CHEMISTRY

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question, or part question.

This document consists a total of **9** printed pages.

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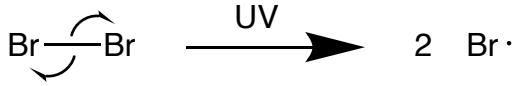
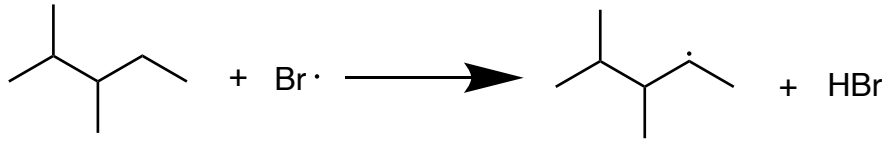
1 **(a)** It is observed that there were many products formed when liquid bromine was added to 2,3-dimethylpentane in the presence of sunlight.

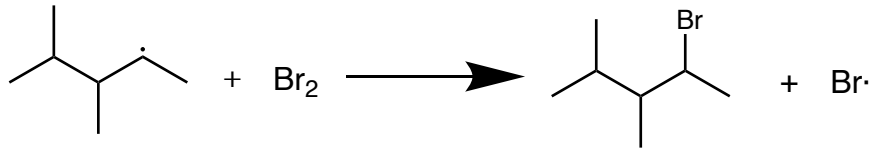
(i) Describe the mechanism where 2-bromo-3,4-dimethylpentane was formed. [4]

B1 – Free Radical Substitution (Name of mechanism)
B1 – Initiation (Must show fish-hook arrows)

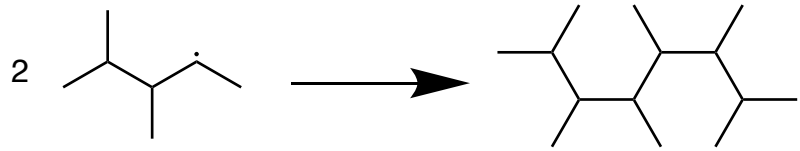


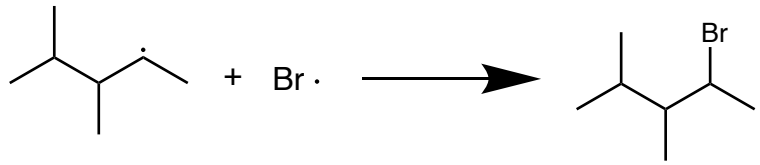
B1 – Propagation (Both steps shown)

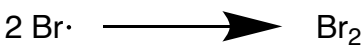




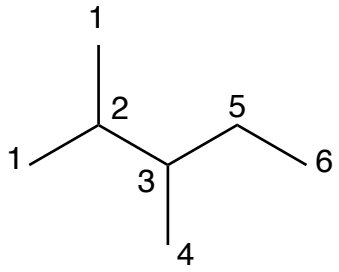
B1 – Termination (All steps shown)







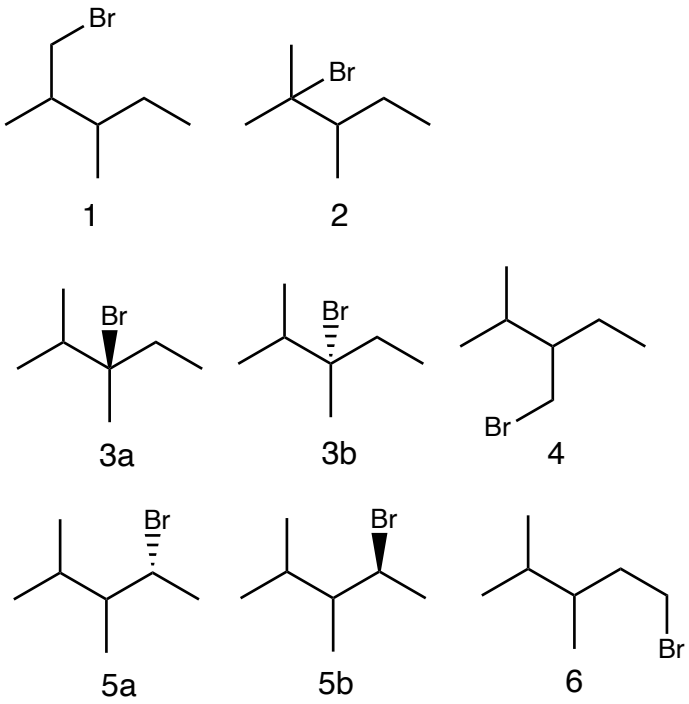
(ii) State the number of different monosubstituted 5-carbon products that can be formed from 1 stereoisomer of 2,3-dimethylpentane, including stereoisomers. [2]



There are 6 chemically equivalent carbons.
Since a bromine atom attached at carbons 3 and 5 will lead to enantiomers being formed, there are a total of 6 + 2 = 8 such products.

B2 for correct answer
B1 only for incorrect answer of 6 is given (candidate forgot to count in stereoisomers)

(iii) State the expected ratio of products formed, assuming that the reactivity for all hydrogen atoms is the same. [2]



B2 – Correct ratio given
Number the products
1 : 2 : 3a : 3b : 4 : 5a : 5b : 6 = **6 : 1 : 0.5 : 0.5 : 3 : 1 : 1 : 3**

How to solve?
Take the number of hydrogen atoms at each position to get the ratio.
For places where stereoisomerism occur, remember to divide by 2 because the radical centre has planar geometry, so equal probability of attack above or below the plane by the Br radical may occur.

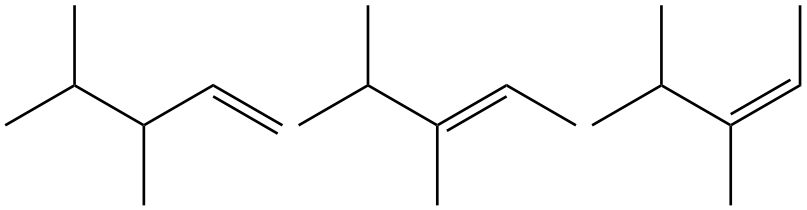
Although you are encouraged to simplify, leaving your answer like this is acceptable.
Award ECF from (ii) of up to 1 mark

(iv) Explain why the reactivity of all hydrogen atoms in 2,3-dimethylpentane, in reality, is **not** the same. [1]

B1 – Possible radicals formed have different number of alkyl groups → different stability of radicals / different rate of formation of respective radicals → different reactivity of the hydrogen atoms.

(b) 2-bromo-3,4-dimethylpentane can also be formed from an appropriate alkene under suitable reaction conditions.

(i) Draw the structure of all alkenes, including stereoisomers, such that when reacted with HBr, will form 2-bromo-3,4-dimethylpentane. [2]

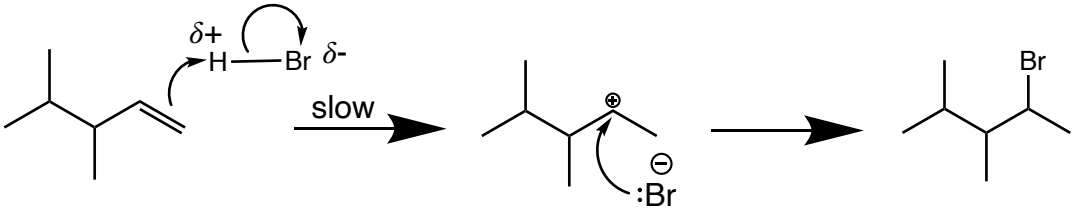


B2 for all 3 correct
B1 for any 2 correct

(ii) Describe the mechanism of the reaction where one of your structures in **(i)** leads to 2-bromo-3,4-dimethylpentane being formed. [3]

B1 – Electrophilic Addition
B2 – Mechanism

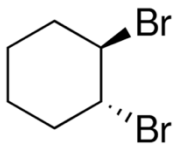
- Partial charges
- Curly arrows
- Slow step



(iii) Explain why this reaction can be conducted in the absence of sunlight, while the reaction in **(a)** must be conducted under sunlight. [2]

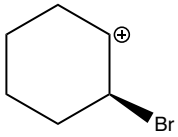
B1 - Pi-electrons in C=C bond are nucleophilic / a source of electrons → reactive → no need for an initiator to kick start the reaction
B1 - C—H bond is not polar (similar electronegativity of C and H), not reactive, not a source of electrons → sunlight imitates the reaction with the reaction of Br radical.

(c) When cyclohexene is reacted with Br_2, only 1 product, **A**, is formed, shown below.



A

(i) Suggest why the proposed structure below **cannot** be the intermediate in the reaction. [1]



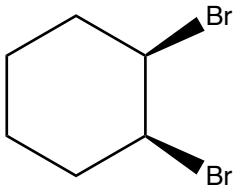
B1 – Because the carbon with the positive formal charge has planar geometry, so the Br^- ion can attack the carbon from above/below the plane. Hence, 2 products will be formed instead of 1. Hence the intermediate cannot be the proposed structure.

Although the information in this question is contrary to the syllabus, drawing the above intermediate is acceptable in H2 Chemistry.

(ii) Suggest how it would have been possible to tell that

- there is only **1** product formed; and
- **A**, not **B**, is the product. [3]

You can assume that the product formed has the molecular formula $C_6H_8Br_2$.



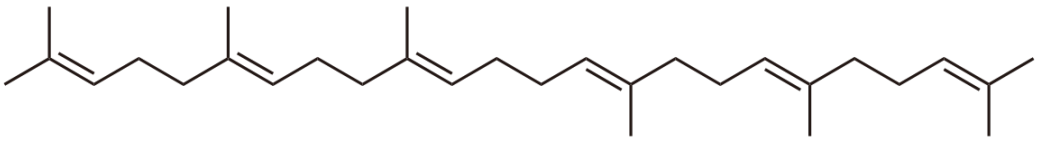
B

B1 – Use of melting/boiling point
"there is only **1** product formed" → Only **1 melting/boiling point recorded** (or **product melts/boils at 1 temperature only**)

B2 – Use of plane-polarised light (Each point is 1 mark)

- The product will **rotate plane-polarised light**.
- The product must be **chiral** → B is achiral/meso compound → A is the product.

2 (a) Squalene is an unsaturated hydrocarbon found in shark liver oil.



Squalene

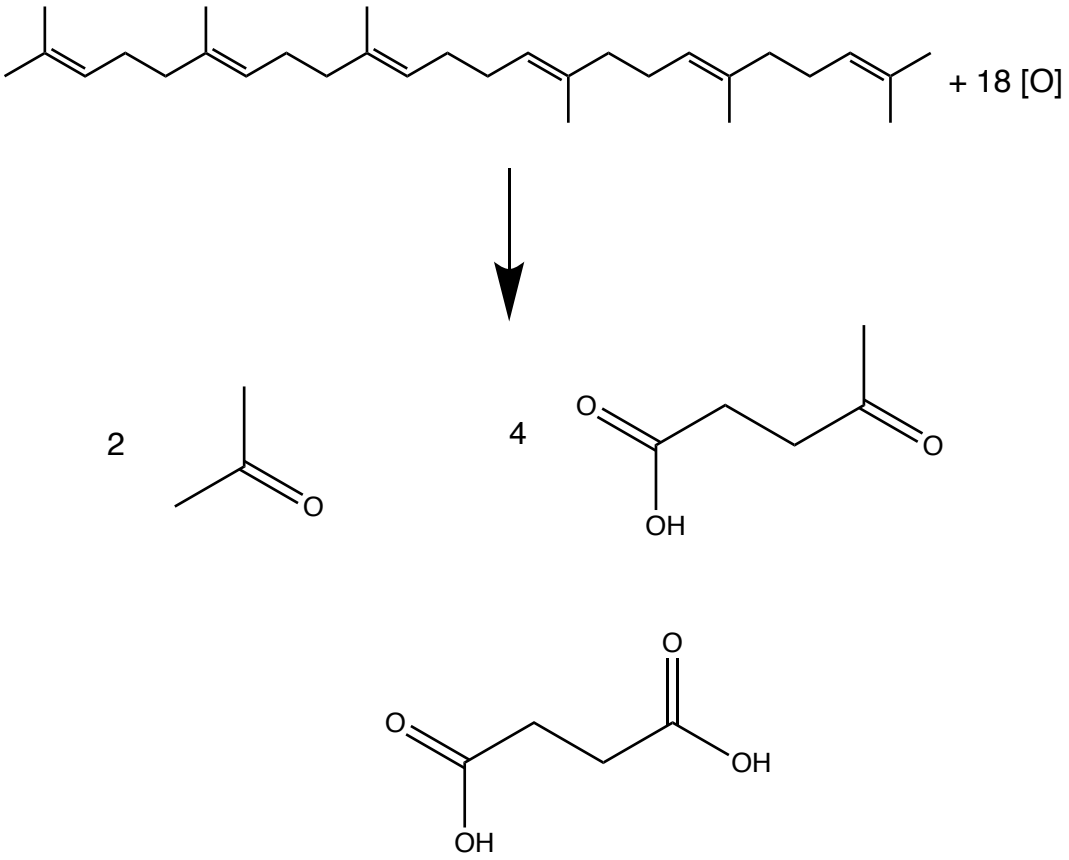
(i) Write a balanced chemical equation when squalene undergoes oxidative cleavage. State the reactants and conditions for oxidative cleavage. [3]

You may use [O] to represent the oxidising agent.

B1 – Correct reactants and conditions
Dilute $KMnO_4$, dilute sulfuric acid, heat
Accept

- Hot dilute $KMnO_4$ in place of "dilute $KMnO_4$, heat"
- State symbols using (aq)

B1 – Correct products formed
B1 – Correct equation



(ii) To determine the degree of unsaturation of squalene, a titration of squalene against an electrophilic reagent is conducted.

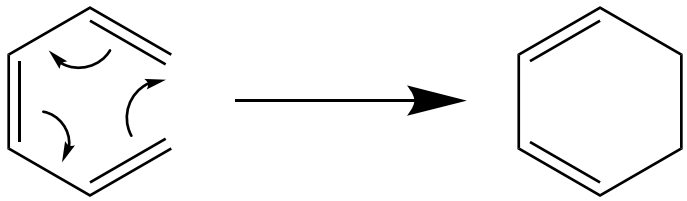
One such reagent is IC*l*.

Explain why IC*l* reacts faster with squalene compared to Cl_2. [1]

B1 – Presence of dipole moment in IC*l* but none in Cl_2. Cl_2 needs to approach the alkene in order to have a stronger temporary induced dipole moment for electrophilic attack.

(b) A class of reactions that can occur between alkenes is the electrocyclic reaction.

A new ring is formed after a conjugated system of double bonds undergo an electrocyclic reaction.

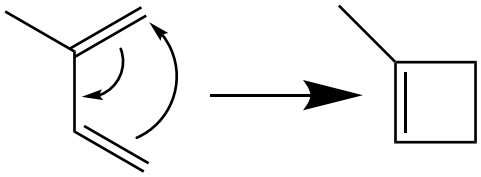


The above shows a 6-pi electron electrocyclic reaction.

In this part, you should ignore stereochemistry.

(i) Draw curly arrows to show how 2-methylbuta-1,3-diene forms a cyclobutene. [1]

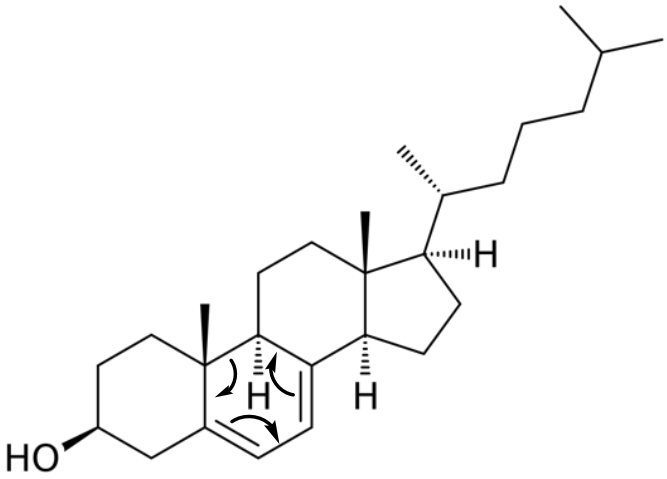
B1 – Correct curly arrows



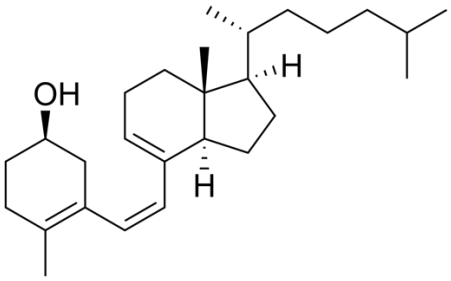
(ii) Electrocyclic reactions are reversible.

Show how 7-dehydrocholestrol forms pre-vitamin D_3 via an electrocyclic reaction using curly arrows to represent electron movement. [1]

B1 – Correct curly arrows

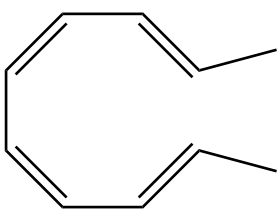


7-dehydrocholestrol

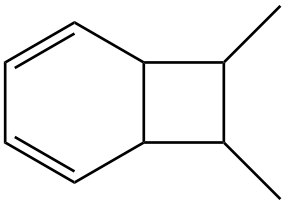


pre-vitamin D_3

(iii) **B** is formed from **A** through 2 electrocyclic reactions. Draw curly arrows, and the intermediate, to show how **B** is formed from **A**. [3]

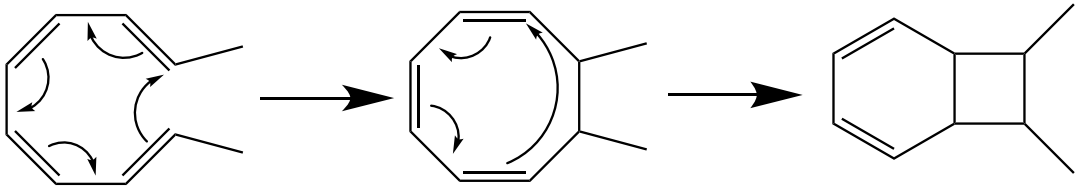


A

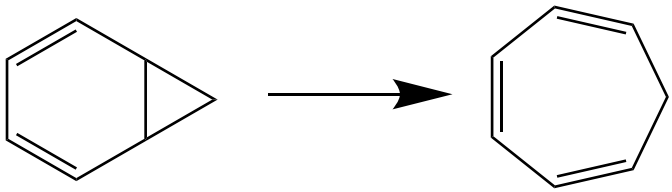


B

B1 – Correct curly arrows for A
B1 – Correct intermediate
B1 – Correct curly arrows for intermediate



(iv) Suggest why this electrocyclic reaction takes place so readily, even at extremely low temperatures. [1]



B1 – Explains why the cyclopropane ring is unstable

Cyclopropane ring is extremely strained/unstable/reactive as the C—C—C bond angle is 60 degrees, far from the ideal angle of 109.5 degrees for a sp^3 hybridised carbon.
OR
The orbital overlap in the C—C bonds of cyclopropane is not very effective due to the far deviation of the C—C—C bond angle from its ideal angle (need to state the value).

Question 2(b) is an ad-hoc question, which is simpler to do, and only requires your basic knowledge of Organic Chemistry + Foundation Topics.