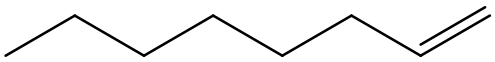
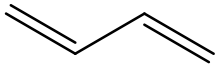
## ALKENES (OLEFINS)

Alkenes form a homologous series of unsaturated hydrocarbons containing a carbon-carbon double bond with the general formula $C_nH_{2n}$.

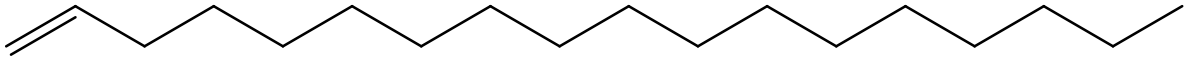
Alkenes are found in nature as well. Ethene is responsible for ripening of fruits, 1-octene is a constituent of lemon oil, octadecene is found in silver fish, butadiene is found in coffee, lycopene and carotenes ($C_{40}H_{56}$) give the attractive colour of red, orange and yellow colours of watermelons, tomatoes, carrots, and other fruits and vegetables. Vitamin A is derived from carotene. Hence, the world would be much less colourful place without alkenes.



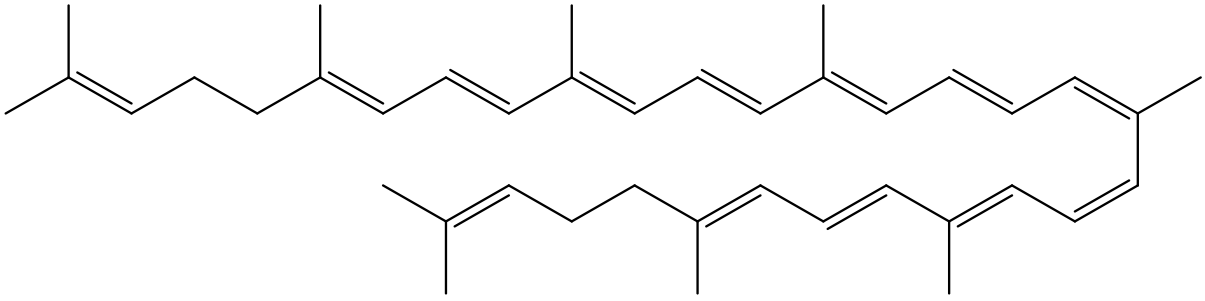
1-Octene



Butadiene



Octadecene



Lycopene

## PHYSICAL PROPERTIES

i. Physical State

These double-bonded compounds are colourless and odourless in nature. However, ethene is an exception because it is a colourless gas with a faintly sweet odour. The first three members of the alkene group are gaseous in nature, the next fourteen members are liquids and the remaining alkenes are solids.

ii. Solubility

The alkenes are insoluble in water due to their nonpolar characteristics. But are completely soluble in nonpolar solvents such as benzene, ligroin, etc.

iii. Boiling Point

The boiling points of the compounds increase as the number of carbon atoms in the compound increases. When alkenes are compared with alkanes, it is found that the boiling points of both are almost similar, as if the compounds are made up of the same carbon skeleton. The boiling point of straight-chain alkenes is more than branched-chain alkenes just as in alkanes.

iv. Melting Point

The melting points of these double-bonded compounds depend upon the positioning of the molecules. The melting point of alkenes is similar to that of alkanes. However, cis-isomer molecules have a lower melting point than trans- isomers as the molecules are packed in a U-bending shape.

Table showing melting and boiling points of some alkanes and alkenes

| **Alkanes** | **Formula** | **Mpt (º C)** | **Bpt (º C)** | **Alkene** | **Formula** | **Mpt (º C)** | **Bpt (º C)** |
|---|---|---|---|---|---|---|---|
| Methane | $CH_4$ | -182 | -164 | | | | |
| Ethane | $C_2H_6$ | -183 | -89 | Ethene | $C_2H_4$ | -169 | -104 |
| Propane | $C_3H_8$ | -188 | -42 | Propene | $C_3H_6$ | -185 | -47 |
| Butane | $C_4H_{10}$ | -138 | -1 | 1-Butene | $C_4H_8$ | -185 | -6 |
| Pentane | $C_5H_{12}$ | -130 | 36 | 1-Pentene | $C_5H_{10}$ | -138 | 30 |
| Hexane | $C_6H1_4$ | -95 | 69 | 1-Hexene | $C_6H_{12}$ | -140 | 63 |
| Heptane | $C_7H_{16}$ | -91 | 98 | 1-Heptene | $C_7H_{14}$ | -119 | 94 |
| Octane | $C_8H_{18}$ | -57 | 125 | 1-Octene | $C_8H_{16}$ | -102 | 121 |

v. Polarity

Alkenes are weakly polar just like alkanes but are slightly more reactive than alkanes due to the presence of double bonds. The π electrons which make up the double bonds can easily be removed or added as they are weakly held. Hence, the dipole moments exhibited by alkenes are more than alkanes. The polarity depends upon the functional group attached to the compounds and the chemical structures.

## NOMENCLATURE OF ALKENES

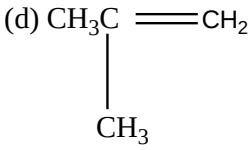
In accordance with the IUPAC system, an alkene is named by dropping the ending *-ane* from the corresponding alkane and replacing it with suffix *-ene.*

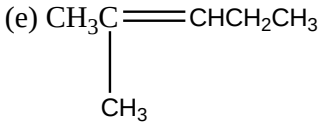
Where required, the position of the double bond is specified by appropriate number between the stem name and ending *-ene* except for ethene and propene without positional isomers.

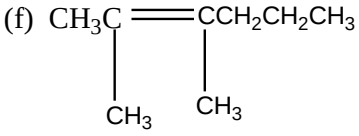
***Example***

Name the following organic compounds using the IUPAC System:

(a) $CH_3CH=CH_2$ (b) $CH_3CH_2CH=CH_2$ (c) $CH_3CH=CHCH_3$

(d) 

(e) 

(f) 

***Solution:***

(a) Propene (b) But-1-ene (c) But-2-ene (d) 2-methylpropene

(e) 2-methylpent-2-ene (f) 2, 3-dimethylhex-2-ene

**Question**

(a) Draw the structure of the following organic compounds:

i. 3, 3-dimethylcyclopentene

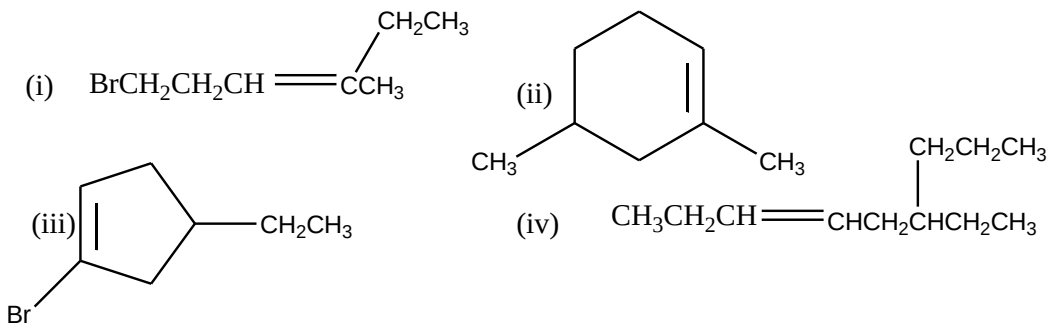
ii. 6-bromo-2, 3-dimethylpent-2-ene

iii. 3, 6-dimethyloct-3-ene

iv. 5-bromo-4-chlorohept-1-ene

v. 4-ethyl-3-methylcyclohexene

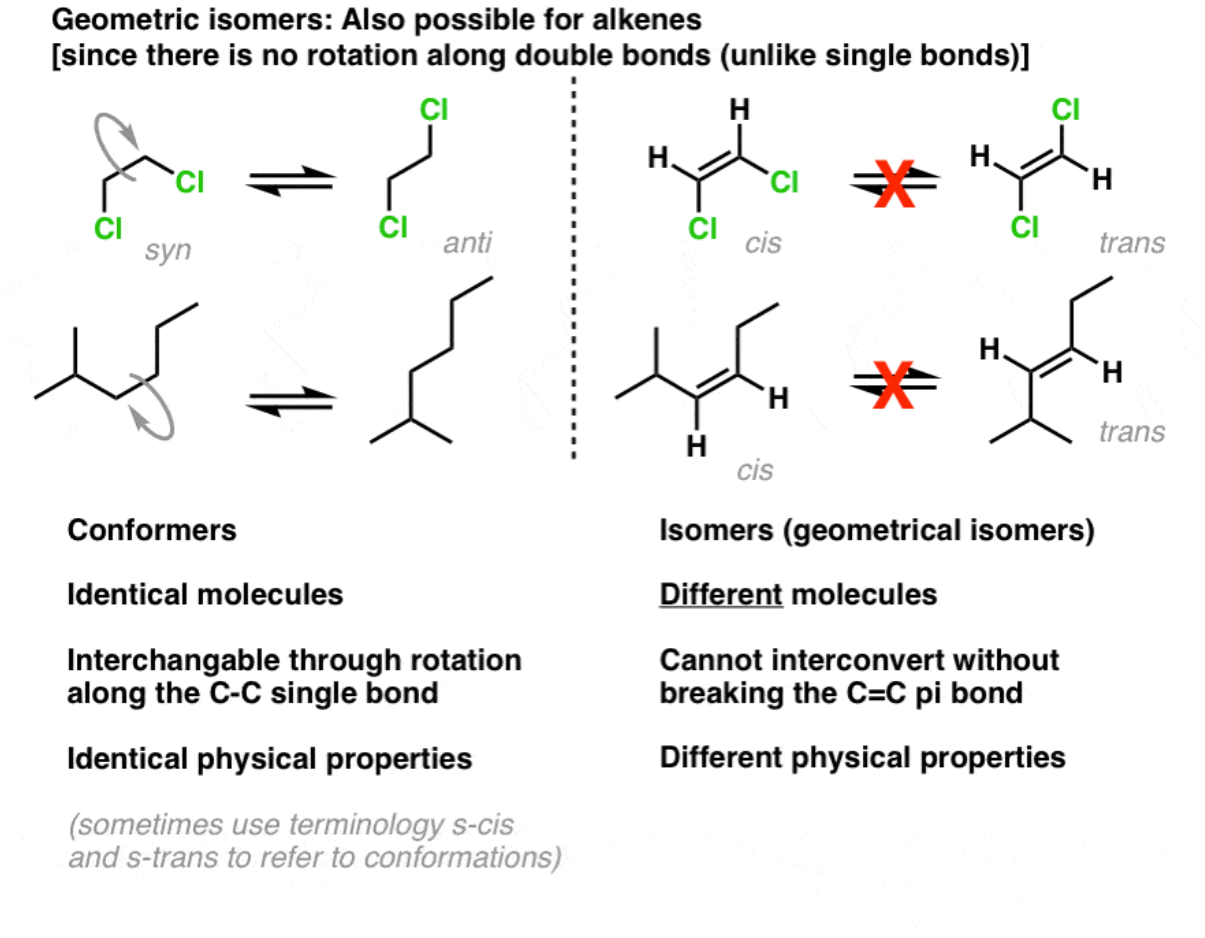
(b) Name the following organic compounds:




***cis*– and *trans*- Isomerism (Geometric Isomerism) In Alkenes**

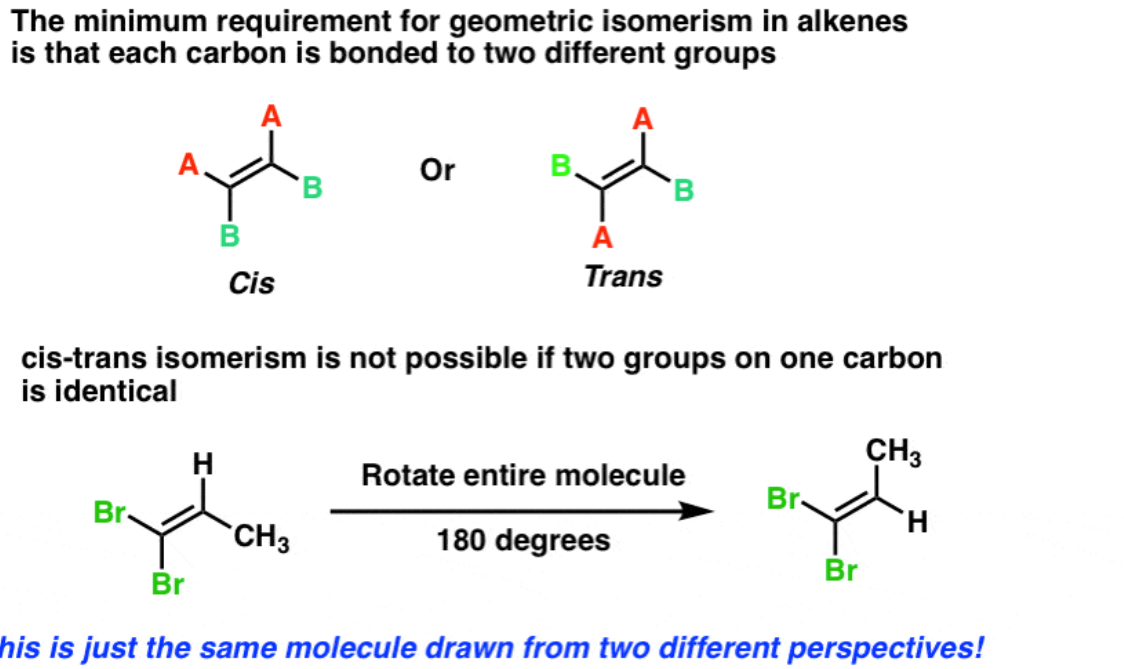
*cis-trans* isomerism is also possible for alkenes. As in small rings, rotation about pi bonds is also constrained: due to the "side-on" overlap of pi bonds, **one can't rotate a pi bond without breaking it**. This stands in contrast to conventional sigma bonds (single bonds) in acyclic molecules, where free rotation is possible: witness 1,2-dichloroethane (below left).

Hence, we can have molecules such as *cis*-1,2-dichloroethene [boiling point 60°C] and *trans*-1,2-dichloroethene [boiling point: 48°C] which can be separated from each other due to their differing physical properties.



We can also use the *cis–trans* nomenclature to distinguish isomers such as 2-methyl-3-hexene (above right). In the *cis* isomer, the two hydrogens are on the same side of the pi bond, and in the *trans* isomer, the two hydrogens are on the opposite side of the bond.

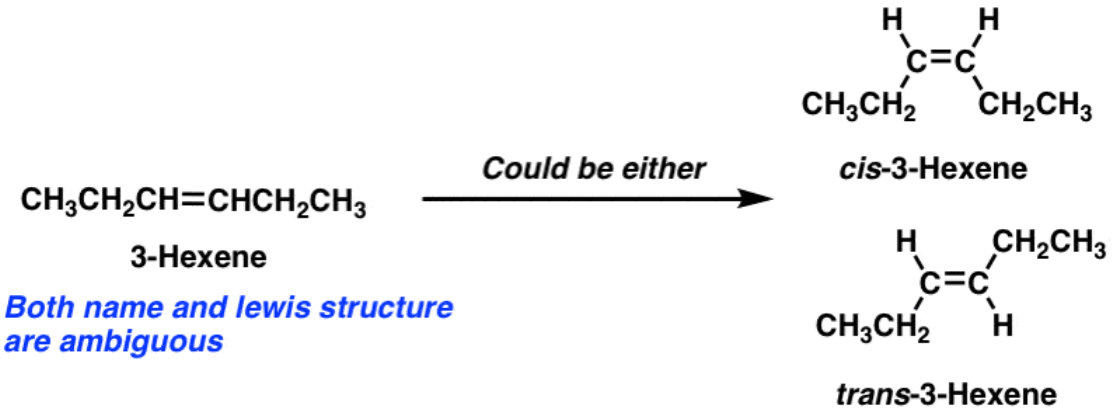
As with rings, the minimum requirement for *cis-trans* isomerism in alkenes is that **each carbon is bonded to two different groups,** and that **the two carbons have at least one substituent in common.** As with rings, *cis-trans* isomerism isn't possible if one of the carbons of the double bond is attached to two identical groups, as with 1,1-dibromo-1-propene, below.




**Ambiguous Names Where Cis/Trans Isomerism Is Possible**

A quick digression: one consequence of our newfound appreciation of geometrical isomerism is that many simple-sounding molecule names are actually ambiguous.

For instance, the descriptor "3-hexene" does not unambiguously describe a specific molecule. To nail down the specific molecule, we need to specify *cis*– or *trans*– 3-hexene.




Note that 1-hexene is still OK, since the 1-position of 1-hexene is attached to two identical groups (hydrogens) and thus no *cis*–*trans* isomers are possible.

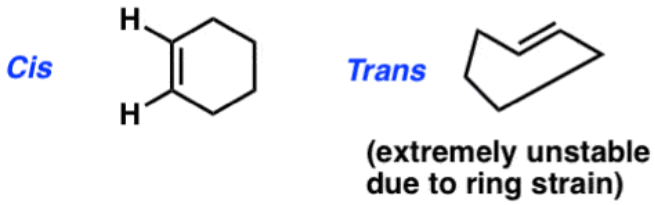
### *Cis*– *Trans*- Isomerism for Cyclic Alkenes

*cis*- and *trans* can also be applied to alkenes in rings. For example, *on paper* it's possible to draw *cis*– and *trans*– cyclohexene, since the pi bond fulfills the requirements for *cis*-*trans*- isomerism. In reality, *trans*-cyclohexene is impossibly strained. For this reason, for ring sizes 7 and below, it's safe to ignore writing "*cis*": the configuration is assumed.

**Cis and trans alkenes in rings**

Double bonds in cycloalkenes of 7 or fewer carbons are exclusively *cis*.

The *trans* isomers are too strained to stable under ordinary conditions

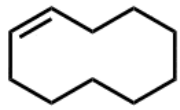



For this reason we can omit the *cis*- when naming "cyclohexene".
A "cis" configuration is assumed.

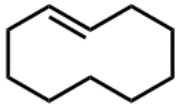
At ring sizes of 8 and above, we *do* need to put a *cis*– or *trans*- in the name, because the *trans*– isomer becomes feasible. (Imagine trying to kiss yourself on the tailbone if you had the neck of a giraffe: suddenly not impossible!)

**Larger rings**

For cycloalkenes containing 8 or more carbons, a non-ambiguous name should indicate the alkene stereochemistry



***cis*-Cyclodecene**



***trans*-Cyclodecene**

**Solution for When "Cis" and "Trans" Fails: The E/Z System**

We saw that *cis* and *trans* fails in rings when the two carbons lacked a common substituent. It also fails for alkenes under these circumstances.

Case in point: try to apply *cis* and *trans* to the alkene below:

**Where "cis" and "trans" fails**


- These alkenes are also geometric isomers: they have the same molecular formula but can't be interconverted through rotation.
- However, all 4 groups attached to the double bond are different. (Br, F, Cl, $CH_3$) .
- Therefore it is impossible to use the "cis" and "trans" nomenclature here.
- Instead we must use "E/Z" nomenclature for these cases

[*note: some textbooks might still refer to this as "cis-trans isomerism" regardless]*

See the problem?

In the absence of two identical groups, **we have no reference point!**

On the left, the chlorine is *cis* to Br and *trans* to F. But does that really justify calling the isomer "*cis*"? How do we decide?

What we need is some way to determine **priorities** in these situations.

**The *E* and *Z* Notation for Alkenes**

Thankfully, we can apply the ranking system developed by Cahn, Ingold, and Prelog for chiral centres for this purpose.

The protocol is as follows:

- Each carbon in the pi bond is attached to two substituents. For **each carbon**, these two substituents are **ranked** (1 or 2) according to the atomic numbers of the atom directly attached to the carbon. (e.g., Cl > F)
- If both substituents ranked 1 are on the **same side** of the pi bond, the bond is given the descriptor *Z* (short for German *Zusammen*, which means "together").
- If both substituents ranked 1 are on the **opposite side** of the pi bond, the bond is given the descriptor *E* (short for German *Entgegen*, which means "opposite").

So, *Z* resembles *"cis"* and *E* resembles *"trans"*. *(Note: they are not necessarily the same and do not always correlate: see Note 2 for an example of a cis alkene which is E . The E/Z system is comprehensive for all alkenes capable of geometric isomerism, including the cis/trans alkene examples above. We often use cis/trans for convenience, but E/Z is the "official", IUPAC approved way to name alkene stereoisomers].*

One easy way to remember *Z* is to say "Zee Zame Zide" in a German accent.

Here's a practical example:

**The E/Z Naming Protocol**

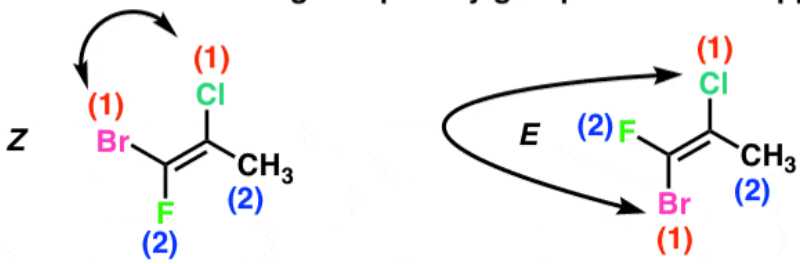
**For <u>each</u> carbon of the pi bond in question:**

**Rank the two atoms directly attached to the pi bond by atomic number. Higher atomic number, higher priority: e.g. I > Br > Cl > F > N**


***For both alkenes, compare Br vs F on the first carbon, and Cl vs C on the second carbon. The atom with the higher atomic number is priority #1.***

**The alkene where the highest priority groups are on the same size is *Z***

**The alkene where the highest priority groups are on the opposite side is *E***



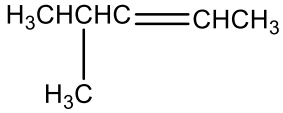

***This alkene is "Z" because highest priorities are on the same side***

***This alkene is "E" because highest priorities are on opposite sides.***

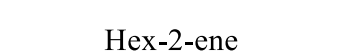
**Useful mnemonic: Z = "Zee zame zide"**

**ISOMERISM**

**Chain isomerism,**

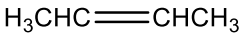



4-methylpent-2-ene

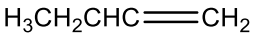



Hex-2-ene

**Positional isomerism,**

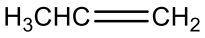


But-2-ene



But-1-ene

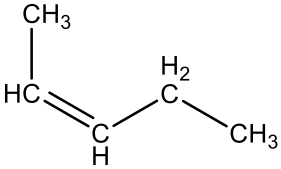
**Functional isomerism,**



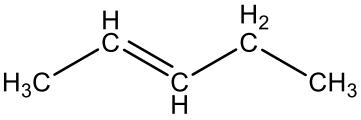
Propene

Cyclopropane

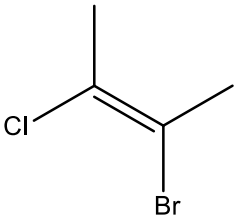
**cis- and trans isomerism**



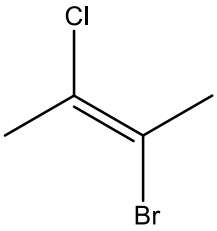
*cis*-Pent-2-ene



*trans*-Pent-2-ene



*cis*-2-Bromo-3-chlorobut-2-ene



*trans*-2-Bromo-3-chlorobut-2-ene

**SYNTHETIC PREPARATIONS OF ALKENES**

Alkenes are generally prepared by elimination of one atom or groups from two adjacent carbon atoms mainly from alcohols and halo alkanes.

The ease of dehydration of alcohols is: $3^o$ Alcohol> $2^o$>$1^o$Alcohol while the ease of dehydrohalogenation of halo alkanes is $3^o$> $2^o$>$1^o$

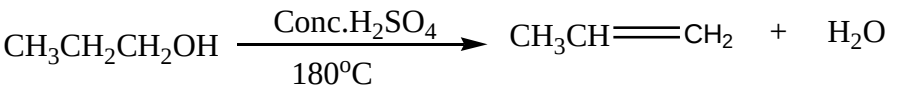
1. **From Alcohols**

Alcohols are heated with excess concentrated sulphuric acid or orthophosphoric acid. The temperature of dehydration depends on the structure of the alcohol.

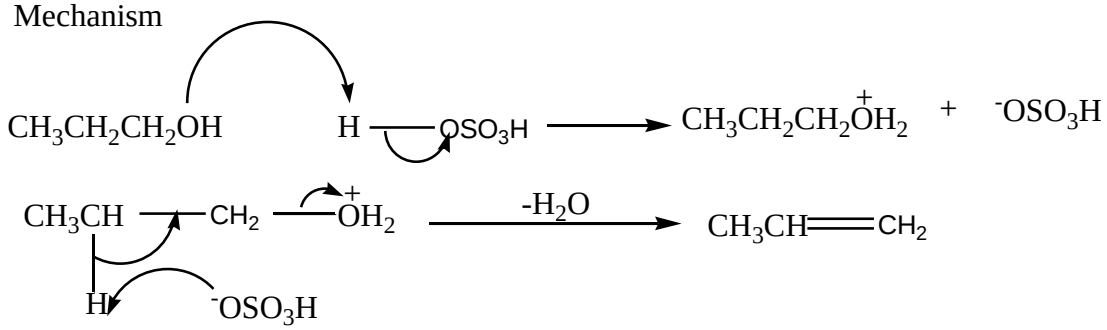
The reaction involves removal of water molecules hence known as *dehydration reaction*

The $1^o$ and $2^o$ alcohols follow the same mechanism while $3^o$ alcohols undergoes partial ionization generating $3^o$ carbocations

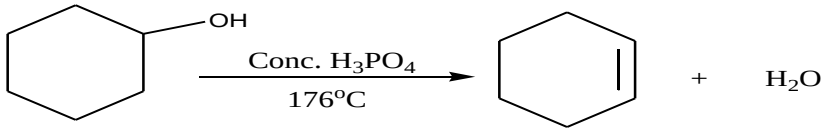
**Example**



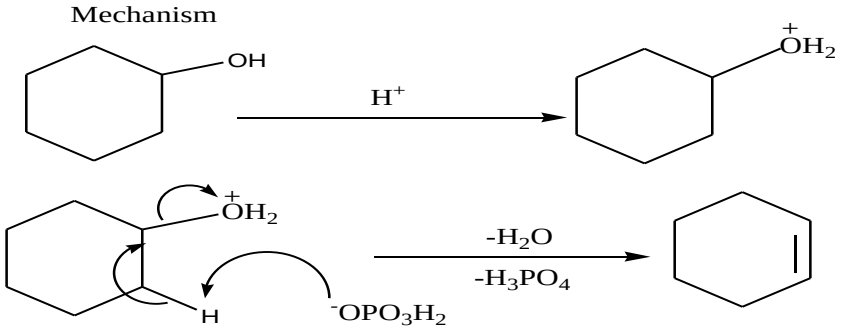

Mechanism



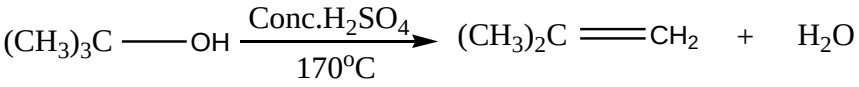

**Example**



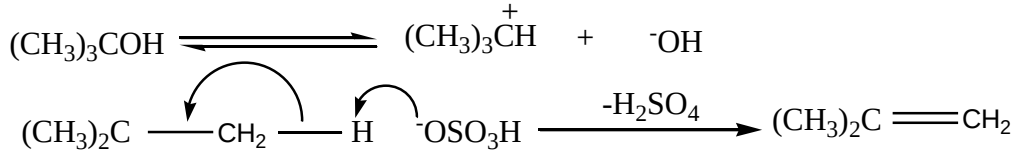

Mechanism



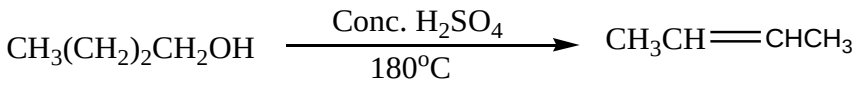

**Example**




Mechanism



**Example**



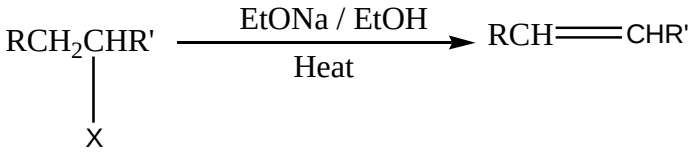

Write the mechanism of the above reaction.

**2. From Haloalkanes**

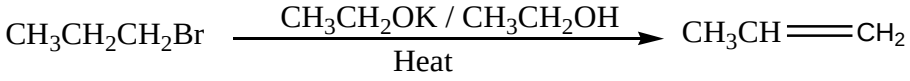
Halo alkanes are heated with a strong base to generate an alkene.

**i. Dehydrohalogenation of alkyl halides.**

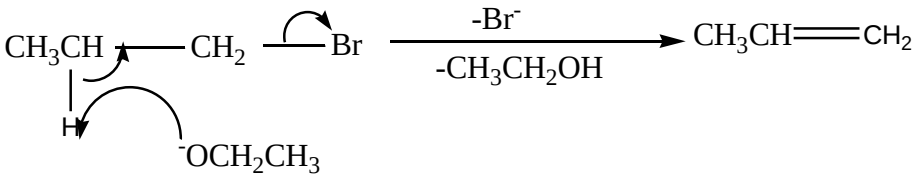
Halo alkanes are heated with a strong base such sodium amide in liquid ammonia or sodium ethoxide in ethanol in order to remove hydrogen halide i.e.



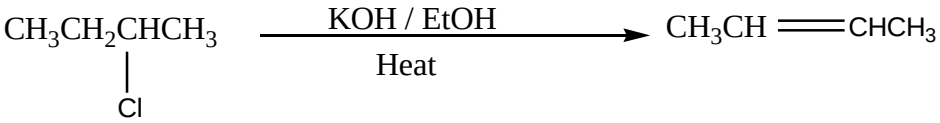

Example



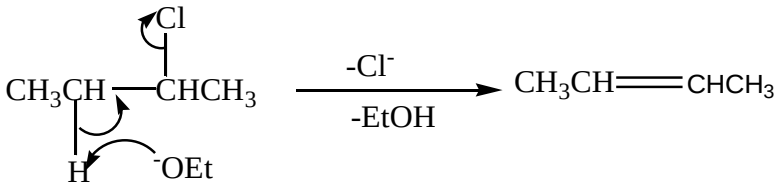

Mechanism



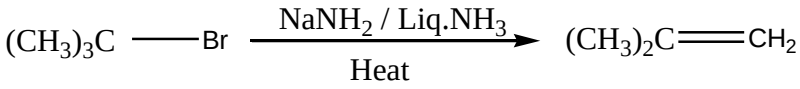

Example



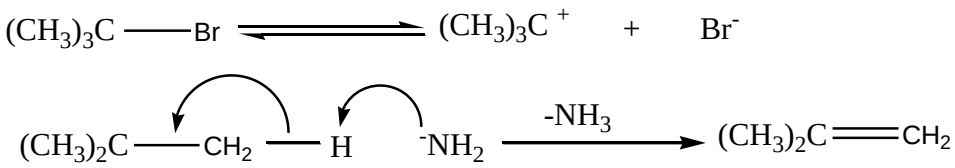

Mechanism




Example

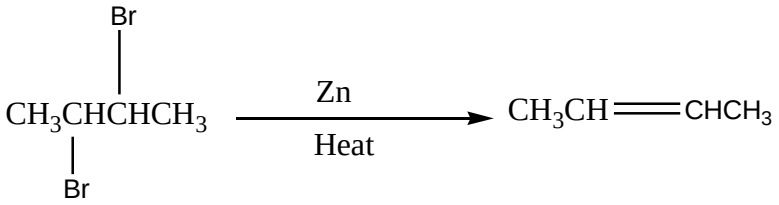



Mechanism




**ii. Dehalogenation of Vicinal dihalides**

When vicinal dihalides are heated with Zinc, alkenes are formed i.e.



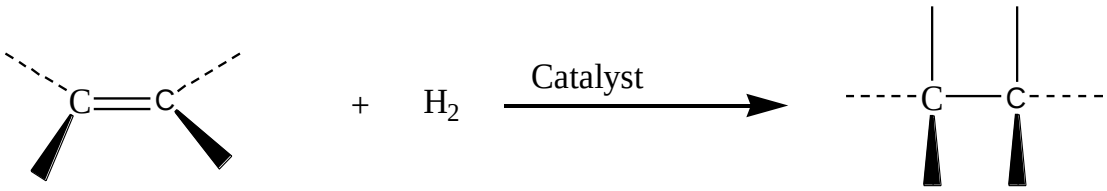

**N.B.** On a large scale, alkenes are obtained by cracking of petroleum products

**REACTIONS OF ALKENES**

Alkenes undergo electrophilic addition, reduction by hydrogen, oxidation and polymerization reactions. Alkenes undergo Electrophilic addition since they are electron rich species.

**1. Addition of Hydrogen to Alkenes**

Alkene react with hydrogen in the presence of a metal catalyst to produce the corresponding saturated alkane addition products. Platinum, nickel and palladium can be used as catalysts




An alkene

An alkane

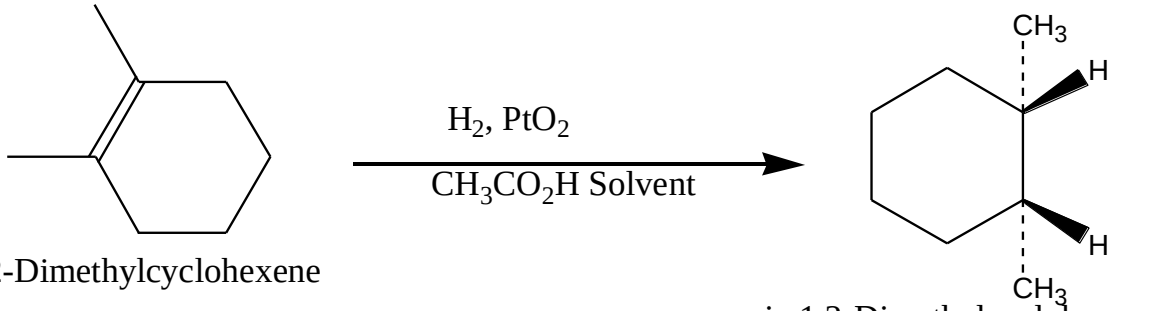
**Examples**,

$$RCH{=}CHR' \xrightarrow[150^oC]{H_2 / Ni} RCH_2CH_2R'$$

e.g.

$$CH_3CH{=}CH_2 \xrightarrow[150^oC]{H_2 / Ni} CH_3CH_2CH_3$$

Platinum and palladium are the most common catalysts for alkene hydrogenation. Palladium is normally used as a very fine powder "supported" on an inert material such as charcoal (Pd/C) to maximize surface area. Platinum is normally used as $PtO_2$, a reagent called Adams' catalyst. The reaction is a heterogeneous one, that is, it takes place on the surface of insoluble catalyst particle. The reaction occurs with **Syn stereochemistry**- both hydrogen atoms add to the double bond from the same face.

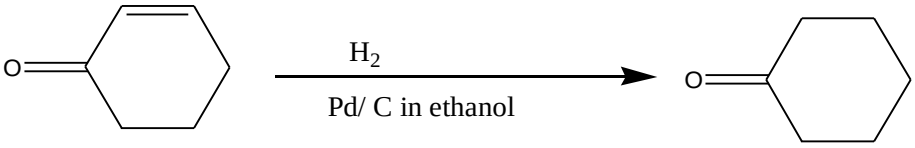



1,2-Dimethylcyclohexene

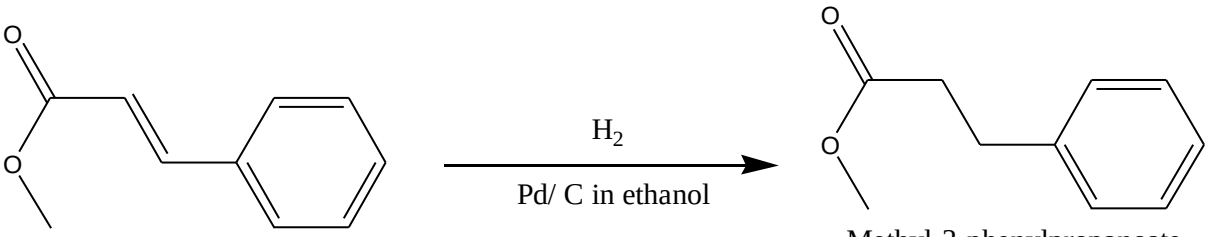
cis-1,2-Dimethylcyclohexane

The first step is the adsorption of hydrogen onto the catalyst surface. Secondly, complexation between catalyst and alkene that occurs as a vacant orbital on the metal interacts with the filled alkene pie orbital. Lastly, hydrogen is inserted into the double bond. The reaction is so sensitive to the steric environment around the double bond, as a result, the catalyst often approaches only the more accessible face of an alkene, giving rise to a single product.

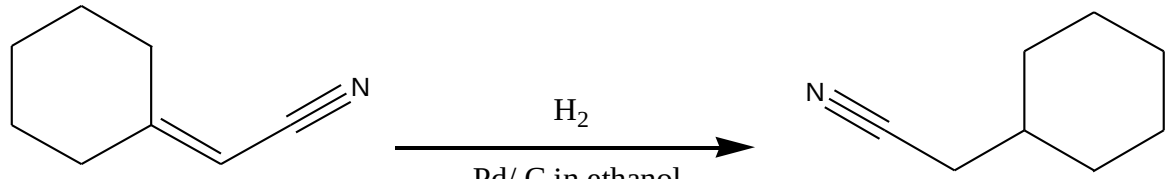
Also, alkenes are much more reactive than most other unsaturated functional groups towards catalytic hydrogenation, and the reaction is therefore quite selective as shown below. Other functional groups such as aldehyde, ketone, esters and nitrile survive normal alkene hydrogenation with conditions unchanged, although reaction with these function groups does occur under more vigorous conditions.




2-Cyclohexenone Cyclohexanone (Ketone NOT reduced)




Methyl-3-phenylpropenoate Methyl-3-phenylpropanoate
(Aromatic ring NOT reduced)



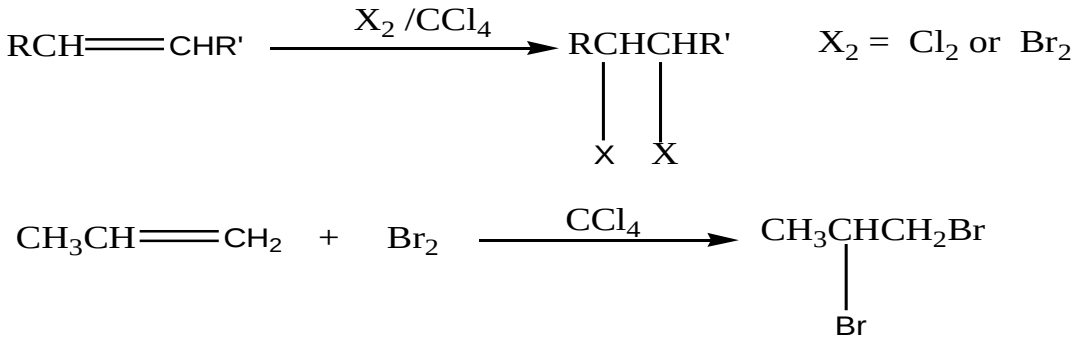

Cyclohexylidene acetonitrile Cyclohexyl acetonitrile
(Nitrile NOT reduced)

This reaction is quite applicable in food industry, where unsaturated vegetable oils are reduced to produce the saturated fats used in margarine and cooking products. Vegetable oils are triesters of glycerol $OHCH_2CH(OH)CH_2OH$ with three long chain carboxylic acids called fatty acids. The fatty acids are generally polyunsaturated and their double bonds invariably have cis stereochemistry. Complete hydrogenation yields the corresponding saturated fatty acids but incomplete hydrogenation often results in partial cis- trans- isomerization of the remaining double. When eaten and digested, the free trans- fatty acids are released, raising blood cholesterol levels and contributing to potential coronary problems.

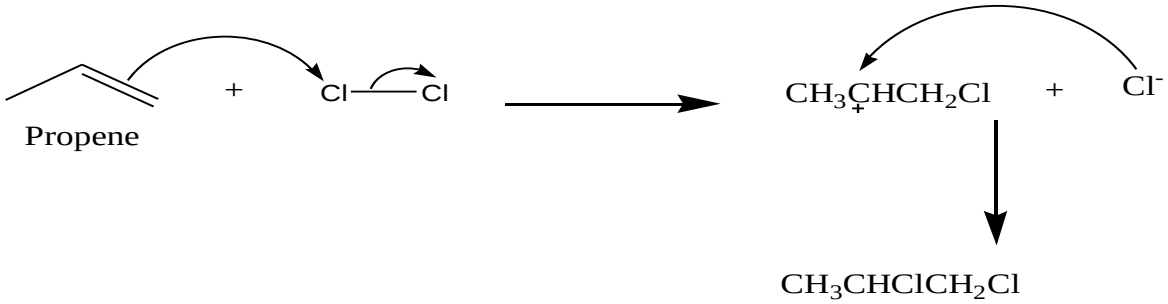
### 2. Addition of Halogens to Alkenes

This reaction is usually carried out in an inert solvent such carbon tetrachloride. Chlorine and Bromine reacts rapidly with alkenes to yield 1, 2- dihalides in a process called halogenation. Fluorine is too reactive and difficult to control for most laboratory applications, and iodine does not react with most alkenes.

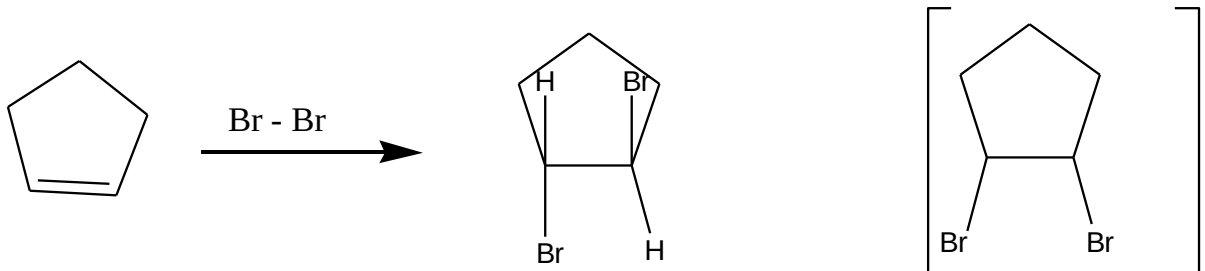
The reddish- brown colour of bromine is turned colourless therefore the reaction is used to test for presence of carbon-carbon double bond and the number of double bonds since the mole ratio is 1:1(Alkene: Bromine)



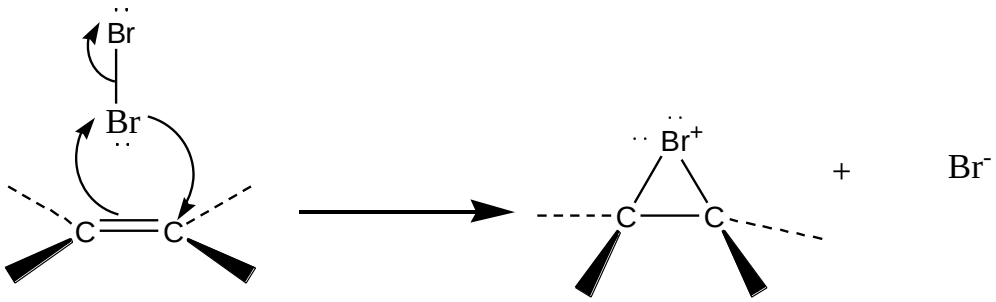

The mechanism involving carbocation seems plausible at first sight. However, it does not explain the stereochemistry of the addition reaction. That is, the mechanism does not tell which product stereoisomer is formed.




When the halogenation reaction is carried out on a cycloalkene, such as cyclopentene, only the trans- stereoisomer of the dihalides addition products is formed rather than the mixture of cis- and trans- isomers that might have been expected if a planar carbocation intermediate were involved.

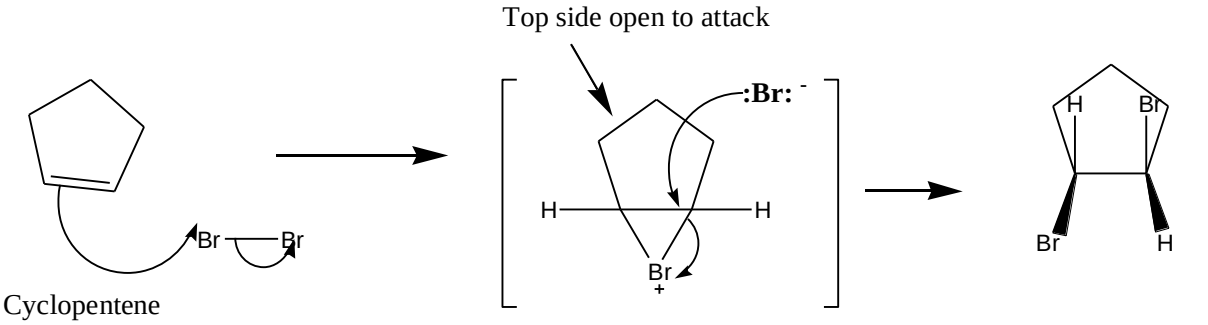



The explanation for the observed **antistereochemstry** of addition was proposed that the reaction intermediate is not a carbocation but instead a bromonium ion, $R_2Br^+$, formed by addition of $Br^+$ to the alkene. Similarly, a chloronium ion contains a positively charged divalent chlorine, $R_2Cl^+$. The bromonium ion is formed in a single step by interaction of the alkene with $Br_2$ and simultaneous loss of $Br^-$.




An alkene A bromonium ion

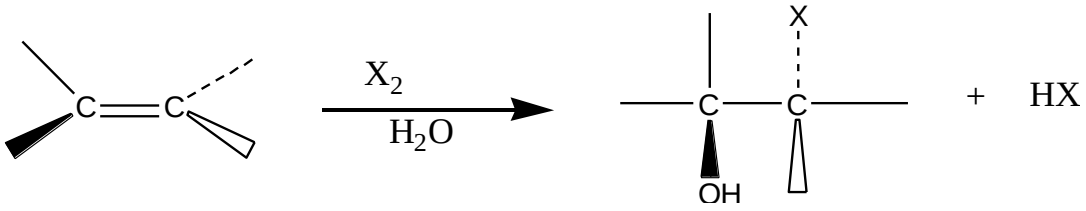
Reaction with $Br^-$ ion in the second step could then occur only from the opposite, unshielded side to give trans- product.



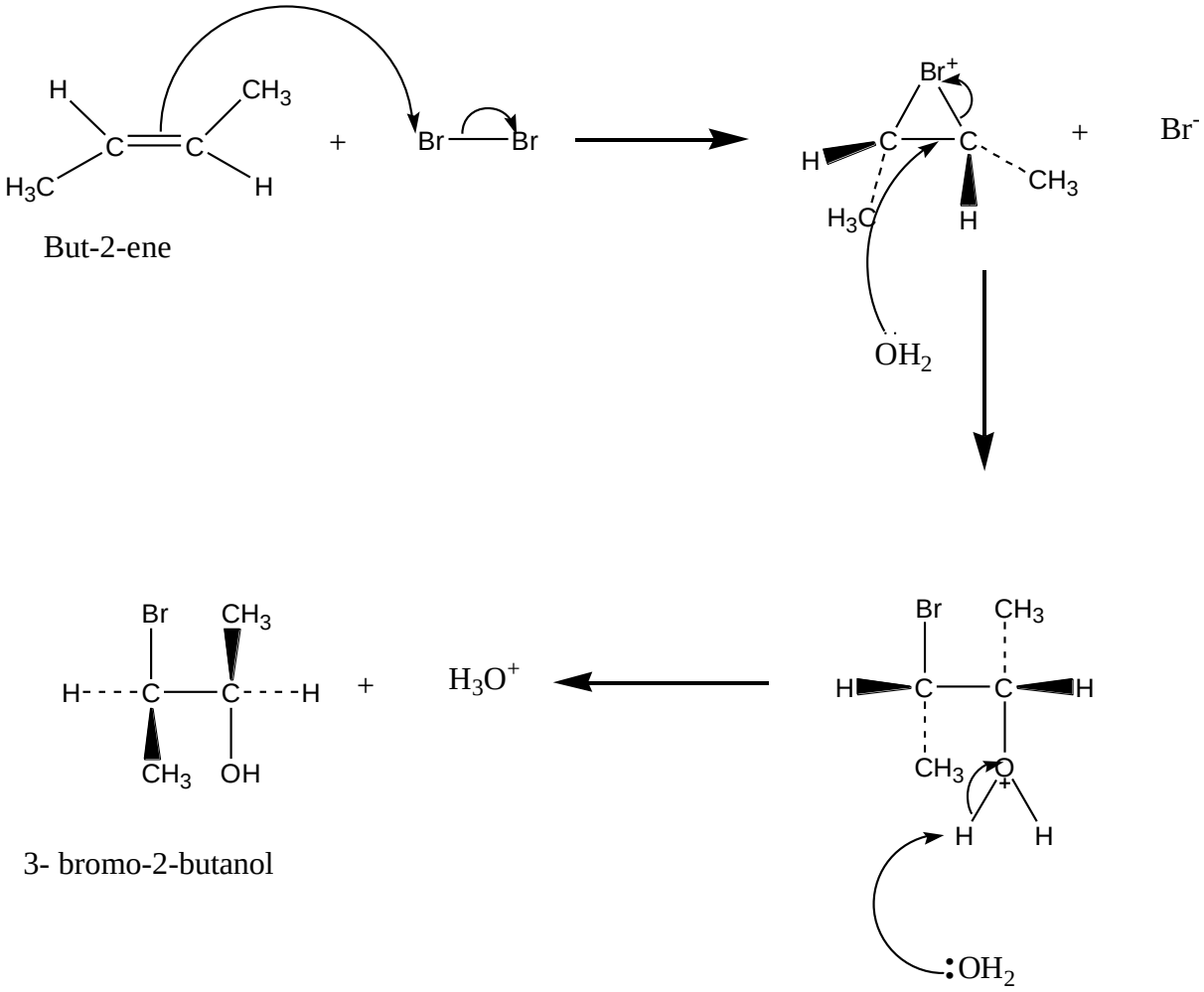

Cyclopentene A bromonium ion intermediate trans- 1,2-Dibromocyclopentane

### 3. Addition of Hypohalous acids to Alkenes: - Halohydrin Formation

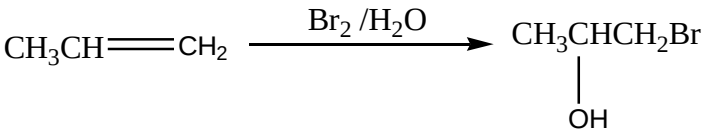
Reaction of alkenes with hypohalous acids HO - Cl or HO- Br to yield 1,2- halo alcohols, called halohydrins. The reaction takes place indirectly by reaction of an alkene with either $Br_2$ or $Cl_2$ in the presence of water.




**Mechanism**

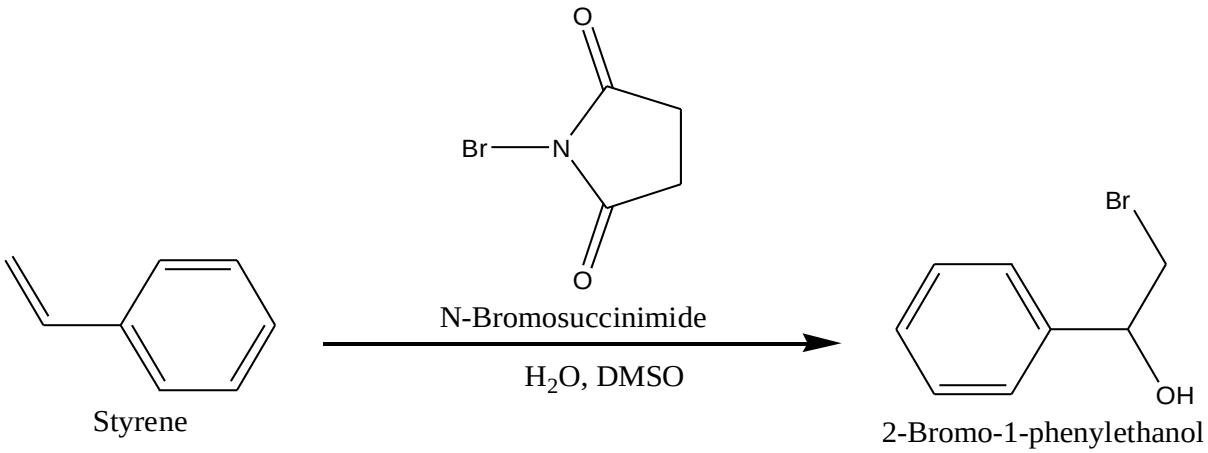



**Other examples**



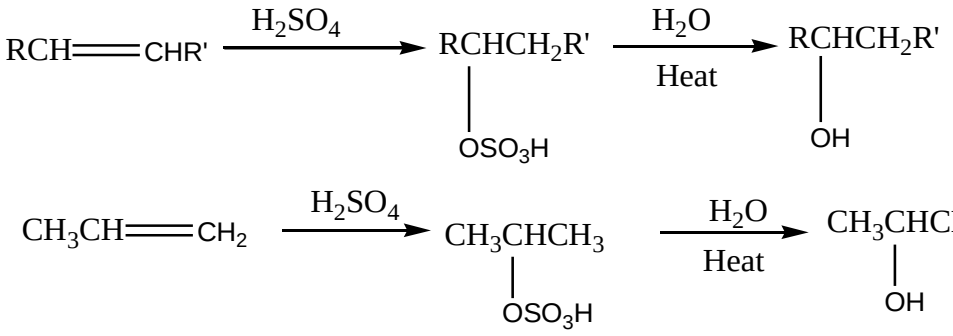
In practice, few alkenes are soluble in water, and bromohydrin formation is often carried out in a solvent such as aqueous dimethyl sulfoxide $CH_3SOCH_3$ (DMSO) using a reagent called N-bromosuccinimide (NBS) as a source of $Br_2$.

NBS is stable, easily handled compound that slowly decomposes in water to yield $Br_2$ at a controlled rate. Bromine itself can be also used in the addition reaction, but it is more dangerous and more difficult to handle than NBS.



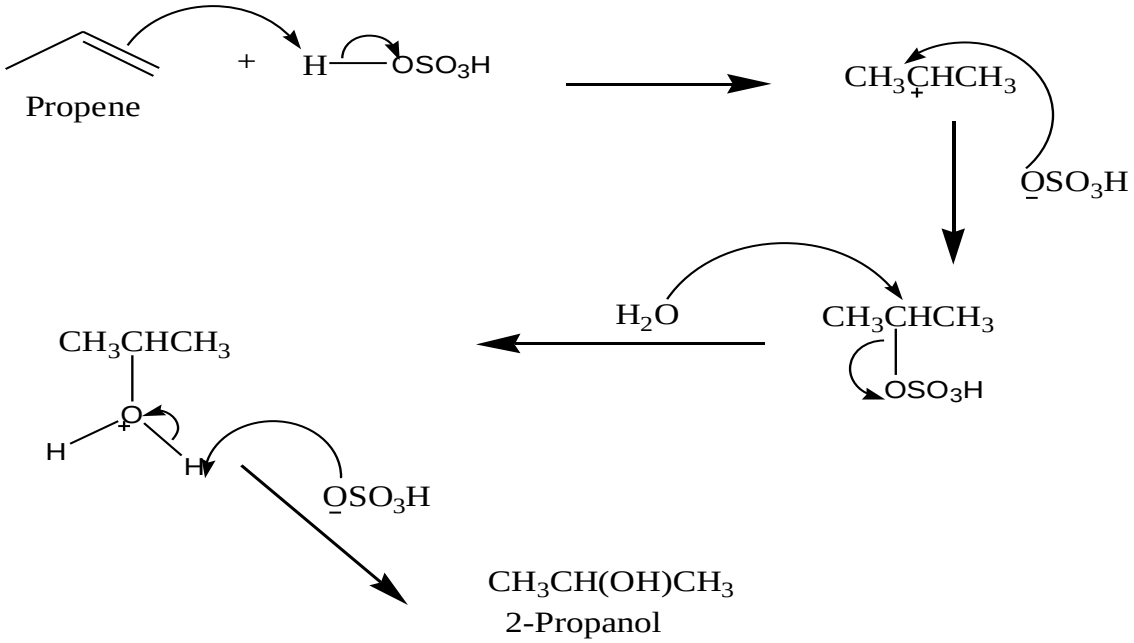

### 4. Addition of Water / Hydration to Alkenes

Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulphate which reacts with water on heating to form alcohol.



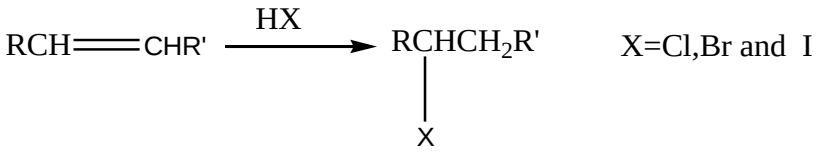

**Mechanism**

The mechanism follows Markovnikov's rule.

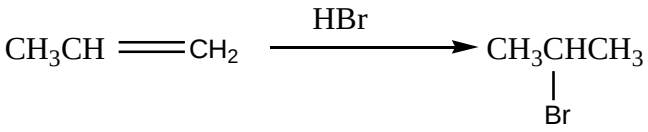



### 5. Addition of Hydrogen Halides to Alkenes

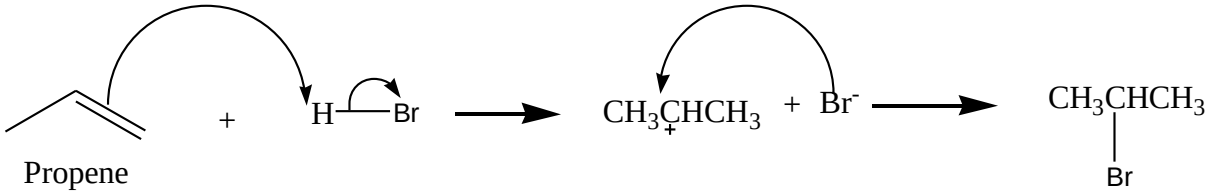
Hydrogen halides react with alkenes forming alkyl halides.



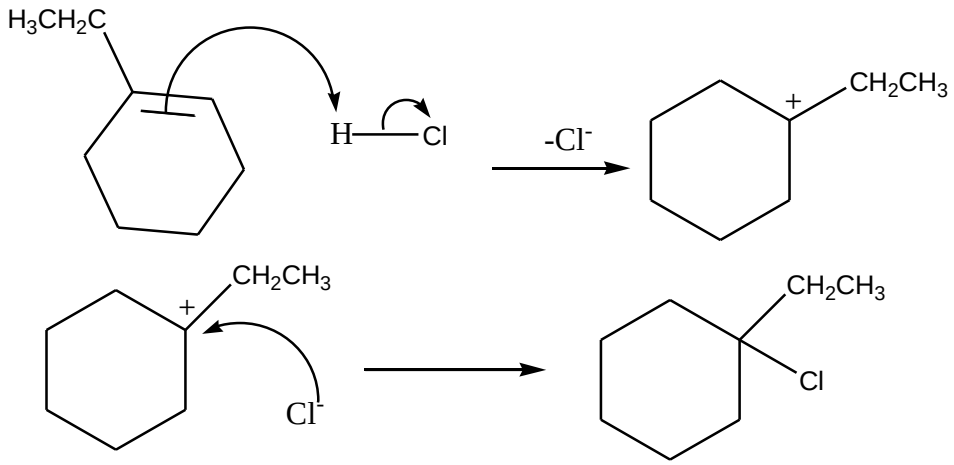

In the reaction above, the hydrogen atom from hydrogen halide adds itself to the carbon atom of the double bond with the larger number of hydrogen atoms. Also, the halogen adds itself to the carbon atom in double bond with lower number of hydrogen atom thus these are known as **Markovnikov's rule.**




**Mechanism**



**Example**




**N.B.** The hydrogen bromide is usually generated by action of concentrated Sulphuric acid on sodium bromide.

### 6. Addition of Hydrogen Bromide to Alkenes in presence of Peroxide

In this reaction, the bromine atom adds itself to the carbon atom of the double bond having higher number of hydrogen atoms with hydrogen atom (from Hydrogen bromide) to lower carbon atom.

This observation is known as anti-Markovnikov's rule.

$$RCH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} RCH_2CH_2Br$$

e.g.

$$CH_3CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2CH_2Br$$

Mechanism

$$RO{-}OR \longrightarrow 2\dot{O}R$$

$$RO\cdot + H{-}Br \longrightarrow ROH + Br\cdot$$

$$CH_3CH{=}CH_2 + Br\cdot \longrightarrow CH_3\dot{C}HCH_2Br$$

$$CH_3\dot{C}HCH_2Br + HOR \longrightarrow CH_3CH_2CH_2Br + \dot{O}R$$

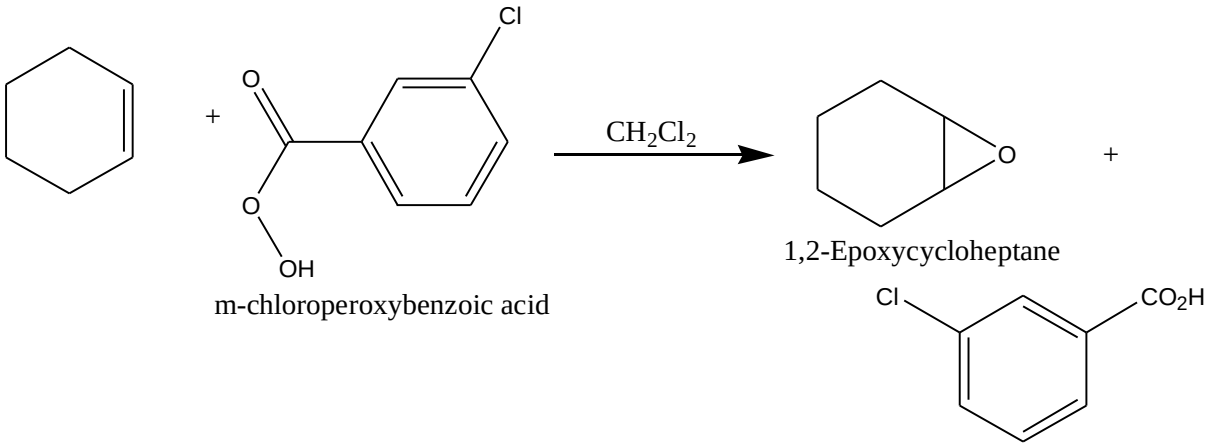
## 7. Oxidation of Alkenes: Epoxidation and Hydroxylation

This decreases electron density on carbon by either forming C-O, C-N, C-X or breaking C-H bond.

### Epoxidation

Alkenes are oxidized to give epoxides on treatment with a peroxy acids ($RCO_3H$), such as meta-chloro peroxybenzoic acid. An epoxide, also called an oxirane, is a cyclic molecule with an oxygen atom in a three membered ring.

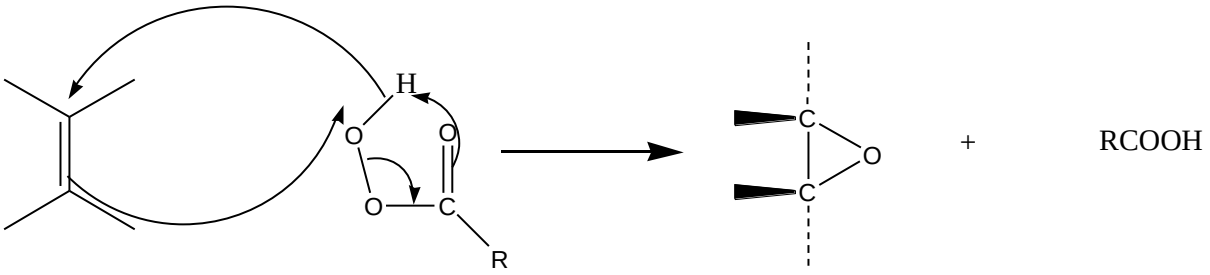
### Example




m-chloroperoxybenzoic acid

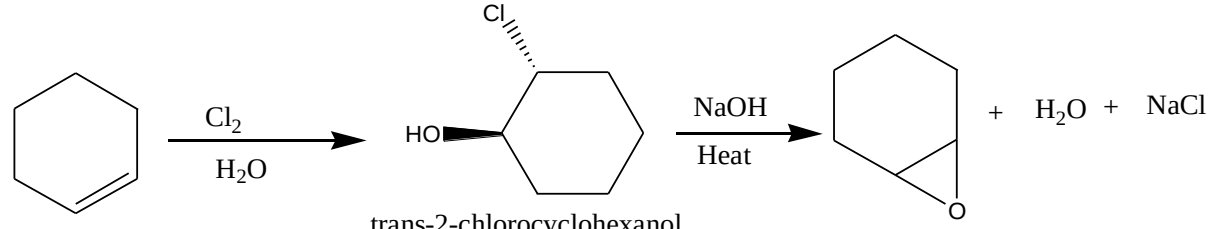
1,2-Epoxycycloheptane

### Mechanism




Epoxide

Also, halohydrins can generate epoxides. Halohydrins are prepared by addition of HO-X to alkenes. Heating halohydrins with a base eliminates HX and produces epoxides.

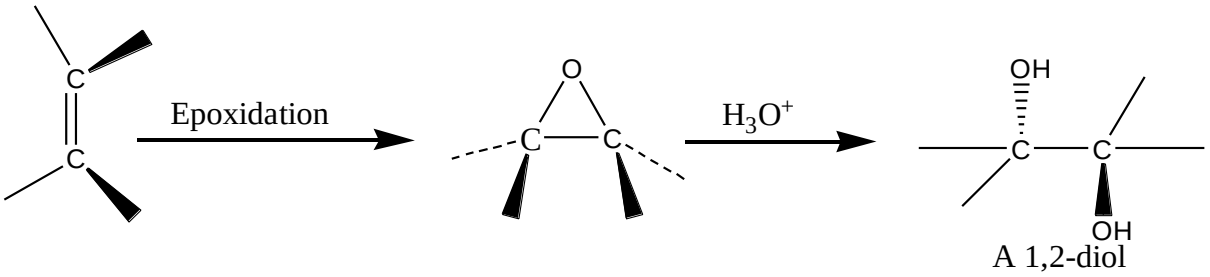



Cyclohexene

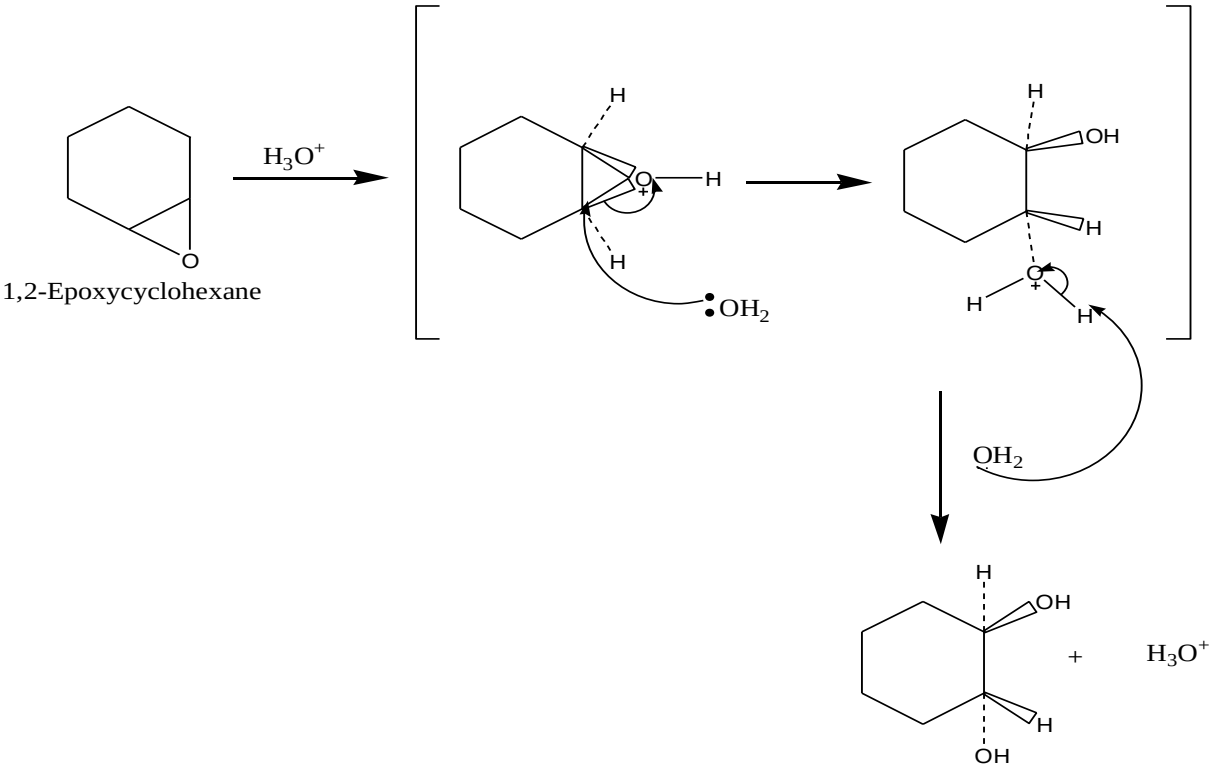
trans-2-chlorocyclohexanol

1,2-Epoxycyclohexane

Epoxides undergo acid catalyzed hydrolysis to give the corresponding diols also called glycols. Hydroxylation is the net result of Epoxidation and hydrolysis reactions- adding –OH group to each of the two double bond carbon atoms.

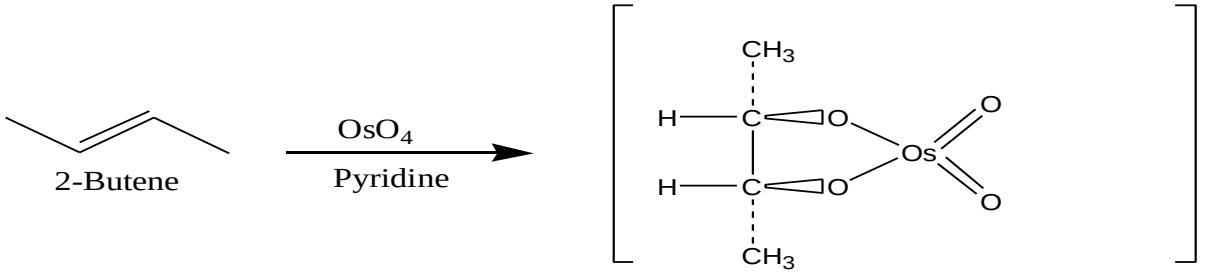



**Mechanism**

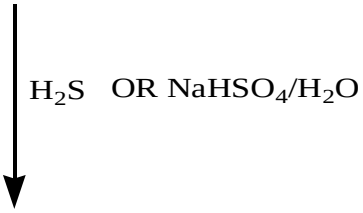


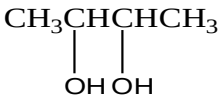

trans-1,2-cyclohexanediol (86%)

**Hydroxylation,** can be done using Osmium tetroxide, $OsO_4$. The reaction occurs with Syn stereochemistry**.** The cyclic intermediate formed maybe reduced with sodium hydrogen sulphate in the presence of water.



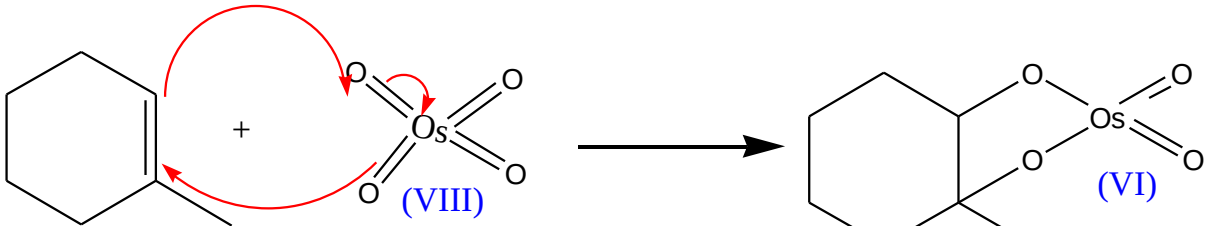

A cyclic Osmate intermediate

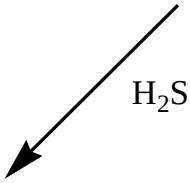


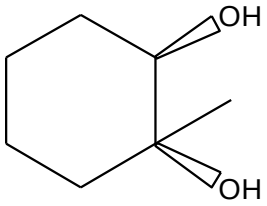




cis-2,3-Butanediol (87%)

Mechanism



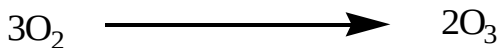

1-Methyl-cyclohexane-1,2-diol

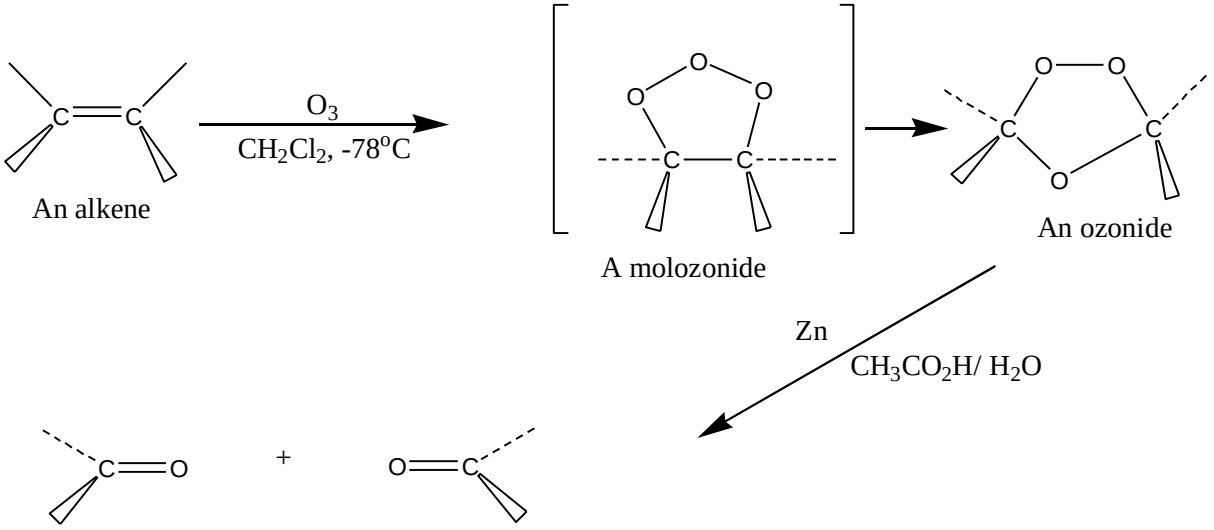
## 8. Oxidation of Alkenes: Cleavage to Carbonyl compounds

There are powerful oxidizing reagents that cleave C = C bonds to produce two carbonyl compounds.

**Ozonolysis**: Ozone ($O_3$) is the most useful reagent.

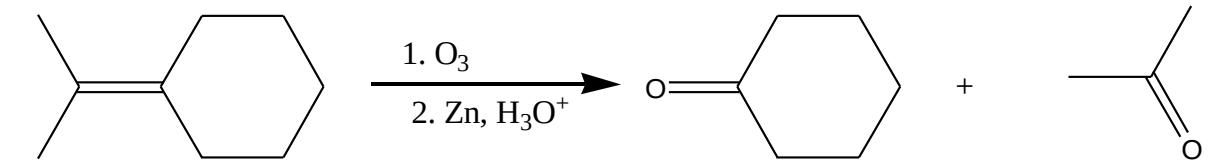
When a stream of oxygen is passed through a high voltage electrical discharge, oxygen adds rapidly to an alkene at low temperature to give cyclic intermediate called a molozonide, which rearranges to form an ozonide.




The ozonide is treated with a reducing agent such as Zinc metal in acetic acid to convert it to carbonyl compounds. The net result of the Ozonolysis/ reduction sequence is that the C = C bond is cleaved and oxygen becomes double bonded to each of the original alkene carbon.

**Example**



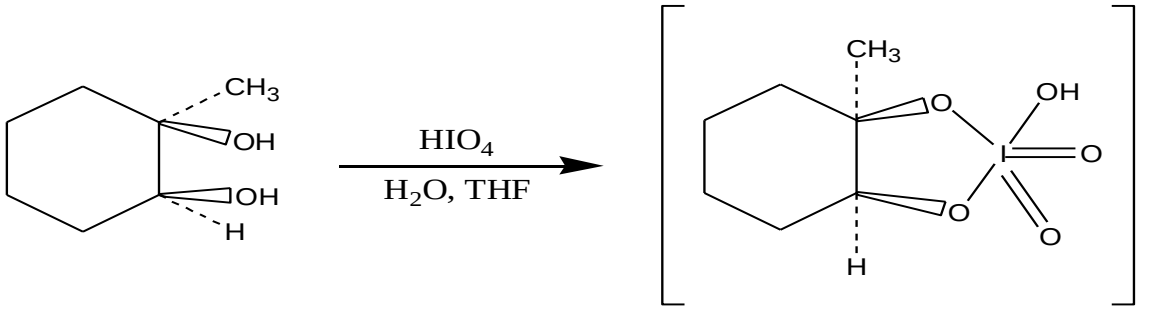

Isopropylidenecyclohexane  Cyclohexanone  Acetone

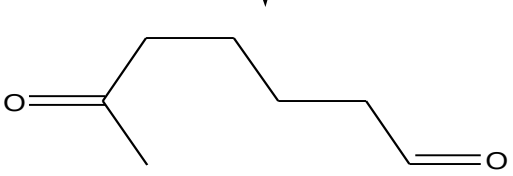
Several oxidizing reagents other than ozone also cause double bond cleavage. For example, potassium permanganate ($KMnO_4$) in neutral or acidic solution cleaves alkenes to give carbonyl containing products. If hydrogen atoms are present on the double bond, carboxylic acids are produced. If two hydrogen atoms present on a carbon atom, $CO_2$ is formed.

$$CH_3CH = CH_2 \xrightarrow[H_3O^+]{KMnO_4} CH_3COOH + CO_2$$

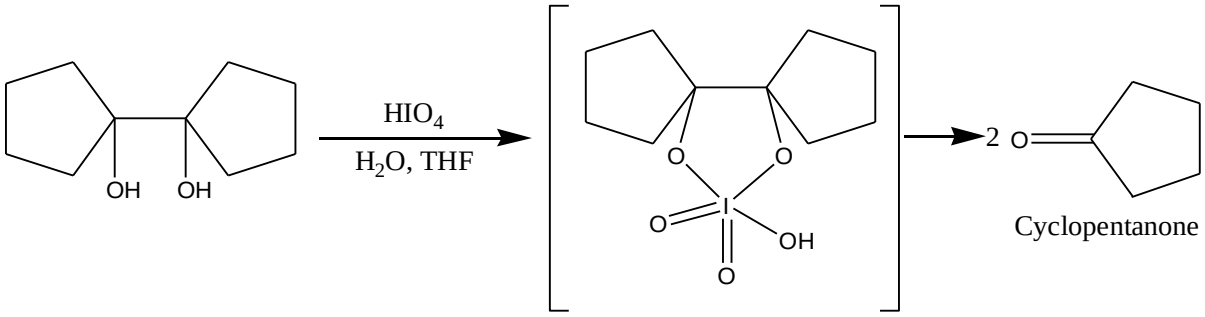
In addition to direct cleavage with ozone or $KMnO_4$ an alkene can also be cleaved by initial hydroxylation to a 1,2- diols followed by treatment with periodic acid, $HIO_4$, if the two –OH groups are in an open chain, two carbonyl compounds result. If the two –OH groups are on a ring, a single open chain dicarbonyl compound is formed.

**Example,**




6-Oxoheptanal

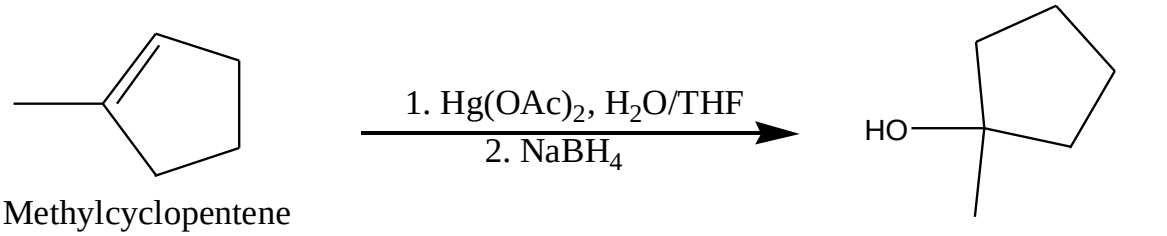



Cyclopentanone

Cyclic periodate intermediate

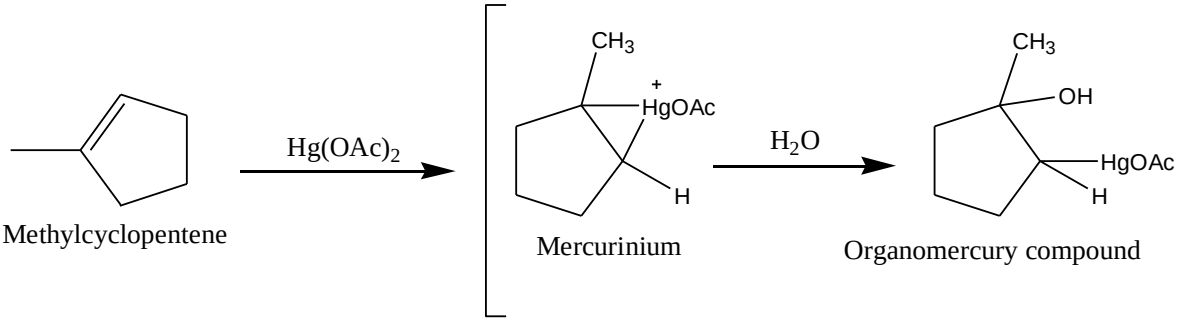
### 9. Oxidation of Alkenes: Oxymercuration

When an alkene is treated with mercury (II) acetate $Hg(O_2CCH_3)_2$, often abbreviated as $Hg(OAc)_2$ in aqueous tetrahydrofuran, THF, electrophilic addition of $Hg^{2+}$ to the double bond rapidly occurs. The intermediate organomercury compound is then treated with sodium borohydride, $NaBH_4$ and an alcohol is produced. The reaction yields Markovnikov's product.




1- Methylcyclopentene

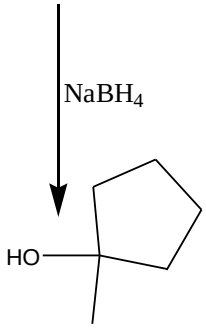
1- Methylcyclopentanol




1- Methylcyclopentene

Mercurinium

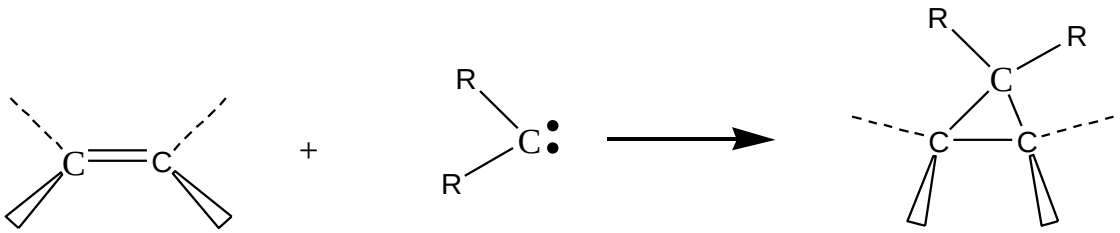
Organomercury compound




1- Methylcyclopentanol

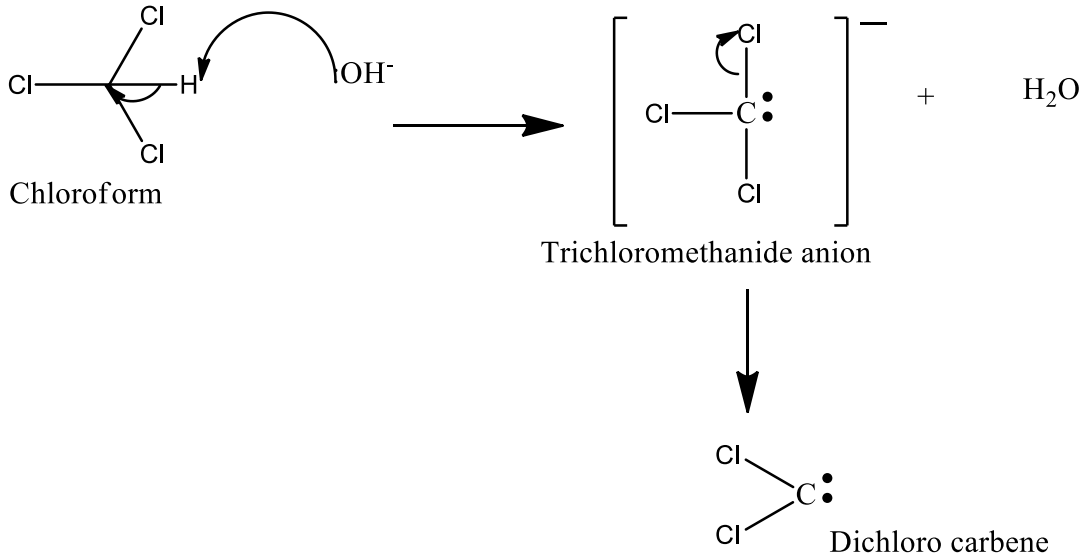
### 10. Addition of Carbenes to Alkenes: Cyclopropane synthesis

A carbene, $R_2C$**:** is a neutral molecule containing a divalent carbon with only six valence electrons in its valence shell. It is highly reactive and generated only as a reaction intermediate, rather than an isolable molecule. Because they are electron- deficient, carbenes behave as electrophiles and react with Nucleophilic C = C bonds. The reaction occurs in a single step without intermediates.

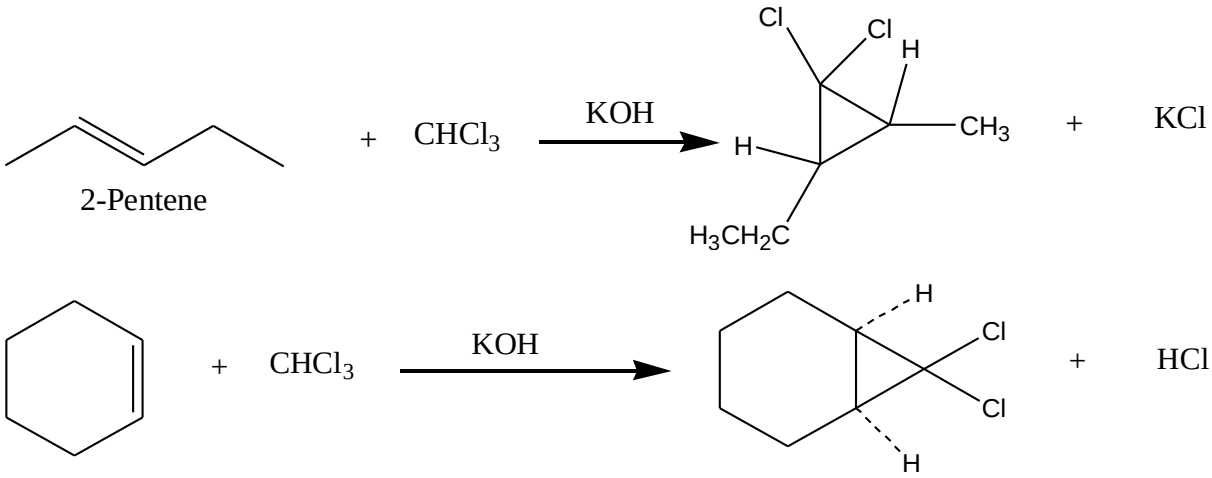


The carbene can be generated by treatment of chloroform, $CHCl_3$ with a strong base KOH. Loss of a proton from chloroform gives trichloromethanide anion, - $CCl_3$, which expels a $Cl^-$ ion to yield dichloro carbene : $CCl_2$

**Mechanism**

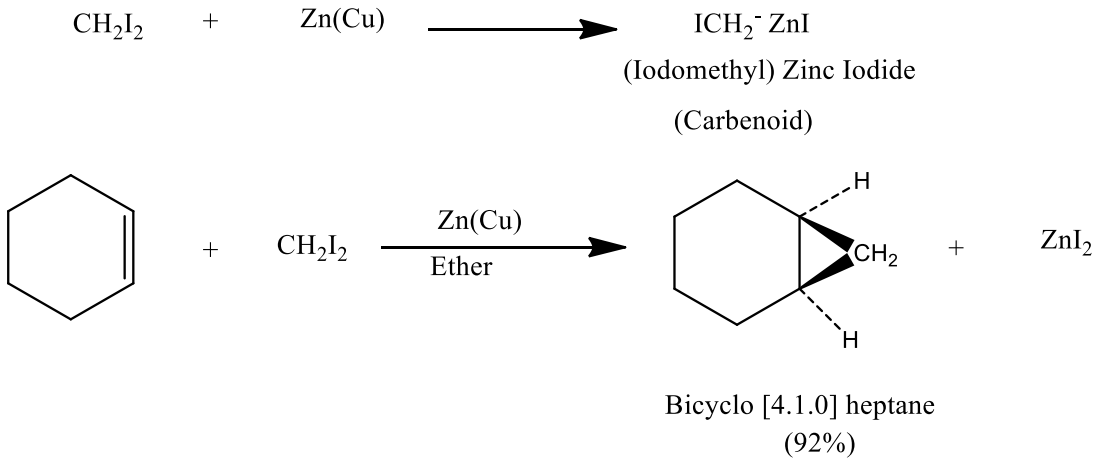



**Examples**



Simmons – Smith reaction produces non – halogenated Cyclopropane. It uses carbenoids – a metal complexed reagent with carbene – like reactivity.

**Example**



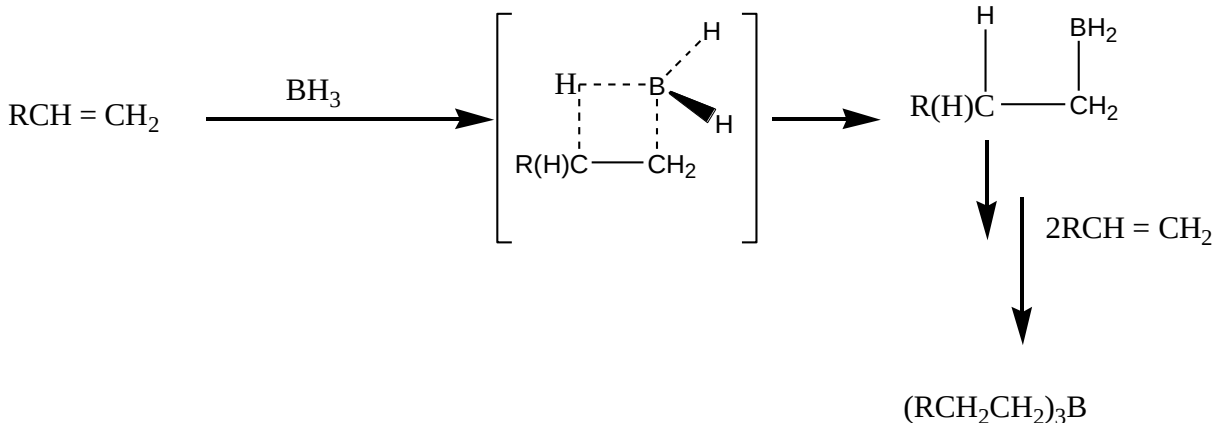

Bicyclo [4.1.0] heptane
(92%)

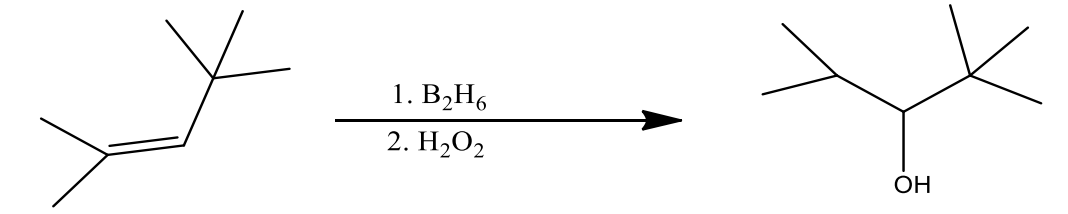
### 11. Hydroboration of Alkenes

This refers to the addition of hydrogen- boron bond to a C-C, C-N and C-O double bonds, as well as C-C triple bonds. It produces organoboranes compounds, which react with a variety of reagents to produce useful compounds, such as alcohols, amines and alkyl halides.

**For Alkenes**:

It is **anti- Markovnikov's** reaction

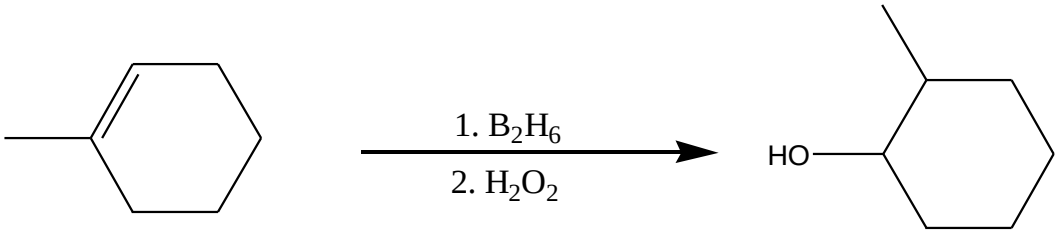





2,4,4-trimethylpent-2-ene

2,2,4-trimethylpentan-3-ol

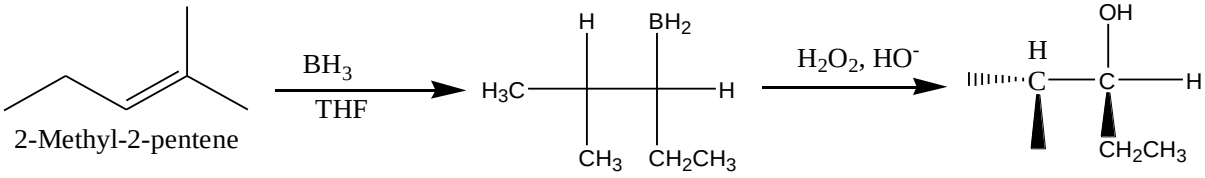
**(99%)**




1-Methylcyclohexene

2-Methylcyclohexanol (90%)

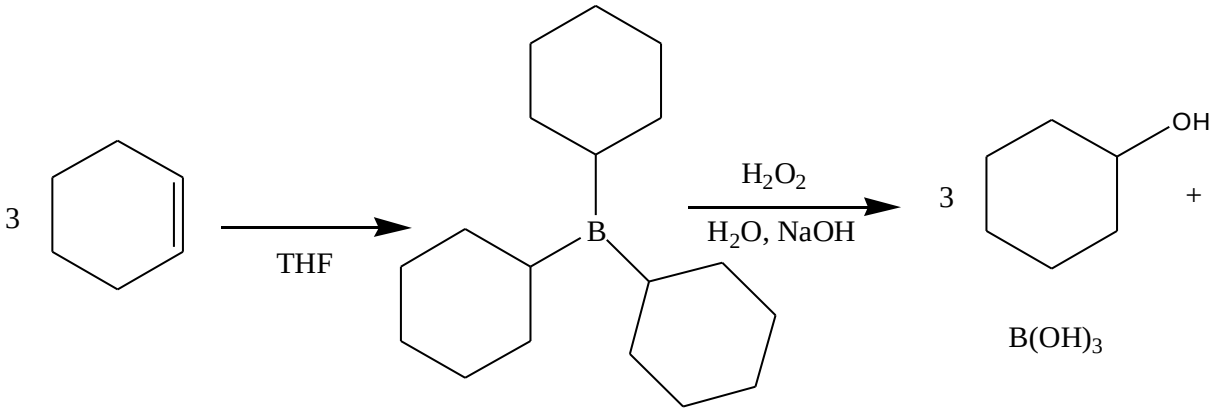
Oxidation of organanoboranes with basic hydrogen peroxide yields alcohol.



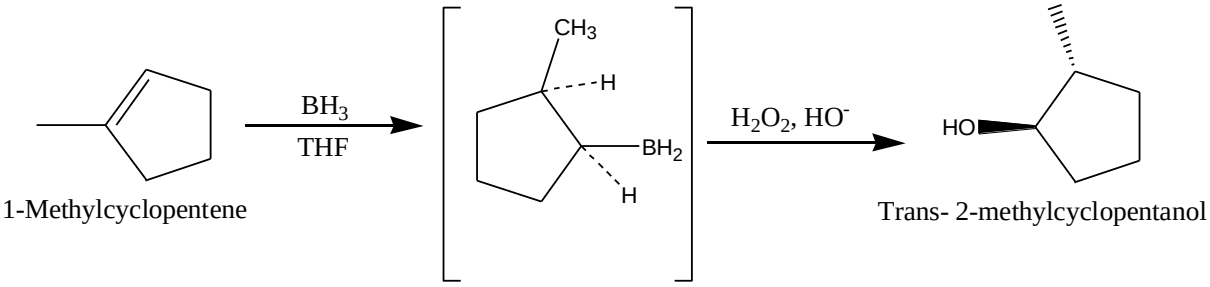

2-Methyl-2-pentene

2-Methyl-3-pentanol

Also**,**




The reaction is useful because of regioselectivity

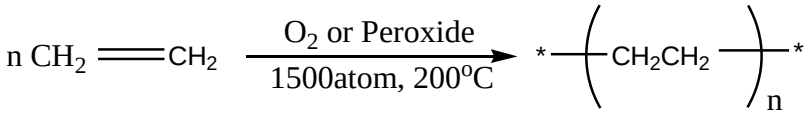



1-Methylcyclopentene

Trans- 2-methylcyclopentanol

12. **Polymerization Reaction**

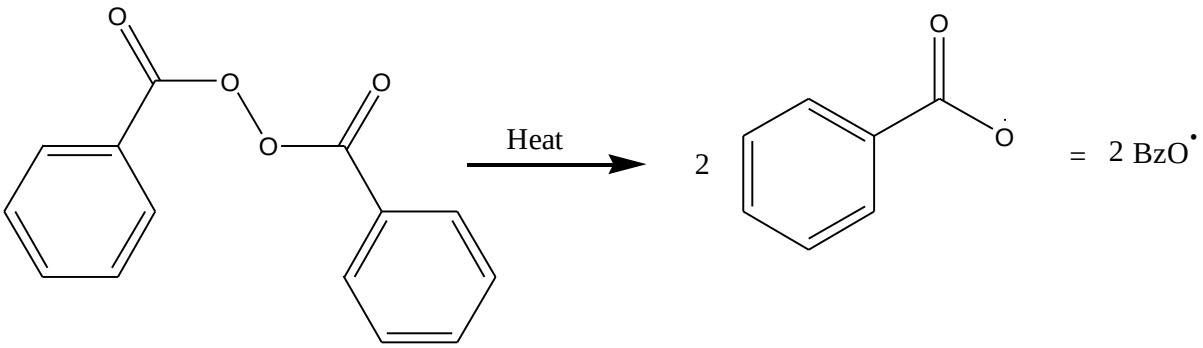
Alkenes undergo addition polymerization to form polymers. The mechanism of polymerization is by radical mediated, cationic and anionic catalyzed. Ethene polymerizes to form polyethene which is an important plastic material used as packing material.



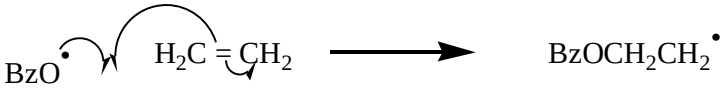

Historically, ethylene polymerization was carried out at high pressure and temperature in the presence of catalyst such as benzoyl peroxide, although other catalysts and reaction conditions are now more often used. The key step is the addition of a radical to the ethylene double bond, a reaction similar in many respects to what takes place in the addition of the electrophile.

**Radical mechanism**

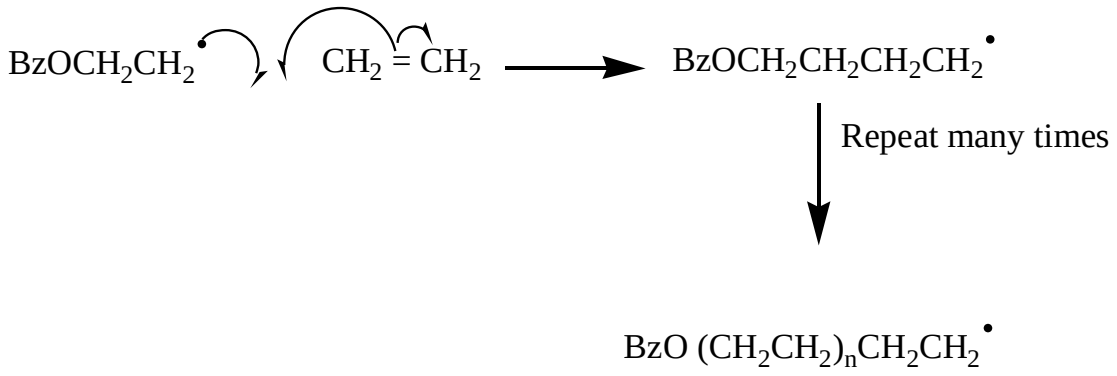
***Initiation***




Benzoyl peroxide

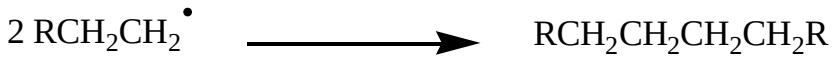



***Chain propagation step***




***Chain termination step***

The chain process is eventually ended by a reaction that consumes the radical. Combining the two growing chains is one possible chain termination reaction.

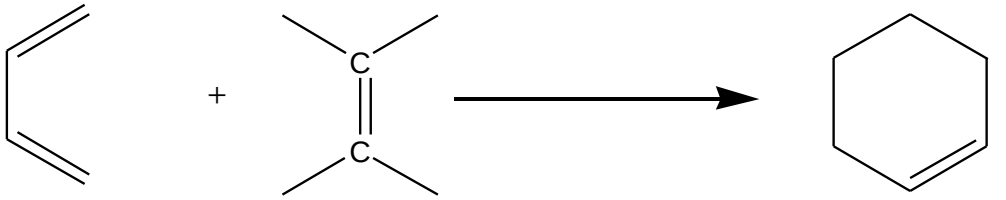



**Examples of Polymers synthesized from Alkenes**.

| **Monomer** | **Polymer** | **Trade/ Common name of polymer** | **Uses** |
|---|---|---|---|
| Ethylene | $H_2C = CH_2$ | Polyethylene | Packaging, bottle |
| Propene (Propylene) | $H_2C = CHCH_3$ | Polypropylene | Molding, rope, carpets |
| Chloroethylene (Vinyl chloride) | $H_2C = CHCl$ | Poly (vinyl chloride) Tedlar | Insulation, films, pipes |
| Styrene | $H_2C = CHC_6H_5$ | Polystyrene | Foam, molding, |
| Tetrafluoroethylene | $F_2C = CF_2$ | Teflon | Caskets, non-sticky coatings |
| Acrylonitrile | $H_2C = CHCN$ | Orlon, Acrilan | Fibers |
| Methylmethacrylate | $H_2C = C(CH_3)CO_2CH_3$ | Plexiglas, Lucite | Paints, sheets, moldings |
| Vinyl acetate | $H_2C = CHOCOCH_3$ | Poly (vinylacetate) | Paint, adhesives, foam |

### 13. Cycloaddition of alkenes

Alkenes undergo diverse Cycloaddition reactions. Most notable is the Diels- Alders reaction with 1, 3 – dienes to give cyclohexene.




Diene Dienophile Cyclohexene

**Assignment**

*A hydrocarbon **A** contains 87.8% carbon. Its relative molecular mass is 82. A decolorizes bromine and in presence of Nickel it reacts with hydrogen to form **B**. 0.1g of **A** was found to absorb 27.3cm$^3$ of hydrogen (measured at s.t.p). **B** does not decolorize bromine.*

*(a) Determine the:*

*(i) Empirical formula*

*(ii) Molecular formula of A.*

*(b) Calculate the:*

*(i) Number of moles hydrogen that reacted with one mole of A*

*(ii) Number of double bonds in the molecule of A*

*(c) Write the possible Isomers of A.*