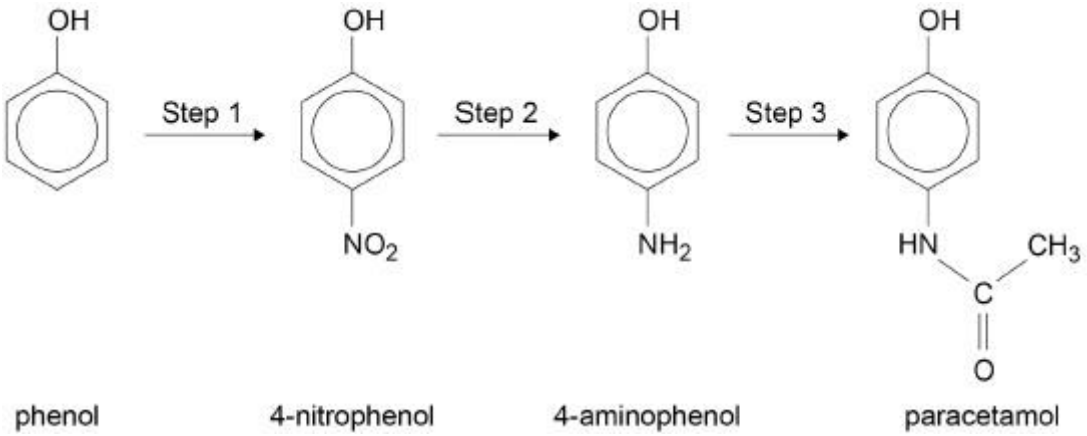
Q1.

Paracetamol is a medicine commonly used to relieve mild pain.

Traditionally, paracetamol has been made industrially in a three-step synthesis from phenol.

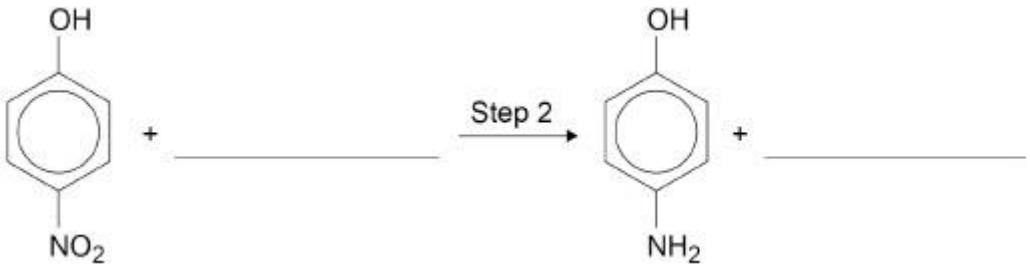


(a) Name the mechanism of the reaction in Step **1**.

_____

(1)

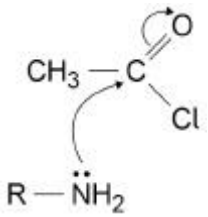
(b) Complete the equation for the reaction in Step **2**.



(1)

(c) In theory, either ethanoyl chloride or ethanoic anhydride could be used in Step **3**.

Complete the mechanism for the reaction of 4-aminophenol with ethanoyl chloride.
RNH_2 is used to represent 4-aminophenol in this mechanism.



(2)

(d) In practice, ethanoic anhydride is used in the industrial synthesis rather than ethanoyl chloride.

Give **one** reason why ethanoyl chloride is **not** used in the industrial synthesis.

_____

_____

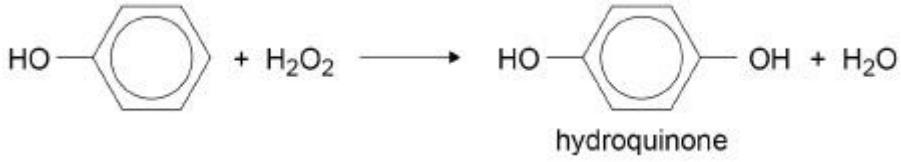
(1)

(e) In Step **3** other aromatic products are formed as well as paracetamol.

Draw the structure of **one** of these other aromatic products.

(1)

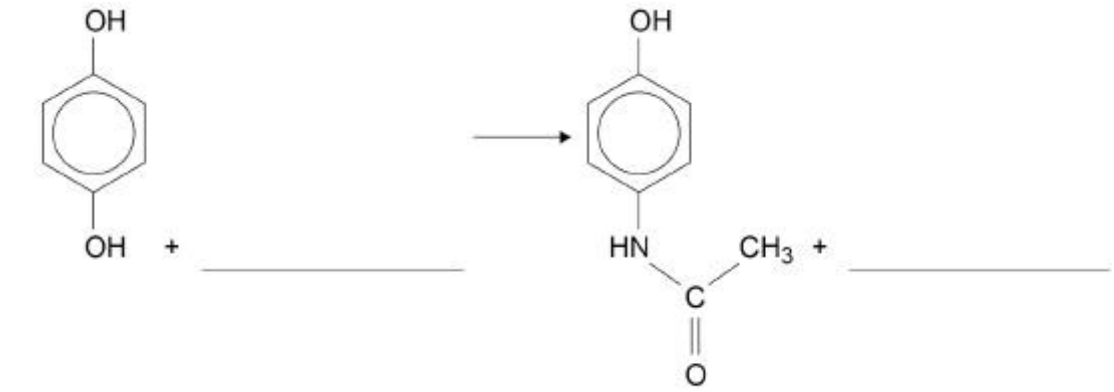
(f) Chemists have recently developed a two-step process to produce paracetamol from phenol.
In the first step, phenol is oxidised to hydroquinone.



hydroquinone

In the second step, hydroquinone reacts with ammonium ethanoate to form paracetamol.

Complete the equation for this second step.



hydroquinone paracetamol

(1)

(g) Calculate the mass, in kg, of hydroquinone (M_r = 110.0) needed to produce 250 kg of paracetamol.

Mass _____ kg

(3)

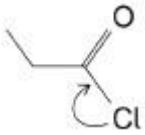
(Total 10 marks)

Q2.

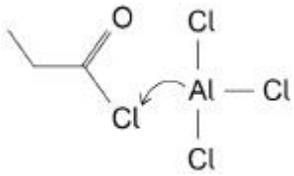
The reaction between propanoyl chloride and benzene is an example of acylation.

Which is a correct representation of part of the mechanism of this reaction?

A



B



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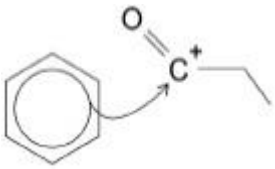

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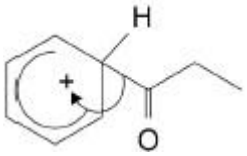
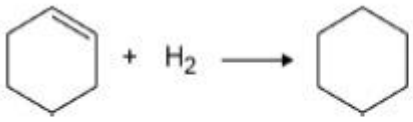


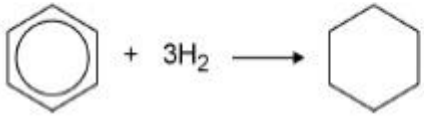
(Total 1 mark)

Q3.

Data about the hydrogenation of cyclohexene and of benzene are given.



$\Delta H^{\ominus} = -120 \text{ kJ mol}^{-1}$



$\Delta H^{\ominus} = -208 \text{ kJ mol}^{-1}$

(a) Explain the bonding in and the shape of a benzene molecule.
Compare the stability of benzene with that of the hypothetical cyclohexa-1,3,5-triene molecule.
Use the data in your answer.

_____

_____

_____

(6)

(b) The enthalpy of hydrogenation of cyclohexa-1,3-diene is **not** exactly double that of cyclohexene.

Suggest a value for the enthalpy of hydrogenation of cyclohexa-1,3-diene and justify your value.

(3)

(Total 9 marks)

Q4.

The nitration of benzene uses a nitrating mixture of concentrated nitric acid and concentrated sulfuric acid.

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Which statement is correct?

A HNO_3 acts as a base. ⬭

B HNO_3 acts as a catalyst. ⬭

C HNO_3 acts as an electrophile. ⬭

D HNO_3 acts as a reducing agent. ⬭

(Total 1 mark)

Q5.

This question is about nitrobenzenes.

(a) Nitrobenzene reacts when heated with a mixture of concentrated nitric acid and concentrated sulfuric acid to form a mixture of three isomeric dinitrobenzenes.

Write an equation for the reaction of concentrated nitric acid with concentrated sulfuric acid to form the species that reacts with nitrobenzene.

_____

(1)

(b) Name and outline a mechanism for the reaction of this species with nitrobenzene to form 1,3-dinitrobenzene.

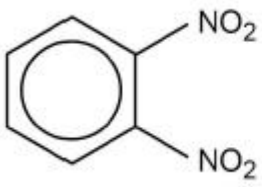
Name of mechanism

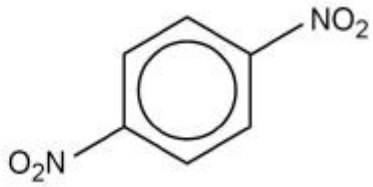
_____

Mechanism

(4)

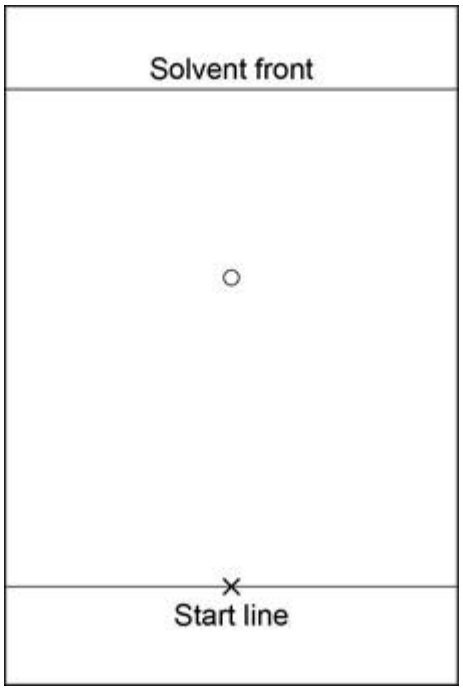
(c) The dinitrobenzenes shown were investigated by thin layer chromatography (TLC).





In an experiment, carried out in a fume cupboard, a concentrated solution of pure 1,4-dinitrobenzene was spotted on a TLC plate coated with a solid that contains polar bonds. Hexane was used as the solvent in a beaker with a lid.

The start line, drawn in pencil, the final position of the spot and the final solvent front are shown on the chromatogram in the diagram below



Use the chromatogram in the diagram above to deduce the R^f value of 1,4-dinitrobenzene in this experiment.

Tick (✓) **one** box.

A 0.41 ⬭

B 0.46 ⬭

C 0.52 ⬭

D 0.62 ⬭

(1)

(d) State in general terms what determines the distance travelled by a spot in TLC.

_____

_____

_____

(1)

(e) To obtain the chromatogram, the TLC plate was held by the edges and placed in the solvent in the beaker in the fume cupboard. The lid was then replaced on the beaker.

Give one other practical requirement when placing the plate in the beaker.

_____

_____

_____

(1)

(f) A second TLC experiment was carried out using 1,2-dinitrobenzene and 1,4-dinitrobenzene. An identical plate to that in part (c) was used under the same conditions with the same solvent. In this experiment, the Rf value of 1,4-dinitrobenzene was found to be greater than that of 1,2-dinitrobenzene.

Deduce the relative polarities of the 1,2-dinitrobenzene and 1,4-dinitrobenzene and explain why 1,4-dinitrobenzene has the greater R_f value.

Relative polarities

_____

Explanation

_____

_____

_____

(2)

(g) A third TLC experiment was carried out using 1,2-dinitrobenzene. An identical plate to that in part (c) was used under the same conditions, but the solvent used contained a mixture of hexane and ethyl ethanoate.

A student stated that the R_f value of 1,2-dinitrobenzene in this third experiment would be greater than that of 1,2-dinitrobenzene in the experiment in part (f)

Is the student correct? Justify your answer.

_____

_____

_____

_____

(2)

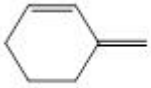
(Total 12 marks)

Q6.

Use your understanding of the bonding in benzene to identify the compound that has the most exothermic enthalpy of hydrogenation.

A  ☐

B  ☐

C  ☐

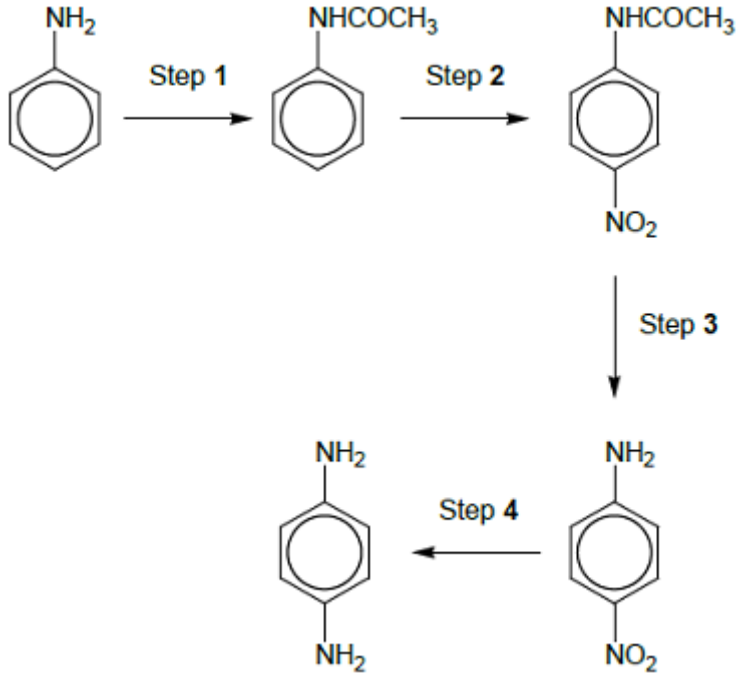
D  ☐

(Total 1 mark)

Q7.

1,4-diaminobenzene is an important intermediate in the production of polymers such as Kevlar and also of polyurethanes, used in making foam seating.

A possible synthesis of 1,4-diaminobenzene from phenylamine is shown in the following figure.



(a) A suitable reagent for step **1** is CH_3COCl

Name and draw a mechanism for the reaction in step **1**.

Name of mechanism

_____

Mechanism

(5)

(b) The product of step **1** was purified by recrystallisation as follows.

The crude product was dissolved in **the minimum quantity of hot water** and the hot solution was filtered through a hot filter funnel into a conical flask. This filtration removed any insoluble impurities. The flask was **left to cool to room temperature**.
The crystals formed were filtered off using a Buchner funnel and a clean cork was used **to compress the crystals in the funnel. A little cold water was then poured through the crystals.**
After a few minutes, the crystals were removed from the funnel and weighed.
A small sample was then used to find the melting point.

Give reasons for each of the following practical steps.

The minimum quantity of hot water was used

_____

_____

_____

The flask was cooled to room temperature before the crystals were filtered off

_____

_____

_____

The crystals were compressed in the funnel

_____

_____

_____

A little cold water was poured through the crystals

_____

_____

_____

(4)

(c) The melting point of the sample in part (b) was found to be slightly lower than a data-book value.

Suggest the most likely impurity to have caused this low value and an improvement to the method so that a more accurate value for the melting point would be obtained.

_____

_____

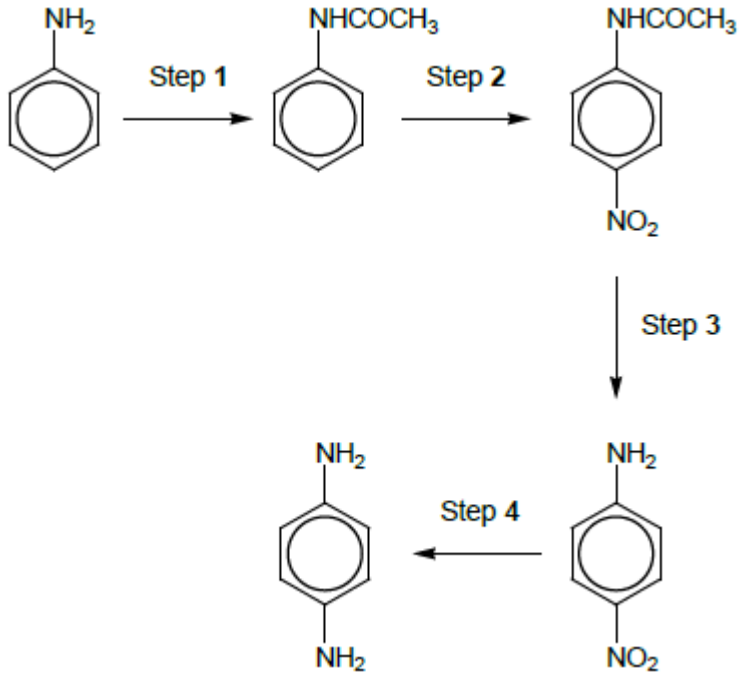
_____

_____

_____

(2)

The figure above is repeated here to help you answer the following questions.



(d) In an experiment starting with 5.05 g of phenylamine, 4.82 g of purified product were obtained in step **1**.

Calculate the percentage yield in this reaction.
Give your answer to the appropriate number of significant figures.

Percentage yield = _____%

(3)

(e) A reagent for step **2** is a mixture of concentrated nitric acid and concentrated sulfuric acid, which react together to form a reactive intermediate.

Write an equation for the reaction of this intermediate in step **2**.

_____

(1)

(f) Name a mechanism for the reaction in step **2**.

_____

(1)

(g) Suggest the type of reaction occurring in step **3**.

_____

(1)

(h) Identify the reagents used in step **4**.

_____

(1)

(Total 18 marks)