## HYDROCARBONS

## ALKENE

#### INTRODUCTION

Alkenes are hydrocarbons with carbon-carbon double bonds, Alkenes are sometimes called **olefins**, a term derived from olefiant gas, meaning 'oil forming gas'. Alkenes are among the most important industrial compounds and many alkenes are also found in plants and many alkenes are also found in plants and animals. Ethylene is the largest-volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals. Alkenes polymeries to give many important polymers.

#### Structure and bonding in Alkenes

- (a) Alkenes are unsaturated hydrocarbons having at least one double bond.
- (b) They are represented by general formula (G.F.)  $C_nH_{2n}$  (one double bond)
- (c) In Ethene C = C bonds length is 1.34 Å
- (d) Its bond energy is 146 kcal.  $mol^{-1}$
- (e) The hybridization of (C = C) alchemic carbon is sp<sup>2</sup>
- (f) The  $\pi$  e<sup>-</sup> cloud is present above and below the plane of s-bonded skeleton.
- (g) They are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.
- (h) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes



**Note:** That angle a < b since repulsion due to  $\pi$  electrons (double bond - single bond repulsion < single bond - single bond repulsion according to VSEPR theory.

Table – 1				
Sr. No.	Compound	Name	Туре	
1.	$(CH_3)_2C = CH_2$	2-Methylpropane	Alkene	
2.	$CH_3-CH = CH - CH_2 - CH = CH_2$	Hexa-1, 4-diene	Isolated diene	
3.	$CH_2 = CH - CH = CH_2$	Buta-1, 3-diene	Conjugated diene	
4.	$CH_3 - CH = C = CH - CH_3$	Penta-2, 3-diene	Cumulated diene	
5.	$ \begin{array}{c} Cl \\ 1 & 2 & 3 \\ CH_3 - CH_2 - CH = CH - CH_2 - CH - CH_3 \end{array} $	6-Chlorohept-3-ene	Alkene	
6.	$ \overset{1}{C} \overset{2}{H}_{2} = \overset{2}{C} \overset{3}{H} - \overset{3}{C} \overset{4}{H} = \overset{5}{C} - \overset{5}{C} \overset{4}{H}_{3} $	4-methoxypenta-1, 3-diene	Conjugated diene	
7.		3-Ethynylpenta-1, 4- diene	Isolated diene	
8.	$\begin{array}{c} CH_{3}C_{2}H_{5} \\ 6 \\ CH_{3} - CH_{2} - C = C - CH_{2} - CH_{3} \end{array}$	3-Ethyl-4-methylhex- 3-ene	Alkene	
9.	$6$ $5$ $4$ $CH_3$ $CH_3$	2, 3- Dimethylcyclohex-1- ene	Cycloalkene	
10.	CH <sub>2</sub> =C=CH <sub>2</sub>	Propidine	Cumulated diene	
11.	$CH_2=C=O$	Ethenone	Alkene	
12.		Methylene cyclopentane	Alkene	
13.		Cyclopentolate	Alkene	



### **ISOMERISM IN ALKENES**

Alkenes show chain, Ring or functional, Position, Geometrical isomerism and optical isomerism.

### METHOD OF PREPARATION

### (I) By Elimination Reaction

### E-1 Mechanism

- (a) It is called unimolecular elimination reaction
- (b) It takes place in two steps.

I<sup>st</sup> Step: Departure of leaving group from a molecule to form carbocation.



II<sup>nd</sup> Step: Carbocation formed above loses a proton to the base and forms the

$$- \begin{matrix} \mathsf{I} \\ \mathsf{C} \\ \mathsf{C} \end{matrix} - \begin{matrix} \mathsf{C} \\ \mathsf{C} \\ \mathsf{C} \end{matrix} = \begin{matrix} \mathsf{C} \\ \mathsf{Fast} \end{matrix} \qquad \mathbf{C} = \mathbf{C} \end{matrix}$$

alkene.

- (c) **I**<sup>st</sup> step of E-1 mechanism is the rate determining step (R.D.S.)
- (d) Since in R.D.S. only substrate undergoes covalency change i.e., it follows first order kinetics with respect to substrate
   Rate = K [substrate]

### Chemistry

- (e) Since in R.D.S. carbocation is formed as an intermediate to the reactivity order of different substrate follows the stability of order of carbocation formed. Allylic > Tertiary > Secondary > Primary
- (f) Loss of leaving group is the part of R.D.S. therefore the order of reactivity of alkyl halide in elimination reaction is

$$R-I > R - Br > R - CI > R - F$$

Above order is parallel to order of leaving group ability

$$I^{\Theta} > Br^{\Theta} > CI^{\Theta} > F^{\Theta}$$

- (g) E-1 mechanism does not show isotopic effect as the loss of hydrogen is not the part of R.D.S.  $\frac{K_{\rm H}}{K_{\rm D}} = 1$
- (h) Since the ionization take place in step I. Therefore, polar solvent favors the E-1 mechanism.
- E-1 mechanism involves carbocation as an intermediate so rearrangement of carbocation can take place if possible. More stable carbocation forms the major product in the reaction.

### E-2 Mechanism

- (a) It is known as bimolecular elimination mechanism.
- (b) It takes place in single step.
- (c) It involves the formation of transition state



**Transition State** 

- (d) Formation of transition state is the rate determination step.
- (e) Ratre of reacting depends on the concentration of substrate as well as of base **i.e.**, it follows the second-order kinetics.

R = [Substrate] [Base]

(f) E-2 mechanism shows the isotopic effect as the loss of hydrogen is a part of R.D.S.

$$\frac{K_{\rm H}}{K_{\rm D}} = \frac{7}{1}$$

- (g) E-2 mechanism shows the halogen effect as loss of leaving group is a part of R.D.S.
- ∴ Reactivity of different alkyl halides follows the sequence Reactivity order of different substrate follows

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

- (h) The rate of reaction increases with increasing strength and concentration of the base.
- (i) Non-polar solvent favors the E-2 mechanism.
- (j) Since E-2 mechanism involves the transition state rearrangement is not possible.

### E 1 CB Mechanism

- (a) In this mechanism, the reaction take place in two steps.
  - (i) The first step involves rapid removal of a proton from the  $\alpha$ -carbon (carbon adjacent to the carbon bearing halogen atom) forming a carbanion.
  - (ii) The carbanion formed then loses the halides ion in the second-rate determining step.

- (b) The overall rate of the reaction is limited to slower second step & hence the rate of reaction depends only on the concentration of carbanion.
- (c) Since carbanion is the conjugate base of the alkyl halide and rate of reaction depends on concentrating of carbanion hence the mechanism is designated as E1cB mechanism.

#### Mechanism of $\alpha$ -Eliminating

 $\alpha$ -elimination does not occur frequently and completes in two stages, the second of which is rate determining.

for eq.

$$CHCl_{3} + OH^{-} \xrightarrow{Fast} CCl_{3} + H_{2}O$$

$$\stackrel{\Theta}{\longrightarrow} : CCl_{2} + Cl^{-}$$
Di chlorocarbon

Another example of  $\alpha$ -elimination of reaction's formation of diphenylacetylene from 2, 2-diphenyl vinyl bromide and soda lime.

#### Class-XI



Mechanism



# (II) HYDROGENATION OF ALKYNE

### By partial reduction of Alkynes

- (a) By catalytic Hydrogenation of Alkynes in presence of poisoned catalyst (A) Syn Addition of Hydrogen Synthesis of cis-Alkenes: This is performed by
  - (i) **Landlar's catalyst:** Metallic palladium deposited on calcium carbonate conditioned with lead acetate and quinoline.
  - (ii) P-2 catalyst (Ni<sub>2</sub>B nickel boride)

### **General reaction**

$$R - C \equiv C - R \qquad \frac{(\text{Lindlar's catalyst})}{\text{quinoline}} \qquad R = C = C + H$$

### Mechanism of hydrogenation



**Steps:** The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorpti0on.) It this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply boned carbon atoms from the same side of  $\pi$  bond and a **cis or syn addition product** is formed. The product alkene now escapes away from the surface of the catalyst. Quinoline occupies the metal surface in hiding further

#### Chemistry

reduction to alkanes **Quinoline** therefore is called catalyst poison and such palladium is called deactivated catalyst or poisoned catalyst.

Ex.

$$CH_{3}CH_{2}C \equiv CCH_{2}CH_{3} \xrightarrow{H_{2}/Ni_{2}B(P_{2}) \text{ or } H_{2}/Pd/CaCO_{3}}_{\text{(syn addition)}} \xrightarrow{CH_{3}CH_{2}}_{H} \xrightarrow{C=C}_{H} \xrightarrow{CH_{2}CH_{3}CH_{3}}_{H}$$

$$(Z)-3-Hexene$$

$$(97\%)$$

(b) Birch Reduction: (Anti addition of hydrogen: synthesis of trans-alkenes)

$$R-C \equiv C-R \quad \frac{Na/Li}{Liq.NH_3} \quad \stackrel{R}{H} C = C \stackrel{H}{R}$$

**General reaction** 

**Mechanism**: Reagents Na (or Li, K) + liq NH<sub>3</sub>  $\rightarrow$  Na<sup>+</sup> + e<sup>-</sup> (solvated electron)



**Note**: This process of reduction is not eligible when terminal alkynes are taken (R−C=CH) because terminal alkynes form sodium salt with Na metal.

#### Chemistry









Sol. H<sub>2</sub>/Landlar's catalyst A $\frac{H}{Lindlar's catalyst}$  cis – Jasmone





### (III) FROM ALKYL HALIDES

**FROM MONO HALIDES:** When mono halide reacts with alcoholic KOH or NaOH then respective alkenes are formed



This is in accordance with the say Zeff rule.

#### Class-XI

**Mechanism**:  $E_2$  and  $E_1$  are possible.

E<sub>2</sub> Mechanism

![](_page_8_Figure_4.jpeg)

As molecularity of slowest step is two i.e.,  $E_2$  mechanism.

E<sub>1</sub> Mechanism

$$\begin{array}{cccc} CH_2 - H & CH_2 - H \\ | \\ CH_3 - C - Cl & -\frac{-Cl}{slow} & CH_3 - C + & -\frac{Fast}{-H^+} & CH_3 - C \\ | \\ CH_3 & CH_3 & CH_3 & CH_3 \end{array}$$

As molecularity of slowest step in one. That is why it is termed as  $E_1$ .

**Remember**: Possibility of E<sub>1</sub> increases with increasing stability of carbo cation.

Similarly, possibility of E<sub>2</sub>

increases with decreasing stability of expected carbocation.

#### **From Dihalides**

#### From vicinal dihalides

When vicinal dihalides are heated with Zn dust, alkene of same no. of carbon is obtained.

**From gem dihalides:** When gem dihalides is heated with Na in ether then higher alkenes are formed.

$$\begin{array}{l} \text{R-CH.X}_2 + 2\text{Zn} & \xrightarrow{\Delta} & \text{R-CH} = \text{CH} - \text{R} \\ \text{CH}_3 - \text{CHCl}_2 + 2\text{Zn} & \xrightarrow{-2 \text{ZnCl}_2} & \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \\ & 2 - \text{butene} \end{array}$$

**Conclusion** – If we take two different types of gems dihalides then we obtain three different types of alkenes.

Note: The above react in is used in the formation of symmetrical alkenes only because if we take two different types of halides then mixture of alkenes is obtained so the yield of are individual alkene is reduced and is improper to separate each alkene from the mixture because the difference of boiling points in alkenes is very less.

#### FROM ALCOHOLS: (IV)

Alkenes can be prepared from monohydric alcohols or alkanols by the loss of H<sub>2</sub>O and the reaction is known as **dehydration reaction**.

$$\begin{array}{cccc} |\beta & |\alpha & & | & | \\ -C & -C & - & -C = C & + & H_2O \\ | & | & | & H \\ H & H \\ Alcohol & & Alkene \end{array}$$

The dehydration can be carried with Al<sub>2</sub>O<sub>3</sub> or with mineral acid upon heating.

(a) Dehydration with Al<sub>2</sub>O<sub>3</sub>: Ethene is prepared by heating ethanol with Al<sub>2</sub>O<sub>3</sub> at 620 K.

$$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{OH} & \frac{Al_2O_3}{620 \text{ K}} & \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O} \\ \text{Ethanol} & \text{Ethene} \end{array}$$

(b) Dehydration with mineral acid: Alcohols upon heating with conc. H<sub>2</sub>SO<sub>4</sub> form alkenes and the reaction is called acidic dehydration.

> 95%H<sub>2</sub>SO<sub>4</sub> CH<sub>3</sub>-CH<sub>2</sub>-OH  $CH_2 = CH_2 + H_2O$ Ethanol Ethene

OH  $CH_3 - CH - CH_3 = \frac{60\% H_2 SO_4}{373 K}$  $CH_3 - CH = CH_2 + H_2O$ Propene

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Propan-2-ol
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$$\begin{array}{c} CH_{3} \\ CH_{3}-C-CH_{3} \\ 0H \\ 2-Methylpropan-2-ol \end{array} \xrightarrow{\begin{array}{c} CH_{3} \\ 30\% H_{2}SO_{4} \\ 363 K \\ 2-Methylpropan-2-ol \end{array}} CH_{3} \\ CH_{3}-C = CH_{2} + H_{2}O \\ 2-Methylpropene \\ 2-Methylpropene \\ \end{array}$$

From the above reactions, it is clear that the order of acidic dehydration in different alcohols is

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Tertiary > Secondary > Primary
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Cycloalkenes can be prepared in the same way be the dehydration of cycloalkanols.

![](_page_10_Figure_0.jpeg)

![](_page_10_Figure_2.jpeg)

Regioselectivity of  $\beta$  elimination is governed by Zaitsev's Rule.

**Mechanism of Reaction:** The acidic dehydration of alcohol proceeds through the formation of a carbocation intermediate and is explained as follows:

**Step - I**: Alcohol being a Lewis base accepts a proton (H<sup>+</sup>) from the acid in a reversible step as follows.

$$CH_3 - CH_2 - \overset{\bigoplus}{O} - H + \overset{\bigoplus}{H} \Rightarrow CH_3 - CH_2 - \overset{\bigoplus}{O} - H$$
  
Ethanol (From acid)  
Protonated ethanol

Step - II: Due to presence of positive change on electronegative oxygen, its electron accepting tendency increases. As a result, C – O bond becomes weak and cleaves as follows:

$$CH_3 - CH_2 \xrightarrow{\frown} O - H \xrightarrow{Slow} CH_3 - CH_2 + H_2O$$
  
H Ethyl carbocation

This is a slow and is regarded as rate determining step.

**Step - III**: Carbocation is unstable in nature and loses a H<sup>+</sup> and changes into ethane in a fast step as follows:

$$H - CH_2 - \overset{\oplus}{C}H_2 \xrightarrow{Fast} CH_2 = CH_2 + H^+$$

**Note:** Dehydration of secondary and tart alcohol is best carried out by using dil. H<sub>2</sub>SO<sub>4</sub>. Since alkenes produced from those alcohols have a tendency to form polymers under the influence of concentrated acid.

#### Chemistry

**Say Zeff Rule**: When two possible alkenes are obtained by the elimination reaction than that alkene will be in good yield, containing maximum number of alkyl group on double bonded C-atoms.

$\begin{array}{c} OH\\ I\\ CH_3 - CH_2 - CH - CH_3 \end{array}  \frac{H_2 SO_2}{\Delta}$	<sup>4</sup> CH <sub>3</sub> − Cl	$H = CH - CH_3 + CH_3$	$_{3}$ -CH <sub>2</sub> – CH = CH <sub>2</sub>
2-butanol	Main 2-but	Product ene 80%	l-butene 20%
CH <sub>3</sub> – CH <sub>2</sub> – CH <sub>2</sub> – CH <sub>2</sub> -OH	$\xrightarrow{H_2SO_4}$	$CH_3 - CH = CH -$	$CH_3 + CH_3CH_2CH = CH_2$
1-butanol		2-butene 80% Main product	1-butene 20%

**Mechanism**: Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.

#### Characteristic of dehydration of alcohol

(1) Since the carbocation is formed s an intermediate in the R.D.S. of dehydration of alcohol The relative reactivity of alcohols decreases in the order.

Tertiary > Secondary > Primary

(2) Since the R.D.S. is reversible it is necessary to remove the  $H_2O$  molecule produced in the reaction.

Therefore, in experimented condition conc.  $H_2SO_4$  is added in a regular interval.

- (3) For dehydration, different dehydrating agent like Al<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub> ca also be employed.
- (4) Rearrangement of carbocation can take place.
- (5) -OH, is not a good leaving group. in alcohols so turn it into a good leaving group, it is converted into H<sub>2</sub>O by protonation.
- (6)  $H_2O$  is a good leaving group.

### Rearrangement in Alcohol Dehydration

- (1) Some alcohols undergo dehydration to form alkene having carbon selector different from those of the straight alcohol.
- (2) This is due to rearrangement of carbocation formed in the reaction to more stable carbocation.

$$\begin{array}{c} CH_{3} \\ CH_{3} - C - CH - CH_{3} \\ I \\ CH_{3} OH \end{array} \xrightarrow{H_{2}SO_{4}} CH_{3} - C - CH = CH_{2} \\ I \\ CH_{3} \\ CH_{3} \\ (3\%) \end{array} \xrightarrow{H_{3}C} C = CH_{3} \\ H_{3}C \\ CH_{3} \\ H_{3}C \\ CH_{3} \\ H_{3}C \\ CH_{3} \\ H_{3}C \\ CH_{3} \\ CH_{3} \\ (3\%) \end{array} \xrightarrow{CH_{3}} (64\%) \xrightarrow{H_{3}C} C - C - CH_{3} \\ H_{3}C \\ H_{3}C \\ CH_{3} \\ CH_{3} \\ (3\%) \end{array}$$

- (3) An example of alcohol dehydration that is accompanied by rearrangement is.
- (4) Percent yield of alkenes formed from rearranged carbocation is greater than the percent yield of alkene obtained from unrearranged carbocation.
- (5) Rearrangement of carbocation can also lead to a change in ring size, as the following example shows

![](_page_12_Figure_13.jpeg)

### Regioselectivity in alcohol dehydration

- 1. In alcohols such as 2-methyl-2-butanol, dehydration can occur in two different directions to give alkenes that are constitution isomers.
- 2. More substituted alkene forms the major product and is called Say Zeff alkene or Zaitsev alkene.
- 3. Less substituted forms the minor product and is called Hofmann's alkene.

$$\begin{array}{c} \begin{array}{c} OH\\ CH_3 - C - CH_2 - CH_3 \end{array} \xrightarrow{H_2 SO_4} \\ CH_3 \end{array} \qquad CH_2 = CH_2 = C \xrightarrow{CH_2 CH_3} \\ \begin{array}{c} H_3 C \end{array} \xrightarrow{H_3 C} \\ CH_3 \end{array} \xrightarrow{H_2 SO_4} \\ CH_2 = CH_2 = C \xrightarrow{CH_2 CH_3} \\ \begin{array}{c} H_3 C \end{array} \xrightarrow{H_3 C} \\ CH_3 \end{array} \xrightarrow{H_2 SO_4} \\ CH_3 \end{array} \qquad CH_2 = CH_2 = C \xrightarrow{CH_2 CH_3} \\ \begin{array}{c} H_3 C \end{array} \xrightarrow{H_3 C} \\ CH_3 \end{array} \xrightarrow{H_3 C} \\ CH_3 \end{array} \xrightarrow{H_2 SO_4} \\ CH_3 \end{array} \xrightarrow{H_2 SO_4} \\ CH_3 \xrightarrow{H_3 SO_4$$

#### Class-XI

### (V) FROM ESTERS

When esters are heated in presence of liq.  $N_2$  and glass wool, then alkyl part of ester converts into respective alkene while alkenoate part of ester is converted into respective acid.

 $\begin{array}{c} CH_3-CO-O & H\\ | & |\\ CH_2-CH_2 \end{array} \quad \frac{Glass \ wool \ 450^\circ}{liq. \ N_3} \quad CH_3-COOH+CH_2=CH_2 \end{array}$ 

The reaction is called as 'Pyrolysis of Ester.'

**Mechanism**: Pyrolysis of Ester is a type of  $E_1$  elimination which proceed via cyclic T.S. that is why the product becomes 'cis.

It is interesting to note that, in this case major produce is 1-alkene in the comparison to 2-alkene.

Major product is obtained by removal of –H from less hindered carbon.

#### (VI) KOLBE'S SYNTHESIS

When aqueous solution of K or Na succinate is electrolysed, ethylene is released at anode.

Class-XI

At Anode

![](_page_14_Figure_3.jpeg)

At Cathode

 $2K^{+} + 2e^{-} \longrightarrow 2K$  $2K + 2H_{2}O \longrightarrow 2KOH + H_{2}$ 

Note: If we use methyl succinic acid as reactant then propylene is formed.

(VII) FROM QUATERNARY AMMONIUM HYDROXIDE

$$CH_{3} \xrightarrow[CH_{3}]{\oplus} -CH_{2} \xrightarrow[CH_{2}]{\oplus} CH_{2} \xrightarrow[OH]{OH} CH_{3} -N + CH_{2} = CH_{2} + H_{2}O$$

Ex.

$$\begin{array}{c} \begin{array}{c} CH_{3} \\ H_{3}-N^{\oplus}-CH-CH_{2}-CH_{3} \\ H_{3}-N^{\oplus}-CH-CH_{2}-CH_{3} \\ H_{3}-H_{2}O \end{array} \xrightarrow{\circ} \begin{array}{c} OH \\ -H_{2}O \end{array} \xrightarrow{\circ} \begin{array}{c} CH_{3}-N^{\oplus}-CH-CH_{2}-CH_{3} \rightarrow CH-CH_{2}CH_{3} \\ CH_{3}-C^{\oplus}H_{2} \\ H_{2} \\ CH_{2} \\ H_{2} \\ CH_{2} \\ H_{2} \\ CH_{2} \\ H_{2} \\ CH_{3} \\ CH$$

CH<sub>3</sub>

Ex.  $\begin{array}{c} \underset{l}{\overset{H}{\overset{\Theta}}} CH_{3} \\ CH_{3} - \underset{l}{\overset{H}{\overset{\Theta}}} CH_{2} - CH_{2} - CH_{2} - CH_{3} \\ \overset{H}{\overset{\Theta}} \\ CH_{2} \end{array} \xrightarrow{\begin{array}{c} \Theta \\ -H_{2} - CH_{3} \end{array}} \xrightarrow{\begin{array}{c} \Theta \\ -OH \\ -H_{2} O \end{array}} \xrightarrow{\begin{array}{c} \Theta \\ -H_{2} - OH \\ -H_{2} O \end{array}} \xrightarrow{\begin{array}{c} CH_{2} = CH_{2} - CH_{3}(minor) \\ CH_{2} = CH_{3}(major) \end{array}$ 

- (a) In this reaction  $\beta$ -hydrogen of tetra-alkyl ammonium ion is attached by a base and alkene is formed.
- (b) In this reaction intermediate is carbanion. So, yield of product depends on stability of carbanion.
- (c) In this reaction Hoffmann's Rule is followed.

### (VIII) THE COPE ELIMINATION

Tertiary amine oxide undergoes the elimination of a dialkylhydroxylamine when they heated. This reaction is called the Cope elimination. **Reaction:** 

Mechanism:

$$CH_{3} - CH_{2} - N - CH_{3}$$

$$CH_{3} - CH_{3} - CH_{3}$$

$$CH_{3} - CH_{3} - CH_{3}$$

$$CH_{3} - CH_{2} + N - CH_{3}$$

$$CH_{3} - CH_{2} + N - CH_{3}$$

### (IX) WITTING REACTION

The aldehydes and ketones are converted into alkenes by using a special class of compounds called phosphorus ylides, also called Witting reagents.

The Triphenyl group of phosphorane has a strong tendency to pull oxygen atom of the aldehyde or ketone via a cyclic transition state forming an alkene.

(R, R', R'' and R''' may be hydrogen or any alkyl group)

Ex.

 $\begin{array}{c} PH_{3}P:+CH_{3}\text{-}Br \longrightarrow [Ph_{3}P^{\oplus}\text{-}CH_{3}]\overset{\ominus}{Br} & \xrightarrow{Bu-Li} [Ph_{3}P^{\oplus}\text{-}\ddot{C}H_{2}] & \xrightarrow{Me} \\ Me & \xrightarrow{C=o} & Ph_{3}P=O+ & Me \\ Me & & Ylide & Product alkene \end{array}$ 

#### PHYSICAL PROPERTIES OF ALKENES / HYDROCARBON

S.No.	Physical properties	Homologues series	Isomers
1.	Physical state	C <sub>1</sub> – C <sub>3</sub> gases	
		C <sub>4</sub> – C <sub>20</sub> liquids	
		> C <sub>20</sub> : solids	
2.	Dipole moment ( $\mu$ )	-	cis > trans

#### Chemistry

3.	Polarity	-	cis > trans (Fro C <sub>ab</sub> =
			C <sub>ab</sub> type of alkenes)
4.	Melting point	increases with M.W.	trans > cis (due to
			more packing capacity)
5.	Boiling point	increases with M.W.	cis > trans #
			branching decreases
			B.P.
			C
			C-C=C <c-c=c-c< td=""></c-c=c-c<>
			Polarity increases,
			boiling point increases
6.	Solubility	Practically	cis > trans Polarity
		insoluble	increases, solubility in
		in water but fairly	polar solvents
		soluble in nonpolar	increases.
		solvents like	
		benzene petroleum	
		ether, etc.	
7.	Stability Waals		trans > cis (cis
			isomers has more
			Vander repulsion)

### **CHEMICAL PROPERTIES OF ALKENES**

Alkenes are more reactive than alkane this is because -

- (a) The  $\pi$  electrons of double bond are located much far from the carbon nuclei and are thus less firmly bound to them.
- (b)  $\pi$  bond is weaker than  $\sigma$  bond and more easily broken.

The reactivity order for alkenes -

 $CH_2 = CH_2 > R - CH = CH_2 > R_2C = CH_2 \approx RCH = CHR > R_2C = CR_2$ 

### (Trans < Cis)

The reactivity order of alkenes has been delt in terms of heat of hydrogenation of alkene, more is the heat of hydrogenation ( $\Delta H = -ve$ ), more is the reactivity, the reactivity of alkene is however also related to

(i) Steric hinderence

(ii) Hyperconjugation

(iii)Heat of Combustion.

All four butanes may be compared, since all give the same products on combustion viz.

$$4CO_2 + 4H_2O$$

#### Chemistry

#### Alkenes give the following type of reactions:

- (1) Addition reaction
- (2) Oxidation reaction
- (3) Ozonolysis
- (4) Substitution reaction
- (5) Polymerization Reaction
- (6) Isomerisation

#### (1) Addition Reaction

### (a) REACTION WITH HYDROGEN -

![](_page_17_Figure_11.jpeg)

**Mechanism:** The reaction takes place at the surface of Ni; therefore, the addition is cis addition.

Ex.

![](_page_17_Figure_14.jpeg)

![](_page_18_Figure_2.jpeg)

#### Reduction of alkene via hydroboration

(i) Alkene can be converted in to alkane by hydroboration followed by proteolysis:

$$R-CH=CH_2 \xrightarrow{H-BH_2} R-CH-CH_2 \xrightarrow{R-CH_2-CH_2} R-CH_2 \xrightarrow{H^+/H_2O} R-CH_2$$

This reaction is also represented as:

$$\text{RCH} = \text{CH}_2 \xrightarrow{\text{H}-\text{BH}_2} (\text{R}-\text{CH}_2-\text{CH}_2)_3\text{B} \xrightarrow{\text{H}^+/\text{H}_2\text{O}} 3\text{R} = \text{CH}_2 - \text{CH}_3 + \text{H}_3\text{BO}_3$$

(ii) Alkene can be converted into alkane by hydroboration followed by treatment with  $AgNO_3 + NaOH$ .

CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-
$$CH_2$$
  $H_3$   $H_6$   $H_3$ -CH<sub>2</sub>-CH<sub>2</sub>- $CH_2$   $H_3$   $H_3$   $H_3$ -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH

#### (b) HALOGENATION

In presence of polar of medium alkene form vicinal dihalide with halogen.

$$\begin{array}{cccc} H & H & H & H & H & H \\ | & | & | & & \\ R-C=C-H+X-X & \xrightarrow{CCl_4} & & R-C=C-H & \\ & & | & | & \\ & & X & X & \\ Vicinal dihalide \end{array}$$

#### Chemistry

Order of reactivity of halogens is:  $F_2 > Cl_2 > Br_2 > I_2$ 

**Mechanism**: It is an electrophilic addition by molecular attack in which the addition takes place in trans manner.

![](_page_19_Figure_4.jpeg)

#### (c) REACTION WITH HX (HYDROHALOGENATION)

Markownikoff's Rule

 $CH_{3}-CH=CH_{2} \xrightarrow{H^{+}} CH_{3} - CH \xrightarrow{-} CH_{2} \xrightarrow{X^{-}} CH_{3}-CH-CH_{2}$  Iess stable (Minor)  $CH_{3} \xrightarrow{H} \xrightarrow{C} CH_{4} \xrightarrow{Br_{2}} H \xrightarrow{CH_{3}} H \xrightarrow{-} CH_{3}$   $H \xrightarrow{-} CH_{3} \xrightarrow{H} H \xrightarrow{-} CH_{3}$   $H \xrightarrow{-} CH_{3} \xrightarrow{-} CH_{3}$   $H \xrightarrow{-}$ 

When an unsaturated unsymmetrical hydrocarbon reacts with HX then halogen goes on that unsaturated carbon which has minimum number of hydrogen atom. Mechanism of the reaction is based on.

### Mechanism

$$CH_3-CH=CH_2 \xrightarrow{H^+} CH_3 \xrightarrow{\oplus} CH_3 - CH_3 \xrightarrow{X^-} CH_3-CH-CH_3$$
  
more stable (major)

- (i) Formation of Carbocation is Rate determining step.
- (ii) Rearrangement of carbocation to more stable carbocation can occur to form a more stable product.
- (iii) Regio chemistry Markovnikov's Addition of HX.
   Addition of HX on unsymmetrical alkenes (R CH = CH<sub>2</sub>) takes place according to Markownikaoff's rule which states that, "the negative part of addendum is added on the carbon atom carrying lesser number of hydrogen atoms."
- (iv) Reactivity order of different hydrogen haloed towards addition.

### HI > HBr > HCl > HF

### Anti Marchenko's Principle / Kharasch Effect/ Peroxide Effect

To understand anti Markovnikov's pri0nciple let us consider the following reactions

$$CH_{3}-CH=CH_{2} + HBr \longrightarrow H H \\ CH_{3}-CH=CH_{2} + HBr \xrightarrow{Peroxide} CH_{3} - C - C - H \\ Br H \\ CH_{3} - CH = CH_{2} + HBr \xrightarrow{Peroxide} H H \\ H \\$$

It is bases on free radical mechanism.

#### (a) Mechanism Concept -

(i)  $R - 0 - 0 - R \rightarrow R0 + 0R$ Peroxide

(ii)  $RO + H - Br \rightarrow ROH + {}^{x}Br$ 

(iii) 
$$x_{Br + CH_3 - C = C - H} \rightarrow$$

Class-XI

![](_page_21_Figure_2.jpeg)

**Note:** It is interesting to note that anti Markovnikov addition in the presence of peroxide is not applicable for HCl and HI

(i) In the case of H – Cl, the step

$$\begin{array}{c} \mathsf{Cl} & \mathsf{Cl} & \mathsf{H} \\ \mathsf{l} & \mathsf{CH}_2 - \mathsf{CH}_2 & \xrightarrow{H-Cl} & \mathsf{Cl} & \mathsf{l} \\ \mathsf{CH}_2 - \mathsf{CH}_2 & \xrightarrow{-Cl} & \mathsf{CH}_2 - \mathsf{CH}_2 + \mathsf{Cl} \end{array}$$

is endothermic (as  $\Delta = +$  12.6 KJ mol<sup>-1</sup>)

(ii) In the case of H – I, the step

$$CH_{2} = CH_{2} + I^{\bullet} \rightarrow CH_{2} + -CH_{2}$$

Is endothermic (as  $\Delta H = +46 \text{ KJ mol}^{-1}$ )

But in the case of HBr both of the steps are exothermic, which results spontaneous reaction CCl<sub>4</sub>, CBrCl<sub>3</sub> etc. can also be added to alkene in anti-Markovnikov manner.

### (d) REACTION WITH HYPOHALOUS ACID -

$$\mathbf{R} - \mathbf{C}\mathbf{H} = \mathbf{C}\mathbf{H}_{2} + \overset{\delta_{-}}{\mathbf{H}}\mathbf{O} - \overset{\delta_{+}}{\mathbf{C}}\mathbf{l} \rightarrow \mathbf{R} - \overset{\mathbf{C}}{\mathbf{C}}\mathbf{H} - \overset{\mathbf{C}}{\mathbf{C}}\mathbf{H}_{2}$$
$$\begin{vmatrix} \mathbf{H} & \mathbf{H} \\ \mathbf{H} & \mathbf{H} \\ \mathbf{H} & \mathbf{H} \end{vmatrix}$$

(i) When chlorine water or bromine water is used.

![](_page_21_Figure_14.jpeg)

#### **Class-XI**

(ii) When aq. solution of HOCl is added in the presence of strong acid.

$$Cl - O - H \xrightarrow{H^{+}}_{-H_{2}O} H \xrightarrow{Cl}_{-H_{2}O} Cl \xrightarrow{CH_{2}=CH-R}_{-H_{2}O} CH_{2}-CH-R \xrightarrow{H_{2}O}_{-H_{2}O} CH_{2}-CH-R \xrightarrow{H_{2}O}_{-H_{2}O} CH_{2}-CH-R \xrightarrow{-H^{+}}_{-H_{2}O} CH-R \xrightarrow{-H^{+}}$$

(e) REACTION WITH  $H_2SO_4$  –

(a) With conc.  $H_2SO_4$ 

(b) With dil. H<sub>2</sub>SO<sub>4</sub>

$$R - CH = CH_2 \qquad \frac{H - SO_4H}{H_2O} \qquad \begin{array}{c} R - CH - CH_2 \\ I \\ OH \end{array}$$

Mechanism

The hydration of alkene is not stereoselective, as in the case of HCl addition. This fact can be explained on the basis of classical carbon cation formation.

Since hydration proceeds via carbocation intermediate therefore rearrangement is always probable.

#### Chemistry

![](_page_23_Figure_2.jpeg)

Rearrangement, however, may be avoided by treatment of alkene by oxymercurationdemarcation method.

![](_page_23_Figure_4.jpeg)

Sodium borohydride (NaBH<sub>4</sub>) converts the carbon-mercury bond into a carbonhydrogen bond. Because the reaction results in the loss of mercury, it is called demarcation.

$$\begin{array}{c} CH_{3}CHCH_{2} - Hg - OAc \begin{array}{c} \frac{NaBH_{4}}{HO^{-}} \\ | \\ OH \end{array} CH_{3}CHCH_{3} + Hg + AcO^{-} \\ | \\ OH \end{array}$$

### (f) ADDITION OF NITROSYL HALIDE -

Alkene with nitrosyl bromide or nitrosyl chloride (Tilden reagent) react according to Markowinkoff's rule to give alkene nitroso bromide and alkene nitroso chloride respectively.

Class-XI

$$R - CH = CH_{2} + O = \overset{\delta \oplus}{N} - \overset{\delta \oplus}{Cl} \longrightarrow R - CH - CH_{2}$$

$$Cl \quad NO$$

$$R - CH = CH_{2} - O = \overset{\delta \oplus}{N} - \overset{\delta \oplus}{Br} \longrightarrow R - CH - CH_{2}$$

$$Br \quad NO$$

$$CH_{3} - CH = CH_{2} + O = \overset{\delta \oplus}{N} - \overset{\delta \oplus}{Cl} \longrightarrow CH_{3} - CH - CH_{2}$$

$$CH_{3} - CH = CH_{2} + O = \overset{\delta \oplus}{N} - \overset{\delta \oplus}{Cl} \longrightarrow CH_{3} - CH - CH_{2}$$

$$CH_{3} - CH = CH_{2} + O = \overset{\delta \oplus}{N} - \overset{\delta \oplus}{Cl} \longrightarrow CH_{3} - CH - CH_{2}$$

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$$CH_{3} - CH = CH_{2} + O = \overset{\delta \oplus}{N} - \overset{\delta \oplus}{Cl} \longrightarrow CH_{3} - CH - CH_{2}$$

$$CH_{3} - CH = CH_{2} + O = \overset{\delta \oplus}{N} - \overset{\delta \oplus}{Cl} \longrightarrow CH_{3} - CH - CH_{2}$$

$$CH_{3} - CH = CH_{2} + O = \overset{\delta \oplus}{N} - \overset{\delta \oplus}{Cl} \longrightarrow CH_{3} - CH - CH_{2}$$

$$CH_{3} - CH = O$$

$$CH_{3} - CH =$$

(g) ADDITION OF WATER (HYDRATION OF ALKENES): Propene and higher alkenes react with water in the presence of acid to form alcohol. This reaction is known as the hydration reaction. Intermediate in this reaction is carbo cation, so rearrangement will take place.

$$CH_{3} - CH = CH_{2} + H_{2}O \xrightarrow{H^{+}} CH_{3} - CH_{3} = CH_{3}$$

$$Cl$$

$$Cl$$

$$Propene$$

$$Propan-2-ol$$

(ii)  

$$CH_{3} - C = CH_{2} + H_{2}O \xrightarrow{H^{+}} CH_{3} - C = CH_{3}$$

$$CH_{3} \xrightarrow{CH_{3}} CH_{3}$$
2-Methylpropene 2=Methylpropene-2-Ol

### Mechanism

CH<sub>3</sub> → CH = CH<sub>2</sub> + H<sup>+</sup> 
$$\xrightarrow{\text{(Slow)}}$$
 CH<sub>3</sub> -  $\overset{\oplus}{\text{CH}}$  - CH<sub>3</sub>  
Carbocation (2°)

$$CH_{3} - \overset{\bigoplus}{CH} - CH_{3} + H - \overset{\square}{O} - H \xrightarrow{(Fast)} CH_{3} - \overset{-H}{CH} - CH_{3} \xrightarrow{-H^{+}} CH_{3} - \overset{-H^{+}}{CH} \xrightarrow{(Fast)} CH_{$$

Class-XI

![](_page_25_Figure_2.jpeg)

(h) HYDROFORMYL OR OXO REACTION: Alkenes react with Carbon monoxide and hydrogen at 100 - 150°C temperature and high pressure (1200 atm) in the presence of Cobalt catalyst to produce an aldehyde. It does not follow markonikoff's rule. The net reaction is the addition of a H-atom to one of the Olefinic bond and a formyl (-CHO) group to the other.

$$R-CH=CH_2+CO+H_2 \xrightarrow{Co./150^{\circ}C} R-CH_2-CH_2-CH_0$$

$$R-CH=CH_2+CO+H_2 \xrightarrow{High pressure} R-CH_2-CH_2$$

(i) **ALKENYLATION (ADDITION OF ALKENE)** In presence of H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> at 80°C dimerization of isobutylene take place gives two isomers of octene.

$$\begin{array}{c} CH_{3} \\ \downarrow \\ 2CH_{3}-C=CH_{2} \\ \end{array} \xrightarrow{H_{2}SO_{4,}80^{\circ}C} CH_{2}=C-CH_{2}-C-CH_{3}+CH_{3}-C=CH-C-CH_{3}\\ \downarrow \\ CH_{3} \\ \end{array} \xrightarrow{CH_{3}} CH_{3} \\ CH$$

#### Class-XI

Mechanism

![](_page_26_Figure_3.jpeg)

(j) ADDITION OF CARBENE: The addition of carbene to alkene is always carried by diazomethane CH<sub>2</sub>N<sub>2</sub> Carbene group obtained from diazomethane is added to alkene and give cycloalkanes.

$$CH_2 = CH_2 + CH_2N_2 \xrightarrow{\Delta} CH_2 - CH_2 + N_2$$

$$CH_3 - CH = CH_2 + :CH_2 \longrightarrow CH_3 - CH - CH_2$$
  
 $CH_2 \to CH_3 - CH - CH_2$ 

**Since**:  $CH_2$  is an electrophilic (neutral) and there is more electron density on double bond so first attack of:  $CH_2$  will be at double bond.

### (k) ADDITION OF HCN:

$$\begin{array}{cccc} & \delta^+ & \delta^- & \delta^- & \delta^- \\ CH_3 - CH = CH_2 + HCN & \longrightarrow & CH_3 - CH - CH_3 \\ & & \downarrow \\ & & CN \end{array}$$

### (2) Oxidation Reaction:

Alkenes are easily oxidised by oxidising agents. Odidising agents attack on double bond and product formed during oxidation depends on oxidising agents.

#### Chemistry

### (a) ALKENE ON COMBUSTIION GIVES $CO_2$ AND $H_2O$

$$C_nH_{2n} + \frac{3n}{2}O_2 \rightarrow nCO_2 + nH_2O_2$$

one mole of alkene requires  $\frac{3n}{2}$  moles of  $O_2$  for complete combustion.

### (b) WITH ACIDIC KMNO<sub>4</sub> / HOT KMNO<sub>4</sub>

![](_page_27_Figure_6.jpeg)

### (c) WITH ALKALINE KMNO<sub>4</sub> / BAYER'S REAGENT

![](_page_27_Figure_8.jpeg)

**Mechanism**: Hydroxylation by alkaline  $KMnO_4$  (Bayer's reagent) is cis addition and the mechanism is cyclic.

![](_page_28_Figure_3.jpeg)

### (3) Ozonolysis

This is the two-step reaction

(i) Ozonide formation

(ii) decomposition of ozonide (reductive hydrolysis)

![](_page_29_Figure_6.jpeg)

**Remember:** Ozonolysis gives oxidative cleavage of alkene to form two carbonyl group for each >C=C<. Whether it is in acyclic or cyclic or in aromatic compound. e.g.: -

Epoxidation by O<sub>2</sub>/Ag

(i) 
$$CH_2 = CH_2 + \frac{1}{2} O_2 \xrightarrow{Ag} CH_2 - CH_2$$

(ii) 
$$CH_3 - CH = CH_2 + \frac{1}{2} O_2 \xrightarrow{Ag} CH_3 - CH - CH_2$$

#### Class-XI

Epoxidation by per acid

![](_page_30_Figure_3.jpeg)

(ii) 
$$CH_3 - CH = CH_2 \xrightarrow{H - C - 0 - 0 - H} CH_3 - CH - CH_2$$

$$R - CH = CH - R \xrightarrow{CF_3COOOH} R - CH - CH - R$$

### Hydroboration

Alkene with borane hydride form an important compound called trialkyl borane.

$$3R - CH = CH_2 + BH_3 \rightarrow (R - CH_2 - CH_2)_3B$$

(a) Trialkyl borane is an important compound because it gives respective alkane on acidic hydrolysis.

$$(R - CH_2CH_2)_{3}B + 3H_2O \xrightarrow{HCl} 3R - CH_2 - CH + B(OH)_3$$

- (b) It gives respective alcohol on alkaline hydrolysis  $(R - CH_2CH_2)_3B + 3H_2O_2 + 3NaOH \rightarrow 3RCH_2CH_2OH + 3NaCl + H_3BO_3$
- (c) It gives I° amine on alkaline hydrolysis with chloramine  $(R - CH_2CH_2)_3B + 3NH2Cl + 3NaOH \rightarrow 3R - CH_2CH_2NH_2 + 3NaCl + H_3BO_3$
- (d)  $(R-CH_2CH_2)_{3B} \xrightarrow{AgNO_3} 3R-CH_2-CH_2-R$
- (e) In the overall hydroboration-oxidation reaction, three moles of alkene read with one mole of BH<sub>3</sub> to form three moles of alcohol.
- (f) Because carbocation intermediates are not formed in the reaction carbocation rearrangements do not occur.
- (g) Regio chemistry Anti-markownikoff's Addition of water.
- (h) Alkyl boranes undergo coupling by means of silver nitrate in the presence of NaOH at 25°C. Higher alkanes are the products of this reaction.

#### (4) Substitution Reaction

(a) Except ethene other higher alkene having alkyl hydrogen when treated with chlorine or bromine ' $\alpha$ ' H is substituted.

![](_page_31_Figure_4.jpeg)

$$CH_3 - CH = CH_2 + Cl_2 \xrightarrow{500^\circ C} -600^\circ C + CH_2 - CH = CH_2 + HCl$$

allyl chloride (3-chloropropene)

![](_page_31_Figure_7.jpeg)

(b) Allylic bromination can be easily done by NBS (N-bromo succinimide)

![](_page_31_Figure_9.jpeg)

#### (5) Polymerization

- (i) Two or more than two molecules of same compound unit with each other to form a long chain molecule with same empirical formula. This long chain molecules having repeating structural units called polymer, and the starting simple molecule as monomer and process is called addition polymerization.
- (ii) Molecular weight of polymer is simple multiple of monomer.
- (iii) The presence of oxygen initiates free radical mechanism.
- (iv) Addition polymerization can also be carried out by ionic mechanism by using Ziegler - Natta Catalysts (R<sub>3</sub>Al + TiZl<sub>4</sub>)

## Chemistry

Name of	Structure of	Structure of	Properties	Uses Properties
1. Polyvinyl chloride (PVC)	$CH_2 = CH - Cl$	(-H <sub>2</sub> C – H C –)   СI	Pliable (easily moulded)	Used in handbag, raincoats, vinyl flooring, good electrical insulator for wires
2. Polypetalous- ethylene or Teflon (PTFE)	F <sub>2</sub> C=CF <sub>2</sub>	(-F <sub>2</sub> C - CF <sub>2</sub> -) <sub>n</sub>	Flexible and inert to solvents, boiling acids, even aquaregia stable up to 598K.	For making non- stick utensils coating
3. Natural rubber vulcanized rubber which is strong	$CH_2 = CH_1 - CH_3$ isoprene $CH_3 = CH_3$		Waxy and non- elastic	Used as raw material for making and elastic vulcanized rubber is used in making tyres hose, pipes etc.
4. Orlon	acrylonitrile	(-H <sub>2</sub> C-H С -)   СN	Fibrous	Used in making Fabrics
5. Poly methyl methacrylate (PMMA)	$CH_2 = C^{CH_3}$ $CH_2 = C^{CH_3}$ $COOCH_3$	Methyl methacrylate	$ \begin{pmatrix} CH_{3} \\ -CH_{2} - C \\ C = 0 \\ 0 \\ OCH_{3} \end{pmatrix}_{n} $	

## (6) Isomerisation

Alkenes isomerase when heated at high temperature or at lower temperature in the presence of various catalysts as AlCl<sub>3</sub>.

Ex.

(i)  $CH_3 - CH_2 - CH_2 - CH = CH_2 \xrightarrow{AlCl_3} CH_3 - CH_2 - CH = CH - CH_3$ 

(ii) 
$$\begin{array}{c} CH_3 & CH_3 \\ | & AlCl_3 & | \\ CH_2 - CH = CH_2 \xrightarrow{AlCl_3} CH_2 = C - CH_3 \end{array}$$

the mechanism proceeds through carbocation

Uses

- (a) In plastic formation.
- (b) In oxy ethylene welding
- (c) As food preservatives and ripening fruits.
- (d) As general anaesthetic ( $C_2H_4$  with 8 10%  $O_2$ )
- (e) In preparation of mustard gas

$$\begin{array}{cccc} CH_2 & CH_2 \rightarrow CH_2 & CH_2Cl \\ | + S_2Cl_2 | & | & | +S \\ CH_2 & CH & CH_2 - S - CH_2 \\ & & 2,2' \text{or } (\beta,\beta') \text{trichloro diethyl-sulphide} \\ & & (\text{mustard gas}) \end{array}$$

Functional Group	Reagent	Observation	Reaction	Remarks
(1) Bayer's Reagent alk. dil. cold KMnO4	Pink colour Disappears C = C	CH <sub>2</sub> =CH <sub>2</sub> + H <sub>2</sub> O+O	$\xrightarrow{\text{alk.KMnO}_{4}} \xrightarrow{\text{CH}_{2} - \text{CH}_{2}} \xrightarrow{\text{CH}_{2} - \text{CH}_{2}} \xrightarrow{\text{I}} \xrightarrow{\text{I}} \xrightarrow{\text{OH}} \xrightarrow{OH} \xrightarrow{OH} \xrightarrow{OH} \xrightarrow{OH} \xrightarrow{OH} O$	Dihydroxylation
(2) Br <sub>2</sub> /H <sub>2</sub> 0	Red colour decolorizes	Br <sub>2</sub> +CH <sub>2</sub> = CH <sub>2</sub> →	$\begin{array}{c} C H_2 - CH_1 \\   &  ^2 \\ Br & BR \\ White ppt. \end{array}$	Debromination
(3) 0 <sub>3</sub> (ozone)	C=0 Compounds	CH <sub>2</sub> =CH <sub>2</sub> + 0 <sub>3</sub>	Zn/H <sub>2</sub> O	Ozonolysis

### Dienes

Dienes are the unsaturated hydrocarbons with carbon-carbon double bonds in the molecules. These are represented by the general formula  $C_nH_{2n-2}$  which means that they are isomeric with alkynes (functional isomers). However, their properties are quite different from those of alkynes. Depending upon the relative positions of the two double bond, dienes are classified in three types:

**Isolated dienes or non-conjugated dienes:** In an isolated diene, the two double bonds are separated by more than one single bond. **For example,** 

$$\begin{array}{c} CH_{3} \\ CH_{2} = CH - CH_{2} - CH = CH_{2} \\ penta - 1.4 - diene \end{array}$$

$$\begin{array}{c} CH_{3} \\ 1 \\ CH_{2} = CH - CH - CH = CH_{2} \\ 3 - Methylpenta - 1.4 - diene \end{array}$$

**Conjugated dienes**: In a conjugated diene, the two double bonds are present in the conjugated or alternate positions and are separated by a single bond.

1 2 3 4	1 2 3 4 5
$CH_2 = CH - CH_2 = CH_2$	$CH_2 = C - CH - CH = CH_3$
Buta — 1,3 — diene	2 – Methylpenta – 1,3 – diene

**Cumulate dienes:** In this case, the two double in the molecules are present at adjacent positions.

### For example,

**Comparison of relative stabilities of isolated and conjugated dienes Resonance Theory**: The relative stabilities of the two types dienes can also be justified on the basis of the theory of resonance. Penta-1, 3-diene (conjugated diene) is a hybrid of the following contributing structures.

 $CH_2 = CH - CH = CH - CH_3 \iff CH_2 - CH - CH = CH - CH_3 \iff CH_2 - CH = CH - CH_3$ The delocalization of  $\pi$ -electron charge because of resonance decreases the energy of the molecule or increases its stability.

Penta-1, 4-diene (isolated diene) has only two contributing structures.

$$\overset{1}{\mathbf{C}} \overset{2}{\mathbf{H}}_{2} = \overset{2}{\mathbf{C}} \overset{3}{\mathbf{H}}_{2} - \overset{4}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} = \overset{5}{\mathbf{C}} \overset{2}{\mathbf{H}}_{2} - \overset{2}{\mathbf{C}} \overset{2}{\mathbf{H}}_{2} - \overset{3}{\mathbf{C}} \overset{4}{\mathbf{H}}_{2} = \overset{5}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} - \overset{2}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} - \overset{2}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} - \overset{4}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} = \overset{5}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} - \overset{1}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} - \overset{1}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} - \overset{1}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} - \overset{1}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} = \overset{1}{\mathbf{C}} \overset{1}{\mathbf{H}}_{2} - \overset{1}{\mathbf{H$$

Since the carbon atom  $C_3$  is not involved in any resonance, the contributing structures are less number are compared to the conjugated diene. The isolated diene is, therefore, less stable than a conjugated diene.

### **PROPETIES OF CONJUGATED DIENES**

The properties of the isolated dienes are similar to those of simple alkene but those of conjugated dienes are somewhat modified because of delocalization of the  $\pi$ -electron charge. However, they also patriate in the addition reactions. The important chemical characteristics of the conjugated dienes are briefly discussed.

**1. Addition Reaction**: Conjugated or 1, 3-dienes take part in the addition reactions which can proceed by electrophilic as well as free radical mechanism depending upon the nature of the attacking reagent and the reaction conditions.

**Electrophilic Addition Reactions:** The electrophilic addition is illustrated by the attack of halogen and halogen acid on Buta--1,3-diene, a conjugated diene.

**Addition of halogen:** If one mole of halogen attacks per mole of the diene, two types of addition products are formed. There are 1, 2 and 1, 4 addition products. For example,

![](_page_35_Figure_8.jpeg)

1, 2- addition is a normal addition in which one mole of halogen has been added to one of the double bonds. But 1, 4- addition is somewhat unexpected.

**Mechanism**: The addition is electrophilic in nature and the halogen molecule (bromine) provides the electrophilic for the attack.

$$CH_{2} = CH - CH = CH_{2} + \overset{\delta_{+}}{B}r - \overset{\delta_{-}}{B}r \rightarrow CH_{2} = CH - \overset{\oplus}{C}H - CH_{2}Br + \overset{\Theta}{B}r$$
  
Buta-1,3-diene Carbocation (2°)

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The 2° carbocation get stablised by resonance as follows -

The attack of ion on carbocation (I and II)

Addition of H - X

$$CH_2 = CH - CH = CH_2 \xrightarrow{HBr} ?$$

**Mechanism**: The addition is electrophilic in nature as H<sup>+</sup> ion is the electrophilic

$$CH_{2} = CH - CH = CH_{2} + H^{\delta_{+}} - B^{\delta_{-}} \rightarrow CH_{2} = CH - CH_{3} + Br^{\bullet}$$
  
Carbocation(2°)

The carbocation gets resonance stablised as follows:

$$CH_{2} = \underbrace{CH}_{(I)} - \underbrace{CH}_{G} + CH_{3} \rightarrow CH_{2} - CH = CH - CH_{3}$$
(II)

The attack of Br<sup>-</sup> ion on the carbocation (I) gives 1, 2-addition product whereas the attack on the carbocation (II) yields 1,4-addition product.

$$CH_{2} = CH - CH - CH_{3}$$

$$|$$

$$Br$$

$$Br^{-} + CH_{2} = CH - \overset{\oplus}{C}H - CH_{3} \rightarrow 1, 2 - Addition product$$

$$Br^{-} + \overset{\oplus}{C}H_{2} - CH = CH - CH_{3} \rightarrow CH_{2} - CH = CH - CH_{3}$$

$$|$$

$$Br$$

$$1, 4 - Addition product$$

(2) Free Radical Addition Reaction: The addition to conjugated dienes can also proceed by free radical mechanism provided it is carried in the presence of a suitable regent which can help in forming a free radical. However, the addition also yields 1, 2 and 1, 4 addition products. The free radical is illustrated by the attack of

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bromodichloromethane (BrCCl<sub>3</sub>) on buta-1,3-diene in the presence of an organic peroxide such as benzoyl peroxide.

$$\overset{1}{C}H_{2} = \overset{2}{C}H - \overset{3}{C}H = \overset{4}{C}H_{2} + \operatorname{BrCCl}_{3} \xrightarrow{\text{Benzyl}} Cl_{3}C\overset{4}{C}H_{2}\overset{3}{C}H - \overset{2}{C}H = \overset{1}{C}H_{2} + Cl_{3}C\overset{4}{C}H_{2} - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_{2} + \overset{1}{C}H_{2} + Cl_{3}C\overset{4}{C}H_{2} - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_{2} + \overset{1}{C}H_{2} + Cl_{3}C\overset{4}{C}H_{2} - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_{2} + \overset{1}{C}H_{2} + Cl_{3}C\overset{4}{C}H_{2} - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_{2} + \overset{1}{C}H_{2} + Cl_{3}C\overset{4}{C}H_{2} - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_{2} + Cl_{3}C\overset{4}{C}H_{2} - \overset{3}{C}H - \overset{2}{C}H - \overset{2$$

**Mechanism**: The mechanism of addition is free radical in nature which is initiated by benzyol free radical. It is explained in the following steps:

Step - IGeneration of free radical.
$$C_eH_5CO-O-O-COC_eH_3$$
Itemshuis $C_eH_5-CO-\dot{O}+\dot{O}-COC_eH_3$  $C_eH_5-CO-\dot{O}$  $\rightarrow$  $\dot{C}_eH_5-CO-\dot{O}+\dot{O}-COC_eH_3$  $C_eH_5-CO-\dot{O}$  $\rightarrow$  $\dot{C}_eH_5-Br+\dot{C}CI_3$  $\dot{C}_eH_5+BrCCI_3$  $\rightarrow$  $C_eH_5-Br+\dot{C}CI_3$ Trichloromethyl free radicalTrichloromethyl free radicalStep-IIAttack of free radical on buta-1, 3-diene. $\dot{C}CI_3+CH_2=CH-CH=CH_2$  $\rightarrow$  $CI_3C-CH_2-\dot{C}H-CH=CH_2$ Free radical gets resonance stablised. $CI_3C-CH_2-CH=CH-\dot{C}H_2$  $CI_3C-CH_2=\dot{C}H-CH=CH_2$  $\leftrightarrow$  $CI_3C-CH_2-CH=CH-\dot{C}H_2$ Step-IIIChange of free radical into addition product.The free radical takes up  $Br$  from the attacking reagent to give the desired addition products.i.e., 1, 2 and 1, 4 addition products. $Br$  $(I,4-Addition Product)$ BrCCI\_3+CI\_3C-CH\_2-CH =  $\dot{C}H_2$  $\rightarrow$  $CI_3C-CH_2-CH = CH_2-CH_2$  $BrCI_3+CI_3C-CH_2-CH=\dot{C}H_2$  $\rightarrow$  $CI_3C-CH_2-CH=CH=CH_2$  $Br$  $(I,4-Addition product)$  $BrCCI_3+CI_3C-CH_2-CH=\dot{C}H_2$ 

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## 3. Cyclo-Addition Reaction (Diel Alder Reaction)

Cyclo-addition reactions are one of the most important reactions of conjugated dienes. Cyclo-addition involves the combination between a conjugated diene ( $4\pi$ -electron system) and a compound containing a double bond ( $2\pi$ -electron system) called dienophile which means a diene loving or attracting molecule. As a result, a six membered ring gets formed and the reaction is therefore known as cyclo-addition reaction. It is quite often termed as **(4 + 2) cyclo-addition reaction** because four  $4\pi$ -electron system adds to a two  $2\pi$  electron system.

The addition products are called **Diel Alder Adduct**. **For example.** 

![](_page_38_Figure_5.jpeg)