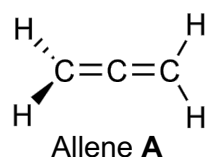


- 1 (a) Allenes are a class of molecules that have 2 adjacent C=C bonds.

One of the simplest allene is shown below.



- (i) Name allene A. [1]

B1 – Propadiene

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

B1 – All correct

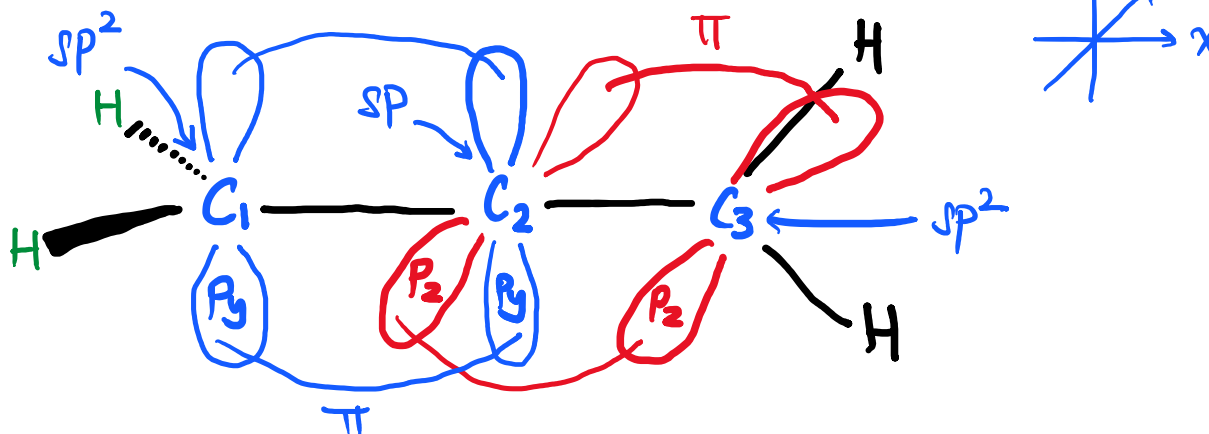
- Terminal carbons: sp^2
- Middle carbon: sp

Candidates are reminded to unambiguously refer to the carbon atoms, either through drawing a diagram or using proper terminology

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

B1 – Middle carbon illustrates 2 unhybridised p orbitals

B1 – Diagram illustrates pi bonds in C=C bonds



B1 – Convincing explanation based on the diagram

- Since the pi bonds in the C=C bonds whose p orbitals are in different axes, the resultant hydrogen atoms reside in different planes.
- Candidate may also show that the C1-H-H plane (xz plane) is perpendicular to the C3-H-H plane (xy plane) from the diagram.

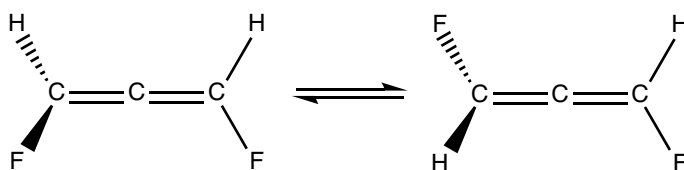
- (iv) Explain why *cis-trans* convention **cannot** be used to differentiate between stereoisomers of allenes. [1]

B1 – cis-trans convention only applies to when the 4 groups are all residing in a plane. However allenes are not planar / 4 groups are not residing in a plane.

This question isn't about why propadiene has no cis-trans isomers, or why cis-trans convention cannot be used on propadiene.

(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]

B1 – A chiral centre is where 4 different groups are covalently bonded to that centre in tetrahedral geometry

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

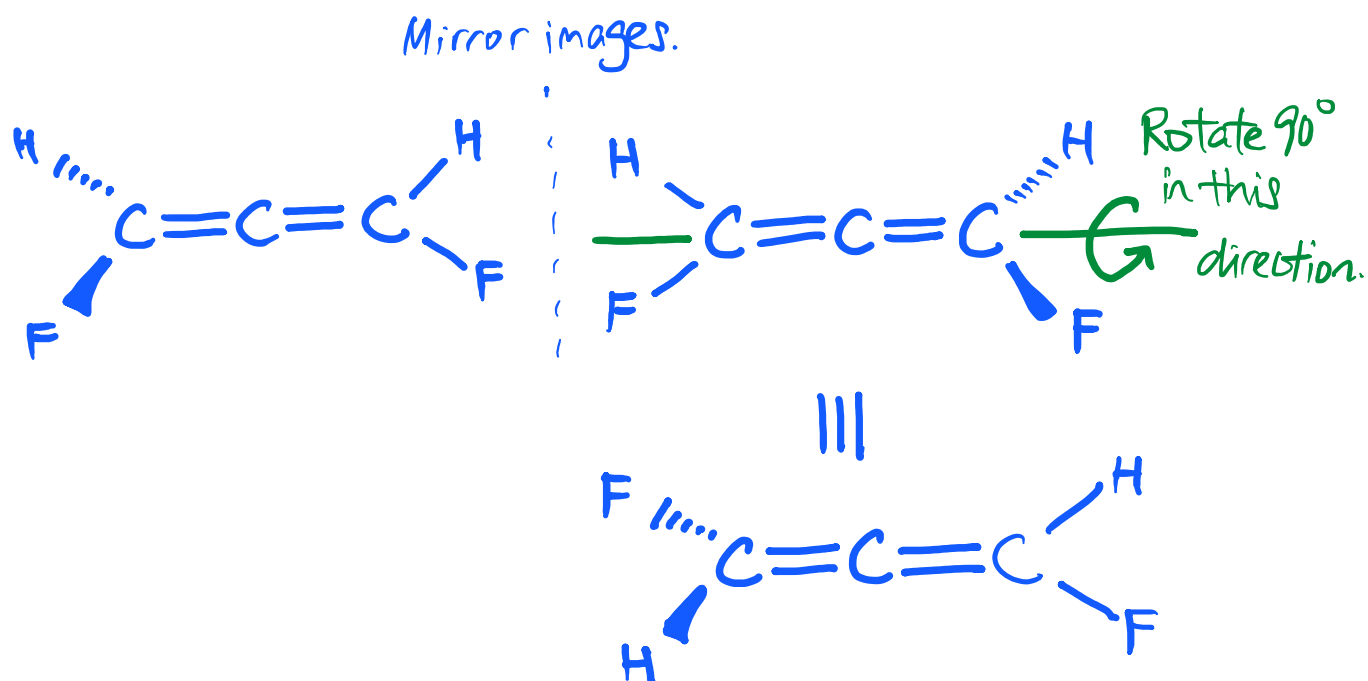
B1 – Restricted rotation about a C=C bond

B1 – Because it takes significant energy to break the pi bond / disrupt the p-p orbital overlap in the C=C bond

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

B1 – Mirror image of either left or right hand side

B1 – Explains clearly how the mirror image molecule is the same as the other molecule



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

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

[1]

B1 – Reduction

(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.

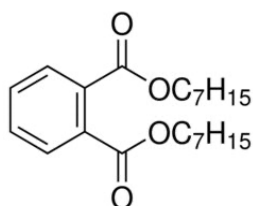
[3]

B1 – Substrates (hydrogen and allene) adsorbs onto active sites of catalyst

B1 – Catalyst weakens covalent bonds AND orientates the molecules into the correct orientation for reaction → lowers activation energy

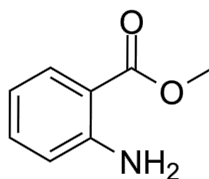
B1 – Product is formed, desorbs from active site of catalyst

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



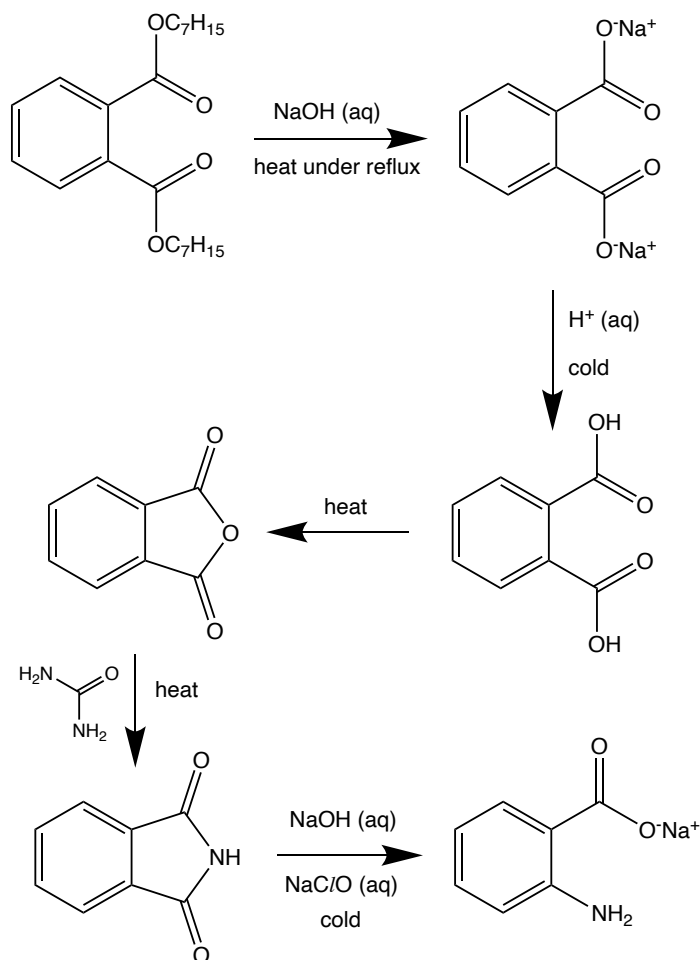
Phthalate ester

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]

B2 – All correct (1 pt for any 3 correct)

Step 1: Hydrolysis

Step 2: Acid-base reaction (accept acidification)

Step 3: Condensation

Step 4: Substitution

Step 5: Oxidation

(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.

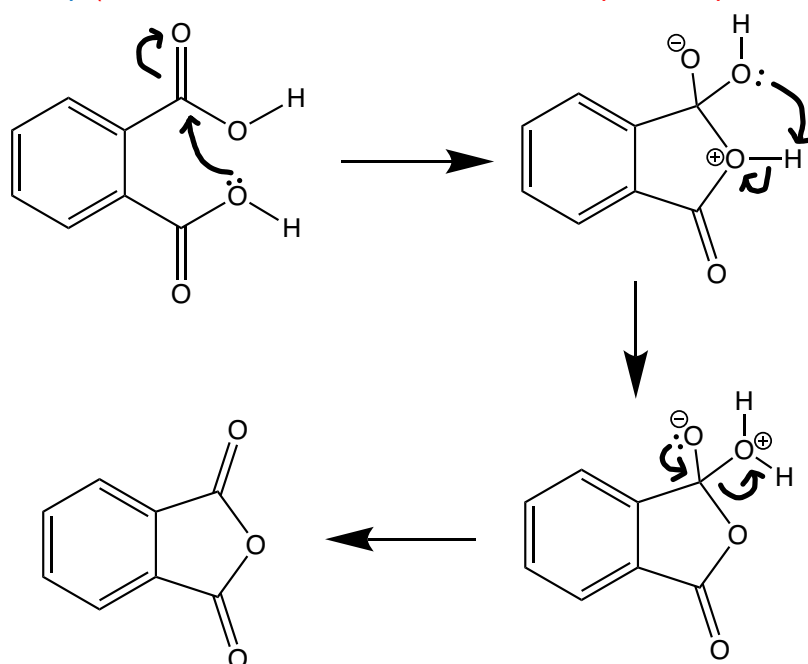
Explain the difference between the solubility of phthalic acid and its conjugate base salt form in water. [2]

B1 – The conjugate base salt form can form favourable ion-dipole interactions with water

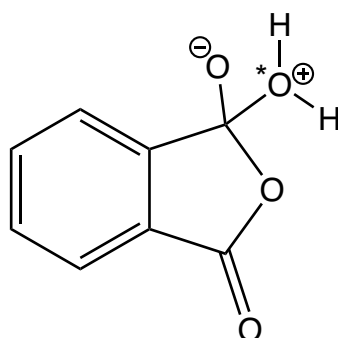
B1 – But phthalic acid can only form weaker hydrogen bonds with water (which releases insufficient energy to overcome the stronger dispersion forces between phthalic acid molecules and hydrogen bonds between water molecules)

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

B1 each per step (arrows should come from a bond/lone pair and point to an atom!)



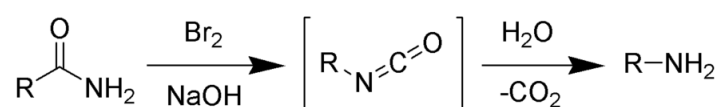
- (iv) State the geometry and bond angle with respect to the oxygen atom marked with an asterisk (*) below. [1]



B1 – sp^3 and 107 degrees

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

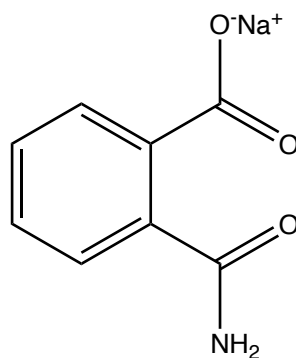
The general version of the Hoffman rearrangement reaction is shown below.



Chlorine can be used in place of bromine in this reaction. You may assume that NaClO is a source of chlorine.

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

B1 – Correct structure (do not accept conjugate acid version)



Note that the -NCO compound is not accepted because the question asks for something that formed before the rearrangement.

Accept (and for subsequent questions) if the benzene ring is represented as



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

B1 – Increase in entropy due to gaseous CO₂ being eliminated (more gas molecules being formed)

- (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]

B1 - C₈H₉NO₂

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

Student 1: conc. H₂SO₄, methanol, heat

Student 2: PCl₅, then methanol

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

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

B1 – A Lewis Base OR a specie that has (an) electron pair(s) (reject lone pair)

- (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]

B1 – Correctly circles -NH₂ group

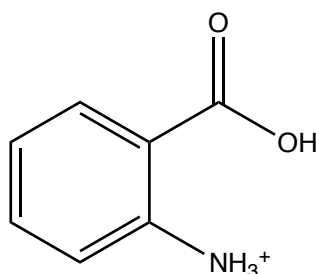
Candidates are reminded to follow the instructions in the question and copy the product!

- (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 H₂SO₄ 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]

B1 – Correct structure



B1 – The lone pair is not available