

Chapter-4

THE HYDROCARBONS (ALKENES)

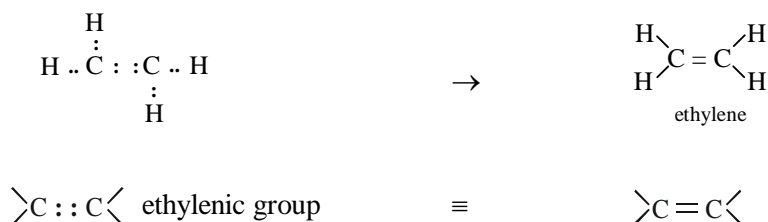
Alkenes

Alkenes are substances which contain less Hydrogen than the maximum quantity of Hydrogen which a Carbon atom can have. Hence these are referred to as unsaturated hydrocarbon. They have general formula C_nH_{2n} .

Structure: Any alkene consists of two Carbon atoms linked via a Carbon–Carbon π -bond.

The simplest member is ethene. *i.e.* $C_2H_4 \rightarrow CH_2 = CH_2$

According to Lewis concept of electron dot structure, the ethene molecule or ethylenic group can be represented as :

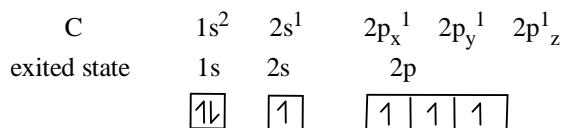


Hence the carbon–carbon double bond is the distinguishable feature of the alkene structure :

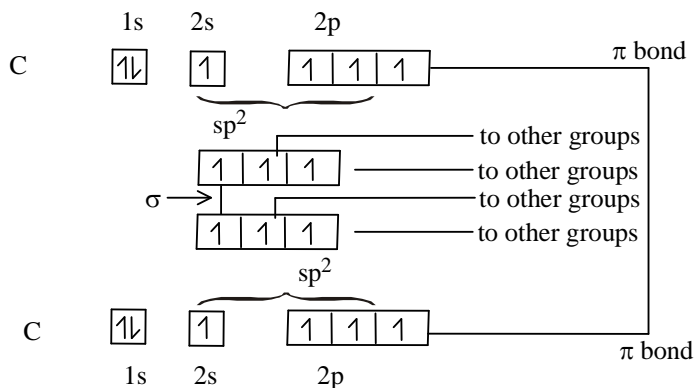
Quantum Mechanics: It provides a much more detailed picture. Every Carbon atom has an electronic configuration of $C = 1s^2 2s^2 2p_x^1 2p_y^1$

To take part in bonding it requires 4 unpaired electrons.

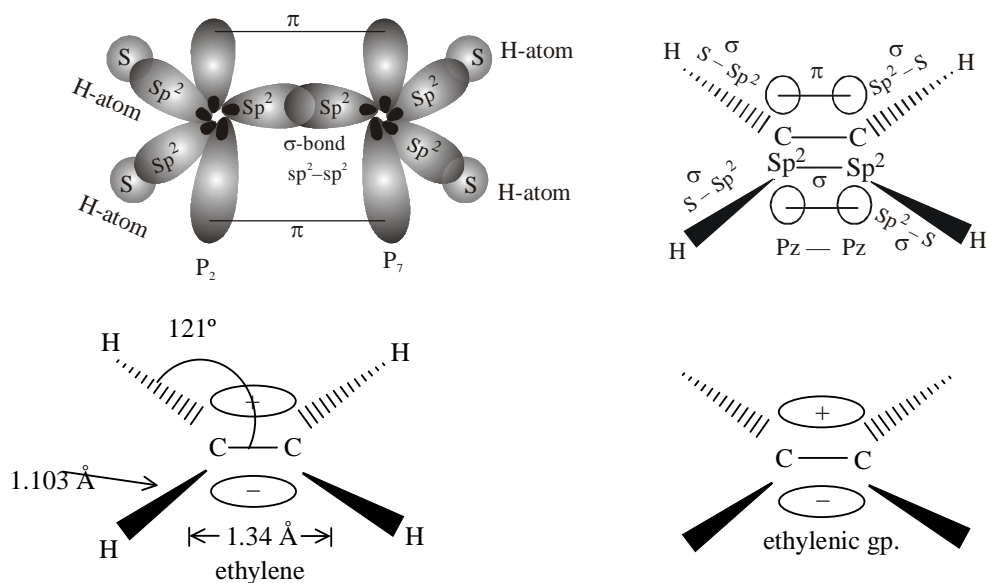
Hence the carbon atom in the excited state has an electronic configuration of



In ethene each Carbon atom has 3 σ bond and one π -bond. so every Carbon atom in order to form 3 bonds requires 3 unpaired electrons and so Carbon makes use of 3 equivalent hybrid orbital *i.e.* sp^2 hybrid orbitals.



One of the sp^2 hybrid orbital of one Carbon atom is used for overlap with one of the sp^2 hybrid orbital of other carbon atom for sp^2 – sp^2 overlap (1-bond) and the remaining 2– sp^2 hybrid orbital of each Carbon atom are either used to form σ -bonds with 4-different s orbital of Hydrogen to form ethene or with other groups *i.e.*



Hybridization, orbital size and comparative bond length: The Carbon-Carbon double bond in alkenes is shorter than the Carbon-Carbon single bond in alkanes because four electrons bind more tightly than two. In addition, certain other bonds in alkenes are significantly shorter than their counterparts in alkanes : for example, the C-H distance is 1.103 Å in ethylene compared with 1.112 Å in ethane. To account for this and other differences in bond length, we must consider difference in hybridization of Carbon.

The Carbon-Hydrogen bonds of ethylene are single bonds just as in, say ethane, but they are formed by overlap of sp^2 orbitals of carbon, instead of sp^3 orbitals as in ethane. Now, compared with an sp^3 orbital, an sp^2 orbital has less p-character and more s-character. A p-orbital extends more distance from the nucleus, s orbital, on the other hand, lies close to the nucleus. As the s character of a hybrid orbital increases, the effective size of the orbital decreases and, with it, the length of the bond to a given second atom. Thus an sp^2-s Carbon-Hydrogen bond should be shorter than an sp^3-s Carbon-Hydrogen bond.

Benzene, in most ways a quite different kind of molecule from ethylene also contains sp^2-s Carbon-Hydrogen bonds; the C-H bond distance is 1.10 Å, almost exactly the same as in ethylene. Acetylene contains sp -hybridized Carbon which, in view of the even greater s character of the orbitals, should form even shorter bonds than in ethylene; this expectation is correct, the sp-s bond being only 1.079 Å.

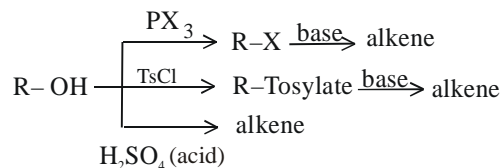
A consideration of hybridization and orbital size would lead one to expect an sp^2-sp^3 bond to be shorter than an sp^3-sp^3 bond. In agreement, the Carbon-Carbon single bond distance in propylene is 1.501 Å, as compared with the Carbon-Carbon distance of 1.534 Å in ethane. The $sp-sp^3$ Carbon-Carbon single bond in methylacetylene is even shorter, 1.459 Å.

Preparation of Alkene

The most important of the methods of preparation of alkenes are

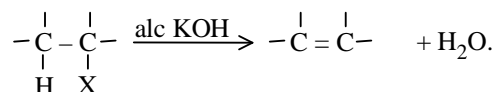
- Dehydrohalogenation of alkyl halide promoted by base
- Dehydration of alcohols catalysed by acids

It is also possible to get alkenes from alkyl sulfonates under a base-promoted elimination close by analogous to dehydrohalogenation. But remember both alkyl halides and alkyl sulfonates are prepared from alcohols

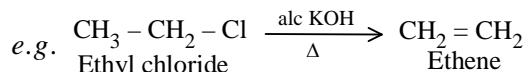


Dehydrohalogenation Method

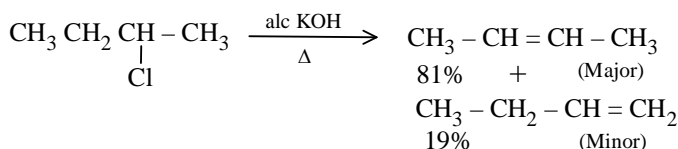
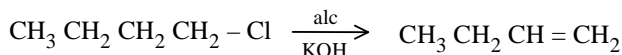
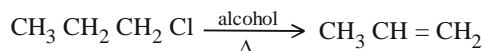
From alkyl halide



The reaction of an alkyl halide with alcoholic KOH is called dehydro halogenation. It can also be termed as elimination reaction. The ease of dehydrohalogenation of alkylhalide is $3^\circ > 2^\circ > 1^\circ$.



In such reactions the Hydrogen from the β -position is lost. Hence these are also called β -elimination reactions.

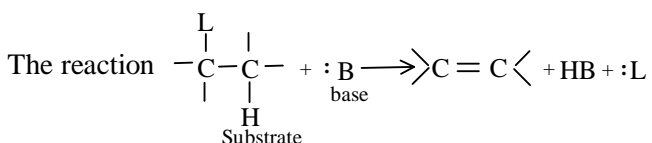


The fact that 1-Chlorobutane yields only But-1-ene and not But-2-ene proves beyond doubt that the β -H atoms to the Carbon carrying halogen is removed. Also the fact that 2-Chlorobutane which contains 2- β -Carbon atoms gives both But-1-ene and But-2-ene confirms that the reaction is β -elimination reaction.

Elimination Reactions

Elimination reaction occurs in two ways

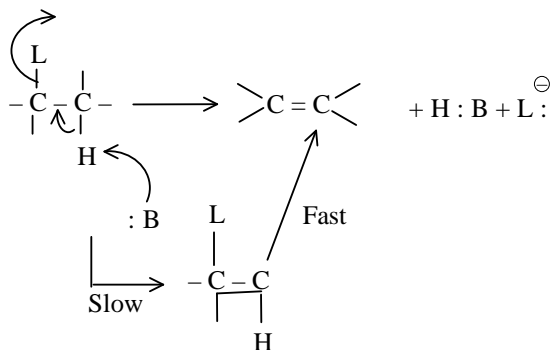
1. Bimolecular mechanism.
2. unimolecular mechanism



L = Leaving - group

The two ways in which such a reaction can take place are.

E-2 Mechanism



The transition state has a higher energy. Here since the formation of transition state is different, therefore formation of transition state is rate determining.

Applying kinetics. Rate $\propto [R-X][B:]$

The molecularity involved in the rate determining step is 2. Hence it is a bimolecular reaction.

This reaction involves the transition state where there is simultaneous removal of halogen from α -Carbon with simultaneous removal of H-atoms from β -Carbon atom. Hence known as 1,2 elimination or β -elimination.

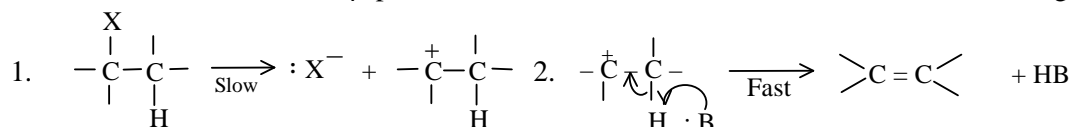
Such reactions are characterised by

- Leaving group, an atom, or group that leaves the molecule taking its pair of electrons with it
- In a position β - to leaving group, the substrate contains a H-atom.
- Reaction is brought about by action of above. (OH^- , $\text{C}_2\text{H}_5\text{O}^-$, $(\text{CH}_3)_3\text{C-O}^-$ etc.)

Sometimes the solvent itself behaves as a base (alcohol or water)

In elimination, a good leaving group is a weakly basic anion. The examples given under dehydro halogenation are all examples of E-2 mechanism.

E-1 Mechanism : Hughes and Ingold proposed that in the 1st step the halogen atom leaves first giving rise to a carbocation and then from the β -position to the carbocation the -H atom leaves as H^+ forming the alkene.

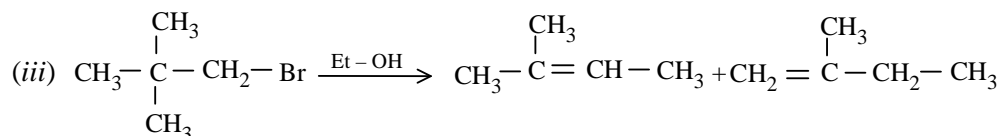
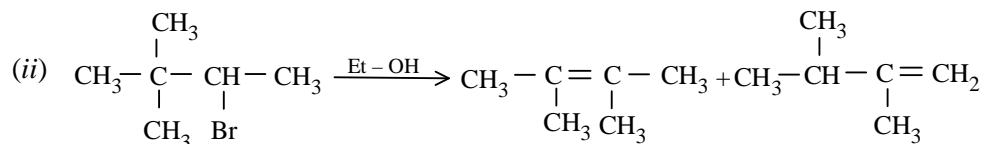
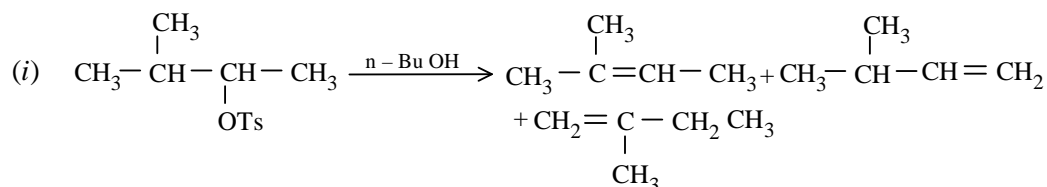


Here the 1st step involves only the breakage of bond where as step-2 involves the removal of H^{\oplus} and forming of π -bond. This leads to the formation of alkene.

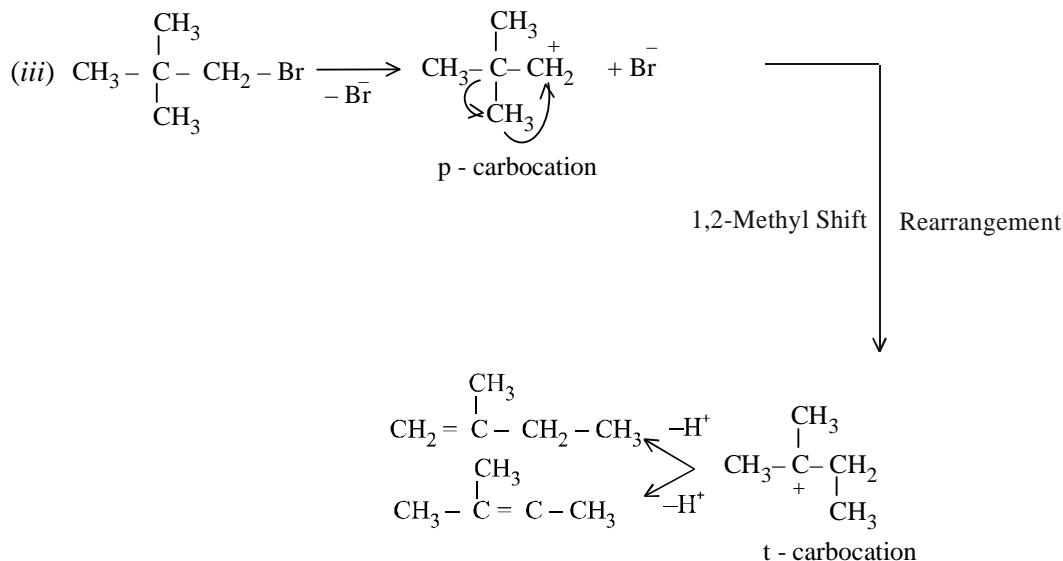
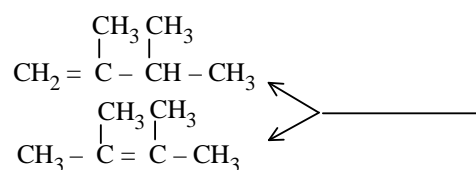
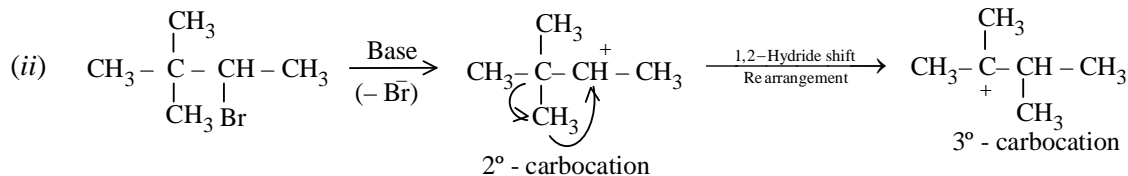
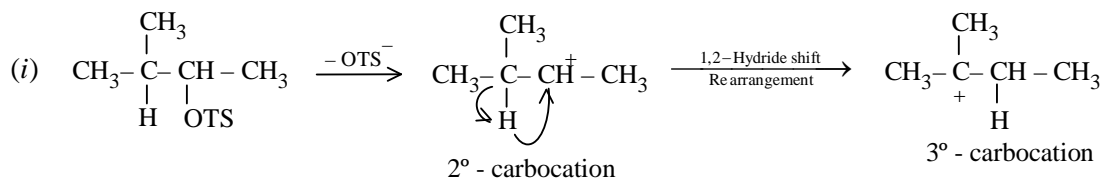
Since step -1 involves only cleavage of bond so it is the rate determining step. Hence Rate = $K[R-X]$

On the proposed mechanism in step-2 it is possible that the carbocation

- may combine with nucleophile to form substituted product
- rearrange to form stable carbocation
- eliminate proton to form alkene.



Mechanism



Evidence for E-1 mechanisms

- (1) Follows 1st order kinetics
- (2) Are not accompanied by primary Hydrogen isotope effect
- (3) Where structure permits, are accompanied by rearrangement

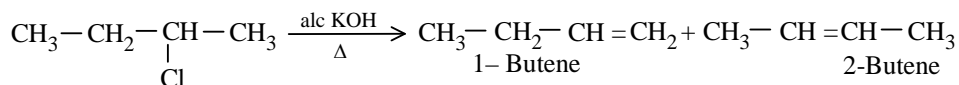
The general reactivity order of alkyl halides for eliminations are. (Both E-1 and E-2)

- (a) R-I > R-Br > R-Cl.
- (b) 3° > 2° > 1°

- (c) The general ease of formation of alkenes is

$\text{R}_2\text{C} = \text{CR}_2 > \text{R}_2\text{C} = \text{CHR} > \text{R}_2\text{C} = \text{CH}_2 > \text{RCH} = \text{CHR} > \text{RCH} = \text{CH}_2$ This is because the general order of stability of alkene is $\text{R}_2\text{C} = \text{CR}_2 > \text{R}_2\text{C} = \text{CHR} > \text{R}_2\text{C} = \text{CH}_2 > \text{RCH} = \text{CHR} > \text{RCH} = \text{CH}_2 > \text{CH}_2 = \text{CH}_2$

On the basis of this we can support Saytzeff's Rule according to which greater the number of alkyl groups attached to the doubly bonded Carbon atoms greater is stability of alkene. *i.e.*



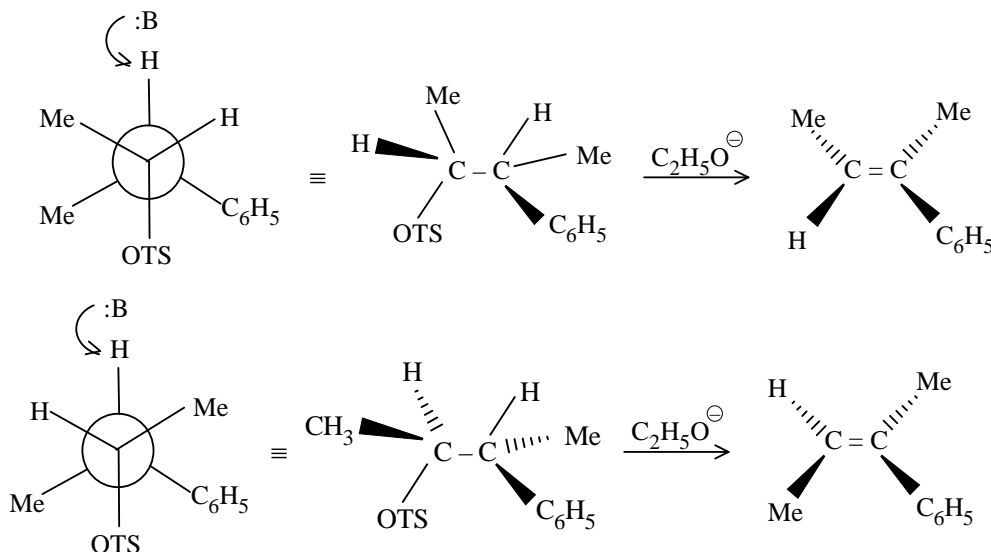
Here 2-Butene is the saytzeff's product.

Now if we see the number of hyperconjugations in 1-Butene it is 3 and the number of hyperconjugations in 2-Butene is 7. Hence 2-Butene is more stable than 1-Butene.

Hence 2-Butene is the predominant compound. We can also recast Saytzeff's rule as : in dehydrohalogenation, the more stable the alkene, the faster it is formed also the predominant formation of the more stable isomer is Saytzeff's orientation.

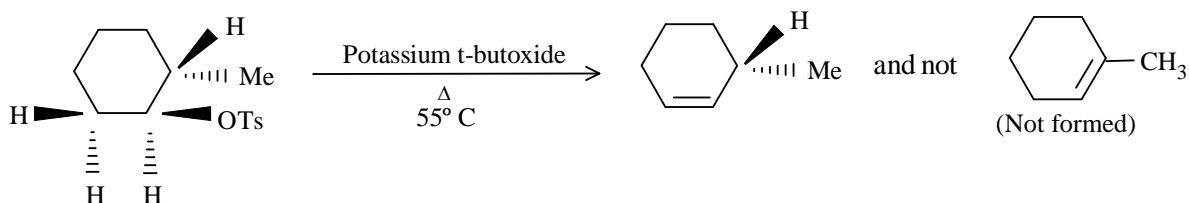
Stereochemistry of Elimination Reaction: There is evidence that an E-2 elimination proceeds only when the Hydrogen atom to be removed and the leaving group are in an anti conformation with respect to each other.

e.g. (2R, 3R)-3-Phenyl-2-butyl tosylate gives exclusively (E)-2-Phenyl-2-butene where as its diastereomer (2S, 3R)-3-Phenyl-2-butyl tosylate gives (Z) 2-Phenyl-2-butene.



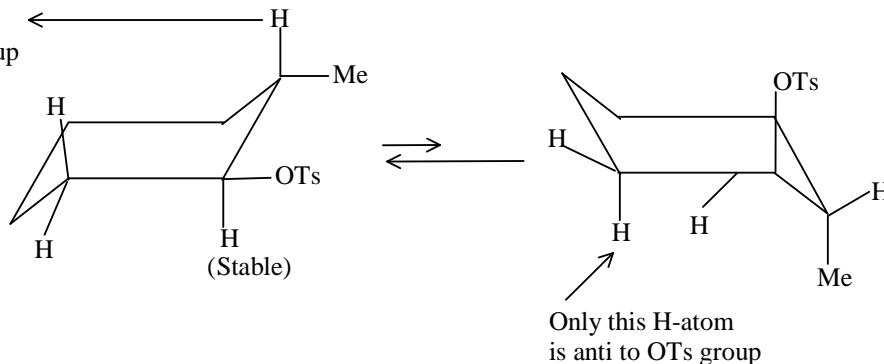
In an E-2 reactions, the stereochemistry of alkene that is formed is governed by the conformation that the starting material adopts in the transition state. So that the leaving group and the protons being removed by the base are anti to each other. There is no such stereochemical requirement for E-1 reaction, because the leaving group is lost and a carbocation has been formed before the proton is removed.

This can be illustrated with an example. The compound :



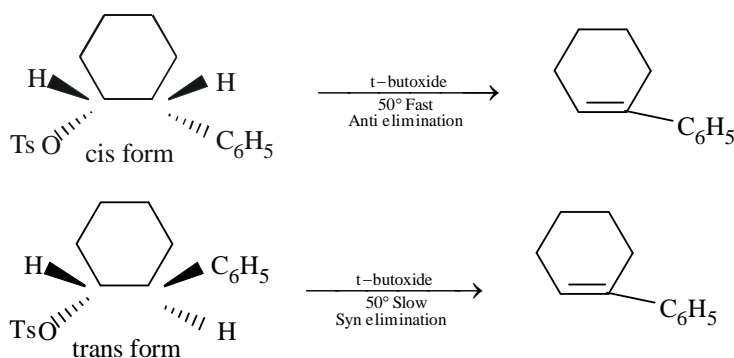
For this molecule in the most stable diequatorial conformation of trans-2-Methyl cyclohexyl-tosylate, no H-atom is anti to the leaving group but if the conformation of ring changes then one H-atom becomes anti to the leaving tosylate group.

The H-atom on the carbon adjacent to the leaving group are gauche not anti

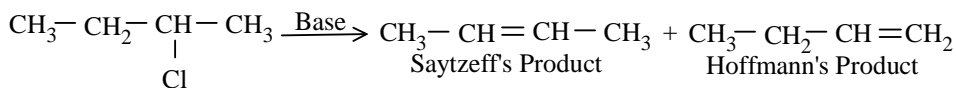


Although the anti orientation is the most favourable it is not essentially the only one possible form.

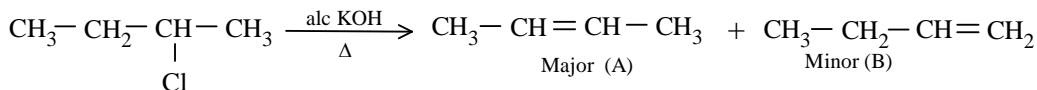
Reactions have suggested that as-2-Phenyl cyclohexyl tosylate and trans-2-Phenyl cyclohexyl tosylate both give 1-Phenyl cycloheptene but the rate at which the cis form reacts is nine times the rate at which the trans form reacts.



Saytzeff's Elimination vs Hoffmann Elimination: According to Hoffmann's elimination when an alkyl halide is treated with bulkier base, then an alkene with least substitution is found to be the major product.

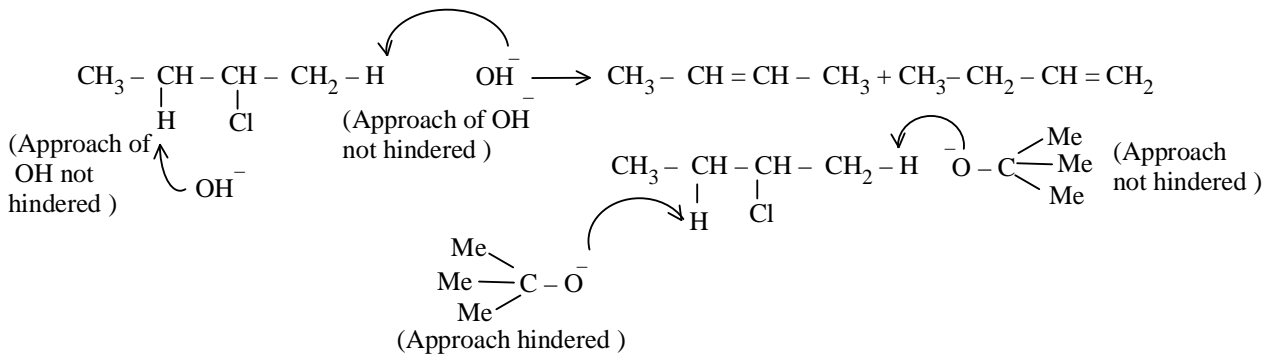


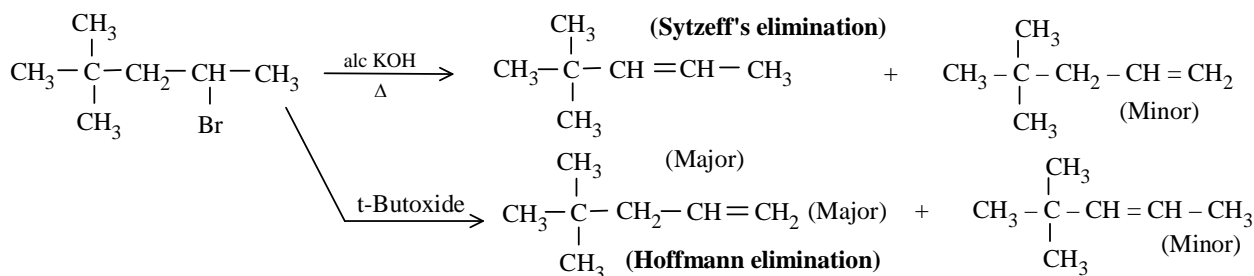
It is observed that when 2-Chlorobutane is heated with alcoholic KOH then the major product formed is 2-Butene and minor product formed is 1-Butene.



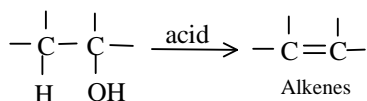
Here product (A) is the major product formed. Which is the Saytzeff's product.

However when 2-Chlorobutane is reacted with Potassium t-butoxide the yield of 1-Butene increases. This is because of the bulkiness of $(\text{CH}_3)_3\text{CO}^-$ which makes it more difficult to abstract the more hindered 2°H -atom.





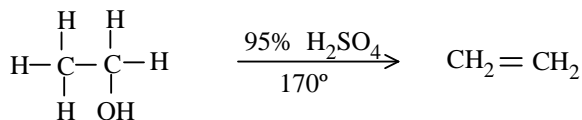
Dehydration of Alcohols



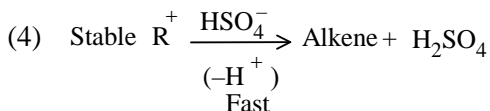
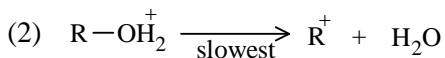
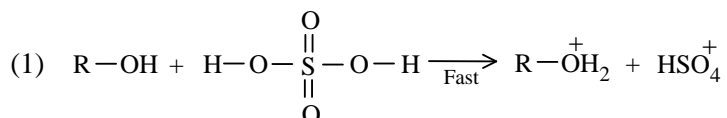
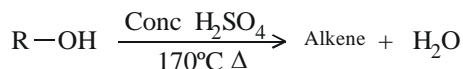
Ease of dehydration of alcohols is $t > s > p$

Alkenes are obtained by dehydration of alcohols. Dehydration can be done under two conditions.

- By heating alcohol with H_2SO_4 on Phosphoric acid at 200°C
- By passing vapours of alcohols over Alumina (Al_2O_3) at $350^\circ - 400^\circ$



General Mechanism



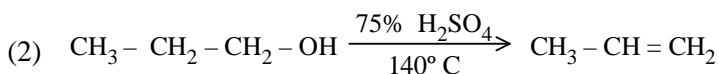
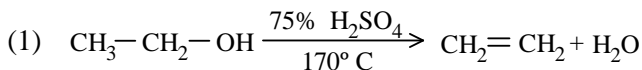
The slowest step is the rate determining step. Hence Rate = $K[\text{R} - \overset{+}{\text{O}}\text{H}_2]$

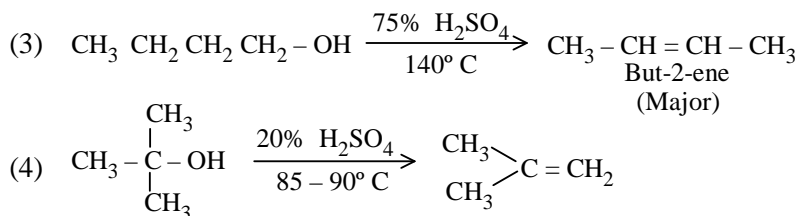
$$\Rightarrow \text{Rate} = K[\text{R-OH}] \Rightarrow [\text{R} - \overset{+}{\text{O}}\text{H}_2] \propto [\text{R} - \text{OH}]$$

Hence it is a First order reaction

It is a E-1 reaction.

This reaction is always accompanied by rearrangements.

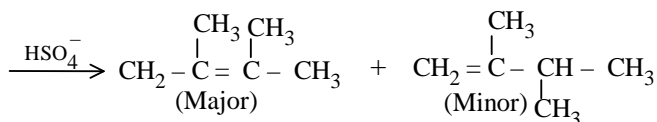
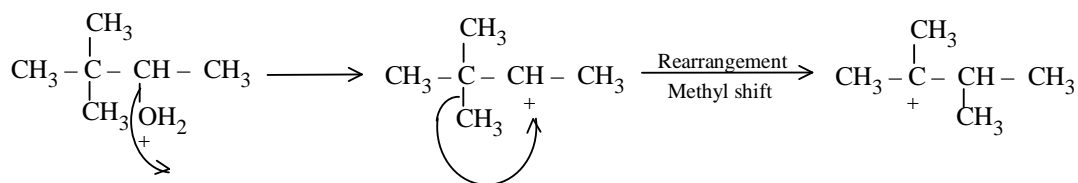
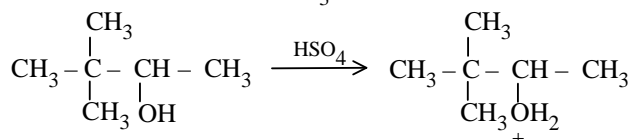
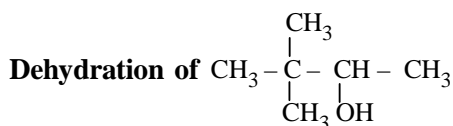
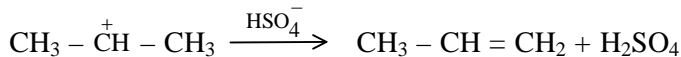
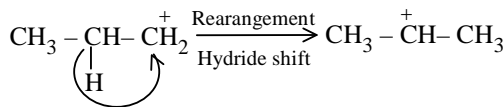
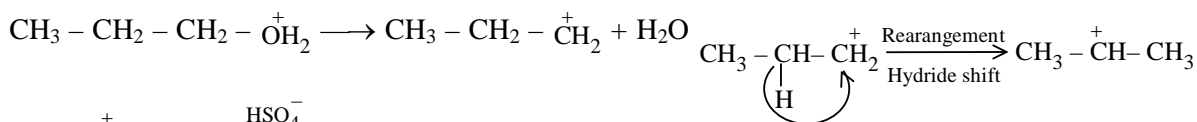




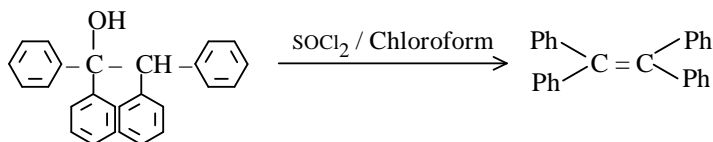
If one looks at the various reactions and conditions it clearly tells us that for dehydration of p-alcohol, one required highly concentrated acid while for t-alcohol, one requires less concentrated acid. This proves that the reactivity order of alcohols for dehydration is t > s > p-

Which could be reasoned out on the fact that during C—C bond cleavage, the substrate undergoes easy dehydration where the intermediate formed is most stable. Since the stability order of carbocation of alcohol is t > s > p. hence the reactivity of alcohol is t > s > p.

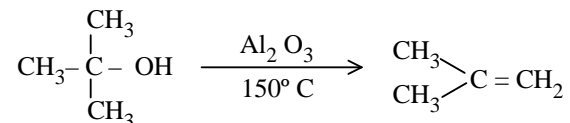
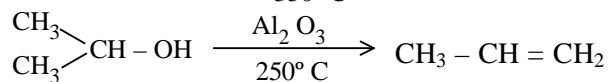
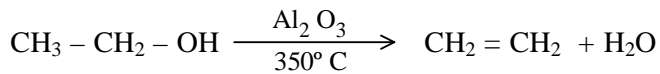
Dehydration of *n*-propyl alcohol.



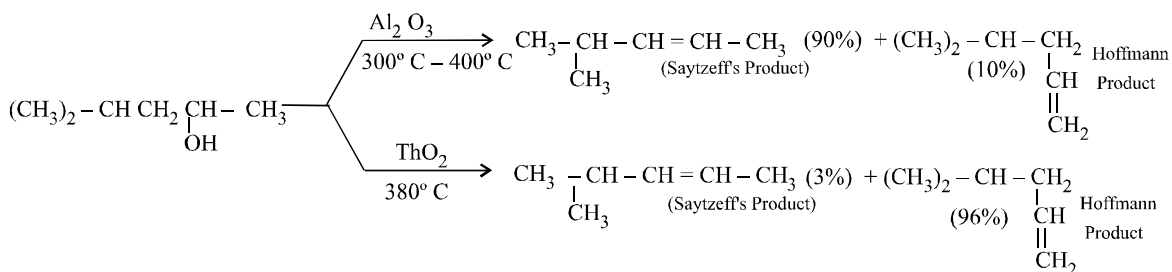
Thionyl chloride and Phosphorous halides convert hydroxy group to a good leaving group when heated with alcohol and thereby promote the dehydration.



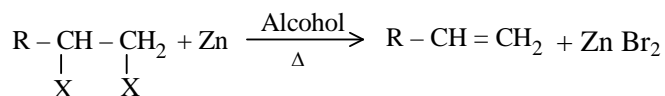
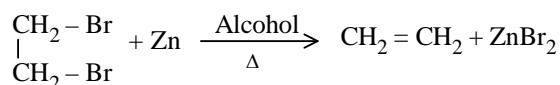
The second method of converting alcohol into alkene is by passing alcohol vapours over alumina or Thorium oxide as catalyst.



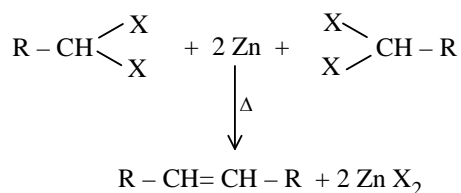
Dehydration of alcohols using Al_2O_3 follows Saytzeff's elimination, but dehydration of alcohols using Thorium oxide favours the Hoffmann elimination.



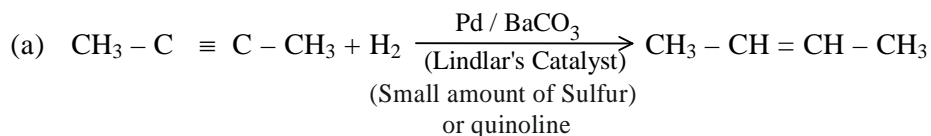
Dehalogenation of Vicinal Dihalides



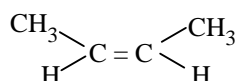
Dehalogenation of Geminal Dihalide



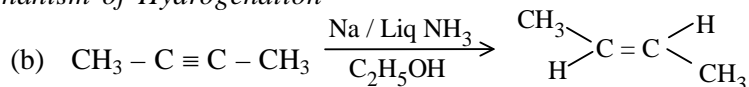
By Controlled Hydrogenation of Alkynes



This reaction always gives cis-isomer



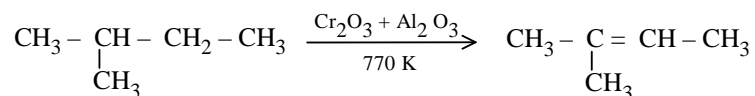
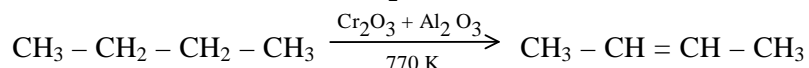
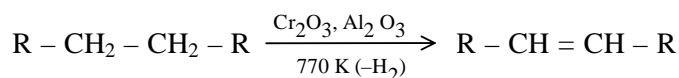
Mechanism of Hydrogenation



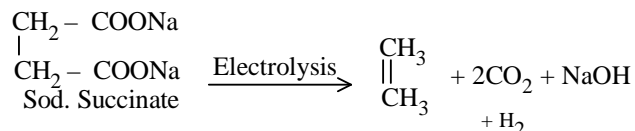
This is Birch reduction

Here in this reaction the product formed is a trans-isomer.

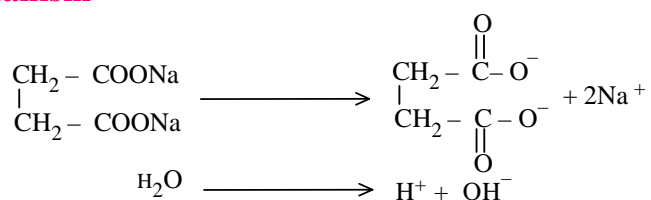
Dehydrogenation of Alkane



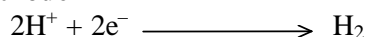
Kolbe's Electrolytic Decarboxylation: Electrolysis of aqueous solutions of Sodium salts of vicinal dicarboxylic acids leads to the decarboxylation of the compound leading to the formation of alkenes.



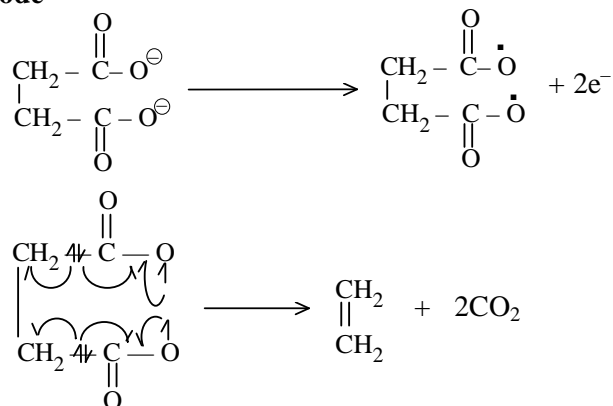
Mechanism



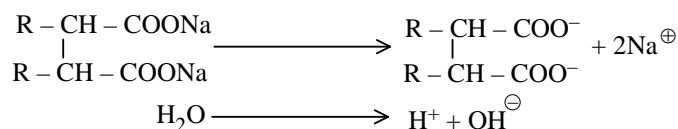
At Cathode



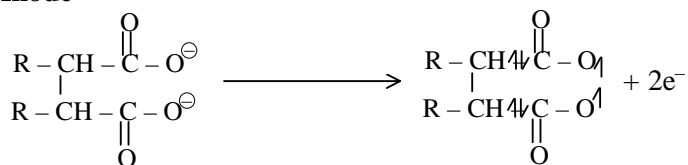
At Anode

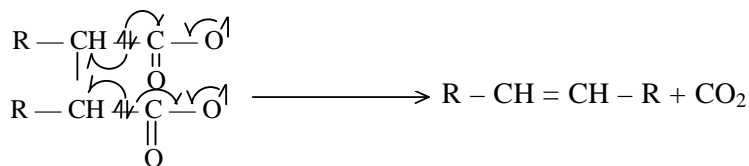


The solution hence contains Na^+ and OH^- there by becoming more and more basic. Here no other side product is formed because the elimination of CO_2 takes place without the formation of new free Radical.

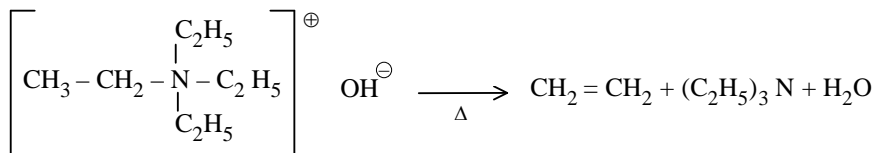


At Anode

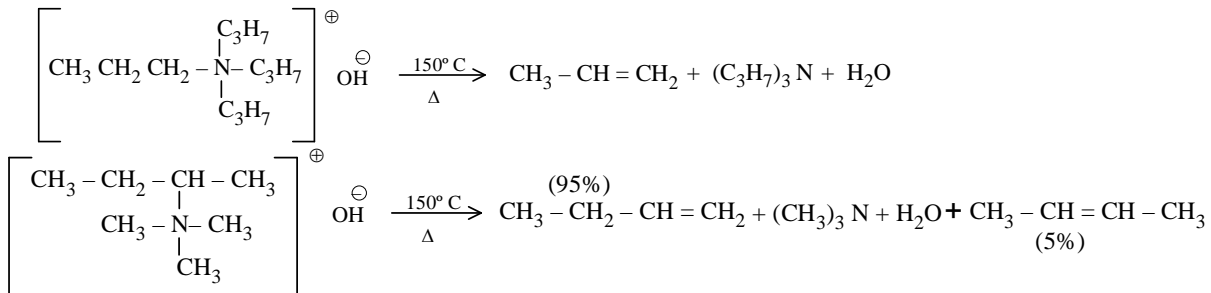




By Heating Quaternary Ammonium Hydroxide

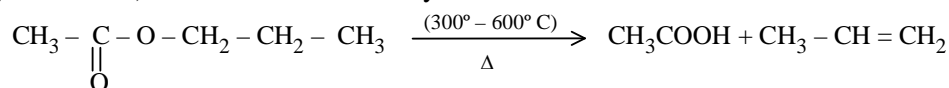


Here the alkene formed is an substituted alkyl groups. i.e. the Hoffmann product is formed.

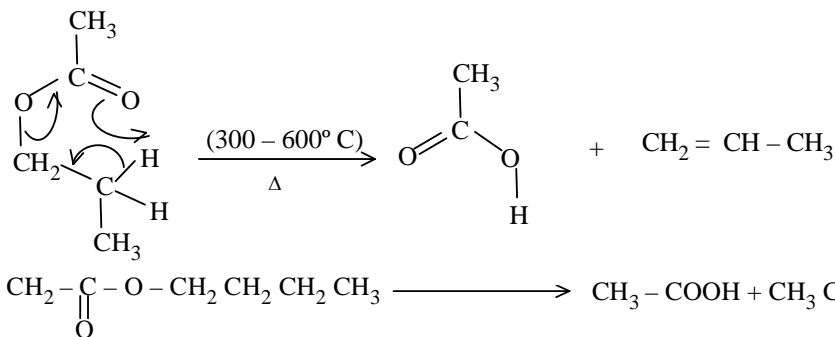


Pyrolysis

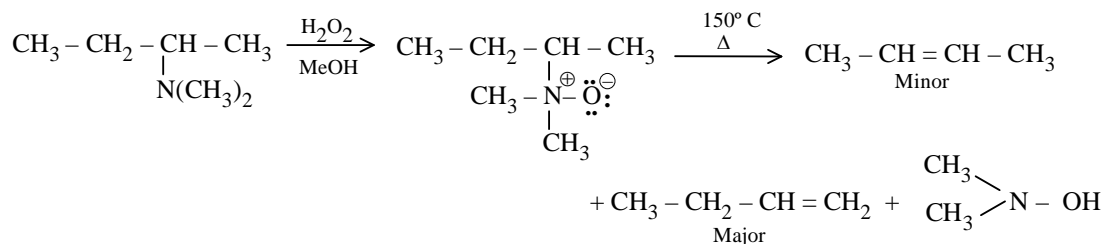
(a) **Pyrolysis of Esters:** When an ester containing α -H atom on the alkyl portion of the molecule is heated to (300-600 °C) an alkene and a carboxylic acid is formed.



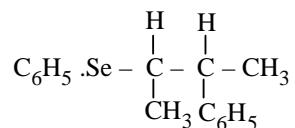
Mechanism



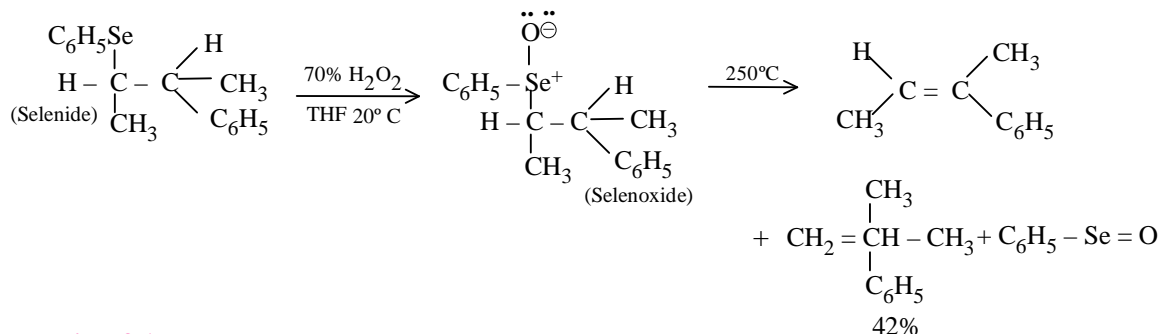
(b) **Pyrolysis of Amineoxide (Cope Reaction):** This method of alkene synthesis is closely related to ester pyrolysis. The oxygen atom of an amine oxide has a formal negative charge which functions as the internal base. Amine oxides are generally formed by peroxide oxidation of the corresponding tertiary amine. Here the alkene formed is the Hoffmann's product only.



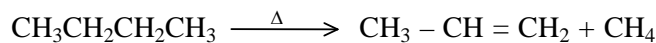
(c) Pyrolysis of Selenoxides



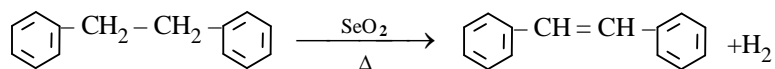
Selenoxides are organoselenium analogues of amine oxide and sulfoxides readily undergo elimination at or near room temperature to give good yield of alkenes. Selenoxides are obtained by peroxidation of corresponding selenides.



(d) Pyrolysis of Alkane



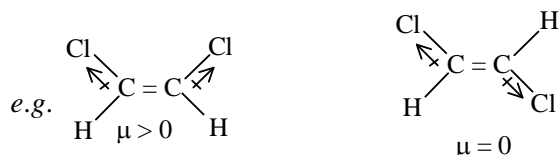
Heating with Selenium Oxide



Structure And Physical Properties

1. Physical Properties

- Alkenes containing two to four Carbon atoms are gases, those containing five to fifteen are liquids and higher alkenes are solids
- These are insoluble in water but soluble in organic Solvents.
- The boiling points of cis alkenes are higher where as melting points of trans-alkenes are more.



As Cis isomers being more polar, boils at a higher temperature, where as trans isomers being more symmetrical fits well into the crystal lattice and have higher melting point

2. Structure

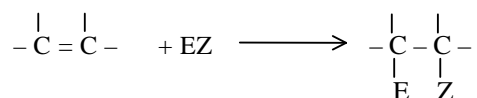
- The characteristic feature of the alkene structure, is the Carbon Carbon double bond. It is thus the functional group of alkenes and as the functional group, it determines the characteristic reactions that alkenes undergo.

These reactions are of two types.

- First, there are those that take place at the double bond itself and, in doing this, destroy the double bond.

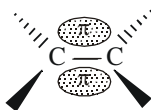
- (b) There are some reactions that take place, not at the double bond, but at certain positions having special relationships to the double bond. Outwardly the double bond is not involved; it is found intact in the product. Yet it plays an essential, though hidden, role in the reaction : it determines how fast reactions take place and by which mechanism or whether it takes place at all.

Reactions at the Carbon–Carbon double bond. Addition: The double bond consists of a strong σ bond and a weak π bond; we expect, therefore, that reaction would involve breaking of this weaker bond. This expectation is correct; the typical reactions of the double bond are of the sort where the π bond is broken and two strong σ bonds are formed in its place.



A reaction in which two molecules combine to yield a single molecule or product is called an addition reaction. The reagent is simply added to the substrate, in contrast to a substitution reaction where part of the reagent is substituted for a part of the substrate. Addition reactions are necessarily limited to compounds that contain atoms sharing more than one pair of electrons, that is, to compounds that contain multiply bonded atoms. Formally, addition is the opposite of elimination; just as elimination generates a multiple bond, addition destroys it.

In the structure of the bond there is a cloud of π electrons above and below the plane of the atoms. These π electrons are less involved than the σ electrons in holding together the Carbon nuclei.



As a result, they are themselves held less tightly. These loosely held electrons are particularly available to a reagent that is seeking electrons. It is not surprising, then, that in many of its reactions the carbon–carbon double bond serves as a source of electrons : that is, it acts as a base. The compounds with which it reacts are those that are deficient in electrons, that is, are acids. These acidic reagents that are seeking a pair of electrons are called electrophilic reagents. The typical reaction of an alkene is electrophilic addition, or, in other words, addition of acidic reagents.

Reagents of another kind i.e., free radicals also seek electrons—or, rather, seek an electron. And so we find that alkenes also undergo free-radical addition.

Electrophilic Addition Reaction – Mechanism

Addition of the acidic reagent, HZ, involves two steps : (Z may be $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{CN}$, $-\text{OH}$, $-\text{OSO}_3\text{H}$ etc.)

Step (1) the first step involves the addition of H^\oplus leading to the formation of carbocation.

Step (2) is the combining of the carbocation with the base : Z.

The evidence for this mechanism includes.

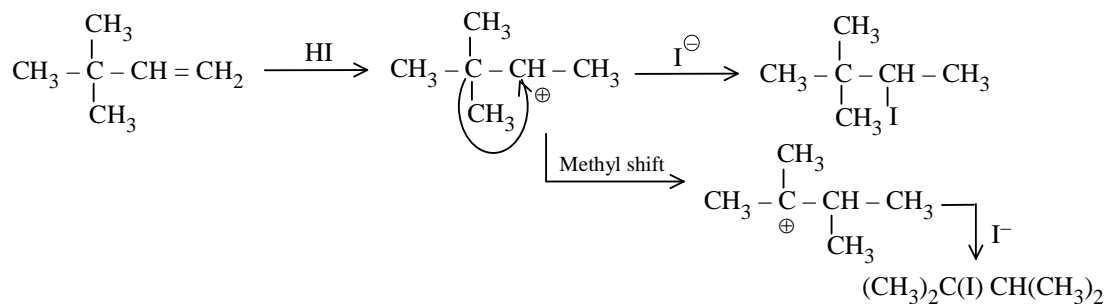
- The rate of reaction depends upon the concentration of both the alkene and the reagent HZ.
- Where the structure permits, reaction is accompanied by rearrangements. In addition, the mechanism is consistent with structures :
- The orientation of addition; and
- The relative reactivities of alkenes.

Rearrangements in Electrophilic Addition Reaction: Where the structure permits, the reaction is accompanied by rearrangements. The product sometimes contains the group Z attached to a Carbon that

was not doubly bonded in the substrate; sometimes the product even has a Carbon skeleton different from that of the substrate.

These “unexpected” products, are readily accounted for by rearrangements of the carbocations proposed as intermediates. These rearrangements follow exactly the same pattern that we have come to expect from our study of carbocations in S_N1 substitution and in $E1$ elimination.

For example, addition of hydrogen iodide to 3,3-dimethyl-1-butene yields not only the expected 2-Iodo-3, 3-dimethylbutane, but also 2-Iodo-2, 3-dimethylbutane:

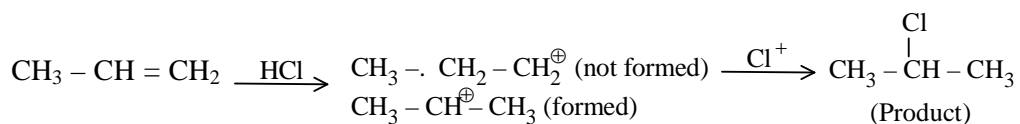


Since a 1,2-shift of a methyl group can convert the initially formed secondary cation into a more stable tertiary cation, such a rearrangement does occur, and much of the product is derived from this new ion and hence the product obtained is 2-Iodo-2, 3-dimethyl butane.

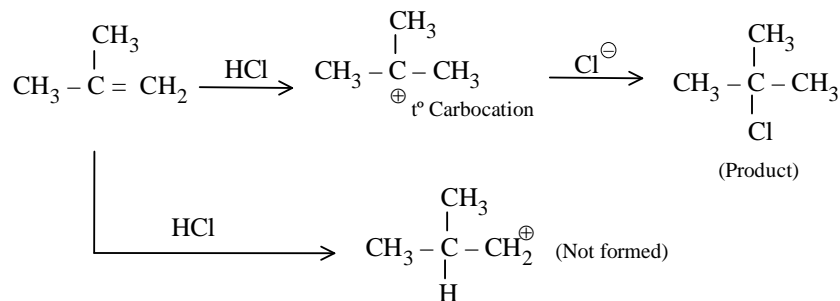
Electrophilic Addition : Orientation and Reactivity

The mechanism is consistent with the orientation of addition of acidic reagents, and the effect of structure on the relative reactivities of alkenes.

Addition of hydrogen chloride to two of the typical alkenes is outlined below, with the two steps of the mechanism shown. In accordance with Markownikov’s rule, propylene yields isopropyl chloride, isobutylene yields tert-butyl chloride, and 2-Methyl-2-butene yields tert-pentyl chloride.



According to the mechanism, Hydrogen from the reagent adds to one or the other of the two doubly bonded Carbons to give one or the other of two possible carbocations. For example, if Hydrogen goes to C-2 of propylene, we get the n-propyl cation; if it goes to C-1, we get isopropyl cation. Once formed, the carbocation rapidly reacts to yield product. Which halide is obtained, then depends upon which carbocation is formed in the first step. The fact that propylene yields isopropyl chloride rather than n-propyl chloride shows that the isopropyl cation is formed, faster than the n-propyl cation. Thus, orientation in electrophilic addition is determined by the relative rates of two competing reactions : formation of one carbocation or the other.

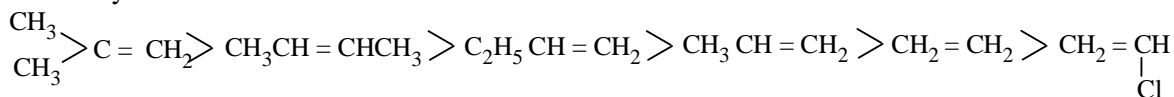


In each of the examples given above, the product obtained shows that in the initial step a secondary cation is formed faster than a primary, or a tertiary faster than a primary, or a tertiary faster than a secondary. Examination of the orientation in many cases shows that this is a general rule : in electrophilic addition the rate of formation of carbocations follow the sequence

Rate of formation of carbocations $3^\circ > 2^\circ > 1^\circ$

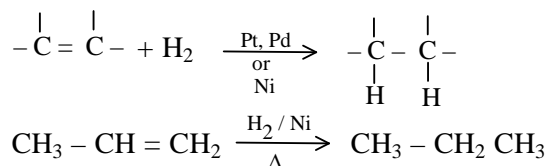
Stability of carbocations $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

Reactivity of alkenes towards acids is



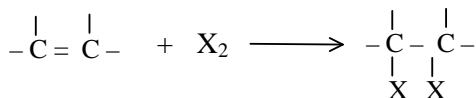
Chemical Reaction

1. Hydrogenation Reaction

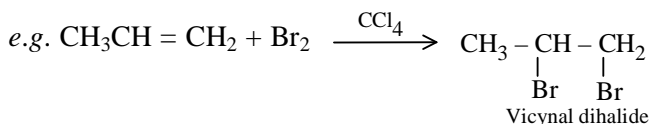


The reaction has been discussed at length in the heading of preparations of alkanes

2. Addition of Halogens



Here $\text{X}_2 = \text{Cl}_2$ or Br_2

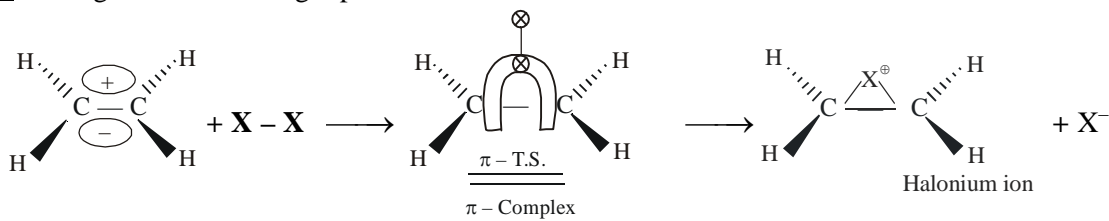


The reaction is carried out simply by mixing together the two reactants, usually in the solvents like Carbon tetrachloride. The addition proceeds rapidly at room temperature and does not require exposure to ultraviolet light.

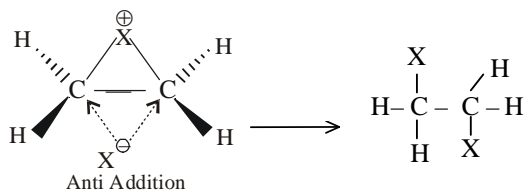
Note : If high temperature, exposure of light or presence of excess halogen is there substitution might become an important side reactions. This reactions leads to the formations of vicinal dihalide.

Mechanism: The additions of halogens to alkenes involves two steps.

Step - 1: Halogen transfer losing a pair of electrons.



Step - 2:

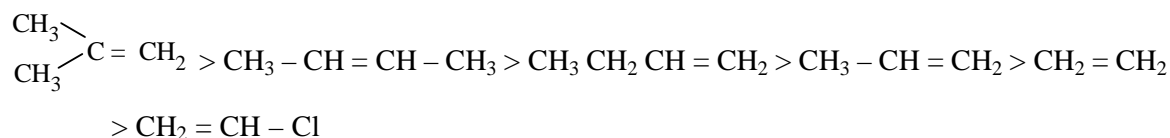


The second step involves the attack of X^- ion on the halonium ion to form the dihalogen derivatives.

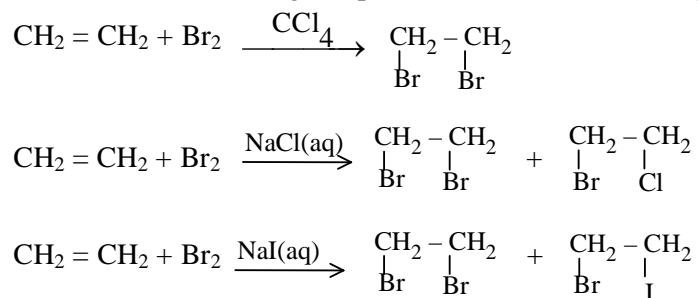
This mechanism is proposed based upon the fact that the reaction depends upon

- (i) effect of the structure of alkene.
- (ii) effect of added nucleophile on the product obtained.
- (iii) the fact that halogen adds with complete stereoselectivity and in the anti sense.
- (iv) the role played by halonium ion in neighbouring group effects.

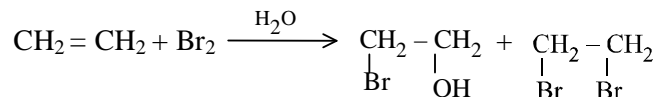
- (a) **Effect of Structure of Alkene:** Alkenes show the same order of reactivity towards halogens or towards acid.



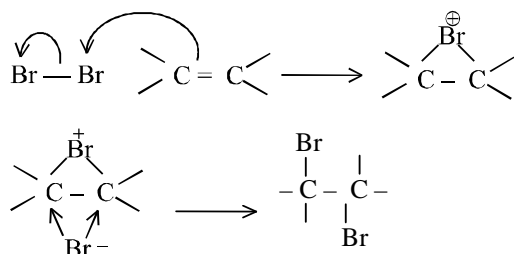
- (b) **Effect of Nucleophiles on Products Formed:** If a halonium ion is the intermediate and capable of reacting with halide ion, then we might expect it to react with almost any negative ion or basic molecule.



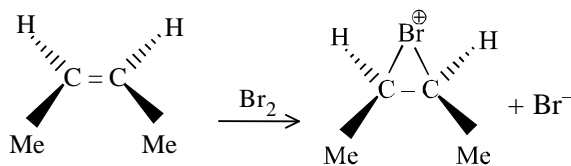
But also $\text{CH}_2 = \text{CH}_2 + \text{NaCl (aq)} \longrightarrow \text{No reaction}$

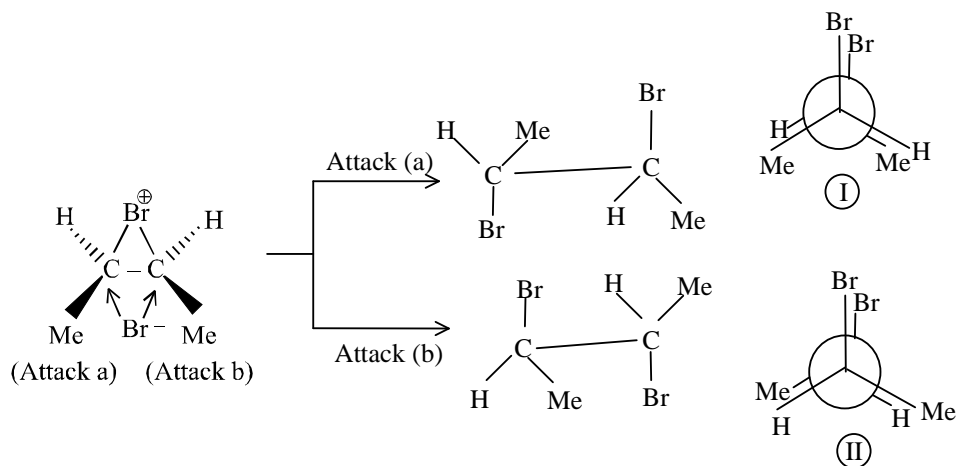


Stereochemistry of Addition: The stereochemistry of the reaction can be understood by the mechanism.



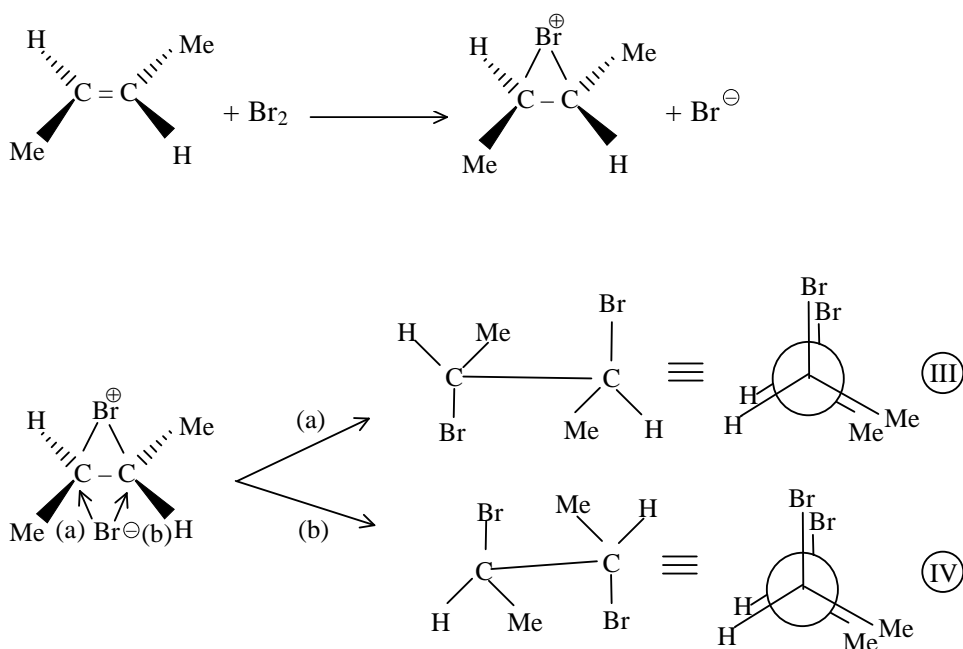
When *cis* But-2-ene is brominated, a racemic mixture of 2,3-Dibromo butane is obtained, this could be explained by the mechanism as proposed above.





Compounds I and II are mirror images of each other. Also attack of Br^{\ominus} anti to Br^{\oplus} can be by 50% attack a and 50% attack b thus leading to racemization.

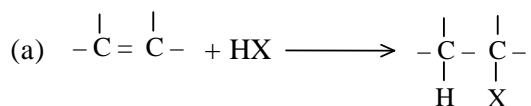
However Bromination of trans But-2-ene leads to meso compound formation.



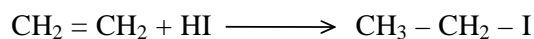
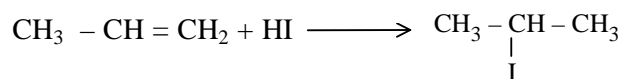
Compound III and IV are identical and possess a plane of symmetry and hence are meso form

3. Addition of Hydrogen halides

An alkene is converted to alkyl halide by HCl or HBr or HI.

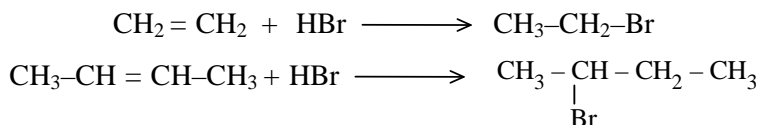


Here HX = HCl, HBr, HI



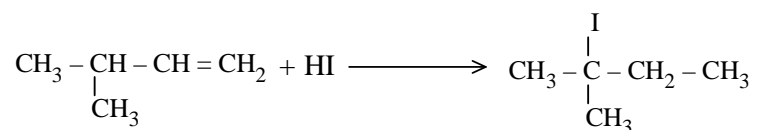
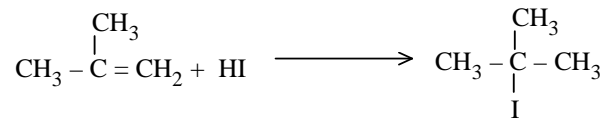
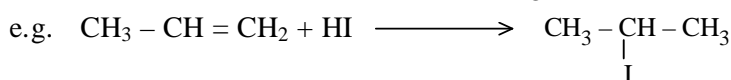
The reaction is frequently carried out by passing dry gaseous Hydrogen chloride into alkene. Sometimes it is carried out in moderately polar solvents like CH_3COOH , which dissolves both the polar HX and the non polar alkene.

When the alkene is symmetrical like $\text{CH}_2 = \text{CH}_2$ or $\text{CH}_3\text{-CH=CH-CH}_3$ etc., then the addition of HX may go to any C-atom carrying a double bond.

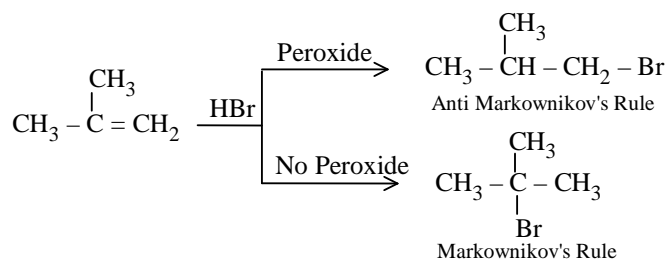
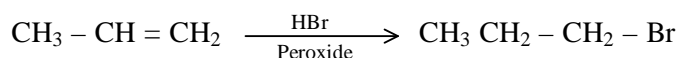
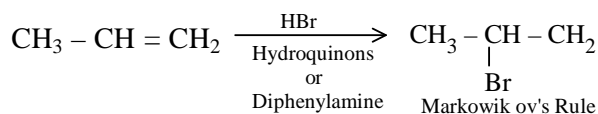


But if the alkene is not a symmetrical like $\text{CH}_3\text{-CH=CH}_2$, $\text{C}_2\text{H}_5\text{-CH=CH}_2$ then addition of HX takes place according to Markownikov's rule.

“In addition of an acid to Carbon-Carbon double bond of an alkene, the Hydrogen atom of the HX attaches itself to the Carbon atoms that has greater number of Hydrogen.”

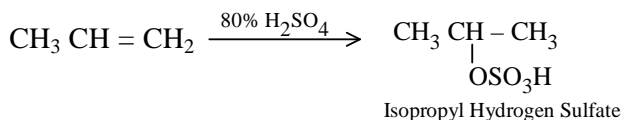
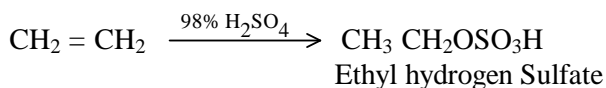


- (b) **Peroxide Effect:** Addition of HCl and HI to alkenes follows Markownikov's rule. But HBr addition was reported to be a mixture of both Markownikov's rule and Anti Markownikov's rule., Until in 1933 M.S. Kharasch and Mayo solved this confusion by discovering the orientations of addition of HBr solely in the presence or absence of peroxides.



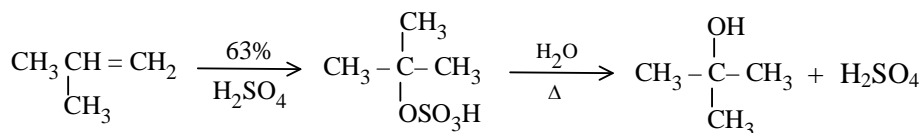
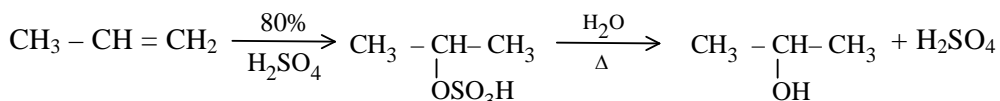
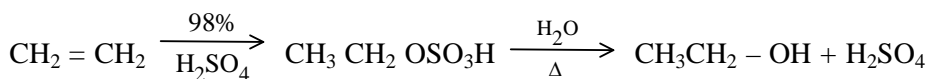
Mechanism of Free radical addition

4. **Addition of H_2SO_4 :** Alkenes react with cold concentrated Sulfuric acid to form compounds of general formula ROSO_3H , known as alkyl hydrogen sulfates. The reactions are again highly regioselective and follow the Markownikov's Rule.



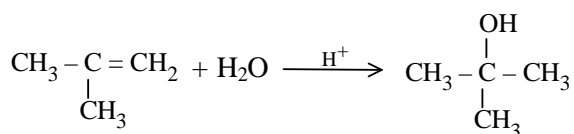
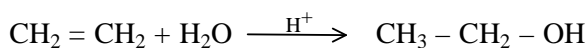
The alkyl hydrogen sulfates are deliquescent solids and are difficult to isolate.

When such an alkyl hydrogen sulfate is diluted with water and heated, we get an alcohol bearing the same alkyl group. The ester of the sulfuric acid is cleaved to get an alcohol and sulfuric acid.

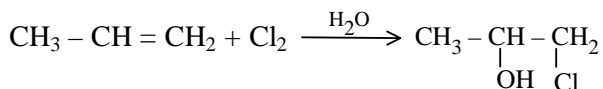
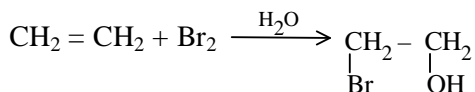


This sequence of the reaction provides a good route for preparing alcohols.

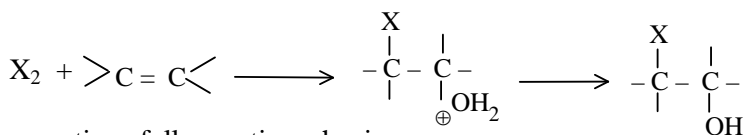
5. **Addition of H₂O:** Water may be added to alkenes in the presence of acids to yield alcohols. This reaction also follows Markovnikov's rule.



6. **Addition of Hypohalous Acids:** The addition of Cl₂ or Br₂ in the presence of water can yield compounds containing halogen and OH on adjacent C-atoms such compounds are called halohydrins.



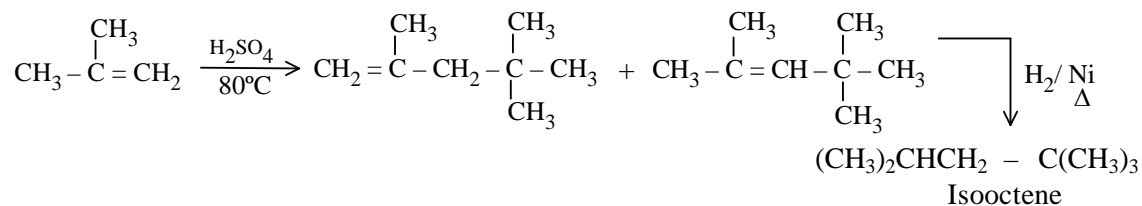
There is evidence of a kind that these compounds are not formed due to the formation of HOX but by reactions of alkene with halogen and water.



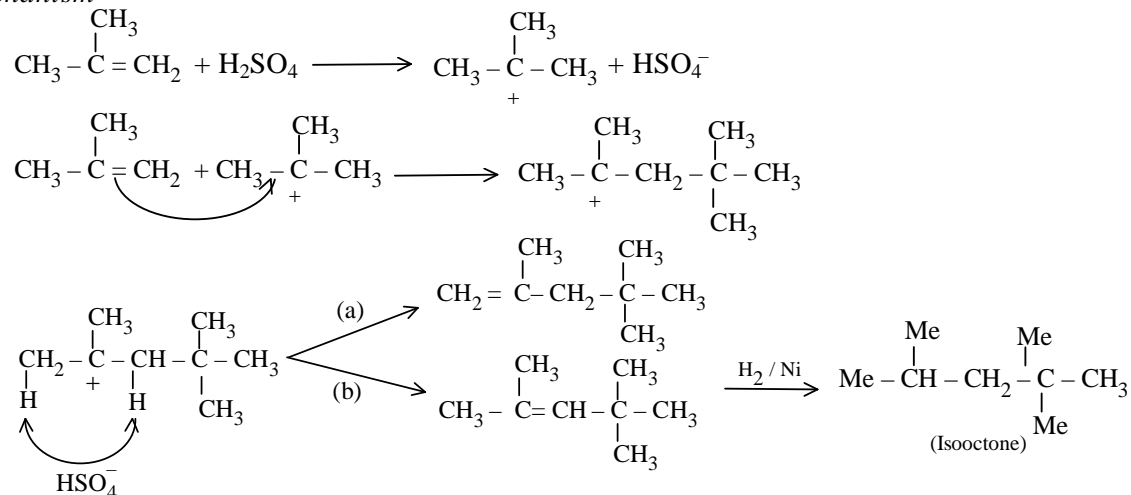
These reactions follow anti mechanism.

Though these reactions proceed to form products which are in accordance with Markownikov's rule, the stereochemistry suggests that the reaction is via halonium ion formation and not via formation of an open carbocation.

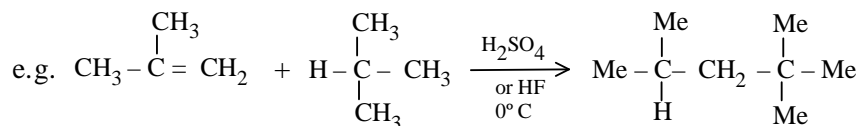
7. **Addition of Alkenes, Dimerization:** When Isobutene is reacted with H_2SO_4 or H_3PO_4 that is a protic acid then we get a mixture of two alkenes with molecular formula C_8H_{16}



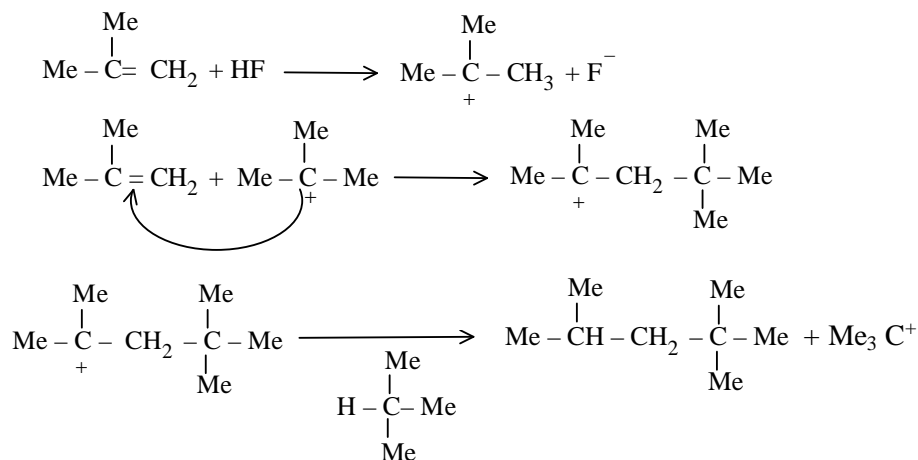
Mechanism



8. **Addition of Alkanes (Alkylation):** When alkenes are reacted with alkanes in the presence of H_2SO_4 or HF at 0°C then we get a higher homologue of alkane.

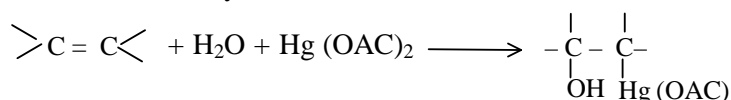


Mechanism

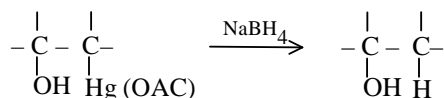


9. **Oxymercuration - Demercuration :** Alkenes react with mercuric acetate in the presence of water to give hydroxy mercurial compounds which on reduction yields alcohols.

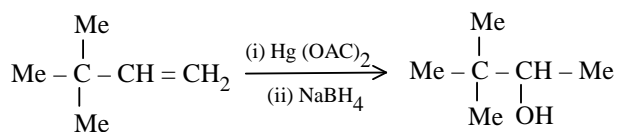
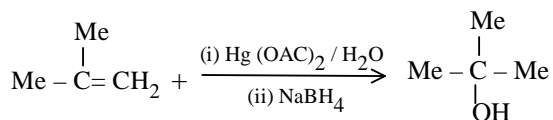
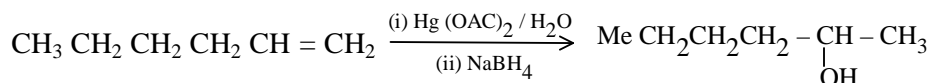
Step - 1 \longrightarrow Oxymercuration



Step - 2 \longrightarrow Demercuration

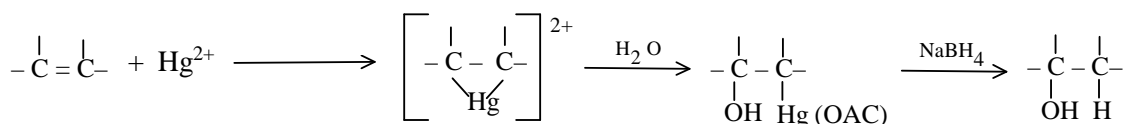


Oxymercuration-Demercuration is highly regioselective and gives alcohols corresponding to Markovnikov's Rule.



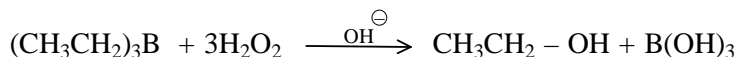
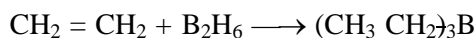
Oxymercuration involves electrophilic addition to carbon-carbon double bond with the mercuric ion acting as electrophile.

Since $\begin{array}{c} \text{Me} \\ | \\ \text{Me}-\text{C}-\text{CH}=\text{CH}_2 \\ | \\ \text{Me} \end{array}$ gives only $\begin{array}{c} \text{Me} \\ | \\ \text{Me}-\text{C}-\text{CH}-\text{Me} \\ | \quad | \\ \text{Me} \quad \text{OH} \end{array}$ and not $\begin{array}{c} \text{Me} \quad \text{Me} \\ | \quad | \\ \text{Me}-\text{C}-\text{CH}-\text{Me} \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$ it is indicated that the mechanism does not involve any rearrangement, thus carbocations are not formed. But it proceeds via a cyclic mercurinium ion.

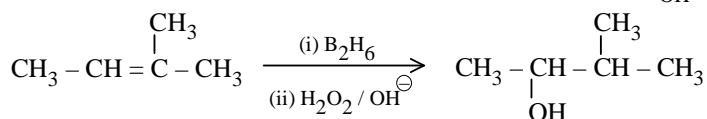
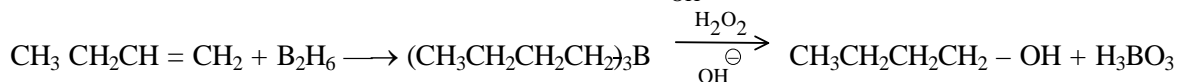
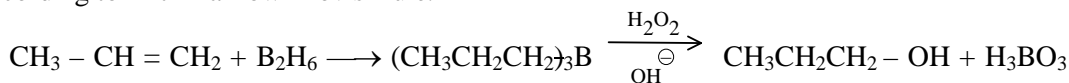


Mercuration can be carried out in different solvents to yield products other than alcohol.

10. **Hydroboration-Oxidation:** When alkenes are reacted with diboranes (B_2H_6) alkenes undergo hydroboration to yield alkyl boranes (R_3B) which on oxidation give alcohols.



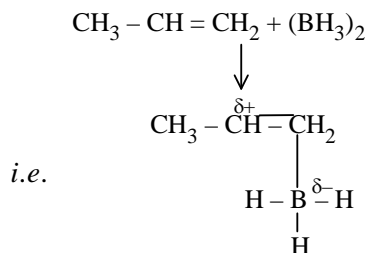
All Hydroboration-oxidation reactions are also highly regioselective, however here the product formed is according to Anti Markovnikov's Rule.



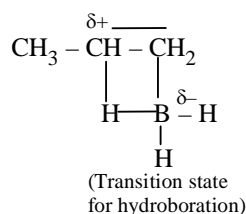
Thus rearrangement does not occur in Hydroboration.

Mechanism

Just as alkenes react with HZ (acidic compounds) so also they react with BH_3 . Which also is a Lewis acid



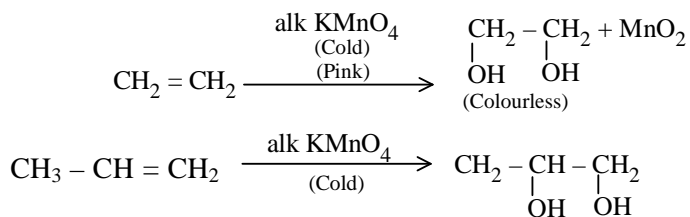
Such a substance is stabilized as



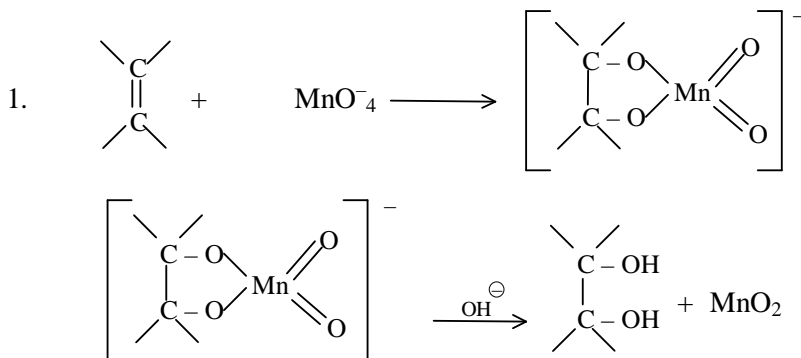
This reaction is a syn-addition reaction

Oxidation Reactions in Alkene

- Hydroxylation (Using Bayer's Reagent):** When an alkene is reacted with dilute alkaline KMnO_4 solution in cold condition then the alkene is converted to vicinal dihydroxy compound.



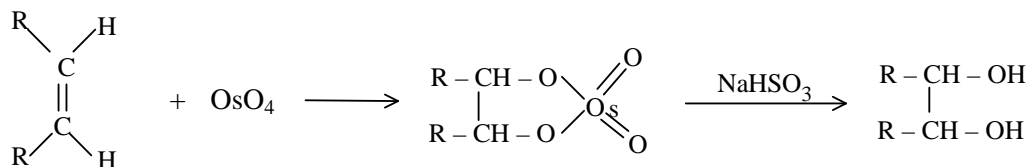
Mechanism



This reaction which gives rise to vicinal diols and is a SYN-ADDITION reaction.

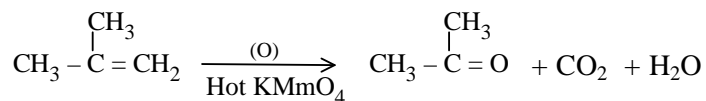
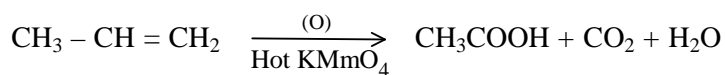
This is supported by the mechanism that the Oxygen atoms of OH group in the diol formed are from the permanganate ions which add to the alkene molecule from the same side and are at gauche position with respect to each other so that effective Hydrogen bond may persist between them.

2. **With Os O₄ (Osmium tetroxide)**

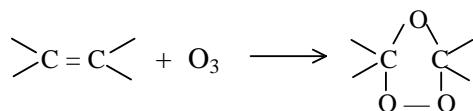


This is again a SYN-ADDITION reaction

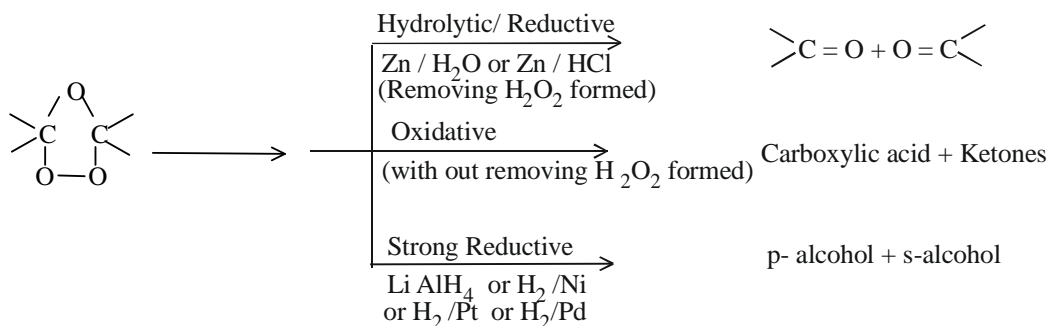
3. **With hot KMnO₄:** Alkenes on reaction with hot alkaline KMnO₄ give a mixture of carboxylic acid and ketones or only ketones or carboxylic acids.



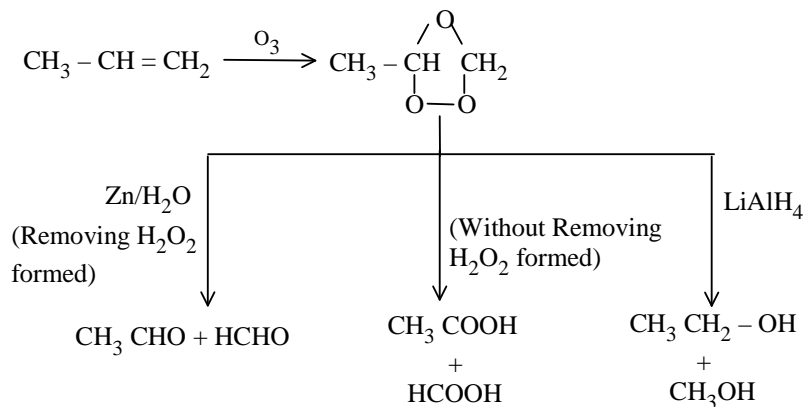
4. **Ozonolysis Reaction:** All alkenes react with Ozone to form an Ozonide.



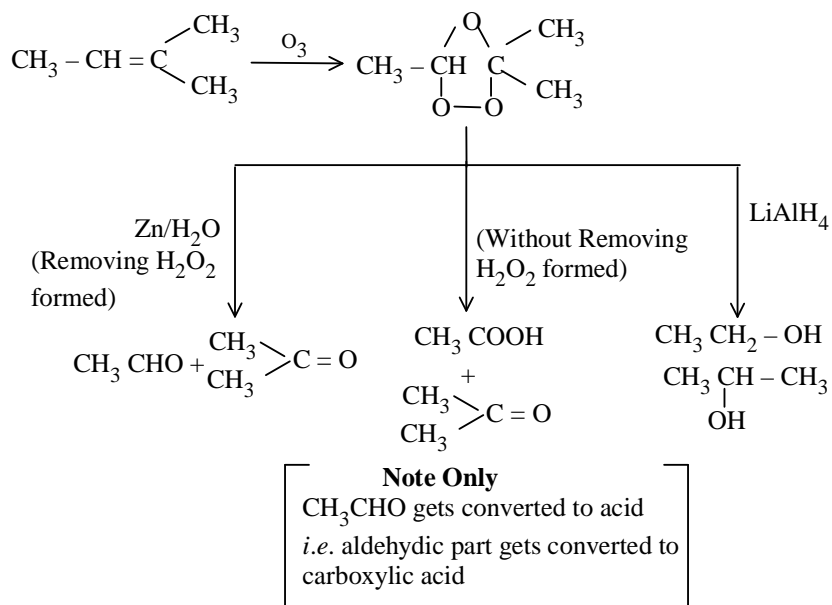
Such Ozonides may be cleaved in 3-ways



(i) Ozonolysis of Propene

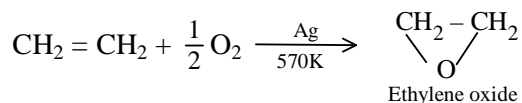


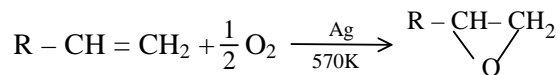
(ii) Ozonolysis of 2-Methyl but-2-ene



Ozonolysis reactions help to locate the positions of double bond in alkene

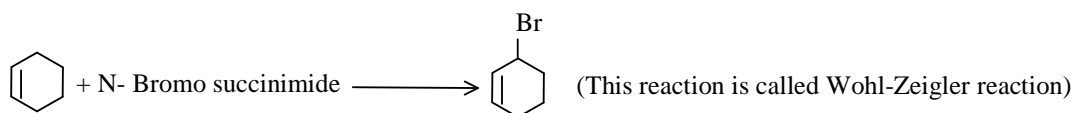
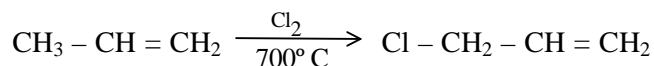
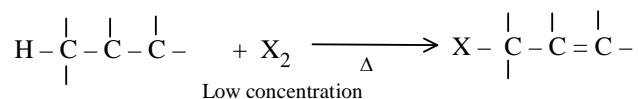
5. **Addition of Oxygen:** Alkenes add on Oxygen in the presence of Silver as catalyst at 570K to form epoxides.



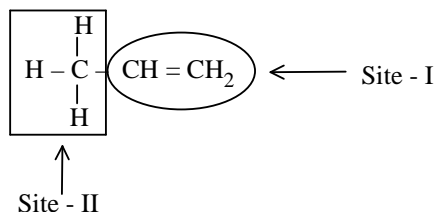


6. **Substitution Reactions:** Most alkenes contain not only the C–C double bond but also alkyl groups which have essentially alkane character. Hence besides the addition reactions which are characteristics of C–C double bonds, Alkenes may undergo the free radical substitution which is a characteristic of alkanes.

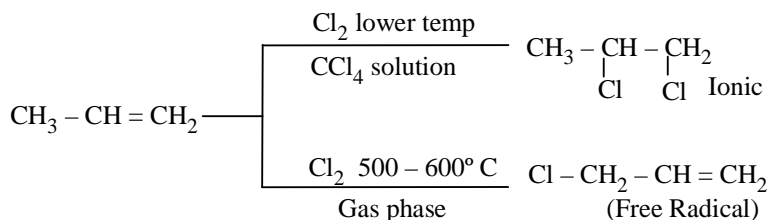
(a) **Halogenation, Allylic Substitution**



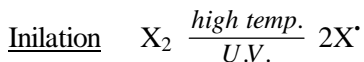
When we consider the molecule of propene



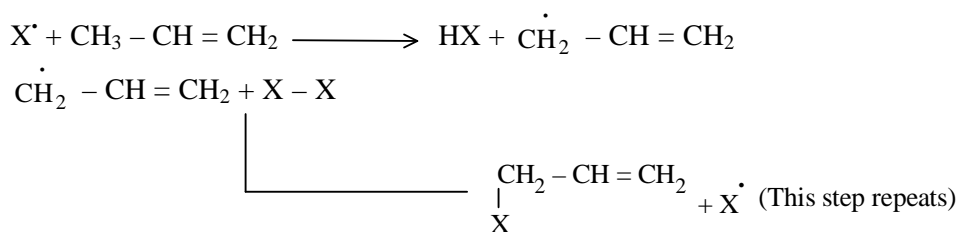
The Site-I is the alkene site where due to the presence of reactive π -bonds the reaction can take place at low temperature, in the absence of light and generally in liquid state. While site-II is the alkane site which requires high temperatures or U.V light. If we try to make the reaction possible at site-II, we must take the necessary condition of high temperature or U.V. radiations.



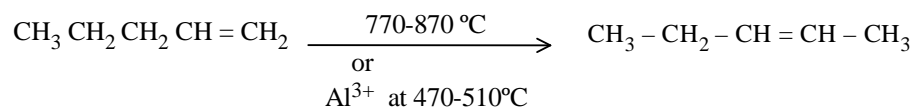
Mechanism



Propagation.



9. Isomerization



10. Polymerization

