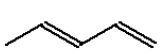
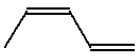
**Answers to Practice Questions**

**1(a)(i)** Molecular formula of **Q** is $C_5H_8$.

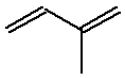
**1(a)(ii)** Isomers of **Q**



*trans*-penta-1,3-diene



*cis*-penta-1,3-diene



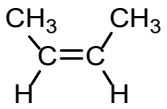
2-methylbuta-1,3-diene

penta-1,4-diene

**1(b)** Squalene has 6 $\pi$ bonds per molecule.

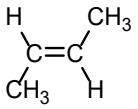
**1(c)** *cis*-pent-2-ene > *trans*-pent-2-ene > 2-methylbut-1-ene

**2(a)** **A:**



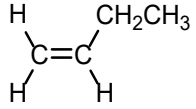
*cis*-but-2-ene

**B:**



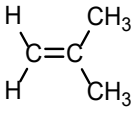
*trans*-but-2-ene

**C:**



but-1-ene

**D:**



2–methylpropene

**E:**

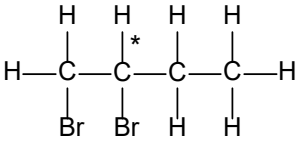
cyclobutane

**F:**

methylcyclopropane

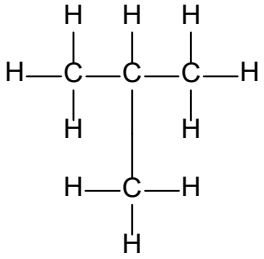
**2(b)**

**G:**



1,2-dibromobutane

**H:**



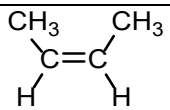
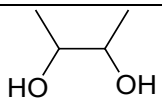
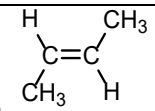
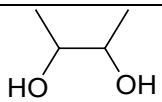
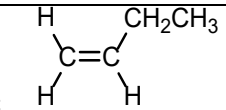
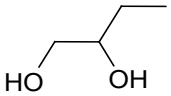
2-methylpropane

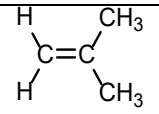
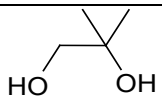
**2(c)** **A** (i.e. *cis*-but-2-ene) is **slightly polar**. In addition to instantaneous dipole-induced dipole attractive forces present between the molecules, there are also permanent dipole-permanent dipole attractive forces.

**B** (i.e. *trans*-but-2-ene) is **non-polar**. Only instantaneous dipole-induced dipole attractive forces exist between the molecules.

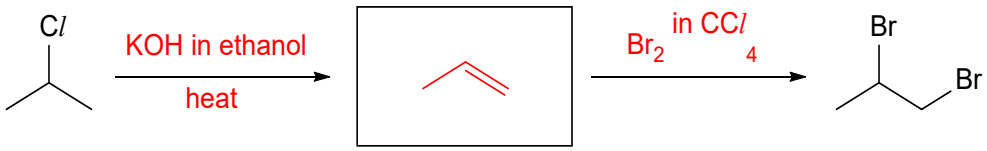
Since **more energy** is needed to **overcome the stronger intermolecular forces** in **A** during boiling, the boiling point of **A** is higher than that of **B**.

**2(d)**

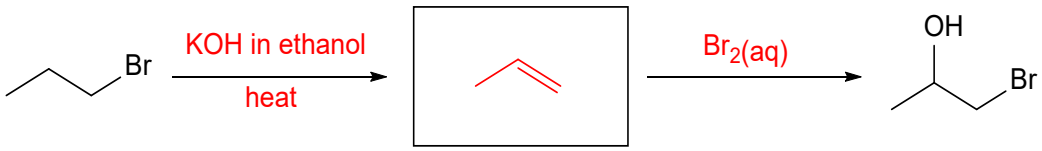
| **Reagent**<br><br>**Alkene** | **(i)** cold, alkaline $KMnO_4(aq)$ | **(ii)** hot $KMnO_4(aq)$ made alkaline with $NaOH(aq)$ | **(iii)** hot $KMnO_4(aq)$ acidified with $H_2SO_4(aq)$ |
|---|---|---|---|
|  **A** |  | $CH_3CO_2^-Na^+$ | $CH_3CO_2H$ |
|  **B** |  | $CH_3CO_2^-Na^+$ | $CH_3CO_2H$ |
|  **C** |  | $CH_3CH_2CO_2^-Na^+$ | $CH_3CH_2CO_2H$ |

| | | | |
|---|---|---|---|
| **D**  |  | $CH_3COCH_3$ | $CH_3COCH_3$ |

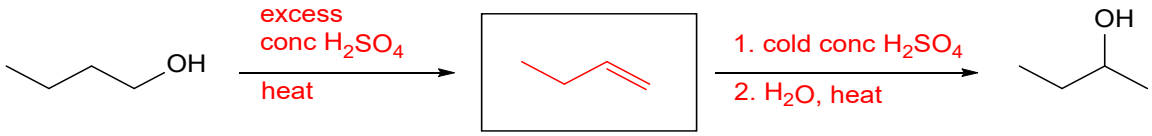
**3(a)**



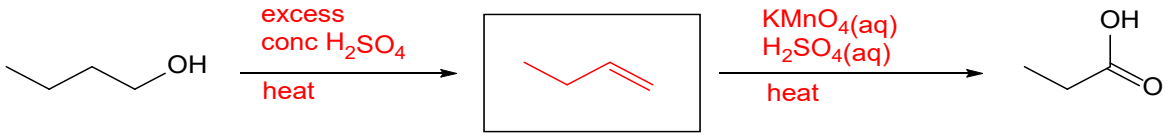

**3(b)**




**3(c)**




**3(d)**




**4(a)** Bubble a sample of each gas through $Br_2(aq)$ in separate test-tubes at room temperature.

For ethene, there is (rapid) decolourisation of the orange $Br_2(aq)$.
For ethane, there is no decolourisation of the orange $Br_2(aq)$.

Equation: $CH_2{=}CH_2 + Br_2 + H_2O \longrightarrow HOCH_2CH_2Br + HBr$

OR

Add two drops of $Br_2$ (in $CCl_4$) to each sample of gas already collected in a stoppered test-tube at room temperature and in the dark. Shake the re-stoppered test-tube.

For ethene, there is (rapid) decolourisation of the orange-red $Br_2$.
For ethane, there is no decolourisation of the orange-red $Br_2$.

Equation: $CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$

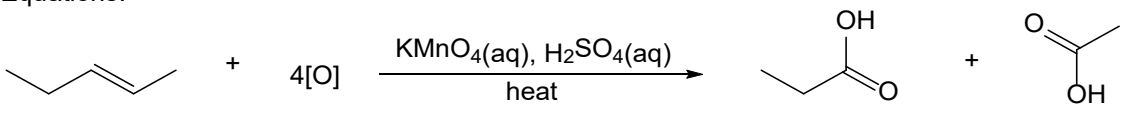
Other possible chemical tests:

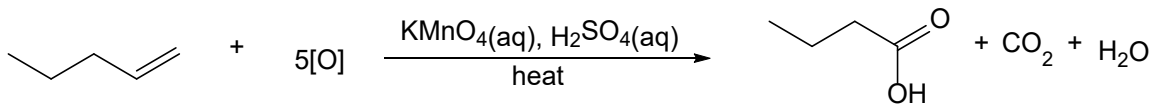
- $KMnO_4(aq)$ acidified with $H_2SO_4(aq)$, heat (Note: DO NOT heat under reflux)
- $KMnO_4(aq)$ and $NaOH(aq)$, cold

**4(b)** Add two drops of $KMnO_4$ acidified with dilute sulfuric acid to each sample in a test-tube, and heat each reaction mixture in a hot water bath. (Note: DO NOT heat under reflux)

For pent-2-ene, there is decolourisation of purple $KMnO_4$.
For pent-1-ene, there is decolourisation of purple $KMnO_4$ **and** evolution of a colourless gas ($CO_2$) which gives a white precipitate with limewater / $Ca(OH)_2(aq)$.

Equations:

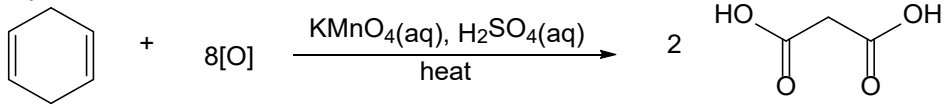


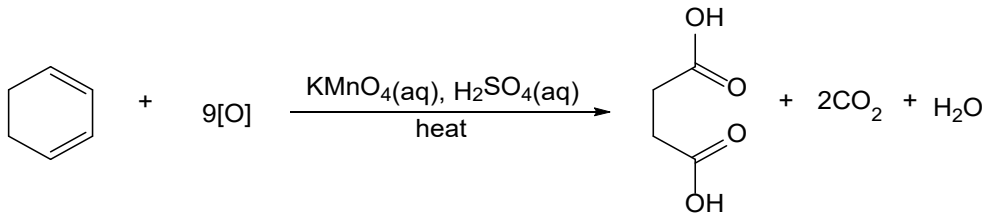



**4(c)** Add two drops of $KMnO_4$ acidified with dilute sulfuric acid to each sample in a test-tube, and heat each reaction mixture in a hot water bath. (Note: DO NOT heat under reflux)

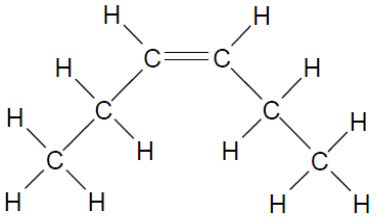
For cyclohexa-1,4-diene, there is decolourisation of purple $KMnO_4$.
For cyclohexa-1,3-diene, there is decolourisation of purple $KMnO_4$ **and** evolution of a colourless gas ($CO_2$) which gives a white precipitate with limewater / $Ca(OH)_2(aq)$.

Equations:

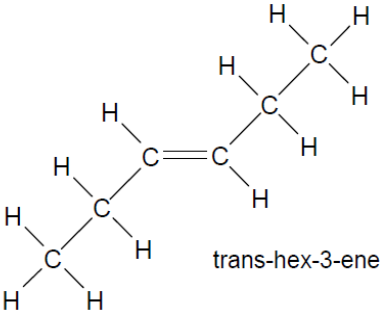



**5(a)**



cis-hex-3-ene

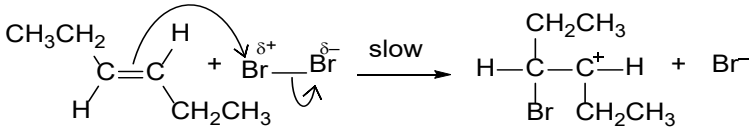


trans-hex-3-ene

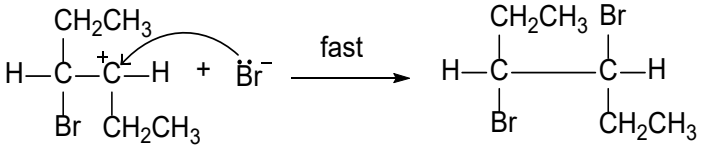
**5(b)** $CH_3CH_2CH{=}CHCH_2CH_3 + Br_2 \longrightarrow CH_3CH_2CHBrCHBrCH_2CH_3$

**5(c)** **<u>Electrophilic Addition</u>**

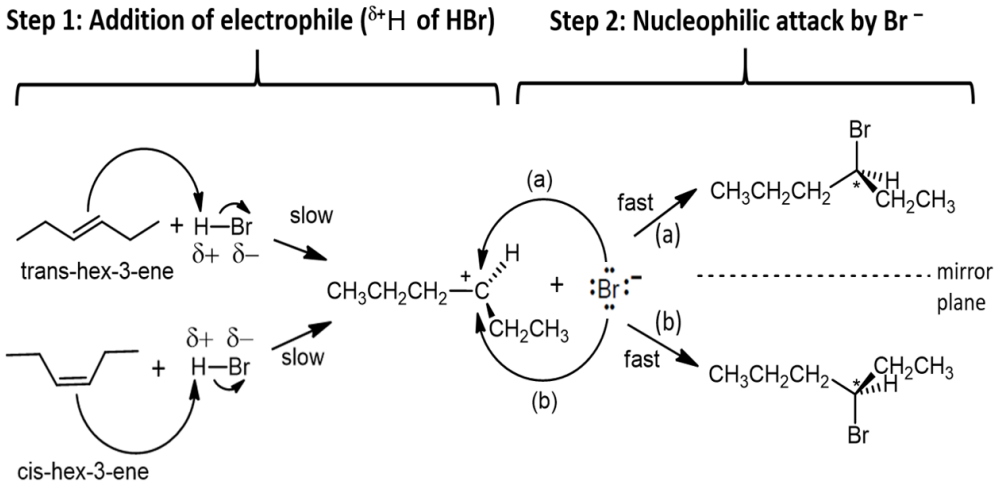
**Step 1:**




**Step 2:**

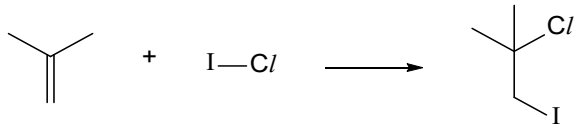


**5(d)**



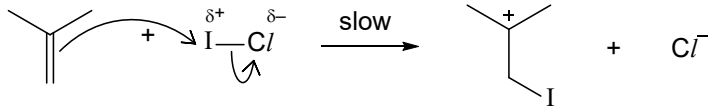

- In step 1, both *cis*-hex-3-ene and *trans*-hex-3-ene react with HBr to give the **same carbocation**. This carbocation is **trigonal planar** with respect to the positively charged carbon.
- In step 2, the $Br^-$ ion can attack the positively charged carbon of the carbocation from either side of the trigonal plane (via **(a)** or **(b)**) **with equal probability**.
- Hence the product is a racemic mixture of the two enantiomers of 3-bromohexane in a 1:1 ratio.

**6**



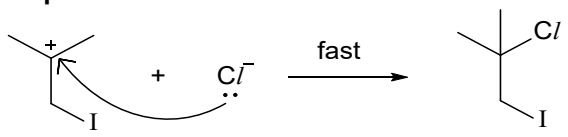
**Electrophilic Addition**

**Step 1:**



more stable carbocation

**Step 2:**



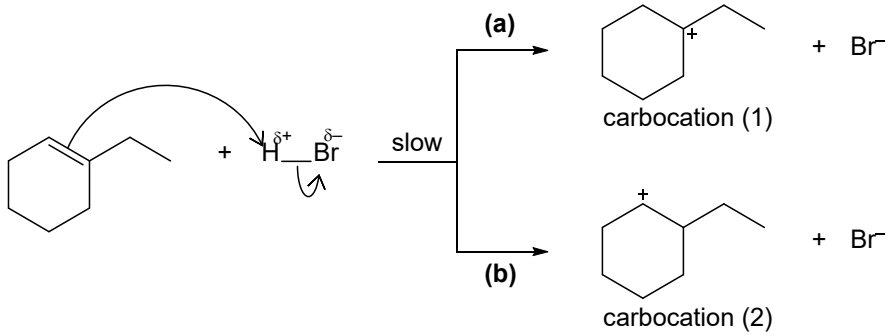
**7(a)** The reaction between ethene and hydrogen halide (HX) takes place via the **electrophilic addition mechanism**. In this case, the **rate-determining step involves the cleavage of the hydrogen-halogen (H–X) covalent bond**.

The **stronger the H–X covalent bond**, the slower is the rate of the reaction and **the lower is the reactivity of HX**.

Since the H–X bond strength decreases from HC*l* to HBr to HI, the rate of the reaction and hence reactivity increases from HC*l* to HBr to HI.

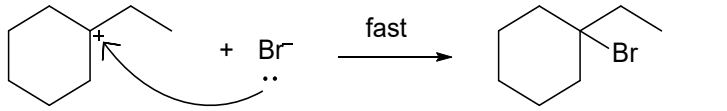
**7(b)** When 1-ethylcyclohexene reacts with HBr, **<u>electrophilic addition</u>** occurs.

In the first step of the mechanism, **<u>two carbocations can be formed</u>**.




Carbocation (1) is a 3° carbocation and its **<u>positive charge is dispersed by three electron-donating alkyl groups</u>**. This carbocation is **<u>more stable</u>** than carbocation (2), a 2° carbocation with its **<u>positive charge being dispersed by only two electron-donating alkyl groups</u>**.

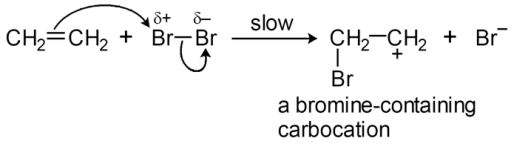
**<u>Being more stable, carbocation (1) is formed faster and is more available</u>** to participate in the second step of the reaction. Consequently, 1-bromo-1-ethylcyclohexane is the major product since it is **formed faster from the more stable carbocation (1)**.




**8** **Answer: A** (only 2-bromoethanol and 1-bromo-2-chloroethane are possible products)

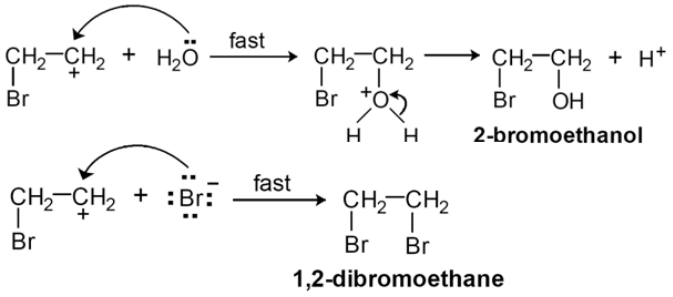
When ethene is shaken with $Br_2$(aq) or shaken with $Br_2$(aq) containing NaC*l*, the mechanism involved in the reactions in each case is **<u>electrophilic addition</u>**.

The **<u>same first step</u>** occurs in each case to give the **<u>same carbocation</u>** since the only electrophile present is $Br_2$:

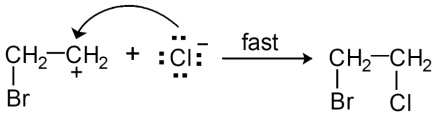



The second step involves the reaction between the bromine-containing carbocation and any nucleophile that is present.

**<u>In $Br_2$(aq), the nucleophiles present are $H_2O$ and $Br^-$</u>**, which react to give 2-bromoethanol and 1,2-dibromoethane respectively.

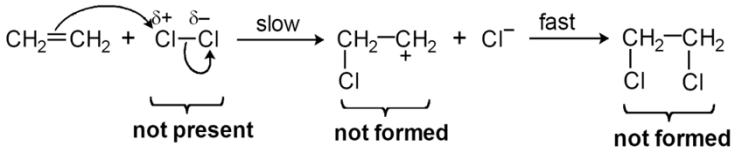


**In $Br_2$(aq) containing NaC*l*, apart from $H_2O$ and $Br^-$, $Cl^-$ is also present as a nucleophile** and it reacts to give the additional product, 1-bromo-2-chloroethane.



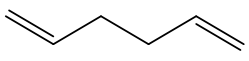
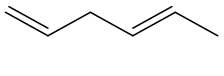
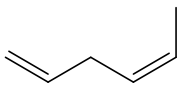
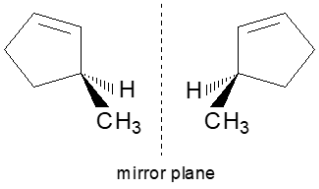

**1-bromo-2-chloroethane**

However, the reaction mixture does **not** contain $Cl_2$. There is no electrophilic $^{\delta+}Cl$ present to react with ethene and a **chlorine-containing carbocation** is **not** formed to react with $Cl^-$.
Hence 1,2-dichlorethane is **not** formed.



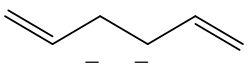

Similarly, in the absence of the **chlorine-containing carbocation**, 2-chloroethanol is **not** formed.

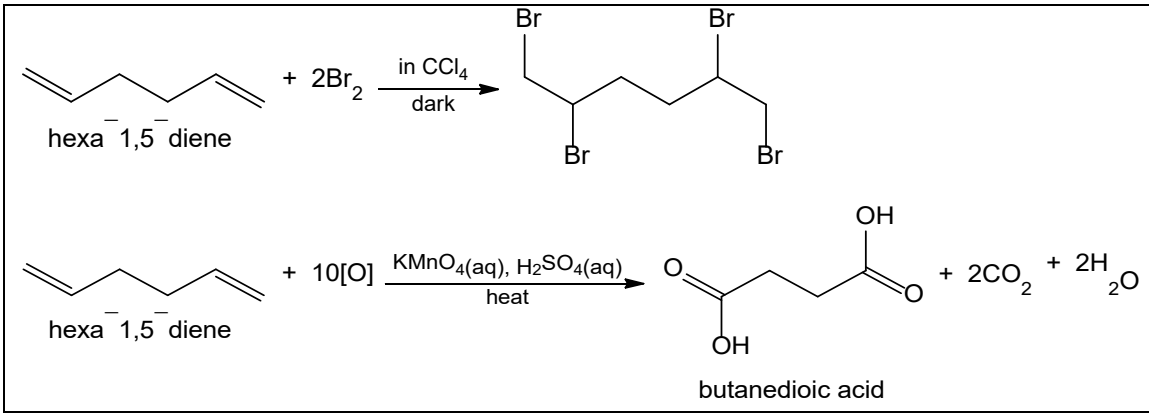
**9**

| | | |
|---|---|---|
|  hexa 1,5 diene |  *trans*-hexa-1,4-diene  *cis*-hexa-1,4-diene |  mirror plane |
| **A** | **B** | **C** |

**Deductions for Question 9 (for reference only)**

**Compound A**

| Evidence / Information | Deduction and explanation |
|---|---|
| **A** is a structural isomer of cyclohexene. | **A** has the molecular formula, $C_6H_{10}$. |
| $C_6H_{10}$ + $2Br_2$ $\xrightarrow[\text{dark}]{\text{in } CCl_4}$ product<br>**A** | **Electrophilic addition occurs.**<br>**A** is a diene or **A** has two C=C bonds per molecule. |
| $C_6H_{10}$ $\xrightarrow{\text{vigorous oxidation}}$ $C_4H_6O_4$<br>**A** butanedioic acid | **Oxidative cleavage of C=C bond occurs.**<br><br>The six-carbon **A** becomes a four-carbon acid.<br>There is a loss of 2 carbon atoms as $CO_2$ gas.<br>Hence **A** contains two $=CH_2$ structural units (i.e. two terminal alkene units).<br><br>Since the four-carbon acid is $HO_2C(CH_2)_2CO_2H$,<br>**A** has to be  hexa 1,5 diene<br>**A** does not display any stereoisomerism. |
| **Equations:** | |




**Compound B**

| Evidence / Information | Deduction and explanation |
|---|---|
| **B** is a positional isomer of **A**. | **B** has the molecular formula, $C_6H_{10}$ and can be one of the following:<br>$CH_2=CH–CH_2–CH=CHCH_3$ (hexa-1,4-diene), or<br>$CH_2=CH–CH=CH–CH_2CH_3$ (hexa-1,3-diene), or<br>$CH_3–CH=CH–CH=CH–CH_3$ (hexa-2,4-diene). |
| $C_6H_{10}$ + 2Br$_2$ $\xrightarrow[\text{dark}]{\text{in } CCl_4}$ product<br>**B** | **<u>Electrophilic addition occurs.</u>**<br><br>**B** is a diene or **B** has two C=C bonds per molecule. |
| **B** gives three carbon-containing products upon vigorous oxidation. | **<u>Oxidative cleavage of C=C bond occurs.</u>**<br>**B** is $CH_2=CH–CH_2–CH=CHCH_3$ (hexa-1,4-diene),<br>which upon oxidation produces $CO_2$, $HO_2C–CH_2–CO_2H$ and $CH_3CO_2H$.<br><br>Note: Both hexa-1,3-diene and hexa-2,4-diene give only two carbon-containing products upon oxidation. |

**B** displays *cis-trans* isomerism.

*trans*–hexa–1,4–diene  *cis*–hexa–1,4–diene

**Equations:**

$$CH_2=CH–CH_2–CH=CH–CH_3 + 2Br_2 \xrightarrow{CCl_4} CH_2(Br)–CH(Br)–CH_2–CH(Br)–CH(Br)–CH_3$$

$$CH_2=CH–CH_2–CH=CH–CH_3 + 9\,[O] \xrightarrow[\text{heat}]{KMnO_4(aq),\ H_2SO_4(aq)} CO_2 + H_2O + HO_2C–CH_2–CO_2H + CH_3CO_2H$$

**Note:**

Hexa-1,3-diene and hexa-2,4-diene each gives only 2 carbon-containing products upon vigorous oxidation using hot, acidified $KMnO_4$.

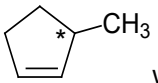
$CH_2=CH–CH=CH–CH_2CH_3 + 10[O] \longrightarrow 3CO_2 + 2H_2O + CH_3CH_2CO_2H$
hexa-1,3-diene

$CH_3–CH=CH–CH=CH–CH_3 + 9[O] \longrightarrow 2CH_3CO_2H + 2CO_2 + H_2O$
hexa-2,4-diene

**Compound C**

| Evidence / Information | Deduction and explanation |
|---|---|
| **C** is a structural isomer of cyclohexene. | **C** has the molecular formula, $C_6H_{10}$. |
| $C_6H_{10}$ + $Br_2$ $\xrightarrow[\text{dark}]{\text{in } CCl_4}$ product<br>**C** | **Electrophilic addition occurs.**<br>**C** has molecular formula $C_6H_{10}$ and has only one C=C bond.<br>$\Rightarrow$ **C** is a cycloalkene with one C=C bond per molecule. |
| Each molecule of **C** possesses one chiral centre. | **C** exhibits enantiomerism. |
| $C_6H_{10}$ $\xrightarrow{\text{vigorous oxidation}}$ product<br>**C**<br>Optically inactive starting sample gives optically inactive product. | The sample of **C** used for oxidation is a racemic mixture (i.e. it contains 1:1 ratio of each enantiomer). |

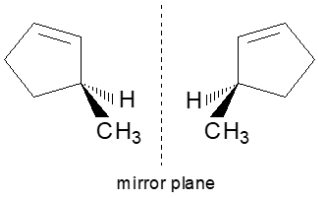
Based on the above information, **C** must contain a ring structure with a C=C bond and a chiral carbon. Hence **C** can be



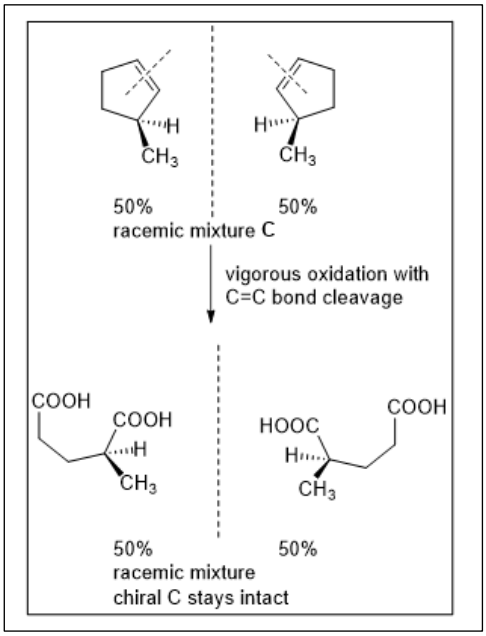

where * denotes chiral carbon

**Note:** Accept all sensible answers.

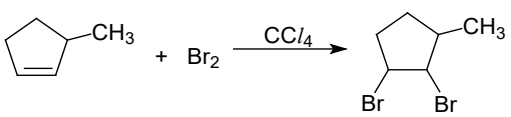
With a chiral carbon, **C** displays enantiomerism and can exist as a pair of enantiomers:

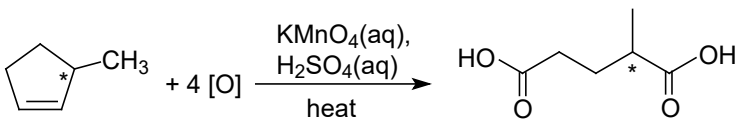



When the sample of **C** containing a racemic mixture undergoes vigorous oxidation, the product obtained is optically inactive because it is also a racemic mixture. The chiral carbon initially present in each enantiomer of **C** remains intact during oxidation and is present in each enantiomeric product molecule.




Equations:




Note:
* denotes chiral C atom