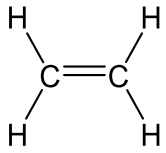
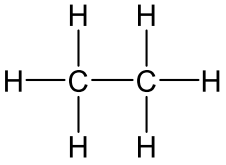
4.1 INTRODUCTION

Alkenes form a homologous series of aliphatic hydrocarbons with the **carbon-carbon double bond** as the distinguishing feature. Alkenes with one C=C bond present in the structure have the general formula, C_nH_{2n}.

Because of its carbon-carbon double bond, an alkene is thus referred to as an **unsaturated hydrocarbon**.



Ethene (C_2H_4)
(presence of C=C) – *unsaturated*)



Ethane (C_2H_6)
(all C-C single bonds – *saturated*)

4.1.1 Nomenclature of Alkenes

Success criteria:
I can deduce the structure of an alkene from its given IUPAC name (and vice versa).

Every name of organic compounds consists of
Prefix — Parent — Suffix

Alkenes have the suffix ***–ene*** to **identify the C=C bond** functional group present in them. When the alkene contains two or three C=C double bonds, it is known as ***di-ene*** and ***tri-ene*** respectively.

- Number the chain from the end closest to the double bonds.
- Lowest number assigned to C=C when it is part of **cyclic ring**.

Cis-trans isomers of alkenes to be distinguished by using the prefix *cis-* or *trans-*.

Checkpoint 1

Give the structural formulae for the following compounds:

(a)	**(b)**
trans-pent-2-ene	2-chloro-3-methylpenta-1,4-diene

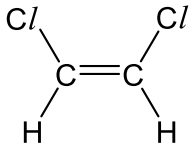
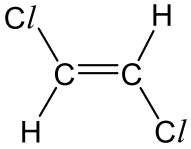
4.2 PHYSICAL PROPERTIES OF ALKENES

Success criteria:
• I can explain the difference in boiling point and melting point between cis and trans isomers.

Similar to alkanes

- Insoluble in water and soluble in non-polar (organic) solvents
- Less dense than water
- Boiling point increases with increasing carbon number
- Branching lowers boiling point

Comparing *cis*- vs *trans*- isomers of 1,2-dichloroethene

	cis-1,2-dichloroethene	*trans*-1,2-dichloroethene
Structural formula		
Boiling point / ºC	60.3	47.5
Melting point / ºC	–81	–49

Explanation of the difference in boiling points between cis-1,2-dichloroethene and trans-1,2-dichloroethene:

Cis-1,2-dichloroethene molecules are polar and has permanent dipole-permanent dipole attractions between the molecules which is stronger than instantaneous dipole-induced dipole attractions between trans-1,2-dichloroethene molecules. Stronger intermolecular forces require more energy to overcome.

Explanation of the difference in melting points between cis-1,2-dichloroethene and trans-1,2-dichloroethene:

FYI:
Crystal lattice: the 3D structural arrangement of atoms, ions or molecules in a crystalline material

Trans-isomers **pack better** into a crystal lattice, leading to more intermolecular forces per unit volume. They generally will have higher melting points than their respective *cis*-isomers.

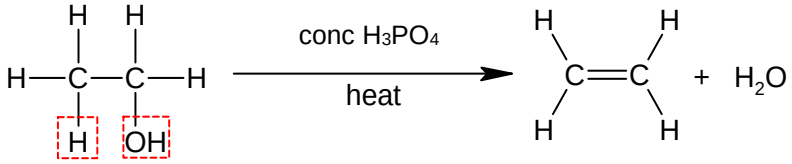
4.3 PREPARATION OF ALKENES

Success criteria:

• I can state the reagents and conditions to convert
  ○ alcohol to alkene
  ○ halogenoalkane to alkene
• I recognize that elimination of H−X from halogenoalkanes and H−OH from alcohol is only possible between two adjacent carbon atoms.
• I can give the structure of the alkene formed from the elimination reaction.

4.3.1 Elimination Reactions

(i) Elimination of water from alcohols

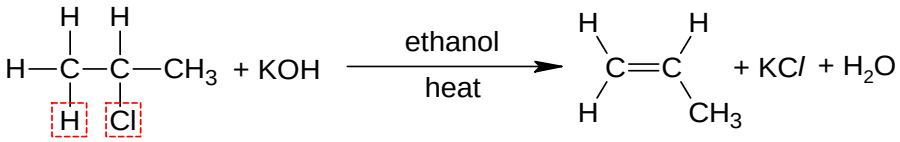


Type of reaction	Elimination
Reagent and condition	concentrated H_3PO_4, heat or Al_2O_3(s), heat (or excess conc. H_2SO_4, heat)

(ii) Elimination of HX from halogenoalkanes

Note: Elimination reaction will cause the degree of unsaturation (no. of π bond) in the product to increase by 1

Note: HC*l* eliminated undergoes acid-base reaction with KOH to form KC*l* and H_2O



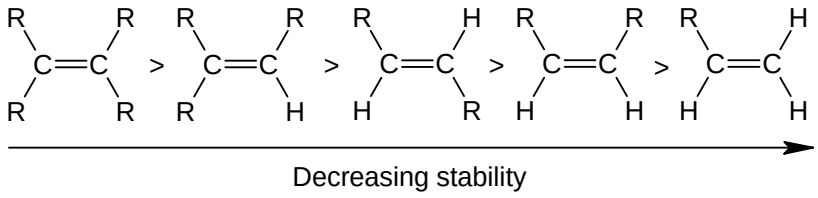
Type of reaction	Elimination
Reagent and condition	ethanolic KOH/NaOH, heat

NOTE:
When group of atoms such as H & C*l* or H & OH are **eliminated** from **different pairs of adjacent carbons**, a mixture of alkene isomers is produced. The relative proportion of each alkene will depend on ***Zaitsev's Rule.***

Explanation:
Btw *cis*- and *trans*-alkenes, bulky groups like alkyl groups are best placed far apart from each other to reduce steric strain. Thus, the *trans*-isomer is more stable and formed in greater quantity.

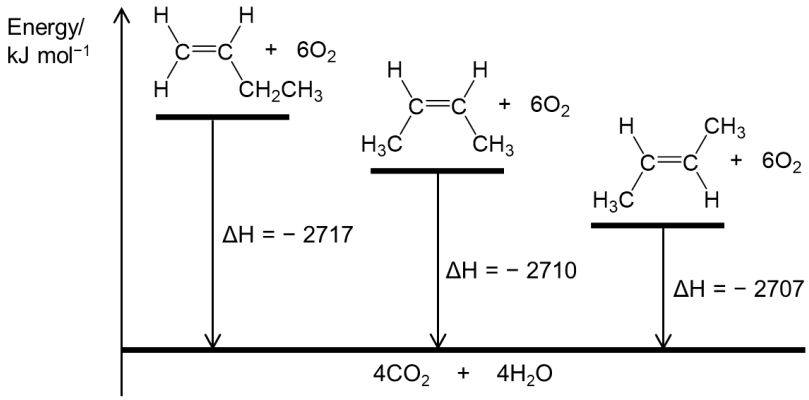
Zaitsev's Rule **(for your info)**

The more highly substituted alkenes are more stable and hence more readily formed in an elimination reaction.



Experimental Evidence (For your info)

The relative chemical stability of the isomers of an alkene can be easily measured by determining their heats of combustion.



The exothermic combustion reaction converts **isomers of butene** to **same set of oxidised products**; carbon dioxide and water.

Differences in chemical stabilities of the isomers of butene result in different amounts of energy released during combustion. The more stable the isomer, the less exothermic is its combustion reaction.

Checkpoint 2

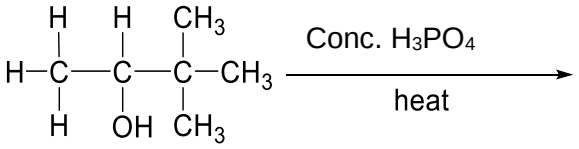
Consider the following molecules. Give the structures of the possible products formed when each undergoes elimination.

Identify the major product, where applicable.

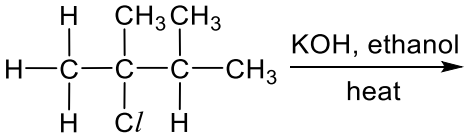
Note: KOH is a base which reacts away the acidic HC*l* molecule from the Halogenoalkane.

Conc H_2SO_4 is a dehydrating agent which can react H_2O away from the alcohol molecule.

(a)

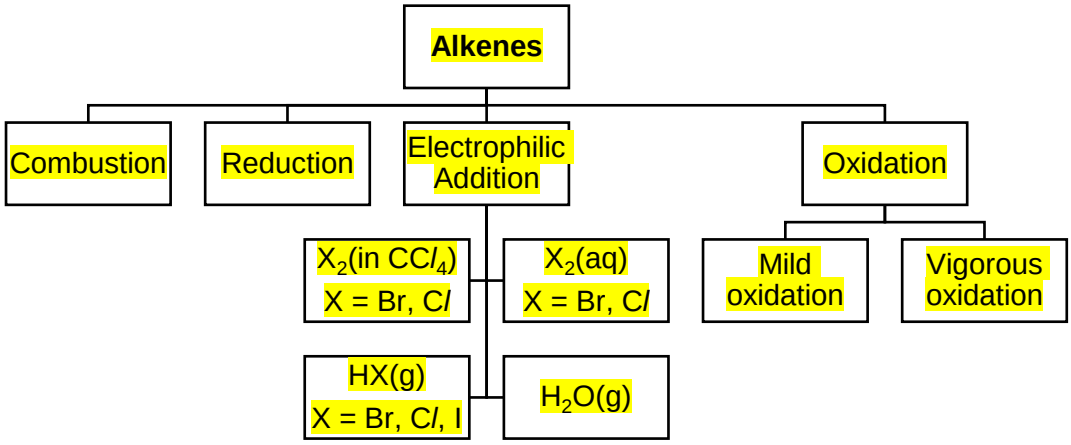


(b)



4.4 REACTIONS OF ALKENES

Success criteria:
• I can state the reagents and conditions for the reactions of alkenes. • I can deduce the structure of alkenes when the organic products and reagents and conditions are given. • I can write balanced equations for the reactions.

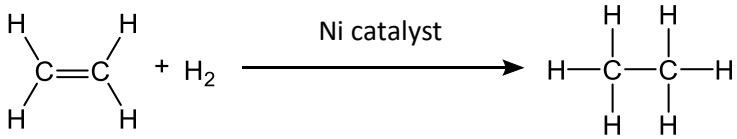


4.4.1 Combustion

Alkenes, being hydrocarbons, undergo complete combustion in excess oxygen to form carbon dioxide and water.

$$C_2H_4\,(g) + 3\,O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(l)$$

4.4.2 Reduction with hydrogen to form alkane



Type of reaction	Reduction
Reagent and condition	H_2(g), Ni(s) catalyst (Or H_2(g), Pt(s) catalyst)

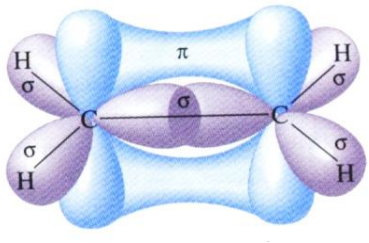
4.4.3 Electrophilic Addition Reactions

Success criteria:
• I can explain why alkenes are reactive towards electrophiles. • I understand why alkenes tend to undergo addition reactions.

(i) Reactivity of Alkene

The C=C bond in alkenes is made up of <u>one σ and one π bond</u>.

- **Sigma bond:** head-on overlap between two $2sp^2$ hybrid orbitals
- **Pi bond:** side-way overlap between two unhybridised 2p orbital



The structure of C=C results in the following reactivity:

- <u>Susceptible to Reactions with Electrophiles</u>

  The π electrons are found in the regions above and below the plane of the molecule. Being less tightly bound to the carbon nuclei, the presence of **π electrons causes a region of relatively high electron density at C=C**, thus alkene is more likely to **react with electrophiles** such as HBr and Br_2 molecules.

- <u>Tendency to Undergo Addition Reactions</u>

  In addition, **less energy** is required to **break** the **π bond** in the C=C bond as the side-way overlap of atomic orbitals is less effective than head-on overlap ones.

Recall:
C=C bond consist of a sigma bond (formed via head on overlap of hybrid orbitals) and **π bond** (formed via side-way overlap of unhybridised orbitals).

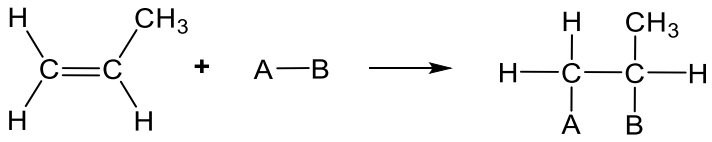
Type of Bond	C—C (σ)	C=C (σ + π)	C—C (π)
Bond Energy/ kJ mol^{-1}	350	610	260

Hence, **alkenes** tend to undergo reactions that **involve** the **breaking** of the weaker **π bond** in the C=C bond, leaving the σ bond intact.

The π electrons are used to form two new σ bonds with the electrophiles to form **one product**.

Note:
How to tell if a reaction is an addition reaction?

One clue is the reaction between 2 reactants (one unsaturated) to form 1 product.
2 Reactants → 1 Product



This reaction is called **<u>electrophilic addition</u>**.

(ii) General Mechanism of Electrophilic Addition

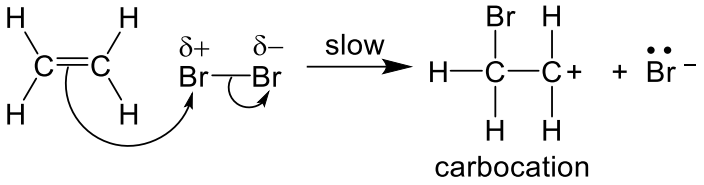
Success criteria:
• I can describe the electrophilic addition mechanism for alkenes using equations, curly arrows and charge when relevant. • I can deduce the structure of the major product from electrophilic addition of an alkene in a *polar* solvent. • I can describe the use of bromine to test for the presence of C=C functional group.

Alkenes tend to undergo **<u>electrophilic addition</u>** reactions.

Important Note:
(i) State the name of mechanism
(ii) Show separation of charges (δ+/δ−) on electrophile and charges on ions
(iii) Between 2 species: Arrows ALWAYS flow from ***electron rich region (π bond of C=C or lone pair of nucleophiles***) to electron deficient region (electrophile or carbocation) Bond breaking within a molecule will be from bond pair to δ− atom.
(iv) Indicate the slow step

***Name of Mechanism*: Electrophilic Addition**

Step 1:

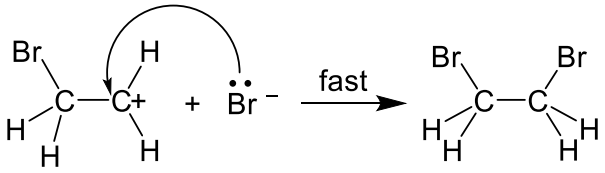


The loosely bound π electrons of the C=C bond is a region of high electron density.

As the bromine molecule approaches the ethene molecule, the <u>π electron cloud of the C=C induces a dipole in the bromine molecule</u> where a bromine atom attains a partial positive charge and <u>react with ethene as an electrophile</u> in the slow step.

The Br–Br bond undergoes **heterolytic** fission producing a <u>reactive carbocation intermediate</u> and a bromide ion.

Step 2:



The negatively charged bromide ion acts as a nucleophile and attacks the unstable positively charge carbocation, forming 1,2-dibromoethane.

Ponder…
1. *Carbocation is a reactive intermediate due to its instability Suggest why.*
2. *What can the carbocation react with to form a stable product based on the "principle of opposite charges attract"?*

(iii) Important Electrophilic Addition Reactions

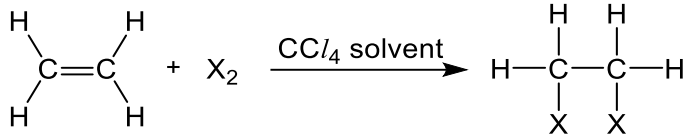
- **Electrophilic Addition of Halogen**

  Electrophilic addition with halogen (Br and C*l*) proceeds as per the general mechanism stated in **4.4.3(ii)**. However, solvents that are nucleophilic in nature (e.g. H_2O) may be involved in the fast step producing a mixture of products.

(a) Halogen dissolved in CC*l*$_4$ (an inert solvent)
(solvent DOES NOT participate in reaction)

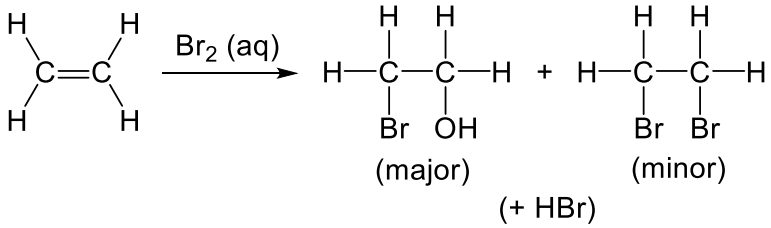
Note:
The rapid and obvious **decolourisation of Br_2** in the above two reactions **(a) and (b)** makes them useful laboratory tests for the presence of unsaturation (presence of C=C double bonds) in organic compounds.

The colours of Br_2 in different medium can be found in the *Data Booklet*. (One page before the Periodic Table)



Type of reaction	Electrophilic Addition
Reagent and condition	X_2 dissolved in CC*l*$_4$ solvent [X = Br or C*l*]
Observation	Orange-red Br_2 decolourised

(b) AQUEOUS Bromine (bromine water)
(solvent CAN participate in reaction)



Video on Br_2(aq) with alkene

https://tinyurl.com/bfnpxz9p

Type of reaction	Electrophilic Addition
Reagent and condition	Br_2(aq)
Observation	Orange Br_2 decolourised

Important points to note:

1. Why do both products have at least one Br attached?

In the 1st step, Br_2 is the only electrophile to react with ethene, hence the first σ bond formed will be with a Br atom.

2. Why are there two products formed?

In the 2nd step, solvent H_2O can also act as a nucleophile to react with the reactive carbocation forming bromoethanol.

Checkpoint 3

Using suitable curly arrows, complete the mechanism shown below to explain the formation of major and minor products when ethene reacts with aqueous bromine shown in **4.4.3(iii)(b)**.

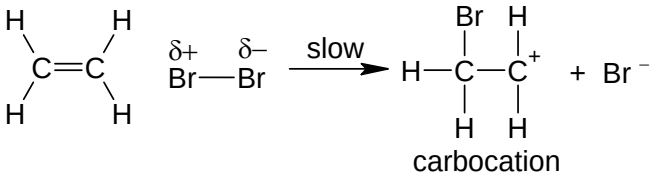
Important Note:
(i) State the name of mechanism

Mechanism:

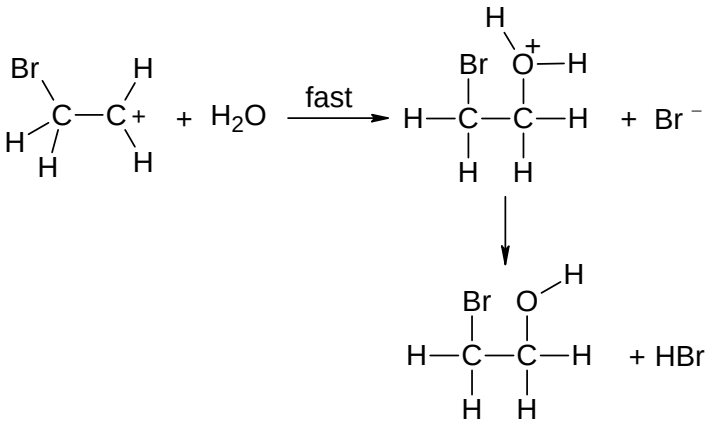
Formation of MAJOR Product

(ii) Show separation of charges (δ+/δ−) on electrophile and charges on ions
(iii) Between 2 species: Arrows ALWAYS flow from ***electron rich region (π bond of C=C or lone pair of nucleophiles***) to electron deficient region (electrophile or carbocation)
(iv) Bond breaking within a molecule will be from bond pair to δ− atom.
(v) Indicate the slow step

Step 1:

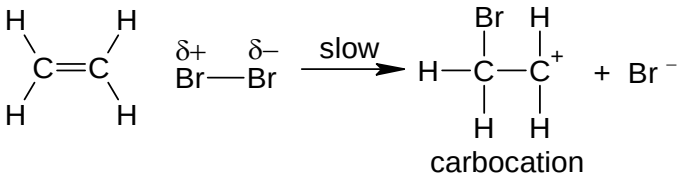


Step 2:

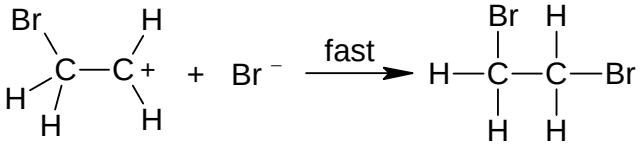


Formation of MINOR Product

Step 1:



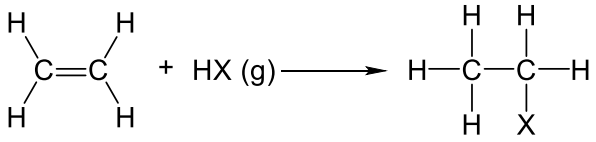
Step 2:



3. Why do you think the carbocation is more likely to react with H_2O: than $:Br^-$ to form the addition product?

The solvent H_2O is present in excess, hence it is more abundant as a nucleophile to react with the reactive carbocation.

- **Electrophilic Addition of Hydrogen Halides**



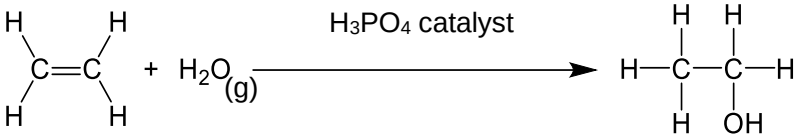
[X = Br or C*l* or I]

Type of reaction	Electrophilic Addition
Reagent and condition	Gaseous HX [X = Br or C*l* or I]

- **Catalytic hydration (Electrophilic Addition of Steam, $H_2O(g)$)**

Since H_2SO_4 is a stronger acid than H_2O, it will be the source of H^+ (electrophile).

The H_2O: will then behave as a nucleophile and react with the carbocation.



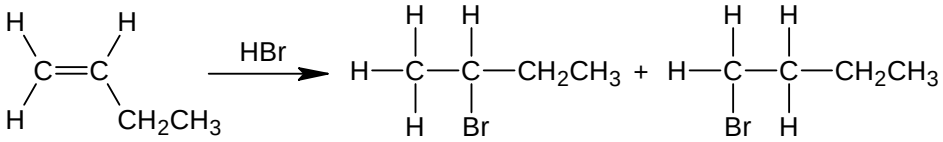
Type of reaction	Electrophilic Addition
Reagent and condition	$H_2O(g)$, H_3PO_4 catalyst (or Conc. H_2SO_4 at room temperature followed by H_2O (l), warm)

Success criteria:
• I can predict the major product from electrophilic addition of an *asymmetric* alkene. • I can explain how the major product is formed by considering the stability of carbocation. • I can understand why the product of electrophilic addition of alkene is optically inactive even if it contains a chiral carbon.

For electrophilic addition across asymmetrical alkenes, **Markovnikov's rule** is used to **predict** the major product formed.

NOTE:
When the atoms that react as the electrophile and nucleophile are different, electrophilic addition of an **asymmetrical alkene** will **yield a mixture of products,** with the major product predicted by **Markovnikov's rule**.

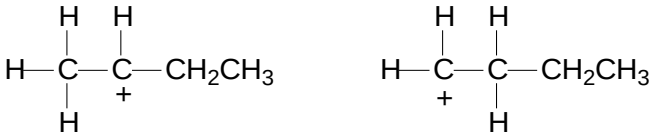
Example: The reaction between hydrogen bromide and but-1-ene will yield two different isomeric products:



asymmetrical alkene — 2-bromobutane (major) — 1-bromobutane (minor)

Why is 2-bromobutane the major product?

The C+ in the 2° carbocation stabilized to a larger extent due to 2 electron-donating alkyl groups. This more stable 2° carbocation is formed more abundantly in the rate-determining step, leading to a higher yield of the product.



2^o carbocation 1^o carbocation

Video on Markovnikov's Rule
Time: 0:30 – 2:38

https://tinyurl.com/dukz7n43

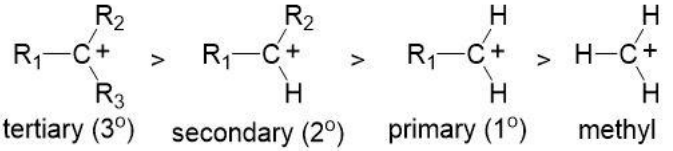
Markovnikov's rule was formulated by Russian chemist Vladimir Vasil'evich Markovnikov in 1870.

The **chemistry principle** behind Markovnikov's Rule is the **formation of the most stable carbocation** in the slow step. The reaction of an electrophile to one carbon atom in C=C creates a positive charge on the adjacent carbon, forming a reactive carbocation intermediate. The more substituted carbocation is formed at a faster rate (lower activation energy due to its greater stability). It will then react with the nucleophile to form the major product.

Explanation of Major product (Important)

Carbocations are generally unstable. The carbocation with more alkyl substituents is more stable as the alkyl groups are **electron donating** and will **reduce the electron deficiency on the carbocation to stabilize it.** The **more stable carbocation is preferentially formed and thus** forms **the major product.**

Therefore, the stability of the carbocations decreases in the following order:

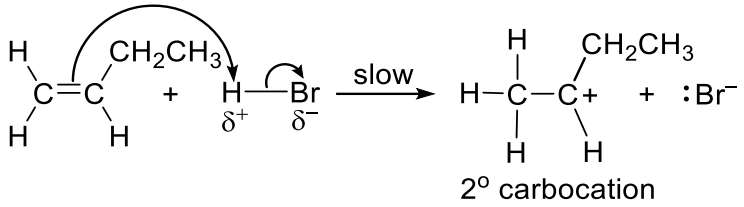


tertiary (3^o) > secondary (2^o) > primary (1^o) > methyl

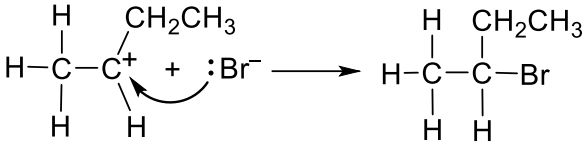
Important Note:
(i) State the name of mechanism
(ii) Show separation of charges (δ+/δ−) on electrophile and charges on ions
(iii) Arrows ALWAYS flow from ***electron rich region (π bond of C=C or lone pair of nucleophiles***) to electron deficient region (electrophile or carbocation)
(iv) Indicate the slow step

Formation of Major Product:

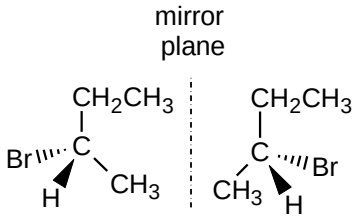
Step 1:



Step 2:



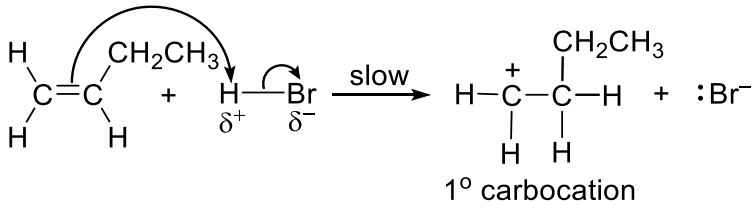
Note:
Even though the product molecule contains a chiral carbon, it is a mixture containing equal amount of the 2 enantiomers of 2-bromobutane (a racemic mixture). The product mixture is optically inactive.



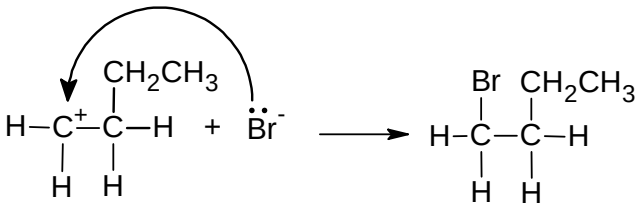
In **Step 2** of the mechanism, Br^- has **equal likelihood** to attack the **trigonal planar carbocation** from **either side of the plane**, thus the 2 enantiomers are formed in equal proportion. The equal but opposite rotation of plane-polarised light by each enantiomer results in net zero optical activity.

Formation of Minor Product:

Step 1:



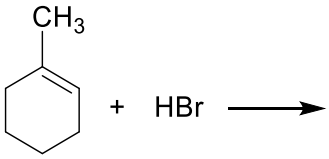
Step 2:

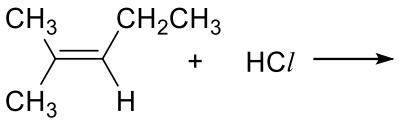


The 2° carbocation, being more stable, is formed more easily. 2-bromobutane is thus formed at higher yield.

Checkpoint 4

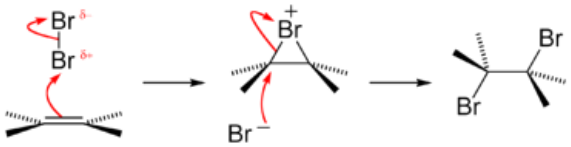
Predict and name the major product of the following reaction:





Electrophilic addition of bromine: The bromonium ion (For your info)
(https://en.wikipedia.org/wiki/Halogen_addition_reaction)

In 1937, Irving Roberts and George E. Kimball first proposed that a cyclic three-membered bromonium ion was formed as an intermediate during the electrophilic addition of Br_2 to an alkenic double bond, to account for the stereoselective *trans*-addition of the two Br atoms.



The reaction mechanism for an alkene bromination can be described as above. In the first step of the reaction, a bromine molecule approaches the electron-rich alkene carbon–carbon double bond. The bromine atom closer to the bond takes on a partial positive charge as its electrons are repelled by the electrons of the double bond.

The atom is electrophilic at this time and is attacked by the pi electrons of the alkene. Due to the large size of bromine, the bromide ion is capable of interacting with both carbons, making a three-membered ring. The bromide ion acquires a positive formal charge and this is known as the "bromonium ion".

When the first bromine atom attacks the carbon–carbon π-bond, it leaves behind one of its electrons with the other bromine that it was bonded to in Br_2. That other atom is now a negative bromide anion and is attracted to the slight positive charge on the carbon atoms. Due to steric repulsion, it can only attack from the other side and forms a bond with one of the carbons. The bond between the first bromine atom and the other carbon atoms breaks, leaving each carbon atom with a halogen substituent.

In this way the two halogens add in an “anti” addition manner, and when the alkene is part of a cycle the dibromide adopts the trans configuration.

4.4.4 Oxidation

Success criteria:
• I can give the structure of products formed when alkene reacts with $KMnO_4$ under different conditions. • I can give the observation when an alkene reacts with $KMnO_4$ in alkaline or acidic medium. • I can deduce the structure of the original alkene from the structure of the oxidised fragments of vigorous oxidation reaction.

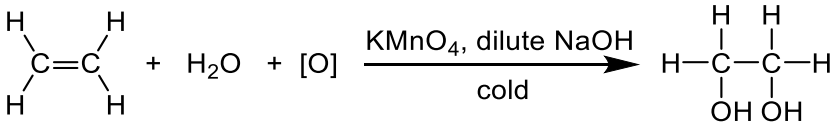
Oxidation of alkenes is a great way to introduce oxygen atom(s) into organic compounds through the formation of carbon−oxygen bonds.

Vigorous and mild oxidation of C=C

The oxidation of carbon-carbon double bonds by the manganate(VII) ion is a well-known reaction in organic chemistry.

(i) Mild Oxidation – formation of diols (two alcohol groups)

The π bond in C=C bond is broken by $KMnO_4$ **at a low temperature** and alkaline medium.



Type of reaction	Mild oxidation
Reagent and condition	$KMnO_4$, NaOH(aq), cold
Observation	Decolourisation of purple $KMnO_4$, brown ppt of MnO_2 formed

Recall:
[O] and H_2O is used to balance the oxidation reaction with $KMnO_4$

This reaction is a useful **distinguishing test** for an alkene from other functional groups.

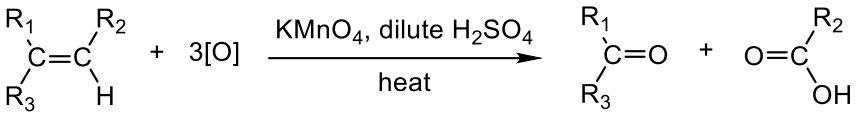
Note: In alkaline medium, purple MnO_4^- is reduced to brown ppt MnO_2

(ii) Vigorous Oxidation

Both the σ AND π bonds in C=C is cleaved by **hot** acidified $KMnO_4$ and produces two fragments.

This process is known as **<u>oxidative cleavage</u>**.

Note:
[O] is used to balance the oxidation reaction with $KMnO_4$

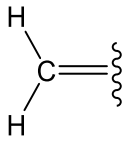
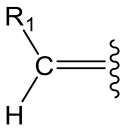
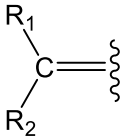
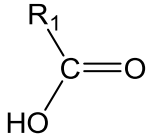
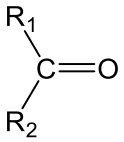


Type of reaction	Vigorous oxidation
Reagent and condition	$KMnO_4$, H_2SO_4(aq), heat
<u>Observation</u>	Decolourisation of purple $KMnO_4$

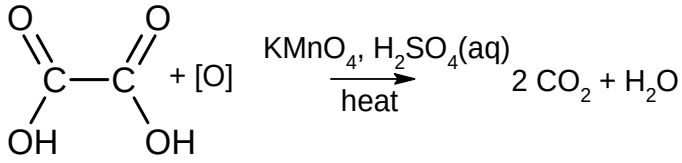
Note: In acidic medium, purple MnO_4^- is reduced to colourless Mn^{2+}.

The **types of product** obtained for vigorous oxidation of alkenes depends on the **number of hydrogen atoms** attached to the C atom of the C=C double bond.

Note:
Oxidation of CH_2= fragment produces H_2CO_3 which decomposes to give CO_2 and H_2O

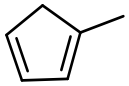
	No. of hydrogen atoms on C=	**2**	**1**	**0**
	Structure	 terminal alkene		
Hot Acidic $KMnO_4$	Observations	• Effervescence due to CO_2(g) formed; • Decolourisation of purple $KMnO_4$	• Decolourisation of purple $KMnO_4$	
	Products after oxidation with hot acidic $KMnO_4$	CO_2 and H_2O	 Carboxylic acid	 Ketone

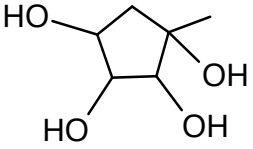
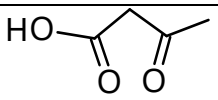
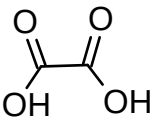
NOTE: Oxidative cleavage of large alkene with multiple C=C bonds may produce ethanedioic acid (HOOC-COOH) as a product. Ethanedioic acid is further oxidised by hot acidified $KMnO_4$ to give CO_2 and H_2O



Worked Example 1

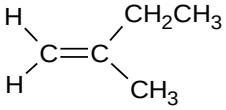
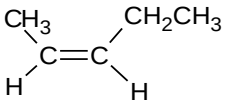
Identify the products when the following compound reacts with $KMnO_4$ under different conditions.



$KMnO_4$, dil NaOH, cold (mild oxidation, breaks π bond ONLY)	
$KMnO_4$, dil H_2SO_4, heat (vigorous oxidation, breaks BOTH σ AND π bonds)	 + 2 CO_2 + H_2O **Note:**  produced undergoes further oxidation by hot acidified $KMnO_4$ to give CO_2 and H_2O

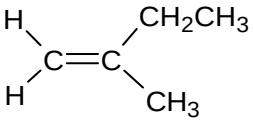
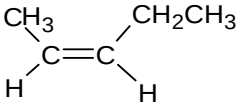
Checkpoint 5

Describe one simple chemical test to distinguish the following set of compounds, stating clearly the **observation** for each compound and support your answer with appropriate **balanced equations**.

 and 

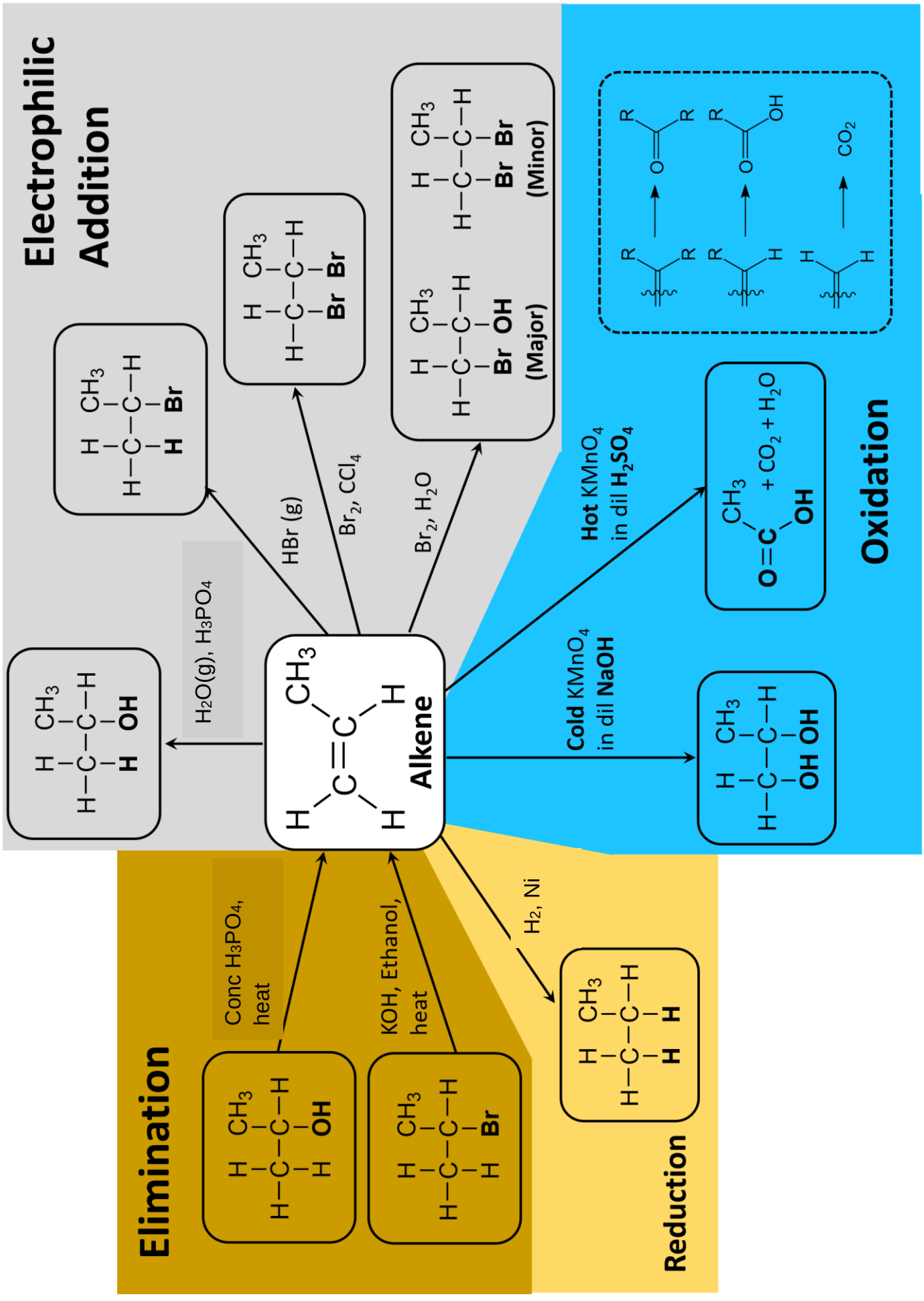
Reagents and conditions: _____

Observations:

Balanced equation:

Success Criteria	Relevant Tutorial questions	What do you still struggle with? Write your queries here.
1. I can deduce the structure of an alkene from its given IUPAC name (and vice versa)	DQ 1,2	
2. I can explain the difference in boiling point and melting point between cis and trans isomers.	DQ13a	
3. I can state the reagents and conditions to convert a. alcohol to alkene b. halogenoalkane to alkene 4. I recognize that elimination of H−X from halogenoalkanes and H−OH from alcohol is only possible between two adjacent carbon atoms. 5. I can give the structure of the alkene formed from the elimination reaction.	KIV	
6. I can state the reagents and conditions for the reactions of alkenes.	DQ11a, 13c	
7. I can deduce the structure of alkenes when the organic products and reagents and conditions are given.	DQ10,12	
8. I can write balanced equations for the reactions of alkenes.	DQ11c	
9. I can explain why alkenes are reactive towards electrophiles. 10. I understand why alkenes tend to undergo addition reactions.	DQ3	
11. I can describe the electrophilic addition mechanism for alkenes using equations, curly arrows and charge when relevant. 12. I can deduce the structure of the major product from electrophilic addition of an alkene in a polar solvent.	DQ5,7	
13. I can describe the use of bromine to test for the presence of C=C functional group.	DQ9	
14. I can predict the major product from electrophilic addition of an asymmetric alkene. 15. I can explain how the major product is formed by considering the stability of carbocation.	DQ4-6	
16. I can understand why the product of electrophilic addition of alkene is optically inactive even if it contains a chiral carbon.	DQ5a,11b	
17. I can give the structure of products formed when alkene reacts with $KMnO_4$ under different conditions.	DQ11c	
18. I can give the observation when an alkene reacts with $KMnO_4$ in alkaline or acidic medium.	DQ9b	
19. I can deduce the structure of the original alkene from the structure of the oxidised fragments of vigorous oxidation reaction.	DQ8, 10c-d	

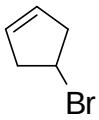

Electrophilic Addition
Alkene
H2O(g), H3PO4
HBr (g)
Br2, CCl4
Br2, H2O
Hot KMnO4 in dil H2SO4
Cold KMnO4 in dil NaOH
Oxidation
Elimination
Conc H3PO4, heat
KOH, Ethanol, heat
H2, Ni
Reduction
CO2

Alkenes Tutorial

Structure and naming

1 Give the IUPAC names of the following compounds.

(a) $(CH_3)_2CHCH=C(CH_3)_2$ **(b)**



2 Draw the structural formulae of the following compounds.

(a) 1-bromo-3-ethylcyclopentene

(b) 3,6-dimethyl-4-propylhepta-1,4-diene

(c) *trans*-hex-2-ene

Electrophilic addition

3 (2021/P1/16) Which statement about propene explains how it reacts with bromine?

A Electrons in the carbon−carbon π bond are donated to an electrophile.

B Electrons in the carbon−carbon σ are donated to an electrophile.

C The sp^2 hybridised carbon is an electrophile and accepts a pair of electrons.

D The σ bond between the sp^2 hybridised carbon atoms is weak and readily broken.

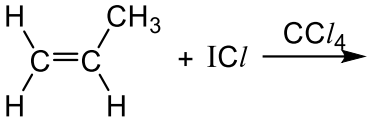
4 For each of the following reactions,

(i) give the structures of the product(s) formed in each of the following reactions.

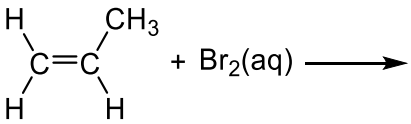
(ii) identify, with explanation, the major product where applicable.

(iii) state the observation during reaction where applicable.

(a)



(b)

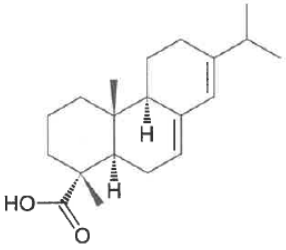


5 Explain each of the following observations, as fully as you can, by making reference to the reaction mechanism of alkenes:

(a) Addition of pure hydrogen iodide to but-1-ene gives a mixture of two enantiomers in equal molar proportions.

(b) Addition of liquid bromine to a solution of ethene in methanol gives a mixture of 1,2-dibromoethane and $CH_2BrCH_2OCH_3$. However, when ethene is shaken with an aqueous solution containing both bromine and sodium chloride, 1,2-dibromoethane, 2-bromoethanol and 1-bromo-2-chloroethane are also formed, but not 1,2-dichloroethane.

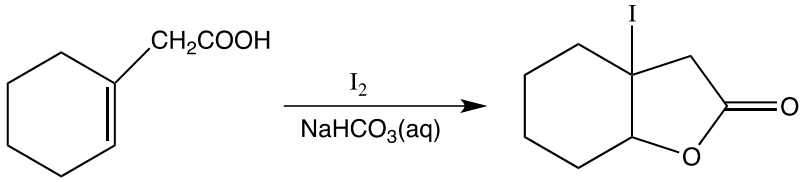
6 (2018 P3 Q4d) Abietic acid is a major component of many resins and has the following structure.



abietic acid, $C_{20}H_{30}O_2$

Draw the structure of the major product when abietic acid is reacted with an excess of HBr. State how many extra chiral centres are formed.

7 When compound **R** is reacted with iodine in the presence of aqueous sodium hydrogencarbonate, iodine does **not** add across the carbon–carbon double bond of compound **R**. Instead, a compound **S**, which has a molecular formula, $C_8H_{11}O_2I$, is formed as shown:



R **S**

$NaHCO_3$ functions as a *base* during this reaction. Suggest an explanation for the observation.

Oxidation

8 For each of the following, identify the alkene which forms the products upon vigorous oxidation by hot acidified $KMnO_4$, giving its structure and IUPAC name.

Draw the cis-trans isomers of the alkene (if any).

(i) $CH_3CH_2CO_2H$ only

(ii) $(CH_3)_2CO$ and $CH_3CH_2CO_2H$

(iii) CO_2 and $CH_3COCH_2CH_2CH_3$

Distinguishing test

9 Describe one simple chemical test to distinguish each set of compounds, stating clearly the observation for each compound in each chemical test. Support your answers with appropriate balanced equations.

(a) cyclohexane and cyclohexene

(b) 

Application question

10 Suggest, with reasons, a possible structural formula for each of the compounds, **A** – **F**, all of which have the molecular formula C_6H_{12}. Note that no two structures should be the same.

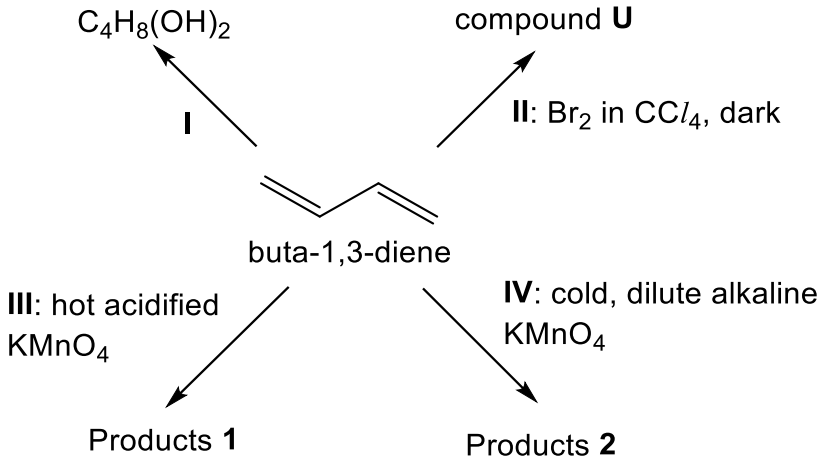
(a) **A** does not decolourises aqueous bromine.

(b) **B** decolourises liquid bromine dissolved in tetrachloromethane and exists as a pair of cis-trans isomers.

(c) **C** undergoes reaction with $KMnO_4$(aq) in dilute acid when heated to give only **one** product, C_3H_6O.

(d) **D** undergoes reaction with $KMnO_4$(aq) in dilute acid when heated to give CH_3CO_2H and $CH_3CH_2COCH_3$.

11 Buta-1,3-diene undergoes the reactions shown in the scheme below



(a) **(i)** Suggest the reagents and conditions for reaction **I**.

(ii) Give the structural formula of the major product formed in reaction **I**.

(b) **(i)** Name the reaction mechansim of reaction **II** and deduce the structure of compound **U**.

(ii) **U** has 2 chiral centers but only 3 stereoisomers. Explain.

(iii) Give 2 reasons why the product mixture from reaction **II** does not exhibit optical activity.

(c) Write balanced equations for reactions **III** and **IV**.

Integrated questions

12 A hydrocarbon, **A**, contains 87.8% carbon and 12.2% hydrogen by mass and has a M_r of 82. **A** decolourises bromine water. In the presence of nickel catalyst, it reacts with hydrogen to form **B**.

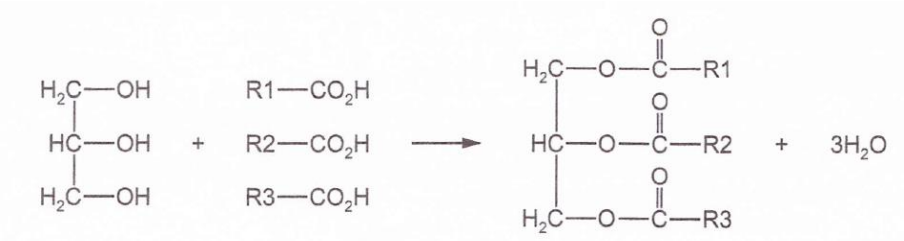
0.1 g of **A** was found to absorb 27.7 cm^3 of hydrogen (measured at s.t.p). **B** does not decolourise bromine water.

(a) Calculate the empirical formula of **A** and hence determine its molecular formula.

(b) Determine the number of moles of hydrogen reacted with 1 mole of **A**. Hence, determine the number of double bonds in a molecule of **A**.

(c) Suggest the structural formulae of **A** and **B**.

13 (Modified from 2016/P2/2) Olive oil contains a mixture of triester formed from glycerol (propane-1,2,3-triol) and three long chain carboxylic acids (fatty acids), as shown by the general equation.



The groups R1, R2 and R3 represent hydrocarbon chains each containing either 15 or 17 carbon atoms. A given oil molecule (triester) can be formed from any combination of the following fatty acids.

name	formula and systematic name	M_r	melting point /°C
palmitic acid	$CH_3(CH_2)_{14}CO_2H$ hexadecanoic acid	256	63
stearic acid	$CH_3(CH_2)_{16}CO_2H$ octadecanoic acid	284	69
oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$ *cis*-9-octadecenoic acid	282	13
linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$ *cis*,*cis*-9,12-octadecadienoic acid	280	–5
linolenic acid	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6CO_2H$ *cis*,*cis*,*cis*-9,12,15-octadecatrienoic acid	278	–11

(a) A particular triester found in olive oils melts at 15°C.

(i) Explain why this triester melts at a lower temperature than any of the individual fatty acids.

(ii) Trans-9-octadecenoic acid melts at 44°C. Explain the difference in its melting point with cis-9-octadecenoic acid.

(iii) State how the presence of C=C bonds affects the melting point of the fatty acids.

(b) The average number of C=C bonds per molecule in different oils can be compared experimentally by determining the mass of iodine that reacts with 100g of the oil.
In one experiment, 0.256g of olive oil was found to react with 0.237g of iodine.

(i) State the name of the mechanism for the reaction occurring between iodine and the C=C bonds in the olive oil.

(ii) Calculate the mass of iodine that would react with the 100g of olive oil.

(iii) Use your answer from b(ii) to calculate the average number of C=C bonds in each oil molecule in olive oil. The average M_r of an olive oil molecule is 782. Give your answer to three significant figures.

(iv) The triesters in olive oil are formed mainly from oleic acid.

Use this information and the data in the table on page 22 to explain the significance of your answer to b(iii) with respect to the composition of olive oil.

(c) Olive oil can be used to make margarine. Part of the manufacturing process involves decreasing the number of C=C bonds in the oil.

(i) State suitable reagents and conditions to carry out this process.

(ii) The conditions in c(i) can also result in isomerization of the C=C bonds, to form trans fatty acids.
Draw a skeletal formula to show the trans isomer of oleic acid, $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$.