\underset{\underset{\overset{|}{CH_3}}{\overset{|}{CH_2}}}{CH}CH_2CH_3$$

4-Ethyl-2-methylhexane

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



$$CH_3CH-\underset{\underset{\overset{|}{CH_3}}{\overset{|}{CH_2}}}{\overset{\underset{|}{CH_3}}{C}}-CHCH_2CH_3$$

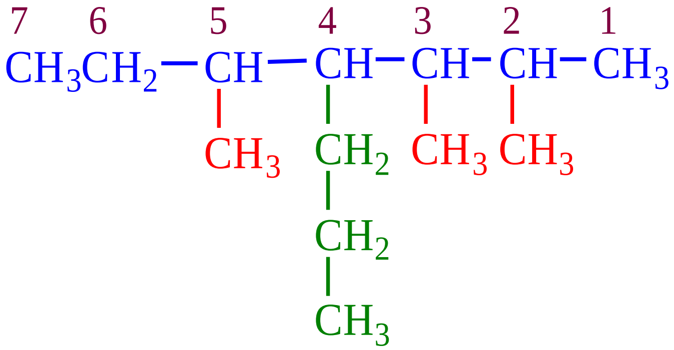
3-Ethyl-3-methylhexane

Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

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



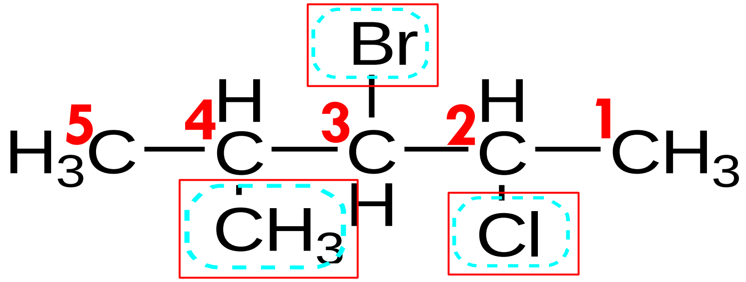
2,3,5-Trimethyl-4-*n*-propylheptane

Saturated Hydrocarbons
1. Alkanes

Nomenclature

The IUPAC Rules

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



$H_3C-CH(CH_3)-CH(Br)-CH(Cl)-CH_3$

2-chloro
3-bromo
4- methyl

3-bromo -2-chloro -4-methyl pentane

Sources of Alkanes

- The two principal sources of alkanes are petroleum and natural gas.

Petroleum and natural gas constitute the chief sources of

- Alkanes up to 40 Carbons
- Aromatic
- Alicyclic (Cyclic aliphtic hydrocarbons)
- Heterocyclic

Saturated Hydrocarbons
1. Alkanes

Sources of Alkanes

Petroleum Refining

Some components of refined petroleum

Fraction	Boiling range (°C)	Caron content
Gas	Below 20	C1 – C4
Petroleum ether	20 – 60	C5 – C6
Naphtha	60 – 100	C6 – C7
Gasoline	40 – 200	C5 – C10
Kerosine	175 – 325	C11 – C18
Gas oil	300 – 500	C15 – C40
Lubricating oil, asphalt, petroleum coke and paraffins	Above 400	C15 – C40

Physical Properties of Alkanes, Alkenes and Alkynes

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

A. Physical States

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

B. Solubility

- Alkanes, Alkenes and Alkynes are nonpolar compounds.
- Their solubility " Like dissolve like"
- Alkanes, Alkenes and Alkynes are soluble in the nonpolar solvents;
  carbon tetrachloride, CCl_4 and benzene,
- Alkanes, Alkenes and Alkynes are insoluble in polar solvents like water.

Saturated Hydrocarbons
1. Alkanes

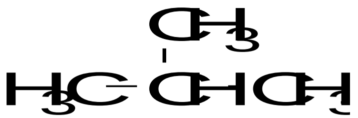
Physical Properties

C. Boiling Points

$CH_3CH_2CH_2CH_3$

n-Butane

bp = 0°C



$H_3C-\overset{CH_3}{\overset{|}{C}}H-CH_3$

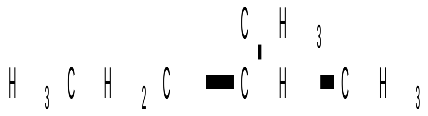
Isobutane

bp = -12°C

$CH_3CH_2CH_2CH_2CH_3$

n-Pentane

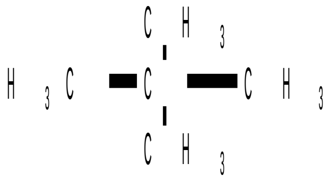
b.p.= 36°C



$H_3CH_2C-\overset{CH_3}{\overset{|}{C}}H-CH_3$

Isopentane

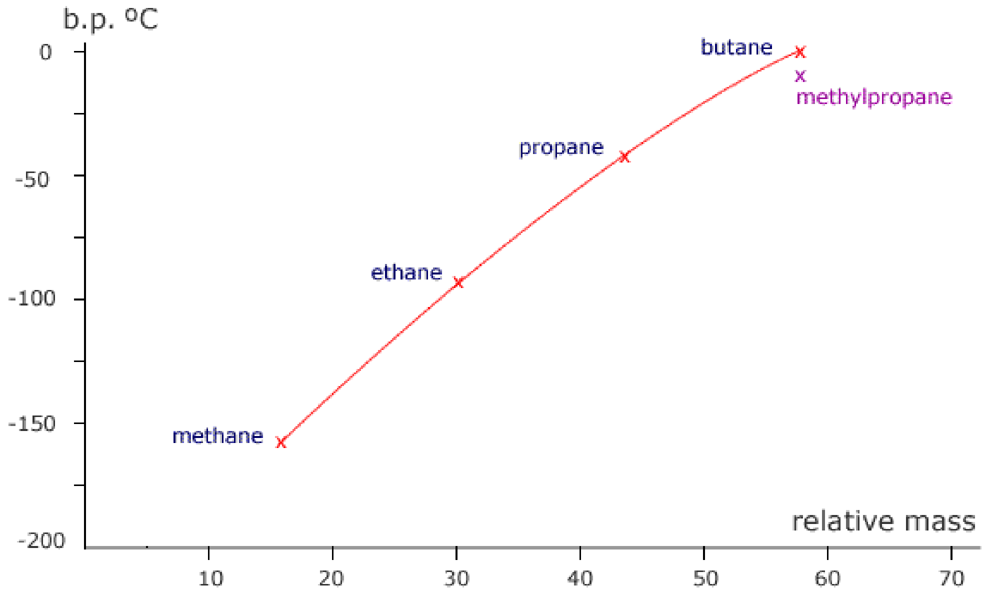
b.p.= 28°C



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

Neopentane

b.p.= 9.5°C



Graph showing boiling point of the alkanes against relative mass

- Boiling point decreases with increasing branches
- Boiling point increases with increasing molecular weight.

Preparation of Alkanes

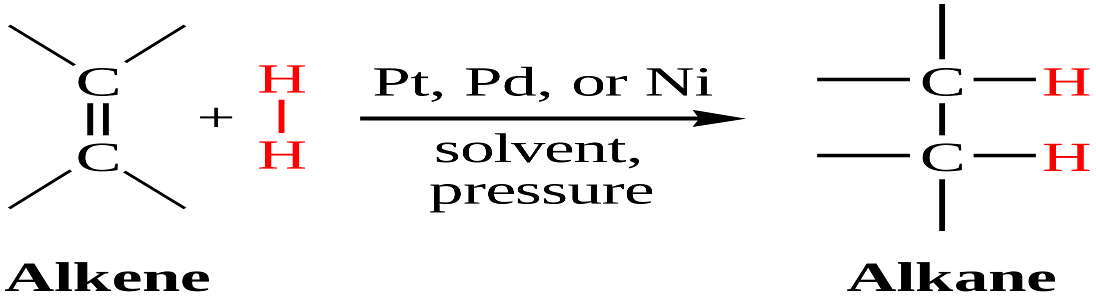
1) Hydrogenation of Alkenes and Alkynes

A great number of alkanes can be obtained by fractional distillation of crude petroleum and subsequent reactions as follows:

1. **Catalytic hydrogenation:**

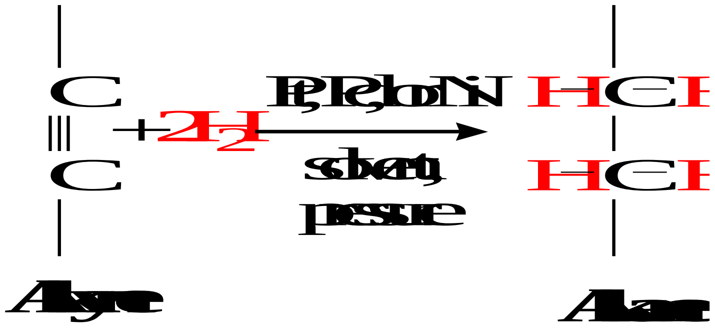
   Alkenes and alkynes react with hydrogen in the presence of metal catalysts such as nickel, palladium, and platinum to produce alkanes.

General Reaction

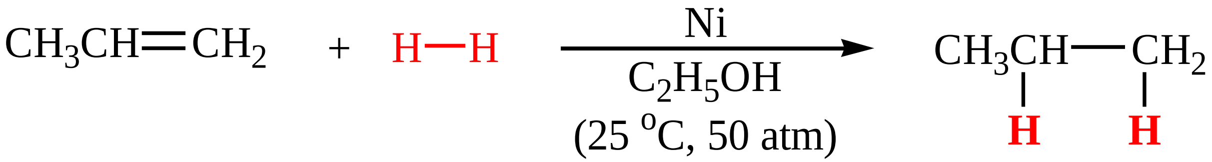


Preparation of Alkanes

1) Hydrogenation of Alkenes and Alkynes

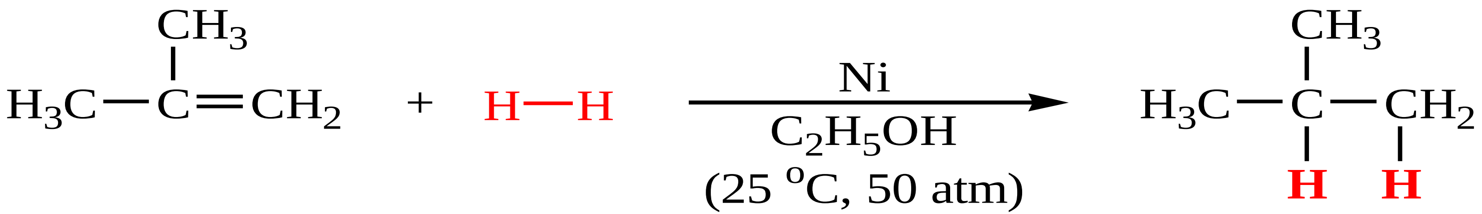


- *Specific Examples*



$$CH_3CH{=}CH_2 + H{-}H \xrightarrow[\text{(25 °C, 50 atm)}]{\text{Ni},\ C_2H_5OH} CH_3CH(H){-}CH_2(H)$$

propene **propane**



$$H_3C{-}C(CH_3){=}CH_2 + H{-}H \xrightarrow[\text{(25 °C, 50 atm)}]{\text{Ni},\ C_2H_5OH} H_3C{-}C(CH_3)(H){-}CH_2(H)$$

2-Methylpropene **Isobutane**

Preparation of Alkanes

2) Hydrolysis of Grignard Reagent

$$RMgX + HOH \longrightarrow RH + MgX(OH)$$

Alkylmagnesium halide
(Grignard reagent)

- ○ *Grignard reagents* **react readily with any source of protons to give hydrocarbons.**

$$CH_3CH_2Br + Mg \xrightarrow{\text{Dry Ether}} CH_3CH_2MgBr$$

Ethyl bromide

Ethyl magnesium bromide
(Grignard reagent)

$$CH_3CH_2MgBr + HOH \longrightarrow CH_3CH_3 + MgBr(OH)$$

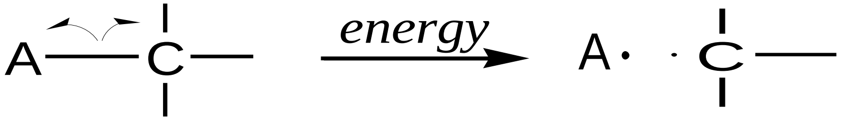
Ethane

3) By coupling of alkyl halides with dialkyl cuprate (all kinds of alkanes)

$$(CH_3CH_2)_2CuLi \xrightarrow{CH_3Br} CH_3CH_2CH_3$$

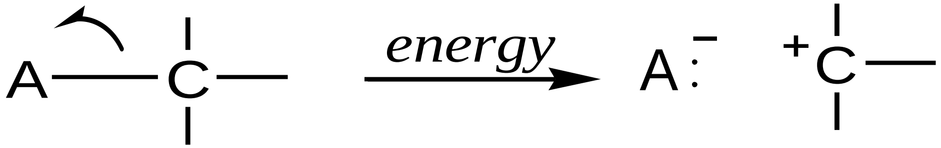
Notations for bond breaking and bond making

- **A covalent bond can be broken in either two ways,**
  - **Homolytic cleavage.**

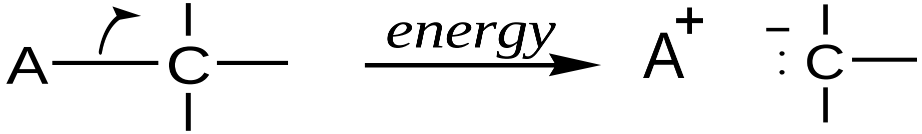


Free radicals

  - **Heterolytic cleavage.**



Carbocation



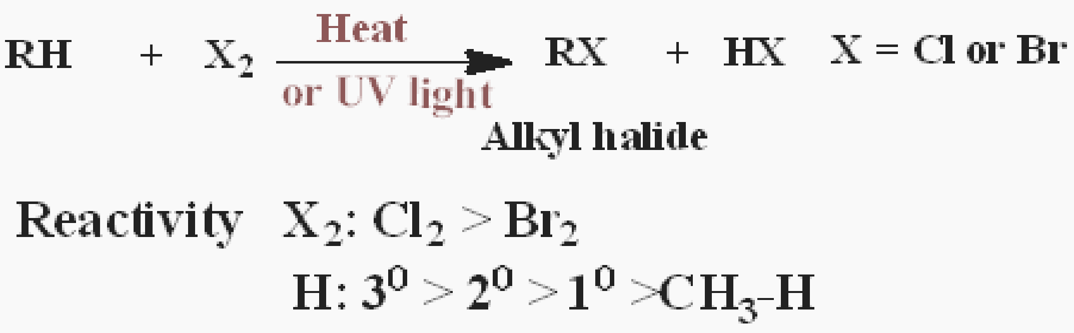
Carboanion

Reactions of Alkanes

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

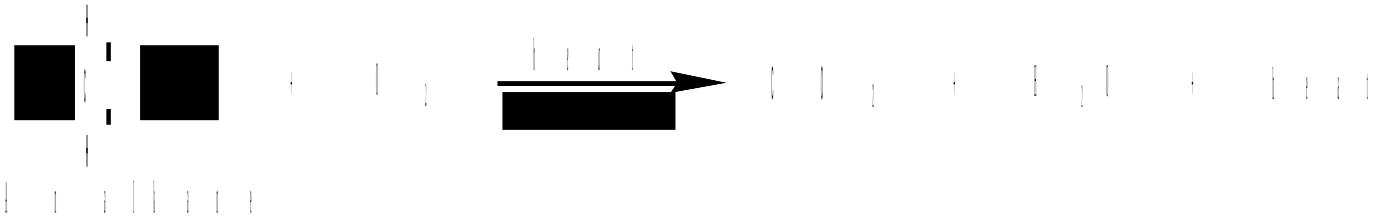


$$RH + X_2 \xrightarrow[\text{or UV light}]{\text{Heat}} \underset{\text{Alkyl halide}}{RX} + HX \quad X = Cl \text{ or } Br$$

$$\text{Reactivity} \quad X_2: Cl_2 > Br_2$$

$$H: 3^0 > 2^0 > 1^0 > CH_3\text{-}H$$

Combustion



Saturated Hydrocarbons
1. Alkanes

Reactions of Alkanes

A. Halogenation

- **Substitution reaction of alkanes,**

  i.e. replacement of hydrogen by halogen,

  usually chlorine or bromine, giving alkyl chloride or alkyl bromide.

- **Flourine reacts explosively with alkanes**

  It is unsuitable reagent for the preparation of the alkyl flourides.

- **Iodine is too unreactive**

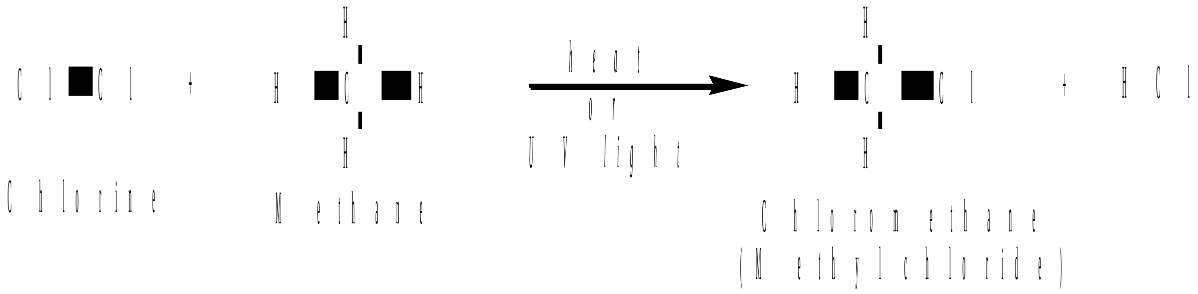
  It is not used in the halogentaion of alkanes.

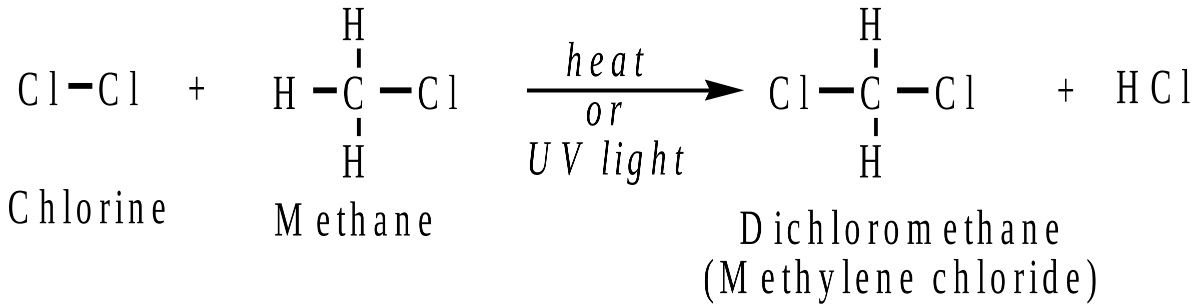
- **Halogenation of alkanes take place at**

  high temperatures or under the influence of ultraviolet light

A. Halogenation

- Chlorination of an alkane usually gives a mixture of products





2. ALKENES

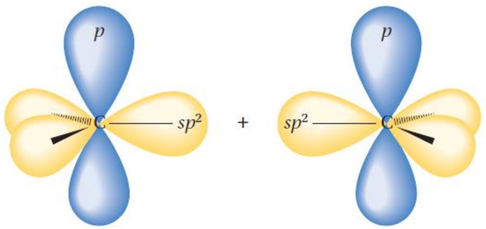
The Structure of Alkenes

- **Alkenes** are hydrocarbons that contain a ***carbon–carbon double bond***.
- **Alkenes are also *Olefins*.**
- **General formula is C_nH_{2n}**
- The simplest members of the **Alkenes** series are **C_2 & C_3**

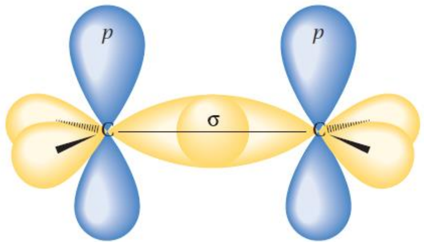
	$CH_2{=}CH_2$	$H_3C-CH{=}CH_2$
Common name:	Ethylene	Propylene
IUPAC name:	Ethene	Propene

The Structure of Alkenes

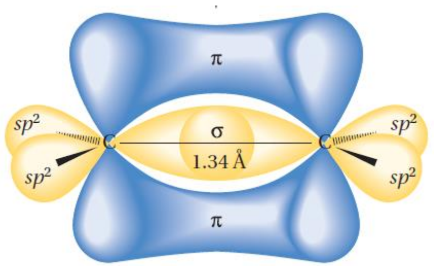
- Hybridization; **sp^2-hybridized orbitals**
- The angle between them is 120° and bond length C=C (1.34 Å).
- A **trigonal planar.**



two sp^2-hybridized carbons with p orbitals parallel



the σ bond is formed by two electrons in overlapping sp^2 orbitals



the π bond is formed by two electrons in overlapping parallel p orbitals

Nomenclature of Alkenes

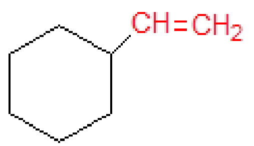
Common Names

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

$CH_2{=}CH_2$	$HC{\equiv}CH$	$CH_3CH{=}CH_2$
ethylene	acetylene	propylene
(ethene)	(ethyne)	(propene)

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

$CH_2{=}CH{-}$	$CH_2{=}CHCl$
vinyl	vinyl chloride
(ethenyl)	(chloroethene)
$CH_2{=}CH{-}CH_2{-}$	$CH_2{=}CH{-}CH_2Cl$
allyl	allyl chloride
(2-propenyl)	(3-chloropropene)



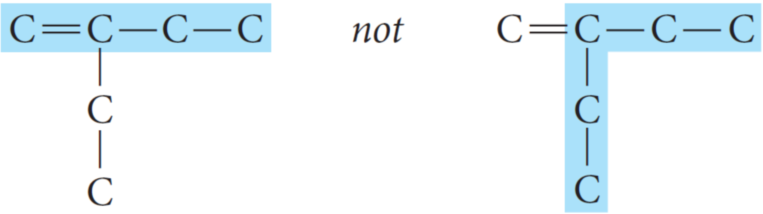
Common name: Vinyl cyclohexane
IUPAC name: Cyclohexylethene

Nomenclature of Alkenes

The IUPAC Rules

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

1. The ending ***-ene*** is used to designate a carbon–carbon double bond.
2. Select the **longest chain that includes *both <u>carbons of the double bond</u>***.

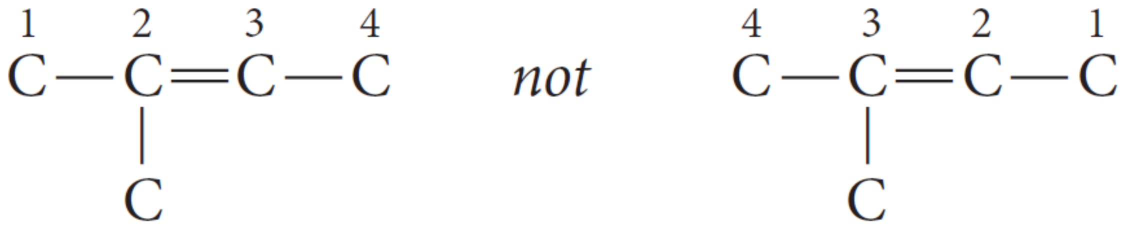


3. **Number the chain from the end nearest the double bond** so that the carbon atoms in that bond have the lowest possible numbers.

$$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C} \quad \textit{not} \quad \overset{5}{C}-\overset{4}{C}=\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$

Nomenclature of Alkenes

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



$$\overset{1}{C}-\overset{2}{\underset{\displaystyle C}{\underset{|}{C}}}=\overset{3}{C}-\overset{4}{C} \quad \textit{not} \quad \overset{4}{C}-\overset{3}{\underset{\displaystyle C}{\underset{|}{C}}}=\overset{2}{C}-\overset{1}{C}$$

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

$$\overset{1}{C}H_2=\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$$

1-butene, *not* 2-butene

Nomenclature of Alkenes

NOTES

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.

No number is necessary in these cases, because in each instance, only one structure is possible.

CH_3CH_3	$CH_2{=}CH_2$	$HC{\equiv}CH$
ethane	ethene	ethyne
$CH_3CH_2CH_3$	$CH_2{=}CHCH_3$	$HC{\equiv}CCH_3$
propane	propene	propyne

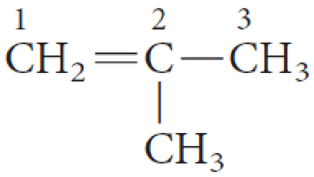
With four carbons, a number is necessary to locate the double bond.

$$\overset{1}{C}H_2{=}\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3 \qquad \overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_3$$

1-butene 2-butene

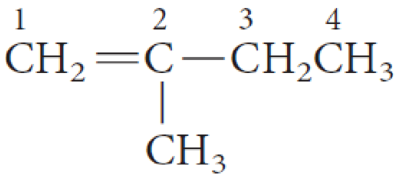
Nomenclature of Alkenes

- Branches are named in the usual way.



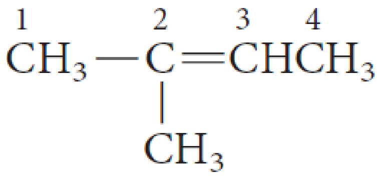
$\overset{1}{\mathrm{CH_2}}=\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{2}{\mathrm{C}}}-\overset{3}{\mathrm{CH_3}}$

methylpropene
(isobutylene)



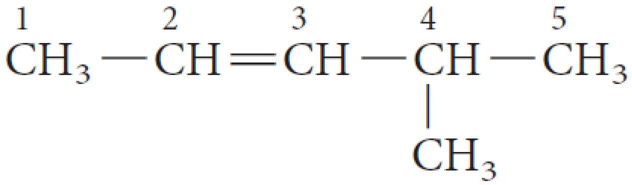
$\overset{1}{\mathrm{CH_2}}=\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{2}{\mathrm{C}}}-\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$

2-methyl-1-butene



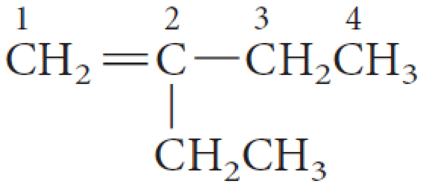
$\overset{1}{\mathrm{CH_3}}-\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{2}{\mathrm{C}}}=\overset{3}{\mathrm{CH}}\overset{4}{\mathrm{CH_3}}$

2-methyl-2-butene



$\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH}}=\overset{3}{\mathrm{CH}}-\underset{\substack{|\\ \mathrm{CH_3}}}{\overset{4}{\mathrm{CH}}}-\overset{5}{\mathrm{CH_3}}$

4-methyl-2-pentene
(*Not* 2-methyl-3-pentene; the chain is numbered so that the double bond gets the lower number.)

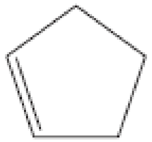


$\overset{1}{\mathrm{CH_2}}=\underset{\substack{|\\ \mathrm{CH_2CH_3}}}{\overset{2}{\mathrm{C}}}-\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_3}}$

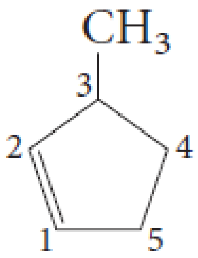
2-ethyl-1-butene
(Named this way, even though there is a five-carbon chain present, because that chain does not include both carbons of the double bond.)

Nomenclature of Alkenes

- With **cyclic hydrocarbons**, we start numbering the ring with the carbons of the double bond.



cyclopentene
(No number is necessary, because there is only one possible structure.)



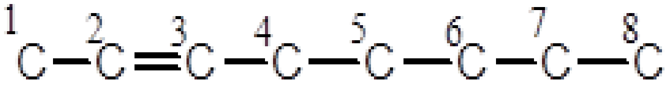
3-methylcyclopentene
(Start numbering at, and number through the double bond; 5-methylcyclopentene and 1-methyl-2-cyclopentene are incorrect names.)

Nomenclature of Alkenes

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

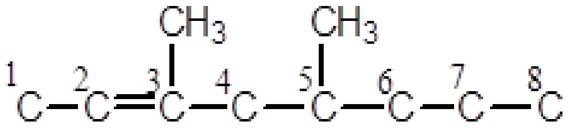
1) The parent carbon chain is an **Octene.**

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



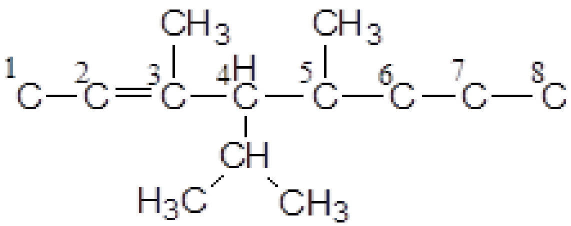
$$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}-\overset{7}{C}-\overset{8}{C}$$

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

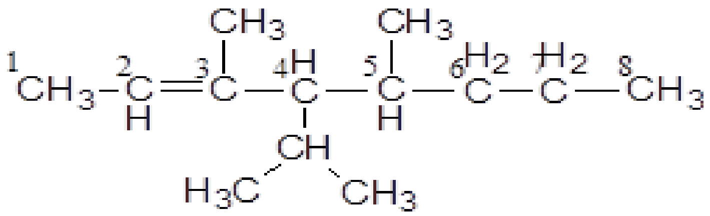


$$\overset{1}{C}-\overset{2}{C}=\overset{\overset{CH_3}{|}}{\overset{3}{C}}-\overset{4}{C}-\overset{\overset{CH_3}{|}}{\overset{5}{C}}-\overset{6}{C}-\overset{7}{C}-\overset{8}{C}$$

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



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

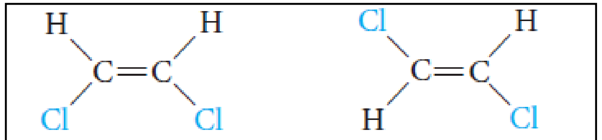


Geometric Isomerism in Alkenes

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

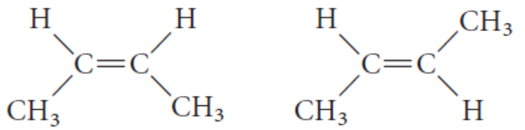
Geometric isomers

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

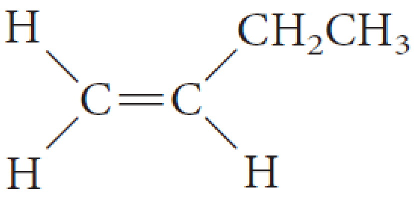
cis-1-Bromo-2-chloroethene

trans-1-Bromo-2-chloroethene

- ***cis* isomer;** when two similar groups are on the **same side** 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.

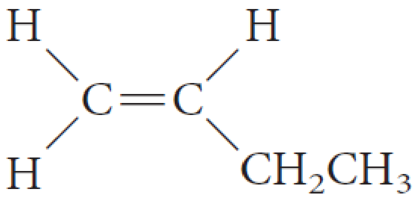
Geometric Isomerism in Alkenes

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

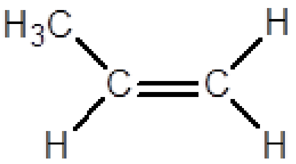


1-butene

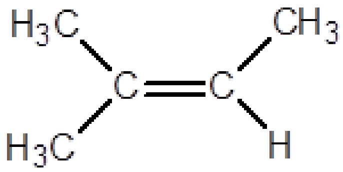
is identical to



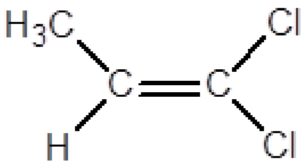
1-butene



Propene



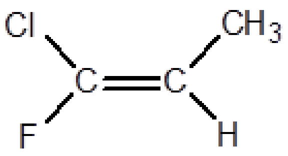
2-Methyl-2-butene



1,1-Dichloropropene

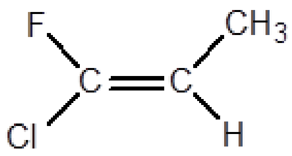
Geometric Isomerism in Alkenes

- 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),

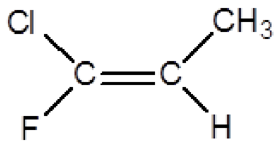
Cl > F, and CH_3 > H.

Geometric Isomerism in Alkenes

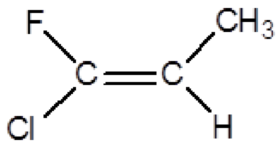
- If the two groups of **higher priority** are on the **same side** of the C=C plane,
  The isomer is labeled *Z;* (from the German *zusammen*, together).

- **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

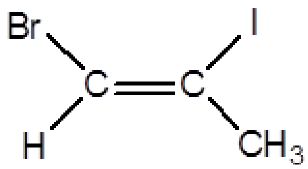


Z-1-Chloro-1-fluoropropene
(Cl and CH_3 on same side)



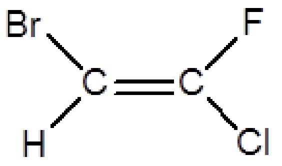
E-1-Chloro-1-fluoropropene
(Cl and CH_3 on opposite side)

Priority: Br > H, I > CH_3



Z-1-Bromo-2-iodopropene

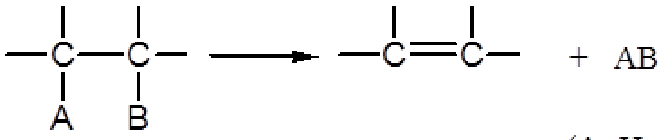
Priority: Br > H, Cl > F



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

Preparation of Alkenes

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

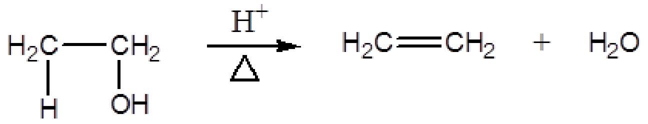


$$-\underset{A}{\overset{|}{\underset{|}{C}}}-\underset{B}{\overset{|}{\underset{|}{C}}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}- \quad + \quad AB$$

(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.***



$$\underset{H}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH_2}} \xrightarrow[\Delta]{H^+} H_2C=CH_2 + H_2O$$

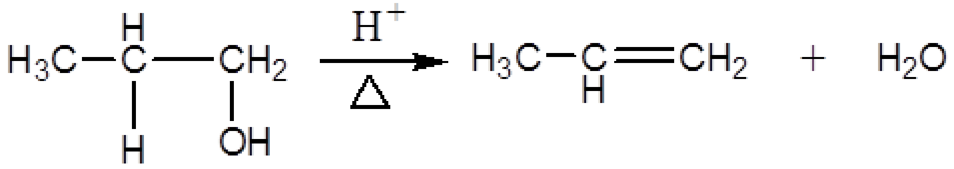
IUPAC name:	Ethanol	Ethene
Common name:	Ethyl alcohol	Ethylene

- The acid *catalysts* most commonly used are sulfuric acid, H_2SO_4, and phosphoric acid, H_3PO_4.

Preparation of Alkenes

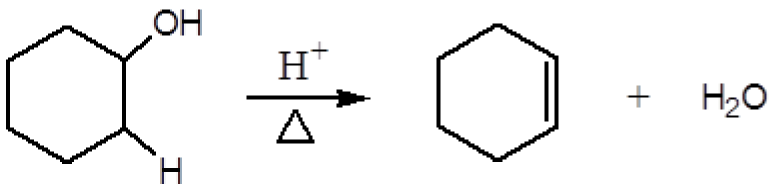
1) Dehydration of Alcohols

Removal of OH group and a proton from two adjacent carbon atoms using mineral acids such as H_2SO4 or H_3PO_4



$$H_3C-CH_2-CH_2OH \xrightarrow[\Delta]{H^+} H_3C-CH=CH_2 + H_2O$$

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



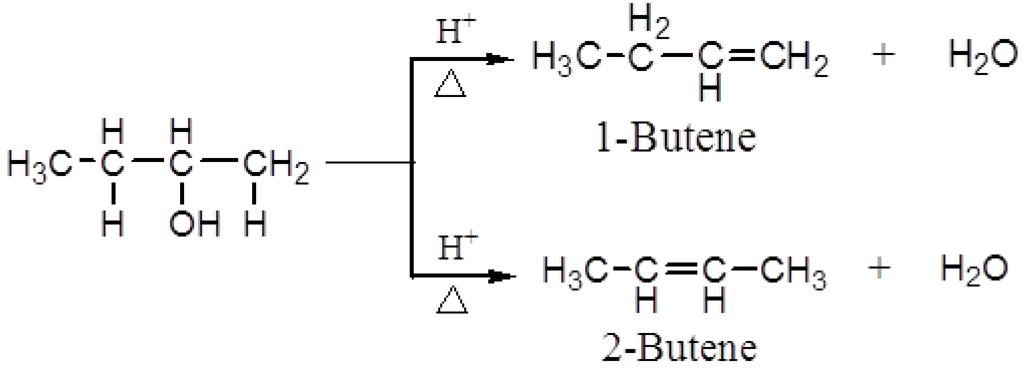
IUPAC name:	Cyclohexanol	Cyclohexene
Common name:	Cyclohexyl alcohol	

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.*



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

Saytzeff's Rule applies

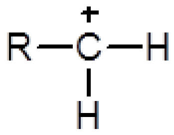
In every instance in which more than one Alkene can be formed

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

Preparation of Alkenes

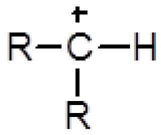
1) Dehydration of Alcohols

- **Classes of Carbocations**



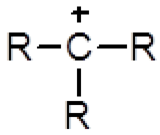
$R-\overset{+}{\underset{H}{C}}-H$

1° carbocation



$R-\overset{+}{\underset{R}{C}}-H$

2° carbocation



$R-\overset{+}{\underset{R}{C}}-R$

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

$3^\circ > 2^\circ > 1^\circ$

Ease of formation and stabilities of carbocations

- **Generally**

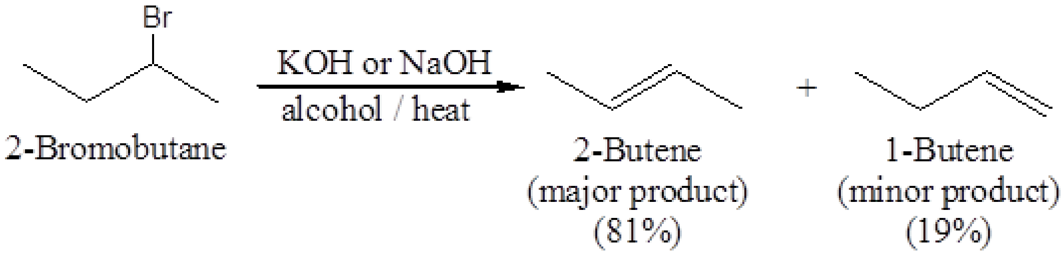
1. The dehydration of alcohols requires an acid catalyst.
2. The predominant alkene formed follows Saytzeffs rule.
3. The reaction proceeds *via* a carbocation intermediate.
4. The stabilities of carbocations and the ease of dehydration of alcohols follows the order $3^\circ > 2^\circ > 1^\circ$.

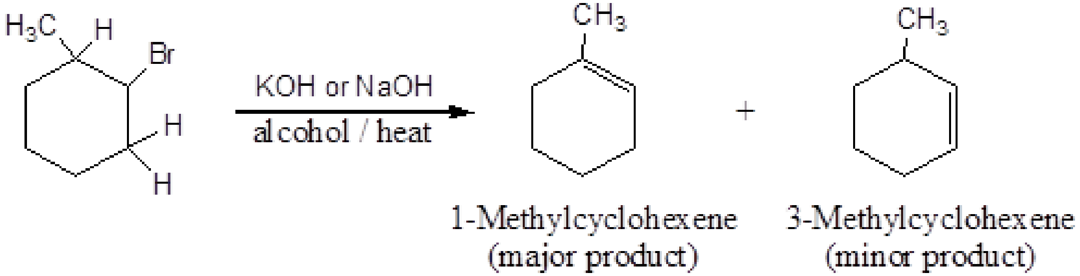
Preparation of Alkenes

2) Dehydrohalogenation of Alkyl Halides

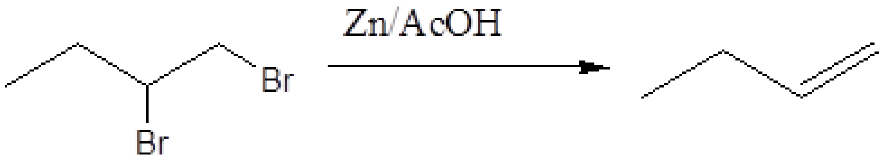
- Alkenes can also be prepared under alkaline conditions.

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





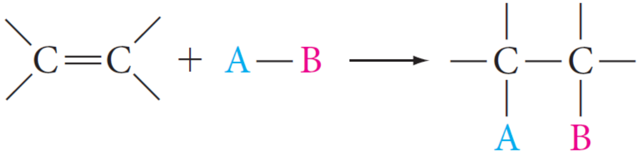
3) Dehalogenation of Vicinal Dibromides



Reactions of Alkenes

- The chemistry of alkenes can be divided into two general types of reactions:

(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

Reactions of Alkenes

(2) Substitution Reactions

$$R{-}H + A{-}B \longrightarrow R{-}A + H{-}B$$

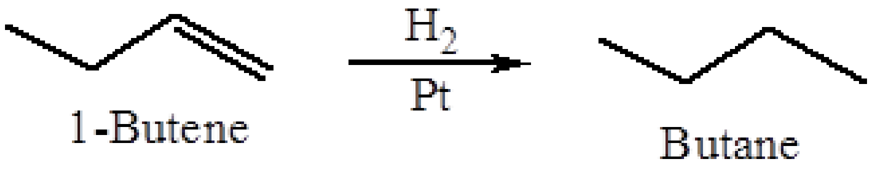
(3) Oxidation Reactions

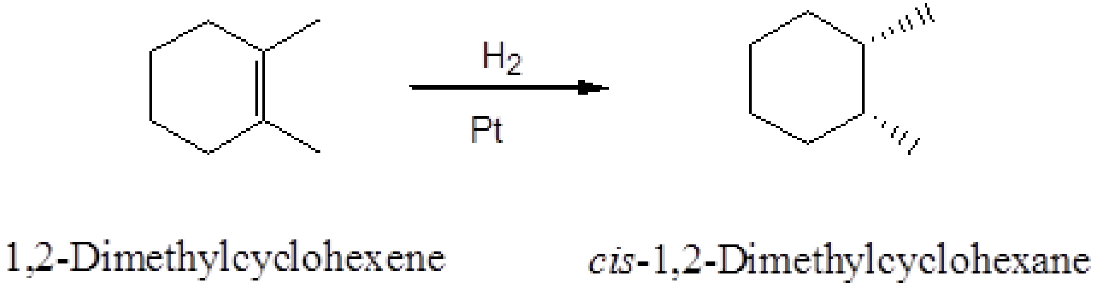
1. Ozonolysis
2. Oxidation Using $KMnO_4$

Electrophilic Addition Reactions

1. Addition of Hydrogen: Hydrogenation

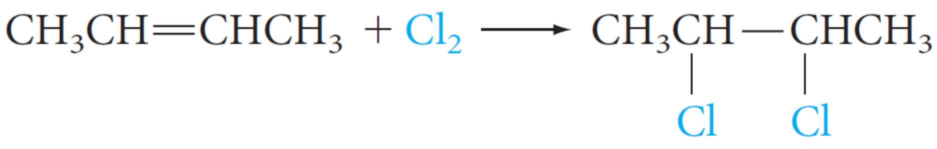
Addition of a mole of hydrogen to carbon-carbon double bond of Alkenes in the presence of suitable catalysts to give an Alkane.





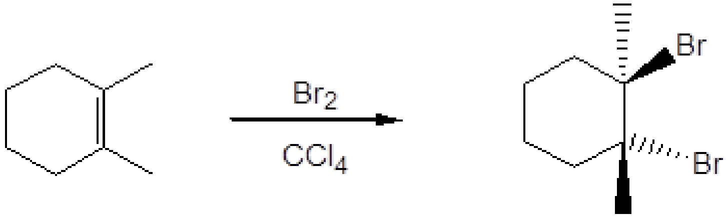
2. Addition of Halogen: Halogenation

*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



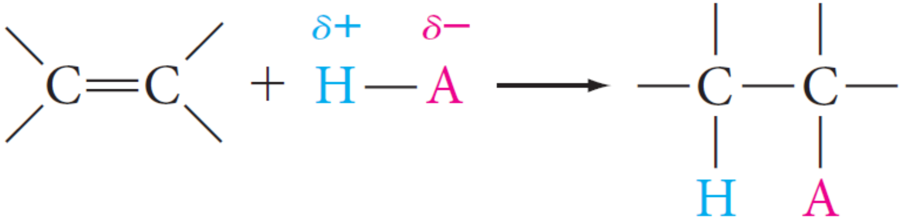
1,2-Dimethylcyclohexene *trans*-1,2-Dibromocyclohexane

- **Iodine** is too unreactive and will not add to the double bond.
- **Fluorine** is too reactive and reacts explosively with an alkene.

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).

Note that

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

Electrophilic Addition Reactions

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 $AlCl_3$.

iv) Metal ions that contain vacant orbitals: the silver ion (Ag^+), the mercuric ion (Hg^{2+}), and the platinum ion (Pt^{2+}).

Examples of Nucleophile:

a)Negative ions

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

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

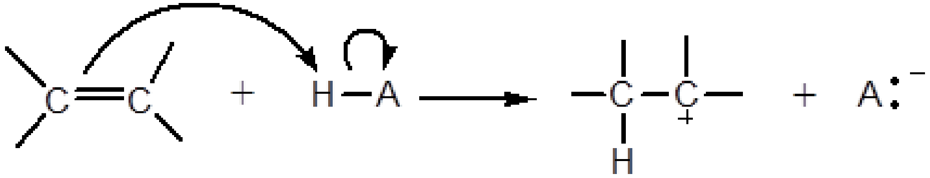
b) Neutral molecules

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

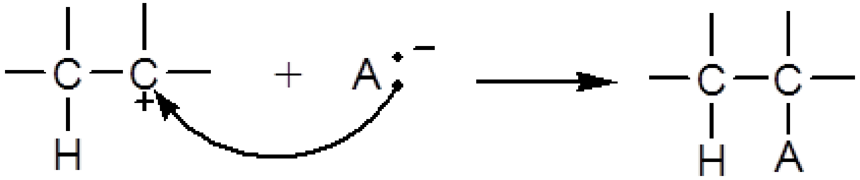
3. Addition of Acids

- **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.



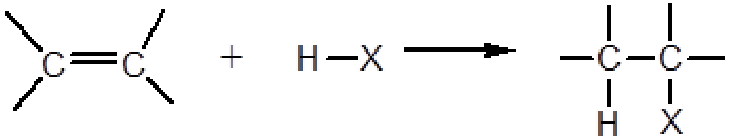
- The attack by an electrophilic reagent on the ∏-electrons, falls in a general category called **electrophilic addition reactions**.

Electrophilic Addition Reactions

3.1. Addition of Hydrogen Halide

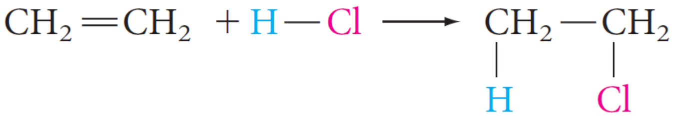
Alkenes react with hydrogen chloride, HC1, hydrogen bromide, HBr and hydrogen iodide, HI, to form alkyl halides, RX.

General equation



(X = Cl, Br or I)

Examples;



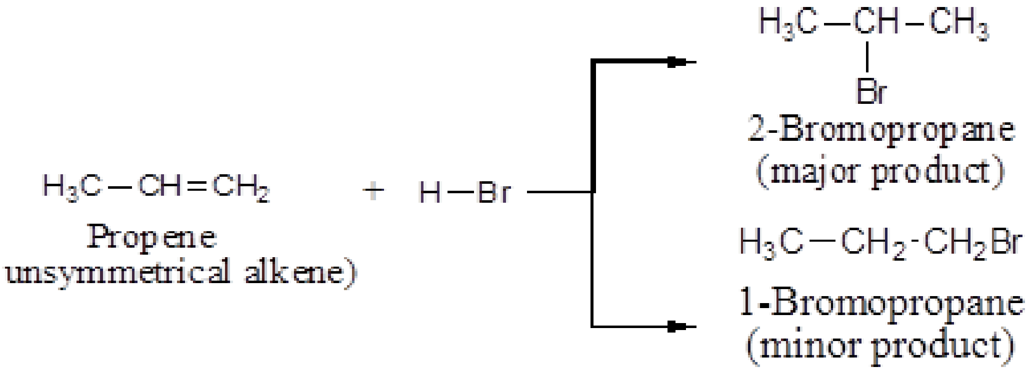
$$CH_2{=}CH_2 + H{-}Cl \longrightarrow \underset{H}{CH_2}{-}\underset{Cl}{CH_2}$$

(or CH_3CH_2Cl)

ethene

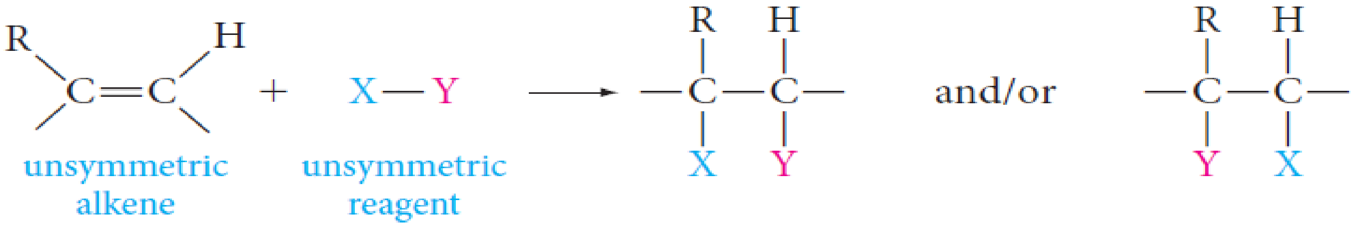
hydrogen chloride

chloroethane
(ethyl chloride)



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.



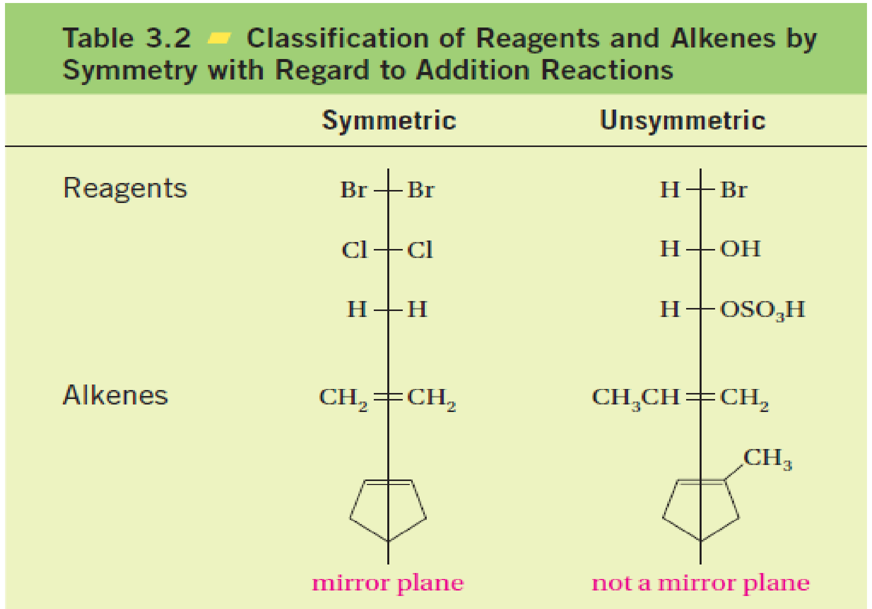


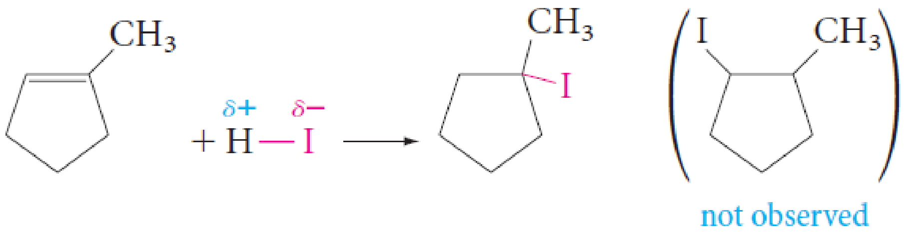
Table 3.2 Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

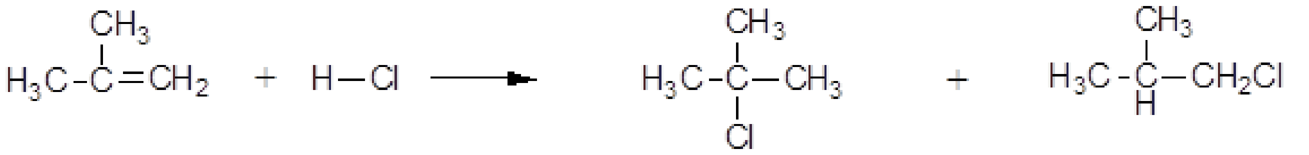
	Symmetric	Unsymmetric
Reagents	Br—Br	H—Br
	Cl—Cl	H—OH
	H—H	H—OSO_3H
Alkenes	$CH_2=CH_2$	$CH_3CH=CH_2$
	mirror plane	not a mirror plane

Electrophilic Addition Reactions

Markovnikov's Rule

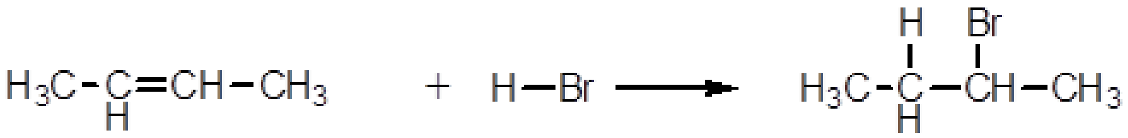
In electrophilic addition of H—X *to* ***Unsymmetrical Alkenes*** *the hydrogen of the hydrogen halide adds to the double-bonded carbon that bears the greater number of hydrogen atoms and the negative halide ion adds to the other double-bonded carbon.*





2-Chloro-2-methylpropane
(major product)

1-Chloro-2-methylpropane
(minor product)

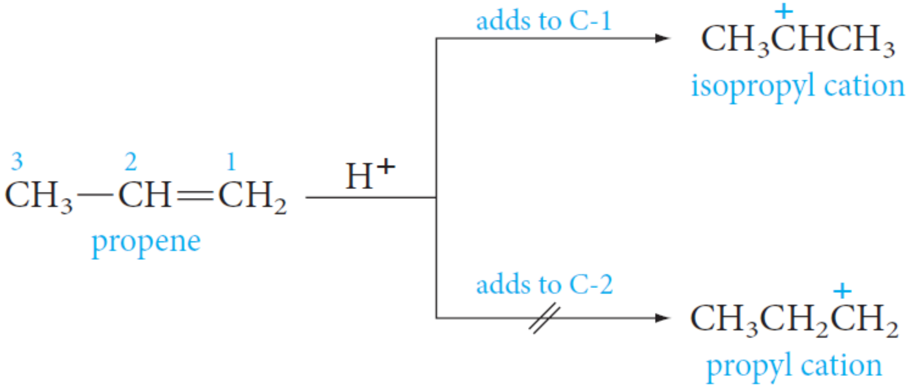


2-Butene
(a symmetrical alkene)

2-Bromobutane
(only one product possible)

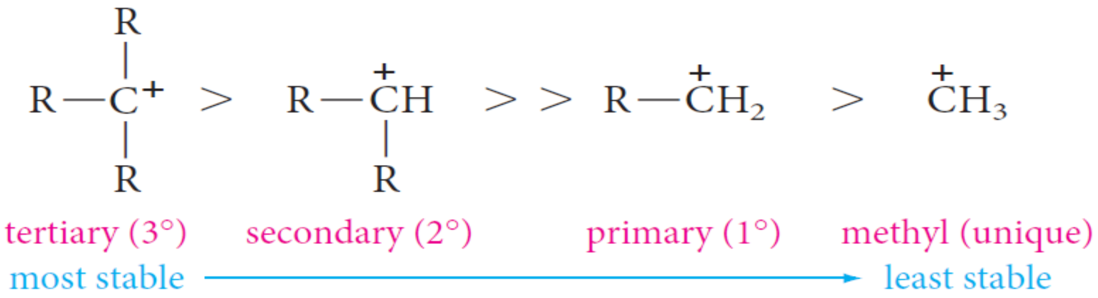
Explanation for Markovnikov's Rule

Example; *Addition of HBr to propene*



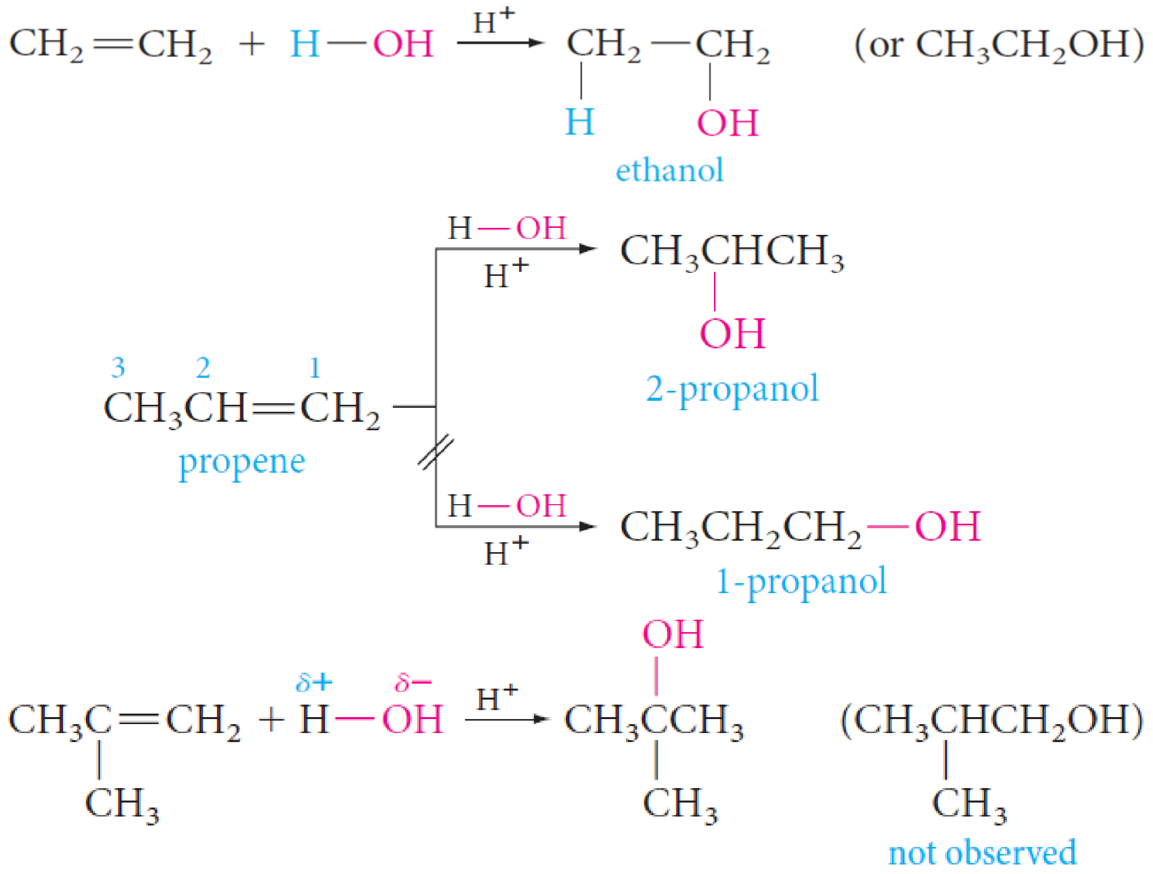
- **In modern terms Markovnikov's rule can be restated:**

  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

$$\overset{3}{CH_3}\overset{2}{CH}{=}\overset{1}{CH_2} \xrightarrow[H^+]{H{-}OH} CH_3\underset{OH}{CH}CH_3$$

propene

2-propanol

$$CH_3CH{=}CH_2 \not\xrightarrow[H^+]{H{-}OH} CH_3CH_2CH_2{-}OH$$

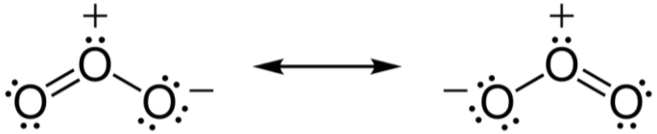
1-propanol

$$CH_3\underset{CH_3}{C}{=}CH_2 + \overset{\delta+}{H}{-}\overset{\delta-}{OH} \xrightarrow{H^+} CH_3\overset{OH}{\underset{CH_3}{C}}CH_3 \quad (CH_3\underset{CH_3}{CH}CH_2OH)$$

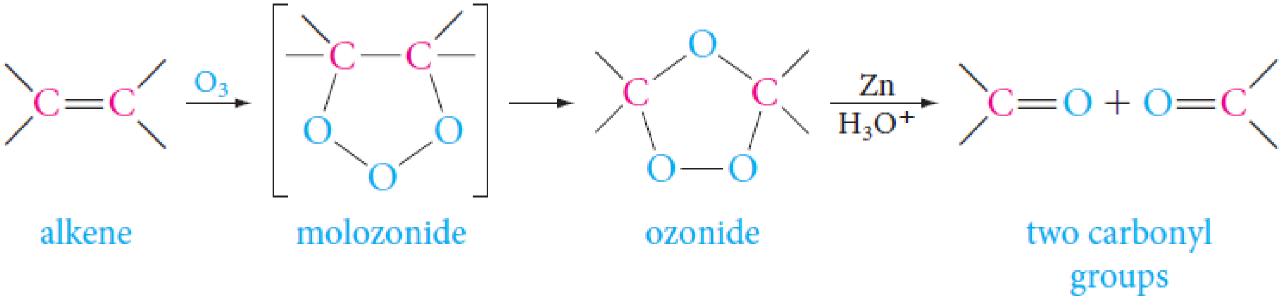
not observed

Oxidation Reactions

1. Ozonolysis



- The first product, a molozonide, is formed by cycloaddition of the oxygen at each end of the ozone molecule to the carbon–carbon double bond.
- This product then rearranges rapidly to an ozonide (explosive if isolated).
- They are usually treated directly with a reducing agent, commonly zinc and aqueous acid, to give carbonyl compounds as the isolated products.



Oxidation Reactions

1. Ozonolysis

- Ozonolysis can be used to locate the position of a double bond.
- **Example;**

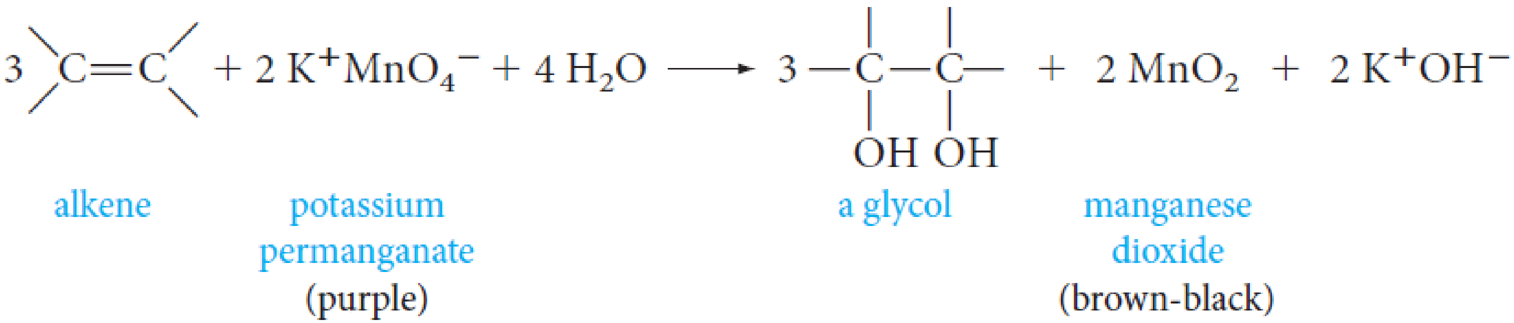
Ozonolysis of 1-butene gives two different aldehydes, whereas 2-butene gives a single aldehyde.

$$\underset{\text{1-butene}}{CH_2{=}CHCH_2CH_3} \xrightarrow[\text{2. Zn, H}^+]{\text{1. O}_3} \underset{\text{formaldehyde}}{CH_2{=}O} \quad \underset{\text{propanal}}{O{=}CHCH_2CH_3}$$

$$\underset{\text{2-butene}}{CH_3CH{=}CHCH_3} \xrightarrow[\text{2. Zn, H}^+]{\text{1. O}_3} \underset{\text{ethanal}}{2\ CH_3CH{=}O}$$

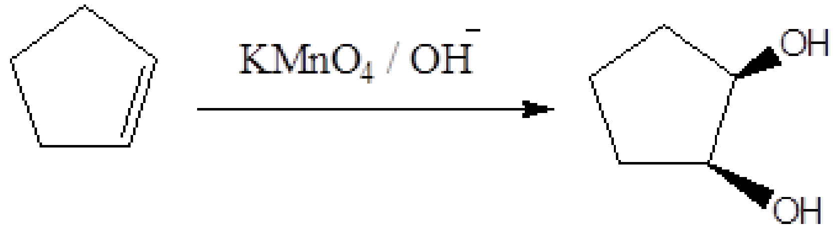
2. Oxidation Using $KMnO_4$

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



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

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



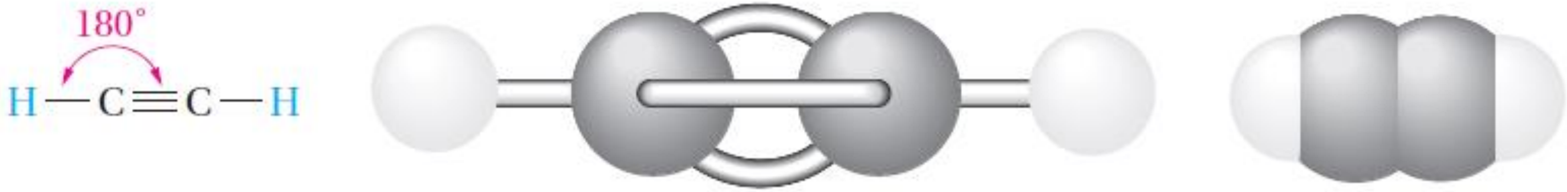
Cyclopentene

cis-Cyclopentane-1,2-diol

3. ALKYNES

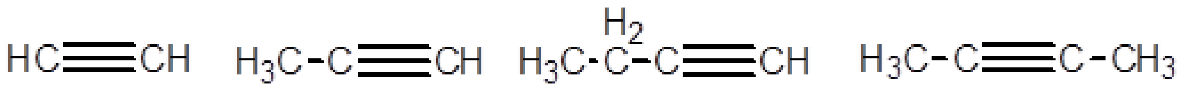
The Structure of Alkynes

- **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°**
- **Linear.**



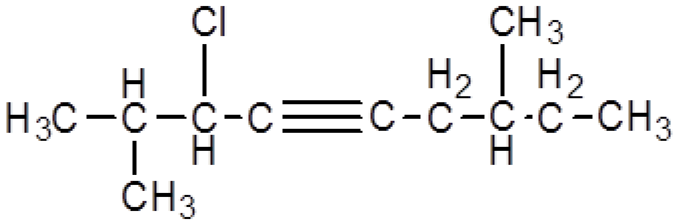
Nomenclature of Alkynes

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



	$HC\equiv CH$	$H_3C-C\equiv CH$	$H_3C-CH_2-C\equiv CH$	$H_3C-C\equiv C-CH_3$
IUPAC name:	Ethyne	Propyne	1-Butyne	2-Butyne
Common name:	Acetylene			

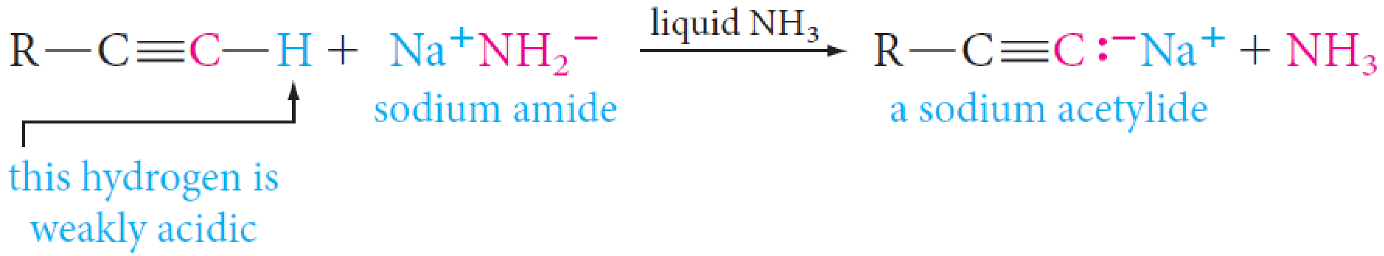
- **Example:**



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).

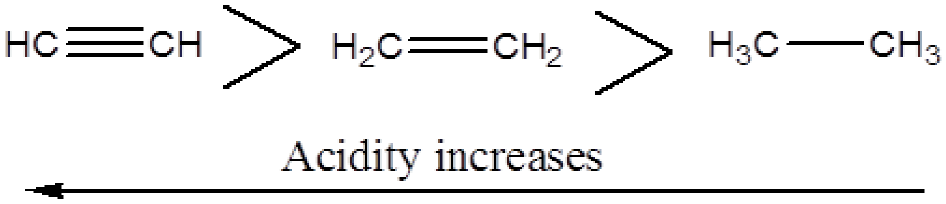


$$R-C\equiv C-H + Na^{+}NH_2^{-} \xrightarrow{\text{liquid } NH_3} R-C\equiv C:^{-}Na^{+} + NH_3$$

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

  - Relative Acidity of the Hydrocarbon.

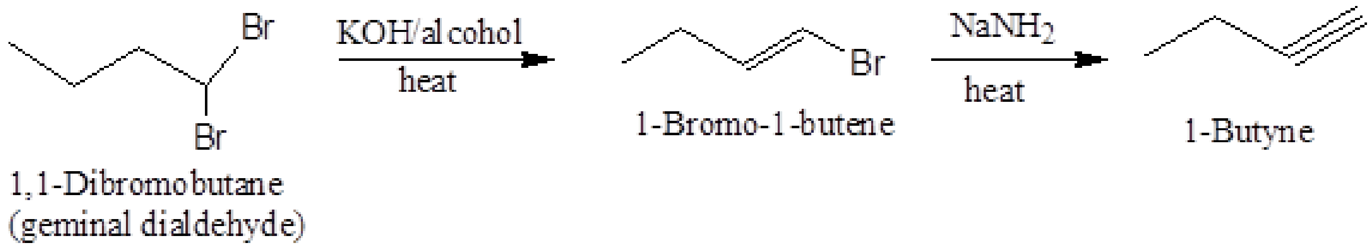
    Terminal alkynes, are more acidic than other hydrocarbons

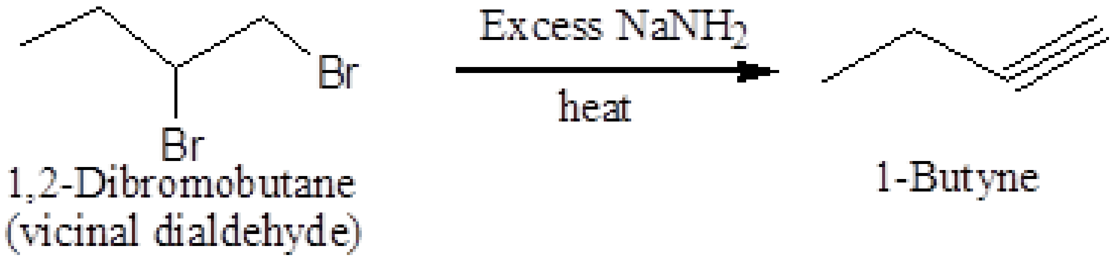


$$HC\equiv CH > H_2C=CH_2 > H_3C-CH_3$$

Preparation of Alkynes

1) Dehydrohalogenation of Alkyl dihalides

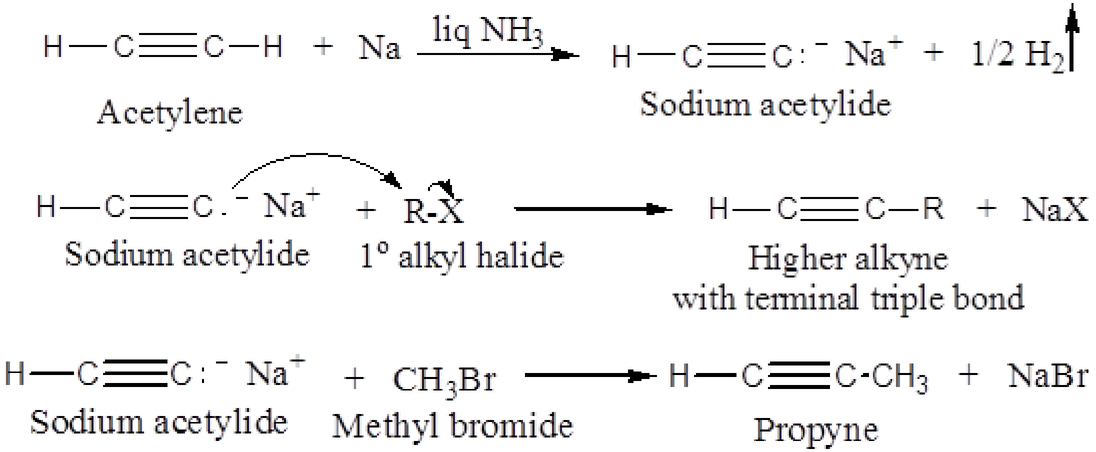




Preparation of Alkynes

2) Reaction of Sodium Acetylide with Primary Alkyl Halides

- **Acetylene**



$$H{-}C{\equiv}C{-}H + Na \xrightarrow{\text{liq } NH_3} H{-}C{\equiv}C{:}^{-}\ Na^{+} + 1/2\ H_2\uparrow$$

Acetylene; Sodium acetylide

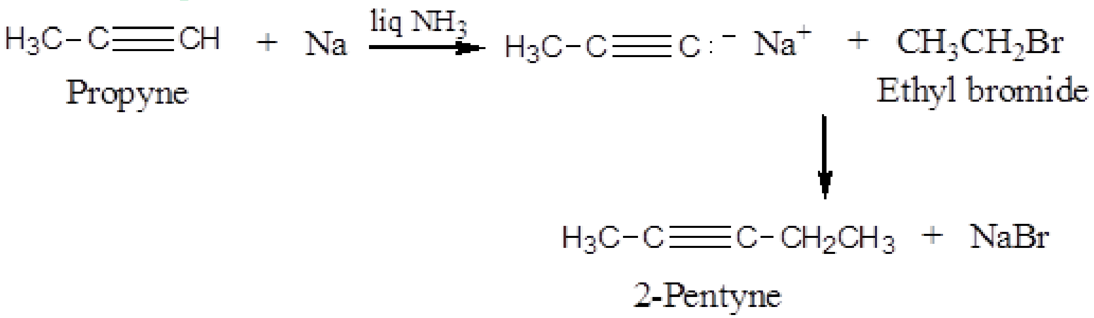
$$H{-}C{\equiv}C{:}^{-}\ Na^{+} + R{-}X \longrightarrow H{-}C{\equiv}C{-}R + NaX$$

Sodium acetylide; 1° alkyl halide; Higher alkyne with terminal triple bond

$$H{-}C{\equiv}C{:}^{-}\ Na^{+} + CH_3Br \longrightarrow H{-}C{\equiv}C{-}CH_3 + NaBr$$

Sodium acetylide; Methyl bromide; Propyne

- **Monosubstituted Acetylenes**



$$H_3C{-}C{\equiv}CH + Na \xrightarrow{\text{liq } NH_3} H_3C{-}C{\equiv}C{:}^{-}\ Na^{+} + CH_3CH_2Br \longrightarrow H_3C{-}C{\equiv}C{-}CH_2CH_3 + NaBr$$

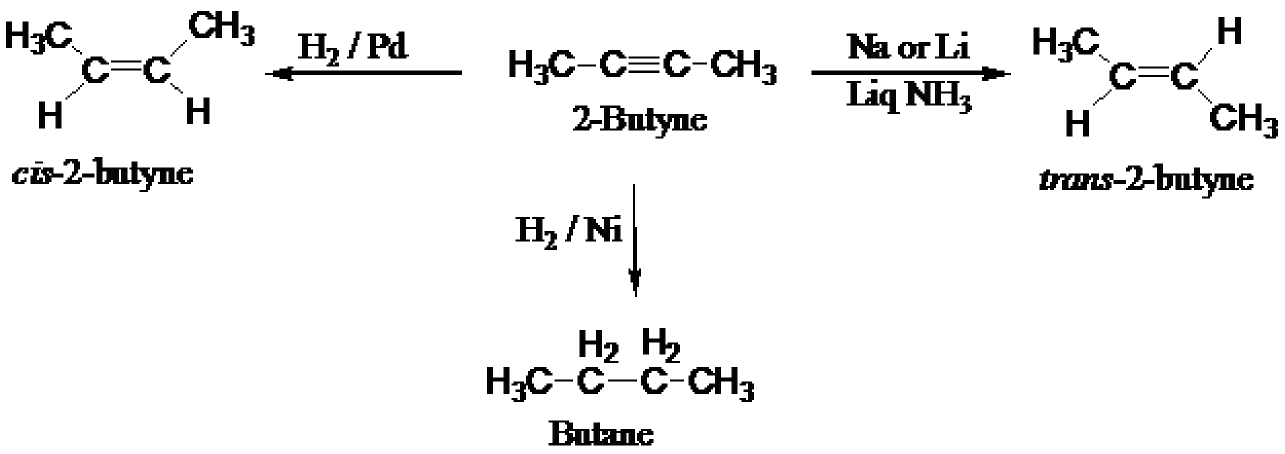
Propyne; Ethyl bromide; 2-Pentyne

Preparation of Alkenes

Electrophilic Addition Reactions

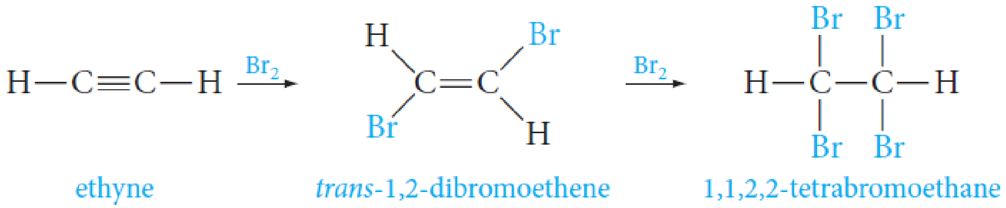
1. Addition of Hydrogen: Hydrogenation

- 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.



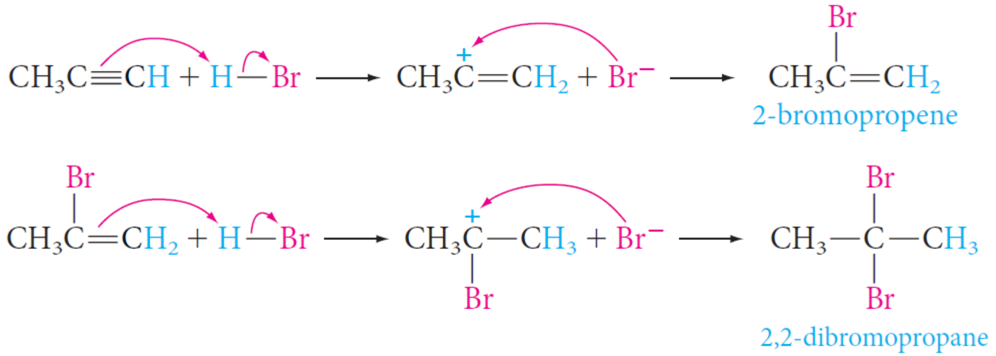
2. Addition of Halogen: Halogenation

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



3. 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:



Electrophilic Addition Reactions

4. Addition of Water: Hydration

- **Addition of water to alkynes** requires not only an acid catalyst but mercuric ion as well.
- Although the reaction is similar to that of alkenes, the initial product - a vinyl alcohol or enol - rearranges to a carbonyl compound (keto form).
- The keto form of aldehydes and ketones are in equilibrium with the enol form.
- The keto from predominates at equilibrium for most simple aldehydes and ketones.
- The inter conversion is called **keto-enol tautomerization.**