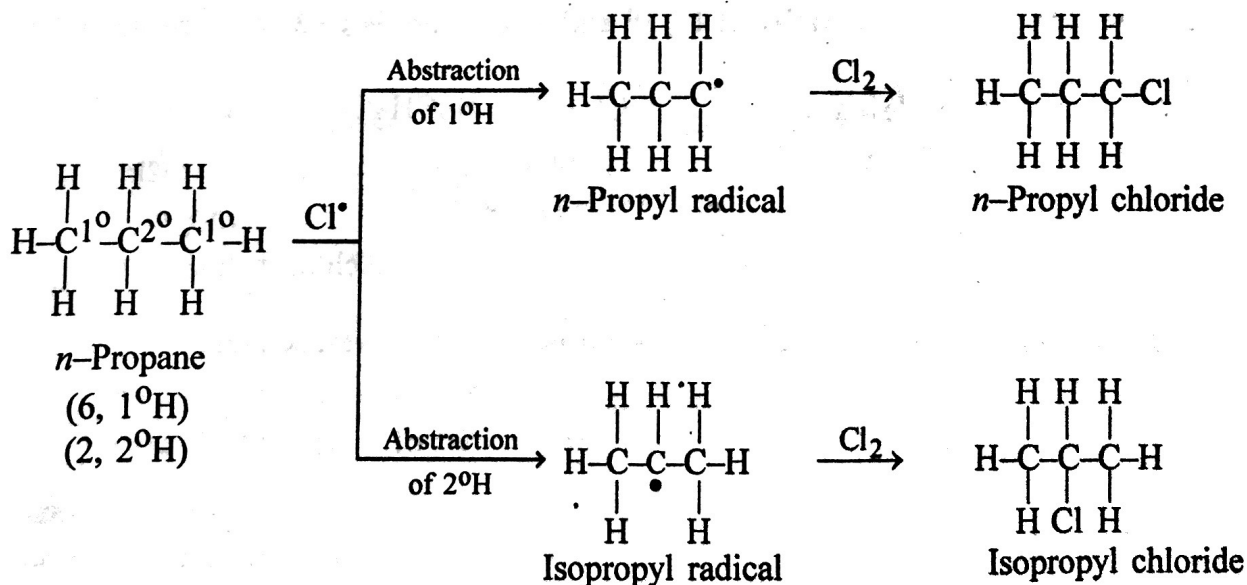


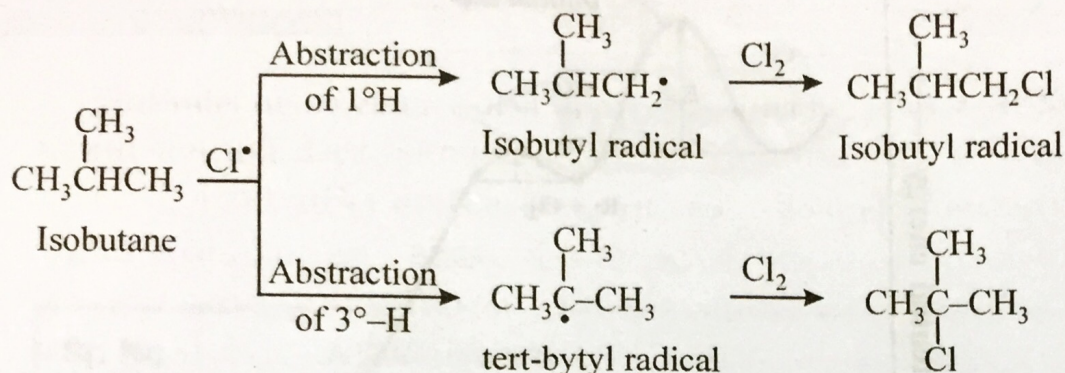
### 1.14 Orientation of halogenation :

Alkanes undergo free radical substitution. Reaction with halogen ( $\text{X} = \text{Cl}, \text{Br}$ ) upon heating or in presence of ultra violet (uv) light resulting in to mono substitution or poly substitution product.

This orientation is determined by the relative rate of competing reactions. e.g.



i.e. by considering the collision frequency one can predict that : chlorination of propane would yield n-propyl chloride and isopropyl chloride in the ratio of 3:1.



Chlorination of isobutane undergo abstraction of one of the nine hydrogen give isobutyl radical and abstraction of a single tertiary hydrogen give tert-butyl radical.

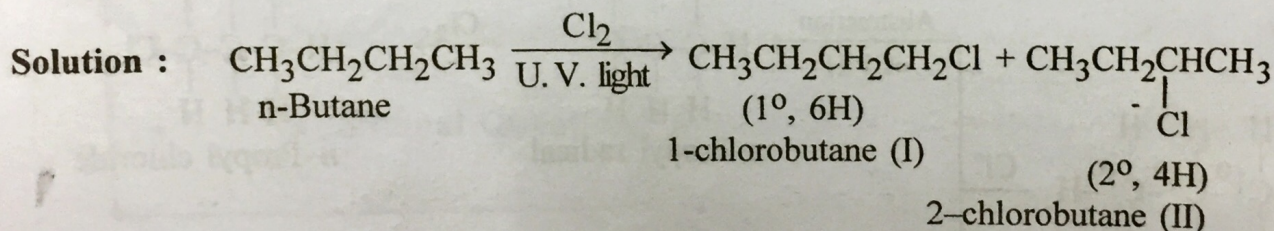
Here percentage yield of two different isomeric product is different due to two factor.

1. The type of hydrogen replaced and its number.
2. Relative reactivity of H atoms replaced by chlorine or bromine.

For chlorine : relative reactivity, 5 : 3.8 : 1 for  $3^\circ$  :  $2^\circ$  :  $1^\circ$

Bromine : Relative reactivity, 1600 : 82 : 1 for  $3^\circ$  :  $2^\circ$  :  $1^\circ$

**Problem :** Calculate percentage yield of the product obtained upon mono chlorination of n-butane. The relative reactivity of  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  H-atom is 1 : 3.8 : 5 respectively.



The relative reactivity of  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$  H-atom is 1 : 3.8 : 5 respectively.

$$\begin{aligned}
 \% \text{ yield} &= \frac{\% \text{ yield of 1-chlorobutane (I)}}{\% \text{ yield of 2-chlorobutane (II)}} = \frac{\text{No. of concerned H-atom}}{\text{No. of concerned H-atom}} \times \frac{\text{reactivity of concerned H-atom}}{\text{reactivity of concerned H-atom}} \\
 &= \frac{6}{4} \times \frac{1}{3.8} \\
 &= \frac{6}{15.2}
 \end{aligned}$$

$$\text{Relative yield} = 0.394$$



Let 'x' be the % yield of 1-chlorobutane. We know that total % must be equal to 100.  
 $\therefore (100 - x)$  will be the % yield of 2-chlorobutane.

$$\text{Now, Relative yield} = 0.394 = \frac{x}{100 - x}$$

$$\therefore x = 28\%$$

$\therefore$  % yield of 1-chlorobutane is 28%

$\therefore$  % yield of 2-chlorobutane is  $(100 - 28) = 72\%$

#### OR (another method)

$$\begin{aligned} \text{Reactivity of 1-chlorobutane} &= \text{No. of } 1^\circ \text{ H-atom} \times \text{reactivity of } 1^\circ \text{ H-atom} \\ &= 6 \times 1 = 6 \end{aligned}$$

$$\begin{aligned} \text{Reactivity of 2-chlorobutane} &= \text{No. of } 2^\circ \text{ H-atom} \times \text{reactivity of } 2^\circ \text{ H-atom} \\ &= 4 \times 3.8 = 15.2 \end{aligned}$$

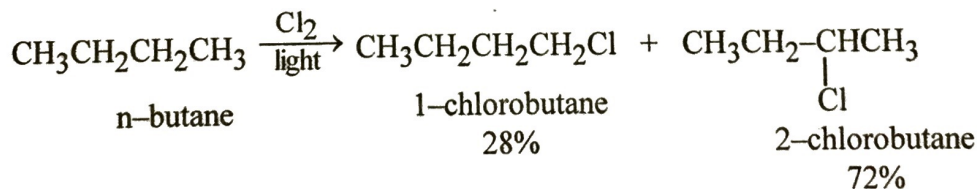
$$\text{Total reactivity of propane} = 6 + 15.2 = 21.2$$

It means  $21.2 = 100\%$ , so how many % for reactivity of 6 and 15.2 ? Hence,

$$\% \text{ yield of 1-Chlorobutane} = \frac{6}{21.2} \times 100 \cong 28\%$$

$$\% \text{ yield of 2-Chlorobutane} = \frac{15.2 \times 100}{21.2} \cong 72\%$$

**Problem : Chlorination of n-butane yields 1-chlorobutane and 2-chlorobutane in 28% and 72% respectively. Find out relative reactivity for concerned hydrogen.**



- Types of H-atom replaced by Cl :	$1^\circ$	$2^\circ$
- Number of H-atom	6	4
- Yield per one H-atom	$\frac{28}{6} = 4.66$	$\frac{72}{4} = 18$

$$\therefore \text{Relative reactivity} = \frac{\text{yield per one } 2^\circ \text{ H}}{\text{yield per one } 1^\circ \text{ H}} = \frac{18}{4.66} = 3.86$$





Reactivity of I = No. of  $1^\circ\text{H}$   $\times$  Reactivity of  $1^\circ\text{H}$  =  $3 \times 1 = 3.0$

Reactivity of II = No. of  $2^\circ\text{H}$   $\times$  Reactivity of  $2^\circ\text{H}$  =  $2 \times 3.8 = 7.6$

Reactivity of III = No. of  $3^\circ\text{H}$   $\times$  Reactivity of  $3^\circ\text{H}$  =  $1 \times 5 = 5.0$

Reactivity of IV = No. of  $1^\circ\text{H}$   $\times$  Reactivity of  $1^\circ\text{H}$  =  $6 \times 1 = 6.0$

$\therefore$  Total reactivity of isopentane =  $3 + 7.6 + 5 + 6 = 21.6$

Now,

$$\% \text{ of 1-chloro-3-methylbutane (I)} = \frac{3 \times 100}{21.6} = 13.89\% \cong 14\%$$

$$\% \text{ of 2-chloro-3-methylbutane (II)} = \frac{7.6 \times 100}{21.6} = 35.18\% \cong 35\%$$

$$\% \text{ of 2-chloro-2-methylbutane (III)} = \frac{5 \times 100}{21.6} = 23.15\% \cong 23\%$$

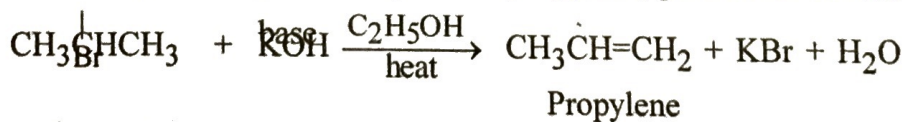
$$\% \text{ of 1-chloro-2-methylbutane (IV)} = \frac{6 \times 100}{21.6} = 27.78\% \cong 28\%$$

### 1.15 Preparation of alkene :

#### (a) From Dehydrohalogenation of alkyl halides. 1,2-elimination (Formation of alkene) :

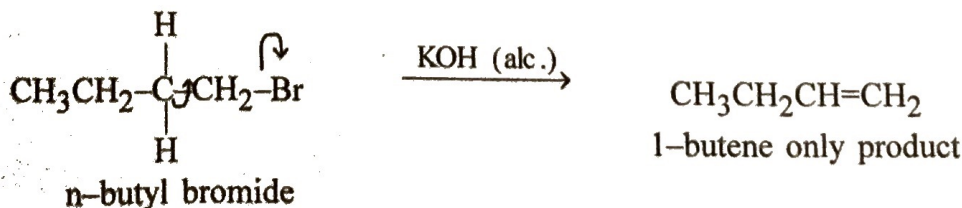
The reagent for dehydrohalogenation is alcoholic KOH.

Alkene can be prepared by the reagent for dehydrohalogenation is alcoholic KOH like  $\text{C}_2\text{H}_5\text{OH}/\text{KOH}$ . When alkyl halide (RX) react with alcoholic KOH, heat give alkene. This reaction is called **dehydrohalogenation**. (De = to remove hydrohalogenation = HX) e.g. when. isopropyl bromide treated with a hot concentrated alcoholic solution of a strong base like potassium hydroxide, KOH it produce propylene, potassium bromide and water.

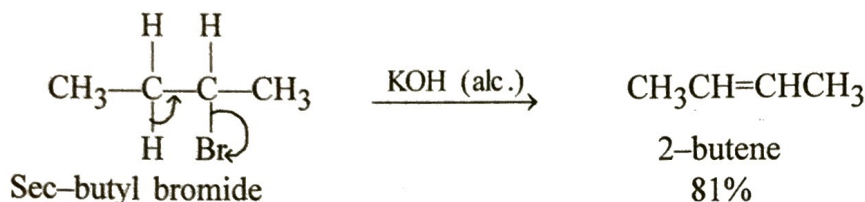
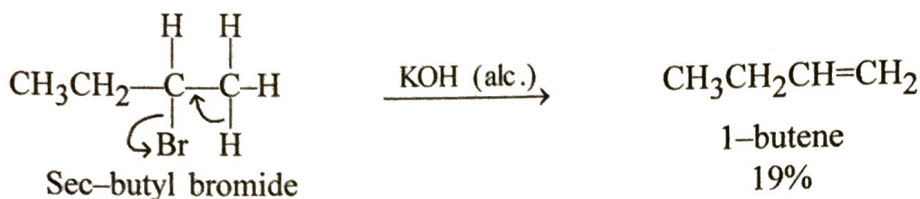


Isopropyl bromide  
(2-bromo propane)

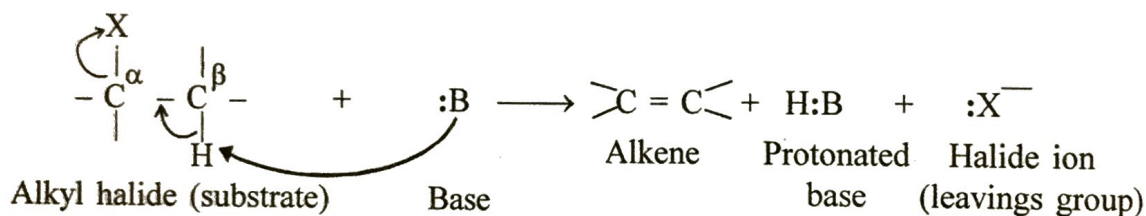
For example, n-butyl bromide can loss hydrogen only from C-2 and yields 1-butene.



while sec-butyl bromide can lose hydrogen either from C-1 to yield 1-butene and can loss hydrogen from C-3 to yield 2-butene.



### Dehydrohalogenation : Mechanism for 1,2-elimination of HX



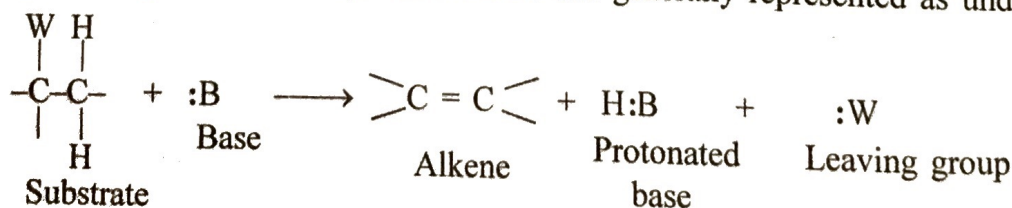
Dehydrohalogenation involves loss (elimination) of the halogen atom and of a hydrogen atom from a carbon adjacent to the one losing the halogen.

**In step-I :** Base (:B) abstracts the hydrogen as a proton, leave its electron pair behind.

**In step-II :** The electron pair is available to form the  $\pi$ -bond between the two carbon atoms upon loss of halogen as halide ion. step-I and step-II occurs **simultaneously**.

In some cases, dehydrohalogenation yields a single alkene and in other cases yields a mixture. Formation of alkenes can be predicted from the structure of the substrate according to Saytzeff rule : "Alkene in which doubly bonded carbon atom have less number of hydrogen atom becomes MAJOR product."

Dehydrohalogenation is a 1,2-elimination and generally represented as under.



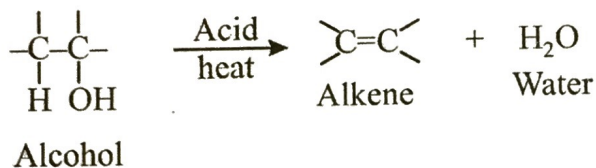
Elimination reactions are characterized by the following : **(Characteristics of elimination reaction)**



- (a) The substrate contains a **leaving group** (W), an atom or group that leaves the molecule, taking its electron pair with it.
- (b) In a position beta to the leaving group, the substrate contains an atom or group – nearly always **hydrogen** – that can be abstracted by a base, leaving its electron pair behind.
- (c) Reaction is brought about by action of a **base**.

**(b) Dehydration of alcohol (De = To remove ; Hydration = Water)**

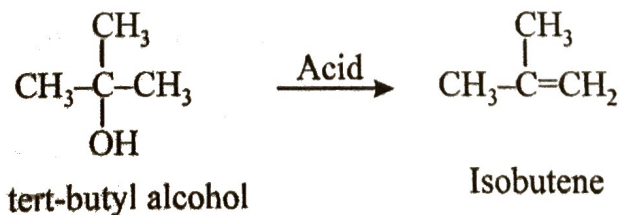
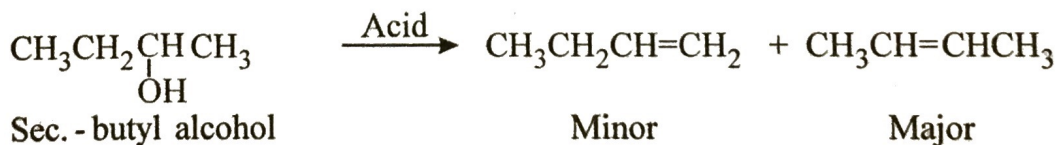
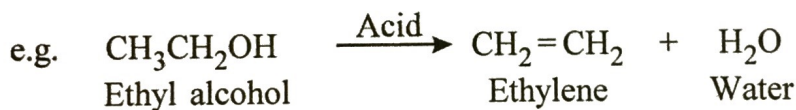
Let us turn to 1,2-elimination that is catalyzed by acid. An alcohol is converted into an alkene by dehydration i.e. removal of water molecule. The common reagents for dehydration are strong acid like  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  or hot alumina ( $\text{Al}_2\text{O}_3$ ).



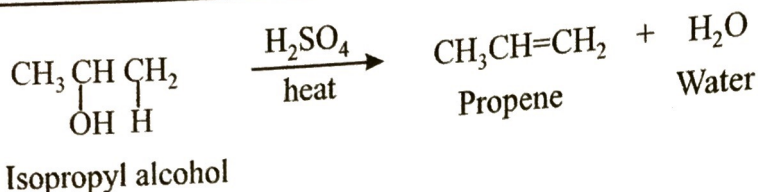
Dehydration : 1,2 - elimination of  $\text{H}_2\text{O}$

Ease of dehydration of alcohols is  $3^\circ > 2^\circ > 1^\circ$

The common reagents are sulphuric acid, Phosphoric acid or hot alumina.



The product which is formed by the loss of hydrogen from the more (highly) substituted carbon adjacent to the hydroxyl group containing carbon predominates. Therefore ease of dehydration of alcohol is  $3^\circ > 2^\circ > 1^\circ$ .



### • Elimination Reaction :

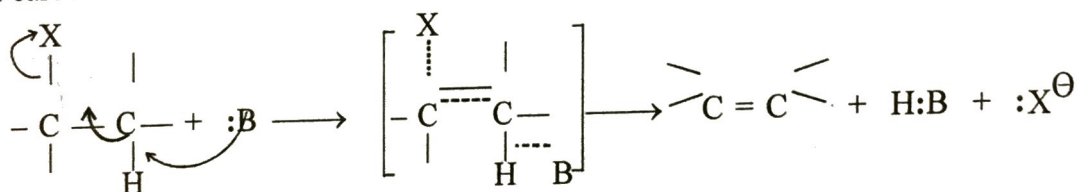
**Elimination :** It is the process in which atoms or groups of atoms, from two adjacent carbon of an alkane molecule are eliminated to form a carbon-carbon double bond is called elimination and such reaction is called elimination reaction.

To carry out such a reaction three types of mechanisms are expected i.e. E1, E2, E1cB.

**Mechanism :** Stepwise detail description of chemical reaction is called mechanism.

### 1.16 The E2 mechanism (Bimolecular elimination) :

For the reaction that proceeds by **second order kinetics**. Hughes and Ingold proposed the E2 mechanism. The carbon-halogen bond C-X start to break and  $\pi$ -bond between carbon-carbon atoms start to form.



It is a **single step reaction** where bond formation and bond breaking take place **simultaneously via pentavalent transition state** formation. For such reaction, reaction rate will be determined as :

$$\text{Rate} = K [\text{R-X}] [:\text{B}]$$

It follows **second order kinetics**. Since rate depends upon **both** substrate and nucleophile concentration.

### 1.17 Evidence for the E2 mechanism : Kinetics and absence of rearrangement :

Elimination reaction that,

- follow second order kinetics.
- are not accompanied by rearrangement.
- shows a large hydrogen isotope effect.
- are not accompanied by hydrogen exchange.
- shows a large element effect.

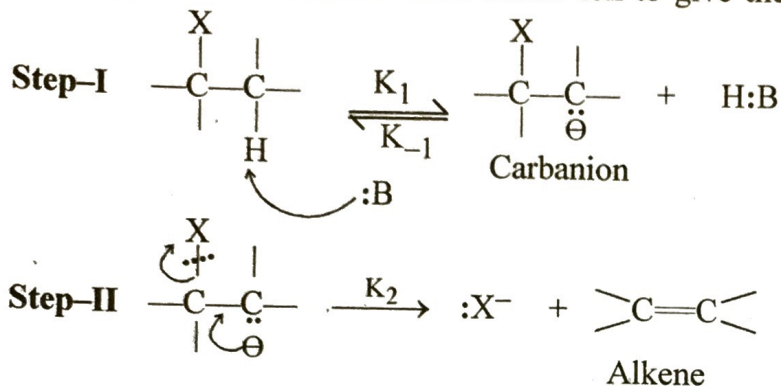
**Evidence for the E2 mechanism. Absence of hydrogen exchange :**

Facts (a), (b) and (c) are consistent with E2 mechanism. But there is another possibility that we must consider : the **carbanion mechanism**. Such a mechanism involves two steps.

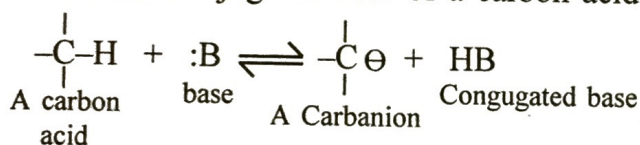


**In step (1) :** The substrate loses a proton by the base to form a negatively charged particle (carbanion).

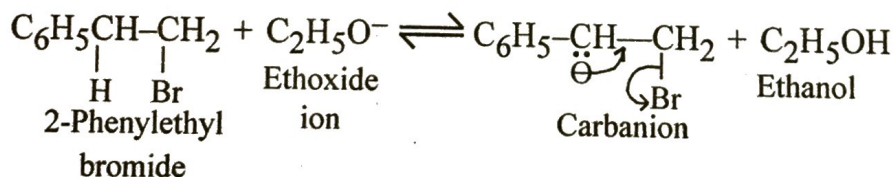
**In step (2) :** This carbanion loses halide ion to give the alkene.



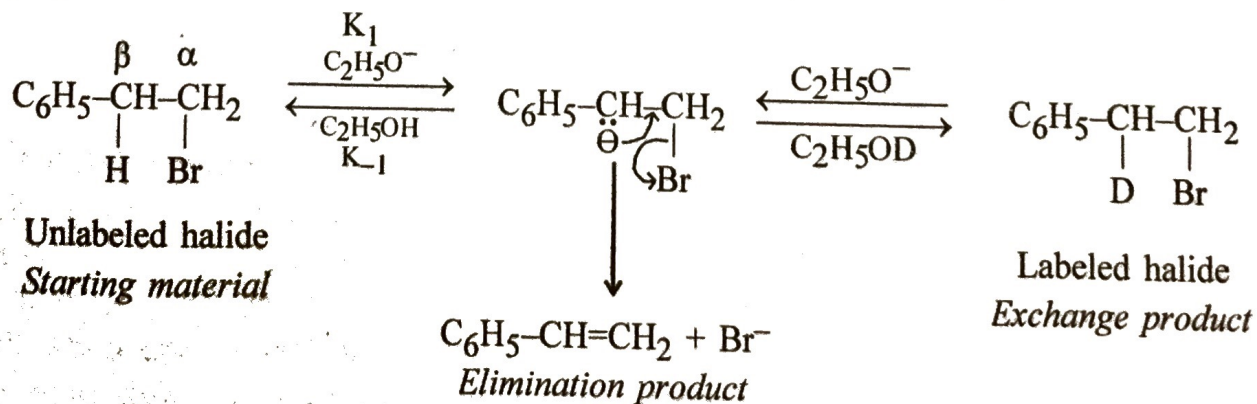
Step-1 is an acid-base reaction. The substrate acting as an acid. Since the acidic proton is attached to carbon, the substrate is called a carbon acid. The products of step-1 are the conjugated acid of the base and the conjugated base of the carbon acid, a carbanion. A carbanion is the conjugated base of a carbon acid.



To understand carbanion mechanism and test for hydrogen exchange let us carry out experiment using 2-phenylethyl bromide and labeled ethanol.



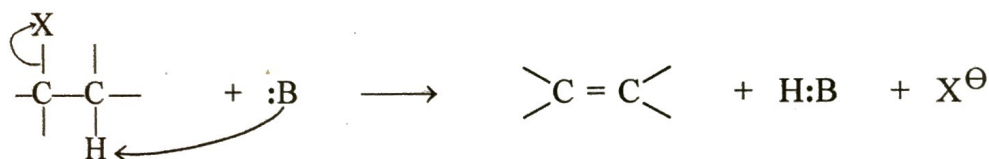
2-Phenylethyl bromide upon dehydrohalogenation by strong base like sodium ethoxide ( $\text{C}_2\text{H}_5\text{ONa}$ ) give carbanion and ethanol.



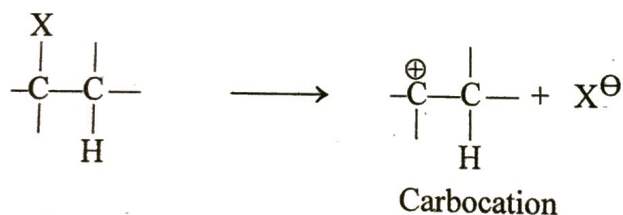
Consider the dehydrohalogenation of 2-phenylethyl bromide in the presence of strong base in labeled ethanol ( $C_2H_5OD$ ) solution. If carbanion formed reversibly it would regain base in labeled ethanol to generate starting material. The reaction was allowed to run until about half the substrate had been converted in to alkene. Reaction was then interrupted and unconsumed 2-phenylethyl bromide was recovered. Mass spectrometric analysis showed that it does not contain deuterium. It shows that there is absence of deuterium and there is absence of reversibly carbanion formation and hence absence of hydrogen exchange [fact (d)].

### 1.18 The E1 mechanism :

For the reaction that proceeds by first order kinetics. **Hughes and Ingold** proposed E1 mechanism. In this mechanism the bond breaking and bond forming (electronic changes) are the same as in E2. However, they are taking place, not simultaneously, but one after the other. Where **E2 involves a single step and E1 involves two steps.**



**In step (1) :** Substrate undergo slow heterolysis to form carbocation and halide ion. Base  $:\text{B}$  not participate in first step.



**Step (2) :** Carbocation rapidly loses an acidic proton to the base resulting in to an alkene.



Here 1<sup>st</sup> step is the rate determining step since it is slow step. Thus, it will follow first order kinetics.

$$\text{Rate} = K \cdot [\text{R} - \text{X}]^1$$

Step (1) of E1 is identical to the first step in  $S_N1$ . In the second step of  $S_N1$ , the carbocation combines with a nucleophile to give the substitution product. In the step (2) of E1, the carbocation reacts with the base to give the elimination product. The reaction of a carbocation have a common end : they provide a pair of electrons to complete the octet of the electron-deficient carbon. In  $S_N1$  these electrons are an unshared pair on the nucleophile; in E1 they are the pair originally shared by the proton and available by departure of the proton.



## 1.19 Evidence for the E1 mechanism :

Elimination reaction that,

- (a) are accompanied by rearrangement.
- (b) shows the same effect of structure on reactivity as  $S_N1$  do; and
- (c) are not accompanied by primary hydrogen isotope effect.
- (d) follow first order kinetics.

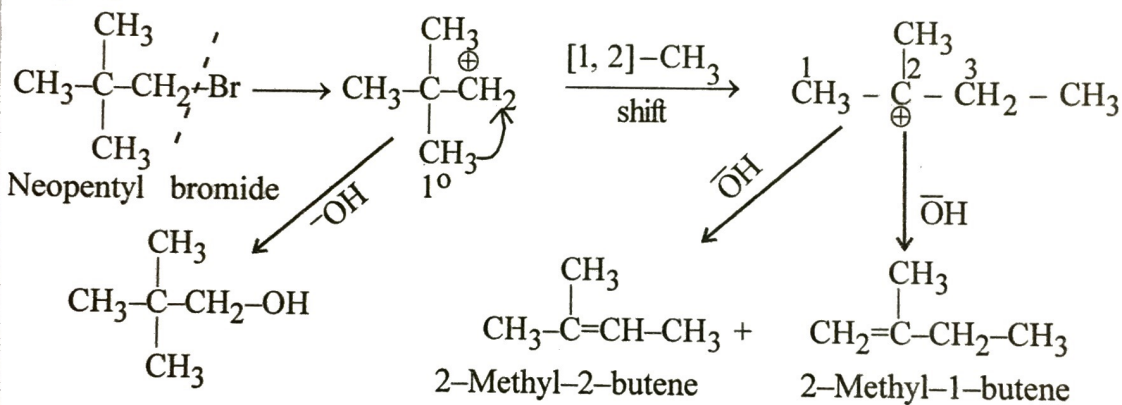
The mechanism which is consistent with all the above facts follows first order kinetics.

**(a) are accompanied by rearrangement**

In E1 mechanism there is formation of carbocation. The rate of formation of carbocation depends upon its stability. Thus less stable carbocation will try to rearrange for more stable carbocation. Thus stability order  $3^\circ > 2^\circ > 1^\circ > CH_3^\oplus$ .

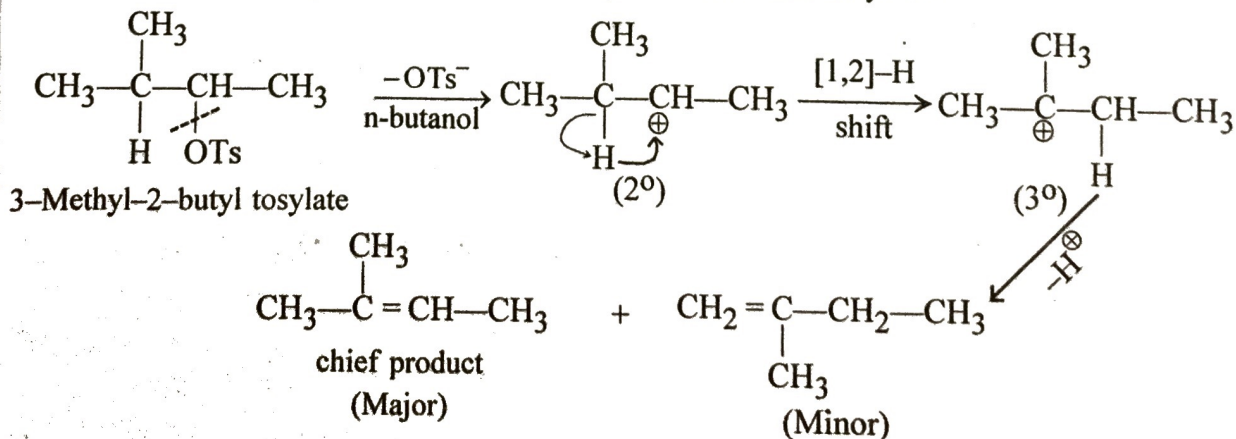
Therefore, E1 mechanism is consistent with the fact (d).

**e.g. Que. Neopentyl bromide upon E1 elimination yields 2-methyl-2-butene as a major product.**

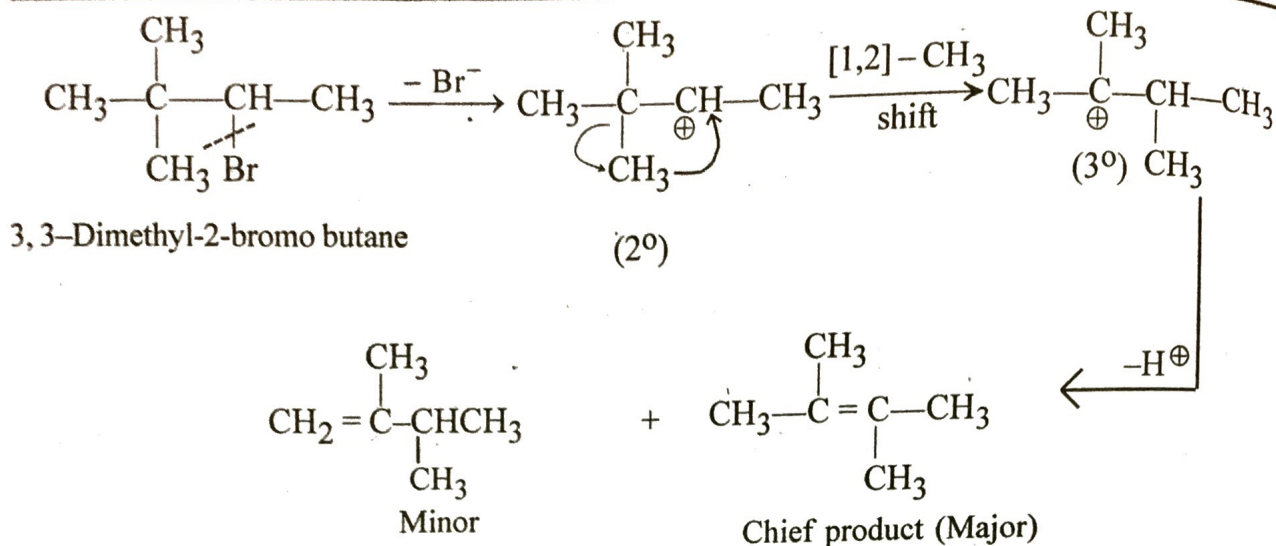


Neopentyl bromide upon heterolysis gives  $1^\circ$  carbocation which upon rearrangement more stable gives  $3^\circ$ -carbocation by  $[1,2]-CH_3$  shift, which upon loss of  $\beta$ -proton gives 2-methyl-2-butene which is more stable, will be in major amount.

Let us see rearrangement in various alkyl chloride and tosylate.



3-Methyl-2-butyl tosylate upon E1 elimination give 2-Methyl-2-butene as a major product.



3,3-dimethyl-2-bromobutane upon E1 elimination give 2,3-dimethyl-2-butene as a major product.

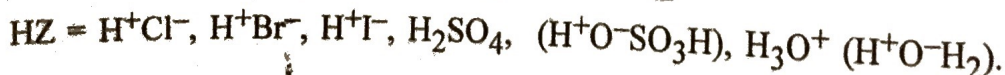
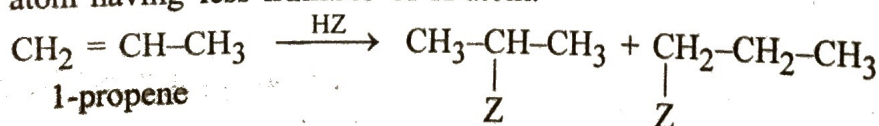
### 1.20 Difference between E1 and E2 :

E1 Mechanism	E2 Mechanism
<ul style="list-style-type: none"> <li>– It is unimolecular elimination.</li> <li>– It follows the first order kinetics.</li> <li>– It is accompanied by rearrangement.</li> <li>– Hydrogen isotope effect does not take place.</li> <li>– Rate = <math>K[\text{RX}]</math>.</li> <li>– It depends on structure of RX.</li> <li>– Carbocation is an intermediate.</li> </ul>	<ul style="list-style-type: none"> <li>– It is bimolecular elimination.</li> <li>– It follows second order kinetics.</li> <li>– It is not accompanied by rearrangement.</li> <li>– Have large hydrogen isotope effect.</li> <li>– Rate = <math>K[\text{RX}][\text{:B}]</math></li> <li>– It not depends on structure of RX.</li> <li>– Pentavalent transition state is an intermediate.</li> </ul>

**Electrophile :** The reagent or species which have tendency to accept a pair of electron is called electrophile. e.g.  $\text{NO}_2^+$ ,  $\text{Br}^+$  etc.

### 1.21 Electrophilic addition : Mechanism :

Alkene undergo addition reactions and reaction take place at double bond. According to Markovnikov's rule, the **positive part** of reagent attach to double bonded carbon atom have **more number** of H-atom and **negative** part of reagent is attach to double bonded carbon atom having **less number** of H-atom.



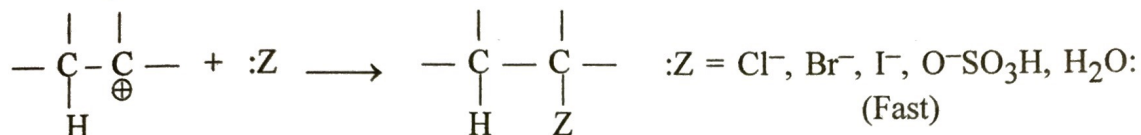
The **general mechanism** for the addition of the **acidic reagent (HZ)** to propene (alkene) can be proceeds via two steps.



**Step (1)** is the transfer of hydrogen ion ( $H^+$ ) from acidic reagent to the alkene to form a carbocation.



**Step (2)** is combining of  $:Z$  (negatively charge or neutral) to the carbocation to yield addition product.

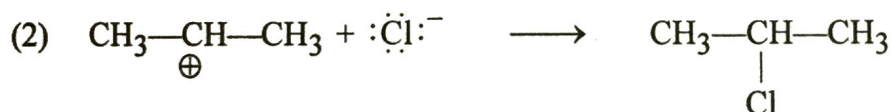


Here step (1) is the slow rate determining step. This step involves attack by an acidic reagent, the reaction is an example of electrophilic addition.

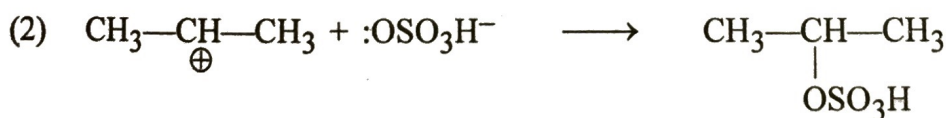
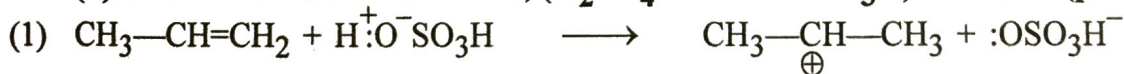
Let us consider specific examples : The addition of :

### 1.21 (a) Hydrogen chloride (HCl) to alkene (Propene) :

The description of each steps of mechanism is as according to above step (1) and (2) in topic 1.21. Here  $:Z = Cl$ .



### 1.21 (b) The addition of Sulfuric acid, ( $H_2SO_4$ i.e. $H^+ O^- SO_3H$ ) to alkene (propene) :



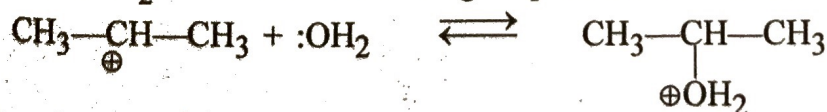
The description of each steps of mechanism is as according to above step (1) and (2) in topic 1.21. Here  $:Z = OSO_3H$ .

### 1.21 (c) The addition of Water (in acidic medium i.e. $H_3O^+ \{H^+ \overline{OH}_2\}$ ) to alkene (propene) :

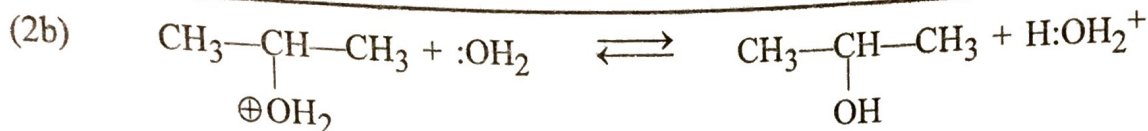
(1) Addition of  $H^+$  to give carbocation.



(2a) Addition of  $H_2O$ : to carbocation on give protonated alcohol.



(2b) Abstraction of  $H^+$  to give alcohol.



The **evidences** for the mechanism of electrophilic addition are as under.

- The rate of reaction depends upon the concentration of both the alkene and the reagent HZ.
- Reaction requires an acidic reagent.
- Reaction is accompanied by rearrangements.
- The orientation of addition and
- The relative reactivities of alkenes.

Let us examine this evidence.

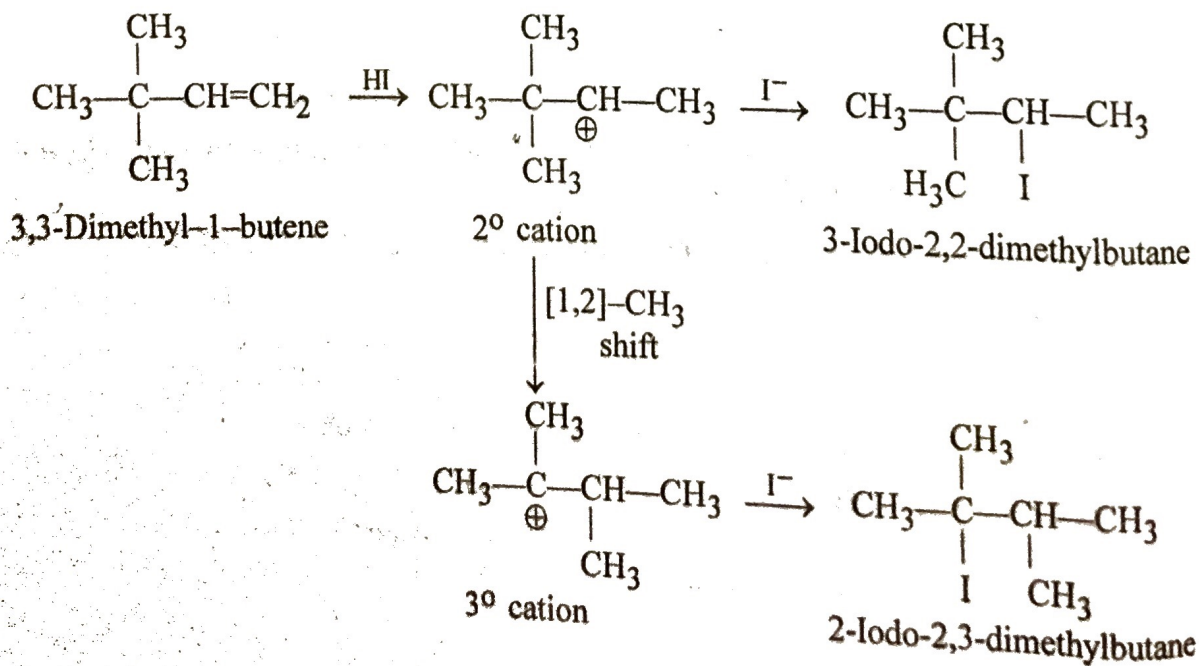
First (a) the rate of reaction depends upon concentration of both the alkene and the reagent HZ. This fact is consistent with a mechanism that starts with reaction between these two reagent.

- Reaction requires an acidic reagent. According to the mechanism, the first step is the transfer of a proton to the alkene. This agrees with the fact that all these reagents are acidic (except water) and can readily transfer protons.

## 1.22 Electrophilic addition. Rearrangements :

Electrophilic addition reaction is accompanied by rearrangements. It is observed that the product sometimes contains the group Z attached to a carbon that was not doubly bonded in the substrate, sometimes the product has a carbon skeleton different from that of the substrate. These unexpected products are the results of rearrangements of the carbocation proposed as intermediates. These rearrangements are the same as in  $\text{S}_{\text{N}}1$  substitution and in  $\text{E}1$  elimination.

**Que :** Addition of hydrogen iodide to 3,3-dimethyl-1-butene yields not only the expected product 3-iodo-2,2-dimethyl butane, but also 2-iodo-2,3-dimethyl butane.

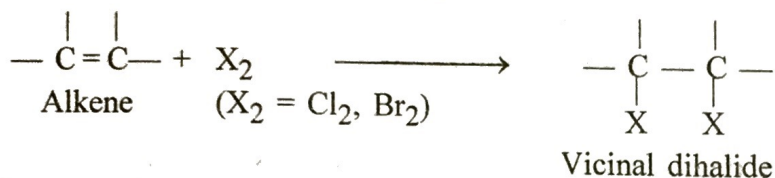




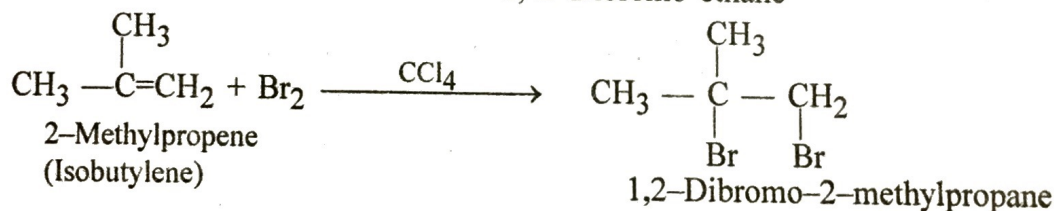
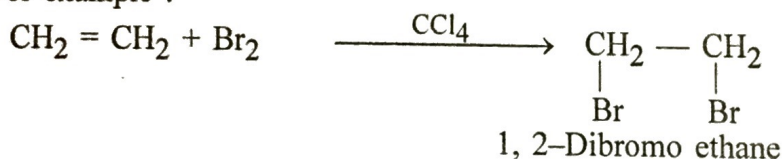
3,3-Dimethyl-1-butene upon addition of HI gives 2° carbocation. This 2° carbocation undergo rearrangement by [1,2]-CH<sub>3</sub> shift to give most stable 3° carbocation. Tertiary carbocation (3°) thus undergo addition of I<sup>-</sup> to yield product 2-iodo-2,3-dimethyl butane.

### 1.23 Addition of halogens :

Alkenes are readily converted by chlorine or bromine into saturated compounds that contain two atoms of halogen attached to adjacent carbons; iodine generally fails to react. The reaction is carried out by mixing together the two reactants, usually in an inert solvent like carbon tetrachloride at room temperature.

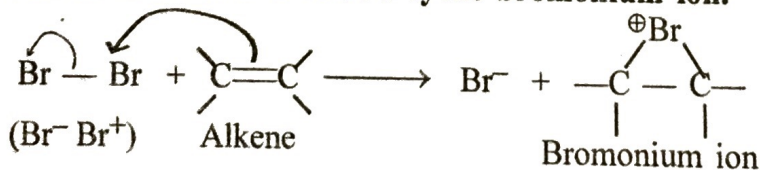


For example :



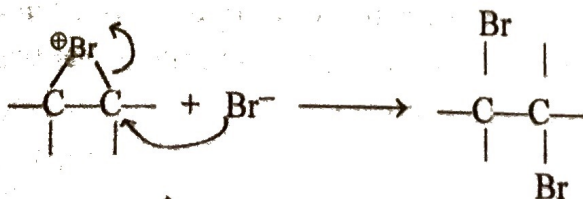
### Mechanism of addition of Halogens : (Addition of bromine Br<sub>2</sub>)

- (i) Bromine is transferred from a bromine molecule as positive bromine i.e. without a pair of electron to the alkene to form a **cyclic bromonium ion**.



Step I is the electrophilic addition, in which bromine is transferred as positive bromine (Br<sup>+</sup>), and left behind newly formed bromide ion (Br<sup>-</sup>). Alkene is base and so halogen is acidic of Lewis type.

- (ii) In step (2) this bromide ion (Br<sup>-</sup>) reacts with the bromonium ion to give the addition product, the dibromide.



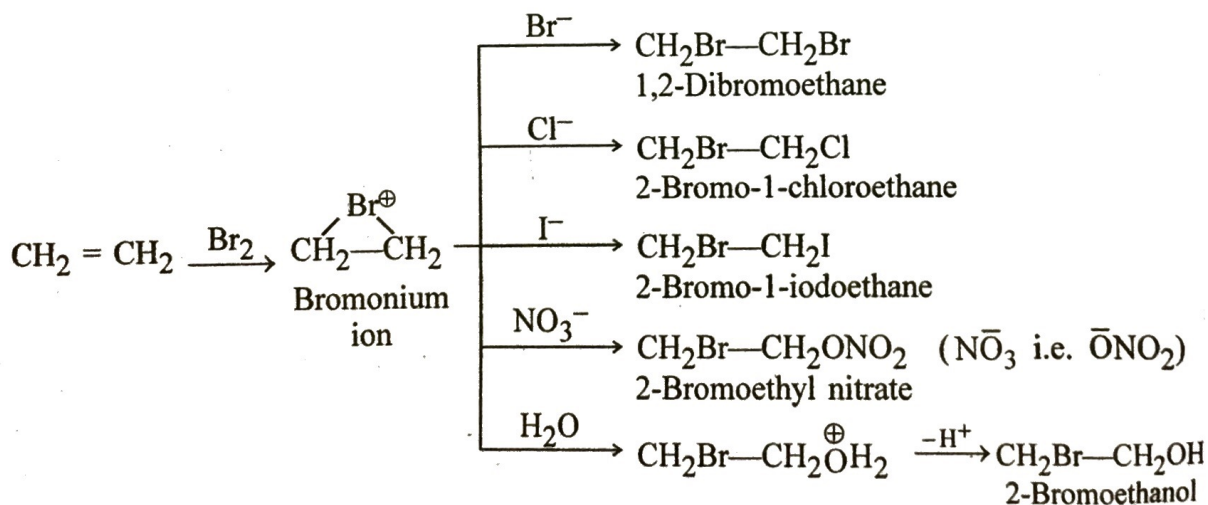


What are the facts upon which this mechanism is based ? They are : (a) the effect of the structure of the alkene on reactivity (b) the effect of added nucleophiles on the products obtained (c) the fact that halogen add with complete stereoselectivity and in the anti sense (d) the direct observation of halonium ions under super acid conditions and (e) the role played by halonium ions in neighboring group effects.

First, there is (a) the effect of the structure of the alkene on reactivity. Alkene show the same order of reactivity towards halogens. Electron releasing substituent activate an alkene and electron withdrawing substituents deactivate. Next, (b) the effect of added nucleophiles on the products obtained. The bromonium ion formed in the reaction between ethylene and bromine, it should be able to react not only with bromide ion but also with  $F^-$ ,  $I^-$ ,  $NO_3^-$  or  $H_2O$ .

Let us consider the **reaction of bromonium ion with various nucleophiles (reagents).**

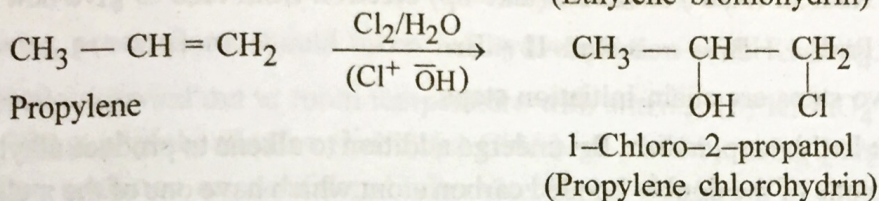
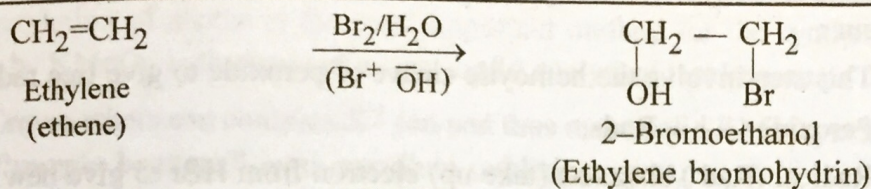
When ethylene is bubbled into an aqueous solution of bromine and sodium chloride, it produce not only dibromo compound but also bromochloro and the bromoalcohol compound.



### 1.24 Halohydrin formation : Addition of the elements of hypohalous acids :

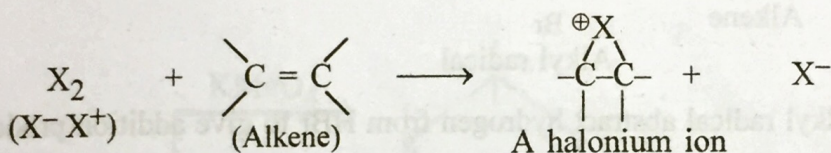
An addition of halogen ( $\text{Br}_2$  or  $\text{Cl}_2$ ) in presence of water, can yield compounds containing halogen and hydroxyl on adjacent carbon atoms are called as halohydrins. These compounds are known as chlorohydrin or bromohydrins. (i.e. compounds which contains halogen atom and  $-\text{OH}$  group is called halohydrins.)



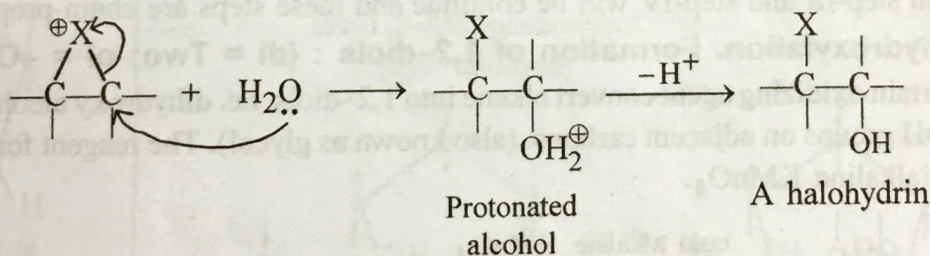


- **Mechanism for the halohydrin formation can be explained as shown below :**

**Step-1 :** The addition of halogen to alkene to form the halonium ion.



**Step (2) :** Halonium ion then react with water to yield the protonated alcohol which on loss of  $\text{H}^+$  (proton) to give halohydrin.



### 1.25 Free-radical addition. Mechanism of the peroxide-initiated addition of HBr (Peroxide effect) :

Addition of HBr to unsymmetrical alkene in the absence of peroxide (like  $\text{H}_2\text{O}_2$ ) follow the Markovnikov's rule, but in the presence of peroxide it follow Anti-Markovnikov's rule. This is known as **peroxide effect**. This peroxide effect account by Kharasch and Mayo.

Markovnikov's addition take place by the **electrophilic** mechanism and Anti-Markovnikov's addition take place by a **free-radical** mechanism.

This peroxide effect mechanism involve free-radical chain reaction mostly addition rather than substitution. Let us consider the addition of HBr to alkene in presence of peroxide.



**Mechanism :**

**Step-I :** This step involve the homolytic cleave of peroxide to give free radical (Rad•).

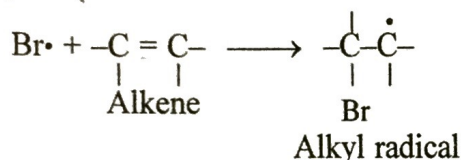


**Step-II :** Radical (Rad•) abstracts (take up) electron from HBr to give new radical Br•.

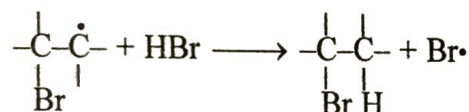


Above two steps are chain-initiation steps.

**Step-III :** In this step, radical Br• undergo addition to alkene to produce alkyl radical. Br• attach itself to one of the doubly bonded carbon atom which have one of the  $\pi$  electrons. The other doubly bonded carbon atom have an odd electron (free radical).



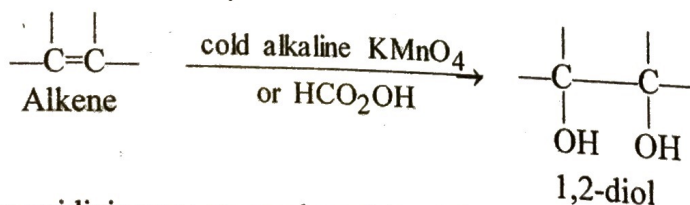
**Step-IV :** Alkyl radical abstract hydrogen from HBr to give addition product and Br•.



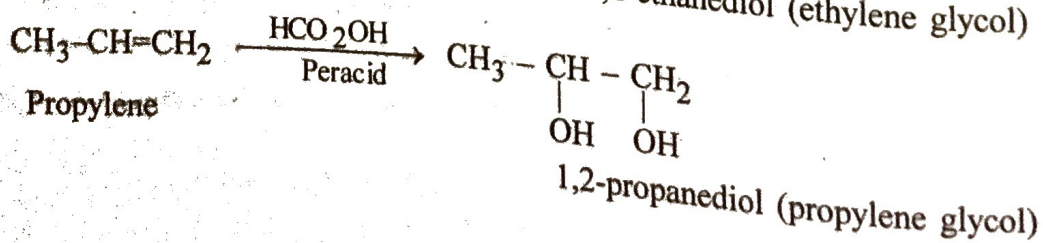
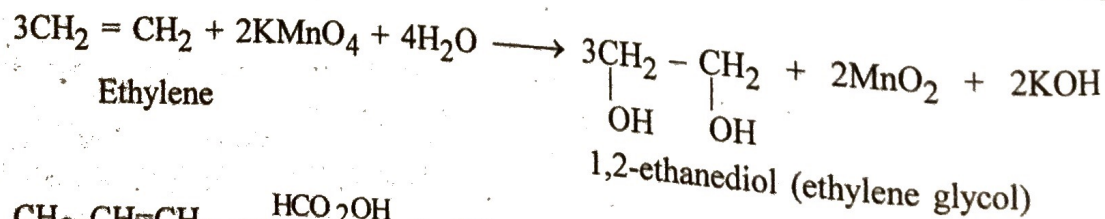
then step-III and step-IV will be continue and these steps are chain-propagation steps.

### 1.26 Hydroxylation. Formation of 1,2-diols : (di = Two; ol = -OH group) :

Certain oxidizing agent convert alkene into 1,2-diols. i.e. dihydroxy alcohols, containing two -OH groups on adjacent carbons. (also known as glycol). The reagent for hydroxylation is cold alkaline  $\text{KMnO}_4$ .



The oxidizing agents used are (a) cold alkaline potassium permanganate ( $\text{KMnO}_4$ ) give **syn** (cis) addition and (b) *peroxy acids* (per acids), such as peroxy formic acid ( $\text{HCO}_2\text{OH}$ ) give **anti** (trans) addition.



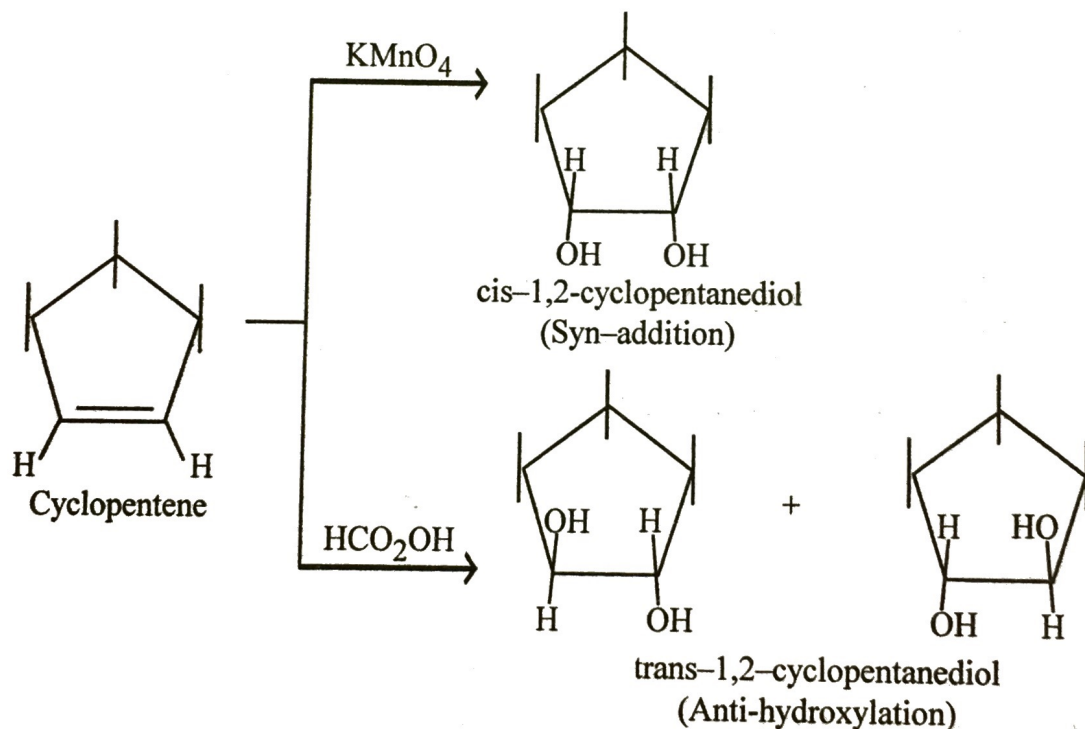
Hydroxylation of alkene is the most important method for the synthesis of 1,2-diols. Oxidation by  $\text{KMnO}_4$  is the basis of a very useful analytical test **known as the Baeyer test**.

The Crown ethers can complex  $\text{K}^+$  ion and thus make solid  $\text{KMnO}_4$  soluble in benzene is called "**purple benzene**" is an excellent oxidizing agent.

Following **precautions** should taken for **hydroxylation** with  $\text{KMnO}_4$ .

(a) Reaction carried out at room temperature with stirring. (b)  $\text{KMnO}_4$  solution either neutral or better, slightly alkaline (basic) (c) Give high yield by using purple benzene (d) Mild reaction condition are considered otherwise further oxidation of diol take place (e). Heat and addition of acid are avoided.

**Que.** What are the precautions should be taken for hydroxylation of alkene with  $\text{KMnO}_4$ .



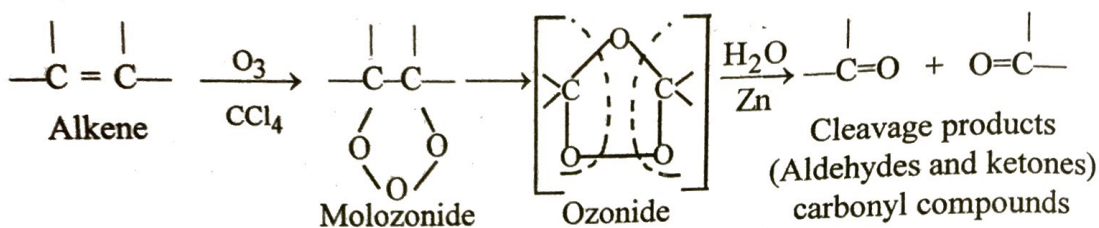
Stereoselective hydroxylation of cyclopentene.

### 1.27 Ozonolysis : Cleavage. Determination of structure by degradation :

The reagent used for cleavage of carbon – carbon double bond is ozone. Ozonolysis (cleavage by Ozone) is carried out in two stages : first, addition of ozone to the double bond to form an ozonide and second, hydrolysis of the ozonide to give the cleaved products carbonyl compound. (Small molecules). The ozone gas is passed into a solution of the alkene in inert solvent like  $\text{CCl}_4$ .

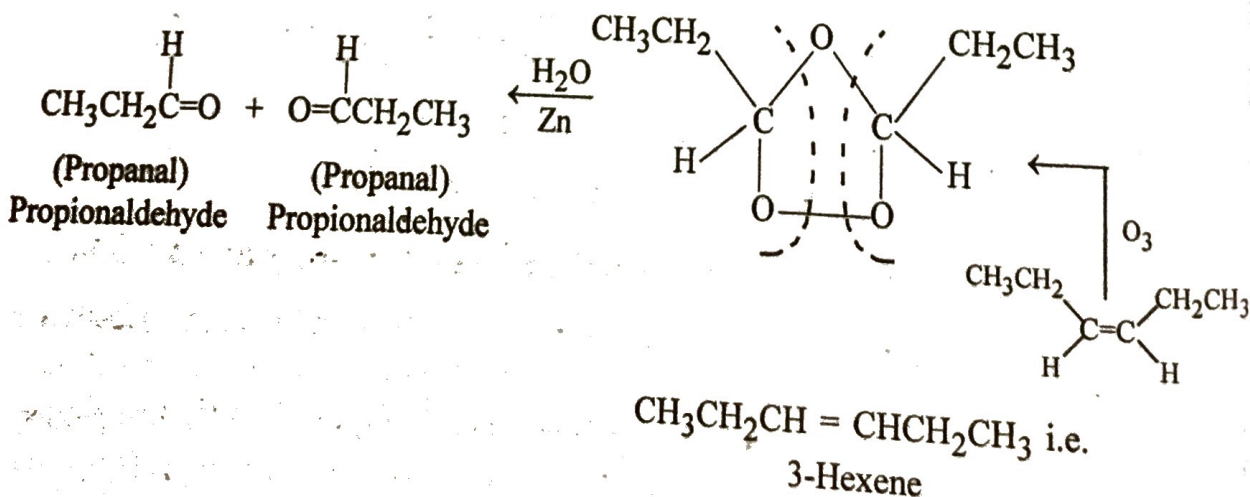
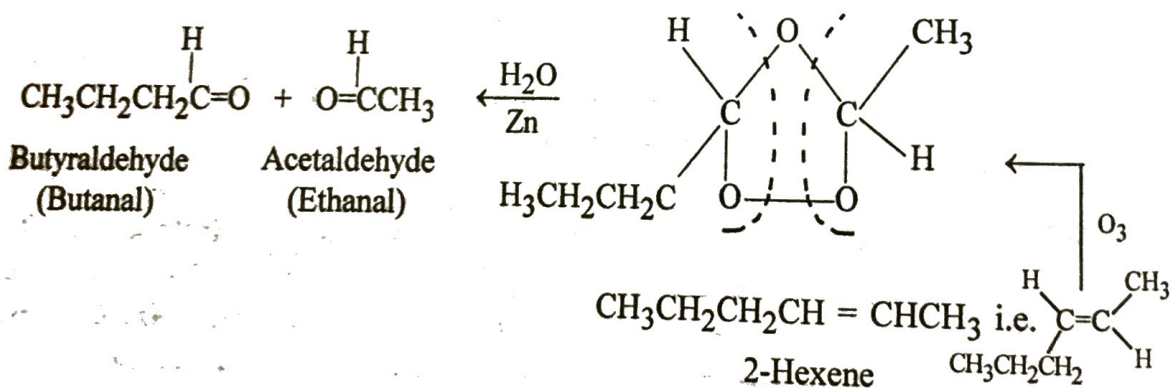


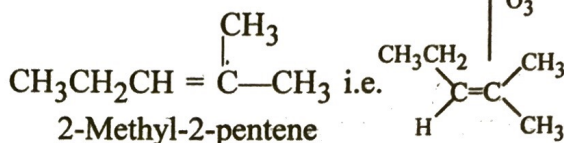
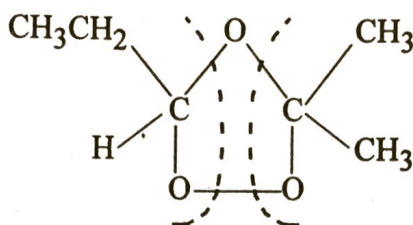
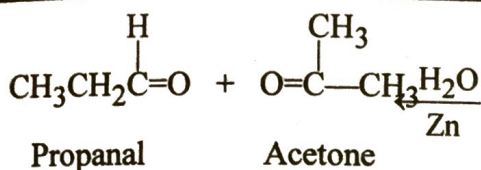
## Ozonolysis



These compounds containing the C=O group are aldehydes and ketones. The function of the reducing agent, (zinc dust) is to prevent formation of hydrogen peroxide which would otherwise react with the aldehydes and ketones. (Aldehydes, RCHO, are converted into acids, RCOOH, for ease of isolation.)

Knowing the number and arrangement of carbon atoms in these aldehydes and ketones, one can work back to the structure of the original alkene. If doubly bonded carbon atom of starting alkene have **one** hydrogen atom then it give **aldehyde** and if doubly bonded carbon atom of alkene have **no** hydrogen atom (but two alkyl groups) then it give **ketone**.  
e.g.

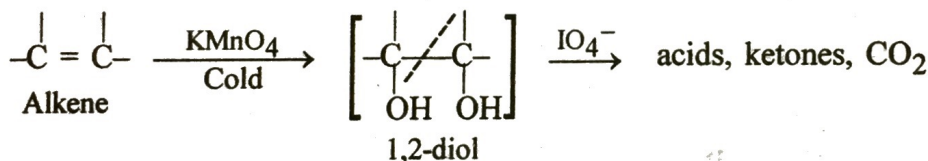




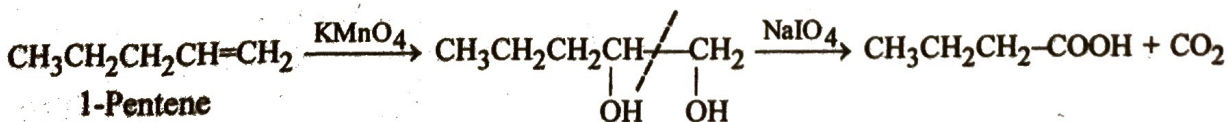
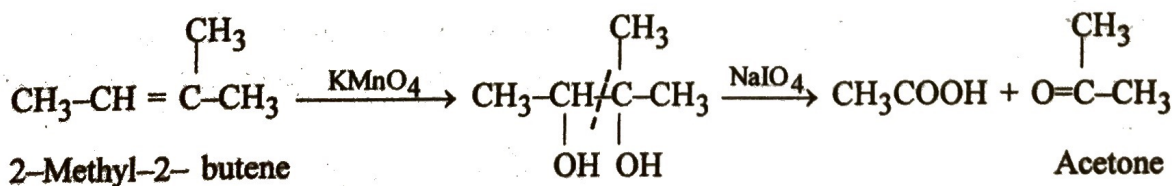
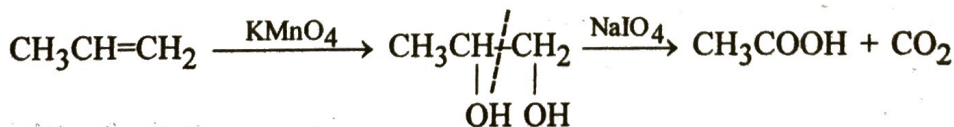
Ozonolysis is a typical means of degradation and desired carbonyl compounds can be prepared by selecting appropriate alkene.

Another method of degradation is oxidation by sodium periodate ( $\text{NaIO}_4$ ) in presence of catalytic amount of periodate.

The permanganate hydroxylates the double bond to give the 1,2-diol, and is itself reduced to the manganate state. The periodate then (a) cleaves the 1,2-diol and (b) oxidized manganate back up to permanganate, and the reaction continues. The C-C bond of 1,2-diol is broken by  $\text{NaIO}_4$  ( $\text{IO}_4^-$ ).



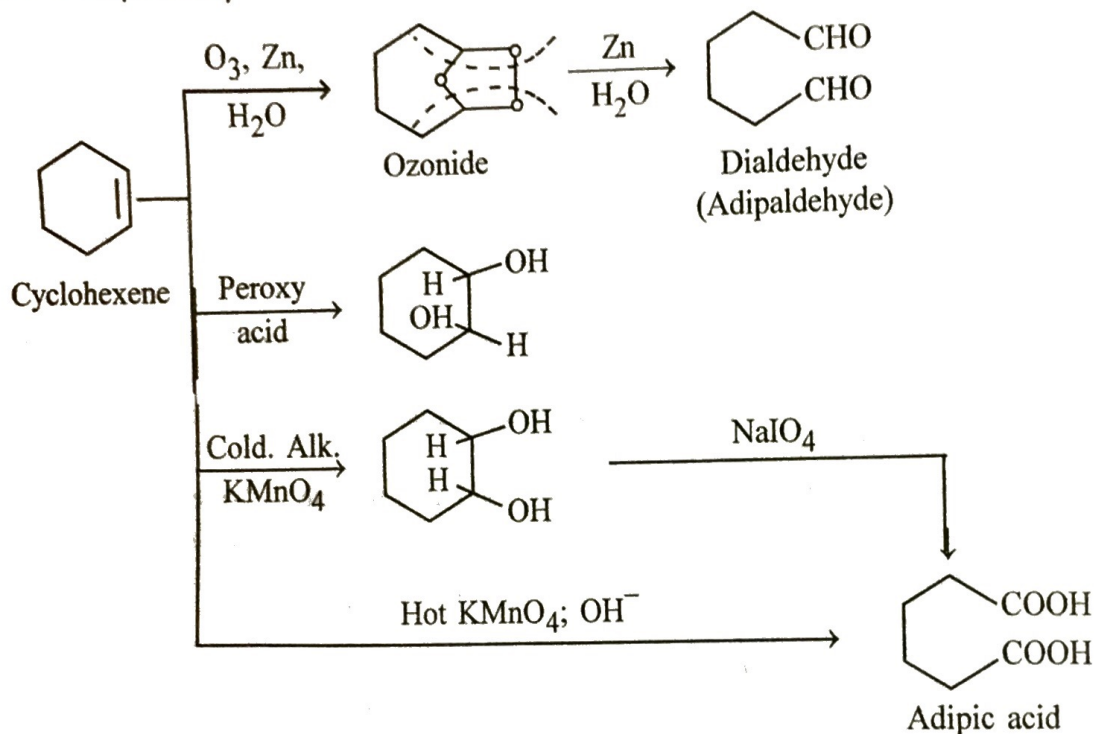
Carboxylic acids,  $\text{RCOOH}$  are generally obtained (instead of aldehydes  $\text{RCHO}$ ). A terminal  $=\text{CH}_2$  group is oxidized to  $\text{CO}_2$  and if initial alkene in which doubly bonded carbon atom have **one hydrogen** atom then it always give **acid** and if there is **no one hydrogen** atom in initial alkene but two alkyl groups then it give **ketone**. e.g.





Write the reaction of cyclohexene towards :

- (a)  $\text{O}_3$ ,  $\text{Zn}/\text{H}_2\text{O}$  (b) Cold alk.  $\text{KMnO}_4$  (c) Peroxyacid (d) Hot.  $\text{KMnO}_4$ ;  $\text{OH}^-$   
 (e)  $\text{KMnO}_4$ ;  $\text{NaIO}_4$



Oxidative cleavage of an alkene produces an acid / ketone /  $\text{CO}_2$ .

→ Write the structures and reaction of an alkene; which upon oxidation produces :

- (a) Alkene  $\xrightarrow{[\text{O}]}$  Acetic acid +  $\text{CO}_2$  (Ans : 1-propene)  
 (b) Alkene  $\xrightarrow{[\text{O}]}$  Butyric acid + Acetone (Ans : 2-methylhexene)  
 (c) Alkene  $\xrightarrow{[\text{O}]}$  Succinic acid  $\text{HOOC}-\text{CH}_2\text{CH}_2\text{COOH}$  (Ans : cyclobutene)  
 (d) Alkene  $\xrightarrow{[\text{O}]}$  Adipic acid (Ans : cyclohexene, as above example)  
 (e) Alkene  $\xrightarrow{[\text{O}]}$  Propionic acid + Methyl ethyl ketone (Ans : 3-methyl-3-hexene)  
 (f) Alkene  $\xrightarrow{[\text{O}]}$  2 mole of acetone (Ans : 2,3-dimethyl-2-butene)

→ Give the structure and reaction of the alkene that give following products on ozonolysis :

- (a) Acetone and acetaldehyde (Ans. : 2-Methyl-2-butene)  
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$  and  $\text{HCHO}$  (Ans. :  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ )  
 (c)  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CHO}$  and  $\text{CH}_3\text{CHO}$  (Ans. :  $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH}=\text{CHCH}_3$ )

(e) Only two moles  $\text{CH}_3 - \text{CO} - \text{CH}_3$  (Ans : 2,3-dimethyl-2-butene)

(e) What would each of above alkenes give upon cleavage by  $\text{NaIO}_4/\text{KMnO}_4$  ?

### 1.28 Alkynes :

The alkynes are named according to two systems. In one, alkynes are considered to be derived from acetylene by replacement of one of both hydrogen atoms by alkyl groups.

$\text{CH} \equiv \text{CH}$  or  $\text{H}-\text{C} \equiv \text{C}-\text{H}$  Acetylene (Ethyne)

$\text{H}-\text{C} \equiv \text{C}-\text{CH}_2-\text{CH}_3$  Ethyl acetylene (1-Butyne)

$\text{CH}_3-\text{C} \equiv \text{C}-\text{CH}_3$  Dimethyl acetylene (2-Butyne)

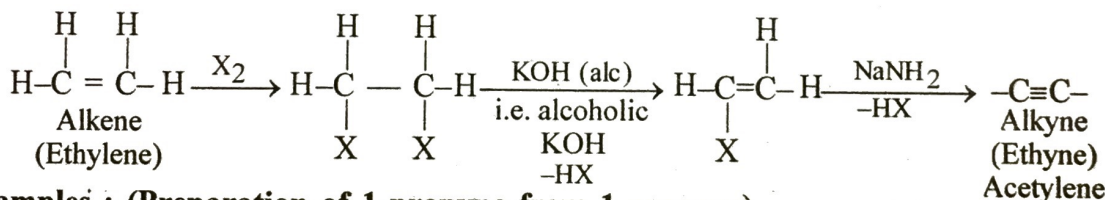
$\text{CH}_3-\text{C} \equiv \text{C}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$  Isopropyl methyl acetylene (4-Methyl-2-pentyne)

### 1.29 Preparation of alkynes :

Alkynes can be prepared by two processes (i) by generating carbon – carbon triple bond (ii) by increasing the size of a molecule that already contains a triple bond.

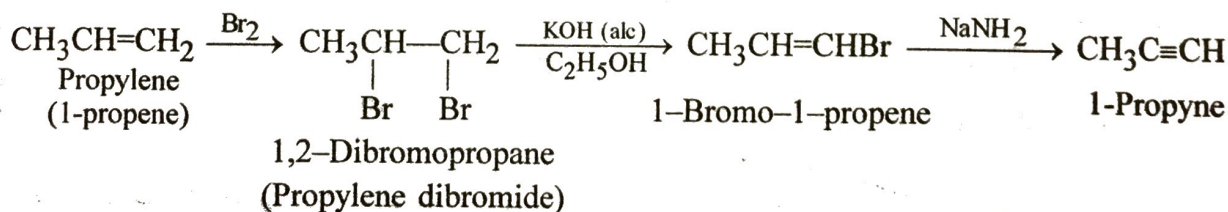
#### 1. Dehydrohalogenation of alkyl dihalides. (i.e. Ethylene to acetylene)

The reagent for dehydrohalogenation of alkyl dihalide is alcoholic KOH and  $\text{NaNH}_2$  (sodamide)

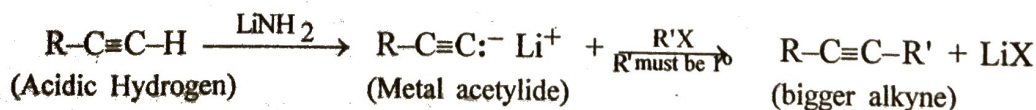


#### Examples : (Preparation of 1-propyne from 1-propene)

Synthesis of alkynes from alkenes having same number of carbon atoms.

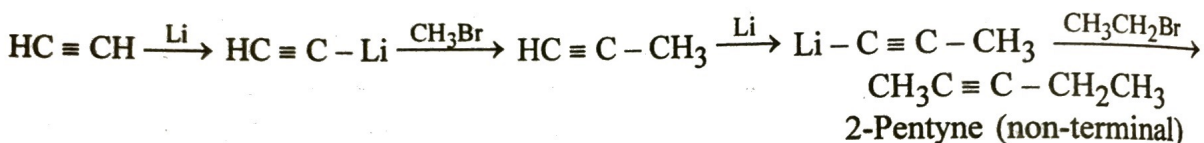
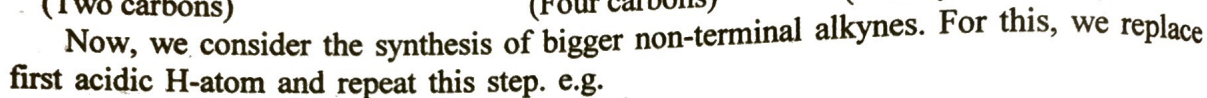


**2. Reaction of metal acetylides with primary alkyl halides.** (synthesis of bigger alkynes from smaller alkynes). The general method for preparation of bigger alkyne is as under.



The H-atom attached to triply bonded carbon atom is acidic hence easily replaced by alkali (Na, Li, etc) or heavy metals (like Cu, Ag etc.) e.g. synthesis of **bigger terminal alkynes**.




$$\text{CH}_3(\text{CH}_2)_4\text{C}\equiv\text{C}^- \text{Li}^+ + \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{Cl} \longrightarrow \text{CH}_3(\text{CH}_2)_4\text{C}\equiv\text{C}-\text{CH}_2(\text{CH}_2)_3\text{CH}_3$$

Lithium-*n*-pentylacetylide      *n*-pentyl chloride                                  6-dodecyne

$$\begin{array}{c} \text{W} \quad \text{X} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{Y} \quad \text{Z} \end{array} \longrightarrow \begin{array}{c} \text{W} \quad \text{H} \\ | \quad | \\ -\text{C}=\text{C}- \end{array} \longrightarrow -\text{C}\equiv\text{C}-$$

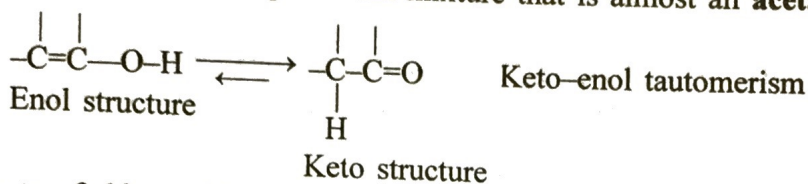
Dehydrohalogenation can generally be carried out in two stages as shown below.



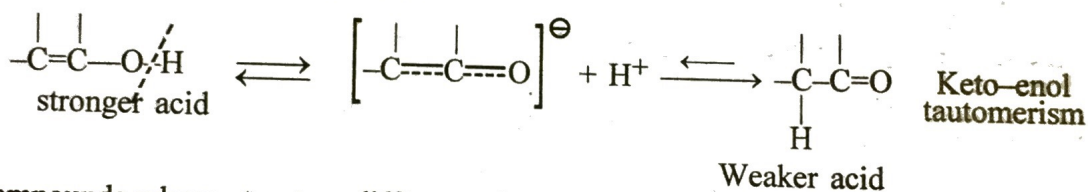
$$\text{H}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{HgSO}_4]{\text{H}_2\text{O}, \text{H}_2\text{SO}_4} \text{H}-\text{C}=\underset{\text{H}}{\underset{\text{O}-\text{H}}{\text{C}}}-\text{H} \rightleftharpoons \text{H}-\underset{\text{H}}{\text{C}}-\underset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{H} \quad \text{i.e. } \text{CH}_3\text{C}(=\text{O})\text{H}$$

Acetylene Vinyl alcohol [enol form] Acetaldehyde [Keto form]

A structure with  $\text{-OH}$  attached to doubly bonded carbon is called an enol ( $\text{-ene}$  for the carbon-carbon double bond,  $\text{-ol}$  for alcohol). We try to make a compound with the enol structure, we obtain instead a compound with the keto structure (one that contains a  $\text{C=O}$  group). There is an equilibrium between the two structures, but it generally lies very much in favor of the keto form. Thus, **vinyl alcohol** is formed initially by hydration of acetylene, but it is rapidly converted into an equilibrium mixture that is almost all **acetaldehyde**.



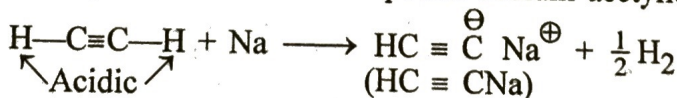
Rearrangements of this enol-keto kind take place particularly easily because of the polarity of the  $\text{-O--H}$  bond. A hydrogen ion separates readily from oxygen to form a hybrid anion; but when a hydrogen ion returns, it may attach itself either to oxygen or to carbon of the anion. When it returns to oxygen, it may readily come off again; but when it attaches itself to carbon, it tends to stay there.



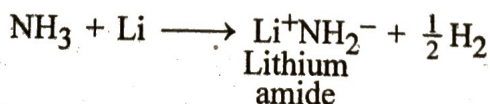
Compounds whose structure differ mostly in arrangement of atoms, but which exist in easy and rapid equilibrium, are called **tautomers**. The most common kind of tautomerism involves structures that differ in the point of attachment of hydrogen. In keto-enol tautomerism, the tautomeric equilibrium generally favors the structure in which hydrogen is bonded to carbon rather than to a more electronegative atom.

### 1.31 Acidity of alkynes :

A **triple bonded carbon** acts as a more **electronegative species**. As a result, hydrogen attached to triply bonded carbon shows acidity. For example sodium reacts with acetylene to liberate hydrogen gas and form the compound sodium acetylide.



Lithium metal reacts with ammonia to form lithium amide ( $\text{LiNH}_2$ ), which is the salt of the weak acid,  $\text{H--NH}_2$ .



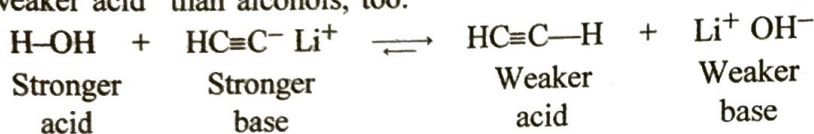
Addition of acetylene to lithium amide dissolved in ether gives ammonia and lithium acetylide.



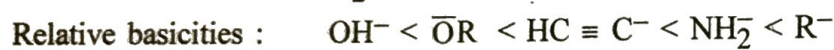


The weaker acid,  $\text{H}-\text{NH}_2$ , is displaced from its salt by the stronger acid,  $\text{HC}\equiv\text{C}-\text{H}$ . In other language, the  $\text{NH}_2^-$  pulls the proton away from the weaker base,  $\text{HC}\equiv\text{C}$ ; if  $\text{NH}_2^-$  holds the proton more tightly than  $\text{HC}\equiv\text{C}-\text{H}$ .

**Que. Acetylene is a weaker acid than water.** When water is added to an acetylide, hydroxide ion is formed and acetylene is liberated. In a similar way, acetylene can be shown to be a weaker acid than alcohols, too.

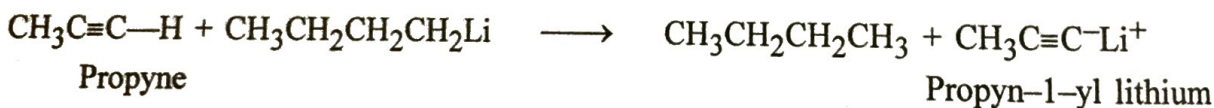
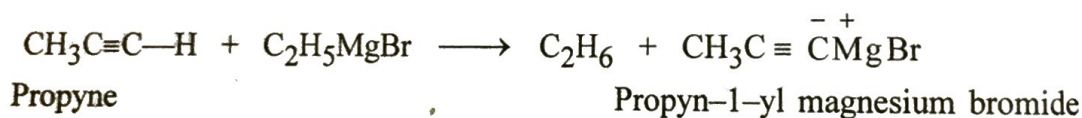


We can now insert acetylene into our sequences of relative acidity and basicity. Other alkynes that contain a hydrogen attached to triply bonded

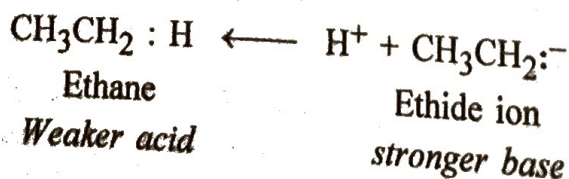
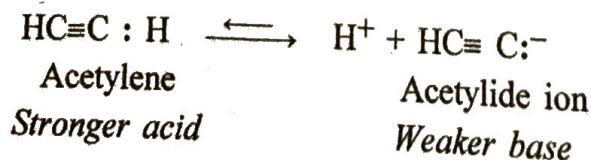


Carbon – that is, *terminal alkynes* – show comparable acidity.

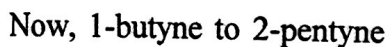
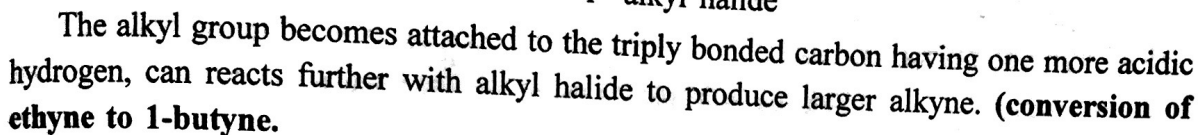
According to our sequence acetylene should be a stronger than an alkane,  $\text{RH}$ . If a terminal acetylene is treated with an alkyl magnesium halide or an alkyl lithium, the alkane is displaced from its “salt”, and the metal acetylide is obtained. For example :



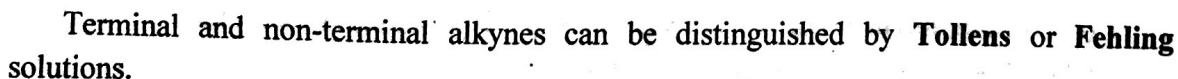
**Que. If acetylene is a stronger acid than ethane,** then the acetylide ion must be a weaker base than the ethide ion,  $\text{C}_2\text{H}_5^-$ . In the **acetylide anion** the unshared pair of electrons occupies an  $sp$  orbital; in the **ethide anion** the unshared pair of electrons occupies an  $sp^3$ -orbital. **The availability of this pair for sharing with acids determines the basicity of the anion.** Now, compare with an  $sp^3$ -orbital, an  $sp$ -orbital has less  $p$ -character and more  $s$ -character. An electron in a  $p$ -orbital is away from the nucleus and is held relatively loosely than an electron in an  $s$ -orbital, on the other hand, is close to the nucleus and is held more tightly. **The acetylide ion is the weaker base since its pair of electrons is held more tightly, in an  $sp$ -orbital.**



Metal acetylides are an important organometallic compounds. They can react with primary alkyl halides to give bigger alkynes.



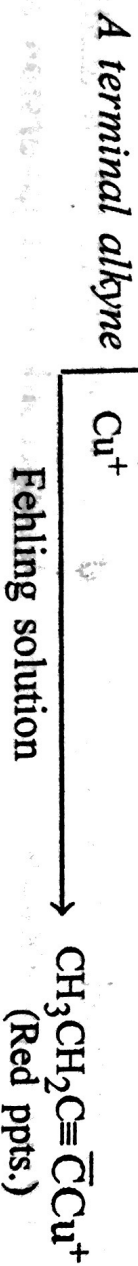
In chemical characterization test, alkynes resembles alkenes. They decolorize bromine in carbon tetrachloride without evolution of HBr and they decolorize cold, neutral, dilute  $\text{KMnO}_4$ . They are not oxidized by chromic acid. Alkynes are more unsaturated than alkenes. Upon ozonolysis **alkynes** give **carboxylic acids**, whereas **alkenes** give **aldehydes** and **ketones**. For example :



**Acidic alkynes** react with certain heavy metal ions, like  $\text{Ag}^+$  and  $\text{Cu}^+$ , to form insoluble acetylides. Formation of a precipitate upon addition of an alkyne to a solution of  $\text{AgNO}_3$  in alcohol, is an indication of hydrogen attached to triply bonded carbon. This reaction can be used to differentiate terminal alkynes (those with the triple bond at the end of the chain) from non-terminal alkenes. Terminal alkynes like 1-butyne or 1-pentyne can reduce Tollens' reagent (silver amonium ion  $\text{Ag}(\text{NH}_3)_2^+$ ) or Fehling solution (alkaline solution of cupric ion).



The H-atom attached to triply bonded carbon atom (terminal H-atom) is highly acidic and easily replaced by heavy metals like Cu, Ag etc. This way we can distinguished terminal and non-terminal alkynes.



A non-terminal alkyne