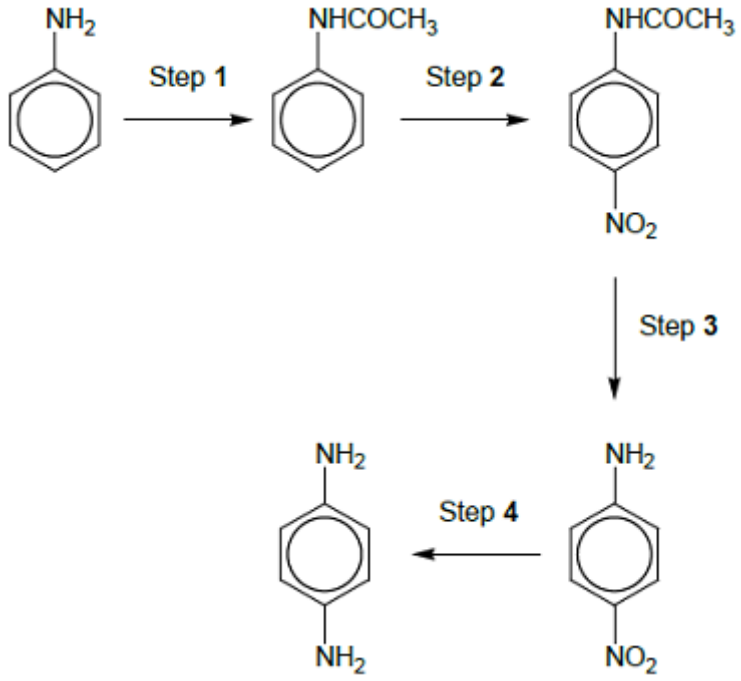
Q1. 1,4-diaminobenzene is an important intermediate in the production of polymers such as Kevlar and also of polyurethanes, used in making foam seating.

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.

_____

_____

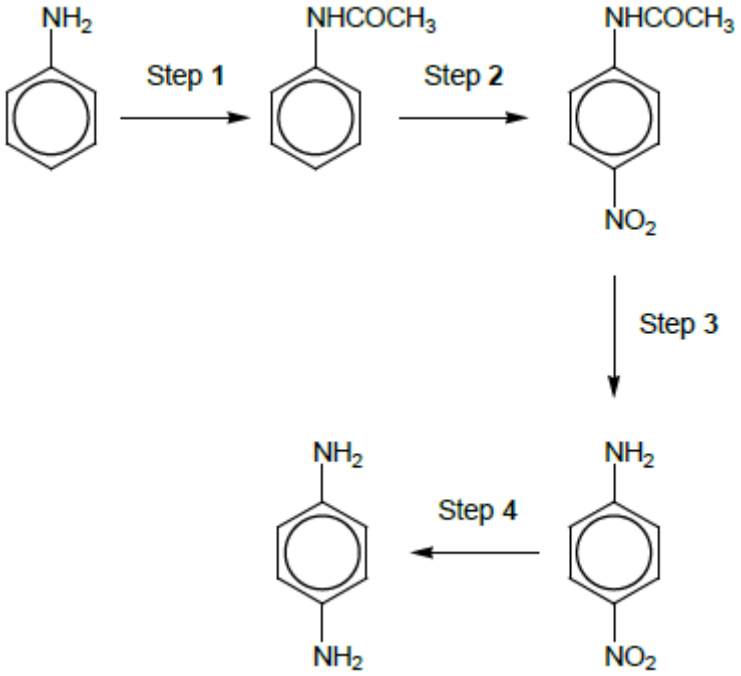
_____

_____

_____

(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)

Q2. 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.

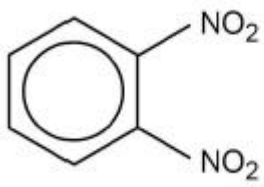
Name of mechanism

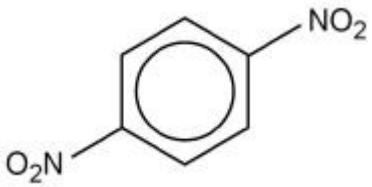
_____

Mechanism

(4)

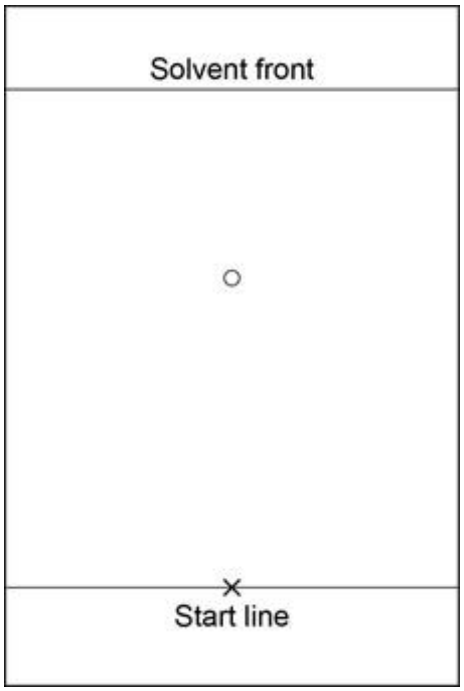
(c) The dinitrobenzenes shown were investigated by thin layer chromatography (TLC).





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.

_____

_____

_____

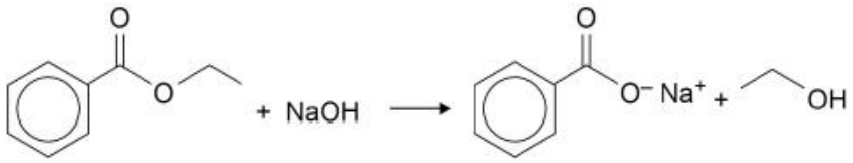
_____

(2)

(Total 12 marks)

Q3. Benzoic acid can be prepared from ethyl benzoate.

Ethyl benzoate is first hydrolysed in alkaline conditions as shown:



A student used the following method.

Add 5.0 cm^3 of ethyl benzoate (density = 1.05 g cm^{-3}, M_r = 150) to 30.0 cm^3 of aqueous 2 mol dm^{-3} sodium hydroxide in a round-bottomed flask.

Add a few anti-bumping granules and attach a condenser to the flask. Heat the mixture under reflux for half an hour. Allow the mixture to cool to room temperature.

Pour 50.0 cm^3 of 2 mol dm^{-3} hydrochloric acid into the cooled mixture.

Filter off the precipitate of benzoic acid under reduced pressure.

(a) Suggest how the anti-bumping granules prevent bumping during reflux.

_____

_____

(1)

(b) Show, by calculation, that an excess of sodium hydroxide is used in this reaction.

(2)

(c) Suggest why an excess of sodium hydroxide is used.

_____

(1)

(d) Suggest why an electric heater is used rather than a Bunsen burner in this hydrolysis.

_____

(1)

(e) State why reflux is used in this hydrolysis.

_____

_____

(1)

(f) Write an equation for the reaction between sodium benzoate and hydrochloric acid.

_____

(1)

(g) Suggest why sodium benzoate is soluble in cold water but benzoic acid is insoluble in cold water.

_____

_____

_____

_____

(2)

(h) After the solid benzoic acid has been filtered off, it can be purified.

Describe the method that the student should use to purify the benzoic acid.

_____

_____

_____

_____

_____

_____

_____

(6)

(i) In a similar experiment, another student used 0.040 mol of ethyl benzoate and obtained 5.12 g of benzoic acid.

Calculate the percentage yield of benzoic acid.

Suggest why the yield is not 100%.

Percentage yield _____ %

Suggestion _____

_____

_____

(3)

(Total 18 marks)

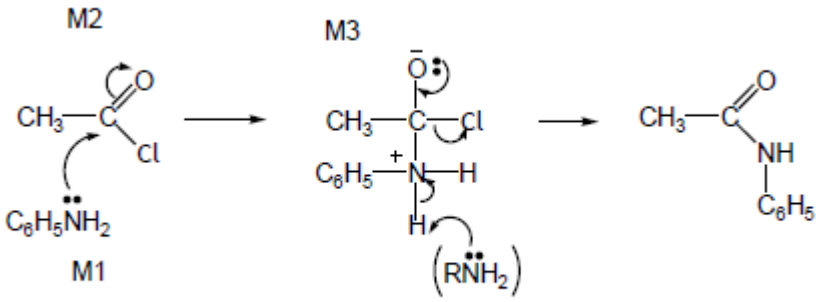
Mark Scheme

Q1.

(a) (nucleophilic) addition-elimination

Not electrophilic addition-elimination

1



Allow C_6H_5 or benzene ring

Allow attack by :$NH_2C_6H_5$

M2 not allowed independent of M1, but allow M1 for correct attack on C+

M3 for correct structure <u>with charges</u> but lone pair on O is part of M4

M4 (for three arrows and lone pair) can be shown in more than one structure

4

(b) **The minimum quantity of hot water was used:**

To ensure the hot solution would be saturated / crystals would form on cooling

1

The flask was left to cool before crystals were filtered off:

Yield lower if warm / solubility higher if warm

1

The crystals were compressed in the funnel:

Air passes through the sample not just round it

Allow better drying but not water squeezed out

1

A little cold water was poured through the crystals:

To wash away soluble impurities

1

(c) Water

Do not allow unreacted reagents

1

Press the sample of crystals between filter papers

Allow give the sample time to dry in air

1

(d) M_r product = 135.0

1

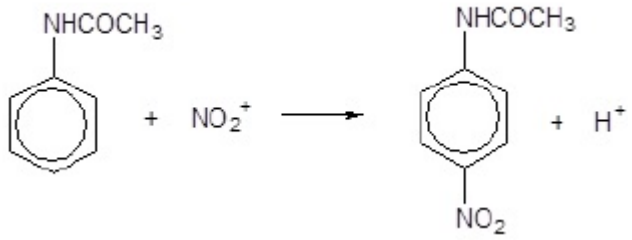
Expected mass = $5.05 \times \frac{135.0}{93.0} = 7.33$ g

1

Percentage yield = $\frac{4.82}{7.33} \times 100 = 65.75 = 65.8(\%)$

Answer must be given to this precision

(e)



OR

$C_6H_5NHCOCH_3 + NO_2^+ \rightarrow C_6H_4(NHCOCH_3)NO_2 + H^+$

1

(f) Electrophilic substitution

1

(g) Hydrolysis

1

(h) Sn / HCl

Ignore acid concentration; allow Fe / HCl

1

[18]

Q2.

(a) $HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

Allow $H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + HSO_4^- + H_2O$

Allow a combination of equations which produce NO_2^+

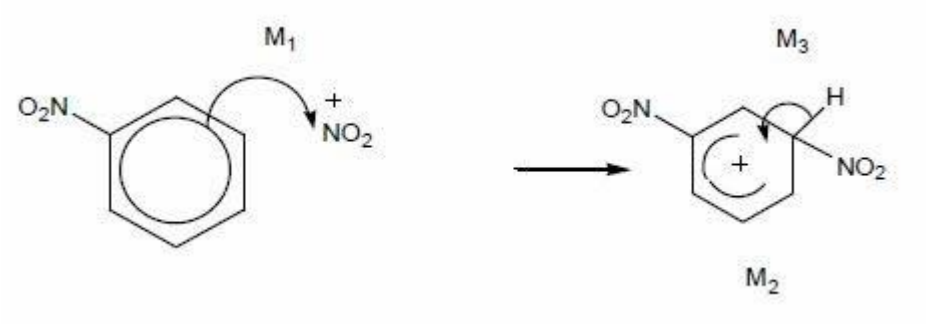
Penalise equations which produce SO_4^{2-}

1

(b) Electrophilic substitution.

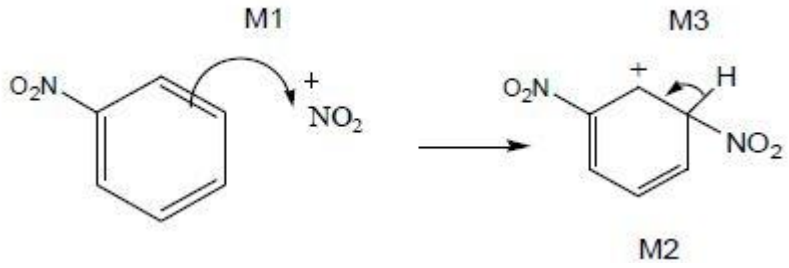
Ignore nitration

1



3

OR Kekule



M1 Arrow from inside hexagon to N or + on N (Allow NO_2^+)

M2 Structure of intermediate

- *horseshoe centred on C1 and must not extend beyond C2 and C6, but can be smaller*
- *+ in intermediate not too close to C1 (allow on or "below" a line from C2 to C6)*

M3 Arrow from bond into hexagon (Unless Kekule)

- *Allow M3 arrow independent of M2 structure*
- *+ on H in intermediate loses M2 not M3*

(c) D

1

(d) (Balance between) solubility in moving phase and retention by stationary phase

OR (relative) affinity for stationary / solid and mobile / liquid / solvent (phase)

(e) Solvent depth must be below start line

Ignore safety

1

(f) 1,2- is more polar **OR** 1,4- is less polar
OR 1,2 is polar, 1,4- is non-polar

1

1,4- (or Less/non polar is) less attracted to (polar) plate / stationary phase / solid **OR** (Less/non polar is) more attracted to / more soluble in (non-polar) solvent / mobile phase / hexane

1

M2 dependent on correct M1

If M1 is blank then read explanation for possible M1 and M2

Allow converse argument for 1,2

(g) No CE = 0

Yes - mark on but there is **NO MARK FOR YES**

Mark independently following yes

Solvent (more) polar or ethyl ethanoate is polar

1

Polar isomer more attracted to / more soluble in / stronger affinity to the solvent (than before)

Penalise bonded to mobile phase in M2

1

[12]

Q3.

(a) allows smaller bubbles to form / prevents the formation of (very) large bubbles

ALLOW provides large surface area for bubbles to form on

IGNORE 'air'

NOT no bubbles form / prevents bubbles forming

1

(b) (Mass of ester = 1.05 × 5.0 = 5.25g)
amount of ester = 5.25 / 150.0 = 0.0350 mol

1

amount of NaOH = 30 × 2 / 1000 = 0.06 mol

1

OR

(Mass of ester = 1.05 × 5.0 = 5.25g)
amount of ester = 5.25 / 150.0 = 0.0350 mol

1

Vol of 0.035 mol of NaOH = (0.035/2) × 1000 = 17.5 cm^3
(so 30 cm^3 used is an excess)

1

OR

amount of NaOH = 30 × 2 / 1000 = 0.06 mol

1

0.06 mol of ester = 9 g = 8.57 cm^3
(only 5 cm^3 used so NaOH in excess)

1

Mark independently

Max 2

(c) To ensure that the ester is completely hydrolysed / to ensure all the ester reacts

ALLOW to ensure the other reagent has completely reacted

1

(d) Many organic compounds / the ester / ethanol are flammable

ALLOW prevent ignition of any flammable vapours formed

1

(e) Reflux allows reactant vapours (of volatile organic compounds) to be returned to the reaction mixture / does not allow any reactant vapour to escape

IGNORE reference to products

1

(f) $C_6H_5COONa + HCl \longrightarrow C_6H_5COOH + NaCl$

Allow ionic equation.

ALLOW molecular formulae ($C_7H_5O_2Na$ and $C_7H_6O_2$)

ALLOW skeletal benzene ring

1

(g) Sodium benzoate soluble because it is ionic

IGNORE polar

1

Benzoic acid insoluble because: despite the polarity of the COOH group / ability of COOH to form H-bonds, the benzene ring is non-polar.

ALLOW 'part of molecule' or 'one end' for COOH

1

(h) Dissolve crude product in <u>hot</u> solvent/water

ALLOW ethanol

If no M1 max = 4

1

of minimum volume

ALLOW reference to saturated soln as alternative to 'min vol'

1

Filter (hot to remove insoluble impurities)

IGNORE use of Buchner funnel here

1

Cool to recrystallise

apply list principle for each additional process in an incorrect method but IGNORE additional m.pt determination

1

Filter under reduced pressure / with Buchner/Hirsch apparatus

1

wash (with cold solvent) **and** dry

1

(i) 5.12 / 122 (= 0.042 mol)

method mark

1

(0.042/0.04) × 100 = 105 %

ecf for M1/0.04

or calculation that 0.04 mol of benzoic = 4.88 g (M1) so

% yield = (5.12/4.88) × 100 = 105%

1

Product not dried / impurities present in product

Only allow M3 if M2>100%

1

[18]