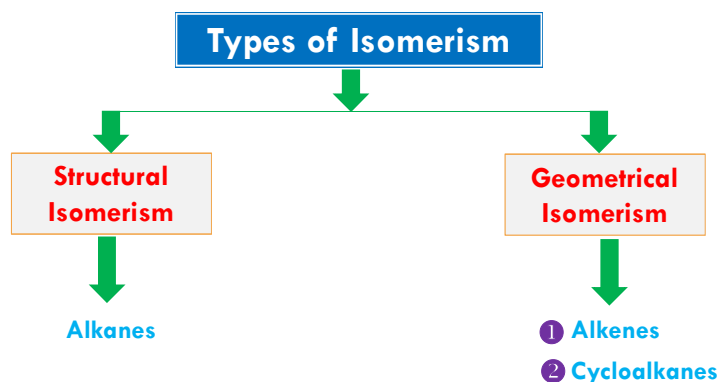


37

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

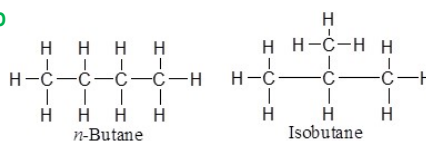


Structural Isomerism in Alkanes

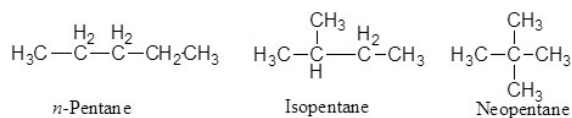
38

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

- **Butanes, C₄H₁₀**



- **Pentanes, C₅H₁₂**



Geometric Isomerism in Alkenes

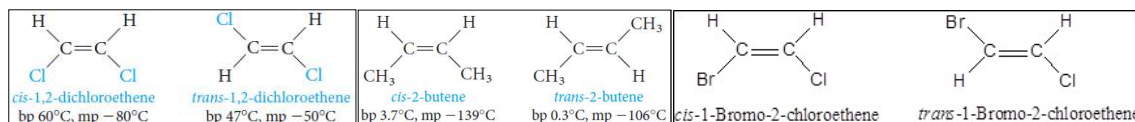
39

- 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**

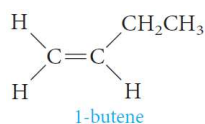
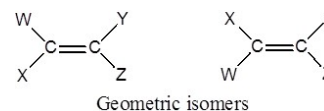


- cis isomer**; when two similar groups are on the **same side or same side** of the double bond.
- trans isomer**; when two similar groups are on the **opposite direction or opposite sides** of the double bond.
- They have **different physical properties** and can be separated by **fractional crystallization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

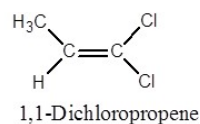
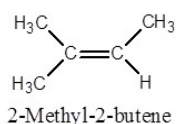
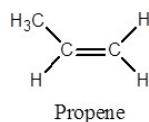
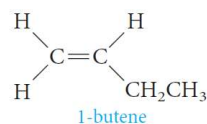
Geometric Isomerism in Alkenes

40

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



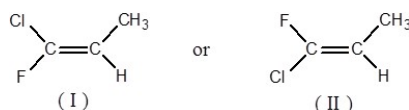
is identical to



Geometric Isomerism in Alkenes

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- 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**.

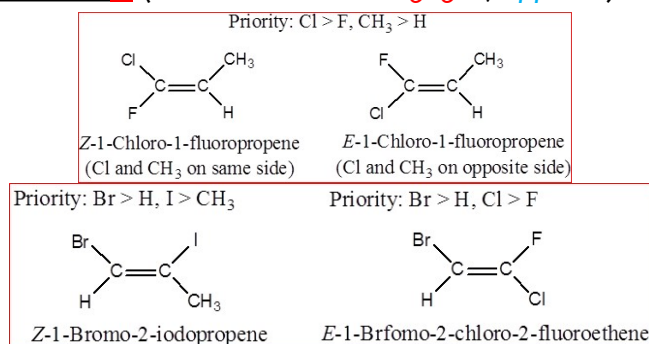
Thus, in structure (I),



Geometric Isomerism in Alkenes

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- 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).

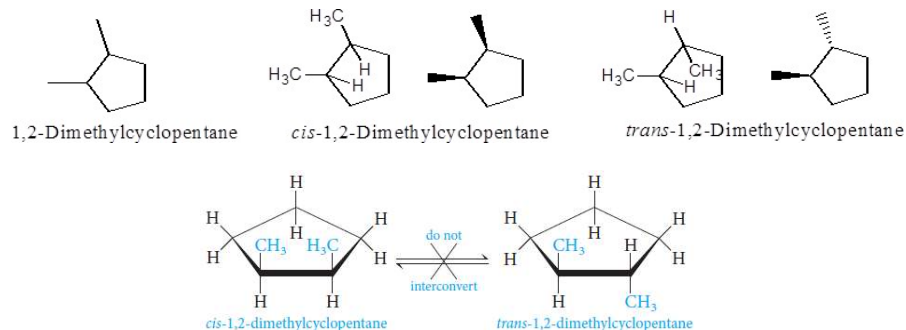


Geometric Isomerism in Cycloalkanes

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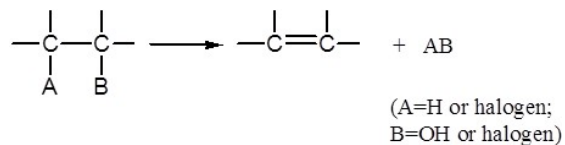
cis-trans Isomerism in Cycloalkanes

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



Preparation of Unsaturated hydrocarbons

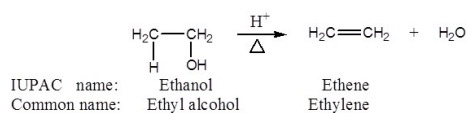
- Unsaturated hydrocarbons are prepared by **Elimination** of an atom or group of atoms from adjacent carbons to form **carbon-carbon double or triple bond**.



1) Dehydration of Alcohols

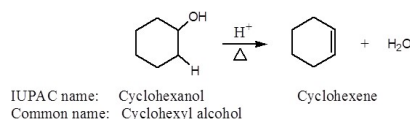
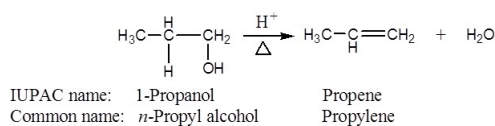
When an alcohol is heated in the presence of a mineral acid catalyst, it readily loses a molecule of **water** to give an **alkene**.

Preparation of Unsaturated hydrocarbons (Alkenes)



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

- Removal of OH group and a proton from two adjacent carbon atoms using mineral acids such as HCl, H_2SO_4 and H_3PO_4



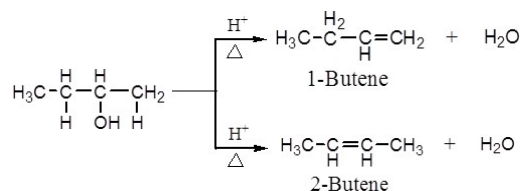
1) Dehydration of Alcohols

Preparation of Unsaturated hydrocarbons (Alkenes)

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

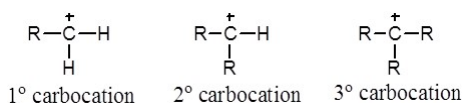
The major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.

1) Dehydration of Alcohols

Preparation of Unsaturated hydrocarbons (Alkenes)

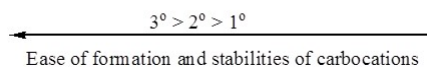
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Classes of Carbocations



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

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



Generally

1. The dehydration of alcohols requires an **acid catalyst**.
2. The predominant alkene formed follows **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 $3^\circ > 2^\circ > 1^\circ$.

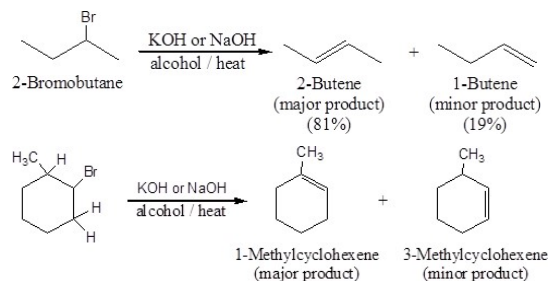
2) Dehydrohalogenation of Alkyl Halides

Preparation of Unsaturated hydrocarbons (Alkenes)

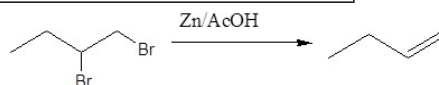
48

- Alkenes can also be prepared under alkaline conditions.

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

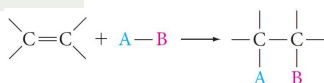


3) Dehalogenation of Vicinal Dibromides



Reactions of Unsaturated hydrocarbons

(1) Electrophilic Addition Reactions



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

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

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

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

(2) Oxidation Reactions

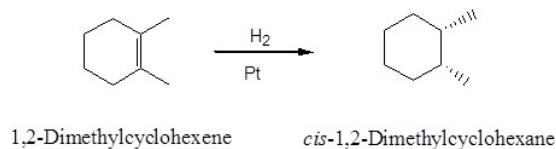
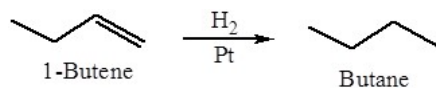
1. Ozonolysis
2. Oxidation Using KMnO_4

Reactions of Unsaturated hydrocarbons (Alkenes)

Electrophilic Addition Reactions

1. Addition of Hydrogen: Hydrogenation

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



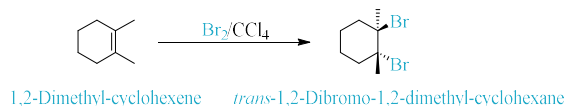
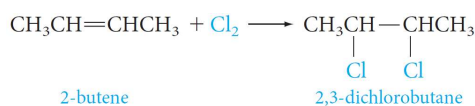
Electrophilic Addition Reactions

Reactions of Unsaturated hydrocarbons (Alkenes)

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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)



Electrophilic Addition Reactions

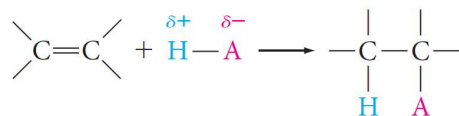
Reactions of Unsaturated hydrocarbons (Alkenes)

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3. Addition of Acids

- A variety of acids add to the double bond of alkenes.

The hydrogen ion (or proton) adds to one carbon of the double bond, and the remainder of the acid becomes connected to the other carbon.



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

Electrophilic Addition Reactions

Reactions of Unsaturated hydrocarbons (Alkenes)

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

Examples of Electrophile:

- Positive reagents:** protons (H^+), alkyl group R^+ , nitronium ion (NO_2^+), etc....
- Neutral reagents having positively polarized centers:** HCl, bromine (because it can be polarized so that one end is positive).
- Lewis acids:** molecules or ions that can accept an electron pair \Rightarrow BF_3 and $AlCl_3$.

Examples of Nucleophile:

a) Negative ions

e.g. $H\ddot{O}^-$: Hydroxide ion, $H\ddot{S}^-$: Hydrosulphide ion, $R\ddot{O}^-$: Alkoxide ions,
 $:N\equiv C^-$: Cyanide ion, $:X^-$: Halide ions, ...etc.

b) Neutral molecules

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

Electrophilic Addition Reactions

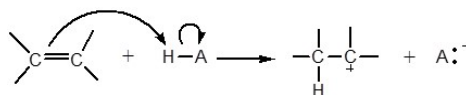
Reactions of Unsaturated hydrocarbons (Alkenes)

54

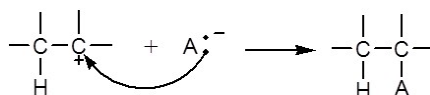
3. Addition of Acids

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

Electrophilic Addition Reactions

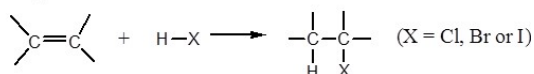
Reactions of Unsaturated hydrocarbons (Alkenes)

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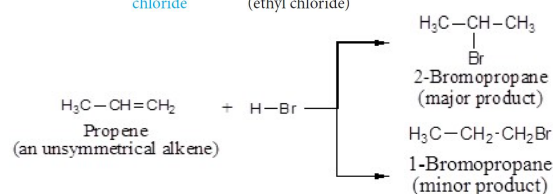
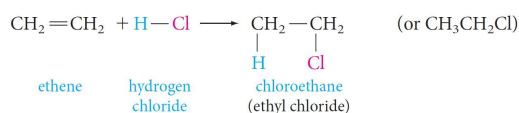
3.1. Addition of Hydrogen Halide

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

General equation



Examples;



Electrophilic Addition Reactions

Reactions of Unsaturated hydrocarbons (Alkenes)

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- 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.

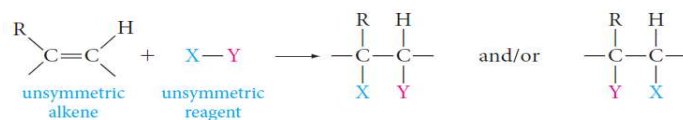




Table 3.2 Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

	Symmetric	Unsymmetric
Reagents	$\begin{array}{c} \text{Br}-\text{Br} \\ \quad \\ \text{Cl}-\text{Cl} \\ \quad \\ \text{H}-\text{H} \end{array}$	$\begin{array}{c} \text{H}-\text{Br} \\ \\ \text{H}-\text{OH} \\ \\ \text{H}-\text{OSO}_3\text{H} \end{array}$
Alkenes	$\text{CH}_2=\text{CH}_2$  <p style="text-align: center;">mirror plane</p>	$\text{CH}_3\text{CH}=\text{CH}_2$  <p style="text-align: center;">not a mirror plane</p>

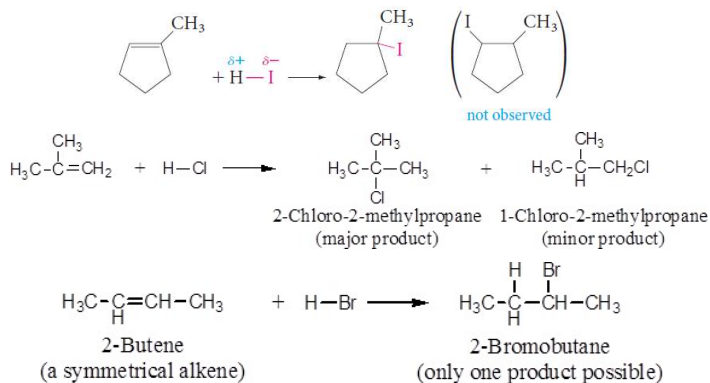
Electrophilic Addition Reactions

Reactions of Unsaturated hydrocarbons (Alkenes)

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Markovnikov's Rule

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



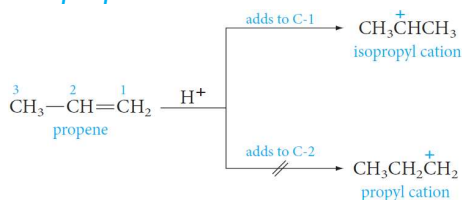
Electrophilic Addition Reactions

Reactions of Unsaturated hydrocarbons (Alkenes)

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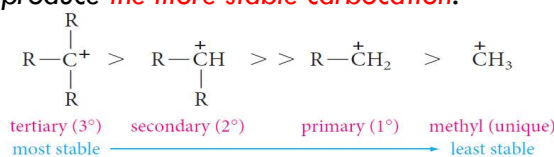
Explanation for Markovnikov's Rule

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**.



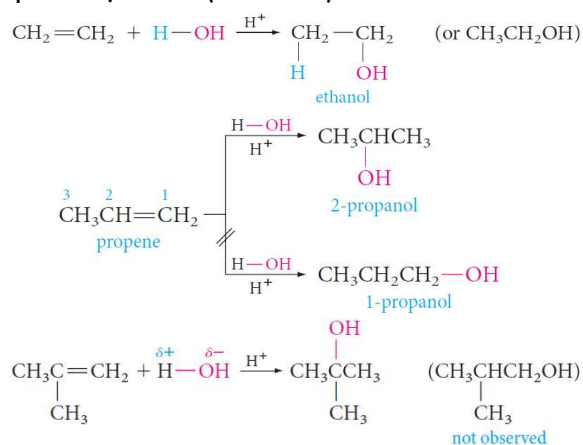
Electrophilic Addition Reactions

Reactions of Unsaturated hydrocarbons (Alkenes)

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3.2. Addition of Water: Hydration

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

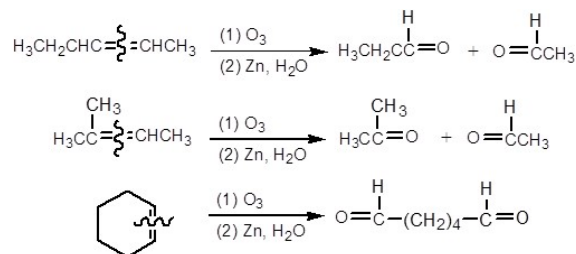


Oxidation Reactions

Reactions of Unsaturated hydrocarbons (Alkenes)

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.



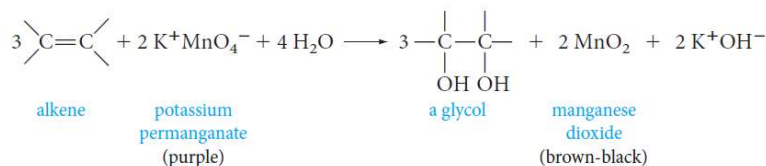
Oxidation Reactions

Reactions of Unsaturated hydrocarbons (Alkenes)

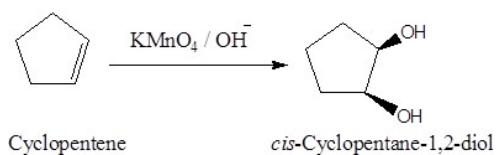
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2. Oxidation Using KMnO_4

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



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



Uses of Alkenes

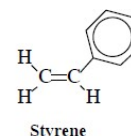
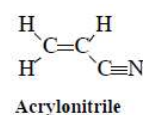
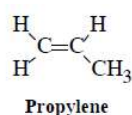
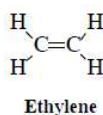
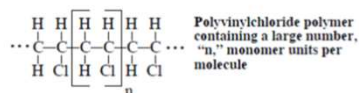
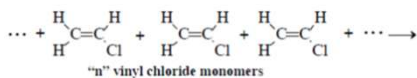
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SYNTHETIC POLYMERS

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

An important example:

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



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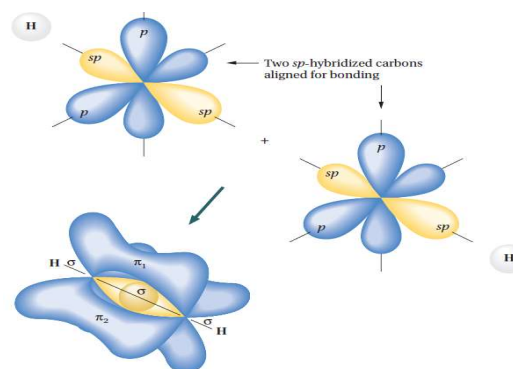
3. ALKYNES

Unsaturated hydrocarbons 2. Alkynes

The Structure of Alkynes

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- **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 \AA**
- The geometry is **Linear**.



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

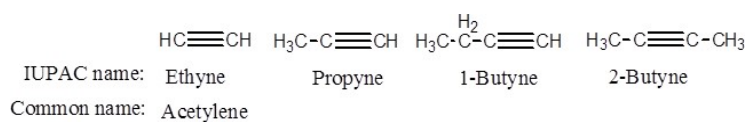
Unsaturated hydrocarbons

2. Alkynes

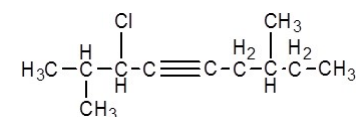
The Structure of Alkynes

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



- Example:**



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

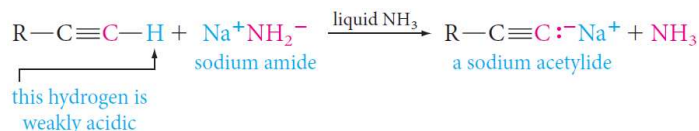
Unsaturated hydrocarbons

2. Alkynes

Acidity of Alkynes

66

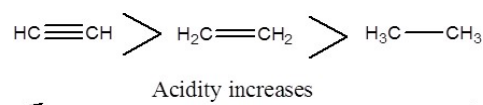
- A hydrogen atom on a triply bonded carbon (**Terminal Alkyne**) is weakly acidic and can be removed by a very strong base (as Sodium amide).



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

- Relative Acidity of the Hydrocarbon.

Terminal alkynes, are more acidic than other hydrocarbons

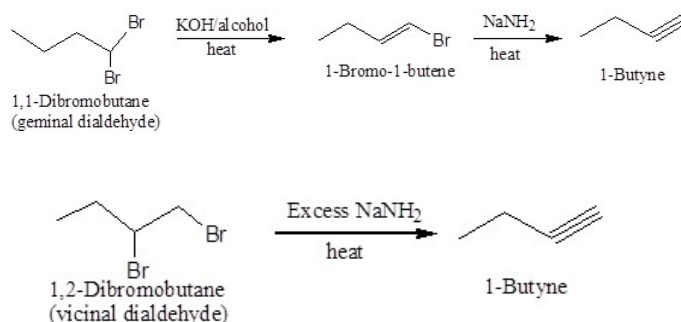


1) Dehydrohalogenation of Alkyl dihalides

Preparation of Unsaturated hydrocarbons (Alkynes)

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

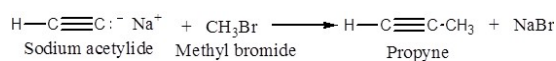
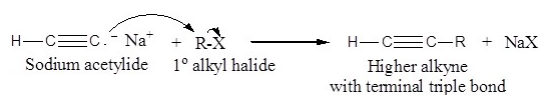
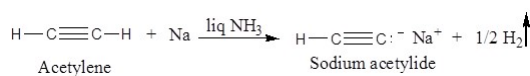


2) Reaction of Sodium Acetylide with Primary Alkyl Halides

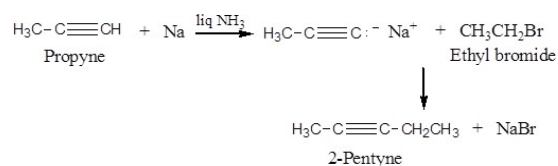
Preparation of Unsaturated hydrocarbons (Alkynes)

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○ Acetylene



○ Monosubstituted Acetylenes



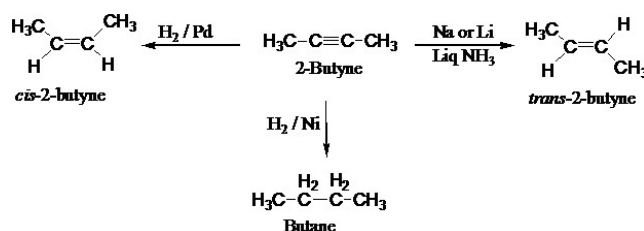
Electrophilic Addition Reactions

Reactions of Unsaturated hydrocarbons (Alkynes)

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1. Addition of Hydrogen: Hydrogenation

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



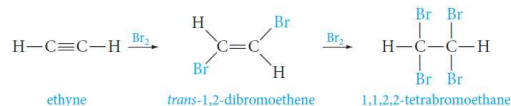
Electrophilic Addition Reactions

Reactions of Unsaturated hydrocarbons (Alkynes)

70

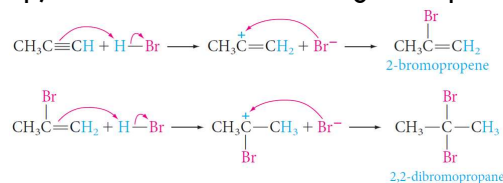
2. Addition of Halogen: Halogenation

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



3. Addition of Hydrogen Halide

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



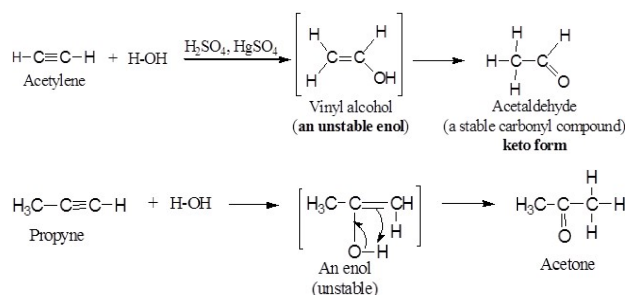
Electrophilic Addition Reactions

Reactions of Unsaturated hydrocarbons (Alkynes)

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4. Addition of Water: Hydration

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



Uses of Alkynes

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Alkynes;

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

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

- Drug production

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

- General uses;

- Making organic compounds
- Organic solvents