

## Alkenes (olefins)

Alkenes are unsaturated hydrocarbons which contain a carbon-carbon double bond. They are represented by the general formula  $C_nH_{2n}$ ; where  $n \geq 2$ .

### Nomenclature of alkenes

According to the IUPAC, the alkenes in general, are named by replacing the ending *-ane* of the name of the corresponding alkanes by *-ene*.

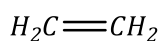
The first and the simplest member is ethene since we cannot have a carbon to carbon double bond in a single carbon atom.

The rules for naming the alkenes are similar to those used for naming the alkanes.

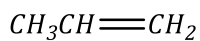
Important to note are:

1. The longest continuous chain containing the carbon-carbon double bond is selected as the parent chain which is named by replacing the ending *-ane* of the name of the corresponding alkane by *-ene*. This will be the parent name of the alkene.
2. Number the chain beginning with the end nearest to the first carbon atom containing the double bond.
3. Indicate the location of the substituents by the number of the carbon atom to which they are bonded.

Examples are:



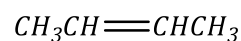
Ethene



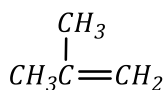
Propene



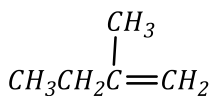
But-1-ene



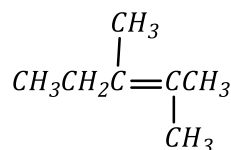
But-2-ene



2-methylpropene



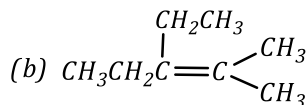
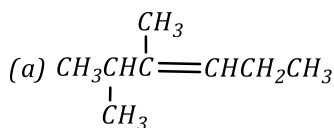
2-methylbut-1-ene



2,3-dimethylpent-2-ene

#### Task

1. Write the IUPAC names of the following compounds



2. Give the structural formula for:

(a) 3-ethylpent-1-ene

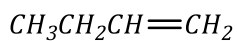
(b) 2,2-dimethylhex-3-ene

(c) 2-methylhept-3-ene

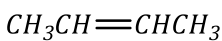
## Isomerism in alkenes

Higher alkenes exhibit chain isomerism, position isomerism and functional group isomerism.

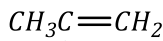
For example  $C_4H_8$  has the following isomers;



*But-1-ene*



*But-2-ene*



*2-Methylpropene*



*Cyclobutane*

### Task

- Write the names and structures of all the possible isomers of the following compounds.
  - $C_5H_{10}$
  - $C_6H_{12}$
- A compound **Q**, on combustion gave 0.629 g of carbon dioxide and 0.257 g of water.
  - Determine the empirical formula of **Q**.
  - At s.t.p, compound **Q** has a vapour density of  $2.5 \text{ gdm}^{-3}$ . Calculate the molecular mass of **Q**.
  - Determine the molecular formula of **Q** hence write the structural formulae and names of the possible open chain isomers of **Q**.

## Physical properties of alkenes

Just like alkanes, alkenes exhibit only weak **van der waals interactions**. This makes their physical properties similar to corresponding alkanes.

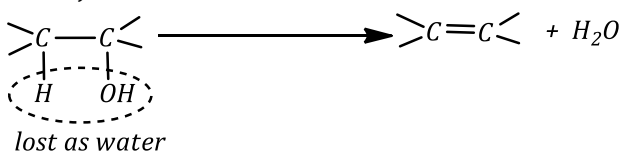
- Ethene, propene and but-1-ene are colourless gases while the rest are either colourless liquids or soft solids (waxy solids) at room temperature.
- The volatility and solubility of alkenes are similar to those of the corresponding alkanes.

## Sources of alkenes

- On a large/ industrial scale, alkenes are obtained by cracking of petroleum. (Refer to alkanes).
- In the laboratory, alkenes can be obtained in the following ways:

### 1. Dehydration of alcohols.

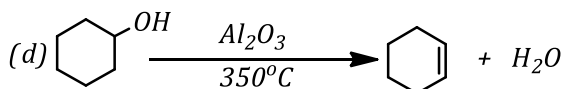
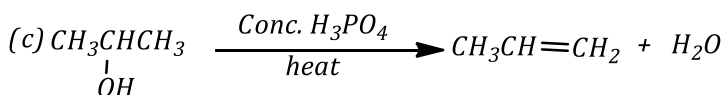
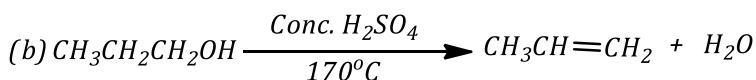
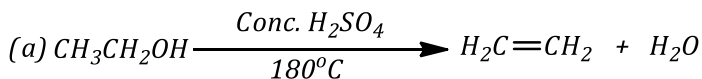
This is an elimination reaction in which the elements of water are removed from the adjacent carbon atoms.



Conditions for the reactions are:

- Excess concentrated sulphuric acid,  $H_2SO_4$  at  $170-180^\circ C$ .
- Or concentrated phosphoric acid,  $H_3PO_4$ , heat
- Or commercial alumina ( $Al_2O_3$  containing silicon dioxide and other oxides) at about  $350-400^\circ C$ .

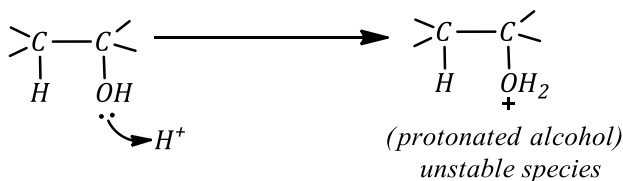
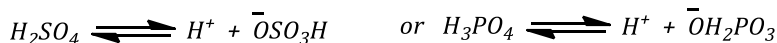
Example



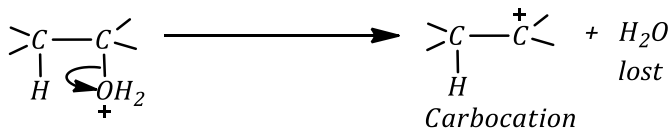
### Mechanism for the reaction.

The mechanism for acid dehydration of alcohols proceeds as follows:

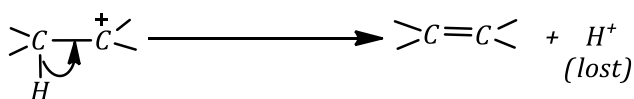
- Protonation of the alcohol.



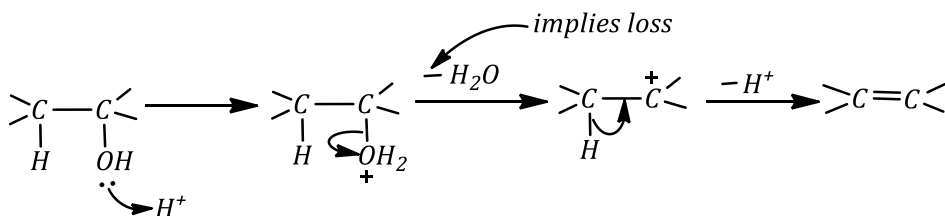
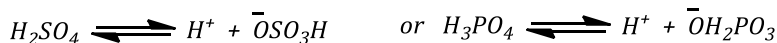
- Loss of a water molecule to form a carbocation as an intermediate.



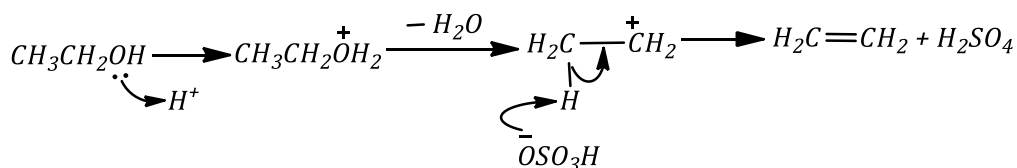
- Loss of a proton from a  $\beta$  carbon atom (the carbon atom next to the positively charged carbon atom) to form an alkene.



The above three steps can be summarized as follows:

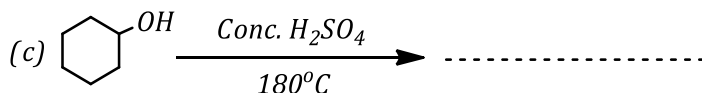
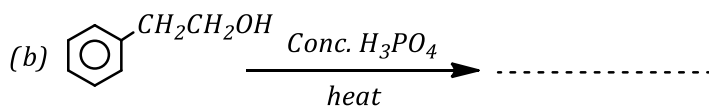
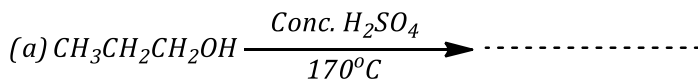


For example; the mechanism for the reaction in (a) above proceeds as follows:



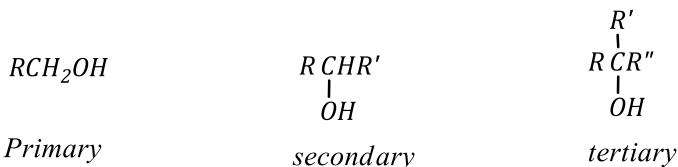
### Task

Complete the equations below and outline the mechanism for each of the reactions.



### NOTE:

- There are three classes of alcohols namely;



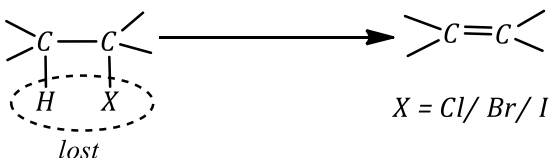
- Each class of alcohol forms a carbocation with varying stability.

Carbocation	Description	Structure
(a) Primary carbocation ( $1^\circ$ ) (least stable)	This has one alkyl group attached to the carbon atom carrying the positive charge.	$R\overset{+}{C}H_2$



## 2. Dehydrohalogenation of monoalkyl halides.

The process involves removal of hydrogen and halogen atoms from the adjacent carbon atoms in a molecule of a monohaloalkane to form an alkene. This is also an elimination reaction.

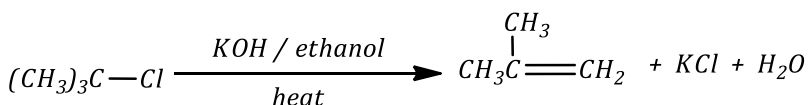
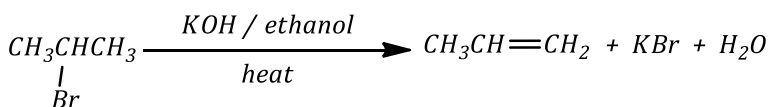
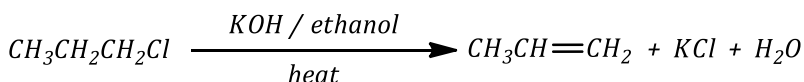


This is done by heating or refluxing an alkylhalide with alcoholic solution of potassium hydroxide.

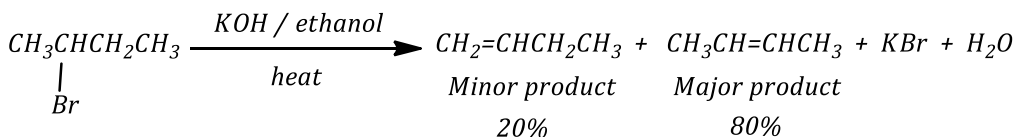
Better yields of alkenes are obtained when secondary or tertiary alkylhalides are used.

Primary alkylhalides (in particular  $\text{CH}_3\text{CH}_2\text{X}$ ) gives very poor yields of alkenes. Thus their use for this purpose is limited.

For example:

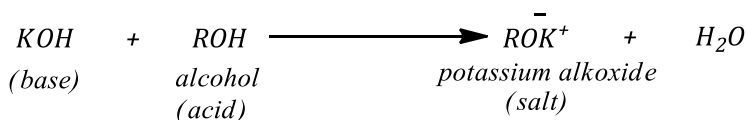


**NOTE:** In reactions where two alkenes are possible, the most favoured alkene is predicted by use of Saytzeff's rule. The rule state that "during elimination reaction, the hydrogen atom is removed from an adjacent carbon atom with fewer number of hydrogen atoms". For example;



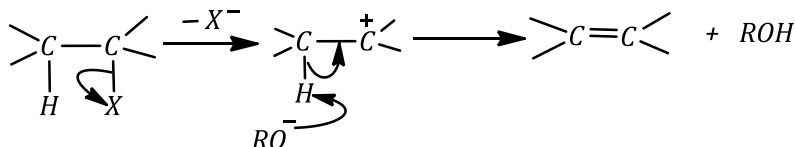
### Mechanism

The mechanism proceeds according to the following mechanism:

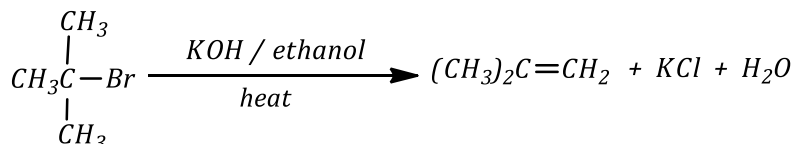


The alkoxide ion formed acts as a stronger base than the hydroxyl ions and removes a proton from the substrate (alkylhalide).

- Tertiary alkylhalides first form carbocations as intermediates by loss of a halogen atom. This is because their carbocations are relatively stable. The carbocation formed then loses a proton.

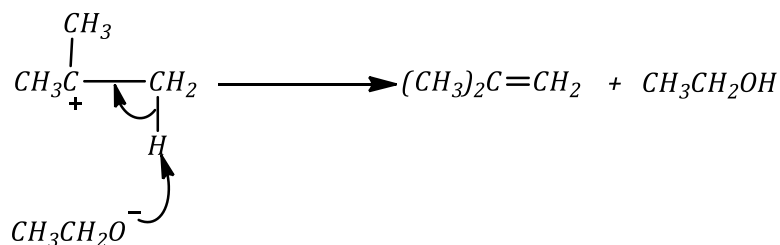
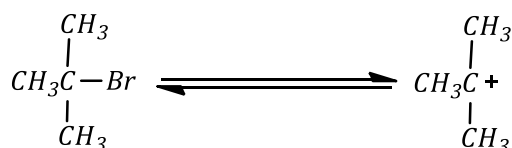
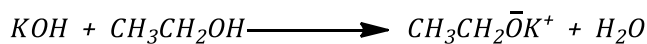


Example:

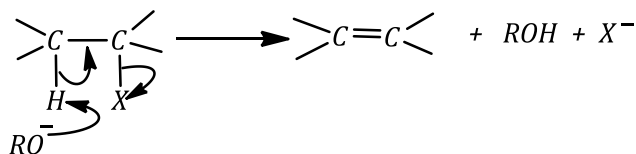


The mechanism for the above reaction proceeds as follows:

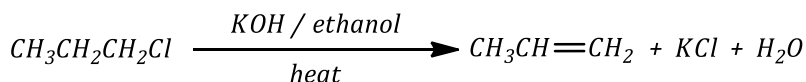
*Mechanism:*



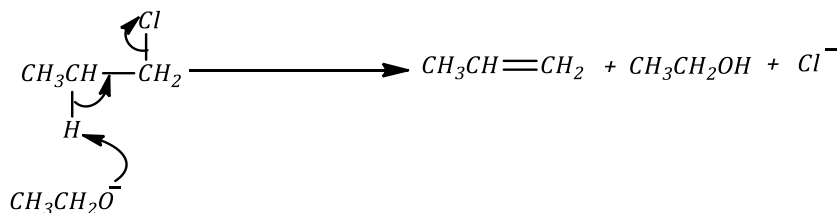
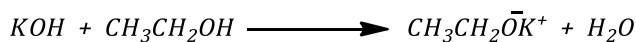
- Primary alkylhalides follow a concerted mechanism (“come in I go away”). This is because their carbocations are very unstable and cannot be easily formed.



Example;



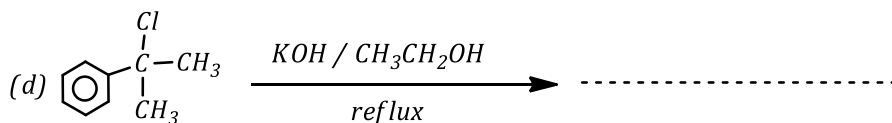
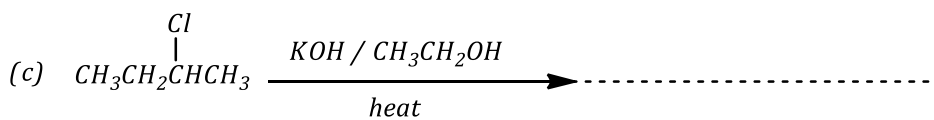
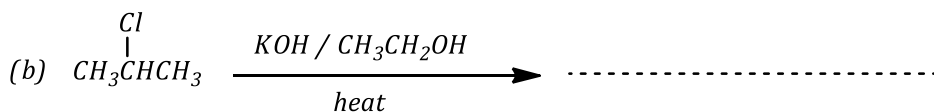
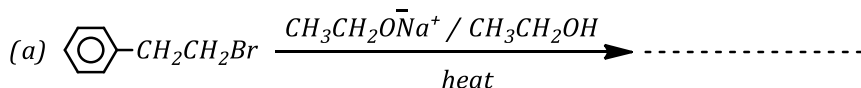
The mechanism for the above reaction proceeds as follows:



- Secondary alkylhalides are intermediate in behaviour between tertiary and primary alkylhalides.

### Task

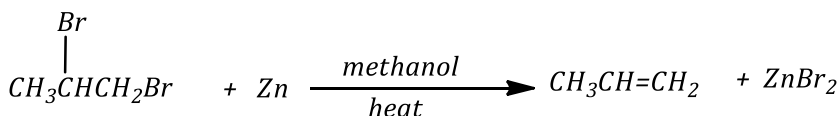
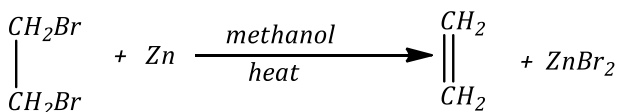
Complete the equations below and outline the mechanism for each reaction.



### 3. Dehalogenation of vicinal dihalides

Vicinal dihalides are halides with two halogen atoms attached to adjacent carbon atoms.

When vicinal dihalide are heated with zinc-copper couple in a solution of methanol, pure alkene is formed.

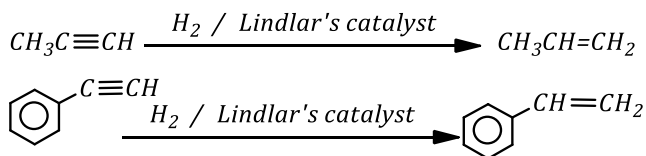


### 4. Partial hydrogenation of alkynes.

This involves reacting alkynes with hydrogen in the presence of Lindlar's catalyst (a poisoned/ deactivated catalyst).



For example:



## Reactions of alkenes.

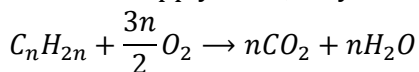
The presence of localised pi electrons in the double bond makes alkenes act as electron rich species.

Thus, alkenes;

- are more reactive than alkanes.
- undergo majorly electrophilic addition reactions across the double bond.

### 1. Combustion

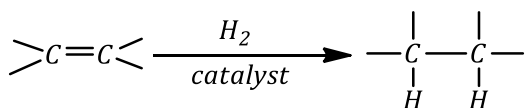
In excess supply of air, they burn to form carbon dioxide and water.



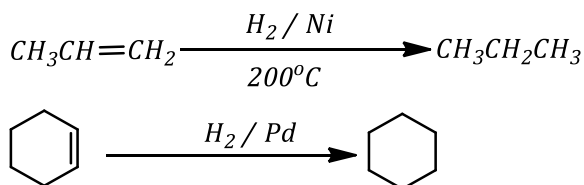
### 2. Addition reactions

#### (a) Hydrogenation (reduction)

In the presence of a suitable catalyst, hydrogen adds across the carbon-carbon double bond to form an alkane.

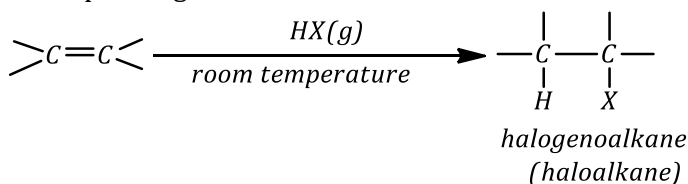


For example:



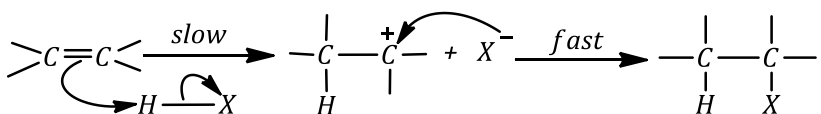
#### (b) Addition of hydrogen halides/ halogen acids, HX; X = Cl/ Br/ I.

At room temperature, alkenes react with gaseous hydrogen halides to give the corresponding haloalkanes.



## Mechanism

The general mechanism for the reaction is as follows:

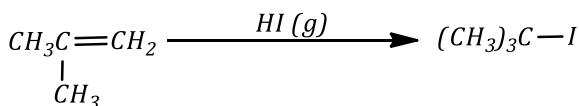
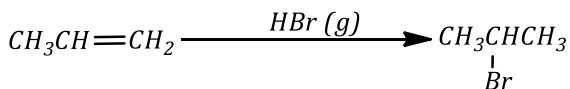
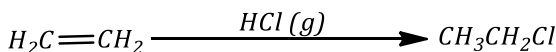


In unsymmetrical alkenes, two products are possible due to the formation of two carbocations; one is stable and the other is unstable.

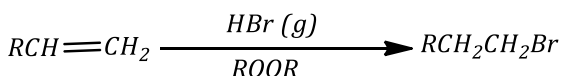
The major product (preferred product) proceeds via the formation of a stable carbocation which is formed in higher concentrations.

This is in accordance with Markovnikov's rule which states that: "In the addition of reagents across the double bond of an unsymmetrical alkene, the more positive part of the reagent becomes attached to the carbon atom of the double bond containing the greater number of hydrogen atoms"

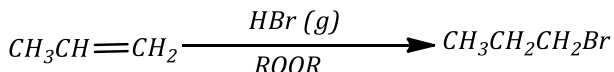
Examples:



In the presence of an organic peroxide,  $ROOR$ , hydrogen bromide adds to the alkene to form a product different from that predicted by Markovnikov's rule. This is anti-Markovnikov's addition rule.



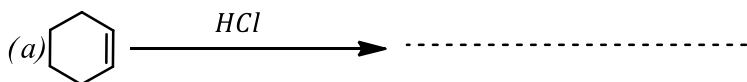
For example;

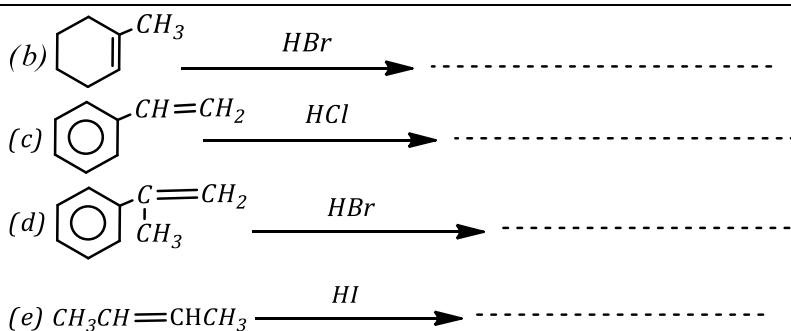


**NOTE:** Peroxide effect is effective only in the case of  $HBr$  and not effective in the case of  $HCl$  and  $HI$ .

### Task

1. Complete the equation below and outline the mechanism for the reaction.





2. Explain the following observations:

- (a) When 2-methylpropene is reacted with hydrogen bromide, the major product is 2-bromo-2-methylpropane rather than 1-bromo-2-methylpropane.
- (b) Hydrogen chloride reacts with but-2-ene to form 2-chlorobutane as the only product whereas with but-1-ene, two products are possible i.e. 2-chlorobutane and 1-chlorobutane.

**Note:**

The rate of addition of halogen acids to an alkene increases in the order  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ .

**Reason**

From Fluorine to iodine, atomic radius increases. The hydrogen-halogen bond length increases in the order  $\text{H} - \text{F} < \text{H} - \text{Cl} < \text{H} - \text{Br} < \text{H} - \text{I}$ .

The hydrogen-halogen bond strength decreases in the order  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$ .

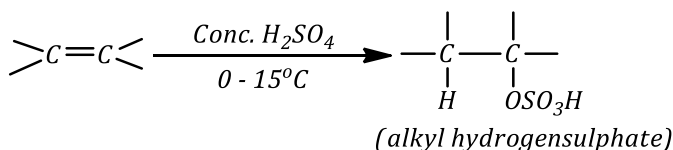
Hence hydrogen iodide readily donates a proton and thus readily reacts faster with an alkene whereas hydrogen fluoride doesn't readily donate and thus it reacts very slowly with an alkene.

**Task**

Propene readily reacts with hydrogen iodide than with hydrogen chloride. Explain this observation.

(c) **Reaction with concentrated sulphuric acid.**

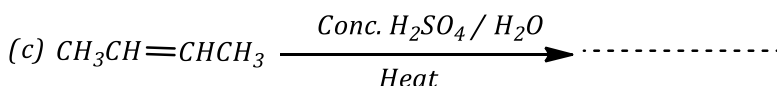
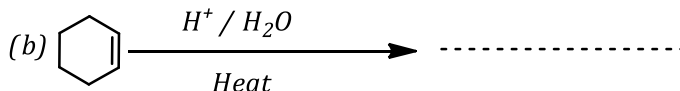
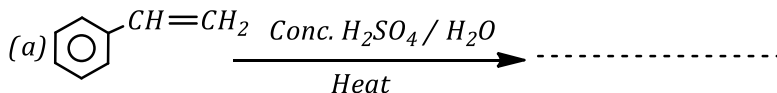
In the cold ( $0-15^\circ\text{C}$ ), alkenes react with concentrated sulphuric acid to form alkylhydrogensulphates.





**Task**

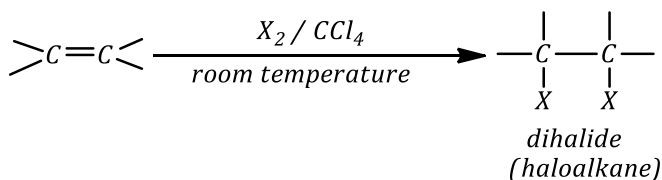
- Complete the following equations and in each case outline a mechanism for the reaction.



- Discuss the reactions of ethene with sulphuric acid. Include equations and mechanism of the reactions that took place.

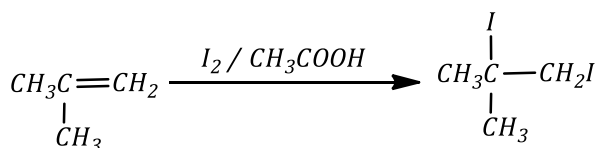
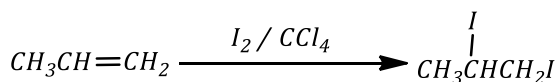
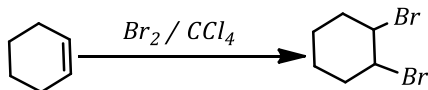
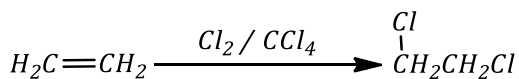
**(d) Addition of halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$  or  $\text{I}_2$ ).**

Alkenes readily react with halogens in carbon tetrachloride or ethanoic acid at room temperature to give a dihaloalkanes.



Carbon tetrachloride acts as an inert solvent and provides a medium for the reaction.

Examples:

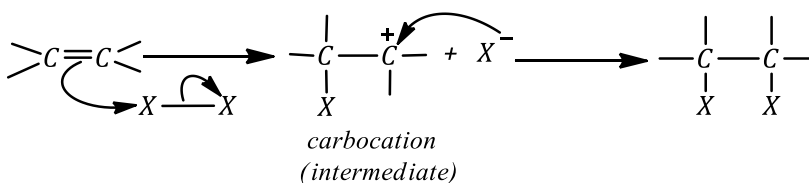
**Mechanism**

Addition of halogens across the double bond is a two-step reaction. The  $\text{X}_2$  is a non-polar molecule. When it approaches the alkene molecule, the  $\pi$ -electron

cloud polarizes the  $X - X$  bond. Thus, a partial positive charge is induced in the nearest halogen atom. The  $\pi$ -electrons then attracts the atom with a partial positive charge.

The halogen atom with a partial positive charge forms a covalent bond with one of the unsaturated carbon atoms and breaks from the other halogen atom. A halide ion is formed and a carbocation is formed.

The halide ion then attacks the carbocation to complete the process.

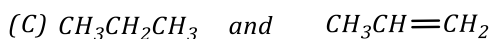
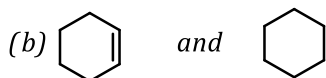
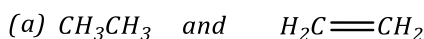


The reaction of bromine in carbon tetrachloride with alkenes is used to:

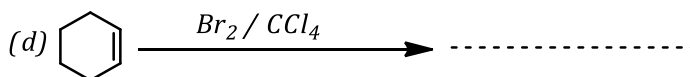
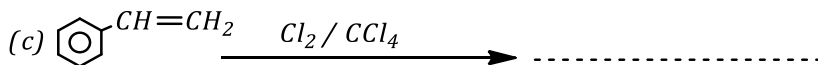
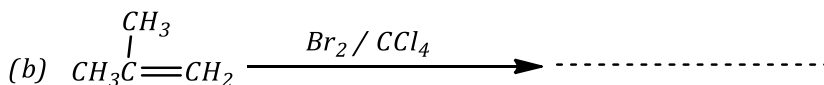
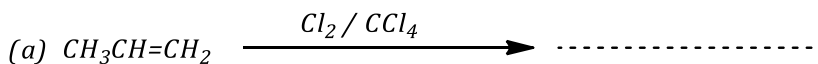
- test for the presence of a carbon-carbon double bond/ unsaturation in alkenes. Alkenes turn the red liquid to colourless.
- distinguish alkenes from alkanes.

### Task

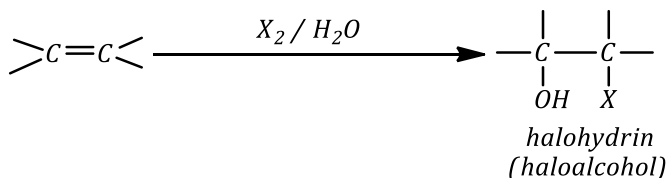
1. name one reagent that can be used to distinguish between the following pairs of compounds. In each case, state what would be observed if each member is separately treated with the reagent you have named.



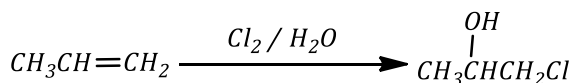
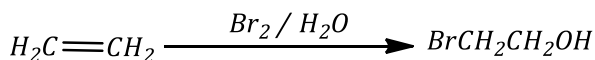
2. Complete the equations below and outline a mechanism for each of the reactions.



If the addition of bromine or chlorine is carried out in aqueous solution (in the presence of water) instead of carbon tetrachloride, the major product is not a dihalogen compound but a haloalcohol.

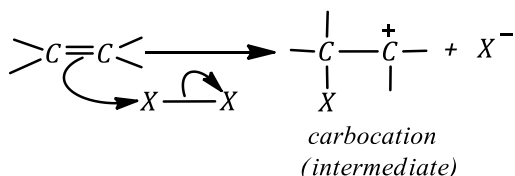


Examples:

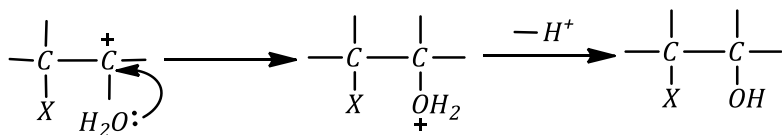


### Mechanism:

The mechanism for halohydrin formation is similar to the mechanism for halogenation in the presence of an inert solvent.



Even though  $X^-$  is formed in first step of the mechanism, its concentration is low compared to  $H_2O$ . Thus, the carbocation is mostly attacked by  $H_2O$  and not  $X^-$  ions in the second step.



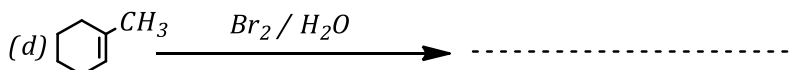
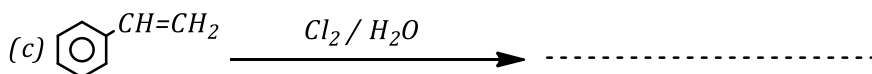
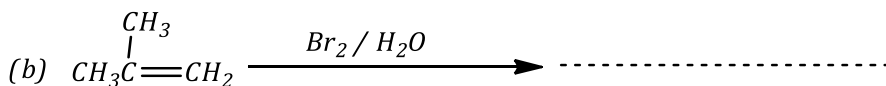
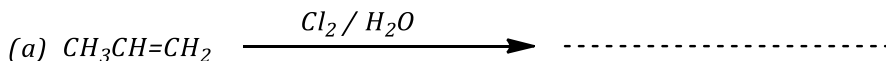
**NOTE:** The reaction of alkenes with bromine in the presence of water (bromine water) is used to:

- identify carbon-carbon double bonds in alkenes.
- differentiate alkenes from alkanes.

Observation: reddish-brown solution turns colourless.

**Task**

1. Complete the equations below and outline a mechanism for each of the reactions.



2. Explain the following observations:

- (a) Bromine in carbon tetrachloride reacts with but-2-ene to form 2,3-dibromobutane as the major product whereas bromine in aqueous solution forms 3-bromobutan-2-ol as the major product.
- (b) Bromine water reacts with propene to form 1-bromopropan-2-ol as the major product rather than 1,2-dibromopropane.
3. 4.20 g of a hydrocarbon **Z** on combustion gave 13.20 g of carbon dioxide and 5.40 g of water.
- (a) Determine the empirical formula of **Z**.
- (b) When 14.0g of **Z** was vapourised, it was found to occupy 8.0 dm<sup>3</sup> at room temperature. If 1 mole of a gas at room temperature occupies 24dm<sup>3</sup>, calculate the;
- (i) molecular mass of **Z**
- (ii) molecular formula of **Z**. [Answer: C<sub>3</sub>H<sub>6</sub>]
- (c) Write down all the structural isomers of **Z**.
- (d) When the vapour of **Z** was passed through bromine water, the bromine water turned from brown to colourless. Identify **Z**.
- (e) Write equation for the reaction between **Z** and acidified water and outline the mechanism for the reaction.

#### 4. Oxidation of alkenes

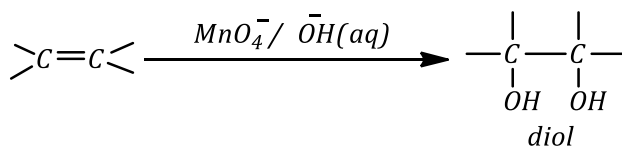
Alkenes undergo oxidation when treated with a number of oxidising agents.

The product of the reaction depends on the oxidising agent and the reaction conditions employed.

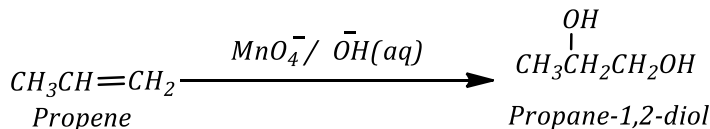
**(a) Reaction with alkaline potassium manganate(VII) solution.**

Alkenes are oxidised by cold alkaline potassium manganate(VII) solution to form diols.





Example



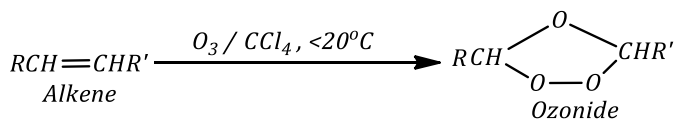
The reaction of alkenes with cold alkaline potassium manganate(VII) solution is used to:

- test for carbon-carbon double bonds in alkenes.
- differentiate alkenes from alkanes.

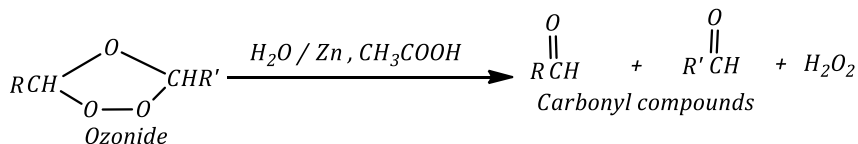
Observation: purple solution turns colourless and a brown precipitate is formed.

### (b) Addition of ozone (Ozonolysis)

When a stream of ozone is passed through an alkene in an inert solvent (e.g. carbon tetrachloride), at low temperature ( $< 20^\circ C$ ), a molecule of ozone adds up to the alkene to form an ozonide.

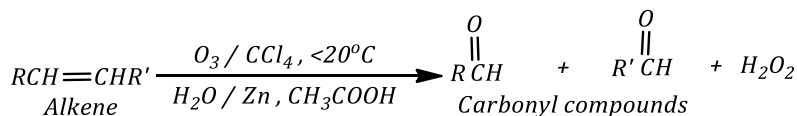


The ozonide formed is unstable, explosive compound and easily decomposes. Hydrolysis of the ozonide gives carbonyl compounds. This process is known as ozolysis.

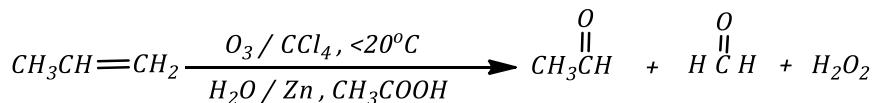
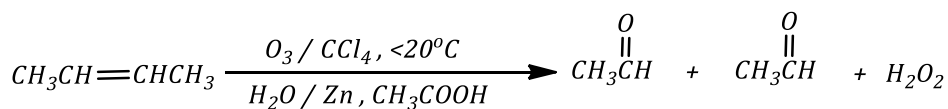


The presence of zinc dust and ethanoic acid during hydrolysis removes the hydrogen peroxide which would oxidise the carbonyl compounds formed.

The above reaction can be simply represented as follows:

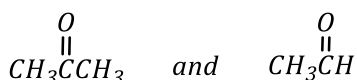


Symmetrical alkenes produce the same type of carbonyl compound while unsymmetrical alkenes give two different types of products.

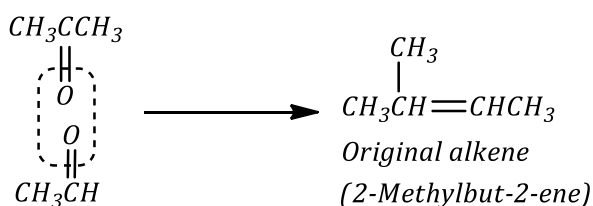


This reaction is used to determine the structure of alkenes.

For example, if the products of ozonolysis are:



Then the alkene that formed the above compounds is determined as below:



### Task

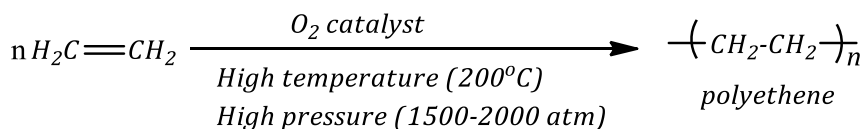
1. A hydrocarbon **Y** contains 85.7% carbon and has a density of  $2.5\text{g l}^{-1}$ .
  - (a) Determine the empirical formula of **Y**
  - (b) Determine molecular formula of **Y**.
  - (c) Write the structural formula of all the possible open chain isomers of **Y**.
  - (d) Ozonolysis of **Y** and subsequent work-up gave one type of compound. Identify **Y**.
  - (e) Write down an equation to show how **Y** can be synthesized from butan-2-ol and indicate a mechanism for the reaction.
2. The molecular formula of a hydrocarbon **X** is  $\text{C}_4\text{H}_8$ 
  - (a) Write the names and formulae of all the possible isomers of **X**.
  - (b) Ozonolysis of **X** followed by hydrolysis gave only one compound. Identify **X** and the compound formed.
  - (c) Write an equation to show how **X** can be converted to an alcohol and outline the mechanism for the reaction.

### (c) Polymerisation.

Poly- means many.

Polymerisation is a process by which small organic molecules (monomers) combine to form large complex molecules (polymers). Therefore, a polymer is a molecule with recurring units.

For example, ethene in the presence of trace/ a little oxygen as a catalyst, high pressure (1500-2000 atm) and high temperature (200°C), undergoes addition polymerisation to form polyethene.



#### Properties of polyethene

- Rigid/ tough
- Insoluble in all solvents at room temperature
- Does not rot
- Does not corrode/ react with common chemical reagents.

#### Uses of polyethene

Polyethene has a number of uses which include:

Making;

- |                    |                        |
|--------------------|------------------------|
| • Bags             | • electrical insulator |
| • plastic bottles  | • tubing               |
| • plastic toys     | • packaging film       |
| • bottles for milk |                        |

Other examples are shown in the table below.

Monomer	Polymer	Properties	Uses
Propene $CH_3CH=CH_2$	$\left( \begin{array}{c} CH-CH_2 \\   \\ CH_3 \end{array} \right)_n$ Poly(propene)	<ul style="list-style-type: none"> <li>tough</li> <li>resistant to boiling water, atmospheric conditions.</li> </ul>	<ul style="list-style-type: none"> <li>ropes</li> <li>packaging materials.</li> </ul>
Tetrafluoroethene $nCF_2=CF_2$	$\left( CF_2-CF_2 \right)_n$ Teflon (polytetrafluoroethene)	<ul style="list-style-type: none"> <li>tough/ very strong</li> <li>resistant to chemicals</li> <li>low coefficient of friction</li> <li>anti-stick properties</li> <li>high softening point of <math>327^\circ C</math></li> </ul>	<ul style="list-style-type: none"> <li>non-stick cooking utensils</li> <li>insulators</li> <li>low-friction bearings</li> </ul>
Chloroethene or vinyl chloride $\begin{array}{c} Cl \\   \\ HC=CH_2 \end{array}$	$\left( \begin{array}{c} Cl \\   \\ CHCH_2 \end{array} \right)_n$ Polychloroethene/polyvinyl chloride (PVC)	<ul style="list-style-type: none"> <li>rigid</li> <li>flexible/ easy to mould</li> </ul>	<ul style="list-style-type: none"> <li>insulators</li> <li>water pipes</li> <li>rain coats</li> <li>hand bags</li> <li>floor tile, hoses etc.</li> </ul>
Phenylethene or styrene $\begin{array}{c} CH=CH_2 \\   \\ \text{C}_6\text{H}_5 \end{array}$	$\left( \begin{array}{c} CHCH_2 \\   \\ \text{C}_6\text{H}_5 \end{array} \right)_n$ Polystyrene (polyphenylethene)	<ul style="list-style-type: none"> <li>brittle</li> <li>flammable</li> <li>hard transparent plastic</li> <li>does not corrode/ rot and resistant to chemicals.</li> <li>melts at <math>230^\circ C</math></li> </ul>	<ul style="list-style-type: none"> <li>electrical insulator</li> <li>plastic toys</li> <li>decorative purposes.</li> </ul>

Methyl 2-methylpropenoate $\begin{array}{c} H_2C=CCH_3 \\   \\ COOCH_3 \end{array}$	$\left[ CH_2-\overset{\overset{CH_3}{ }}{\underset{\underset{COOCH_3}{ }}{C}} \right]_n$ Perspex	<ul style="list-style-type: none"> <li>transparent</li> <li>strong/ hard</li> </ul>	<ul style="list-style-type: none"> <li>substitute for glass in aircrafts, helicopters and buildings.</li> <li>lenses</li> <li>plastic jewellery etc.</li> </ul>
2-methylbuta-1,3-diene $\begin{array}{c} CH_3 \\   \\ H_2C=CCH=CH_2 \end{array}$	$\left( CH_2\overset{\overset{CH_3}{ }}{C}=CHCH_2 \right)_n$ Natural rubber	When vulcanised, it has several purposes such as: <ul style="list-style-type: none"> <li>harder</li> <li>tougher</li> <li>durable</li> <li>less temperature sensitive</li> <li>resistant to chemicals</li> </ul>	<ul style="list-style-type: none"> <li>condoms</li> <li>gloves</li> <li>car tyres</li> <li>shoe soles.</li> </ul>
2-chlorobuta-1,3-diene $\begin{array}{c} Cl \\   \\ H_2C=CCH=CH_2 \end{array}$	Neoprene rubber $\left( CH_2\overset{\overset{Cl}{ }}{C}=CHCH_2 \right)_n$	<ul style="list-style-type: none"> <li>Expensive to produce</li> <li>High resistance to chemicals and autoxidation</li> </ul>	<ul style="list-style-type: none"> <li>manufacture of synthetic rubber</li> </ul>

## Uses of alkenes

- Making plastics like polyethene for buckets, bowls, bags etc.
- Manufacture of polystyrene used in making car battery cases and parts of the refrigerator.
- Making ethane-1,2-diol used as anti-freezing for motor car radiators.
- Manufacture of ethanol.

## Summary of the reactions of alkenes

