ALKENES (OLEFINS)

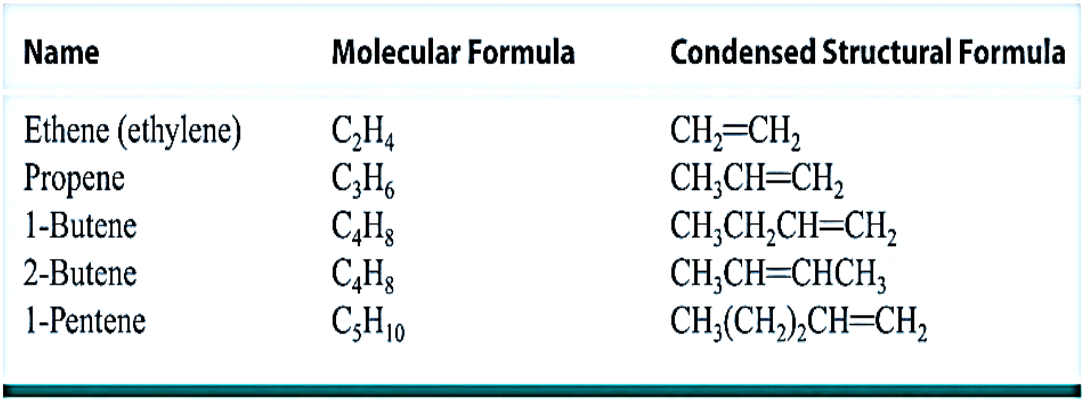
are an unsaturated hydrocarbons which contain carbon–carbon double bonds. The chemical formula : (C_nH_{2n+2}).

They are colourless, nonpolar, and combustable. The physical state depends on molecular mass: like the corresponding saturated hydrocarbons, the simplest alkenes, ethene, propene, and butene are gases at room temperature. Linear alkenes of approximately five to sixteen carbons are liquids, and higher alkenes are waxy solids. The melting point of the solids also increases with increase in molecular mass.

IUPAC NAME

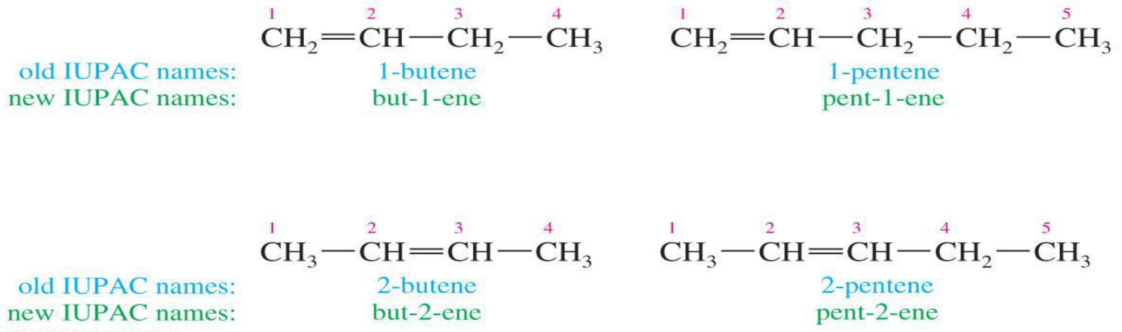
1. **The parent name will be the longest carbon chain that contains both carbons of the double bond. Drop the -ane suffix of the alkane name and add the –ene suffix**

alk**ane** + -ene = alk**ene**



Name	Molecular Formula	Condensed Structural Formula
Ethene (ethylene)	C_2H_4	$CH_2{=}CH_2$
Propene	C_3H_6	$CH_3CH{=}CH_2$
1-Butene	C_4H_8	$CH_3CH_2CH{=}CH_2$
2-Butene	C_4H_8	$CH_3CH{=}CHCH_3$
1-Pentene	C_5H_{10}	$CH_3(CH_2)_2CH{=}CH_2$

When the chain is longer than 3 carbons, number the atoms such that the *double bond* is given the lowest number (i.e. start at the end nearest the double bond).



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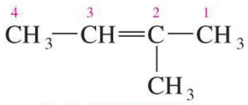
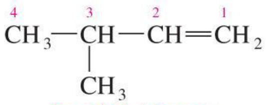
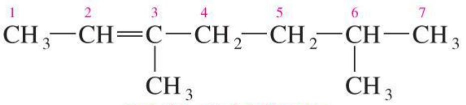
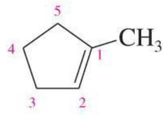
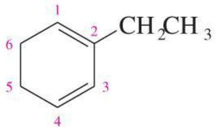
-For branches, each *alkyl* group is given a number, but the double bond is still given preference when numbering the chain

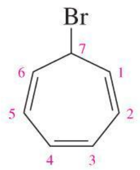

2-methyl-2-butene
2-methylbut-2-ene

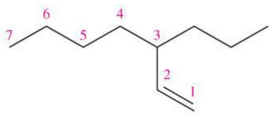

3-methyl-1-butene
3-methylbut-1-ene


3,6-dimethyl-2-heptene
3,6-dimethylhept-2-ene


1-methylcyclopentene
1-methylcyclopentene


2-ethyl-1,3-cyclohexadiene
2-ethylcyclohexa-1,3-diene


7-bromo-1,3,5-cycloheptatriene
7-bromocyclohepta-1,3,5-triene


3-propyl-1-heptene
3-propylhept-1-ene

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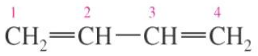
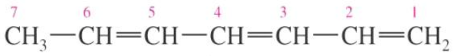
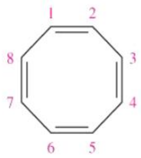
- **Compounds with 2 double bonds are called *dienes*, 3 double bonds are *trienes*, etc.**







old IUPAC names:	1,3-butadiene	1,3,5-heptatriene	1,3,5,7-cyclooctatetraene
new IUPAC names:	buta-1,3-diene	hepta-1,3,5-triene	cycloocta-1,3,5,7-tetraene

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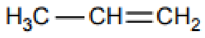
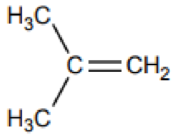
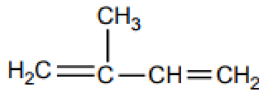
Common name :

The parent name will be the longest carbon chain that contains both carbons of the double bond. Drop the -ane suffix of the alkane name and add the –ylene suffix


ethylene


propylene


isobutylene

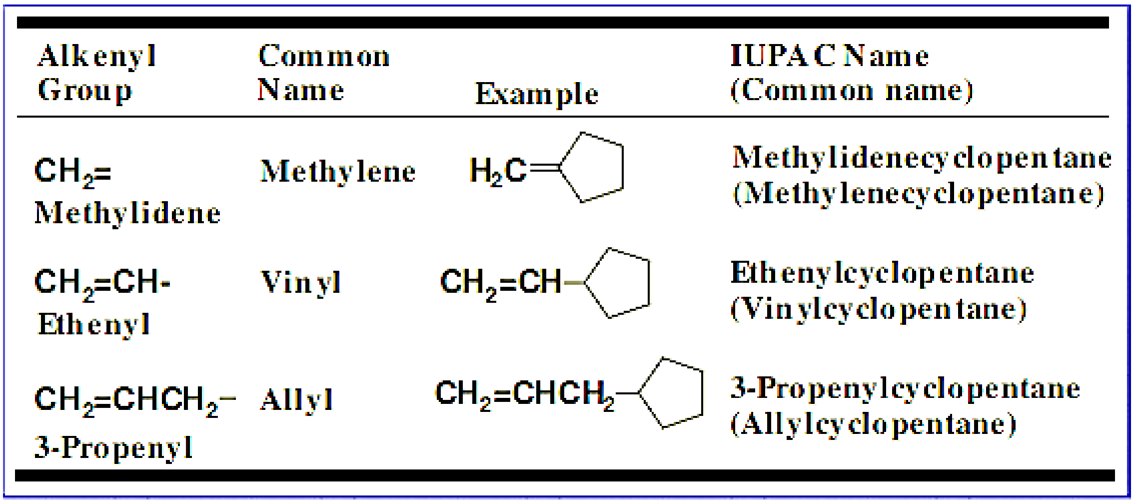

isoprene

Common Names of Unsubstituted and Substituted Alkenes.

Structure	Common Name	Systematic Name
$CH_2=CH_2$	ethylene	ethene
$CH_3-CH=CH_2$	propylene	propene
$(CH_3)_2C=CH_2$	isobutylene	2-methylpropene
$CH_2=C=CH_2$	allene	propadiene
$CH_2=C(CH_3)CH=CH_2$	isoprene	2-methyl-1,3-butadiene
$CH_2=CH-Cl$	vinyl chloride*	chloroethene
$CH_2=CH-CH_2-Cl$	allyl chloride*	3-chloropropene
$CH_2=CH-CH_2-OH$	allyl alcohol	2-propenol
$CH_2=CH-CH_2-NH_2$	allyl amine	2-propenamine

Alkenyl groups

The common names methylene, vinyl, and allyl are often used to show the presence of the following alkenyl groups:



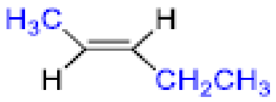
Alkenyl Group	Common Name	Example	IUPAC Name (Common name)
$CH_2=$ Methylidene	Methylene	$H_2C=$	Methylidenecyclopentane (Methylenecyclopentane)
$CH_2=CH-$ Ethenyl	Vinyl	$CH_2=CH-$	Ethenylcyclopentane (Vinylcyclopentane)
$CH_2=CHCH_2-$ 3-Propenyl	Allyl	$CH_2=CHCH_2-$	3-Propenylcyclopentane (Allylcyclopentane)

Geometric isomers

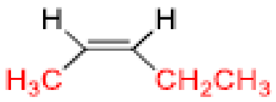
The *rigidity* of a bi bond gives rise to geometric isomers. Geometric isomers are compound that differ only in the arrangement of their atoms in space because of restricted rotation around the double bond

When similar groups (not H's) are bound to the same side of the double bond the alkene is said to be *cis.*

When similar groups are bound to opposite sides of the double bond it is said to be *trans.*



trans-pent-2-ene



cis-pent-2-ene

Stability of Alkenes:there are three factors that affect the stability of alkenes

1-Degree of substitution ;more highly substituted double bonds are more stableso tetra >tri>di.> monosustituted

R2C=CR2 > R2C=CRH > RHC=CHR and R2C=CH2 > RCH=CH2

2-Stereochemistry :trans >cis due to reduced steric interaction when substituted groups are opposite sides of double bonds

3-Conjugation :conjugated alkenes are more stable than isolated one

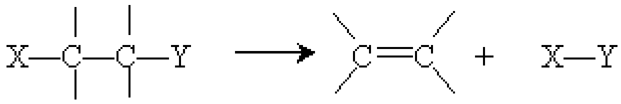
The C-H bonds are formed by overlap of sp_2 orbitals.

The ethene C-H bonds contain more s character than the ethane C-H bonds and are therefore *shorter* and *stronger*).

Preparation of alkenes

Alkenes can be prepared by 1,2- elimination involves removing of H& X or OH of a molecule to form a new structure. The general form of this reaction is shown below, where X and Y are OH & H substituent groups of the alkane such as

- **Dehydrohalogenation of alkyl halides**
- **Dehydration of alcohols**
- **Dehalogenation of Vicinal Dihaloalkenes**



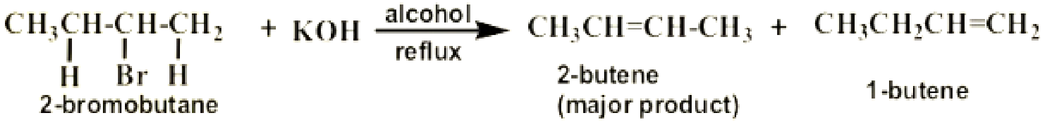
Dehydrohalogenation can be performed in the presence of a base,alcoholic potassium hydroxide

$$R\text{-}CH_2\text{-}CH_2\text{-}X \xrightarrow[\text{reflux}]{\text{NaOH/ethanol}} R\text{-}CH{=}CH_2 + HX$$

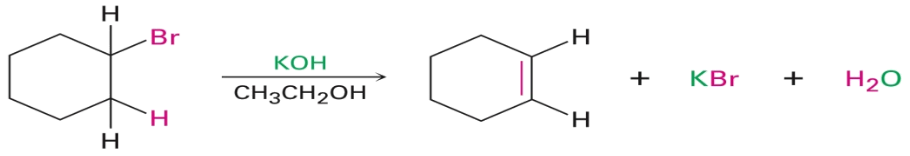
$$RCH_2CH_2X \xrightarrow[\text{-HX}]{\text{alc. KOH}} RCH{=}CH_2$$

The Saytzeff rule predicts the major alkene product from an elimination to be the more highly substituted alkene.

Sometimes, strong, bulky bases can form products that are *not* Saytzeff products.



$$CH_3CH(H)\text{-}CH(Br)\text{-}CH_2(H) + KOH \xrightarrow[\text{reflux}]{\text{alcohol}} CH_3CH{=}CH\text{-}CH_3 + CH_3CH_2CH{=}CH_2$$



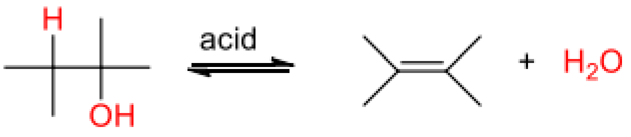
Bromocyclohexane **Cyclohexene (81%)**

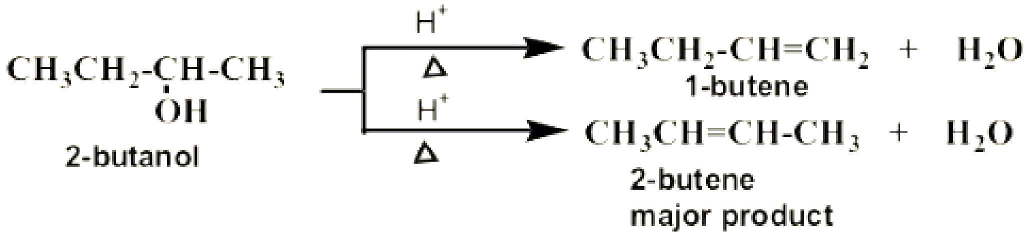
Dehydration of alcohols

alkenes can form by Dehydration of alcohols **using elimination mechanism by** one of two processes: the **E1 mechanism** or the **E2 mechanism.** Consider ethanol in a solution of sulfuric acid (H_2SO_4) at a temperature of about 160°C. According to the Bronsted-Lowry model, sulfuric acid produces hydronium ions (H_3O^+), which interact with the hydroxyl group of ethanol.

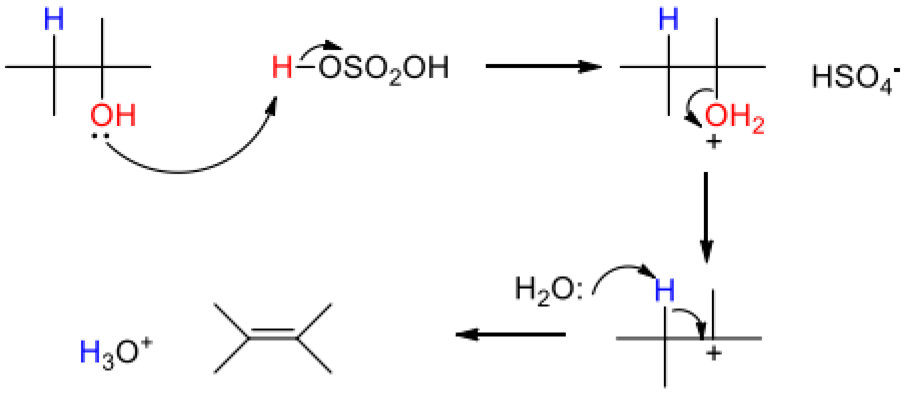
$$CH_3CH_2OH \longrightarrow H_2C{=}CH_2 + H_2O$$

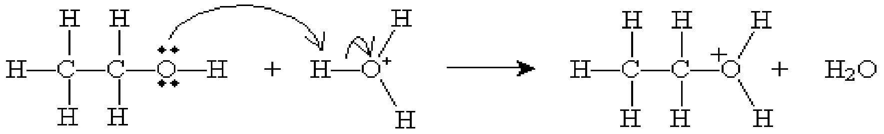
$$R\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow[\triangle]{\text{conc. } H_2SO_4} R\text{-}CH{=}CH_2 + H_2O$$





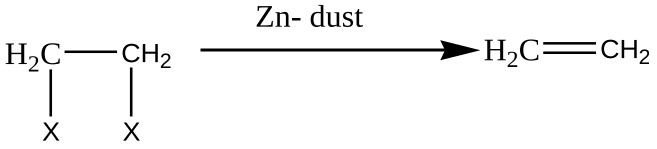
The mechanism of dehydration is similar to the E1 mechanism.



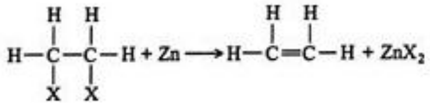


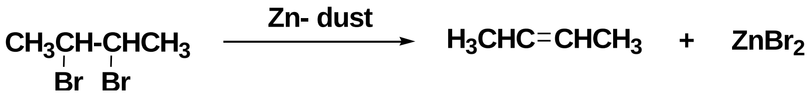
Dehalogenation of Vicinal Dihalides:

Treatment of vicinal dihalides (usually vicinal dibromide) with Zn metal in acetic acid or NaI in acetone produce alkene by elimination reactions

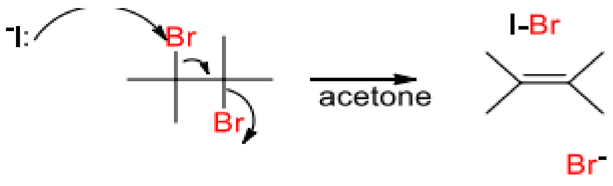


$$\underset{X}{H_2C}-\underset{X}{CH_2} \xrightarrow{\text{Zn- dust}} H_2C{=}CH_2$$





$$CH_3\underset{Br}{CH}-\underset{Br}{CH}CH_3 \xrightarrow{\text{Zn- dust}} H_3CHC{=}CHCH_3 + ZnBr_2$$



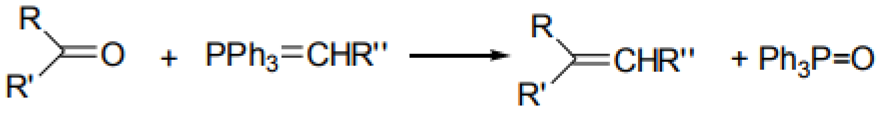
Hydrogenation of alkynes

Hydrogenation of alkynes in presence of Lindlar catalyst (Lindlar catalyst is Pd on CaCO3 deactivated by lead acetate which prevents further hydrogenation) gives alkenes

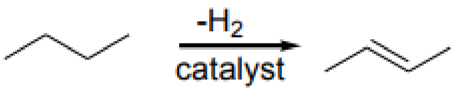
$$HC\equiv CH \xrightarrow[\text{lindlar catalyst}]{H_2,\ \Delta} H_2C=CH_2$$

$$RC\equiv CR \xrightarrow[\text{lindlar catalyst}]{H_2,\ \Delta} RHC=CH_2$$

Wittig Reaction



Dehydrogenation of Alkanes



Diverse Reactions of Alkenes

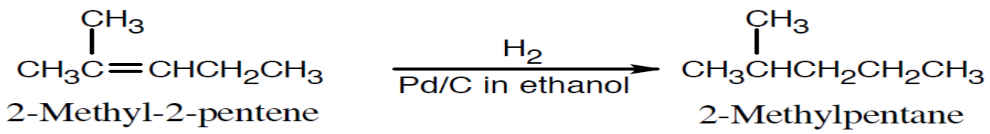
Alkenes undergo electrophilic addition reactions to give many useful products.

1-)Hydrogenation

Hydrogenation of alkenes produces the corresponding alkanes. The reaction is carried out under pressure at a temperature of 200 °C in

the presence of a metallic catalyst. Common industrial catalysts are based on platinum, nickel or palladium.

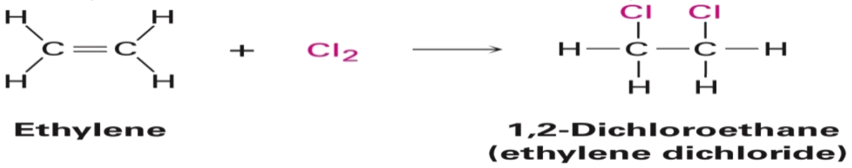
$$H_2C{=}CH_2 \xrightarrow[H_2]{Ni} CH_3CH_3$$



$$\underset{\text{2-Methyl-2-pentene}}{CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_3} \xrightarrow[\text{Pd/C in ethanol}]{H_2} \underset{\text{2-Methylpentane}}{CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3}$$

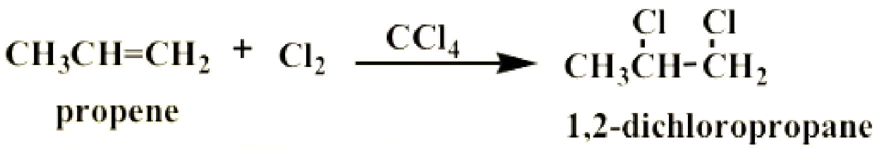
2-)Halogenation of Alkenes: Addition of X2

Halogen adds to alkenes by electrophilic addition reaction to form vicinal dihalides. Addition of Bromine and chlorine to alkenes to give 1,2-dihalides or vicinal dihalides takes place rapidly at room temperature in a variety of inert solvent including carbon tetrachloride, chloroform and methylene chloride Example;1,2-dichloroethane is formed by addition of Cl_2 to ethylene



Ethylene

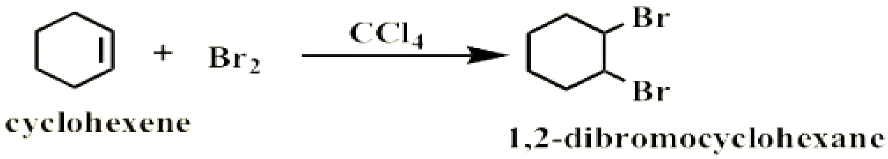
1,2-Dichloroethane
(ethylene dichloride)



$$CH_3CH{=}CH_2 + Cl_2 \xrightarrow{CCl_4} CH_3\overset{Cl}{\overset{|}{C}}H-\overset{Cl}{\overset{|}{C}}H_2$$

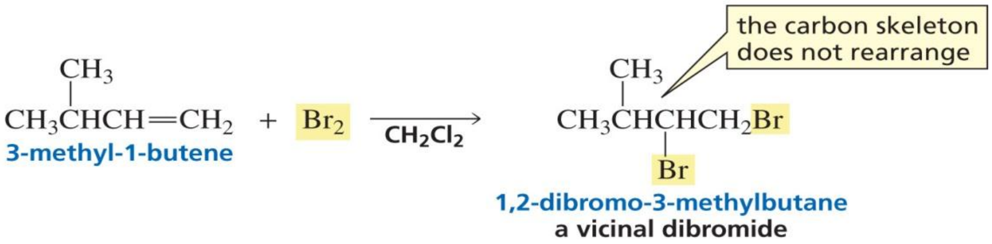
propene

1,2-dichloropropane



cyclohexene

1,2-dibromocyclohexane



$$CH_3\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2 + Br_2 \xrightarrow{CH_2Cl_2} CH_3\overset{CH_3}{\overset{|}{C}}H\underset{Br}{\underset{|}{C}}HCH_2Br$$

3-methyl-1-butene

the carbon skeleton does not rearrange

1,2-dibromo-3-methylbutane
a vicinal dibromide

$$CH_2{=}CH_2 + Br_2 \rightarrow BrCH_2\text{-}CH_2Br$$

Fluorine is too reactive and iodine is less reactive so it does not react with majority of alkenes

3- Addition of Hydrogen Halides:

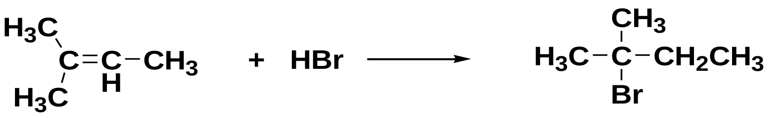
Hydrohalogenation is the addition of hydrogen halide HX such as HCl or HBr or HI to alkenes to yield the corresponding halo alkanes.

-The relative reactivity of HX : HI>HBr>HCl>HF

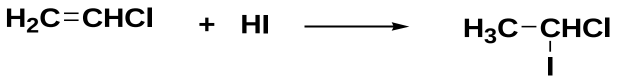
-The addition of HX to unsymmetrical alkene obeys Markovnikov's rule.

Markovnikov's rule: - **when an unsymmetrical alkene reacts with a hydrogen halide to give an alkyl halide the hydrogen adds to the carbon of the alkene that has the greater number of hydrogens and halogen to the carbon of the alkene with the fewer number of hydrogen .**

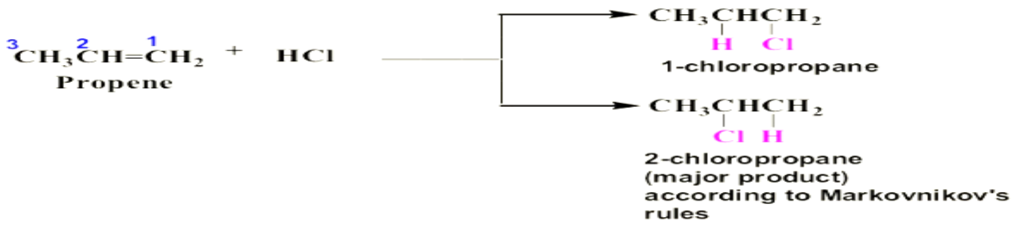
So the addition of HX is regiospecific because in each case only one of the two orientation of addition is observed



2-bromo-2-methylbutane

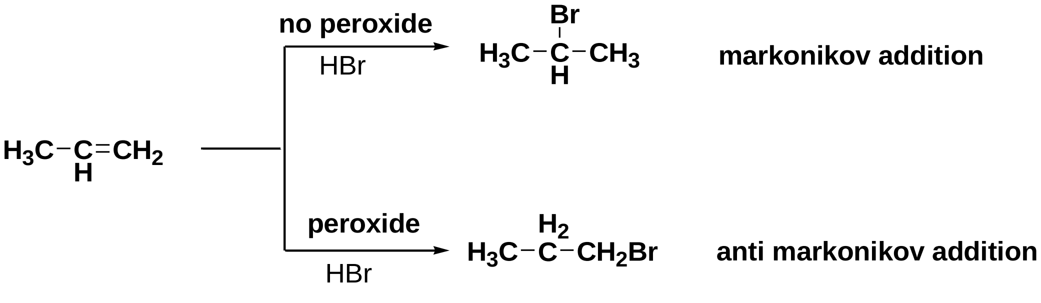


1-chloro-1-iodoethane



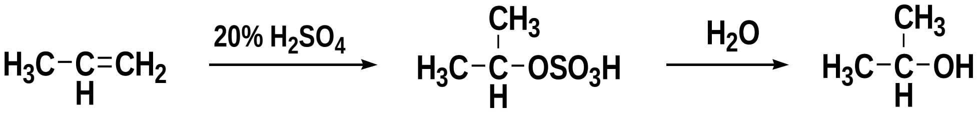
Anti Markovnikov:

In addition of HBr only the presence of peroxide follow anti Markovnilov rule so the hydrogen will attached to the carbon atom which contain lower number of hydrogen atoms

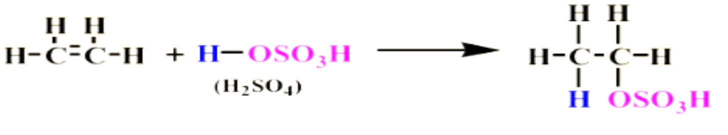


4- Addition of diluted H_2SO_4:

This addition reaction is regeoselective and follows Markovnikov's rule and convert alkenes into alcohols. Alkene react with conc. H_2SO_4 to give alkyl hydrogen sulphate which can be hydrolyzed with water to produce alcohol.



$$H_3C-\underset{H}{C}=CH_2 \xrightarrow{20\%\ H_2SO_4} H_3C-\underset{H}{\overset{CH_3}{C}}-OSO_3H \xrightarrow{H_2O} H_3C-\underset{H}{\overset{CH_3}{C}}-OH$$



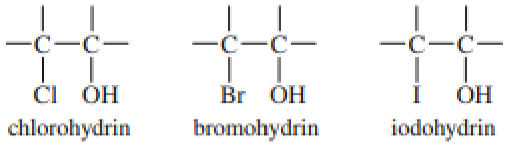
ethyl hydrogensulphate

$$CH_3CH_2OSO_3H + \underset{(H_2O)}{H\text{-}OH} \longrightarrow CH_3CH_2OH + H_2SO_4$$

5-Halohydrins formation of Alkenes: Addition of HOX

Reaction of alkenes with hypohalous acids HO–Cl or HO–Br yields 1,2-halo alcohol, called a halohydrin

Addition takes place by reaction of the alkene with either Br2 or Cl2 in the presence of water.

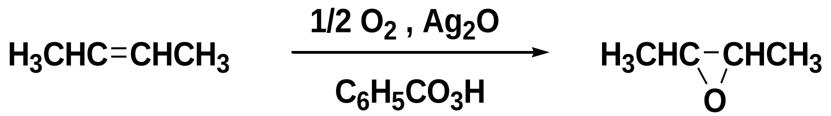


$$H_2C{=}CH{-}CH_3 + Cl_2 + H_2O \longrightarrow H_2\underset{Cl}{C}{-}\underset{OH}{CH}{-}CH_3 + HCl$$

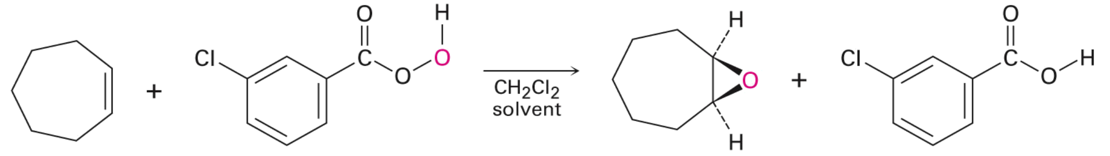
6-Oxidation reaction of alkenes:
i-Epioxidation
ii-Hydroxylation
iii-Ozonolysis

i)Epoxidation

Oxidation using oxygen only by Ag_2O or peracids (RCOOOH) leads to the formation of alkylene oxides (epoxides).e. g.



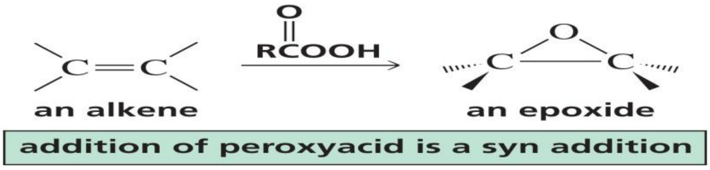
$$H_3CHC{=}CHCH_3 \xrightarrow[C_6H_5CO_3H]{1/2\ O_2\ ,\ Ag_2O} \underset{O}{H_3CHC-CHCH_3}$$

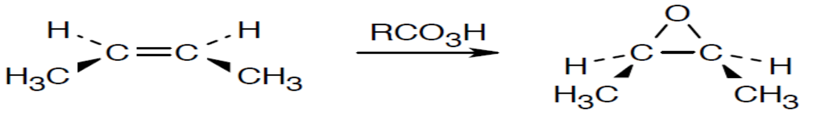


Cycloheptene ***meta*-Chloroperoxybenzoic acid** **1,2-Epoxycycloheptane** ***meta*-Chlorobenzoic acid**

Only Syn Addition is Observed

The addition of a peroxyacid to an alkene to form an epoxide is a concerted reaction: the oxygen atom adds to the two sp2 carbons at the same time. Therefore, it must be a syn addition.





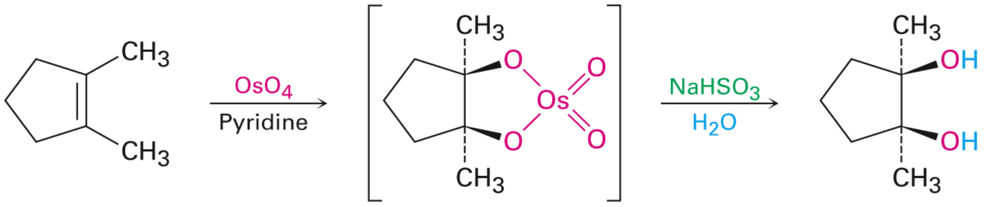
cis-2-Butene *cis*-2,3-Epoxybutane

ii) Hydroxylation

Hydroxylation can be carried out directly by treating an alkene with osmium tetroxide

Reaction occurs with syn stereochemistry

Does not involve a carbocation intermediate

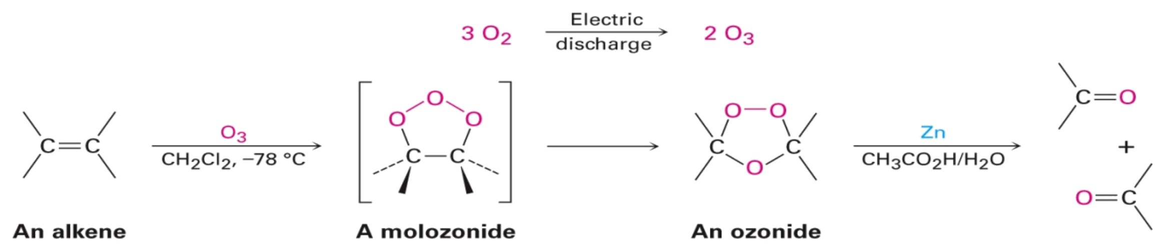


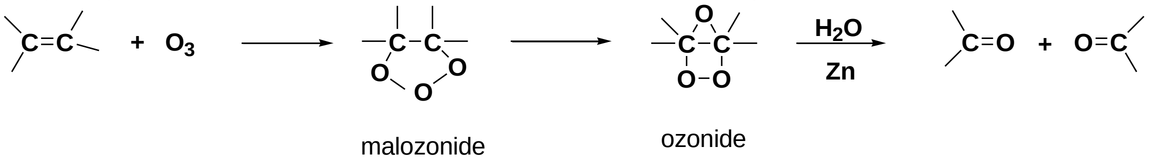
1,2-Dimethylcyclopentene **A cyclic osmate intermediate** ***cis*-1,2-Dimethyl-1,2-cyclopentanediol (87%)**

iii)ozonolysis

Ozone (O_3) adds to C=C bond, at low temperature, to form molozonide

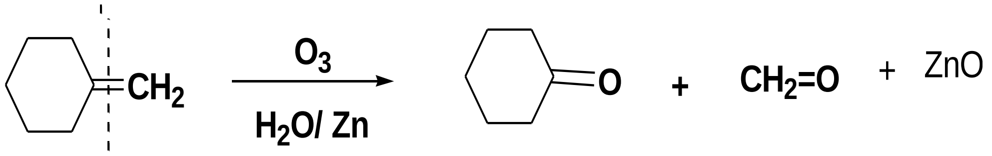
Molozonide rearranges to form ozonide





$$H_3CHC{=}CHCH_3 \xrightarrow[H_2O/\ Zn]{O_3} H_3CHC{=}O + O{=}CHCH_3 + ZnO$$

$$CH_3CH{=}CH_2 \xrightarrow[H_2O/\ Zn]{O_3} H_3CHC{=}O + CH_2{=}O + ZnO$$

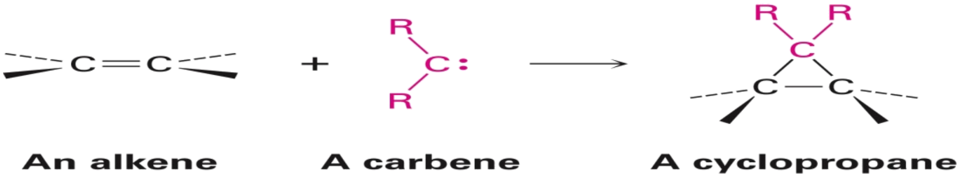


7-)Addition of Carbenes to Alkenes: Cyclopropane Synthesis

Carbene, R_2C: A neutral molecule containing a divalent carbon with only six electrons in its valence shell

Electrophilic addition of a carbene to an alkene yields a cyclopropane

Adds symmetrically across the double bond



8-)Hydroboration-Oxidation:

an Anti- Markovnikov Hydration

$$RCH{=}CH_2 + BH_3 \longrightarrow (RCH_2CH_2)_3B \xrightarrow{H_2O_2} 3\ RCH_2CH_2OH$$

$$(CH_3)_2CHCH_2CH{=}CH_2 \xrightarrow[2.\ H_2O_2,\ NaOH,\ H_2O]{1.\ BH_3,\ THF} (CH_3)_2CHCH_2CH_2CH_2\ddot{O}H$$