



Content

Alkenes (exemplified by ethene)

- (i) electrophilic addition, including Markovnikov's rule
- (ii) reduction and oxidation reactions

Learning Outcomes

Candidates should be able to:

- (a) explain the general reactivity of alkenes towards electrophilic reagents / electrophiles
- (b) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:
 - (i) electrophilic addition of water/steam, hydrogen halides and halogens
 - (ii) reduction via catalytic hydrogenation (catalytic addition of hydrogen)
 - (iii) oxidation by cold, alkaline solution of manganate(VII) ions to form the diol
 - (iv) oxidation by hot, acidified solution of manganate(VII) ions leading to the rupture of the carbon-to-carbon double bond in order to determine the position of alkene linkages in larger molecules
- (c) describe the mechanism of electrophilic addition in alkenes, using bromine with ethene as an example
- (d) apply Markovnikov's rule to the addition of hydrogen halides to unsymmetrical alkenes, and explain the composition of products in terms of the stability of carbocation intermediates

Lecture outline

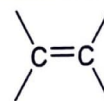
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References

- 1 Chemistry in Context
by G C Hill & J S Holman
- 2 'A' Level Chemistry
by E N Ramsden
- 3 Principles of Organic Chemistry
by Peter R.S. Murray
- 4 Cambridge International AS and A Level
Chemistry Coursebook
by Lawrie Ryan and Roger Norris
- 5 <http://www.chemguide.co.uk>

1.1 Alkenes

Alkenes are hydrocarbons that contain one or more **carbon-carbon double (C=C) bond**. The functional group of an alkene is the C=C bond.

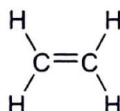


- Non-cyclic alkenes that contain one C=C bond per molecule form a homologous series of unsaturated aliphatic hydrocarbons with the general formula C_nH_{2n} , where n is an integer greater than or equal to 2.

Name	Molecular formula C_nH_{2n}	Structural formula	Skeletal formula
ethene	C_2H_4	$CH_2=CH_2$	
propene	C_3H_6	$CH_3CH=CH_2$	
but-1-ene	C_4H_8	$CH_3CH_2CH=CH_2$	
pent-1-ene	C_5H_{10}	$CH_3CH_2CH_2CH=CH_2$	
hex-1-ene	C_6H_{12}	$CH_3CH_2CH_2CH_2CH=CH_2$	

- A **terminal alkene** contains the **=CH₂ structural unit** (i.e. the C=C bond is located at one end of the carbon chain). The alkenes in the table above are all terminal alkenes.
- A **cycloalkene** contains one or more C=C bond in a **ring structure**.
- Alkenes occur abundantly in nature. Some examples are given below.

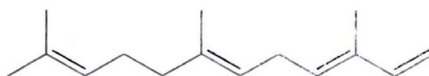
ethene is a plant hormone that induces ripening in fruits



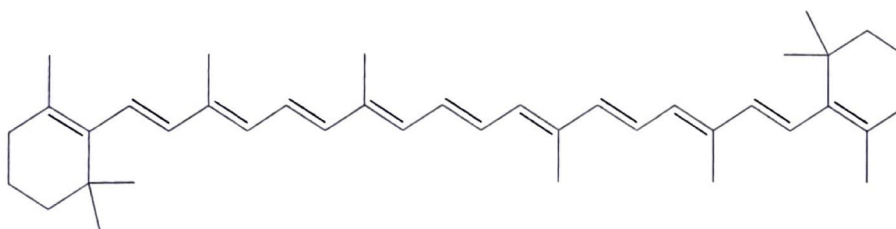
limonene is found in lemon and orange oils



α -farnesene is found in the waxy coating on apple skin



β -carotene is an orange pigment responsible for the orange colour of carrots



1.2 Nomenclature of alkenes

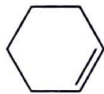
- The IUPAC name of an organic compound generally has the following three parts.

prefix	+	parent name	+	suffix
What and where are the substituents?		What is the longest carbon chain?		What is the functional group?

- In the IUPAC system, an alkene is identified by the suffix **-ene**. The nomenclature rules for alkenes are similar to those used to name alkanes, but with the suffix **-ene** instead of **-ane**.

- Steps to take note:

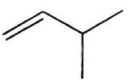
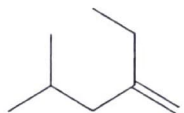
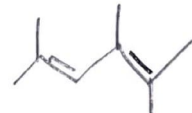
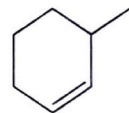
- Identify the longest carbon chain that contains the C=C bond. Note that C=C bonds take precedence over alkyl groups and halogens in determining the main carbon chain and the direction in which it is numbered.
- Number the carbon atoms in the chain in the direction that gives the doubly bonded carbon atoms the lowest possible numbers.
- Specify the numerical position of the C=C bond (if necessary) by placing the appropriate number before the -ene suffix. This number corresponds to the numerical position of the lowest numbered carbon in the C=C bond.

Structural formula	IUPAC name
$\text{CH}_2=\text{CH}_2$	ethene
$\text{CH}_3\text{CH}=\text{CH}_2$	propene
$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	but-1-ene
$\text{CH}_3\text{CH}=\text{CHCH}_3$	but-2-ene (not but-3-ene)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	pent-1-ene
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$	pent-2-ene (not pent-3-ene)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	hex-1-ene
	cyclohexene

- Alkenes with two C=C bonds are named as **dienes**. Alkenes with three C=C bonds are named as **trienes**, and so forth. The numbers in the IUPAC names indicate the position of each C=C bond.

$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	buta-1,3-diene
$\text{CH}_2=\text{CHCH}_2-\text{CH}=\text{CHCH}=\text{CH}_2$	hepta-1,3,6-triene

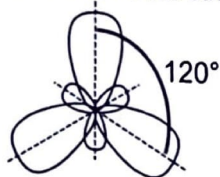
- Examples

(a)  3-methylbut-1-ene	(b)  2-ethyl-4-methylpenta-1-ene	(c)  2,3,5-trimethylhexa-2,4-diene	(d)  3-methylcyclohexene
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1.3 Structure and bonding

(a) Structure of the ethene molecule

- The two carbon atoms in the ethene molecule are sp^2 hybridised.



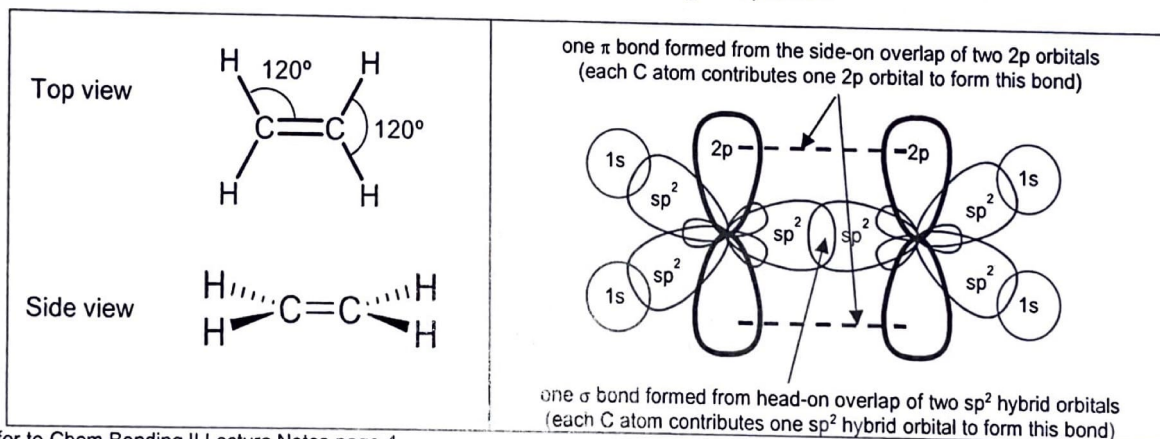
top view of three sp^2 hybrid orbitals

Three sp^2 hybrid orbitals (around a carbon atom) lie in a trigonal plane.

- For each carbon atom,

(a) two sp^2 hybrid orbitals overlap with the 1s orbitals of two hydrogen atoms to form two carbon-hydrogen σ bonds	
(b) one remaining sp^2 hybrid orbital overlaps head-on with the sp^2 hybrid orbital of the neighbouring carbon atom to form one carbon-carbon σ bond	
(c) the unhybridised 2p orbital overlaps side-on with the unhybridised 2p orbital of the neighbouring carbon atom to form one π bond	

- The shape about each C atom in ethene is trigonal planar and ethene is a planar molecule. The π -electron cloud lies above and below the plane formed from the two trigonal planes.



Refer to Chem Bonding II Lecture Notes page 4.

(b) Strength of the carbon-carbon π bond

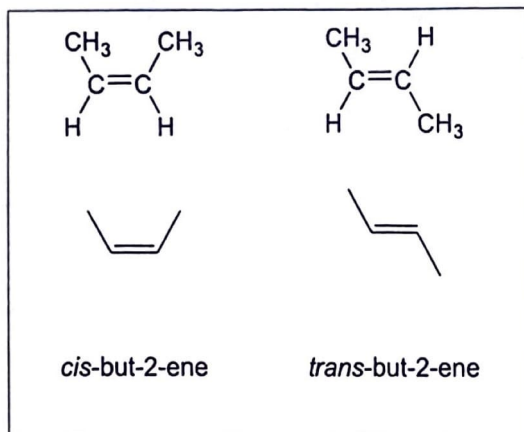
Type of bond	C=C (ethene)	C-C (ethane)
Bond energy / kJ mol^{-1}	610	346
Bond length / nm	0.134	0.154

- Bond energy of the C=C bond > Bond energy than the C-C bond
 $\Rightarrow$ the C=C bond is stronger than the C-C bond
- Bond energy of the C=C bond < 2 x Bond energy of the C-C bond
 $\Rightarrow$ the π bond is weaker than the σ bond

Reason: side-on overlap of the p orbitals is less effective than the head-on overlap of orbitals

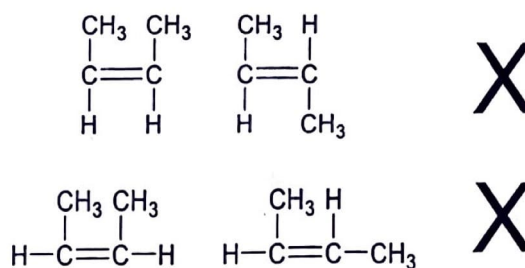
1.4 *Cis-trans* isomerism in alkenes

- Rotation about the C=C bond requires breaking of the π bond. Hence, there is restricted rotation about any C=C bond.
- This restricted rotation of the C=C bond can give rise to *cis-trans* isomerism when each doubly bonded carbon atom is joined to two different atoms or groups.
- **Example 1:** But-2-ene displays *cis-trans* isomerism.

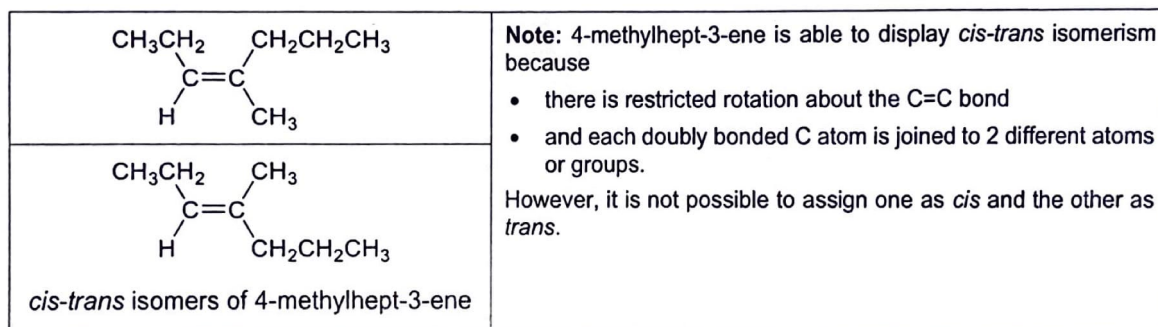


Note:

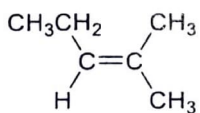
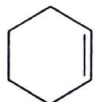
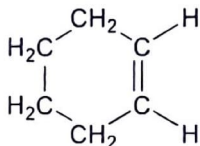
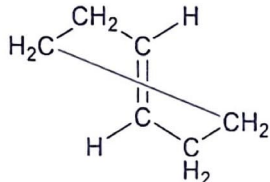
When asked to draw the structures of *cis-trans* isomers, the diagrams shown below are not acceptable. The **trigonal planar** shape about each carbon atom is an examination requirement.



- **Example 2:** 4-methylhept-3-ene displays *cis-trans* isomerism.

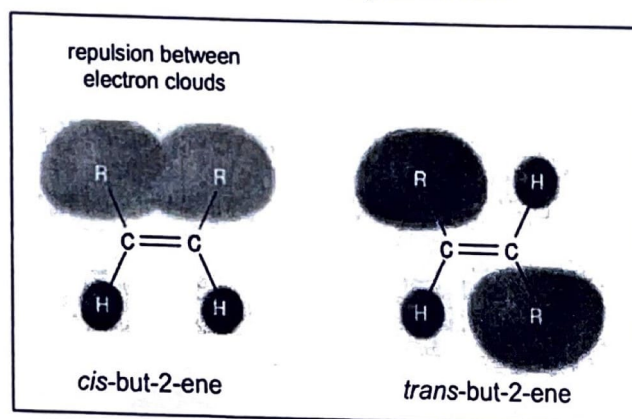


- Examples of alkenes which do **not** display *cis-trans* isomerism.

Alkene	Remark
	• 2-methylpent-2-ene does not display <i>cis-trans</i> isomerism because one of the doubly bonded carbon atoms is joined to two identical groups ($-\text{CH}_3$).
 cyclohexene or 	• Cyclohexene does not display <i>cis-trans</i> isomerism because "<i>trans</i>-cyclohexene" is too unstable to exist at room temperature due to its highly strained structure. 

1.5 Relative stabilities of *cis-trans* isomers

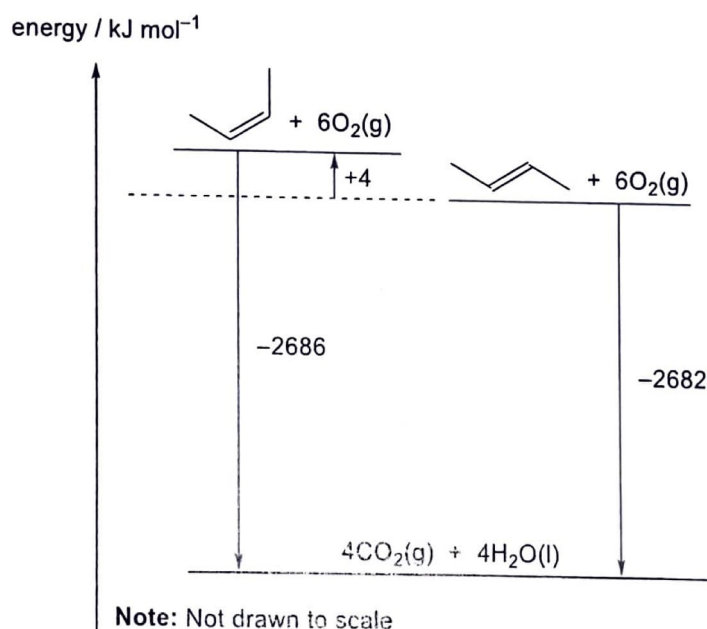
- In general, a *cis* alkene is less stable than its stereoisomeric *trans* alkene.
- This is because of steric strain (due to repulsion between electron clouds) arising from crowding between two alkyl groups in the *cis* isomer as shown in the diagrams below.



- The difference in stability between *cis*-but-2-ene and *trans*-but-2-ene can be quantified by comparing their standard enthalpy change of combustion data.

Alkene	standard enthalpy change of combustion / kJ mol^{-1}
<i>cis</i> -but-2-ene	-2686
<i>trans</i> -but-2-ene	-2682

- The data indicates that *trans*-but-2-ene is more stable than *cis*-but-2-ene by 4 kJ mol^{-1} . This greater stability of *trans*-but-2-ene can be seen more clearly from the energy level diagram below.

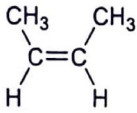
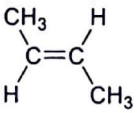


2.1 Some physical properties of alkenes

- The alkenes possess physical properties that are essentially the same as those of the alkanes.
 - They are insoluble in water, but quite soluble in non-polar solvents (e.g. CCl_4).
 - They are less dense than water.
 - The boiling point increases with increasing number of carbon atoms.

Name	Structural formula	melting point/ $^{\circ}\text{C}$	boiling point/ $^{\circ}\text{C}$	state at 25 $^{\circ}\text{C}$
ethene	$\text{CH}_2=\text{CH}_2$	-169	-102	gas
propene	$\text{CH}_3\text{CH}=\text{CH}_2$	-185	-48	gas
but-1-ene	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	-185	-6.5	gas
pent-1-ene	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	-165	30	liquid
hex-1-ene	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	-138	63.5	liquid
hept-1-ene	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	-119	93	liquid
oct-1-ene	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	-104	122.5	liquid

2.2 Physical properties of *cis-trans* isomers

	 <i>cis</i> -but-2-ene	 <i>trans</i> -but-2-ene
Net dipole moment	non-zero (small)	zero
Boiling point / $^{\circ}\text{C}$	4	1
Melting point / $^{\circ}\text{C}$	-139	-106

- The boiling point of *cis*-but-2-ene is **higher** than that of *trans*-but-2-ene.

Cis-but-2-ene is slightly polar. There exists both instantaneous dipole-induced dipole and permanent dipole-permanent dipole attractive forces between the *cis*-but-2-ene molecules.

Trans-but-2-ene is non-polar. Only instantaneous dipole-induced dipole forces exist between the *trans*-but-2-ene molecules.

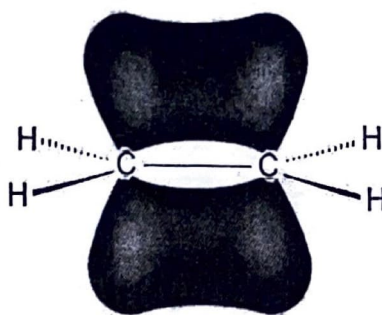
Since more energy is needed to overcome the stronger intermolecular forces present in *cis*-but-2-ene than in *trans*-but-2-ene, *cis*-but-2-ene has a higher boiling point than *trans*-but-2-ene.

- The melting point of *cis*-but-2-ene is **lower** than that of *trans*-but-2-ene.

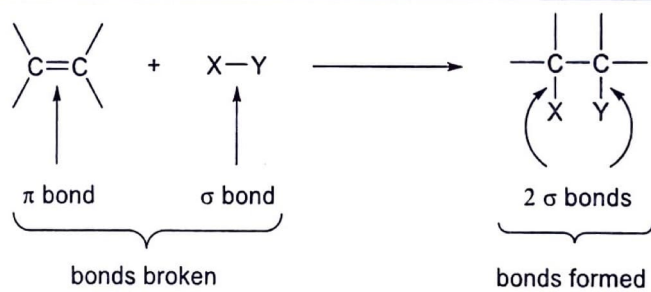
The molecules of *cis*-but-2-ene pack poorly in the solid lattice because the two bulky methyl groups are located on the same side in the molecule. The poor packing results in larger distances between molecules, which lead to weaker intermolecular forces and hence a lower melting point for *cis*-but-2-ene.

3.1 Chemical reactivity of alkenes

- Alkenes are highly reactive compounds in comparison with alkanes.
- The high reactivity of alkenes is attributed to the presence of the **electron-rich C=C bond**. The π electrons in the C=C bond act as a source of electrons during many reactions and they attract reagents known as **electrophiles**.

 π electron cloud - is a source of electrons - is nucleophilic - attracts electrophiles	What is an electrophile? - An electrophile is an electron-pair acceptor which is attracted to an electron-rich site. - An electrophile is electron-deficient. It can be a species with - a positive charge (e.g. CH_3CH_2^+) or - a partial positive charge (e.g. $^{\delta+}\text{H}-\text{Br}^{\delta-}$) or - an incomplete octet (e.g. BH_3). Note: - Alkenes are nucleophiles and they react with electrophiles. - A nucleophile is a species that is able to donate an electron pair to an electron-deficient atom to form a covalent bond.
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- Because the π bond is much weaker than the σ bond in a C=C bond, it is much more easily broken. As a result, alkenes undergo **addition** reactions in which the π bond is broken and two new σ bonds are formed.

Addition reaction - only occurs when there is unsaturation in the reactant molecules 2 species react to give a single product - a π bond is broken to form two new σ bonds (decrease in unsaturation) - the σ bond of the unsaturated bond remains unbroken	
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- Since alkenes **attract electrophiles** and undergo **addition reactions**, the characteristic reactions of alkenes are termed **electrophilic addition reactions**. (refer to sections 4 to 7)

3.2 Reactions of alkenes

- Common reactions of alkenes

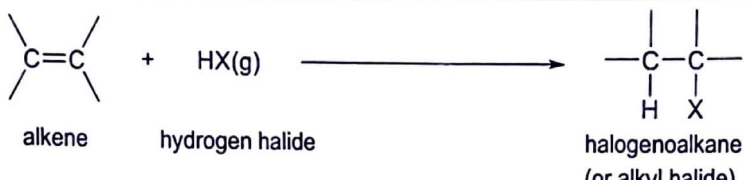
Electrophilic addition	Addition of hydrogen halides (HX)	$\text{C}=\text{C} + \text{HX} \xrightarrow{\text{dry HX(g)}} \begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \text{X} \end{array}$
	Addition of water (laboratory method)	$\text{C}=\text{C} + \text{H}_2\text{O} \xrightarrow[2. \text{H}_2\text{O, heat}]{1. \text{cold conc H}_2\text{SO}_4} \begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \text{OH} \end{array}$
	Addition of steam (industrial method)	$\text{C}=\text{C} + \text{H}_2\text{O(g)} \xrightarrow[\text{high pressure, high temperature}]{\text{H}_3\text{PO}_4 \text{ on silica}} \begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \text{OH} \end{array}$
	Addition of halogens (X ₂) in CCl ₄	$\text{C}=\text{C} + \text{X}_2 \xrightarrow[\text{in CCl}_4]{\text{X}_2} \begin{array}{c} \quad \\ \text{---C---C---} \\ \text{X} \quad \text{X} \end{array}$
	Addition of halogens (X ₂) in H ₂ O	$\text{C}=\text{C} + \text{X}_2 + \text{H}_2\text{O} \xrightarrow[\text{in H}_2\text{O}]{\text{X}_2} \begin{array}{c} \quad \\ \text{---C---C---} \\ \text{X} \quad \text{OH} \end{array} + \text{HX}$
Oxidation	Mild oxidation in cold, alkaline medium	$\text{C}=\text{C} + \text{H}_2\text{O} + [\text{O}] \xrightarrow[\text{cold}]{\text{KMnO}_4(\text{aq}), \text{NaOH}(\text{aq})} \begin{array}{c} \quad \\ \text{---C---C---} \\ \text{OH} \quad \text{OH} \end{array}$
	Strong oxidation in hot, acidic medium	$\text{C}=\text{C} \xrightarrow[\text{heat}]{\text{KMnO}_4(\text{aq}), \text{H}_2\text{SO}_4(\text{aq})} \begin{array}{l} \bullet \text{ carboxylic acids} \\ \bullet \text{ ketones} \\ \bullet \text{ CO}_2 \text{ and H}_2\text{O} \end{array}$ (depending on structure of alkene)
Reduction	Addition of H ₂ using Ni catalyst	$\text{C}=\text{C} + \text{H}_2 \xrightarrow[\text{Ni, heat}]{\text{H}_2} \begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \end{array}$
	Addition of H ₂ using Pt or Pd catalyst	$\text{C}=\text{C} + \text{H}_2 \xrightarrow[\text{Pt or Pd}]{\text{H}_2} \begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \end{array}$
Combustion		$\text{C}_n\text{H}_{2n} + \frac{3n}{2}\text{O}_2(\text{g}) \longrightarrow n\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\text{l})$

- Note:**

$\text{C}=\text{C}$	$\xrightarrow[\text{heat}]{\text{K}_2\text{Cr}_2\text{O}_7(\text{aq}), \text{H}_2\text{SO}_4(\text{aq})}$	oxidation of alkenes does not occur	Alkenes do not undergo oxidation with hot, acidified K ₂ Cr ₂ O ₇ (aq).
$\text{C}=\text{C}$	$\xrightarrow{\text{LiAlH}_4 \text{ in dry ether}}$	reduction of alkenes does not occur	Alkenes do not react with reducing agents such as LiAlH ₄ and NaBH ₄ . Note: Refer to lecture notes on Carbonyl Compounds.
$\text{C}=\text{C}$	$\xrightarrow{\text{NaBH}_4 \text{ in methanol}}$	reduction of alkenes does not occur	

4.1 Reaction with hydrogen halides

- The hydrogen halides (e.g. HCl, HBr and HI) are polar reagents which react with alkenes to give halogenoalkanes at room temperature.

Electrophilic Addition (hydrohalogenation reaction)	 alkene hydrogen halide halogenoalkane (or alkyl halide)
Reagent	HX(g) where X = Cl, Br or I
Conditions	dry HX(g), room temperature
Mechanism	Electrophilic addition

- The reaction essentially involves the addition of H and X atoms across the C=C bond of the alkene.
- Dry** gaseous hydrogen halides must be used. Aqueous solutions of hydrogen halides such as hydrochloric acid cannot be used for this reaction because it will result in the formation of alcohols (refer to section 7).
- Example 1:** Ethene reacts with hydrogen chloride to produce chloroethane.



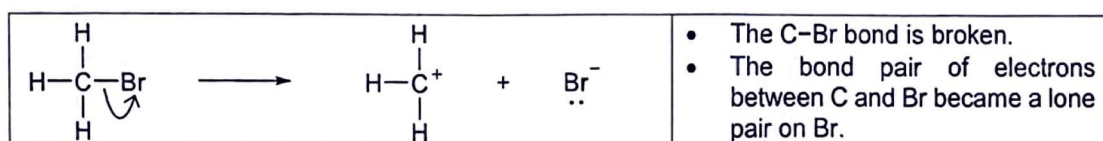
- Example 2:** Cyclohexene reacts with hydrogen bromide to produce bromocyclohexane.



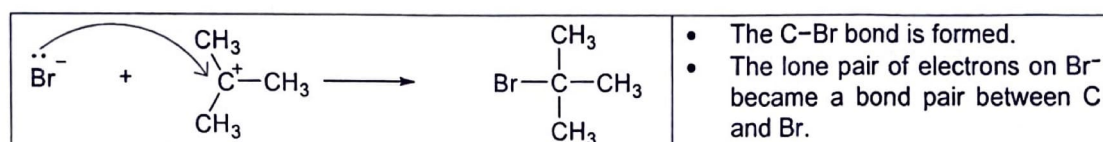
4.2 Use of curly arrows in mechanism

- Curly arrows are used in organic chemistry to illustrate the **forming/breaking of bonds** via the movement of electron(s).
- Full arrow () is used when it involves the movement of two electrons, whereas half arrow () is used when it involves the movement of one electron (refer to Alkanes lecture notes).
- A curly arrow always starts from electrons such as bond pair or a lone pair.
- Some examples of using full arrow to illustrate the process of bond breaking and/or bond forming are given below:

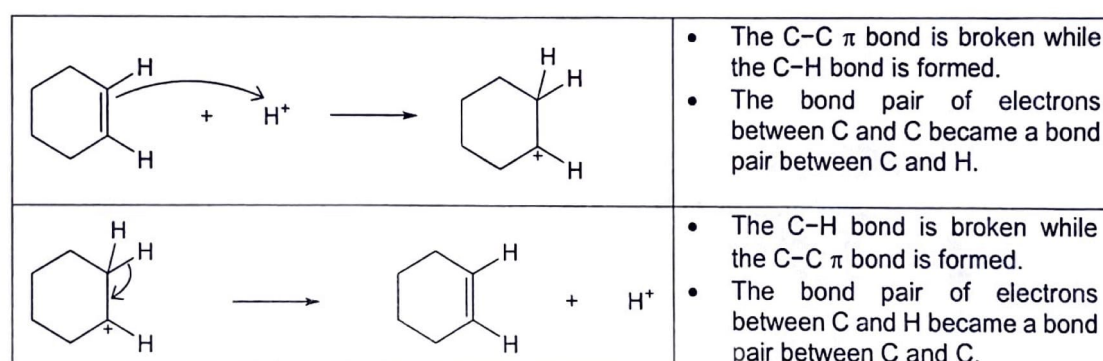
1. Bond breaking



2. Bond forming



3. Bond breaking and bond forming



Example 1:

Draw the curly arrows for the following reaction. Show all relevant lone pairs.

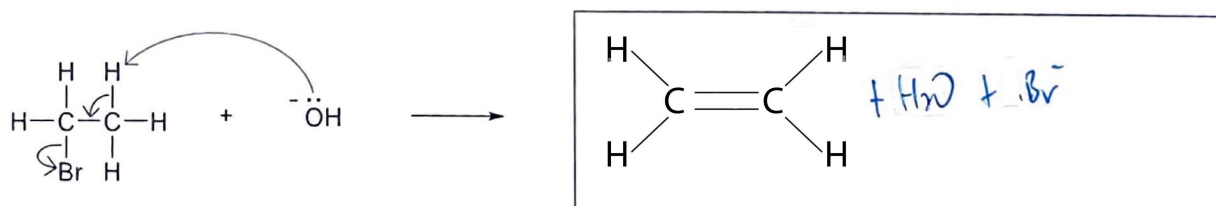


Strategy:

- Identify bonds that are being broken.
- Identify new bonds that are being formed.

Example 2:

Draw the product(s) of the following reaction by considering the curly arrows drawn.

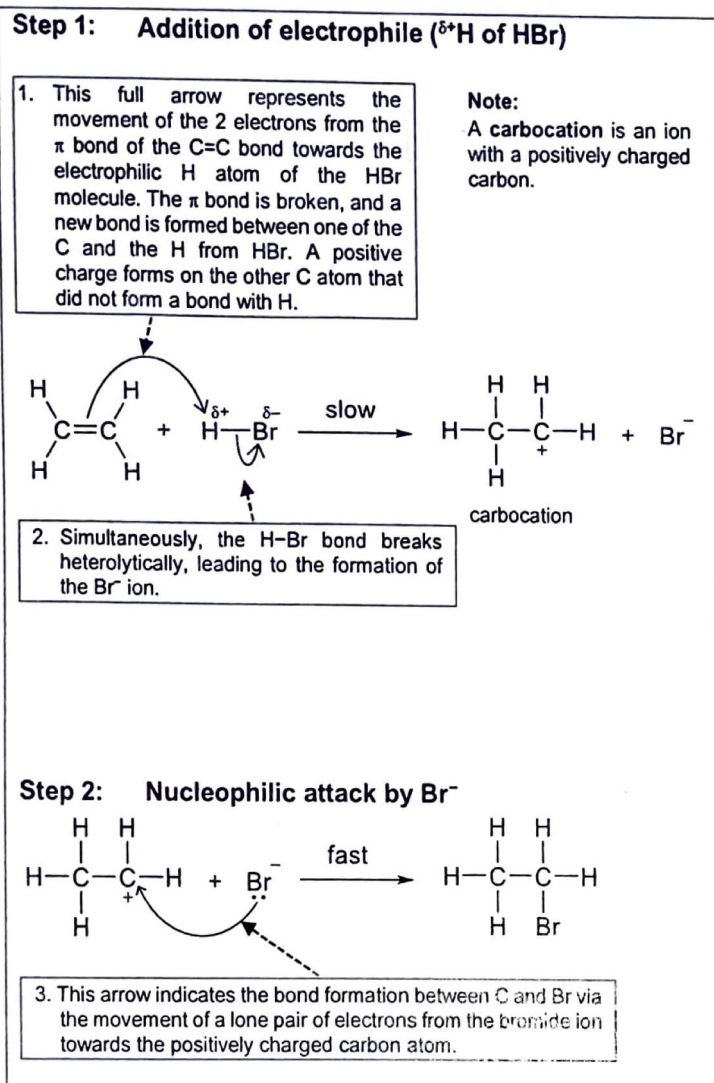


4.3 Electrophilic addition mechanism

- Consider the reaction between ethene and gaseous hydrogen bromide to give bromoethane. The reaction essentially involves the addition of H and Br atoms across the C=C bond.

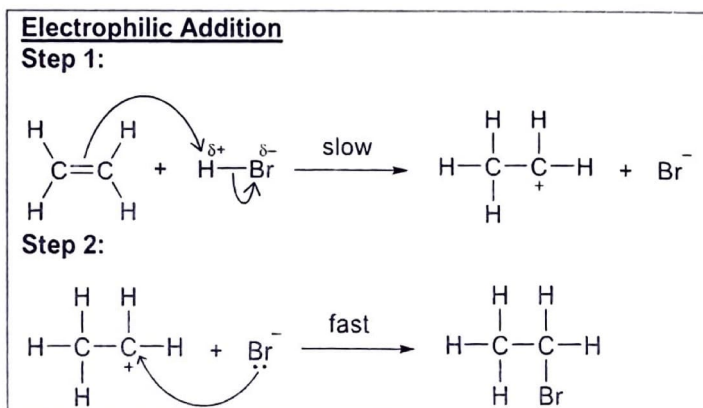
Equation	$\text{CH}_2=\text{CH}_2 + \text{HBr} \longrightarrow \text{CH}_3\text{CH}_2\text{Br}$
Mechanism	Electrophilic addition

- The mechanism involved is **electrophilic addition** which consists of the following two steps:



- The C=C bond of ethene is electron-rich.
- The HBr molecule is polar with the H atom having a partial positive charge (δ^+) and the Br atom having a partial negative charge (δ^-) since the Br atom is more electronegative than the H atom.
- How does the reaction start?** The $\delta^+\text{H}$ atom in the HBr molecule is an electrophile and is strongly attracted to the π electron cloud of the electron-rich C=C bond in the ethene molecule.
- This first step is the slow step because it involves the cleavage of the π bond in the C=C bond and also the heterolytic fission of the H-Br bond, and hence it has a higher activation energy than the second step.
- This first step results in the formation of a carbocation, $\text{CH}_3\text{-CH}_2^+$ (a reactive intermediate), and a Br^- ion.
- In the second step, the negatively charged bromide ion is attracted to the positively charged carbon atom of the carbocation.
- In this fast step, the bromide ion acts as a nucleophile and forms a bond with the carbocation to yield the bromoethane molecule as the product.

- Summary: The reaction mechanism involved is **electrophilic addition**.



Note:

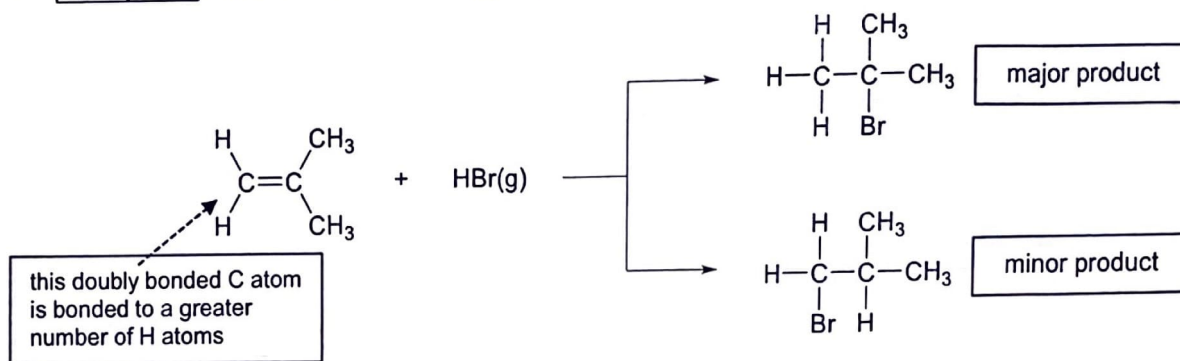
- Name the mechanism
- Indicate partial charges, δ^+ and δ^- (if any).
- Use full arrows to show bond breaking/forming via the movement of electrons.
- Show lone pair of electrons on nucleophile.
- Indicate slow and fast step for each elementary step.
- Draw the formula of any intermediate.
- Draw the formula of product, identifying major and minor products (if applicable).

4.4 Markovnikov's rule

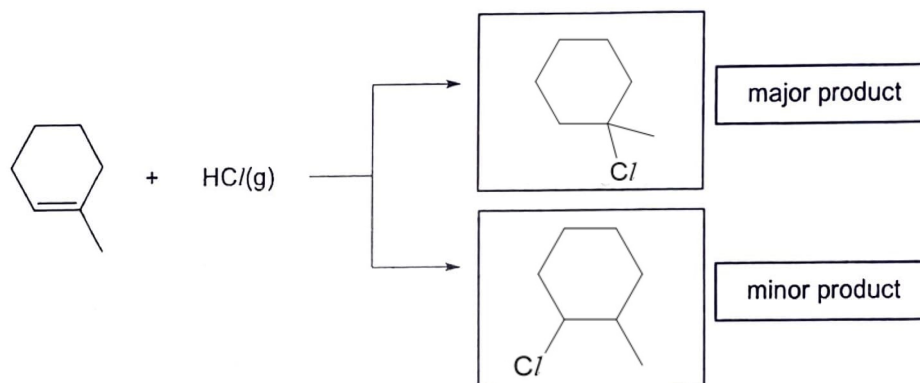
- When an **unsymmetrical alkene** reacts with a hydrogen halide, two isomeric products are formed. However, they are not formed in equal amounts. The product formed in
 - greater amount is termed the 'major product'.
 - smaller amount is termed the 'minor product'.
- In 1869, the Russian chemist, Vladimir Markovnikov, formulated a rule to predict the orientation of the addition of a hydrogen halide to an **unsymmetrical alkene** after studying many addition reactions of alkenes with hydrogen halides.

Markovnikov's rule	In the addition of a hydrogen halide (HX) to the C=C bond of an unsymmetrical alkene, the major product is the one in which the hydrogen (H) atom of HX attaches itself to the doubly bonded carbon atom already bonded with the greater number of hydrogen atoms.
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- Example 1:** Reaction between methylpropene and hydrogen bromide



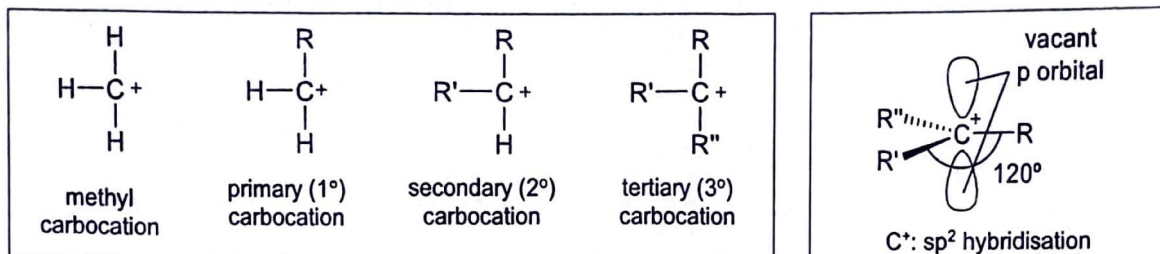
- Example 2:** Reaction between 1-methylcyclohexene and hydrogen chloride



- Note that Markovnikov's rule stated above is only predictive – indicating which product is formed predominantly but **not** explaining why it is formed.
- To understand why Markovnikov's rule works, there is a need to take a closer look at the mechanism for the reaction between an unsymmetrical alkene and a hydrogen halide. The mechanistic explanation of why one product predominates over the other possible product lies in the **relative energetic stabilities of the carbocation intermediates** formed during the reaction.

4.5 Stability of carbocations

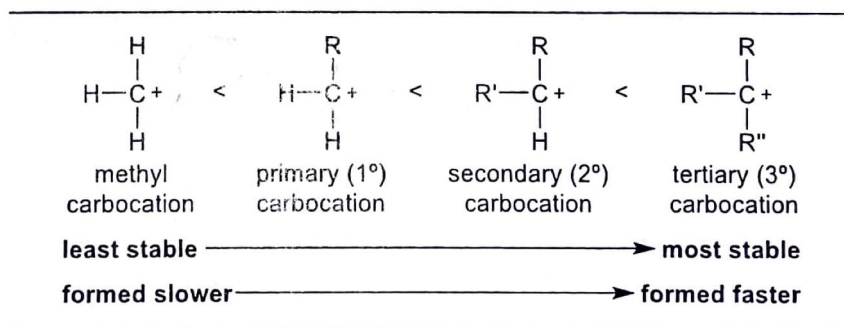
- A **carbocation** is an ion with a positively charged carbon. It is extremely reactive and has a strong tendency to accept a pair of electrons.
- A carbocation can be classified as **primary** (1°), **secondary** (2°) or **tertiary** (3°) based on the number of alkyl groups ($-R$) bonded to the carbon bearing the positive charge.



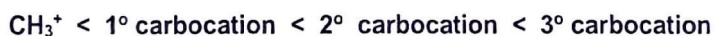
- The **stability** of a charged system is increased by **dispersal of the charge**. Therefore, any factor that tends to *spread out* the positive charge of the electron-deficient carbon and distribute it over the rest of the ion will stabilise the carbocation.
- Consider a substituent, **G**, bonded to a positively charged carbon. Compared to a hydrogen atom, **G** may either be **electron-donating** or **electron-withdrawing**.

If G is an electron-donating group ...		If G is an electron-withdrawing group ...	
$\text{G} \rightarrow \text{C}^+$	Examples: $-\text{CH}_3$ $-\text{CH}_2\text{CH}_3$	$\text{G} \leftarrow \text{C}^+$	Examples: $-\text{NO}_2$ $-\text{COOH}$
G is electron-donating. - It disperses the positive charge on the carbon - and stabilises the carbocation.		G is electron-withdrawing. - It intensifies the positive charge on the carbon - and destabilises the carbocation.	

- Note:** An alkyl group ($-R$) is **electron-donating**.
- The greater the number of electron-donating alkyl groups attached to the carbon bearing the positive charge, the greater the dispersal of the positive charge and hence the greater the stability of the carbocation.
- Consequently, the **stability of carbocations** increases in the following order:



- Note:** The **more stable** a carbocation is, the lower is the activation energy required for its formation and hence the **faster** is its **rate of formation** (see Section 4.7 for the energy profile diagram).
- Hence the **rate of formation** of carbocations **increases** in the following order:

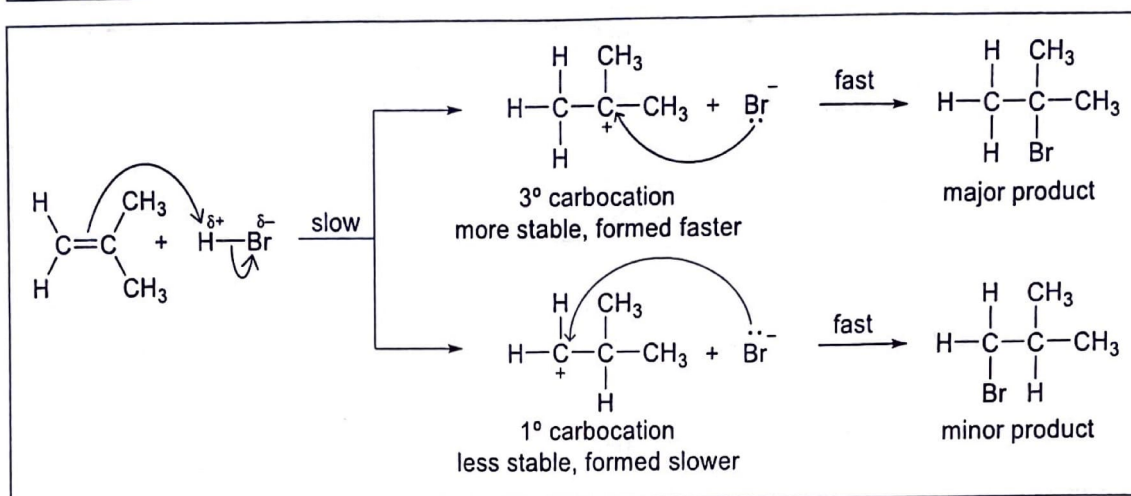


4.6 Mechanistic Explanation of Markovnikov's rule

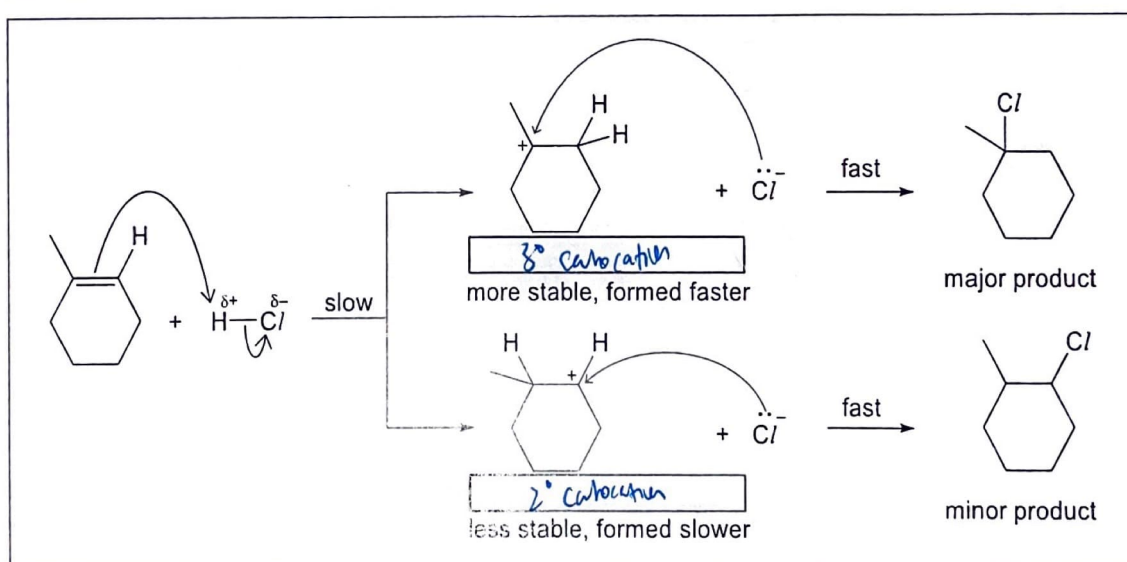
- The basis underlying Markovnikov's rule is the formation of the more stable carbocation.
- How an electrophile adds to an alkene can now be generalised by the modern version of Markovnikov's rule.

Mechanism-based Markovnikov's rule	In an electrophilic addition reaction, the electrophile adds to an unsymmetrical alkene to produce the more stable carbocation intermediate . Being formed faster in the slow step, the more stable carbocation is more available to participate in the fast step to give the major product.
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- Example 1:** Mechanism for the reaction between methylpropene and HBr

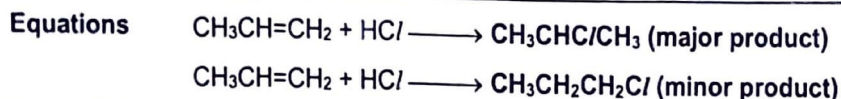


- Example 2:** Mechanism for the reaction between 1-methylcyclohexene and HCl



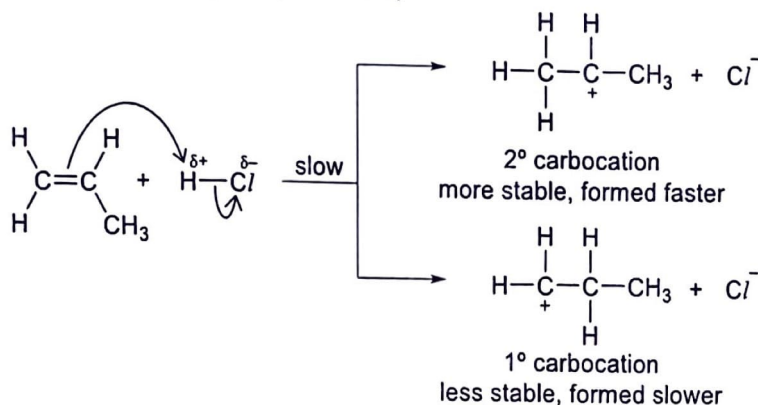
4.7 Energy profile diagram

- Consider the electrophilic addition reaction between propene and hydrogen chloride.

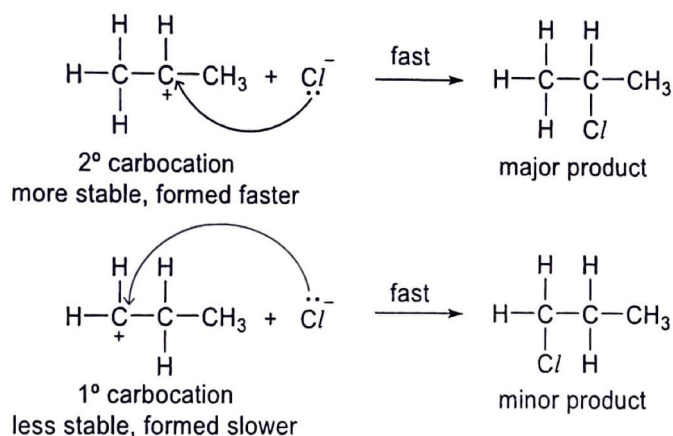


- The mechanism involved is **electrophilic addition** which consists of the following two steps:

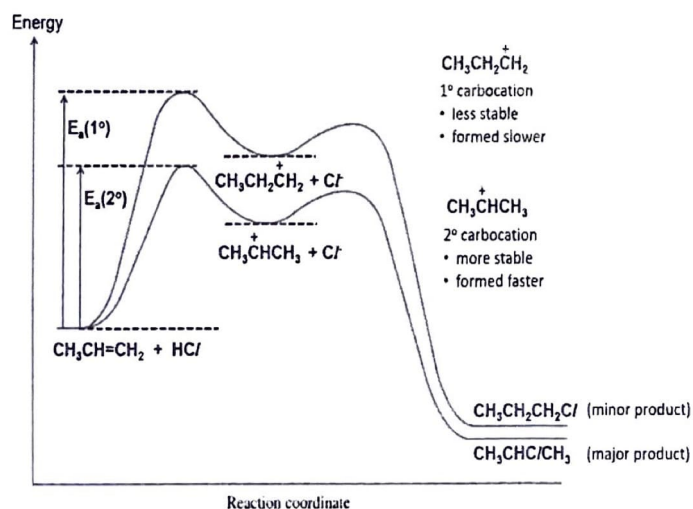
Step 1: Addition of electrophile ($\delta^+\text{H}$ of HCl)



Step 2: Nucleophilic attack by Cl^-



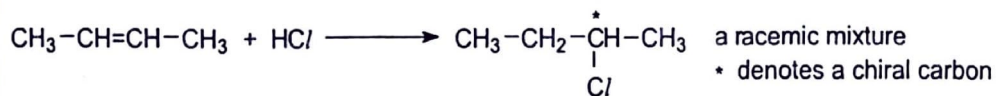
- The energy profile diagram for the above reaction is shown below.



- Between the two isomeric carbocations, the 2° carbocation is more stable (i.e. exists at a lower energy level) than the 1° carbocation.
- The reaction leading to the formation of the more stable 2° carbocation has a lower activation energy. Hence the rate of formation of the more stable 2° carbocation is faster.

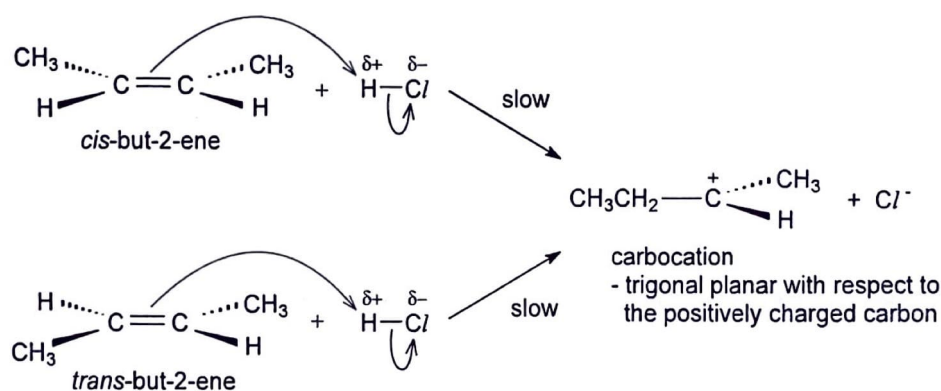
4.8 Stereochemistry of electrophilic addition of HX

- Consider the reaction between but-2-ene and HCl.



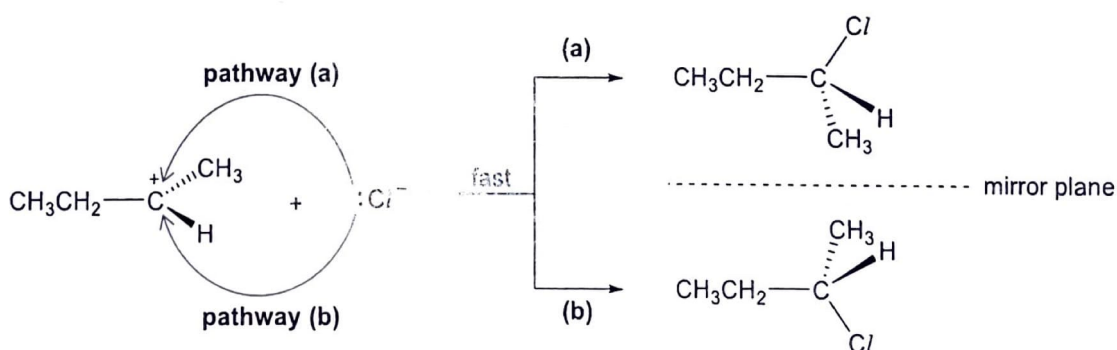
- The product obtained is a **racemic mixture** i.e. it contains equimolar mixture of the two enantiomers of 2-chlorobutane.
- Why is this so?**
- The reaction occurs via **electrophilic addition** mechanism which consists of the following steps:

Step 1: Addition of electrophile ($\delta^+\text{H}$ of HCl)



- In step 1, both *cis*-but-2-ene and *trans*-but-2-ene react with HCl to give the same carbocation. This carbocation is **trigonal planar** with respect to the positively charged carbon.

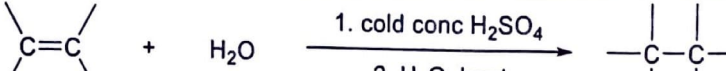
Step 2: Nucleophilic attack by Cl^-



- In step 2, the Cl^- ion can attack the positively charged carbon of the trigonal planar carbocation from **either side** of the trigonal plane with **equal likelihood**.
- Hence the product is a **racemic mixture** of the two enantiomers of 2-chlorobutane.

Recap: A racemic mixture contains equal proportion of each enantiomer, where the rotating power of one enantiomer exactly cancels that of the other. Hence, a racemic mixture does not rotate the plane of plane-polarised light and is not optically active.

- Alkenes do not react with water directly.
- In the laboratory, the addition of H_2O across the $\text{C}=\text{C}$ bond of an alkene to form an alcohol can be carried out via a two-step process as shown below.

Electrophilic Addition (hydration of alkene; laboratory method)	 alkene alcohol
Reagents and conditions	Step 1: cold conc H_2SO_4 Step 2: H_2O , heat

- Details of the two-step process are given below.

Step 1:

Electrophilic addition

$$\begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{C} \\ \diagdown \quad \diagup \end{array} + \text{H}_2\text{SO}_4 \xrightarrow{\text{cold}} \begin{array}{cc} | & | \\ -\text{C} & -\text{C}- \\ | & | \\ \text{H} & \text{OSO}_2\text{OH} \end{array}$$

alkene

an alkyl hydrogensulfate

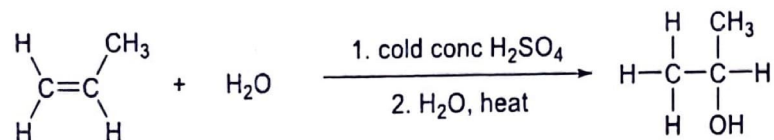
Note: For unsymmetrical alkenes, the reaction follows the mechanism-based Markovnikov's rule. During the reaction, the more stable carbocation is formed faster and hence more available to react further to give the major product.

$$\text{C}=\text{C} + \text{H}-\text{O}-\text{S}(=\text{O})_2\text{OH} \xrightarrow{\text{slow}} \text{C}-\text{C} + \text{HSO}_4^-$$
$$\begin{array}{c} | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{H}^+ \end{array} + \begin{array}{c} \text{O} \\ || \\ \text{O}^- - \text{S} - \text{OH} \\ || \\ \text{O} \end{array} \xrightarrow{\text{fast}} \begin{array}{c} | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{O} - \text{S} - \text{OH} \\ \quad \quad || \\ \quad \quad \text{O} \end{array}$$

Step 2: Hydrolysis	$\begin{array}{c} \text{---C---C---} \\ \quad \\ \text{H} \quad \text{O} \\ \qquad \parallel \\ \qquad \text{S} \\ \qquad \parallel \quad \backslash \\ \qquad \text{O} \quad \text{OH} \end{array} + \text{H}_2\text{O} \xrightarrow{\text{heat}} \begin{array}{c} \text{---C---C---} \\ \quad \\ \text{H} \quad \text{OH} \end{array} + \text{H}_2\text{SO}_4$ alkyl hydrogen sulfate alcohol
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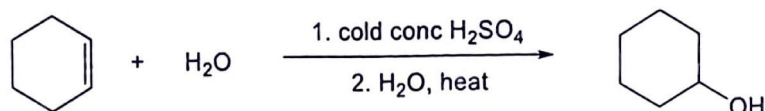
Alkyl hydrogensulfates can be converted to alcohols by heating them with water. This is called **hydrolysis** because a covalent bond is cleaved by reaction with water.

- Example 1:** Reaction of propene to form propan-2-ol



Note: Propan-2-ol is the major product formed because this reaction follows Markovnikov's rule.

- Example 2:** Reaction of cyclohexene to form cyclohexanol.

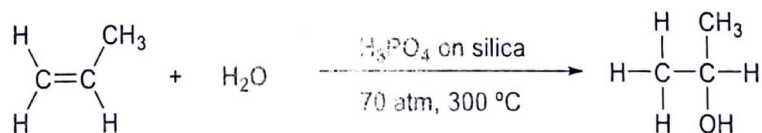


5.2 Addition of steam (Industrial method)

- The addition of steam across the C=C bond of an alkene is an industrial method to produce an alcohol.

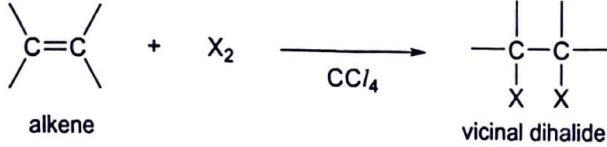
Electrophilic Addition (hydration of alkene; industrial method)	$ \begin{array}{c} \diagup & & \diagdown \\ & \text{C}=\text{C} \\ \diagdown & & \diagup \end{array} + \text{H}_2\text{O(g)} \xrightarrow[\text{high pressure, high temperature}]{\text{H}_3\text{PO}_4 \text{ on silica}} \begin{array}{c} & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{OH} \end{array} $ alkene alcohol
Reagent	H ₂ O(g)
Conditions	concentrated H ₃ PO ₄ (catalyst) on a silica support under high pressure and high temperature
Mechanism	Electrophilic addition

- In this case, the alkene and steam are passed over a phosphoric acid catalyst deposited on a silica support under high pressure and high temperature.
- Example:** Hydration of propene to form propan-2-ol



6.1 Reaction with halogens (in CCl_4)

- The addition of a halogen X_2 ($\text{X} = \text{Cl}$ or Br) to an alkene produces a vicinal dihalide (i.e. an organic molecule in which the 2 halogen atoms are on adjacent carbon atoms).

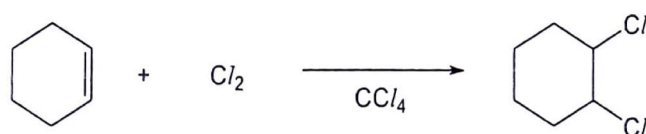
Electrophilic Addition (halogenation)	 alkene vicinal dihalide
Reagent	X_2 dissolved in an inert solvent (e.g. CCl_4 or CH_2Cl_2) where $\text{X} = \text{Cl}$ or Br
Conditions	dark (i.e. absence of ultra-violet light), room temperature
Mechanism	Electrophilic addition

- Br_2 and Cl_2 are the two halogens that are normally used in halogen addition to an alkene.
- F_2 and I_2 are seldom used for halogenation of alkenes. This is because F_2 reacts explosively with alkenes while the addition of I_2 to an alkene is a thermodynamically unfavourable reaction. The vicinal diiodides are unstable at room temperature and decompose back to the corresponding alkenes and I_2 .
- Inert solvents such as tetrachloromethane (CCl_4) or dichloromethane (CH_2Cl_2) are typically used for halogen additions because these solvents dissolve both the halogen and the alkene.
- Example 1:** Reaction between ethene and bromine (in CCl_4) to give 1,2-dibromoethane



Note:

- When ethene is bubbled into Br_2 in CCl_4 at room temperature, Br_2 is added across the $\text{C}=\text{C}$ bond to give 1,2-dibromoethane
- Observation:** (Rapid) decolourisation of orange-red Br_2 occurs.
(refer to Data Booklet Section 9(d) Colours of halogens)
- The use of Br_2 (in CCl_4) is a useful distinguishing test for alkenes (and also for phenol and phenylamine functional groups) (refer to section 11).
- The amount of Br_2 reacted per mole of alkene is a measure of the number of $\text{C}=\text{C}$ bonds present in the alkene molecule. One mole of $\text{C}=\text{C}$ reacts with one mole of Br_2 .
- Example 2:** Reaction between cyclohexene and chlorine (in CCl_4) to give 1,2-dichlorocyclohexane



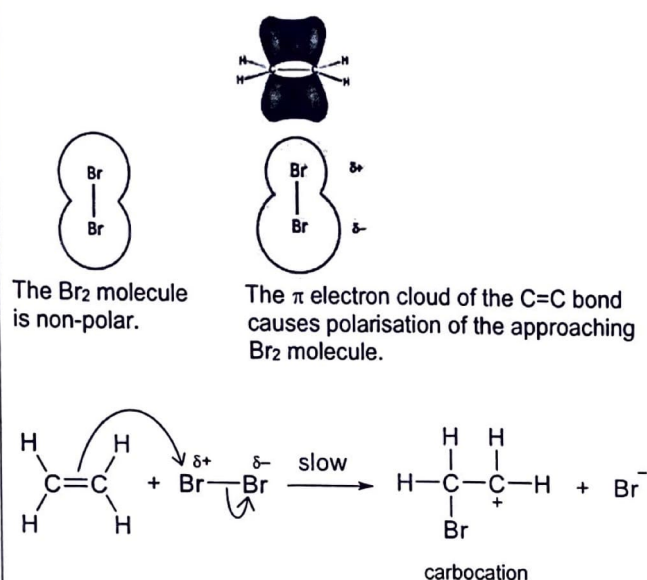
6.2 Electrophilic addition mechanism

(a) Reaction between ethene and bromine (in CCl_4) to give 1,2-dibromoethane.

Equation	$\text{CH}_2=\text{CH}_2 + \text{Br}_2 \longrightarrow \text{CH}_2\text{BrCH}_2\text{Br}$
Mechanism	Electrophilic addition

- The mechanism involved is **electrophilic addition** which consists of the following two steps:

Step 1: Addition of electrophile ($\delta^+\text{Br}$ of polarised Br_2)



- The $\text{C}=\text{C}$ bond of the ethene molecule is electron-rich.
- The Br_2 molecule is non-polar.
- How does the reaction start?** When a Br_2 molecule approaches an ethene molecule, the π electron cloud of the ethene molecule interacts with the approaching Br_2 molecule's electron cloud. Like charges repel, so the distortion of the electron cloud and hence polarisation of the $\text{Br}-\text{Br}$ bond occurs i.e. the Br_2 molecule becomes: $\delta^+\text{Br}-\text{Br}\delta^-$, with the $\delta^+\text{Br}$ closer to the $\text{C}=\text{C}$ bond and the $\delta^-\text{Br}$ further away from the $\text{C}=\text{C}$ bond.

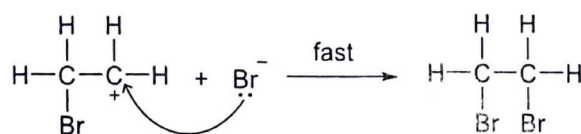
- In the first step of the mechanism, the $\delta^+\text{Br}$ of the polarised Br_2 molecule acts as an **electrophile** and is strongly attracted to the electron rich $\text{C}=\text{C}$ bond in the ethene molecule.
- This first step is the slow step because it involves the cleavage of the π bond in the $\text{C}=\text{C}$ bond and also the heterolytic fission of the $\text{Br}-\text{Br}$ bond, and hence it has a higher activation energy than the second step.

- This first step results in the formation of a carbocation, $\text{CH}_2\text{Br}-\text{CH}_2^+$, and a Br^- ion.

- In the second step, the negatively charged Br^- ion is attracted to the positively charged carbon of the carbocation.

- In this fast step, the bromide ion acts as a nucleophile and forms a bond with the carbocation to yield the 1,2-dibromoethane molecule as the product.

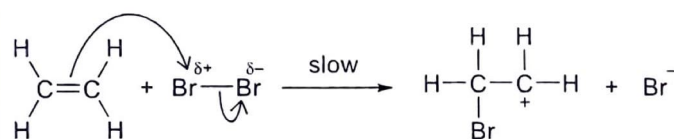
Step 2: Nucleophilic attack by Br^-



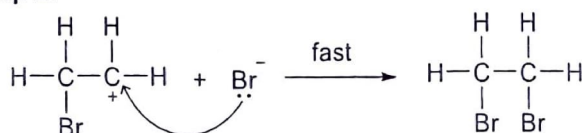
- Summary: The reaction mechanism involved is **electrophilic addition**.

Electrophilic Addition

Step 1:



Step 2:



Note:

- Name the mechanism
- Indicate **partial charges**, δ^+ and δ^- (if any).
- Use **full arrows** to show bond breaking/forming via the movement of electrons.
- Show **lone pair of electrons** on nucleophile.
- Indicate **slow or fast step** for each elementary step.
- Draw the formula of any intermediate.
- Draw the formula of product, identifying major and minor products (if applicable).

(b) Reaction between propene and bromine (in CCl_4) to give 1,2-dibromopropane.

Equation	$\text{CH}_3\text{CH}=\text{CH}_2 + \text{Br}_2 \longrightarrow \text{CH}_3\text{CHBrCH}_2\text{Br}$
Mechanism	Electrophilic addition

- The mechanism involved is **electrophilic addition** which consists of the following steps:

Step 1: Addition of electrophile ($\delta^+\text{Br}$ of polarised Br_2)

Step 2: Nucleophilic attack by Br^-

Note:

- In this case, there are two possible carbocations that can be formed.

more stable 2° carbocation

less stable 1° carbocation

- Draw the more stable carbocation when describing the mechanism.

(c) Reaction between 1-methylcyclohexene and chlorine to give 1,2-dichloro-1-methylcyclohexane.

Equation	
Mechanism	Electrophilic addition

- The mechanism involved is **electrophilic addition** which consists of the following steps:

Step 1: Addition of electrophile ($\delta^+\text{Br}$ of polarised Br_2)

Step 2: Nucleophilic attack by Br^-

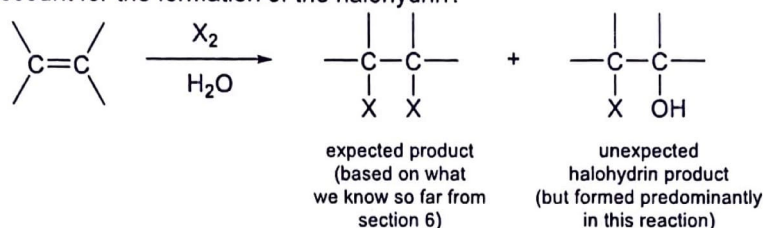
- Draw the more stable carbocation when describing the mechanism.

7.1 Reaction with halogens (in H₂O)

- When an alkene is reacted with a halogen dissolved in H₂O, a halogen atom and an –OH group are added across the C=C bond to form a halohydrin product.

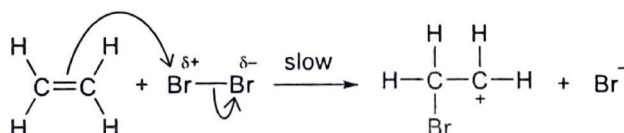
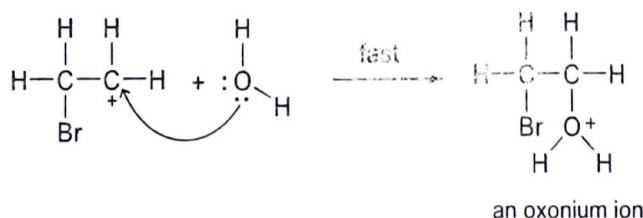
Electrophilic Addition (halohydrin formation)	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array} + \text{X}_2 + \text{H}_2\text{O} \longrightarrow \begin{array}{c} \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{X} \quad \text{OH} \\ \text{halohydrin} \end{array} + \text{HX}$
Reagent	X ₂ in water or X ₂ (aq) or X ₂ /H ₂ O where X = Cl, Br and I
Conditions	dark, room temperature
Mechanism	Electrophilic addition

- How can we account for the formation of the halohydrin?

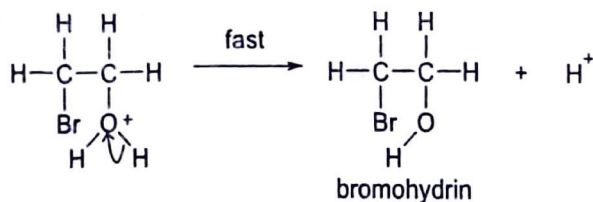
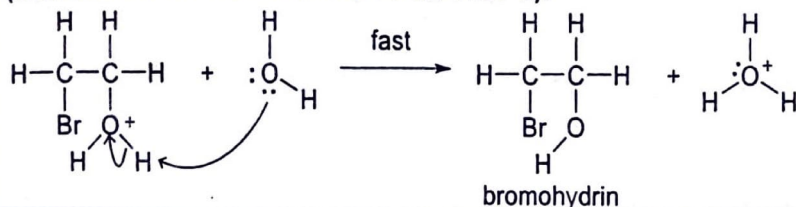


7.2 Mechanistic Explanation For the Formation of 2-Bromoethanol From the Reaction Between Ethene and Aqueous Bromine

Equation	$\text{CH}_2=\text{CH}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow \text{BrCH}_2\text{CH}_2\text{OH (major product)} + \text{HBr}$
Mechanism	Electrophilic addition

Step 1: Addition of electrophile ($\delta^+\text{Br}$ of polarised Br₂)Step 2: Nucleophilic attack by H₂O (in excess)

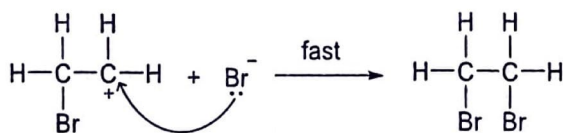
- This elementary step is the same as on page 21.
- This step also fits the kinetics data that the **slow step involves only the alkene and the halogen molecule**.
- In the second step, instead of Br[−] ion, H₂O (which is present in large excess as compared to the Br[−] ion, and is also a nucleophile) is attracted to the positively charged carbon of the carbocation.
- The O atom of the H₂O molecule forms a bond with the positively charged C of the carbocation to form an oxonium ion.
- Note:** An oxonium ion is a species which contains a positively charged oxygen.

Step 3: Loss of proton**(ALTERNATIVE PRESENTATION FOR STEP 3):**

- In this third step, the oxonium ion loses a proton (i.e. H^+) to form a bromohydrin.

- In reality, a water molecule gains the proton to form the H_3O^+ ion (another oxonium ion).

- Note:** In step 2, nucleophilic attack by Br^- also occurs to give 1,2-dibromoethane as the minor product.

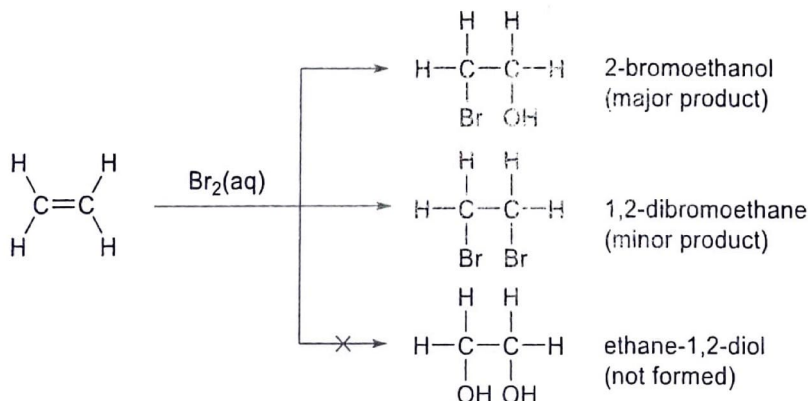
Alternative Step 2: Nucleophilic attack by Br^- **Note:**

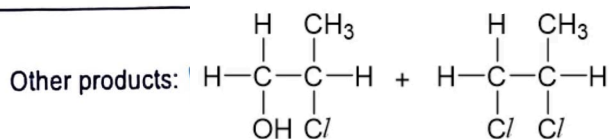
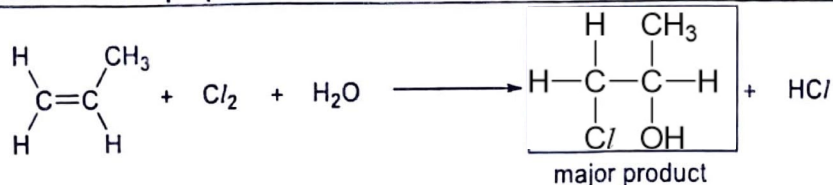
If other nucleophiles (e.g. Cl^- , CH_3OH , etc.) are also present in the reaction mixture, they can react with the carbocation to give other products.

- Example 1:** Ethene reacts with Br_2 in H_2O to produce a bromohydrin



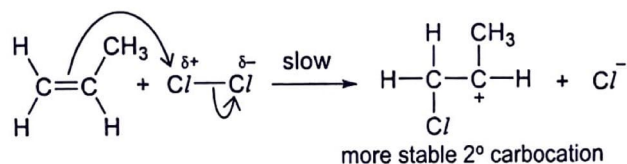
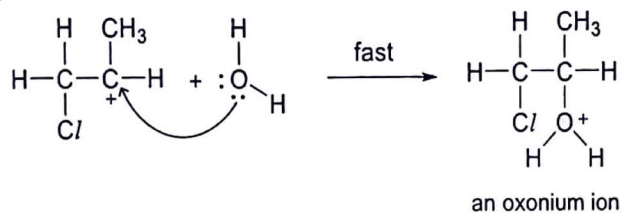
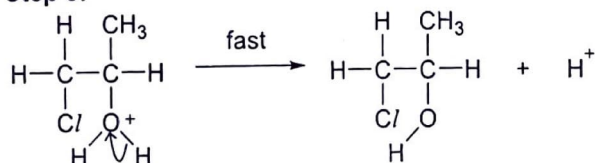
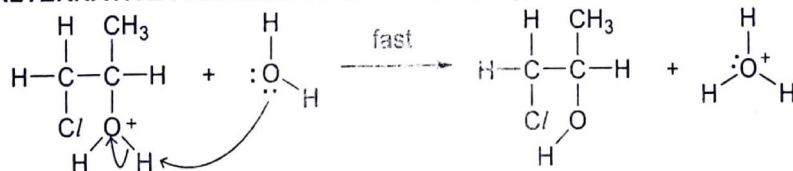
- When ethene is bubbled into $\text{Br}_2(\text{aq})$ at room temperature, an electrophilic addition reaction occurs. Br and OH are added across the $\text{C}=\text{C}$ bond to give 2-bromoethanol.
- Observation:** (Rapid) decolourisation of orange $\text{Br}_2(\text{aq})$ occurs.
(refer to Data Booklet Section 9(d) Colours of halogens)
- Note:** In this reaction, 1,2-dibromoethane is also formed.



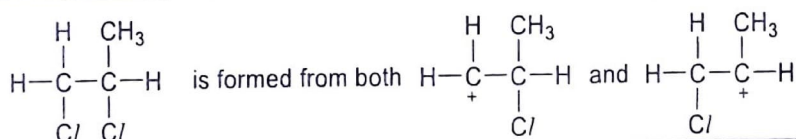
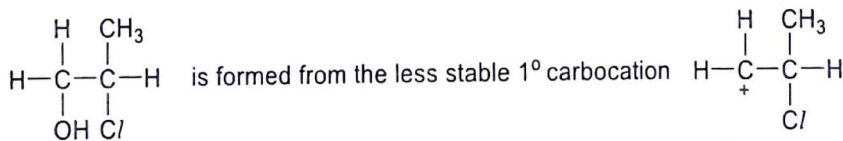
Example 2: Reaction between propene and chlorine in water**Equation****Mechanism****Electrophilic addition**

Note: During the reaction, the more stable carbocation (i.e. 2° carbocation) is formed faster and hence more available to react further to give the above major product.

- The mechanism involved in the reaction is **electrophilic addition**.

Step 1:**Step 2:****Step 3:****(ALTERNATIVE PRESENTATION FOR STEP 3):**

- Note:**

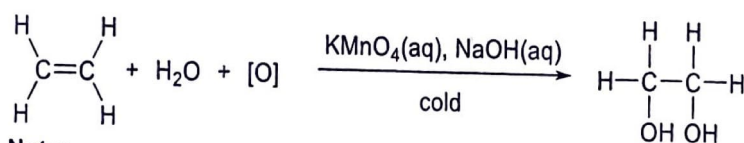


8.1 Reaction with cold, alkaline potassium manganate(VII)

- Alkenes undergo mild oxidation with **cold**, alkaline potassium manganate(VII) to form diols. This reaction involves the addition of two -OH groups across the $\text{C}=\text{C}$ bond of an alkene.

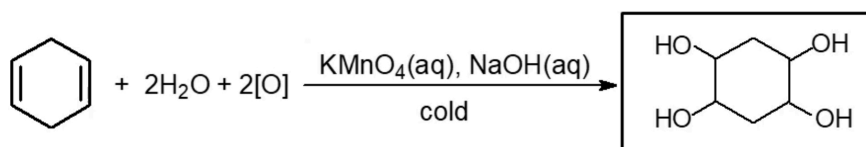
Mild oxidation	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array} + \text{H}_2\text{O} + [\text{O}] \xrightarrow[\text{cold}]{\text{KMnO}_4(\text{aq}), \text{NaOH}(\text{aq})} \begin{array}{c} \quad \\ \text{---C---C---} \\ \quad \\ \text{OH OH} \\ \text{a diol} \end{array}$ alkene
Reagents	$\text{KMnO}_4(\text{aq}), \text{NaOH}(\text{aq})$
Condition	cold
Type of reaction	Oxidation
Observations	- Purple KMnO_4 is decolourised. - A brown-black precipitate of MnO_2 is observed.

- The reaction occurs **without** the complete cleavage of the $\text{C}=\text{C}$ bond and is usually regarded as mild oxidation of an alkene.
- Example 1:** Ethene is oxidised by cold, alkaline KMnO_4 to produce ethane-1,2-diol.



Note:

- When ethene is bubbled into cold, alkaline KMnO_4 , mild oxidation of ethene occurs to produce ethane-1,2-diol.
- Observations:
 - Purple KMnO_4 is decolourised.
 - A brown-black precipitate of MnO_2 is observed.
- The use of cold KMnO_4 made alkaline with $\text{NaOH}(\text{aq})$ is a useful distinguishing test for alkenes (refer to section 11).
- Example 2:** Mild oxidation of a cycloalkene



8.2 Reaction with cold, acidified potassium manganate(VII)

- The mild oxidation of an alkene to form a diol can also be carried out using **cold KMnO_4** acidified with dilute H_2SO_4 although this is less common.
- Observation: Purple KMnO_4 is decolourised.

9.1 Reaction with hot, acidified potassium manganate(VII)

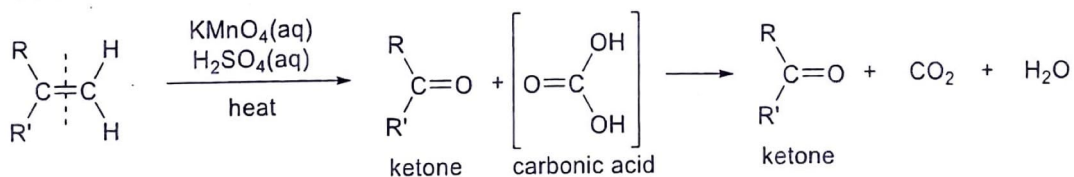
- Alkenes undergo strong oxidation with hot, acidified potassium manganate(VII) to give various products, which may include ketones, carboxylic acids and/or carbon dioxide gas. The exact oxidation products obtained depends on the structure of the alkene.
- The reaction is also called **oxidative cleavage** because the oxidation takes place with the complete cleavage of the C=C bond.

Strong oxidation (oxidative cleavage)	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$ alkene	$\xrightarrow[\text{heat}]{\text{KMnO}_4(\text{aq}), \text{H}_2\text{SO}_4(\text{aq})}$ - carboxylic acids - ketones - CO₂ and H₂O Note: The actual oxidation products obtained depends on the structure of the alkene.
Reagents	KMnO ₄ (aq), H ₂ SO ₄ (aq)	
Condition	heat / heat under reflux (see page 32)	
Type of reaction	Oxidation	
Observations	- Purple KMnO₄ is decolourised. - For terminal alkenes (=CH₂), a colourless gas (CO₂) which forms a white precipitate with limewater is evolved.	

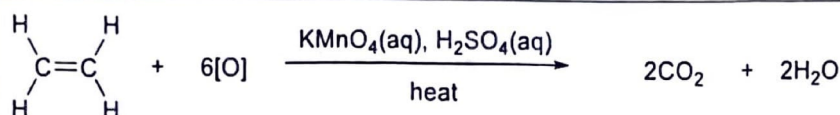
- The **degree of substitution** on the C=C bond of the alkene (i.e. the number of alkyl substituents attached to the doubly bonded carbon atoms) determines the oxidation products obtained as shown below.

$\begin{array}{c} \text{R} \quad \text{R}'' \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R}' \quad \text{R}''' \end{array}$	$\xrightarrow[\text{heat}]{\text{KMnO}_4(\text{aq}), \text{H}_2\text{SO}_4(\text{aq})}$	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}' \end{array} + \begin{array}{c} \text{R}'' \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{R}''' \end{array}$ ketone ketone	Note: R-, R'-, R''- and R'''- are alkyl groups. Simple rule of thumb: 1. Cleave C=C and put an O on the C= 2. Replace H on C= with OH
$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R}' \quad \text{R}''' \end{array}$	$\xrightarrow[\text{heat}]{\text{KMnO}_4(\text{aq}), \text{H}_2\text{SO}_4(\text{aq})}$	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}' \end{array} + \begin{array}{c} \text{OH} \\ \diagup \\ \text{O}=\text{C} \\ \diagdown \\ \text{R}''' \end{array}$ ketone carboxylic acid	
$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R}' \quad \text{H} \end{array}$	$\xrightarrow[\text{heat}]{\text{KMnO}_4(\text{aq}), \text{H}_2\text{SO}_4(\text{aq})}$	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}' \end{array} + \text{CO}_2 + \text{H}_2\text{O}$ ketone	

Applying "rule of thumb":

**Note:** Carbonic acid readily decomposes to give CO₂ and H₂O.

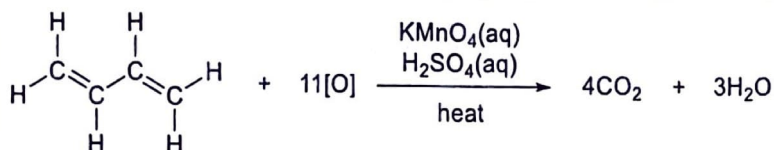
- Example 1:** Oxidation of ethene using hot, acidified KMnO_4 .



Observations:

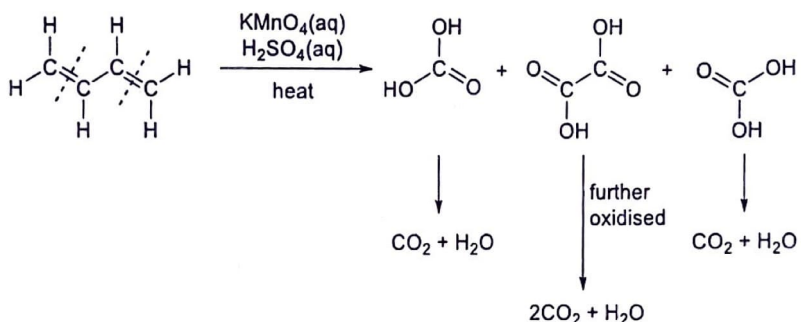
- Purple KMnO_4 is decolourised.
- A colourless gas (CO_2), which forms a white precipitate with limewater, is evolved.

- Example 2:** Oxidation of buta-1,3-diene using hot, acidified KMnO_4 .

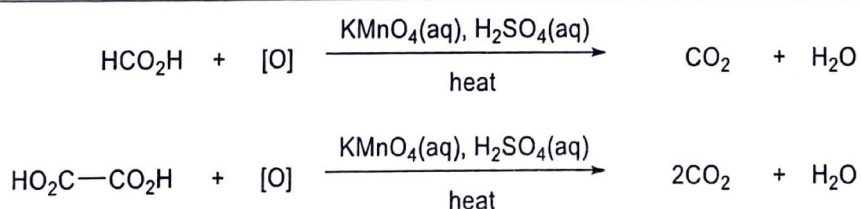


Note:

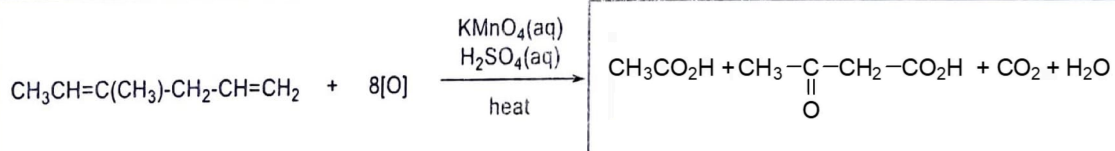
- Buta-1,3-diene is first oxidised to carbonic acid and ethanedioic acid.
- Ethanedioic acid is further oxidised by hot, acidified potassium manganate(VII) to form carbon dioxide and water.



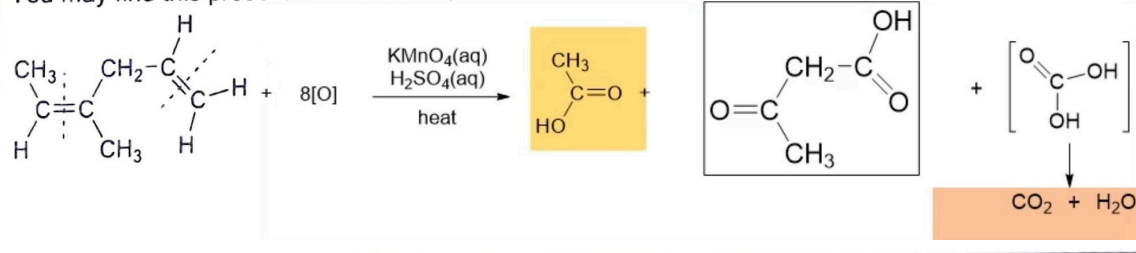
Note: Both HCOOH and $\text{HOOC}-\text{COOH}$ can be oxidised by hot, acidified KMnO_4 to give CO_2 and H_2O .



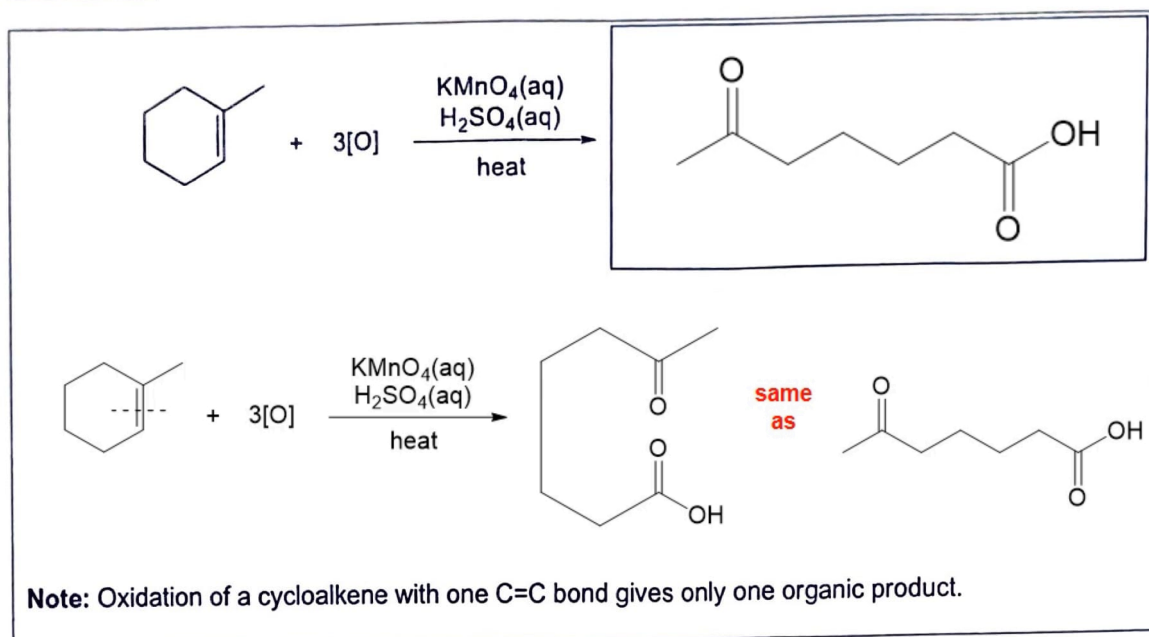
- Example 3:** Oxidation of $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}=\text{CH}_2$ using hot, acidified KMnO_4 .



You may find this presentation of the alkene useful:



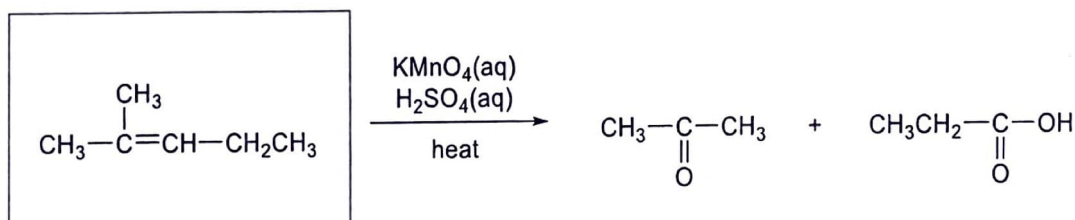
- Example 4:** Oxidation of 1-methylcyclohexene using hot, acidified KMnO_4 .



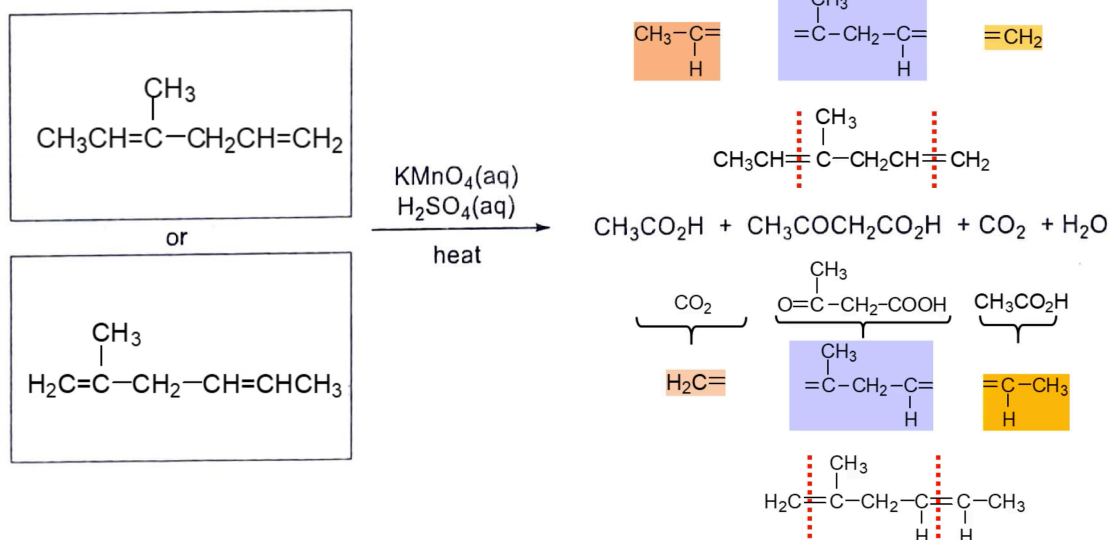
9.2 Determination of the positions of C=C bonds in larger molecules

- When an alkene with one or more C=C bonds undergoes oxidation in the presence of hot, acidified KMnO_4 , analysis of the oxidation products obtained helps to locate the position of each of the C=C bonds in the alkene molecule and this may allow the alkene to be identified.

Example 1



Example 2

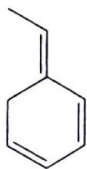
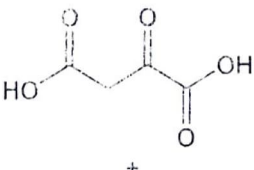
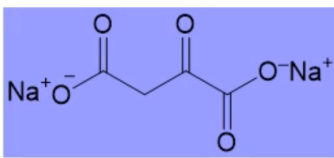


9.3 Reaction with hot, alkaline potassium manganate(VII)

- Alkenes can also undergo strong oxidation using **hot, alkaline KMnO_4** . The medium can be made alkaline using NaOH(aq) . In this case, some of the oxidation products obtained are different from those obtained using acidic medium.

Strong oxidation (oxidative cleavage)	 alkene $\xrightarrow[\text{heat}]{\text{KMnO}_4(\text{aq})}$ NaOH(aq) { and/or $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}'$ ketone and/or $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}^-\text{Na}^+$ carboxylate salt and/or $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ sodium carbonate and water
	Note: The actual oxidation products obtained depends on the structure of the alkene. Note: The counter cation depends on the alkali used.
Reagents	$\text{KMnO}_4(\text{aq}), \text{NaOH(aq)}$
Condition	heat / heat under reflux
Type of reaction	Oxidation
Observations	- Purple KMnO_4 is decolourised. - Brown-black precipitate of MnO_2 is observed.

Examples

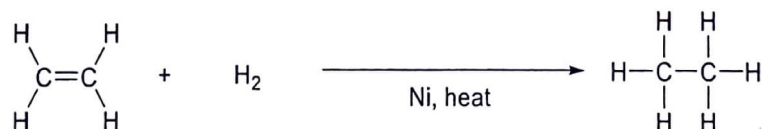
Alkene	Oxidation products obtained when heated with KMnO_4 and $\text{H}_2\text{SO}_4(\text{aq})$	Oxidation products obtained when heated with $\text{KMnO}_4(\text{aq})$ and NaOH(aq)
$\text{CH}_3-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$ + $\text{HO}_2\text{C}-\text{CH}_2-\text{CO}_2\text{H}$ + $\text{CO}_2 + \text{H}_2\text{O}$	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$ + $\text{Na}^+ \text{ } ^-\text{O}_2\text{C}-\text{CH}_2-\text{CO}_2^-\text{Na}^+$ + $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$ +  + $\text{CO}_2 + \text{H}_2\text{O}$	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}^-\text{Na}^+$  $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$

10.1 Reduction

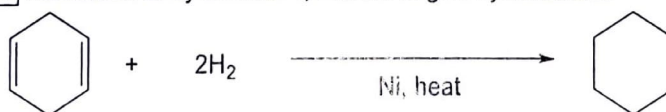
- Alkenes undergo reduction when heated with hydrogen gas in the presence of nickel catalyst to give alkanes. The overall reaction involves the addition of hydrogen atoms across the C=C bond.

Reduction (catalytic hydrogenation)	$ \begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array} + \text{H}_2 \xrightarrow[\text{or Pd or Pt}]{\text{Ni, heat}} \begin{array}{c} \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} $ alkene hydrogen gas alkane
Reagent	H ₂ (g)
Conditions	Ni catalyst, heat or Pt catalyst or Pd catalyst
Type of reaction	Reduction
Mechanism	Refer to heterogeneous catalysis in Kinetics lecture notes.

- Although the addition of hydrogen to an alkene is exothermic, reduction is slow in the absence of a catalyst. Commonly used transition metal catalysts include platinum, palladium, ruthenium and nickel.
- Because the conversion of an alkene to an alkane involves reduction by hydrogen in the presence of a catalyst, the reaction is also called or **catalytic hydrogenation**.
- The amount of H₂ reacted per mole of alkene is a measure of the number of C=C bonds present in the alkene molecule. One mole of C=C bond requires one mole of H₂ to reduce.
- Hydrogenation of alkene is of great commercial value. In the food industry, unsaturated vegetable oils are catalytically hydrogenated on a vast scale to produce the saturated fats used in margarine.
- Example 1:** Reduction of ethene to give ethane



- Example 2:** Reduction of cyclohexa-1,4-diene to give cyclohexane



10.2 Combustion

- Alkenes undergo complete combustion when burned in excess oxygen gas to give carbon dioxide and water.

Combustion	$ \text{C}_n\text{H}_{2n} + \frac{3n}{2} \text{O}_2(\text{g}) \longrightarrow n \text{CO}_2(\text{g}) + n \text{H}_2\text{O}(\text{l}) $ or $ \text{C}_x\text{H}_y + \left(x + \frac{y}{4}\right) \text{O}_2(\text{g}) \longrightarrow x \text{CO}_2(\text{g}) + \frac{y}{2} \text{H}_2\text{O}(\text{l}) \quad \text{where } y = 2x $
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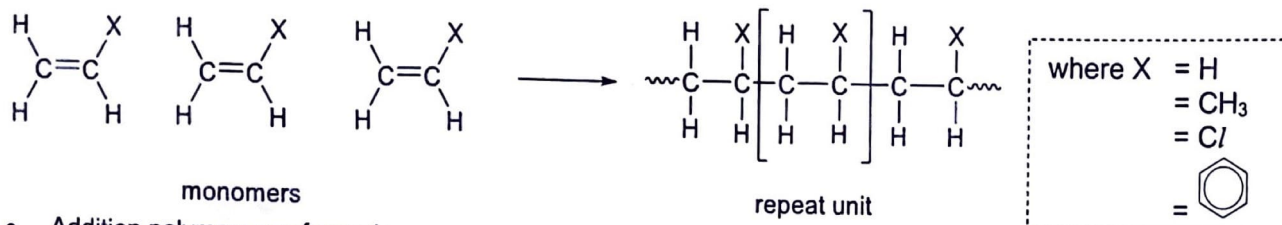
- Example:** $\text{CH}_2=\text{CH}_2(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

10.3 Addition Polymerisation

Recall from Introduction to Organic Chemistry, Lecture Notes 9 Section 6.3
An addition reaction:

- only occurs when there is unsaturation in the reactant molecules.
- 2 species react to give a single product.
- a π bond is broken to form two σ bonds.

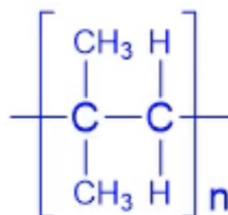
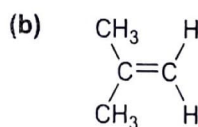
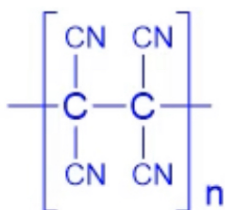
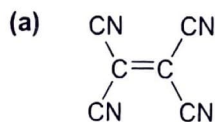
Addition polymers



- Addition polymers are formed:
 - with monomer containing C=C double bonds e.g. alkenes such as ethene and propene
 - by adding monomers to the growing end of a polymer chain
- The empirical formula of polymer is the same as its monomer.
- Polymers are usually named according to the monomers from which they are prepared. The polymer is named by enclosing the name of the monomer(s) in parentheses and adding the prefix poly. Some examples are given below:

Name of polymer	Monomer structure	Polymer structure/formula	The convention for writing polymer formulas is to enclose the repeat unit within brackets, followed by the letter n to indicate the number of repeat units.
poly(ethene)	ethene		
poly(propene)	propene		

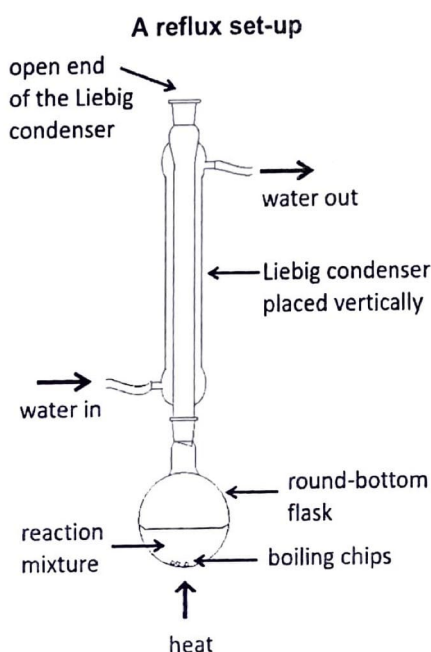
- Example:** Draw the polymer structure formed from the following monomers:



11.1 General points to take note for a distinguishing test

- When asked to describe a simple chemical test that can be carried out to distinguish between one organic compound from another organic compound, take note of the following points:
 - The chemical test is assumed to be performed **using test-tubes** in the laboratory.
 - The test should involve a **chemical reaction** (e.g. redox, addition/substitution, acid-base etc) with the use of chemicals available in the laboratory. For example, to distinguish an acidic compound (e.g. carboxylic acid) from a neutral compound, the addition of aqueous Na_2CO_3 to both samples is accepted but the dipping of litmus paper or addition of universal indicator into each sample are not accepted as a chemical test.
 - The test should be **simple** and does not require the use of apparatus such as the Liebig condenser (see below).
 - So, should a higher temperature be needed as part of the condition for the test, write "heat" and not "heat under reflux" (see below).
 - The chemical test chosen must result in **different observable changes** for the different organic compounds involved in the test. These observable changes may include the following:
 - a change in the colour of the solution
 - the formation of a precipitate
 - the evolution of a gas and the test for the gas
 - the dissolving of a compound due to a chemical reaction
 - The answer to a distinguishing test question usually includes the following parts:
 - reagents and conditions
 - positive and negative observations
 - chemical test for any gas evolved
 - equations (if required by the question)
- What is meant by "heating under reflux"?

Many organic syntheses are carried out at temperatures above room temperature and these syntheses require heating under reflux.



- Heating under reflux is the process of heating a reaction mixture while continuously cooling the vapour produced via a Liebig condenser with running water.
- On heating, the volatile reactants/products vapourise. The vapour condenses on the inner walls of the cooled Liebig condenser and drips back to the flask as a liquid.
- Hence, loss of volatile reactants or products is minimised.
- Heating under reflux is commonly used in organic synthesis which involves heating a reaction mixture containing volatile reactants/products for an extended period of time.

11.2 Distinguishing tests involving alkenes

• Example 1:

Suggest a simple chemical test to distinguish between pentane and pent-2-ene. Write equation for any reaction that occurs.

Answer:

Test	Add Br ₂ in CCl ₄ drop-wise to each sample in a test-tube at room temperature.
Observations	For pent-2-ene, there is <u>rapid decolourisation</u> of the orange-red Br ₂ . For pentane, there is <u>no rapid decolourisation</u> of the orange-red Br ₂ .
Equation	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3 + \text{Br}_2 \longrightarrow \text{CH}_3\text{CHBrCHBrCH}_2\text{CH}_3$

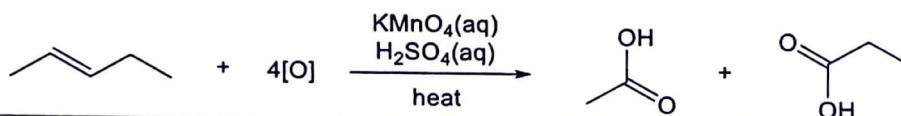
Alternative answer:

Add two drops of KMnO₄ acidified with dilute H₂SO₄ to each sample in a test-tube and heat each reaction mixture in a hot water bath (**do not heat under reflux!**)

For pent-2-ene, there is decolourisation of purple KMnO₄.

For pentane, there is no decolourisation of purple KMnO₄.

Equation:



Other possible chemical tests:

- Br₂(aq), room temperature
→ orange Br₂(aq) decolourises for pent-2-ene but not for pentane
- KMnO₄(aq) and NaOH(aq), cold
→ purple KMnO₄ decolourises, brown-black precipitate of MnO₂ observed for pent-2-ene but not for pentane

• Example 2

Suggest a simple chemical test to distinguish between propane and propene (both are gases). Write a balanced equation for any reaction that occurs.

Answer:

Test	Bubble a sample of each gas through Br ₂ (aq) in separate test-tubes at room temperature.
Observations	For propene, there is (rapid) decolourisation of the orange Br ₂ (aq). For propane, there is no decolourisation of the orange Br ₂ (aq).
Equation	$\text{CH}_3\text{CH}=\text{CH}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{Br} + \text{HBr}$

Alternative answer:

Add two drops of Br₂ in CCl₄ to each sample of gas already collected in a stoppered test-tube at room temperature. Shake the re-stoppered test-tube.

For propene, there is rapid decolourisation of the orange-red Br₂.

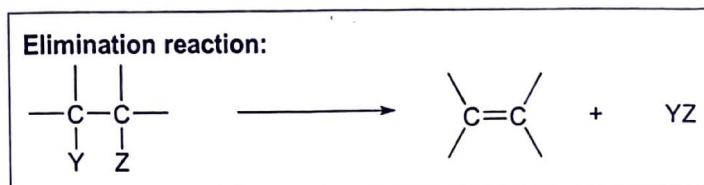
For propane, there is no rapid decolourisation of the orange-red Br₂.

Equation: $\text{CH}_3\text{CH}=\text{CH}_2 + \text{Br}_2 \longrightarrow \text{CH}_3\text{CHBrCH}_2\text{Br}$

Other possible chemical tests:

- KMnO₄(aq) acidified with H₂SO₄(aq), heat
- KMnO₄(aq) and NaOH(aq), cold

- Alkenes can be prepared from the following elimination reactions:
 - dehydrohalogenation of halogenoalkanes (or alkyl halides)
 - dehydration of alcohols
- An **elimination reaction** involves the removal of atoms or groups of atoms from adjacent carbon atoms of the reactant molecule leading to the creation of a new π bond in the product molecule.

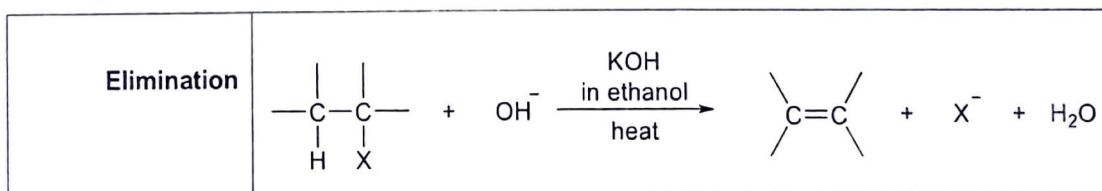


12.1 Elimination of HX from halogenoalkanes

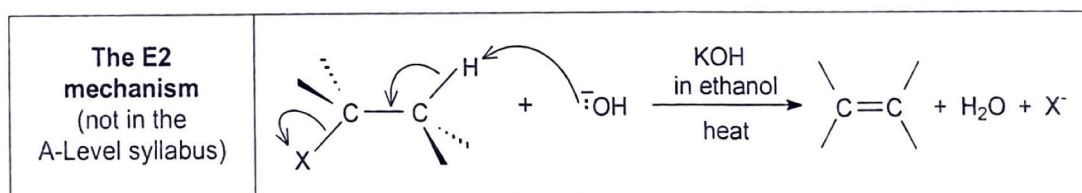
- Halogenoalkanes can undergo elimination reactions when heated with alkali (e.g. KOH) in the presence of alcohol as solvent.

Elimination (dehydrohalogenation)	$ \begin{array}{c} \quad \\ -C-C- \\ \quad \\ H \quad X \\ \text{halogenoalkane} \end{array} \xrightarrow[\text{heat}]{\text{KOH in ethanol}} \begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \\ \text{alkene} \end{array} + HX $ Note: X = Cl, Br or I
Reagent	KOH in ethanol or ethanolic KOH or alcoholic KOH or NaOH in ethanol
Condition	Heat / heat under reflux
Mechanism	Elimination

- During the reaction, a H atom and the X atom attached to adjacent carbon atoms are removed and an alkene is formed. This elimination reaction is known as **dehydrohalogenation** since the elements of HX are eliminated from the halogenoalkane molecule.
- Note:** The reaction is more correctly represented by the equation shown below. This is because HX is actually not obtained as a product of the reaction although elements of HX are effectively removed from the halogenoalkane molecule.



- Note:** In alcoholic medium, the OH^- ion acts as a base and abstracts a proton to form H_2O .



• **Examples:**

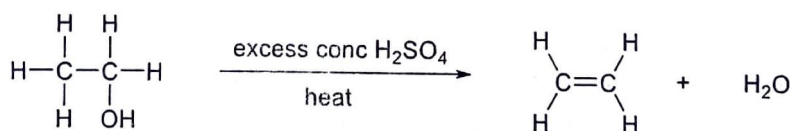
Reaction of 1-bromopropane with hot, ethanolic KOH.	$\begin{array}{c} \text{H} & \text{CH}_3 \\ & \\ \text{H}-\text{C}-\text{C}-\text{H} \\ & \\ \text{Br} & \text{H} \end{array} + \text{OH}^- \xrightarrow[\text{heat}]{\text{KOH in ethanol}} \begin{array}{c} \text{H} & \text{CH}_3 \\ \backslash & / \\ \text{C}=\text{C} \\ / & \backslash \\ \text{H} & \text{H} \end{array} + \text{Br}^- + \text{H}_2\text{O}$
Reaction of chlorocyclohexane with hot, ethanolic KOH.	$\text{Cyclohexyl-Cl} + \text{OH}^- \xrightarrow[\text{heat}]{\text{KOH in ethanol}} \text{Cyclohexene} + \text{Cl}^- + \text{H}_2\text{O}$

12.2 Elimination of H₂O from alcohols

- Alcohols can undergo dehydration to give alkenes. The reaction involves the elimination of H₂O from the alcohol molecule.

Elimination (dehydration)	$\begin{array}{c} & \\ -\text{C}-\text{C}- \\ & \\ \text{H} & \text{OH} \\ \text{alcohol} \end{array} \xrightarrow[\text{heat}]{\text{excess conc H}_2\text{SO}_4} \begin{array}{c} \diagup & \diagdown \\ \text{C}=\text{C} \\ \diagdown & \diagup \\ \text{alkene} \end{array} + \text{H}_2\text{O}$
Reagent and conditions	excess conc. H₂SO₄, heat or Al₂O₃, heat or H₃PO₄, heat
Mechanism	Elimination

- In the dehydration reaction, a H atom and the hydroxyl group (i.e. -OH) from adjacent carbon atoms in the alcohol molecule are eliminated as a molecule of water.
- Example:** Ethanol undergoes dehydration to give ethene.



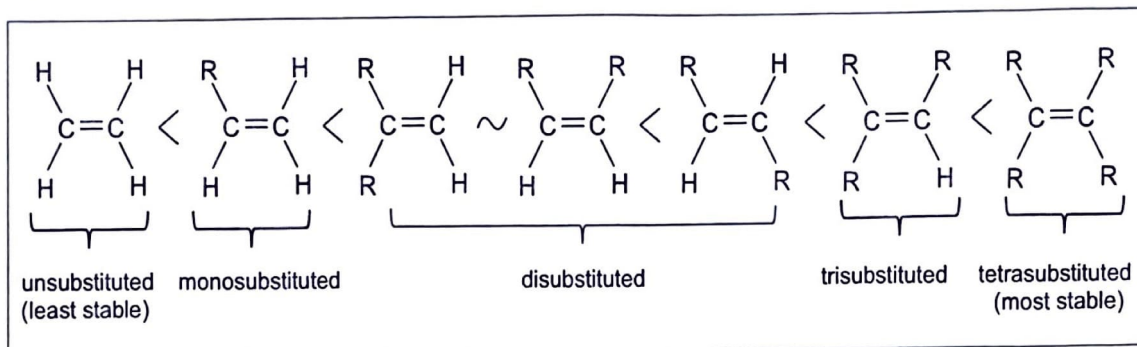
Using excess concentrated H ₂ SO ₄	Using hot Al ₂ O ₃
Note: During the reaction, conc. H₂SO₄ may oxidise some of the ethanol and is itself reduced to SO₂. The acidic SO₂ gas is removed by bubbling the gaseous mixture through sodium hydroxide solution.	

12.3 Saytzeff's Rule (or Zaitsev's Rule)

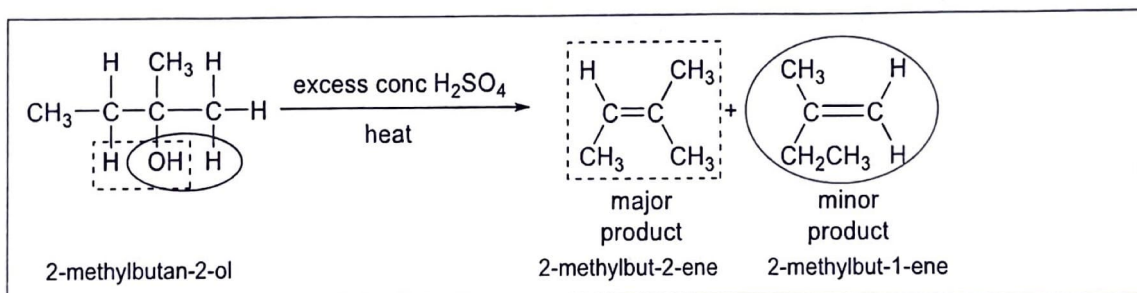
- Saytzeff's Rule (or Zaitsev's Rule) states:

For elimination reactions of alcohols or halogenoalkanes to alkenes, the preferred product is the alkene with the **greater number of alkyl groups** attached to the doubly bonded carbon atoms i.e. the more substituted alkene.

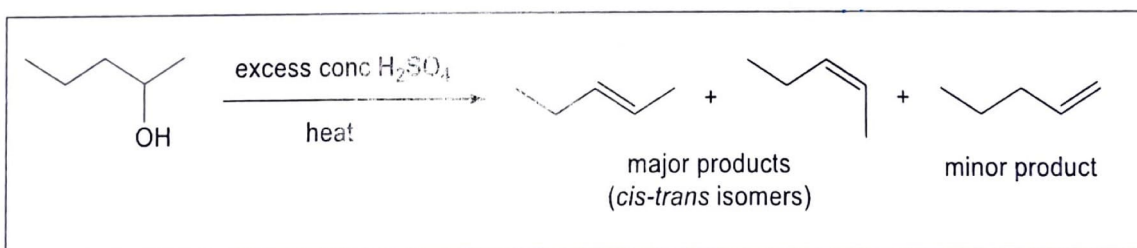
- Note that the more substituted the alkene (i.e. the alkene with more electron-donating alkyl substituents attached to its doubly bonded carbon atoms) is the more stable the alkene.
- In general, the stability of alkenes increases in the order:



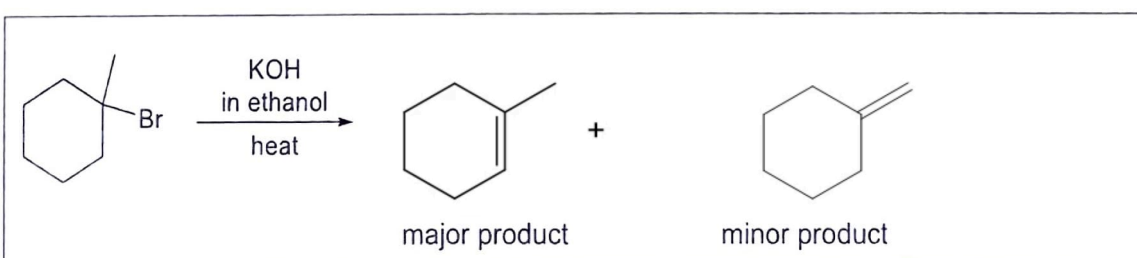
- Example 1:** Dehydration of 2-methylbutan-2-ol



- Example 2:** Dehydration of pentan-2-ol



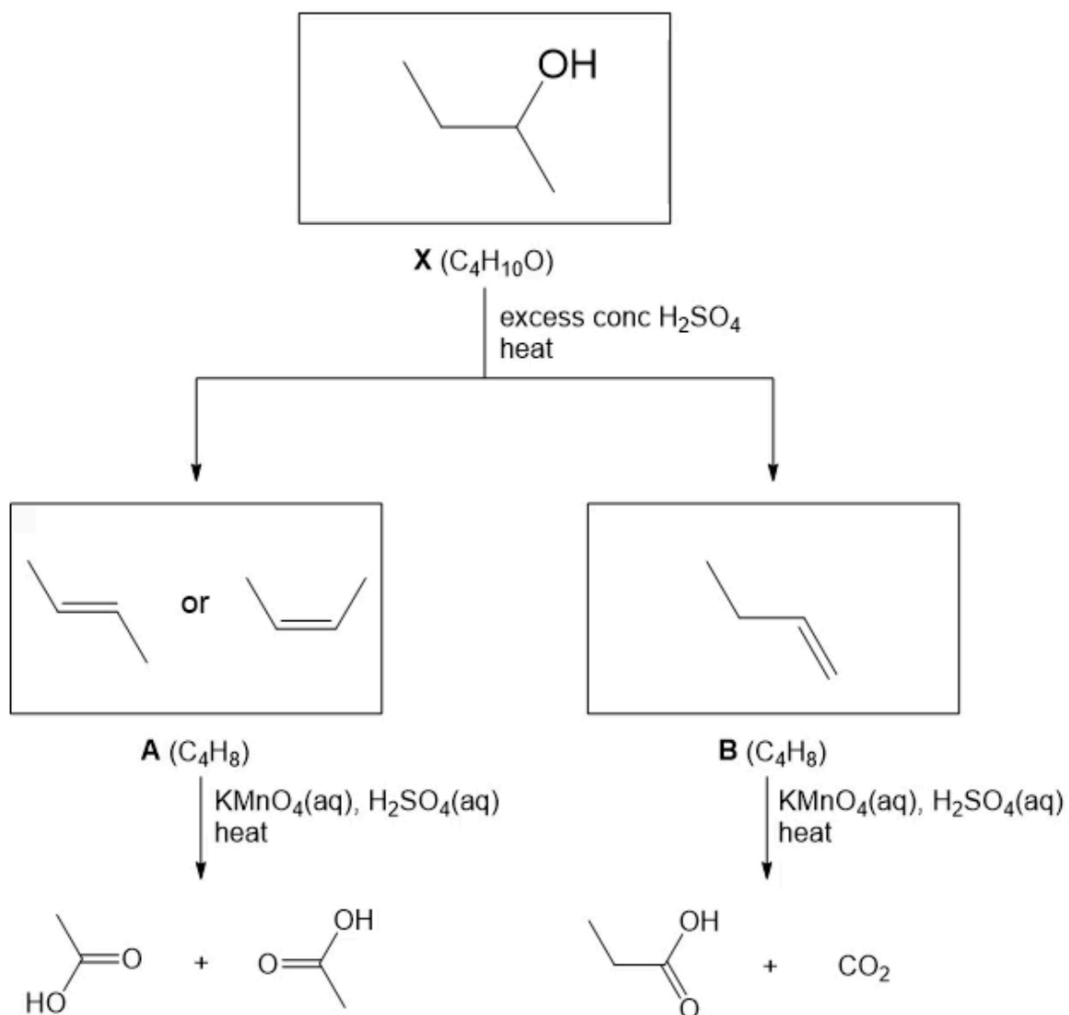
- Example 3:** Dehydrohalogenation of 1-bromo-1-methylcyclohexane

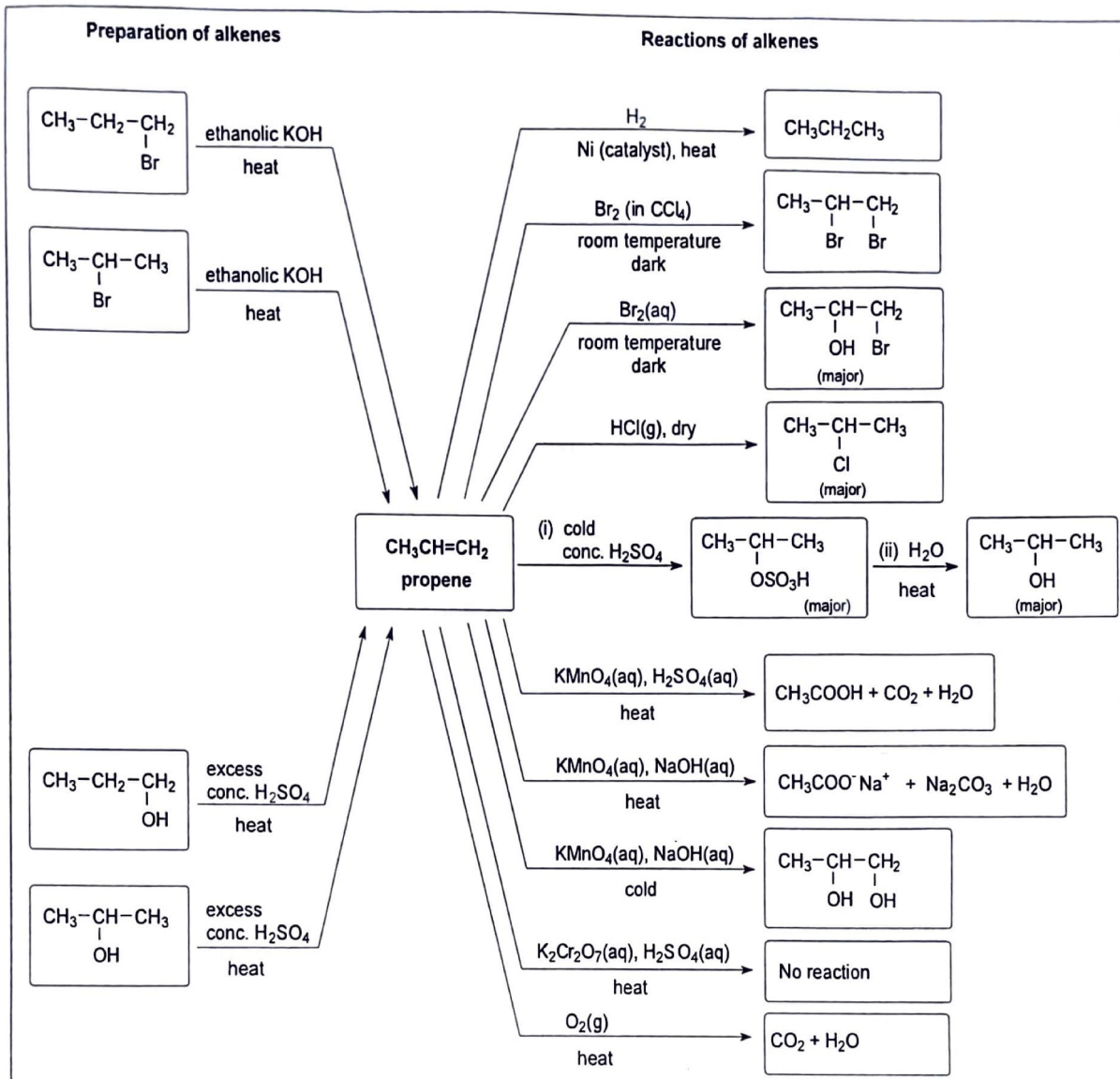


• **Example 4:** Elucidation

An alcohol **X** ($C_4H_{10}O$) was heated with excess concentrated H_2SO_4 to give two alkenes, **A** and **B**. Alkene **A** exhibits cis-trans isomerism but alkene **B** does not. One mole of **A** gives two moles of ethanoic acid when heated with acidified $KMnO_4(aq)$, while one mole of **B** gives one mole of propanoic acid and one mole of CO_2 as the only carbon containing products under the same reaction conditions.

Deduce the structures of **A**, **B** and **X**.

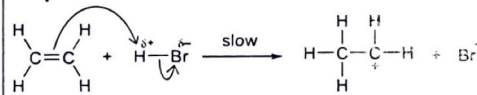




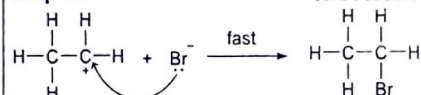
Electrophilic Addition Mechanism

Electrophilic addition of HBr to alkene

Step 1:



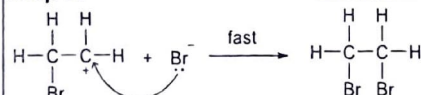
Step 2:

Electrophilic addition of Br₂ to alkene

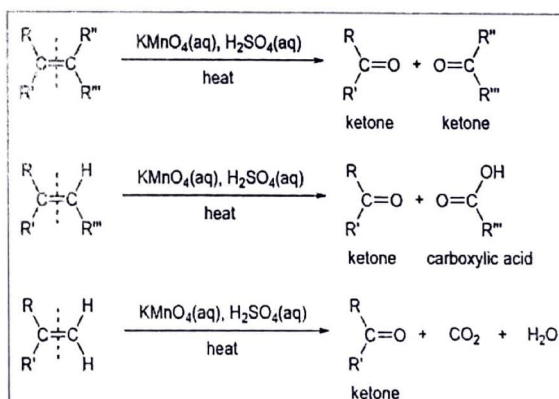
Step 1:



Step 2:



Strong Oxidation of Alkenes



Note:

R¹-, R²-, R³- and R⁴- are alkyl groups.

Simple rule of thumb:

1. Cleave C=C and put an O on the C=
2. Replace H on C= with OH

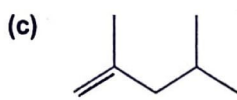
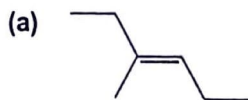


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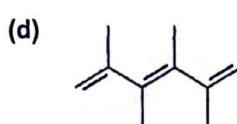
Tutorial 11 – Alkenes

Self-check Questions

1 Give the systematic name or structure of each the following alkenes:



(e) 1,5-dimethylcyclopentene



(f) 1-ethylcyclohexa-1,4-diene

2 (a) A non-cyclic hydrocarbon **Q** contains four sp^2 hybridised carbon atoms and one sp^3 hybridised carbon atom per molecule.

(i) What is the molecular formula of **Q**?

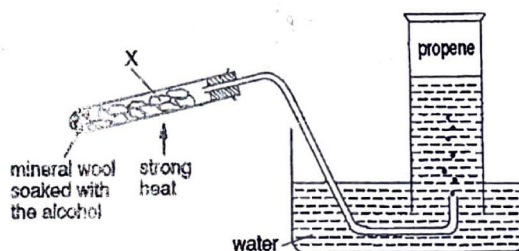
(ii) Draw the skeletal formulae of all the possible structures of **Q** (including both structural isomers and stereoisomers) and name each one.

(b) Squalene, a hydrocarbon with molecular formula $C_{30}H_{50}$, is obtained from shark liver. If squalene is a non-cyclic compound, how many π bonds does it have per molecule?

(c) Arrange the following alkenes in decreasing order of boiling point:

2-methylbut-1-ene, *cis*-pent-2-ene and *trans*-pent-2-ene.

3 Alkenes can be prepared in the laboratory by the dehydration of alcohols. The apparatus shown below can be used to prepare a sample of propene.



(a) Give the skeletal formula of two alcohols which can be used to prepare propene.

(b) Write an equation for the dehydration of an alcohol that you have given in (a).

(c) (i) The material **X** can be pumice or a ceramic such as broken brick or broken crockery. Write the chemical name or a substance that might be present in one of these materials.

(ii) The material **X** becomes black in colour. Suggest what substance is responsible for this black colour, and how it arises in the reaction.

(iii) At the end of the reaction, when no more propene comes over, the apparatus is left to cool with the delivery tube out of the water. Suggest why this is done.

(d) Propene can also be prepared from 2-chloropropane.

(i) Suggest reagent and conditions for this reaction.

(ii) Name the type of reaction which occurs and write a balanced equation for the reaction.

Q4

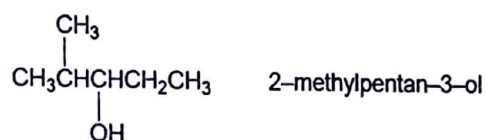
In a preparation of ethene, ethanol is added a drop at a time to a heated reagent Y. The impure ethene is washed by being bubbled through a solution Z and then collected.

What could reagent Y and solution Z be?

	reagent Y	solution Z
A	acidified $\text{K}_2\text{Cr}_2\text{O}_7$	dilute NaOH
B	concentrated H_2SO_4	dilute H_2SO_4
C	concentrated H_2SO_4	dilute NaOH
D	ethanolic NaOH	concentrated H_2SO_4

Q5

How many alkenes (including stereoisomers) can be obtained when 2-methylpentan-3-ol undergoes dehydration?



- | | |
|-----|-----|
| A 2 | B 3 |
| C 4 | D 5 |

Q6

Propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, is dehydrated by passing its vapour over hot aluminium oxide to give a hydrocarbon. What is the product obtained when the hydrocarbon reacts with bromine?

- A 1-bromopropane
 B 2-bromopropane
 C 1,1-dibromopropane
 D 1,2-dibromopropane

Q7

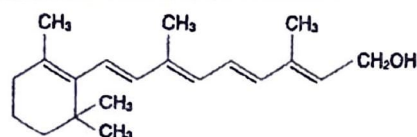
A mixture containing both 2-bromohexane and 3-bromohexane is heated with ethanolic potassium hydroxide.

How many isomeric alkenes (including stereoisomers) could be produced at the end of the reaction?

- | | |
|-----|-----|
| A 3 | B 4 |
| C 5 | D 6 |

Q8

The structure of Vitamin A is shown below.



When it is completely reacted with hydrogen in the presence of a palladium catalyst at room temperature, how many chiral centres does the product molecule possess?

- | | |
|-----|-----|
| A 2 | C 4 |
| B 3 | D 5 |

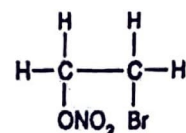
Q9

Which of the following can act as an electrophile?

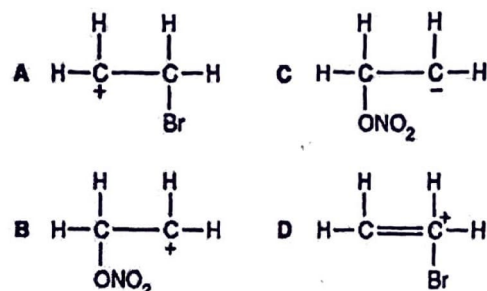
- A Cl_2 B $\text{CH}_2=\text{CH}_2$ C CN^- D H_2O

Q10

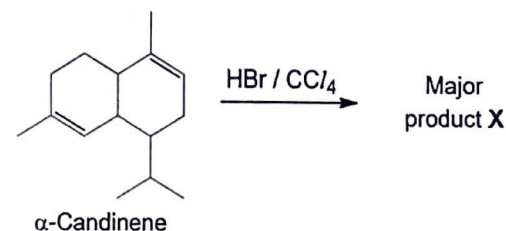
When ethene reacts with bromine in the presence of concentrated aqueous sodium nitrate, the product contains the following compound.



What is the intermediate formed in this reaction?

**Q11**

α -Cadinene can be found in juniper berries. X is the major product formed when α -Cadinene is reacted with HBr in CCl_4 .



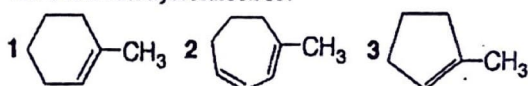
How many stereoisomers does X have?

- | | |
|------|------|
| A 8 | B 16 |
| C 32 | D 64 |

Q12

A hydrocarbon, on heating with an excess of hot concentrated acidic $\text{KMnO}_4(\text{aq})$, produces $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{COCH}_3$.

What could the hydrocarbon be?



- | | |
|----------------|----------------|
| A 1, 2 and 3 | B 1 and 2 only |
| C 2 and 3 only | D 1 only |

4	5	6	7	8	9	10	11	12

Practice Questions

- 1 In each of the blank spaces, suggest a suitable **alkene** for the conversions and state the **reagents and conditions** required for all steps.



- 2 Hex-3-ene occurs in two isomeric forms.

- Draw the displayed formulae of the two isomeric forms of hex-3-ene.
- Write a balanced equation for the reaction between hex-3-ene and bromine in tetrachloromethane.
- Describe the mechanism for the reaction in (b).
- Explain why the reaction of either isomer of hex-3-ene with hydrogen bromide gives the same equimolar (1:1) mixture of two isomers of the product.

- 3 Six isomeric hydrocarbons, A to F, share the same molecular formula, C₄H₈.

A and B are *cis-trans* isomers and A has a higher boiling point than B. C reacts with aqueous bromine to yield a product G, which has a chiral centre. D reacts with hydrogen to form a branched-chain alkane, H. E and F are saturated hydrocarbons. E reacts with bromine in the presence of ultra-violet light to form **only one** mono-brominated product.

- Suggest a structural formula for **each** of the hydrocarbons A to F. Give the IUPAC name of **each** compound.
- Give the displayed formulae and IUPAC names of G and H.
- Explain why the boiling point of A is higher than that of B.
- Give the structural formulae of the organic products obtained when each of the hydrocarbons A to D is treated with
 - cold potassium manganate(VII) made alkaline with aqueous sodium hydroxide,
 - hot potassium manganate(VII) made alkaline with aqueous sodium hydroxide, and
 - hot potassium manganate(VII) acidified with dilute sulfuric acid.

- 4 For each of the following pairs of compounds, describe one **simple** chemical test which would enable you to distinguish between them. State clearly how **each** compound behaves in the test and write balanced equations for the reactions involved.

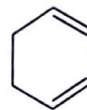
(a) ethane and ethene

(b) pent-1-ene and pent-2-ene

(c)



and



- 5 Methylpropene reacts with iodine monochloride to form 2-chloro-1-iodo-2-methylpropane. Name and describe the mechanism for this reaction. Show relevant charges and dipoles, and use curly arrows to indicate the movement of electron pairs.

- 6 Explain the following observations:

(a) When ethene reacts with hydrogen halides, the reactivity increases in the order: $\text{HCl} < \text{HBr} < \text{HI}$.

(b) When 1-ethylcyclohexene reacts with hydrogen bromide, 1-bromo-1-ethylcyclohexane is the major product obtained.

- 7 When ethene is shaken with aqueous bromine, the main reaction products are 2-bromoethanol and 1,2-dibromoethane. When ethene is shaken with an aqueous solution containing **both** bromine and sodium chloride, which of the following are possible products?

- 1 2-bromoethanol
- 2 1-bromo-2-chloroethane
- 3 2-chloroethanol
- 4 1,2-dichloroethane

A 1 and 2 only B 1 and 3 only C 3 and 4 only D 1, 2 and 3 only

- 8 There are many structural isomers of cyclohexene and three of them, **A**, **B** and **C**, are described below. Note that the molecules of **A**, **B** and **C** do not contain any *sp* hybridised carbon atom.

1 mole of **A** reacts with 2 moles of bromine in CCl_4 in the dark. Under vigorous oxidation, **A** forms butanedioic acid ($\text{C}_4\text{H}_6\text{O}_4$).

B is a positional isomer of **A**. 1 mole of **B** also reacts with 2 moles of bromine in CCl_4 in the dark, but gives three carbon-containing products upon vigorous oxidation.

1 mole of **C** reacts with 1 mole of bromine in CCl_4 in the dark. Each molecule of **C** possesses one chiral centre. When an optically inactive sample of **C** underwent vigorous oxidation, the final reaction mixture was found to be optically inactive.

Draw the structures of isomers **A**, **B** and **C**, illustrating the possible stereoisomeric forms, if any.