UNIT-III

UNSATURATED HYDROCARBONS (ALKENES AND ALKYNES)

General methods of preparation, physical and chemical properties, Saytzeff and Hoffmann eliminations (with mechanism), Electrophilic Additions, (H2, HX) mechanism (Markonikoff's/ Anti Markonikoff's addition) with suitable examples-syn and anti-addition. addition of X2, HX. Oxymercuration demercuration, ozonolysis, hydroxylation, Diels Alder reaction,1,2- and1,4-addition reactions in conjugated dienes. Reactions of alkynes; acidity, electrophilic and nucleophilic additions, hydration to form carbonyl compounds, Alkylation of terminal alkynes

General methods of preparation, physical and chemical properties:

Alkenes (CnH_2n)

- Definition: Hydrocarbons containing at least one C=C double bond.
- Hybridization: Each carbon in the double bond is sp^2 hybridized, planar geometry (~120°).
- Bonding: One σ-bond (overlap of sp^2 orbitals) + one π-bond (sidewise overlap of p orbitals).
- General formula: CnH_2n (acyclic, one double bond).

. General Methods of Preparation of Alkenes

(A) From Alkyl Halides (Dehydrohalogenation)

- Reagent: **Alcoholic KOH**, heat.
- Reaction:

$$R-CH_2-CH_2X \xrightarrow{\Delta\ \text{alc.KOH}} R-CH=CH_2 + HX$$

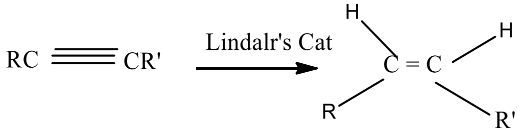
(B) From Alcohols (Dehydration)

- Reagent: **Conc. H_2SO_4** or **H_3PO_4,** heat.
- Reaction:

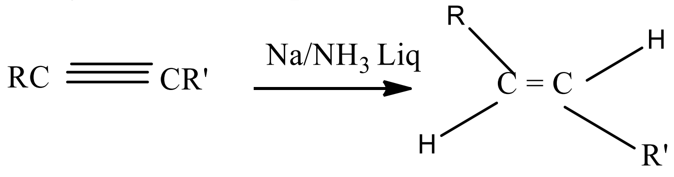
$$R-CH_2-CH_2OH \xrightarrow[\Delta]{\text{conc.}H_2SO_4} R-CH=CH_2+H_2O$$

C) By Partial Hydrogenation of Alkynes

- Catalyst: **Lindlar's catalyst** → **cis-alkenes**.



- Catalyst: **Na / NH_3 (liq.)** → **trans-alkenes**.



D)From Geminal or Vicinal Dihalides

Reagent: Zn/alcohol or $NaNH_2$.
Reaction: R-CHX-CHX-R' → R-CH=CH-R' + 2HX

2. Physical Properties of Alkenes

State: C_2–C_4 gases; C_5–C_{17} liquids; higher → waxy solids.
Boiling point increases with molecular mass; cis isomers have higher b.p. than trans due to dipole moment.
Insoluble in water (nonpolar), soluble in organic solvents.
Density < 1 (lighter than water).
Lower alkenes have a faint sweet odour.

Saytzeff's Rule (Zaitsev's Rule)

Saytzeff's Rule, also known as Zaitsev's Rule, is an empirical rule formulated by Russian chemist Alexander Zaitsev that predicts the major product in elimination reactions. The rule states that in an elimination reaction, the alkene formed in greatest amount is the one that corresponds to removal of hydrogen from the β-carbon having the fewest hydrogen substituents[1][2]. This results in the formation of the most substituted and thermodynamically stable alkene as the major product

Definition and Statement

The rule can be formally stated as: "When more than one elimination product is possible, the most substituted alkene is formed as the major product" The stability order of alkenes follows: monosubstituted < disubstituted < trisubstituted < tetrasubstituted

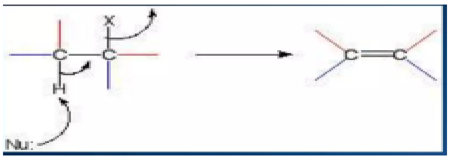
Mechanism of Saytzeff's Rule

Saytzeff's rule applies to both **E1 and E2 elimination mechanisms**

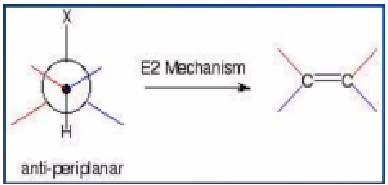
E2 Mechanism (Bimolecular Elimination)

The E2 mechanism involves a **concerted, one-step process** where bond breaking, and formation occur simultaneously

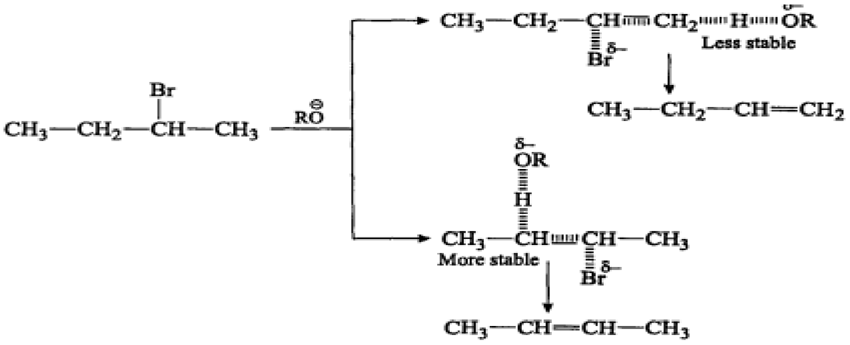
1. **Concerted Process**: A strong base removes a β-hydrogen while the leaving group departs simultaneously



2. **Stereochemical Requirement**: The β-hydrogen and leaving group must be **antiperiplanar** (180° apart) for optimal orbital overlap



3. **Rate Law**: Second-order kinetics: Rate = k[RX][Base]
4. **Product Formation**: The more substituted alkene forms preferentially due to its greater thermodynamic stability. The Transition state has Double bond character which lowers energy and gives stable alkene

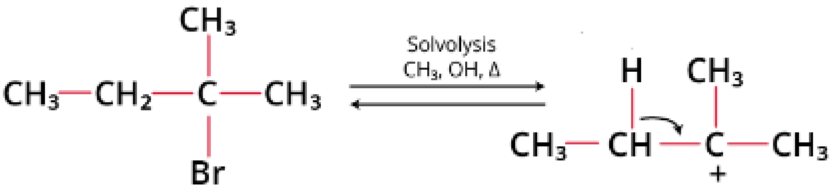


E1

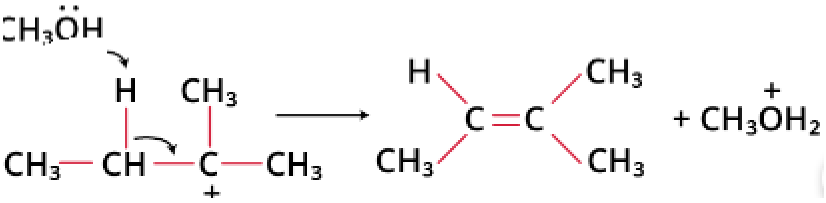
Mechanism (Unimolecular Elimination)

The E1 mechanism follows a **two-step process** involving carbocation formation

1. **Step 1 (Rate-determining)**: Loss of leaving group to form a carbocation intermediate



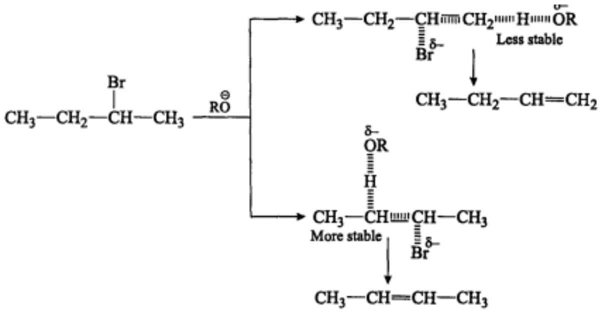
2. **Step 2**: Base removes a β-hydrogen from the carbocation, forming the alkene



3. **Carbocation Stability**: Tertiary > Secondary > Primary carbocations
4. **Rate Law**: First-order kinetics: Rate = k[RX]

Example of Saytzeff's Rule

When **2-bromobutane** undergoes dehydrohalogenation with alcoholic KOH



Major product: 2-butene (disubstituted, more stable)

Minor product: 1-butene (monosubstituted, less stable)

The **2-butene is favoured** because it has two alkyl groups attached to the double bond, making it more substituted and thermodynamically stable

Hofmann's Rule

Hofmann's Rule represents the opposite trend to Zaitsev's rule and applies specifically to elimination reactions involving quaternary ammonium salts The rule states that the major alkene product is the least substituted and least stable product

Definition and Statement

Hofmann's Rule: In eliminations involving quaternary ammonium salts or other bulky leaving groups, **the** least substituted alkene becomes the major product due to steric hindrance effects

Mechanism of Hofmann Elimination

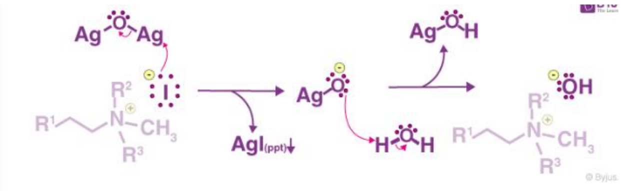
The **Hofmann elimination** (also called **exhaustive methylation**) occurs through a multi-step process

Step 1: Exhaustive Methylation

1. **Primary, secondary, or tertiary amine** reacts with **excess methyl iodide (CH_3I)**
2. **Complete methylation** occurs, forming a **quaternary ammonium iodide salt**
3. **SN2 mechanism**: Each methylation follows nucleophilic substitution

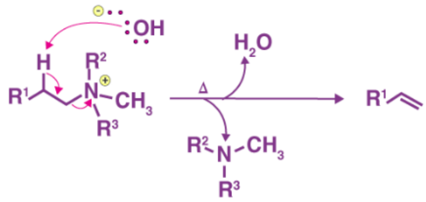
Step 2: Anion Exchange

1. **Silver oxide (Ag_2O)** treatment replaces iodide with hydroxide
2. **AgI precipitates** as an insoluble salt
3. **Quaternary ammonium hydroxide** is formed



Step 3: E2 Elimination

1. **Heating (100-200°C)** initiates the elimination
2. **Hydroxide acts as base**, abstracting β-hydrogen
3. **Trimethylamine (NR_3) leaves** as the leaving group
4. **Antiperiplanar requirement** still applies, but steric effects dominate



Why Hofmann Rule Gives Less Substituted Products

The **steric bulk** of the quaternary ammonium leaving group causes the base to preferentially abstract hydrogens from **less hindered positions**

1. **Steric Hindrance**: The bulky NR_3^+ group creates unfavourable interactions with alkyl substituents
2. **Conformational Effects**: The conformation required for Zaitsev product formation becomes energetically unfavourable
3. **Accessibility**: β-hydrogens on less substituted carbons are more accessible to the base

Example of Hofmann Elimination

Propylamine exhaustive methylation

1. **$CH_3CH_2CH_2NH_2$ + excess CH_3I → $CH_3CH_2CH_2N^+(CH_3)_3I^-$**
2. **Ag_2O/H_2O treatment → $CH_3CH_2CH_2N^+(CH_3)_3OH^-$**
3. **Heat → $CH_2{=}CHCH_3$** (propene) + **$N(CH_3)_3$**

The **propene** (less substituted) forms as the major product rather than a more substituted alternative[22].

Key Differences Between Saytzeff and Hofmann Rules

Aspect	**Saytzeff Rule**	**Hofmann Rule**
Product Preference	Most substituted alkene[25][26]	Least substituted alkene[25][26]
Stability	More stable product[25][3]	Less stable product[25][22]
Leaving Groups	Halides, hydroxyl groups[1][2]	Quaternary ammonium salts[16][17]
Mechanism	E1 and E2 both applicable[3][5]	Primarily E2[17][20]
Driving Force	Thermodynamic stability[2][3]	Steric hindrance effects[18][20]

Exceptions to Saytzeff's Rule

Several important exceptions exist to Zaitsev's rule

1. Bulky Bases

When **bulky bases** like **tert-butoxide** are used with bulky substrates, the **Hofmann product** becomes favored due to steric hindrance

2. Poor Leaving Groups

Fluoride and other poor leaving groups can lead to non-Zaitsev products

3. Conformational Constraints

In **cyclohexane rings**, E2 elimination requires **antiperiplanar geometry**, which may not be available for the most substituted pathway

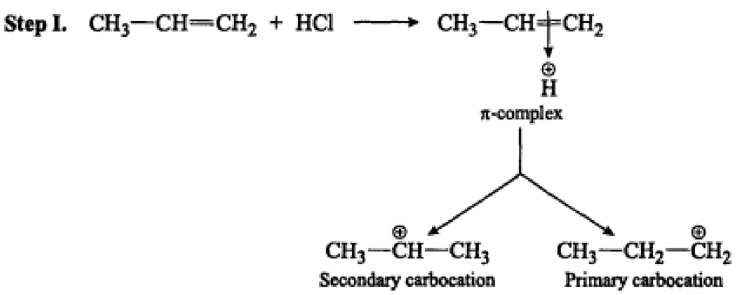
4. Conjugation Effects

When **conjugated systems** can form, they may override the normal substitution preference

Markovnikov's Addition: In the ionic addition of HX to an alkene (no peroxides), the hydrogen attaches to the carbon with more hydrogens, and the halogen attaches to the more substituted carbon. This outcome is controlled by carbocation stability.

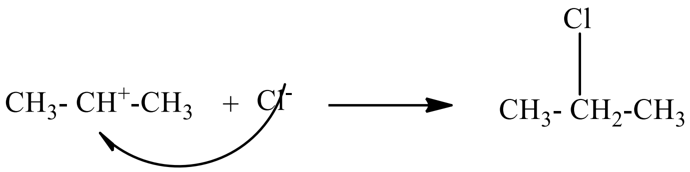
Mechanistic Steps

1. Step 1: Protonation of double bond — π electrons attack H of HCl; bond between H–Cl breaks, generating Cl^-. Intermediate: Carbocation on more substituted carbon.



More Stable

2. Step 2: Nucleophilic attack — Cl⁻ attacks the carbocation, forming the alkyl halide product.



$$CH_3\text{-}CH^+\text{-}CH_3 + Cl^- \longrightarrow CH_3\text{-}\overset{Cl}{C}H_2\text{-}CH_3$$

Reaction Conditions that Favor Markovnikov

- Acidic ionic conditions.
- HX (HCl, HBr, HI) with no peroxides or radical initiators.
- More stable carbocation intermediate determines regiochemistry.
- Hyperconjugation and resonance stabilize carbocations.

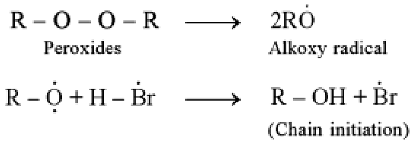
Example Reactions

- CH3CH=CH2 + HBr → CH3CHBrCH3 [HBr, no peroxides]
- CH2=CHCH3 + HCl → CH3CHClCH3 [HCl]
- CH3CH=CHCH3 + HI → CH3CHI–CH2CH3 [HI]

  Anti-Markovnikov's Addition: In the radical addition of HX to an alkene (with peroxides, light, or radical initiators), the regiochemistry is reversed: the halogen attaches to the less substituted carbon. This is due to radical stability controlling the reaction pathway.

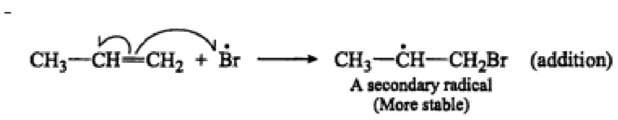
Mechanistic Steps

1. Initiation: Peroxide decomposes into radicals (RO·). RO· abstracts H from HBr to create Br· radical.



   1. Propagation Step 1: Br· radical attacks double bond and new C–Br bond on less substituted carbon; carbon radical forms on more substituted carbon. halogen bonds to less substituted carbon to maximize stability of intermediate radical.

2.



3. Propagation Step 2: Carbon radical abstracts H from HBr and the product is (anti-Markovnikov) + Br· radical regenerated.

$$CH_3-\dot{C}H-CH_2Br+H-Br \longrightarrow CH_3-CH_2-CH_2Br+\dot{B}r$$

(Chain propagation) 1-Bromopropane

4. Termination:

Two radicals combine (minor pathways).

$$\dot{R}+\dot{R}' \longrightarrow R-R'$$

$$\dot{B}r+\dot{B}r \longrightarrow Br_2$$

This was supported by small addition of H_2O_2 can influence a large no of molecules on Alkene and it can be inhibited by addition of Hydroquinone or Diphenyl Amine

Conditions that Favour Anti-Markovnikov

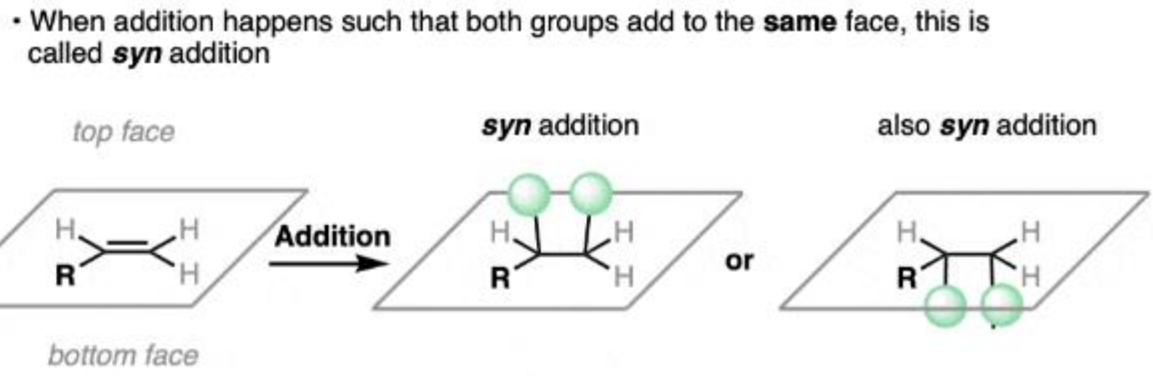
- Presence of peroxides (RO–OR).
- Radical initiators or light (hv).
- radical stability under radical conditions
- The peroxide effect is observed only in addition of HBr but not observed in addition of HCI and H-1.

Example Reactions

- $CH3CH=CH2 + HBr \rightarrow CH3CH2CH2Br$ [HBr, peroxides]
- $CH2=CHCH3 + HBr \rightarrow CH3CH2CH2Br$ [HBr, ROOR]

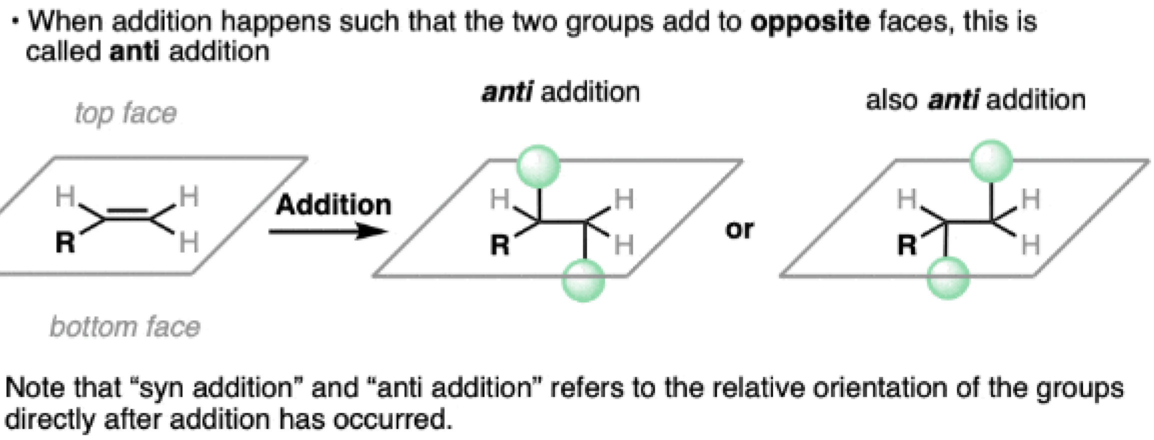
Syn and Anti Addition in Alkenes

Syn Addition: This is an addition reaction where **two groups/atoms are added to the same side (or face) of a double bond** in an alkene. As a result, both substituents are oriented in the same direction in the resulting product



- When addition happens such that both groups add to the **same** face, this is called ***syn*** addition

- **Anti Addition**: Here, **the two groups/atoms are added on opposite sides (or faces) of the double bond**. The substituents end up on different sides, leading to a trans orientation in the product



- When addition happens such that the two groups add to **opposite** faces, this is called **anti** addition

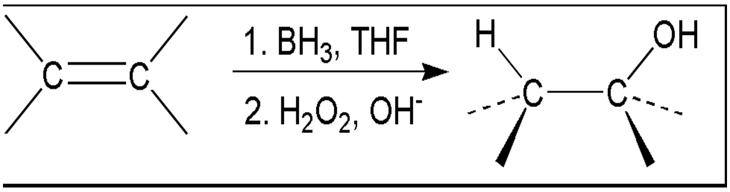
Note that "syn addition" and "anti addition" refers to the relative orientation of the groups directly after addition has occurred.

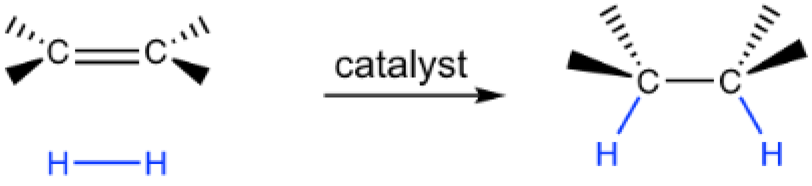
Key Differences

Criteria	Syn Addition	Anti Addition
Definition	Addition to **same side/face** of double bond	Addition to **opposite sides/faces** of double bond
Stereochemistry	Leads to **cis/isomers** or groups together	Leads to **trans/isomers** or groups apart
Common Examples	Hydroboration-oxidation, catalytic hydrogenation, dihydroxylation with OsO_4 or $KMnO_4$[2][3][4][5]	Halogenation (e.g., Br_2), oxymercuration-demercuration, epoxidation then ring opening[2][3][4][6]

Mechanistic Insight & Examples

- **Syn Addition**:
  - Both substituents add from the same side of the π-bond.
  - Examples:
    - **Hydroboration-Oxidation**: Addition of BH_3 followed by oxidation (adds H and OH syn to each other).

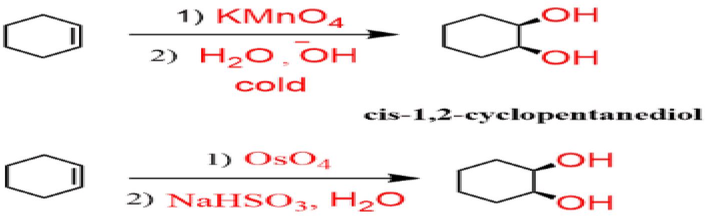




catalytic hydrogenation: syn addition

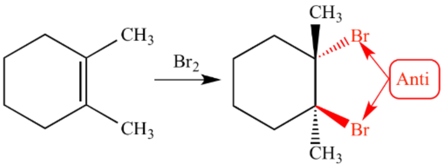
Catalytic Hydrogenation: Addition of H_2 using metal catalysts (Pd, Pt, Ni) — both hydrogens add to the same face.

- **Dihydroxylation**: Using OsO_4 or cold, dilute $KMnO_4$, both OH groups add to the same side.

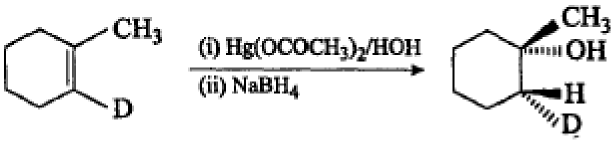


Anti- addition: One group adds from one side of the π-bond, while the other adds from the opposite side. In **anti addition**, the first group blocks one face, so the second must add from the opposite face, causing a trans or anti spatial relationship

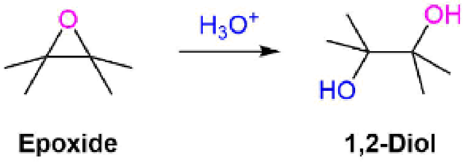
- **Halogenation**: When Br_2 adds to an alkene, a three-membered bromonium ion intermediate is formed; then the Br^- attacks from the opposite side — yielding anti addition and a trans product.



- **Oxymercuration-Demercuration**: Adds OH and Hg(OAc), often in anti fashion.

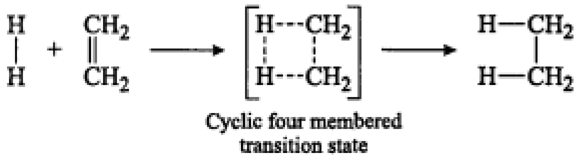


- **Epoxidation followed by Acidic Ring Opening**: Produces trans/anti-diol.

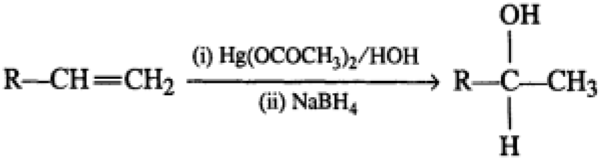


Mechanism

- In **syn addition**, both groups are delivered to the same face of the alkene's plane.

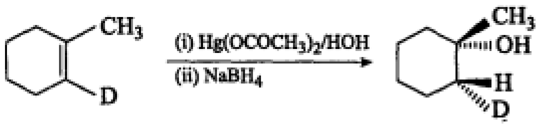


Oxymercuration demercuration: Addition of alkene with mercuric acetate in the presence of water is called oxymercuration reaction. In this case product formation takes place by the formation of bridged carbocation as reaction intermediate. The adduct on reduction with sodium borohydride gives alcohol. This step is known as demercuration, and the overall reaction is also called oxymercuration reduction.

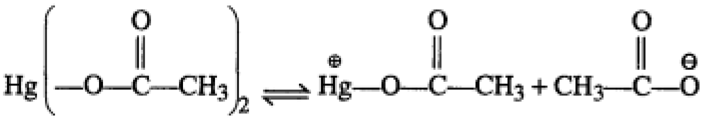


$$R\text{—}CH{=}CH_2 \xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } Hg(OCOCH_3)_2/HOH} R\text{—}\overset{\overset{\large OH}{|}}{\underset{\underset{\large H}{|}}{C}}\text{—}CH_3$$

Experimentally it has been found that the product of the reaction is result of the anti addition reaction.

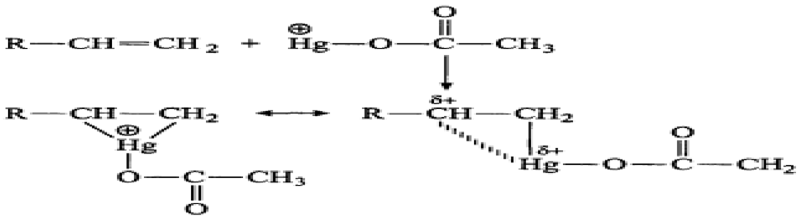


Mechanism:

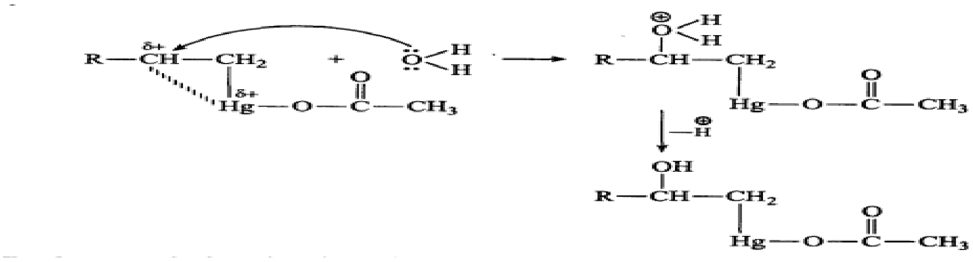


$$Hg\left(\text{—}O\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3\right)_2 \rightleftharpoons \overset{\oplus}{Hg}\text{—}O\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3 + CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\ominus}{O}$$

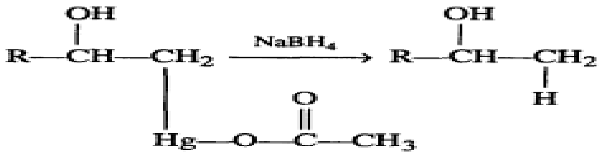
First step:



Second step : In the second step nucleophile attacks on the opposite face of the Hg. Nucleophile will attack on the carbon which has more carbocation character.

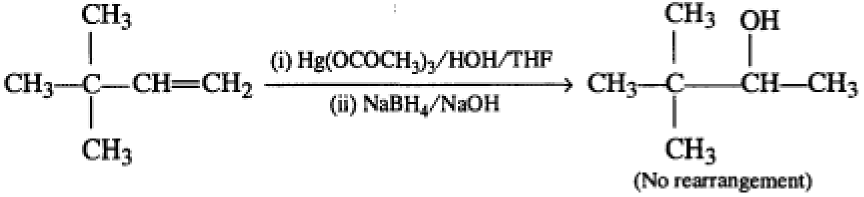


Third step: Sodium borohydride converts carbon-mercury bond into a carbon-hydrogen bond. Because the reaction results in the loss of mercury. it is called demercuration.



In the product both -OH and H are anti to each other.

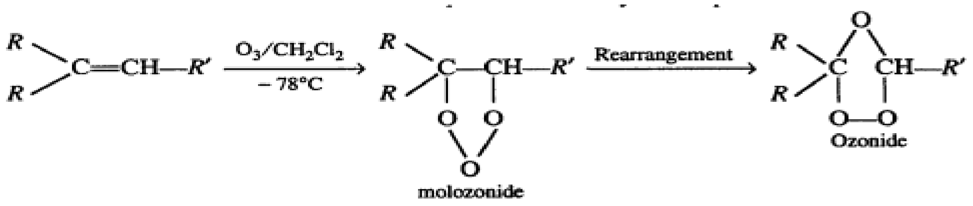
Note 1. Oxymercuration-demercuration allows the Markovnikov addition of -H and -OH without any rearrangement. The net result of the reaction is addition of HOH.



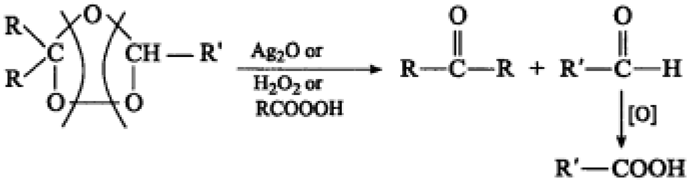
OZONOLYSIS

Ozone undergoes a reaction with olefins in an inert solvent at low temperatures to yield unstable addition compounds called 'ozonides'. These ozonides are not easily isolated and yield carbonyl compounds on further treatment either with boiling water and Zn or zinc and acetic acid.

This overall reaction is called as Ozonolysis.

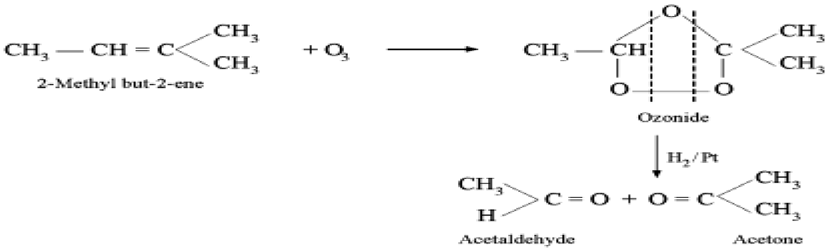


Ozonide converts into carbonyl compound by the addition of reducing agents or oxidizing agents



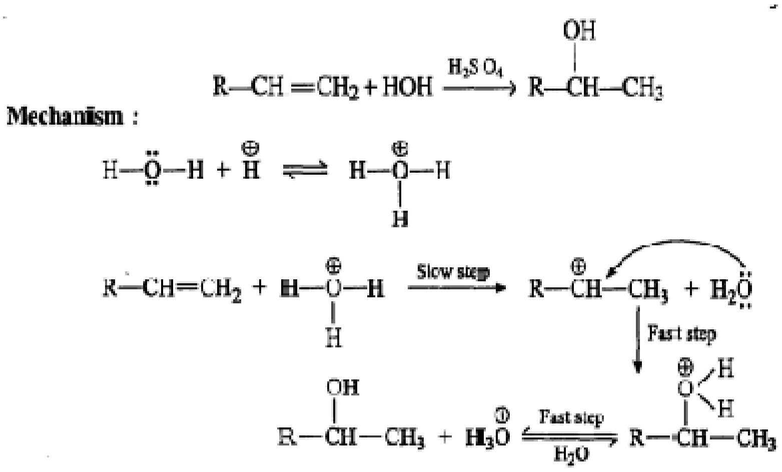
In this sequence of reactions doubly bonded carbon having no hydrogen converts into keto group and doubly bonded carbon having hydrogens converts into aldehydes and further aldehydes oxidized into carboxylic acids

Examples



Hydration of Alkenes : Addition of water

Alkenes give addition reaction with water only in the presence of acid as catalyst. The catalyst of the reaction is sulphuric acid.

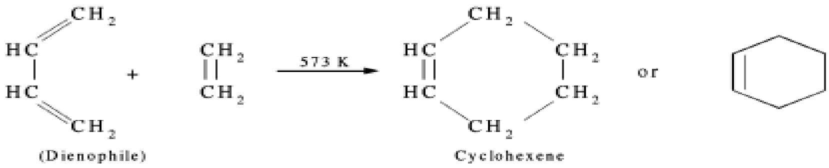


Diels–Alder Reaction

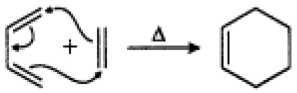
This reaction involves the formation of a six membered ring by the1, 4-addition of an alkene to a conjugated diene. Alkene used in this reaction is generally referred as dienophile and the product formed is called Diels-Alder adduct

Key Features

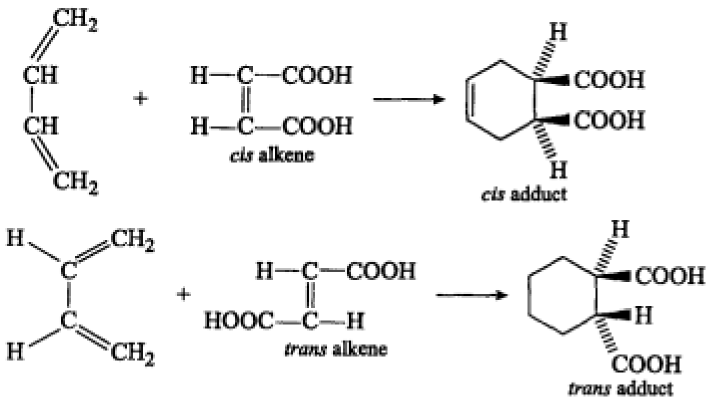
- Type: [4+2] cycloaddition
- Concerted: all bonds form/break in one step
- Pericyclic: cyclic transition state, no intermediates



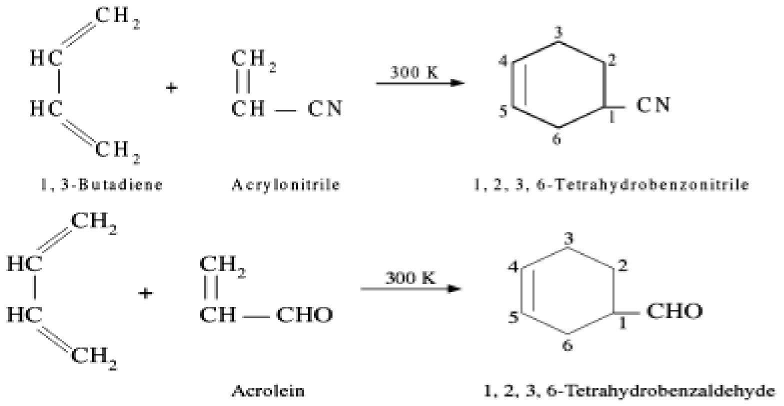
Or



The Diels-Alder reaction is highly stereospecific. The stereochemistry of the diene and dienophile are preserved during adduct formation. This can be seen when cis and trans disubstituted alkenes are used as dienophile



This reaction proceeds faster when the dienophile has electron withdrawing substituents such as -COOH, CHO-NO, and - CN. Thus following reactions take place at low temperatures.



1,2- and1,4-addition reactions in conjugated dienes

1,2-Addition in Alkenes

1,2-addition refers to the addition of a reagent (like HX, H_2, or other electrophiles) to an alkene, where the addition occurs at the **first and second carbon atoms** of the double bond.

- **Mechanism**:
  In 1,2-addition, the double bond of the alkene reacts with the reagent, breaking the pi bond and creating a carbocation intermediate at the more stable position (or the position of least steric hindrance). The electrophile (or nucleophile, depending on the reaction) then attacks the carbocation, leading to the formation of the product.

- **Example**:
  Consider the addition of HBr to but-2-ene:
  $CH_3CH{=}CHCH_3{+}HBr{\rightarrow}CH_3CH_2CHBrCH_3$

  In this case, the HBr adds to the first and second carbons of the double bond, resulting in 1-bromobutane (a 1,2-addition product).

- **Product Structure**:
  The product of a 1,2-addition generally retains the original placement of the substituents on the carbons involved in the double bond. The major product in this case is often the one where the electrophile adds to the carbon of the double bond that forms the more stable carbocation intermediate.

1,4-Addition in Alkenes

1,4-addition, also known as **conjugate addition**, occurs when the reagent adds to the **1st and 4th carbons** of a conjugated system (like a diene or a compound with a conjugated double bond system).

- **Mechanism**:
  In a conjugated diene system (such as buta-1,3-diene), the double bond is shared between two carbon atoms (C1 and C2) and the conjugated system has additional possibilities for electrophilic attack. In **1,4-addition**, the reagent adds to the C1 (where the double bond starts) and the C4 (the terminal carbon of the conjugated system).
- **Example**:
  Consider the addition of HBr to buta-1,3-diene:

  $CH_2{=}CHCH{=}CH_2{+}HBr{\rightarrow}CH2CHBrCH_2CH_3$

  In this case, HBr adds to C1 and C4, leading to **3-bromo-1-butene** (a 1,4-addition product).

- **Product Structure**:
  The 1,4-addition product places the new substituent (e.g., Br) on the terminal carbon of the conjugated diene, which may lead to a more stable product depending on the reaction conditions.

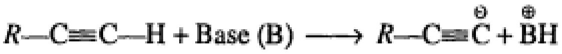
Key Differences Between 1,2- and 1,4-Addition:

1. **Position of Addition**:
   - 1,2-addition occurs directly at the two carbons of the original double bond.
   - 1,4-addition occurs between the first carbon and the fourth carbon of a conjugated system.
2. **Reaction Conditions**:
   - 1,2-addition is typically favoured in conditions where the reaction occurs quickly and with strong electrophiles.
   - 1,4-addition tends to be favoured in conditions with weaker electrophiles or under conditions that stabilize the intermediate anion (e.g., in the presence of a stabilizing solvent or at lower temperatures).
3. **Stability of Products**:

In conjugated systems, 1,4-addition can lead to a more thermodynamically stable product due to conjugation, while 1,2-addition can be a kinetic product

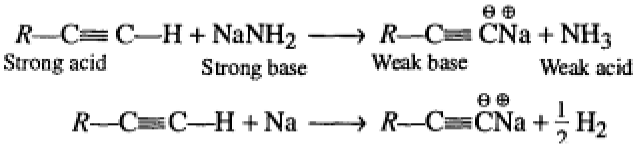
Acidity of Alkynes

The hydrogens in terminal alkynes are relatively acidic because they readily donate proton to strong bases.



$$R-C\equiv C-H + \text{Base (B)} \longrightarrow R-C\equiv\overset{\ominus}{C} + \overset{\oplus}{B}H$$

When terminal alkynes are treated with sodarnide in liquid ammonia or passed over molten sodium they convert into the corresponding carbanions.



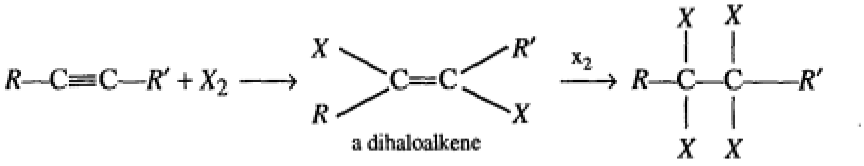
$$\underset{\text{Strong acid}}{R-C\equiv C-H} + \underset{\text{Strong base}}{NaNH_2} \longrightarrow \underset{\text{Weak base}}{R-C\equiv\overset{\ominus\,\oplus}{CNa}} + \underset{\text{Weak acid}}{NH_3}$$

$$R-C\equiv C-H + Na \longrightarrow R-C\equiv\overset{\ominus\,\oplus}{CNa} + \frac{1}{2}H_2$$

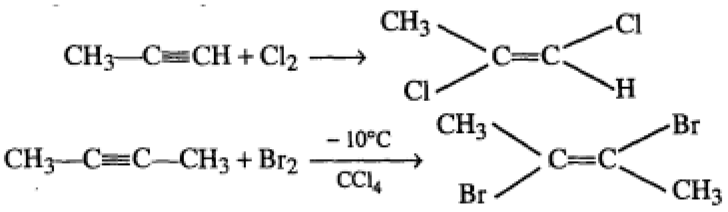
The above two reactions suggest the acidic character of hydrogen in l-alkynes.
Carbon atoms in l-alkynes are sp hybridized, hence have more s character than in
As s electrons are closer to the nucleus than p electrons, s orbitals are more electronegative than p orbitals Therefore, increasing the s character of a hybrid orbital makes the orbital more electronegative and hence they are acidic

ALKYNES ELECTROPHILIC ADDITION REACTIONS

Alkynes undergo addition reactions with 2 molecules of chlorine or bromine

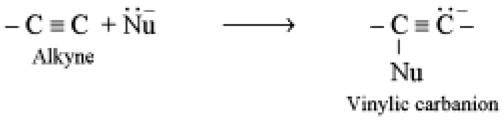


A dihaloalkene is an intermediate in this reaction dihaloalkenes can be prepared by adding calculated amount of halogen (1 mole) to the alkyne at low temperatures. This addition of halogen to an alkyne is predominately an anti-addition.



ALKYNES NUCLEOPHILIC ADDITION REACTIONS

Alkynes undergo nucleophilic addition reactions because of the greater stability of the resulting carbanion is more stable formed by the attack of nucleophile . Since the rate determining step involves the formation of vinylic (Sp^2) carbanion

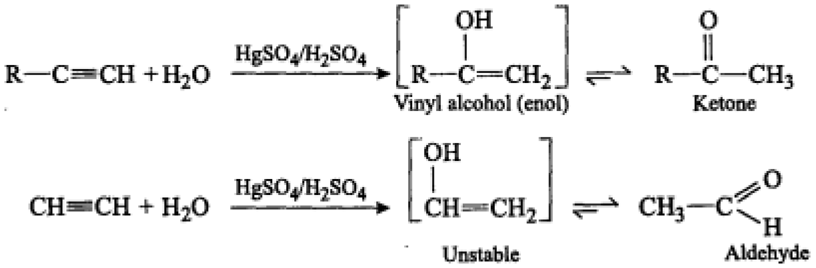


HYDRATION TO FORM CARBONYL COMPOUNDS

Hg metal ions form some sort of complex with alkyne by coordinating with the electrons of the pie (n) bonds This complex formation decreases the electron density around the triply bonded carbon atoms and thus helps in the attack by the nucleophilic reagent

$$-\overset{}{\underset{|}{C}}\equiv\underset{|}{C}- + Hg^{2+} \longrightarrow -C\equiv\underset{\underset{Hg^{2+}}{\downarrow}}{C}-$$

Water adds to carbon-carbon triple bond in the presence of mercuric sulphate and sulphuric acid to form a vinyl alcohol (enol) which readily tautomerizes to the corresponding carbonyl compound. the addition follows Markovnikov rule



Important Questions (Long Answer)

1. Describe the mechanism of electrophilic addition in alkenes, focusing on the Markovnikov's and Anti-Markovnikov's additions.
2. Discuss the Saytzeff and Hoffmann eliminations with suitable examples.
3. Explain the mechanism and importance of ozonolysis in alkenes.
4. Discuss the reactions of alkynes, including their acidity, electrophilic additions, and nucleophilic additions.
5. Explain the Diels-Alder reaction with mechanisms and its significance in organic synthesis.

Important Questions (Short Answer)

1. What is the mechanism of electrophilic addition in alkenes?
2. Write a note on the hydration of alkynes to form carbonyl compounds.
3. Describe the process of syn and anti-addition in alkenes.
4. What is the significance of ozonolysis in organic chemistry?
5. Explain the 1,2- and 1,4-addition reactions in conjugated dienes.