Chapter 5

Hydrocarbons: Alkanes, cycloalkanes, alkenes, alkynes

Introduction:

Alkanes belong to the hydrocarbon family: molecules composed exclusively of carbon and hydrogen.

Hydrocarbons are subdivided into two categories of compounds, according to their chemical structure: saturated and unsaturated (Figure 5.1).

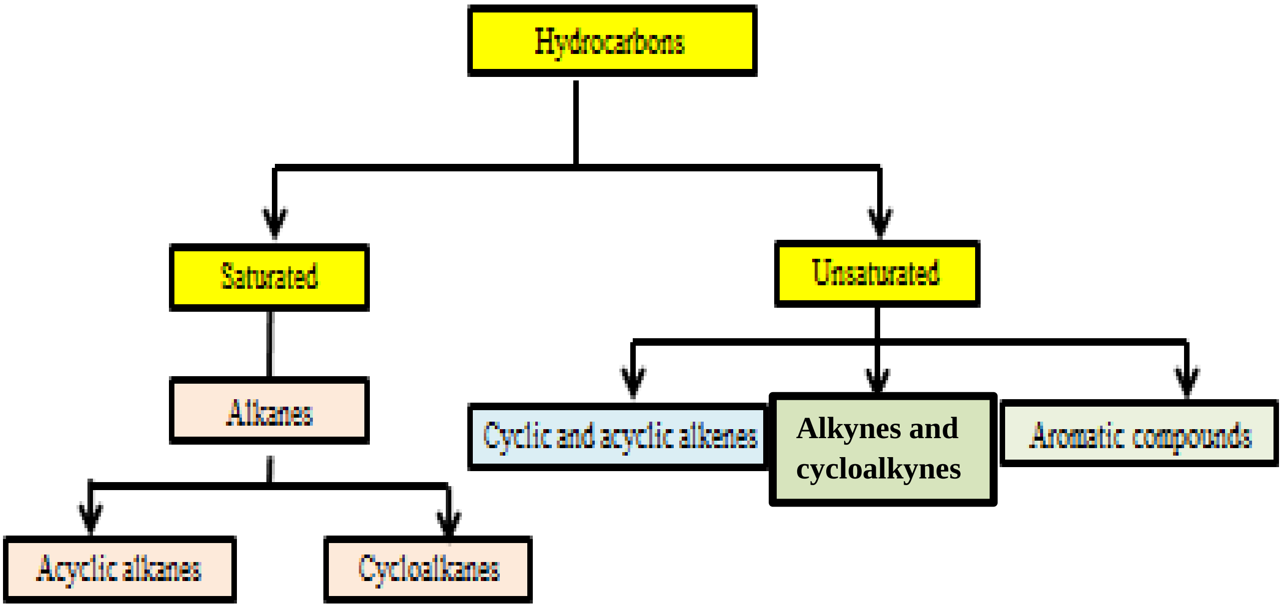


Figure 5.1: Classification of hydrocarbons.

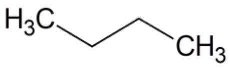
5.1. Alkanes :

5.1.1. Definition :

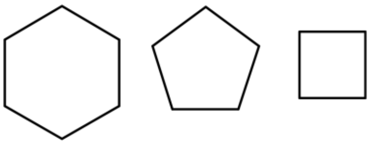
Alkanes, also called paraffins, have the molecular formula C_nH_{2n+2}. They are saturated hydrocarbons (no multiple bonds). SP^3 hybridized carbons are linked by σ bonds.

Alkanes are classified into various types based on their structure:

- ✓ Linear alkanes (n-alkanes)



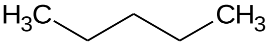
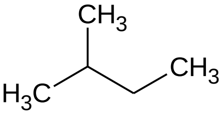
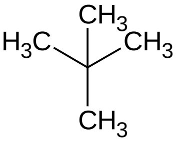
- ✓ Branched alkanes (branched)
- ✓ Cyclic alkanes (cycloalkanes) with the general formula C_nH_{2n}



5.1.2. Physical properties of alkanes:

- ✓ Alkanes are nonpolar molecules; they are soluble in several nonpolar organic solvents. However, they are insoluble in water because water molecules are polar and engage in intermolecular attractions such as hydrogen bonding. Therefore, alkanes are hydrophobic.
- ✓ Alkanes have lower boiling points for a given molecular weight than most other organic compounds. The boiling and melting points increase with molecular mass. However, at equal molecular masses, the boiling point is lower the more branched the molecule is.

  Example:

Name	**Formula**	**Boiling point, °C**
Pentane		36
2-methylbutane (isopentane)		28
2,2-dimethylpropane (neopentane)		10

- ✓ Under normal temperature and pressure conditions, alkanes are distributed as follows:

C_1 to C_4 Gas
C_5 to C_{16} Liquid
C_{17} and above Solid

- ✓ Cyclic alkanes generally have higher boiling and melting temperatures than linear alkanes of the same number of carbon atoms.

5.1.3. Chemical properties of alkanes:

The name paraffins initially given to alkanes summarizes their chemical behavior: paraffins: low affinity. They are not very reactive. They only have carbon-carbon and carbon-hydrogen σ bonds. They do not undergo addition reactions. The bonds are weakly polarized and not very polarizable. They are not attacked by electrophiles or nucleophiles. The only possible reactions are radical substitution reactions and oxidation reactions.

5.1.3.1. Halogenation of Alkanes:

This is a radical substitution reaction, initiated photochemically (light, hυ), thermally (heat), or using a radical initiator (peroxides R-O-O-R').

Chlorine and bromine produce alkyl halides. Fluorine produces the same type of product if initially diluted in an inert gas in an apparatus that removes the heat produced. No simple reaction has been observed with iodine.

$$RH + X_2 \xrightarrow[\text{Or peroxydes}]{h\upsilon \text{ or } \Delta} RX$$

The mechanism for obtaining alkyl halides is a chain mechanism. The reaction is regioselective.

The reaction takes place in three stages:

- **Initiation:**

$$X{-}X \xrightarrow[\text{Or peroxydes}]{h\upsilon \text{ or } \Delta} 2X^{\cdot}$$

- **Propagation:**

$$R{-}H + X^{\cdot} \longrightarrow R^{\cdot} + H{-}X$$

$$R^{\cdot} + X{-}X \longrightarrow R{-}X + X^{\cdot}$$

- **Termination:**

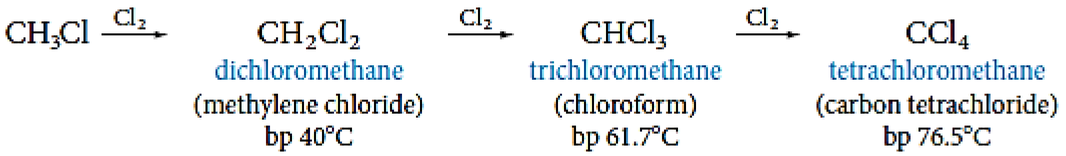
$$R^{\cdot} + X^{\cdot} \longrightarrow R{-}X$$

$$R^{\cdot} + R^{\cdot} \longrightarrow R{-}R$$

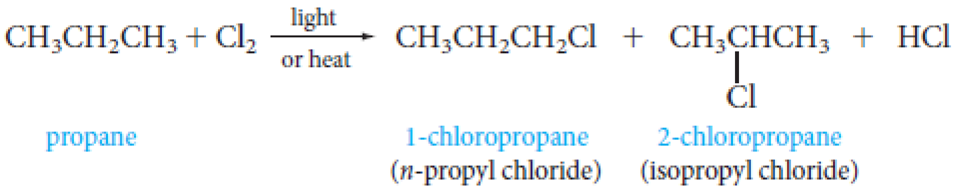
$$X^{\cdot} + X^{\cdot} \longrightarrow X{-}X$$

Notes:

If excess halogen is present, the reaction can continue further to give polyhalogenated products. Thus, methane and excess chlorine can give products with two, three, or four chlorines.

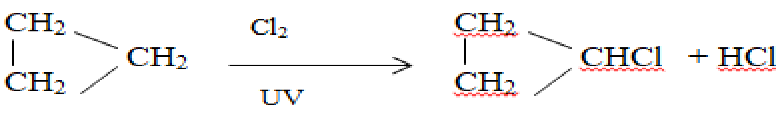


With longer chain alkanes, mixtures of products may be obtained. For example, with propane:



$$CH_3CH_2CH_3 + Cl_2 \xrightarrow[\text{or heat}]{\text{light}} CH_3CH_2CH_2Cl + \underset{\displaystyle Cl}{CH_3\overset{}{C}HCH_3} + HCl$$

Halogenation of cycloalcanes:



5.1.3.2. Combustion :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow n\,CO_2 + (n+1)\,H_2O$$

$$C_nH_{2n} + \left(\frac{3n}{2}\right) O_2 \longrightarrow n\,CO_2 + n\,H_2O$$

5.1.4. Preparation of alkanes and cycloalkanes :

5.1.4.1. From petroleum and natural gas:

The main source of alkanes is in petroleum. Their distillation in the presence of catalysts (based on silica or alumina) under high pressure (up to 80 kg/cm^2) and at high temperatures (400 to 700°C) allows for the collection of different hydrocarbon fractions.

5.1.4.2. Reduction of a halogenated derivative by hydrolysis of the corresponding organomagnesium compound :

$$RX + Mg \longrightarrow RMgX \xrightarrow{H_2O} RH + MgXOH$$

5.1.4.3. Wurtz reaction:

$$2\,RX + 2\,Na \longrightarrow R-R + 2\,NaX$$

$$2\,RX + Zn \longrightarrow R-R + ZnX_2$$

5.1.4.4. Reduction of halogenated derivatives by zinc in the presence of an acid:

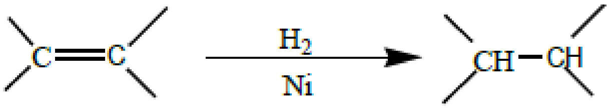
$$RX + Zn + H^+ \longrightarrow RH + Zn^{2+} + X^-$$

5.1.4.5. From carboxylic acids (Decarboxylation):

The overall reaction is of the type:

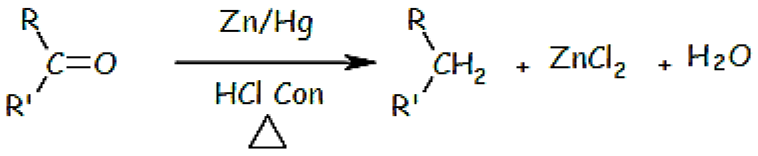
$$R-COOH \xrightarrow{NaOH} R-COONa \xrightarrow{NaOH,\ \Delta} R-H + Na_2CO_3$$

5.1.4.5. Catalytic hydrogenation of alkenes:

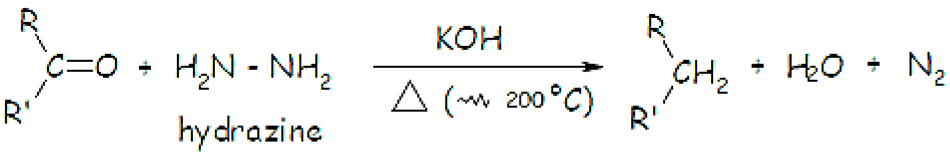


5.1.4.6. From carbonyl derivatives:

Reduction according to CLEMENCEN (in concentrated acid medium)

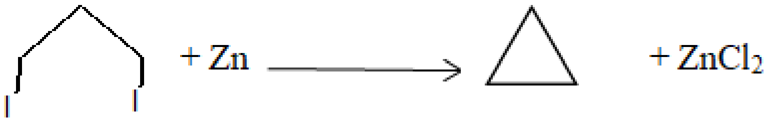


Reduction according to WOLFF-KISHNER (in basic medium)

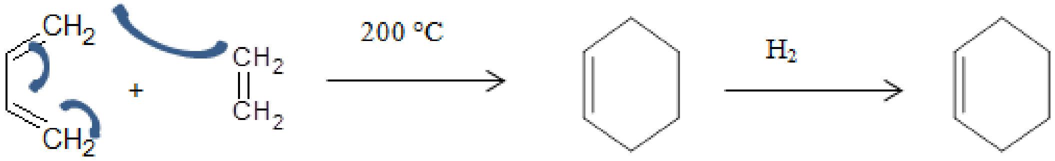


Preparation of cycloalcanes:

Preparation of cyclopropane by the action of zinc on a dihalogenated derivative.



Cyclohexane derivatives can be obtained by condensation of a molecule of a conjugated diene and an alkene. This is a cycloaddition or Diels-Alder reaction:



5.2. Alkenes :

5.2.1. Definition:

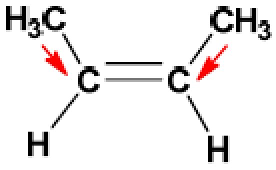
Alkenes or ethylenic compounds (or olefins) are unsaturated hydrocarbons with at least one double bond. Their general formula is C_nH_{2n}. That of cycloalkenes C_nH_{2n-2}

The double bond is formed by two pairs of shared electrons. The carbon atoms that form the double bond are in a state of sp2 hybridization.

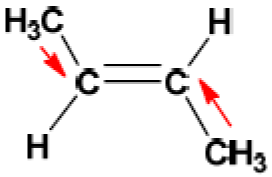
5.2.2. Physical properties of alkanes:

- ✓ Alkenes have physical properties similar to those of alkanes. They are therefore insoluble in water and soluble in nonpolar organic solvents.
- ✓ The boiling point of alkenes increases with their molar mass, as is the case for alkanes. Geometric isomers of the same alkene (Z and E) do not always have the same boiling point.

  Example :

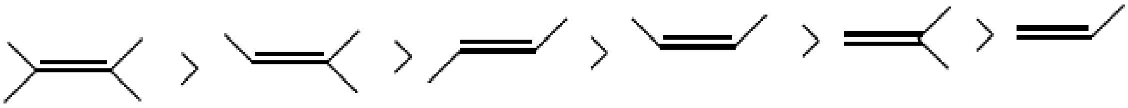


(Z)-but-2-ene
bp 3,7°C



(E)-but-2-ene
bp 0,8°C

- ✓ The stability of alkenes increases with the number of alkyl groups carried by the double bond. This characteristic determines the regiochemistry of elimination and addition reactions.



5.2.3. Chemical properties of alkenes:

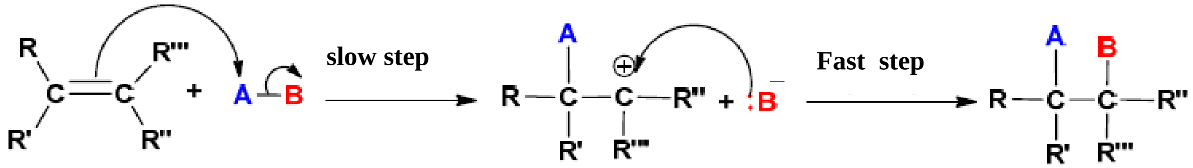
There are three distinct categories of chemical reaction for alkenes:
Addition reaction, polymerisation and oxidation reaction.

5.2.3.1. Addition reaction :

The reaction involves the addition of a reagent A-B, which carries a polar covalent bond, to an alkene. This reaction occurs in two steps:

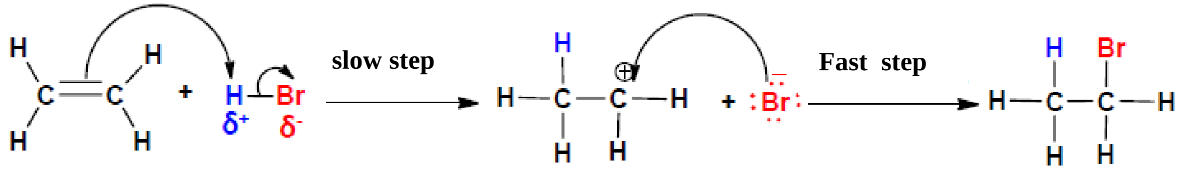
In the first step, the alkene acts as a nucleophile and attacks the electrophilic atom $A^{\delta+}$ of the reagent using the electrons from the π bond, leading to the cleavage of the σ bond in A-B and the formation of a carbocation.

In the second step of the mechanism, the anion B- acts as a nucleophile, attacking the carbocation and resulting in the formation of the final product.

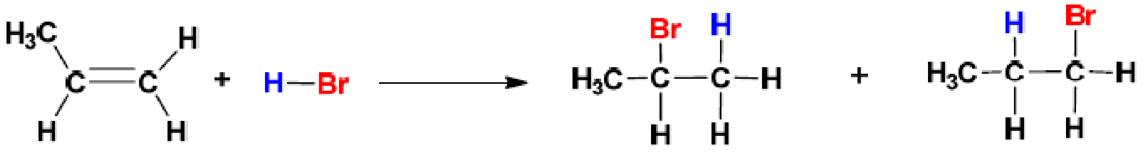


Acid addition:

The different halohydric acids HX (X = Cl, Br, I) add onto alkenes to yield monohalogenated derivatives.



If the alkene is asymmetric (Markovnikov rule):

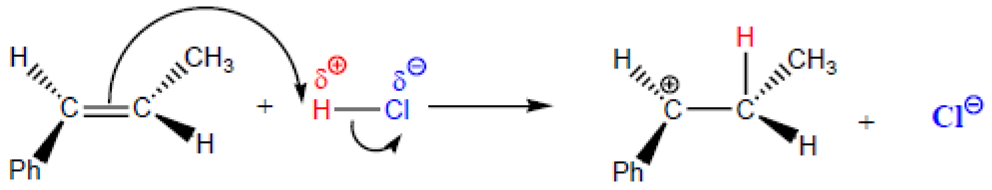


majority product **minority product**

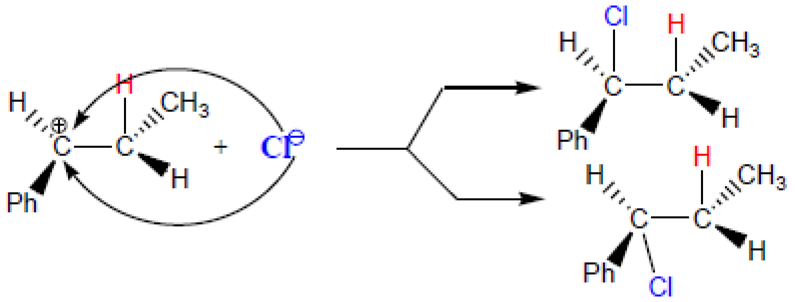
Markovnikov rule : “Addition of a reactant A-B (where B ≠ A), the electropositive species A adds to the carbon of the alkene with the greatest number of hydrogens. The main product is the one formed by the most stable reaction intermediate”.

Example: the addition of HCl to an ethylenic

1st step: formation of a carbocation

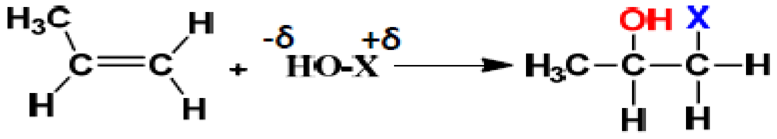


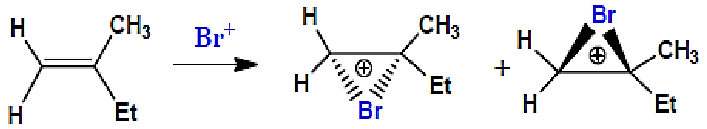
2nd step: attack of the Cl^- nucleophile on the electrophilic site.

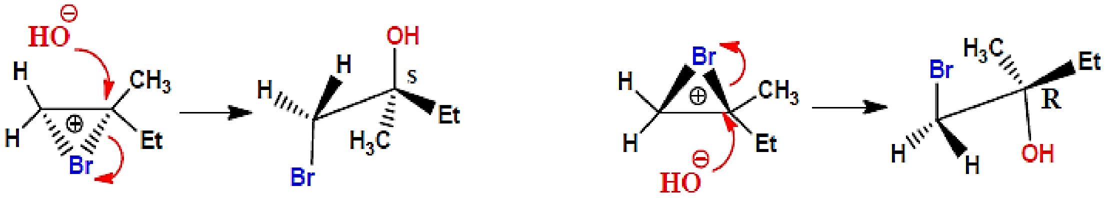


Addition of hypohalous acids HOX:

The addition of hypochlorous (HOCl) or hypobromous (HOBr) acid to an alkene leads respectively to a chlorohydrin or a bromohydrin (α-halogenated alcohol). In this reaction the halogen attaches to the less substituted carbon, and the OH to the more substituted carbon; this reaction is regioselective.







The halonium ion can form above or below the plane of the double bond.

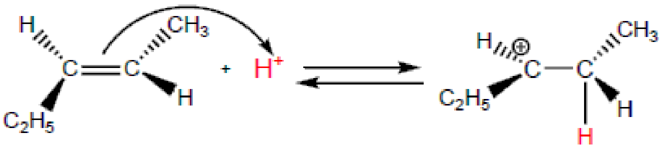
Hydration of alkenes - addition of water:

The addition of water to ethylenic compounds leads, in the presence of an acid catalyst (H_3PO_4, H_2SO_4), to the formation of alcohols. Regioselectivity obeys Markovnikov's rule.

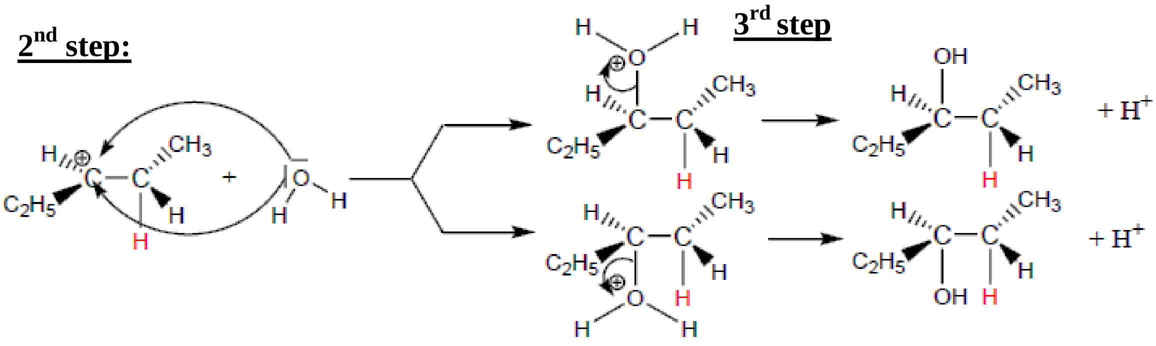
If the alkene is reactive (highly substituted), a dilute sulfuric acid solution is sufficient to hydrate the alkene. In the case of a lightly substituted alkene, the reaction requires a concentrated acid solution.

In a dilute acid medium at 25°C

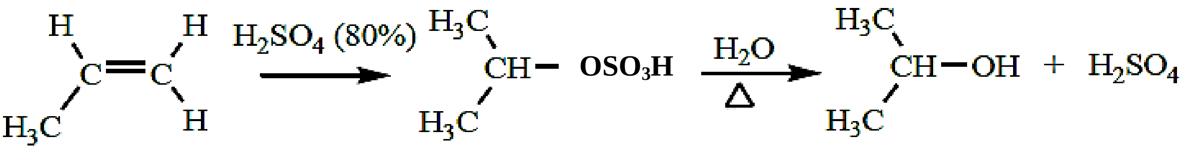
1st step:



2nd step:

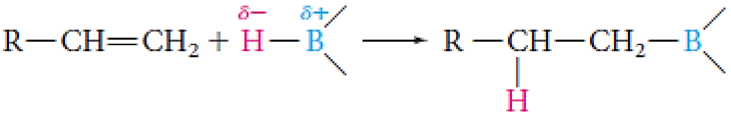


In concentrated acid medium at 100°



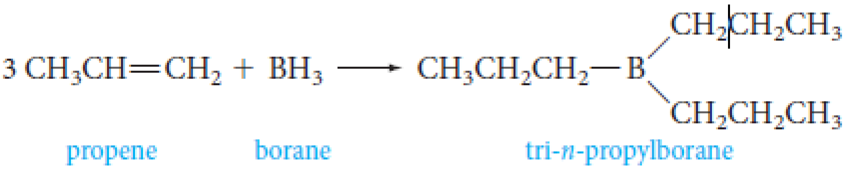
Hydroboration-Oxidation:

Definition: Hydroboration-oxidation is an electrophilic addition reaction leading to the formation of an alcohol according to the anti-Markovnikov principle.



$$R-CH=CH_2 + \overset{\delta-}{H}-\overset{\delta+}{B}\langle \longrightarrow R-\underset{\displaystyle H}{\underset{|}{CH}}-CH_2-B\langle$$

Because it has three B — H bonds, one molecule of borane, BH_3, can react with three molecules of an alkene. For example, propene gives tri-*n*-propylborane.

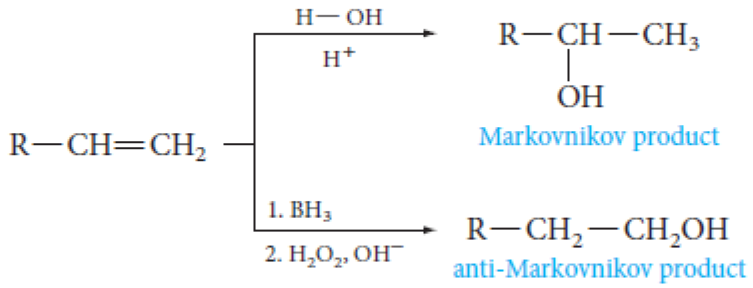


$$\underset{\text{propene}}{3\,CH_3CH=CH_2} + \underset{\text{borane}}{BH_3} \longrightarrow \underset{\text{tri-}n\text{-propylborane}}{CH_3CH_2CH_2-B\begin{matrix}CH_2CH_2CH_3\\ \\ CH_2CH_2CH_3\end{matrix}}$$

Trialkylboranes can be oxidized by hydrogen peroxide and base to give alcohols.

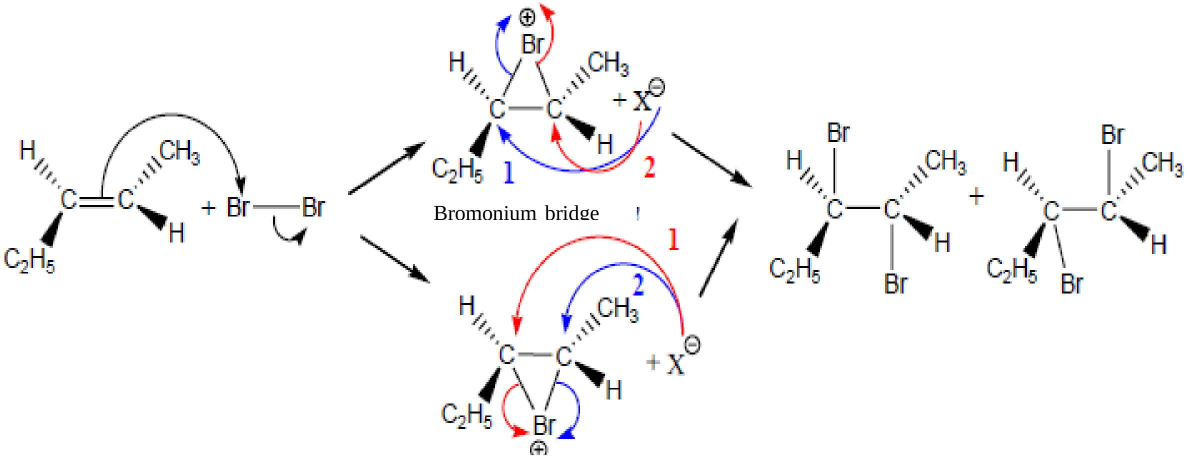
$$\underset{\text{tri-}n\text{-propylborane}}{(CH_3CH_2CH_2)_3B} + 3\,H_2O_2 + 3\,NaOH \longrightarrow$$

$$3\,\underset{n\text{-propyl alcohol}}{CH_3CH_2CH_2OH} + \underset{\text{sodium borate}}{Na_3BO_3} + 3\,H_2O$$



Addition of dihalogens X_2:

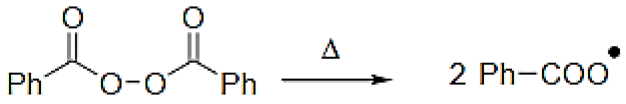
The addition of dihalogens to the double bond gives α, β dihalogenated derivatives. Generally, it is a trans addition, the reaction is stereospecific. It goes through a halonium intermediate. (In this case also the halonium ion can form above or below the plane of the double bond).



Free Radical addition:

The reaction occurs in three steps:

Initiation:



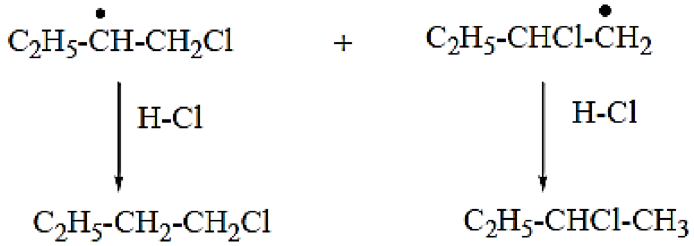
$$Ph{-}COO^{\bullet} + H{-}Cl \longrightarrow Ph{-}COOH + Cl^{\bullet}$$

Propagation:

$$C_2H_5\text{-}CH{=}CH_2 + Cl^{\bullet} \longrightarrow C_2H_5\text{-}\dot{C}H\text{-}CH_2Cl + C_2H_5\text{-}CHCl\text{-}\dot{C}H_2$$

More stable secondary radical ; Less stable primary radical

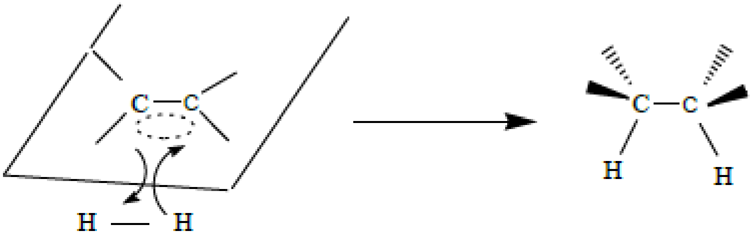
Anti-Markovnikov addition



majority product **minority product**

Catalytic hydrogenation of alkenes (catalytic examples: Pt, Pd, Ni):

It is a syn addition (the two hydrogen atoms enter through the same face of the double bond). The addition of dihydrogen can generate two asymmetric centers.



5.2.3.2. Oxidation reaction

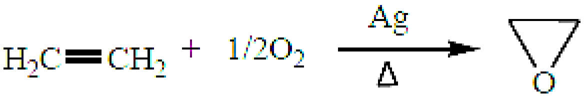
a. CombustionCombustion :

$$C_nH_{2n} + \left(\frac{3n}{2}\right) O_2 \longrightarrow n\ CO_2 + n\ H_2O$$

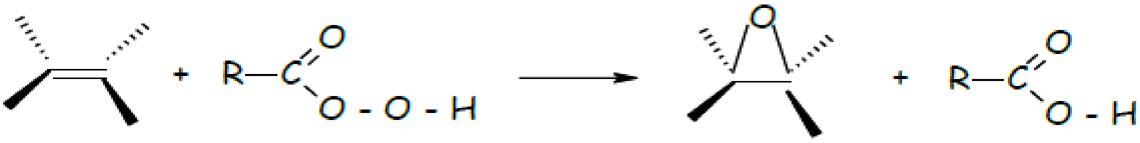
b. Oxygen addition: Epoxidation and hydroxylation

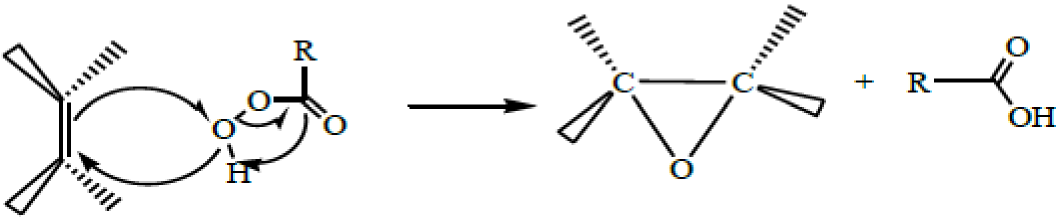
b1. Epoxidation :

Catalytic oxidation of ethylene by air



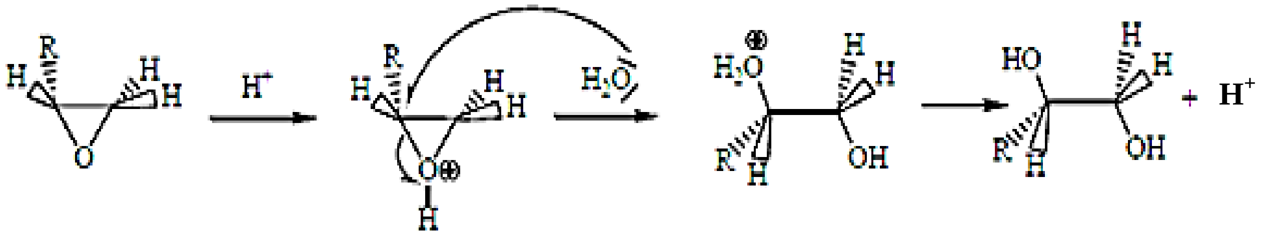
Epoxidation in the presence of peracids



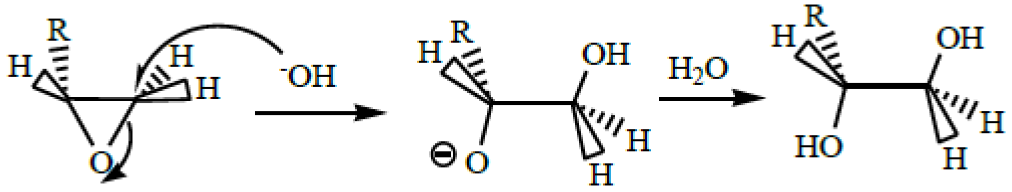


b.2. Trans hydroxylation:

In acidic medium:

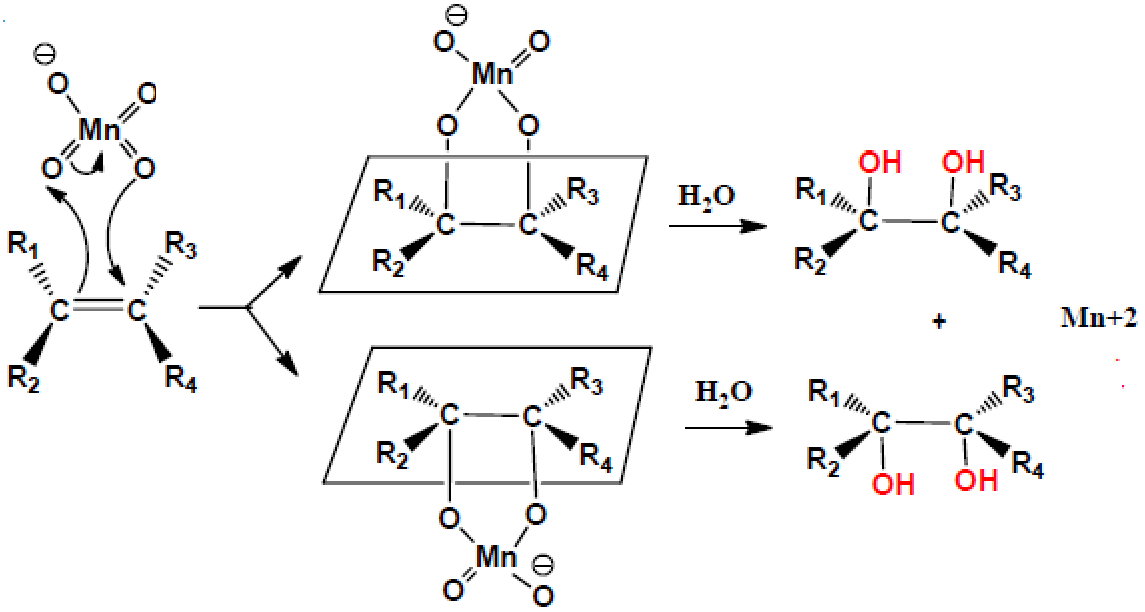


In a basic medium :

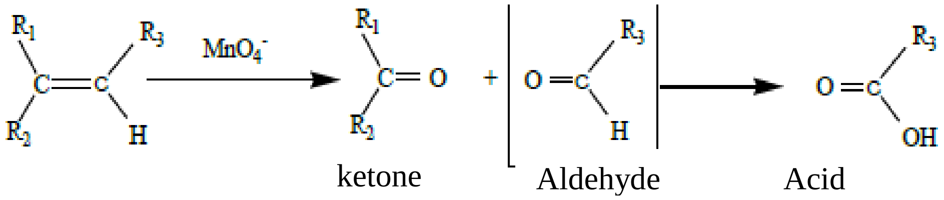


Formation of cis 1,2-diols (syn1,2-dihydroxylation)

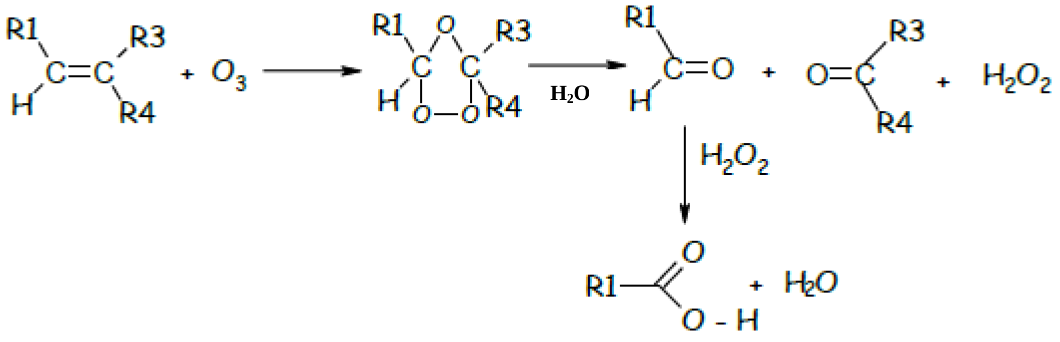
This formation can take place either in the presence of osmium tetroxide (OsO4) with H_2S or through potassium permanganate ($KMnO_4$) in a cold diluted basic medium, which constitutes the Baeyer test.



Addition of concentrated $KMNO_4$ or $K_2Cr_2O_7$:

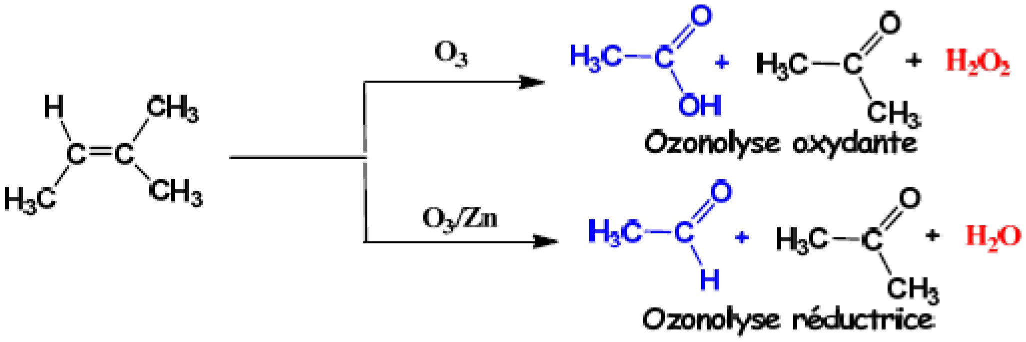


Ozonolysis of an alkene:



If we repeat the same reaction in the presence of powdered Zn, we stop at the aldehyde stage, because Zn (powder) destroys H2O2 at the moment of its formation.

$$Zn \; + \; H_2O_2 \longrightarrow ZnO \quad H_2O$$



5.2.3.3. Polymerization:

Polymerization is a process by which an organic compound reacts with itself to form a high-molecular-weight compound composed of repeating units of the original compound.

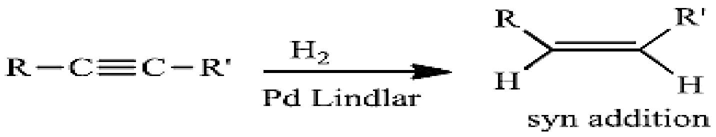
$$\underset{\text{Ethene}}{CH_2{=}CH{-}H \; + \; CH_2{=}CH_2} \xrightarrow[\text{(ii) Pressure, (iii) Catalyst}]{\text{(i) High temp.}} \underset{\text{Butene}}{CH_2{=}CH{-}CH_2{-}CH_3}$$

$$\xrightarrow{CH_2{=}CH_2} \underset{\text{Polyethylene or Polythene}}{({-}CH_2{-}CH_2)_n}$$

5.2.4. Preparation of alkenes:

Partial hydrogenation of alkynes:

The alkynes have a triple bond in the molecule and their controlled hydrogenation by passin the alkynes with hydrogen gas in equimolar ratio over heated catalysts, gives alkenes. The catalyst used may be finely Lindlar's catalyst.



Pyrolysis or cracking:

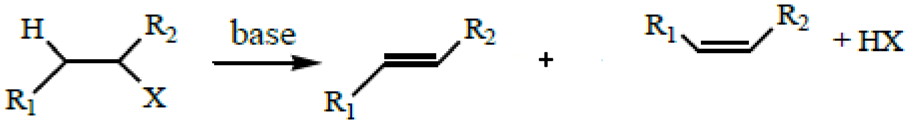
Higher alkanes when heated to a high temperature under pressure decompose to give a mixture of lower alkanes and alkenes.

$$\underset{\text{Alkane}}{R.CH_2.CH_2R} \xrightarrow[\text{200 Atmos.}]{500°C} \underset{\text{Alkene}}{R.CH{=}CH_2} + \underset{\text{Alkane}}{R{-}H}$$

$$\underset{\text{Hexane}}{CH_3.CH_2.CH_2.CH_2.CH_2.CH_3} \xrightarrow[\text{200 Atmos.}]{500°C} \underset{\text{Propene}}{CH_3CH{=}CH_2} + \underset{\text{Propane}}{CH_3.CH_2.CH_3}$$

Elimination reactions (E1 or E2)

By dehydrohalogenation.



Dehydratation of alcohols:

Alcohols when dehydrated in presence of catalysts give alkenes. The best procedure is to pass the vapours of alcohol over heated alumina.

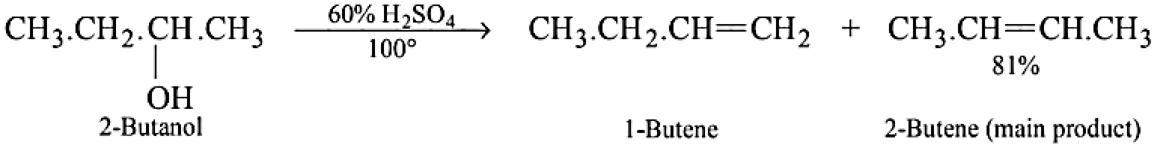
$$\underset{\text{Alcohol}}{R{-}CH_2.CH_2.OH} \xrightarrow[350{-}450°C]{Al_2O_3} \underset{\text{Alkene}}{R.CH{=}CH_2} + H_2O$$

Other substances like P_2O_5, H_2SO_4 (conc), H_3PO_4 are also used for dehydratation. The ease of dehydratation of various alcohols is in the order:

Tertiary > Secondary > Primary

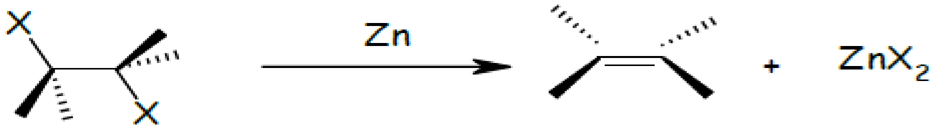
In the dehydratation of secondary and tertiary alcohols, when there is a possibility of the formation of two alkenes, the hydrogen atom is preferentially eliminated from the carbon with fewer number of hydrogens, to give an olefin having maximum number of alkyl groups about the double bond (Saytzeff rule).

Example:



$$\underset{\text{2-Butanol}}{CH_3.CH_2.\underset{\displaystyle OH}{\underset{|}{CH}}.CH_3} \xrightarrow[100°]{60\%\ H_2SO_4} \underset{\text{1-Butene}}{CH_3.CH_2.CH{=}CH_2} + \underset{\text{2-Butene (main product)}}{\underset{81\%}{CH_3.CH{=}CH.CH_3}}$$

By dehydrohalogenation of vicinal dihalides:



5.3. Alkynes:

5.3.1. Definition:

Alkynes, or acetylenic compounds with the general formula C_nH_{2n-2}, are compounds that possess a triple bond. The two carbons involved in the triple bond are sp-hybridized (resulting in a linear shape for the carbons). The triple bond consists of one σ bond and two π bonds. The simplest member of this family is ethyne, or acetylene (H−C≡C−H).

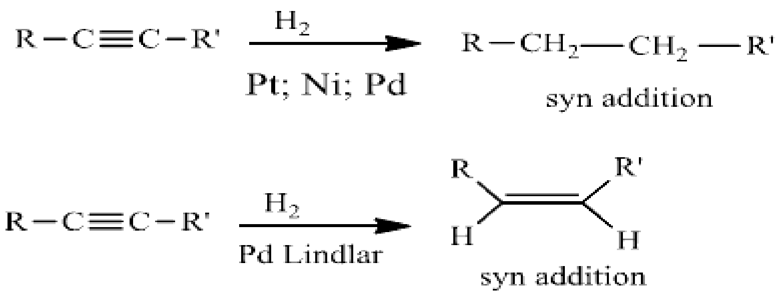
We distinguish substituted alkynes, which are in the form R-C≡C-R' (with R and R' ≠ H), whereas true alkynes are in the form H-C≡C-R' (with R' = H or R' ≠ H).

5.3.2. Reactions of Alkynes :

5.3.2.1. Hydrogenation:

a. Catalytic hydrogenation:

The use of a catalyst such as Pd, Pt, or Ni leads to alkanes. To stop at the alkene stage, a catalyst called **Lindlar palladium** is required.

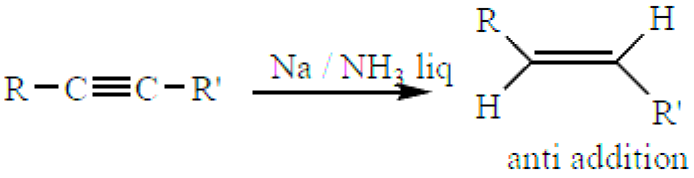


Alkane

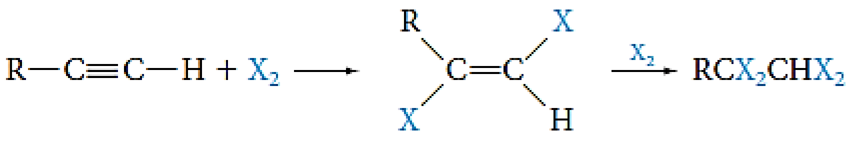
Alkene

b. Chemical Hydrogenation:

It is possible to obtain an ethylenic compound (alkene) by reducing the triple bond using an **alkali metal** (Li, Na, K).

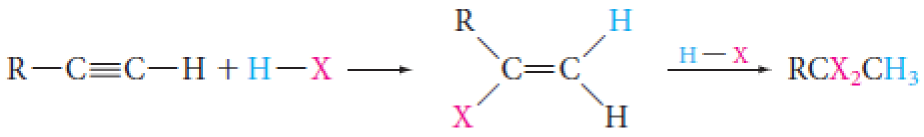


5.3.2.2. Dihalogen Addition (halogenation) :

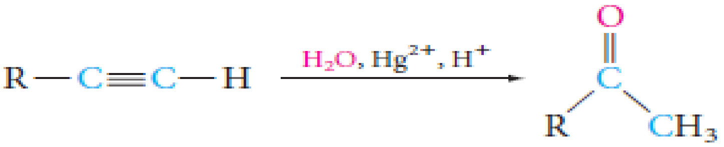


5.3.2.3. Hydrogen Halide Addition (Hydrohalogenation):

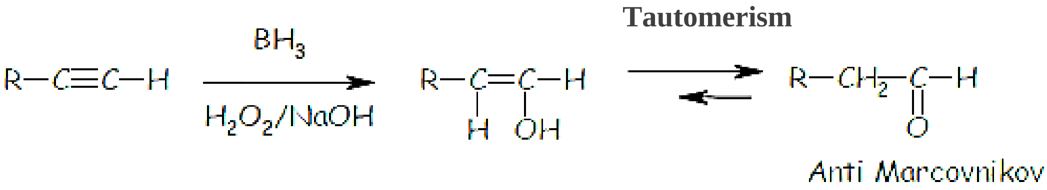
The **addition of hydrogen halides (HX, where X = Cl, Br, I)** to alkynes follows **Markovnikov's rule**, leading to the formation of **haloalkenes** and, with excess HX, **geminal dihaloalkanes**.



5.3.2.3. Hydration of Alkynes :



5.3.2.4. Borane Addition (Hydroboration-Oxidation of Alkynes)

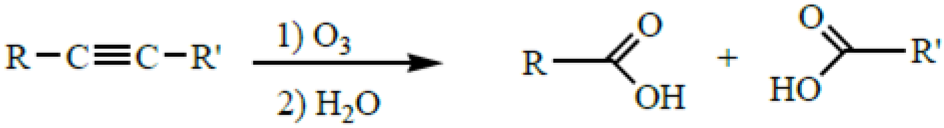


5.3.2.5. Formation of Acetylide Anions :

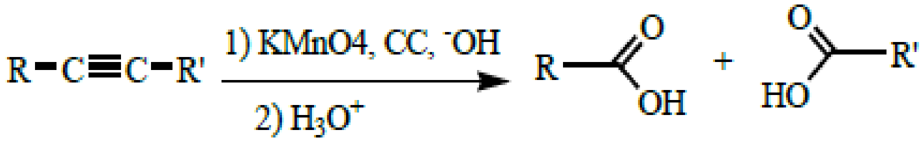
$$R-C\equiv C-H + Na^+ NH_2^- \xrightarrow{NH_3} R-C\equiv C:^- Na^+ + NH_3$$

5.3.2.6. Oxidation reaction:

The same ozonolysis reactions used for alkenes lead to the formation of carboxylic acids.



Oxidation with $K_2Cr_2O_7$ or $KMnO_4$ yields the same result.



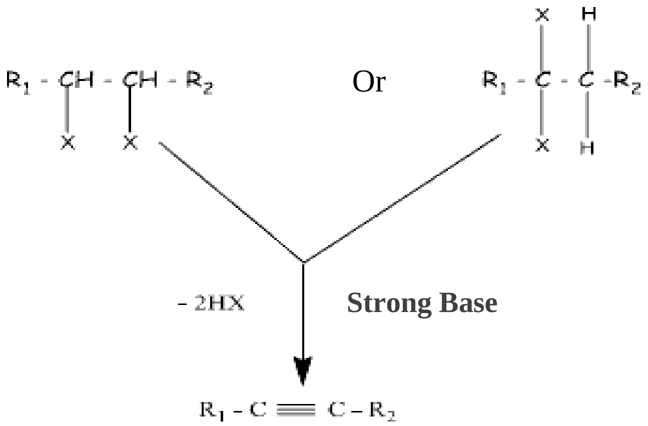
5.3.3. Preparation of alkynes:

The preparation is broadly based on two processes:

5.3.3.1. Formation of a triple bond :

Double Dehydrohalogenation of Dihalides:

(Elimination of 2 HX molecules from vicinal or geminal dihalides)



- A **vicinal dihalide** (halogens on adjacent carbons) or **geminal dihalide** (halogens on the same carbon) is treated with a strong base (e.g., **$NaNH_2$ in liquid NH_3** or alcoholic **KOH**).
- Two successive **E2 eliminations** remove **HX**, forming the alkyne.

Example:

$$CH_3-CH_2-CBr_2-CH_3 \xrightarrow[\text{Ammoniac liquid}]{2NaNH_2} CH_3-CH_2-C\equiv CH + 2NH_3$$

$$CH_3-CH_2-CBr_2-CH_3 \xrightarrow{2KOH/EtOH} CH_3-C\equiv C-CH_3 + 2H_2O$$

5.3.3.2. Increase in the carbon skeleton :

$$H-C\equiv C-H \xrightarrow[NH_3\ liq]{NaNH_2} H-C\equiv C-Na \xrightarrow{R-X} H-C\equiv C-R$$

Example :

$$CH_3-CH_2-C\equiv CH + NaNH_2 \xrightarrow[-NH_3]{\text{Ammoniac liquid}} CH_3-CH_2-C\equiv C-Na$$

$$CH_3-CH_2-C\equiv C-Na \xrightarrow{CH_3-I} CH_3-CH_2-C\equiv C-CH_3 + NaI$$