

Chapter – V Alkenes

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Chapter – V Alkenes

Introduction: Alkenes are **unsaturated hydrocarbons** containing at least one carbon-carbon double bond and are represented by the general formula C_nH_{2n} . They are also called as **olefins**. The word olefin was derived from the word olefiant gas.

Example: The name of ethylene that is **oil forming gas**, which on treatment with Cl_2 or Br_2 forms oily liquids.

Nomenclature of alkenes:

A) Common name system: Alkenes are named by replacing ending “**ane**” of the corresponding alkane by “**ylene**”.

B) IUPAC Nomenclature:

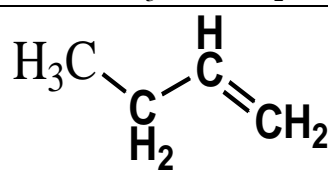
Rule-I: select the longest chain containing double bond as parent alkane.

Rule-II: The suffix “**ane**” of the parent alkane is replaced by “**ene**”

Rule-III: The position of $C=C$ is indicated by the lowest possible number.

Rule-IV: The number indicating the position of double bond is placed before the name of the alkene or suffix “**ene**”.

Rule-V: The positions of other substituents on the longest carbon chain are indicated by proper numbers.

Sr. No	Structure of alkene	Parent alkane	Common name	IUPAC name
1	$H_2C=CH_2$	Ethane	Ethylene	Ethene
2	$CH_3-CH=CH_2$	Propane	Propylene	Propene or prop-1-ene
3		Butane	1 or α -Butylene	1-Butene or but-1-ene

4	$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{HC}=\text{CH} \\ \diagup \\ \text{CH}_3 \end{array}$	Butane	2 or β -Butylene	2-Butene or but-1-ene
5	$\begin{array}{c} \text{H}_3\text{C} \quad \text{H}_2 \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{H}_2 \quad \text{H} \end{array} \quad \text{C}=\text{CH}_2$	Pentane	1 or α -Pentylene	1-Pentene or pent-1-ene
6	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}=\text{CH}_2 \end{array}$	Propane	Iso-butylene	2-Methyl-1-propene (2-Methyl-prop-1-ene)
7	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{C}=\text{CH}_2 \\ \\ \text{H}_3\text{C} \\ \text{H} \end{array}$	Butane	Neo-Hexylene	3,3-dimethyl-1-butene (3,3-Dimethyl-but-1-ene)

Methods of formation of alkene:

A) Dehydration of alcohols:- (-H₂O): Alcohols on heating in the presence of dehydrating agents, eliminates water (-H₂O) molecule to form corresponding alkenes. 1^o, 2^o and 3^o

Alcohols differ in their relative ease of dehydration. The order is

Tertiary alcohol > Secondary alcohol > Primary alcohol

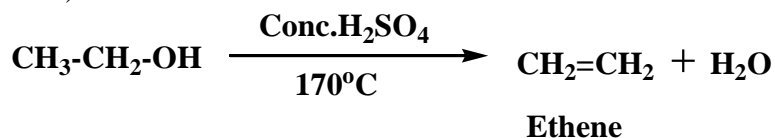


(Faster dehydration)



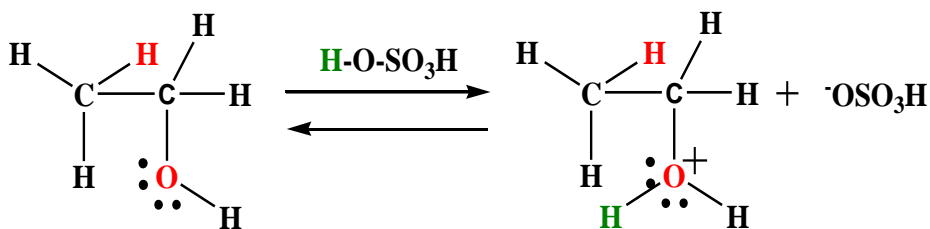
(Slower dehydration)

- 1) A primary alcohol e.g. ethanol on heating with Conc.H₂SO₄ or phosphoric acid at 170 °C (443K) forms Ethene.

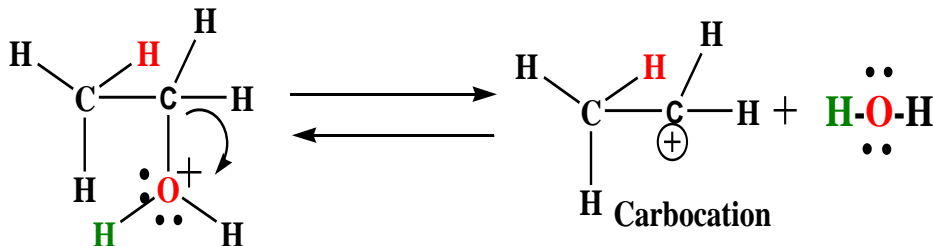


Mechanism of dehydration of alcohol involves three steps.

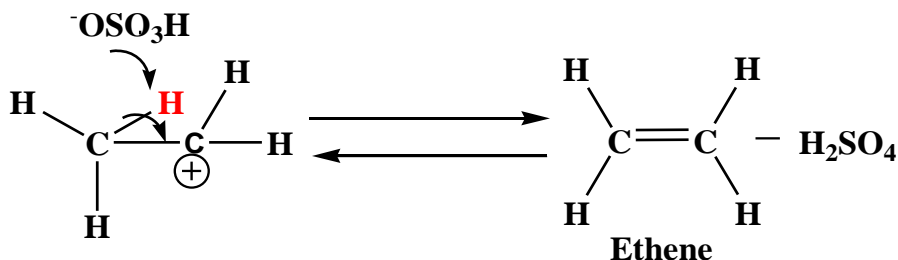
Step-I : Conc. H_2SO_4 protonates alcohol to transform the **very poor leaving group** $-\text{OH}$ into the **very good leaving group** $-\text{OH}_2$ and **results** into formation of **protonated alcohol** and conjugate base of acid.



Step-II: The protonated alcohol undergoes heterolysis to form the carbocations and water.

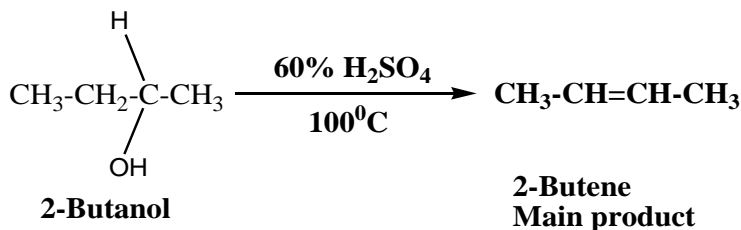


Step-III: In this step, Carbocations loses a proton to the base to form alkene.

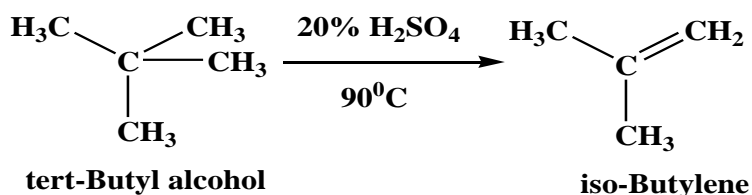


- Dehydration of alcohols is a **unimolecular elimination (E1)** reaction.
- It is **reversible reaction**.
- Under the condition of dehydration, the alkene, being quite volatile, is removed from reaction mixture and thus the **equilibrium in third step is shifted to the right** to get more quantity of alkene.
- Dehydration of primary alcohol is carried out by passing alcohol vapors over alumina (Al_2O_3) catalyst at 350-400C, here alumina acts as a Lewis acid to remove $-\text{OH}$ from primary alcohol.

- 2) **Dehydration of Secondary alcohol** e.g. 2-butanol on heating with 60% H_2SO_4 to 100°C forms 2-butene as main product.



- 3) Dehydration of tertiary alcohol e.g. 2-methyl-2-propanol on heating with 20% H_2SO_4 at 90°C gives 2-methyl-1-propene.

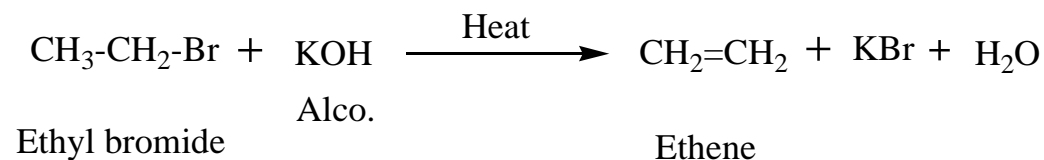


Note: 2° and 3° alcohols undergo dehydration more rapidly than primary alcohols because they easily form more stable secondary and tertiary carbocations respectively.

B) Dehydrohalogenation of alkyl halides: (-HX)

When alkyl halide on heating with alcoholic alkali solution (NaOH or KOH) or **sodium ethoxide** eliminate **hydrogen and halogen atoms (-HX)** from adjacent (α , β carbon atoms to form alkenes. Since the reaction takes place with loss of hydrogen halide, it is called as **dehydrogenation**.

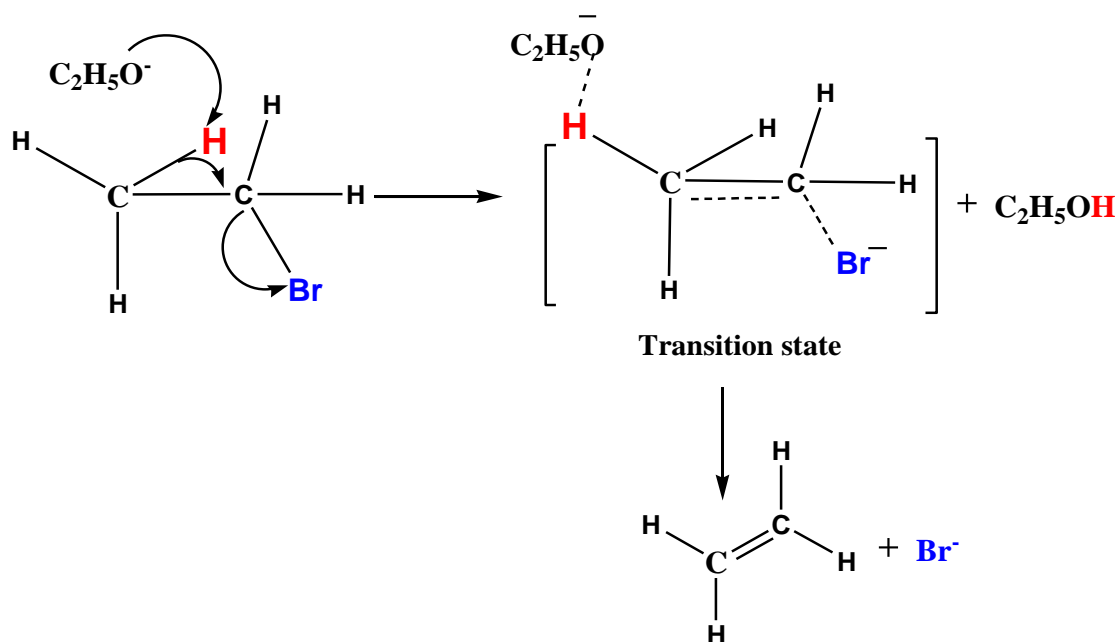
A primary alkyl halide e.g. ethyl bromide on heating with alcoholic NaOH or KOH solution or sodium ethoxide undergoes elimination reaction gives Ethene.



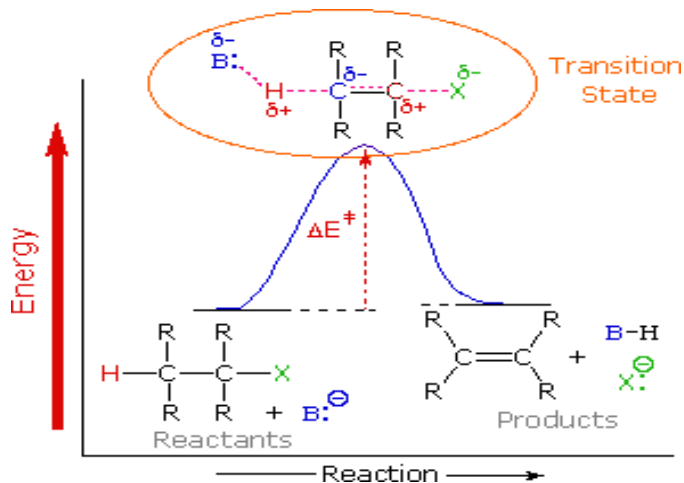
- It is bimolecular elimination reaction (E^2).
- The rate of reaction is found to be proportional to the concentration of alkyl halide and base. Hence, it is second order reaction.
- $R \propto [\text{CH}_3\text{CH}_2\text{Br}] [\text{C}_2\text{H}_5\text{O}^-]$

Mechanism:

- Ethoxide ion ($\text{C}_2\text{H}_5\text{O}^-$) acting as base, abstracts β -hydrogen atom of alkyl halide. Simultaneously, there is weakening of covalent bond between α -carbon atom and departing halogen atom resulting in the formation of transition state. In T.S., due to delocalization of electrons of C-H σ bond, the bond between α and β .
- The unstable T.S. then ultimately loses hydrogen atoms to form alkene.

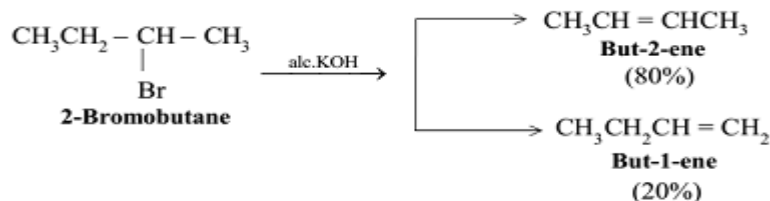


- Reaction takes place with loss of hydrogen atom from β carbon and halogen atom from α -carbon, it is called 1,2 or α , β elimination or simply β -elimination reaction.
- Most ' E^2 ' reactions proceed more rapidly when the departing groups, hydrogen atom from β -carbon and halogen atom from α -carbon, are trans than when they are cis. i.e. E^2 reactions are **anti-elimination reactions**. Hence, these reactions are **stereo specific**.
- Some substrates (alkyl halides) possess alternative β -hydrogen atoms; hence, there is possibility of formation of more than one alkene product.

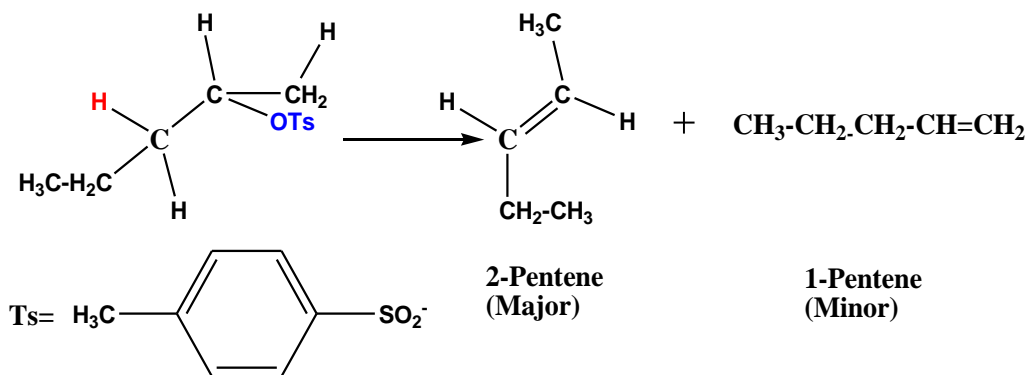
Energy profile diagram:

Saytzeff rule: Neutral substrates like alkyl halides or alkyl sulphonates possessing alternative β -hydrogen atoms on heating with base preferably yield that alkene (main product) in which there is greater number of alkyl groups attached to the carbon-carbon double bond.

Example-1: 2-bromobutane on heating with sodium ethoxide gives 2-butene with more alkyl substituent's on double bond as main product (80%) and 1-butene with less alkyl substituent's on double bond as minor product (20%).

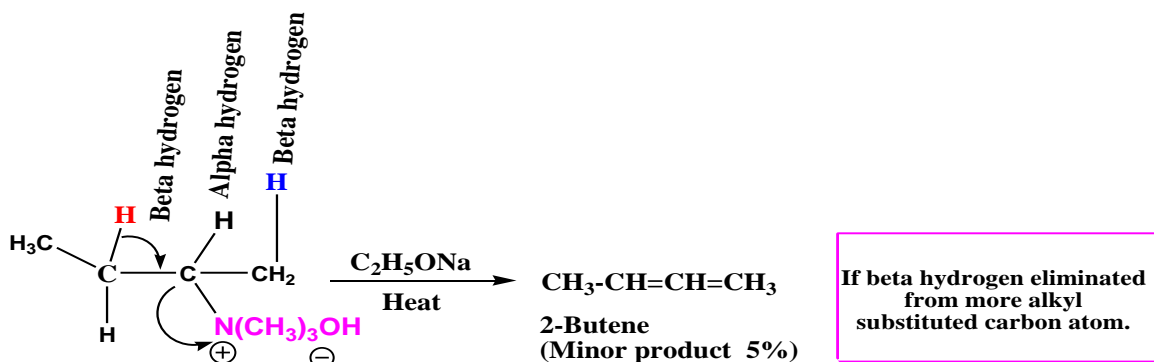
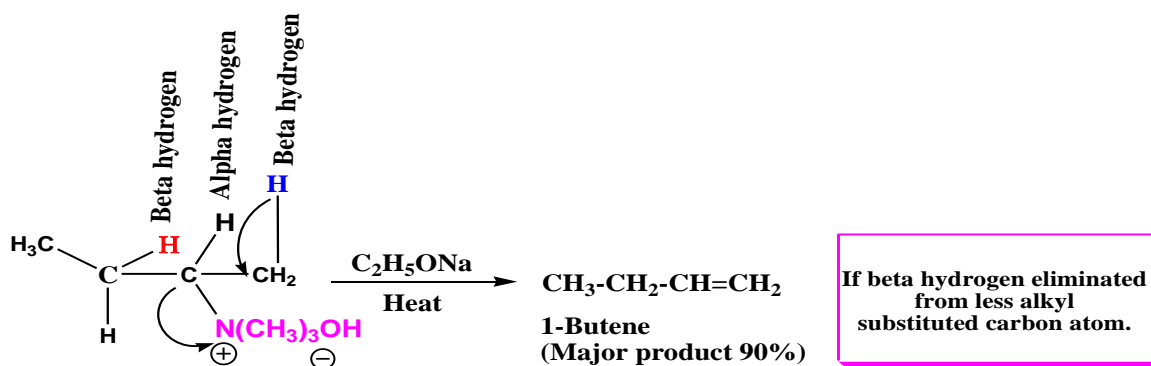


Example-2: Pentane -2-p-toluene sulphonate on heating with sodium ethoxide gives 2-pentene as main product and 1-pentene as minor product.



Hofmann rule: It states that charged substrates like quaternary ammonium or sulphonium salts possessing alternative β -hydrogen atoms on heating with base undergo elimination reaction to yield alkene which has last alkyl substituent's on the carbon-carbon double bond as main product.

- **Example:** Sec.butyl trimethyl ammonium hydroxide (+vely charged) on heating with sodium ethoxide gives 1-butene as main product and $(\text{CH}_3)_3\text{N}$ trimethyl amine and H_2O as biproducts.



Physical Properties of Alkenes:

- 1) Alkenes have characteristic smell or generally colorless and odorless compounds.
- 2) Alkenes having two to four carbon atoms are gases, those containing five to fifteen carbon atoms are liquids while higher alkenes are solids.
- 3) Alkenes are insoluble in water (due to its non polar or weak polar character) but soluble in organic solvents or polar solvents like alcohol, ether etc.
- 4) Rotation is restricted around the double bond in alkenes, resulting in diastereoisomers with different substitution patterns around the double bond.

- 5) Alkenes have less density than water (Lighter than water).
- 6) The B.P. and M.P. of alkenes is usually lower than that of an alkane with same number of carbon atoms.
- 7) The B.P. and M.P. of alkene increases as number of carbon atoms in the compound increases.
- 8) The M.P./B.P. of straight chain alkenes is more than that of branched chain alkenes as similar to alkanes.
- 9) The M.P. /B.P. of cis isomer is lower than trans isomer as the molecule is placed in a U-bending tube.
- 10) Dipole moments of alkenes is more than that of alkane due to presence of double bonds, polarity depends upon functional group attached on alkenes.
- 11) Alkenes are more reactive than related alkanes due to relative instability of the pi-bond.

Reactivity of Alkenes:

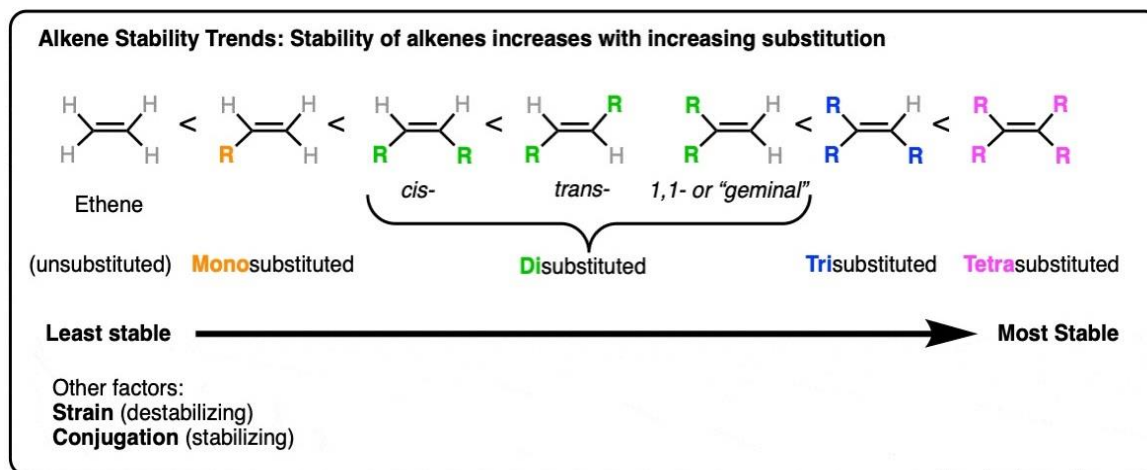
Alkenes are more reactive than their related alkanes due to the relative instability of the double bond. They are more likely to participate in a variety of reactions, including combustion, addition, hydrogenation, and halogenations reactions. Alkenes can also be reacted, typically in the presence of a catalyst, to form polymers.

Relative stabilities of alkenes: The major product formed in Saytzeff rule can be correlated with the relative stability of various alkenes. Heat of combustion and heat of hydrogenation suggests that the stability of alkene is increased by alkyl substitution on double bonded carbon atoms.

Greater stability of alkenes with increase of alkyl substituent's can be explained by hyper conjugation (**Refer Chapter No.-I hyper conjugation**). Attachment of more number of alkyl substituent's to the double bonded carbon atom gives more number of hyper conjugative structures. Thus in below series tetra substituted alkene shows forms 12 hyper conjugative structures which makes most stable while ethylene does not shows hyper conjugative structure making it least stable.

Tri substituted alkene shows 9 hyper conjugative structures, disubstituted alkene shows 6, and mono substituted alkene shows 3 structures.

Thus, the stability order is as follows,



Chemical Reactions of Alkenes: Alkenes are rich source of loosely held pi electrons, due to which they show electrophilic addition reaction. Electrophilic addition reactions of alkenes are accompanied by large energy changes so these are energetically favorable than that of electrophilic substitution reactions. In special conditions alkenes also undergo free radical substitution reactions.

1)Catalytic hydrogenation and its mechanism: Addition of molecular hydrogen to C=C in the presence of a transition metal catalyst such as Ni, Pt, Pd, Ru, Rh etc. is called as catalytic hydrogenation e.g. Ethene reacts with hydrogen gas in the presence of Raney Ni catalyst to form ethane.

It is an exothermic reaction.



Ethylene

Ethane

Propene reacts with hydrogen gas in the presence of Raney nickel catalyst to form propane.

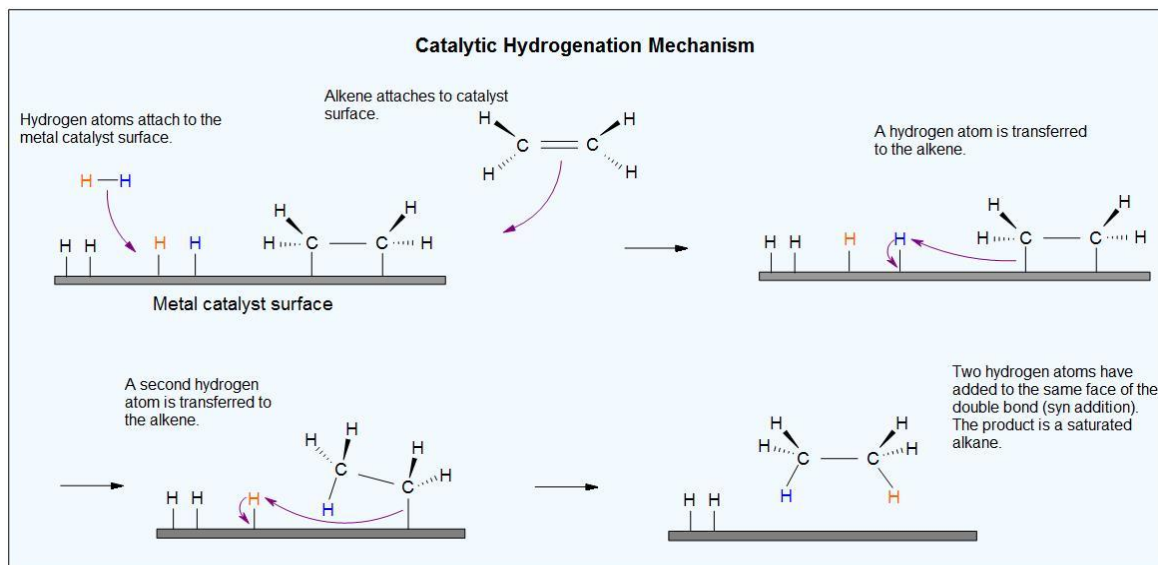


1-Propene

Propane

Mechanism:

- Finely divided (powdered) Raney nickel acts as adsorbing material.
- Ethylene and hydrogen gas get adsorbed on the metal surface by which H-H σ - bond becomes weak.
- Two hydrogen atoms from adsorbed metal surface add stepwise to the double bond of alkene forming alkane.
- Metal surface desorbs (removes) alkane immediately and become free for further alkene adsorption.
- Hydrogen also ads to adsorbed ethylene forming ethane.
- Addition of hydrogen to C=C of alkene is rapid and cis. Hence it is a stereo specific reaction.

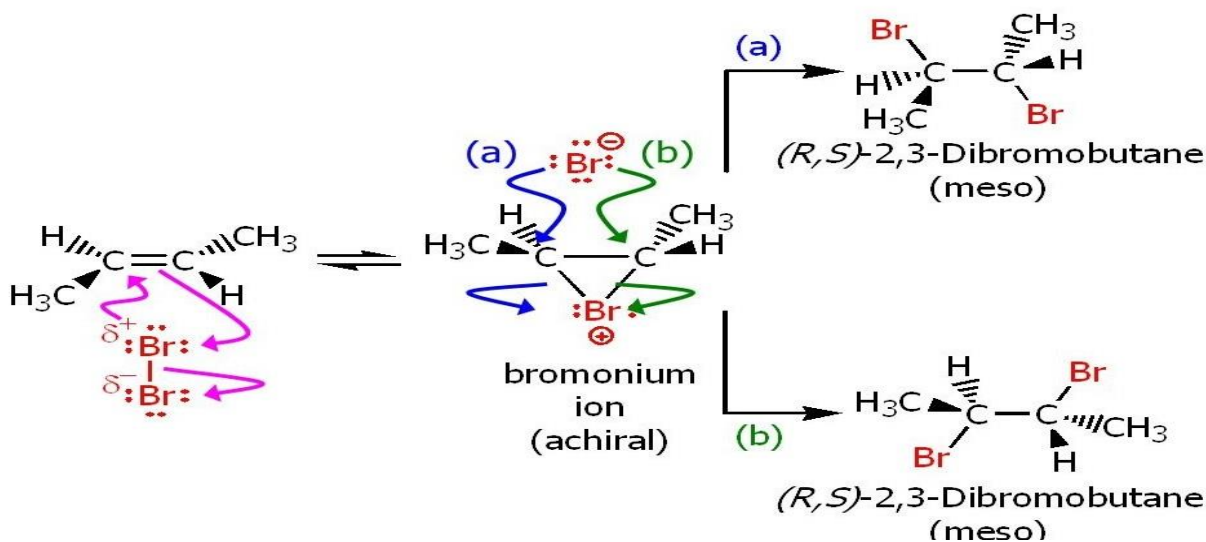
**2) Electrophilic and free radical additions:**

A) Addition of halogens: When chlorine and bromine add to C=C of alkene under ordinary conditions of temperature and pressure in a solvent medium gives dibromo or dichloro alkane as a addition product.

Example: When bromine in CCl_4 or CH_3COOH adds to C=C of alkene to form dibromo derivative. In this reaction decolorisation of bromine without evolution of HBr takes place.

This is important test for confirmation of unsaturation character of alkenes.

Reaction of bromine to trans-2-butene gives meso 2, 3 dibromobutane.



Mechanism: It involves two step mechanisms.

- In first step of this reaction one end of Br_2 molecule becomes positively polarized through electron repulsion by the pi-electrons of alkene, thereby forming pi-complex with it.
- It then breaks down to form cyclic bromonium ion.
- In second step, nucleophile Br^- attacks from the opposite side of the cyclic ring on either carbon atoms to produce trans-dibromo product.

Stereochemistry: There is formation of cyclic halonium ion (bromonium ion), addition of chlorine or bromine to $\text{C}=\text{C}$ of alkene is always opposite, that is anti. Hence it is a stereo selective reaction. Anti addition of bromine, with respect to two stereo isomers, becomes stereo specific reaction.

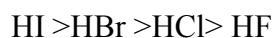
Example: Due to anti addition, trans-2-butene reacts with bromine to form meso dibromide while cis-2-butene reacts with bromine to form racemic product.

Under the catalytic influence of light, halogens (Cl_2 , Br_2) add to $\text{C}=\text{C}$ of alkenes by a free radical reaction. This radical addition is favored in the vapor phase or in a non-polar solvent like CCl_4 .

B) Addition of hydrogen halides (HX):

Markownikov's rule: In unsymmetrical alkene, the negative part of a molecule (hydrogen halide) adds to more substituted carbon atom of double bonded carbon atoms of alkene. It is known as Markownikov's rule.

The order of reactivity of hydrogen halides to alkene is as follows,

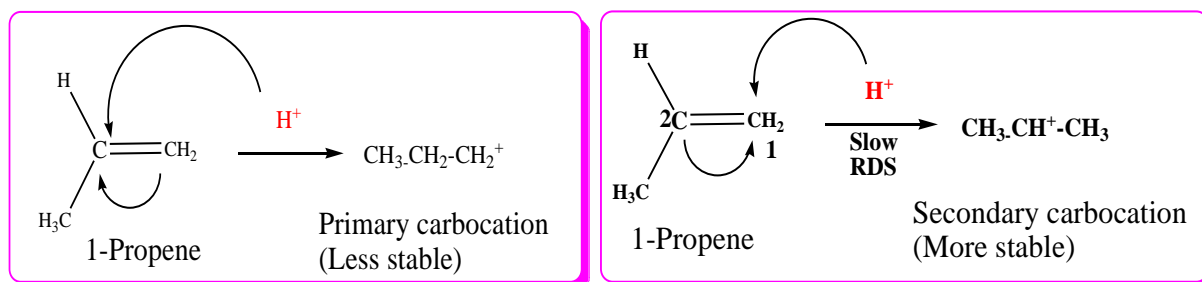


That is the order of their acid strength, it indicates that the addition of proton as electrophile to $\text{C}=\text{C}$ is the rate determining step.

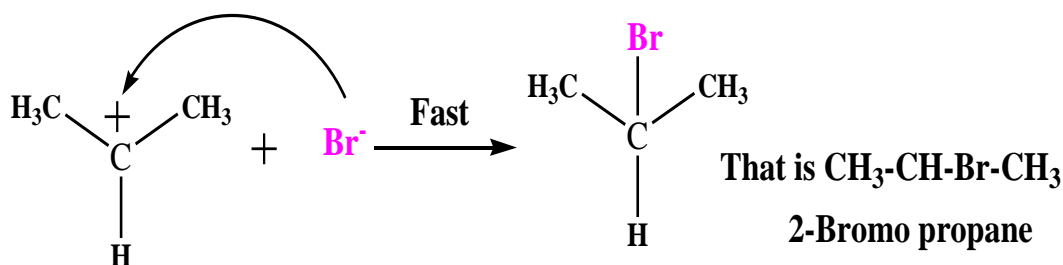
Example: Propylene reacts with bromine to form 2-bromopropane rather than 1-bromopropane.

Mechanism:

- H-Br ionizes to give H^+ as electrophile and Br^- as nucleophile. H^+ as electrophile prefers to attack one of the carbon atom of $\text{C}=\text{C}$ which results in the formation of more stable secondary carbocations.



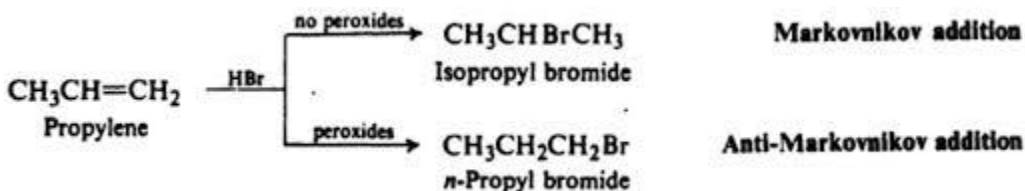
- Secondary carbocations are stabilized by hyper conjugative effect.
- Nucleophile Br^- then attacks positively charged carbon atom of secondary carbocations to form 2-bromo propane.
- Thus this addition of HBr to propene is according to Markownikov's rule.



Effect of substituent's on the rate of addition: Any effect that increases the electron density of C=C will enhance the reactivity of alkene towards electrophilic reagents. The electro donating substituent's like alkyl and OH on C=C increase the rate of addition by stabilizing the intermediate carbocations with hyper conjugative effect, Vice versa effect is shown if electron attracting group/substituent's present on alkene.

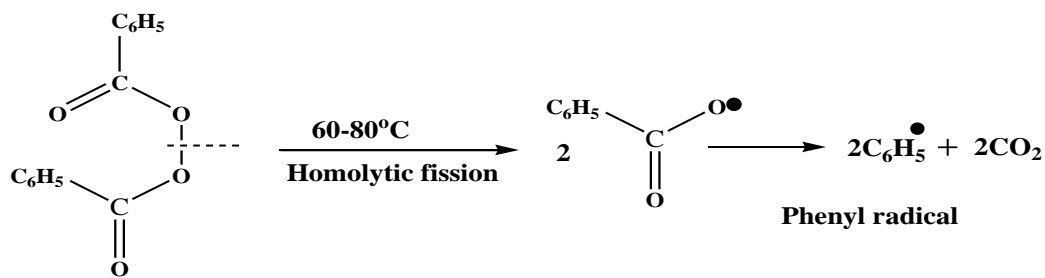
C) Free radical reactions (Peroxide effect/Kharasch effect/anti-Markownikov's rule):

In a presence of UV light or a small amount of initiator such as dibenzoyl peroxide, the addition of HB to an unsymmetrical alkene takes place according to anti-Markownikov's rule; it is called as Peroxide effect.



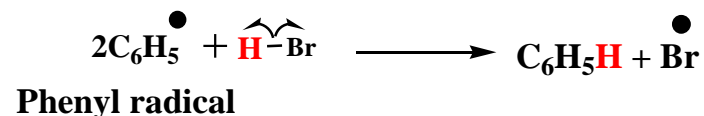
Mechanism: The reaction involves free radical mechanism pathway.

I) Initiation step: Dibenzoyl peroxide on thermolysis forms benzoyl peroxy radical which decomposes to give phenyl radical.

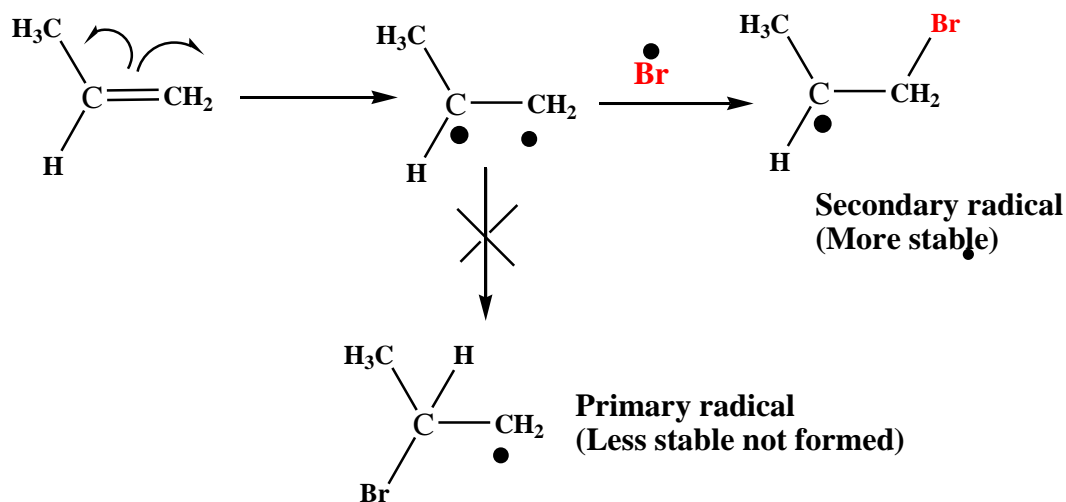


Dibenzoyl peroxide

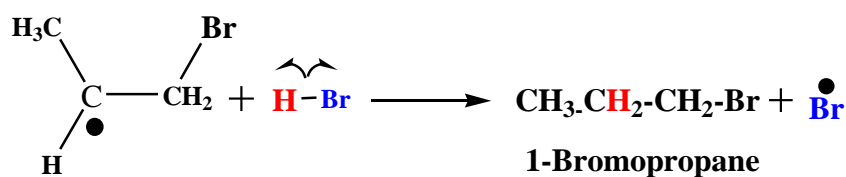
Phenyl radical abstracts H free radical from H-Br to generate Br free radical.



II) Propagation step: Br free radical acts as an electrophile and adds to C=C to form stable secondary radical.

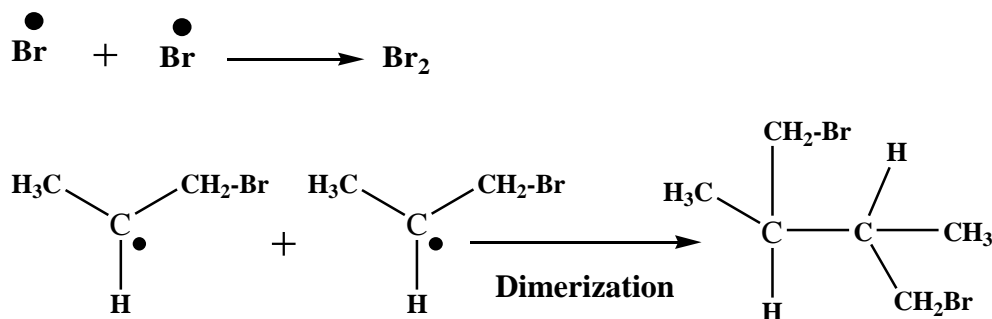


Secondary radical abstracts hydrogen free radical from another molecule of HBr to form 1-bromopropane rather than 2-bromopropane.



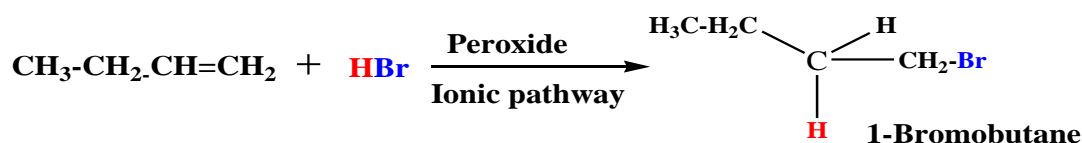
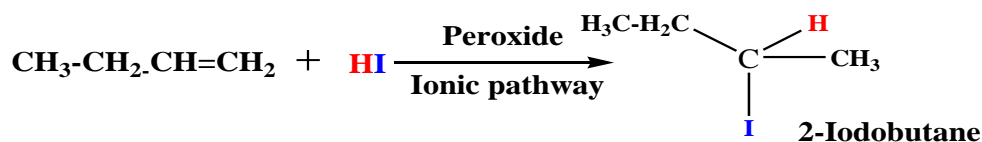
Generally Br free radical acts as an electrophile and thus continues the reaction.

III) Termination step: Br free radicals and secondary free radicals dimerize to give Br_2 and dibromo compound as minor byproducts.



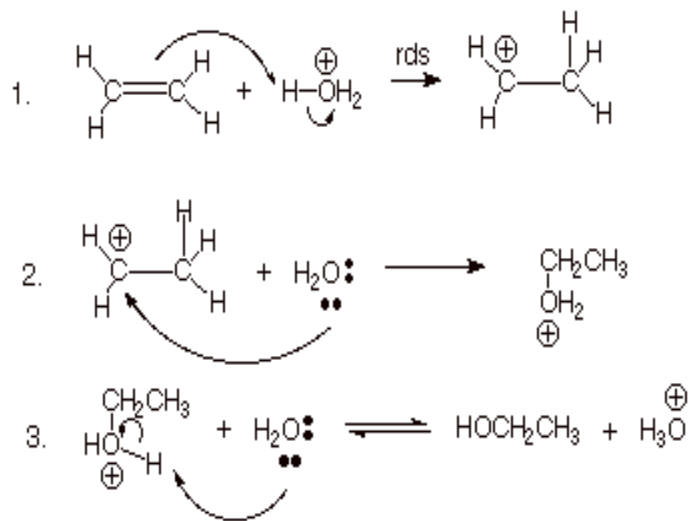
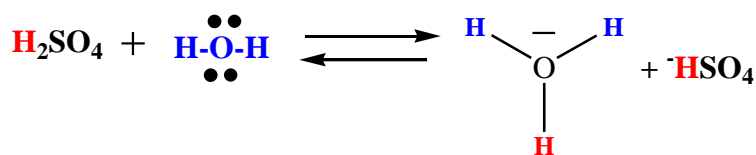
Note: Peroxide effect is not observed in the addition of HCl, HI and HF to an unsymmetrical alkene because these reactions are not energetically favorable for them. Hence addition of HCl,

HI and HF to an unsymmetrical alkene, even in the presence of dibenzoyl peroxide, takes place according to Markownikov's rule.



D) Hydration: The addition of water on C=C is called as hydration of alkenes. Alkenes on hydration give alcohols. This reaction is carried out at low temperature with dilute sulphuric acid which provides high concentration of water. It shifts the equilibrium to the right.

Mechanism:



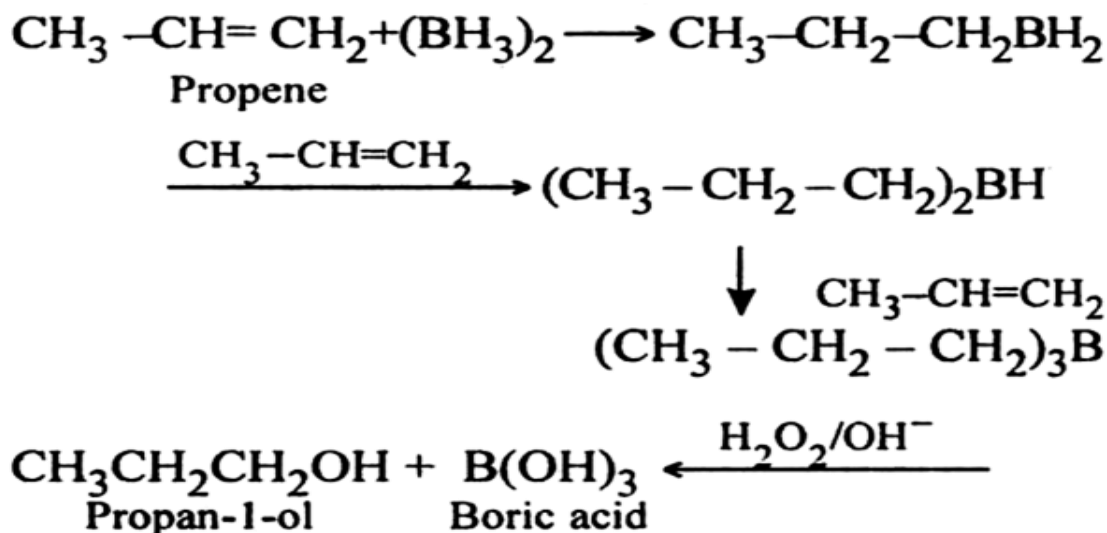
Hydration reaction takes place according to Markownikov's rule.

HSO_4^- is a weaker nucleophile than water and hence it does not attack carbocations.

Furthermore, water molecules envelop the HSO_4^- ion by solvation and thus it fails to come in contact with carbocations.

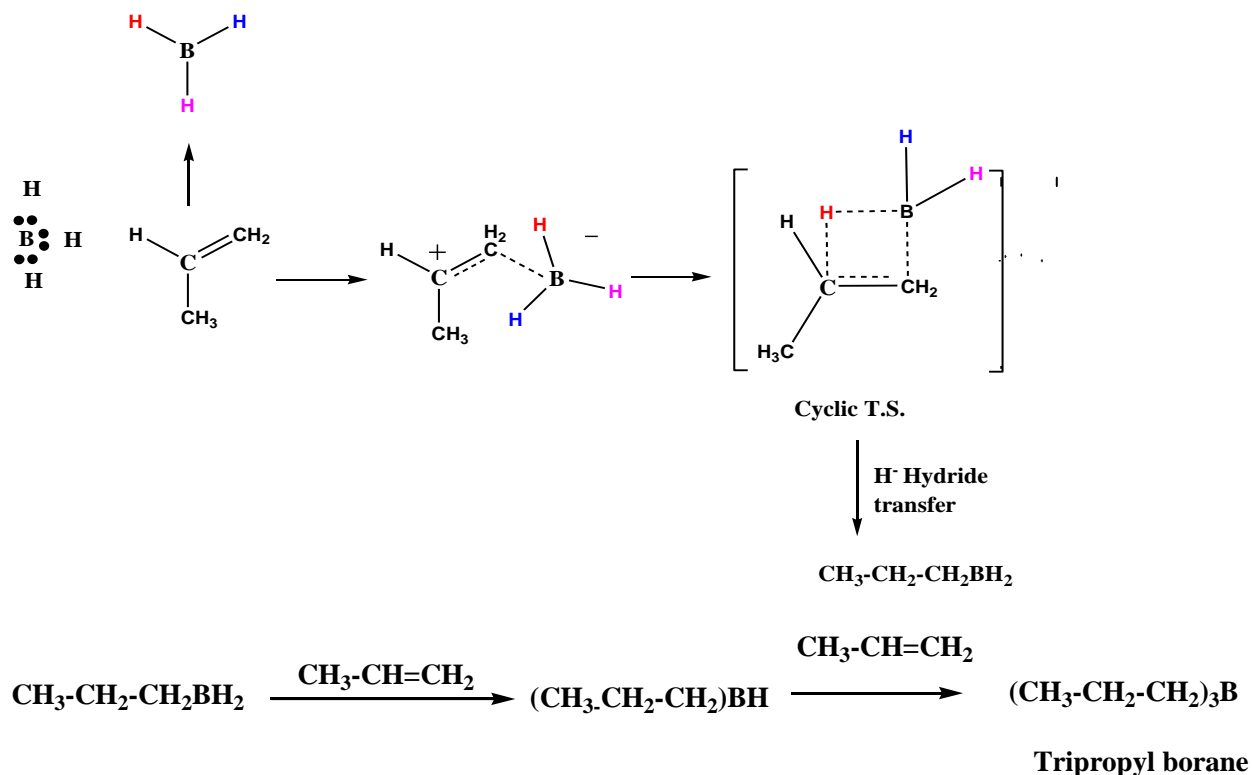
Hydroboration reaction: Alkene when reacted with diborane with tetrahydrofuran as solvent media forms trialkyl boranes which on oxidation with alkaline hydrogen peroxide solution afford primary alcohols. The reaction is called as hydroboration-oxidation reaction.

Example: Propene on treatment with alkaline diborane forms tripropyl borane which on oxidation with alkaline diborane forms tripropyl borane which on oxidation with alkaline H_2O_2 solution forms 1-propanol. The overall reaction takes place as an anti-Markownikov's rule.



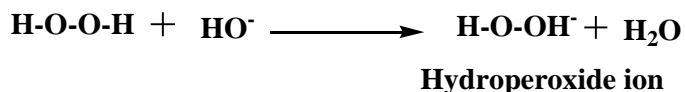
Mechanism:

- B_2H_6 , diborane, acts as monomer of $(\text{BH}_3)_2$.
- In BH_3 , there are six electrons around boron atom. This makes the boron atom in borane an electron deficient center and acts as Lewis acid.
- This BH_3 attacks on pi-electrons of an alkene and adds to the least substituted carbon atom of an alkene.
- While hydrogen atom of the borane attaches itself to the more electropositive carbon forming cyclic T.S.
- Transfer of H^- (Hydride) ion to positively polarized carbon atom takes place to form $\text{CH}_3-\text{CH}_2\text{CH}_2-\text{BH}_2$.
- It follows the same mechanism and transfers two hydride (H^-) ions to the more molecules of 1-propene to form tripropylborane.

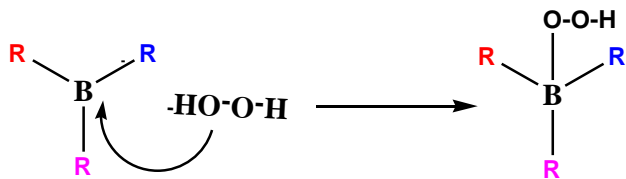


The mechanism for the oxidation stage involves the following steps.

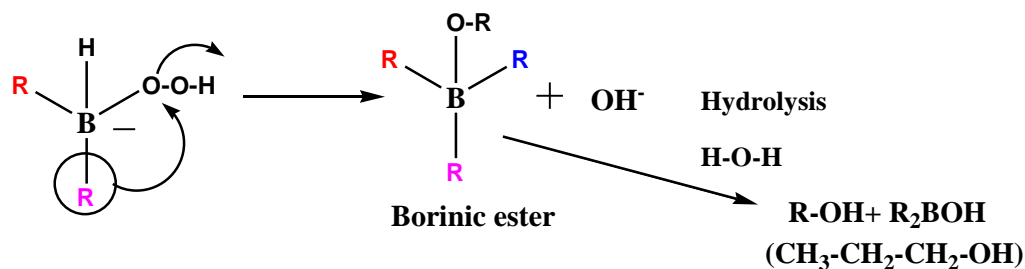
- H_2O_2 with NaOH solution forms hydro peroxide ion.



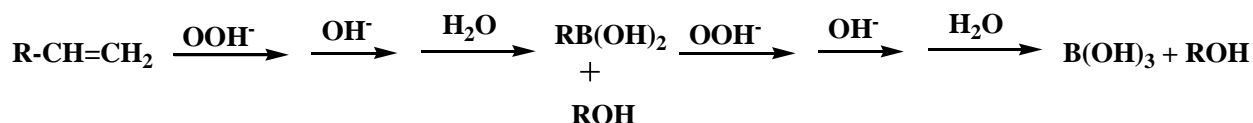
- Hydro peroxide ion acts as nucleophile and attacks on electron deficient boron of tripropylborane.



- The resulting hydro peroxide undergoes rearrangement which involves 1,2-anionic shift of an alkyl group with its bonded electron pair from boron to oxygen and forms borinic ester
- This ester on hydrolysis forms primary alcohol.

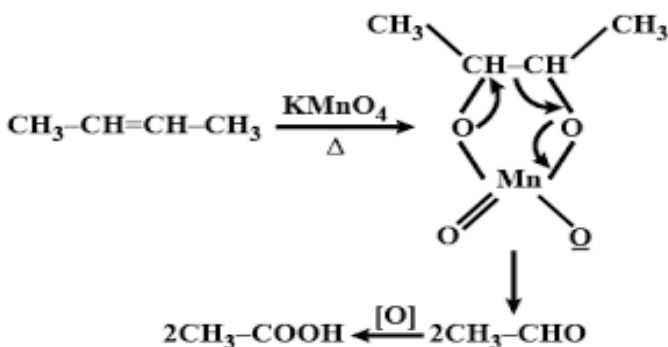


R₂BOH follows the same mechanism to give two more molecules of 1-propanol.



Oxidation with KMnO₄: Alkenes are oxidatively cleaved to salts of carboxylic acids by hot permanganate solutions.

Example: Cis or Trans -2-butene on oxidation with alkaline KMnO₄ solution undergoes oxidative cleavage to two molar equivalents of acetate ion. In this oxidation reaction, the intermediate may be a glycol; that is further oxidized with cleavage at the carbon-carbon bond.

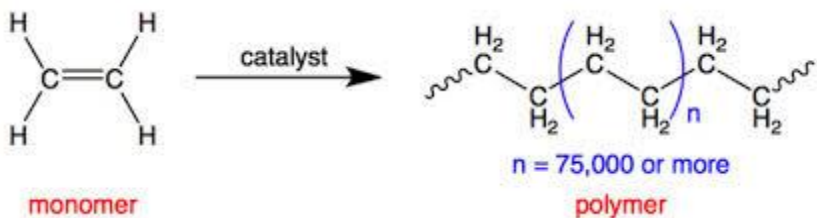


Polymerization of alkenes: The process in which a large number of small molecules unite to form larger molecule (Macromolecule) is called as polymerization. A small molecule is called as monomer and larger molecule is called polymer.

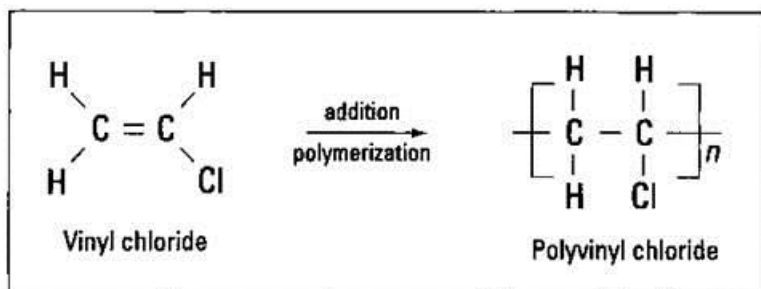
Example: A monomer like ethylene on heating under pressure with oxygen undergoes polymerization to form a polymer known as polyethylene.

It is having high molecular weight (about 20,000). The reaction is called as poly addition.

Polyethylene is used as plastic material for packaging films.



A substituted alkene like vinyl chloride under similar experimental conditions undergoes polyaddition reaction to form polymer known polyvinyl chloride. It is used to prepare phonographs records, plastic pipes, raincoats etc.





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DEPARTMENT OF CHEMISTRY

Question Bank

Class: B.Sc. Semester -I

Name of Paper: Organic Chemistry (Paper -II) CHE-102

Title of Chapter: Alkenes

Questions:

1. What are alkenes? Describe mechanism involved in the following methods of preparation of alkenes

A) Dehydrohalogenation of alkyl halides

B) Dehydration of alcohols.

2. Illustrate with suitable examples Saytzeff and Hoffmann rules to predict the orientations of elimination on the basis of molecular structure.

3. Offer examples of two different kinds of addition products when propylene reacts with HBr under different conditions. Give appropriate mechanism.

4. Explain the mechanism of hydration of alkenes using

A) Sulphuric acid

B) Diborane followed by oxidation with H_2O_2/OH

5. Write short notes on following

A) Relative stability of alkenes.

B) Polymerization of alkenes

C) Oxidation of alkene by $KMnO_4$

D) Reactivity of alkenes.

6. Discuss in detail the process of hydrogenation of alkenes.

7. Write in short physical properties of alkenes.

8. Describe with example Markownikov's addition on unsymmetrical alkenes.