CHEM 108

FUNDAMENTALS OF ORGANIC CHEMISTRY

FOR B.Sc. PROGRAMS OF SCIENTIFIC COLLEGES

PRE-REQUISITES COURSE; CHEM 101

CREDIT HOURS; 4 (3+1)

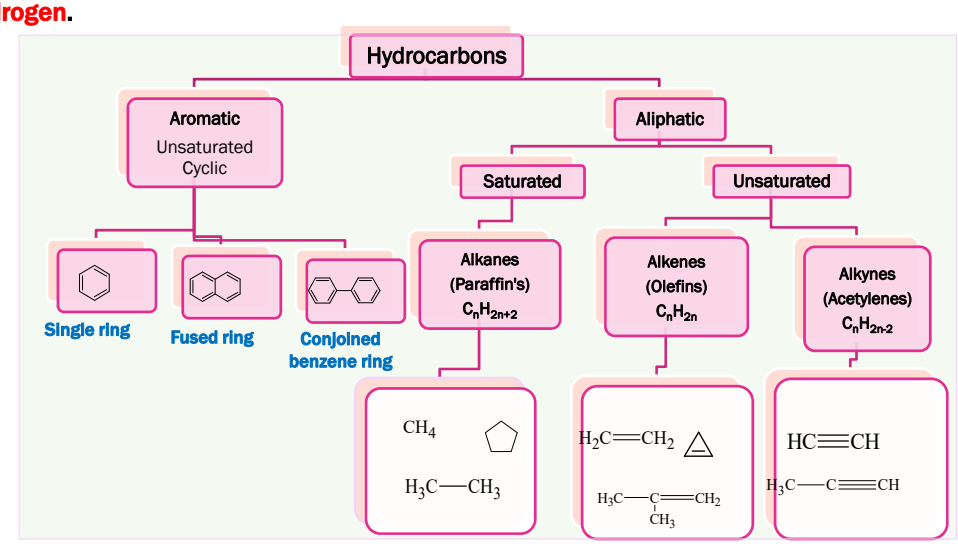
Chemistry Department, College of Science, King Saud University

CHAPTER 2

ALIPHATIC HYDROCARBONS

Hydrocarbons

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



Hydrocarbons

- **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_nH_{2n-2} (contain ***carbon-carbon triple bond)***

Saturated Hydrocarbons;

ALKANES

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.

Alkanes

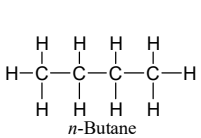
Names, Molecular formulas and Number of Isomers of the first ten Alkanes

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

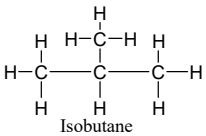
Alkanes; Structural Isomerism

- **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}.**

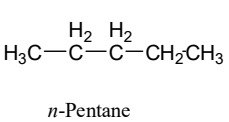


n-Butane

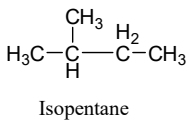


Isobutane

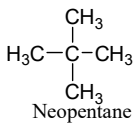
➢ **Pentanes, C_5H_{12}.**



n-Pentane



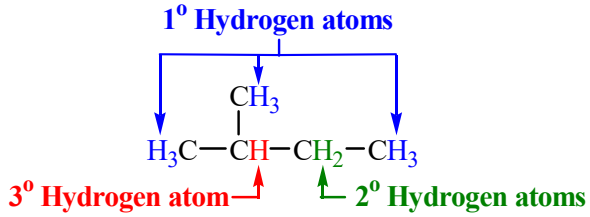
Isopentane



Neopentane

Alkanes; 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.



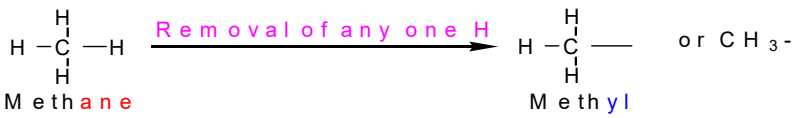
- **Hydrogens** are also referred to as **1°, 2°, or 3°** according to the type of carbon they are bonded to.

Alkanes; 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*.

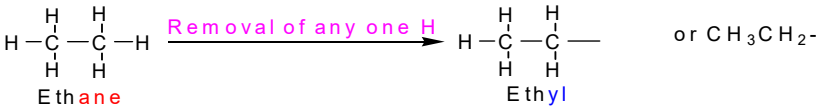
  i.e. Alkane – ane + yl = Alkyl
- **Examples:**
  - ***Methane***



CH_3- (Methane – ane + yl) = methyl

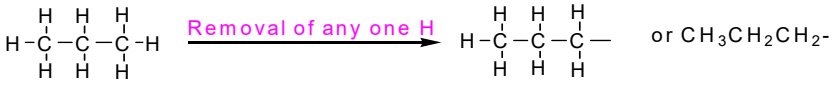
Alkanes; Alkyl Groups

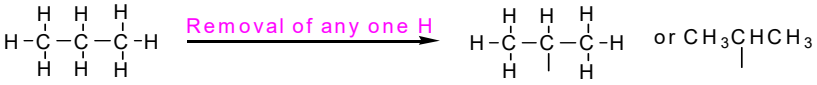
- **Ethane**



CH_3CH_2- (Ethane – ane + yl) = ethyl

- **Propane**





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

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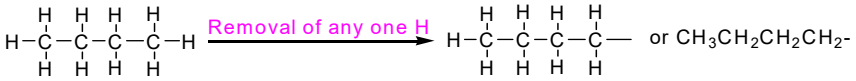
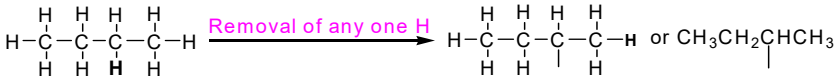
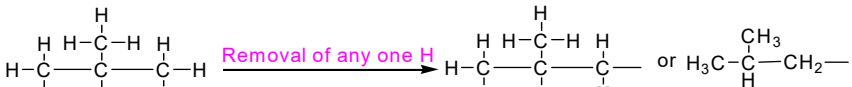
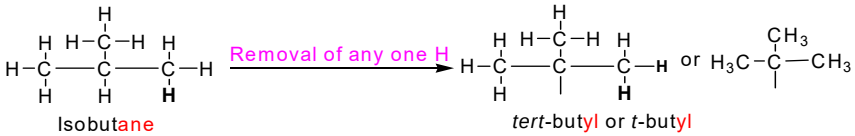
Alkanes; Alkyl Groups

- **Butane**









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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–

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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

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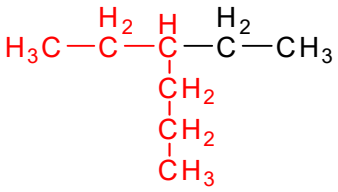
Alkanes; Nomenclature

The IUPAC Rules

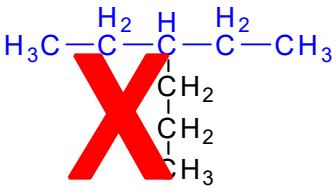
1) Select the parent structure .

the longest continuous chain



Ethyl hexane

not



Propyl pentane

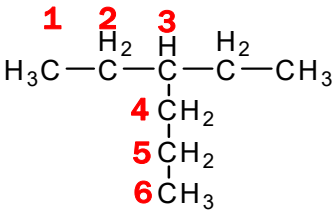
The longest continuous chain is not necessarily straight.

Alkanes; Nomenclature

The IUPAC Rules

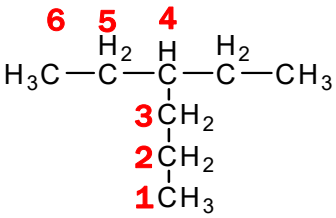
2) Number the carbons in the parent chain

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



3-Ethyl hexane

not

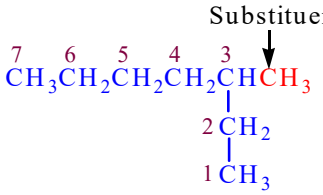


4-Ethyl hexane

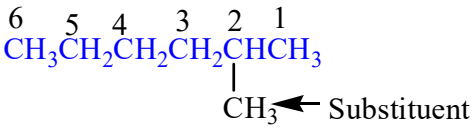
Alkanes; Nomenclature

The IUPAC Rules

2) Number the carbons in the parent chain



3-Methylheptane



2-Methylpentane

Alkanes; 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).

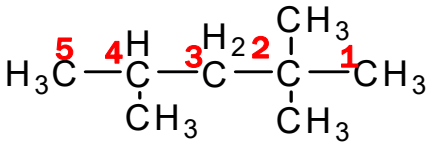
4) The parent carbon chain (hexane)

3- Ethyl hexane

Alkanes; Nomenclature

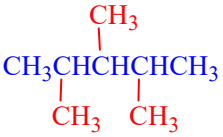
The IUPAC Rules

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.

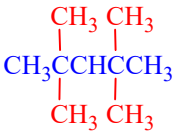


2,2,4- Tri methylpentane

2,3-Dimethylbutane



2,3,4-Trimethylpentane

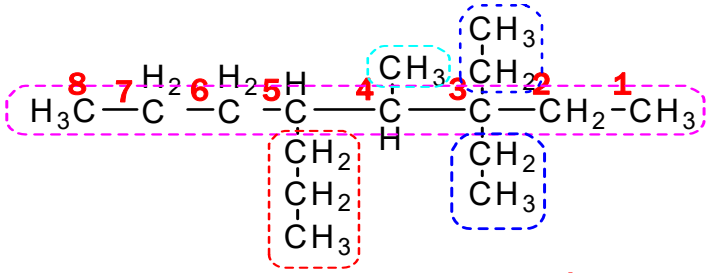


2,2,4,4-Tetramethylpentane

Alkanes; Nomenclature

The IUPAC Rules

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



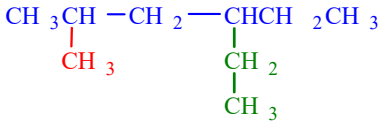
3,3-di ethyl
4- methyl
5- propyl

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

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.

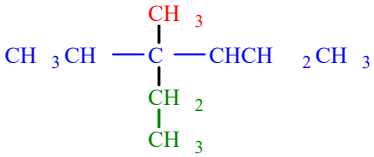


4-Ethyl-2-methylhexane

Alkanes; Nomenclature

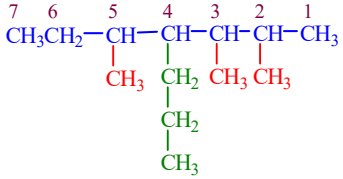
The IUPAC Rules

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



3-Ethyl-3-methylhexane

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



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

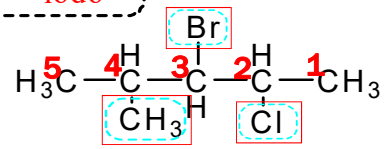
Alkanes; Nomenclature

The IUPAC Rules

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

-F fluoro
-Cl chloro
-Br bromo
-I iodo

$-NO_2$ nitro
$-NH_2$ amino
-CN cyano



2-chloro
3-bromo
4-methyl

3-bromo-2-chloro-4-methylpentane

Alkanes; 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 aliphatic hydrocarbons)
  - Heterocyclic

Alkanes; Sources of Alkanes

Petroleum Refining

Some components of refined

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

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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.

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Physical Properties of Alkanes, Alkenes and Alkynes

C. Boiling Points

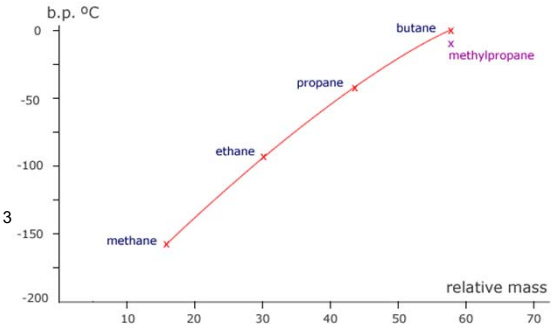
$CH_3CH_2CH_2CH_3$
n-Butane
b.p.=0°C

$H_3C-CH(CH_3)-CH_3$
Isobutane
b.p.=-12°C

$CH_3CH_2CH_2CH_2CH_3$
n-Pentane
b.p.=36°C

$H_3CH_2C-CH(CH_3)-CH_3$
Isopentane
b.p.=28°C

$H_3C-C(CH_3)_2-CH_3$
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.

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Alkanes; Preparation of Alkanes

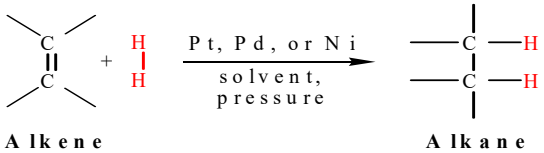
1) Hydrogenation of Alkenes and Alkynes

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



Alkene Alkane

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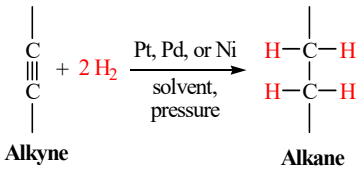
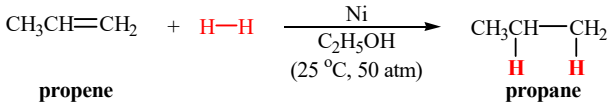
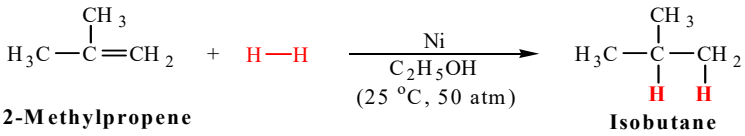
Alkanes; Preparation of Alkanes

1) Hydrogenation of Alkenes and Alkynes



- *Specific Examples*





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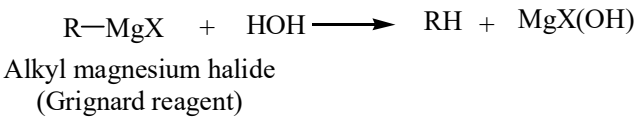
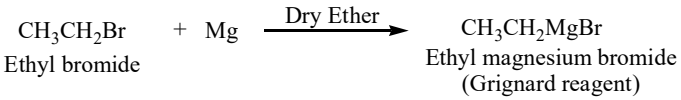
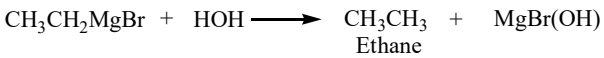
Alkanes; Preparation of Alkanes

2) Hydrolysis of Grignard Reagent

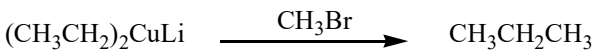


- ***Grignard reagents* react readily with any source of protons to give hydrocarbons.**





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



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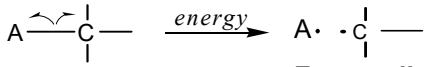
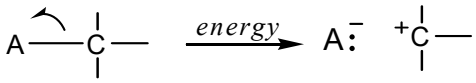
Alkanes; Notations for Bond Breaking and Bond Making

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

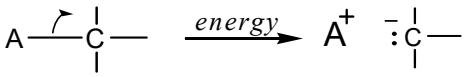


Free radicals

  - **Heterolytic cleavage.**



Carbocation



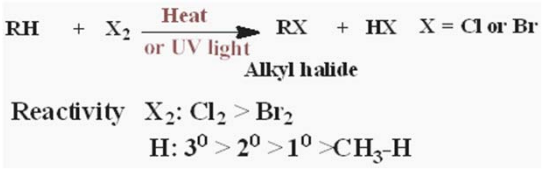
Carboanion

Alkanes; Reactions of Alkanes

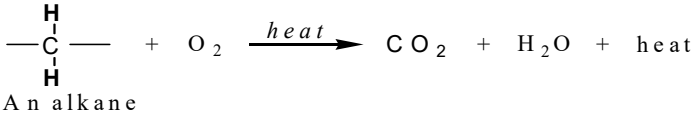
Saturated hydrocarbons undergo very few reactions, so they are called Paraffinic hydrocarbons. (Latin *parum*, little; *affinis*, affinity)

1) 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



2) Combustion



Alkanes; Reactions of Alkanes

1) 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

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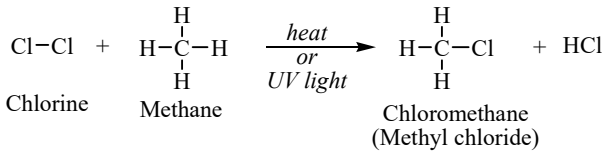
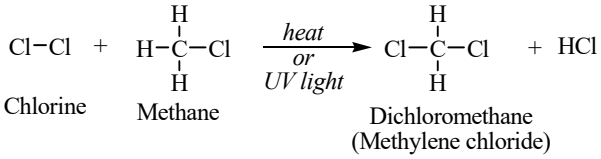
Alkanes; Reactions of Alkanes

1) Halogenation

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





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Unsaturated Hydrocarbons;

ALKENES

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**

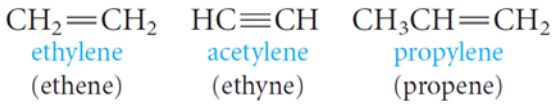
	$CH_2{=}CH_2$	$H_3C{-}CH{=}CH_2$
Common name:	Ethylene	Propylene
IUPAC name:	Ethene	Propene

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

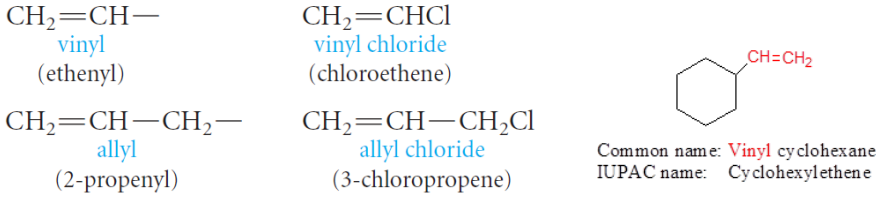
Alkenes; Nomenclature

Common Names

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



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



Common name: Vinyl cyclohexane
IUPAC name: Cyclohexylethene

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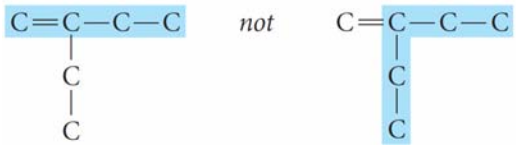
Alkenes; Nomenclature

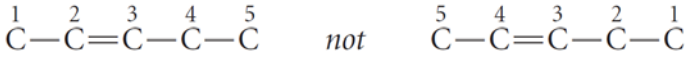
The IUPAC Rules

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 carbons of the double bond*.



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



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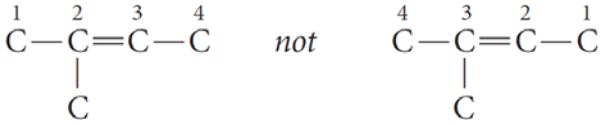
Alkenes; Nomenclature

The IUPAC Rules

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



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

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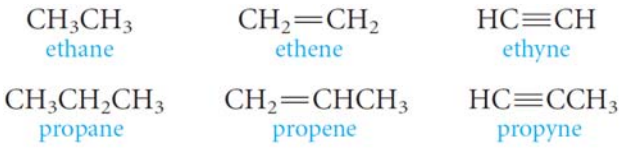
Alkenes; Nomenclature

The IUPAC Rules

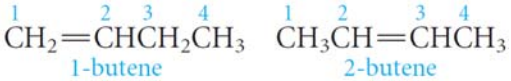
NOTES

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.



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



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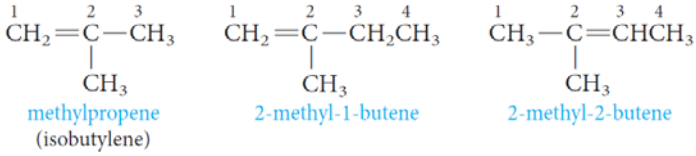
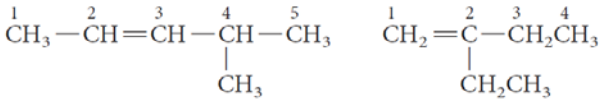
Alkenes; Nomenclature

The IUPAC Rules

- Branches are named in the usual way.



methylpropene (isobutylene) | 2-methyl-1-butene | 2-methyl-2-butene



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

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.)

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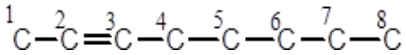
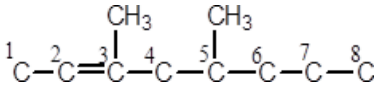
Alkenes; Nomenclature

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

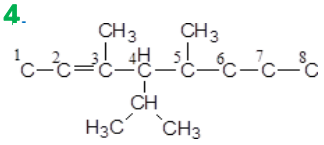
1) The parent carbon chain is an **Octene.**
   The double bond is located between the 2nd and 3rd carbons.



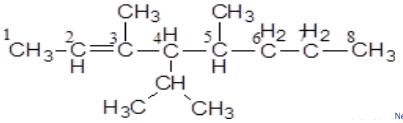
2) Two **methyl groups** are attached on the parent carbon chain, one on **carbon 3** and the other on **carbon 5.**



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



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



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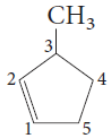
Alkenes; Nomenclature of Cycloalkenes

- 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.)



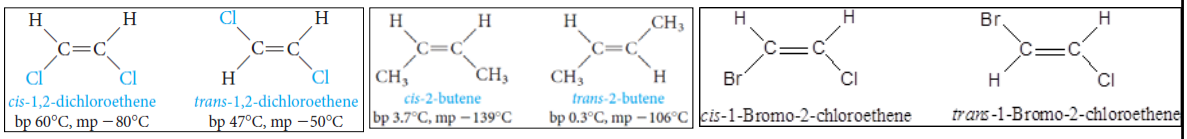
3-methylcyclopentene
(Start numbering at, and number through the double bond; 5-methylcyclopentene and 1-methyl-2-cyclopentene are incorrect names.)

Alkenes; Geometric Isomerism

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

Geometric isomers

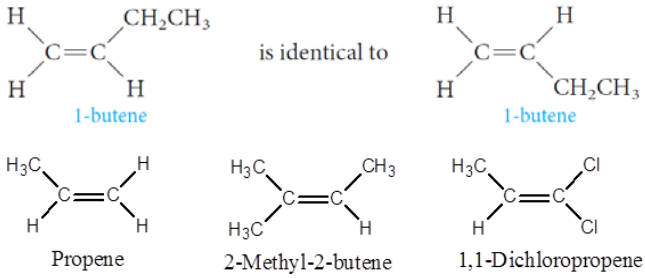
A) when W differs from X and Y from Z, Alkenes exist as geometric isomers



- ***cis* 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.

Alkenes; Geometric Isomerism

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



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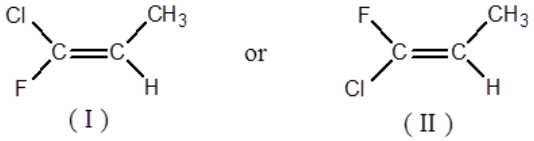
Alkenes; Geometric Isomerism

- For alkenes with four different substituent such as



Another system, the *E, Z* system,

- **Basically, the E,Z system works as follows;**
  Arrange the groups on each carbon of the C=C bond in order of priority
- **The priority depends on atomic number:**
  The higher the atomic number of the atom directly attached to the double-bonded carbon, the higher the priority.

Thus, in structure (I),

Cl > F, and CH_3 > H.

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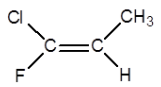
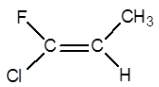
Alkenes; Geometric Isomerism

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

Priority: Cl > F, CH_3 > H

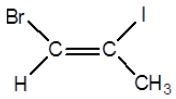


Z-1-Chloro-1-fluoropropene (Cl and CH_3 on same side)



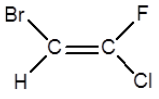
E-1-Chloro-1-fluoropropene (Cl and CH_3 on opposite side)

Priority: Br > H, I > CH_3



Z-1-Bromo-2-iodopropene

Priority: Br > H, Cl > F



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

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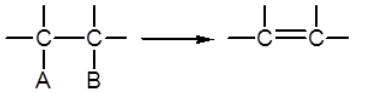
Alkenes; Preparation of Alkenes

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

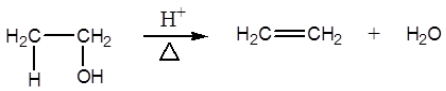


+ AB

(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.*



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.

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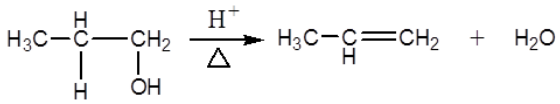
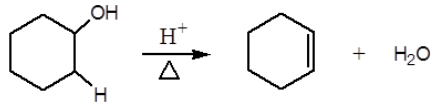
Alkenes; Preparation of Alkenes

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



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



IUPAC name: Cyclohexanol — Cyclohexene
Common name: Cyclohexyl alcohol

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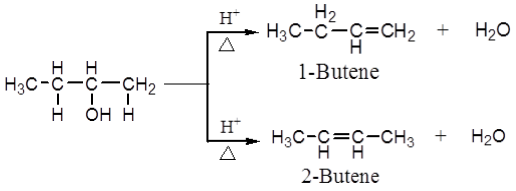
Alkenes; Preparation of Alkenes

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.*



1-Butene

2-Butene

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

Saytzeff's Rule applies

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

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

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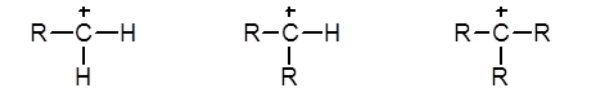
Alkenes; Preparation of Alkenes

- **Classes of Carbocations**



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

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

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

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 $3^{\circ} > 2^{\circ} > 1^{\circ}$.

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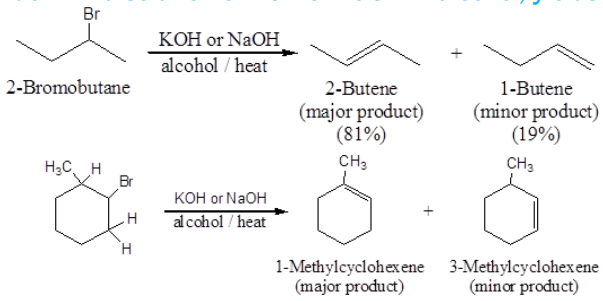
Alkenes; Preparation of Alkenes

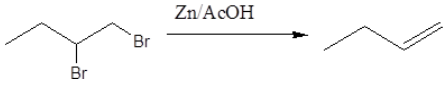
2) Dehydrohalogenation of Alkyl Halides

- 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



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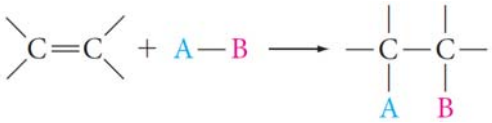
Alkenes; Reactions of Alkenes

- 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 Rul

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

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Alkenes; Reactions of Alkenes

(2) Substitution Reactions

(3) Oxidation Reactions

1. Ozonolysis
2. Oxidation Using $KMnO_4$

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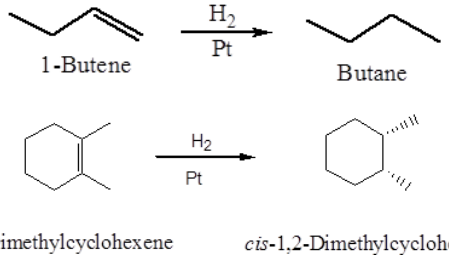
Alkenes; Electrophilic Addition Reactions

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.



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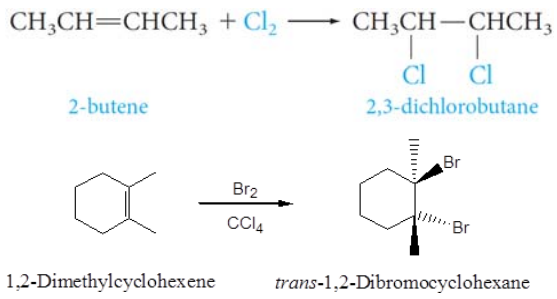
Alkenes; Electrophilic Addition Reactions

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)



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

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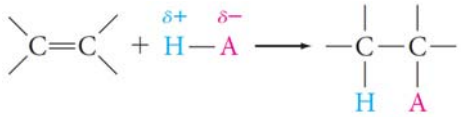
Alkenes; Electrophilic Addition Reactions

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).

Note that

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

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Alkenes; 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. HO^- Hydroxide ion, HS^- Hydrosulphide ion, RO^- Alkoxide ions, $N\equiv C^-$ Cyanide ion, X^- Halide ions, ...etc.

b) Neutral molecules — e.g. H_2O , $R—O—H$, $R—O—R$, H_3N , R_3N , ...etc.

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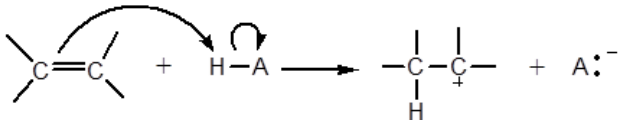
Alkenes; Electrophilic Addition Reactions

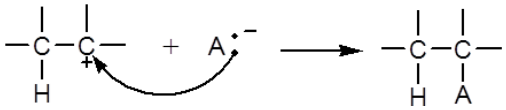
3. Addition of Acids

- **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.



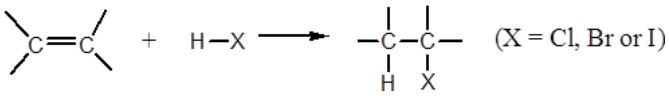
- The attack by an electrophilic reagent on the ∏-electrons, falls in a general category called **electrophilic addition reactions.**

Alkenes; Electrophilic Addition Reactions

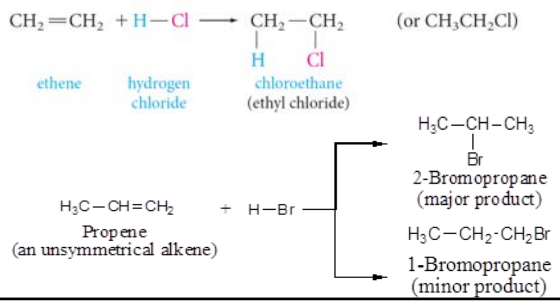
3.1. Addition of Hydrogen Halide

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

General equation



Examples;



Alkenes; 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.

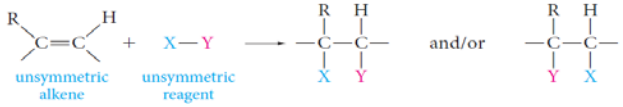


Table 3.2 Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

	Symmetric	Unsymmetric
Reagents	Br_2, Cl_2, H_2	HBr, HOH, $HOSO_3H$
Alkenes	$CH_2=CH_2$ (mirror plane)	$CH_3CH=CH_2$ (not a mirror plane)

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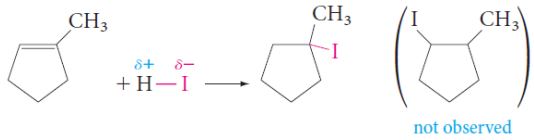
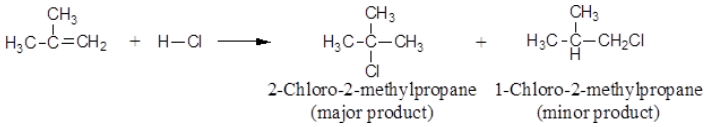
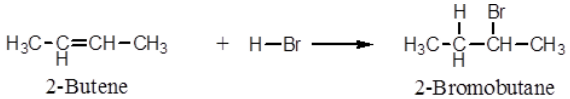
Alkenes; Electrophilic Addition Reactions

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.







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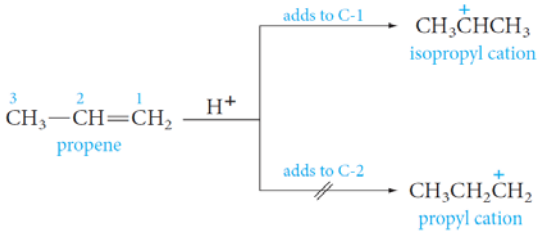
Alkenes; Electrophilic Addition Reactions

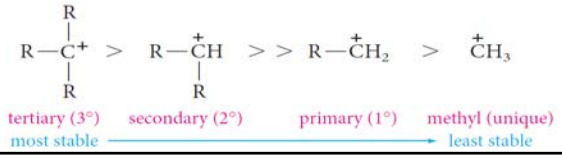
Explanation for Markovnikov's Rule

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.***



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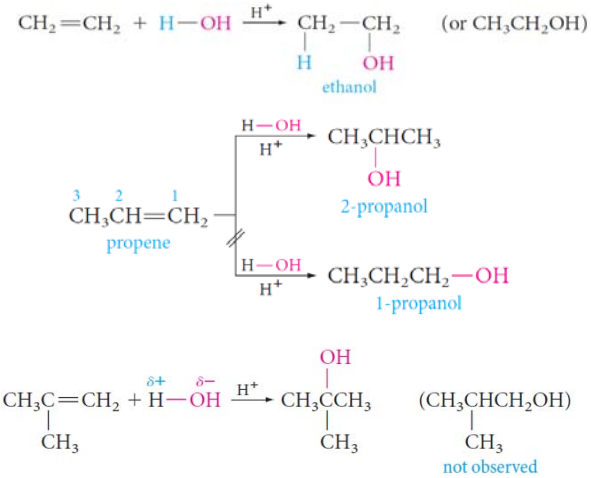
Alkenes; Electrophilic Addition Reactions

3.2. Addition of Water: Hydration

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



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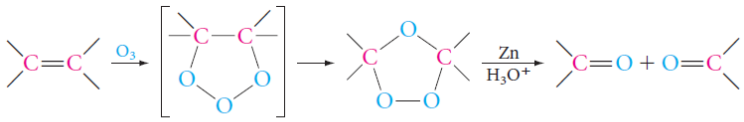
Alkenes; Oxidation Reactions

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.



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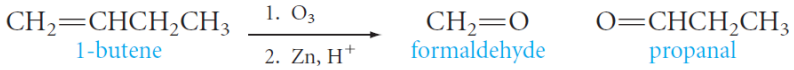
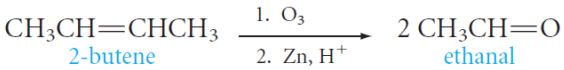
Alkenes; Oxidation Reactions

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.





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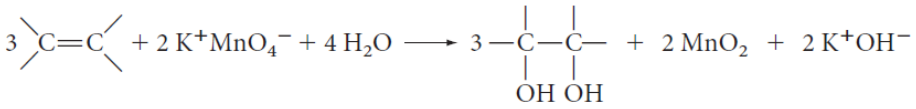
Alkenes; Oxidation Reactions

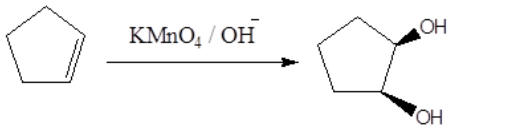
2. Oxidation Using $KMnO_4$

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



alkene — potassium permanganate (purple) — a glycol — manganese dioxide (brown-black)

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

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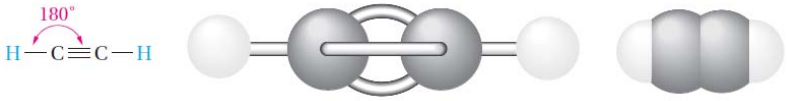
Unsaturated Hydrocarbons;

ALKYNES

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.**



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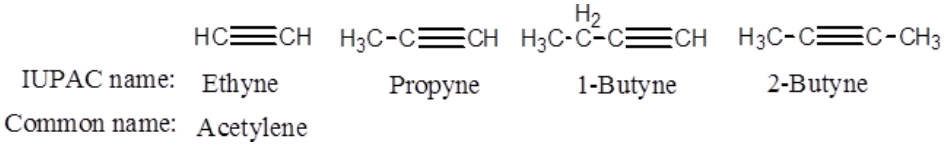
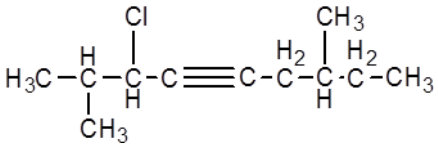
Alkynes; Nomenclature

- **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 .**



- **Example:**



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

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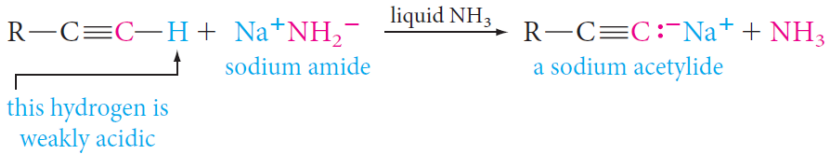
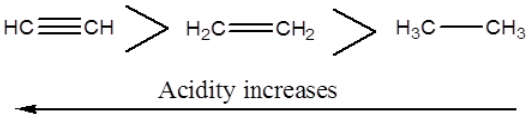
Alkynes; Acidity

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



- Internal alkynes (**Non-Terminal Alkyne**) have no exceptionally acidic hydrogens.
  - Relative Acidity of the Hydrocarbon.
    Terminal alkynes, are more acidic than other hydrocarbons



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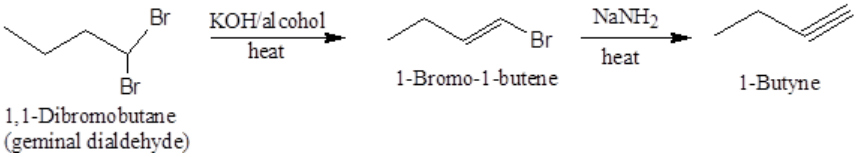
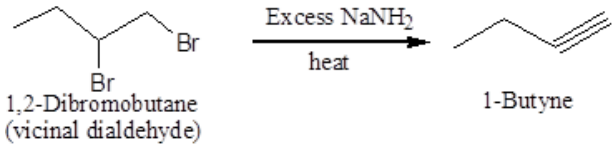
Alkynes; Preparation of Alkynes

1) Dehydrohalogenation of Alkyl dihalides





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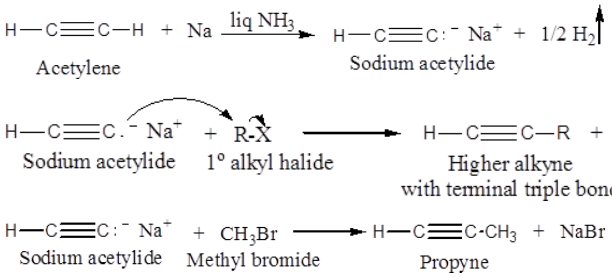
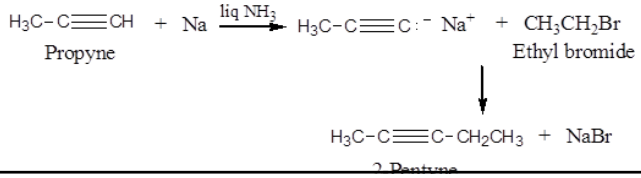
Alkynes; Preparation of Alkynes

2) Reaction of Sodium Acetylide with Primary Alkyl Halides

- **Acetylene**



- **Monosubstituted Acetylenes**



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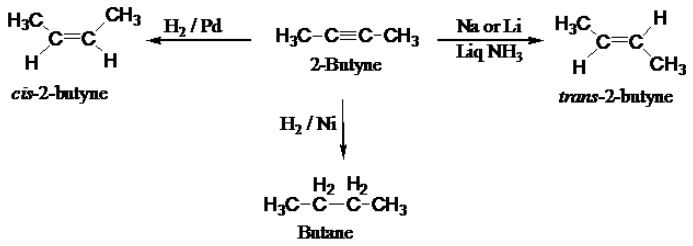
Alkynes; Reactions of Alkynes (Electrophilic Addition)

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.



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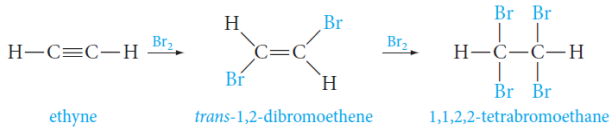
Alkynes; Reactions of Alkynes (Electrophilic Addition)

2. Addition of Halogen: Halogenation

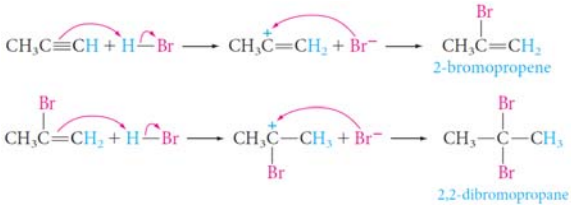
Bromine adds as follows; In the first step, the addition occurs mainly *trans*.



ethyne — *trans*-1,2-dibromoethene — 1,1,2,2-tetrabromoethane

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:



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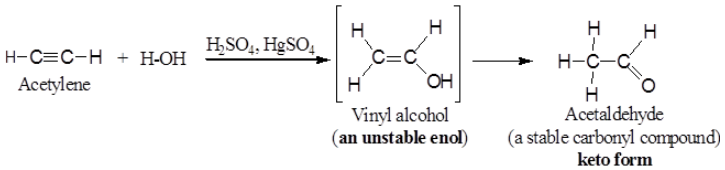
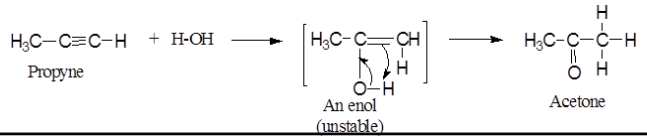
Alkynes; Reactions of Alkynes (Electrophilic Addition)

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.





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