2022 JC1 H2 CHEMISTRY (9729)
EXTENSION TOPIC – ORGANIC CHEMISTRY
Topic 3: HYDROCARBONS - ALKENES

Name: ____ Civics Group: _________

Students 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; see also Reaction Kinetics)
  (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

REFERENCES

1 **Chemistry for Advanced Level**, Peter Cann, 2002
2 **Chemistry (2nd edition)**, Chris Conoley and Phil Hill
3 **Chemistry in Context**, Hill & Holman
4 **Organic Chemistry (3rd edition)**, David R Klein
5 **Understanding Chemistry for Advanced Level**, Ted Lister, Janet Renshaw

LECTURE CONTENT

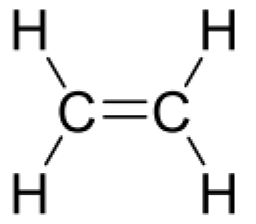
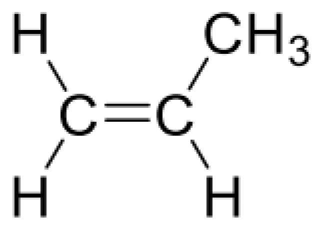
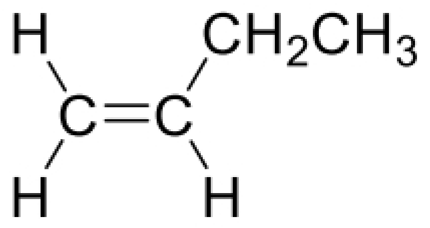
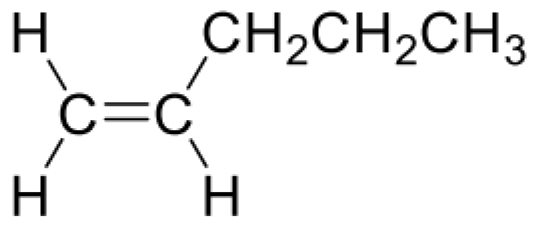
1 Introduction

- Alkenes are **unsaturated** hydrocarbons containing C=C double bonds as the functional group in their structures.

- The double bond constitutes a reactive site which allows the alkene greater chemical reactivity compared to the corresponding alkane.

- Alkenes have the general formula $\mathbf{C_{n}H_{2n}}$ where *n* is an integer greater than or equal to 2. Compare to an alkane with the general formula of C_nH_{2n+2}, the presence of a double bond corresponds to two hydrogen atoms lesser.

Examples of **straight chain** alkenes*

n	**name**	**molecular formula**	**structural formula**		
2	ethene	C_2H_4			$CH_2=CH_2$
3	propene	C_3H_6			$CH_2=CHCH_3$
4	but-1-ene	C_4H_8			$CH_2=CHCH_2CH_3$
5	pent-1-ene	C_5H_{10}			$CH_2=CHCH_2CH_2CH_3$

* The examples in the table only show alkenes with double bonds in the **terminal position** (at the end of the molecule) or between carbon positions **number 1 and 2**.

1.1 Hybridisation of carbon atoms in C=C

Note for H1 Chemistry students:

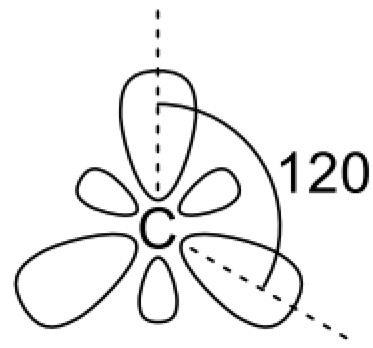
Knowledge of hydridisation is **not required**.

- Each carbon atom in the C=C is **<u>sp^2</u>** hybridised, and bonded to other atoms in a **trigonal planar** manner with a bond angle of **120º**.

Using ethene ($CH_2=CH_2$) as an example,

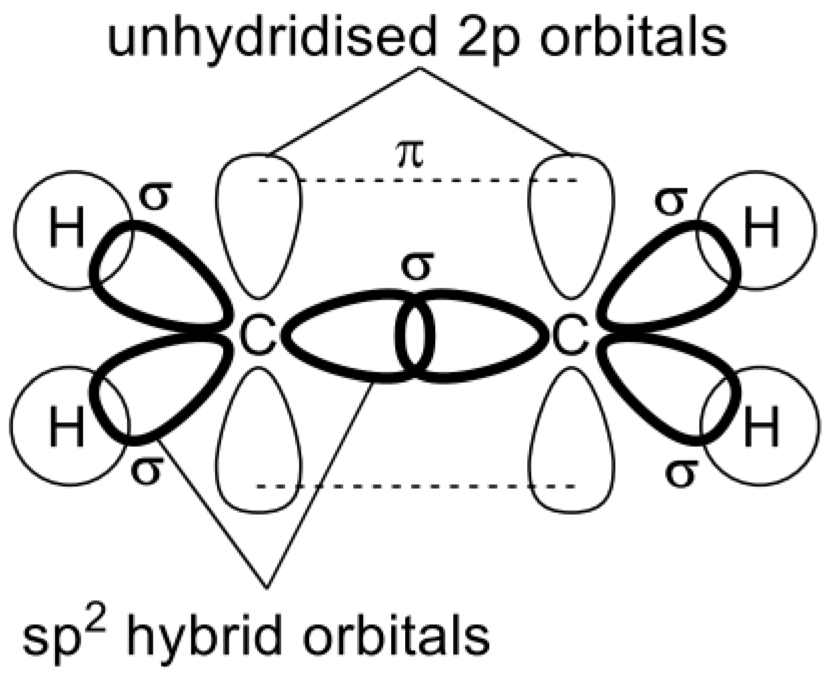
- Two of the three sp^2 hybrid orbitals of the carbon atom overlap head-on with the 1s orbitals of two hydrogen atoms to form two C–H sigma (σ) bonds.

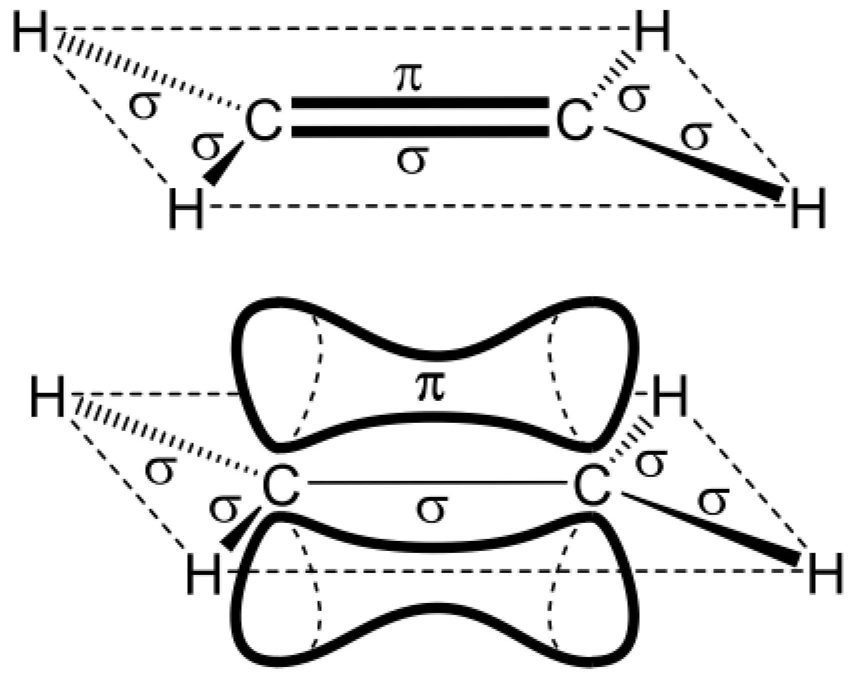
- The remaining sp^2 hybrid orbital overlaps head-on with the sp^2 hybrid orbital of the neighbouring carbon atom to form a C–C sigma (σ) bond.



three sp^2 hybrid orbitals lie in a trigonal planar geometry

- The unhybridised 2p orbital, which is perpendicular to the plane containing the atoms, 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 containing the atoms.





1.2 Strength of π bond in C=C

type of bond	**C–C (ethane)**	**C=C (ethene)**
bond energy / kJ mol^{-1}	350	610
bond length / nm	0.154	0.134

- As more energy is required to break a C=C bond than a C−C bond, a C=C bond is stronger than a C−C bond. This is due to **stronger electrostatic force of attraction for the more electrons shared** between the two carbon atoms.

- The energy required to break a C=C bond is less than twice the energy required to break a C–C bond as in a C=C, the **π bond is weaker than the σ bond** because the side-on overlap of orbitals is less effective than head-on overlap of orbitals.

- In terms of orbital overlap, the C=C bond in an ethene molecule is shorter than the C–C bond in an ethane molecule as the two carbon atoms in ethene are closer together to allow the formation of a π bond via side-on overlap of two unhybridised 2p orbitals.

2 Nomenclature (using the IUPAC system)

Steps in naming alkenes:

Step 1: Name the parent chain

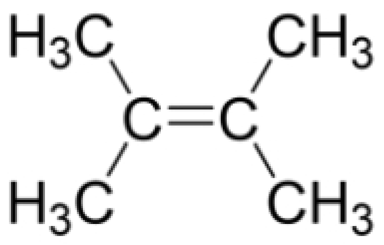
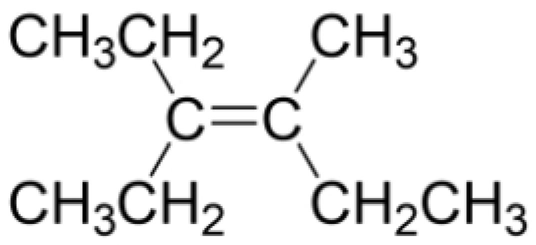
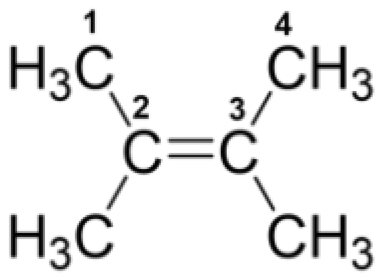
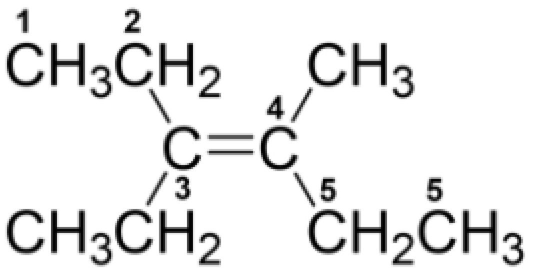
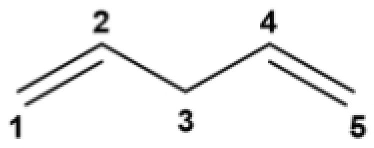
- Determine the *longest continuous carbon chain* which contains **both carbon atoms of the double bond** as the parent chain.
- Name parent chain with the suffix –*ene*
- If there are two double bonds within a molecule, name it with the suffix *'-**diene**'.*

Step 2: Assign numbers to the carbons on the parent chain so that the carbon atoms of the double bond have the smallest number possible. (*i.e.* assign the functional group the smallest number)

Step 3: Name every **side group** that branches off according to their position on the chain.

Step 4: Write the name as a single word.

Self Check 2A

Alkene			
Step 1: identify parent chain	4 carbons ⇒ **but**ene	6 carbons ⇒ **hex**ene	5 carbons ⇒ **pent**ene
Step2: assign numbers to double bond position	 ⇒ but-2-ene	 ⇒ hex-3-ene	 ⇒ penta-1,4-diene
Step 3: side groups	methyl group (×1) at C2 methyl group (×1) at C3	ethyl group (×1) at C3 methyl group (×1) at C4	N.A.
Name			

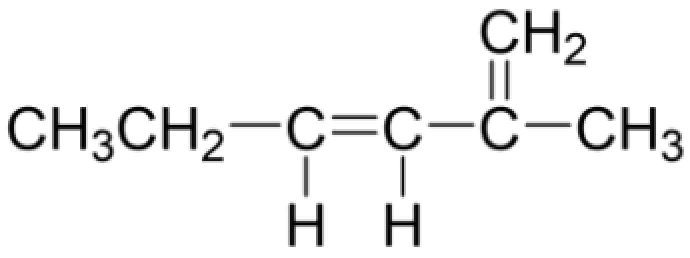
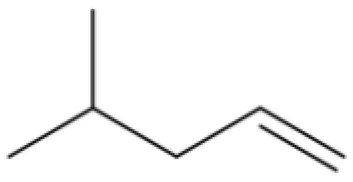
Example 2A

Write the displayed formula for the following compounds.

3-methylpent-2-ene	cyclohexa-1,4-diene

Example 2B

Write the IUPAC name of the following compounds.

 $CH_3CH_2-\underset{H}{\underset{\vert}{C}}=\underset{H}{\underset{\vert}{C}}-\overset{CH_2}{\overset{\Vert}{C}}-CH_3$	

3 Isomerism

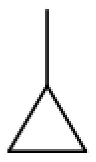
In the previous topics, we have seen that alkanes can show both constitutional (structural) isomerism and enantiomerism.

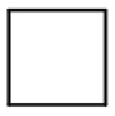
- Alkenes can exhibit **constitutional** isomerism and ***cis-trans*** isomerism due to the C=C.

- *Cis-trans* isomerism exists in alkenes as a result of:
  - ⇒ presence of **restricted rotation** about a C=C double bond due to the **presence of π bond**
  - ⇒ each carbon atom in C=C is **joined to two different groups**

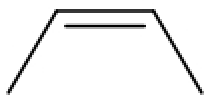
- In cyclohexene, only the *cis* isomer exists (with alkyl groups on the same side of C=C). No *trans* isomer due to severe ring strain in small ring systems. However, *cis-trans* isomerism is possible only in cycloalkenes with ring size larger than seven carbon atoms.

Example: Isomers of C_4H_8

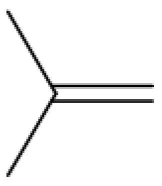




trans-but-2-ene

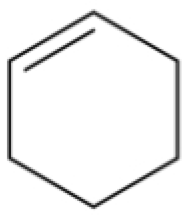
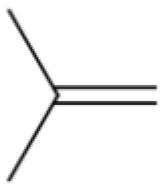
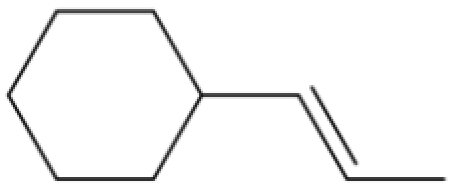
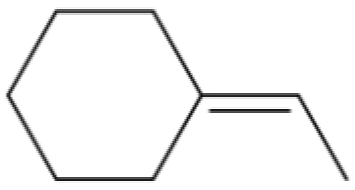


cis-but-2-ene



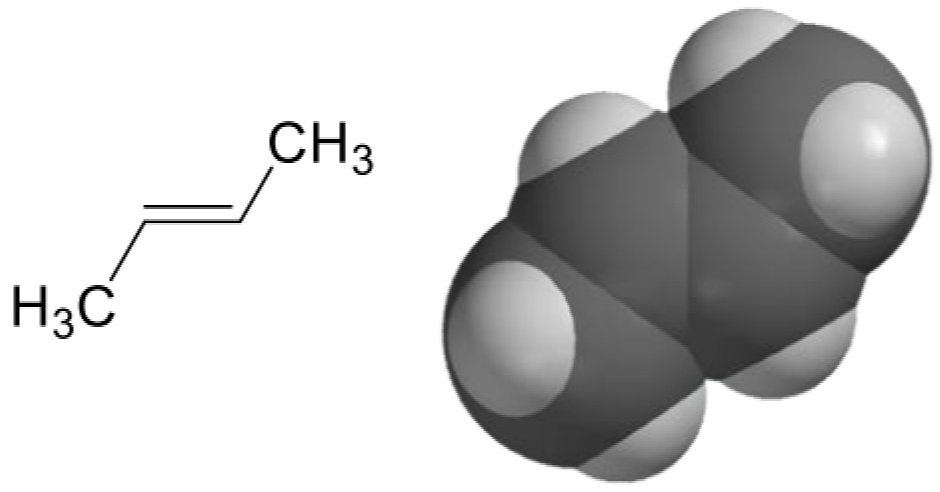
Example 3A

Identify the compounds that can exhibit *cis-trans* isomerism.

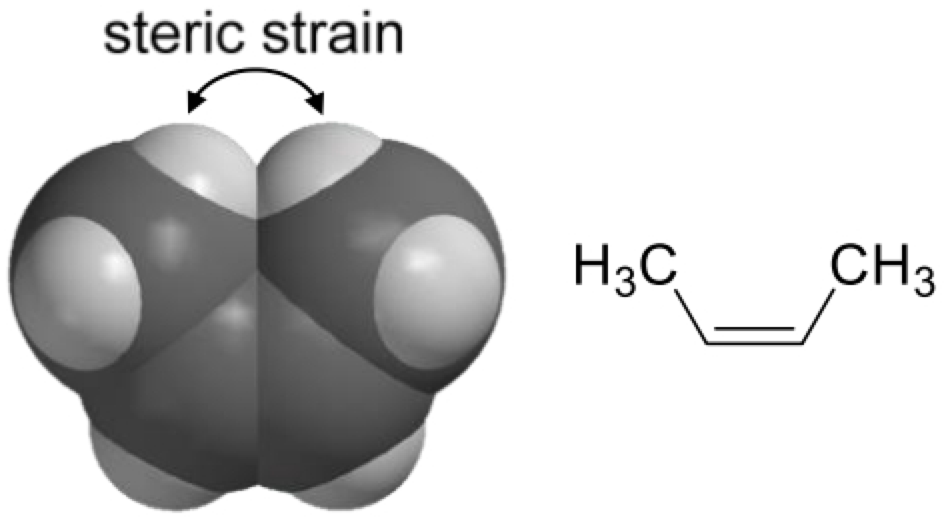
			

3.1 Relative stability of *cis-trans* isomers

- *Trans* isomers are usually more stable than the corresponding *cis* isomers as the latter experience greater steric strain. In this case, the steric strain is due to inter-electronic repulsion between the electron clouds.



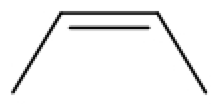
trans-but-2-ene



cis-but-2-ene

- The difference in stability can be quantified by comparing the enthalpy change of combustion.

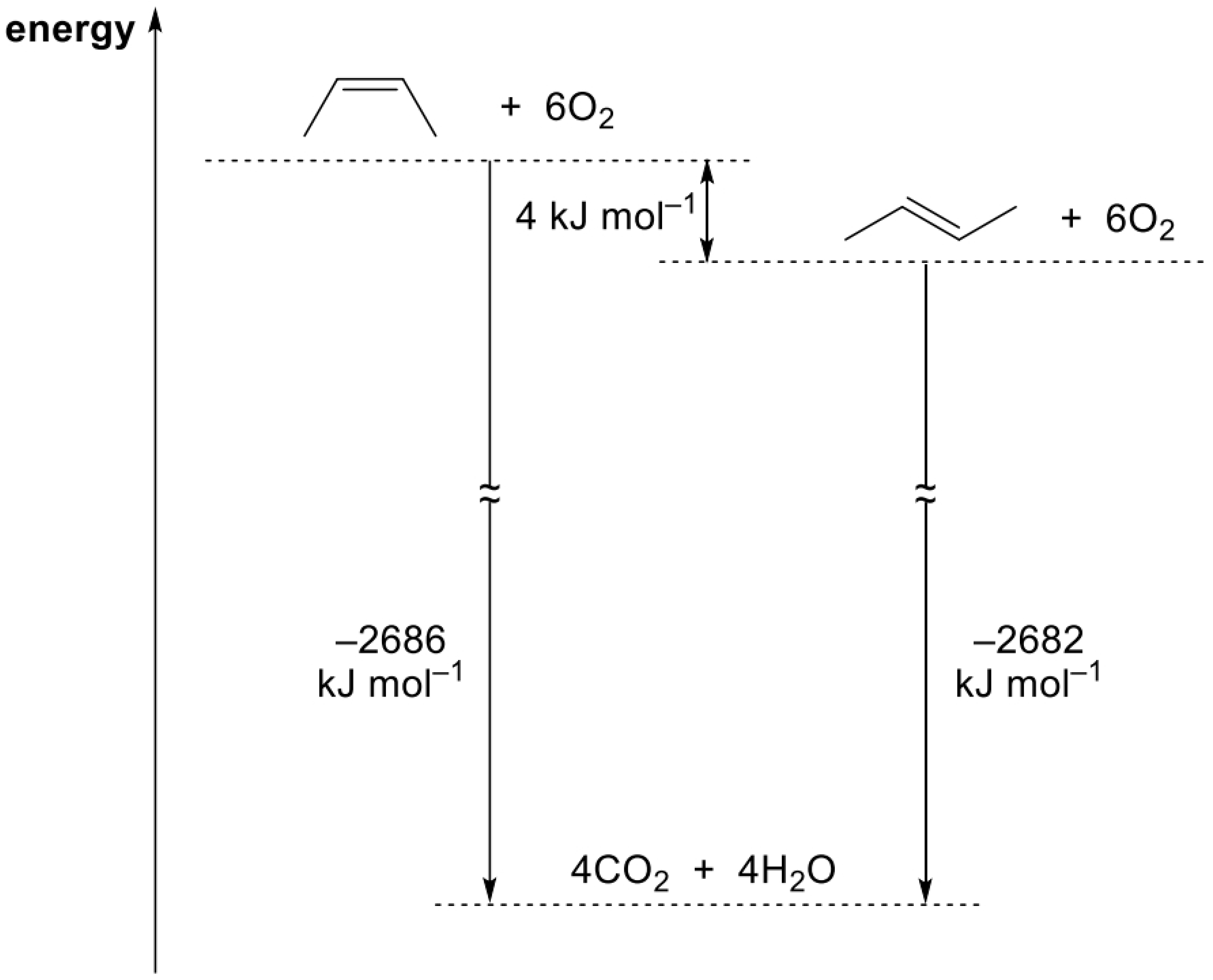
 $+\ 6O_2 \longrightarrow 4CO_2 + 4H_2O$ $\qquad \Delta H_c^\ominus = -2682\ \text{kJ mol}^{-1}$

 $+\ 6O_2 \longrightarrow 4CO_2 + 4H_2O$ $\qquad \Delta H_c^\ominus = -2686\ \text{kJ mol}^{-1}$

How does the enthalpy change of combustion relate to stability of the isomers?

The same products are obtained when the isomers are completely burnt in oxygen.

A more exothermic $\Delta H_c^\ominus$ means that the isomer is ________ stable because of the higher energy content it has.



4 Physical Properties

4.1 Boiling point and melting point

- For straight chain alkenes, the boiling point/melting point increases as the number of C atoms increases.

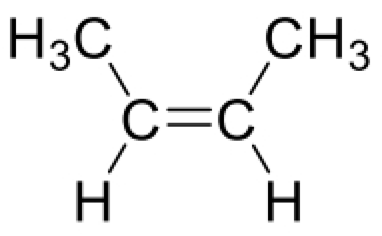
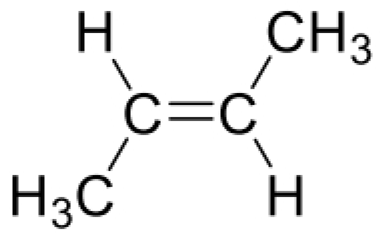
  ⇒ Alkenes are **non-polar molecules** which experience instantaneous dipole-induced dipole forces of attraction between molecules.

  As **number of electrons** (as seen from the M_r of alkenes) increase, the boiling point increases.

  - ✓ **<u>bigger and more polarisable electron cloud</u>**
  - ✓ **<u>strength of instantaneous dipole-induced dipole interactions between molecules</u>** increases
  - ✓ **<u>more energy</u>** is needed to overcome the stronger electrostatic forces of attraction between molecules.

- The greater the degree of branching in the isomer, the lower the boiling point due to weaker instantaneous dipole-induced dipole interactions between molecules since branched alkenes are more spherical in shape. Hence, **<u>lesser surface area of contact</u>** between molecules.

- *cis*-*trans* isomers may have some differences in their physical properties.

	 *cis*-but-2-ene	 *trans*-but-2-ene
net dipole moment	non–zero (small)	zero
boiling point / ºC	4	1

⇒ *cis*-but-2-ene is slightly **polar** while *trans*–but–2–ene is **non-polar**. The intermolecular forces in *cis*-but-2-ene (permanent dipole–permanent dipole and instantaneous dipole–induced dipole interactions) are **stronger** than those in *trans*-but-2-ene (only instantaneous dipole–induced dipole interactions).

⇒ Since boiling involves the overcoming of intermolecular forces, *cis*-but-2-ene has a higher boiling point than *trans*-but-2-ene.

⇒ However, the melting point of *cis*-but-2-ene (−138.9 ºC) is lower than *trans*-but-2-ene (105.5 ºC). Why?

The more symmetrical *trans*-but-2-ene molecules pack into the crystal lattice better, allowing closer approach and larger attractive forces, thus resulting in higher melting points.

4.2 Solubility

Alkenes are insoluble in water, but soluble in **non-polar solvents**, *e.g.* benzene, hexane, CCl_4. Why?

Reason:

Between alkene and non-polar solvent:

The energy released in forming the **instantaneous dipole−induced dipole (i.d.–i.d.)** interactions between the alkene molecules and non-polar solvent molecules is sufficient to overcome the **i.d.–i.d. interactions between the alkene molecules** and the **i.d.–i.d. interactions between the non-polar solvent molecules**.

Between alkene and water/polar solvent:

The energy released in forming the **permanent dipole−induced dipole (p.d.–i.d.)** interactions between the alkene molecules and water molecules / polar solvent molecules is insufficient to overcome the **i.d.–i.d. interactions between the alkene molecules** and the **hydrogen bonds / permanent dipole-permanent dipole (p.d.–p.d.) interactions between the water molecules / polar solvent molecules**.

Self Check 4A

Arrange the alkenes in order of increasing boiling point.

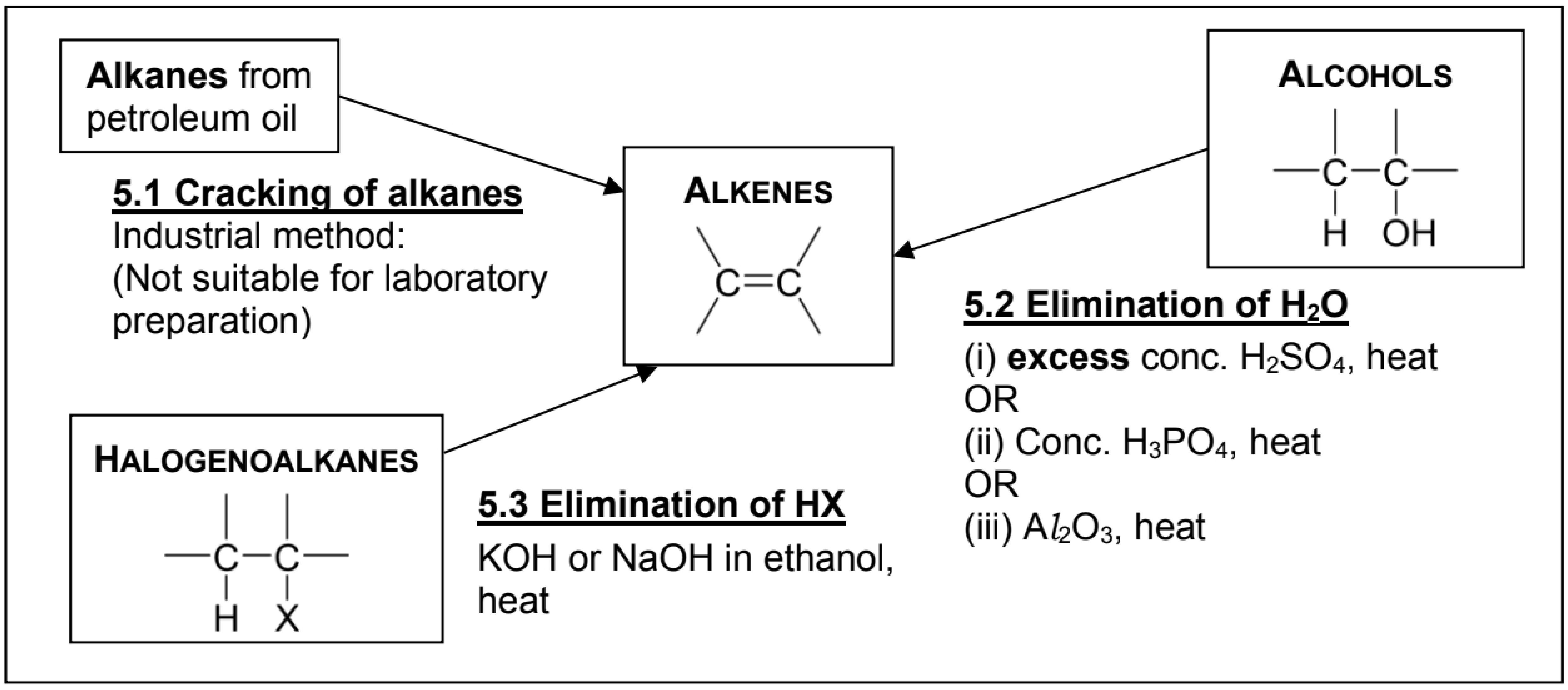
cis-hex-2-ene *trans*-hex-2-ene 2,3-dimethylbut-2-ene

Checkpoint for Section 1–4

At the end of these sections, you must be able to:

- Understand that alkenes are unsaturated hydrocarbons, with the general formula $\mathbf{C_nH_{2n}}$.
- Describe the hybridisation of carbon atoms in C=C and the bonding between adjacent atoms in terms of orbital overlap with the aid of suitable diagrams.
- Explain the difference in bond strength between a C=C and C-C.
- Write IUPAC names of simple alkene molecules given the structural formula and vice versa.
- Describe the type of isomerism that exists in alkenes, and explain how is arises.
- Describe the physical properties of alkenes such as the boiling points and solubility, and the factors affecting them (refer to Chemical Bonding).

5 Preparation of Alkenes



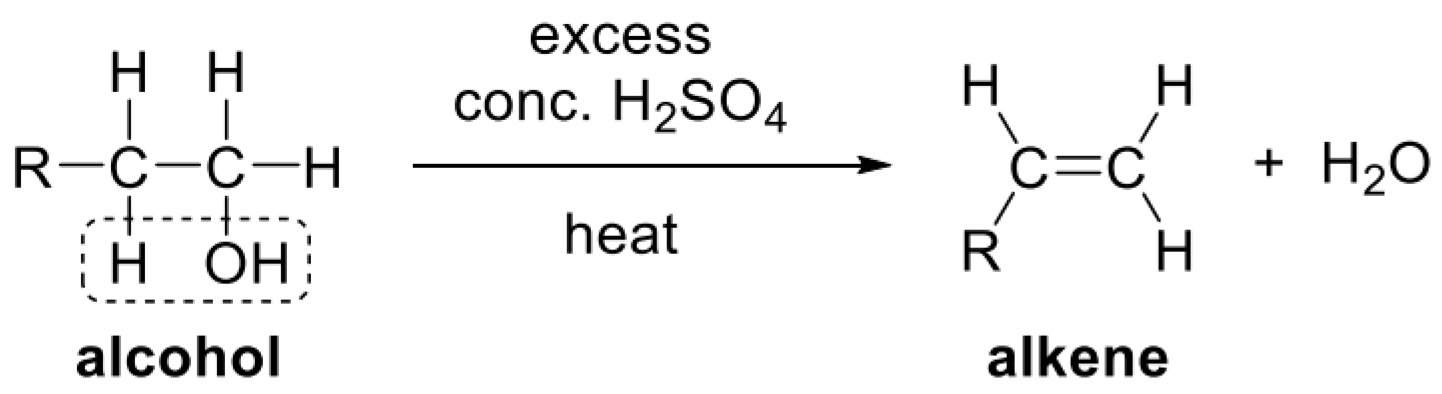
5.1 Cracking of alkanes

- Cracking is an industrial process used to split large alkane molecules into smaller fragments, through strong heating. Alkenes can be obtained from alkanes during the cracking of petroleum. Large amounts of ethene are produced for industrial purposes this way.

$$\underset{\text{big alkane molecule}}{C_{22}H_{46}} \rightarrow \underset{\text{smaller alkane molecule}}{C_{12}H_{26}} + \underset{\text{ethene molecules}}{5C_2H_4}$$

5.2 Dehydration of alcohol (*i.e.* elimination of H_2O)

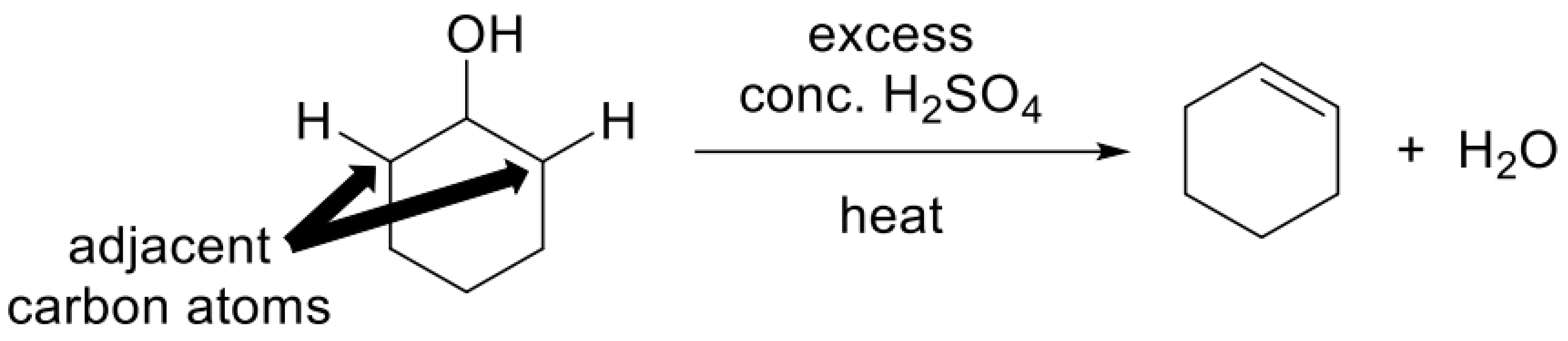
- **Alcohols** with H and OH on **adjacent** carbons atoms can be **dehydrated to yield alkenes**. This is an **elimination reaction**, whereby H_2O is eliminated.



Sets of reagents and corresponding conditions:

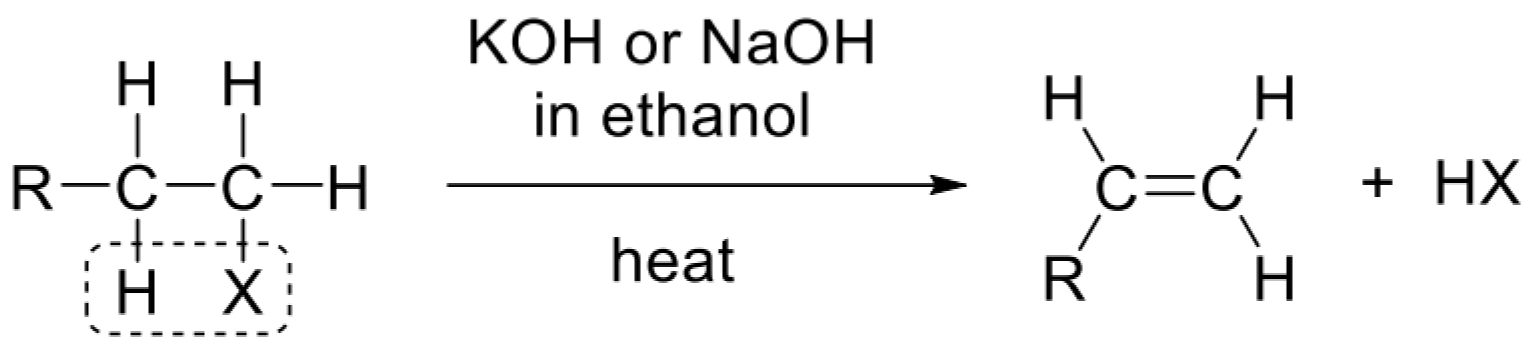
reagents	conditions
excess concentrated sulfuric acid, H_2SO_4	heat
solid alumina, $A\ell_2O_3$	heat
concentrated phosphoric acid, H_3PO_4	heat

Example:



5.3 Dehydrohalogenation of alkyl halides (***i.e.*** elimination of HX)

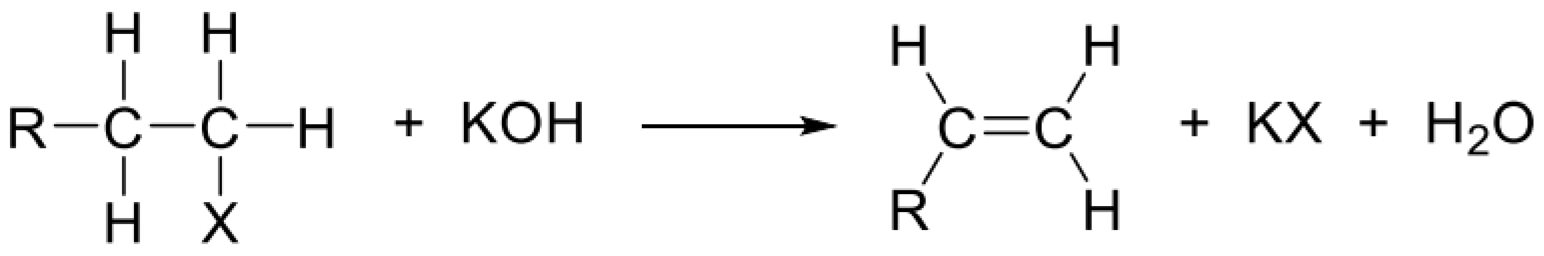
- Alkyl halides with H and X (e.g. C*l* or Br or I) on adjacent carbon atoms are **dehydrohalogenated (eliminate HX) to yield alkenes.**



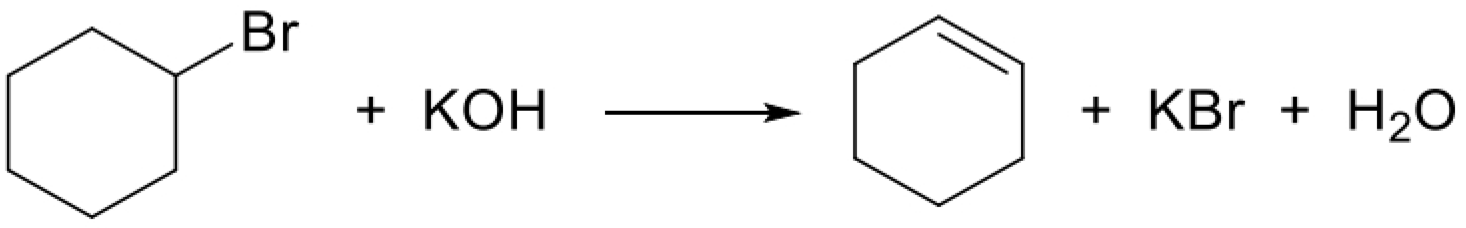
alkyl halide **alkene**

Reagents and condition: KOH or NaOH in ethanol, heat

A more accurate equation to represent the reaction is

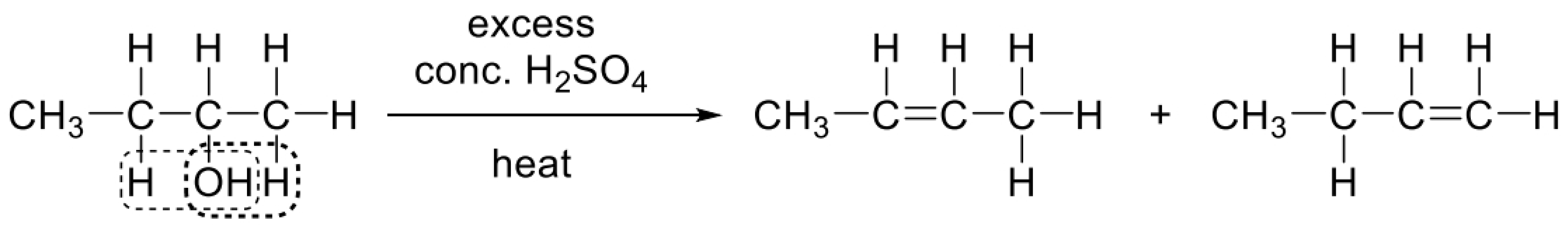


Example:



- Using **Saytzeff's Rule** to predict major products of an elimination reaction **(FYI only)**

⇒ Consider a reaction of butan-2-ol with excess concentrated sulfuric acid and heat. A mixture of products is obtained.



butan-2-ol

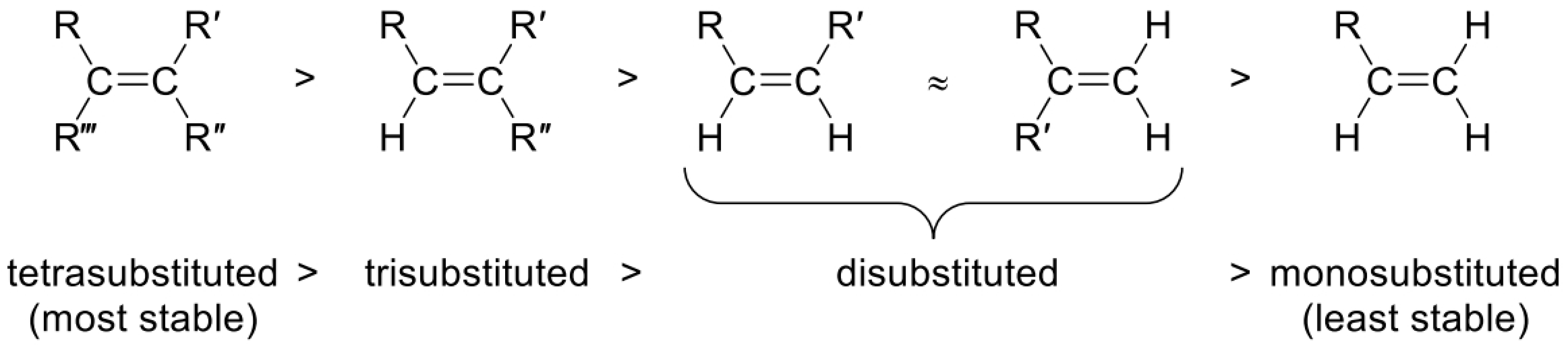
(*cis*- & *trans*-)but-2-ene (major product)

but-1-ene (minor product)

⇒ Saytzeff rule states that if an elimination results in the formation of more than one type of alkenes, the more highly substituted alkenes (*i.e.* the one with more alkyl groups attached to the double bonded carbon atoms) will be the **most stable** alkene formed.

⇒ The most stable alkene is the **major product** (*i.e.* the product formed in greater amounts).

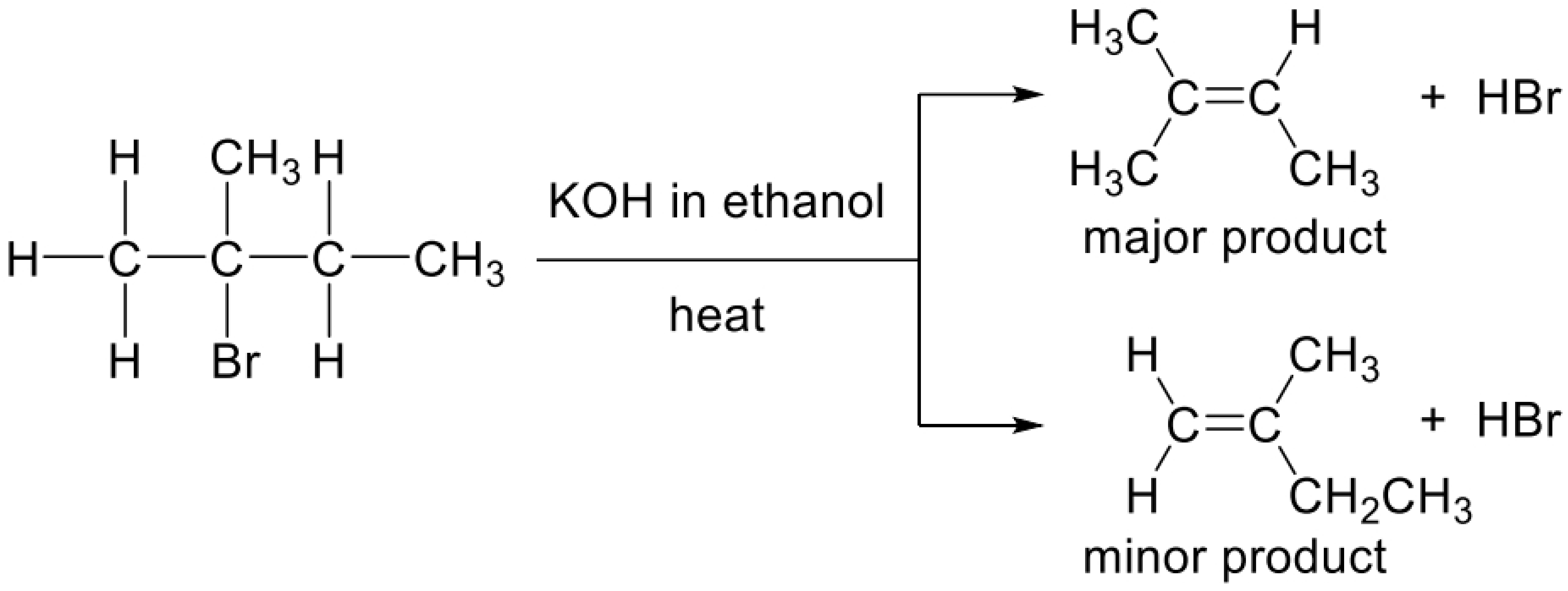
In order of decreasing stability,



⇒ Hence in the elimination reaction of butan-2-ol, but-2-ene (more highly substituted) is formed as the major product, and but-1-ene (less highly substituted) is formed as the minor product.

⇒ As the alkyl groups of the *cis*-isomer would be spatially closer together, they experience more steric strain than in the *trans*-isomer. The *trans*-isomer is thus more stable than the *cis*-isomer, and more of it would be produced.

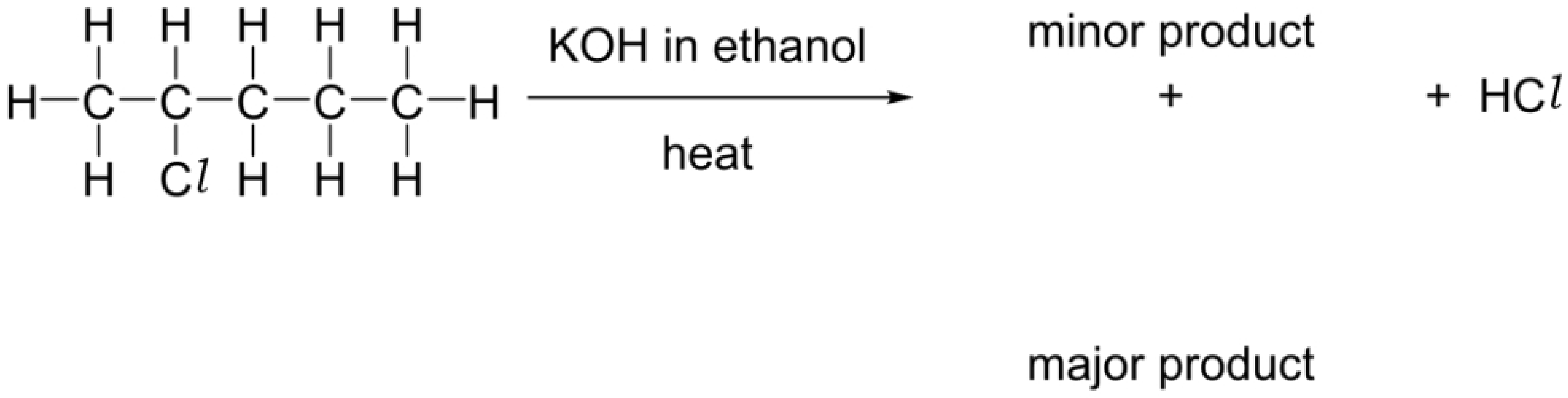
Example: Elimination of HBr



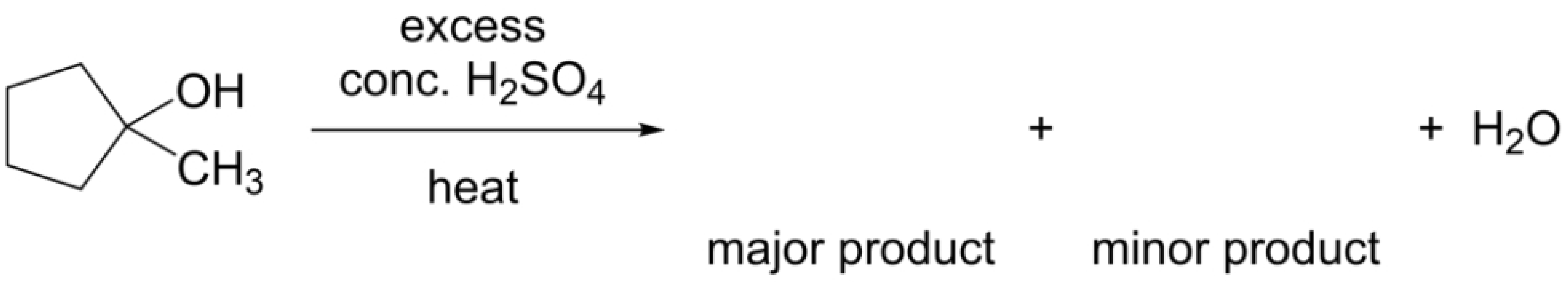
Example 5A

(a) Draw the structural formulae of the products for the reactions.
(Apply Saytzeff's Rule where applicable.)

(i)



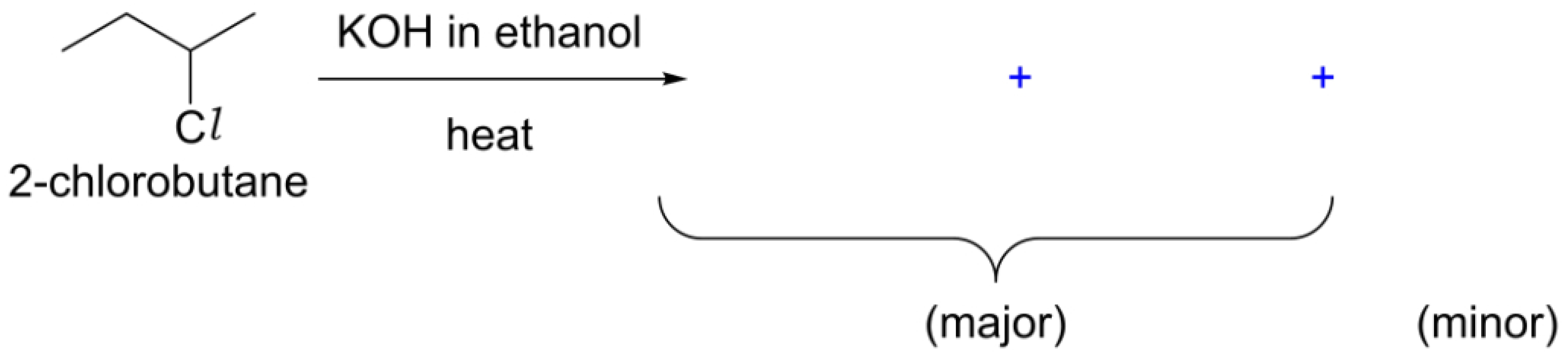
(ii)



Example 5A (cont'd)

(b) When an alcohol is heated with excess concentrated H_2SO_4, only pent-2-ene is obtained. Deduce the structural formula of this alcohol.

(c) Draw the structural formulae of all alkenes formed when 2-chlorobutane is heated under reflux with ethanolic KOH.
Rank the products in order of increasing amounts formed.



Relative amount of each alkene formed:

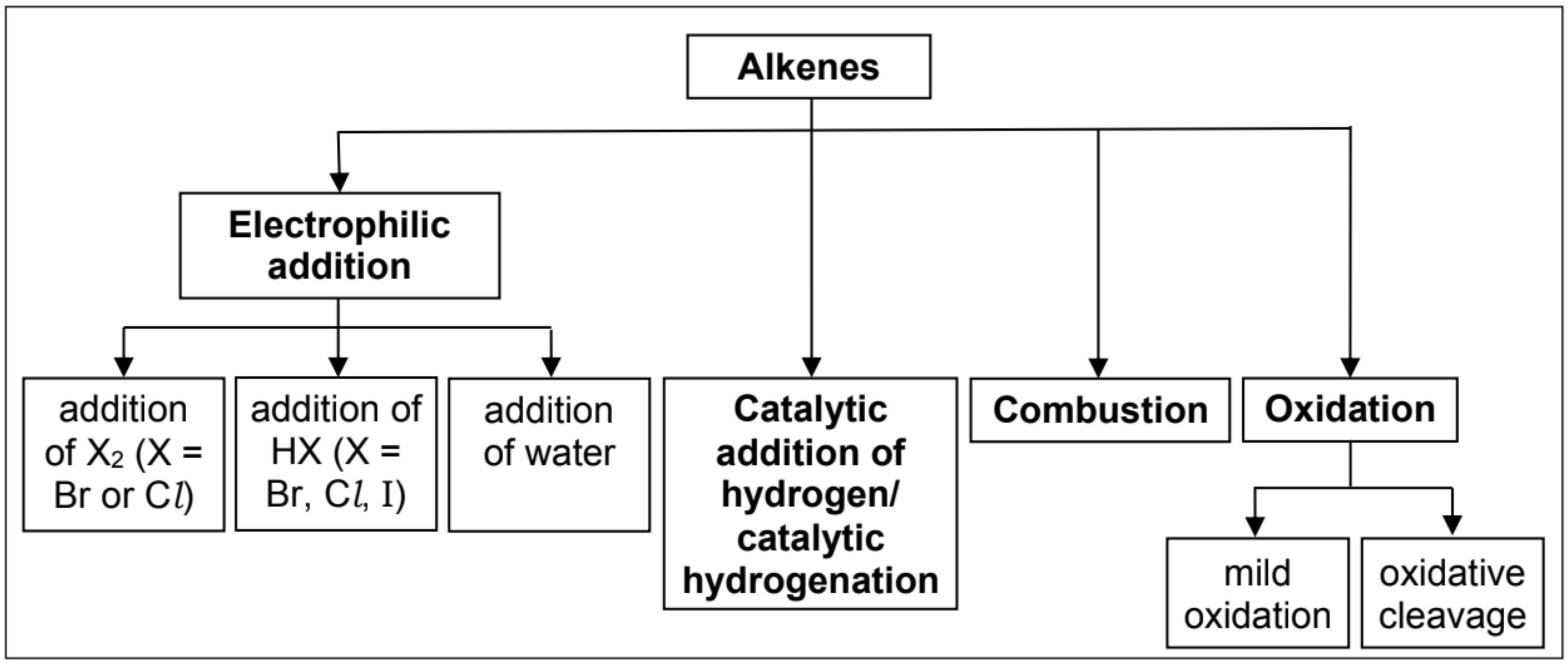
Note: The *trans*-isomer of but-2-ene is more stable than the *cis*-isomer hence more of it is produced as there is less steric strain from the alkyl groups on the opposite sides of the alkene.

Checkpoint for Section 5

At the end of this section, you must be able to:

- Describe the reagents and conditions to prepare alkenes by:
  - Elimination of water from alcohols
  - Elimination of HX from halogenoalkanes
- Understand that elimination may lead to formation of more than one type of alkene:
  - The alkenes may be *cis-trans* isomers.
  - The more highly substituted alkene is the major product (formed in larger proportions).

6 Reactions of Alkenes



6.1 Combustion

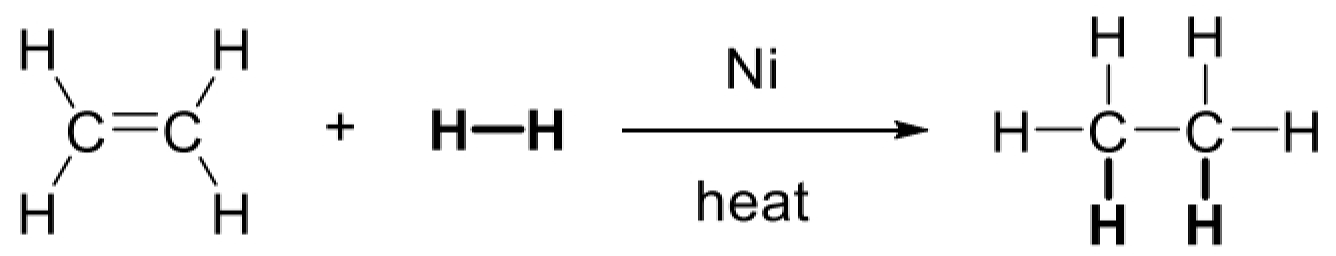
Alkenes undergo complete combustion in air to form carbon dioxide and water.

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \quad \text{or} \quad C_nH_{2n} + \frac{3n}{2}O_2 \rightarrow nCO_2 + nH_2O$$

6.2 Reduction (catalytic hydrogenation / catalytic addition of hydrogen)

LO (b) Describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:
(ii) reduction via catalytic hydrogenation (catalytic addition of hydrogen; see also Reaction Kinetics)

Alkenes are hydrogenated to give **alkanes.**



Reagents and conditions: H_2(g), nickel (catalyst), heat

This reaction is an example of **heterogeneous catalysis**.
Hydrogenation can be carried out using more active catalysts such as platinum (Pt) and palladium (Pd) at room temperature.

Other reducing agents such as $LiAlH_4$ cannot be used for hydrogenation of alkene. Why?
$LiAlH_4$ which is a source of hydride ions, H^-, will be repelled by the electron-rich π electron cloud in C=C bond. It will not be able to add hydrogen atoms across the C=C double bond.

Applications

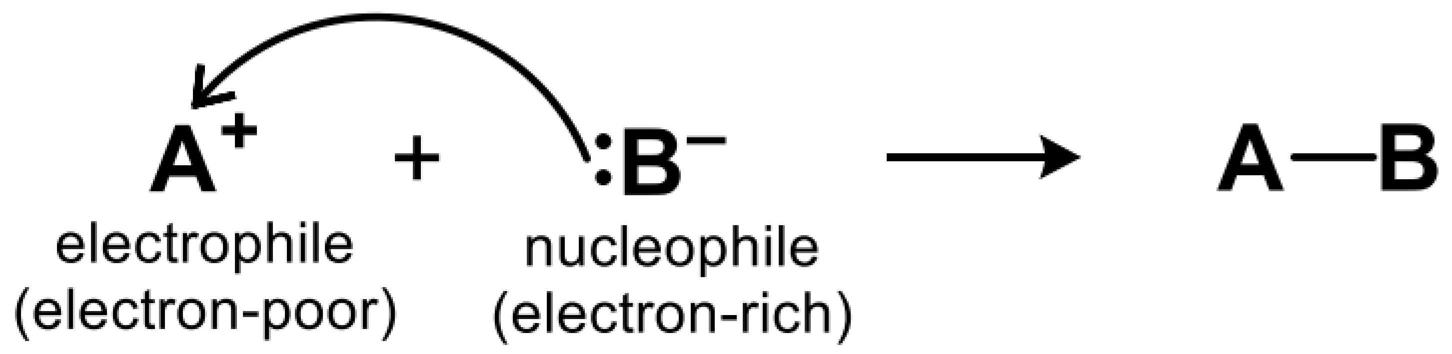
Catalytic hydrogenation is used to 'harden' unsaturated fats and oils in the making of margarine. It is also used in the conversion of alkenes, obtained from petroleum cracking, into alkanes in the manufacturing of high-octane gasoline and aviation fuels.

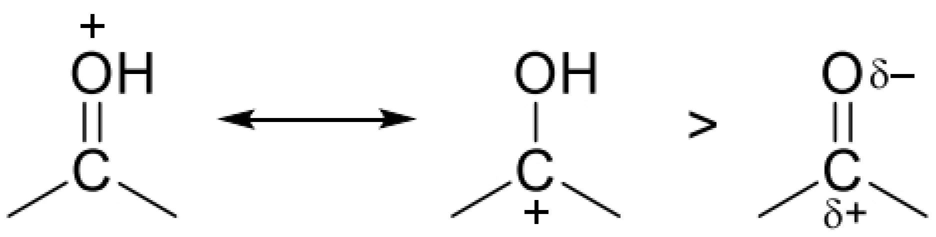
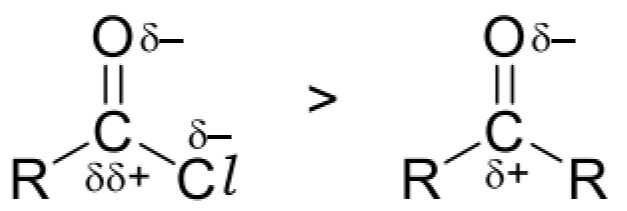
6.3 Electrophilic addition reactions

Not in H1 Syllabus except 6.3.3 i)

6.3.1 Electrophiles and nucleophiles

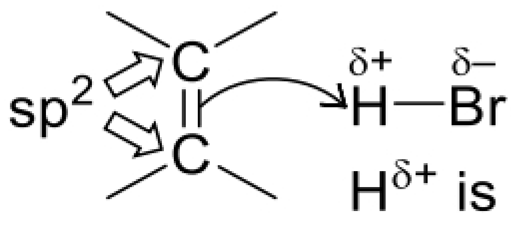
Most organic reactions are polar reactions which take place between an **electron-poor site** and an **electron-rich site**. Such reactions involve the **donation of an electron pair** from a **nucleophile** to an **electrophile**.



electrophile (Lewis acid) ('electron-loving')	**nucleophile (Lewis base)** ('nucleus-loving')
electron-poor species • **positively charged ions** • neutral molecules carrying a **partial positive charge** (δ+)	electron-rich species e.g. • **negatively charged ions** • neutral molecules that contain **lone pair of electrons**
forms covalent by **accepting** an electron pair from an **electron-rich** site	form a covalent bond by **donating** an electron pair to an **electron-deficient** site
strength of electrophile depends on **size and stability of positive charge** • cations are more powerful electrophiles than neutral molecules  **protonated ketone** **ketone** • carbon atoms are electrophilic when attached to electronegative atoms. The more electronegative the atom(s) bonded to carbon, the more electrophilic the carbon atom.  **acyl chloride** **ketone**	strength of nucleophile depends on **availability of lone pair of electrons** • anions are more powerful nucleophiles than neutral molecules $H\ddot{O}^- > H_2\ddot{O}$ • the more electronegative the atom bearing the negative charge or lone pair, the tighter the electrons are held to the nucleus, the weaker the nucleophile. $R-\ddot{N}H_2 > R-\ddot{O}H > R-\ddot{F}$ • down the group, electrons are held less tightly to the nucleus as the atom size increases, and hence they are more available for forming bonds, making the nucleophile stronger. $H_2\ddot{S} > H_2\ddot{O}$ $I^- > Br^- > Cl^- > F^-$

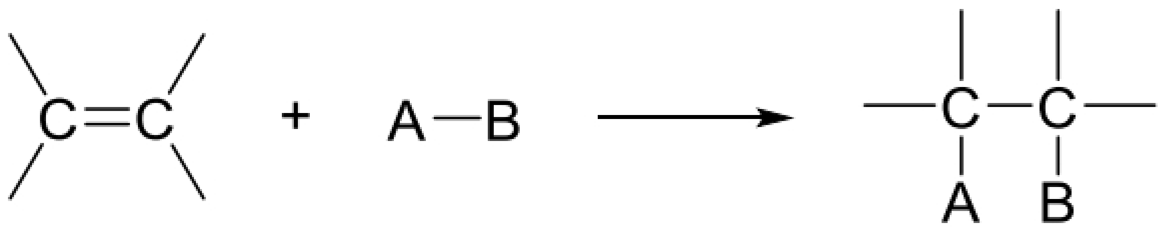
LO (a) Explain the general reactivity of alkenes towards electrophilic reagents/electrophiles

- Alkenes, though generally non-polar, are **highly reactive** as compared to the alkanes because of the **π electron cloud** between the doubly bonded carbon atoms.
- These **loosely held π electrons** will attract **electrophiles** or even induce dipoles, creating electrophilic sites in some nearby neutral molecules.



H$^{\delta+}$ is the electrophilic site as it is electron-deficient

- Alkenes are **<u>unsaturated</u>**, thus they undergo addition reactions. The reactions of alkenes mainly involve **<u>electrophilic addition</u>** reactions.

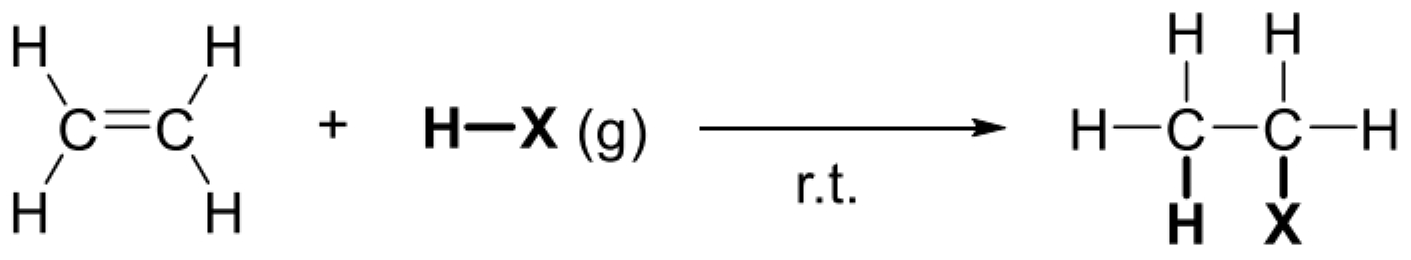


- During the reaction, the **<u>weaker π bond</u>** (due to less effective overlapping of p orbitals) is **<u>broken</u>** instead of the σ bond. In place, two **<u>strong σ bonds</u>** are formed in the saturated product.
- The **<u>shape of the C atom in C=C now changes from trigonal planar to tetrahedral</u>** (the **<u>hybridisation of the C atom changes from sp^2 to sp^3</u>**).

LO (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
(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

6.3.2 Electrophilic addition of hydrogen halides (hydrohalogenation)

- The addition of **hydrogen halides (HX)** to alkenes produces **halogenoalkanes (alkyl halides).**



X = C*l*, Br, I

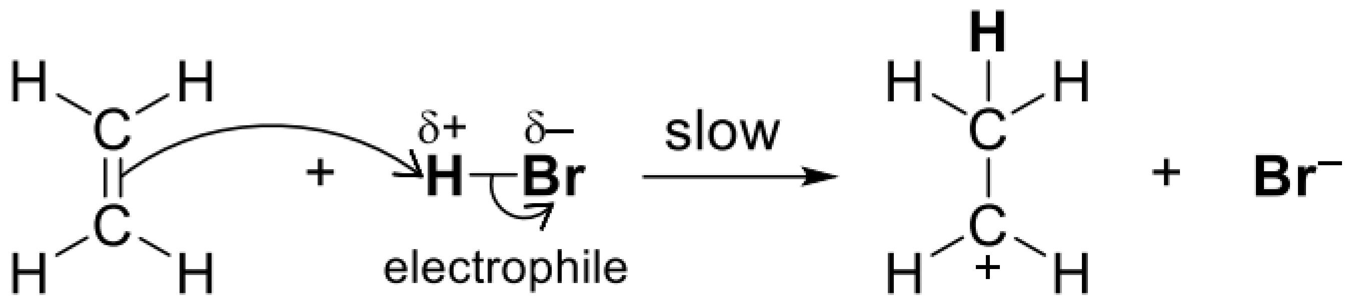
Reagents and conditions: gaseous HC*l* or HBr or HI, room temperature

- The order of reactivity of HX is HI > HBr > HC*l*. The weaker the H–X bond strength, the greater the reactivity with alkenes.
- This takes place via the mechanism **electrophilic addition** with the formation of an **intermediate carbocation**.
- The electrophilic site is the partially positive hydrogen atom of HX. Hence it is the hydrogen that first adds to the alkene to give the intermediate carbocation.

Name of mechanism: **Electrophilic Addition**

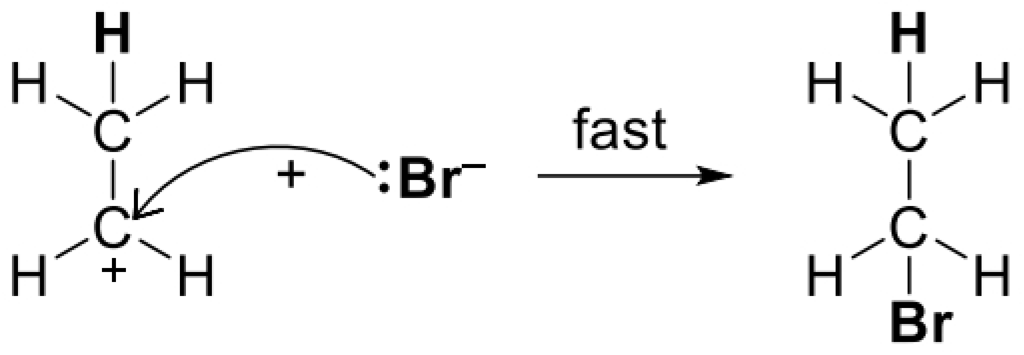
Step 1: (Slow step)

- In the first step of the mechanism, heterolytic fission of the H–Br bond (Lewis acid) occurs and the π bond of the ethene molecule (Lewis base) cleaves. This results in the formation of a bromide ion and a positively charged intermediate.



Step 2: (Fast step)

- In the second step, the negatively charged bromide ion (Lewis base) donates a lone pair with the carbocation intermediate (Lewis acid) to form the product.



Points to note when describing the mechanism:

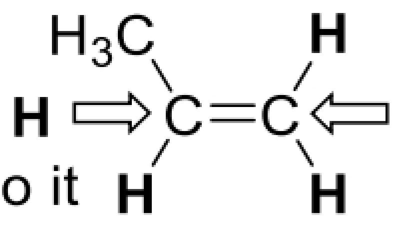
- **Name** the type of reaction undergone, i.e. electrophilic addition
- Show the **movement of electrons** during the reaction using curved arrows (full arrow head for a pair of electrons).
  Remember that electrons flow from electron donor/electron-rich region (Lewis base) to electron acceptor/electron-deficient region (Lewis acid), and thus the arrow should point in the same direction.
- Show **lone pair of electrons** on Br⁻(or any other species that reacts with the carbocation intermediate) in the fast step.
- Indicate **partial charges**, δ+ and δ–.
- Indicate **slow step** for each elementary step (if any).

- Using **Markovnikov's Rule** to predict major products of an electrophilic addition reaction

⇒ When HX is added to an **unsymmetrical alkene** (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 of the HX attaches itself to the C atom already carrying having the greater number of hydrogen atoms**.

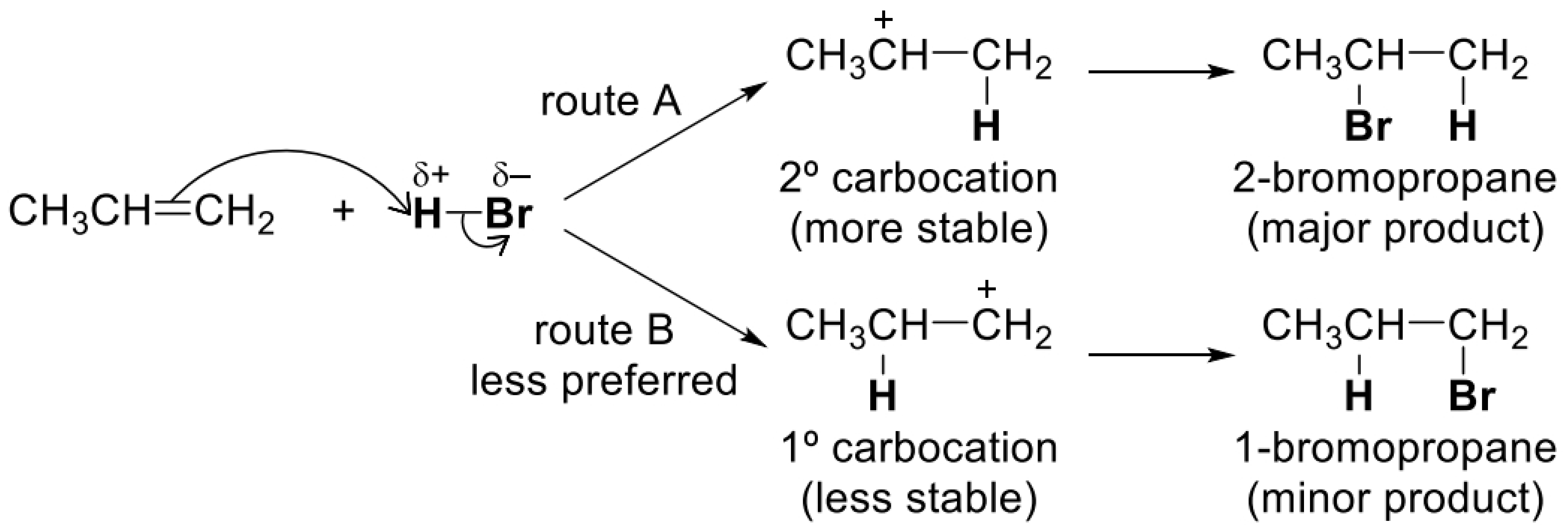
this carbon has only **1 H** atom directly bonded to it



this carbon has **2 H** atoms directly bonded to its

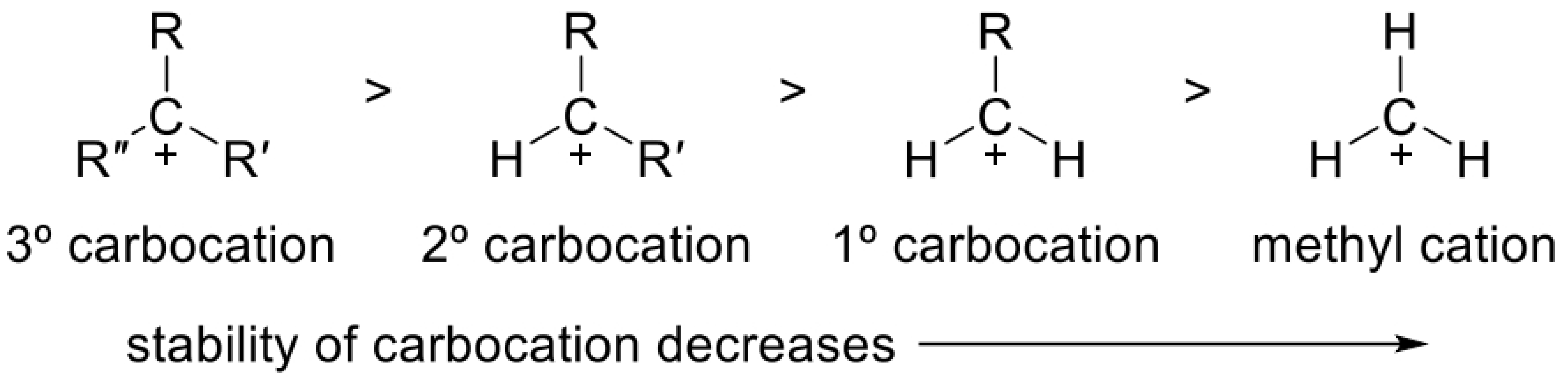
- **Explanation of Markonikov's rule**

⇒ This reaction can proceed via two routes (either Route A or B), which in turn generate 2 possible carbocation intermediates (1º and 2º carbocation). However, 2-bromopropane is the predominant product as it is formed via the **more stable 2º carbocation**.



⇒ Markovnikov's Rule can be explained by comparing the **<u>stability of carbocation intermediates</u> formed during the electrophilic addition.**

Order of stability of carbocations:



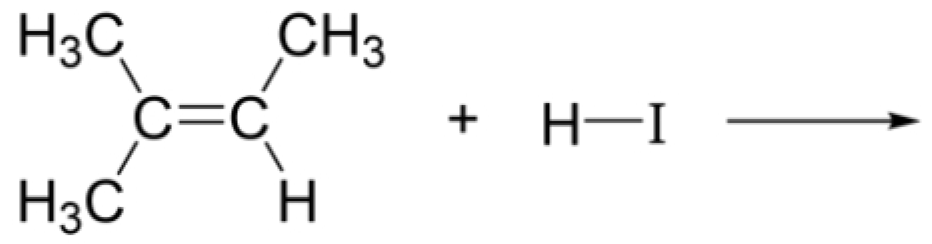
Reason:

- ✓ Alkyl groups are electron-donating, they help to disperse the positive charge on the carbocation thus stabilising it.
- ✓ Therefore, the more highly substituted carbocation has greater stability, hence more products will be formed from it.

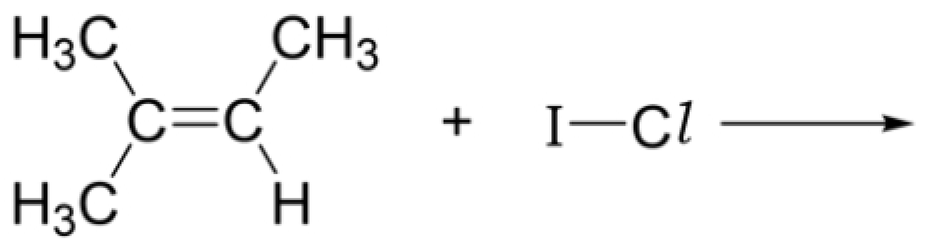
Example 6A

Identify the major product formed for the reactions.

(a)



(b)



6.3.3 Electrophilic addition of halogens

Note for H1 Chemistry students:

Knowledge of electrophilic nature or mechanism is **not required**.

The products obtained in the reaction are dependent on the solvent used.

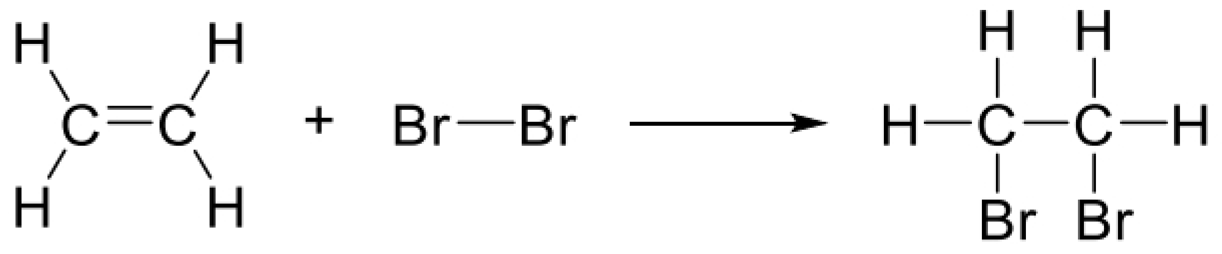
i) Inert Solvent – CCl_4

Reagents and conditions: Cl_2 in CCl_4 or Br_2 in CCl_4, room temperature

- This reaction is conducted in the absence of uv light to prevent any free radical substitution that can happen on the alkyl groups.

- This reaction may be used as a simple laboratory **test to check for unsaturation** (*i.e.* the presence of the **C=C bond**). The amount of Br_2 required indicates the number of C=C bonds present in the molecule.

  For example, when ethene is bubbled into Br_2 in CCl_4 at room temperature (no light or **in the dark**):



  Observation: The orange-red colour of Br_2 in CCl_4 is rapidly **decolourised**
  Explanation: Br_2 is added across the C=C bond to give colourless 1,2-dibromoethane

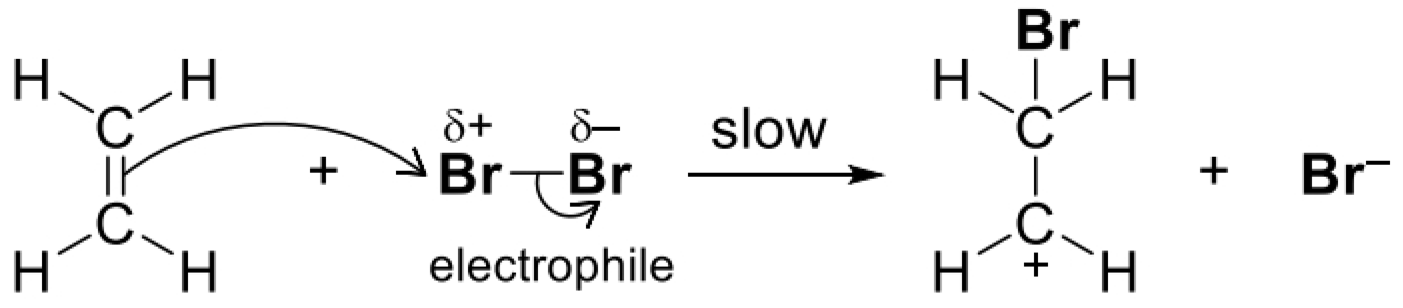
  Note:
  - Fluorine is too reactive and reacts explosively with alkenes under laboratory conditions;
  - Iodine does not react with most alkenes.

Name of mechanism: **Electrophilic Addition**

Step 1: (Slow step)

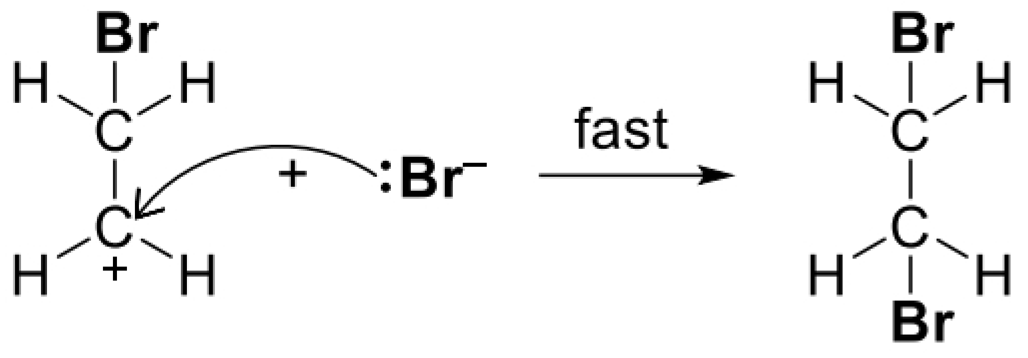
- As the bromine molecule approaches the alkene, the Br–Br bond is **polarised** by the π electron cloud of the C=C double bond.

- The positive end of the polarised Br–Br (Lewis acid) acts as an electrophilic site, attacking the C=C double bond (Lewis base), to give an **intermediate carbocation**.



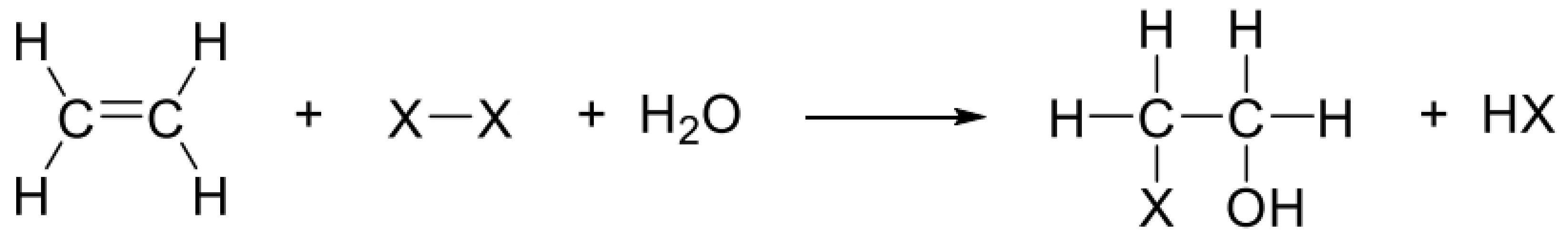
Step 2: (Fast step)

- The bromide ion (acting as a nucleophile) attacks the intermediate carbocation to give the final product.



ii) Nucleophilic Solvent – H_2O

If water is used as a solvent, a halohydrin is obtained as the major product.

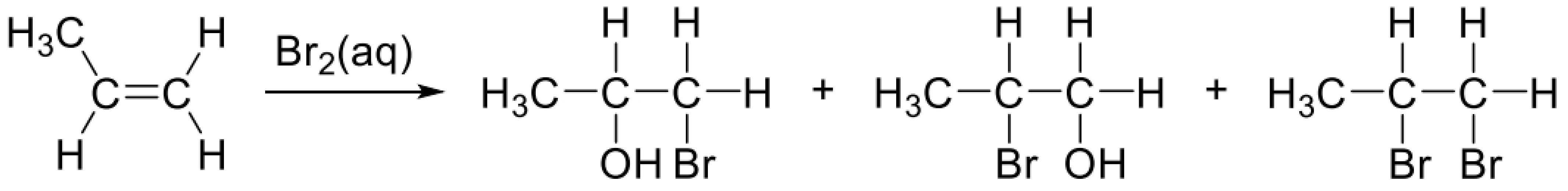


halohydrin
(major product)

Reagents and conditions: Cl_2(aq) or Br_2(aq), room temperature

- If an alkene reacts with a halogen dissolved in a solvent that can act as a nucleophile, such as H_2O, the product mixture includes a halohydrin.

  For example,

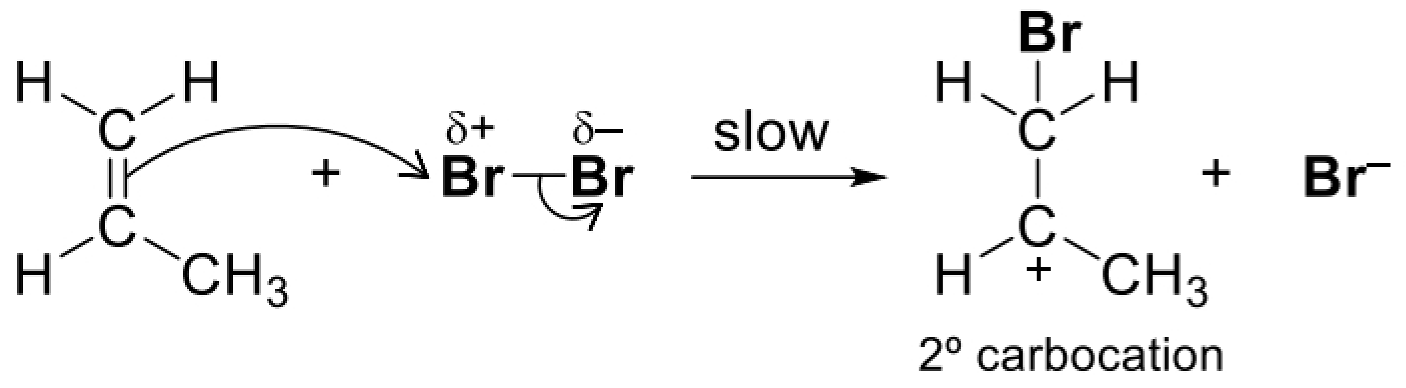


(major product)

Name of mechanism: **Electrophilic Addition**

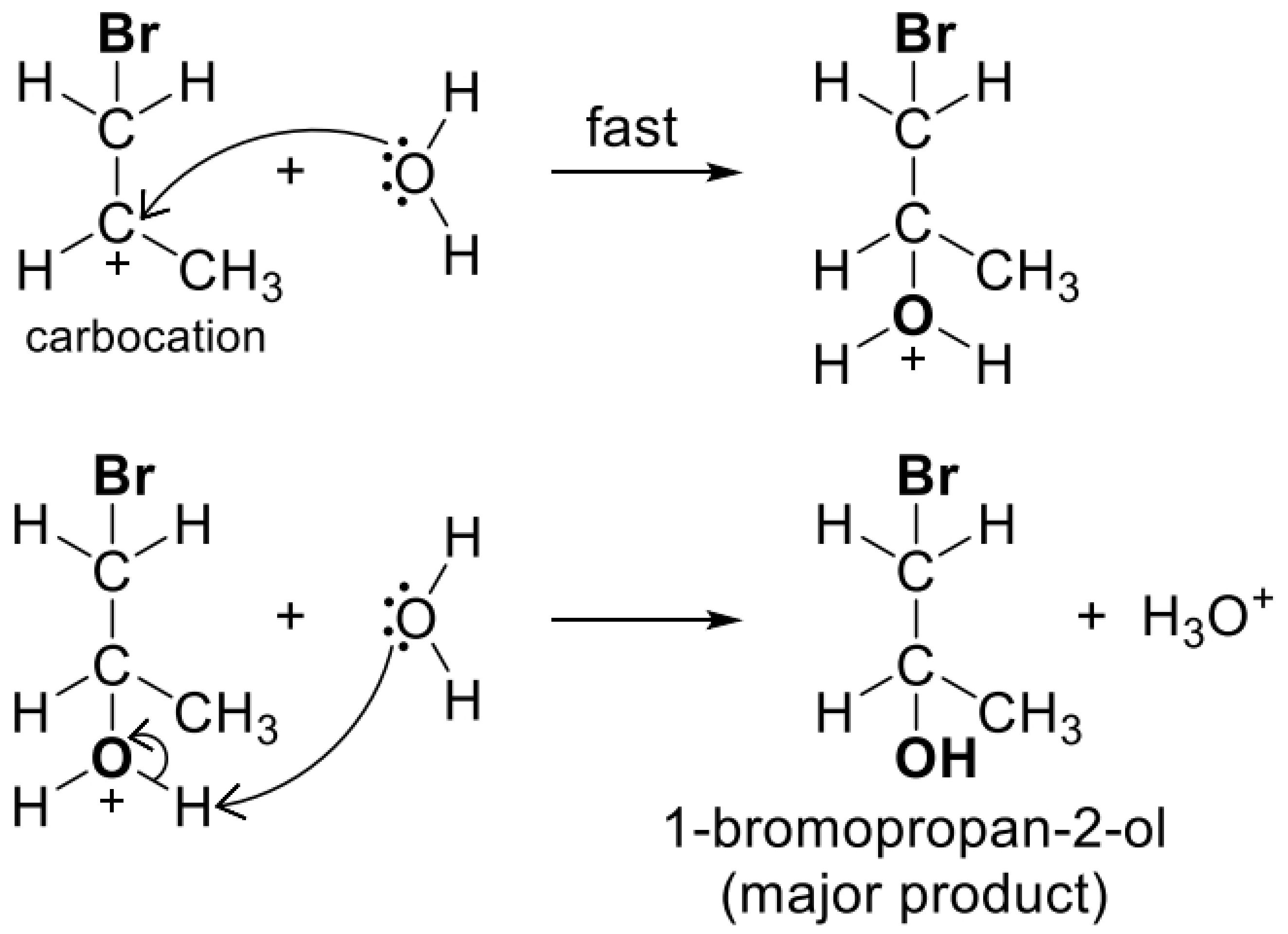
Step 1: (Slow step)

- The more stable 2º carbocation intermediate is formed preferentially.



Step 2: (Fast step)

- There are two types of nucleophiles present: H_2O and Br^-. Either can attack the carbocation intermediate in the fast step, leading to two different products. The **halohydrin** is formed as the **major product** as **water is present in excess**. There are more water molecules present than Br^- ion to attack the intermediate carbocation formed. The water molecules also effect the deprotonation to form 1-bromopropan-2-ol.



The formation of the halohydrin can be seen as the addition of $\overset{\delta+}{Br}—\overset{\delta-}{OH}$ across the C=C double bond. As propene is an unsymmetrical alkene, Br will be attached to the carbon carrying more H atoms as this gives a more stable carbocation intermediate.

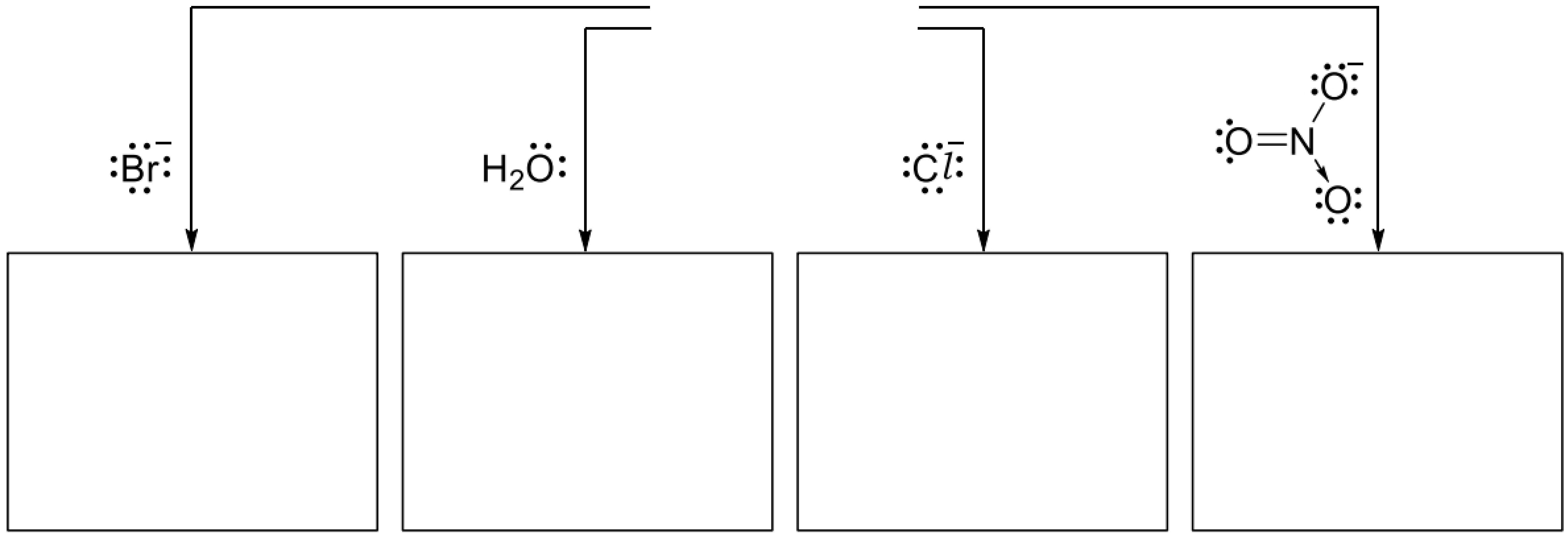
- If the reaction is done in presence of other anions, such as F^-, Cl^-, CN^-, NO_3^-, these anions can also attack the carbocation in the fast step to form other **minor** products.

- **The reaction of alkenes with Br_2(aq) can also be used as a test for unsaturation**. The orange aqueous Br_2 is rapidly decolourised indicating the presence of the C=C bond.

Example 6B

Draw the carbocation intermediate and hence four possible products formed when ethene reacts with aqueous bromine in the presence of sodium chloride and sodium nitrate.

(carbocation formed when ethene first reacts with Br_2)

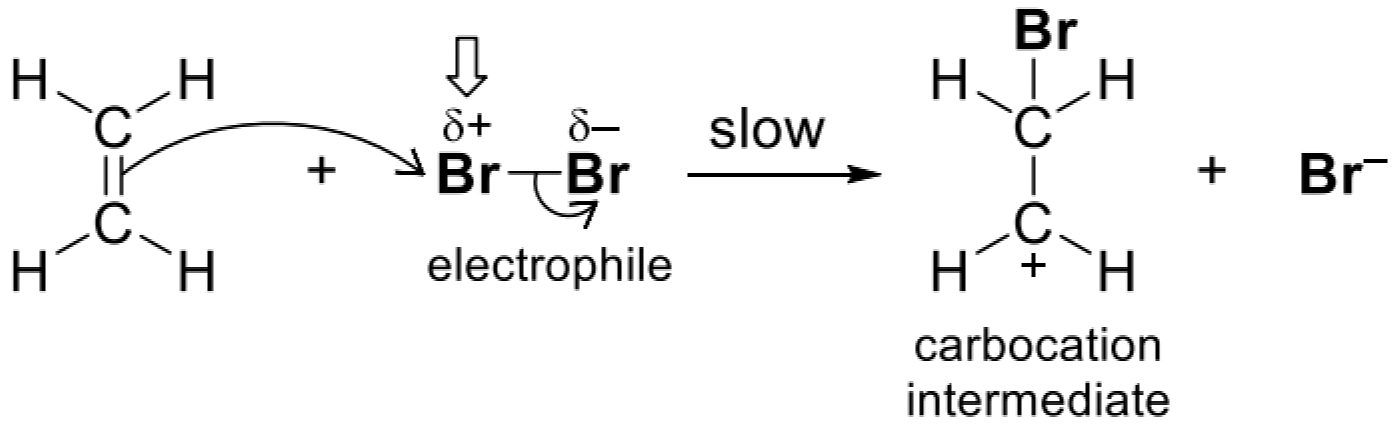


(Br^-, H_2O, Cl^- and NO_3^- are the nucleophiles present in the mixture)

*Note that ALL products have **at least one Br atom (from halogen electrophile)** present.

Why do compounds such as 1,2-dichloroethane or 2-chloroethanol not exist in the product mixture?

The slow step of the reaction involves the π electrons attacking the **halogen electrophile**, Br_2 to form a carbocation intermediate.



The carbocation formed will have a Br atom bonded to it. Thus, all products must have at least one Br atom bonded.

H_2O, NO_3^- and Cl^- are all electron-rich nucleophiles and thus they can attack the resulting carbocation.
Since they are electron-rich, they will NOT be attacked by ethene in the slow step.

Self Check 6A

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?

A $CH_2Br–CH_2Br$ $CH_2Cl–CH_2Cl$

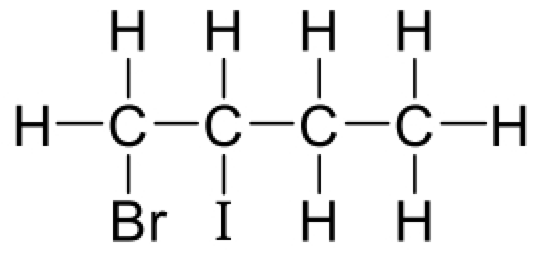
B $CH_2Br–CH_2Br$ $CH_2Cl–CH_2Br$

C $CH_2Br–CH_2Br$ $CH_2(OH)–CH_2Cl$

D $CH_2(OH)–CH_2Br$ $CH_2Cl–CH_2OH$

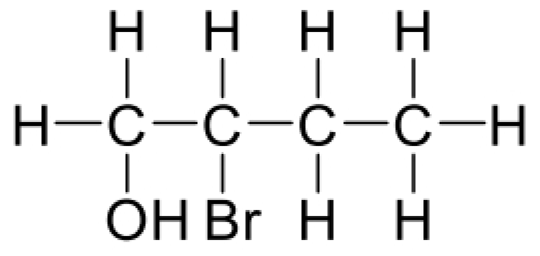
2 Which of the following is **not** a product formed when but-1-ene reacts with IBr(aq)?

A



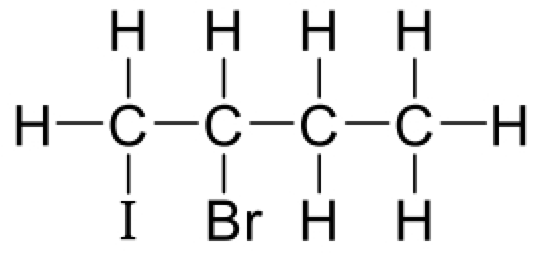
$CH_2Br–CHI–CH_2–CH_3$

C



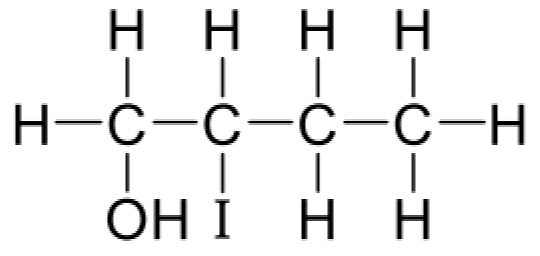
$CH_2(OH)–CHBr–CH_2–CH_3$

B



$CH_2I–CHBr–CH_2–CH_3$

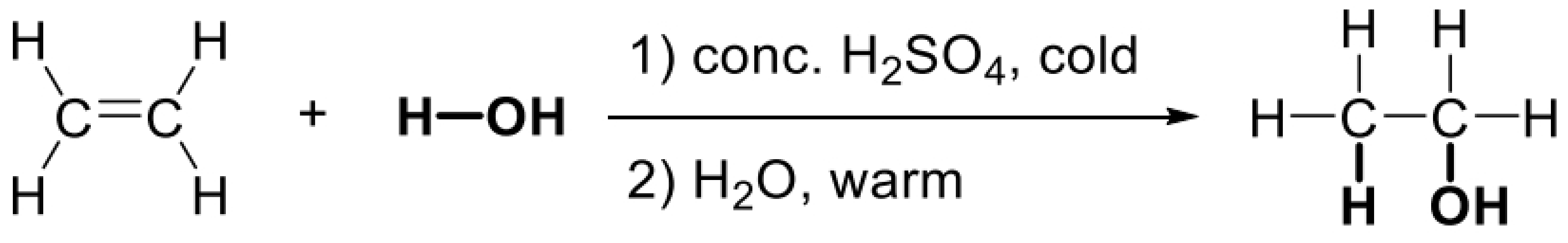
D



$CH_2(OH)–CHI–CH_2–CH_3$

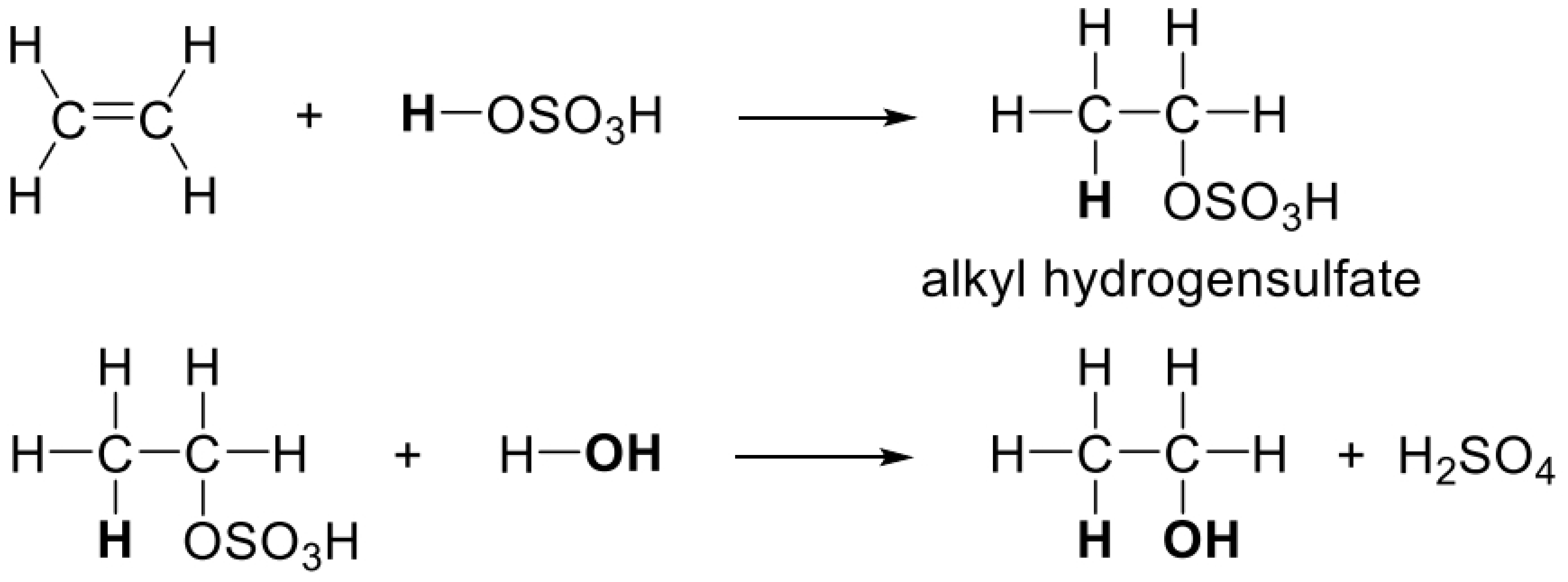
6.3.4 Electrophilic addition of water (hydration)

The addition of water to alkenes produces **alcohols**:

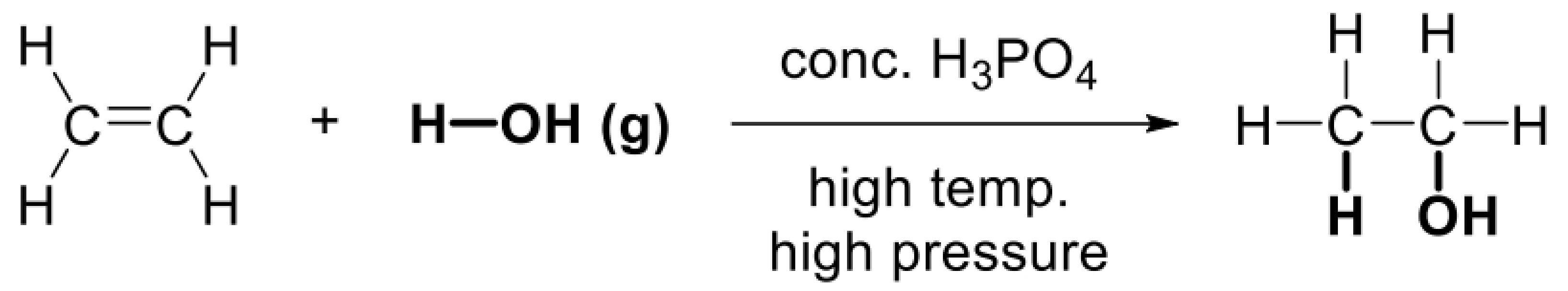


Reagents and conditions: 1) concentrated H_2SO_4, cold
2) warm with water

- In the laboratory, this is achieved *via* a two-stage process, involving reaction of the alkene with concentrated sulfuric acid in the cold to give an alkyl hydrogensulfate, which is then *hydrolysed* by warming with water to give the alcohol:



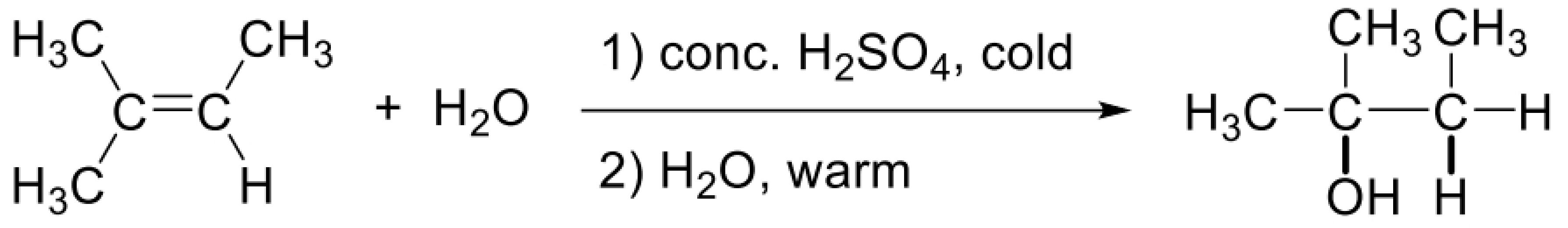
- Industrially, the reaction is performed using **steam** with **phosphoric acid catalyst under high temperature and pressure**:



Reagents and conditions: steam, H_3PO_4 (catalyst) at high temp. and pressure

- Water is not a good electrophile, hence, the addition of water has to be acid-catalysed.

- Hydration of **unsymmetrical** alkenes follows Markovnikov's rule.



2-methylbut-2-ene

Checkpoint for Section 6.1 – 6.3

At the end of these sections, you must be able to:

– Describe the reagents and conditions for reactions that alkenes undergo:
  - Reduction of alkenes
  - Electrophilic addition of hydrogen halides, halogens (in inert solvent and in water), water

– Explain what electrophiles are and why alkenes generally reacts with it.

– Compare and explain the differences in general reactivity of alkanes and alkenes.

– Describe the mechanism of electrophilic addition, drawing curly arrows to show the movement of electron pairs during the reaction and label all the partial charges and/or charges of the species involved

– Apply Markovnikov's rule to electrophilic addition to unsymmetrical alkenes to determine the major product of a reaction.

– Explain the composition of products in terms of stability of carbocation intermediate

6.4 Oxidation

Not in H1 Syllabus

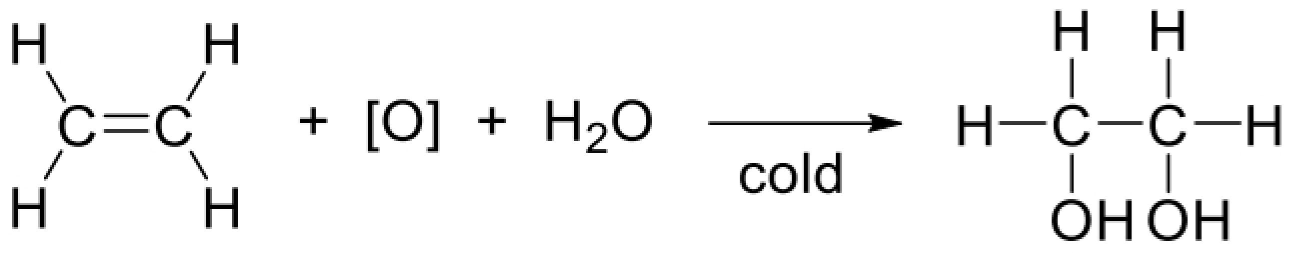
LO (b) Describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:
  (v) oxidation by cold, alkaline solution of manganate(VII) ions to form the diol
  (vi) oxidation by hot, acidified solution of manganate(VII) ions leading to the rupture of the carbon-to-carbon double bond in order to determine the position of alkene linkages in larger molecules

Alkenes can undergo different types of oxidation:

- cleavage of the π bond of the C=C bond (**mild oxidation**)
- cleavage of the C=C bond (**vigorous oxidation**)

6.4.1 Mild oxidation (without cleavage of the C=C bond)

The reagents and conditions is strong enough to break the π bond but not the σ bond of the alkene, and hence a **diol** is produced.

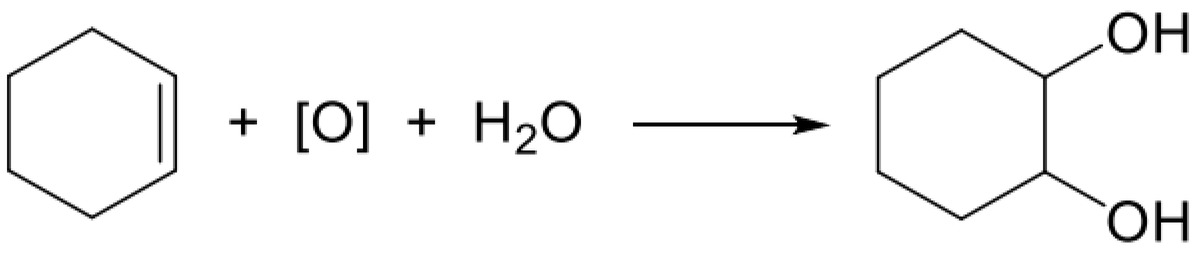


Reagents and conditions: $KMnO_4$(aq), NaOH(aq), cold
Observations: Decolourisation of purple $KMnO_4$ and formation of brown precipitate (MnO_2)

OR

Reagents and conditions: $KMnO_4$(aq), H_2SO_4(aq), cold
Observations: Purple $KMnO_4$ solution is decolourised

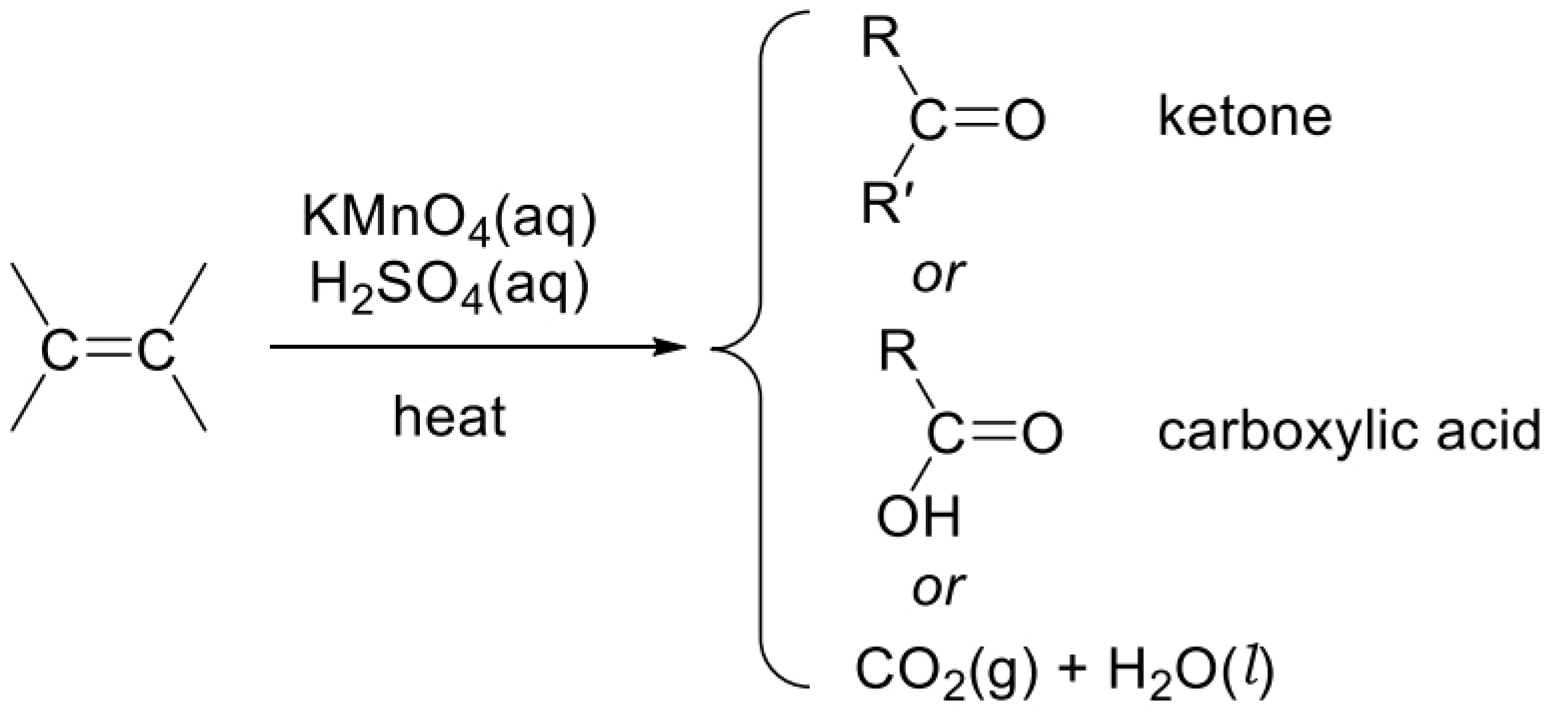
Example:



- Cyclohexene is oxidised to give cyclohexane-1,2-diol.
- This reaction can also be used as a test for the presence of C=C bond.

6.4.2 Oxidative cleavage (with the cleavage of C=C bond)

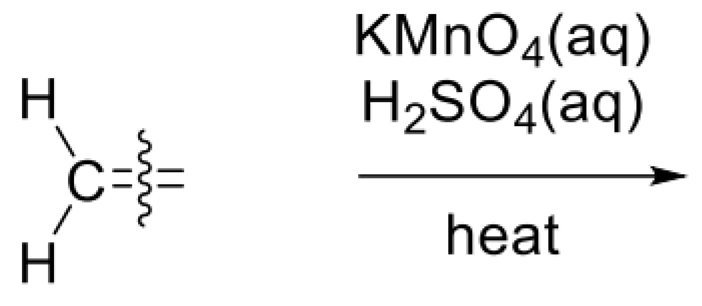
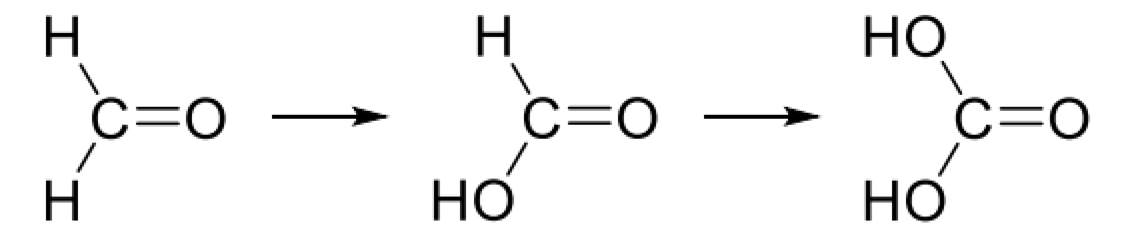
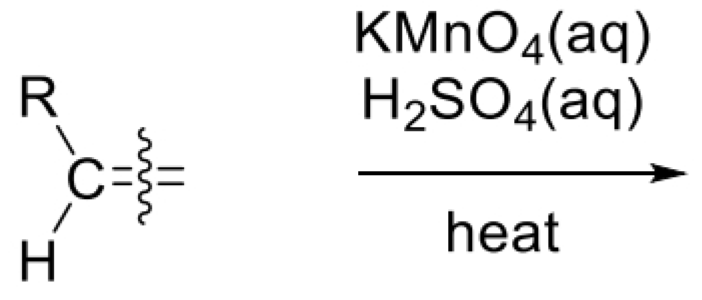
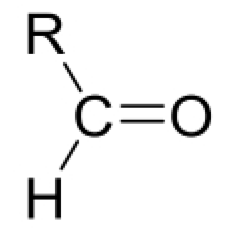
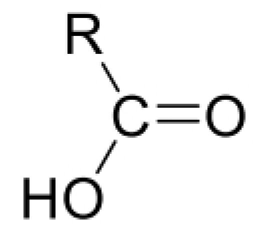
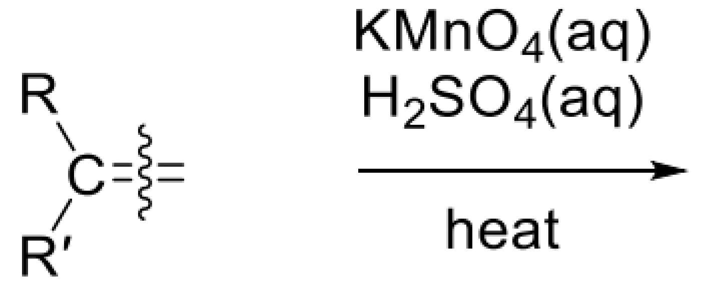
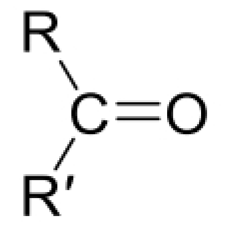
In acidic medium:



Reagents and conditions: $KMnO_4$(aq), H_2SO_4(aq), heat
Observations: Purple $KMnO_4$ solution is decolourised

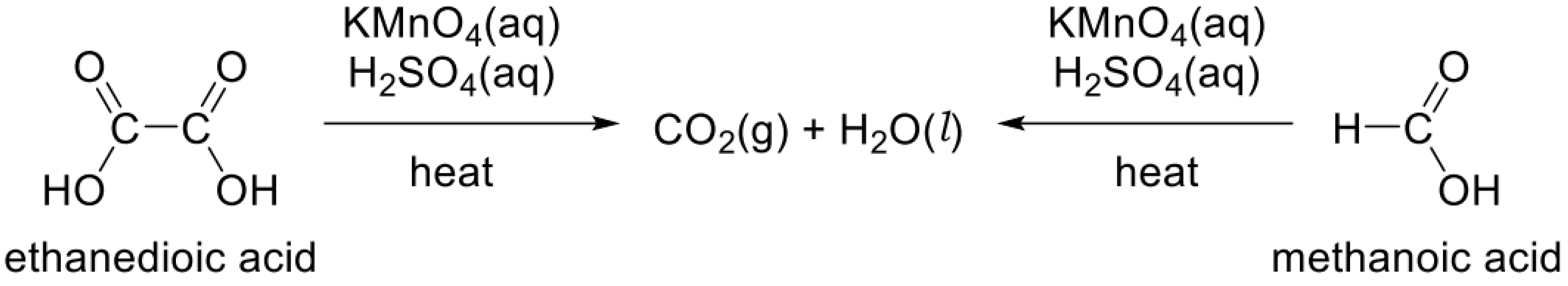
- Both the π bond as well as the σ bond of the alkene are cleaved under the strongly oxidising conditions, resulting in a variety of products such as **ketones, carboxylic acids or CO_2**.

- The oxidation products formed depends on the structure of the alkene. Therefore, vigorous oxidation of alkenes can be used to **determine the position of the C=C bond** in an alkene.

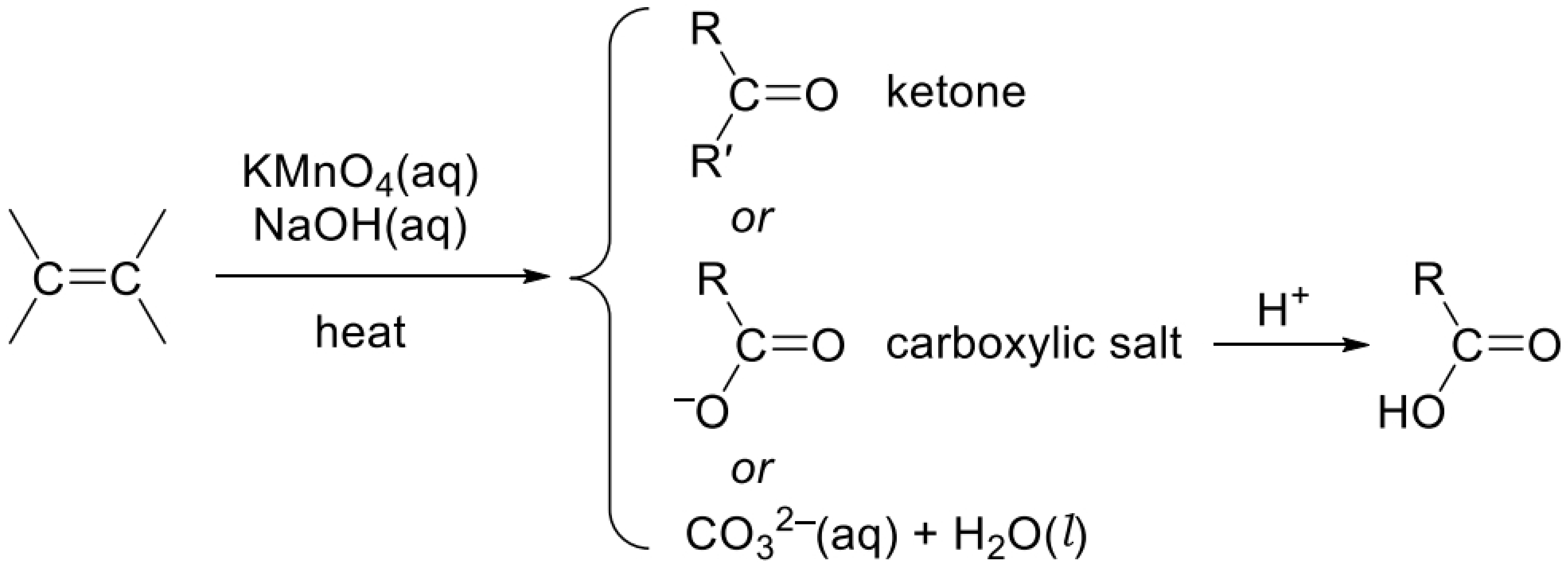
	intermediates	final product(s)
case 1: sp^2 C atom bonded to 2 H atoms (terminal alkene) 	 **methanal** **methanoic acid** **carbonic acid**	$CO_2 + H_2O$
case 2: sp^2 C atom bonded to 1 H and 1 R group 	 **aldehyde**	 **carboxylic acid**
case 3: sp^2 C atom bonded to 2 R groups 	Nil	 **ketone**

- Oxidative cleavage can be used as a test to differentiate alkenes with terminal C=C double bond and those without. For terminal C=C double bond, upon oxidation, **CO_2 is liberated which forms a white precipitate when bubbled through limewater, $Ca(OH)_2$**.

- The carboxylic acids HCO_2H and $HO_2C–CO_2H$ which may be formed from oxidative cleavage are further oxidised by hot, acidified potassium manganate(VII) to form CO_2 and H_2O. (You have learned this under Chapter 1 on Redox reaction)



In alkaline medium:



Reagents and conditions: $KMnO_4(aq)$, NaOH(aq), heat
Observations: Decolourisation of purple $KMnO_4$ and formation of brown precipitate (MnO_2)

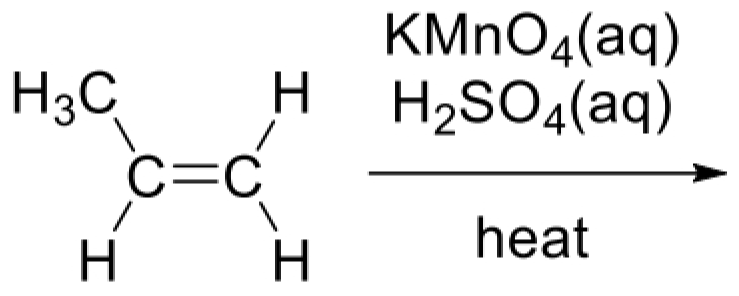
- When the medium for strong oxidation of alkenes is changed from acidic to alkaline using NaOH(aq), some of the products obtained will change. For example, carboxylate salt, RCO_2^- is obtained instead of carboxylic acid, and carbonate, CO_3^{2-} is obtained instead of CO_2. Hence, **no effervescence will be observed**.

Note:
1. The difference in mild and vigorous oxidation of alkene lies in the **temperature used and NOT the medium used.**
2. $K_2Cr_2O_7$ is not strong enough as an oxidising agent for oxidation of alkenes.

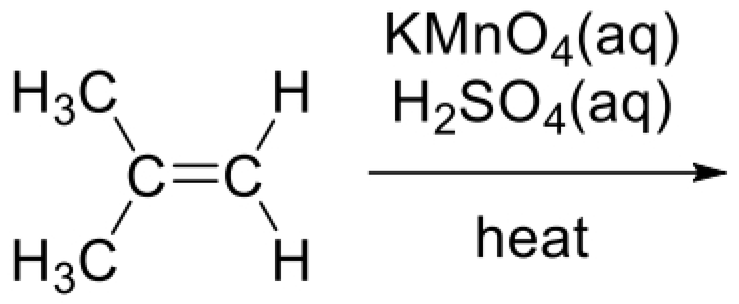
Example 6C

1 Give the structural formula of the products formed for each reaction.

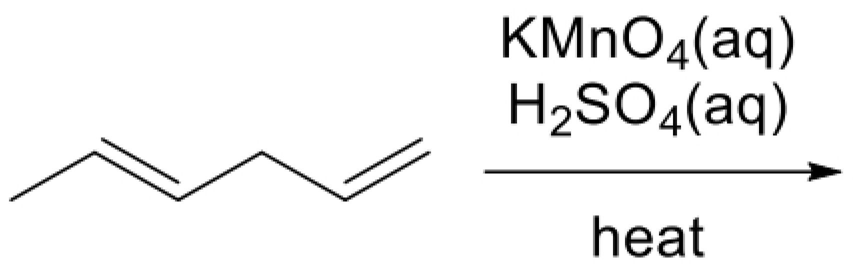
(a)



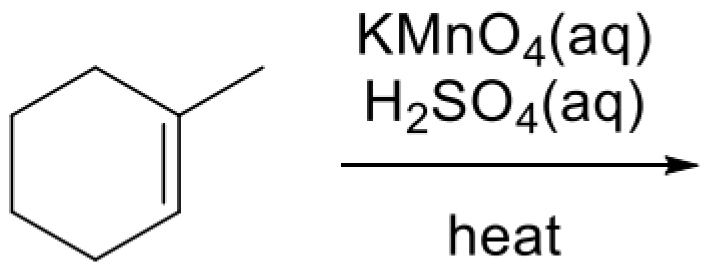
(b)



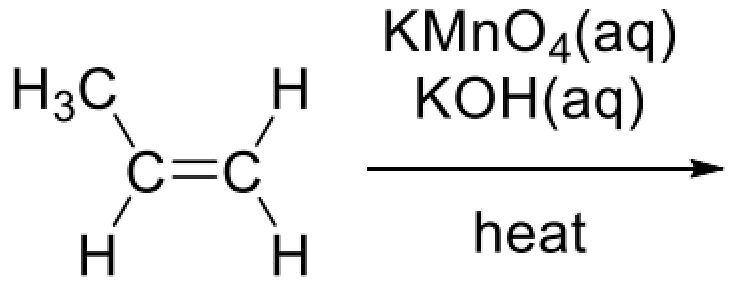
(c)



(d)

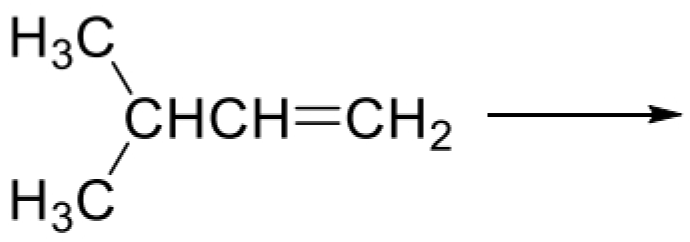


(e)



*compare the products of this reaction with that in (a)!

2 Draw the structure of the organic compound(s) formed when the following compound is heated with concentrated alkaline $KMnO_4$, followed by acidification.
(modified N2008/II/3(a))



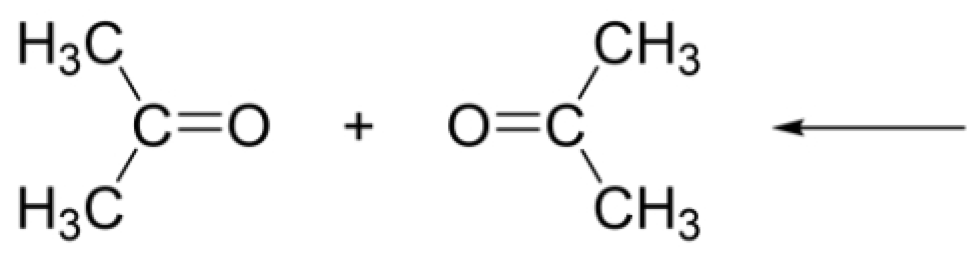
$(CH_3)_2CHCH{=}CH_2 \longrightarrow$

Example 6D

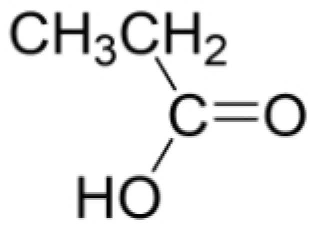
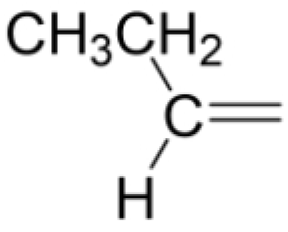
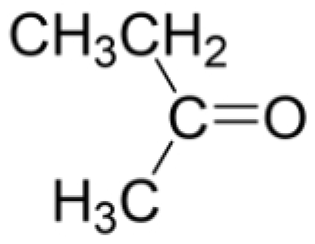
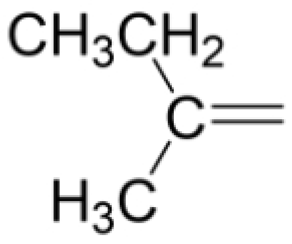
Draw the structure of the alkene that forms the given oxidation products.

(a) **A** (C_6H_{12}) → CH_3COCH_3 only

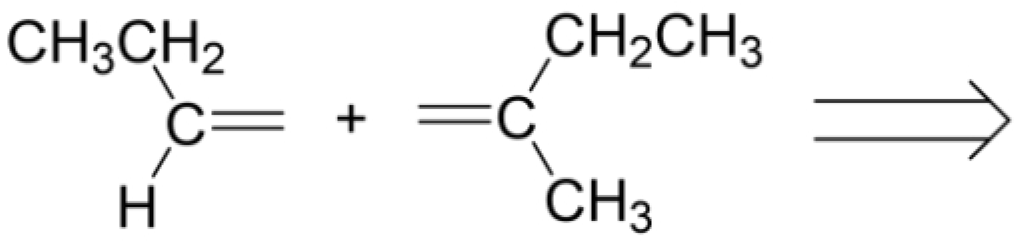
Since only one 3 C product is formed from a 6 C alkene, it means the alkene is symmetrical, resulting in the formation of the same oxidation product.



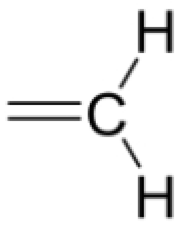
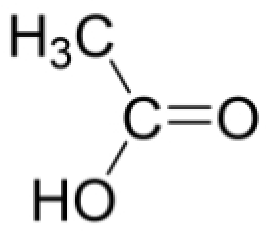
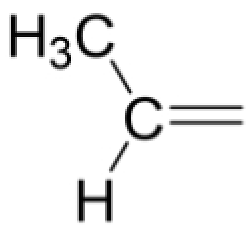
(b) **B** (C_7H_{14}) → $CH_3CH_2CO_2H + CH_3CH_2COCH_3$

-  indicates the presence of the  fragment
-  indicates the presence of the  fragment

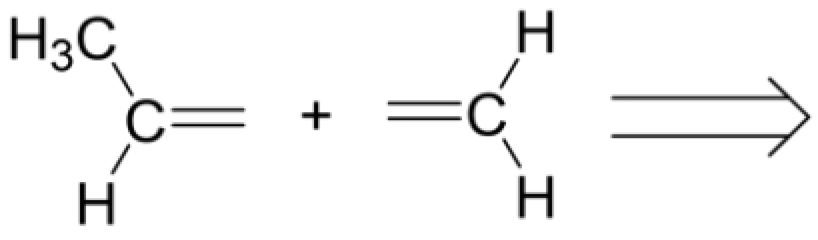
By arranging the groups, the alkene is



(c) **C** (C_3H_6) → $CH_3CO_2H + CO_2 + H_2O$

- $CO_2 + H_2O$ formed indicates the presence of terminal alkene, 
-  indicates the presence of the  fragment

By arranging the groups, the alkene is



Checkpoint for Section 6.4

At the end of this section, you must be able to:

– Describe the reagents and conditions for reactions that alkenes undergo:
  - Mild oxidation of alkenes
  - Oxidative cleavage of C=C in alkenes

– Understand that the difference in condition determines the type of oxidation that occur.

– Determine the products of vigorous oxidation depending on the structure of the alkene, and the medium that was used (acidic or alkaline).

– Use the products of vigorous oxidation to determine the structure of the alkene.

7 Chemical Tests for Alkenes

Note for H1 Chemistry students:

Only reaction with Br_2 in inert solvent is **required**.

- The following reactions may be used as test for unsaturation because they give rise to easily observable colour changes:

test	expected observations if an alkene is present	type of reaction
reagent: Br_2 in CCl_4 or Br_2(aq) **condition:** room temperature	The reddish-brown bromine or orange bromine water turns colourless	addition
reagent: $KMnO_4$(aq), NaOH(aq) **condition:** cold/heat	The purple $KMnO_4$ solution is decolourised, a brown solid is observed.	oxidation
reagent: $KMnO_4$(aq), H_2SO_4(aq) **condition:** cold/heat	The purple $KMnO_4$ solution is decolourised	oxidation

Self Check 7A

A hydrocarbon **P**, C_5H_8, can be extracted from mature leaves of some plants. Compound **P** is subjected to the following tests to analyse its structure.
State **all** deductions about compound **P** that you can make in each of the tests.

(a) Compound **P** reacts with hydrogen in the presence of palladium catalyst to give a compound, C_5H_{12}.

(b) Upon heating compound **P** with concentrated aqueous $KMnO_4$, only **one organic product**, CH_3COCO_2H, is formed.

(c) Use your deductions to draw a displayed formula for compound **P**.

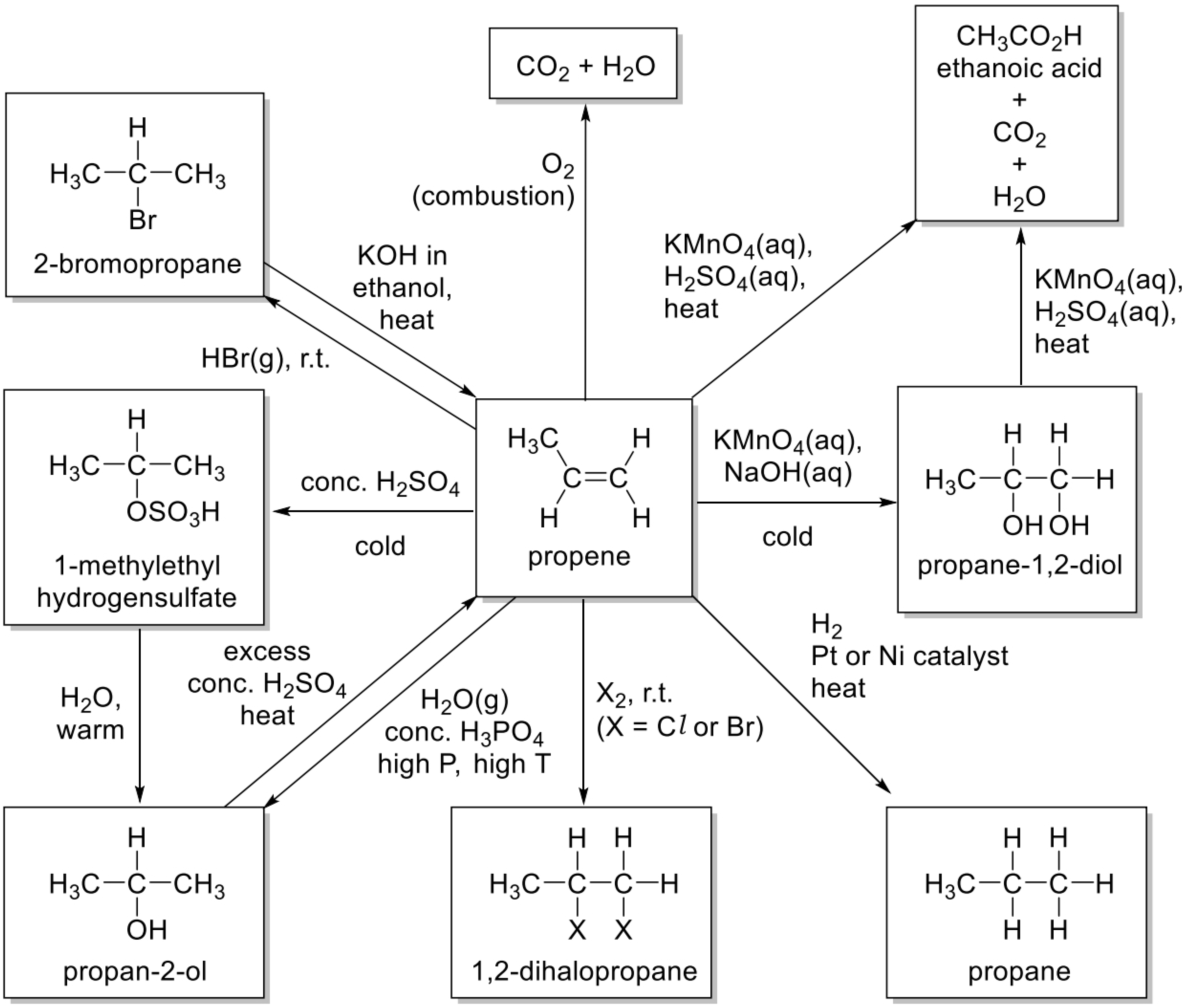
(d) Suggest **one other reagent** that can be used to test the presence of the functional group in compound **P**. State what you would expect to observe in the test.

Checkpoint for Section 7

At the end of this section, you must be able to:

– Describe the reagents and conditions for reactions that can be used to test for presence of unsaturation (C=C) in a compound.

8 Summary



Self Check Answers

2A – 2,3-dimethylbut-2-ene; 3-ethyl-4-methylhex-3-ene; penta-1,4-diene

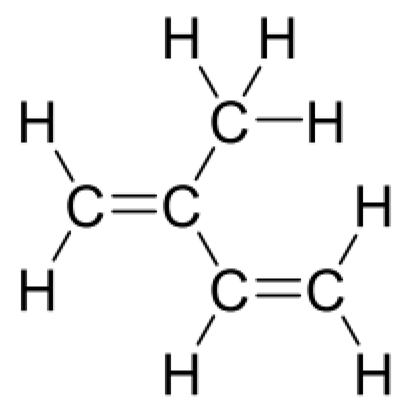
4A – 2,3-dimethylbut-2-ene < *trans*-hex-2-ene < *cis*-hex-2-ene

6A – **B**; **C**

7A – **(a)** 1 mol of **P** reacts with 2 mol of H_2 ($C_5H_8 \rightarrow C_5H_{12}$). This indicates that **P** has <u>two C=C groups</u>.

(b) There is a loss of two carbon atoms (in the form of CO_2) after oxidation. This indicates that there are <u>two =CH_2 groups (terminal double-bonded carbon)</u> in **P**.

(c)



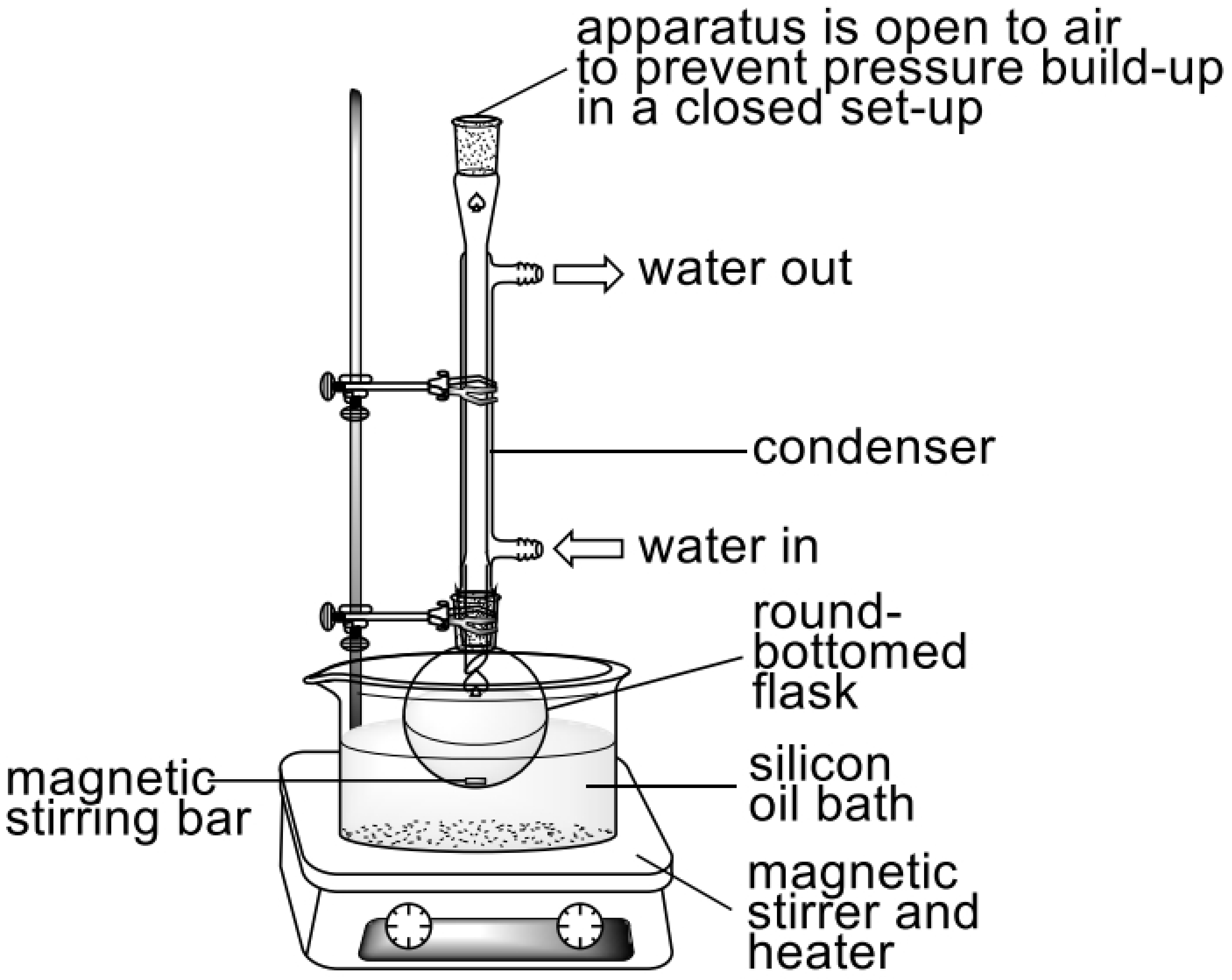
(d) Add aq Br_2 (or Br_2 in CCl_4) to compound **P**, in the absence of light. Orange (reddish-brown) colour of bromine would be rapidly decolourised.

Appendix

Heating under reflux

Some organic reactions like the elimination of HX from halogenoalkanes and vigorous oxidation of alkenes require heating under reflux condition.

A reflux set-up is as shown:



- Heating under reflux is useful for organic reactions that are usually slow and require heat for the reaction to proceed. This condition allows substantial time for reaction to go to completion, without the need to add more solvent during the course of reaction.
- When heated under a reflux, the contents are heated at a constant temperature with the solvent boiling continuously. (i.e., temperature is kept at the boiling point of the solvent)
- In this method, any vapour produced is immediately condensed back into the reaction flask. This prevents highly volatile components, either the reactants or solvents, from boiling off and allows the reaction to go to completion.