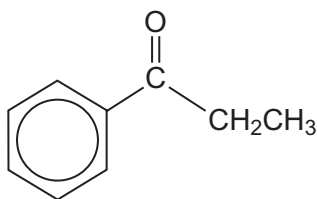


Aromatic Compounds
and Amines

- 8 Consider compound **P** shown below that is formed by the reaction of benzene with an electrophile.

**P**

- 8 (a) Give the **two** substances that react together to form the electrophile and write an equation to show the formation of this electrophile.

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(3 marks)

- 8 (b) Outline a mechanism for the reaction of this electrophile with benzene to form **P**.

(3 marks)



- 8 (c)** Compound **Q** is an isomer of **P** that shows optical isomerism. **Q** forms a silver mirror when added to a suitable reagent.

Identify this reagent and suggest a structure for **Q**.

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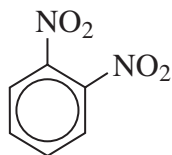
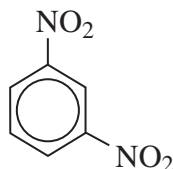
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(2 marks)

8

END OF QUESTIONS



SECTION BAnswer **all** questions in the spaces provided.**8** Three isomers of $C_6H_4(NO_2)_2$ are shown below.**W****X****Y****8** (a) (i) Give the number of peaks in the ^{13}C n.m.r. spectrum of each isomer.

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*(3 marks)***8** (a) (ii) Draw the displayed formula of the compound used as a standard in recording these spectra.*(1 mark)*

- 8** (b) Isomer **X** is prepared from nitrobenzene by reaction with a mixture of concentrated nitric acid and concentrated sulfuric acid.

The two acids react to form an inorganic species that reacts with nitrobenzene to form **X**.

- 8** (b) (i) Give the formula of this inorganic species formed from the two acids and write an equation to show its formation.

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(2 marks)

- 8** (b) (ii) Name and outline a mechanism for the reaction of this inorganic species with nitrobenzene to form **X**.

(4 marks)

Question 8 continues on the next page

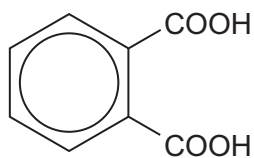
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5 Items softened with plasticisers have become an essential part of our modern society.

Compound **S**, shown below, is commonly known as phthalic acid.

Esters of phthalic acid are called phthalates and are used as plasticisers to soften polymers such as PVC, poly(chloroethene).



S

5 (a) Give the IUPAC name for phthalic acid.

..... (1 mark)

5 (b) Draw the displayed formula of the repeating unit of poly(chloroethene).

(1 mark)

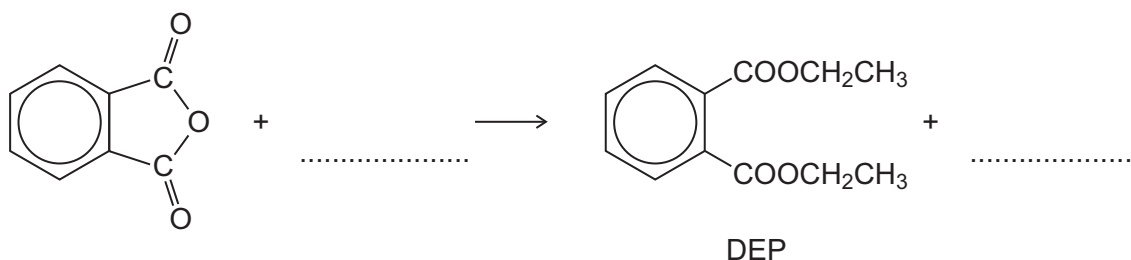
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5 (c) The ester diethyl phthalate (DEP) is used in food packaging and in cosmetics.

5 (c) (i) Complete the following equation showing the formation of DEP from phthalic anhydride.



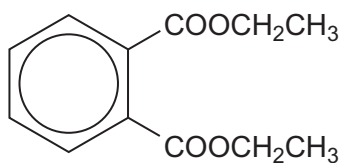
(2 marks)

5 (c) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of DEP.

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(1 mark)

5 (c) (iii) One of the peaks in the ^{13}C n.m.r. spectrum of DEP is at $\delta = 62$ ppm. **Table 3** on the Data Sheet can be used to identify a type of carbon atom responsible for this peak.

Draw a circle around **one** carbon atom of this type in the structure below.



(1 mark)

5 (d) The mass spectrum of DEP includes major peaks at $m/z = 222$ (the molecular ion) and at $m/z = 177$

Write an equation to show the fragmentation of the molecular ion to form the fragment that causes the peak at $m/z = 177$

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(2 marks)



5 (e) Because of their many uses, phthalates have been tested for possible adverse effects to humans and to the environment.

The European Council for Plasticisers and Intermediates is an organisation that represents the manufacturers of plasticisers.

The text below is taken from a document written by the organisation.

‘Research demonstrates that phthalates, at current and foreseeable exposure levels, do not pose a risk to human health or to the environment. Experimental evidence shows that phthalates are readily biodegradable and do not persist for long in the environment.’

5 (e) (i) Hydrolysis of DEP in an excess of water was found to follow first order kinetics. Write a rate equation for this hydrolysis reaction using DEP to represent the ester.

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(1 mark)

5 (e) (ii) Suggest what needs to be done so that the public could feel confident that the research quoted above is reliable.

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(2 marks)

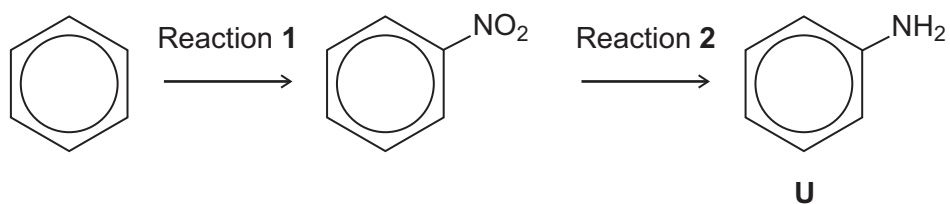
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8 (b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



The mechanism of Reaction 1 involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction 1.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

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(6 marks)

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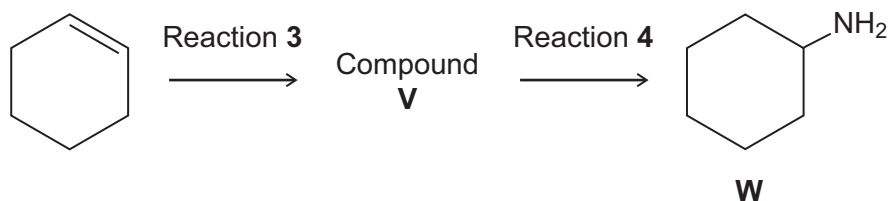
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8 (c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

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(6 marks)

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8 (d) Explain why amine **U** is a weaker base than amine **W**.

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(3 marks)

(Extra space)

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19

END OF QUESTIONS

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Section B

Answer **all** questions in the spaces provided.

6 Many synthetic routes need chemists to increase the number of carbon atoms in a molecule by forming new carbon–carbon bonds. This can be achieved in several ways including

- reaction of an aromatic compound with an acyl chloride
- reaction of an aldehyde with hydrogen cyanide.

6 (a) Consider the reaction of benzene with $\text{CH}_3\text{CH}_2\text{COCl}$

6 (a) (i) Write an equation for this reaction and name the organic product.

Identify the catalyst required in this reaction.

Write equations to show how the catalyst is used to form a reactive intermediate and how the catalyst is reformed at the end of the reaction.

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(5 marks)

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6 (a) (ii) Name and outline a mechanism for the reaction of benzene with this reactive intermediate.

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(4 marks)

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Question 6 continues on the next page

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Section B

Answer **all** questions in the spaces provided.

6 Benzene reacts with ethanoyl chloride in a substitution reaction to form $C_6H_5COCH_3$. This reaction is catalysed by aluminium chloride.

6 (a) Write equations to show the role of aluminium chloride as a catalyst in this reaction. Outline a mechanism for the reaction of benzene.

Name the product, $C_6H_5COCH_3$

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(6 marks)



- 6 (b)** The product of the substitution reaction ($\text{C}_6\text{H}_5\text{COCH}_3$) was analysed by mass spectrometry. The most abundant fragment ion gave a peak in the mass spectrum with $m/z = 105$
Draw the structure of this fragment ion.

(1 mark)

- 6 (c)** When methylbenzene reacts with ethanoyl chloride and aluminium chloride, a similar substitution reaction occurs but the reaction is faster than the reaction of benzene. Suggest why the reaction of methylbenzene is faster.

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(2 marks)

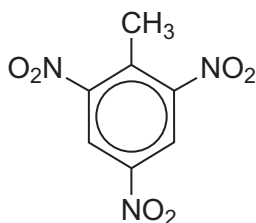
9

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- 9 Many aromatic nitro compounds are used as explosives. One of the most famous is 2-methyl-1,3,5-trinitrobenzene, originally called trinitrotoluene or TNT. This compound, shown below, can be prepared from methylbenzene by a sequence of nitration reactions.



- 9 (a) The mechanism of the nitration of methylbenzene is an electrophilic substitution.

- 9 (a) (i) Give the reagents used to produce the electrophile for this reaction.
Write an equation or equations to show the formation of this electrophile.

Reagents

.....

Equation

.....

(3 marks)

- 9 (a) (ii) Outline a mechanism for the reaction of this electrophile with methylbenzene to produce 4-methylnitrobenzene.

(3 marks)



9 (b) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TNT.

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(1 mark)

9 (c) Deduce the number of peaks in the ^1H n.m.r. spectrum of TNT.

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(1 mark)

9 (d) Using the molecular formula ($\text{C}_7\text{H}_5\text{N}_3\text{O}_6$), write an equation for the decomposition reaction that occurs on the detonation of TNT. In this reaction equal numbers of moles of carbon and carbon monoxide are formed together with water and nitrogen.

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(1 mark)

9

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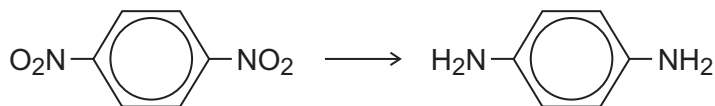


Section B

Answer **all** questions in the spaces provided.

7 Each of the following conversions involves reduction of the starting material.

7 (a) Consider the following conversion.



Identify a reducing agent for this conversion.

Write a balanced equation for the reaction using molecular formulae for the nitrogen-containing compounds and [H] for the reducing agent.

Draw the repeating unit of the polymer formed by the product of this reaction with benzene-1,4-dicarboxylic acid.

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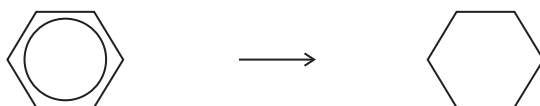
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7 (b) Consider the following conversion.



Identify a reducing agent for this conversion.

State the empirical formula of the product.

State the bond angle between the carbon atoms in the starting material and the bond angle between the carbon atoms in the product.

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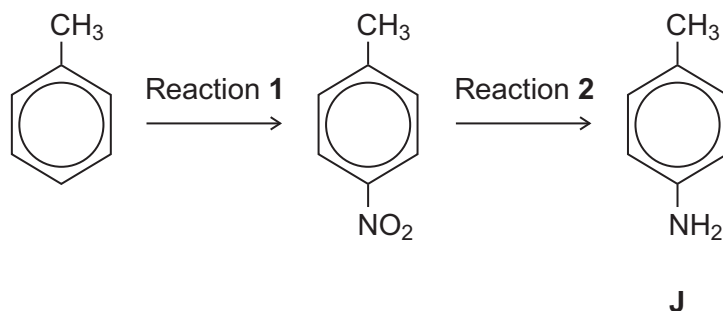
(4 marks)

Question 7 continues on the next page

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5 Consider the following reaction sequence starting from methylbenzene.



5 (a) Name the type of mechanism for reaction 1.

[1 mark]

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5 (b) Compound J is formed by reduction in reaction 2.

5 (b) (i) Give a reducing agent for this reaction.

[1 mark]

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5 (b) (ii) Write an equation for this reaction. Use [H] to represent the reducing agent.

[1 mark]

.....

5 (b) (iii) Give a use for J.

[1 mark]

.....



- 5 (c)** Outline a mechanism for the reaction of bromomethane with an excess of compound **J**. You should represent **J** as RNH_2 in the mechanism.

[4 marks]

- 5 (d)** Compound **K** ($\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$) is a structural isomer of **J**.

Explain why **J** is a weaker base than **K**.

[3 marks]

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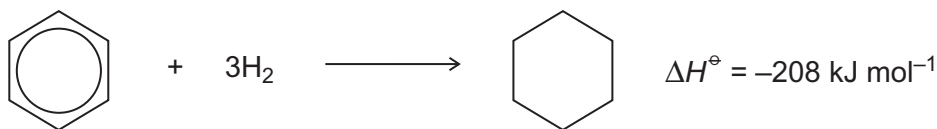
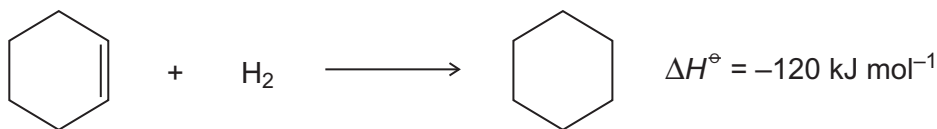
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- 8 Equations for the hydrogenation of cyclohexene and of benzene, together with the enthalpies of hydrogenation, are shown.



- 8 (a) (i) Use these data to show that benzene is 152 kJ mol^{-1} more stable than the hypothetical compound cyclohexa-1,3,5-triene.

[1 mark]

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- 8 (a) (ii) State, in terms of its bonding, why benzene is more stable than cyclohexa-1,3,5-triene.

[1 mark]

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- 8 (b) Three carbon-carbon bonds are labelled on the structures shown. These bonds are of different lengths.



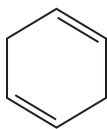
Write the letters **w**, **x** and **y** in order of **increasing** bond length.

[1 mark]

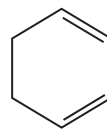
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8 (c) The structures of two cyclic dienes are shown.



cyclohexa-1,4-diene



cyclohexa-1,3-diene

8 (c) (i) Use the enthalpy of hydrogenation data given opposite to calculate a value for the enthalpy of hydrogenation of cyclohexa-1,4-diene.

[1 mark]

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8 (c) (ii) Predict a value for the enthalpy of hydrogenation of cyclohexa-1,3-diene.

[1 mark]

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8 (c) (iii) Explain your answers to Questions **8 (c) (i)** and **8 (c) (ii)** in terms of the bonding in these two dienes.

[3 marks]

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