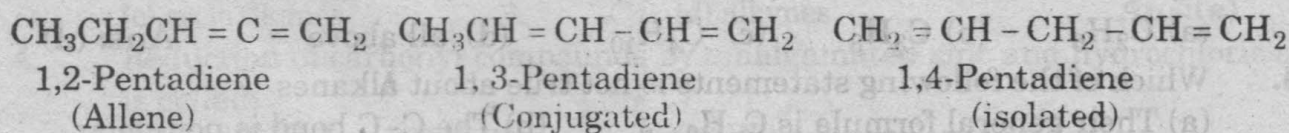# 5. UNSATURATED HYDROCARBONS ALKENES AND ALKYNES

5.1 Introduction

Hydrocarbons in which all the four valencies of carbon are not fully satisfied, contain less than maximum number of hydrogen atoms, and have carbon – carbon multiple bonds, are called *unsaturated hydrocarbons.* Unsaturated hydroc rbons can be divided into two main classes, alkenes and alkynes. The aturated hydrocarbons which contain at least one carbon-carbon double bo are called **alkenes.** They have the general formula C_nH_{2n} (n = number of C atoms). As a class alkenes are commonly known as **olifines** (Latin; oleum = oil ; ficare = to make) because the lower members form oily products on treatment with chlorine or bromine.

Many alkenes contain more than one carbon - carbon double bond. They are called **alkadienes,** if the number of double bonds is two, **alkatriens** for three double bonds etc. If two double bonds are adjacent, they are called comulated double bonds and the alkenes with comulated double bonds are called **allenes.** The allenes are highly reactive compounds and are therefore difficult to prepare, thus only few allenes are known. If the two double bonds are separated by a single bond, they are called **conjugated** double bonds and the diene is called conjugated diene. If the two double bonds are separated by two or more single bonds, they are called **isolated** double bonds and the diene is called isolated diene.

$$CH_3CH_2CH = C = CH_2 \quad CH_3CH = CH - CH = CH_2 \quad CH_2 = CH - CH_2 - CH = CH_2$$

| 1,2-Pentadiene | 1, 3-Pentadiene | 1,4-Pentadiene |
| (Allene) | (Conjugated) | (isolated) |

The term alkene is specifically used for those unsaturated hydrocarbons which have isolated carbon–carbon double bonds. The carbon–carbon double bond is called olifinic bond.
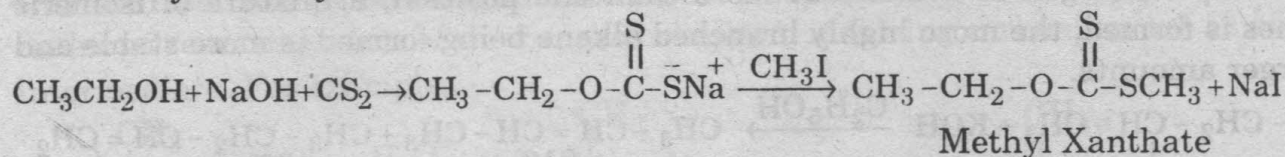
The unsaturated hydrocarbons that contain a triple bond (–C ≡ C–) in their molecules are called alkynes and are isomeric with **alkadienes.** A triple bond is comprised of one strong σ bond and two weaker π bonds. The general formula for alkyne is C_nH_{2n-2}. The first and the most important member of the alkyne series is acetylene, HC ≡ CH, and hence they are also called **Acetylenes,** and the triple bond is often referred to as the acetylenic linkage.
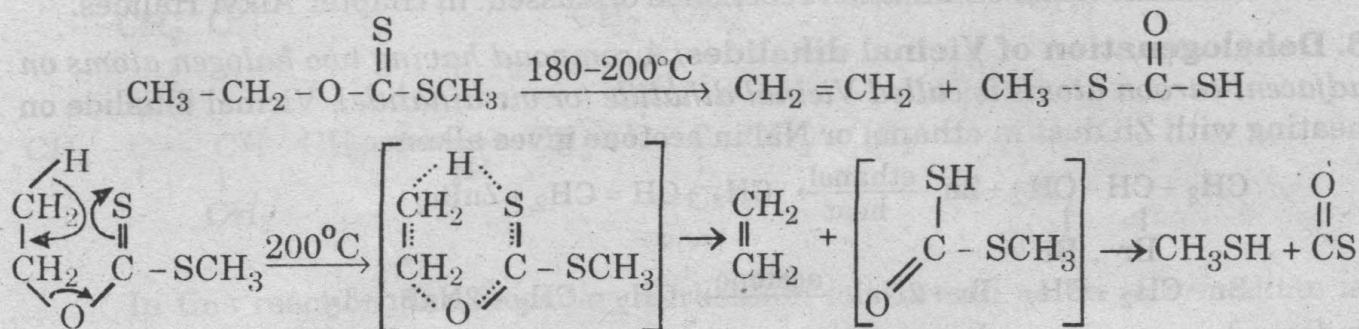
5.2 ALKENES

Methods of preparation of Alkenes

Alkenes may be prepared from saturated compounds by the elimintion of atoms or groups from two adjacent (vicinal) carbon atoms. Such reactions are called elimination reactions. *"Reactions in which two atoms or groups are eliminated from two adjacent carbon atoms of the substrate molecule to form a multiple bond are*
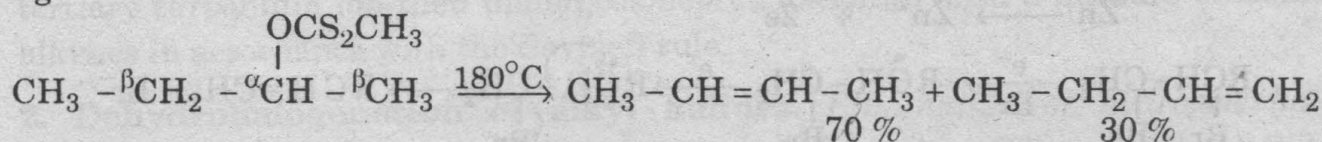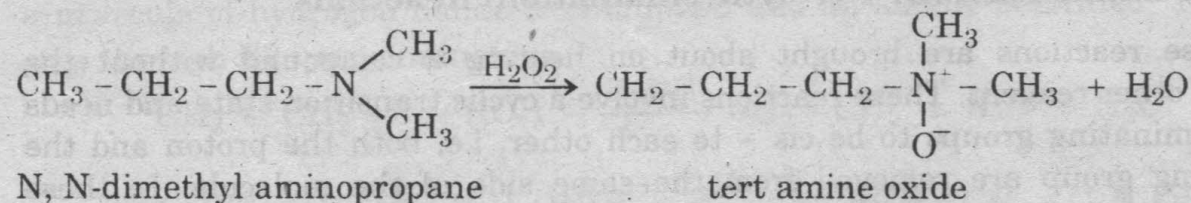
with methyl iodide yields xanthate ester.

$$CH_3CH_2OH + NaOH + CS_2 \rightarrow CH_3-CH_2-O-\overset{\overset{\displaystyle S}{||}}{C}-\bar{S}\overset{+}{N}a \xrightarrow{CH_3I} CH_3-CH_2-O-\overset{\overset{\displaystyle S}{||}}{C}-SCH_3 + NaI$$

Methyl Xanthate

The xanthate ester is then heated to 180 – 200 C to produce alkene.

$$CH_3-CH_2-O-\overset{\overset{\displaystyle S}{||}}{C}-SCH_3 \xrightarrow{180-200°C} CH_2=CH_2 + CH_3-S-\overset{\overset{\displaystyle O}{||}}{C}-SH$$

When more than one β-hydrogens are available, isomeric alkenes are obtained, e.g.

$$CH_3-\overset{\beta}{CH_2}-\overset{\overset{\displaystyle OCS_2CH_3}{|}}{\overset{\alpha}{CH}}-\overset{\beta}{CH_3} \xrightarrow{180°C} CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$$
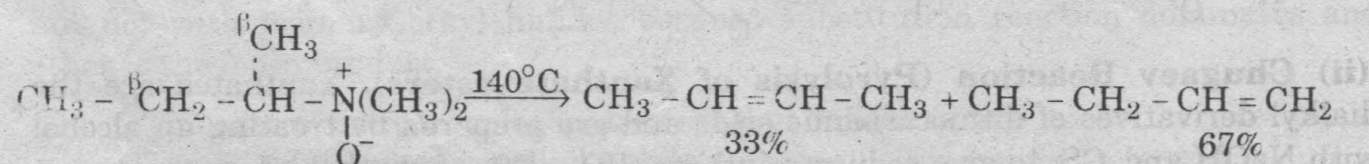$$\phantom{CH_3-CH_2-CH-CH_3 \xrightarrow{180°C}} \underset{70\%}{} \underset{30\%}{}$$

(iii) Cope Reaction (Pyrolysis of amine oxide). Tertiary amine oxides are obtained by treating tirtiary amine with hydrogen peroxide, H_2O_2.
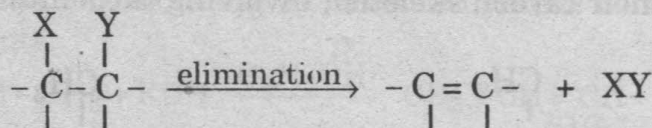
$$CH_3-CH_2-CH_2-N\overset{CH_3}{\underset{CH_3}{<}} \xrightarrow{H_2O_2} CH_2-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle O^-}{|}}{N^+}}-CH_3 + H_2O$$

N, N-dimethyl aminopropane   tert amine oxide

The amine oxide when heated to 120 – 150°C gives alkene via a cyclic transition state.

$$CH_3-CH_2-CH_2-\overset{+}{\underset{\underset{\displaystyle O^-}{|}}{N}}-(CH_3)_2 \xrightarrow{120°C} CH_3-CH=CH_2 + (CH_3)_2NOH$$

$$H_3C-\overset{\overset{\displaystyle CH_2}{|}}{\underset{\underset{\displaystyle H}{|}}{CH}}\overset{CH_3}{\underset{\underset{\displaystyle O^-}{}}{\overset{+}{N}}}CH_3 \xrightarrow{120°C} \left[H_3C-\overset{\overset{\displaystyle CH_2}{||}}{\underset{\underset{\displaystyle O^{\delta-}}{}}{CH}} \quad \overset{\delta+}{N}(CH_3)_2 \right] \longrightarrow CH_3-CH=CH_2 + (CH_3)_2NOH$$
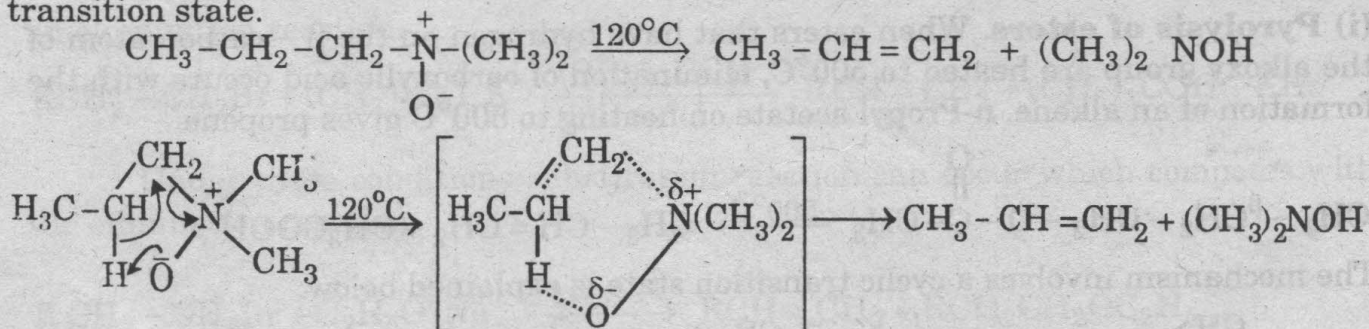
If two β – hydrogens are available, isomeric alkene would result.

$$CH_3-\overset{\beta}{CH_2}-\overset{\overset{\displaystyle \overset{\beta}{CH_3}}{|}}{CH}-\overset{+}{N}(CH_3)_2 \xrightarrow{140°C} CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$$
$$\phantom{CH_3-CH_2-CH-N(CH_3)_2 \xrightarrow{140°C}} \underset{33\%}{} \underset{67\%}{}$$

called **elimination reactions"**

$$\underset{\underset{\displaystyle -}{|}}{\overset{\overset{\displaystyle X}{|}}{-}}C-\underset{\underset{\displaystyle -}{|}}{\overset{\overset{\displaystyle Y}{|}}{C}}- \xrightarrow{\text{elimination}} -C=C- \; + \; XY$$
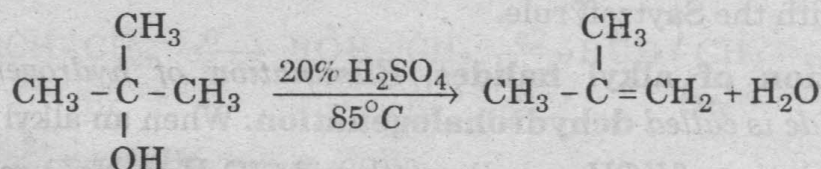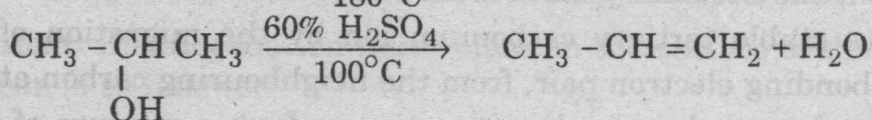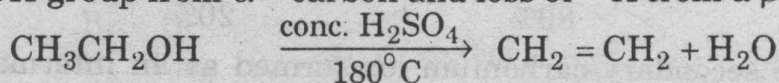
There are three common types of elimination reactions.

1. Dehydration of alcohols   2. Dehydrohalogenation of alkyl halides
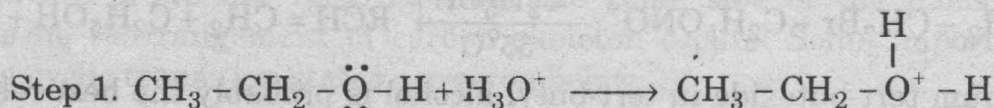3. Dehalogenation of vicinal dihalides.

1. Dehydration of Alcohols. Alcohols on heating in the presence of a Bronsted acid such as sulphuric acid, phosphoric acid or a Lewis acid such as alumina (Al_2O_3) lose a molecule of water to form an alkene. The dehydration of a alcohol involves loss of the $-OH$ group from α – carbon and loss of $-H$ from a β–carbon.

$$CH_3CH_2OH \xrightarrow[180°C]{\text{conc. } H_2SO_4} CH_2=CH_2+H_2O$$

$$\underset{\overset{\displaystyle |}{OH}}{CH_3-CH\,CH_3} \xrightarrow[100°C]{60\% \; H_2SO_4} CH_3-CH=CH_2+H_2O$$

$$\underset{\underset{\displaystyle OH}{\overset{\displaystyle |}{|}}}{\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{|}}}{CH_3-C-CH_3}} \xrightarrow[85°C]{20\% \; H_2SO_4} \overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{|}}}{CH_3-C=CH_2}+H_2O$$

The ease of dehydration of alcohols is: tert > sec > primary.

Mechanism. The most accepted mechanism for the acid catalysed dehydration of alcohols involves the following three steps.

1. In the first step, a proton is rapidly transferred from the acid to one of the unshared electron pair of the oxygen atom of alcohols to form protonated alcohol.
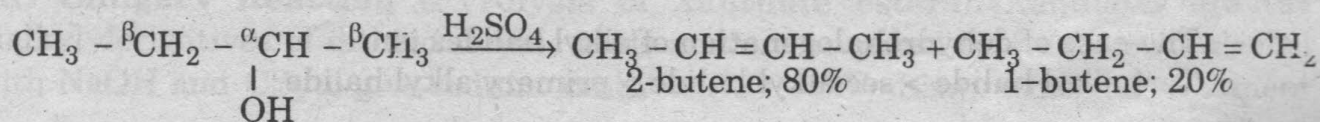
Step 1. $CH_3-CH_2-\overset{\displaystyle \cdot\cdot}{\underset{\displaystyle \cdot\cdot}{O}}-H+H_3O^+ \longrightarrow CH_3-CH_2-\overset{\overset{\displaystyle H}{|}}{O^+}-H$

2. The positive charge on the oxygen of the protonated alcohol weaken the $C-O$ bond. Thus the C–O bond breaks to form carbonium ion, leaving a water molecule.
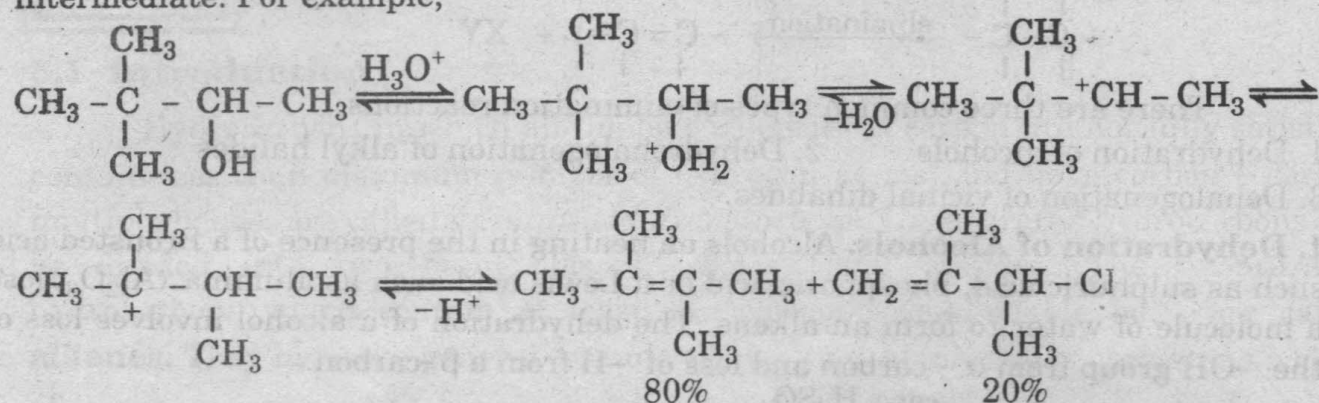
Step 2. $CH_3-CH_2-\overset{\overset{\displaystyle H}{|}}{O^+}-H \longrightarrow CH_3-{}^+CH_2+H_2O$
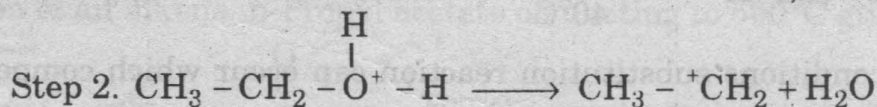
3. The carbonium ion stabilizes itself by transferring a proton to a water molecule, resulting in the formation of alkene.

Step 3. $CH_3-{}^+CH_2+H_2O \longrightarrow CH_2=CH_2+H_3O^+$
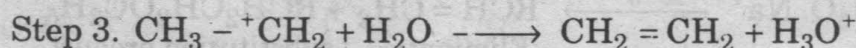
Orientation in Elimination. Alcohols containing more than one β-carbon bearing hydrogen atoms, on dehydration gives mixture of alkenes in accordance with Saytzeff rule. The rule states *that when alternative exist, hydrogen is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms. For example,*
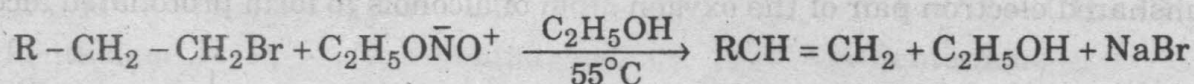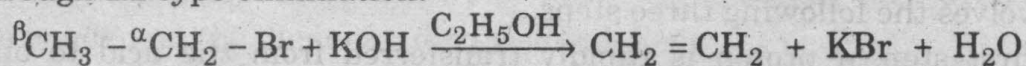
$$\underset{\overset{\displaystyle |}{OH}}{CH_3-{}^\beta CH_2-{}^\alpha CH-{}^\beta CH_3} \xrightarrow{H_2SO_4} \underset{\text{2-butene; 80\%}}{CH_3-CH=CH-CH_3}+\underset{\text{1–butene; 20\%}}{CH_3-CH_2-CH=CH_2}$$

Carbonium Ion Rearrangement. Some primary and secondary alcohols also under go rearrangement of their carbon skeleton, involving carbonium ion as an intermediate. For example,

$$CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH - CH_3 \xrightleftharpoons{H_3O^+} CH_3 - \underset{\underset{^+OH_2}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH - CH_3 \underset{-H_2O}{\rightleftharpoons} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - {}^+CH - CH_3 \rightleftharpoons$$

$$CH_3 - \underset{\overset{+}{\underset{CH_3}{|}}}{\overset{\overset{CH_3}{|}}{C}} - CH - CH_3 \underset{-H^+}{\rightleftharpoons} CH_3 - \underset{\underset{CH_3}{|}}{C} = C - CH_3 + CH_2 = \underset{\underset{CH_3}{|}}{C} - CH - Cl$$

80%   20%

In this reaction, the secondary carbonium ion formed as an intermediate is converted into a more stable tertiary carbonium ion by the migration of methyl group, along with its bonding electron pair, from the neighbouring carbon atom. The tertiary carbonium ion then undergoes deprotonation to form a mixture of isomeric alkenes in accordance with the Saytzeff rule.
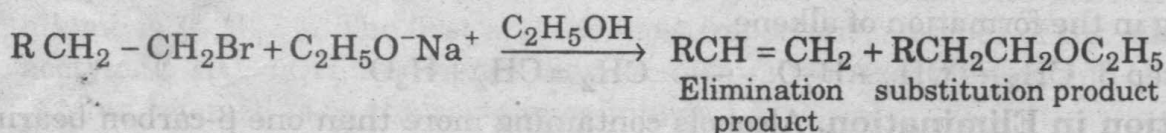
2. Dehydrohalogenation of alkyl halides. *Elimination of hydrogen halide molecule from alkyl halide is called* **dehydrohalogenation.** When an alkyl halide is heated with ethanolic solution of KOH or sodium ethoxide $(C_2H_5O^-Na^+)$ in ethanol, a molecule of hydrogen halide is eliminated and an alkene is formed. The reaction goes through E2 type elimination.

$${}^\beta CH_3 - {}^\alpha CH_2 - Br + KOH \xrightarrow{C_2H_5OH} CH_2 = CH_2 + KBr + H_2O$$

$$R - CH_2 - CH_2Br + C_2H_5O\bar{N}O^+ \xrightarrow[55°C]{C_2H_5OH} RCH = CH_2 + C_2H_5OH + NaBr$$

Potassium tert-butoxide in tert-butyl alcohol is probably the best reagent for an elimination reaction.

$$RCH_2 - CH_2Br + (CH_3)_3CO^-K^+ \xrightarrow[40°C]{(CH_3)_3COH} RCH = CH_2 + (CH_3)_3COH + KBr$$
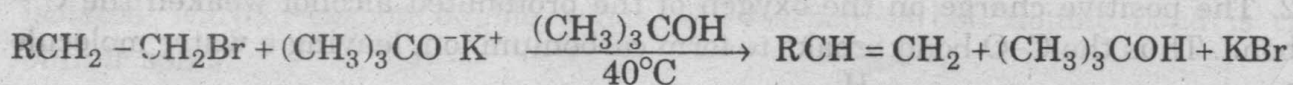
Under these conditions substitution reaction can occur which competes with the elimination reaction.

$$R\,CH_2 - CH_2Br + C_2H_5O^-Na^+ \xrightarrow{C_2H_5OH} RCH = CH_2 + RCH_2CH_2OC_2H_5$$

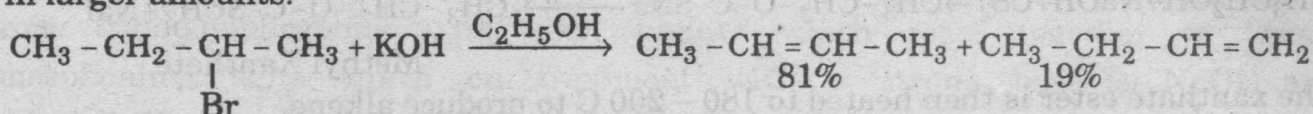Elimination   substitution product
product

This method gives satisfactory results only with secondary and tertiary alkyl halides but not with primary alkyl halides because substitution reaction dominates and ether is the main product.

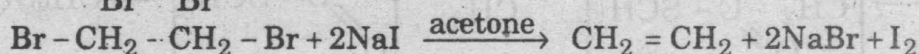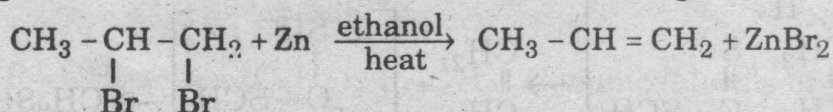The ease of dehydrohalogenation of alkyl halides is:
Tert alkyl halide > sec alkyl halide > primary alkyl halide.

If β–hydrogen is availble at more than one position, a mixture of isomeric alkenes is formed, the more highly branched alkene being formed is more stable and in larger amounts.
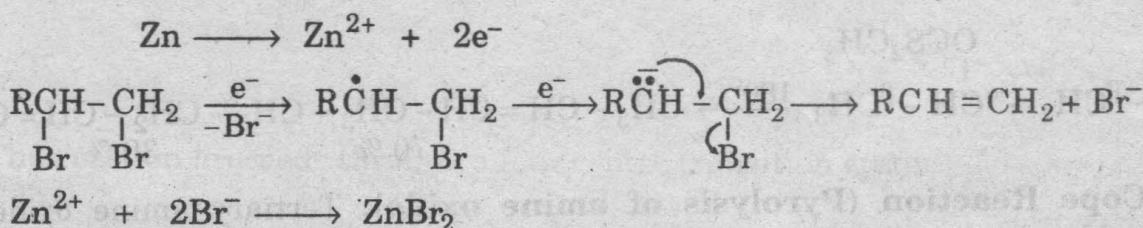
$$CH_3 - CH_2 - \underset{\underset{Br}{|}}{CH} - CH_3 + KOH \xrightarrow{C_2H_5OH} \underset{81\%}{CH_3 - CH = CH - CH_3} + \underset{19\%}{CH_3 - CH_2 - CH = CH_2}$$

The mechanism of the elimination reaction is discussed in chapter Alkyl Halides.

3. Dehalogenation of Vicinal dihalides. *A compoud having two halogen atoms on adjacent carbon atoms is called Vicinal dihalide (or vic-dihalide).* Vicinal dihalide on heating with Zn dust in ethanol or NaI in acetone gives alkenes.

$$CH_3 - \underset{\underset{Br}{|}}{CH} - \underset{\underset{Br}{|}}{CH_2} + Zn \xrightarrow[heat]{ethanol} CH_3 - CH = CH_2 + ZnBr_2$$

$$Br - CH_2 - CH_2 - Br + 2NaI \xrightarrow{acetone} CH_2 = CH_2 + 2NaBr + I_2$$

Mechanism: Dehalogenation takes place on the surface of the metal and a possible mechanism is as follows:

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$\underset{\underset{Br}{|}}{RCH} - \underset{\underset{Br}{|}}{CH_2} \xrightarrow[-Br^-]{e^-} \underset{\underset{Br}{|}}{R\overset{\cdot}{C}H - CH_2} \xrightarrow{e^-} R\overset{\cdot\cdot}{C}H - \underset{\underset{Br}{|}}{CH_2} \longrightarrow RCH = CH_2 + Br^-$$

$$Zn^{2+} + 2Br^- \longrightarrow ZnBr_2$$

4. Thermal Elimination (Or Pyrolytic elimination) Reactions

These reactions are brought about on heating a compound without the presence of other reagent. These reactions involve a cyclic transition state and needs the two eliminating groups to be cis - to each other, i.e, both the proton and the other leaving group are removed from the same side of the molecule. In these reactions no rearrangement of carbon skeleton occurs. Some important reactions involving cyclic transition states are given below:

(i) Pyrolysis of esters. When esters that have hydrogen on the β – carbon atom of the alkoxy group are heated to 500°C, elimination of carboxylic acid occurs with the formation of an alkene. n-Propyl acetate on heating to 500°C gives propene.

$$CH_3 - {}^{\beta}CH_2 - CH_2 - O - \overset{\overset{O}{\|}}{C} - CH_3 \xrightarrow{500°C} CH_3 - CH = CH_2 + CH_3COOH$$
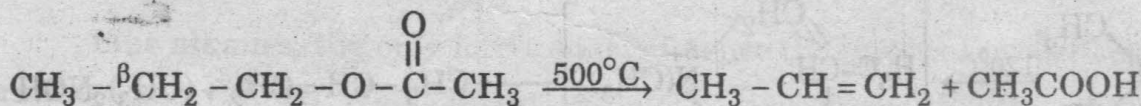
The mechanism involves a cyclic transition state is explained below:
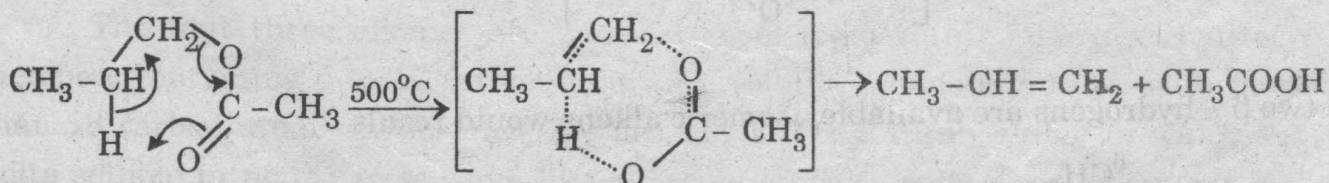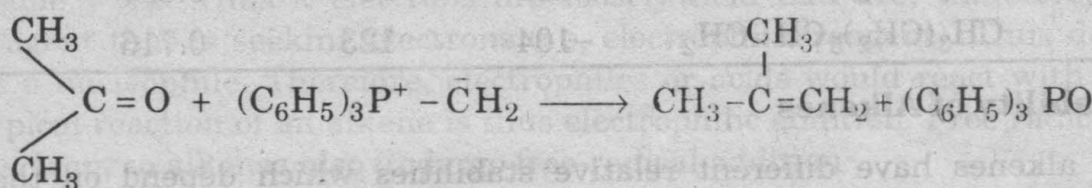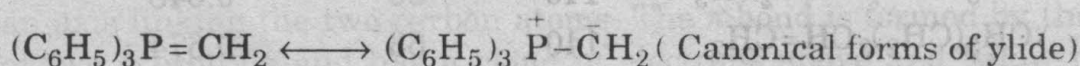

(ii) Chugaev Reaction (Pyrolysis of Xanthate esters). Xanthates are the dialkyl derivatives of dithiocarbamic acids and are prepared by treating an alcohol with NaOH and CS$_2$ to give sodium xanthate (RO – CS – SNa), which on treatment
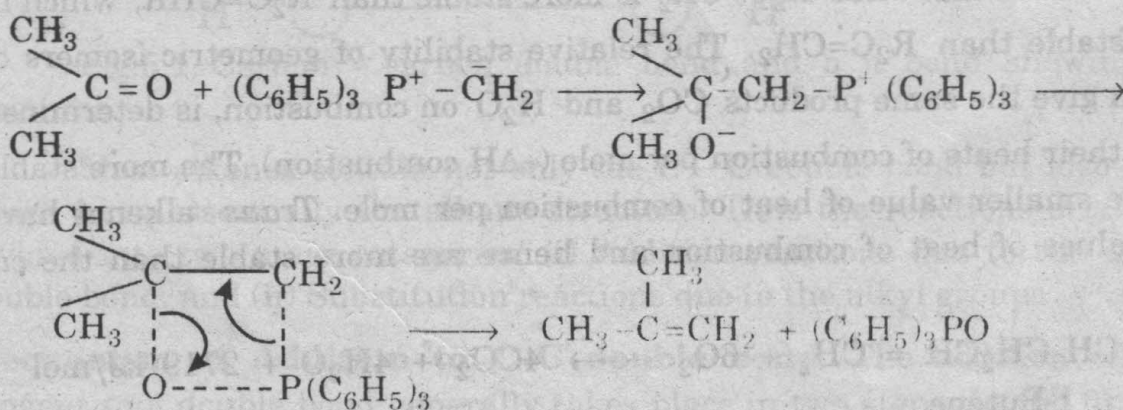
(iv) Wittig Reaction. In the Wittig reaction an aldehyde or ketone is treated with a phosphorus ylide to give an alkene through a four centre transition state. Phosphorus ylides, which are hybrids of two canonical forms, are usually prepared from triphenylphosphine and alkyl halides which react together to form phosphonium salts which on treatment with a strong base as NaOH or n–butyllithium or phenyllithium in dry ether, gives a phosphorus ylide.

$$(C_6H_5)_3P: \ + \ CH_3I \longrightarrow (C_6H_5)_3P^+CH_3I^- \xrightarrow{C_6H_5Li} (C_6H_5)_3 P = CH_2 + C_6H_6 + LiI$$
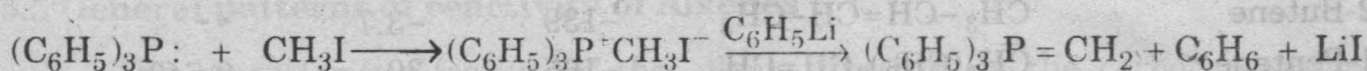
Triphenyl phosphine   methyltriphenylphosphonium   phosphorus ylide
                    iodide

$$(C_6H_5)_3P = CH_2 \longleftrightarrow (C_6H_5)_3 \overset{+}{P} - \overset{-}{C}H_2 \ (\text{Canonical forms of ylide})$$

$$\underset{CH_3}{\overset{CH_3}{>}} C = O \ + \ (C_6H_5)_3P^+ - \overset{-}{C}H_2 \longrightarrow CH_3 - \underset{|}{\overset{CH_3}{C}} = CH_2 + (C_6H_5)_3 PO$$

The reaction proceeds through a four centre transition state:

$$\underset{CH_3}{\overset{CH_3}{>}} C = O \ + \ (C_6H_5)_3 \ P^+ - \overset{-}{C}H_2 \longrightarrow \underset{CH_3 \ O^-}{\overset{CH_3}{>}} \underset{|}{C} - CH_2 - P^+ (C_6H_5)_3 \longrightarrow$$

$$\begin{array}{c} \underset{CH_3}{\overset{CH_3}{>}} C \text{----} CH_2 \\ | \qquad\qquad | \\ O \text{-----} P(C_6H_5)_3 \end{array} \longrightarrow CH_3 - \underset{|}{\overset{CH_3}{C}} = CH_2 + (C_6H_5)_3 PO$$

5.3 Physical properties of Alkenes

Like alkanes, the only forces that influence the physical properties of alkenes are the weak van der Waals attractive forces. Therefore, the physical properties of alkenes are essentially the same as those of the corresponding alkanes.
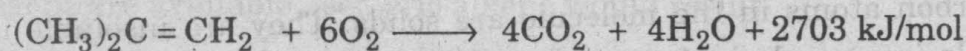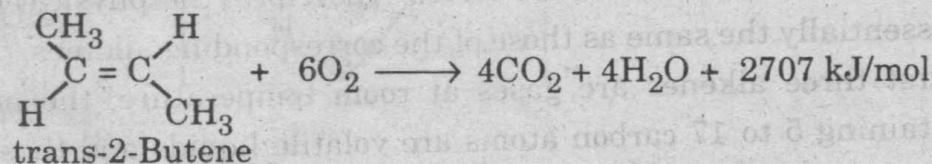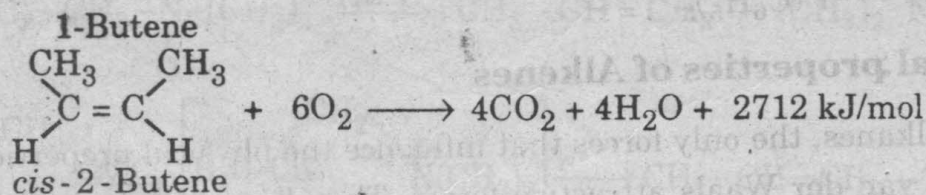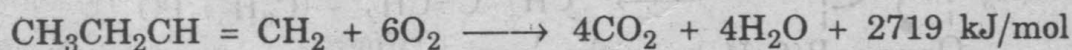
The first three alkenes are gases at room temperature, the next fourteen members containing 5 to 17 carbon atoms are volatile liquids and those with more than 18 carbon atoms in the molecule are solids. They are insoluble in water but quite soluble in nonpolar solvents like benzene, ether or chloroform. They are less dense than water. The boiling and melting points, in general, rise with increasing molecular mass. Branching, however, lowers the boiling point.

Table 5.1 Physical Constants of Alkenes

Name	Formula	M.p.(°C)	B.p.(°C)	Density (g/cm³)
Ethene	$CH_2=CH_2$	−169	−102	0.6100
Propene	$CH_3-CH=CH_2$	−185	−47	0.6104
1-Butene	$CH_3-CH_2-CH=CH_2$	−185	−6.5	0.6255
2-Butene	$CH_3-CH=CH-CH_3$	−139	−3.7	--
1-Pentene	$CH_3(CH_2)_2CH=CH_2$	−165	30	0.643
2-Pentene(cis)	$CH_3CH=CH\ CH_2CH_3$	−151	37	0.656
2-Pentene(trans)	$CH_3CH=CH\ CH_2CH_3$	−140	36	0.648
1-Hexene	$CH_3(CH_2)_3CH=CH_2$	−140	63	0.674
1-Heptene	$CH_3(CH_2)_4CH=CH_2$	−119	93	0.697
1-Octene	$CH_3(CH_2)_5CH=CH_2$	−104	123	0.716

5.4 Relative stability of Alkenes

Different alkenes have different relative stabilities which depend on the position of the double bond in the molecule, and the number, nature and relative positions of the substituents on the double-bonded carbon atoms. The greater the number of alkyl groups attached to the double-bonded carbon atoms, the greater is the stability of the alkene. Thus $R_2C=CR_2$ is more stable than $R_2C=CHR$, which in turn is more stable than $R_2C=CH_2$. The relative stability of geometric isomers of alkenes, which give the same products CO_2 and H_2O on combustion, is determined by comparing their heats of combustion per mole ($-\Delta H$ combustion). The more stable isomer has the smaller value of heat of combustion per mole. *Trans* alkenes have the smaller values of heat of combustion and hence are more stable than the *cis* isomers.

$$CH_3CH_2CH = CH_2 + 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2719\ kJ/mol$$
1-Butene

$$\begin{matrix} CH_3 & CH_3 \\ C & = & C \\ H & & H \end{matrix} + 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2712\ kJ/mol$$
cis-2-Butene

$$\begin{matrix} CH_3 & H \\ C & = & C \\ H & & CH_3 \end{matrix} + 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2707\ kJ/mol$$
trans-2-Butene

$$(CH_3)_2C = CH_2 + 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2703\ kJ/mol$$
Isobutylene

The *cis* isomer has higher energy because there is greater steric repulsion between its alkyl groups on the same side of the double bond than between an alkyl group and H in the *trans* isomer. These repulsions are greater with larger alkyl

groups, which produce larger energy differences between geometric isomers.

In 1-butene, there is virtually no steric strain. Therefore, 2-butene is more stable because of steric repulsion than 1-butene which is supported by the heat of combustion. Thus the generally order of relative stabilities of alkenes is;

$$R_2C = CR_2 > R_2C = CHR > R_2C = CH_2 > RCH = CHR > RCH = CH_2 > H_2C = CH_2$$
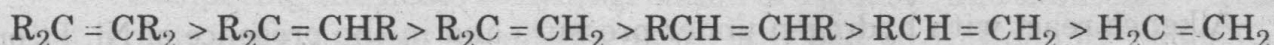
5.5 General patterns of reactivity of Alkenes

The characteristic feature of the alkene structure is the carbon – carbon double bond, which consists of a strong σ bond and a weak π bond. The σ bond is formed by the overlap of sp^2 hybrid orbitals end –to–end and is symmetrical about an axis linking the two carbon atoms. The π bond is formed by the sidewise overlap of two p orbitals and has a cloud of electrons above and below the plane of the σ frame work. Thus π electrons are loosely held and are, therefore, available to a reagent that is seeking electrons (i.e, electrophilic reagent). Thus double bond acts as a nucleophile. Therefore, electrophiles or acids would react with an alkene. The typical reaction of an alkene is thus electrophilic addition. Free radicals also seek an electron, so alkenes also undergo free-radical addition.
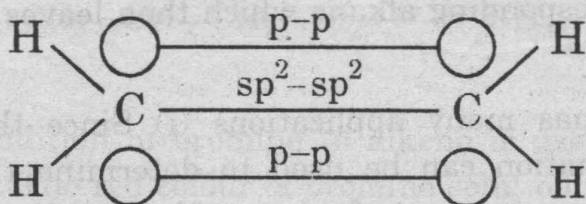

Fig.5.1 Carbon - carbon double bond and a π bond showing cloud of π electrons.

Most alkenes contain not only the C – C double bond but also alkyl groups, which have essentially the alkane structure. Thus the reactions of alkenes can be divided into two main catagories. (i) Addition reactions due to the carbon–carbon double bond, and (ii) Substitution reactions due to the alkyl groups.

Mechanism of Addition to C–C double bond. The addition of electrophilic reagent to a double bond generally takes place in two steps. In the first step one of the double-bonded carbon forms a bond with an electrophilic part of the reagent to from an intermediate carbocation, which then rapidly combines with the other part of reagent which now acts as a nucleophile to give the addition product in the second step.
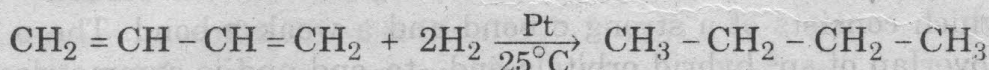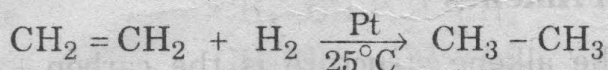
For example,
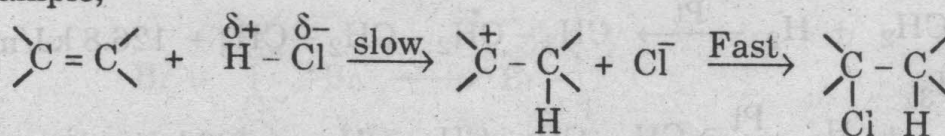
5.6 Chemical properties (Reactions) of Alkenes

1. Hydrogenation (Addition of Hydrogen). *The reaction of an unsaturated compound with hydrogen in the presence of a finely divided metal catalyst to form a saturated compound is called* **catalytic hydrogenation.**

The most commonly used catalysts are platinum, palladium and nickel. Pt is used as PtO, Pd is employed as a fine powder supported on charcoal, nickel is used as **Raney Nickel** which is obtained by dissolving Ni-Al alloy in NaOH which dissolves Al leaving Ni as a fine suspension, called **Raney Nickel.**

Alkenes react with hydrogen under pressure and in the presence of Ni, Pt or Pd catalyst to form alkanes.
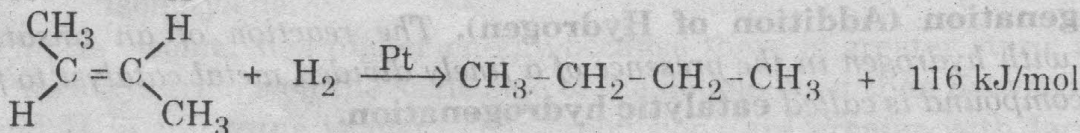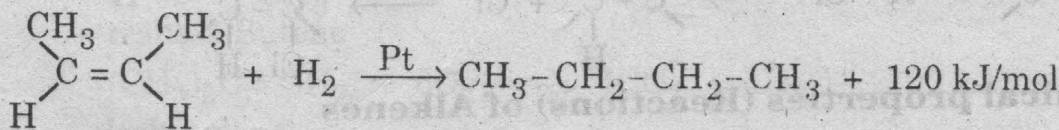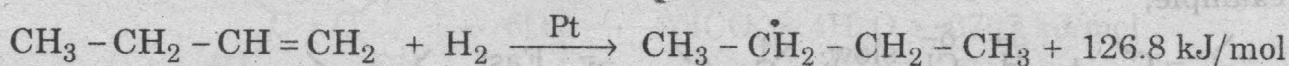
$$CH_2 = CH_2 + H_2 \xrightarrow[25°C]{Pt} CH_3 - CH_3$$

$$CH_2 = CH - CH = CH_2 + 2H_2 \xrightarrow[25°C]{Pt} CH_3 - CH_2 - CH_2 - CH_3$$

Hydrogenation is carried out in a a solvent; alcohol, acetic acid and ethyl acetate are generally employed. The addition of hydrogen to an alkene is a cis addition. The hydrogenation of alkenes occurs at the surface of the metal catalyst. The metal adsorbs hydrogen by providing electrons to form the metal hydrogen bonds. At the same time, alkene is also adsorbed on the surface of the matal that breaks the π bond of the alkene and helps in a step-wise transfer of hydrogen atoms to the alkene to produce the corresponding alkane which then leaves the surface of the metal.

Catalytic hydrogenation has many applications (i) Since the reaction is quantitative, therefore, hydrogenation can be used to determine the number of double bonds in a polyalkene by measurement of volume of hydrogen used. Vitamin A requires five molecules of hydrogen for complete reduction and hence has five double bonds in its molecule.

(ii) An important industrial application of catalytic hydrogenation is the preparation of vegetable ghee from vegetable oil.
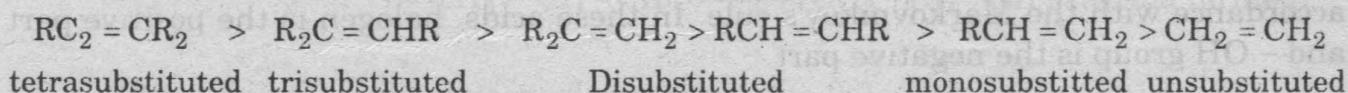
(iii) Heats of Hydrogenation. Hydrogenation of alkenes is an exothermic reaction. *The amount of heat evolved when one mole of an alkene is hydrogenated is called* **heat of hydrogenation.** The heat of hydrogenation of most alkenes is about 126 kJ for each double bond in a molecule. However, the heats of hydrogenation of individual alkenes may slightly differ from this value. These differences in heats of hydrogenation allow us to measure the relative stabilities of alkene isomers when hydrogenation convert them to the same product. Consider, for example, the hydrogenation of isomeric alkenes, 1-butene, cis-2-butene and trans-2-butene, each of which adds one molecule of hydrogen to produce the same product, n-butane,

$$CH_3 - CH_2 - CH = CH_2 + H_2 \xrightarrow{Pt} CH_3 - CH_2 - CH_2 - CH_3 + 126.8 \text{ kJ/mol}$$

$$\underset{H}{\overset{CH_3}{>}}C = C\underset{H}{\overset{CH_3}{<}} + H_2 \xrightarrow{Pt} CH_3 - CH_2 - CH_2 - CH_3 + 120 \text{ kJ/mol}$$

$$\underset{H}{\overset{CH_3}{>}}C = C\underset{CH_3}{\overset{H}{<}} + H_2 \xrightarrow{Pt} CH_3 - CH_2 - CH_2 - CH_3 + 116 \text{ kJ/mol}$$
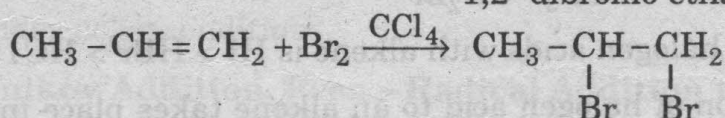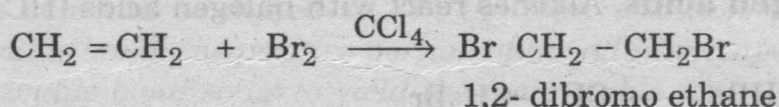
This can be seen that of the three isomeric alkenes, that 1-butene evolves the largest amount of heat of hydrogenation and trans-2-butene evolves the least. Thus trans-2- butene is the most stable and 1-butene is the least stable isomer and cis-2-butenes lies in between.

Comparing the heats of hydrogenation of 1-butene and 2-butene, we conclude that greater the number of alkyl groups attached to the doubly bonded carbon atoms, the greater is the stability of the alkene.

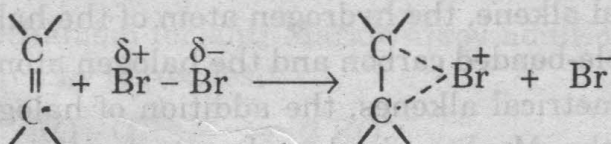The **order of stabilities** of alkenes in general terms is as follows:

$$RC_2 = CR_2 \quad > \quad R_2C = CHR \quad > \quad R_2C = CH_2 > RCH = CHR \quad > \quad RCH = CH_2 > CH_2 = CH_2$$

tetrasubstituted   trisubstituted   Disubstituted   monosubstitted unsubstituted

2. Addition of Halogens.

Alkenes react with chlorine or bromine in an inert solvent like CCl_4 at room temperature to form vicinal dichloride or vic-dibromide. Fluorine reacts too violently to be controlable and iodine does not give stable vic-diiodides.

$$CH_2 = CH_2 \;+\; Br_2 \xrightarrow{CCl_4} Br\, CH_2 - CH_2Br$$
1,2- dibromo ethane

$$CH_3 - CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3 - \underset{\underset{Br}{|}}{CH} - \underset{\underset{Br}{|}}{CH_2}$$
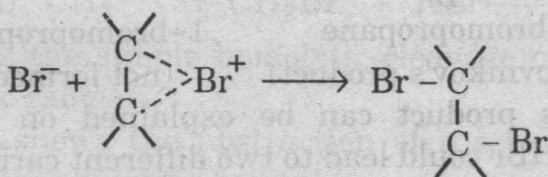
The addition of bromine to alkene is used as a simple qualitative test for unsaturation. The red colour of bromine solution is rapidly discharged when it adds to alkene to form colourless dibromo compound.

Mechanism: The π electrons of the double bond attack on one of the bromine atoms to form cyclic bromonium ion and bromide ion.

$$\begin{array}{c} \diagup C \diagdown \\ \| \\ \diagdown C \diagup \end{array} + \;\; \overset{\delta+}{Br} - \overset{\delta-}{Br} \longrightarrow \begin{array}{c} \diagup C \diagdown \\ | \quad \overset{+}{>}Br \\ \diagdown C \diagup \end{array} + \; \overset{-}{Br}$$

In fact, as the π electrons of the alkene approach the bromine molecule, the Br–Br bond is induced to be polarized and is thus weakened which is finally broken heterolytically.

The bromide ion thus produced then attacks one of the carbon atoms of the bromonium ion from the backside to form the trans–addition product.

$$\overset{-}{Br} + \begin{array}{c} \diagup C \diagdown \\ | \quad \overset{+}{>}Br \\ \diagdown C \diagup \end{array} \longrightarrow \begin{array}{c} Br - C \diagdown \diagup \\ \diagup \diagdown \\ \diagup C - Br \\ \diagup \diagdown \end{array}$$

3. Addition of hypohalous acid.

When halogenation of an alkene is conducted in aqueous solution, halohydrin is formed in addition to vic-dihalide, the major product is halohydrin which shows the addition of hypohalous acid (HOX) across the double bond.