Trinidad and Tobago Chemistry Olympiad

Round 2 - Level B

INSTRUCTIONS TO CANDIDATES:

1. **Do not turn this page until you are told to do so**.
2. This paper consists of **eleven (11)** numbered pages.
3. There are **five (5)** questions; Answer **all** questions.
4. The examination duration is **3 hours**.
5. The total number of marks = **121 marks**.
6. In addition to this question paper, you should also have an answer booklet and graph paper.
7. Show **ALL** working. The majority of marks are awarded for appropriate statements, descriptions and explanations.
8. The use of non-programmable calculators is allowed.
9. A Periodic Table will not be provided.

1. *The first recorded chemist was a woman by the name of Tapputi, who lived in ancient Mesopotamia. She, along with her assistant (-)ninu, was responsible for making perfumes in the kingdom. Many of their techniques, and perfume components, have persisted to modern times. One of these procedures is the distillation of fragrances from plants.*

   (a) Describe the process of: (i) steam distillation, and (ii) vacuum distillation. Identify how they are distinct from simple distillation.

   (6 marks)

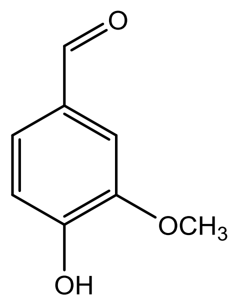
- Simple distillation is typically used for the separation of a few liquids which have significantly different boiling points, at atmospheric pressure.[or separation of a solvent from dissolved impurities (that are solid at room temperature)]. (2 marks)
- (i) Steam distillation, as its name suggests, uses steam generated in a separate flask, and pumped into the flask containing the mixture, to facilitate the separation/purification process. It is used for the separation of sensitive hydrophobic compounds that will otherwise decompose at their normal boiling point. This process allows the targeted compounds to be distilled off at a much lower (benign) temperature. (2 marks)

e.g. the steam distillation of plant materials to yield essential oils for the aromatherapy industry.

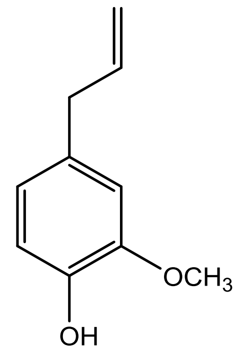
- (ii) Vacuum distillation utilizes the fact that the boiling point of a liquid is directly proportional to the prevailing pressure. By reducing the pressure (lower than atmospheric pressure) that the surface of the liquid is experiencing (through the application of a vacuum), a liquid can be distilled off at a temperature much lower than its boiling point. This is especially advantageous for the purification of liquids that decompose at elevated temperatures. (2 marks)

e.g. dimethylformamide (DMF) is a popular solvent in Organic Synthesis. However it usually requires purification (by drying with calcium hydride) before use. If this mixture is distilled at atmospheric pressure, the majority of DMF will decompose to dimethylamine and carbon monoxide; and hence vacuum distillation is required.

(*b*) *Consider the structures of two naturally occurring fragrant compounds, vanillin and eugenol:*



Vanillin



Eugenol

Vanillin can be extracted from the vanilla bean, while eugenol is the major component of clove oil.

(i) Describe two chemical tests that can be used to distinguish between vanillin and eugenol, providing relevant observations as well. ***(6 marks)***

- Identify the structural points of distinction between the molecules: (a) vanillin has an aldehyde group while eugenol has an alkene linkage

- (Correct test: 1 mark; Correct observation with each compound: 1 mark x 2) x 2

- React each sample with Brady's reagent (2,4-dinitrophenylhydrazine); a red precipitate (*give marks for yellow or orange)* will be formed with vanillin, but no observable reaction will occur with eugenol.

Note: Give marks for correct alternatives e.g. Tollen's reagent, Fehling's, Benedict's etc

- React each sample with bromine in the dark; the orange-brown colour of bromine will be decolourized with eugenol, but no observable reaction will occur with vanillin.

(ii) Spectroscopic methods may also be used to differentiate between vanillin and eugenol. Identify one such method, and describe how it can be used to distinguish between these compounds. ***(5 marks)***

- Infrared (IR) spectroscopy [or Nuclear Magnetic Resonance (NMR) spectroscopy, or Mass Spectrometry (MS)].

IR - identifies differences in functional groups

[NMR - sensitive to differences in chemical and magnetic environments for the type of atom being considered]

[MS - Molecular ion peak, fragmentation pattern]

(2 marks)

- Both compounds have an aromatic ring (with the same type of substitution). Vanillin however has an aldehyde functionality which will have a different IR frequency than that of the alkene system present in eugenol.

(3 marks)

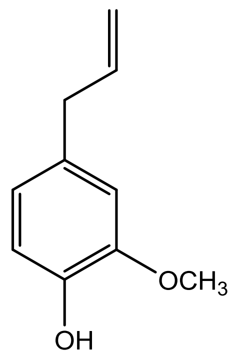
For consideration:

(i) Examine the table of liquids below:

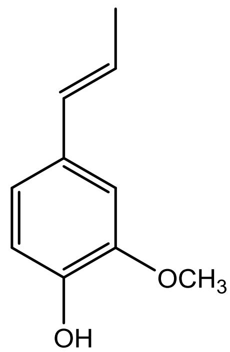
Liquid	*Standard Boiling Point (°C)*	*Miscibility with water*
(a) dimethyl sulphoxide	*189*	*Miscible*
(b) α-Pinene	*155*	*Very low*

- *Would simple distillation be suitable for the separation of a mixture of (a) and (b)?*
- *Would steam distillation be suitable for the purification of (a) from minor dissolved impurities?*

(ii) How would you distinguish between eugenol and isoeugenol?

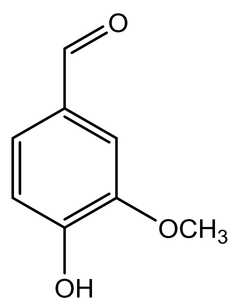


Eugenol

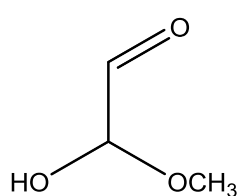


Isoeugenol

(iii) How can Brady's reagent be used to distinguish between vanillin and 2-hydroxy-2-methoxyacetaldehyde

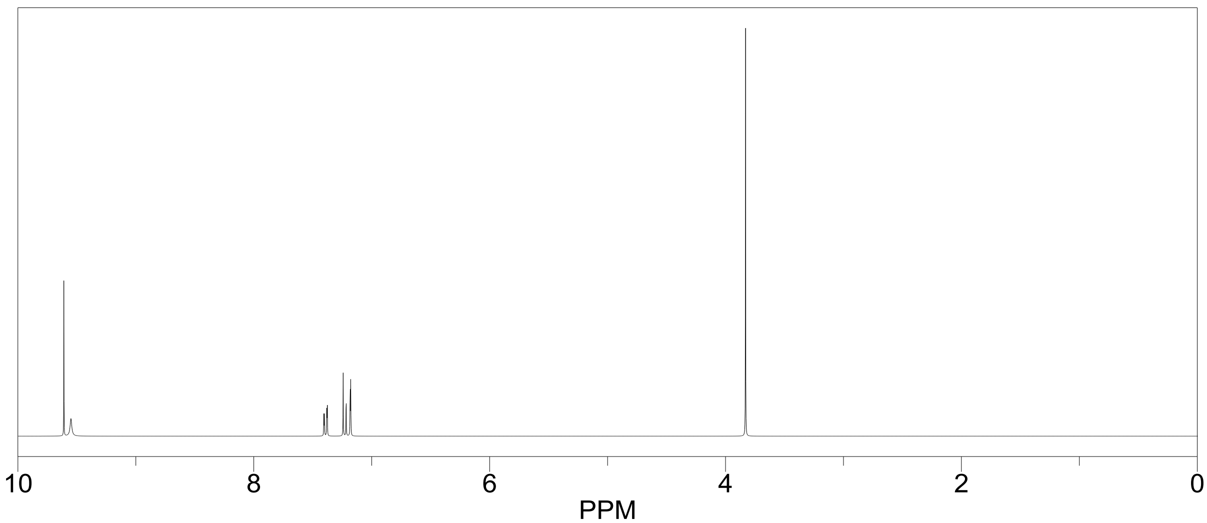


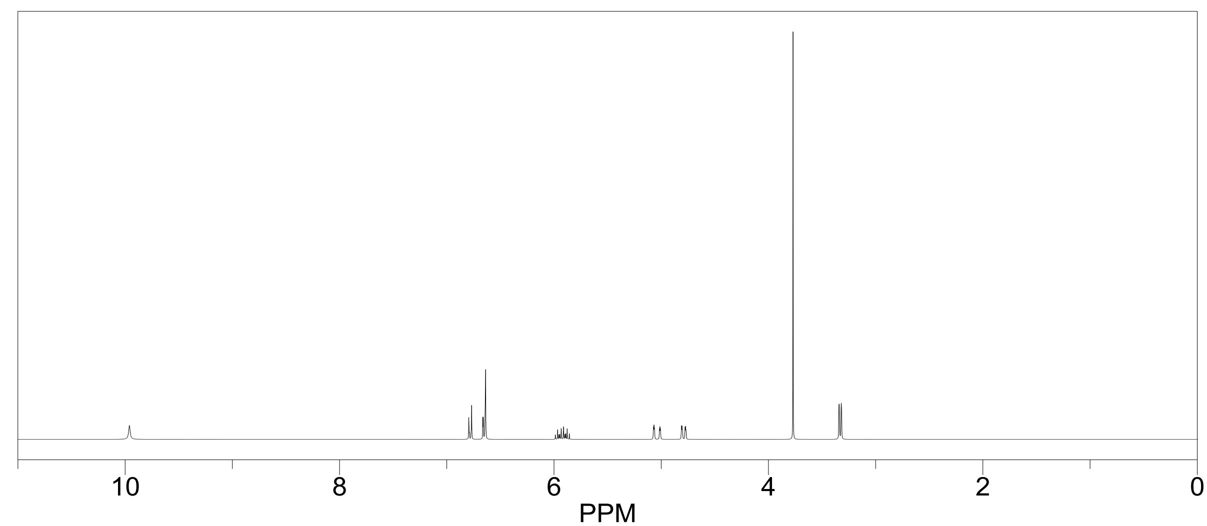
Vanillin



2-hydroxy-2-methoxyacetaldehyde

(iv) Consider the two NMR spectra shown below. Which one is that of vanillin, and of eugenol?





2. *Chalcopyrite is a naturally occurring mineral with the formula: $CuFeS_2$.*

Copper metal can be extracted by the complete open air combustion of Chalcopyrite in the presence of silica. The other products of this reaction are: ferrosilite ($FeSiO_3$) and a colourless gas with a suffocating odour. You have 1 kg of Chalcopyrite which you subject to this reaction.

(a) *The gas produced reacts with NaOH (aq) to yield sodium sulfite. What is the identity of the gas?* ***(2 marks)***

- SO_2 (2 marks)

$$SO_2\,(g) + 2NaOH\,(aq) \longrightarrow Na_2SO_3\,(aq) + H_2O\,(l)$$

(b) *Write the balanced equation for the open air combustion of Chalcopyrite in the presence of silica.* ***(3 marks)***

$$2CuFeS_2\,(s) + 5O_2\,(g) + 2SiO_2\,(s) \longrightarrow 2Cu\,(s) + 2FeSiO_3\,(s) + 4SO_2\,(g)$$

- Representing correct formulae of reactants and products (1 mark)
- Correctly balanced equation (2 marks)

(c) Given that the reaction occurs at 900 K, what is the volume of sulphur dioxide expected to be produced at this temperature? State all assumptions. **(8 marks)**

- M_r $CuFeS_2$ = 64 + 56 + (2 x 32)
  = 184 (1 mark)
- 184 g = 1.0 mole chalcopyrite
- 1000 g = 1.0/184 * 1000 g
  = 5.43 mole chalcopyrite (1 mark)

- From the stoichiometric equation,
- 2 moles $CuFeS_2$ = 4 moles SO_2
- 5.43 moles $CuFeS_2$ = 4/2 * 5.43 moles SO_2
  = 10.87 moles SO_2 (1 mark)

- Assuming that SO_2 is an ideal gas (1 mark)
- Ideal gas equation: (*An acceptable alternative calculation can utilize Charles' Law*)
- PV = nRT (1 mark)

  where P = pressure
  = assume to be 1 atm (1 mark)
  V = volume = ?
  n = number of moles = 10.87 moles
  R = 0.0821 L atm K^{-1} mol^{-1}
  T = 900 K
- Rearranging and substituting:

  V = nRT/P
  = 10.87 * 0.0821 * 900 / 1
  = 803.2

Units Check:

V = (moles x L atm K^{-1} mol^{-1} x K) / atm
= L

V = 803.2 L (1 mark for value; 1 mark for correct units) *(d) Chalcopyrite may also undergo electrolysis to yield copper metal, iron metal, and the sulfide ion.*

(i) Write the half-cell equation for this reaction. ***(4 marks)***

(i) Write equation showing reactants and products:

$CuFeS_2 \longrightarrow Cu + Fe + 2S^{2-}$ (1 mark)

(ii) Assign charges on both sides:

0 (2 x 2-)

0 -4 (1 mark)

(iii) Balance charges by adding electrons:

$CuFeS_2 + 4e^- \longrightarrow Cu + Fe + 2S^{2-}$ (2 marks)

(ii) If a current of 8.60 A is passed through 1 kg of this molten mineral, how long will it take for all of the copper and iron to be deposited? ***(10 marks)***

$F = 96,500\ C\ mol^{-1}$; Ar: Cu = 64; Fe = 56; S = 32

- From the equation in (i):

1 mole $CuFeS_2$ = 4 mole e^- (1 mark)

5.43 moles = 4 * 5.43 moles e^-

= 21.74 moles e^- (2 marks)

- Faraday constant: 96,500 C mol^{-1}
- 1 mole e- = 96,500 C (1 mark)
- 21.74 moles e^- = 96,500 x 21.74 C

= 2.1×10^6 C (2 marks)

- Q = It (2 marks)

where Q = charge = 2.1×10^6 C

I = current = 8.60 A

t = time in s

- Rearranging and substituting:

$t = Q/I$

$= 2.1 \times 10^6$ C / 8.60 A

$= 2.4 \times 10^5$ s (1 mark for value; 1 mark for correct units)

$= 2.4 \times 10^5$ / 3600 hrs

= 67.8 hrs (*also acceptable*)

(e) Chalcopyrite can undergo other types of oxidation reactions. For example, if it is suspended in water, and oxygen gas is bubbled through this mixture, the products / observations include:

(i) A blue solution that: (I) change blue litmus paper red, and also (II) forms a light blue precipitate with dil. NH_3 *(aq), dissolving in excess to form a deep blue solution.*

(ii) A soluble anion that when reacted with acidified $BaCl_2$ *(aq) yields a white precipitate.*

(ii) A red powder (that looks like rust). This red powder will react with dil. HCl (aq) to yield a light brown solution, which when mixed with potassium thiocyanate solution an intense blood red colour is formed.

Explain each of the reactions / observations identified in (i) to (iii), and hence deduce the overall balanced equation for the reaction of Chalcopyrite with oxygen and water.

(20 marks)

- (i): The changing of blue litmus paper red indicates the presence of H^+ in the solution (1 mark)

  A blue solution indicates the presence of $[Cu(H_2O)_6]^{2+}$ (or Cu^{2+}) (1 mark)

  Continuous addition of NH_3 (aq) will eventually neutralize the H^+, and make the solution alkaline. After this has occurred, copper (II) hydroxide will precipitate, and further NH_3 (aq) will coordinate to this complex, forming a deep blue solution. (2 marks)

$$H^+ (aq) + NH_3 (aq) \longrightarrow NH_4^+(aq) \text{ (1 mark)}$$

$$\underbrace{Cu^{2+} (aq) \xrightarrow{NH_3 (aq)} \underset{\text{light blue precipitate}}{Cu(OH)_2 (s)}}_{\text{2 marks}} \underbrace{\xrightarrow{\text{excess } NH_3 (aq)} \underset{\text{deep blue solution}}{Cu(NH_3)_4^{2+}(aq)}}_{\text{2 marks}}$$

- (ii): Indicates the presence of SO_4^{2-} (aq) (1 mark)

  The white precipitate is $BaSO_4$ (1 mark)

$$SO_4^{2-} (aq) + Ba^{2+} (aq) \longrightarrow BaSO_4 (s) \text{ (1 mark)}$$

- (iii): Blood red solution with thiocyanate is a confirmatory test for Fe^{3+} (1 mark)

  Rust is Fe_2O_3, a basic oxide, which will react with acid to form a light brown solution due to the presence of Fe^{3+} (1 mark)

$$Fe_2O_3 (s) + 6HCl (aq) \longrightarrow 2FeCl_3 (aq) + 3H_2O (l) \text{ (1 mark)}$$

$$Fe^{3+} (aq) + SCN^- (aq) \longrightarrow [FeSCN]^{2+} (aq) \text{ (1 mark)}$$

Overall equation:

$$2CuFeS_2\,(s) + 8.5O_2\,(g) + 2H_2O\,(l) \longrightarrow Fe_2O_3\,(s) + 2Cu^{2+}\,(aq) + 4SO_4^{2-}\,(aq) + 4H^+\,(aq)$$

- Representing correct formulae of reactants and products (2 marks)
- Correctly balanced equation (2 marks)

For consideration:

(i) For (c), an alternative approach utilizes Charles' Law. Calculate the volume using this method.

(ii) If the assumption that SO_2 is an ideal gas is incorrect, then the ideal gas equation cannot be used in (c) (neither can Charles' law). How then will the volume be calculated?

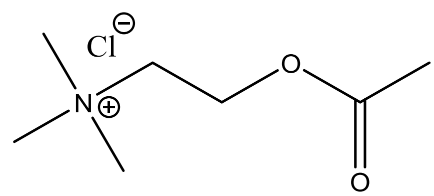
(iii) The actual reactions taking place in (e)(i) regarding the Cu^{2+}(aq) and NH_3 (aq) are:

$$[Cu(H_2O)_6]^{2+}\,(aq) \xrightarrow{NH_3\text{ acting as a base}} \underset{\text{light blue precipitate}}{[Cu(H_2O)_4(OH)_2]\,(s)} \xrightarrow{\text{ligand exchange}} \underset{\text{deep blue solution}}{[Cu(H_2O)_2(NH_3)_4]^{2+}\,(aq)}$$

- *Why does NH_3 displace OH^- and H_2O as a ligand?*
- *Why does the colour change from blue to light blue to finally deep blue occur?*

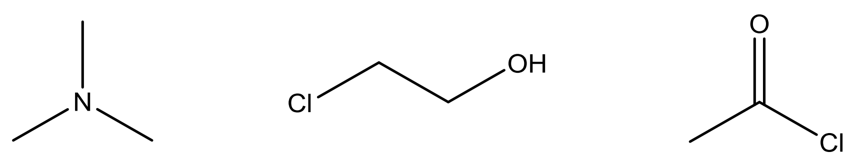
3. *The Lionfish (Pterois spp.) is a recent invasive species to the waters of Trinidad and Tobago, with the capacity to cause significant damage to marine life, partly due to its voracious appetite. Furthermore, the presence of venomous spines means that there are few natural predators. The venom is a combination of a neuromuscular toxin (a protein) and a neurotransmitter (acetylcholine).*

Consider the structure of acetylcholine chloride:



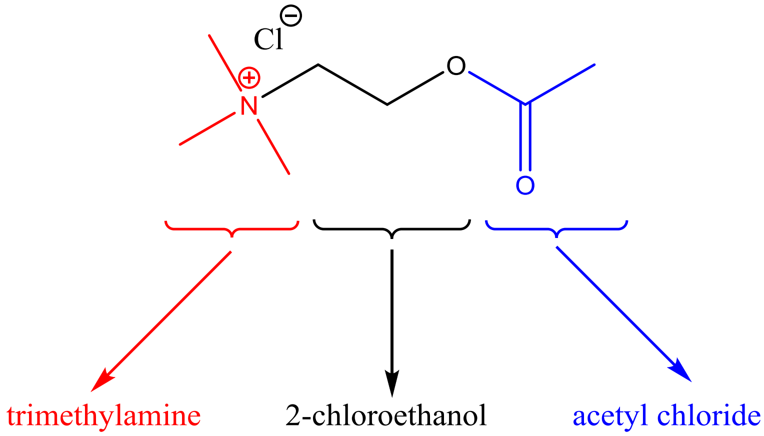
Acetylcholine chloride

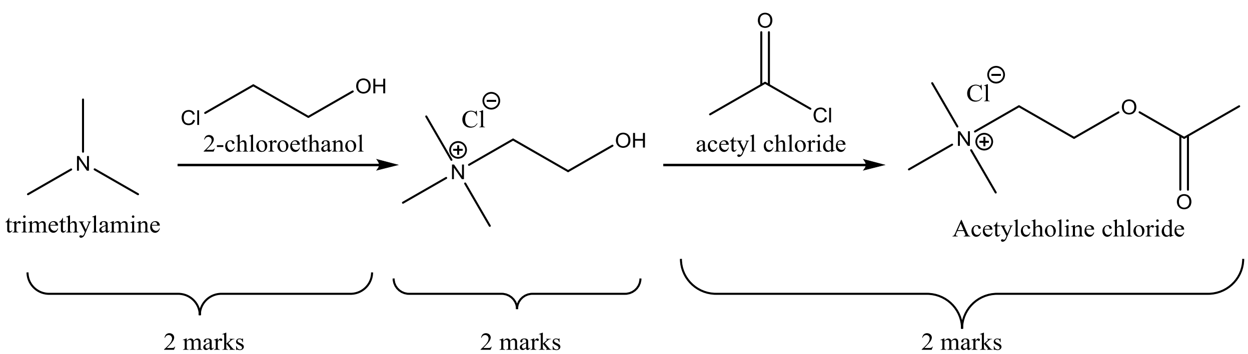
Starting from trimethylamine, utilize the chemicals shown below to devise a synthesis of acetylcholine chloride. Show the identity of the intermediate compound. ***(6 marks)***



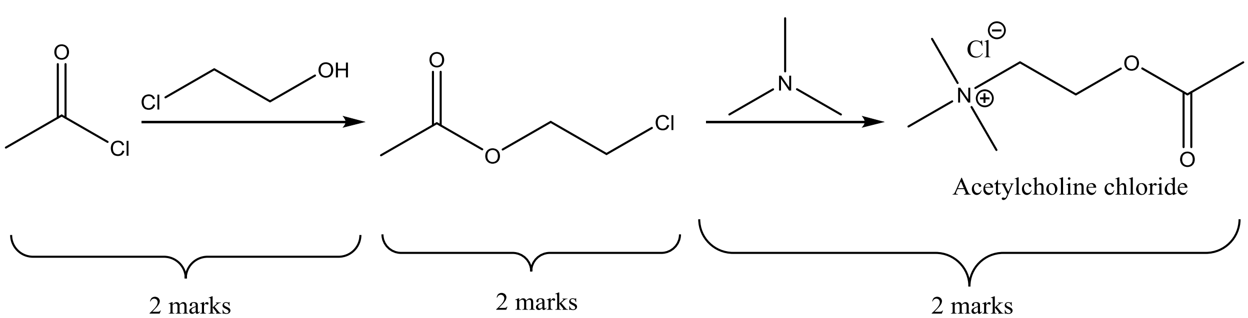
trimethylamine 2-chloroethanol acetyl chloride

- Examine the structure of the final product; one can identify regions corresponding to the various reactants. This strategy (called the "Disconnection Approach") is a powerful technique for synthesizing a given organic compound:



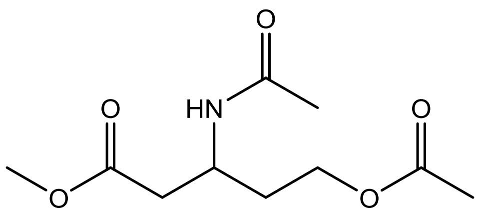


Or



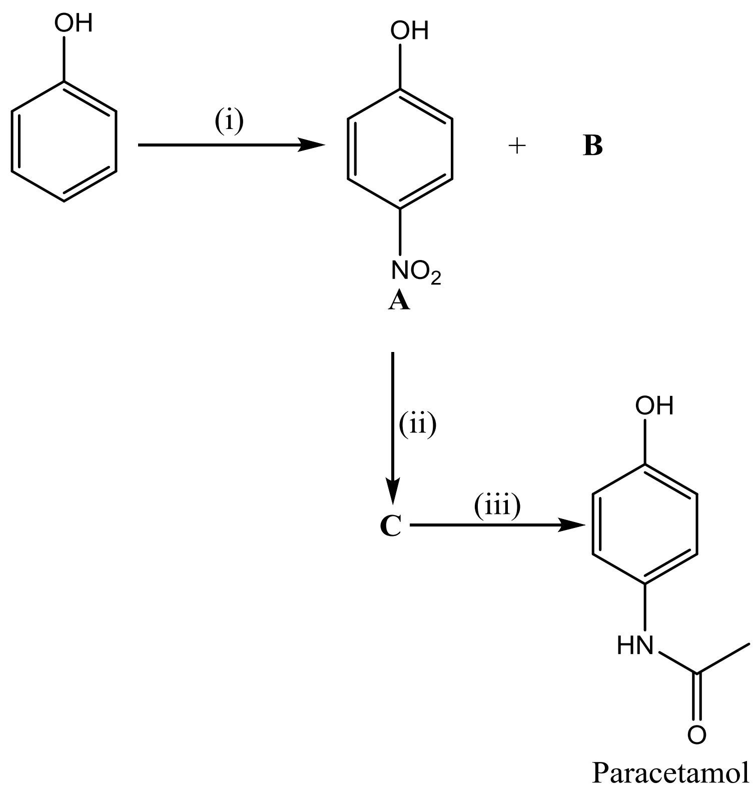
For consideration:

Consider the structure shown below and propose how you will synthesize it from simple building blocks (starting materials).



4. *Pain relieving medications are an indispensable feature of modern society, and are diverse in their structure and origin. Some, such as acetylsalicylic acid (commonly known as Aspirin), are derivatives of naturally occurring compounds. The bark of the Willow tree, which contains a precursor of Aspirin (salicylic acid), was used for the treatment of fever and inflammation by the Ancient Egyptians. Others have been identified through a targeted system of drug discovery.*

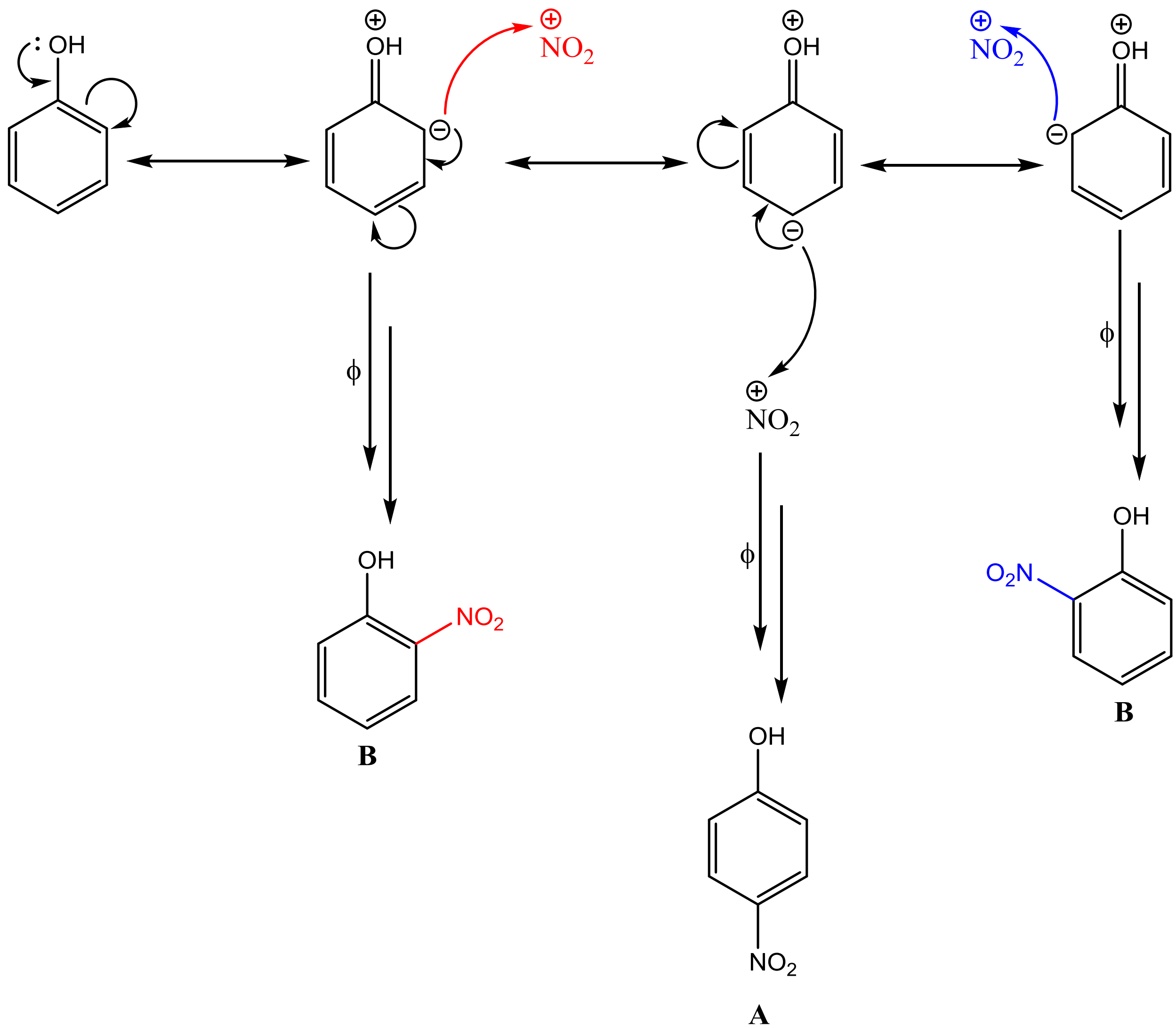
(a) Paracetamol / acetaminophen is marketed under various names - Tylenol, Panadol etc. Consider a possible scheme for its synthesis:



(i) Identify the missing reagents / reactants: (i) - (iii) ***(3 marks)***

- (i): Dilute HNO_3 or $NaNO_3$ / dil. H_2SO_4 (1 mark)
- (ii): Sn / conc. HCl or $NaBH_4$ or any suitable reducing agent (1 mark)
- (iii): Acetic anhydride or acetyl chloride (1 mark)

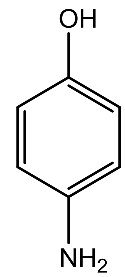
  [A few students had acetic acid. This was accepted] *(ii) Compound **B** is an isomer of **A**, formed in the same reaction. Draw its structure, and account mechanistically for the formation of both **A** and **B**.* ***(5 marks)***



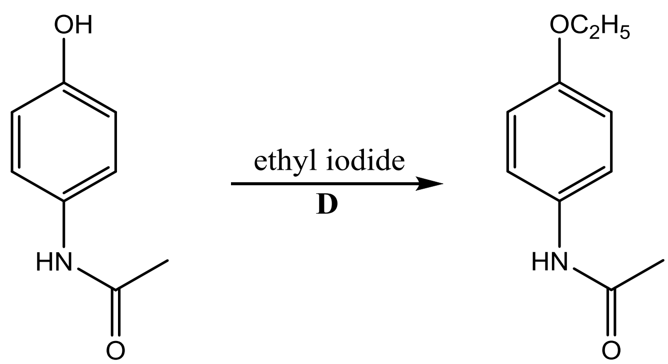
ϕ: Loss of H^+ to faciliate reformation of the aromatic ring, an energetically favourable system

- Resonance structures (2 marks)
- Movement of electrons (2 marks)
- Identity of **B** (1 mark)

[Marks were awarded for reasonable answers] *(iii) Draw the structure of compound **C**.* ***(2 marks)***



*(iv) Phenacetin (shown below), can be obtained from paracetamol in a single step using ethyl iodide and reagent **D**. Suggest an identity for **D**.* ***(2 marks)***

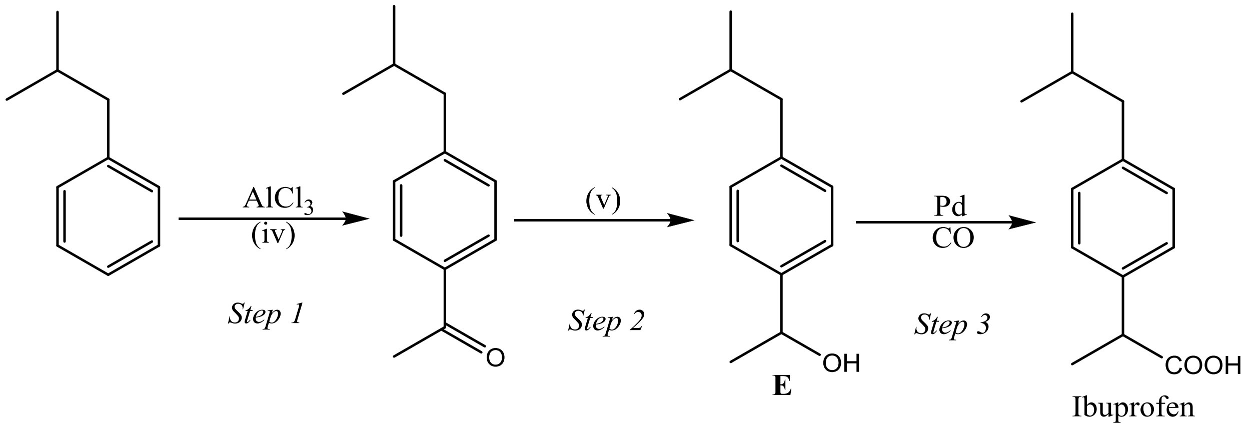


Paracetamol Phenacetin

- Consider the structure of both reactants and determine what change they have undergone in forming a single product: Paracetamol loses an H^+; and ethyl iodide loses an I^-. i.e. HI is produced. What will neutralize this acid, without affecting the amide linkage? - a weak base.

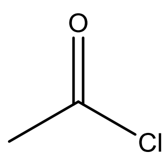
D = K_2CO_3 (give marks for any base that is suggested)

(b) Shown below is a possible synthetic route to ibuprofen, starting from 2-methylpropylbenzene:



(i) Identify the missing reagents / reactants: (iv) and (v) ***(2 marks)***

(iv): an acetyl (ethanoyl) group has been introduced into the aromatic ring. This is a Friedel-Crafts acylation reaction.



(1 mark)

acetyl chloride / ethanoyl chloride

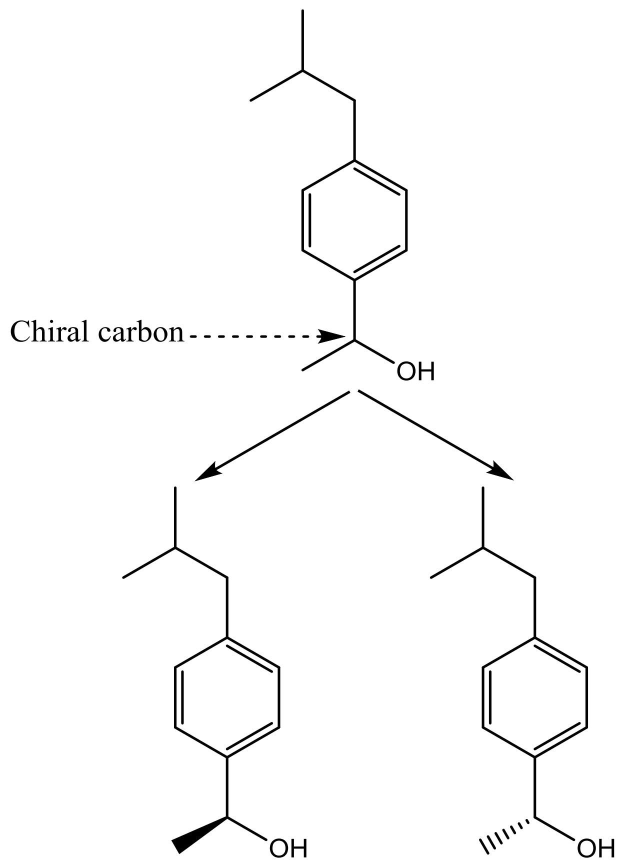
(v): conversion of carbonyl to alcohol requires a reducing agent e.g. $LiAlH_4$ or $NaBH_4$ (1 mark)

(ii) What type of reaction is Step 2? ***(1 mark)***

- Reduction

(iii) Compound ***E*** *is actually a pair of isomers. Draw them.* ***(4 marks)***

- Compound **E** has a chiral carbon, and this gives rise to a pair of stereoisomers:



(2 marks) (2 marks)

[Representing chirality via the use of a mirror plane was also accepted]

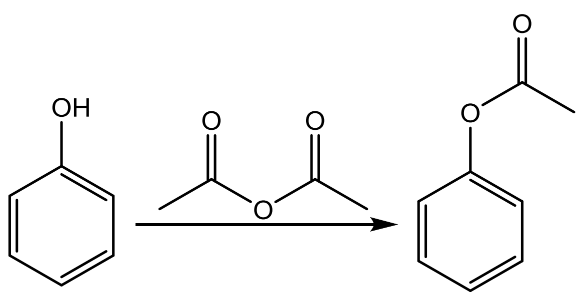
(iv) Even though ibuprofen is marketed as a racemate, only the S isomer is medicinally active. Why do you think that most formulations of ibuprofen do not remove the R isomer prior to sale to the consumer? **(2 marks)**

- The R isomer does not have harmful effects, and hence the cost of separating the R isomer does not make this purification worthwhile.

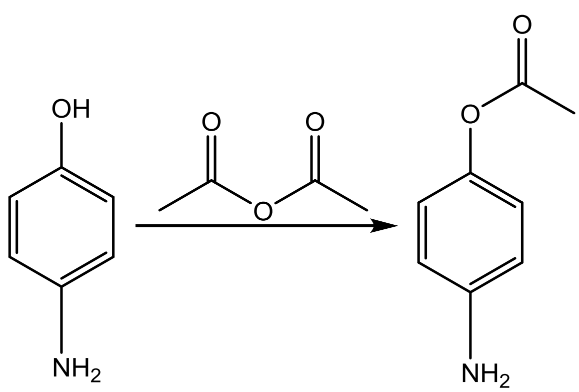
For consideration:

(i) Why is phenol nitrated under milder conditions, compared to benzene? What would be the outcome of the reaction if the same reagents/conditions that are used for the nitration of benzene, be used for phenol?

(ii) Consider this transformation:

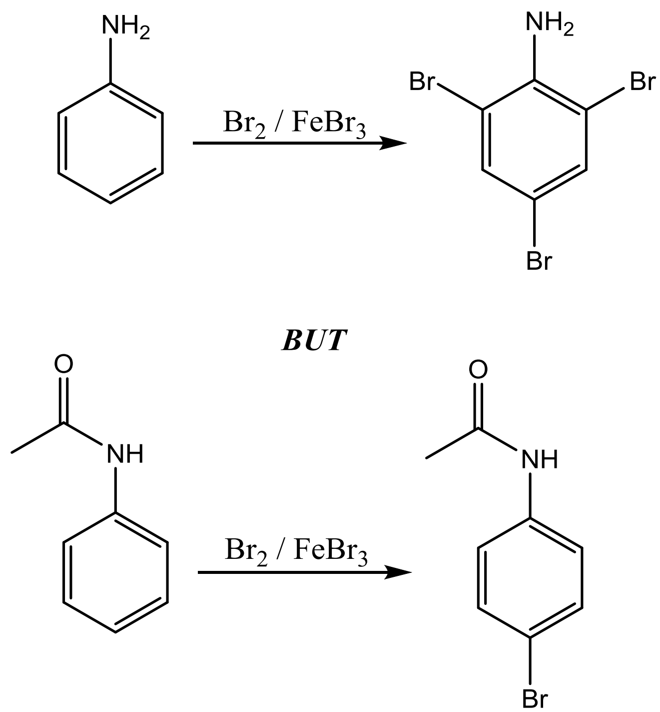


In a (iii), why does the following not occur then?



(iii) In a (iv), what would be the outcome if no base is added to the reaction?

(iv) Account for the following observation:

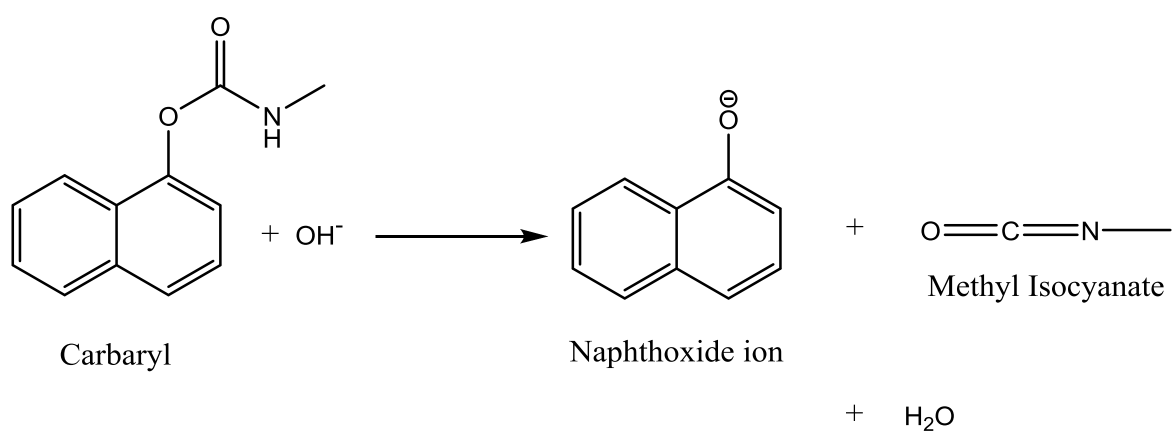


(v) In b (iii), identify the R and S isomers.

5. *The data presented in this question was taken from the article: Darryl Hawker,* ***2015****, 92, 1531 - 1535. Kinetics of Carbaryl Hydrolysis: An Undergraduate Environmental Chemistry Laboratory.*

Carbaryl is the first commercially successful pesticide, with the worldwide quantities deployed being greater than that of all other carbamate pesticides. It is commonly known by its trade name, Sevin. Ideally, pesticides should not persist indefinitely in the environment, but rather undergo some transformation to inactive and non-toxic products. One such transformation pathway is hydrolysis, which may occur by either acidic, basic, or enzymatic, mechanisms.

For carbaryl, it has been shown that the acidic mechanism requires too low of a pH (< 5) to be of environmental relevance. The base-mediated hydrolysis occurs at pH > 10, and can be represented as follows:



*Experiments were conducted to determine the rate of base-mediated hydrolysis of carbaryl at different pHs. The progress of the reaction was monitored by following the absorbance (A) of carbaryl at a specific wavelength - that corresponding to its maximum absorbance (**Figure 1**).*

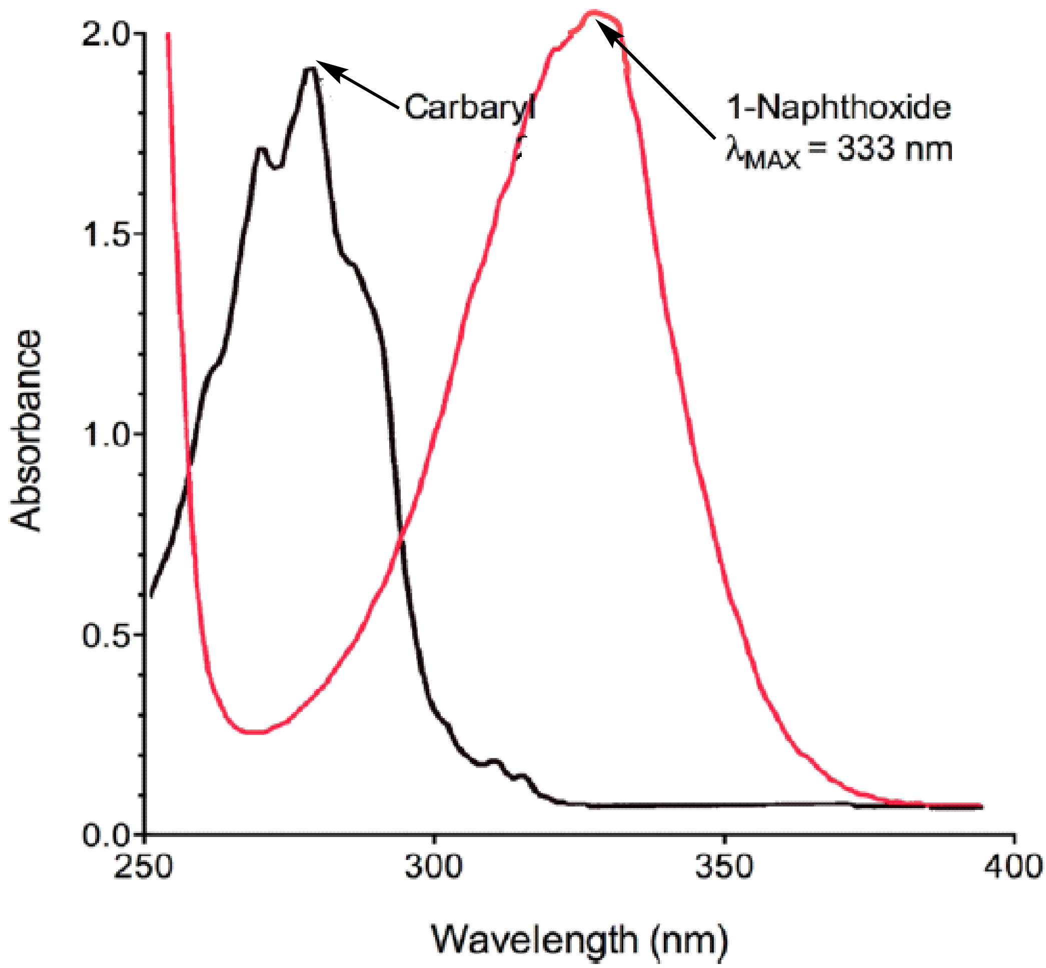


Figure 1: Ultraviolet absorption spectra of carbaryl and 1-naphthoxide

The concentration of carbaryl, at a given time "t", can be replaced by a corrected absorbance: A_t - A_∞ (Absorbance at time "t" - Absorbance at infinity i.e. when maximum hydrolysis of carbaryl has occurred). The following equation which models a straight line can be derived:

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k't$$

where A_0 = initial absorbance; k' = pseudo-first-order rate constant

*This was done for pHs: 10.0, 10.5, and 11.0 at 20 °C (**Figure 2**).*

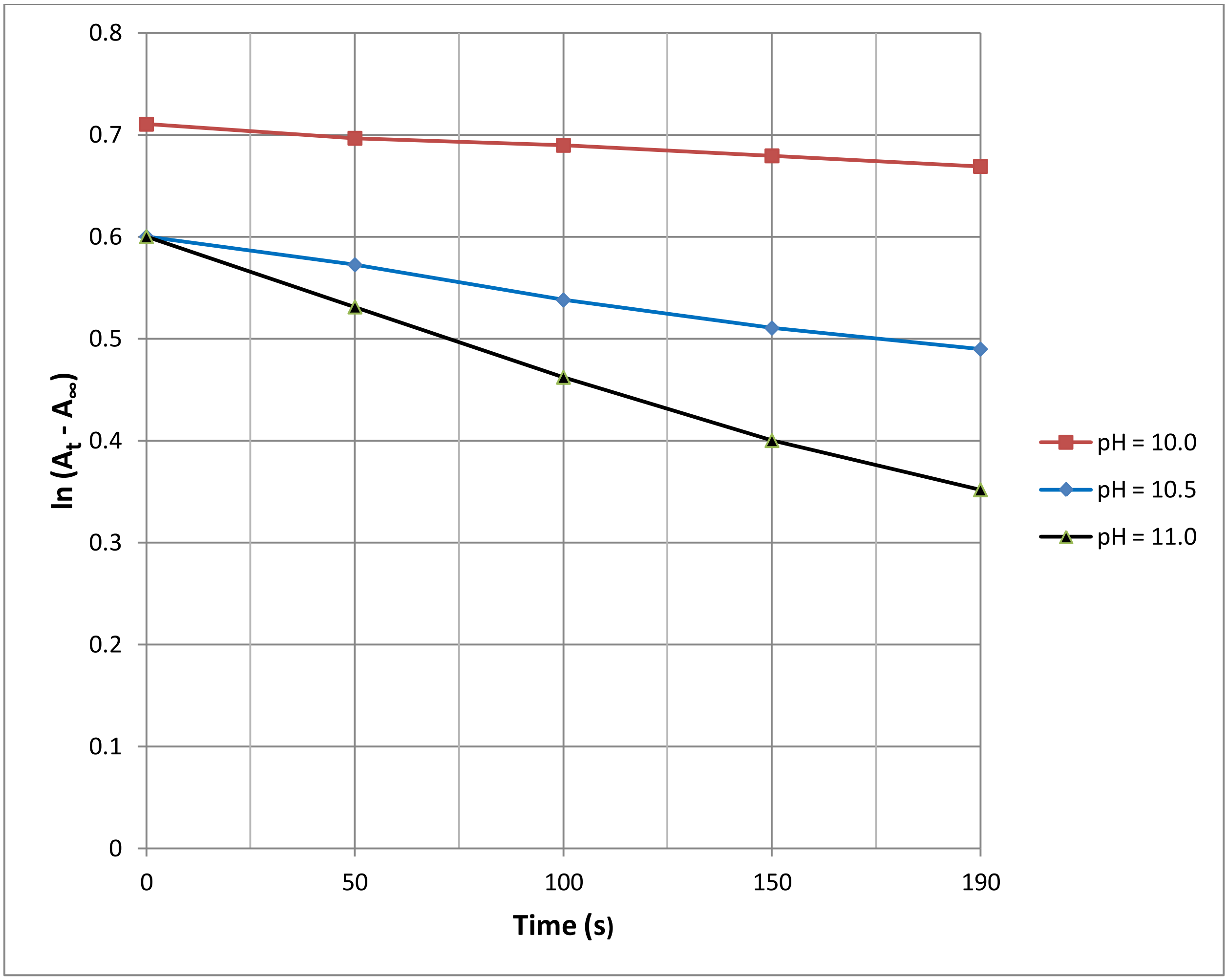
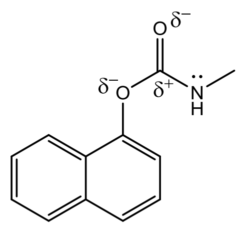


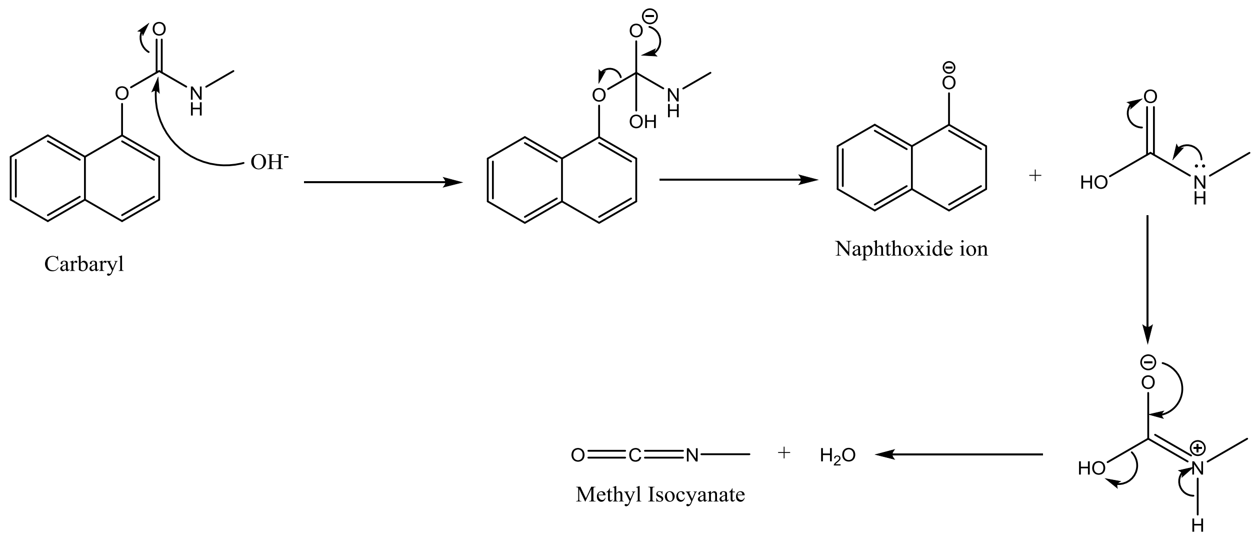
Figure 2: Pseudo-first-order kinetic experiments at different pHs

(a) Suggest a mechanism for the base-mediated hydrolysis of carbaryl to form the naphthoxide ion and methyl isocyanate. ***(3 marks)***

- When elucidating a mechanism, consider the following:
  - Where are the electron deficient (e.g. bonded to electronegative atoms) and electron rich centres?
  - Which atoms have lone pairs that are capable of being donated?
  - The three most electronegative atoms, in order, are: F, O, N
  - H_2O is an excellent leaving group



Carbaryl



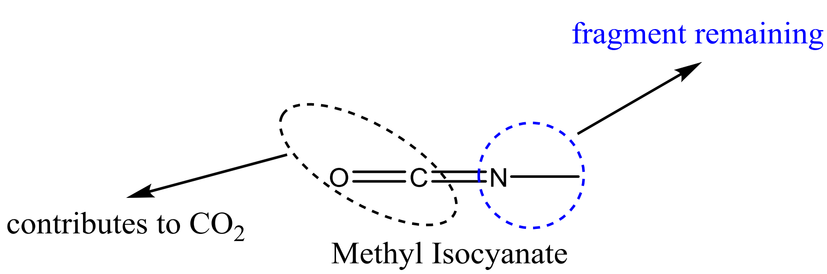
Award full marks for any partial mechanistic details that are correct.

(b) Methyl isocyanate reacts with water to yield:

(i) a colourless gas that turns limewater milky and

(ii) a gas that has a strong odour similar to fish.

Identify products (i) and (ii). ***(3 marks)***



(i) CO_2 (1 mark)

(ii) methylamine / CH_3NH_2 (2 marks)

*(c) From **Figure 1**, calculate the wavelength (λ) at which maximum absorbance of carbaryl occurs. As an example, 1-naphthoxide has a λ_{max} = 333 nm.* ***(3 marks)***

- Identify the point on the x-axis that corresponds to the position of maximum absorbance of carbaryl: 2.1 cm to 2.2 cm

- Identify a suitable distance on the x-axis to determine the scale: 3.8 cm to 3.9 cm = 50 nm (1 mark)

- Therefore: 3.85 cm = 50 nm

  1.00 cm = 13.0 nm

  2.15 cm = 13.0 x 2.15 nm

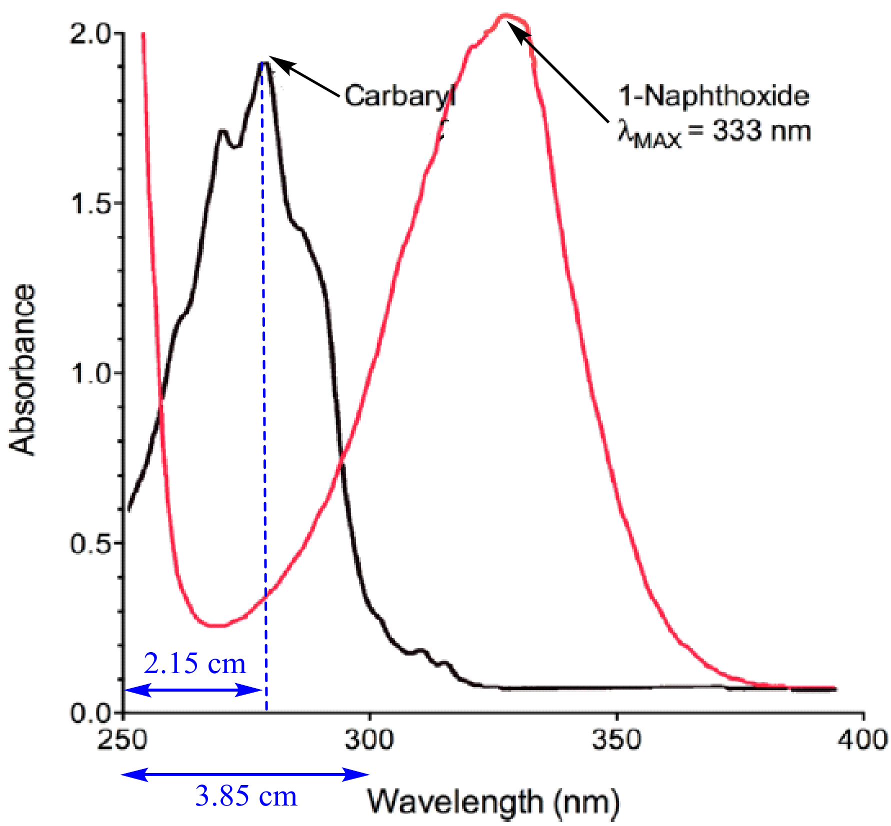
  = 28.0 nm (1 mark)

- Wavelength of maximum absorbance = Origin point + Increment

  = 250 + 28

  = 278 nm (1 mark)

- Acceptable range: 276 - 280 nm



*(d) From **Figure 2**, calculate the $[OH^-]$ at which there is the highest rate of hydrolysis of carbaryl.* ***(6 marks)***

- The highest rate of hydrolysis occurs when there is the greatest change in concentration of carbaryl over the period of monitoring. From Figure 2, this occurs when the pH = 11.0 (1 mark)
- pH + pOH = 14 (1 mark)
- pOH = 14 - 11.0
- pOH = 3.0
- pOH = - $\log[OH^-]$ (1 mark)
- $-\log[OH^-] = 3.0$
- $\log[OH^-] = -3.0$
- $[OH^-] = 10^{-3.0}$ (1 mark)

  $= 0.001$ $moldm^{-3}$ (1 mark for value; 1 mark for appropriate units)

Give marks for alternative calculation routes that are correct e.g. utilizing K_w

(e) The true rate equation can be written as:

$$rate = k_B[OH^-][carbaryl]$$

where k_B = base-mediated hydrolysis rate constant

and $k' = k_B[OH^-]$

(i) What is the overall order of this reaction? ***(1 mark)***

- For the general rate equation: Rate = $k[A]^a[B]^b[C]^c$

  Overall order = a + b + c
- Overall order of this reaction = 1 + 1 = 2 (1 mark)

(ii) In the construction of the graphs in Figure 2, the rate of the reaction was assumed to be dependent upon the [carbaryl], with the [OH^-] being ignored. What does this suggest about the [OH^-] over the course of the reaction? ***(2 marks)***

- This suggests that the [OH^-] is relatively constant over the course of the reaction. For a species that is in fact a reactant, this assumption will be valid when that species is in much higher concentration (stoichiometric excess) than the others. (2 marks)

To obtain the data for this study, buffers at the respective pHs were prepared, and used in a 50-fold excess of the carbaryl.

(*iii) By plotting a suitable graph, determine the value of k_B.* ***(12 marks)***

For this question, award marks for correct calculations and steps, obtaining the exact values shown below is not necessary.

- Consider this equation: $k' = k_B[OH^-]$,

and compare it to the equation of a straight line: $y = mx + c$,

$y = k'$

$m = k_B$

$x = [OH^-]$

$c = 0$ (graph passes through Origin)

- Therefore, a plot of k' vs [OH^-], will yield a graph from which k_B can be determined

- k' can be calculated from each graph in Figure 2 as follows:

For pH 11:

- Using any two suitable points that are on the straight line: (0, 0.6) and (150, 0.4)

- Gradient $= (y_2 - y_1) / (x_2 - x_1)$ (1 mark)

$= (0.4 - 0.6) / (150 - 0)$

$= - 0.0013$ (1 mark)

- Gradient = - k'

- $k' = -$ Gradient
  $= 0.0013\ s^{-1}$ (1 mark for value; 1 mark for correct units)

- Similarly for the two other pHs:

pH = 10.5

Points: (0, 0.6) and (190, 0.49)

Gradient $= (y_2 - y_1) / (x_2 - x_1)$

$= (0.49 - 0.6) / (190 - 0)$

$= - 0.00058$

$k' = 0.0006\ s^{-1}$ (1 mark)

pH = 10.0

Points: (0, 0.71) and (190, 0.67)

Gradient $= (y_2 - y_1) / (x_2 - x_1)$

$= (0.67 - 0.71) / (190 - 0)$

$= - 0002$

$k' = 0.0002\ s^{-1}$ (1 mark)

- Calculating $[OH^-]$ from pH as in (d):

pH = 10.5

pOH = 3.5

$[OH^-] = 10^{-3.5}$

$= 0.0003$ M

pH = 10.0

pOH = 4.0

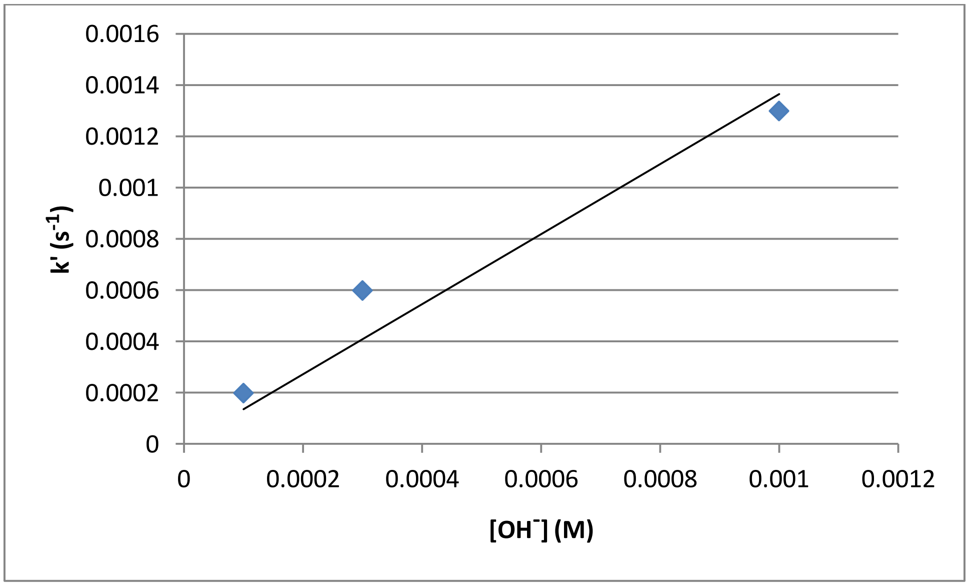
$[OH^-] = 10^{-4.0}$

$= 0.0001$ M

- Plot a graph of k' vs $[OH^-]$:

$[OH^-]$ (M)	k' (s^{-1})
0.0001	0.0002
0.0003	0.0006
0.001	0.0013

Graph of k' vs [OH⁻]



- Allocation of Marks

  Title (1 mark)

  Identification of Scale (1 mark)

  Suitable axes (1 mark)

  Best fine straight line passing through Origin (1 mark)

- Using any two suitable points that are on the straight line e.g.: (0, 0) and (0.001, 0.00136)
- Gradient $= (y_2 - y_1) / (x_2 - x_1)$

  $= (0 - 0.00136) / (0 - 0.001)$

  $= 1.36$
- Gradient $= k_B$
- $k_B = 1.36\ s^{-1}M^{-1}$ (1 mark for value; 1 mark for correct units)

For consideration:

(i) What is the mechanism for the reaction between methyl isocyanate and water?

(ii) Provide an alternative approach to answering question (d).

(iii) How would you prepare 500 mL of a buffer at pH 10? You have the following chemicals available: distilled water, NaOH (s), $NaHCO_3$ (s), 0.1 M HCl (aq).

END OF EXAMINATION PAPER