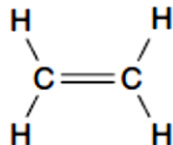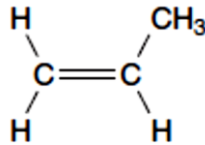# ALKENES

- Alkenes are hydrocarbons that contains carbon – carbon double bonds.
- C = C is the functional group and an important structural unit.

Nomenclature

1) Choose the longest continuous carbon chain that contain the double bond. The suffix -ane is replaced with -ene to indicate the presence of double bond.
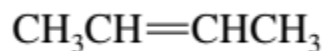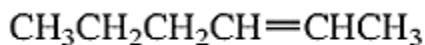

Ethene   **Propene**

2) When the chain contains more than three carbon atoms, a number is used to give the location of the double bond. The chain is numbered starting from the end closest to the double bond, and the double bond is given the lower number of its two double – bonded carbon atoms.
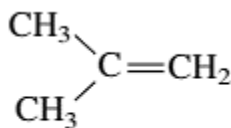
$$CH_2=CHCH_2CH_3$$
1-Butene

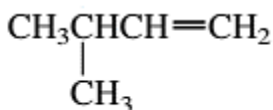$$CH_3CH=CHCH_3$$
2-Butene

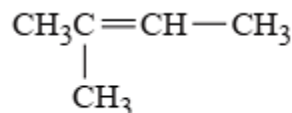$$CH_3CH_2CH_2CH=CHCH_3$$
2-Hexene

3) Substituents are arranged alphabetically (note that the double bond is given preference in numbering). e.g.
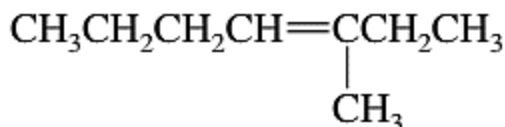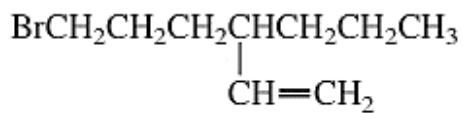

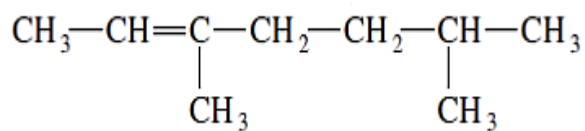2-Methylpropene   3-Methyl-1-butene   2-Methyl-2-butene

3-Methyl-3-heptene   2-Methyl-2-heptene

$BrCH_2CH_2CH_2CHCH_2CH_2CH_3$
$CH=CH_2$

6-Bromo-3-propyl-1-hexene

$CH_3-CH=C-CH_2-CH_2-CH-CH_3$
CH_3 CH_3

3,6-dimethylhept-2-ene
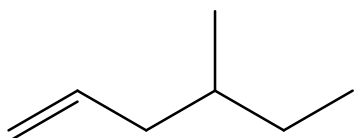
4-methyl-1-hexene
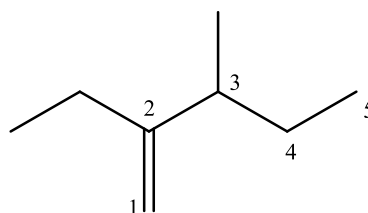
2-ethyl-3-methylpent-1-ene
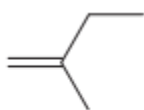
2-Methyl-1-butene

2,3-dimethylpent-2-ene

4-ethylhept-3-ene

3-propylhept-1-ene

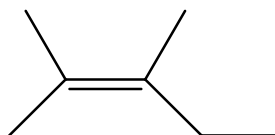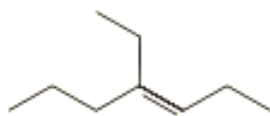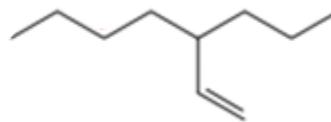4) Cyclic alkenes are named by adding the prefix cyclo- to the name of acyclic, unbranched alkene with the same number of carbon atoms.
The double bond is usually located between C_1 and C_2. The locant is usually omitted in the name.
e.g.

Cyclopropene   Cyclobutene   Cyclopentene   Cyclohexene
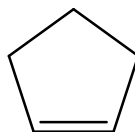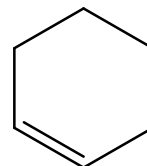
– Substituted cycloalkenes are numbered beginning with the double bond, proceeding through it and continuing in sequence around the ring. Substituents are given the lowest numbers possible.

Priority is assigned at the first point of difference.

e.g
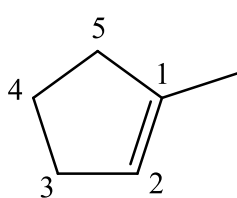
1-Methylcyclopentene
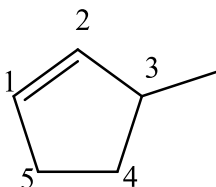
3-methylcyclopentene
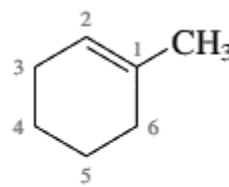
1-Methylcyclohexene
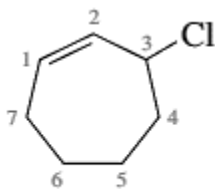
3-Chlorocycloheptene
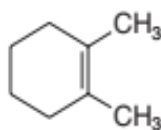
1,2-Dimethylcyclohexene
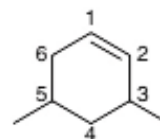
3,5-Dimethylcyclohexene
(*not* 4,6-dimethylcyclohexene)
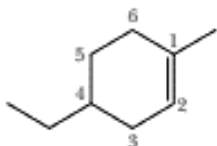
4-Ethyl-1-methylcyclohexene

5) A compound with two double bonds is a diene.

   Triene - 3 double bonds

   Tetraene - 4 double bonds

   Numbers are used to specify the location of the double bonds.

   $CH_2 = CH - CH = CH_2$
   Buta-1,3-diene

CH_2=$CHCH_2CH$=CH_2

1,4-Pentadiene

CH_2=CCH=CH_2
        |
       CH_3
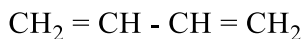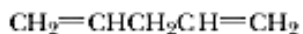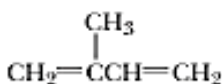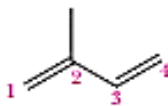
2-Methyl-1,3-butadiene

1,3-Cyclopentadiene
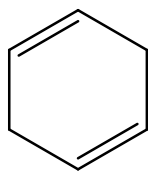
Cyclohexa-1,4-diene
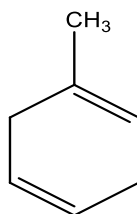
1-methylcyclohexa-1,4-diene
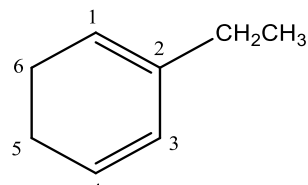
2-ethyl-1,3-cyclohexadiene
2-ethylcyclohexa-1,3-diene

Trienes. e.g.

$$\underset{1}{CH_2} = \underset{2}{CH} - \underset{3}{CH} = \underset{4}{CH} - \underset{5}{CH} = \underset{6}{CH} - \underset{7}{CH_3}$$
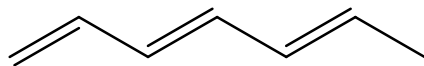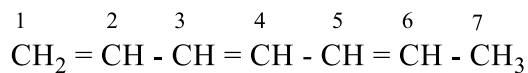
Hepta-1,3,5-triene

Alkenes as Substituents

(i) =CH₂

Methylene

(ii) —CH=CH₂

vinyl
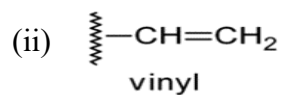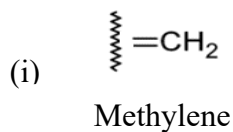
e.g
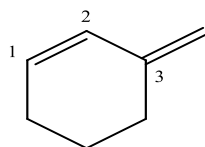
3-methylenecyclohexene

3-vinyl-1,5-hexadiene
3-vinylhexa-1,5-diene

(iii) $\{$—CH_2—CH=CH_2

allyl group

(iv)

phenyl group

CH_2=CH—CH_2—Cl

allyl chloride
3-chloropropene

2-phenyl-1,3-cyclopentadiene
2-phenylcyclopenta-1,3-diene
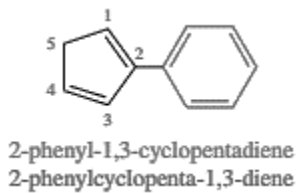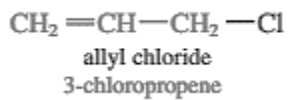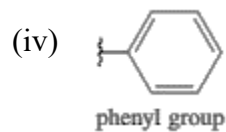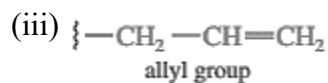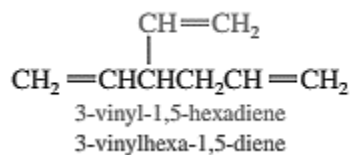
ISOMERISM IN ALKENES

– Stereoisomers are molecules that have the same molecular formula, and atoms are connected in the same way but are arranged differently in space.

– Stereoisomers can be subdivided into two general categories:

(i) Enantiomers – Are stereoisomers that are non – superposable mirror images of each other.

(ii) Diastereoisomers - Are stereoisomers whose molecules are not mirror image of each other.

Examples of diastereoisomers include;
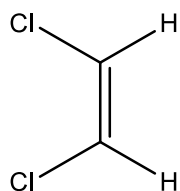
Cis-1,2-dichloroethene   trans-1,2-dichloroethene
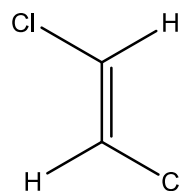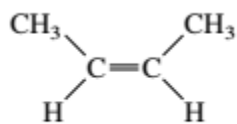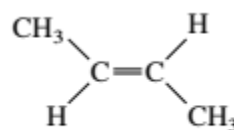
cis-2-Butene   *trans*-2-Butene
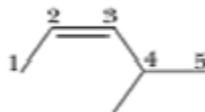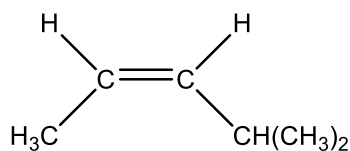
Cis-4-methylpent-2-ene
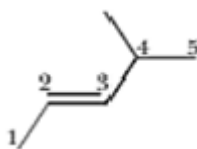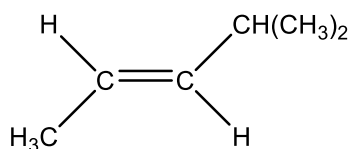
trans-4-methylpent-2-ene

E/Z Nomenclature of Alkenes

- The cis – trans nomenclature for geometric isomers sometimes gives an ambiguous name. e.g., isomers of 1-bromo – 1- chloropropene are not clearly cis or trans because it is not obvious which substituents are referred to as being cis or trans.
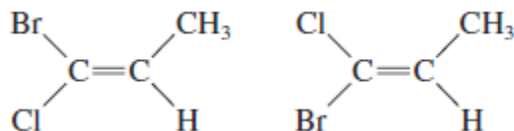
- To deal with this problem, E -Z system of nomenclature is used.

➤ **Cahn – Ingold – Prelog priority rules are used.**
- To name an alkene by E-Z system, mentally separate the double bond into two ends.
1) Priority is based on atomic number. The higher the atomic number, the higher the priority.
   e.g.
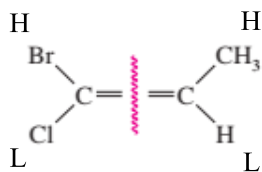
   Z- Configuration

- When atoms of higher atomic number are on the *same* side of the double bond, we say that the double bond has the **Z** configuration, where Z stands for the German word **zusammen** "together".
- When atoms of higher atomic number are on *opposite* sides of the double bond, we say that the configuration is **E.** Where E stands for the German word **entgegen,** meaning "opposite."

2) When atoms are directly attached to the double bond are identical, compare atoms attached to these two on the bases of their atomic numbers.
- Priority is determined at the first point of difference.
   e.g.,

H   C(H,H,H) L

Br CH_3

$C=C$

Cl CH_2CH_3

L

           C(C,H,H) H
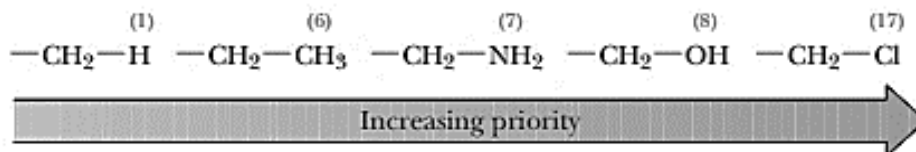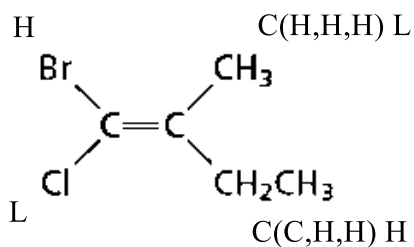
     E- Configuration

3) Work outward from the point of attachment, comparing all atoms attached to a particular atom before proceeding further along the chain.
Always evaluate substituent atoms one by one, never as a group.
e.g.,

Higher   C(C,H,H) Lower

Br CH_2CH_2OH

$C=C$

Cl $CH(CH_3)_2$

Lower

          C(C,C,H) Higher

    E- configuration

Higher   C(O,H,H) Higher

Br CH_2OH

$C=C$

Cl $C(CH_3)_3$

Lower

        C(C,C,C) Lower

    Z- configuration

Higher

C(C,H,H)   C(O,H,H) Higher

H_3CH_2C*   *CH_2OH

$C=C$

*H_3C *$C(CH_3)_3$

C(H,H,H)

Lower   C(C,C,C) Lower

     Z- configuration

Note: One high – priority atom takes priority over any number of lower – priority atoms.

4) Treat double and triple bonds as if each were a bond to a separate atom. i.e., imagine that each Pi bond is broken and the atoms at both ends duplicated.

e.g.,

$$-CH=CH_2 \longrightarrow -\overset{\overset{\displaystyle C}{|}}{CH}-\overset{\overset{\displaystyle C}{|}}{CH_2}$$

$$-\overset{\overset{\displaystyle O}{\|}}{CH} \longrightarrow -\overset{\overset{\displaystyle O-C}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O$$

Higher   C(O,H,H) Lower

Br.   CH₂OH
    C═C
Cl   CH=O
Lower
                C(O,O,H) Higher
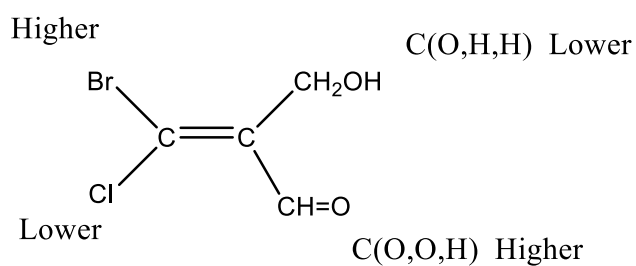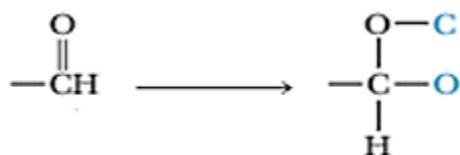
E- configuration

5) With different isotopes of the same element, the heavier isotopes have higher priority. e.g., (T) tritium (^3H) has higher priority than (D) deuterium (^2H), followed by hydrogen (^1H).

e.g.,
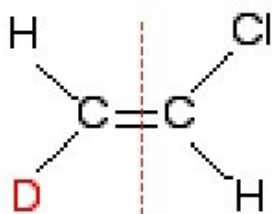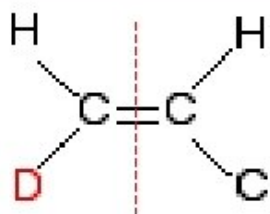
E - Configuration   Z- Configuration

EXERCISE

1. Give the IUPAC names for each of the following using E/Z designation.

i)

Br H

$C=C$

Cl $CH_2CH_2CH_3$
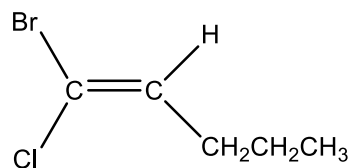
(*E*)-1-bromo-1-chloropent-1-ene

ii)

Cl Br

$C=C$

I CH_2CH_3
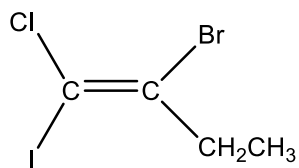
(*E*)-2-bromo-1-chloro-1-iodobut-1-ene

iii)

H_3C $CH_2CH(CH_3)_2$

$C=C$

H CH_3
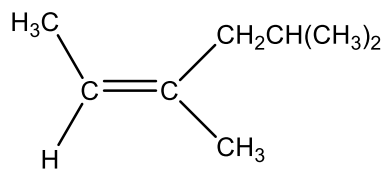
(*Z*)-3,5-dimethylhex-2-ene

iv)

Cl CH_3

$C=C$

I CH_2CH_3
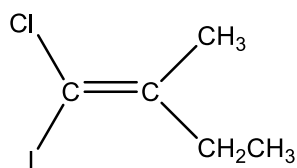
(*Z*)-1-chloro-1-iodo-2-methylbut-1-ene

2. Determine the configuration of each of the following alkenes as Z or E as appropriate:

(i)

H_3C CH_2OH

$C=C$

H CH_3

Higher   (C) ⟶ H₃C   CH₂OH ⟵ Higher
                    C=C
Lower   (H) ⟶ H   CH₃   ⟵ Lower
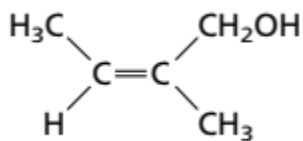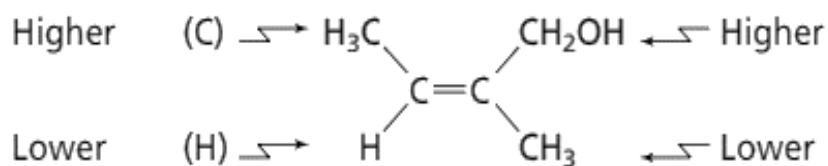
Higher ranked substituents are on the same side of the double bond; the configuration is *Z*

(ii)

H_3C CH_2CH_2F
        C=C
H $CH_2CH_2CH_2CH_3$

Higher CH_3 CH_2CH_2F Higher
                C=C
Lower H $CH_2CH_2CH_2CH_3$ Lower
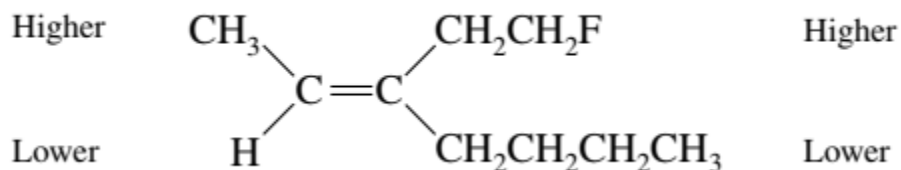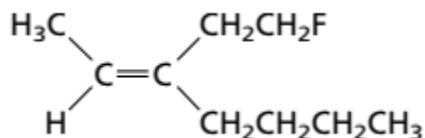
Higher ranked substituents are on the same side of the double bond; the alkene has the *Z* configuration

(iii)

H_3C CH_2CH_2OH
        C=C
H $C(CH_3)_3$

—CH_2CH_2OH —$C(CH_3)_3$
—$C(C,H,H)$ —$C(C,C,C)$
Lower priority   Higher priority
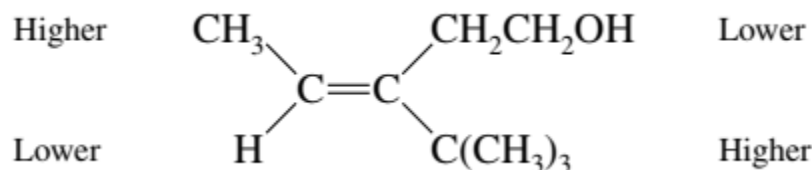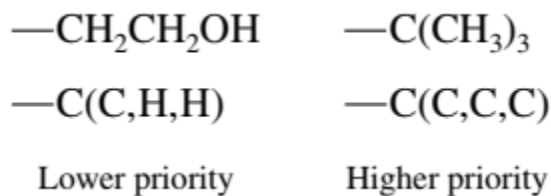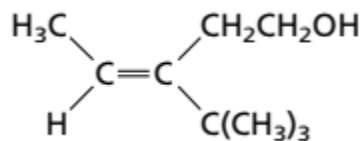
Higher CH_3 CH_2CH_2OH Lower
                C=C
Lower H $C(CH_3)_3$ Higher
Higher ranked groups are on opposite sides; the configuration of the alkene is *E*.

(iv)
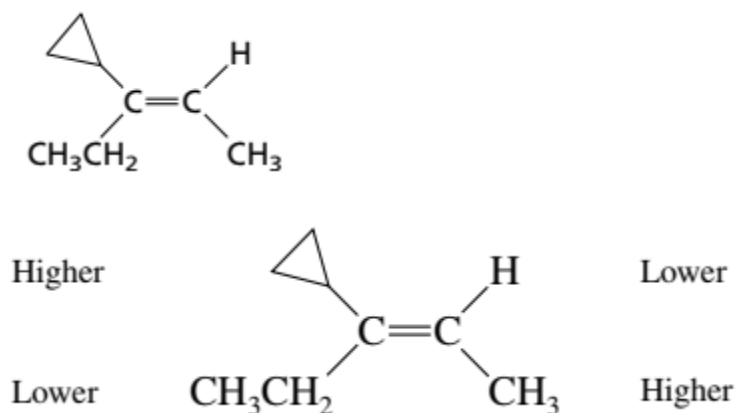
Higher ranked groups are on opposite sides; the configuration of the alkene is *E*.

PHYSICAL PROPERTIES OF ALKENES

- Most alkenes exhibit only weak van der waal interactions, so their physical properties are similar to alkanes of comparable molecular weight.
i. Low molecular weight alkenes, up to C_4H_8 are gases at ambient temperature and pressure. Ethene, propene and butene - colorless gases.
$C_5 - C_{14}$ – liquids
≥ 15 – Solids

ii. Boiling points.
The boiling points of alkenes increases with molecular weight, due to increase in surface area leading to higher molecular forces (van der waal forces).
Each alkene has a boiling point which is a few degrees lower than the corresponding alkane.
Van der waal forces depend on;
  o Shape of molecules
  o Number of electrons in the molecule (each alkene has 2e- fewer than corresponding alkane).
- The cis isomers have slightly higher boiling points than the trans isomers due to presence of net dipole. i.e., they are polar, hence dipole - dipole forces in addition to the van der waal forces.
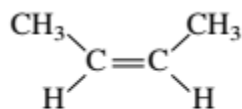
cis-2-Butene

Bpt = 4°C
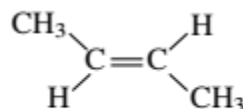
trans-2-Butene

Bpt = 1°C

- The methyl group (sp^3 hybridized) donates electrons to the carbon of the double bond (sp^2 hybridization).
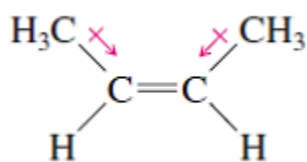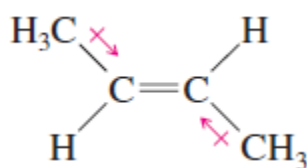
        Higher Bpt   Low Bpt

- In the cis-isomers, the dipole reinforces each other, giving a small net dipole (dipole – dipole intermolecular forces).
- In the trans isomers, the two bond dipoles cancels.
- A cis alkene is more polar than a trans alkene, giving it a slightly higher boiling point and making it more soluble in polar solvents.
- Branching lowers the boiling points of alkenes, due to decrease in surface area and the van der waal forces.

    e.g
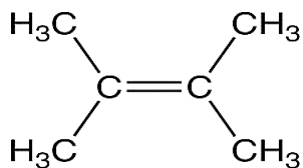
– No net dipole	- no net dipole	- Net dipole
– Lower surface area due to branching	-intermediate bpt	- Highest bpt
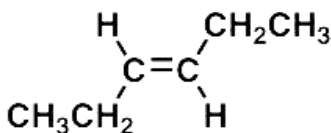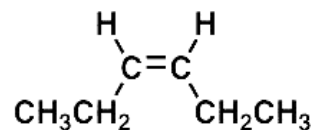
iii. Melting points
Melting points increases as the number of carbon atoms increases due to increase in surface area.
Cis isomers have lower melting points than trans isomers due to lower packing in the solid state due to the presence of "u-bond".
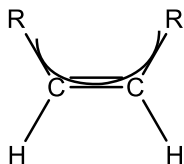
iv. Density
Alkenes are less dense than water (0.6 – 0.7 g/ml).

v. Solubility
- Alkenes are relatively non-polar.
- They are insoluble in water
- Soluble in non-polar organic solvents e.g., hexane, gasoline, ethers etc.
- Cis isomers are slightly more soluble in polar solvents compared to trans – isomers due to the presence of a small dipole. i.e are more polar.

Exercise
1. Explain the difference in the boiling points of the following alkenes
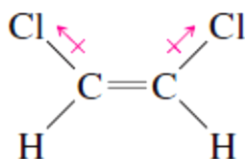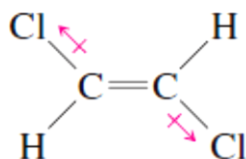
Bpt = 60°C   Bpt = 48°C

2. For each of the pair of compounds, predict the one with higher boiling points. Justify your answers.
   i)   Cis -1,2 -dichloroethane or Cis -1,2-dibromoethene,
   ii)   Cis or trans -2, 3-dichlorobut-2-ene
   iii)   Cyclohexene or 1,2-dichlorocyclohexene

STABILITY OF ALKENES
- In general, the cis alkenes are less stable than their trans isomers because of steric strain between the two larger substituents on the same side of the double bond.

e.g
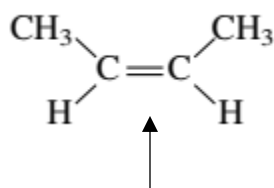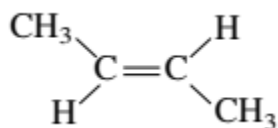
Bulky groups on the same side of double bond leading to steric strain

- Heat of hydrogenation of alkenes can be used to measure their relative stabilities.
- An example of such an experiment is one involving platinum catalyzed hydrogenation of three butene isomers shown below.

The figure shows an enthalpy diagram with three hydrogenation reactions, labelled with $+ H_2$, energy differences of $7\ \text{kJ mol}^{-1}$ and $5\ \text{kJ mol}^{-1}$, and $\Delta H^\circ = -127\ \text{kJ mol}^{-1}$, $\Delta H^\circ = -120\ \text{kJ mol}^{-1}$, and $\Delta H^\circ = -115\ \text{kJ mol}^{-1}$.
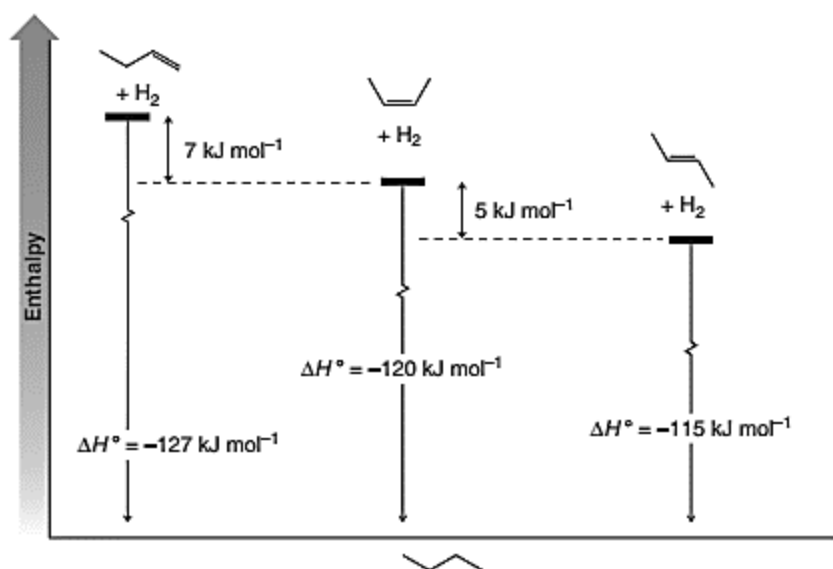
- The trans isomer is more stable than the cis isomer since less energy is released when the trans isomer is converted to butane.
- In addition, it shows that the terminal alkene but–1-ene, is less stable than either of the disubstituted alkenes, since its reaction is the most exothermic.
- Overall, the greater the number of attached alkyl groups (i.e the more highly substituted the carbon atoms of the double bond), the greater is the alkene's stability.
  i.e.,
  Monosubstituted < Disubstituted < Trisubstituted < Tetrasubstituted.
- Alkyl groups are electron donating, hence increases the electron density of the π – bond leading to stabilization.

Tetrasubstituted   Trisubstituted   ←————— Disubstituted —————→   Monosubstituted   Unsubstituted
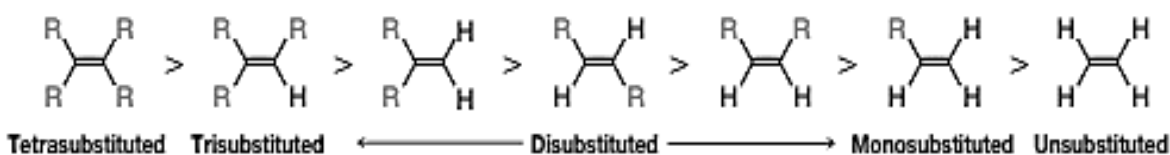
Example

1. Consider the two alkenes 2-methylpent-1ene and 2-methylpent-2-ene and decide which would be more stable.
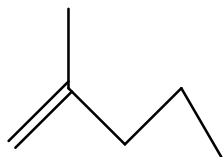
2-methylpent-1-ene
(Disubstituted, less stable)
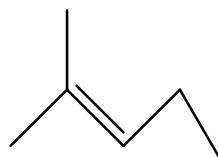
2-methylpent-2-ene
(Trisubstituted, more stable)

2-methylpent-2-ene has 3 substituents on its double bond whereas 2-methylpent-1-ene has two and therefore 2-methyl-2-pentane is more stable.

2. Rank the following cycloalkenes in order of increasing stability.

Solution

$<$ $<$ Order of increasing stability
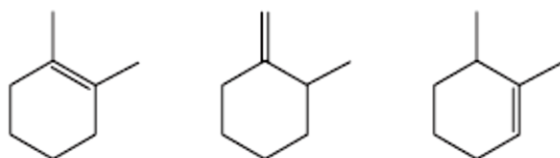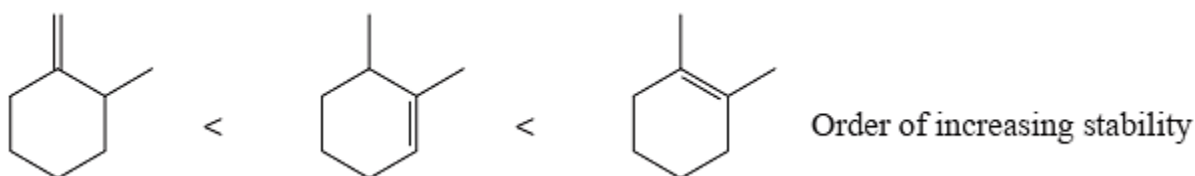
1. Predict the more stable alkene of each pair.
   a) 2-methylpent-2-ene or 2,3-dimethylbut-2-ene
   b) Cis-3-hexene or trans-hex-3-ene
   c) 1-hexene or cis-3-hexene
   d) trans-2-hexene or 2-methylpent-2-ene

   Solution
   a) 2,3-Dimethylbut-2-ene would be more stable because the double bond is tetrasubstituted, 2-methylpent-2-ene has trisubstituted double bond.
   b) Trans-hex-3-ene would be more stable because alkenes with trans double bonds are more stable than those with cis double bonds
   c) Cis-hex-3-ene would be more stable because its double bond is disubstituted. The double bond of hex-1-ene is monosubstituted.
   d) 2-methy-2-pentene would be more stable because its double bond is trisubstituted. Double bond of trans-hex-2-ene is disubstituted.

PREPARATION OF ALKENES
- Alkenes can be prepared via elimination reactions in which a proton and a leaving group are removed to form a π – bond.
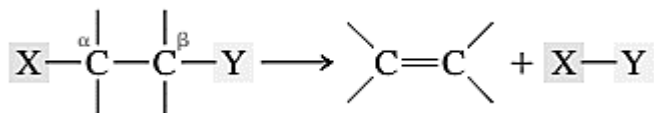
- Alkene formation requires that X and Y be substituents on adjacent carbon atoms. By making X the reference atom and identifying the carbon attached to it as the carbon, it can be seen that atom Y is a substituent on the β carbon.

e.g

X = Cl, Br, I
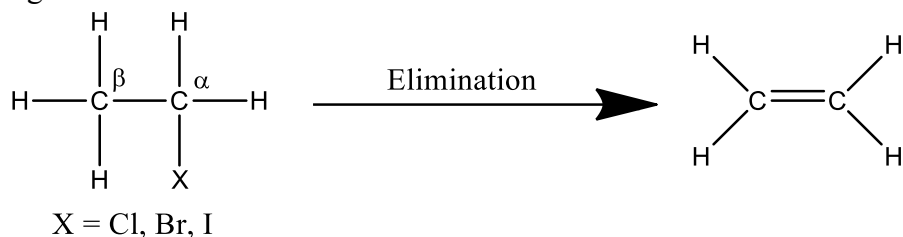
β – elimination reactions or 1,2-elimination reactions.

1. Dehydrogenation of Alkenes
− Ethylene and propene are prepared on an industrial scale by high temperature of ethane and propane.

$$CH_3CH_3 \xrightarrow{750°C} CH_2=CH_2 + H_2$$

$$CH_3CH_2CH_3 \xrightarrow{750°C} CH_3CH=CH_2 + H_2$$
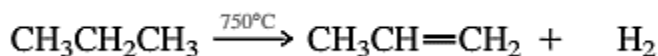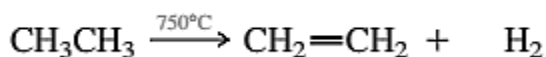
Not practical for laboratory synthesis of most alkenes.

2. Dehydrohalogenation of Alkyl halides
− Involves elimination of hydrogen and a halogen from an alkyl halide to form an alkene.
− The best reaction condition to use when synthesizing alkenes by dehydrohalogenation are those that promote an E_2 elimination.
− Reaction conditions that favor elimination by an E_1 mechanism should be avoided because the results can be too variables (rearrangements).

How to Favor an E_2 Mechanism
a. Use a secondary or tertiary alkyl halide if possible.
   Reason – Steric hinderance in the substrate will inhibit substitution.
b. When a synthesis must begin with a primary alkyl halide, use a bulky base.
   Steric hinderance of the base inhibit substitution.
c. Use a high concentration of a strong and non-polarizable base such as an alkoxide.
d. Sodium ethoxide in ethanol (EtONa / EtOH) and potassium tert-butoxide in tert-butyl alcohol (t-BUOK/t-BUOH).
e. Use elevated temperature because heat generally favors elimination over substitution.

- A strong base is used to abstract a proton from a β – carbon atom.

:B = base
X = halogen
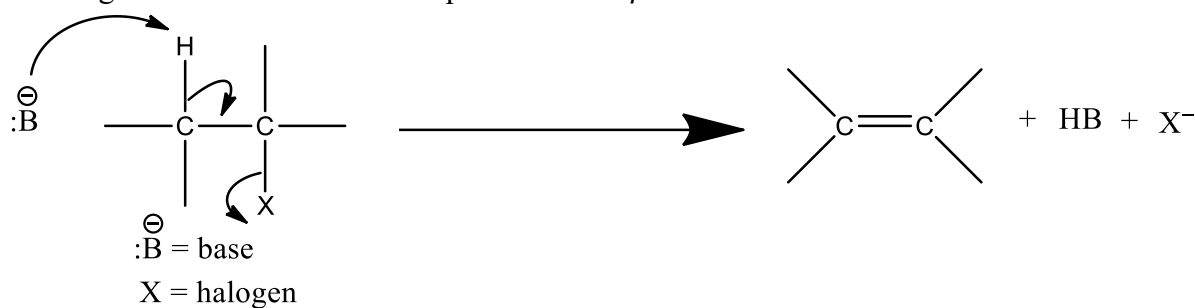
- Excellent yields are obtained with 2° and 3° bulky alkyl halides
- Strong bases that are commonly used include;
  - i) $NaOCH_2CH_3$ in ethanol
  - ii) $NaOCH_3$ in methanol
  - iii) KOH in ethanol
  - iv)   tert-butoxide (t-BUOK) in tert-butyl alcohol (t-BUOH)

Examples

$$CH_3(CH_2)_{15}CH_2CH_2Cl \xrightarrow[\text{KOC(CH}_3)_3]{\text{DMSO}} CH_3(CH_2)_{15}CH = CH_2$$
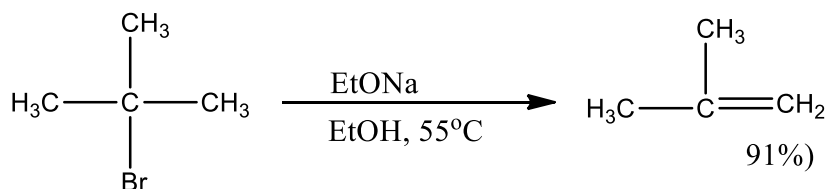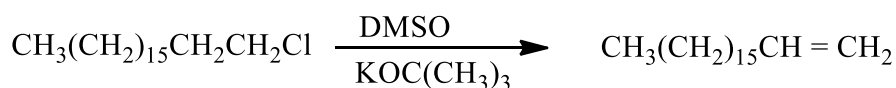
Regioselectivity

- Elimination reactions produce more than one product when the β-positions are not identical.
- If we use a small base (e.g CH_3CH_2ONa or NaOH), the major product is the highly substituted (more stable) alkene e.g

2-methyl-2-butene
(69%)
Trisubstituted:
more stable

+

2-methyl-1-butene
(31%)
Disubstituted
less stable

2-Methyl-1-butene
Minor

2-Methyl-2-butene
Major
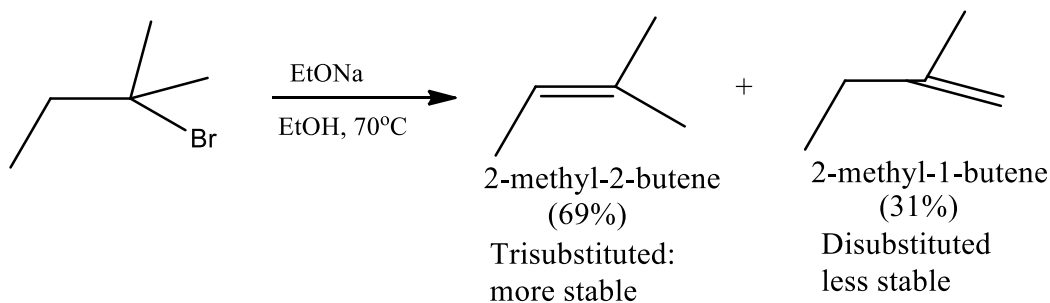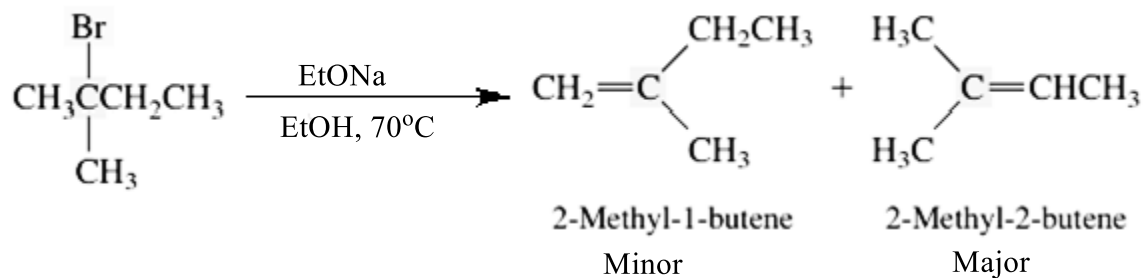
– Whenever an elimination occurs to give the more stable, more highly substituted alkene, it's said that the elimination follows <u>Zaitsev's rule.</u>
e.g

2,3-Dimethyl-1-butene
(minor product)

2,3-Dimethyl-2-butene
(major product)

Minor
Monosubstituted

Major
Trisubstituted
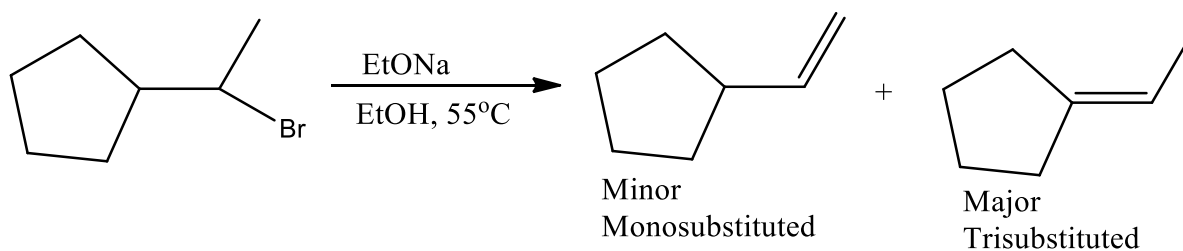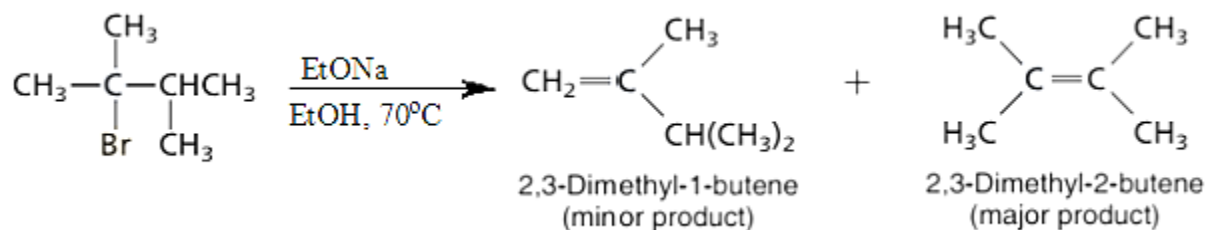
Formation of the Hoffmann Product

– Carrying out dehydrohalogenation with a bulky base such as potassium tert-butoxide (t-BUOK) in tert-butyl alcohol (t-BUOH) favors the formation of less substituted alkenes.
– When elimination yields the less substituted alkene, it is said to follow <u>Hofmann rule.</u>
e.g

Minor

Major
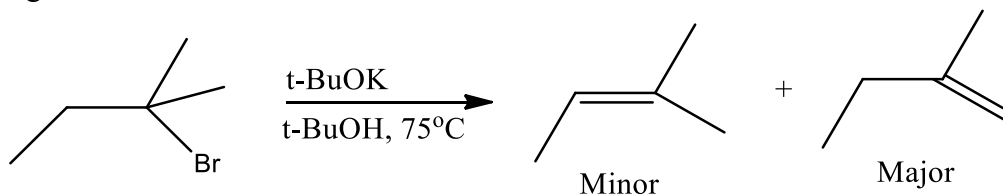
Example

i) What base would you use to maximize the yield at this specific alkene?
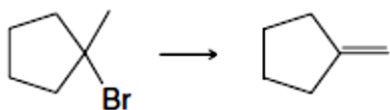
Here you want the less substituted alkene.

Therefore, a bulky base should be used such as potassium tert-butoxide in tert-butyl alcohol.

Stereoselectivity

−   Dehydrohalogenation favors the formation of the more stable isomer (the trans isomer), (E isomer).
    e.g

Minor

Major

2-Bromobutane		1-Butene	cis-2-Butene	trans-2-Butene
		Least		Major
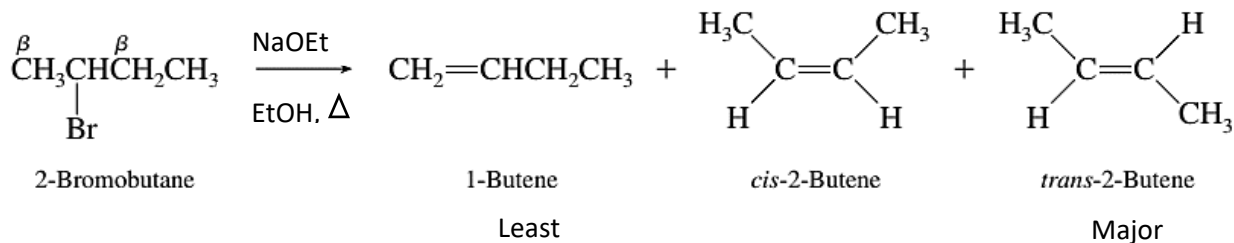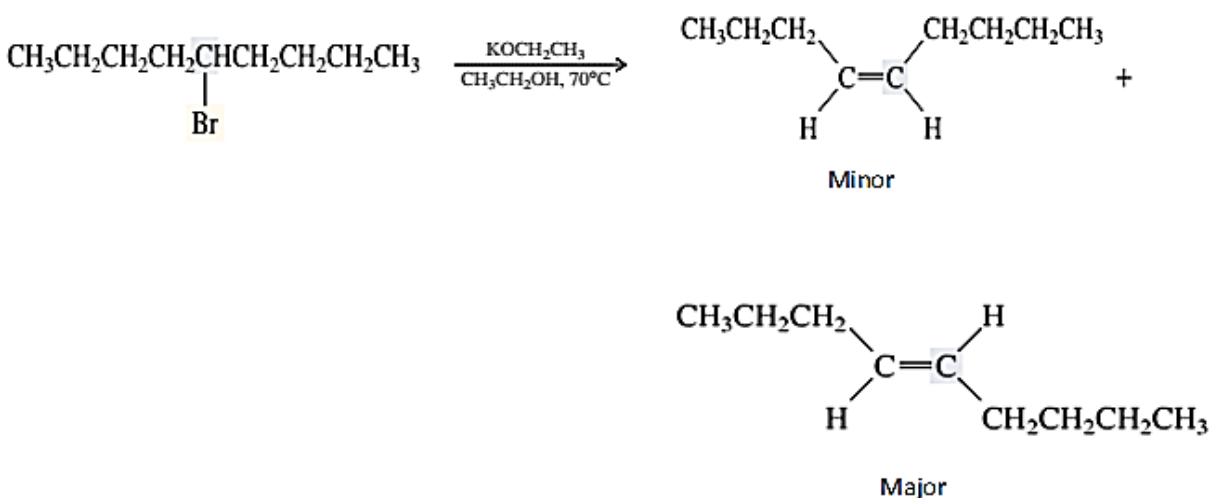
−   Dehydrohalogenation of cycloalkyl halides leads exclusively to cis cycloalkenes when the ring has fewer than ten carbon atoms. Larger rings give mixture of cis and trans isomers.

Bromocyclodecane   *cis*-Cyclodecene   *trans*-Cyclodecene
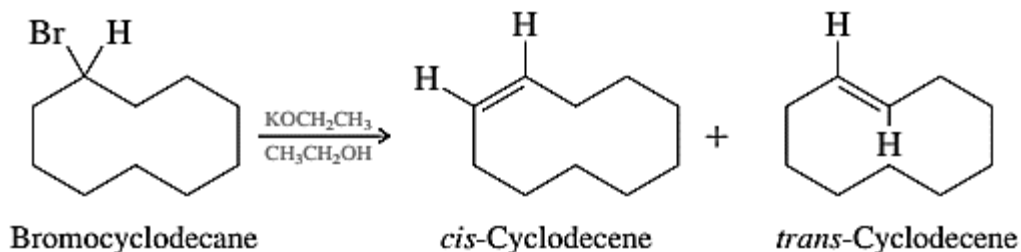
3. Acid – catalyzed dehydration of alcohols

- Most alcohols undergo dehydration (lose a molecule of water) to form an alkene when heated with a strong acid.
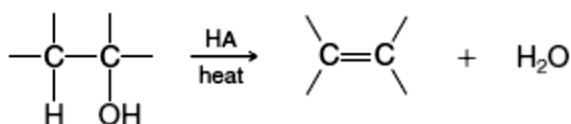
- The reaction is an elimination and is favored by high temperatures.
- Bronsted acids (proton donors) are commonly used in the laboratory. e.g., H_2SO_4, H_3PO_4 etc.
- Temperature and concentration of acid required depend on the structure of the alcohol substrates.
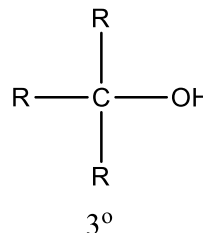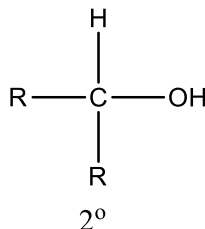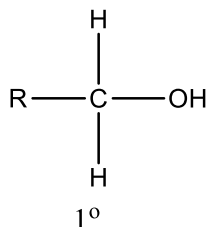
i) Primary alcohols: - most difficult to dehydrate.

  e.g., dehydration of ethanol requires conc H_2SO_4 and a temperature of 180^oC.
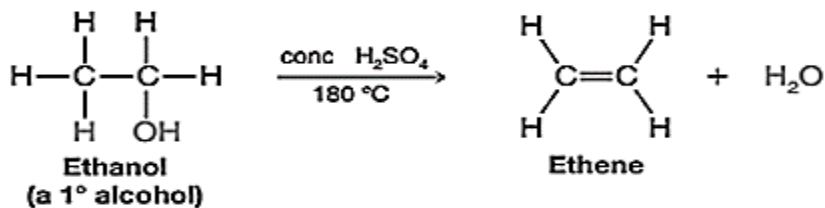
ii) Secondary alcohols: - usually dehydrated under milder conditions.
    e.g., cyclohexanol dehydrates in 85% phosphoric acid at 165-170°c

$$\text{(80\%)}$$
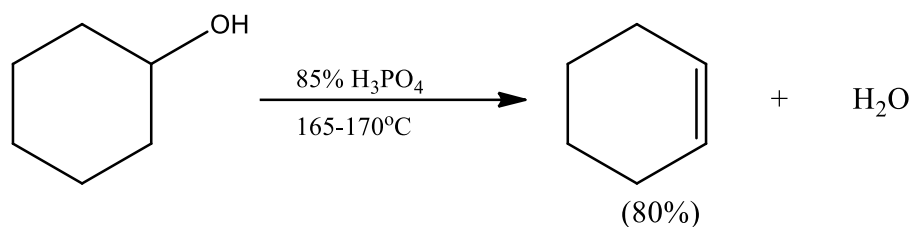
iii) Tertiary alcohols are easily dehydrated under relatively mild conditions.

e.g.,
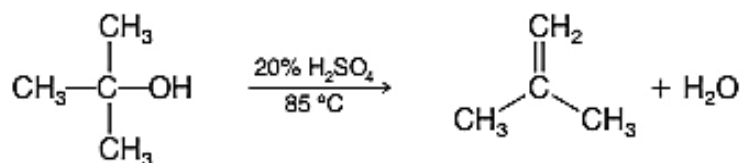
- Relative ease of dehydration: $3° > 2° > 1°$

Regioselectivity

- Dehydration of alcohols follows Zaitsev's rule (always) e.g.,

| 2-Methyl-2-butanol | 2-Methyl-1-butene (10%) | 2-Methyl-2-butene (90%) |

| 2-Methylcyclohexanol | 1-Methylcyclohexene (84%) | 3-Methylcyclohexene (16%) |

2,3-Dimethyl-2-butanol → 2,3-Dimethyl-1-butene (minor product) + 2,3-Dimethyl-2-butene (major product)
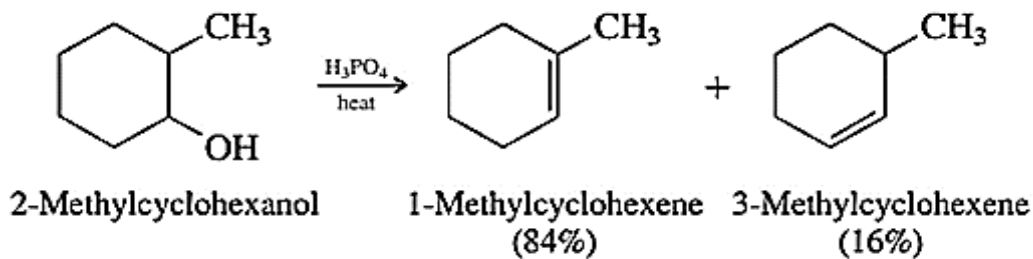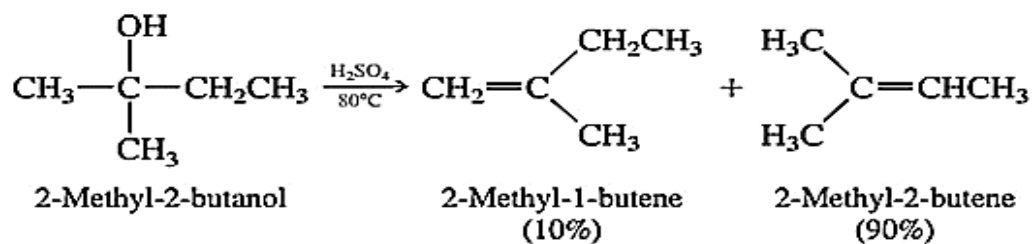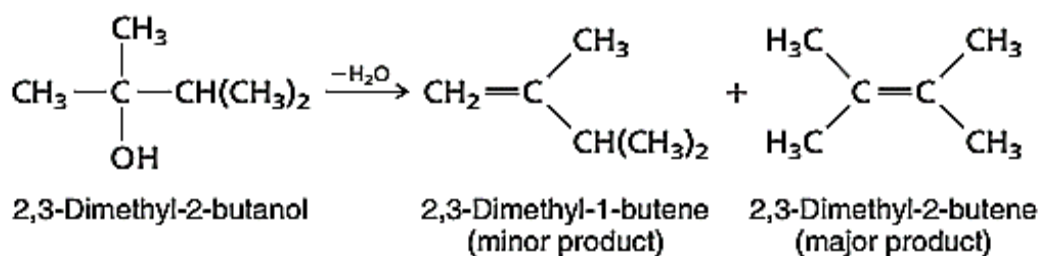
Stereoselectivity

− Alcohol dehydration tend to produce the more stable isomers. (stereoisomer).

3-Pentanol → cis-2-Pentene (25%) (minor product) + trans-2-Pentene (75%) (major product)

2-Pentanol → 1-Pentene (Least) + cis-2-Pentene + trans-2-Pentene (Major)
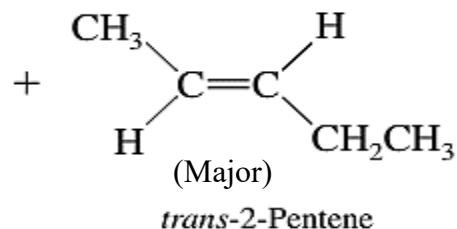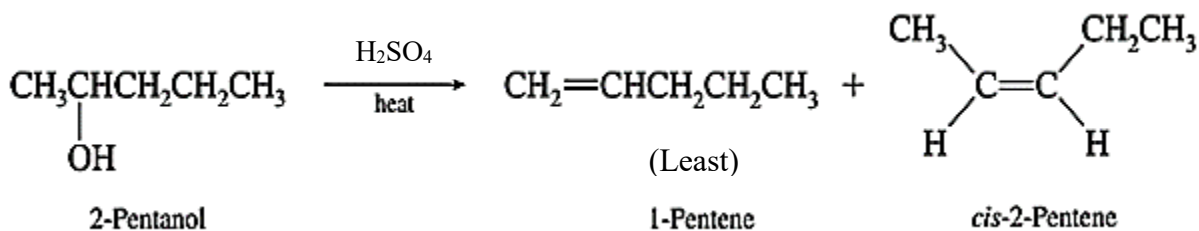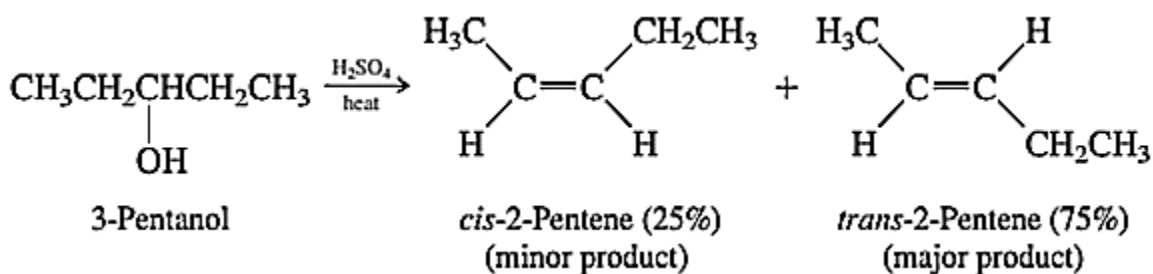
REACTIONS OF ALKENES

− Because single bonds (sigma bonds) are more stable than Pi bonds, the most common reactions of alkenes arise from the reactivity of the carbon – carbon double bond, transforming the Pi bond into a sigma bond.

$$\text{C}=\text{C} \quad + \quad \text{E} - \text{Nu} \xrightarrow{\text{addition}} \text{E}-\text{C}-\text{C}-\text{Nu}$$
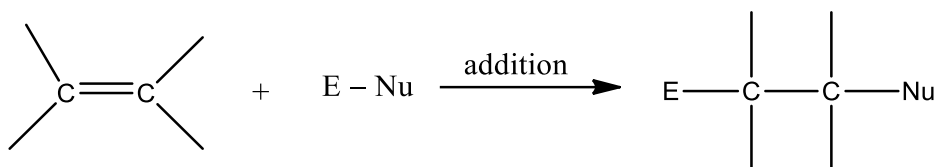
a) Hydrogenation of alkenes

- Alkenes react with hydrogen in presence of a variety of metal catalysts to add one hydrogen atom to each carbon atom of the double bond.

$$\text{C}=\text{C} \quad + \quad H_2 \xrightarrow[\substack{\text{solvent,} \\ \text{pressure}}]{\text{Pt, Pd or Ni}} \overset{|}{\underset{H}{-C}}-\overset{|}{\underset{H}{C}}-$$

e.g

$$(CH_3)_2C{=}CHCH_3 + \quad H_2 \xrightarrow{\ Pt\ } (CH_3)_2CHCH_2CH_3$$
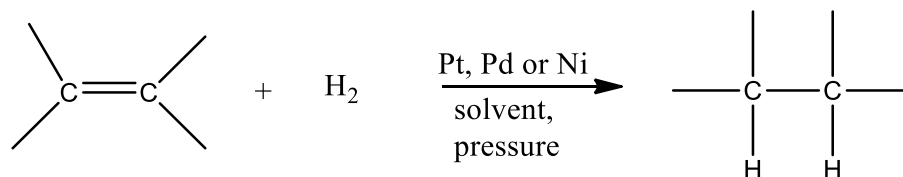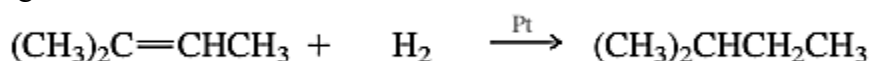
- The solvent is chosen for its ability to dissolve alkene and is typically ethanol, hexane or acetic acid.

b) Addition of hydrogen halides.

$$\text{C}=\text{C} + \text{H}-\text{X} \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{X}{C}}-$$
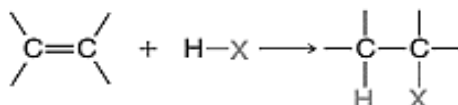
- These additions are sometimes carried out by dissolving the hydrogen halide in a solvent, such as acetic acid, or by bubbling the gaseous hydrogen halide directly into the alkenes (using the alkene itself as the solvent).
- The order of reactivity of the hydrogen halides in alkenes addition is;

    HI > HBr > HCl > HF
- Unless the reaction is highly substituted, HCl reacts so slowly that the reaction is not one that is useful as a preparative method.
  HBr adds readily but unless precautions are taken, the reaction may follow alternatively route.
  e.g

2-Bromopropane   1-Bromopropane
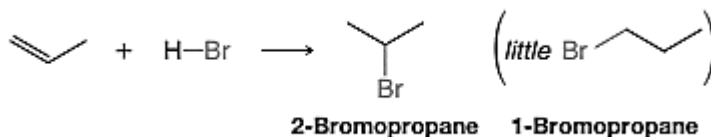
- Vladimir – Markonikov observed this regioselectivity and made the generalization known as Markonikov's rule.

- The addition of HX to an unsymmetrical alkene such as propene could conceivably yield two constitutional isomers. However, the reaction yields only one and is therefore regioselective.

Regioselectivity

- Addition of hydrogen halides follows markonikov's rule.
- Markonikov's rule states that in the addition of HX to an alkene, the hydrogen atom adds to the carbon atom of the double bond that already has the greater number of hydrogen atoms e.g

$$CH_3CH_2CH{=}CH_2 + \quad HBr \quad \longrightarrow \quad CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$$

1-Butene   Hydrogen bromide   2-Bromobutane (80%)

$$\underset{H_3C}{\overset{H_3C}{>}}C{=}CH_2 + \quad HBr \quad \longrightarrow \quad CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}Br$$

2-Methylpropene   Hydrogen bromide   2-Bromo-2-methylpropane (90%)

1-Methylcyclopentene   Hydrogen chloride   1-Chloro-1-methylcyclopentane (100%)
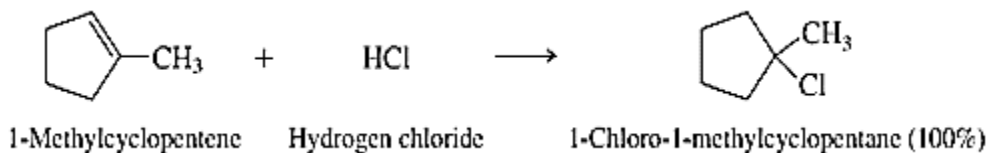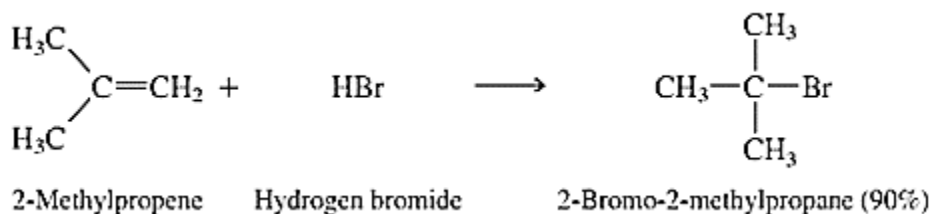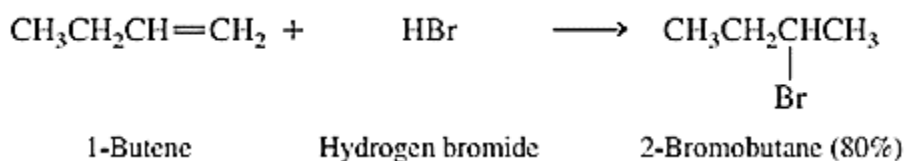
Free Radical Addition of HBr to Alkanes

- It was found that addition of HBr (but not HCl or HI) to alkenes gave products that are opposite to those expected from Markonikov's rule when peroxides are present.
- When alkenes are treated with HBr in the presence of peroxides (ROOR), an anti–Markonikov addition occurs in the sense that the hydrogen atom becomes attached to the carbon atom with the fewer hydrogen atoms. e.g

$$CH_2{=}CHCH_2CH_3 + \quad HBr \quad \xrightarrow{\text{peroxides}} \quad BrCH_2CH_2CH_2CH_3$$

1-Butene   Hydrogen bromide   1-Bromobutane
(only product; 95% yield)
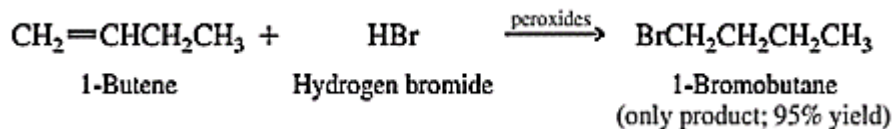
- Alkenes can be contaminated with small amounts of alkyl hydroperoxides (ROOH) if exposed to atmospheric oxygen.
- Free radical addition of HBr can also be initiated photochemically, with or without adding peroxides.

Methylenecyclopentane   Hydrogen bromide   (Bromomethyl)cyclopentane (60%)
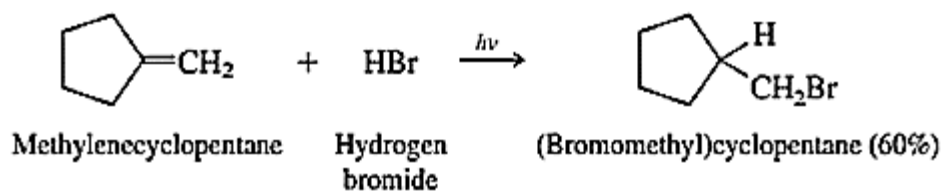
- This anti-markonikov addition occurs only when HBr is used in the presence of peroxides and does not occur significantly with HF, HCl, and HI even when peroxides are present.

c) Addition of water to alkene

- Acid - Catalyzed addition of water to the double bond of an alkene (hydration of an alkene) is a method for the preparation of low – molecular weight alcohols.
- Acids most commonly used to catalyze the hydration of alkenes are – dilute aqueous H_2SO_4 and H_3PO_4 (Phosphoric acid).
- These reactions too are usually regioselective, and the addition of water to the double bond follows Markonikov's rule.
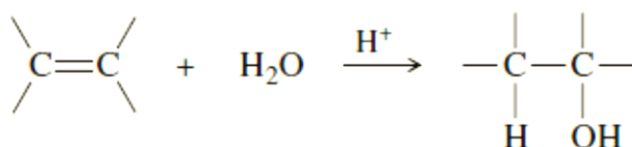
- Because the reaction follows Markonikov's rule, acid – catalyzed hydrations of alkenes do not yield primary alcohols except in special case of hydration of ethene.

$$CH_2 = CH_2 \ + \ H_2O \ \xrightarrow[300°C]{H_3PO_4} \ CH_3CH_2OH$$

Examples

$$(CH_3)_2C{=}CH_2 \ + \ H_2O \ \xrightarrow{H_3O^+} \ (CH_3)_3COH$$
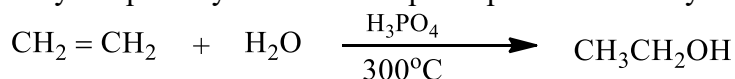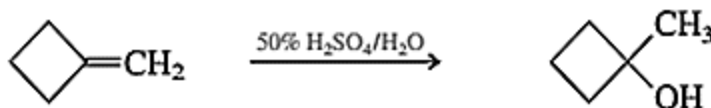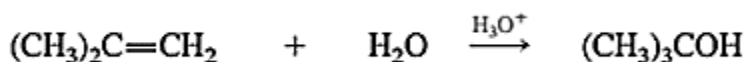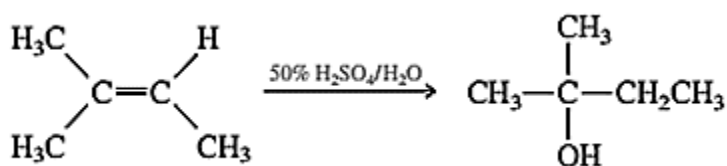
Draw a structural formula for the product of the acid – catalyzed hydration of 1-methylcyclohexene.

1-methylcyclohex-1-ene   **1-methylcyclohexanol**
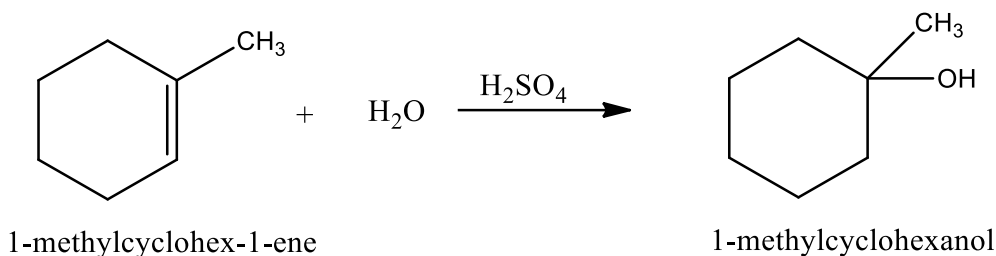
(i)   Hydration of oxymercuration – Demercuration.

- Many alkenes do not easily undergo hydration in aqueous acid.
- Some alkenes are nearly insoluble in aqueous acids, and others undergo side reactions under the strongly acidic conditions.
- Oxymercuration – demercuration is another method for converting alkenes to alcohols with Markonikov orientation.
- Oxymercuration – demercuration works with many alkenes that do not easily undergo direct hydration, and it takes place under milder conditions.
- Alkenes react with mercuric acetate $(Hg(OCOCH_3)_2)$ in a mixture of tetrahydrofuran (THF) and water to produce (hydroxyalkyl) mercuric compounds, which can be reduced to alcohols with Sodium borohydride $(NaBH_4)$)

Step 1: Oxymercuration
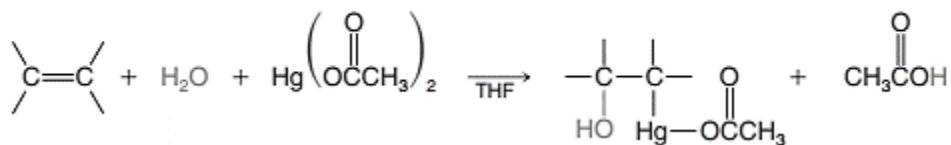
- Water and mercuric acetate add to the double bond.

Step 2: Demercuration
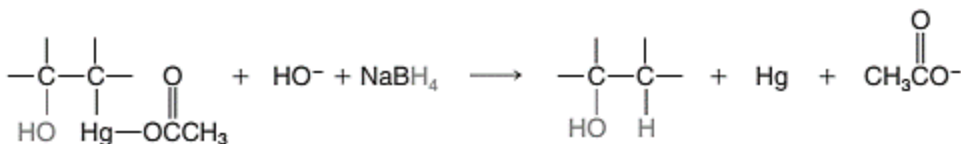
- Sodium borohydride reduces the acetoxymercury group and replaces it with hydrogen. (Acetate group is abbreviated OAC).
- Both steps can be carried out in the same vessel, and both reactions take place very rapidly at room temp or below.
- The overall reaction gives alcohols in very high yields usually greater that than 90%.
- The net orientation of the addition of the elements of water is in accordance with Markonikov's rule.
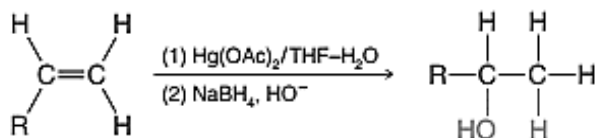
e.g
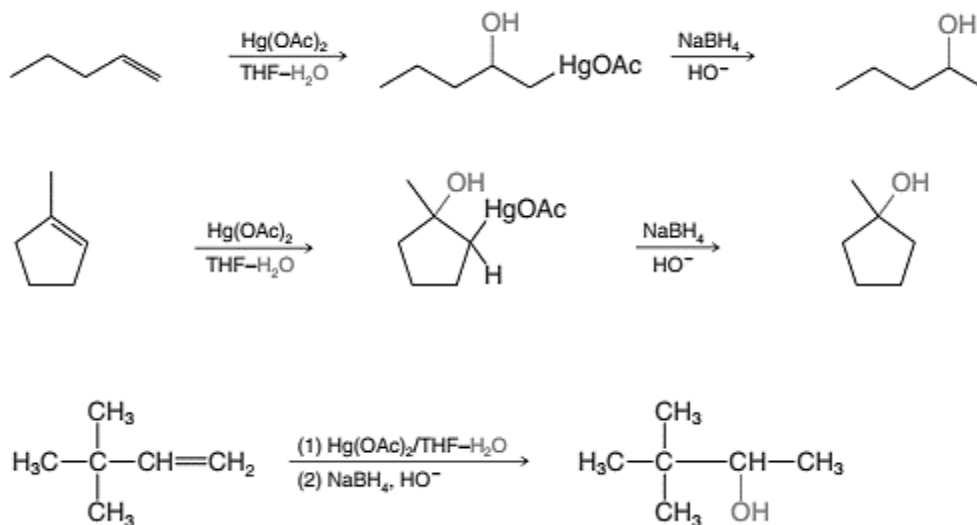
(ii) Hydration through Hydroboration – Oxidation

− Anti – markonikov hydration of a double bond can be achieved through use of diborane (B_2H_6) or a solution of borane in tetrahydrofuran (BH_3: THF).

e.g
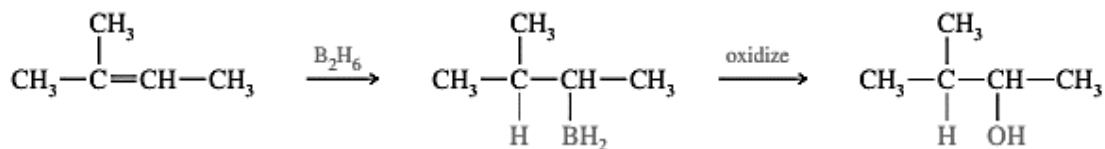
− The BH_3. THF reagent is the form of borane commonly used in organic reactions.
− BH_3 adds to the double bond of an alkene to give an alkylborane.
− Basic hydrogen peroxide oxidizes the alkylborane to an alcohol.

$$CH_3(CH_2)_7CH=CH_2 \xrightarrow[\text{2)H}_2\text{O}_2,\ \text{OH}^-]{\text{1) BH}_3:\ \text{THF}} CH_3(CH_2)_7CH_2CH_2OH$$

$$(CH_3)_2C=CHCH_3 \xrightarrow[\text{2)H}_2\text{O}_2,\ \text{OH}^-]{\text{1) BH}_3:\ \text{THF}} (CH_3)_2CHCHCH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad OH$$
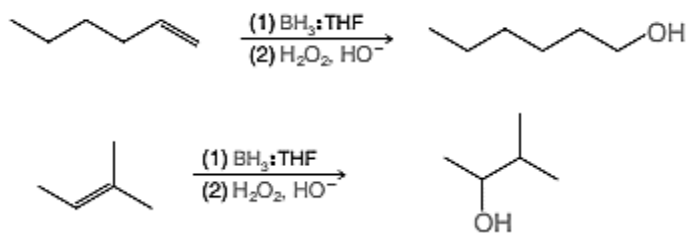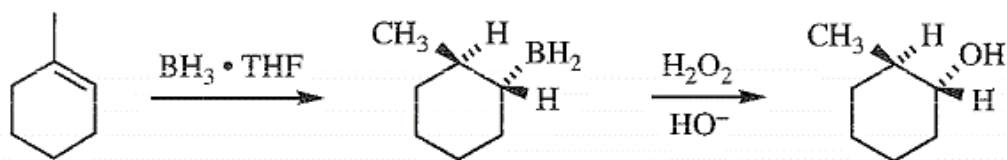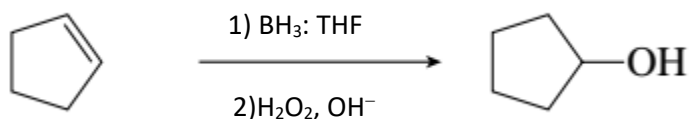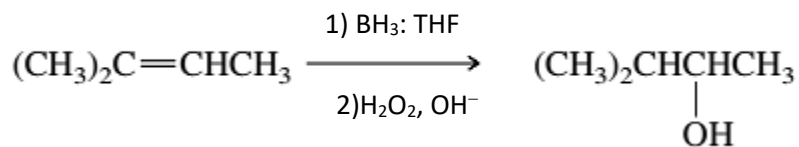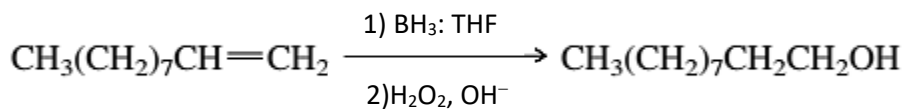
d) Addition of Halogen to Alkenes (Halogenation)

- Chlorine (Cl_2) and bromine (Br_2) react with alkenes at room temperature by the addition of halogen atoms to the two carbon atoms of the double bond, forming two new carbon – halogen bonds. Any solvents used must be inert to the halogens. e.g methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4)

usually anti addition

$$CH_2=CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$$
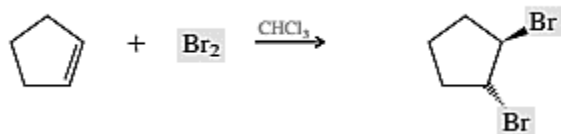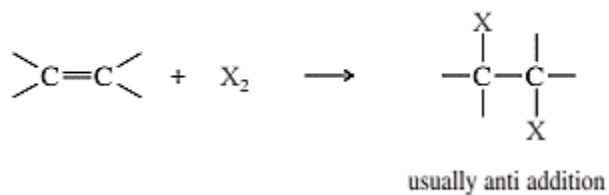
e) Halohydrin Formation

- When bromination occurs in non-nucleophilic solvent (e.g $CHCl_3$), the result is addition of bromine across the double bond.

$$CH_2{=}CH_2 + :\ddot{B}r{-}\ddot{B}r: \longrightarrow \overset{+}{C}H_2{-}CH_2{-}\ddot{B}r: + :\ddot{B}r:^-$$

Ethylene   Bromine   2-Bromoethyl cation   Bromide ion
(nucleophile)   (electrophile)   (leaving group)
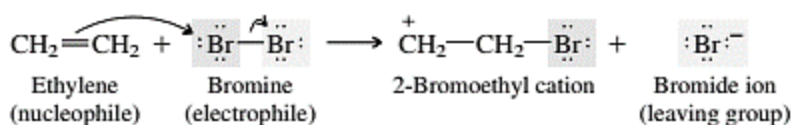
- A carbocation (such as 2-bromoethyl cation) has been demonstrated to be less stable than an alternative structure called a cyclic bromonium ion, in which the positive charge resides on bromine, not carbon.

$$H_2C{-}CH_2$$
$$\diagdown \overset{+}{}\diagup$$
$$:\ddot{B}r:$$

Ethylenebromonium ion

$$:\ddot{B}r:^-$$

$$CH_2{-}CH_2 \qquad \longrightarrow \qquad :\ddot{B}r{-}CH_2{-}CH_2{-}\ddot{B}r:$$
$$\overset{+}{:}\ddot{B}r:$$
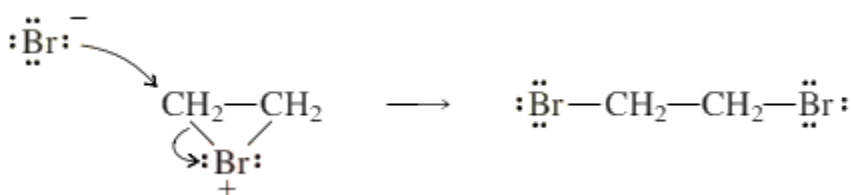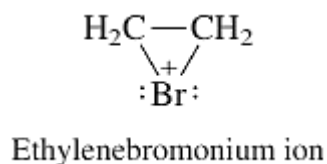
- However, when the reaction is performed in the presence of water, the halonium ion is attacked by a water molecule rather than bromide.

$$\overset{}{C}{=}\overset{}{C} + :\ddot{X}{-}\ddot{X}: \longrightarrow \overset{\ddot{X}^+}{-\overset{}{C}{-}\overset{}{C}{-}} \quad :\ddot{X}:^-$$

(X = Cl, Br or I)   halonium ion

$$\overset{\ddot{X}^+}{-\overset{}{C}{-}\overset{}{C}{-}} \longrightarrow \overset{:\ddot{X}:}{-\overset{|}{C}{-}\overset{|}{C}{-}} \longrightarrow \overset{:\ddot{X}:}{-\overset{|}{C}{-}\overset{|}{C}{-}} + H_3O^+ \; X^-$$
$$H_2\ddot{O}: \qquad\qquad H_2\ddot{O}: H \diagup^{:\ddot{O}:}\diagdown H \qquad :\ddot{O}H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad halohydrin$$
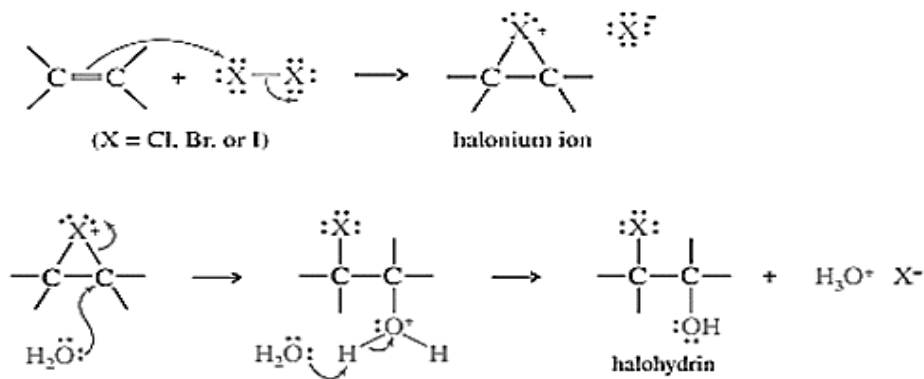
- The net result is the addition of Br and OH across the alkene.
- Products are; -Bromohydrin (bromine + water)

              -Chlorohydrin (Chlorine + water)

- The reactions are generally referred to as **halohydrin formation**.
- Markonikov orientation is observed in halohydrin formation i.e., the nucleophile (water) attacks the more substituted carbon.
- The OH add to the more substituted carbon atom of the double bond (i.e add to carbon with less hydrogens)

$$\underset{}{\overset{}{\text{C}}}=\underset{}{\overset{}{\text{C}}} \;+\; X_2 \;+\; H_2O \;\longrightarrow\; -\underset{\underset{\text{X}}{|}}{\overset{}{\text{C}}}-\underset{}{\overset{\overset{\text{OH}}{|}}{\text{C}}}- \;+\; HX$$

X = Cl or Br   **Halohydrin**

e.g

$$H_2C\!=\!CH\!-\!CH_3 \;+\; Cl_2 \;+\; H_2O \;\longrightarrow\; H_2C\!-\!\underset{\underset{\text{OH}}{|}}{\overset{\overset{}{}}{C}}H\!-\!CH_3 \;+\; HCl$$
$$Cl$$

$$CH_3CH_2\underset{\underset{\text{CH}_3}{|}}{C}\!=\!CH_2 \;+\; Br_2 \;\xrightarrow{\;H_2O\;}\; CH_3CH_2\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{OH}}{|}}{C}}\!-\!CH_2Br$$
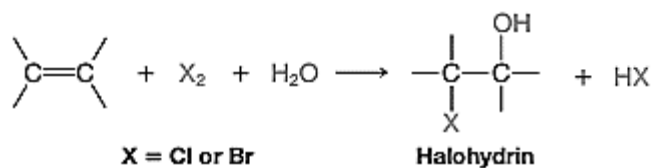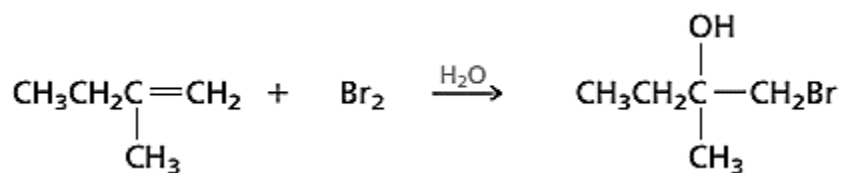
f) Addition of Sulphuric Acid

$$\overset{}{\underset{}{C}}\!=\!\overset{}{\underset{}{C}} \;+\; H\!-\!OSO_2OH \;\longrightarrow\; H\!-\!\overset{|}{\underset{|}{C}}\!-\!\overset{|}{\underset{|}{C}}\!-\!OSO_2OH$$

Alkene   Sulfuric acid   Alkyl hydrogen sulfate
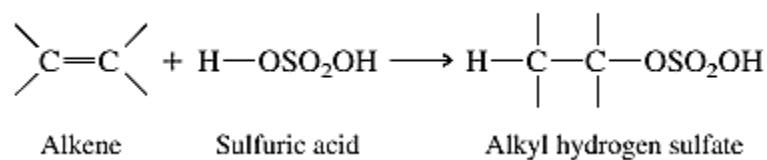
− Markonikov's addition e.g

$$CH_3CH\!=\!CH_2 \;+\; HOSO_2OH \;\longrightarrow\; CH_3\underset{\underset{\text{OSO}_2\text{OH}}{|}}{C}HCH_3$$
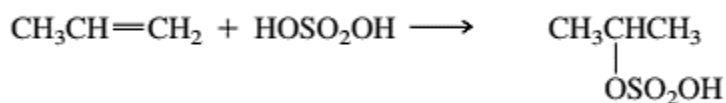
− Alkyl hydrogen sulfates can be converted to alcohols by heating with steam or water (i.e., hydrolysis).

Cleavage occurs here during hydrolysis

$$H\!-\!\overset{|}{\underset{|}{C}}\!-\!\overset{|}{\underset{|}{C}}\!-\!O\!-\!SO_2OH \;+\; H_2O \;\xrightarrow{\text{heat}}\; H\!-\!\overset{|}{\underset{|}{C}}\!-\!\overset{|}{\underset{|}{C}}\!-\!OH \;+\; HOSO_2OH$$

Alkyl hydrogen sulfate   Water   Alcohol   Sulfuric acid
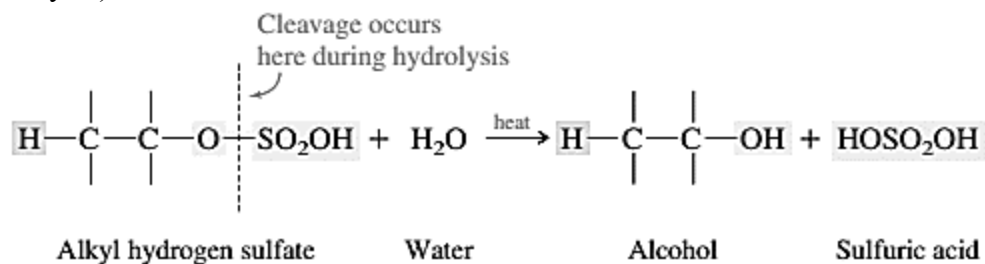
e.g
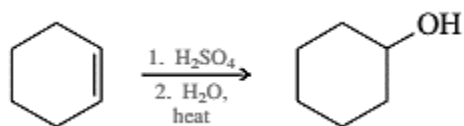
OXIDATION OF ALKENES

- Alkenes undergo a number of reactions in which the carbon – carbon double bond is oxidized.

a) Dihydroxylation

- Addition of OH and OH across a double bond of alkenes
  e.g.,

- 1,2-Dihydroxylation is an important oxidative addition reaction of alkenes.
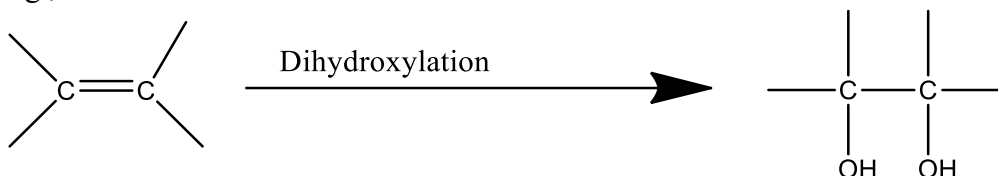- The two most common reagents for this purpose are osmium tetroxide (OsO_4) and potassium permanganate.

i) Osmium tetroxide (OsO_4)

- Widely used to synthesize 1,2-diols (sometimes called glycols).

An osmate ester
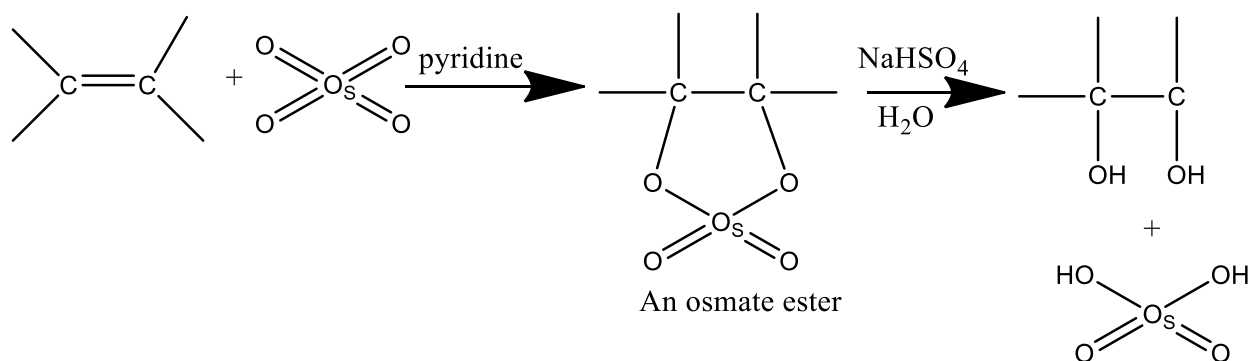
- After formation of the cyclic intermediate with osmium, cleavage at the oxygen–metal bonds take place without altering the stereochemistry of the two new C–O bonds.
  e.g

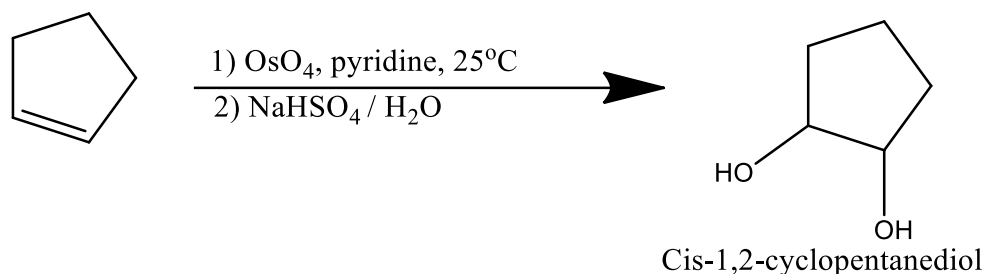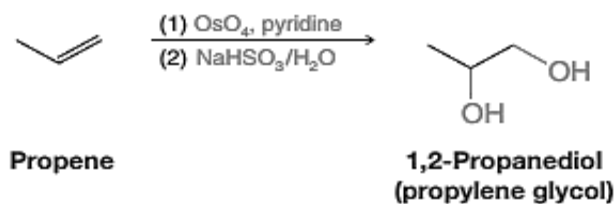Propene → 1,2-Propanediol (propylene glycol)

Reagents: (1) OsO$_4$, pyridine (2) NaHSO$_3$/H$_2$O

1) OsO$_4$, pyridine, 25°C
2) NaHSO$_4$ / H$_2$O

Cis-1,2-cyclopentanediol

ii) Potassium Permanganate (cold)

− Can also be used for dihydroxylation, although because it is a stronger oxidizing agent it is prone to cleave the diol through further oxidation.

e.g

CH_2=CH_2 + $KMnO_4$ → (HO⁻, H$_2$O, cold) → HO–CH$_2$CH$_2$–OH

Ethene → 1,2-Ethanediol (ethylene glycol)
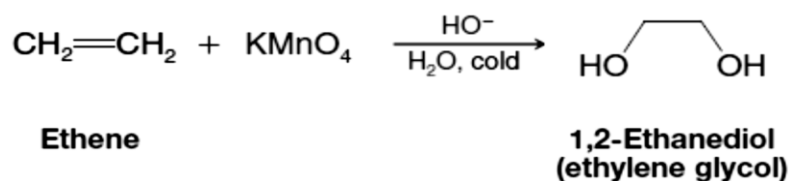
b) Oxidative Cleavage of Alkene
i) Cleavage by permanganate

− In a potassium permanganate dihydroxylation, if the solution is warm or acidic or too concentrated, <u>oxidative cleavage</u> of the glycol may occur.
− In effect, the double bond is cleaved to two carbonyl groups.
− The products are initially aldehydes and ketones, but aldehydes are oxidized to carboxylic acids under these strong oxidizing conditions.
− If a molecule contains a terminal =CH_2 group, that group is oxidized to CO_2 and water.

glycol   ketone (stable)   aldehyde (oxidizable)   acid

$KMnO_4$ (warm, concd.)
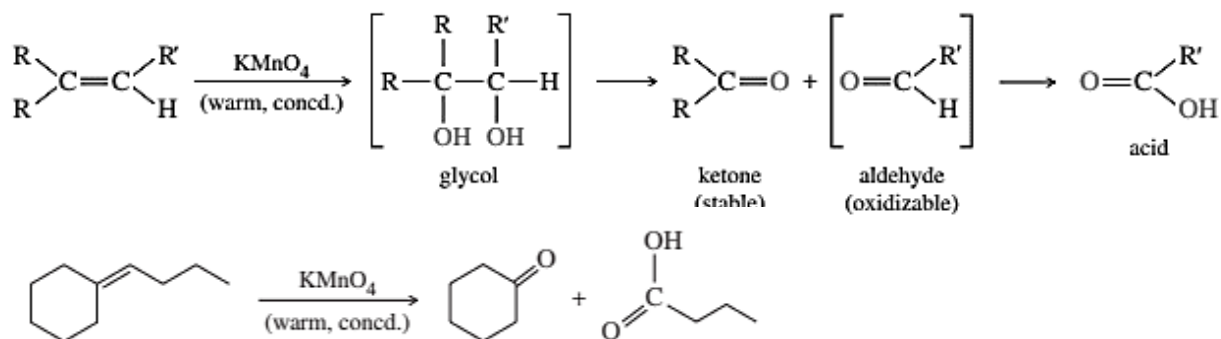
- One of the uses of potassium permanganate, other than for oxidative cleavage, is a chemical test for unsaturation in an unknown compound.
- If an alkene (or alkyne) is present, the purple colour of a potassium permanganate solution is discharged and a brown precipitate of manganese dioxide (MnO_2) forms as the oxidation takes place.

ii) Cleavage with Ozone
- The most useful method for cleaving alkenes is to use ozone (O_3).
- Ozonolysis consists of bubbling ozone into a very cold (-78°C) solution of the alkene in CH_2Cl_2, followed by treatment of the solution with dimethyl sulfide (or zinc or acetic acid).

reaction scheme 1: cyclopentene with methyl substituent → 1)O₃, CH₂Cl₂, -78°C 2) (CH₃)₂S → product with CH₃

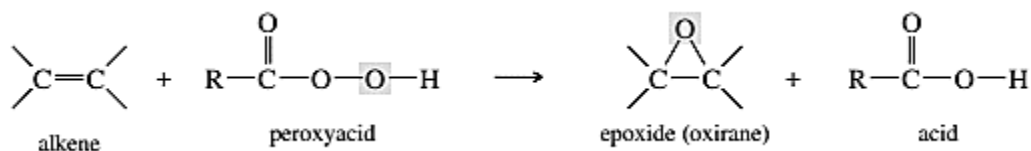reaction scheme 2
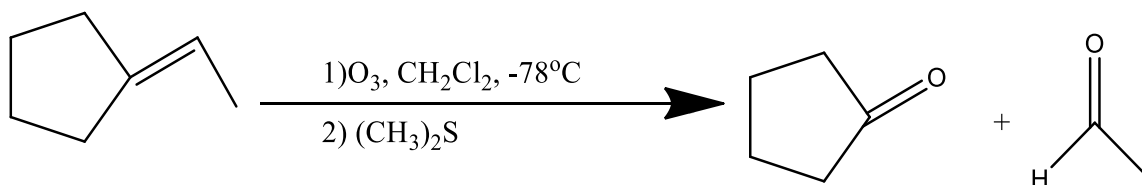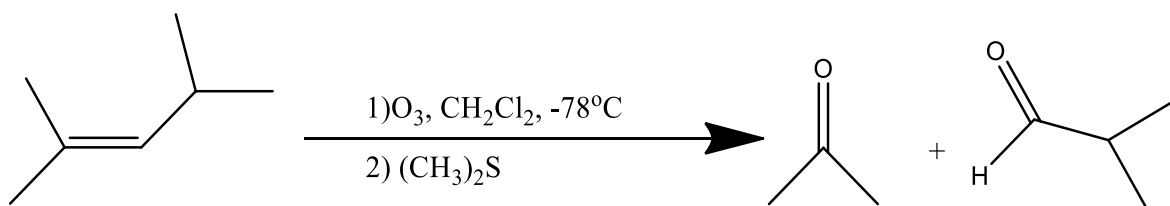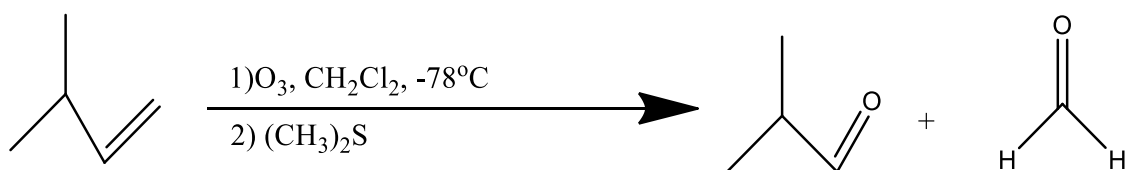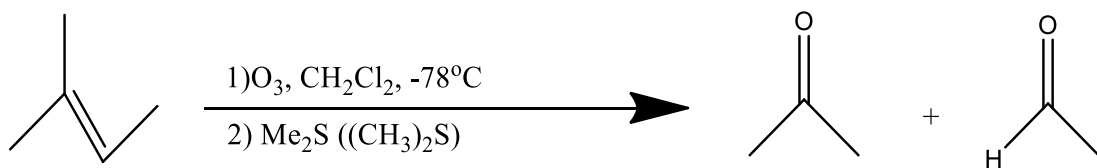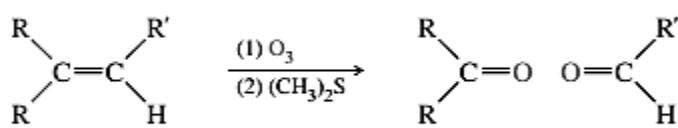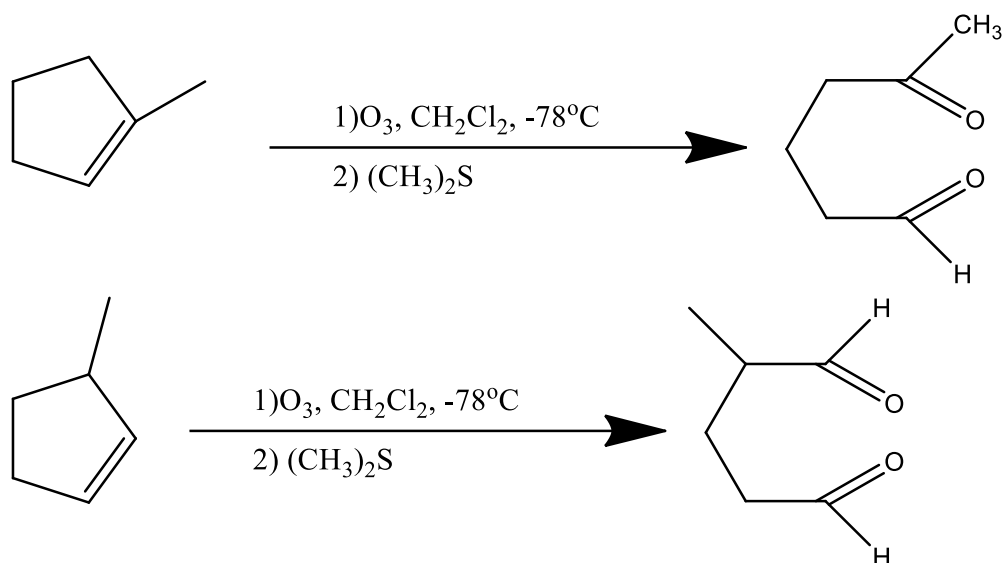
Epoxidation of Alkenes

− An epoxide is a three-membered cyclic ether, also called oxirane.
− An alkene is converted to an epoxide by a peroxyacid, a carboxylic acid that has an extra oxygen atom.

− The epoxidation of an alkene is clearly an oxidation since an oxygen atom is added. Peroxyacids are highly selective oxidizing agents.
− m-chloroperoxybenzoic acid (MCPBA) is usually used to convert alkenes to epoxides having the same cis or trans stereochemistry. It is commonly used for its desirable solubility properties.
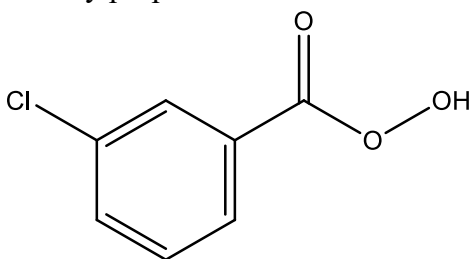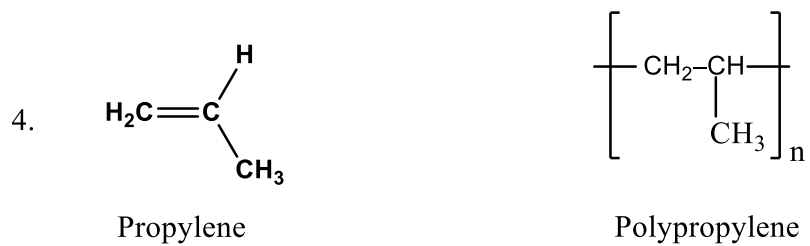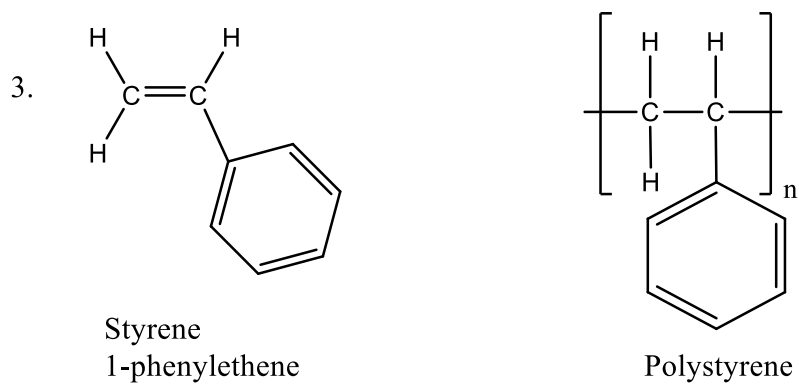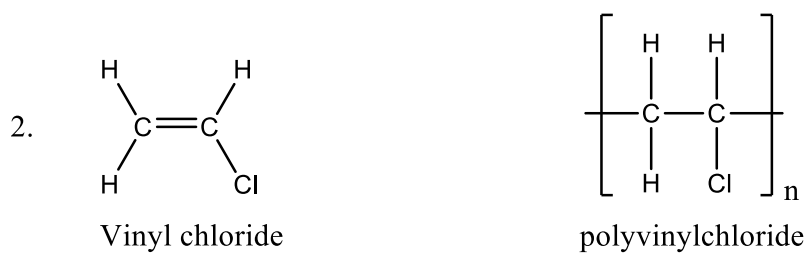

m-chloroperoxybenzoic acid (MCPBA)

− The peroxyacid dissolves, then the spent acid precipitates out of solution.
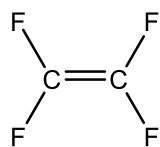 e.g
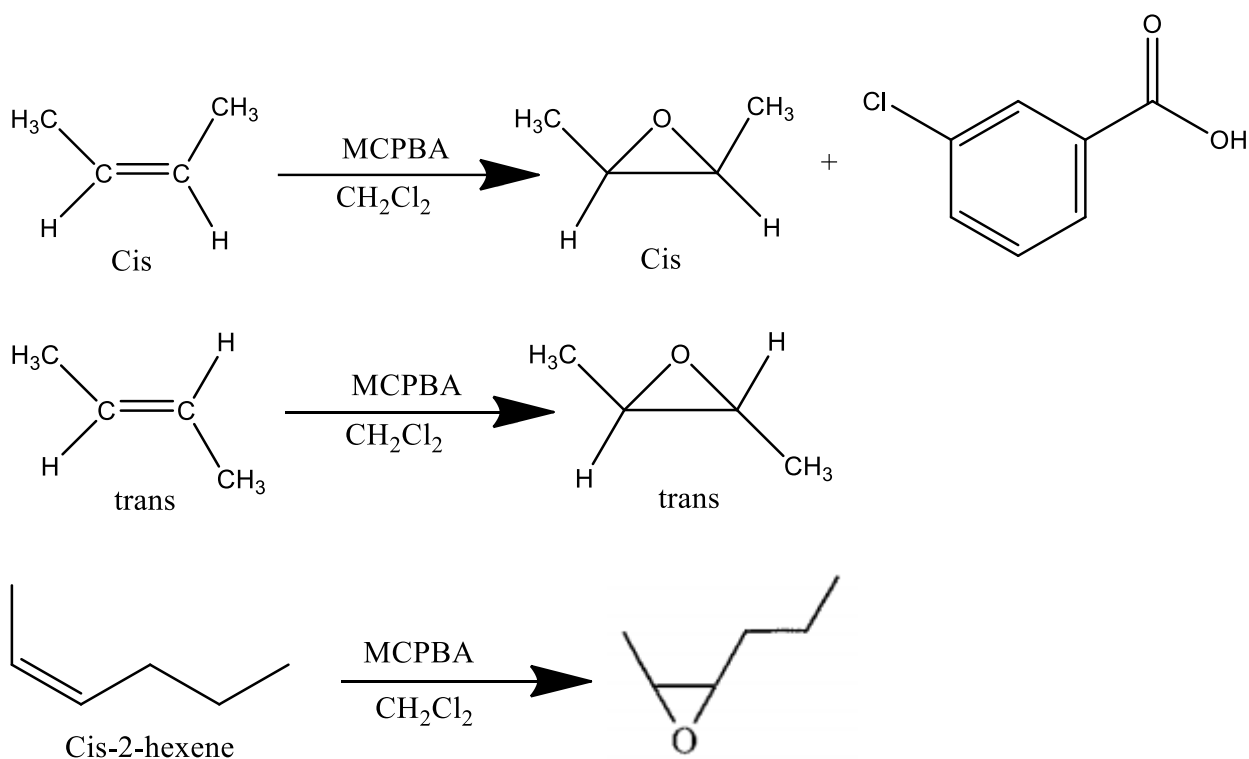
POLYMERIZATION OF ALKENES

- A polymer is a large molecule composed of many smaller repeating units (monomers) bonded together.
- Alkenes serve as monomers for some of the most common polymers, such as polyethylene, polypropylene, polystyrene, polyvinylchloride et.c
- Polymers can be classified on their method of synthesis;
(i) Addition polymers- they are made by directly adding monomer units together.
    These polymers contain all the atoms of monomers.
(ii) Condensation polymers- they are made by combining monomer units and eliminating/splitting out a small molecule often water.

- Alkenes polymerize to give addition polymers resulting from repeated addition reactions across their double bonds.
- Addition polymers generally form by chain-growth polymerization, the rapid addition of one molecule at a time to a growing polymer chain.
- There is generally a reactive intermediate (cation, anion or radical) at the growing end of the chain.
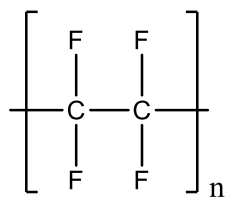
Common addition/ Chain-growth polymers

1.

Ethylene

polyethylene polymer

2.

Vinyl chloride

polyvinylchloride

3.

Styrene
1-phenylethene

Polystyrene

4.

$H_2C=C$

Propylene

Polypropylene

5.

| Tetrafluoroethene | Polytetrafluoroethylene |

Mechanism of polymerization

1. Free radical polymerization

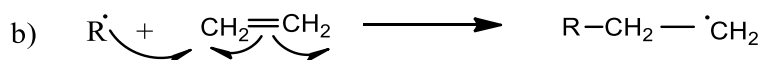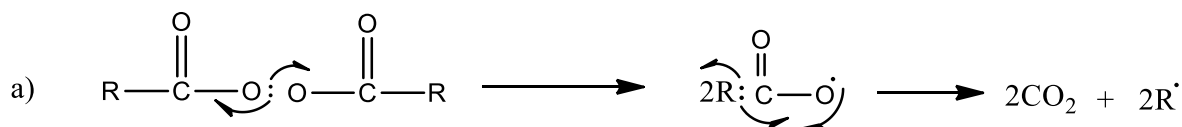2. Ionic polymerization — Cationic polymerization / Anionic polymerization

3. Coordination polymerization

Free radical polymerization

- Formed through homolytic cleavage.
- Involves odd electron species-free radical.
- It is carried out in three steps:

Step 1: Initiation step

Initiators are needed. e.g diacylperoxide

$$R-\overset{O}{\underset{\|}{C}}-O-O-\overset{O}{\underset{\|}{C}}-R$$

diacyl peroxide

a) $R-\overset{O}{\underset{\|}{C}}-O \cdot O-\overset{O}{\underset{\|}{C}}-R \longrightarrow 2R \cdot \overset{O}{\underset{\|}{C}}-O \cdot \longrightarrow 2CO_2 + 2R \cdot$

b) $R \cdot + CH_2 = CH_2 \longrightarrow R-CH_2 - \cdot CH_2$

Step 2: Propagation step

$R-CH_2 - \cdot CH_2 + nCH_2 = CH_2 \longrightarrow R\left(CH_2 - CH_2\right)_n CH_2 \cdot CH_2$

n monomer
units
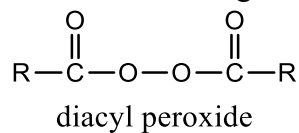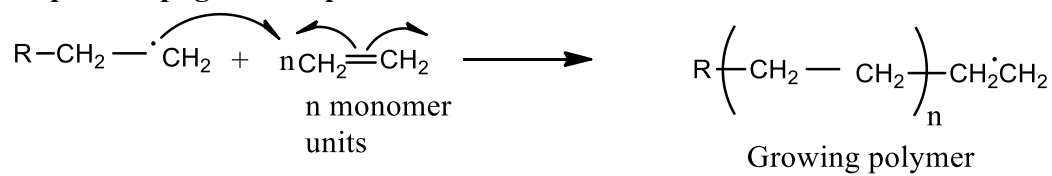
Growing polymer

Step 3: Termination step
Takes place in two steps;
Coupling- The two growing polymers combine with each other to form a dead polymer.

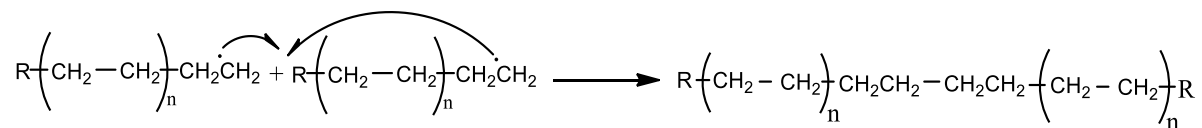$$R + CH_2 - CH_2 \overline{)_n} CH_2\dot{C}H_2 \ + \ R + CH_2 - CH_2 \overline{)_n} CH_2\dot{C}H_2 \longrightarrow R + CH_2 - CH_2 \overline{)_n} CH_2CH_2 - CH_2CH_2 + CH_2 - CH_2 \overline{)_n} R$$

Disproportionation – involves hydrogen transfer from one growing chain to another. The hydrogen moves as hydrogen free radical.

$$R + CH_2 - CH_2 \overline{)_n} CH_2\dot{C}H_2 \ + \ R + CH_2 - CH_2 \overline{)_n} \overset{H}{\underset{}{CH}} - \dot{C}H_2 \longrightarrow R + CH_2 - CH_2 \overline{)_n} CH_2CH_3 \ + \ R + CH_2 - CH_2 \overline{)_n} CH = CH_2$$