57th INTERNATIONAL

CHEMISTRY OLYMPIAD

2025

UK Round One

STUDENT QUESTION BOOKLET

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- **The time allowed is two hours.**
- **Attempt all six questions.**
- **Write your answers in the student answer booklet.**
- **Write only the essential steps of your calculations in the answer booklet.**
- **Always give the appropriate unit and number of significant figures.**
- **A copy of the periodic table and some useful physical constants and formulae are provided as a separate document.**
- **Do *NOT* write anything in the right-hand margin of the answer booklet.**
- **The marks available for each question are shown below. These may be helpful when dividing your time between questions.**

Question	1	2	3	4	5	6	**Total**
Marks Available	8	9	20	12	19	15	**83**

Some of the questions will contain material you will not be familiar with. However, you should be able to work through the problems by applying the skills you have learnt as a chemist. There are different ways to approach the tasks – even if you cannot complete certain parts of a question, you may find later parts straightforward.

Q1 This question is about clay pigeon shooting

Team GB enjoyed success in the clay pigeon shooting at the 2024 Olympics, with Nathan Hales winning gold with an Olympic record score and Amber Rutter winning silver only three months after becoming a mum for the first time.

Fast burning powders, such as nitrocellulose are used in clay pigeon shooting cartridges. Their burn rate is designed for lighter loads such as the clay pigeon load of 28 g.

Nitrocellulose is a highly flammable compound which is primarily composed of cellulose trinitrate. This can be prepared by adding cellulose, (empirical formula $C_6H_7(OH)_3O_2$), to a mixture of concentrated nitric acid and concentrated sulfuric acid. This forms cellulose trinitrate (empirical formula $C_6H_7(ONO_2)_3O_2$) and one other product.

The nitronium ion, NO_2^+, generated in the acid mixture, nitrates the alcohol groups on cellulose to form the nitrate ester group, $CONO_2$.

(a) **(i)** Write an equation for the reaction between cellulose and nitric acid to form cellulose trinitrate.

(ii) Draw the dot-and-cross diagram for the nitronium ion.

The nitric acid acts as a Lewis base and accepts a proton from the sulfuric acid to form an intermediate, $H_2NO_3^+$. This intermediate decomposes to form the nitronium ion.

(b) Write the equation for the formation of the intermediate from nitric acid and sulfuric acid.

(c) Write the equation for the decomposition of the intermediate to form the nitronium ion.

Complete combustion of cellulose trinitrate produces carbon dioxide, water, and a gaseous element.

(d) Write the equation for the complete combustion of cellulose trinitrate, $C_6H_7N_3O_{11}$.

(e) Calculate the standard enthalpy of combustion of cellulose trinitrate.

$\Delta H^{\ominus}_{f}$ (CO) = –110.5 kJ mol^{-1}; $\Delta H^{\ominus}_{f}$ (CO_2) = –393.5 kJ mol^{-1};
$\Delta H^{\ominus}_{f}$ (H_2O) = –285.8 kJ mol^{-1}; $\Delta H^{\ominus}_{f}$ (cellulose trinitrate) = –653.1 kJ mol^{-1}.

When a shot is fired, complete combustion does not occur as there is not enough time to react with oxygen from air. Instead, the cellulose trinitrate decomposes to gaseous products which help to propel the shot. Heat is released and the products of this decomposition can reach temperatures over 200 °C.

(f) Write the equation for the decomposition process. Assume that all products are gaseous and no oxygen is formed in the reaction.

(g) Calculate the total volume of gaseous products produced from the decomposition of 5.00 g of cellulose trinitrate at 200 °C in m^3.

Q2 This question is about BrAt

While Charlie XCX's *Brat Summer* of 2024 may be over, this summer will be Paddington's *BrAt Bear Summer*. Much like *Brat Summer*, the compound BrAt doesn't last forever. This is due to the radioactive decay of astatine. Astatine is the rarest naturally occurring element in the Earth's crust, with a total estimated mass of 30 g at any point in time.

(a) Estimate how many At atoms occur naturally on the Earth at any point in time. Assume all astatine is the most stable naturally occurring isotope, ^{219}At.

Astatine can be made synthetically from bismuth through a nuclear reaction. Bismuth is obtained as a by-product of lead purification. During the purification, magnesium and calcium are added to a mixture of lead and bismuth. Bismuth forms an alloy **A**. Alloy **A** contains 7.91% Ca and 9.60% Mg by mass. There is no lead in alloy **A**.

(b) Determine the empirical formula of alloy **A**.

Alloy **A** is separated from the lead and undergoes reaction with chlorine gas to form bismuth and two ionic compounds **B** and **C** in a 2:1 ratio.

(c) Write the formulae of compounds **B** and **C**.

Astatine can be made by bombarding bismuth atoms with alpha particles. Alpha particles are high energy helium-4 nuclei which are emitted by a radioactive source. When an alpha particle collides with a bismuth atom the nuclei fuse to form one isotope of astatine, $^{x}_{y}At$, and two neutrons.

$$^{209}_{83}Bi + \alpha \rightarrow {}^{x}_{y}At + 2\,{}^{1}_{0}n$$

(d) Write the mass and atomic numbers for the isotope of astatine, $^{x}_{y}At$, that is formed.

Most bismuth atoms do not react and must be removed from the reaction mixture. Upon addition of concentrated nitric acid, the remaining bismuth reacts to form bismuth(III) nitrate, water, and a colourless gas with a molar mass of 30.01 g mol^{-1}. Pure astatine, At_2, is isolated by extraction from the aqueous reaction mixture with an organic solvent.

(e) Write an equation for the reaction of bismuth with concentrated nitric acid.

BrAt can be made from astatine in two steps. First, Br_2 reacts with **D** to make compound **E** only. Compound **E** reacts with At_2 to give BrAt and **D**. The mass spectrum of compound **E** shows two major peaks of almost equal intensity at m/z values of 205.82 and 207.82.

(f) Write the formulae of **D** and **E**.

As astatine undergoes radioactive decay, samples of BrAt do not last for long.

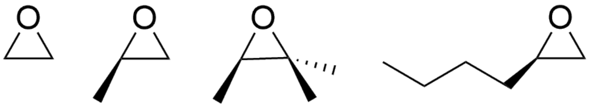
3.60 g of BrAt will be synthesised at the beginning of this summer. The half-life for the decay of this isotope of At is 433 minutes. Assume that Paddington's *BrAt Bear Summer* is over when only 3.65 mg of the BrAt remains.

(g) How long will Paddington's *BrAt Bear Summer* be? Give your answer to the nearest hour.

Q3 This question is about epoxides

Epoxy is an extremely durable and chemically resistant family of plastics. Epoxy has a variety of applications, including high-strength adhesives, carbon fibre, and decorative furniture.

Epoxy plastic is synthesised from epoxide molecules. An epoxide contains a three-membered ring with two carbon atoms and one oxygen atom. Epoxides are highly reactive due to ring strain in the three-membered ring.



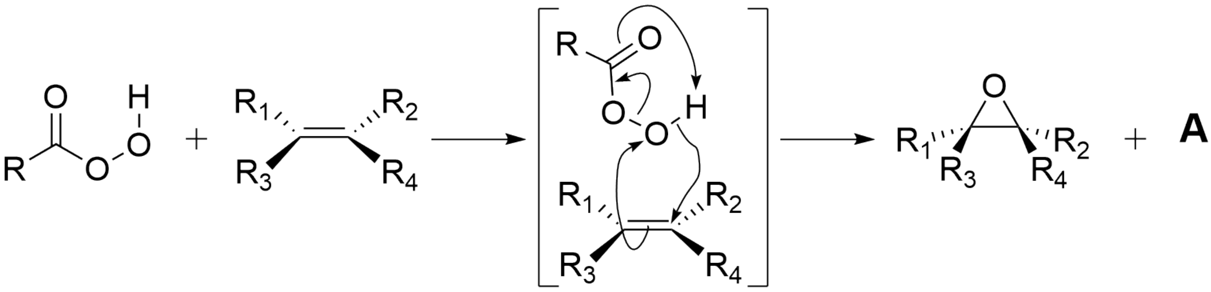
Examples of epoxides.

(a) State the general formula of an epoxide that contains n carbon atoms.

(b) In the answer booklet, tick the approximate C–C–O bond angle for the following molecules.

	60°	90°	104.5°	107°	109.5°	120°	180°
$C_2H_5OC_2H_5$							
							

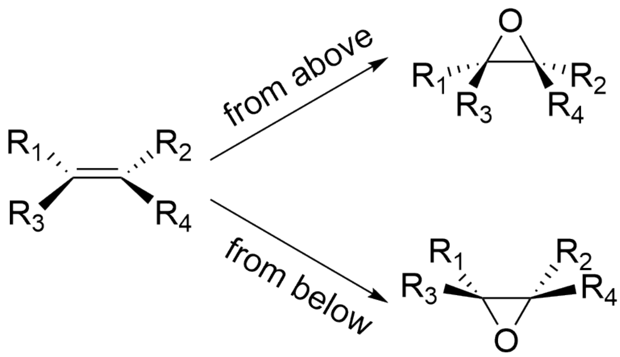
A common method of forming epoxides is the reaction of alkenes with organic peroxyacids. The mechanism for this reaction is shown with the transition state given in square brackets.



(c) Draw the structure of compound **A**.

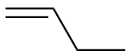
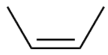
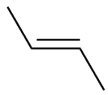
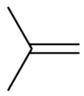
These peroxyacids can add an oxygen atom to either the top or bottom of the double bond depending on whether they approach from above or below.

This can result in the formation of stereoisomers.

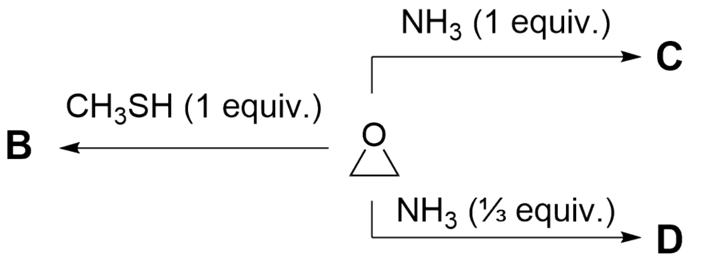


(d) Draw the structures of both stereoisomers formed when propene reacts with a peroxyacid.

(e) In the answer booklet, tick the number of epoxide isomers that would be formed on the reaction of each of the C_4H_8 isomers.

C_4H_8 isomer	1	2	3	4
				
				
				
				

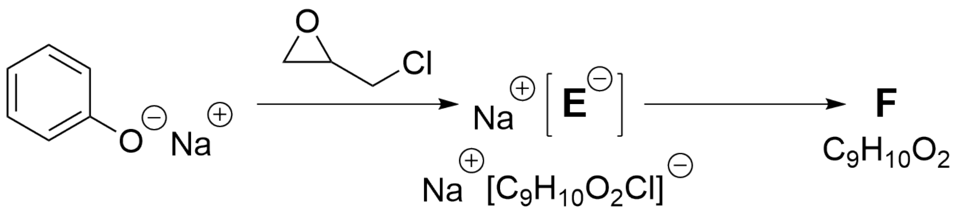
When epoxides react with nucleophiles their three-membered ring opens, as shown in the general scheme to the right.



Some specific examples of the reaction of the simplest epoxide are shown on the left.

(f) Draw the structures of compounds **B**, **C**, and **D**.

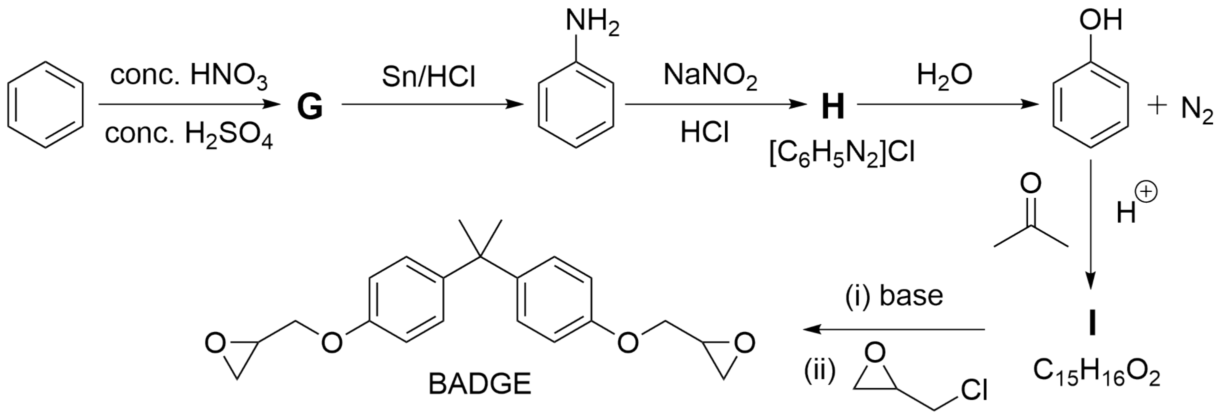
A particularly useful epoxide is called epichlorohydrin (C_3H_5OCl). Sodium phenoxide reacts with epichlorohydrin to form intermediate anion **E**⁻, which then cyclises, forming product **F.**



(g) Draw the structures of intermediate anion **E**⁻ and compound **F**. Stereochemistry is not required.

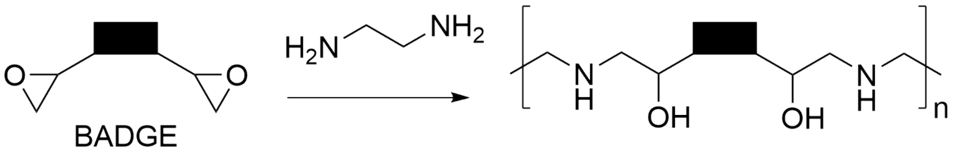
To make epoxy plastic, an epoxy resin (which contains the epoxide) is mixed with a hardener (which contains the nucleophile).

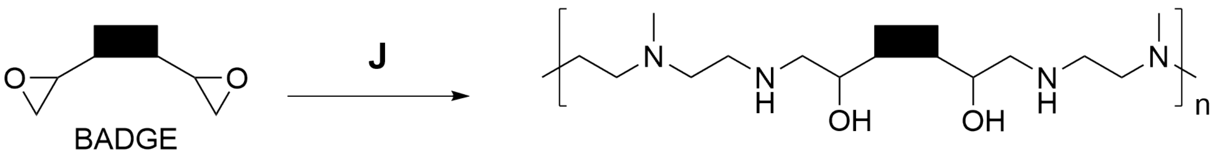
A common ingredient in epoxy resin is **b**isphenol **A** **d**i**g**lycidyl **e**ther, commonly known as BADGE. It is possible to synthesise BADGE from benzene.

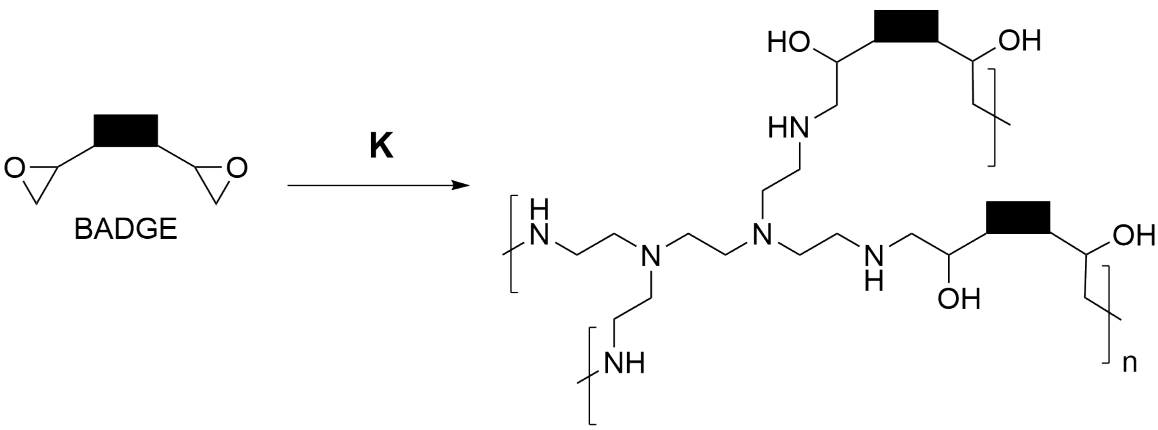


(h) Draw the structures of compounds **G**, **H**, and **I**. Stereochemistry is not required.

BADGE reacts with a hardener to form epoxy. The repeating units of some epoxides are shown. The structure of BADGE has been simplified with a rectangular block.

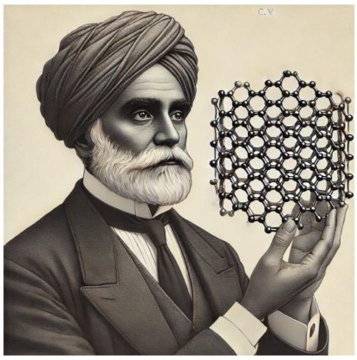






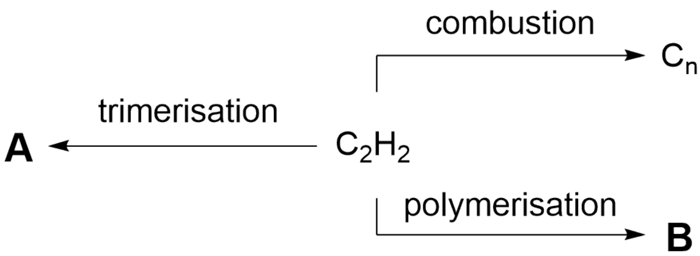
(i) Draw the structures of hardeners **J** and **K**.

Q4 This question is about carbon nanotubes and Raman spectroscopy



Carbon nanotubes have promising applications in nanotechnology due to their high tensile strength and variable electrical conductivity. Nanotubes can have different diameters, and these can be determined through Raman spectroscopy.

The technique of Raman spectroscopy was developed by Indian physicist C.V. Raman. He was the first Asian to win any science Nobel Prize.



Carbon nanotubes can be formed as a side product during the combustion of ethyne (C_2H_2).

(a) Write an equation for this side reaction, which occurs during the combustion of ethyne, to form nanotubes with chemical formula C_n.

40.00 dm^3 of ethyne gas at 298 K was combusted at atmospheric pressure and gave 242 mg of carbon nanotubes.

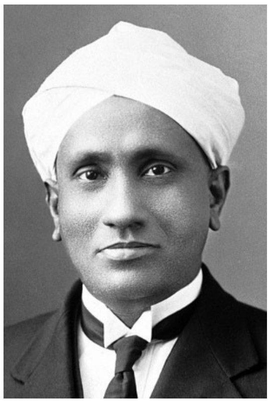
(b) Calculate the percentage by mass of carbon that ends up in the nanotubes in this reaction.

Ethyne can react with itself when different catalysts are added. In one reaction, three molecules of ethyne trimerise to make compound **A**.

(c) Draw the structure of compound **A.**

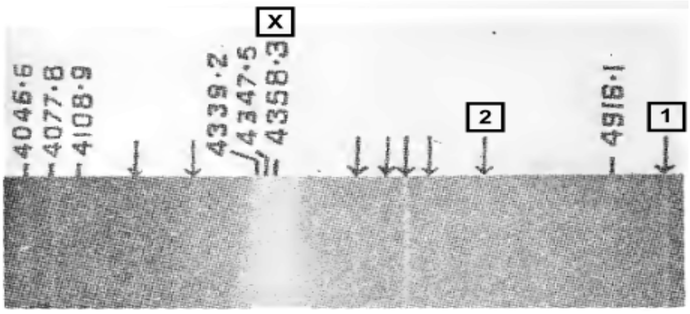
Alternatively, ethyne can polymerise to give polymer **B**.

(d) Draw the repeat unit of polymer **B**.



Carbon nanotubes can be studied using Raman spectroscopy. This probes vibrations of molecules. Molecular vibrations can be studied using infrared (IR) spectroscopy. However, Raman spectroscopy can find vibrations that are not observable by IR spectroscopy.

Raman spectroscopy works by shining light of a precise frequency at the sample. The scattered light is observed. The frequency of the scattered light is measured. The deviation in frequency between the incident and scattered light provides information about the bonds involved in the vibration.



C. V. Raman reported the first such spectrum in 1928, measuring a sample of compound **A.** The spectrum is shown on the left. Two significant lines were observed at wavelengths of 5028.8 Å (line 1) and 4683.9 Å (line 2). The incident light had a wavelength of 4358.3 Å (line X).

Although you might be familiar with characterising light by its frequency or its wavelength, in spectroscopy measurements are commonly of the wavenumber, $\tilde{\nu}$. The unit of wavenumber is cm^{-1}.

$$\tilde{\nu} = \frac{1}{\lambda}$$

where λ is the wavelength given in cm.

(e) Calculate the difference between:

(i) the frequency of line 1 and the incident line X (in Hz).

(ii) the wavenumber of line 2 and the incident line X (in cm^{-1}).

When a vibration is visible in both Raman and IR spectra, the Raman deviation and IR absorption peaks are visible at the same wavenumber. In an IR spectrum of **A**, peaks can be seen at just above 3000 cm^{-1} and around 1600 cm^{-1}.

(f) In the answer booklet, tick which vibration is responsible for each Raman line.

	C≡C stretch	conjugated C=C stretch	C–H stretch	C–C stretch	O–H stretch
Line 1					
Line 2					

Vibrations in molecules often involve more than just one bond. Vibrations of multiple bonds may give rise to different modes of vibration.

The diameter, d, of a carbon nanotube can be studied by looking at the wavenumber of a particular mode measured using Raman spectroscopy. The wavenumber of this mode, $\tilde{\nu}$, in cm^{-1}, is related to the diameter, d, in nm, by the equation $\tilde{\nu} = A/d$, where A is a constant.

A sample of nanotubes of known radii was irradiated with laser light of a precise frequency and the wavenumber of the scattered light was measured. Unfortunately, nobody remembered to note down the frequency of the laser used.

radius / nm	1.16	1.31	1.42	1.56
wavenumber / cm^{-1}	9302.2	9313.3	9319.9	9327.1

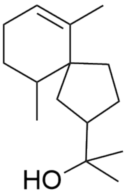
(g) **(i)** Determine the value of constant A with appropriate units.

(ii) Calculate the wavelength of the laser used in nm.

(iii) If in his day, C. V. Raman had used his spectrometer with incident light line X to investigate a nanotube with a 2.4 nm diameter, at what wavelength would he have observed the scattered light in Å?

Q5 This question is about agarwood

Agarwood, also known as “Wood of the Gods”, has a rich and complex scent. It is commonly used to make perfumes which are particularly popular in the UAE (the host of the 2025 IChO), where they are known as ‘oud’. Agarwood comes from *Aquilaria* trees. However, these trees only produce agarwood once they’re infected with a mould called *P. parasitica*. Unfortunately, this means many trees are deliberately infected and then chopped down.



agarospirol

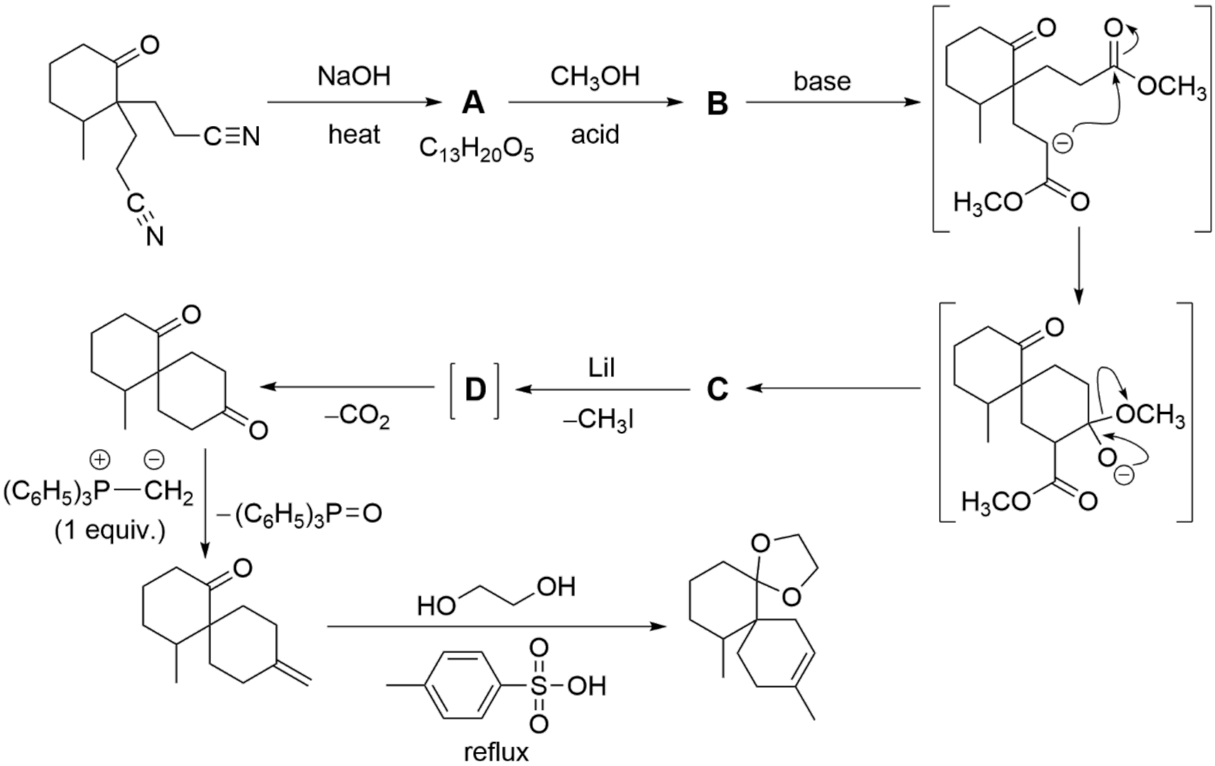
One fragrant compound found in agarwood is called agarospirol. Natural agarospirol is a single isomer, but the structure is shown here without any stereochemistry.

Agarospirol is an example of a spiro compound, where two rings are joined by only one atom.

Instead of infecting and chopping down endangered trees, chemists can synthesise agarospirol in a lab.

(a) In the answer booklet, circle the stereocentres in agarospirol.

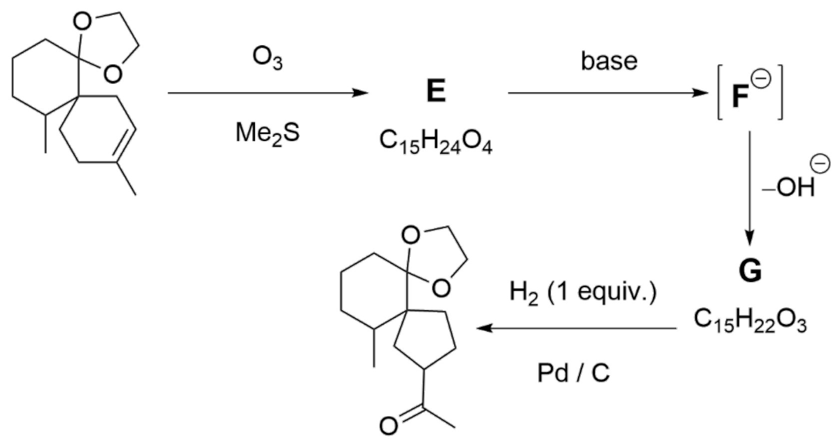
The first part of the synthesis of agarospirol is given below. On treatment with base, compound **B** is deprotonated to form an anion, which cyclises as shown to form compound **C**.



In the remaining parts of this question you do not have to show any stereochemistry in the structures drawn.

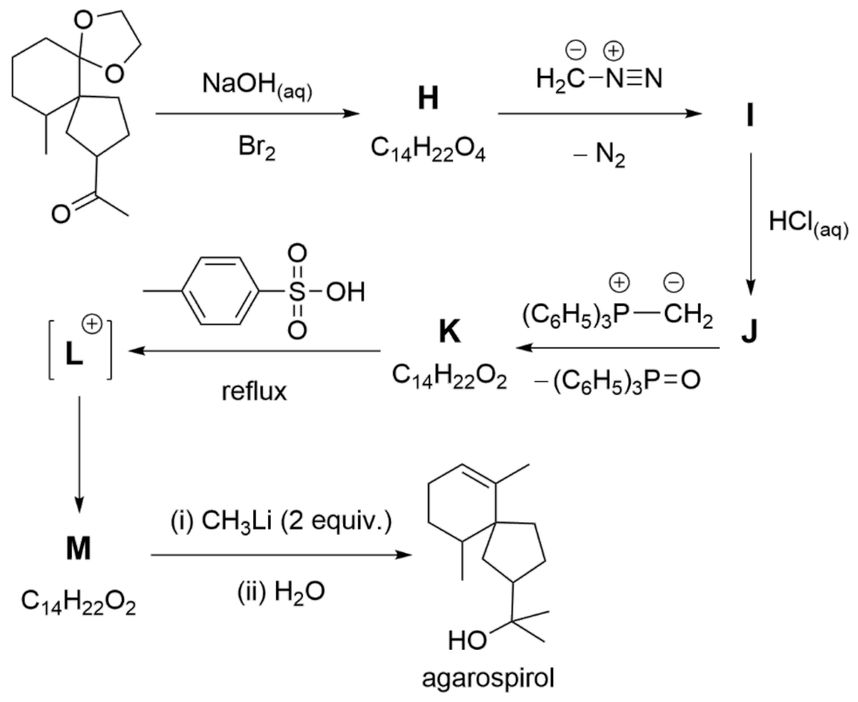
(b) Draw the structures of compounds **A**, **B**, and **C**, and intermediate **D**.

The next part of the synthesis is shown. Compound **E** is formed by ozonolysis. Upon treatment with base, compound **E** forms intermediate anion **F**⁻, which cyclises and then dehydrates to form compound **G**.



(c) Draw the structures of compound **E,** anion **F**⁻, and **G**.

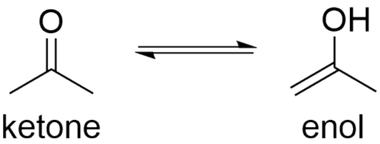
The final part of the synthesis is shown. Compounds **K** and **M** are isomers. Compound **K** isomerises into compound **M** via intermediate cation **L**⁺ under the action of an acid catalyst.



(d) Draw the structures of compounds **H**, **I**, **J**, **K**, intermediate cation **L**⁺, and compound **M**.

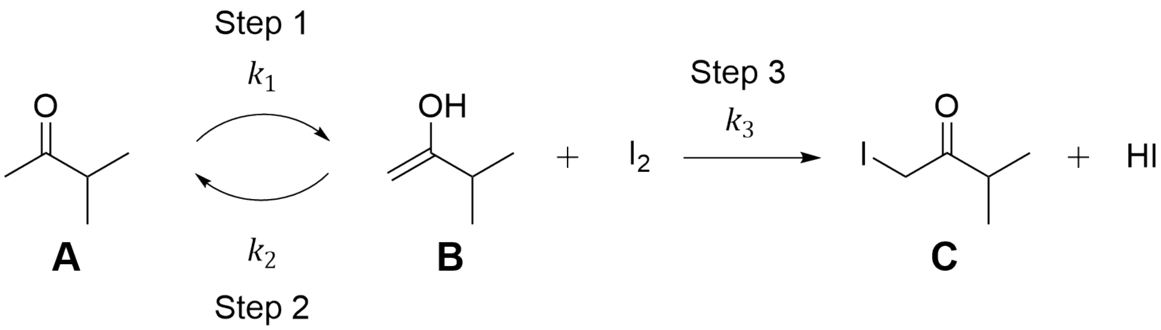
Q6 This question is about the iodination of ketones

Many ketones exist in equilibrium with one or more enol forms.



Upon the addition of iodine to a ketone, iodine can react with any of the enols present.

Iodine was added to a solution of ketone **A**. The reaction can be broken down into three steps with their rate equations given below.



Step	Reaction	Rate equation
1	**A** → **B**	rate = k_1[**A**]
2	**B** → **A**	rate = k_2[**B**]
3	**B** + I_2 → **C** + HI	rate = k_3[**B**][I_2]

where: $k_2 = 8.3\ \mathrm{s^{-1}}$ and $k_3 = 5.2 \times 10^5\ \mathrm{mol^{-1}dm^3s^{-1}}$.

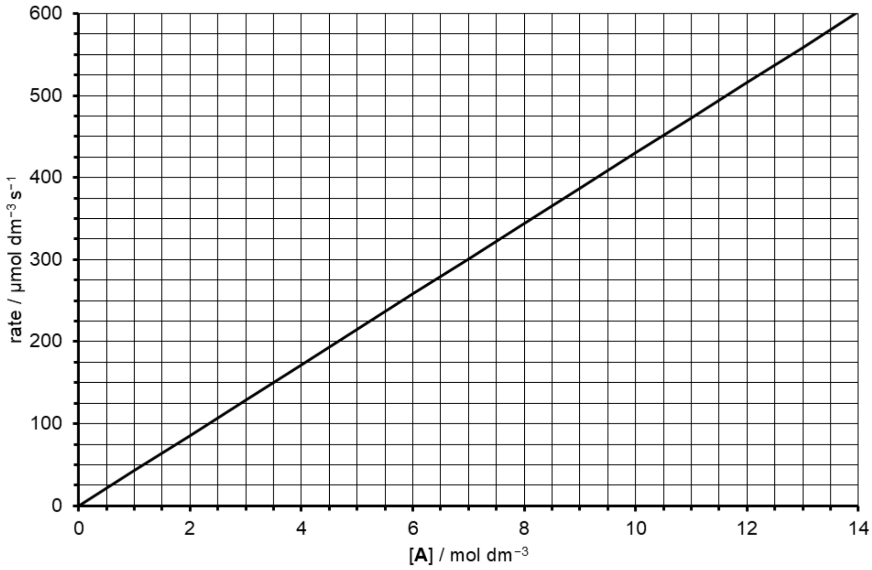
Any species involved in or before the rate determining step could affect the overall rate and therefore appear in the rate equation.

At high concentrations of I_2, the rate determining step is Step 1*;* once enol **B** is formed it reacts immediately with I_2 to form **C**.

(a) Which of the following species will be included in the rate equation for the formation of **C** at high concentrations of I_2? Tick all correct answer(s) in the answer booklet.

A **B** **C** I_2 HI

The initial rate of formation of **C** was measured at different concentrations of **A** and plotted on a graph.



(b) Using the graph, or otherwise:

(i) Write the rate equation for the initial rate of formation of **C** at high concentrations of I_2, in terms of the concentrations of reactants **A** and I_2, and an appropriate combination of k_1, k_2, and k_3.

(ii) Determine the value of rate constant k_1 with appropriate units.

At low concentrations of I_2, the rate determining step is Step 3.

Under these conditions the ketone and enol forms exist in an equilibrium. The equilibrium between **A** and **B** can be described using the equilibrium constant, K_{eq}.

$$K_{eq} = \frac{k_1}{k_2}$$

(c) Write an expression for [**B**] at equilibrium in terms of [**A**], k_1, and k_2.

(d) Using your answer from part **(c)** or otherwise, write an expression for the rate of formation of **C** in terms of the concentrations of reactants **A** and I_2, and an appropriate combination of k_1, k_2, and k_3.

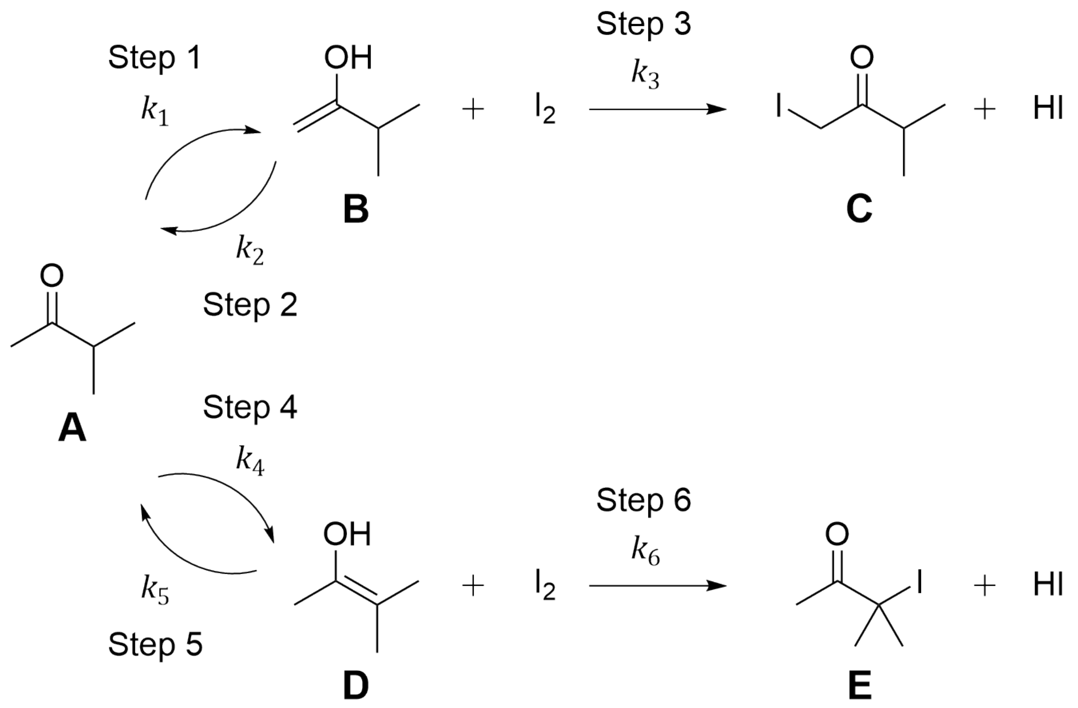
At intermediate concentrations of I_2, Step 2 and Step 3 occur at similar rates. Therefore we cannot assume that the ketone and enol forms are in an equilibrium.

Under these conditions the concentration of **B** can be written as:

$$[\mathbf{B}] = \frac{k_1[\mathbf{A}]}{k_2 + k_3[I_2]}$$

(e) Write the rate of formation of **C** at intermediate concentrations of I_2 in terms of the concentrations of reactants **A** and I_2, and an appropriate combination of k_1, k_2, and k_3.

Compound **A** can also form enol **D** which can react separately with I_2 to form compound **E**. A scheme for the formation of **C** and **E** is shown below.



Where: $k_4 = 2.9 \times 10^{-6}\ \mathrm{s^{-1}}$, $k_5 = 2.1 \times 10^{-2}\ \mathrm{s^{-1}}$, and $k_6 = 5.2 \times 10^{5}\ \mathrm{mol^{-1}\ dm^{3}\ s^{-1}}$.

(f) In the answer booklet, for each row tick whether each statement is correct for compound **C** or compound **E**.

Statement	**C**	**E**
Product whose reaction pathway has a larger rate constant for the first step		
Is the major product at high [I_2]		
Product whose reaction pathway has a larger K_{eq}		
Is the major product a low [I_2]		

(g) Calculate the concentration of I_2 required to form the products **C** and **E** at the same rate. Hint: You will need use an expression for the rate at intermediate concentrations of I_2.

Acknowledgements & References

References will be added to the version of the paper uploaded to the web later.

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Q2 The image is © Dr Ben Pilgrim.

Q3 The image of the table is © Sky Kang and was generated by ChatGPT.
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Authors of 2025 UK Round One Paper (listed alphabetically)
Dr Helen Alonzi (St Bartholomew's School)
Dr Peter Bolgar (University College London)
Richard Danylyuk (University of Cambridge)
Oliver Evans (University of Cambridge)
Sky Kang (Up Learn)
Dr JL Kiappes (University College London)
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