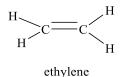
Unsaturated hydrocarbons

In our discussion of the alkanes we mentioned briefly another family of hydrocarbons, the **alkene** which contain less hydrogen, carbon for carbon than the alkanes, and which can be converted into alkanes by addition of hydrogen. The alkenes were further described as being obtained from alkanes by loss hydrogen in the cracking process. The alkenes called **Unsaturated hydrocarbons** because the alkenes contain less than the maximum quantity of hydrogen. The simplest member of the alkene family is ethylene, C_2H_4 .



Physical properties of alkenes

As a class the alkenes possess physical properties that are essentially the same as those of the alkanes .they are insoluble in water but quite soluble in nonpolar solvents like. benzene ,chloroform ,ether or ligroin. they are Less dense than water .,Like alkanes alkenes are at most only weakly polar, trans isomer more stable than the cis isomer in alkenes.

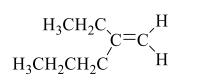
The general formula for alkenes is CnH_2n we say that carbon atoms are joined by a double bond, the carbon –carbon double bond is the distinguishing feature of the alkene structure .

IUPAC name of alkenes

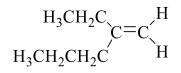
Alkenes are named using a series of rules similar to those for alkane with the suffix –ene used instead of –ane to identify the functional group There are three steps.

STEP1

Name the parent hydrocarbon. Find the longest carbon chain containing the double bond, and name the compound accord nary, using the suffix - ene.



Named as a pentene NOT



as a hexane, the double bond is not contained in the six carbon chain.

1

STEP 2

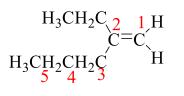
Number the carbon atoms in the chain. Being at the end nearer the double bond or, if the double bond equidistant from the two ends, Being at the end nearer the first branch point. This rule ensure that the double bond carbon receive the lowest possible numbers.

 $\begin{array}{c} CH_{3}\\ CH_{3}CH_{2}CHCH \longrightarrow CHCH_{3}\\ 6 5 4 3 2 1\\ 4\text{-methyl-2-hexene} \end{array}$

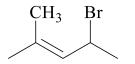
 $\begin{array}{c} Br\\ CH_3CH_2CH = CHCH_2CHCH_3\\ 1 & 2 & 3 & 4 & 5 & 6 & 7\\ 6-bromo-3-heptene \end{array}$

STEP 3

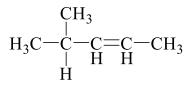
Writ the full name. Number the substituents according to their positions in the chain, and the list them alphabetically. Indicate the position of the double bond by giving the number of the first alkene carbon and the placing that number directly before the parent name.



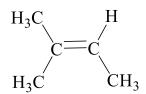
2-Ethyl-1-pentene



4-bromo-2-methyl-2-pentene

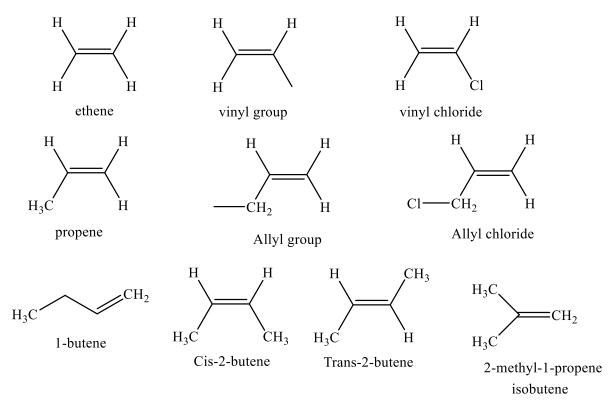


4-methyl-2-pentene

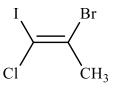


2-methyl-2-butene trimethylethylene

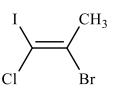
ISOMERS AND COMMON NAMES OF SIMPLE ALKENES



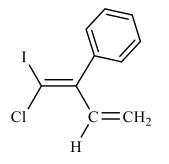
If the groups attached to the double bond are different, we distinguish the two isomers by adding the prefix -Z (Zusammen)(the same side) or E (Entgegen) (opposite side) depending on the atomic number of the atoms attached to each end of the double bond. The Cahn-Ingold-Prelog system(C-I-P) system is used for prioritizing of groups.



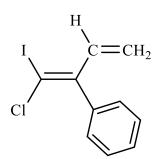
(*Z*)-2-bromo-1-chloro-1-iodopropene



(E)-2-bromo-1-chloro-1-iodopropene



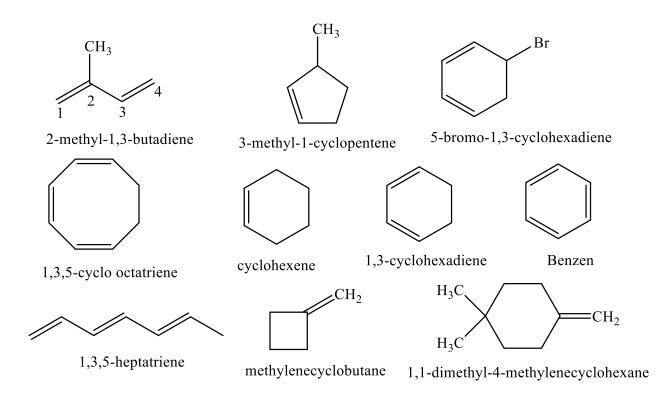
(Z)-1-chloro-1-iodo-2-phenyl-1,3-butadiene



(E)-1-chloro-1-iodo-2-phenyl-1,3-butadiene

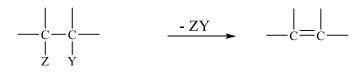
3

Compounds containing more than one double bond



Preparation of alkenes

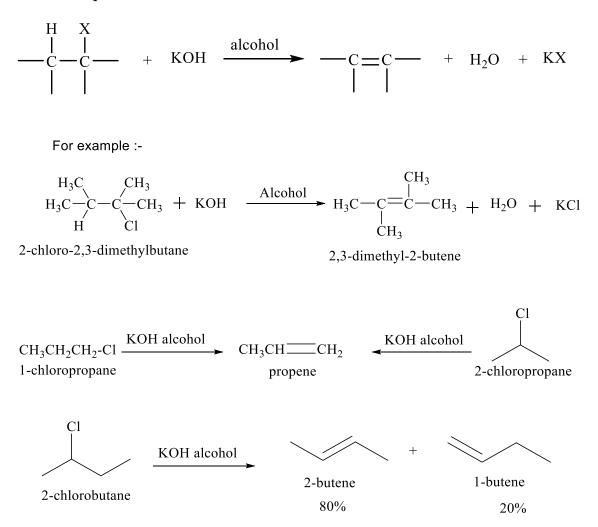
The introduction of the carbon- carbon double bond into a molecule containing only single bonds must necessarily involve the elimination of atoms or groups form two adjacent carbons.



1- Dehydrohalogenation of alkyl halide

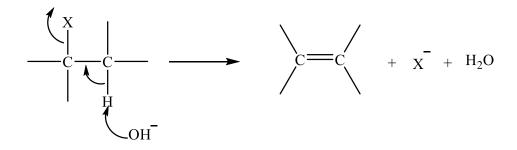
The most important of these methods of preparation alkenes .alkyl halides are converted into alkenes by Dehydrohalogenation : elimination of the elements of hydrogen halide . Dehydrohalogenation involves removal of the halogen atom together with a hydrogen atom from a carbon adjacent to the one bearing the halogen it. The alkenes is prepared by simple heating together the alkyl halide and a solution of potassium hydroxide in alcohol.

General equation:-



Mechanism of Dehydrohalogenation of alkyl halides

The function hydroxide ion is to pull a hydrogen ion away from carbon together halide ion separates and the double bond forms we can.



2- Dehydration of alcohols

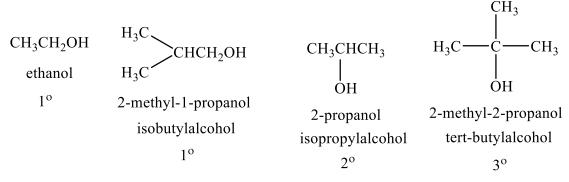
Alcohols are compound of the general formula **ROH**, R is any alkyl group, an alcohol is converted into an alkene by **dehydration** :elimination of a molecule of water, Dehydration required the presence of an acid and the application of heat. It is generally carried out in either of two ways: (a) by heating the alcohol with sulphuric acid or phosphoric acid, or (b) by passing the alcohol vapour over alumina (Al_2O_3) , at high temperature , alumina function as an acid serve as Lewis acid.

notice the various classes of alcohol differ widely in ease of dehydration the order of reactivity being .

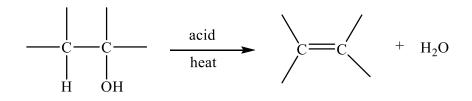
easy dehydration of alcohol

 $3^{\circ} > 2^{\circ} > 1^{\circ}$

Classification of alcohols



general equation



Example :-

 $\begin{array}{cccc} CH_{3}CH_{2}CHCH_{3} & \xrightarrow{60\% H_{2}SO_{4}} & CH_{3}CH \Longrightarrow CHCH_{3} \\ OH & & 2-butene \\ 2-butanol \\ sec-butylalcohol & cheif product \end{array}$

mechanism of dehydration of alcohols

the general accepted mechanism for the dehydration of alcohols is summarized in the following equations :for the sake of simplicity ,ethyl alcohol is used as the example :-

the ethyl alcohol unites (step 1) with a hydrogen ion to form the protonated alcohol ,which dissociates (step 2) into water and a carbonium ion ; the carbonium ion then loses (step 3) a hydrogen ion form the alkene

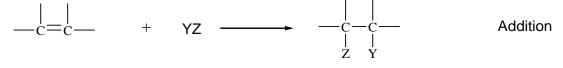
step (1)
$$CH_3CH_2OH + H:B \longrightarrow CH_3CH_2OH_2 + B:$$

step (2) $CH_3CH_2OH_2 - H_2O - CH_3CH_2 + H_2O$:

step (3)
$$CH_3CH_2 + B: \xrightarrow{-H} H_2C = CH_2 + H:B$$

Reaction of the carbon – carbon double bond

Alkene chemistry is the chemistry of the carbon – carbon double bond .What kind of reaction can we expect of the double bond consists of the a strong sigma bond and a weak pi bond ;we might expect ,therefore that reaction would involve the breaking of this weaker bond .this expectation is correct ;the typical reaction of the double bond are of the sort. Where the pi bond is broken and the two strong sigma bonds are formed in its place.



Addition Reaction

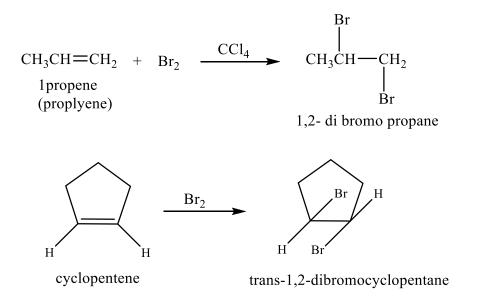
1- Addition of halogens

Alkenes are readily converted by chlorine or bromine into saturated compounds that contain two atoms of halogen attached to adjacent carbons ; iodine generally fails to react .

$$-\overset{i}{C} = \overset{i}{C} - + X_2 \longrightarrow -\overset{i}{C} - \overset{i}{C} - \overset{i}{C} - X_2 = CI_2, Br_2, I_2$$

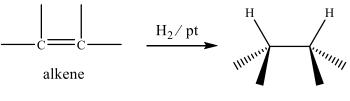
vicinal di halide

7



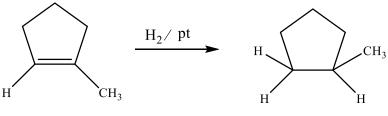
2- Hydrogenation

Reduction of alkenes by catalytic hydrogenation

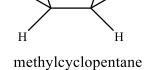


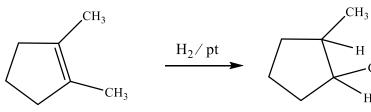
alkane

Reduction occurs on metal surface the addition of hydrogen is syn (cis)



1-methyl-1-cyclopentene





1,2-dimethyl-1-cyclopentene

Cis-1,2-dimethylcyclopentane

Η -CH₃

Η

3- Addition of hydrogen halide Markonikov`s rule

An alkene is converted by hydrogen chloride or hydrogen bromide and hydrogen iodide into the corresponding alkyl halide .

$$-\overset{|}{C}=\overset{|}{C}- + HX \longrightarrow -\overset{|}{C}-\overset{|}{C}-\overset{|}{C}- HX = HCI, H Br, HI$$

In this way ethylene is converted into an ethyl chloride, the hydrogen becoming attached to one double –bonded carbon and the chlorine to the other

 $H_2C=CH_2 + HC1 \longrightarrow CH_3CH_2C1$ ethylene ethyl chloride

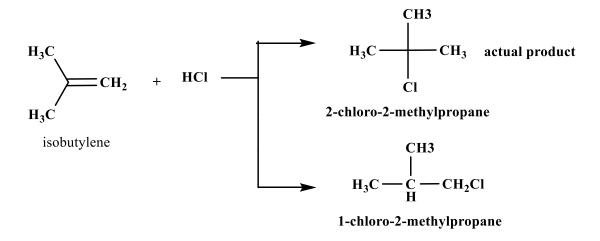
propylene could yield either of two products, the n-propyl iodide or the iso propyl iodide, depending upon the orientation of addition that is depending upon which carbon atoms the hydrogen and iodine become attached to actually only the isopropyl iodide is formed.

$$H_{3}C-C=CH_{2} + HI \longrightarrow H_{3}C-C=CH_{2}I$$

$$H_{3}C-C=CH_{2} + HI \longrightarrow CH_{3}CH-CH_{3}$$
 actual product

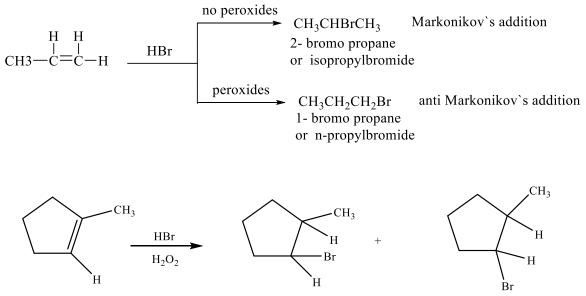
$$H_{3}C-C=CH_{2} + HI \longrightarrow CH_{3}CH - CH_{3}$$
 isopropyl iodide

in the same way, isobutylene could yield either of two products iso butyl halide or *tert* – butyl halide.



Addition of hydrogen bromide. Peroxide effect

Addition of hydrogen chloride and of hydrogen iodide to alkenes follows Markonikov's rule. the addition of hydrogen bromide (HBr) to alkenes follows Markonikov's rule, but the addition of hydrogen bromide (HBr) presence of peroxide in reaction system to actual product don't follow Markonikov's rule (anti Markonikov's rule).

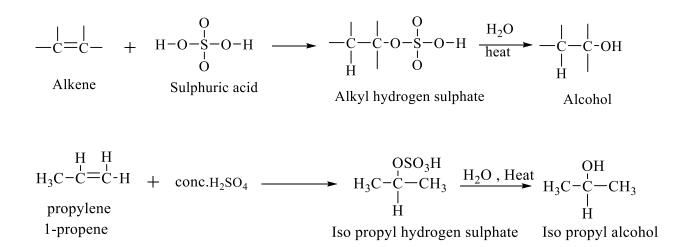


1-methyl-1-cyclopentene Z-1-bromo-2-methylcyclopentane E-1-bromo-2-methylcyclopentane

Addition of sulphuric acid

Alkenes react with cold concentrated sulphuric acid for compound of the general formula $ROSO_3H$, known as **alkyl hydrogen sulphates** .these products are formed by addition of hydrogen ion to one side of the double bond and bisulphate ion to the other . it is important to notice that carbon is bonded to oxygen and not to sulphur.

If the sulphuric acid solution of the alkyl hydrogen sulphate is diluted with water and heated, there is obtained an alcohol bearing the same alkyl group as the original alkyl hydrogen sulphate. alkyl hydrogen sulphate has been cleaved by water to form the alcohol and sulphuric acid.



4-Addition of water (hydration)

Water adds to the more reactive alkenes in the presence of acid to yield alcohols .this addition follows Markonikov`s rule

$$-\overset{|}{C} = \overset{|}{C} - + \text{ HOH} \xrightarrow{H^{+}} -\overset{|}{C} - \overset{|}{C} - \overset{|}{C} - \overset{|}{H} \overset{|}{OH}$$

For example

$$\begin{array}{c} H & H \\ H_{3}C - C = C - H \\ 1 - \text{propene} \end{array} + HOH \xrightarrow{H^{+}} H_{3}C - C - C - H \\ 1 - \text{propene} \end{array}$$

Electrophilic Addition :mechanism

We shall take up first the addition of those reagent which contain ionisable hydrogen : the hydrogen halide ,sulphuric acid ,and water. The general accepted mechanism will be outlined, and then will shall notice certain facts. Like dehydration of alcohols addition as pictured

As involving carbonium ions.

Addition of the acidic reagent ,**HZ** {electron deficient molecule, Lewis acid } is believed to proceed by two steps

Step (1) involves transfer of hydrogen ion from $:\mathbb{Z}$ to the alkenes to form carbonium ion.

The step (2) is the combining of the carbonium ion with the base :Z

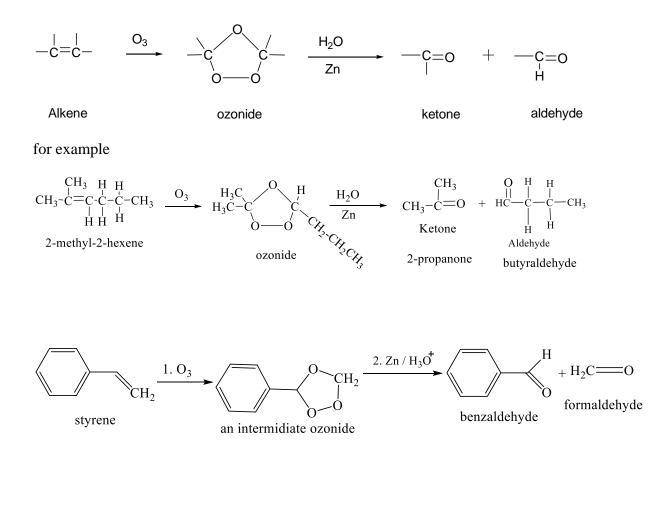
Notice the step (1) is the difficult step



Ozonolysis, determination of structure by degradation

The classical reagent for cleaving the carbon –carbon double bond is ozone . **Ozonolysis** (cleavage by ozone) is carried out in two stages :-

First stage :- addition of ozone to the double bond to form an ozonide ;and **second stage** :- hydrolysis of the ozonide to yield the cleavage products.



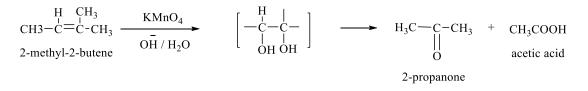
Oxidation of alkene by permanganate :-

Addition of permanganate which is believed to involve formation and cleavage of intermediate glycols

$$-\overset{|}{C} = \overset{|}{\overset{C}{C}} - \overset{KMnO_4}{\xrightarrow{OH/H_2O}} \left[\begin{array}{c} -\overset{|}{\overset{|}{C}} - \overset{|}{\overset{|}{C}} - \overset{|}{\overset{|}{OH}} \end{array} \right] \longrightarrow Acid , Ketones , CO_2$$

Carboxylic acids , RCOOH , are obtained instead of aldehydes RCHO . A terminal = CH₂ Group is oxidized to CO_2 .

for example :-



CH ₃ CH ₂ CH ₂ CH=CH ₂	KMnO ₄	CH ₃ CH ₂ CH ₂ COOH	+	CO ₂
1-pentene	OH / H_2O	butyric acid butanoic acid		