UNIT 5 ADDITION TO CARBON-CARBON MULTIPLE BOND SYSTEM

Structure

5.1 INTRODUCTION

In the last two units you have studied about substitution reactions. In this unit you will study addition reactions of carbon-carbon double bond and carbon-carbon triple bond.

The most characteristic way in which carbon-carbon double (alkenes) or carbon-carbon triple bonds (alkynes)reacts,is by addition to the multiple (double or triple) bonds. Alkenes consist of one σ bond and one π bond, while alkynes contain one σ bond and two π bonds. Since π bonds are weaker than σ bonds, most of the reactions would involve the breaking of the weak π bond(s).

Addition reactions at the carbon-carbon multiple bonds can be divided into three types:

- Electrophilic additions
- Free radical additions
- Concerted additions

In this unit we shall discuss each type of the addition reactions in detail.

Objectives

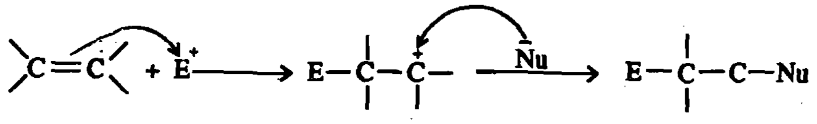
After studying this unit, you should be able to:

- list types of addition reactions,
- discuss the mechanism of electrophilic addition reactions,
- explain the 1, 2 and 1,4-addition of dienes,
- explain the mechanism of free radical addition reactions, and
- explain the mechanism of concerted addition reactions.

5.2 ELECTROPHILIC ADDITION REACTIONS

Most reactions of alkenes or alkynes occur when an electron-deficient substance (an electrophile) attacks the π bond. Most commonly the attacking reagents are acid, either a mineral acid or a Lewis acid, i.e., any species which is electron-deficient and seeks to share an electron pair of some other substance. By contrast, there is little tendency for a double or a triple bond to react with a base.

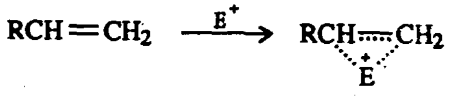
In addition reaction of an alkene, the π bond is broken and its pair of electrons are used in the formation of two new σ bonds. The sp^2 hydridised carbon atoms are rehybridised to sp^3 in the process. Compounds containing π bonds are usually of higher energy than those having σ bonds. Consequently, an addition reaction is usually an exothermic process.



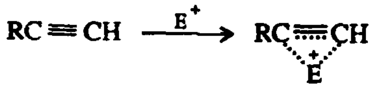
In the region of the double bond there is a cloud of π-electrons above and below the plane of the bonded atoms. The π electrons are loosely held by the nuclei and are thus easily available to electron seeking reagents. Such reagents are called electrophilic reagents or electrophiles and the reactions are called electrophilic addition reactions.

In general, alkynes undergo almost the same types of reactions as alkenes. Electron density around the carbon-carbon triple bond is higher than that around carbon-carbon double bond. So, we might expect alkynes to be more reactive towards electrophilic reagents than alkenes, but the reverse is true, i.e., alkenes are more reactive than alkynes. You may be surprised at this trend. To understand the reason, consider the nature of the carbon atoms of alkenes and alkynes. You may recall that in alkenes carbon atoms are sp^2 hydridised and in alkynes, these are sp hydridised. Since an sp hybridised carbon is more electronegative than an sp^2 hybridised carbon atom, the π electrons are more tightly held by the carbon nuclei in the former case and, hence, they are less easily available for combination with an electrophile. Thus, electrophilic addition at the sp hybridised carbon atoms in an alkyne should be less facile.

Another explanation may be attributed to the formation of highly strained unstable cyclic alkenyl cation from an alkyne as compared to strain-free alkyl cation formed from an alkene.



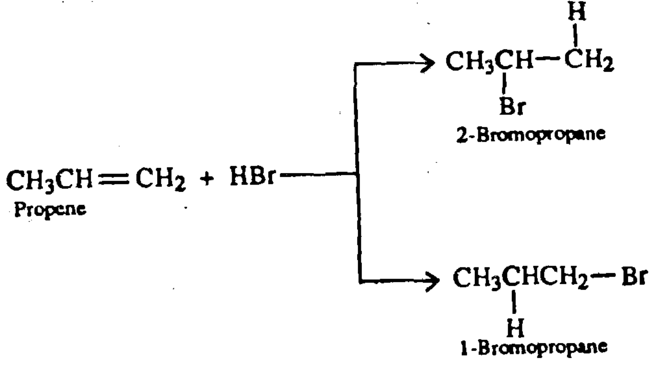
Alkyl cation



Both these factors may account for the diminished reactivity of alkynes towards electrophilic addition. Let us study some important electrophilic addition reactions of alkenes and alkynes.

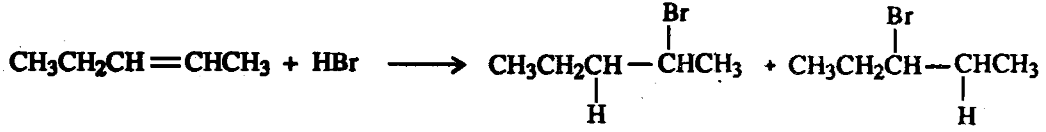
5.2.1 Addition of Hydrogen Halides

Alkyl halide is formed when an alkene reacts with hydrogen halide. This reaction is known as **hydrohalogenation**. The order of reactivity of HX towards alkene is: HI > HBr > HCl > HF. In the case of a symmetrical alkene we get only one product but in case of unsymmetrical alkene we get two different products. Actually only one of the two products is formed in significant amount. For example, when HBr adds to an unsymmetrical alkene like propene, in principle, two products could be formed, i.e., 1-bromopropane and 2-bromopropane.



However, only one product, 2-bromopropane is produced. One would like to know why only one product is formed. A Russian chemist Valdimir Markownikoff studied this question in 1870 and made a generalisation based empirically on his observation. According to the rule named after him as, Markownikoff's rule, the addition of a hydrogen halide to an unsymmetrical alkene takes place in such a way that the negative part of the substrate goes to the carbon atom that contains lesser number of hydrogen atoms.

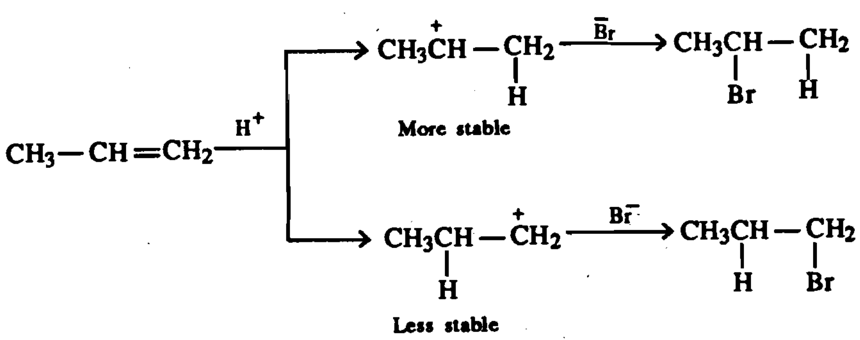
However, when both carbon atoms forming the double bond have the same number of hyrogen atoms in a unsymmetrical alkene, a mixture of products results. For example, when 2- pentene reacts with hydrogen bromide, it gives a mixute of 2-bromopentane and 3-bromopentane.



$$CH_3CH_2CH{=}CHCH_3 + HBr \longrightarrow CH_3CH_2\underset{H}{CH}-\overset{Br}{C}HCH_3 + CH_3CH_2\overset{Br}{C}H-\underset{H}{CH}CH_3$$

2-Pentene **2-Bromopentane** **3-Bromopentane**

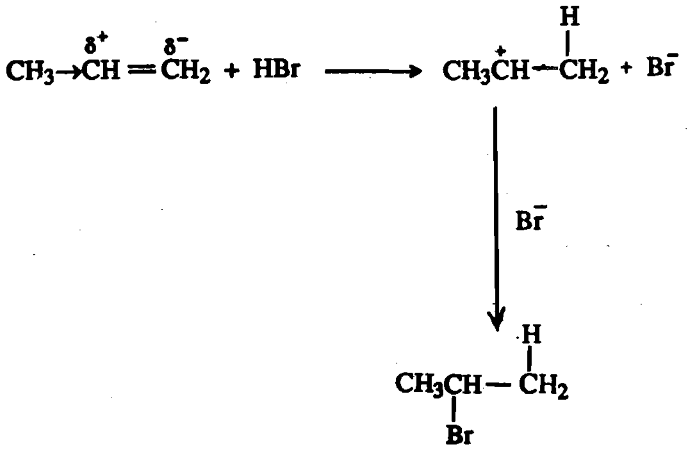
Markownikoff's rule can be explained on the basis of relative stabilities of the carbocations. In the first step i.e., the addition of H$^+$ to propene, there is a possibility of the formation of either primary or secondary carbocation. Since the secondary carbocation is more stable, it will form of 2-bromopropane.



$$CH_3-CH{=}CH_2 \xrightarrow{H^+} CH_3\overset{+}{C}H-\underset{H}{CH_2} \xrightarrow{Br^-} CH_3\underset{Br}{CH}-\underset{H}{CH_2}$$

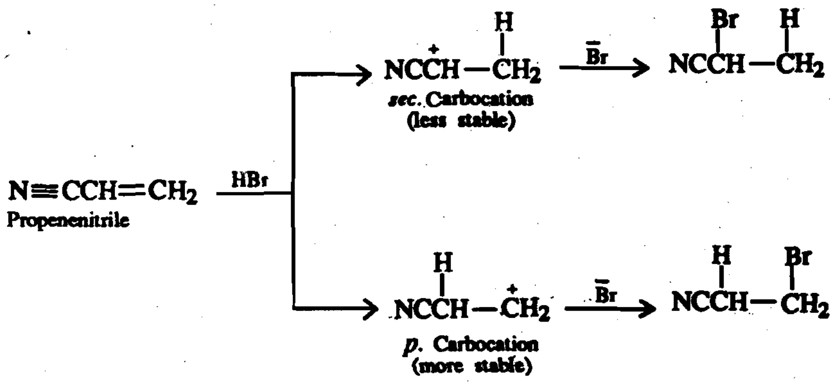
$$CH_3-CH{=}CH_2 \xrightarrow{H^+} CH_3\underset{H}{CH}-\overset{+}{C}H_2 \xrightarrow{Br^-} CH_3\underset{H}{CH}-\underset{Br}{CH_2}$$

We can also understand the Markownikoff's rule by considering the electronic effect of the substitutent on the double bond. For example in propene, due to +I effect of the methyl group, the π electrons are displaced towards the terminal carbon atom which acquires partial negative charge. So, the proton adds on the carbon atom farthest from the methyl group, and then the halide ion adds to the carbocation formed at the adjacent carbon atom.



$$CH_3\rightarrow\overset{\delta^+}{C}H=\overset{\delta^-}{C}H_2 + HBr \longrightarrow CH_3\overset{+}{C}H-\overset{H}{C}H_2 + Br^- \xrightarrow{Br^-} CH_3\underset{Br}{CH}-\overset{H}{C}H_2$$

Now consider another example, *viz.*, addition of HBr to propenenitrile. Addition of HBr to propenenitrile gives 1-bromopropanenitrile as the major product, which is obtained from the primary carbocation.



In the case of propenenitrile, because of the strong electron withdrawing effect of the nitrile group, the secondary carbocation is less stable than primary carbocation. Further the carbocation is separated from the CN group by two carbon atoms and the destabilisation by the inductive effect is less.

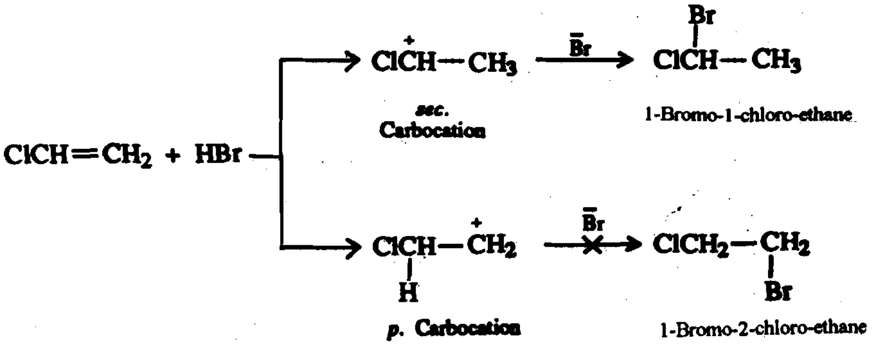
Thus, the Markownikoff's rule can be modified to the following statement — "In the addition of hydrogen halide to alkenes, the more stable carbocation is formed which then adds the negative ion to form the product." This rule is adequate to predict the orientation pattern of addition of unsymmetrical reagents to unsymmetrical alkenes. However, it may be emphasised that this rule is applicable only to the addition of electrophilic reagents.

The products formed from the addition of HBr to some substituted alkene are given in Table 5.1.

Table 5.1 : Orientation pattern addition HBr to substituted ethenes

	Alkene	Product
1.	$CH_3CH=CH_2$	$CH_3\underset{Br}{CH}-CH_3$
2.	$(CH_3)_2C=CH_2$	$(CH_3)_2\underset{Br}{C}-CH_3$
3.	$C_6H_5CH=CH_2$	$C_6H_5\underset{Br}{CH}-CH_3$
4.	$ClCH=CH_2$	$Cl\underset{Br}{CH}-CH_3$
5.	$NCHC=CH_2$	$NCCH_2-CH_2Br$
6.	$(CH_3)_3N^+CH=CH_2$	$(CH_3)_3N^+CH_2-CH_2Br$
7.	$HOOCCH=CH_2$	$HOOCCH_2-CH_2Br$
8.	$F_3CCH=CH_2$	$F_3CCH_2-CH_2Br$

Entry 4 of Table 5.1 is of special interest and illustrates certain general features.

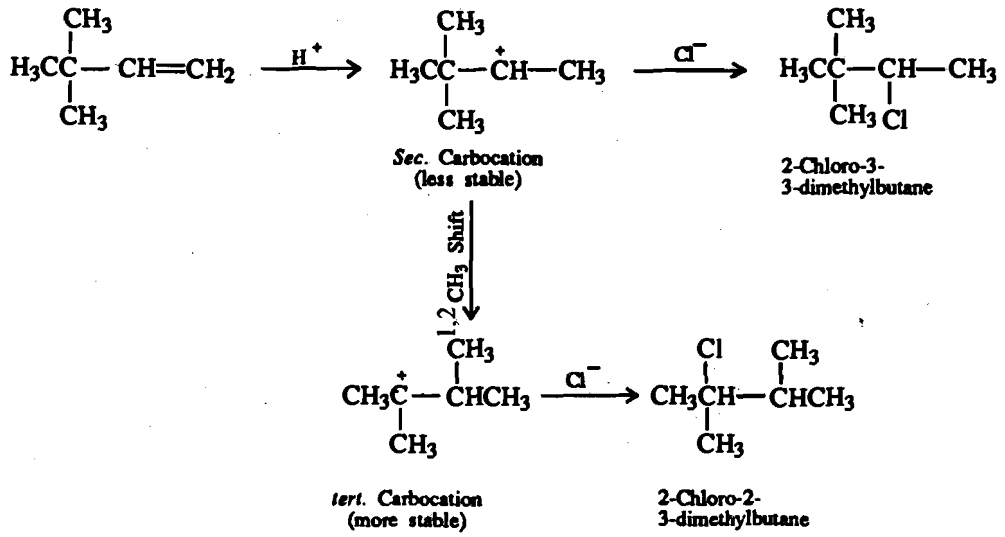


In chloroethene (and other haloethenes), the primary carbocation would be more stable due to inductive effect (similar to the addition of HBr to propenenitrile given earlier).

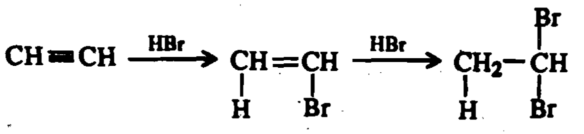
If this were the only effect in operation, the prodcut would be 1-bromo-2-chloroethane because its corresponding carbocation is more stable. There is, however, another effect arising from delocalisation of the lone pair on the chlorine atom with the vacant *p*-orbital of carbocation at C-2 (resonance effect) which stabilises the secondary carbocation. The question is, which of these effects predominates? Formation of 1-bromo-1-chloroethane implies that the lone apir effect apparently prevails over the inductive effect rendering secondary carbocation stabler than the primary carbocation.

Rearrangements take place in other electrophilic additions like hydration, halogenation, etc. also.

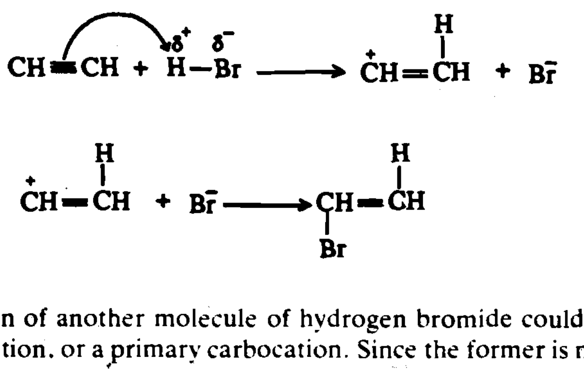
Rearrangement: Rearrangement is one of the characteristics of a carbocation. A carbocation formed, in an addition reaction of a hydrogen halide to an unsymmetrical alkene, often undergoes rearrangement (alkyl or hydride shift) to give a more stable carbocation. For example, addition of HCl to 3,3-dimethyl-1-butene gives two products, 2-chloro-3,3-dimethyl butane (normal product) and 2-chloro, 2,3-dimethylbutane (rearranged product) as shown in following scheme:



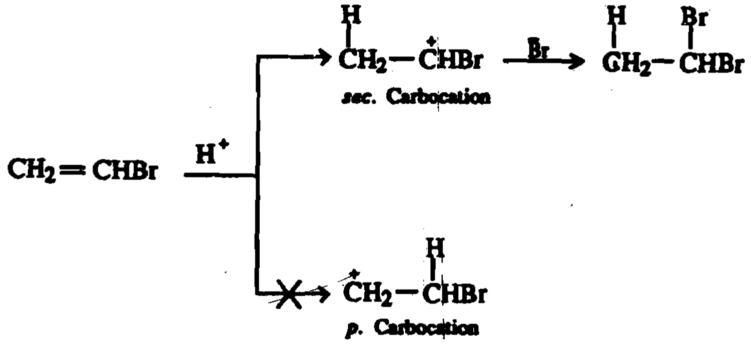
Alkynes also undergo hydrohalogenation. Like alkenes, the addition is in accordance with Markownikoff's rule. For example, ethyne reacts with hydrogen bromide to form first 1-bromoethene and then 1,1-dibromoethane.



The mechanism of the reaction is same as in the hydrohalogenation of alkenes. Addition of one molecule of HBr gives bromoethene.



Addition of another molecule of hydrogen bromide could give either secondary carbocation, or a primary carbocation. Since the former is more stable than the latte. the reaction proceeds via the former to form 1,1-dibromoethane, i.e.,



Because of the electron withdrawing nature of bromine atom, the availability of π electrons in 1-bromoethene is less than that in ethyne. Hence addition of HBr to 1-bromoethene is much slower than to ethyne.

SAQ 1

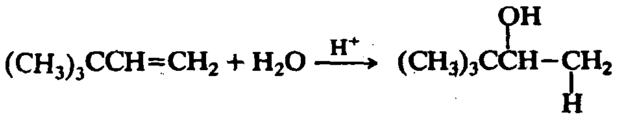
Predict the relative rates of the following alkenes towards HBr

a) $CH_3CH_2CH=CH_2$ b) $CH_2=CH_2$ c) $CH_3CH_2CH=C(CH_3)_2$

……

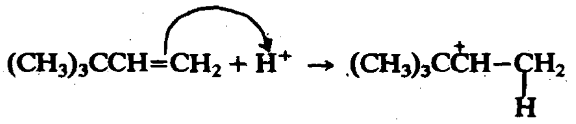
5.2.2 Addition of Water

In the presence of a mineral acid, water adds to the carbon-carbon double bond to give an alcohol. This reaction is called hydration of an alkene.

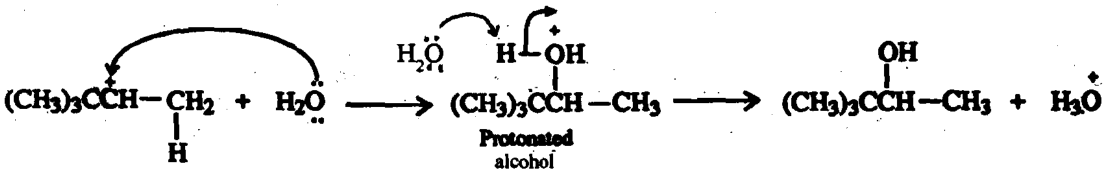


$$(CH_3)_3CCH{=}CH_2 + H_2O \xrightarrow{H^+} (CH_3)_3C\overset{OH}{C}H-\underset{H}{C}H_2$$

This reaction also follows Markownikoff's rule, a pattern with which we are now familiar. As expected, the reaction occurs in two steps. The alkene is first protonated to give a carbocation. Attack of the nucleophile (H_2O) on the carbocation, in the second step, and loss of a proton from the resulting adduct completes the reaction.

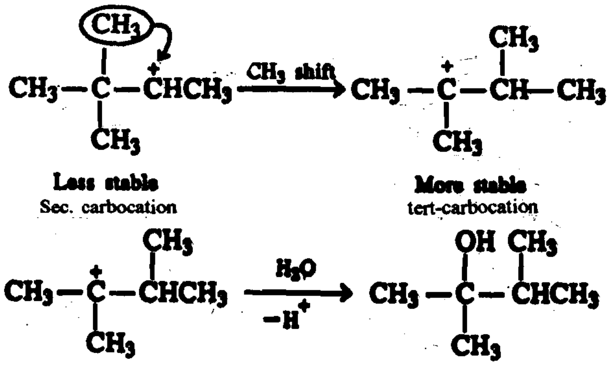


$$(CH_3)_3CCH{=}CH_2 + H^+ \rightarrow (CH_3)_3C\overset{+}{C}H-\underset{H}{C}H_2$$



$$(CH_3)_3C\overset{+}{C}H-\underset{H}{C}H_2 + H_2\ddot{O} \longrightarrow (CH_3)_3C\overset{H-\overset{+}{O}H}{C}H-CH_3 \longrightarrow (CH_3)_3C\overset{OH}{C}H-CH_3 + H_3\overset{+}{O}$$

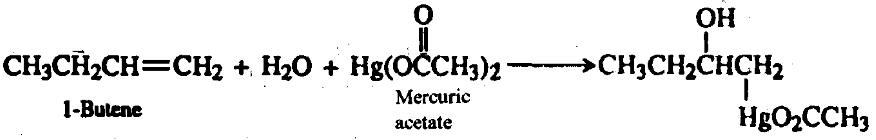
Because a carbocation is involved, rearrangement is possible. Carbocation can undergo a 1,2-shift of CH_3 group to yield the more stable carbocation, e.g.



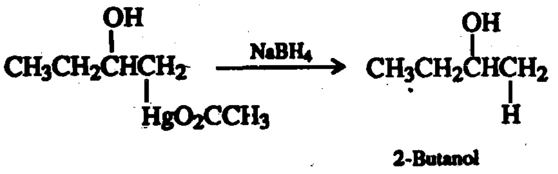
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{C}HCH_3 \xrightarrow{CH_3\ shift} CH_3-\underset{CH_3}{\overset{+}{C}}-\overset{CH_3}{C}H-CH_3$$

$$CH_3-\underset{CH_3}{\overset{+}{C}}-\overset{CH_3}{C}HCH_3 \xrightarrow[-H^+]{H_2O} CH_3-\underset{CH_3}{\overset{OH}{C}}-\overset{CH_3}{C}HCH_3$$

Another method used to accomplish Markownikoff's hydration of an alkene is **oxymercuration-demercuration**. Alkene reacts with mercuric acetate in the presence of water to give hydroxy-mercurial compounds which on reduction accomplishes demercuration and produces an alcohol. The product of oxymercuration is usually reduced with sodium borohydride ($NaBH_4$). Oxymercuration-demercuration reaction usually gives a better yield of alcohols than acid catalysed hydration.



$$CH_3CH_2CH{=}CH_2 + H_2O + Hg(O\overset{\displaystyle O}{\overset{\|}{C}}CH_3)_2 \longrightarrow CH_3CH_2\overset{\displaystyle OH}{\overset{|}{C}}H\underset{\displaystyle HgO_2CCH_3}{\underset{|}{C}}H_2$$

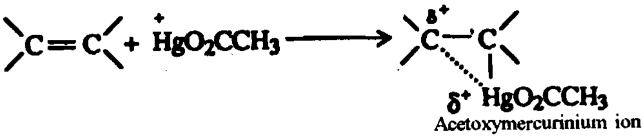


$$CH_3CH_2\overset{\displaystyle OH}{\overset{|}{C}}H\underset{\displaystyle HgO_2CCH_3}{\underset{|}{C}}H_2 \xrightarrow{NaBH_4} CH_3CH_2\overset{\displaystyle OH}{\overset{|}{C}}H\underset{\displaystyle H}{\underset{|}{C}}H_2$$

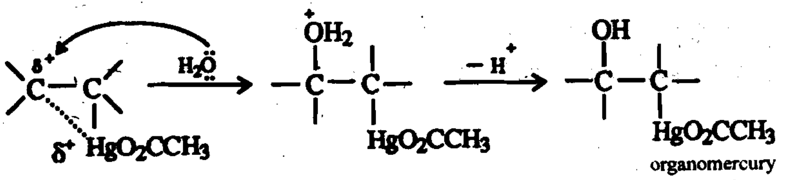
Mechanism: The mechanism of oxymercuration is very similar to that of hydrohalogenation. First mercuric acetate dissociate into $\overset{+}{Hg}O_2CCH_3$ and $\bar{O}_2CCH_3$ e.g.,

$$Hg(O_2CCH_3)_2 \rightleftharpoons \overset{+}{Hg}O_2CCH_3 + \bar{O}_2CCH_3$$

In the first step electrophile $\overset{+}{Hg}O_2CCH_3$ attacks the carbon-carbon double bond and forms a cyclic intermediate called acetoxymercurinium ion.

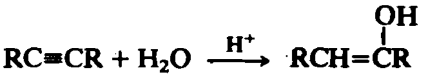

Acetoxymercurinium ion

In the next step nucleophile H_2O attacks on the partially positively charged carbon atom from the side opposite to mercury to give the stable organomercury compound. The organomercury compound on reduction with $NaBH_4$ gives alcohol. We will study about the reduction by $NaBH_4$ in Unit 8.


organomercury compound

Oxymercuration is regiospecific and stereospecific (*anti* addition). The stereospecificity is attributed to formation of a cyclic intermediate.

Like alkenes addition of water to alkyne should give alcohol, e.g.,



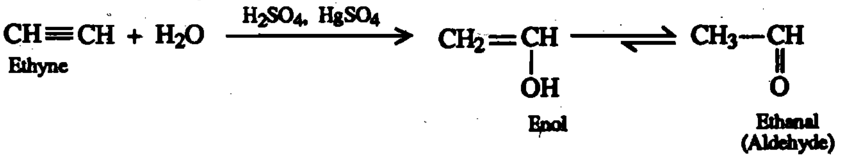
$$RC{\equiv}CR + H_2O \xrightarrow{H^+} RCH{=}\overset{\displaystyle OH}{\overset{|}{C}}R$$

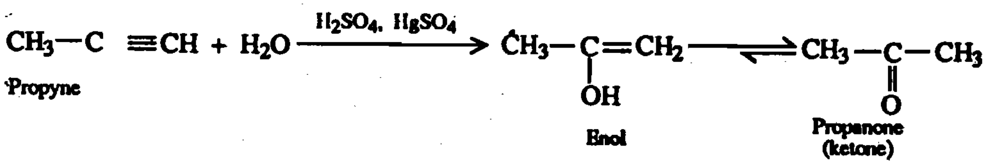
The alcohol produced by hydration of an alkyne, however, is of a special kind known as enol. As the name (en-ol) indicates it has OH group attached to a carbon atom forming a double bond. Infact enols are very unstable and generally undergo isomerization (tautomerism) to give either an aldehyde or a ketone.

$$RCH{=}\overset{\displaystyle OH}{\overset{|}{C}}R \rightleftharpoons RCH_2-\overset{\displaystyle O}{\overset{\|}{C}}R$$

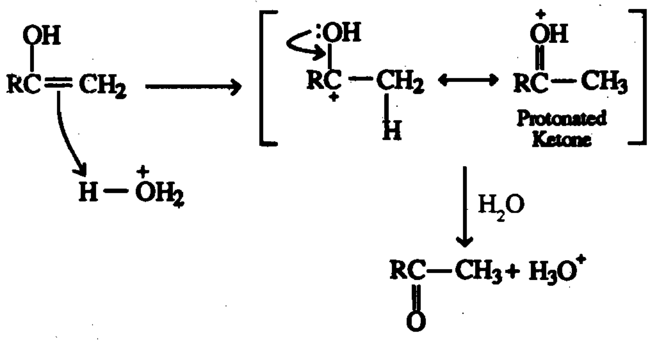
Keto-enol tautomerism does not require acid catalysis though acids expedite the equilibrium.

Enols are converted to aldehydes or ketones by prototropic shift, i.e., shift of a proton from oxygen to carbon. This phenomenon is known as **Keto-enol tautomerism**, and the individual compounds are known as **tautomers**. For example, when ethyne reacts with water, it gives ethanal, an aldehyde, while 1-propyne gives propanone a ketone, i.e.,

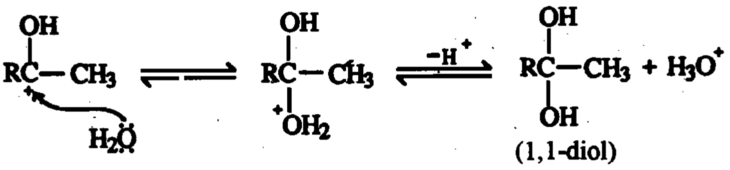




The enol is converted into aldehyde or ketone by a mechanism that is similar to hydration of a double bond. The enol double bond is protonated to give a carbocation. The carbocation in this example, as its resonance structures show, is a protonated ketone. Instead of adding water, this ion loses a proton to give ketone.

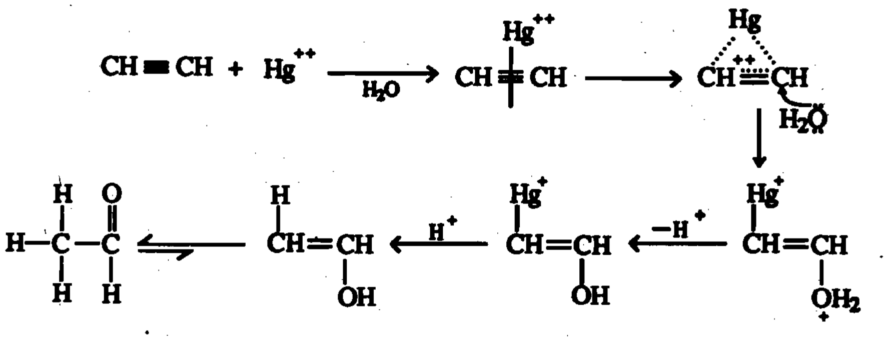


You may now ask why the carbocation is not attacked by a water molecule., i.e. ?



The answer is that this reaction is reversible and the equilibrium between the ketone and the corresponding diol in most cases favours ketone.

Alkynes cannot be hydrated as easily as simple alkenes, because of their lower reactivity towards electrophilic addition. However, in the presence of mercuric sulphate, a catalyst, hydration occurs readily. A possible explanation of the function of the catalyst is that Hg^{++} ion being of a large size, readily forms a bridged ion, a π complex, which then reacts as shown below:



SAQ 2

Predict the product(s) of the following reactions

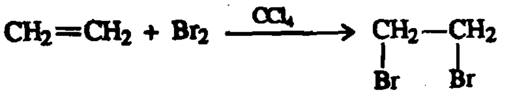
a) $(CH_3)_3CCH=CH_2 + H_2O \xrightarrow{H^+}$

b) $CH_3CH_2CH=CH_2 + H_2O + Hg(OCCH_3)_2 \rightarrow \overset{A}{\ldots\ldots} \xrightarrow{NaBH_4} \overset{B}{\ldots\ldots}$

c) $CH_3C\equiv CH + H_2O \xrightarrow{H^+} \ldots\ldots\ldots$

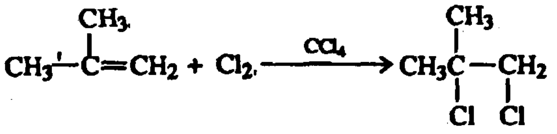
5.2.3 Addition of Halogen

Treatment of alkenes with halogens gives 1,2-dihalogenated alkanes or dihalides. Bromine and chlorine are effective electrophilies. This reaction is by far the best method of preparing vicinal dihalides, e.g.,



$$CH_2{=}CH_2 + Br_2 \xrightarrow{CCl_4} \underset{Br}{CH_2}{-}\underset{Br}{CH_2}$$

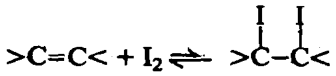
1,2-Dibromoethane



$$CH_3{-}\overset{CH_3}{C}{=}CH_2 + Cl_2 \xrightarrow{CCl_4} CH_3\overset{CH_3}{\underset{Cl}{C}}{-}\underset{Cl}{CH_2}$$

1,2-Dichloro
2-methylpropane

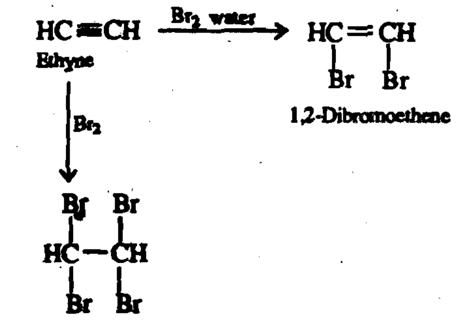
Fluorine and iodine generally do not add to the carbon-carbon double bond or carbon-carbon triple bond. Fluorine undergoes explosive reaction with alkenes or alkynes, the reaction, therefore, require special techniques. Addition of iodine to alkene is a reversible reaction, i.e., the 1,2-diiodo product is unstable and loses I_2 to reform the alkene.



$$>C{=}C< + I_2 \rightleftharpoons >\overset{I}{C}{-}\overset{I}{C}<$$

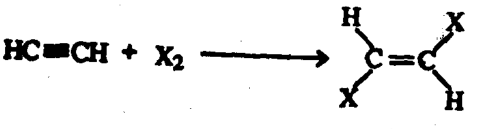
These reactions are generally carried out in an inert solvent (e.g., CCl_4). Since at high temperature substitution products may be formed, hence these reactions are carried out at room temperature.

Like alkenes, alkynes also react with chlorine and bromine to yield tetrahaloalkanes. Two molecules of halogen add to the triple bond. A dihaloalkene is an intermediate and can be isolated using proper reaction conditions. Ethyne, for instance, on treatment with bromine water gives only 1,2-dibromoethene whereas with bromine alone, it forms 1,1,2,2-tetraboromoethane.



1,1,2,2,-Tetrabromoethane

Addition of halogens to ethyne is stereoselective; the predominant product is the *trans* isomer.

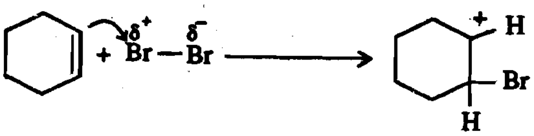


trans Product

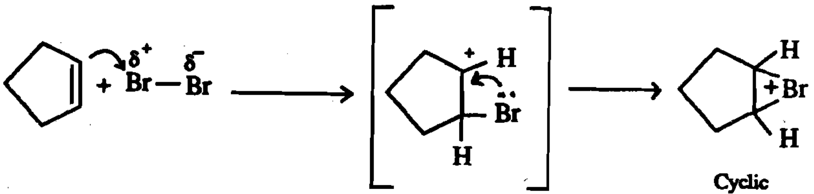
This reaction is very useful for detection of the carbon-carbon double bond. The test reagent (Br_2 in CCl_4) has a reddish brown colour of bromine while the dihalide is colourless. After addition of Br_2 to carbon-carbon double bond, rapid decolourisation occurs, which confirms the presence of carbon-carbon double bond.

Mechanism: Although bromine is non-polar, it is nevertheless highly polarisable. In the vicinity of carbon-carbon double bond, the bromine molecule becomes polarised and, hence, partial positive charge (δ^+) is developed on one bromine atom and partial negative (δ^-) charge is developed on the other bromine atom.

In the first step, the π electrons attack the positive end of the polarised bromine molecule, displacing bromide ion and forming carbocation.

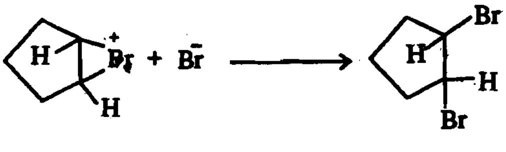


Immediately in the next step, Br^- attacks the carbocation to yield the additon product. Since carbocation is coplanar,, and sp^2 hybridised, Br^- can attack from both the sides to give a mixture of *cis* and *trans* products. However, only the *trans* product was observed. The explanation was suggested in 1937 by Kimball and Roberts who postulated that true reaction intermediate is not a carbocation but a cyclic bromonium ion.



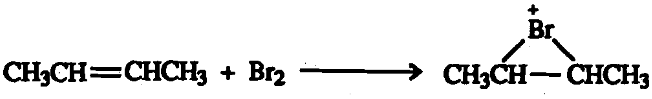
Cyclic bromonium ion

The bromide ion must attack from the rear side of the leaving group in the nucleophilic displacement reaction. Therefore, the bromide ion attacks exclusively on the side opposite to the bromonium ion to yield only the *trans* product. This is also known as *anti* addition.



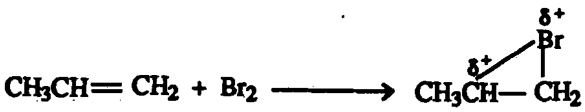
trans Product

Addition of Br_2 to a symmetrical alkene gives a symmetrical bromonium ion. However, addition of Br_2 to an unsymmetrical alkene gives an unsymmetrical bromonium ion, in which, most of the positive charge is carried on the more substituted carbon. i.e.,



$$CH_3CH{=}CHCH_3 + Br_2 \longrightarrow CH_3\overset{}{CH}{-}CHCH_3 \;(\overset{+}{Br} \text{ bridging})$$

Symmetrical bromonium ion



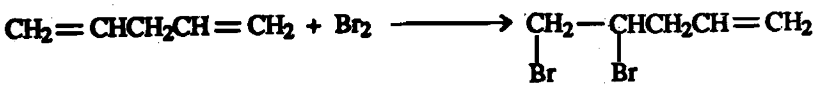
$$CH_3CH{=}CH_2 + Br_2 \longrightarrow CH_3\overset{\delta+}{CH}{-}CH_2 \;(\overset{\delta+}{Br} \text{ bridging})$$

Unsymmetrical bromonium ion

In the symmetrical bromonium ion the attack by a nucleophile could take place at either carbon. However, in case of unsymmetrical bromonium ion the nucleophile will attack the more substituted carbon.

5.2.4 Addition to Conjugated Dienes

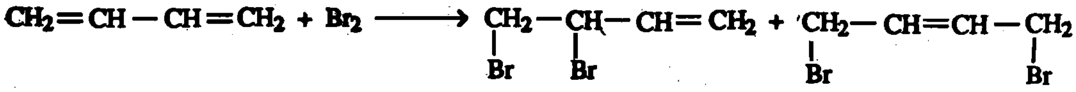
In isolated diene both the double bonds react independently, as though they are in different molecules. Reaction of an isolated diene say 1,4-pentadiene with bromine gives 4,5-dibromo-1-pentene.



$$CH_2{=}CHCH_2CH{=}CH_2 + Br_2 \longrightarrow \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{C}}HCH_2CH{=}CH_2$$

1,4-Pentadiene 4,5-Dibromo-1-pentene

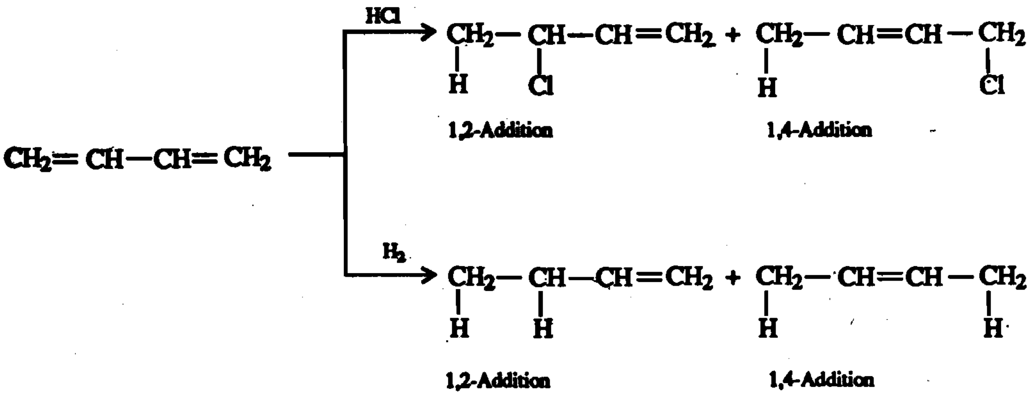
Conjugated dienes behave differently from isolated dienes. Conjugated dienes undergo normal as well as unexpected addition reactions. When a conjugated diene, say 1,3-butadiene is treated with bromine, two dibromo derivatives are obtained. One of these is the expected 3,4-dibromo-1-butene due to 1,3-butadiene. The first step the unexpected 1,4-dibromo-2-butene due to 1,4-addition (major product).



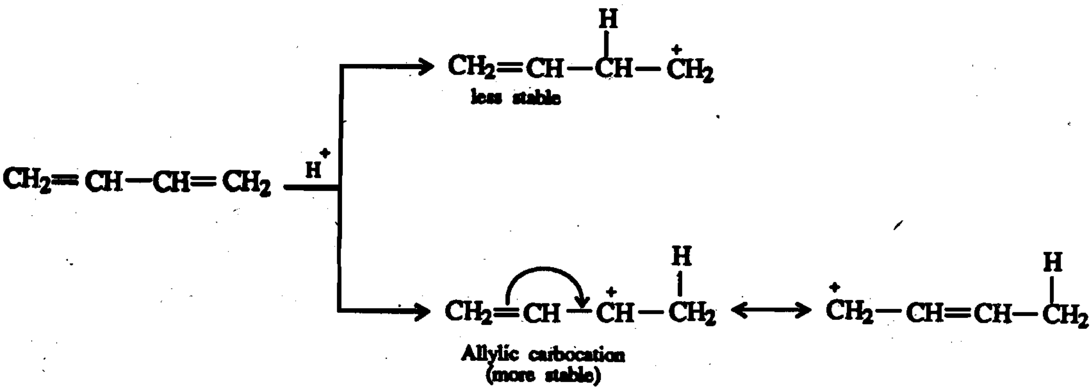
$$CH_2{=}CH-CH{=}CH_2 + Br_2 \longrightarrow \underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH}}-CH{=}CH_2 + \underset{Br}{\underset{|}{CH_2}}-CH{=}CH-\underset{Br}{\underset{|}{CH_2}}$$

1,2-Addition 1,4-Addition

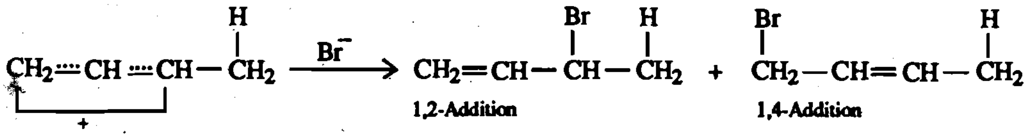
Similarly reactions of HCl and H_2 with conjugated diene provide not only 1,2-addition product but also 1,4-addition product, e.g.



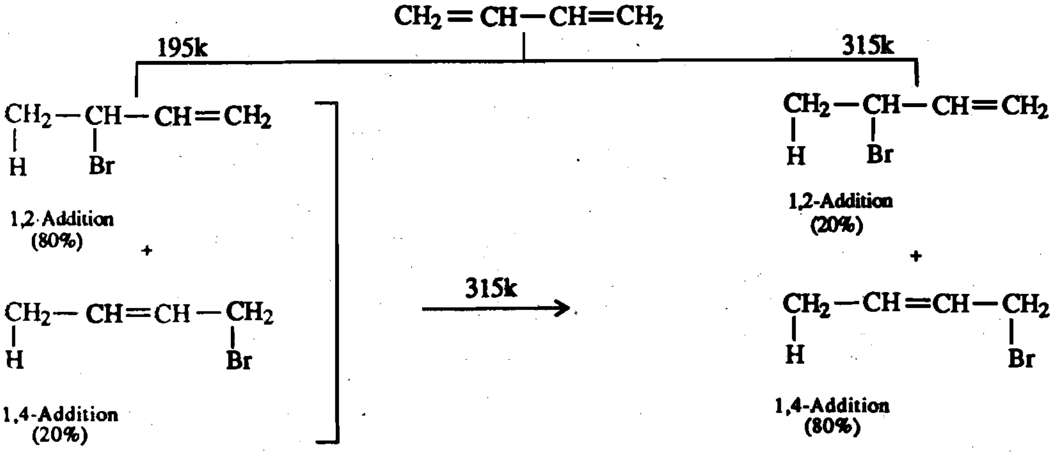
Addition at 1,2-position is understandable but how can we account for the products that are obtained due to 1,4-addition. To understand this, let us examine the mechanism of the addition of hydrogen bromide to 1,3-butadiene. The first step involves the formation of carbocation. Hydrogen may attach itself to either C_1 or C_2. The addition of the hydrogen at C_2 would give rise to a unstable primary localised carbocation. But the addition at C_1 results in the formation of resonance stabilised allylication. This also explain the enhanced reactivity of dienes over isolated double bonds.



In the second step Br^- can attack at either C_1 or C_3 since both share the positive charge. Thus a mixture of 1,2- and 1,4-addition products is obtained.

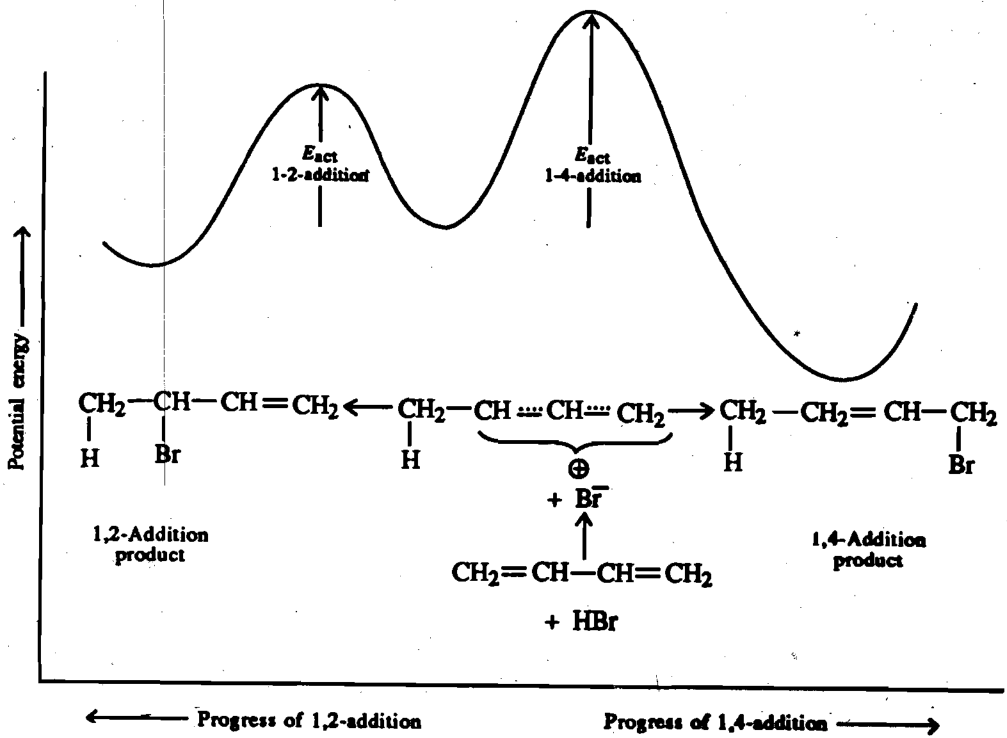


Now one can ask whether these two products are formed in equal amounts or in different ratio. It is interesting to note that the product composition in these reactions varies at different temperature. To understand this take the example of addition of HBr to 1,3-butadiene. HBr when added to 1,3-butadiene at low temperature (195 K), the 1,2-product (80%) predominates over 1,4-product (20%). While at higher temperature (315 K) the 1,4-product (80%) predominates over 1,2-product (20%). At intermediate temperature, a mixtures of intermediate composition are obtained.



It has also been observed that warming 1,2-product to 315 K with a trace of acid results in an equilibrium mixture in which 1,4-product predominates.

How can we explain these observations? Let us examine the reaction by drawing a potential energy diagram (Fig. 5.1). At low temperature, the addition of HBr to 1,3-butadiene gives 80% 1,2-product. This shows that 1,2-addition has the low energy of activation (E_{act}) and thus, the 1,2-product is formed faster than the 1,4-product. The relative rates of the reaction control the product ratio.



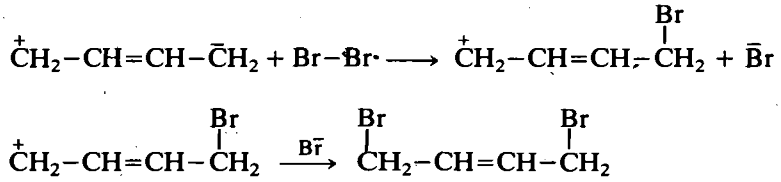
At higher temperature, a greater percentage of molecules can reach the higher-energy state, and the more stable, 1,4-product predominates. At higher temperature, the relative stabilities of the products control the product ratio. Thus, we can say 1,2-product is kinetically controlled while the 1,4-product is thermodynamically controlled.

Formation of 1,4-product can also be explained on the basis of electrometic effect. Butadiene can undergo the electromieric effect in two stages.

i) $CH_2{=}CH{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}\overset{+}{C}H{-}\bar{C}H_2$

ii) $CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\bar{C}H_2$

Second ionic species is more stable as the charges are further apart in this as compared with the first. In an ionising solvent the addition of Br_2 takes place in the second species to give 1,4-addition product.



$$\overset{+}{C}H_2{-}CH{=}CH{-}\bar{C}H_2 + Br{-}Br \longrightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\underset{}{\overset{Br}{\overset{|}{C}}}H_2 + \bar{B}r$$

$$\overset{+}{C}H_2{-}CH{=}CH{-}\overset{Br}{\overset{|}{C}}H_2 \xrightarrow{Br^-} \overset{Br}{\overset{|}{C}}H_2{-}CH{=}CH{-}\overset{Br}{\overset{|}{C}}H_2$$

SAQ 3

Fill in the blanks:

a) When a conjugated diene is treated with halogen it gaves normal .... product and unexpected .... product.

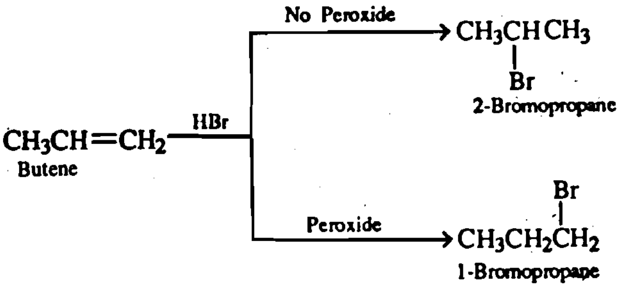
b) Addition of H^+ to 1,3-butadiene gives .... carbocation and .... carbocation.

c) When HBr is added to 1,3-butadiene at low temperature .... predominate and at high temperature .... predominates.

d) In the addition of HBr to conjugated diene the .... is kinetically controlled and the .... is thermodynamically controlled.

5.3 FREE RADICAL ADDITION REACTIONS

The above discussion may give you the impression that addition of hydrogen halides to unsaturated hydrocarbons always gives Markownikoff's product. But it is not so. After extensive study of the mechanism of addition of HBr to different alkenes, it was found by Kharasch and Mayo that in the presence of a peroxide the product obtained was contrary to Markownikoff's rule. Such additions are sometimes referred to as anti-Markownikoff additions. Since the orientation is reversed in the persence of a peroxide, this is also known as the peroxide effect. For example, the addition of hydrogen bromide to propene in the presence of peroxides gives 1-bromopropane rather than 2-bromopropane. However, this effect is not observed with HCl or HI.

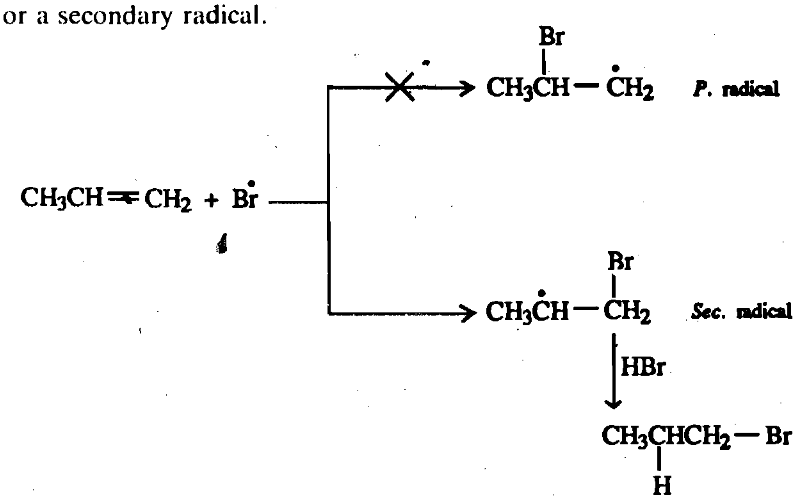


The intermediate in the peroxide catalysed reaction is a free radical and not a carbocation. The function of peroxide is to generate the free radical:

$$(RCO_2)_2 \longrightarrow 2RC\dot{O}_2 \longrightarrow 2\dot{R} + 2CO_2$$

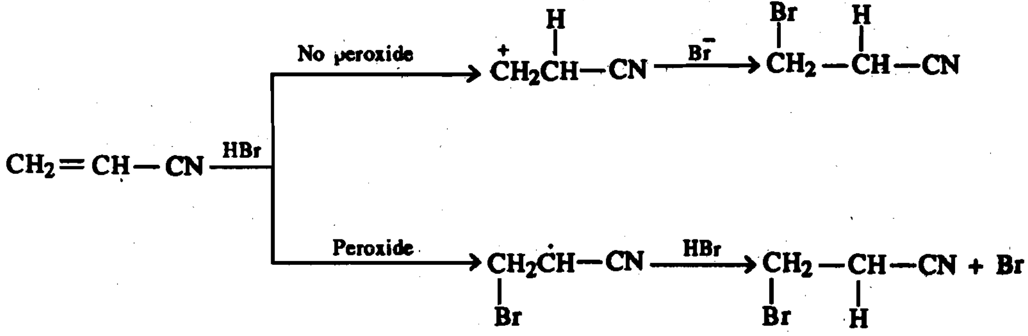
$$\dot{R} + HBr \longrightarrow RH + \dot{B}r$$

Bromine radical can add to either of the two carbon atoms producing either a primary or a secondary radical.



The bromine radical prefers to react at the terminal carbon to give a secondary radical because, the secondary radical is more stable than a primary radical. The orientation of addition of the free radical is controlled on the principle that it takes place in a manner such that the more stable radical, of the possible alternatives, is generated. Consequently, the final product of reaction of HBr is (in presence of peroxide) generally the one with bromine attached to the less substituted carbon atom.

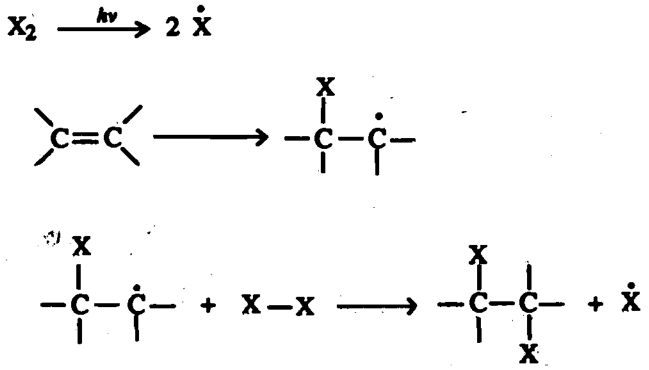
Now let us take the example of propenenitrile. How would propenenitrile react with HBr in the presence of peroxides? Reaction of propenenitrile with HBr both in the presence as well as and in the absence of peroxide yields 1-bromopropanenitrile



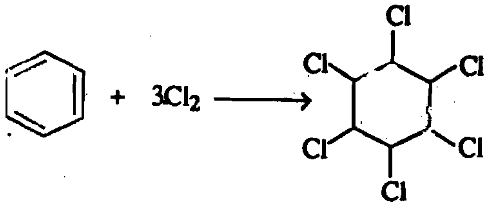
We see that the same product is formed by an entirely different mechanisms. On the basis of the principles discussed above, it is possible to predict the direction of orientation in either case.

Now let us see what is the stereochemistry of free radical addition?. In most of the reported cases, it is *trans*. 1-Bromocyclohexene reacts with HBr in the presence of peroxide to give *cis* 1,2-dibromocyclohexane, in which the two components of the addendum, viz., H and Br have *trans* stereochemistry.

In section 5.2.3 you have studied the halogenation of alkene by ionic mechanism. Halogenation of alkenes can also be carried in the presence of light or peroxides, which follows free radical mechanism as shown below:



An industrial process involving addition of free radicals across double bonds is the reaction of chlorine with benzene in presence of light. Of the theoretically possible eight isomers only three, viz., α, β and γ are formed in substantial amounts. It is well known that the γ-isomer, called gammexane is a potent insecticide.



In this process chlorine radical is formed by homolytic fission of Cl_2.

You will study free radical addition reactions in more detail in Unit 10.

SAQ 4

Complete the following reactions

a) $CH_3\overset{CH_3}{C}{=}CH_2 + HBr \xrightarrow{\text{Peroxide}}$ ......

b) $CH_2{=}CHCN + HBr \xrightarrow{\text{Peroxide}}$ ......

c) $CH_2{=}CHCN + HBr \longrightarrow$ ....

5.4 CONCERTED ADDITION REACTIONS

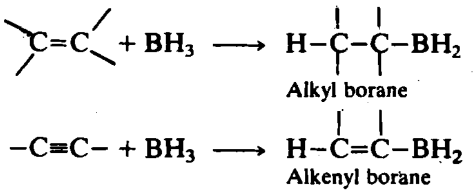
In contrast to electrophilic addition reaction there are group of reagents which react with double bond from the same face of the double bond. These do not involve highly charged intermediates like carbocation. These are known as concerted addition reactions. Some important examples of concerted addition reactions are discussed below.

Organoboranes were discovered in the 1950s by Herbert C. Brown, who was awarded a Nobel Prize in 1979 for his work with organoboron compounds.

5.4.1 Hydroboration

Hydroboration is a reaction in which diborane, $(BH_3)_2$ adds to a carbon-carbon double bond or carbon-carbon triple bond to yield an organoborane. A new carbon-hydrogen bond and a new carbon-boron bond are formed.

Addition of borane to alkenes gives alkyl boranes while addition of borane to an alkyne gives alkenyl borane.

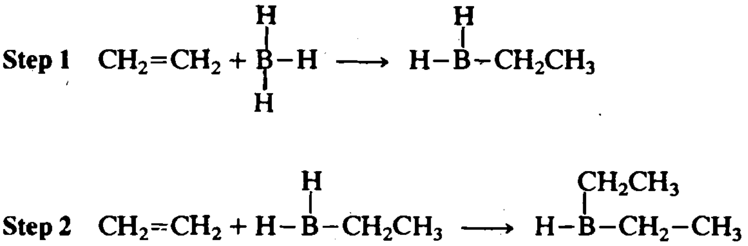


Alkyl borane

Alkenyl borane

This reaction is very facile and requires only a few seconds for completion at 275 K and gives organoboranes in quantitative yield in ether solvents.

The addition takes place in a stepwise fashion via successive addition of each boron hydrogen bond to the alkene. The sequence of reaction is called **hydroboration**.

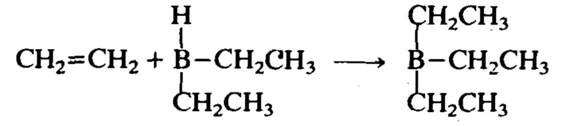


Step 1 $CH_2{=}CH_2 + H{-}\underset{H}{\overset{H}{B}}{-}H \longrightarrow H{-}\overset{H}{B}{-}CH_2CH_3$

Step 2 $CH_2{=}CH_2 + H{-}\overset{H}{B}{-}CH_2CH_3 \longrightarrow H{-}\overset{CH_2CH_3}{B}{-}CH_2{-}CH_3$

Borane (BH_3) itself is unknown but its dimer, diborane (B_2H_6) behaves as if it were the hypothetical monomer.

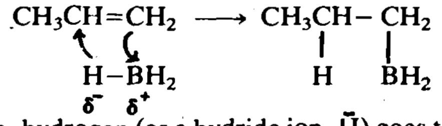
Step 3



$$\mathrm{CH_2{=}CH_2 + \overset{\displaystyle H}{\underset{\displaystyle CH_2CH_3}{B}}{-}CH_2CH_3 \longrightarrow \overset{\displaystyle CH_2CH_3}{\underset{\displaystyle CH_2CH_3}{B}}{-}CH_2CH_3}$$

Triethyl borane

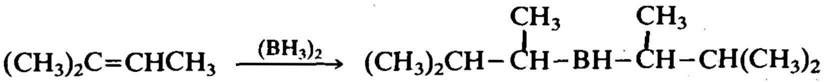
Sometimes the hydroboration reaction is described as *anti*-Markownikoff's addition. This is true only in a literal sense, because in this reaction hydrogen is the electronegative portion of the molecule instead of being the electropositive portion as in other cases.



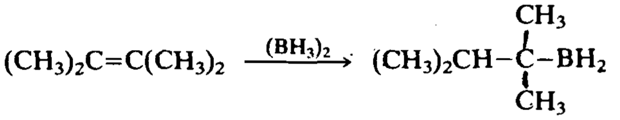
$$\mathrm{\underset{\underset{\delta^-\ \ \delta^+}{H-BH_2}}{CH_3CH{=}CH_2} \longrightarrow CH_3\underset{H}{CH}-\underset{BH_2}{CH_2}}$$

As shown above, hydrogen (as a hydride ion, $\bar{H}$) goes to the more substituted carbon atom. The result appears to be *anti*-Markownikoff's addition.

The ease of reaction decreases with the increase in the alkyl substituents on the double bond, e.g., trisubstituted alkenes form dialkylboranes and tetrasubstituted alkenes yield only monoalkylboranes.



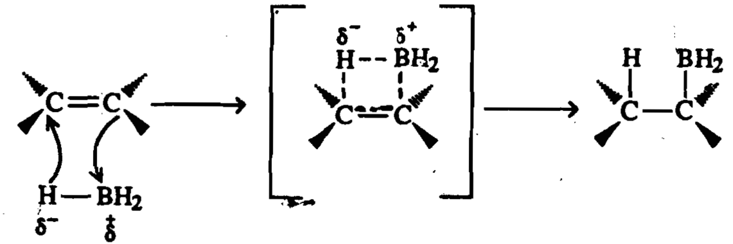
$$\mathrm{(CH_3)_2C{=}CHCH_3 \xrightarrow{(BH_3)_2} (CH_3)_2CH-\overset{CH_3}{CH}-BH-\overset{CH_3}{CH}-CH(CH_3)_2}$$



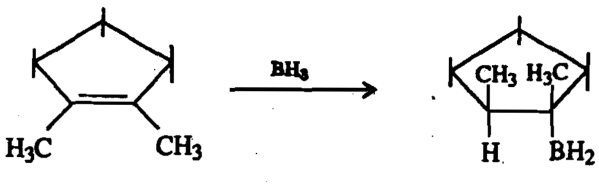
$$\mathrm{(CH_3)_2C{=}C(CH_3)_2 \xrightarrow{(BH_3)_2} (CH_3)_2CH-\overset{CH_3}{\underset{CH_3}{C}}-BH_2}$$

Stereochemistry

In hydroboration the boron and the hydride ion add to the two carbon atoms of the double bond simultaneously. This means that B and H must add from the same side of the double bond. Such addition reactions are called *cis*-additions or *syn*-additions.



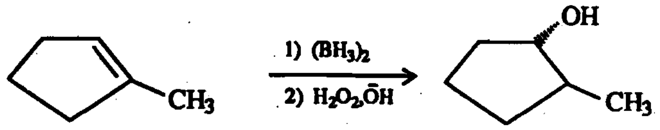
When an organoborane is subsequently oxidised to an alcohol, the hydroxyl group ends up in the same position as the boron atom that it has replaced, that is, with the retention of configuration at that carbon.

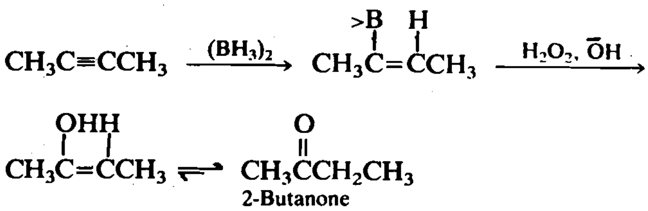


The organoboranes are versatile compounds capable of undergoing a variety of chemical transformations. Some important reactions of organoboranes are given below:

i) One of the most important reactions of organoboranes is H_2O_2 oxidation. Oxidation of an organoborane by alkaline H_2O_2 gives the corresponding alcohol. It appears as if water had been added to the double bond in an *anti*-Markownikoff's manner.

$$\mathrm{3\,CH_3CH_2CH{=}CH_2 \xrightarrow{BH_3} (CH_3CH_2CH_2CH_2)_3B \xrightarrow{H_2O_2,\ \bar{O}H} 3\,\underset{\text{1-Butanol}}{CH_3CH_2CH_2CH_2OH}}$$



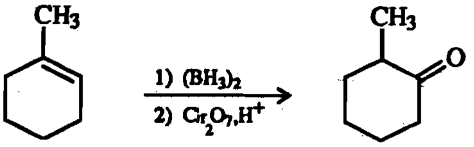


$$CH_3C\equiv CCH_3 \xrightarrow{(BH_3)_2} CH_3\overset{>B}{C}=\overset{H}{C}CH_3 \xrightarrow{H_2O_2,\ \bar{O}H}$$

$$CH_3\overset{OH}{C}=\overset{H}{C}CH_3 \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$$

2-Butanone

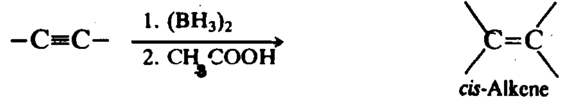
ii) Oxidation of organoboranes with chromic acid yields carbonyl compounds.



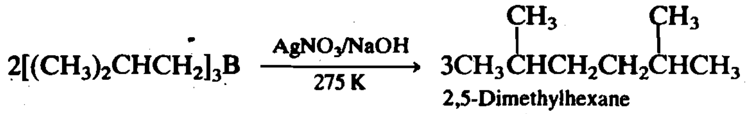
iii) Organoboranes are readily cleared to alkanes by treating with carboxylic acid. Thus, the acid-hydrolysis of organoboranes provides a useful method for carrying out hydrogenation of alkenes and also of alkynes.

$$3\,CH_3CH=CH_2 \xrightarrow{(BH_3)_2} (CH_3CH_2CH_2)_3B \xrightarrow{3\,CH_3COOH} 3\,CH_3CH_2CH_3$$

1-Propene Propane



iv) Reaction of trialkyl boranes with alkaline silver nitrate solution induces a coupling reaction and hence provides a method for the synthesis of higher alkanes.

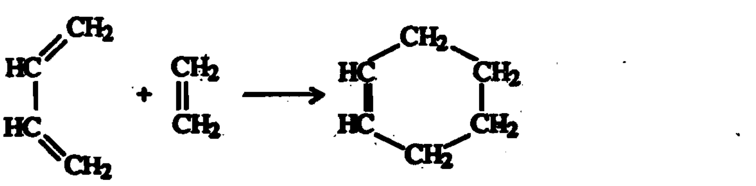


$$2[(CH_3)_2CHCH_2]_3B \xrightarrow[275\,K]{AgNO_3/NaOH} 3CH_3\overset{CH_3}{C}HCH_2CH_2\overset{CH_3}{C}HCH_3$$

2,5-Dimethylhexane

5.4.2 Diels-Alder Reaction

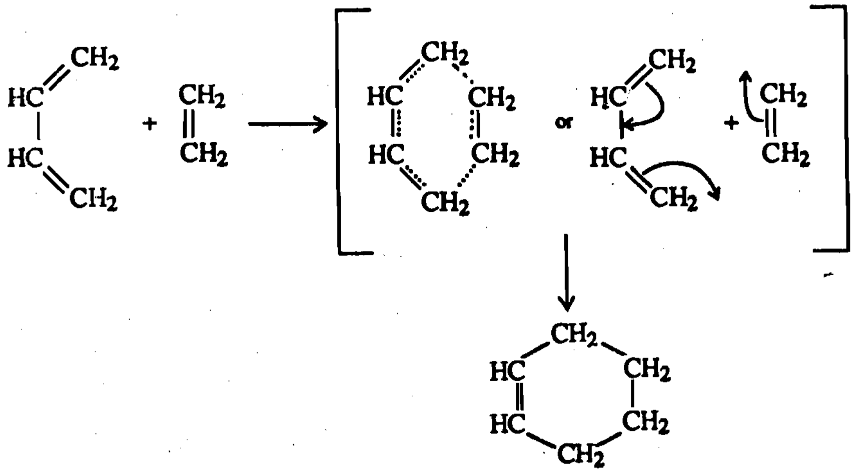
In Diels-Alder reaction, a conjugated diene is treated with certain unsaturated compounds called the dienophiles (diene-lover), to yield an adduct. This is a 1,4-addition of an alkene to a conjugated diene. This reaction is named after the German chemists Otto Diels and Kurt Alder. It is an exceedingly useful reaction used for synthesising cyclic systems. The simplest Diels-Alder reaction is the reaction of 1,3-butadiene and ethene to yield cyclohexene, i.e.,



This is very slow reaction and occurs only under the conditions of heat and pressure. However, this reaction takes place most rapidly giving high yields if the alkene component contains electron withdrawing groups or the diene has electron donating groups.

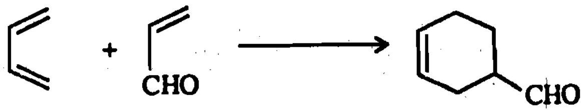
The reaction has a wide scope because also compounds containing multiple bonds other than carbon-carbon double bond may be used. When cyclic dienes are used in the Diels-Alder reaction, bicyclic adducts result. An especially important cyclic diene is cyclopentadiene.

Mechanishm: The mechanism of Diels-Alder reaction is quite different from all others we have studied. It is neither a polar reaction nor a free radical reaction, rather it is concerted (one step) pericyclic process. Both new carbon-carbon single bonds and the new π bond are formed simultaneously, just as the three π bonds in the starting materials break. The concerted nature of the transformation can be shown as a delocalised transition state in which all six π electrons are indicated by dotted line or by the electron pushing technique.

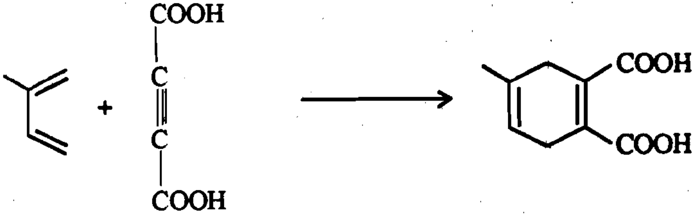


Some important examples of Diels-Alder reaction are given below:

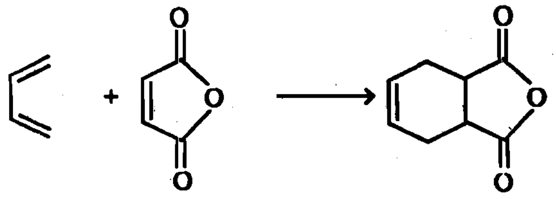
i)



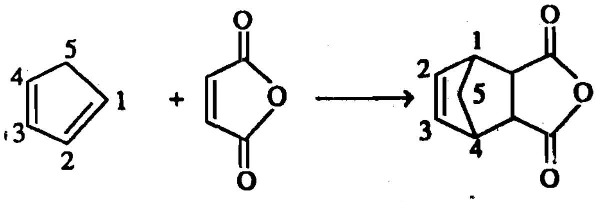
ii)



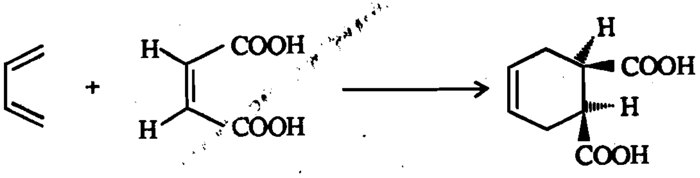
iii)

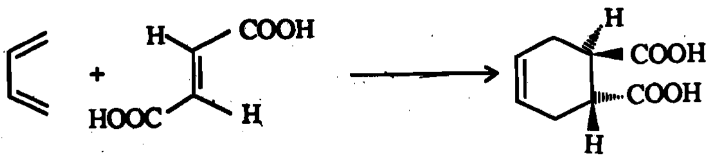


iv)



Another important feature of the Diels-Alder reaction is that it is stereospecific.. The stereochemistry of the starting dienophile is maintained during the reaction. For example, maleic acid gives a *cis* product and fumaric acid gives a *trans* product, e.g.,

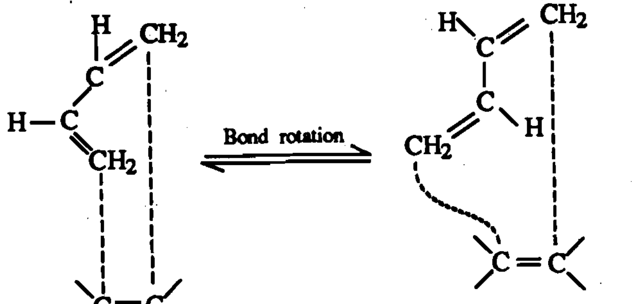




Fumaric acid

trans Acid

To undergo the Diels-Alder reaction, a diene must be able to adopt a *s-cis* geometry (*cis-like* about the single bond) only. The carbon atoms 1 and 4 of the diene in *s-cis* conformation are close enough to react through a cyclic transition state to give a new ring. In the alternative *s-trans* geometry, the ends of the diene are too far apart to overlap the dienophile *p*-orbitals effectively.



s in Confemation
successful reaction

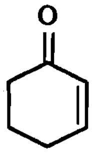
s trans Confermation
No reaction

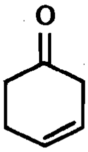
SAQ 5

Which of the following alkenes would you expect to be good Diels-Alder dienophiles?

a) CH = CHNO$_2$

b)


c)


d)


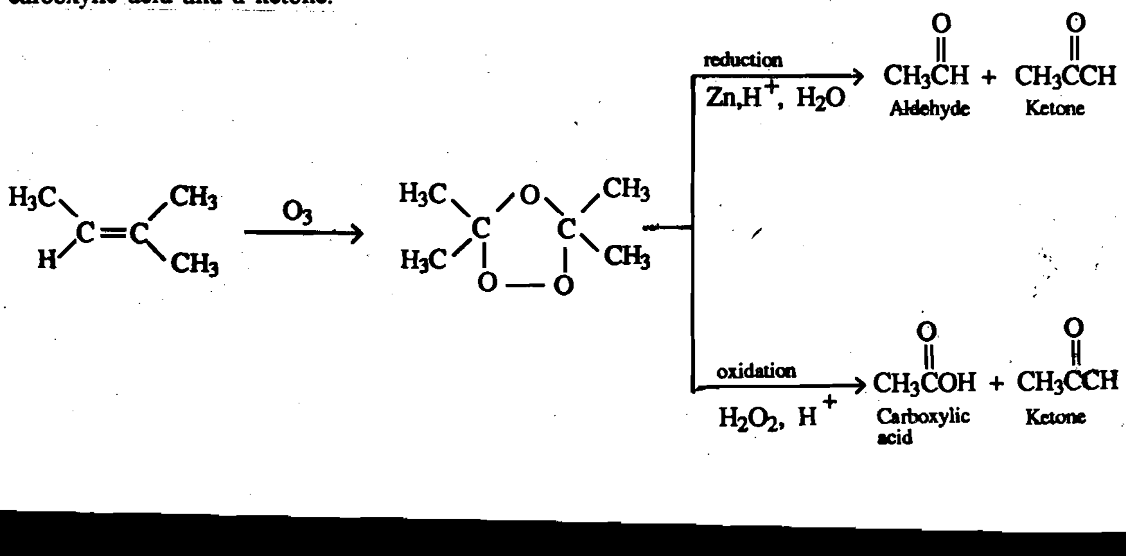
……………………………………………………………………

5.4.3 Ozonolysis

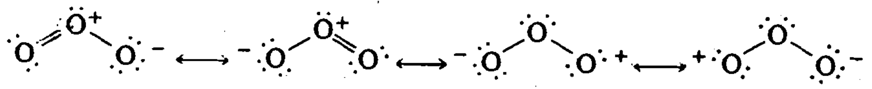
In all the reactions of alkenes and alkynes studied so far, the carbon skeleton of the starting material has been left intact. We have seen the conversion of the carbon-carbon double bond into new functional groups (halide, alcohol, etc.) by addition different reagents, but the carbon skeleton has not been broken. Ozonolysis is a cleavage reaction, in which the double bond is completely altered or broken and the alkene molecule is converted into two smaller molecules.

$$>C=C< + O_3 \longrightarrow >C=O + O=C<$$

Ozonolysis consists of two separate reactions, first is the oxidation of the alkene or alkyne by ozone to give an ozonide; and the second is either oxidation or reduction of the ozonide to yield the cleavage products. For example reductive ozonolysis of 2-methyl-2-butene yields an aldehyde and a ketone, while oxidative ozonolysis give a carboxylic acid and a ketone.

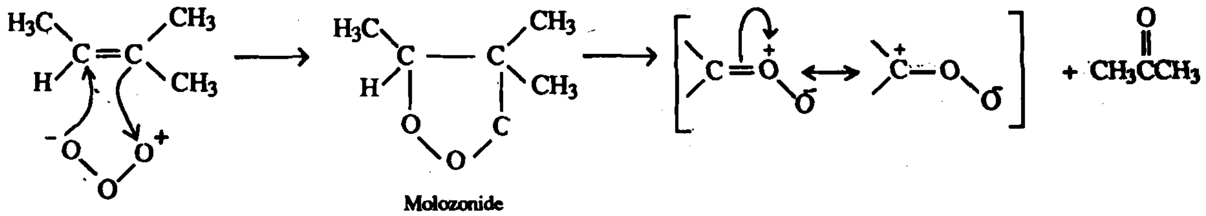


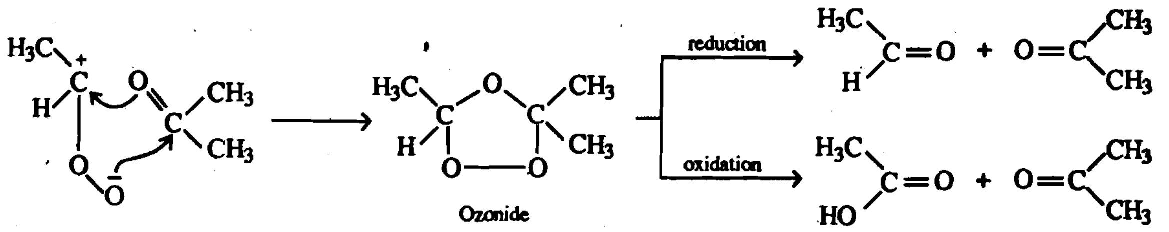
Mechanism : Ozone can be represented as resonance hybrid of the following contributing structure:



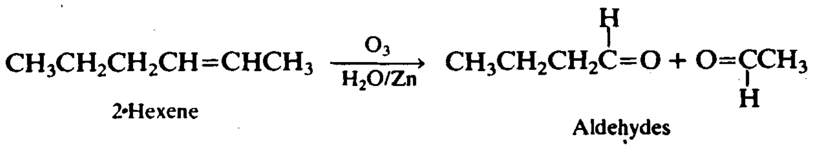
resonance contributors of ozone

The first step consists of a 1,3-dipolar addition of ozone to the double bond forming a molozonide. The molozonide, being unstable, subsequently decomposes into fragments. Recombination of these fragments in an alternative way yields an ozonide.



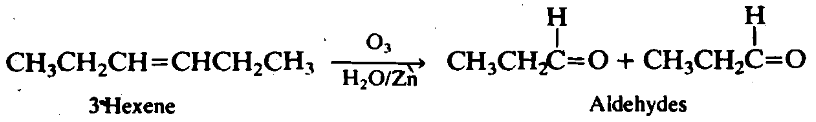


Low molecular-weight ozonides are highly explosive and are, therefore, not isolated. Instead, ozonides are usually further treated with either a reducing agent such as zinc metal in ethanoic acid or an oxidising agent, such as hydrogen peroxide to yield cleaved products. The overall reaction is known as ozonolysis. Knowing the number and arrangement of cabon atoms in those cleaved products, one can locate the position of the double bond in the original alkene. Some examples of ozonolysis are given below:



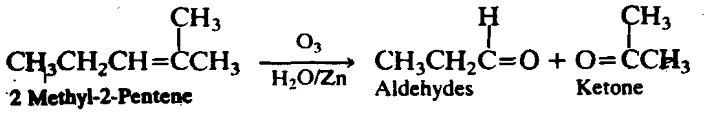
$$CH_3CH_2CH_2CH{=}CHCH_3 \xrightarrow[H_2O/Zn]{O_3} CH_3CH_2CH_2\overset{H}{\overset{|}{C}}{=}O + O{=}\underset{H}{\underset{|}{C}}CH_3$$

2-Hexene Aldehydes



$$CH_3CH_2CH{=}CHCH_2CH_3 \xrightarrow[H_2O/Zn]{O_3} CH_3CH_2\overset{H}{\overset{|}{C}}{=}O + CH_3CH_2\overset{H}{\overset{|}{C}}{=}O$$

3-Hexene Aldehydes

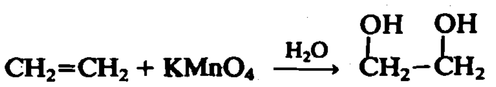


$$CH_3CH_2CH{=}\overset{CH_3}{\overset{|}{C}}CH_3 \xrightarrow[H_2O/Zn]{O_3} CH_3CH_2\overset{H}{\overset{|}{C}}{=}O + O{=}\overset{CH_3}{\overset{|}{C}}CH_3$$

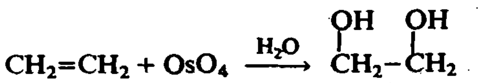
2 Methyl-2-Pentene Aldehydes Ketone

5.4.4 Hydroxylation

Alkenes are readily hydroxylated, (i.e., addition of hydroxyl groups) to form a dihydroxy compound (diol) known as gycols. The most popular reagent used to convert an alkene into diol is cold alkaline aqueous solution of potassium **permanganate ($KMnO_4$) or osmium tetroxide (OsO_4). The yield with $KMnO_4$ is quite low as compared to OsO_4, but the use of OsO_4 is limited because it is both expensive and toxic.**

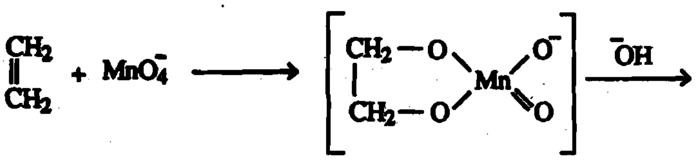


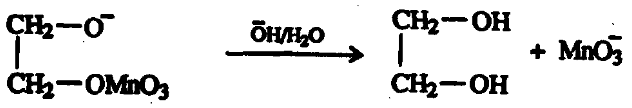
$$CH_2{=}CH_2 + KMnO_4 \xrightarrow{H_2O} \overset{OH}{\overset{|}{C}}H_2{-}\overset{OH}{\overset{|}{C}}H_2$$

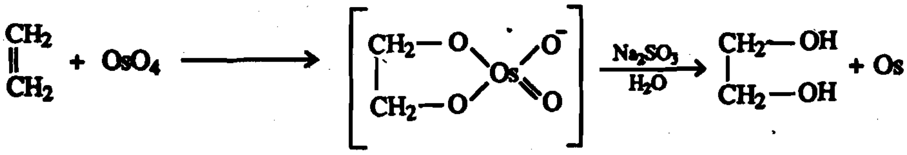


$$CH_2{=}CH_2 + OsO_4 \xrightarrow{H_2O} \overset{OH}{\overset{|}{C}}H_2{-}\overset{OH}{\overset{|}{C}}H_2$$

Both of these hydroxylation reactions occur with *syn*, rather than *anti* stereochemistry and yield *cis* diol. Both the permanganate and the OsO_4 oxidation processes proceed *via* cyclic intermediates.







Oxidation of alkenes (disappearance of pink colour) by cold aq. (neutral or slightly alkaline) permanganate is regarded as a test for the presence of an olefinic bond (Baeyer test).

5.5 SUMMARY

- Addition reaction of carbon-carbon multiple bonds can be divided into three main groups i.e., electrophilic addition, free radical addition and concerted addition.
- Alkenes undergo electrophilic addition more readily than alkynes.
- Alkenes react with hydrogen halides to give alkyl halides.
- Unsymmetrical alkenes on reaction with a hydrogen halide undergo Markownikoff's addition.
- Alkenes react with water to give alcohols, while alkynes give enols. Alcohols can also be obtained by oxymercuration and demercuration.
- Treatment of alkenes with halogens give 1,2-dihalogenated alkanes and that of alkynes give tetrahaloalkanes.
- When conjugated dienes are treated with hydrogen or halogens or hydrogen halide, two addition products are obtained. One is 1,2-addition product and the other is 1,4-addition product.
- Addition of HBr in the presence of peroxide gives *anti*-Markownikoff's product. This reaction occurs via free radical mechanism.
- Reaction of propenenitrile with HBr both in presence of peroxide and in the absence of peroxide yields the same product.
- Borane adds to an alkene or an alkyne to give organoborane, which undergoes a variety of chemical transformations.

5.6 TERMINAL QUESTIONS

1) Predict the products of the following:
   a) $CH_3CH_2CH{=}CHCH_3 + HBr \longrightarrow$ .... + ...
   b) $NCCH{=}CH_2 + HBr \longrightarrow$ ....

c) $ClCH=CH_2 + HBr \longrightarrow$ ....

d) $(CH_3)_3CCH=CH_2 + HBr \longrightarrow$ .... + ...

2) Fill in the following blanks:

a) Addition of H_2O to unsymmetrical alkene follows ..... rule.

b) Carbocation can undergo a 1,2-shift of H or R to yield more stable .....

c) Oxymercuration-demercuration of alkene gives .....

d) Alkyne reacts with halogen to give .....

3) Why are alkenes more reactive than alkynes towards electrophilic reactions?

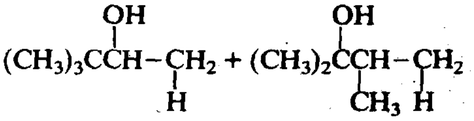
4) A, B and C are isomeric heptenes. On ozonolysis A gives ethanal and pentanal, B gives propanone and butanone and C gives ethanal and pentan-3-one. Give the structure formulae of A, B and C.

5.7 ANSWERS

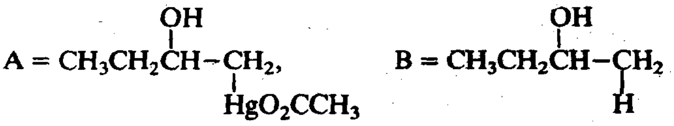
Self-assessment Questions

1) The alkene which forms most stable carbocation has fastest reaction. Thus the rate of reaction towards HBr addition is:

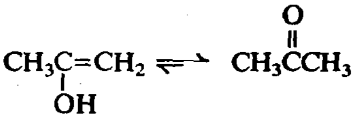
$CH_2=CH_2 < CH_3CH_2CH=CH_2 < (CH_3)_2C=CHCH_2CH_3$

2) a) 

$(CH_3)_3C\overset{OH}{C}H-\underset{H}{C}H_2 + (CH_3)_2\overset{OH}{C}\underset{CH_3}{C}H-\underset{H}{C}H_2$

b) 

$A = CH_3CH_2\overset{OH}{C}H-\underset{HgO_2CCH_3}{C}H_2, \quad B = CH_3CH_2\overset{OH}{C}H-\underset{H}{C}H_2$

c) 

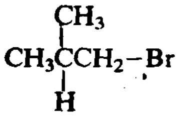
$CH_3\underset{OH}{C}=CH_2 \rightleftharpoons CH_3\overset{O}{\overset{\parallel}{C}}CH_3$

3) a) 1,2-addition, 1,4-addition

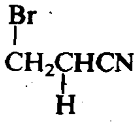
b) primary, secondary

c) 1,2-product, 1,4-product

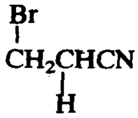
d) 1,2-product, 1,4-product

4) a) 

$CH_3\overset{CH_3}{\underset{H}{C}}CH_2-Br$

b) 

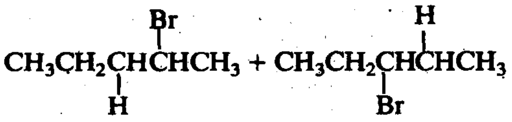
$\overset{Br}{C}H_2\underset{H}{C}HCN$

c) 

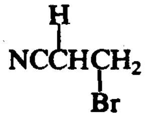
$\overset{Br}{C}H_2\underset{H}{C}HCN$

5) Alkenes (a) and (c) are good dienophiles

Terminal Questions

1) a) 

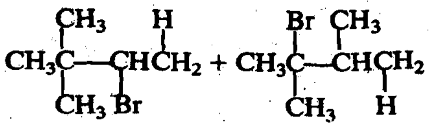
$CH_3CH_2\underset{H}{C}H\overset{Br}{C}HCH_3 + CH_3CH_2\underset{Br}{C}H\overset{H}{C}HCH_3$

b) 

$NC\overset{H}{C}H\underset{Br}{C}H_2$

c) 

$Cl\underset{Br}{C}H\underset{H}{C}H_2$

d) 

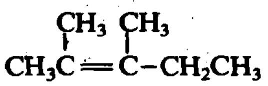
$CH_3\overset{CH_3}{\underset{CH_3}{C}}-\underset{Br}{C}H\overset{H}{C}H_2 + CH_3\overset{Br}{\underset{CH_3}{C}}-\overset{CH_3}{C}H\underset{H}{C}H_2$

2) a) Markownikeff's
b) carbocation
c) alcohol
d) tetrahaloalkane.

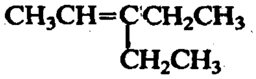
3) Since an *sp* hybridised carbon is more electronegative than sp^2 hybridised carbon, π electrons in alkynes are less easily available for combination with electrophile. Therefore alkynes are less reactive than alkene.

4) >C=O group is introduced at >C=C< after fission, hence:

compound A = $CH_3CH=CHCH_2CH_2CH_2CH_3$

compound B = 

$CH_3\overset{CH_3}{C}=\overset{CH_3}{C}-CH_2CH_3$

compound C = 

$CH_3CH=\underset{CH_2CH_3}{C}CH_2CH_3$