ANDERSON SERANGOON JUNIOR COLLEGE JC1 H2 CHEMISTRY <u>HYDROCARBONS: ALKENES</u>

Content/Outline

Alkenes (exemplified by ethene)

- 1 Introduction
- 2 Nomenclature
- 3 Isomerism
- 4 Physical Properties
- 5 Preparation of alkene
 - Cracking
 - Elimination, including Saytzeff's rule
- 6 Chemical Property
- 7 Reactions of alkene
 - Electrophilic addition, including Markovnikov's rule
 - Oxidation
 - Reduction
- 8 Chemical Tests for alkene
- 9 Electronic Effect (Inductive Effect)

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
 - (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 carbonto-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 the carbocation intermediates

References

- 1. Chemistry for Advanced Level. Peter Cann & Peter Hughes
- 2. Chemistry (2nd edition). Chris Conoley and Phil Hill
- 3. Chemistry in Context. Hill & Holman
- 4. Understanding Advanced Organic and Analytical Chemistry, K.S Chan and Jeanne Tan

1 INTRODUCTION

Alkenes are **unsaturated** hydrocarbons which contain one or more C=C double bonds in their structures.

Alkenes have the general formula C_nH_{2n} . Cycloalkenes have the general formula C_nH_{2n-2} . (Note that cycloalkanes have the same general formula as alkenes e.g. C_3H_6 represents propene as well as cyclopropane.)

Each C atom of the C=C is _____. Hence the geometry (shape) about each of the double bonded C is trigonal planar.





Three sp² hybrid orbitals lie in a trigonal plane

Two of the three sp² hybrid orbitals of the carbon atom overlap head–on with the 1s orbitals of the two hydrogen atoms to form two C–H sigma (σ) bonds.

The remaining sp² hybrid orbital overlaps head–on with the sp² hybrid orbital of the neighbouring carbon atom to form a C–C sigma (σ) bond.

The unhybridised 2p orbital, which is perpendicular to the plane of the inter–nuclear axis, overlaps side–on with the 2p orbital of the neighbouring carbon atom to form a pi (π) bond. The π electron cloud lies above and below the plane of the inter–nuclear axis.



bonding in ethene molecule

2 NOMENCLATURE

The name of an alkene is derived from an alkane with same number of carbon atoms by changing the suffix from **-ane** to **-ene**.

The longest continuous carbon chain that **contains the C=C** is named as the parent chain.

The **position of the double bond** and any substituents are indicated by **numbering the carbon atoms** in the chain, as shown below.

n	Molecular formula	Name	Structural formula
2	C_2H_4	ethene	CH ₂ =CH ₂
3	C_3H_6	propene	CH ₂ =CHCH ₃
4		but-1-ene	CH ₂ =CHCH ₂ CH ₃
		but-2-ene	1 2 3 4 CH₃CH=CHCH₃
	U4⊓8	2–methylpropene	$CH_3 \\ CH_2 = C_2 C_3 CH_3$

If the molecule has two C=C double bonds, it is named as a diene.

Structural formula	Appropriate IUPAC name
1^{2} $CH_2=CH-CH=CH_2$	buta-1,3-diene
$\begin{array}{cccc}1&2&3&4&5\\CH_2=CHCH_2CH=CH_2\end{array}$	penta-1,4-diene
	cyclohexa–1,4–diene

More examples on nomenclature

Ċompound	Appropriate IUPAC name	Inappropriate names
CH ₃ CH ₂ CH=CHCH ₃	Ø pent-2-ene	⊠ pent–3–ene
		The position of the double bond in the chain is indicated by the <i>smallest number</i> possible.
CH=CH ₂	Ø 3–ethylhex–1–ene	⊠3–propylpent–1–ene
CH ₃ CH ₂ CH ₂ —C—CH ₂ CH ₃ H	$\begin{array}{c} \hline CH = CH_2 \\ \hline CH_3CH_2CH_2 - C \\ \hline \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	The parent chain must be the <i>longest continuous</i> carbon chain that <i>contains the C=C</i> .
	Н	⊠4–ethylhex–5–ene
		The position of the double bond in the chain is indicated by the <i>smallest number</i> possible.
CI	☑ 2–chloro–3– methylcyclohexa–1,4–	Image: State S
CH ₃	diene Cl CH ₃ 2 3 1	The position of the double bond in the chain is indicated by the <i>smallest number</i> possible.
	4 6 5	$E CH_3 CI CH_3 CI CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3$
		The number assigned to the C=C must be in <i>consecutive</i> order. (e.g. 1 & 2. Not 1 & 6)
		⊠1–choro–6–methylcyclohexa– 1,4–diene
		The position number assigned to the substituent should be the lowest number possible.
		⊠3–methyl–2–chlorocyclohexa– 1,4–diene
		The substituent should be arranged in alphabetical order.

3 ISOMERISM IN ALKENES

<u>Two</u> types of isomerism to consider in alkenes:

- Constitutional isomerism
- Cis–trans isomerism

3.1 Constitutional isomerism

Isomers that have the same molecular formula but different structural formulae.

Constitutional isomerism in alkenes can arise:

- due to different positions of the C=C double bond in the carbon chain

E.g.

but-1-ene	CH ₂ =CHCH ₂ CH ₃	
but–2–ene	CH ₃ CH=CHCH ₃	

- due to different degree of branching in the carbon chain

E.g.



is a constitutional isomer of but-1-ene and but-2-ene.

3.2 Cis-trans isomerism

Isomers that have the same molecular and structural formula but different spatial arrangements due to the *restricted rotation about a bond*.

Cis–trans isomerism exists in alkenes as a result of the <u>restricted rotation about a C=C double</u> bond due to the presence of π bonds.



- (i) Presence of C=C double bond to prevent free rotation about the double bond
- (ii) Have two different groups / atoms attached to each C atom of the C=C double bond





Exercise 3.1

Which of the following cannot exhibit cis-trans isomerism?



Н

Br

4 PHYSICAL PROPERTIES (Recall and apply Chemical Bonding concepts here)

4.1 Boiling point/volatility

1. Boiling point increases as the number of carbon atoms increases (as with alkanes)

Chain length of alkene	Physical state at room temperature
C2 – C4	gas
C5 – C15	liquid
> C15	waxy solid

Example

Name	Molecular formula	Boiling point / °C	
ethene	C_2H_4	-102	
propene	C_3H_6	-48	
but–1–ene	C_4H_8	-6.5	
pent–1–ene	C_5H_{10}	30	

- As the **size of electron cloud increases**, the ease of distortion of the electron cloud increases.
- This results in stronger instantaneous dipole–induced dipole (id–id) attractions between the alkene molecules.
- Hence, **more energy** is required to overcome the stronger id–id attractions between the molecules.
- 2. For the same molecular formula, branched chain alkenes have lower boiling points than their corresponding straight chain alkenes (as with alkanes).

Example

Alkene	Structural formula	Boiling Point
pent-1-ene	$CH_3CH_2CH_2CH=CH_2$	30 [°] C
3–methylbut–1–ene	$CH_3 \\ CH_3 - C - CH = CH_2 \\ H \\ H$	25 °C

- Pent-1-ene is an **elongated** molecule which provides a **greater surface area** of contact compared to the more **compact (or spherical)** 3-methylbut-1-ene molecule.
- This leads to stronger instantaneous dipole–induced dipole (id–id) attractions between pent–1–ene molecules.
- Hence, **more energy** is required to overcome the stronger id–id attractions between pent–1–ene molecules.

3. <u>Cis-isomers generally have higher boiling points than trans-isomers</u>

Example			
Isomer	CI CI CI CI H	CI CI H CI	
	cis-1,2-dichloroethene	trans-1,2-dichloroethene	
Boiling point/°C	60	48	
Polarity of molecule	The <i>cis</i> isomer is a polar molecule. The C–C <i>l</i> bond is polar and the dipoles of the 2 C–C <i>l</i> bonds in the <i>cis</i> isomer <u>do not cancel each other</u> , the molecule has a <u>net dipole</u> moment.	The <i>trans</i> isomer is a non–polar molecule. The dipoles of the 2 C–C <i>l</i> bonds in the <i>trans</i> isomer <u>cancel each other</u> , the molecule has <u>no net dipole</u> moment.	
Comparing strength of intermolecular forces of attraction	More energy is needed to overcome stronger permanent dipole-permanent dipole attractions between molecules of the polar <i>cis</i> isomer than to overcome the weaker instantaneous dipole-induced dipole attractions between molecules of the non-polar <i>trans</i> isomer.		

FYI:

Trans–isomers generally have higher melting point due to better packing of molecules in the **solid state**. The trans–isomers **pack more efficiently / have closer packing** than the cis– isomers which results in **stronger instantaneous dipole–induced dipole (id–id) attractions between molecules**. Hence, more energy is required to break the stronger id–id attractions between the molecules.

4.2 Solubility

Unsubstituted alkenes, being non-polar, are **insoluble** in water and other highly polar solvents.

This is because the energy **released** during the **formation** of instantaneous dipole–induced dipole (id–id) attractions between the alkene and water molecules is unable to compensate for the energy **absorbed** to **break** the **id–id attractions** between alkene molecules and the **hydrogen bonding** between water molecules during hydration.

On the other hand, alkenes are more soluble in non-polar solvents, e.g. benzene, hexane, CCl_4 .

5 PREPARATION OF ALKENES

Alkenes can be obtained from three main groups of organic compounds, namely, alkanes, alcohols and halogenoalkanes.

5.1 Cracking of alkanes (Refer to 'Alkanes' Lecture Notes for more details)

- 1. Thermal cracking
 - Conditions: heat with steam at high temperature and pressure
 - E.g. C₁₂H₂₆ → CH₃CH₂CH₂CH₂CH₃ + 3 CH₂=CH₂ dodecane hexane ethene
- 2. Catalytic cracking
 - Catalyst: zeolites (mixture of Al₂O₃ and SiO₂).
 - Conditions: high temperature and pressure
 - E.g. $C_{12}H_{26}$ dodecane $CH_3 CH_3$ | | + $CH_3CH_2CH=CH_2$ $CH_3CHCH_2CH_2CHCH_3$ but-1-ene

branched chain C₈H₁₈

5.2 Elimination

A type of reaction which involves the removal of atoms or group of atoms from two adjacent carbon atoms to form a carbon-carbon double bond in the product



5.2.1 Elimination of water (H₂O) from alcohols

A hydrogen atom and a hydroxyl group, –OH, from **adjacent** carbon atoms in an alcohol molecule are eliminated as a molecule of water.



Type of reaction	Reagents	Conditions
Elimination	Excess conc. H ₂ SO ₄	heat under reflux
Elimination	Conc. H ₃ PO ₄	heat under reflux
Elimination	Al_2O_3	heat under reflux for industrial process

Example

$$\begin{array}{cccc} H & H & H \\ H & - C & - C & - C & - H \\ H & OH & H \end{array} \xrightarrow{excess conc. H_2SO_4} H & H & H \\ \begin{array}{c} H & H & H \\ - C & - C & - C & - H \\ H & OH & H \end{array} \xrightarrow{excess conc. H_2SO_4} H & - C & - C & - H \\ \begin{array}{c} H & H & H \\ - & H & - H \\ - & H & - C & - C & - H \\ - & H & H \\ \end{array} \xrightarrow{H} H & - H & - H \\ \begin{array}{c} H & H & H \\ - & H & - H \\ - & H \\$$

Saytzeff's Rule

To predict major/minor alkene product from elimination reaction

- When an unsymmetrical alcohol or halogenoalkane undergoes elimination reaction, a mixture of alkenes is formed as there is more than one possible site for elimination.
- These alkenes formed can be <u>constitutional</u> or <u>cis-trans</u> isomers of each other.
- However, the alkene products are not formed in equal proportions a more stable alkene is formed in larger proportions (the major product), and the less stable alkene is the minor product.
- According to **Saytzeff's Rule**, the <u>most substituted alkene</u> (the alkene with the <u>most number</u> <u>of alkyl (R) groups</u> attached to the C=C double bond) will be the <u>most stable product</u> and is thus the <u>major product</u>.



Example

Elimination of butan–2–ol gives more than one alkene. *Saytzeff's Rule* is applied to determine the major product(s).



<u>3 different alkenes</u> are formed.

Major:

Minor:

5.2.2 Elimination of hydrogen halide (HX) from halogenoalkanes

A hydrogen atom and a halogen atom, -X, from **adjacent** carbon atoms in a halogenoalkane molecule are eliminated as a molecule of hydrogen halide, HX.



Type of reaction	Reagents	Conditions	This reagent is also referred to as
Elimination	KOH in ethanol	heat under reflux	hot ethanolic KOH.

Elimination of unsymmetrical halogenoalkanes may give more than one alkene. *Saytzeff's Rule* is applied to determine the major product(s).

Example

Elimination of 2-chloropentane gives more than one alkene.



3 different alkenes are formed.

Major:	
Minor:	

Exercise 5.1

Which of the following isomers of $C_5H_{11}OH$ gives, on dehydration, the greatest number of different alkenes?



What is meant by 'heat under reflux'?

Heating under reflux is carried out with a condenser connected vertically to the reaction flask. Cooling water is circulated in the outer jacket of the condenser and the vapour formed will be condensed back into the reaction flask as shown in the diagram below.

Why is reflux condition necessary?

Organic reactions are usually slow and heating is often required for the reaction to proceed. Since organic reactants / solvents are highly volatile, the reflux set–up will <u>prevent volatile components of the reaction mixture from boiling off</u>, and hence achieving maximum yield.



6 CHEMICAL PROPERTY

Which classes of reagents do alkenes react with and why? What types of reactions do alkenes undergo and why?

The C=C double bond in alkene is **electron rich** due to the presence of the π electron cloud.

The π electrons provide the reactive site which attracts **electrophiles** or **electrophilic reagents** (electron–deficient species). Thus, alkenes have greater chemical reactivity compared to the corresponding alkanes.



Due to the relatively strong C–H and C–C bonds present in the alkene molecules, the reaction that alkenes undergo is mainly **addition** in nature, which involves the **breaking of the weaker** π **bond**.

Hence, the main type of reaction that alkenes undergo is **ELECTROPHILIC ADDITION**.

6.1 Electrophilic Addition

An addition reaction is a reaction in which two molecules combine to form a single molecule.

Electrophilic addition is an addition reaction in which *an electron–rich molecule donates a pair* of electrons to an electrophile.

Electrophile – a <u>cation</u> or <u>electrically neutral molecule</u> which <u>has</u> an <u>electron-deficient</u> <u>atom</u> (i.e. molecule has an atom with a δ + charge). Electrophiles are 'electron-lovers' and they tend to be attacked by electron-rich regions of organic molecules such as double bonds. They are also known as *Lewis acid* (electron-pair acceptor).

In the <u>electrophilic addition</u> of an alkene, an electrophile is attracted to the C=C bond. The alkene molecule donates a pair of electrons from the π bond to the electrophile and breaks the π bond in the process.



electrophilic reagent is attracted to the $\boldsymbol{\pi}$ bond of alkene molecule

A <u>saturated</u> organic compound (C–C) is thus formed when 'atoms' or 'groups of atoms' are added across the C=C bond of the alkene molecule.



The detailed mechanism for electrophilic addition reaction will be discussed on page 16.

7 REACTIONS OF ALKENES

7.1 Electrophilic Addition Reactions

Alkenes can undergo electrophilic addition with halogens, hydrogen halides or water/steam.

7.1.1 Electrophilic addition of halogen to alkenes

Type of reaction	Electrophilic addition	
Reagent	$Br_2(l)$ or $Br_2(g)$ in $CCl_4 / Cl_2(g)$ in CCl_4	
Condition	room temperature in the absence of light	Why must it be carried out
Observation	reddish brown Br ₂ or pale yellow C	
	decolourised	

Example

When ethene is bubbled into $\underline{Br_2(l)}$ at room temperature (in the dark), the **reddish brown** colour of Br_2 is rapidly <u>decolourised</u>.

 Br_2 is added across the C=C bond to give <u>1,2-dibromoethane</u>.



Application

The reaction of alkenes with $Br_2(l)$ is a <u>test for unsaturation</u>.

The rapid decolourisation of the reddish-brown $\underline{Br_2(l)}$ indicates the presence of C=C double bond.

The amount of Br₂ used is a measure of the number of C=C bonds in an alkene molecule.

One mole of Br₂ is added for each C=C bond present in the alkene.

Note: Cl_2 in CCl_4 is not used as a test for unsaturation as the colour of Cl_2 is difficult to observe.

Mechanism



How do alkenes react with electrophiles?

Notes on Reaction Mechanism

- The sequence of steps by which the reaction takes place is called the reaction mechanism.
- Describes which bonds are broken and formed, and when they are broken and formed.
- In mechanisms of organic reactions, a <u>full</u> curly arrow, is used to represent the <u>movement of a pair of electrons</u>. The arrow tail is where the electron pair originates from and the arrow head is where the electron pair ends up. Electrons usually move from a nucleophile to an electrophile.

Note: Nucleophile ('nucleus-loving' particle)

- A nucleophile is an electron–pair donor.
- It is an anion or a neutral compound with a lone pair of electrons and attacks regions of <u>low electron density</u> (δ+ end of a polar bond or centres of positive charge).
- Examples: :Br⁻, :OH⁻, :CN⁻, NH₃, H₂O

Describe the mechanism of the reaction: $CH_2=CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$



What is the electrophile in the reaction?

Partially positive (δ +) bromine of the polarised Br₂ molecule.

Explanation of the mechanism in words (NOT REQUIRED):

Step 1 (slow)

- When the bromine molecule approaches the alkene, the Br–Br bond is <u>polarised</u> by the π electron cloud of the C=C double bond (i.e. the negatively–charged π electron cloud induces a temporary dipole in the non–polar Br–Br bond.)
- The positive end of the polarised Br–Br acts as an electrophile and is attracted towards the C=C double bond.
- As a pair of electrons from the electron–rich C=C moves to the electrophilic $Br^{\delta+}$ (as shown by the curly arrow), the π bond is broken and the pair of electrons is now shared between the carbon and the bromine atom.
- The adjacent carbon atom becomes positively charged, thus forming a carbocation intermediate.
- Heterolytic fission of the Br–Br bond results in the formation of a Br[–] (bromide) ion.

Step 2 (fast)

• The bromide ion (acting as a nucleophile) attacks the intermediate carbocation to give the final product 1,2–dibromoethane.

Important Note:

- Explanation of the mechanism in words is **NOT** required in the exams.
- When a question asks to 'describe the mechanism' of a reaction, you will need to:
 - > Write the name of the mechanism, e.g. electrophilic addition
 - Show the elementary steps in the mechanism, and label 'slow'/'fast' steps, if applicable
 - Use curly arrows to clearly illustrate the movement of electrons, e.g. full-headed arrows drawn from electron pair donor to electron pair acceptor
 - > Show partial charges, lone pair on relevant particles e.g. nucleophiles
 - > Draw the structural formula of any intermediate and product(s) formed

7.1.2 Electrophilic addition of aqueous bromine to alkenes

Type of reaction	Electrophilic addition	
Reagent	Br₂(aq)	
Condition	room temperature in the absence of light	
Observation	orange Br ₂ (aq) decolourised	

Example

When ethene is bubbled into <u>aqueous Br_2 </u> at room temperature (in the dark), the <u>orange</u> colour of $Br_2(aq)$ is rapidly decolourised.

<u>Two products</u> are obtained: 1,2–dibromoethane and 2–bromoethanol. (Note: In the reaction with <u>liquid or gaseous</u> Br₂, only 1 product – 1,2–dibromoethane – is formed)

Why is a *mixture* of products formed?

- As observed from the electrophilic addition mechanism, a carbocation intermediate is formed in Step 1 (slow step).
- The carbocation, being electron–deficient, will react with any electron–pair donor species (also called 'nucleophiles' e.g. H₂O, OH⁻, Br⁻ and Cl⁻) present in the reaction mixture.
- In this example, the electron-pair donor, the H₂O molecule, can compete with the Br⁻ (formed in Step 1) to react with the carbocation intermediate.
- Hence, if more than one electron-pair donor is present, a mixture of products are formed in Step 2 of the mechanism (fast step).



As H₂O molecules are present in much larger quantity, the chances of the carbocation reacting with H₂O are much higher. Hence, a greater proportion of 2–bromoethanol is formed.

Exercise 7.1

Reaction of ethene with bromine in the presence of aqueous sodium chloride gives a mixture of products.

Which pair of products will be included in this mixture?

$CH_2Br - CH_2Br$	$CH_2Cl - CH_2Cl$
$CH_2Br - CH_2Br$	$CH_2Cl - CH_2Br$
$CH_2Br - CH_2Br$	$CH_2(OH) - CH_2Cl$
$CH_2(OH) - CH_2Br$	$CH_2Cl - CH_2OH$
	$\begin{array}{l} CH_2Br-CH_2Br\\ CH_2Br-CH_2Br\\ CH_2Br-CH_2Br\\ CH_2(OH)-CH_2Br \end{array}$

7.1.3 Electrophilic addition of hydrogen halides, HX to alkenes





What is the major product obtained when an unsymmetrical alkene reacts with hydrogen halide and why?

Markovnikov's rule To predict major/minor product from electrophilic addition reaction of alkene

When HX is added to an unsymmetrical alkene (with different R groups attached to the double bond carbons), two products are possible.

According to Markovnikov's rule, the major product is the one in which the H atom adds to the carbon of the double bond having the <u>greater</u> number of hydrogen atoms bonded to it; the halogen atom (X) adds to the other carbon.

Example

Electrophilic addition of HC*l* to propene gives two products. Markovnikov's rule is applied to determine the major product.



Explanation to Markovnikov's rule

- The rule can be explained by comparing the <u>stability of carbocation intermediates</u> formed during the electrophilic addition of an unsymmetrical molecule to an unsymmetrical alkene.
- Alkyl (R/R') groups are <u>electron-donating</u> groups, which help to <u>disperse</u> the <u>positive</u> <u>charge</u> on the carbocation, hence <u>stabilising</u> it. (Refer to Section 9 on Electronic Effect)
- Therefore, the <u>carbocation with more electron-donating alkyl groups</u> bonded to the electron-deficient carbon can <u>disperse the positive charge to a greater extent</u> and will have a <u>greater stability</u>.
- The stability of carbocations follows the order:



most stable

• The more stable carbocation will be formed at a faster rate. Hence, more of the carbocation with the greater stability will be available for reaction and more product will be formed from it.

Example

In the electrophilic addition of HC*l* to propene, electrons move from the π electron cloud of propene to the electrophilic H^{δ+} end of the polar HC*l* molecule. Two possible carbocations are generated as shown.



The secondary carbocation has <u>more electron–donating alkyl groups</u> attached to the C⁺ which <u>disperses</u> the <u>positive charge</u> on the <u>carbocation</u> to a <u>greater extent</u> and gives rise to a <u>more</u> <u>stable carbocation</u> intermediate.

Subsequently, more of the secondary carbocation is attacked by C*l*⁻ nucleophile in the fast step to form the major product, 2–chloropropane.

Exercise 7.2

(a) In the reaction between but-1-ene and hydrogen bromide, there are 2 possible carbocation intermediates formed in the slow step. Draw the 2 carbocation intermediates, explain why one of them is more stable than the other.



as it has ______ alkyl groups attached to the C⁺ which ______ the _____ charge on the carbocation to a ______ and gives rise to a more stable carbocation intermediate.

(b) Give the structural formulae of the major and minor products formed when each of the following alkenes is reacted with hydrogen bromide gas at room temperature.

Alkene	Major product	Minor product
but–1–ene		
Н Н СН ₃ СН ₂ —С—С—Н		
2-methylbut-2-ene		
$CH_3 CH_3 $		

(c) Explain why the product mixture formed in the reaction between but-1-ene and hydrogen bromide is optically inactive? *Hint: refer to your answer in (a) to help you.*

A ______ is formed. The carbocation intermediate in (a) is ______ about the ______ which allows an ______ probability of attack by the bromide ion from either side of the plane, resulting in a 50:50 mixture of a pair of enantiomers being formed.



Exercise 7.3

Suggest the structure of the product formed when ICl is reacted with propene.

Hints:

- 1) IC*l* is a polar molecule
- 2) Decide which element in ICl is less electronegative
- 3) Recall that the electrophilic end of ICl is attracted to the π electron cloud of the C=C

4) Use Markovnikov's rule to determine the more stable carbocation intermediate and hence the major product





<u>Type</u> of reaction Electrophilic addition

Industrial method

Reagent	steam, with concentrated phosphoric acid, H ₃ PO ₄ , as catalyst
Condition	heat under reflux at high pressure

Laboratory method

Store 1	Reagent	concentrated H ₂ SO ₄
Slage	Condition	cold
Stage 2	Reagent	water
	Condition	warm

Hydration of unsymmetrical alkenes follows Markovnikov's rule.

Exercise 7.4

What is the product obtained when the following alkene undergoes hydration?



7.2 Oxidation

Unlike alkanes, alkenes undergo oxidation easily.

Alkenes are oxidised **only** by potassium manganate(VII), KMnO₄, a strong oxidising agent. The type of organic products formed depends on the temperature at which the oxidation is carried out.

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Oxidation of alkenes can take place:

- without cleavage (rupture) of the C=C bond (mild oxidation) or
- with cleavage of the C=C bond (strong oxidation / oxidative cleavage) •

7.2.1 Mild oxidation

This oxidation involves breaking of the π bond in the alkene to form a diol.

Equation to represent the oxidation:

Type of reaction	Mild oxidation	Mild oxidation	· · · · ·
Reagent	KMnO₄ in NaOH(aq) or KOH(aq)	KMnO ₄ in dilute H ₂ SO ₄	This reagent is also commonly referred to as cold alkaline /
Condition	cold	cold	
Observation	 The <u>purple</u> KMnO₄ solution is <u>decolourised</u>. <u>Brown ppt</u> of MnO₂ is formed (as MnO₄⁻ is reduced to MnO₂ in alkaline medium) 	 The <u>purple</u> KMnO₄ solution is <u>decolourised</u> (as MnO₄⁻ is reduced to Mn²⁺ in acidic medium) 	

Application

This is another useful test for unsaturation; i.e. to detect the presence of a C=C double bond.

Example

When reacted with cold KMnO₄(aq) in NaOH(aq), ethene is oxidised to give ethane-1,2-diol



7.2.2 Strong oxidation (also called oxidative cleavage)

This oxidation is more vigorous as it involves the cleavage of C=C bond; i.e. the double bond is completely broken.

<u>Type</u> of reaction	Strong oxidation / oxidative cleavage	Strong oxidation / oxidative cleavage	
Reagent	KMnO₄ in NaOH(aq) or KOH(aq)	KMnO ₄ in dilute H ₂ SO ₄	This reagent is
Condition	heat under reflux	heat under reflux	also commonly referred to as
Observation	 The <u>purple KMnO₄ solution</u> is decolourised. <u>Brown ppt</u> of MnO₂ formed (as MnO₄⁻ is reduced to MnO₂ in alkaline medium) 	 The <u>purple KMnO₄</u> <u>solution is decolourised</u>. (as MnO₄⁻ is reduced to Mn²⁺ in acidic medium) 	hot concentrated KMnO ₄ .

The types of products obtained <u>depend on the structure of the alkene</u> (i.e. the number of H atoms bonded to the double bond carbon atoms, C=C.)

Case	Structure of alkene	Final products of strong oxidation
1	H C H	CO2 + H2O
2	R C H	R C==0 HO carboxylic acid
3	R C	R C==0 R' ketone

Detailed explanation for each case in oxidative cleavage





Example 1

Carbon dioxide and water are formed when ethene is heated with acidified KMnO₄.



Example 2

A carboxylic acid and a ketone are formed when 3–methylpent–2–ene is heated with KMnO₄ in dilute H_2SO_4 .



Exercise 7.5

When an alkene reacts with an excess of hot acidified potassium manganate(VII), the carbon-to-carbon double bond is broken and the terminal carbon atoms are oxidised to the maximum extent possible without breaking a carbon-to-carbon single bond. Thus, propene undergoes the following reaction.



Predict the carbon–containing products obtained by subjecting each of the following alkenes to the above conditions:

	Reactants	Products
(i)	CH ₃ CH ₂ CH=CH ₂	
(ii)	(CH ₃) ₂ C=CH ₂	

Each of the above two alkenes is treated with *cold* acidified potassium manganate(VII).

Draw the structure of the organic product formed in each case and identify on your formulae any chiral carbon atoms.

	Reactants	Products
(i)	CH ₃ CH ₂ CH=CH ₂	
(ii)	(CH ₃) ₂ C=CH ₂	

Exercise 7.6

Predict the product(s) formed when the following compounds are treated with excess hot acidified KMnO₄.



Note:

Ethanedioic acid (HOOC–COOH) and **methanoic acid (HCOOH)** will give CO₂ and H₂O upon further oxidation.

	KMnO4, H2SO4		KMnO ₄ , H ₂ SO ₄	0
но-с-с-он	heat	- CO ₂ + H ₂ O	heat	Н—Ё—ОН

Application of oxidative cleavage

- Analysis of the different product fragments upon cleavage of an unknown alkene allows us to <u>determine the position of the double bond(s) in the alkene</u> as well as the alkyl groups bonded to the carbon in the double bond.
- Since the overall reaction simply cleaves the molecule at the C=C double bond, the parent alkene can be reconstructed by
 - recombining the ketone and/or carboxylic acid fragments
 - constructing a terminal double bond (=CH₂) if CO₂ + H₂O are formed as products

Steps to deduce structure of the alkene

From the product fragments (ketone and/or carboxylic acid):

- remove O from –OH bonded to each C=
- remove O from each C=
- recombine the resulting fragments at C= to form C=C

<u>Example</u>

Deduce the structural formula of an alkene, C_5H_{10} , which upon strong oxidation yields equimolar mixture of propanone and ethanoic acid.



Structure of alkene:

Some pointers on oxidation of alkenes:		
HOT vs COLD	Determines strong or mild oxidation	
ALKALINE vs ACIDIC	Determines observations and type of Mn products	
	formed	

When <u>conc.</u> KMnO₄ is mentioned, strong oxidation will occur!

Note: K₂Cr₂O₇ CANNOT oxidise the strong C=C bond!!!

7.3 Reduction via Catalytic Hydrogenation



Type of reaction	Reduction	Reduction
Descent	H ₂ gas,	H ₂ gas,
Reagent	catalyst	catalyst
Condition	heat	room temperature and
		pressure

This reaction is an example of **reduction** using <u>heterogeneous</u> catalysis (**NOT** electrophilic addition).

One industrial example of this heterogeneous catalysis reaction is the production of margarine, where polyunsaturated plant oils are hydrogenated.

Application

This reaction is useful in <u>determining the number of C=C double bonds</u> in an organic compound by measuring the amount of hydrogen that reacted with one mole of the compound.

<u>One mole</u> of H_2 reacts with <u>each</u> C=C bond present in the alkene.

8 SUMMARY OF CHEMICAL TESTS FOR ALKENES

The following reactions covered in the earlier sections may be used as **tests for unsaturation** because they give rise to easily observable colour changes:

Reagent	Conditions	Observations if alkene is present
Br ₂ (g) in CCl ₄ or Br ₂ (l)	room temperature, absence of light	The reddish-brown Br2 is rapidly decolourised.
Br ₂ (aq) or bromine water	room temperature, absence of light	The orange Br_2 is rapidly decolourised.
KMnO ₄ in dil. H ₂ SO ₄	cold	The purple KMnO₄ solution is decolourised.
KMnO₄ in KOH(aq)	cold	The purple KMnO ₄ solution is decolourised with the formation of brown precipitate of MnO ₂ .
KMnO4 in dil. H2SO4	heat	The purple KMnO₄ solution is decolourised.
KMnO₄ in KOH (aq)	heat	The purple KMnO ₄ solution is decolourised with the formation of brown precipitate of MnO ₂ .

9 Electronic effect (Inductive effect)

Electronic effect is mainly due to the presence of polar bonds and as a result, there are two possible inductive effects: **electron–donating** and **electron–withdrawing**.

An inductive effect is the <u>shifting of electrons</u> in a σ <u>bond</u> in response to the <u>electronegativity of nearby atoms</u>. Inductive effects play a major role in understanding chemical reactivity of organic compounds.

An atom like fluorine has an <u>electron–withdrawing effect</u> as it can pull the bonding pair away from the atom it is attached to. Most atoms that you will come across have an electron–withdrawing effect when they are attached to a carbon atom, because they are mostly more electronegative than carbon.

However, some groups of atoms have an <u>electron–donating effect</u> and "push" electrons towards the carbon they are attached to, making it slightly negative. Metals, such as lithium and magnesium, inductively donate electrons.

A simple example can be illustrated using the polar covalent bond: H-Cl. Due to the large electronegativity difference between H and Cl, the H atom will possess the δ + charge while Cl atom the δ - charge. The ability of a bond to be polarised is often termed as the "inductive effect".

Inductive effect	Examples			
	Electronegative	atoms	and	groups
	(e.g. halogens, groups)	carbonyl groups	and cyano	(–CN)
vvitndrawing				
		— <u>C</u> →-X		
	Alkyl groups (e.g. –CH ₃ , –CH ₂ CH ₃ etc.)			
Donating		CCH₃		
Note: C is slightly more electron			negative thar	ηΗ

REVIEW CHECKLIST

Concepts	Tick in this box if you are	Questions that you want
Lean describe and symptoin the	able to do so 😊	to clarity
 can describe and explain the physical properties of alkenes with respect to their: Boiling point and volatility Solubility Boiling point for <i>cis</i>-<i>trans</i> isomers 		
 I am able to recall the reagents and conditions for the following types of reaction involving alkenes: EA of X₂ EA of HX EA of H₂O Mild Oxidation Vigorous (Strong) Oxidation Reduction 		
I can describe the EA mechanism.		
Checkpoint: Describe the mechanism when chlorine gas reacts with ethene in the dark.		
I am able to apply Markovnikov's rule to identify the major and minor products of an EA for an unsymmetrical alkene.		
Checkpoint: Draw the major and minor products formed when but–1–ene reacts with HBr(g).		
I am able to draw the products formed when alkenes undergo strong oxidation.		
I am able to determine the original structure of the alkene given its oxidation products.		
 I am able to recall the reagents and conditions of the following reactions to prepare alkenes: Dehydration of alcohols Dehydrohalogenation of halogenoalkanes 		

I am able to apply Saytzeff's rule to identify the major and minor products of an elimination of a secondary and tertiary alcohol / halogenoalkane.	
Checkpoint: Draw the major and minor products formed when butan–2–ol and 2–bromobutane undergoes elimination.	

2024 JC1 H2 Alkenes