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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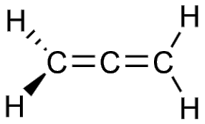
1 **(a)** Allenes are a class of molecules that have 2 adjacent C=C bonds.

One of the simplest allene is shown below.



Allene **A**

(i) Name allene **A**. [1]

(ii) State the hybridisation of the respective carbon atoms of **A**. [1]

(iii) With the aid of a labelled diagram, explain why **A** is **not** planar. [3]

(iv) Explain why *cis-trans* convention **cannot** be used to differentiate between stereoisomers of allenes. [1]

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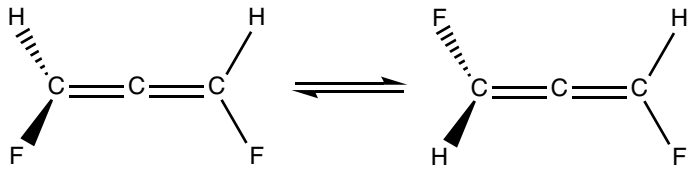
(b) Allenes can be *optically active* although they do not necessarily have a *chiral centre*.

Consider the following reaction below, where there has been a rotation of 180 degrees about only 1 C=C bond.



(i) Define *chiral centre*. [1]

(ii) Explain why the reaction above **cannot** take place freely. [2]

(iii) With the aid of a diagram, show that the 2 allenes are enantiomers. [2]

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(c) Allene **A** may undergo a reaction to form propane.

(i) State the *type of reaction* for this process. [1]

(ii) The reagent used for this process of hydrogen gas. With suitable transition metal catalysts like palladium, platinum or nickel, propane is readily formed.

Describe the mode of action of the metal catalyst. [3]

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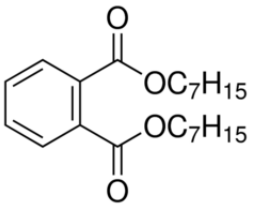
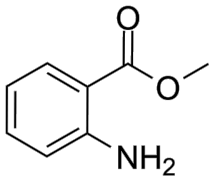
2 (a) The amateur chemist Youtuber NileRed attempted to synthesise a grape flavouring from vinyl gloves.



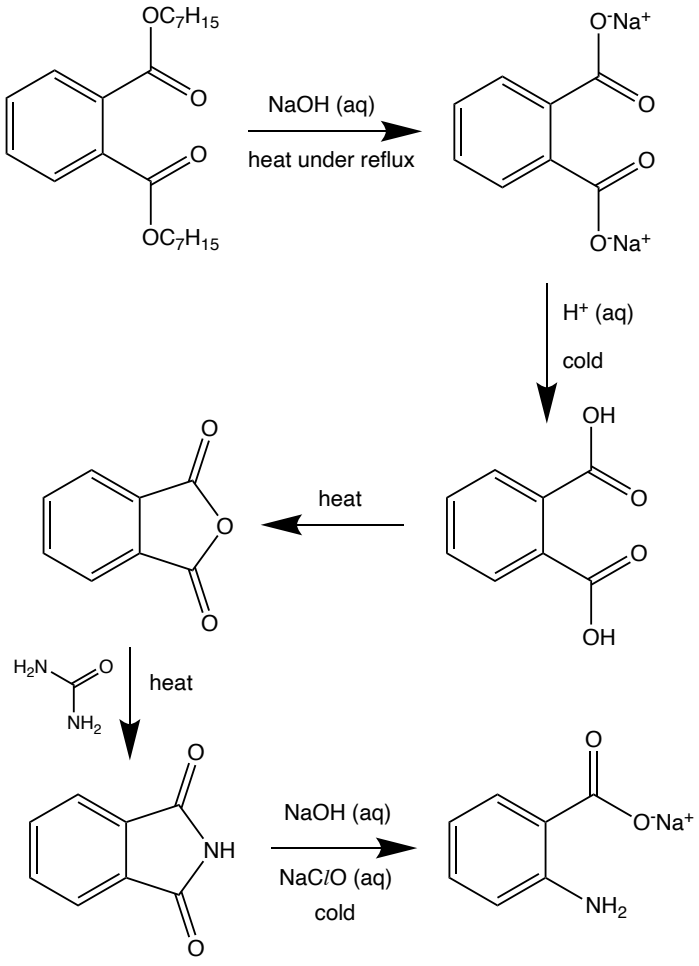
Phthalate ester

Phthalate ester was extracted from vinyl gloves, and a series of steps was conducted to convert the ester to the grape flavouring methyl anthranilate.



Methyl anthranilate

Below shows part of the synthetic steps NileRed used.

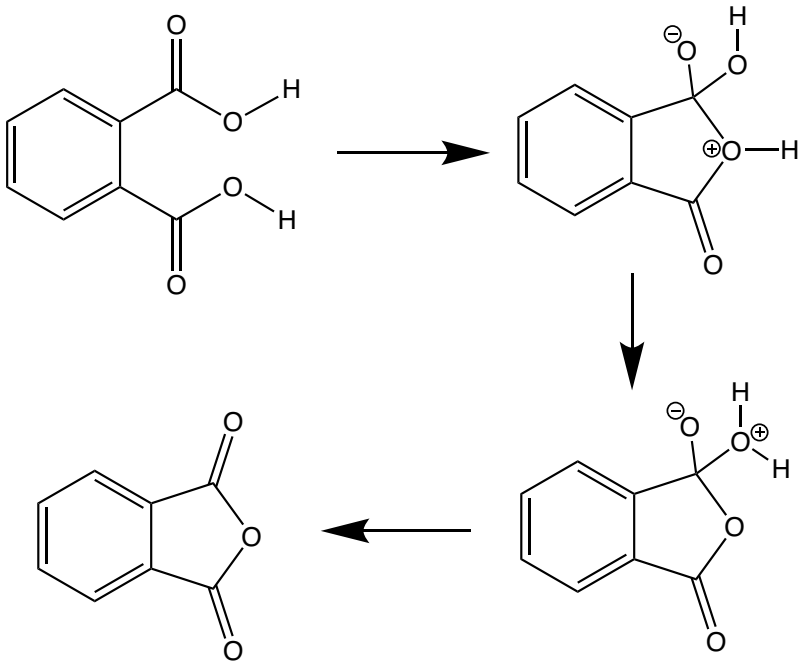


(i) State the *type of reaction* for each step. [2]

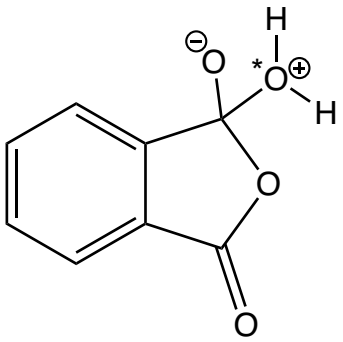
(ii) In step 2 where cold acid was added, the product phthalic acid precipitated out as a white solid due to its poor solubility in water.

Explain the difference between the solubility of phthalic acid and its conjugate base salt form in water. [2]

(iii) In the space below, draw curly arrows and lone pairs where applicable to illustrate how step 3 takes place. [3]



(iv) State the geometry and bond angle with respect to the oxygen atom marked with an asterisk (*) below. [1]



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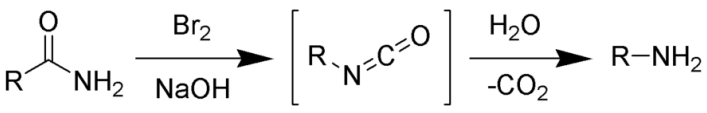
(b) Step 5 is known as the Hoffman rearrangement reaction.

The general version of the Hoffman rearrangement reaction is shown below.



Chlorine can be used in place of bromine in this reaction. You may assume that NaC*l*O is a source of chlorine.

Part **(b)** continues on the next page.

(i) What intermediate must have been formed first before the Hoffman rearrangement in step 5 occurred? Draw its structure. [1]

(ii) Suggest why the Hoffman rearrangement is favourable with respect to a thermodynamic factor of this reaction. [1]

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(c) The final step of this reaction is to convert the product of step 5 into methyl anthranilate.

(i) State the molecular formula of methyl anthranilate. [1]

(ii) 2 students propose different routes for the synthesis.

Student 1: conc. H_2SO_4, methanol, heat
Student 2: PCl_5, then methanol

In both methods, methanol acts as a *nucleophile* in this reaction.

State what is meant by a *nucleophile*. [1]

(iii) There is another group that can act as a nucleophile.

Copy the product of step 5 and indicate where the nucleophilic group is by circling that group. [1]

(iv) Student 2's method is not used in this synthesis as there will be an unintended side product. The nucleophilic group you identified in **(iii)** contributes to the side product.

However, Student 1's method does not pose such a problem. This is because H_2SO_4 may act as a Bronsted-Lowry acid which prevents the side reaction from occurring.

Draw the structure for after the product of step 5 reacts with sulfuric acid (before reacting with methanol), and with reference to this structure, explain why the nucleophilic centre loses its nucleophilicity. [2]

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