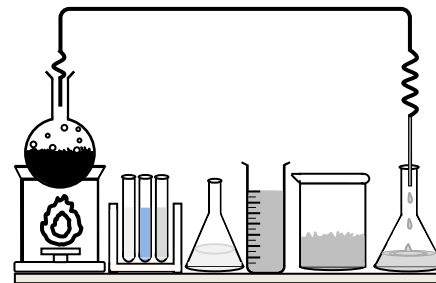


## Chapter – 15



### HYDROCARBON

#### ALKANES

Alkanes are saturated hydrocarbons which can be represented by the general formula  $C_nH_{2n+2}$ . They are also known as paraffins after their poor affinity towards common reagents e.g., acids, bases, oxidising and reducing agents. The molecular formula of alkanes suggests that each individual member differs from its neighbour by  $CH_2$  group. Such a series of compounds is known as homologous series and the individual members being known as homologues.

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#### 1 METHODS PREPARATION OF ALKANES

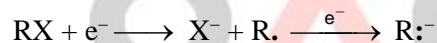
##### 1.1 METHODS INVOLVING NO CHANGE IN THE CARBON SKELETON

##### 1.1.1 Reduction of alkyl halides, $RX$ where $X = F, Cl, Br$ or $I$ :

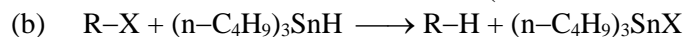
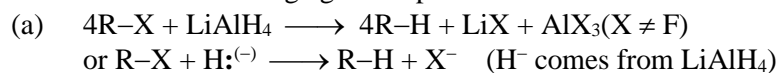
###### (Substitution of halogen by hydrogen)

This may be done in three different ways

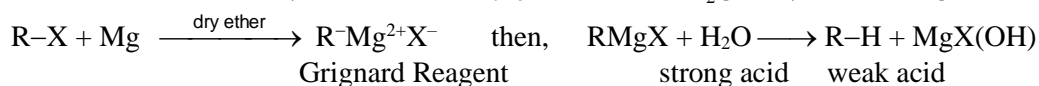
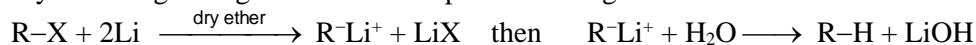
- (i) **Reduction by dissolving metals:** Reduction by dissolving metals e.g. zinc and acetic or hydrochloric acid, zinc and sodium hydroxide, zinc–copper couple and ethanol, etc. In this reaction, earlier ‘nascent’ hydrogen was considered to be the reducing agent. Now it is believed that there is an electron–transfer from the metal to the substrate leading to the formation of carbanion, which is followed by the abstraction of a proton from the solvent. Thus, reduction with a zinc–ethanol couple may be formulated as



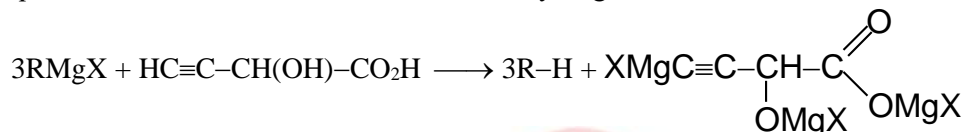
- (ii) **Reduction by reducing agents like  $LiAlH_4$ ,  $NaBH_4$  etc.:** Primary and secondary alkyl halides are readily reduced to alkanes by lithium aluminium hydride ( $LiAlH_4$ ) while reduction of tertiary halides with  $LiAlH_4$  gives mainly alkenes. On the other hand, sodium borohydride ( $NaBH_4$ ) reduces secondary and tertiary halides, but not primary, whereas triphenyltin hydride ( $Ph_3SnH$ ) reduces all three types of alkyl halide. So each reducing agent is specific in its action.



- (iii) **Using organometallic compounds like Grignard Reagent:** Alkyl halides react with either  $Mg$  or  $Li$  in dry ether to give organometallic compounds having a basic carbanionic site.



The net effect is replacement of MgX by H. This reaction can be afforded with any compound that is more acidic than alkane e.g., alcohols, NH<sub>3</sub>, terminal alkynes etc. Thus the net effect of the reaction is the displacement of a weak acid from its salt by a strong acid. Using this reaction, we determine the number of active hydrogens present in a given compound (the one which reacts with Grignard reagent). This quantitative estimation of number of active hydrogens is called Zerewitinoff's method. For example,



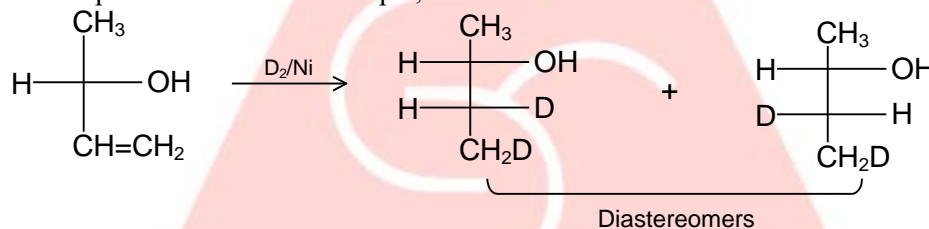
Three moles of alkane formed shows that the compound contains three active (acidic) hydrogens.

### 1.1.2. Hydrogenation of alkenes in the presence of Pd, Pt or Ni:

This addition is an example of heterogeneous catalysis involving syn-addition.



The stereospecificity of the reaction is that the addition of hydrogen to the double bond occurs in syn fashion without disturbing the configuration at the chiral carbon. The mechanism of this reaction will be dealt in the topic "alkenes". For example,

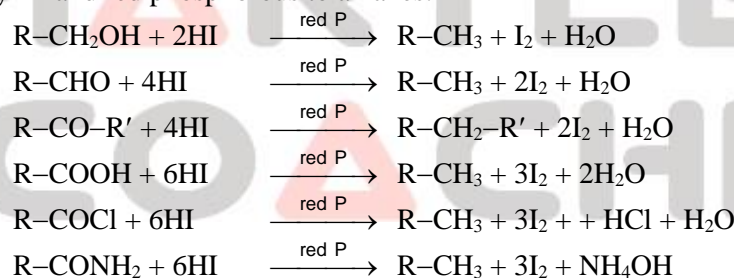


The addition of both the deuterium atoms occurs from the same side. In some molecules, the attack is from the bottom side and in other molecules, D<sub>2</sub> attacks from the top side leading to the formation of 2 isomers called diastereomers.

Raney Nickel is more reactive than the Nickel catalyst. It consists of an alloy containing equal amounts of Ni and Al digested with NaOH, residual part containing mainly nickel is washed, dried and stored under ethanol.

### 1.1.3. Reduction of alcohols, carbonyl compounds, acids and acid derivatives:

Alcohols, aldehydes, Ketones, carboxylic acids and their derivatives like acid halides and acid amides can be reduced by HI and red phosphorous to alkanes.



Carbonyl compounds can also be reduced to alkanes by (i) Zn-Hg amalgam and HCl (Clemmensen Reduction) and (ii) H<sub>2</sub>N-NH<sub>2</sub> and KOH (Wolff Kishner Reduction)



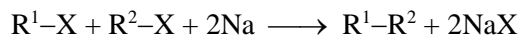
(The mechanism of these reactions will be taken up in the chapter of aldehydes and ketones).

## 1.2 METHODS INVOLVING CHANGE IN THE CARBON SKELETON

### 1.2.1 Methods in which number of carbon atoms increases w.r.t. starting compound:

#### (a) Wurtz Reaction:

An ethereal solution of an alkyl halide (preferably the bromide or iodide) is treated with sodium, when alkane is obtained. For example,

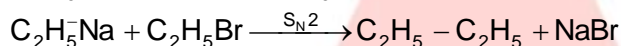
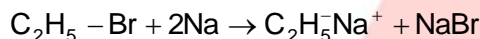


In this reaction, two R groups are coupled by reacting RBr, RCl or RI with Na or K. The yields of the product are best for 1° alkyl halides (60%) and least for 3° alkyl halides (10%).

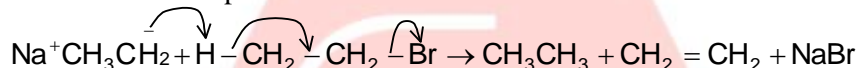
Looking further in the above reaction, it was found that in addition to the desired alkane  $R^1-R^2$ , there will also be present the alkanes  $R^1-R^1$  and  $R^2-R^2$ . Unsaturated hydrocarbons are also obtained. Obviously, then, the best yield of an alkane will be obtained when  $R^1$  &  $R^2$  are same, i.e., when the alkane contains an even number of carbon atoms and is symmetrical. It has been found that the Wurtz reaction gives good yields only for 'even carbon' alkanes of high molecular weight, and that the reaction generally fails with tertiary alkyl halides.

[Note: Metals other than sodium, which can be employed in Wurtz reaction are Ag and Cu in finally divided state]

The reaction probably involves the formation of carbanions as intermediate.



The support for such a mechanism involving carbanions is provided by the observation that optically active halides demonstrate inversion of configuration at the carbon atom undergoing nucleophilic attack. The carbanion can also act as a base and promote elimination.

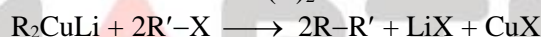
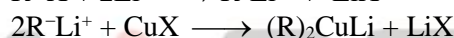
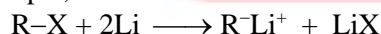


This is often observed as a side reaction to the normal Wurtz reaction proceeding by  $S_N2$  mechanism.

### (b) Corey-House Synthesis:

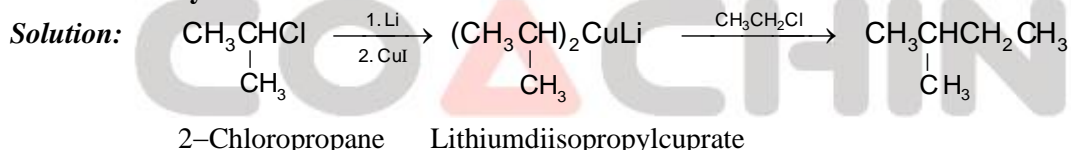
A superior method for coupling is the Corey-House Synthesis which could be employed for obtaining alkanes containing odd number of carbon atoms (unsymmetrical alkanes). An alkyl halide ( $R-X$ ) is first converted into alkyl lithium by treating with lithium. The alkyl lithium is then reacted with cuprous halide to get lithium dialkyl cuprate. The complex is then treated with another alkyl halides ( $R'-X$ ), which must be preferably primary. The reaction follows  $S_N2$  mechanism. With secondary alkyl halides the reaction leads, to partly substitution forming alkane and partly elimination forming alkene, with tertiary alkyl halide only elimination takes place.

For example,



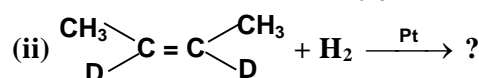
#### Illustration 1

**Question:** Prepare 2-methylbutane from chloroethane and 2-chloropropane using Corey-House synthesis.

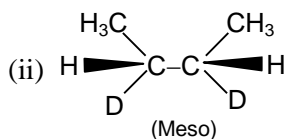


#### Illustration 2

**Question:** Predict the products in the following reactions:

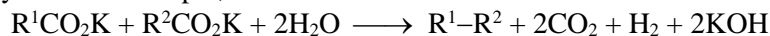


**Solution:** (i) Propane



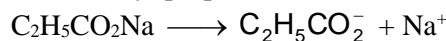
(c) Kolbe's electrolytic method:

A concentrated solution of the sodium or potassium salt of a carboxylic acid or a mixture of carboxylic acids is electrolysed. For example,

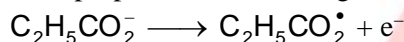


If  $R^1$  and  $R^2$  are different, then hydrocarbons  $R^1-R^1$  and  $R^2-R^2$  are also obtained along with  $R^1-R^2$ .

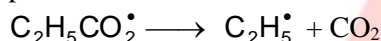
Earlier several mechanisms have been proposed for the Kolbe's reaction. The free-radical theory is the one now favoured, having strong evidences in support of it. For example, when sodium propionate is electrolysed, n-butane, ethylene and ethyl propionate are obtained.



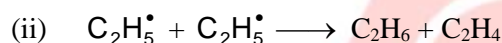
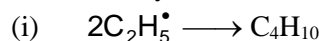
At anode, the propionate ion discharges to form a free radical.



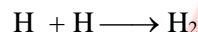
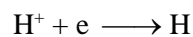
This propionate free radical then breaks up into the ethyl free radical and carbon dioxide.



Then, ethyl radicals undergo chain termination by recombination forming butane. They may also undergo disproportionation reaction forming ethane and ethene as by products. Another possible by product is ethyl propionate formed by recombination of ethyl radical and propionate radical.

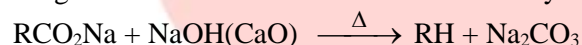


Thus at anode, gases evolved are  $CO_2$ , ethane, ethene and butane. At cathode,  $H^+$  accepts an electron and is converted to H-atom. Two of the H-atoms combine to form  $H_2$  gas.



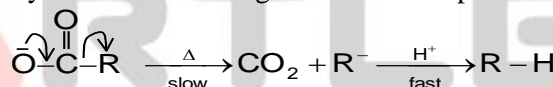
## 1.2.2 Methods in which number of carbon atoms decreases w.r.t. starting compound: Decarboxylation of carboxylate salts:

By heating a mixture of the sodium salt of a carboxylic acid and soda-lime, alkanes can be obtained.



This process of eliminating  $CO_2$  from a carboxylic acid is known as decarboxylation.

This reaction can be employed for decreasing the length of carbon chain i.e. to descend a homologous series. This decarboxylation reaction probably involves following mechanistic steps.



## 2 GENERAL PHYSICAL PROPERTIES OF ALKANES

- (I) The first four alkanes (methane to butane) are colourless gases, the next thirteen (pentane to heptadecane) are colourless liquids and those containing 18 carbon atoms or more are solids at ordinary temperatures.
- (II) Their boiling points show gradual rise as the carbon content increases. In general,

the boiling point difference between two successive members of the homologous series (except for the first few members) is about  $20-30^\circ\text{C}$ . Among the isomeric alkanes, the straight chain (i.e. normal) isomer has a higher boiling point than the branched chain isomer. The greater the branching of the chain, the lower the boiling point. For example,

Alkane	$CH_3CH_2CH_2CH_3$	$CH_3(CH_2)_3CH_3$	$CH_3(CH_2)_4CH_3$
	(n-Butane)	(n-Pentane)	(n-Hexane)
(b.p. in $^\circ\text{C}$ )	0	36	69
Alkane	$(CH_3)_2CHCH_3$	$(CH_3)_2CHCH_2CH_3$	$(CH_3)_4C$
	(Isobutane)	(Isopentane)	(Neopentane)
(b.p. in $^\circ\text{C}$ )	-11.5	28	9.5

In fact, the lowering of boiling point with the branching of the carbon chain is a feature characteristic of all the families of organic compounds.

The vander Waal's forces which hold non-polar molecules are weak and have a very short range.



Therefore, within a family of compounds the strength of intermolecular forces would be directly proportional to the size (or the surface area) of the molecule. In other words, larger the molecule, the stronger would be the intermolecular forces. The process of boiling requires overcoming these intermolecular forces of a liquid and a solid. As the molecules become larger, the intermolecular forces increase and the boiling points should rise with increase in the number of carbon atoms. As the branching increases in a molecule, its shape approaches that of a sphere and there is a reduction in surface area. This renders the intermolecular forces weaker and they are overcome at relatively lower temperature. Therefore, a branched-chain isomer should boil at a temperature lower than that of a straight-chain isomer.

(III) Their melting points also show a rise with the increasing number of carbon atoms, but the rise is not as regular as in the case of boiling points. For example,

n-Alkane	C <sub>4</sub> H <sub>10</sub>	C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>14</sub>	C <sub>7</sub> H <sub>16</sub>	C <sub>8</sub> H <sub>18</sub>
m.p. °C	-135	-130	-95	-90	-57

It is, however, significant that as we move from an alkane having an odd number of carbon atoms to the next higher alkane, the rise in melting point is much higher than that when we move up from an alkane with an even number of carbon atoms.

The intermolecular forces in a crystal depend not only on the size of the molecules but also on how they are packed into a crystal. During melting, these intermolecular forces have to be overcome. Since breaking of crystal structure is a more complicated process, it is understandable that the rise in melting point with increasing molecular weight is not as regular as in the case of boiling points. The structure/geometry of the alkane is of considerable importance.

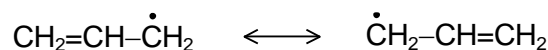
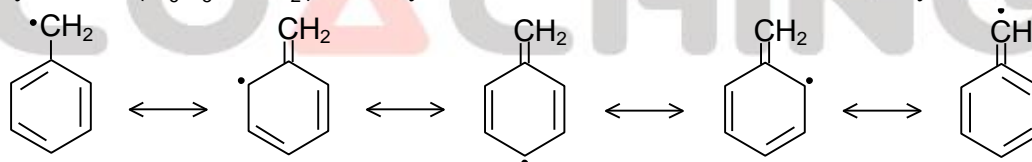
- (IV) Alkanes are made up of carbon and hydrogen atoms only. Since these two elements have almost similar electronegativities, alkanes are non-polar. Therefore, non-polar alkanes are soluble in non-polar solvents like carbon tetrachloride, benzene, etc. but insoluble in polar solvents like water, alcohol, etc.
- (V) The densities of alkanes show a definite rise with increasing molecular weight, but they reach a limiting constant value of about 0.8 g/ml with n-hexadecane (C<sub>16</sub>H<sub>34</sub>). Thus, alkanes are always lighter than water.

### 3 GENERAL CHEMICAL PROPERTIES OF ALKANES

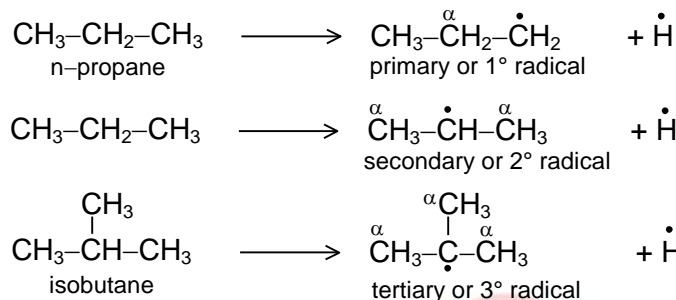
The alkanes are generally stable towards common reagents at room temperature.

The minimum energy required to cause homolytic cleavage of almost non-polar C-H and C-C bonds is not available at room temperature. However, alkanes undergo substitution reactions at high temperature. As the temperature is increased, the C-H and C-C bonds break forming free radicals as intermediates. The reactivity of alkanes is decided on the basis of stability of the free radicals. As the stability of free radical increases, energy required to produce them i.e., energy of activation decreases and hence the rate of reaction increases.

Benzyl radical (C<sub>6</sub>H<sub>5</sub> -  $\dot{\text{C}}\text{H}_2$ ) and allyl radical (CH<sub>2</sub>=CH- $\dot{\text{C}}\text{H}_2$ ) are stabilised by resonance.



Benzyl radical has five resonating structures, while allyl radical has two resonating structures. Therefore, benzyl radical is slightly more stable than allyl radical and hence toluene is more reactive than propene towards substitution reactions. Alkyl radicals, on the other hand, are stabilised by hyperconjugation. Their stability may be compared by the number of hyperconjugation structures. In the reaction given below a primary radical is stabilised by two  $\alpha$ -hydrogen atoms, a secondary radical is stabilised by six  $\alpha$ -hydrogen atoms and a tertiary radical is stabilised by nine  $\alpha$ -hydrogen atoms.



Since resonance supercedes hyperconjugation, the stability order of various free radicals is as given below:



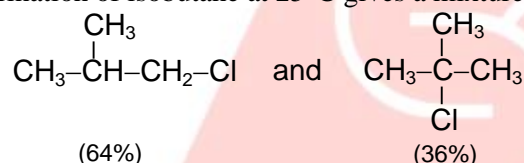
### 3.1 HALOGENATION

Chlorination may be brought about by photo irradiation, heat or catalysts and the extent of chlorination depends largely on the amount of chlorine used. A mixture of all possible isomeric monochlorides is obtained, but the isomers are formed in unequal amounts, due to difference in reactivity of primary, secondary; and tertiary hydrogen atoms.

The order of ease of substitution is

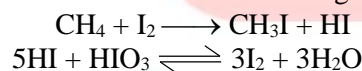
Tertiary Hydrogen > Secondary Hydrogen > Primary Hydrogen

Chlorination of isobutane at 25°C gives a mixture of two isomeric monochlorides.

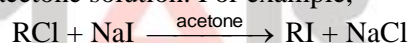


The tertiary hydrogen is replaced about 5 times as fast as primary hydrogen.

Bromination is similar to chlorination, but not so vigorous. Iodination is reversible, but it may be carried out in the presence of an oxidising agent such as HIO<sub>3</sub>, HNO<sub>3</sub> etc., which destroys the hydrogen iodide as it is formed and so drives the reaction to the right.

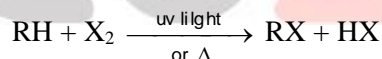


Iodides are more conveniently prepared by treating the chloro or bromo derivative with sodium iodide in methanol or acetone solution. For example,



This reaction is possible because sodium iodide is soluble in methanol or acetone, whereas sodium chloride and sodium bromide are not. This reaction of halide exchange is known as **Conant-Finkelstein reaction**. It will be dealt in detail in chapter of Alkyl Halides.

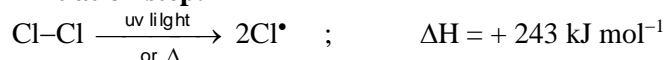
Direct fluorination is usually explosive. So special conditions are necessary for the preparation of the fluorine derivatives of the alkanes.



Reactivity of X<sub>2</sub>: F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > I<sub>2</sub>

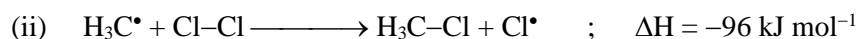
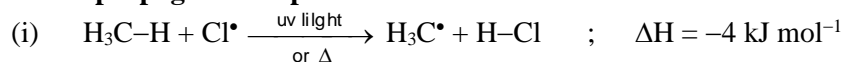
The mechanism of chlorination of methane is as follows.

#### Chain initiation step:



The required enthalpy comes from ultraviolet (uv) light or heat supplied.

#### Chain propagation step:



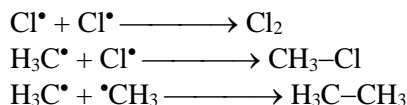
The sum of the two chain propagation steps in the overall reaction is



In propagation steps, the same free radical intermediates, here  $\text{Cl}^\bullet$  and  $\text{H}_3\text{C}^\bullet$ , being formed and consumed.

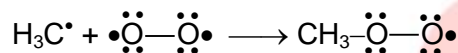
**Chain termination step:**

Chains terminate on those rare occasions when any two free-radical intermediates collide to form a covalent bond.

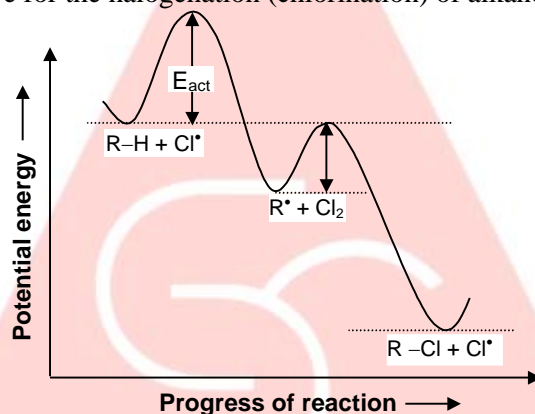


Radical inhibitors stop chain propagation by reacting with free radical intermediates.

For example,



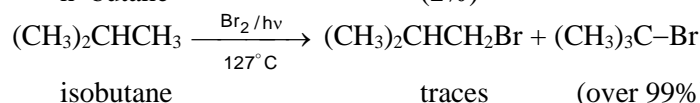
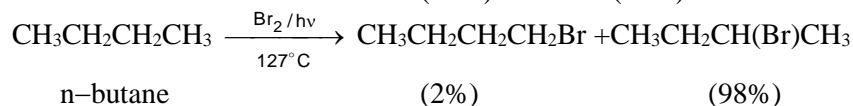
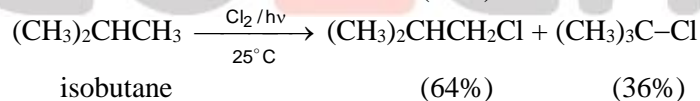
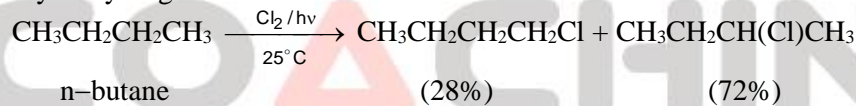
The potential energy curve for the halogenation (chlorination) of alkane is shown as



In more complex alkanes, the abstraction of each different kind of hydrogen atom gives a different isomeric product. Three factors determine the relative yields of isomeric product.

- 1. Probability Factor:** This factor is based on the number of each kind of hydrogen atoms in the alkane molecule. For example, in  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  there are six equivalent  $1^\circ$  H and four equivalent  $2^\circ$  H. The probability of abstracting a  $1^\circ$  H to  $2^\circ$  H is 6 to 4, or 3 to 2.
- 2. Reactivity of  $\text{H}^\bullet$ :** The order of reactivity of hydrogen atoms is  $3^\circ > 2^\circ > 1^\circ$ .
- 3. Reactivity of  $\text{X}^\bullet$ :** The more reactive  $\text{Cl}^\bullet$  is less selective and more influenced by the probability factor.

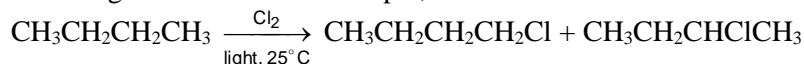
The less reactive  $\text{Br}^\bullet$  is more selective and less influenced by the probability factor, as summarized by the **Reactivity-Selectivity Principle**. If the attacking species is more reactive, it will be less selective and the yields will be determined by the probability factor as well as reactivity of hydrogen atoms while if the species attacking is less reactive and more selective, the yield of the product is governed exclusively by reactivity of hydrogen atoms.



In the chlorination of isobutane abstraction of one of the nine primary hydrogens leads to the formation of isobutyl chlorides, whereas abstraction of a single tertiary hydrogen leads to the formation of tert-butyl chloride. The probability favours formation of isobutyl chloride by the ratio of 9 : 1. But the experimental results show the ratio roughly to be 2 : 1 or 9 : 4.5. Evidently, about 4.5 times as many collisions with the tertiary hydrogen are successful as collisions with the primary hydrogens.

The  $E_{act}$  is less for abstraction of a tertiary hydrogen than for the abstraction of a primary hydrogen.

The rate of abstraction of hydrogen atoms is always found to follow the sequence  $3^\circ > 2^\circ > 1^\circ$ . At room temperature ( $25^\circ\text{C}$ ), the relative rates in chlorination are 5.0 : 3.8 : 1.0 respectively for  $3^\circ$ ,  $2^\circ$  and  $1^\circ$  hydrogen atoms. Using these values, we can predict quite well the ratio of isomeric chlorination products from a given alkane. For example,



$$\frac{\text{n-butyl chloride}}{\text{sec-butyl chloride}} = \frac{\text{number of } 1^\circ \text{ H}}{\text{number of } 2^\circ \text{ H}} \times \frac{\text{reactivity of } 1^\circ \text{ H}}{\text{reactivity of } 2^\circ \text{ H}} = \frac{6}{4} \times \frac{1.0}{3.8} = \frac{3}{7.6} \text{ equivalent to } \frac{28\%}{72\%}$$

In spite of these difference in reactivity, chlorination rarely yields a great excess of any single isomer. In most cases, both the products are formed in considerable amounts.

The same sequence of reactivity,  $3^\circ > 2^\circ > 1^\circ$ , is found in bromination, but with enormously larger reactivity ratios. At  $127^\circ\text{C}$  the relative rates per hydrogen atom in bromination are 1600 : 82 : 1 respectively for  $3^\circ$ ,  $2^\circ$  and  $1^\circ$  hydrogen atoms. Here, differences in reactivity are so marked that it outweighs probability factor. Hence bromination almost exclusively gives selective product.

In bromination of isobutane at  $127^\circ\text{C}$ ,

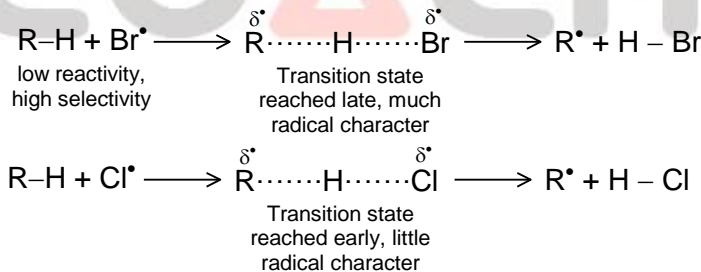
$$\frac{\text{isobutyl bromide}}{\text{tert-butyl bromide}} = \frac{\text{number of } 1^\circ \text{ H}}{\text{number of } 3^\circ \text{ H}} \times \frac{\text{reactivity of } 1^\circ \text{ H}}{\text{reactivity of } 3^\circ \text{ H}} = \frac{9}{1} \times \frac{1}{1600} = \frac{9}{1600} \text{ equivalent to } \frac{0.5\%}{99.5\%}$$

Hence, tert-butyl bromide happens to be the exclusive product (over 99%) with traces of isobutyl bromide.

The reason for the higher selectivity in bromination as compared to chlorination is due to the following explanation.

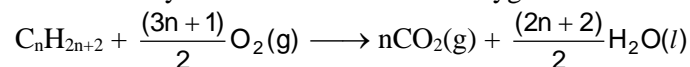
According to the general principle, for comparable reactions, the more endothermic (or less exothermic) reaction has a transition state (TS), which more closely resembles the intermediate and may more closely resemble the ground state (reactants). Since attack by  $\text{Br}^\bullet$  on an alkane is more endothermic than attack by  $\text{Cl}^\bullet$ , its TS shows more C-H bond breaking and more H-Br bond formation. Any stabilization in the intermediate radical also occurs in the corresponding TS. Therefore, a TS leading to a  $3^\circ \text{R}^\bullet$ , has a lower enthalpy than one leading to a  $2^\circ \text{R}^\bullet$ , which in turn has a lower enthalpy than one leading to a  $1^\circ \text{R}^\bullet$ , the relative rates of H-abstraction by  $\text{Br}^\bullet$  are  $3^\circ > 2^\circ > 1^\circ$ . The TS for H-abstraction by  $\text{Cl}^\bullet$  has less C-H bond breaking and less H-Cl bond formation. The nature of the incipient radical has less effect on the enthalpy of the TS and on the rate of its formation. Hence there is less difference in the rate of formation of the three kinds of  $\text{R}^\bullet$ 's. In the attack by the comparatively unreactive bromine atom, the transition state is reached late in the reaction process, after the alkyl group has developed considerable radical character.

In the attack by the highly reactive chlorine atom, the transition state is reached early, when the alkyl group has gained very little radical character. Thus bromination is more selective than chlorination.



### 3.2 OXIDATION

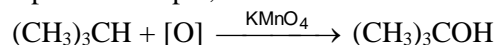
All alkanes readily burn in excess of air or oxygen to form carbon dioxide and water.



On the other hand, controlled oxidation under various conditions, leads to different products. Extensive

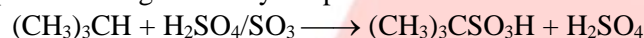


oxidation gives a mixture of acids consisting of the complete range of  $C_1$  to  $C_n$  carbon atoms. Less extensive oxidation gives a mixture of products in which no chain fission has occurred. Under moderate conditions mixed ketones are the major products and oxidation in the presence of boric acid produces a mixture of secondary alcohols. The oxidation of alkanes in the vapour state occurs via free radicals, e.g. alkyl ( $R^\bullet$ ), alkylperoxy ( $ROO^\bullet$ ) and alkoxy ( $RO^\bullet$ ). Oxidising reagents such as potassium permanganate readily oxidise a tertiary hydrogen atom to a hydroxyl group. For example, isobutane is oxidised to t-butanol.



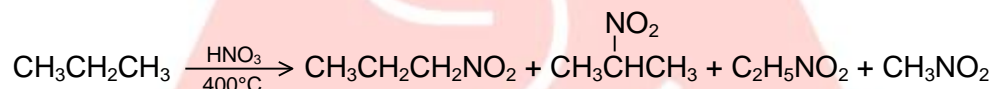
### 3.3 SULPHONATION

It is the process of replacing hydrogen atom by a sulphonic acid group,  $SO_3H$ . Sulphonation of a normal alkane from hexane onwards may be carried out by treating the alkane with oleum (fuming sulphuric acid). The order of ease of replacement of H-atoms in tertiary compounds is very much easier than secondary and in secondary compounds replacement of H-atoms by sulphonic acid group is easier than primary. Replacement of a primary hydrogen atom in sulphonation is very slow indeed. Isobutane, which contains a tertiary hydrogen atom, is readily sulphonated to give t-butyl sulphonic acid.



### 3.4 NITRATION

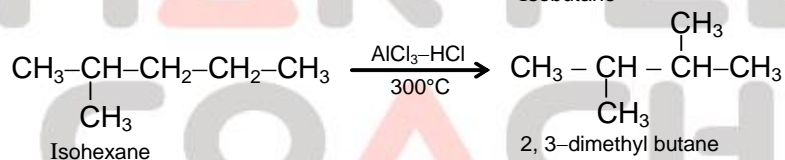
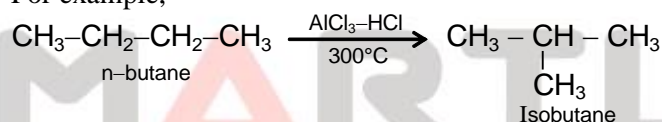
Under certain conditions alkanes react with nitric acid, when a hydrogen atom will be replaced by a nitro-group,  $NO_2$ . This process is known as nitration. Nitration of the alkanes may be carried out in the vapour phase between  $150^\circ$  and  $475^\circ C$ , when a complex mixture of mononitroalkanes is obtained. The mixture consists of all the possible mononitroderivatives and the nitro-compounds formed by every possibility of chain fission of the alkane. For example, propane gives a mixture of 1-nitropropane, 2-nitropropane, nitroethane and nitromethane.



### 3.5 ISOMERISATION

It is a process by which n-alkane is converted into a branched alkane containing a methyl group in the side chain by heating the n-alkane with  $AlCl_3-HCl$  at  $300^\circ C$ .

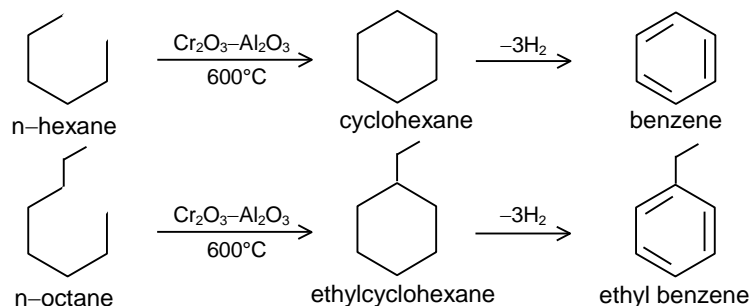
For example,



The isomerisation is believed to be an ionic chain reaction initiated by a carbonium ion followed by 1, 2 shift of hydride or methyl group.

### 3.6 AROMATISATION

Aromatisation of n-alkanes containing six or more carbon atoms into benzene and its homologues takes place at high temperature ( $600^\circ C$ ) in presence  $Cr_2O_3-Al_2O_3$  as a catalyst.

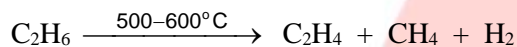


### 3.7 PYROLYSIS OR CRACKING

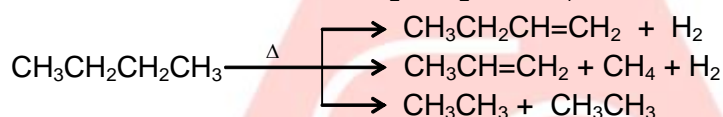
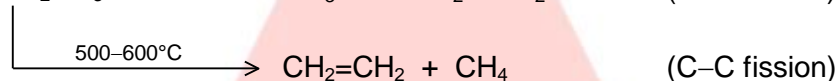
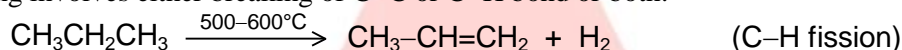
The thermal decomposition of organic compounds is known as pyrolysis and the process of cleavage of complex hydrocarbons into simpler molecules by the application of heat is known as cracking, i.e. the thermal decomposition is called cracking, but when induced by catalyst it is called *catalytic cracking*. Methane is the most stable hydrocarbon because of a higher C–H bond energy through red hot (500–600°C) tube in absence of air we get a mixture of lower compounds.

The products depend on the following factors:

(a) structure of alkane, (b) extent of temperature and pressure, (c) absence or presence of catalysts like SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, etc.



Cracking involves either breaking of C–C or C–H bond or both.



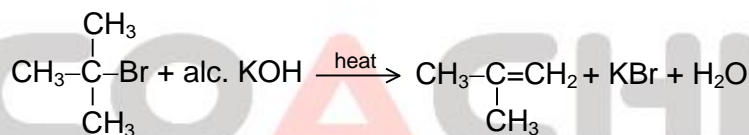
## ALKANES

Alkenes are unsaturated hydrocarbons having one double bond. They are represented by the general formula C<sub>n</sub>H<sub>2n</sub>. They are also known as olefins since ethene, the first member of the homologous series forms oily liquid when treated with chlorine.

### 1 METHODS PREPARATION OF ALKENES

#### 1.1 DEHYDROHALOGENATION OF ALKYL HALIDES

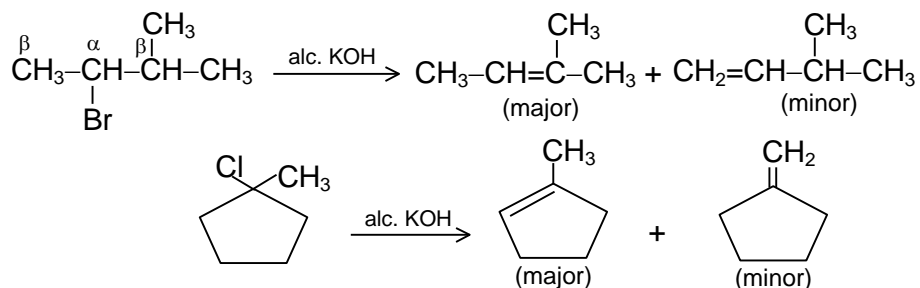
Alkyl halides when treated with a strong base like hot alcoholic solution of KOH undergo elimination of hydrogen halide leading to the formation of alkene. The yield of alkene depends on the nature of alkyl halide used. It is fair with primary and very good with secondary and tertiary alkyl halides. For example tertiary butyl bromide when heated with alcoholic KOH results in the formation of isobutene with the elimination of hydrogen halide.



In this type of elimination reaction the two leaving groups are lost from the adjacent carbon atoms. One of the leaving groups is the halogen atom and the C–atom from which halogen is lost is usually designated as 1 or (α)–carbon atom. Hydrogen, the other leaving group is lost from the neighbouring carbon which is designated as 2 or (β) carbon atom and the reactions are referred to

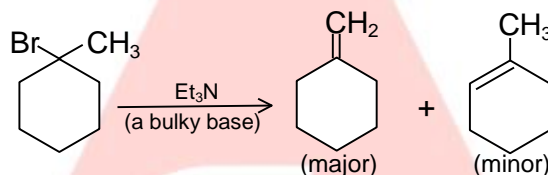
1, 2–elimination or β–elimination (α– is commonly omitted). If the alkyl halide contains only one β–carbon atom, only one alkene is formed as in the above–sited example. However, if the alkyl halide has two or more β–carbon atoms, two or more alkenes are possible. According to

*Saytzeff rule*, dehydrohalogenation of alkyl halides leads to the formation of that alkene as the major product which has maximum number of alkyl groups attached to  $\text{C}=\text{C}$ . It is the stability of the alkene that decides the major product. For example,

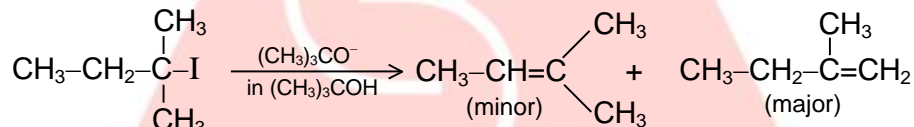
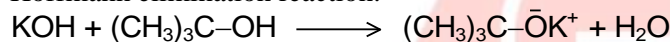


However, if the size of base is increased, it finds it relatively easier to abstract proton from a less substituted  $\beta$ -carbon atom than from more substituted  $\beta$ -carbon atom of alkyl halide. Therefore, less stable alkene becomes the major product. This is known as **Hoffmann's rule**.

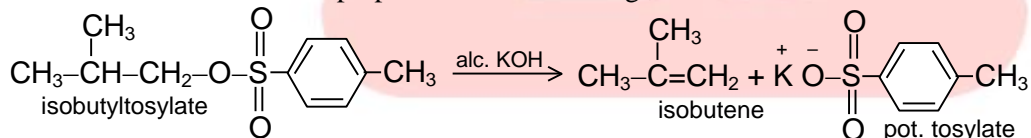
For example,



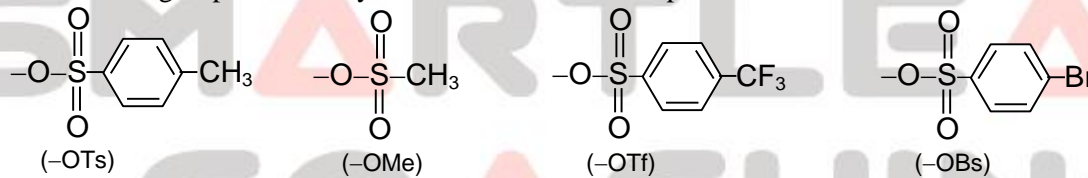
KOH dissolved in tertiary butanol gives potassium tertiary butoxide, which is another bulky base used in Hoffmann elimination reaction.



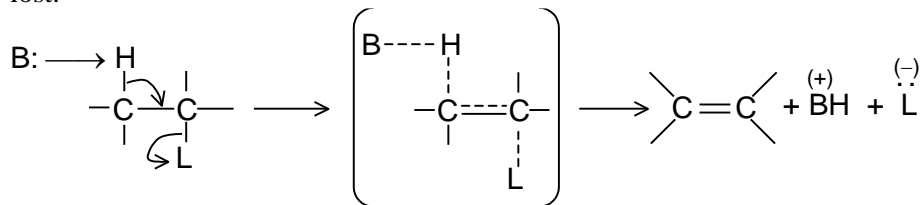
In place of haloalkanes, sulphonyl derivatives of alkanes can also be used in the base catalysed elimination reaction for the preparation of alkenes e.g.,



The groups commonly used in this class of compounds include:

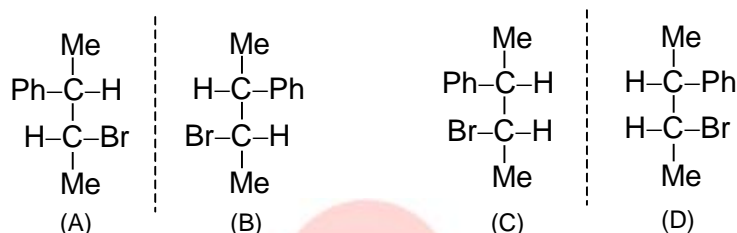


The mechanism of 1, 2 elimination involves simultaneous removal of a proton from the  $\beta$ -carbon atoms by the base and the other leaving group (L) (halogen or sulphonyl group as the case may be) from the  $\alpha$ -carbon atom. The two leaving groups must align themselves at  $180^\circ\text{C}$  to each other and in the same plane before they are lost.

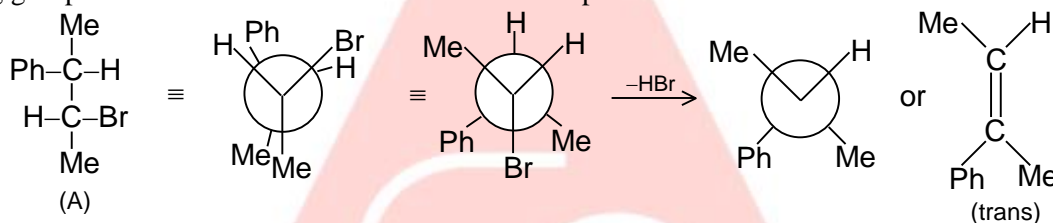


It is a single step bimolecular elimination reaction which passes through a transition state. The rate determining step involves cleavage of the C-H and C-L bonds. The energy required to break these bonds comes from the energy released due to the formation of B:-H bond and  $\pi$ -bond. The cleavage of C-L bond in the rate determining step implies that the reactivity of alkyl halides should follow the order:  $\text{R-I} > \text{R-Br} > \text{R-Cl}$  to match, the bond dissociation energy of carbon-halogen bond. This has indeed been found to be so. The above mechanism helps us to predict the stereochemistry of the alkene wherever possible.

For example 2-bromo-3-phenyl butane contains two dissimilar chiral carbon atoms and hence exists in four optically active isomers (2 pair of enantiomers) as shown below.



What type of alkene is obtained on dehydrohalogenation of compound (A)? In order to answer this question we shall rewrite the structure of compound (A) according to Newmann projection and ensure that the two leaving groups are at  $180^\circ$  to each other and in the same plane.

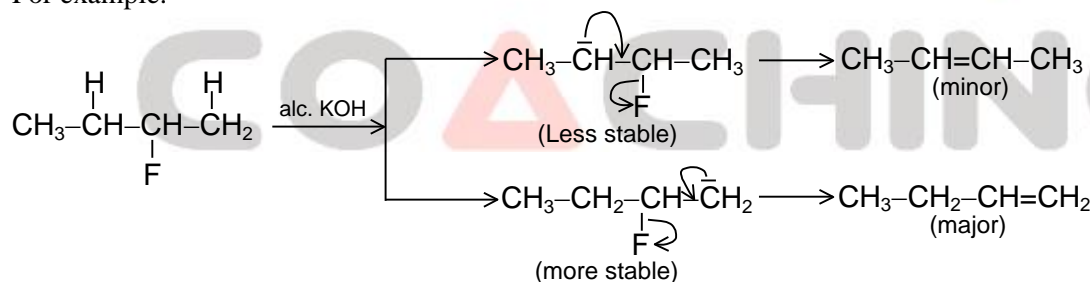


You will be curious to know the stereochemistry of alkenes obtained from (B), (C) and (D). Try it out in the same manner to get the answer. (The enantiomers give the same alkene while diastereomers give different alkenes)

Dehydrohalogenation of alkyl halides with alcoholic KOH invariably leads to the formation of both the Saytzeff product (more stable alkene) as well as Hoffmann product (less stable alkene) with Saytzeff product as the major product for alkyl iodides, alkyl bromides and alkyl chlorides. However with alkyl fluorides, Hoffmann product is the major product. Infact as we move from iodide  $\rightarrow$  bromide  $\rightarrow$  chloride  $\rightarrow$  fluoride, the percentage of Saytzeff product gradually decreases and that of Hoffmann product gradually increases. The change over takes place with fluoride. How do we explain this?

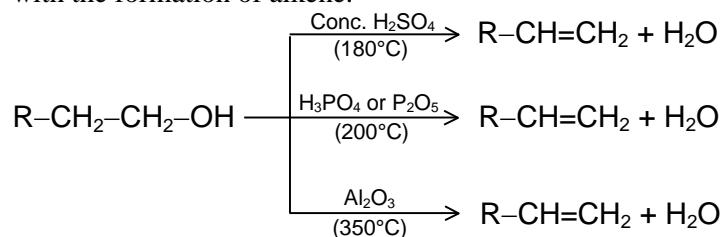
The decrease in the percentage of Saytzeff product is directly linked with carbon-halogen bond dissociation energy. With the increase in carbon-halogen bond dissociation energy it becomes more and more difficult for the leaving group (L) to leave as  $L^-$ . As a result the reaction has a tendency to follow another mechanism called *Elimination from conjugate base*. In this mechanism the base first removes proton from the  $\beta$ -carbon atom forming a carbanion as the intermediate. The carbanion then attacks the  $\alpha$ -carbon atom causing the removal of F.

For example.



## 1.2 DEHYDRATION OF ALCOHOLS

Alcohols when heated in presence of  $H_2SO_4$ ,  $H_3PO_4$ ,  $P_2O_5$ ,  $Al_2O_3$  or  $BF_3$  undergo loss of water molecule with the formation of alkene.



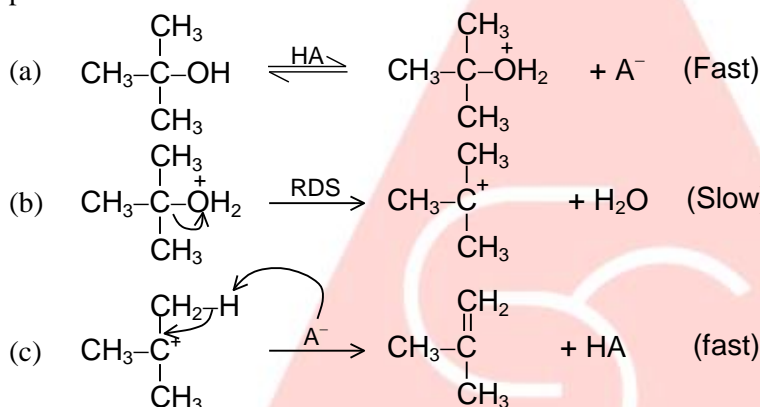


The reaction mechanism involves the following steps:

- In the first step OH group of the alcohol is protonated in a fast reversible reaction. Unlike OH group, protonated OH group is a good leaving group.
- In the second step, water molecule is lost with the formation of a carbonium ion. This is the rate determining step.

**In any reaction if a carbonium ion is formed as an intermediate and there is a possibility of rearrangement in which an atom or a group of atoms migrates from an adjacent carbon atom or a cyclic ring expands so that a more stable carbonium ion is formed, that rearrangement will take place.**

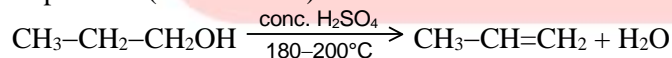
- In the final step carbonium ion loses proton from its adjacent carbon atom which results in more stable alkene. The anions of the acid or another alcohol molecule will function as a base and facilitate loss of proton.



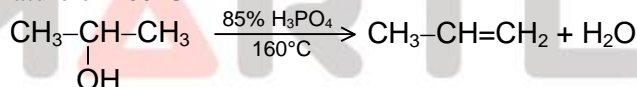
The ease of dehydration follows the order  
tertiary > secondary > primary alcohols.

This is reflected in the reaction conditions used to carry out dehydration of alcohols.

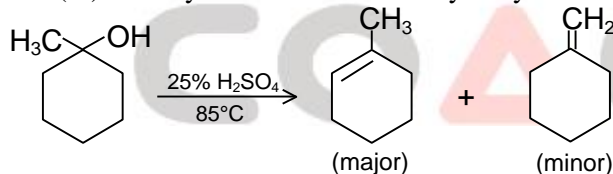
- Primary alcohols require the most stringent conditions to undergo dehydration i.e. use of conc.  $\text{H}_2\text{SO}_4$  and high temperature (180 – 200°C).



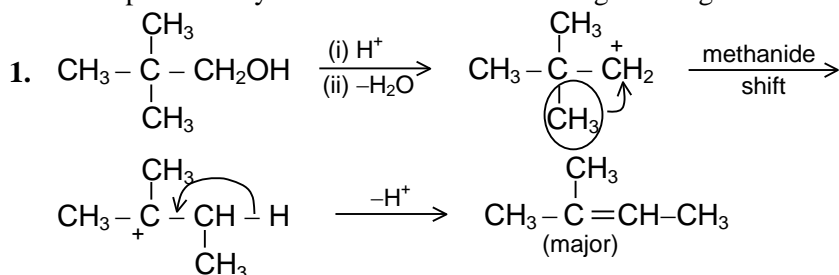
- Secondary alcohols can be dehydrated under relatively milder conditions by the use of 85%  $\text{H}_3\text{PO}_4$  and a temperature of 160°C

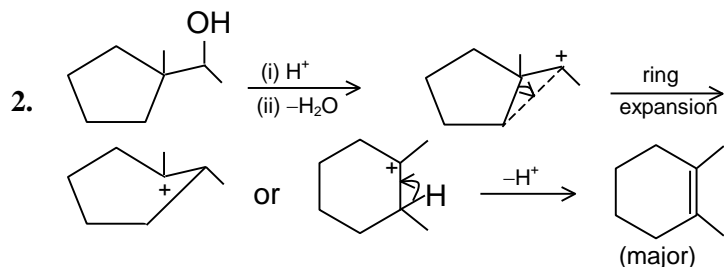


- Tertiary alcohols can be easily dehydrated by using 25%  $\text{H}_2\text{SO}_4$  at 85°C.



Examples of dehydration of alcohols involving rearrangement.

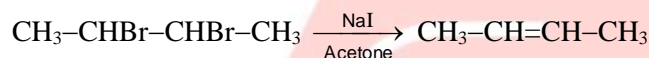
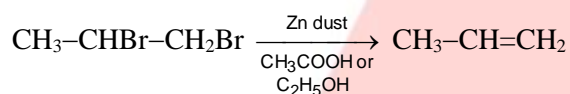




### 1.3 DEHALOGENATION OF VICINAL DIHALIDES

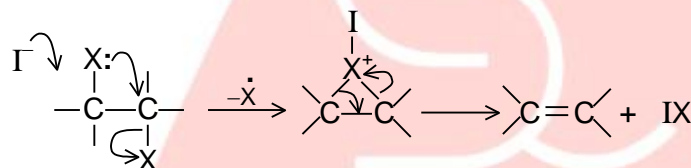
There are two types of dihalides namely gem (or geminal) dihalides in which the two halogen atoms are attached to the same carbon atom and vic. (or vicinal) dihalides in which the two halogen atoms are attached to the adjacent carbon atoms.

Dehalogenation of vic dihalides can be effected by either NaI in acetone or zinc in presence of acetic acid or ethanol.



The reaction mechanism involves loss of the two halogen atoms in two steps. The two halogen atoms align themselves at  $180^\circ$  and in the same plane before they are lost.

#### (i) With NaI in acetone:

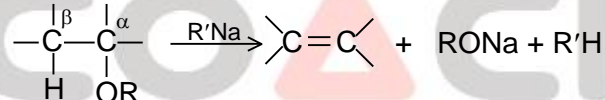


#### (ii) With Zn dust and acetic acid:

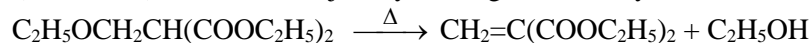


### 1.4 CLEAVAGE OF ETHERS

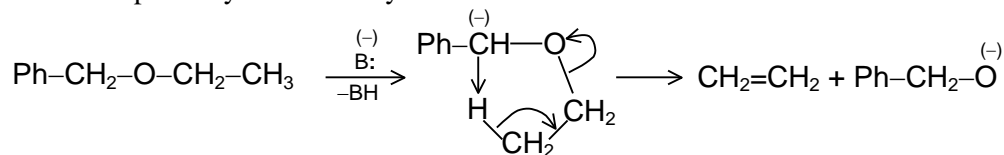
Olefins can be formed by the treatment of ethers with very strong bases such as alkylsodium, alkyllithium or sodamide.



The reaction is aided by electron withdrawing groups in the  $\beta$ -position. For example  $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}(\text{COOC}_2\text{H}_5)_2$  forms alkene just by heating without any base at all.

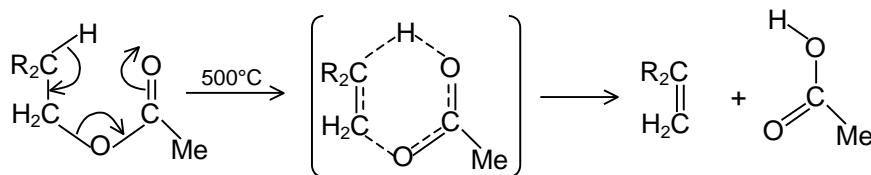


The mechanism probably involves a cyclic intermediate



### 1.5 PYROLYSIS OF ESTERS

Thermal cleavage of an ester usually acetate involves the formations of a six membered ring as the transition state leading to the elimination of acid leaving behind alkene.

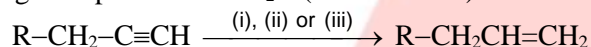


As a direct consequence of cyclic transition state, both the leaving groups namely proton and carboxylate ion are in the cis position. This is an example of cis elimination.

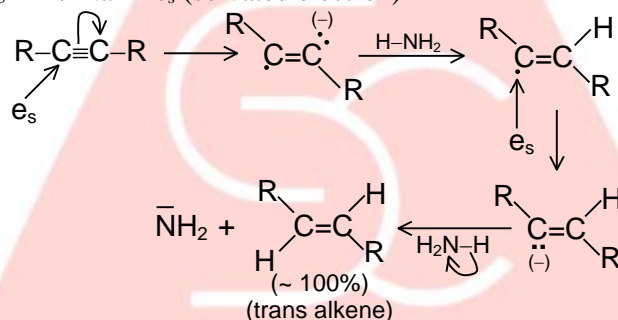
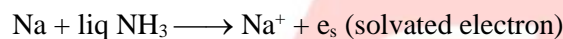
## 1.6 PARTIAL REDUCTION OF ALKYNES

Reduction of alkyne to alkene is brought about by any one of the following reducing agents.

- Alkali metal dissolved in liquid ammonia.
- Hydrogen in presence of palladium poisoned with  $\text{BaSO}_4$  or  $\text{CaCO}_3$  along with quinoline (Lindlar's catalyst).
- Hydrogen in presence of  $\text{Ni}_2\text{B}$  (nickel boride).

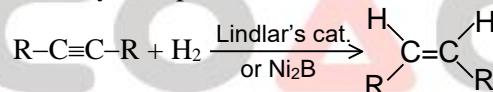


Alkali metal dissolved in liquid ammonia produces nearly 100% trans alkene by the following mechanism:



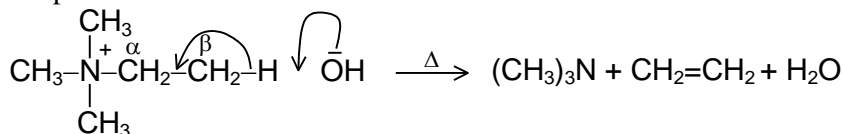
The dissolution of alkali metal in liquid  $\text{NH}_3$  produces solvated electrons. The reaction is initiated by the attack of  $\text{sp}$ -hybridised carbon atom of alkyne molecule with a solvated electron ( $e_s$ ) when the  $\pi$  electrons move to the other  $\text{sp}$  hybridised carbon atom. In order to acquire greater stability the single electron on one carbon atom and the pair of electrons on the adjacent carbon atom orient themselves as far away as possible forcing the two alkyl groups to acquire the farthest position. The carbanion then picks up a proton from  $\text{NH}_3$  to produce a vinylic radical. Attack by another solvated electron gives vinylic anion which produces trans alkene by picking up a proton from  $\text{NH}_3$ .

Hydrogenation of alkynes by Lindlar's catalyst or nickel boride produces nearly 100% cis alkene. The catalyst provides a heterogenous surface on which alkyne molecules get adsorbed. Hydrogen molecules collide with the adsorbed alkyne to produce cis alkene in which both the hydrogen atom come from the same side.

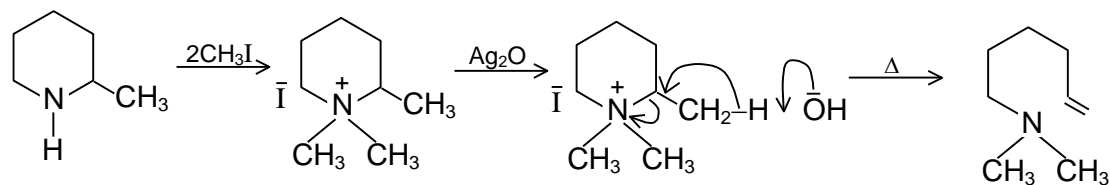


## 1.7 HOFFMANN DEGRADATION METHOD

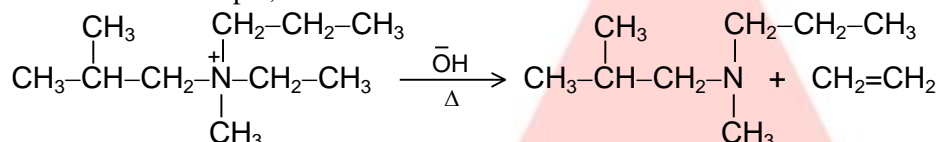
Alkenes can be prepared by heating quaternary ammonium hydroxide under reduced pressure at a temperature between  $100^\circ\text{C}$  and  $200^\circ\text{C}$ .



This is the final step of the overall three step reaction called Hoffmann degradation. In the first step, primary, secondary or tertiary amine is treated with enough  $\text{CH}_3\text{I}$  to convert it to the quaternary ammonium iodide. In the second step, the iodide is converted into hydroxide by treatment with  $\text{Ag}_2\text{O}$ .

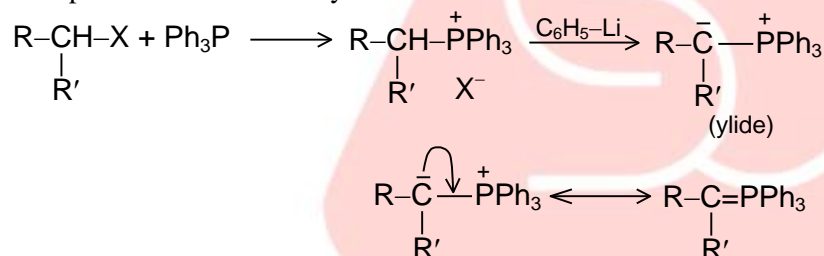


The  $\bar{\text{O}}\text{H}$  ion invariably removes proton from  $\beta$ -carbon atom. If two or more alkyl groups have  $\beta$ -carbon atoms,  $\bar{\text{O}}\text{H}$  removes proton from that  $\beta$  carbon atom which gives more stable carbanion. That means if tetra alkyl ammonium halide contains ethyl group as one of the alkyl groups then ethene will be the major product in this reaction. For example,

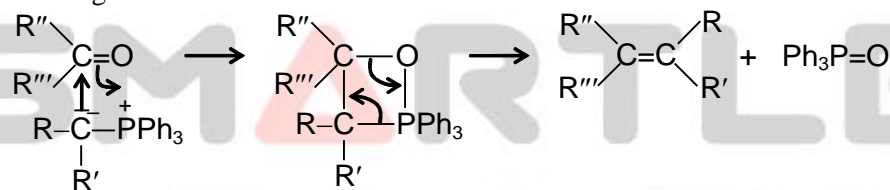


## 1.8 WITTIG REACTION

This method involves a convenient method of converting aldehydes and ketones into alkenes by using a special class of compounds called phosphorous ylides, also called Wittig reagent. Primary or secondary alkyl halide is first treated with triphenyl phosphine the phosphonium halide produced in the above reaction is converted into phosphorane by adding a strong base like  $\text{C}_6\text{H}_5\text{Li}$  or  $n\text{-C}_4\text{H}_9\text{-Li}$ . Phosphorane is stabilised by resonance.



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



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

## 2 GENERAL PHYSICAL PROPERTIES OF ALKENES

The first three alkenes are gases, the next fourteen members are liquids and the higher ones are solids. They are colourless and odourless (except ethylene which has a faint sweet smell), practically insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether, etc. They show a regular gradation in physical properties, such as boiling points, with increasing carbon content. The boiling point of two successive members of the homologous alkene series differ by about 20–30°C, except for very small homologues. The branched chain alkenes have lower boiling points than the corresponding straight chain alkenes. Like alkanes, alkenes are generally non-polar, but certain alkenes are weakly polar. For example, dipole moment of propene and 1-butene is about 0.35D due to their unsymmetrical geometry.

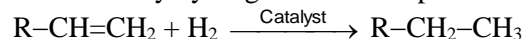
cis-Alkenes, in contrast to trans-alkenes, also have a small dipole moment. Therefore cis-alkenes, boil at somewhat higher temperature than the trans-alkene. cis-alkenes have poorer symmetry and as such do not fit into the crystalline lattice, with respect to the trans-isomers. Consequently, cis-alkenes have generally lower melting points.

## 3 GENERAL CHEMICAL PROPERTIES OF ALKENES



### 3.1 HYDROGENATION

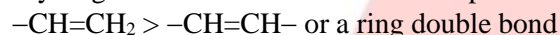
Alkenes are readily hydrogenated under pressure in presence of a catalyst.



The following catalysts have been used satisfactorily in the above reaction.

- Finely divided platinum and palladium are effective at room temperature. Platinum or palladium black i.e., metals in a very finely divided state, may be prepared by reducing their soluble salts with formaldehyde.
- Nickel requires a temperature of 200–300°C. Raney nickel is effective at room temperature and atmospheric pressure. (The method for the preparation of Raney nickel has been described elsewhere in the module).

One molecule of hydrogen is adsorbed for each double bond present in the unsaturated compound. The rate of hydrogenation of alkenes at room temperature and atmospheric pressure is

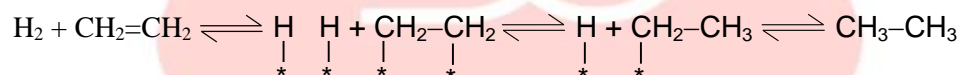


Alkenes of the type  $R_2C=CR_2$  or  $R_2C=CHR$  are difficult to hydrogenate under the above reaction conditions.

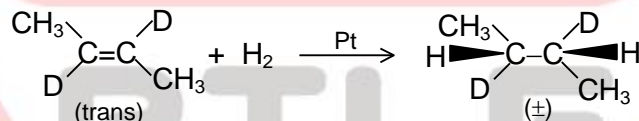
The mechanism of catalytic hydrogenation is not known with certainty. It is widely accepted that hydrogen is adsorbed on the surface of heterogeneous catalyst and is present as atomic hydrogen ( $H_2 \rightarrow 2H\bullet$ ). The alkene is also adsorbed on the catalytic surface.

It appears that the adsorption is more chemical than physical. The chemisorption has converted hydrogen molecule into hydrogen atoms and has broken the weak  $\pi$ -bond of alkene, this is how the catalyst lowers the activation energy of hydrogenation reaction.

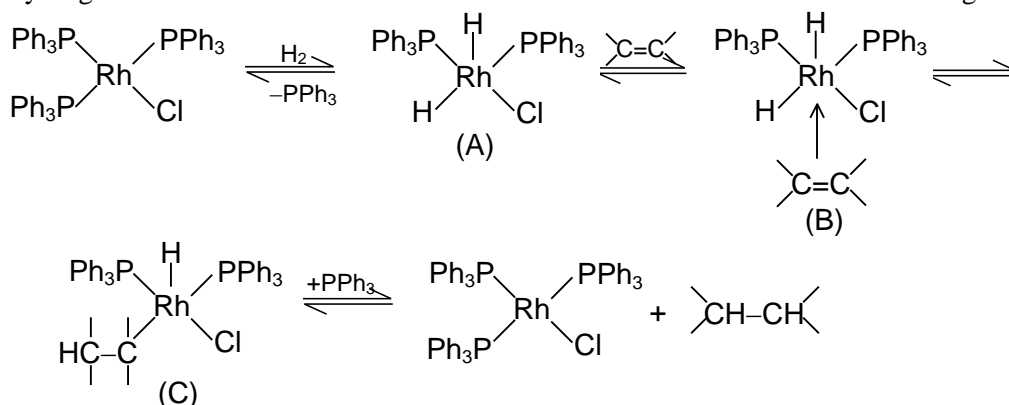
The adsorption is then followed by addition of both the hydrogen atoms from the same side of the double bond. The addition of hydrogen to an alkene is predominantly stereo selectively syn. Various steps involved in the catalytic hydrogenation reaction are given below. The asterisks (\*) indicate metallic sites.



For example,

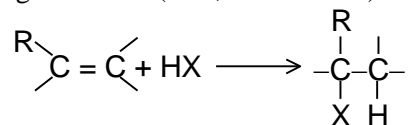


Hydrogenation of alkenes can also be effected by the use of a homogeneous catalyst,  $[RhCl(Ph_3P)_3]$ , also called Wilkinson's catalyst. The overall reaction proceeds in four steps. In the first step,  $H_2$  adds to the rhodium complex and one  $Ph_3P$  group is lost, thereby rhodium changing its oxidation state from +1 to +3. The co-ordination number of rhodium in the compound (A) has also increased from 4 to 5. In the 2<sup>nd</sup> step alkene attacks (A) forming a  $\pi$ -complex (B) which undergoes rearrangement in the 3<sup>rd</sup> step of a H-atom to one of the carbon atoms of the double bond, the other carbon forming a sigma bond with Rh. In the 4<sup>th</sup> step the second hydrogen atom is transferred to the other carbon and the alkane is lost with the regeneration of the catalyst.



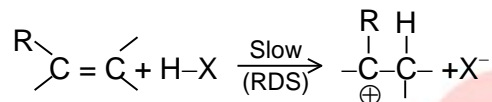
### 3.2 ADDITION OF HYDROGEN HALIDES

Hydrogen halides (HCl, HBr and HI) add to the double bond of alkenes.

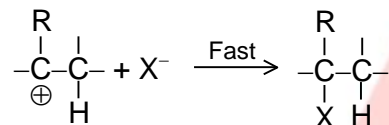


Mechanisms for addition of hydrogen halide to an alkene involves the following two steps.

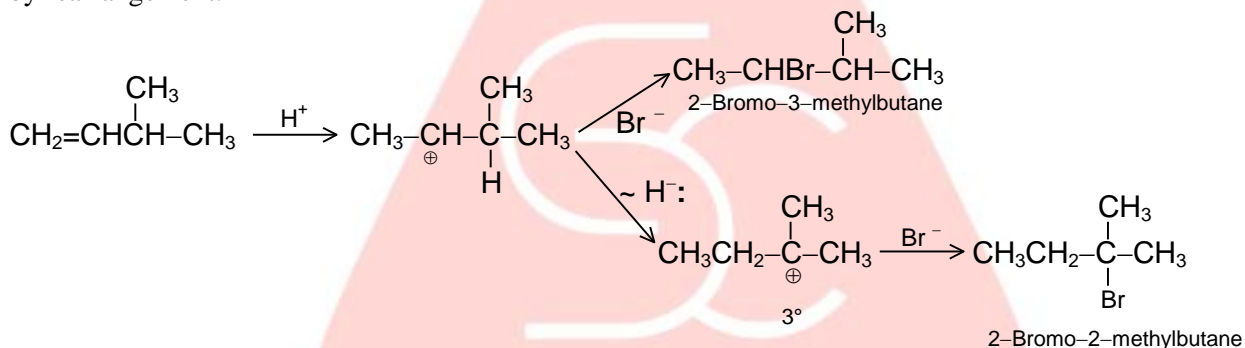
**Step 1.**



**Step 2.**



The addition of HBr to some alkenes gives a mixture of the expected alkyl bromide and an isomer formed by rearrangement.

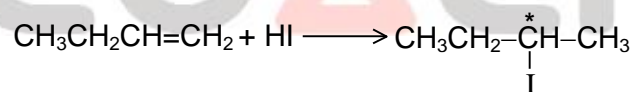


With this understanding of the mechanism for the ionic addition of hydrogen halides to alkenes, a statement can be made as:

In the ionic addition of an unsymmetrical reagent to a double bond, the positive portion of the reagent attaches itself to a carbon atom of the double bond so as to yield the more stable carbocation as intermediate. Because this is the step that occurs first, it is the step that determines the overall orientation of the reaction. In those cases where rearrangement does not occur, the addition of HX to alkenes follows Markovnikov's rule, according to which "the negative part of the unsymmetrical reagent goes to that carbon atom which bears lesser number of hydrogen atoms".

But in those cases, where rearrangement occurs, the overall addition of HX to alkenes does not follow Markovnikov's rule.

When HI is added to 1-butene the reaction leads to the formation 2-iodobutane, that contains a stereocentre.



The product, therefore, can exist as a pair of enantiomers. The carbocation that is formed in the first step of the addition is trigonal planar (sp<sup>2</sup> hybridized) and is achiral. When the iodide ion reacts with this flat carbocation, reaction is equally likely at either face. Thus reaction leads to the formation of two enantiomers and both the enantiomers are produced in equal amounts. Thus, product of the reaction is a racemic mixture.

### 3.3 ADDITION OF HYDROGEN BROMIDE IN PRESENCE OF PEROXIDE

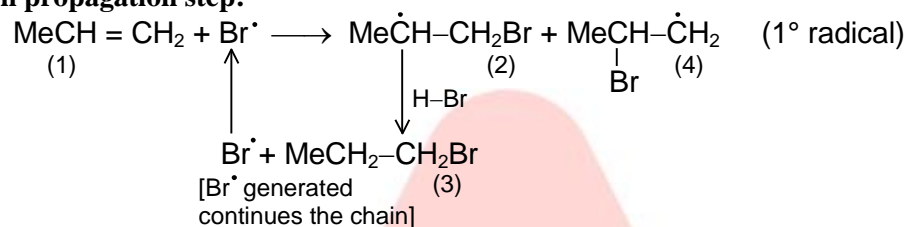
The addition of HBr to propene, MeCH=CH<sub>2</sub>(1), under polar conditions (in absence of peroxide) yields 2-bromopropane. However, in the presence of peroxide (or under other conditions that promote radical formation), the addition proceeds via a rapid chain reaction to yield 1-bromopropane. This addition of HBr in presence of peroxide is generally referred to as the peroxide effect leading to anti-Markovnikov addition. This difference in orientation of HBr addition is due to the fact that in the first (polar) case, the reaction is initiated by H<sup>+</sup> and proceeds via the more stable (secondary) carbocation while in the second (radical) case, it is initiated by

$\text{Br}^\bullet$  and proceeds via the more stable (secondary radical).

**Chain initiation step:**



**Chain propagation step:**



The initiation is by  $\text{Br}^\bullet$ , as hydrogen abstraction by  $\text{RO}^\bullet$  from  $\text{HBr}$  is energetically much more favourable than the alternative of bromine abstraction to form  $\text{ROBr} + \text{H}^\bullet$ . The alternative addition of  $\text{Br}^\bullet$  to (1) to form  $\text{MeCH}(\text{Br})\text{CH}_2^\bullet$  (4) does not occur, as secondary radical  $\text{Me}\dot{\text{C}}\text{HCH}_2\text{Br}$  (2) is more stable than primary radical.

$\text{HBr}$  is the only one of the four hydrogen halides that will add readily to alkenes via a radical pathway. The reason for this is reflected in the  $\Delta H$  values ( $\text{kJ mol}^{-1}$ ) for the two steps of the chain reaction for addition of  $\text{HX}$  to  $\text{CH}_2 = \text{CH}_2$ . For example,

	(1) $\text{X}^\bullet + \text{CH}_2 = \text{CH}_2$	(2) $\text{XCH}_2\text{CH}_2^\bullet + \text{HX}$
H-F	-188	+155
H-Cl	-109	+21
H-Br	-21	-46
H-I	+29	-113

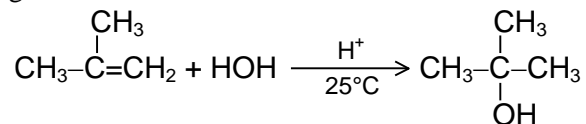
Only for  $\text{HBr}$ , both the chain steps are exothermic while for  $\text{HF}$  the second step is highly endothermic, reflecting the strength of the  $\text{H-F}$  bond and the difficulty of breaking it. For  $\text{HCl}$ , it is again the second step that is endothermic (though not to such a great extent) while for  $\text{HI}$  it is the first step that is endothermic, reflecting the fact that the energy gained in forming the weak  $\text{I-C}$  bond is not as much as that lost in breaking the  $\text{C=C}$   $\pi$  bond. Thus only a few radical additions of  $\text{HCl}$  are known, but the reactions are not very rapid and the reaction chains are short at ordinary temperatures.

Even with  $\text{HBr}$  addition, the reaction chains tend to be rather short, much shorter than those in halogen addition and more than a trace of peroxide is thus needed to provide sufficient initiator radicals. For preparative purposes up to 0.01 mol peroxide per mol of alkene is required. Once initiated, reaction by this pathway is very much faster than any competing addition via the polar pathway and the anti-Markownikov product like (3) will thus predominate. If the Markownikov product, e.g.  $\text{MeCH}(\text{Br})\text{CH}_3$  from propene, is required it is necessary either to purify the alkene rigorously before use or to add inhibitors (good radical acceptors such as phenols, quinines, etc) to mop up any radicals. Essentially complete control of orientation of  $\text{HBr}$  addition, in either direction, can thus be achieved, under preparative conditions, by incorporating either peroxides (radical initiators) or radical inhibitors in the reaction mixture. This is particularly useful as such control is not confined purely to alkenes themselves. For example,  $\text{CH}_2 = \text{CHCH}_2\text{Br}$  can be converted into 1,2- or 1,3-dibromopropane at will.

### 3.4 ADDITION OF WATER

#### 3.4.1 ACID CATALYZED HYDRATION

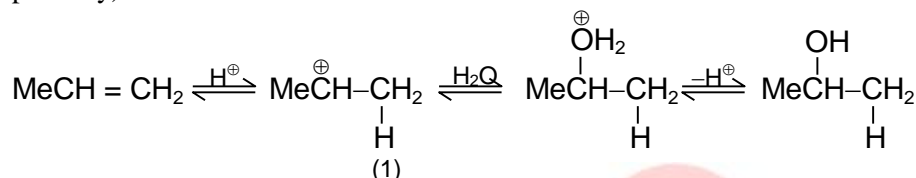
The acid catalyzed addition of water to the double bond of an alkene is a method of preparation of low molecular weight alcohols. The addition of water to the double bond follows Markownikov's rule in those cases where rearrangement is not involved.



As the reactions follow Markownikov's rule acid catalyzed hydration of alkenes do not yield primary

alcohols except in the special case of the hydration of ethene. The occurrence of carbocation rearrangements limits the utility of alkene hydration as a laboratory method for preparing alcohols.

Acid catalysed hydration of an alkene is the reversal of the similarly acid catalysed dehydration (by the E<sub>1</sub> pathway) of alcohols to alkenes.



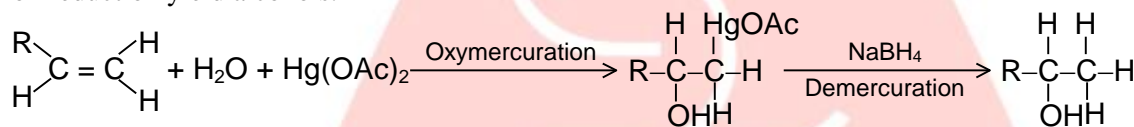
The formation of the carbocationic intermediate (1), either directly or via an initial  $\pi$  complex, appears to be rate limiting and the overall orientation of addition is Markownikov (in the present case).

Acids that have weakly nucleophilic anions (like  $\text{HSO}_4^-$  from dilute aqueous  $\text{H}_2\text{SO}_4$ ) are chosen as catalysts, so that their anions will offer little competition to the actual nucleophile  $\text{H}_2\text{O}$ . In case, if any  $\text{ROSO}_3\text{H}$  is formed, it will be hydrolysed to  $\text{ROH}$  under the conditions of the reactions.

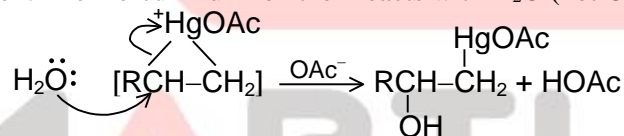
### 3.4.2 OXYMERCURATION-DEMERCURATION

In the overall Oxymercuration-Demercuration reaction,  $\text{H}_2\text{O}$  is added to the double bond. The reaction is free from rearrangement (as it does not involve carbocation intermediate) and involves syn addition using Markownikov's rule.

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds which on reduction yield alcohols.

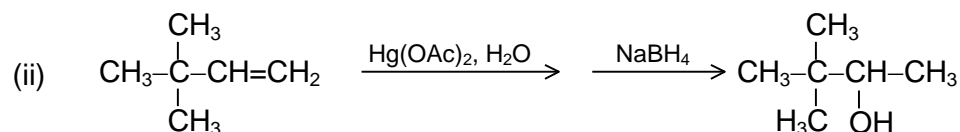
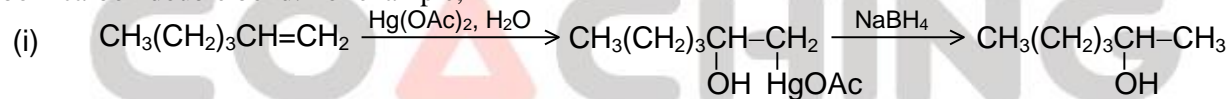


The first stage, oxymercuration involves addition to the carbon-carbon double bond of  $-\text{OH}$  and  $\text{Hg}(\text{OAc})_2$ . The electrophile of  $\text{Hg}(\text{OAc})_2$  is  $\text{AcOHg}^+$  that adds to  $\text{C}=\text{C}$  to form a mercurinium ion similar to a bromonium ion. The mercurinium ion then reacts with  $\text{H}_2\text{O}$  (not  $\text{OAc}^-$ ) at the more substituted carbon.



Then, in demercuration,  $\text{HgOAc}$  is replaced by  $\text{H}$ . The reaction sequence amounts to hydration of the alkene, but is much more widely applicable than direct acid catalysed hydration.

Oxymercuration-demercuration gives alcohols corresponding to Markownikov addition of water to the carbon-carbon double bond. For example,



### 3.4.3 HYDROBORATION-OXIDATION

In the overall Hydroboration-Oxidation reaction,  $\text{H}_2\text{O}$  is added to the double bond. The reaction is free from rearrangement (as it does not involve carbocation intermediate) and involves syn addition using anti-Markownikov's rule overall.

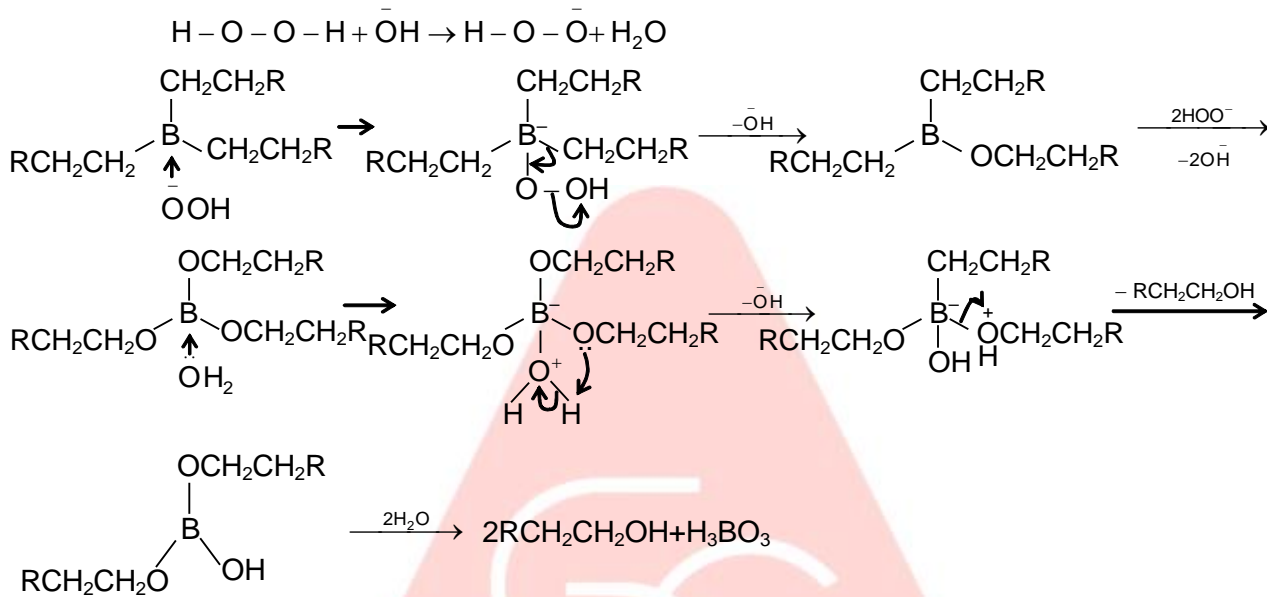
With the reagent diborane,  $\text{B}_2\text{H}_6$ , or disubstituted borane ( $\text{R}'_2\text{BH}$ , in THF solvent, alkenes undergo hydroboration to yield trialkylboranes. The addition follows Markownikov's rule.



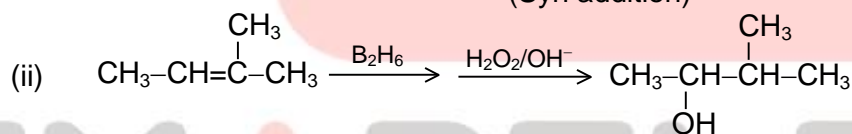
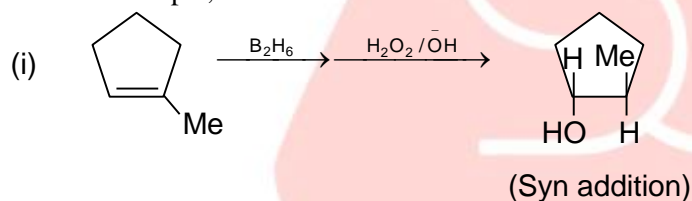




Oxidation of trialkylborane is carried out by alkaline  $H_2O_2$  which results in the formation of alcohol as if water has been added to alkene according to anti Markovnikov's rule.



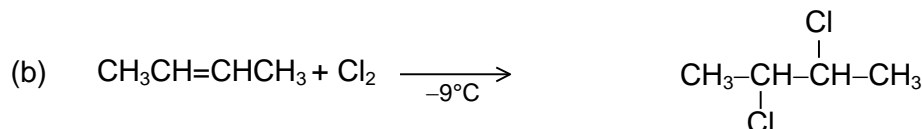
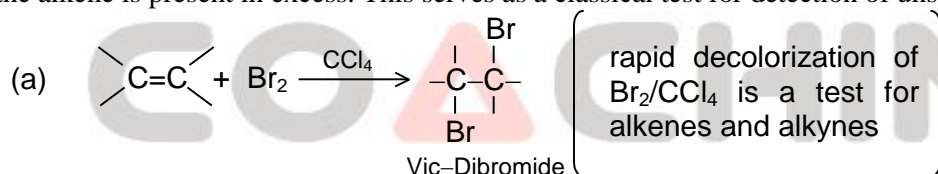
For example,



### 3.5 ADDITION OF BROMINE AND CHLORINE

Alkenes react rapidly with bromine at room temperature and in the absence of light.

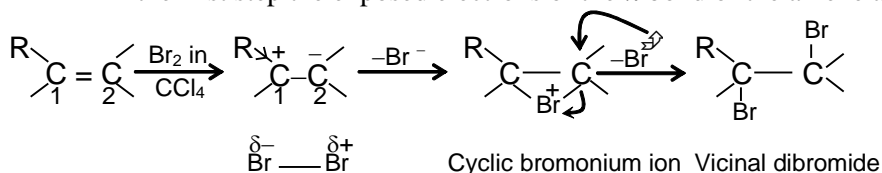
If bromine in  $CCl_4$  is added to an alkene, the red-brown colour of the bromine disappears almost instantly as long as the alkene is present in excess. This serves as a classical test for detection of unsaturation of  $C=C$  or  $C \equiv C$  type.



#### Mechanism:

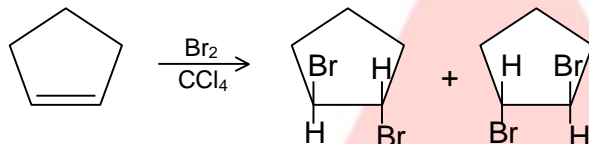
The mechanism proposed for halogen addition is an ionic mechanism.

In the first step the exposed electrons of the  $\pi$  bond of the alkene attack the halogen in the following way.



In this reaction, when reagent (bromine) approaches alkene, the temporary polarization develops on the alkene with C<sub>2</sub> atom gaining a negative charge and C<sub>1</sub> atom acquiring positive charge (as it can be compensated by the +I effect of R group). The alkenes being electron rich compounds (due to the presence of π-electron cloud) are attacked by the electrophile (Br<sup>⊕</sup>) to give a cyclic bromonium ion. Here, the formation of cyclic bromonium ion as intermediate is possible because bromine is of considerably large size having lone pairs to be bonded to both the carbons simultaneously. The cyclic bromonium ion is then attacked by Br<sup>⊖</sup> from the top (as lower side is already blocked) whereby the three membered ring is cleaved by trans opening giving vicinal dibromide as the product. Thus, the overall addition of Br<sub>2</sub> to alkene follows trans stereoselectivity.

When cyclopentene reacts with bromine in CCl<sub>4</sub>, anti-addition occurs and the products of the reaction are trans-1,2-dibromocyclopentane enantiomers (as a racemate).

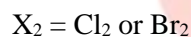
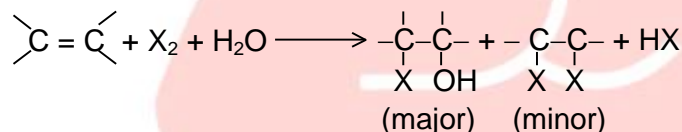


When cis-2-butene adds bromine, the product is a racemic form of 2,3-dibromobutane. When trans-2-butene adds bromine, the product is the meso compound.

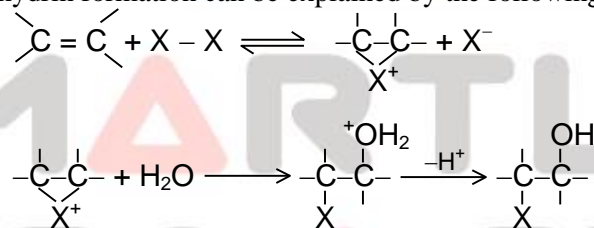
Thus we find that a particular stereoisomeric form of the starting material react in such a way that it gives a specific stereoisomeric form of the product. Thus the reaction is stereospecific.

### 3.6 HALOHYDRIN FORMATION

If the halogenation of an alkene is carried out in aqueous solution (rather than in CCl<sub>4</sub>), the major product of the overall reaction is a halo-alcohol called halohydrin. In this case, the molecules of the solvent become reactant.

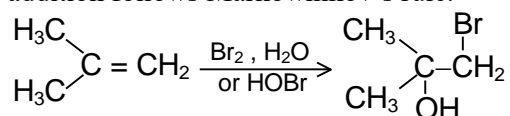


Halohydrin formation can be explained by the following mechanism



The addition of X and OH occurs in the trans manner, as the reaction proceeds by the formation of halonium ion intermediate.

If the alkene is unsymmetrical, the halogen adds up on the carbon atom with greater number of hydrogen atoms i.e. the addition follows Markownikov's rule.

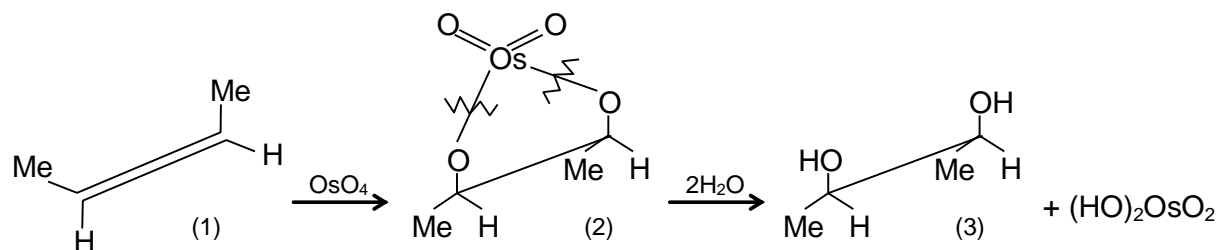


### 3.7 HYDROXYLATION

There are a number of reagents that can add two OH groups to alkenes. The two OH groups can be either added from the same side (syn hydroxylation) or from the opposite side (anti hydroxylation).

#### 3.7.1 SYN HYDROXYLATION

Osmium tetroxide (OsO<sub>4</sub>) adds to alkene to form cyclic osmic ester (2) which can be made to undergo ready hydrolytic cleavage of their Os-O bonds to yield the vic-diol(3).

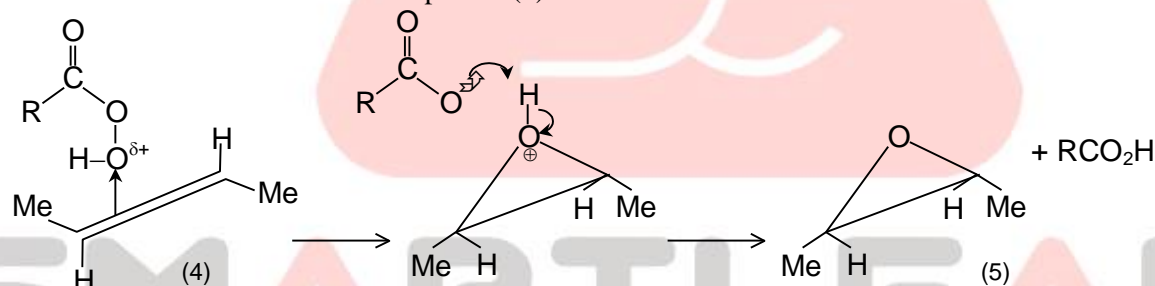


cis-2-butene (1) thus yields the meso butan-2, 3-diol (3), i.e. the overall hydroxylation is stereoselectively syn, as would be expected from Os–O cleavage in a necessarily cis cyclic ester (2). The disadvantage of this reaction as a preparative method is expense and toxicity of  $\text{OsO}_4$ . However, this can be overcome by using it in catalytic quantities in association with  $\text{H}_2\text{O}_2$  which re-oxidises the osmic acid,  $(\text{HO})_2\text{OsO}_2$ , formed to  $\text{OsO}_4$ .

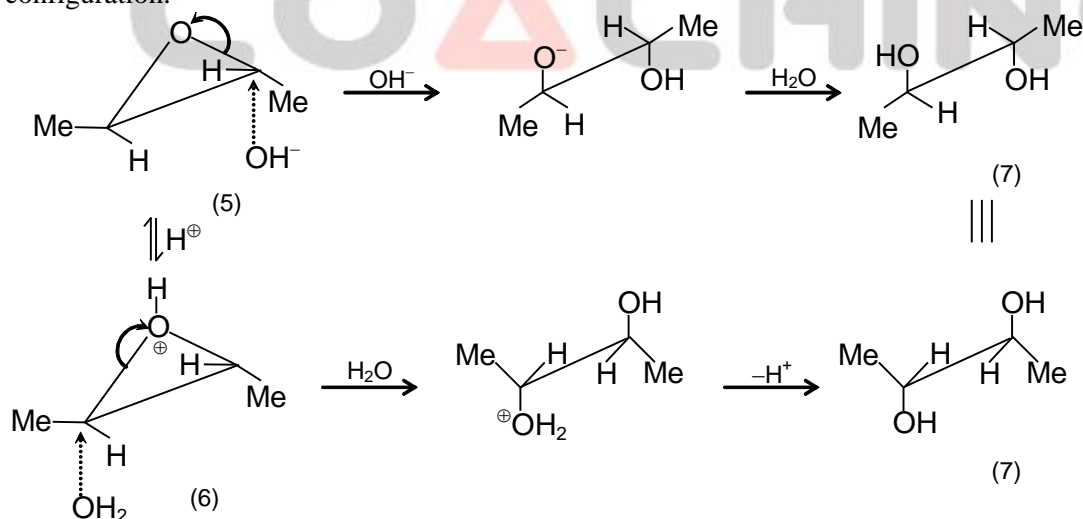
Alkaline permanganate,  $\text{Mn}^{18}\text{O}_4^-$  (a reagent used classically to test for unsaturation), will also effect stereoselective syn addition and this by analogy with the above, is thought to proceed via cyclic (cis) permanganic ester. It has not proved possible actually to isolate such species but use of  $\text{Mn}^{18}\text{O}_4^-$ , was found to lead to a vic-diol in which both oxygen atoms were  $\text{O}^{18}$  labeled. Thus both were derived from  $\text{MnO}_4^-$ , and neither from the solvent  $\text{H}_2\text{O}$ , which provides support for a permanganic analogue of (2) as an intermediate, provided that  $\text{Mn}^{18}\text{O}_4^-$  undergoes no  $\text{O}^{18}$  exchange with the solvent  $\text{H}_2\text{O}$  under these conditions. The disadvantage of  $\text{MnO}_4^-$  for hydroxylation is that the resultant 1,2-diol is very much susceptible to further oxidation by it.

### 3.7.2 ANTI-HYDROXYLATION

Peroxyacids,  $\text{RCOOOH}$  will also oxidize alkenes, e.g. trans-2-butene (4), by adding an oxygen atom across the double bond to form an epoxide (5).

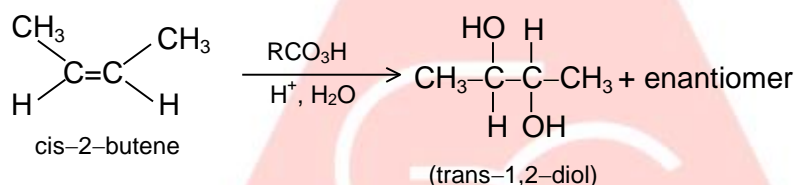
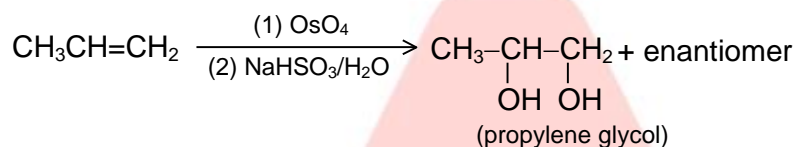
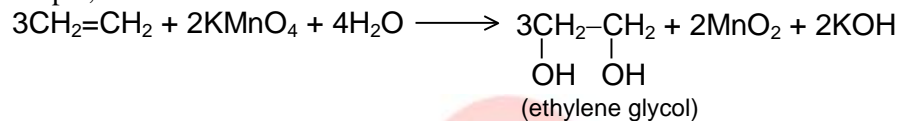


Epoxides (though uncharged) have a formal resemblance to cyclic bromonium ion intermediates, but unlike them are stable and may readily be isolated. However, they undergo nucleophilic attack under either acid or base catalysed conditions to yield the 1,2-diol. In either case attack by the nucleophile on carbon atom will be from the opposite side of the oxygen bridge in (5). Such attack on the epoxide will involve inversion of configuration.



Attack has been shown on only one of the two possible carbon atoms in (5) and (6), though on different ones in the two cases. In each case, attack on the other carbon will lead to the same product, the meso vic-diol (7). By comparing the configuration of (7) with that of the original alkene (4), it can be seen that in overall terms stereoselective anti hydroxylation has been effected. Thus by suitable choice of reagent, the hydroxylation of alkenes can be made stereoselectively syn or anti at will.

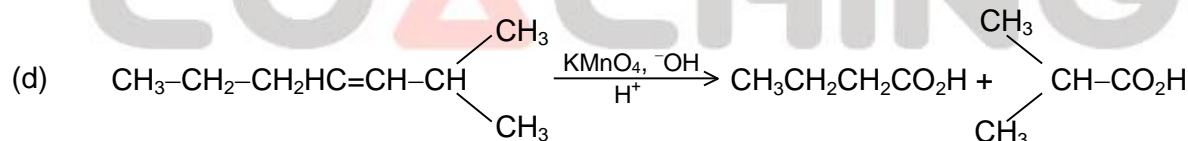
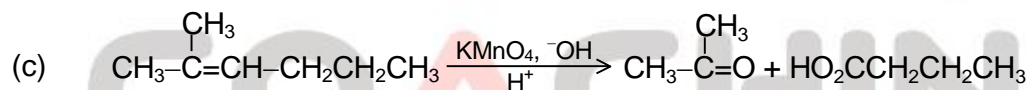
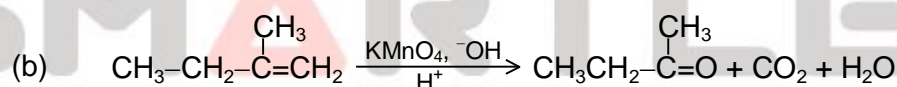
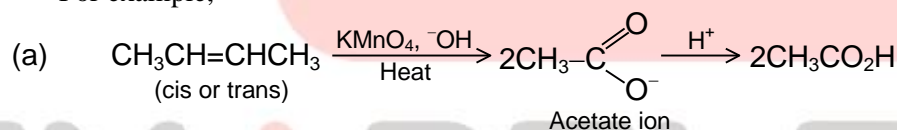
For example,



### 3.8 OXIDATIVE CLEAVAGE BY HOT ALKALINE KMnO<sub>4</sub>

Alkenes are oxidatively cleaved by hot alkaline permanganate solution. The terminal CH<sub>2</sub> group of 1-alkene is completely oxidized to CO<sub>2</sub> and water. A disubstituted atom of a double bond becomes >C=O group of a ketone. A monosubstituted atom of a double bond becomes aldehyde group which is further oxidized to salt of carboxylic acid.

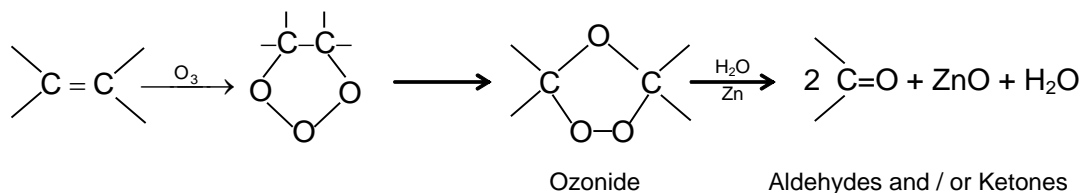
For example,



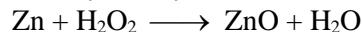
### 3.9 OZONOLYSIS

A more widely used method for locating the position of double bond in an alkene involves the use of ozone (O<sub>3</sub>). Ozone reacts vigorously with alkene to form unstable compound called molozonide, which rearranges spontaneously to form a compound known as ozonide. Ozonides, themselves are unstable and reduced directly with Zn and water. The reduction produces carbonyl compounds (aldehydes and ketones) that can be isolated and identified.

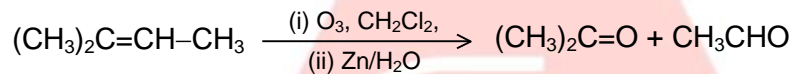
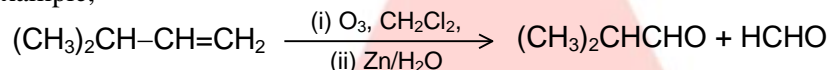




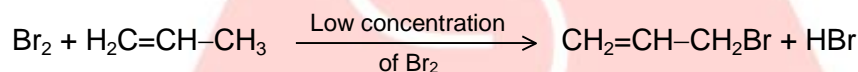
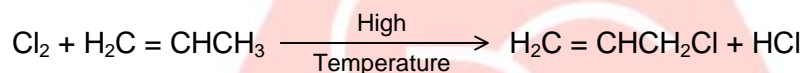
Ozonolysis can be either of reductive type or of oxidative type. The difference lies in the fact that products of reductive ozonolysis are aldehydes and/or ketones while in oxidative ozonolysis, the products are carboxylic acids and/or ketones. This is because  $\text{H}_2\text{O}_2$  formed would oxidize aldehydes to carboxylic acids but ketones are not oxidized. In reductive ozonolysis, we add zinc which reduces  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$  and thus  $\text{H}_2\text{O}_2$  is not present to oxidize any aldehyde formed.



For example,

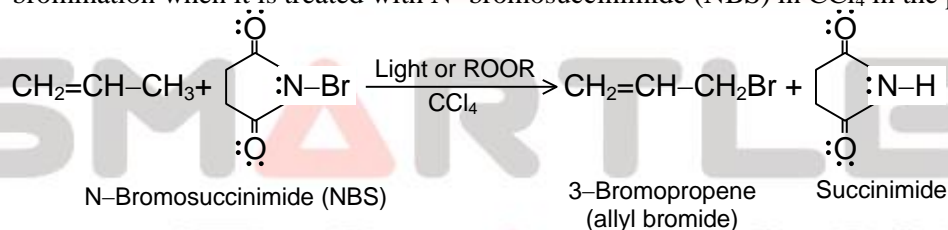


### 3.10 SUBSTITUTION REACTIONS AT ALLYLIC POSITION

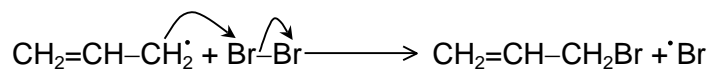
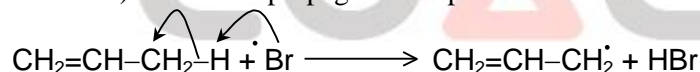


These halogenations are like free radical substitution of alkanes. The order of reactivity of H-abstraction is allyl > 3° > 2° > 1° > vinyl.

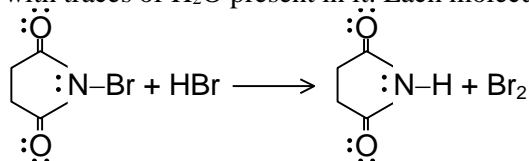
Allylic substitution by chlorine is carried out using  $\text{Cl}_2$  at high temperature and alkene (with  $\alpha$ -carbon) in gaseous phase. Allylic bromination can be carried out using N-Bromosuccinimide. Propene undergoes allylic bromination when it is treated with N-bromosuccinimide (NBS) in  $\text{CCl}_4$  in the presence of peroxide or light.



The reaction is initiated by the formation of a small amount of  $\text{Br}^\cdot$  (possibly formed by dissociation of  $\text{Br}_2$  molecule). The chain propagation steps for this reaction are the same as for chlorination.

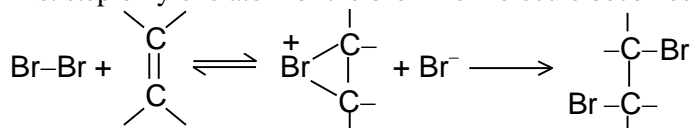


N-Bromosuccinimide is nearly insoluble in  $\text{CCl}_4$  and provides a constant but very low concentration of bromine in the reaction mixture. It does this by reacting very rapidly with the  $\text{HBr}$  formed by the reaction of NBS with traces of  $\text{H}_2\text{O}$  present in it. Each molecule of  $\text{HBr}$  is replaced by one molecule of  $\text{Br}_2$ .



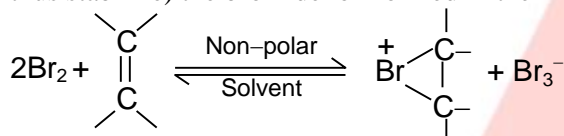
Under these conditions, that is, in a non-polar solvent and with a very low concentration of bromine, very little bromine adds to the double bond, instead it undergoes substitution and replaces an allylic hydrogen atom.

A question must have arisen in your mind that why does a low concentration of bromine favour allylic substitution over addition? To understand this we must recall the mechanism for addition and notice that in the first step only one atom of the bromine molecule becomes attached to the alkene in a reversible step.



The other atom (now the bromide ion) becomes attached in the second step. Now, if the concentration of bromine is low, the equilibrium for the first step will lie far to the left. Moreover, even when the bromonium ion forms, the probability of its finding a bromide ion in its vicinity is also low. These two factors slow the addition to such an extent that allylic substitution competes successfully.

The use of a non-polar solvent also slows addition. Since there are no polar molecules to solvate (and thus stabilize) the bromide ion formed in the first step, the bromide ion uses a bromine molecule as a substitute.



This means that in a non-polar solvent the rate equation is second order with respect to bromine

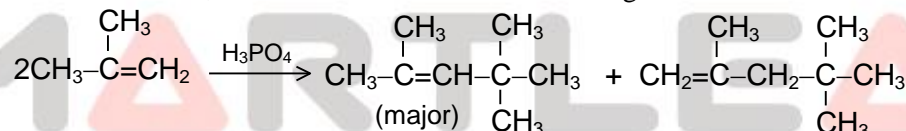
$$\text{rate} = k \left[ \begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array} \right] [\text{Br}_2]^2$$

and that the low bromine concentration has an even more pronounced effect in slowing the rate of addition whereby increasing the tendency to undergo substitution.

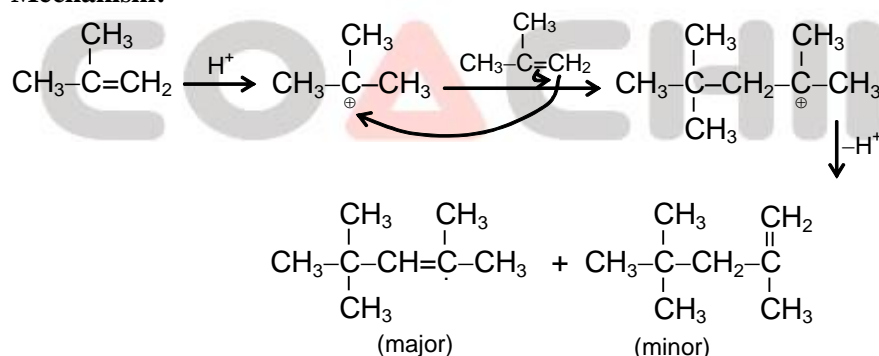
To understand why a high temperature favours allylic substitution over addition requires a consideration of the effect of entropy changes on equilibria. The addition reaction has a substantial negative entropy change because it combines two molecules into one. At low temperatures, the  $T\Delta S$  term in  $\Delta G = \Delta H - T\Delta S$ , is not large enough to offset the favourable  $\Delta H$  term. But as the temperature is increased, the  $T\Delta S$  term becomes more significant,  $\Delta G$  becomes more positive, and the equilibrium becomes more unfavourable for addition and subsequently favours allylic substitution.

### 3.11 ACID CATALYZED DIMERIZATION OF ALKENES

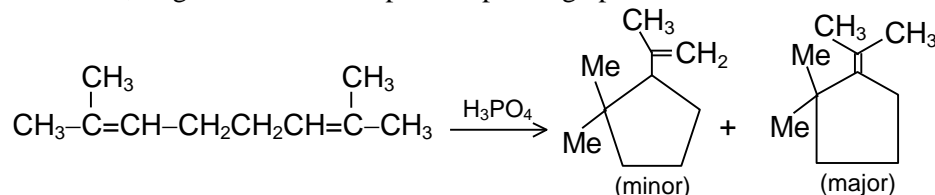
I. In case of monoalkene, two alkenes dimerize to form a larger alkene.



**Mechanism:**

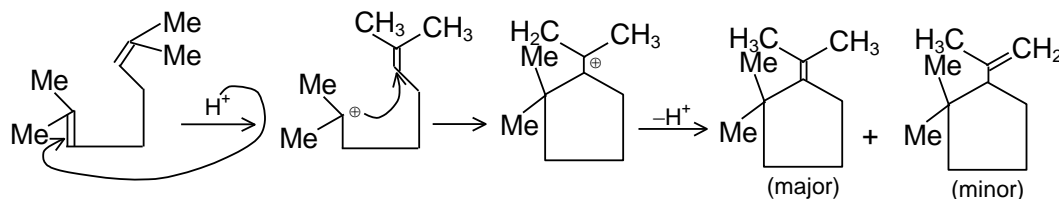


II. In case of diene, ring formation takes place depending upon the structure of diene.



If the ring formed is five or six-membered, this reaction occurs with great ease.

**Mechanism:**



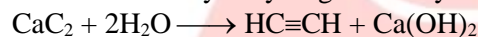
## ALKYNES

Alkynes are hydrocarbons having four hydrogen atoms less than the corresponding alkane. They have two degrees of unsaturation in the form of a triple bond between two carbon atoms. They are isomeric with dienes and cycloalkene and have the general formula  $C_nH_{2n-2}$ . The most important member of the alkyne series is acetylene and hence alkynes are also known acetylenes.

### 1 GENERAL METHODS OF PREPARATION OF ALKYNES

#### 1.1 HYDROLYSIS OF CARBIDES

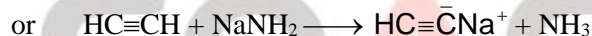
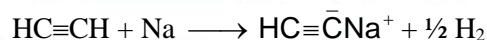
Some of the lower members of alkyne series can be synthesized by the hydrolysis of carbides. For example, calcium carbide on hydrolysis gives acetylene and magnesium carbide on hydrolysis gives propyne.



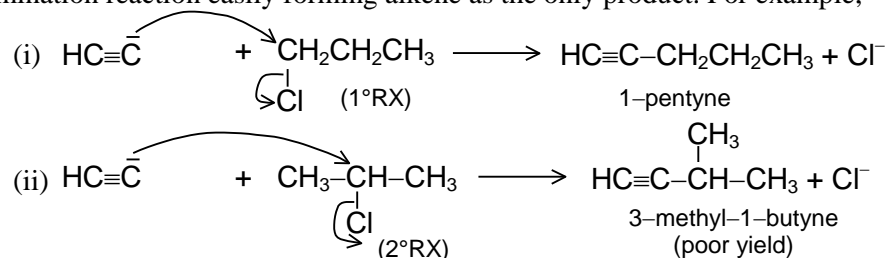
The difference in the behaviour of calcium carbide and magnesium carbide is due to the differences in their structures. Both the carbides are ionic in nature. In calcium carbide, the anion exists as  $\bar{C} \equiv \bar{C}$  while in magnesium carbide, the anion exists as  $\bar{C}^3- C \equiv \bar{C}$ . It is pertinent to note that aluminium carbide ( $Al_4C_3$ ) and beryllium carbide ( $Be_2C$ ) do not form any alkyne on hydrolysis, instead they form methane on hydrolysis. This is due to the fact that their anions exist as  $C^{4-}$ .

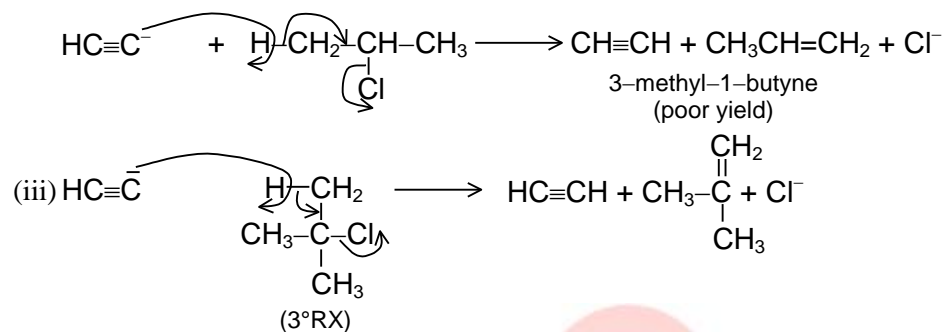
#### 1.2 FROM ACETYLENE

The two hydrogen atoms of acetylene are acidic in nature and can be replaced by a strong base like sodium or sodamide.

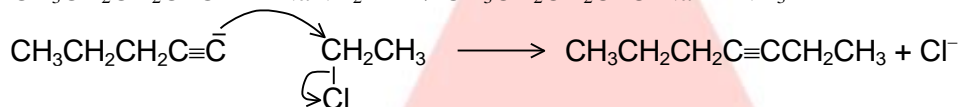
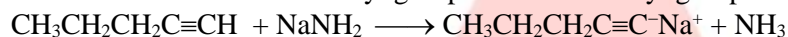


Sodium acetylide when treated with primary alkyl halide gives 1-alkynes following nucleophilic substitution reaction by  $S_N2$  mechanism. Secondary alkyl halide gives poor yield of 1-alkyne because substitution reaction is accompanied by elimination reaction with acetylide ion ( $HC \equiv \bar{C}$ ) functioning as a strong base. Tertiary alkyl halides do not undergo any substitution reaction because of steric hindrance. Instead they undergo elimination reaction easily forming alkene as the only product. For example,





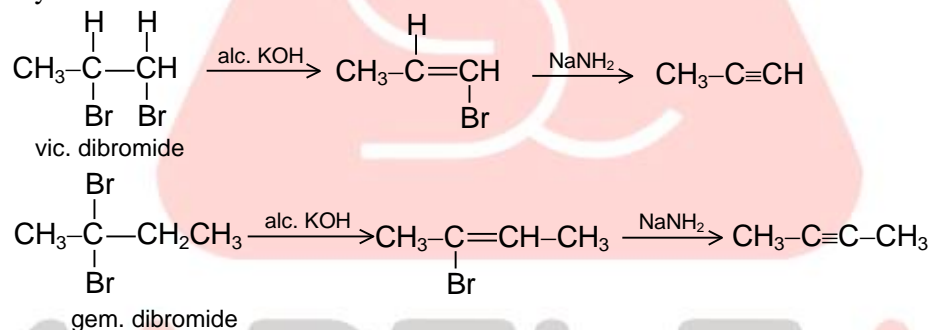
1-alkyne still has one more acidic hydrogen and by repeating the same set of reactions, it is possible to introduce the same alkyl group or different alkyl group at the other sp hybridised carbon atom.



### 1.3 DEHYDROHALOGENATION OF VICINAL OR GEMINAL DIHALIDES

Both vicinal dihalides and geminal dihalides undergo dehydrohalogenation reaction with a strong base to give alkyne in fairly good yield. The reaction follows 1, 2-elimination mechanism.

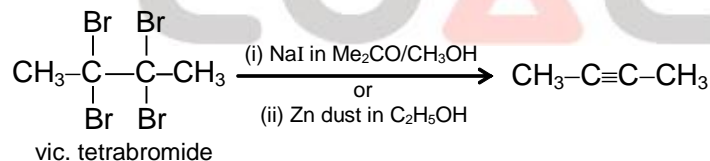
In the first step, the base employed is alcoholic KOH while in the subsequent step, we need a strong base like sodamide as vinyl halide is less reactive towards elimination.



NaNH<sub>2</sub> is preferred over alc. KOH in the second step as alc. KOH finds it difficult to eliminate a hydrogen halide molecule as the two leaving groups are attached to sp<sup>2</sup> hybridised carbon atoms.

### 1.4 DEHALOGENATION OF VICINAL TETRAHALIDES

Vicinal tetrahalides are compounds containing two halogen atoms attached to each of the two adjacent carbon atoms. They lose all the four halogen atoms forming alkynes when treated with either (i) NaI in acetone/methanol, or (ii) Zn dust and ethanol. The mechanism is very similar to the one discussed in the lesson on "Alkenes".



## 2 GENERAL PHYSICAL PROPERTIES OF ALKYNES

Being compounds of low polarity, the alkynes have physical properties that are essentially the same as those of the alkanes and alkenes. They are insoluble in water but quite soluble in the usual organic solvents of low polarity like ether, benzene, carbon tetrachloride etc. Their densities are lower than that of water. Their melting points and boiling points show the usual increase with increase in number of carbon atoms and the usual effects of chain branching.

The CH<sub>3</sub>-C bond in propyne is formed by overlap of an sp<sup>3</sup> hybrid orbital from methyl carbon with a sp hybrid orbital from acetylenic carbon. The bond is between sp<sup>3</sup>-sp carbon. Since one orbital has more 's' character than the other and is thereby more electronegative, the electron density in

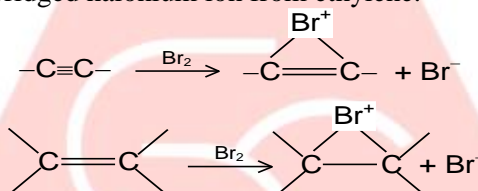


the resulting bond is not symmetrical. The unsymmetrical electron distribution results in a dipole moment larger than alkene but still relatively small. Symmetrically disubstituted alkynes have zero dipole moment.

### 3 GENERAL CHEMICAL PROPERTIES OF ALKYNES

The triple bond of alkynes consists of one sigma bond and two pi bonds, which are perpendicular to each other. The two pi bonds get mixed up and all the four pi electrons are cylindrically distributed around the two sp hybridised carbon atoms. Being unsaturated, alkynes undergo addition reactions to form alkene derivatives with the addition of one molecule and saturated compounds with the addition of two molecules. Under suitable conditions, it is possible to isolate the intermediate alkene.

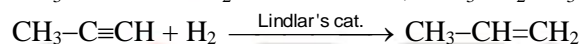
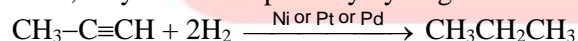
Acetylene is less reactive than ethylene towards most of the electrophilic reagents. This is unexpected in view of the fact that the  $\pi$ -electron density in a triple bond is higher than that in a double bond. Possible reason for decreased reactivity of a triple bond towards electrophiles may be the fact that the bridged halonium ion from acetylene is more strained than the bridged halonium ion from ethylene.



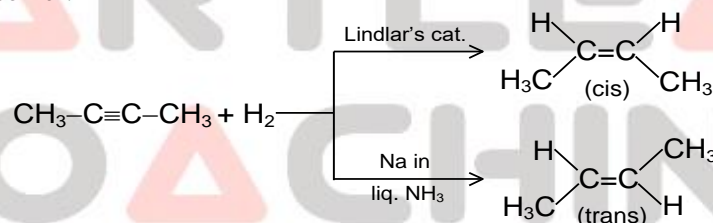
Towards hydrogenation (which do not involve electrophilic attack), alkynes are more reactive than alkenes.

#### 3.1 HYDROGENATION

Alkynes can be reduced directly to alkanes by the addition of  $\text{H}_2$  in the presence of Ni, Pt or Pd as a catalyst. The addition reaction takes place in two steps. It is not possible to isolate the intermediate alkene under the above reaction conditions. By using Lindlar's catalyst [Pd on  $\text{CaCO}_3 + (\text{CH}_3\text{COO})_2\text{Pb}$ ], nickel boride or palladised charcoal, alkynes can be partially hydrogenated to alkenes.

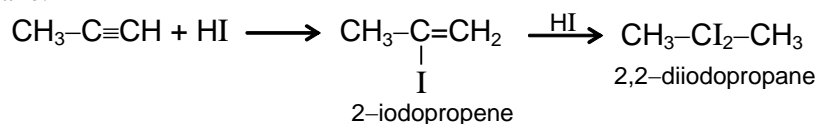


2-butyne when reduced with Lindlar's catalyst gives nearly 100% cis isomer while Na in liquid ammonia gives nearly 100% trans isomer.



#### 3.2 ADDITION OF HALOGEN ACIDS

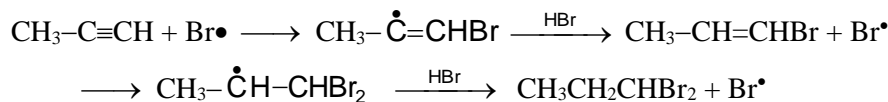
Addition of halogen acids to alkynes occur in accordance with Markownikoff's rule. Addition of one molecule of halogen acid gives an unsaturated halide, which then adds another molecule of hydrogen halide to form gem dihalides. For example, addition of HI to propyne first gives 2-iodopropene and then 2,2-diiodopropane.



The order of reactivity of halogen acids towards addition reaction is  $\text{H-I} > \text{H-Br} > \text{H-Cl}$ .

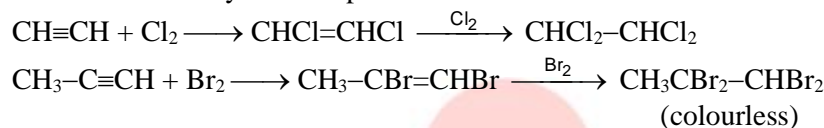
Peroxides have the same effect on addition of HBr to alkyne as that on alkene and the reaction follows free radical mechanism.





### 3.3 ADDITION OF HALOGENS

One or two molecules of halogens can be added to alkynes giving dihalides and tetra halides respectively. Chlorine and bromine add readily to the triple bond while iodine reacts rather slowly.

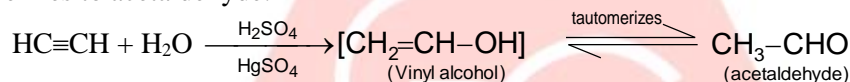


This reaction can be used as a test to detect unsaturation (both alkenes and alkynes) as  $\text{Br}_2$  in  $\text{CCl}_4$  is reddish brown in colour while the product obtained is colourless.

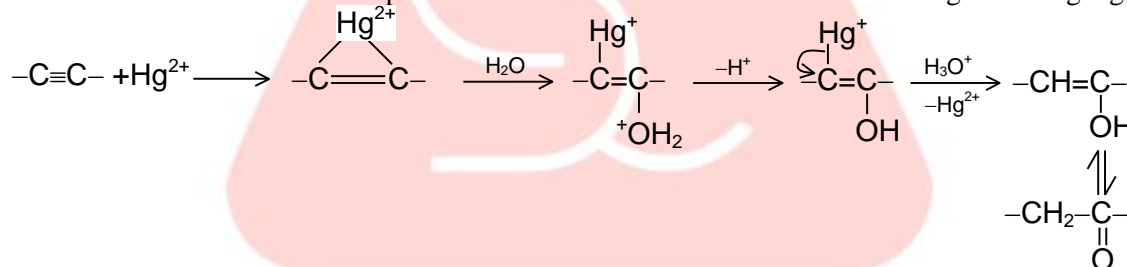
### 3.4 ADDITION OF WATER

Water adds to alkyne when alkyne is treated with 40%  $\text{H}_2\text{SO}_4$  containing 1%  $\text{HgSO}_4$  (as a catalyst) to form a carbonyl compound. The addition of water follows Markownikoff's rule forming enol as intermediate, which tautomerizes to give a more stable carbonyl compound.

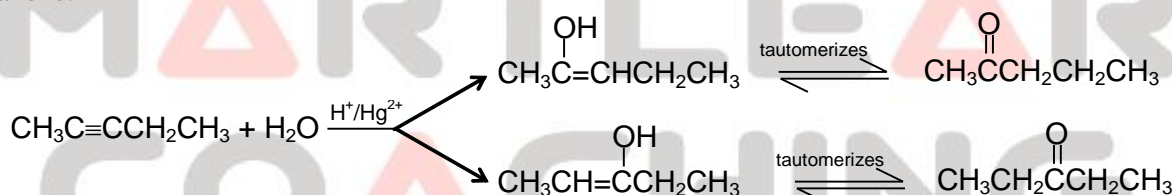
For example, acetylene gas when passed through dil.  $\text{H}_2\text{SO}_4$  containing  $\text{HgSO}_4$  initially forms vinyl alcohol, which tautomerizes to acetaldehyde.



The reaction is believed to take place via the formation of a three membered ring involving  $\text{Hg}^{2+}$  ion.

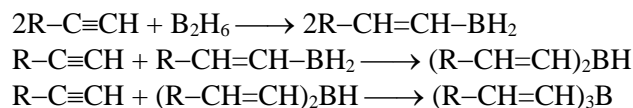


Acetylene is the only alkyne forming an aldehyde in this reaction. Higher homologues of acetylene either form a single ketone or a mixture of ketones. For example, 2-pentyne gives a mixture of 2-pentanone and 3-pentanone.

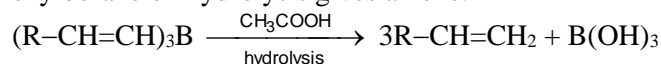


### 3.5 ADDITION OF BORON HYDRIDES

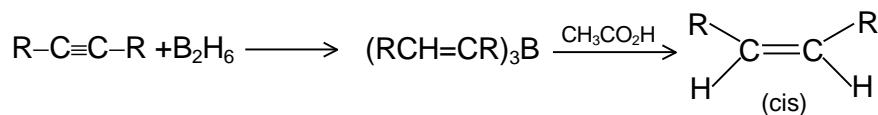
Diborane, the simplest hydride of boron reacts with alkyne to form trialkenylborane. Diborane splits into two  $\text{BH}_3$  units and the addition of  $\text{BH}_3$  takes place following Markownikoff's rule. The addition continues as long as hydrogen is attached to boron atom.



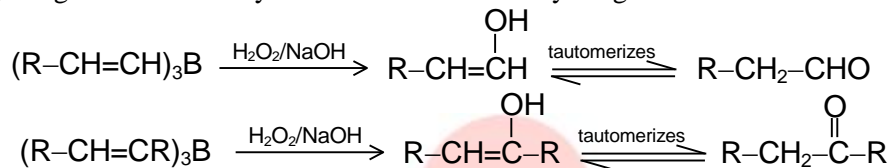
Trialkenylborane on hydrolysis gives alkene.



Internal alkynes give rise to alkenes where geometrical isomerism is possible. Hydroboration followed by hydrolysis of alkynes gives cis alkene as the major product.

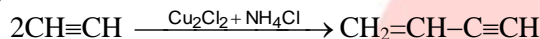


Oxidation of trialkenylborane with alkaline  $H_2O_2$  results in the formation of carbonyl compounds. Terminal alkynes give rise to aldehydes whereas internal alkynes give rise to ketones.



### 3.6 DIMERISATION

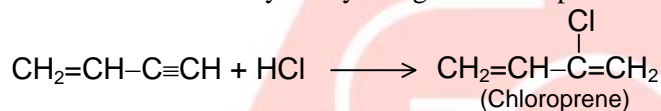
Acetylene dimerises when treated with a mixture of  $Cu_2Cl_2$  and  $NH_4Cl$  to give vinyl acetylene.



The dimer undergoes addition reactions just like any other unsaturated hydrocarbon.

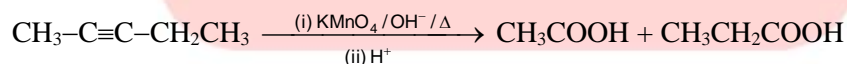
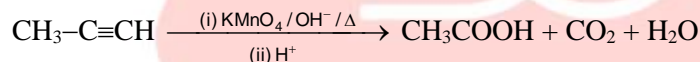
The addition reaction preferably takes place at the triple bond and not at the double bond in spite of the fact that alkynes are less reactive than alkenes towards electrophilic addition reactions.

For example, addition of  $HCl$  to vinyl acetylene gives chloroprene.



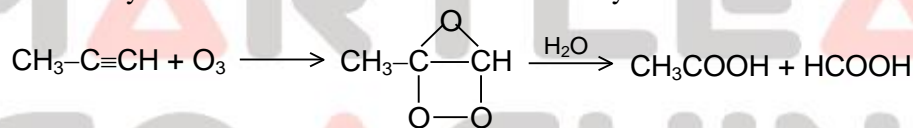
### 3.7 OXIDATION

Alkynes are oxidised by hot alkaline  $KMnO_4$ , which causes cleavage of  $-C\equiv C-$  resulting in the formation of salts of carboxylic acids. The salts on acidification are converted into acids. Internal alkynes give mixture of carboxylic acids while terminal alkynes give a carboxylic acid and the terminal  $C$ -atom is oxidised to  $CO_2$  and  $H_2O$ .

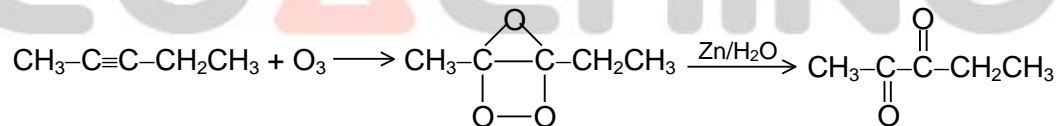


### 3.8 OZONOLYSIS

Reaction of alkynes with  $O_3$  gives rise to the formation of ozonide. Hydrolysis of ozonide with  $H_2O$  gives a mixture of two carboxylic acids. This is called oxidative ozonolysis.



However, if ozonide is hydrolysed with  $Zn$  and  $H_2O$ , a diketone is formed. This is called reductive ozonolysis.

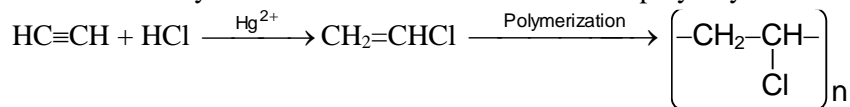


Ethyne behaves differently. Ozonolysis followed by oxidative hydrolysis of ethyne gives a mixture of glyoxal and formic acid.



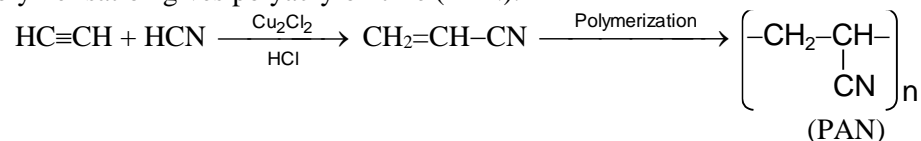
### 3.9 POLYMERISATION REACTIONS

- (i) Hydrochloric acid adds to acetylene in the presence of  $Hg^{2+}$  ion as catalyst to form vinyl chloride. Polymerisation of vinyl chloride results in the formation of polyvinyl chloride (PVC).



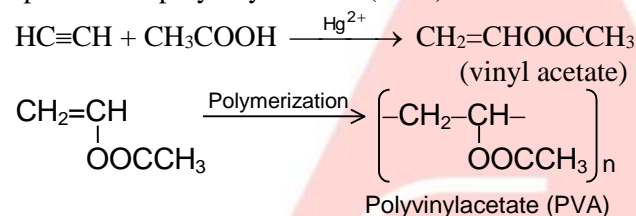
(PVC)

- (ii) Addition of HCN to ethyne is catalysed by  $\text{Cu}_2\text{Cl}_2$  in HCl. The product obtained is acrylonitrile, which on polymerisation gives polyacrylonitrile (PAN).

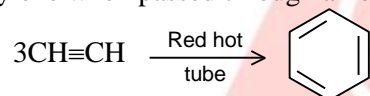


Acrylonitrile is also used in the manufacture of a synthetic rubber called BuNa-N (a copolymer of butadiene and acrylonitrile) and a thermoplastic called ABS (a terpolymer of acrylonitrile, butadiene and styrene).

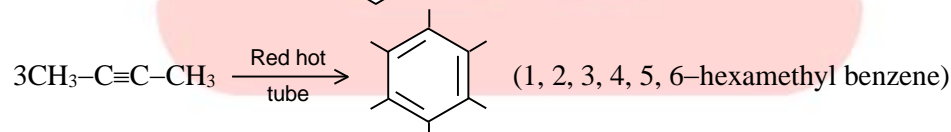
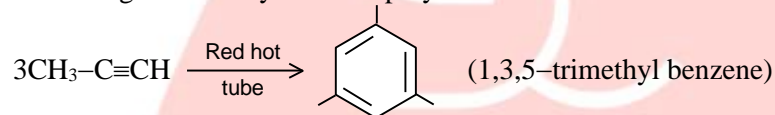
- (iii) Acetic acid adds to ethyne in the presence of  $\text{Hg}^{2+}$  ion to give vinyl acetate, which is used as monomer in the preparation of polyvinyl acetate (PVA).



- (iv) Acetylene when passed through a hot metallic tube polymerizes to give benzene.

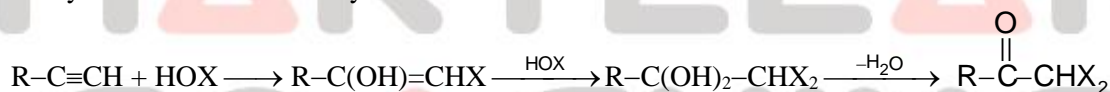


Higher homologues of acetylene also polymerize under similar conditions to give derivatives of benzene.



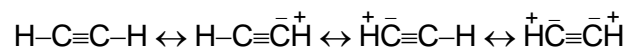
### 3.10 ADDITION OF HYPOHALOUS ACID

Alkynes react with hypohalous acid in the molar ratio of 1 : 2 to give dihalo ketones. Acetylene forms dihaloaldehyde.



### 3.11 ACIDITY OF ALKYNES

The acidic nature of hydrogen in acetylene is characteristic of hydrogen in the group  $\equiv\text{CH}$  and it is because the  $\equiv\text{C---H}$  bond has considerable ionic character due to resonance.



There is, evidence that the electronegativity of a carbon atom depends on the number of bonds by which it is joined to its neighbouring carbon atom. Since  $\pi$ -electrons are more weakly bound than  $\sigma$ -electrons, the electron density around a carbon atom with  $\pi$ -bonds is less than that when only  $\sigma$ -bonds are present. Thus a carbon atom having one  $\pi$ -bond has a slight positive charge compared with a carbon atom, which has only  $\sigma$ -bonds. Hence, the electronegativity of an  $\text{sp}^2$  hybridised carbon atom is greater than that of an  $\text{sp}^3$  hybridised carbon atom. Similarly, a carbon atom, which has two  $\pi$ -bonds, carries a small positive charge, which is greater than that carried by a carbon atom with only one  $\pi$ -bond. Thus the electronegativity of an  $\text{sp}$  hybridized carbon atom is greater than that of an  $\text{sp}^2$  hybridised carbon atom. Thus, more the 's' character a bond has, the more electronegative is that carbon atom. Therefore the attraction for electrons by hybridized carbons will be  $\text{sp} > \text{sp}^2 > \text{sp}^3$ .

Therefore, the hydrogens in terminal alkynes are relatively acidic. Acetylene itself has a  $\text{pK}_a$  of about 25. It is a far weaker acid than water ( $\text{pK}_a = 15.7$ ) or the alcohols ( $\text{pK}_a = 16$  to 19) but it is much more acidic than

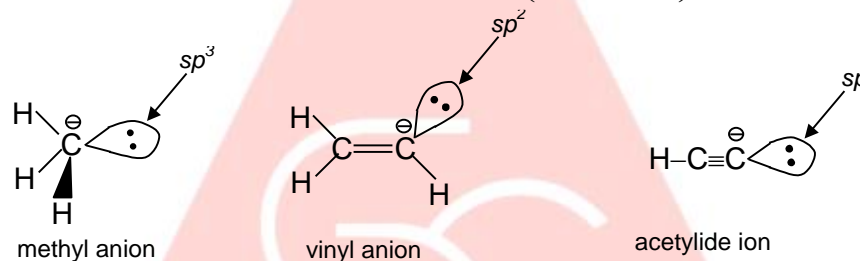


ammonia ( $pK_a = 34$ ). A solution of sodium amide in liquid ammonia readily converts acetylene and other terminal alkynes into the corresponding carbanions.



This reaction does not occur with alkenes or alkanes. Ethylene has a  $pK_a$  of about 44 and methane has a  $pK_a$  of about 50, which means that they are weaker acids than  $NH_3$ .

From the foregoing  $pK_a$ 's we see that there is a vast difference in the basic character of the carbanions  $RC\equiv C^-$ ,  $CH_2=CH^-$  and  $CH_3^-$ . This difference can be explained in terms of the character of the orbital occupied by the lone-pair electrons in the three anions. Methyl anion has a pyramidal structure with the lone-pair electrons in an orbital that is approximately  $sp^3$  ( $\frac{1}{4}s$  and  $\frac{3}{4}p$ ). In vinyl anion, the lone-pair electrons are in an  $sp^2$  orbital ( $\frac{1}{3}s$  and  $\frac{2}{3}p$ ). In acetylide ion, the lone pair is in an  $sp$  orbital ( $\frac{1}{2}s$  and  $\frac{1}{2}p$ ).



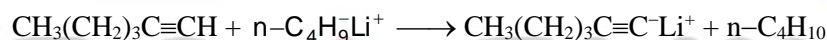
Electrons in  $s$ -orbitals are held closer to the nucleus than they are in  $p$ -orbitals.

This increased electrostatic attraction means that  $s$ -electrons have lower energy and greater stability than  $p$ -electrons. In general, the greater the amount of  $s$ -character in a hybrid orbital containing a pair of electrons, the less basic is that pair of electrons and more acidic is the corresponding conjugate acid. Alternatively, since greater the electronegativity of an atom, the more readily it can accommodate a negative charge and hence less basic the species would be. Basicities of the following carbanions follow the order:  $CH\equiv C^- < CH_2=CH^- < CH_3^-$  and hence the order of acidic strength would be  $HC\equiv CH > CH_2=CH_2 > CH_4$ .

Of course, the foregoing argument applies to hydrogen cyanide as well. In this case, the conjugate base,  $C\equiv N^-$ , is further stabilized by the presence of the electronegative nitrogen. Consequently, HCN is sufficiently acidic ( $pK_a = 9.2$ ) that it is converted to its salt with hydroxide ion in water.



Alkynes are also quantitatively deprotonated by alkyl lithium compounds, which may be viewed as the conjugate base of alkanes.

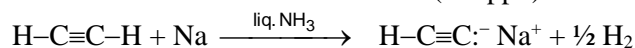
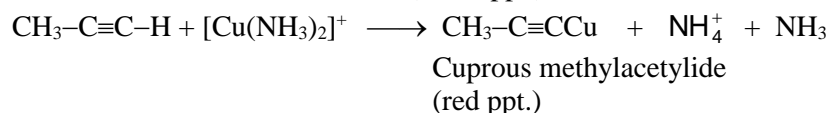
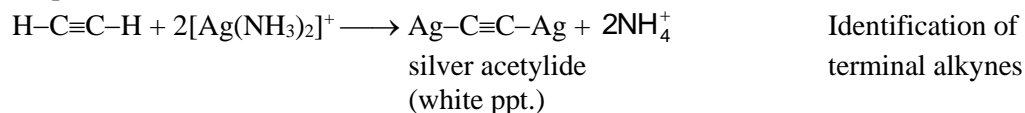


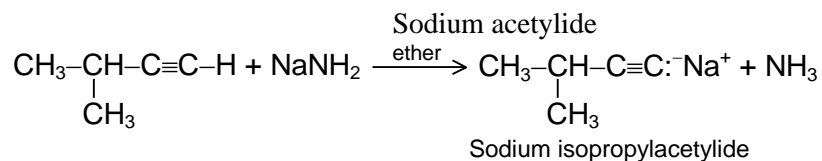
These transformations are simply an acid-base reaction, with 1-hexyne being the acid and  $n$ -butyllithium being the base. Since the alkyne is a much stronger acid than the alkane (by over 20  $pK$  units!), equilibrium lies essentially completely to the right.

Terminal alkynes give insoluble salts with a number of heavy metal cations such as  $Ag^+$  and  $Cu^+$ . The alkyne can be regenerated from the salt and the overall process serves as a method for purifying terminal alkynes. However, many of these salts are explosively sensitive when dry and should always be kept moist.



For example,





### 3.12 DIELS-ALDER REACTION

This is a reaction involving cyclo addition of alkene or alkyne, commonly referred to as the dienophile with a conjugated diene system. The product formed in the reaction is usually a six membered ring and the addition takes place in the 1, 4-position.

