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Level: CIE AS and A Level (9701)

Subject: Chemistry

Topic: CIE Chemistry

Type: Topic Question

2002

XVIII

1583

Chemistry CIE AS & A Level
To be used for all exam preparation for 2025+

CHEMISTRY

AS and A

This to be used by all students studying CIE AS and A level Chemistry (9701) But students of other boards may find it useful



Question 1.

- (a) Benzene can react with aluminium bromide, AlBr_3 , and bromoethane, $\text{CH}_3\text{CH}_2\text{Br}$, to form ethylbenzene.

Write the equation for the formation of the CH_3CH_2^+ species.

(1 mark)

- (b) Name the mechanism for the formation of ethylbenzene from benzene and aluminium bromide.

(1 mark)

- (c) Using the CH_3CH_2^+ electrophile, draw the mechanism for the conversion of benzene into ethylbenzene. Include all necessary curly arrows and charges.

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(3 marks)

- (d) State the type of reaction that occurs in part (c).

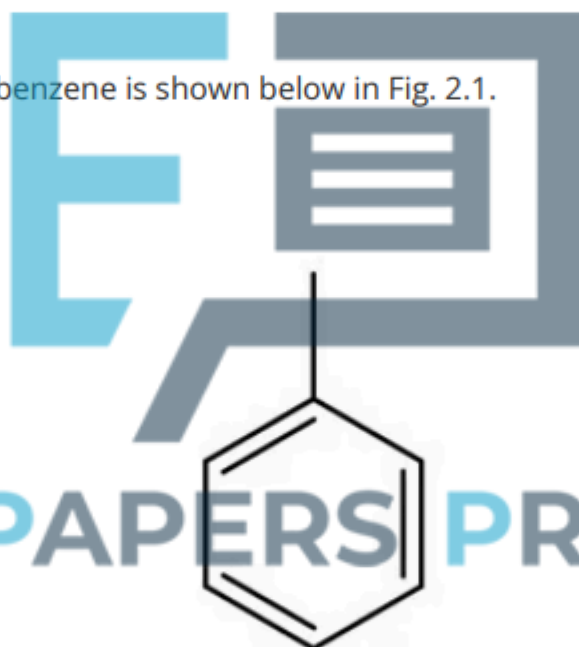
(1 mark)

Question 2.

- (a) Benzene undergoes substitution reactions. State the equation for the reaction of benzene with nitric acid to produce nitrobenzene and water.

(2 marks)

- (b) The structure of methylbenzene is shown below in Fig. 2.1.



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Fig. 2.1

Draw the structures of the two isomers of chloromethylbenzene formed from the reaction of methyl benzene and Cl_2 in the presence of AlCl_3 .

(2 marks)



(c) State the type of reaction that benzene will typically undergo.

(1 mark)

Question 3.

(a) This question is about the bromination of benzene.

State the name of the mechanism that benzene will undergo if reacted with bromine in the presence of a halogen carrier to form bromobenzene, C_6H_5Br .

(1 mark)

(b) Write an equation to show how the halogen carrier generates the Br^+ ion in order to allow the reaction in part (a) to occur.

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(2 marks)

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- (c) Complete the mechanism in Fig. 3.1 for the formation of bromobenzene. Include relevant charges where appropriate.

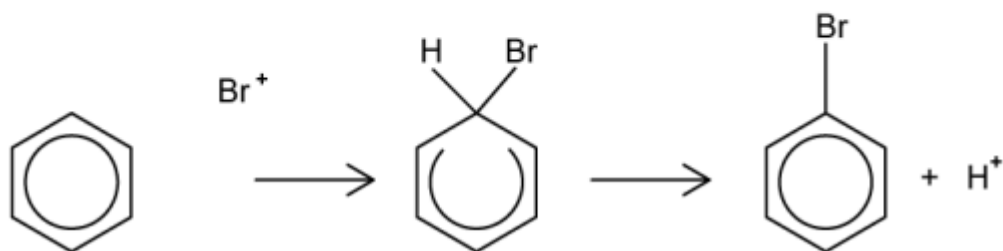


Fig. 3.1

(3 marks)

Question 4.

- (a) This question is about the reactions of methylbenzene.

Draw the structure of compound **A** in Fig. 4.1.

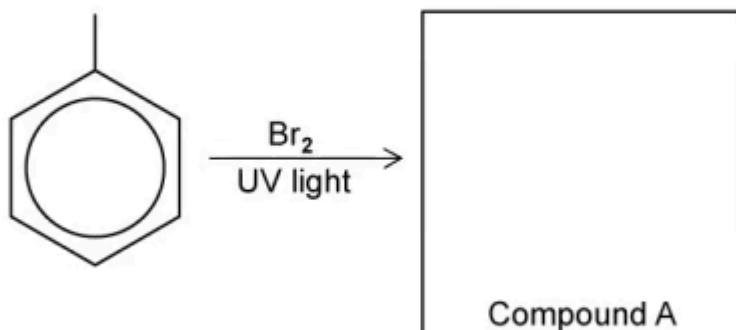
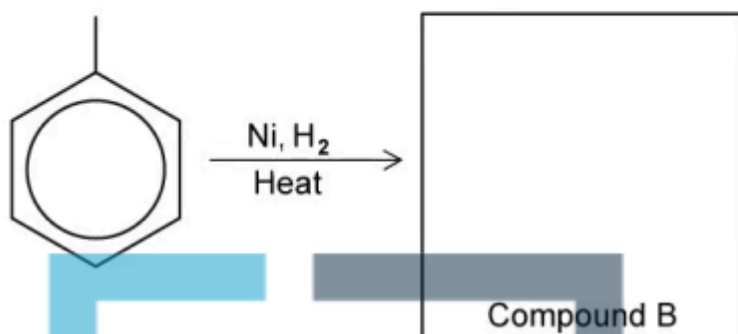


Fig. 4.1

(1 mark)



(b) Draw the structure of compound **B** in Fig. 4.2.



(1 mark)

(c) State the reagents and conditions required for reaction 1 in Fig. 4.3 for the formation of benzoic acid from methylbenzene.

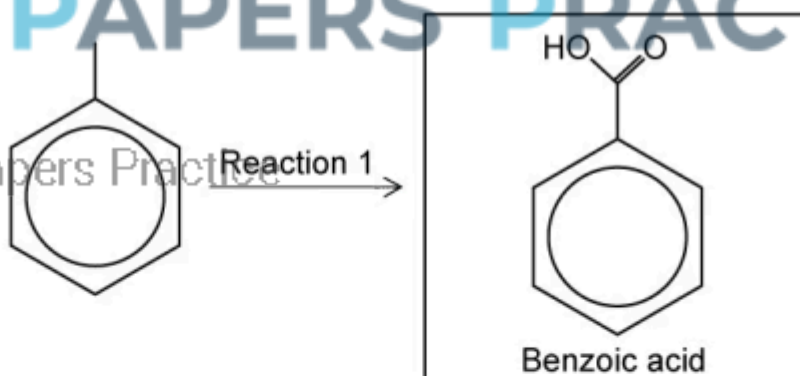
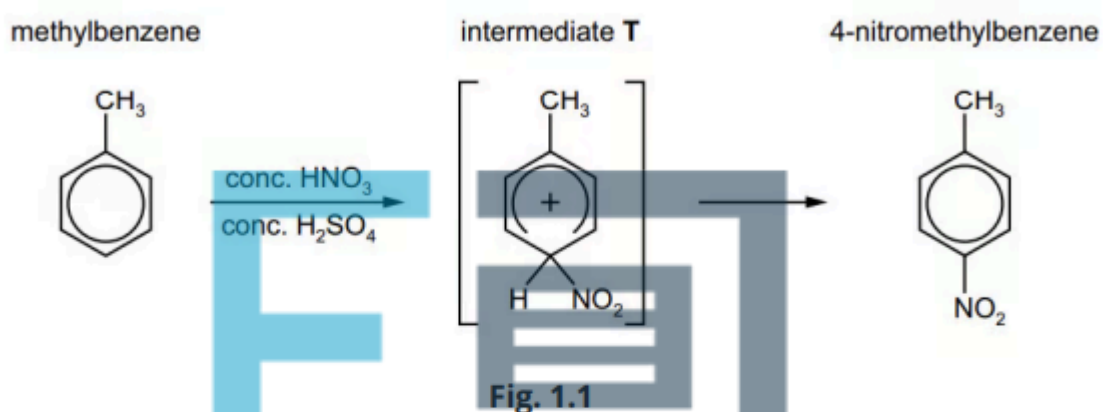


Fig. 4.3

(3 marks)

**Question 5.**

- (a) 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown in Fig. 1.1.



- i) This reaction also forms an isomer of 4-nitromethylbenzene as a by-product. Draw the structure of this by-product.

[1]

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- ii) Write an equation for the reaction between HNO_3 and H_2SO_4 that forms the electrophile for this reaction.

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[1]

- iii) Describe how the structure and bonding of the six-membered ring in intermediate **T** differ from those in methylbenzene. In your answer refer to the hybridisation, the π bonding and the bond angles in the ring system.

[3]

(5 marks)



(b) Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown in Fig. 1.2.

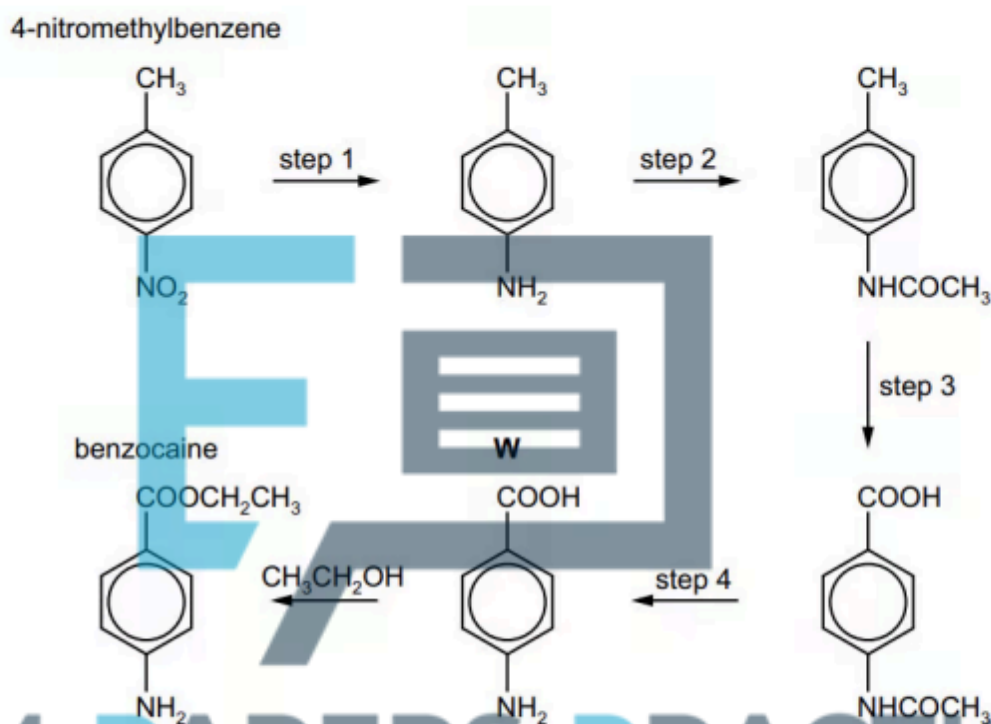


Fig. 1.2

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i) Give the systematic name of compound W.

[1]

ii) Suggest the reagents and conditions for step 1.

step 1

[2]



ii) Suggest the reagent for step 2.

step 2

[1]

iii) Suggest the reagents and conditions for step 3 and step 4.

step 3

step 4

[2]



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(6 marks)

(c) A sample of benzocaine was analysed by carbon-13 NMR and proton NMR spectroscopy.

i) Predict the number of peaks in the carbon-13 NMR spectrum of benzocaine.

[1]

Benzocaine was dissolved in CDCl_3 and the proton NMR spectrum of this solution was recorded as shown in Fig. 1.3.

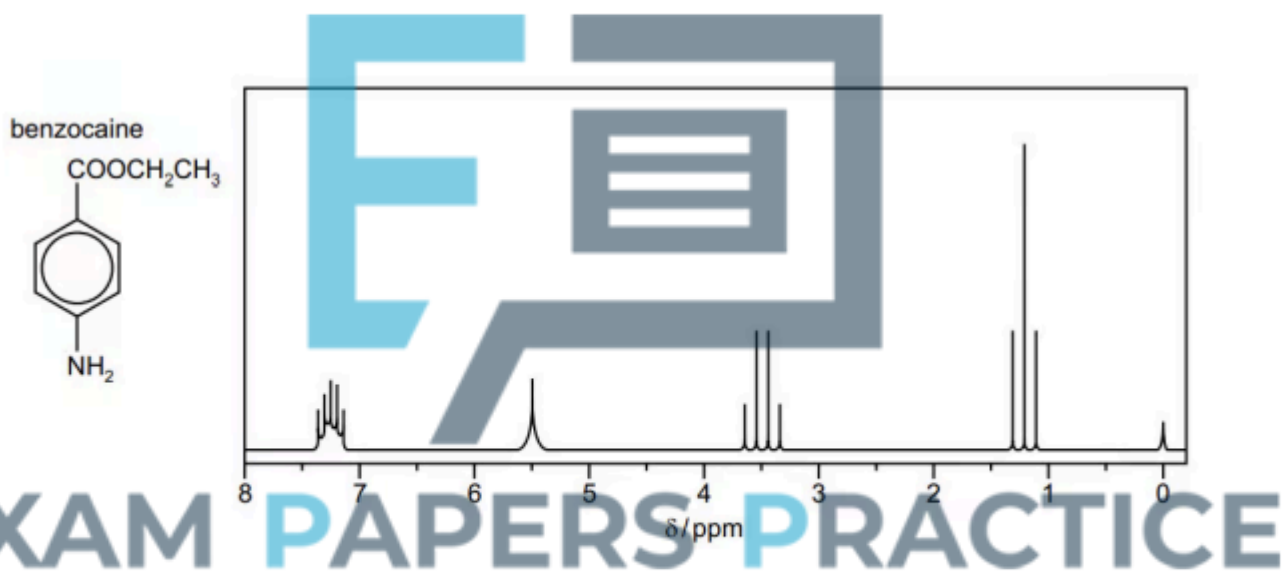


Fig. 1.3

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ii) The data in Table 1.2 should be used in answering this question.

Complete Table 1.1 for the chemical shifts δ 1.2 ppm, 3.5 ppm and 5.5 ppm.

Table 1.1

δ / ppm	environment of proton	number of ^1H atoms responsible for the peak	splitting pattern
1.2			
3.5			
5.5			
7.1-7.4	attached to aromatic ring	4	two doublets

[3]



iii) Explain the splitting pattern for the absorption at δ 1.2 ppm.

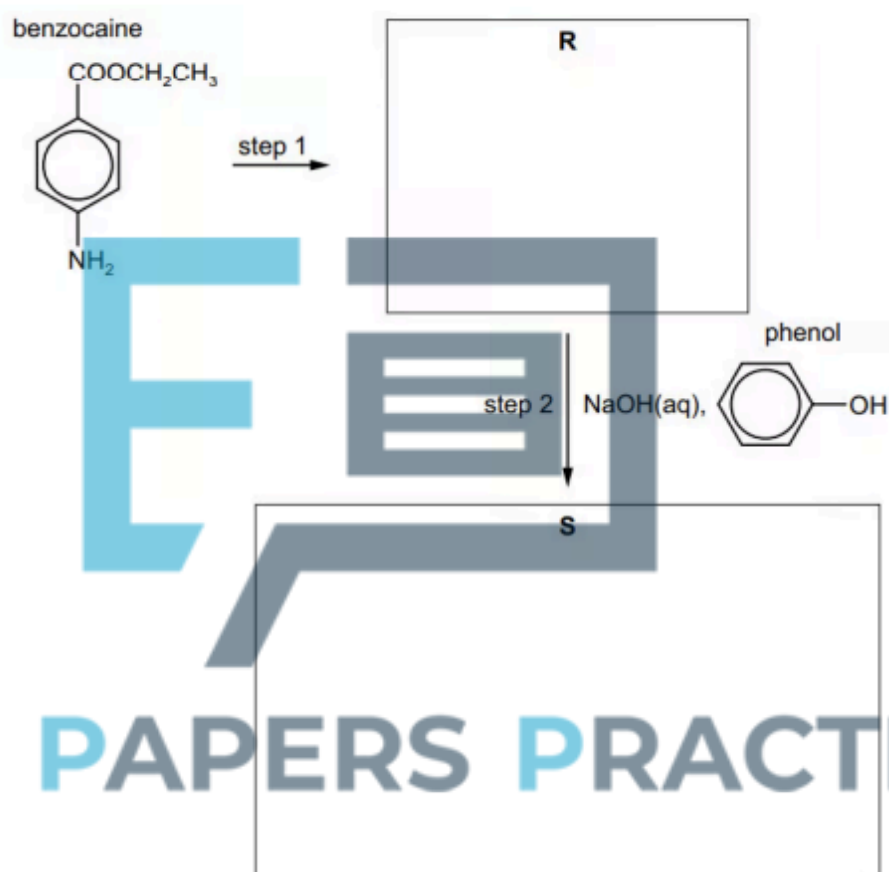
[1]

Table 1.2

Environment of proton	Example	chemical shift range, δ / ppm
alkane	$-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$	0.9–1.7
alkyl next to C=O	$\text{CH}_3-\text{C}=\text{O}$, $-\text{CH}_2-\text{C}=\text{O}$, $>\text{CH}-\text{C}=\text{O}$	2.2–3.0
alkyl next to aromatic ring	CH_3-Ar , $-\text{CH}_2-\text{Ar}$, $>\text{CH}-\text{Ar}$	2.3–3.0
alkyl next to electronegative atom	CH_3-O , $-\text{CH}_2-\text{O}$, $-\text{CH}_2-\text{Cl}$	3.2–4.0
attached to alkene	$=\text{CHR}$	4.5–6.0
attached to aromatic ring	$\text{H}-\text{Ar}$	6.0–9.0
aldehyde	HCOR	9.3–10.5
alcohol	ROH	0.5–6.0
phenol	$\text{Ar}-\text{OH}$	4.5–7.0
carboxylic acid	RCOOH	9.0–13.0
alkyl amine	$\text{R}-\text{NH}-$	1.0–5.0
aryl amine	$\text{Ar}-\text{NH}_2$	3.0–6.0
amide	RCONHR	5.0–12.0

(5 marks)

(d) Benzocaine can also be used to synthesise the azo compound **S** by the following route.



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Fig. 1.4

i) Suggest the reagent(s) used for step 1.

[1]



- ii) Suggest structures for compounds **R** and **S** and draw them in the boxes in Fig. 1.4. [2]

(3 marks)

Question 6.

(a) Benzene can undergo electrophilic substitution with ethanoyl chloride in the presence of aluminium chloride.

- i) Write an equation to show the formation of the electrophile. [1]
- ii) Draw the mechanism for the reaction. [3]

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(4 marks)

(b) The organic product from part (a) can be reduced to form an alcohol.

Name a suitable reducing agent and write a chemical equation to show this reduction, using [H] to represent the reducing agent.

(2 marks)



- (c) Outline the mechanism for the reaction of the ethanoyl chloride with aluminium chloride to form the acylium ion needed for electrophilic substitution.

(2 marks)

- (d) Explain how the catalyst reforms.



(2 marks)

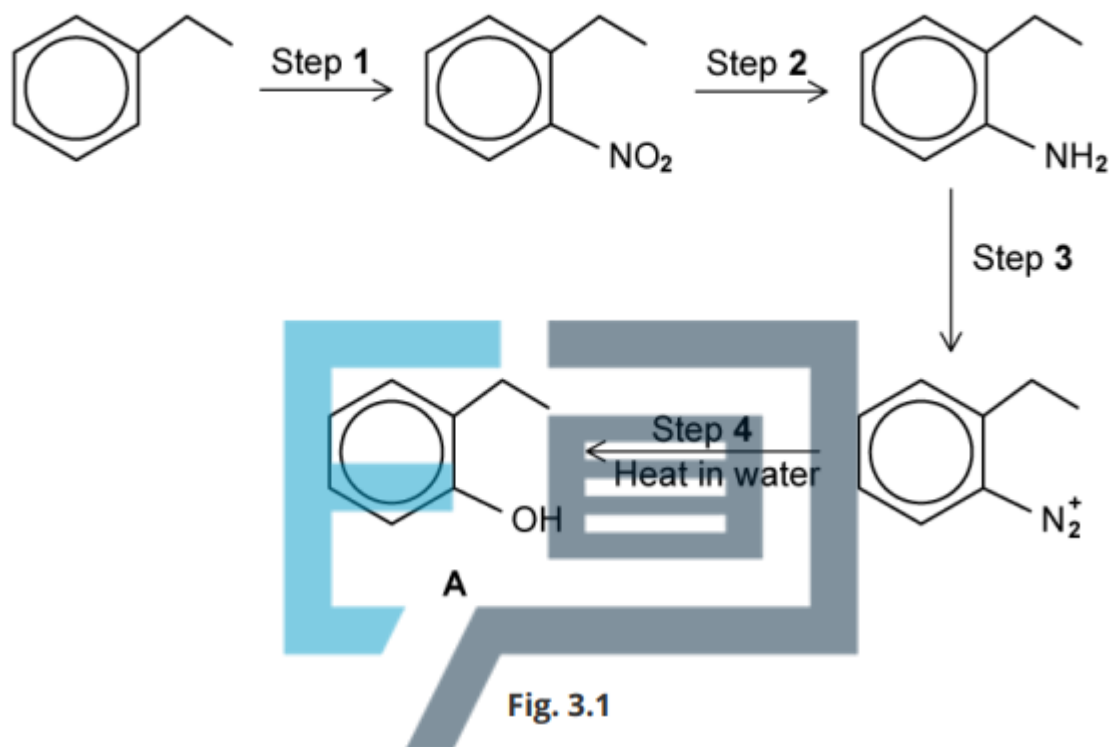
Question 7.

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(a) Compound **A** can be formed from ethylbenzene by the following route in Fig. 3.1.



Suggest reagents and conditions for the following steps.

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Step 1

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Step 2

Step 3

(4 marks)



- (b) Suggest the structures of the organic products of the reactions between each of the compound **A** and the following reagents. If no reaction occurs write 'no reaction'.

Reagent	Product with compound A
Na	
H ⁺ / KMnO ₄	

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(2 marks)

- (c) Explain why ethyl-2-nitrobenzene is formed rather than ethyl-3-nitrobenzene.

(1 mark)

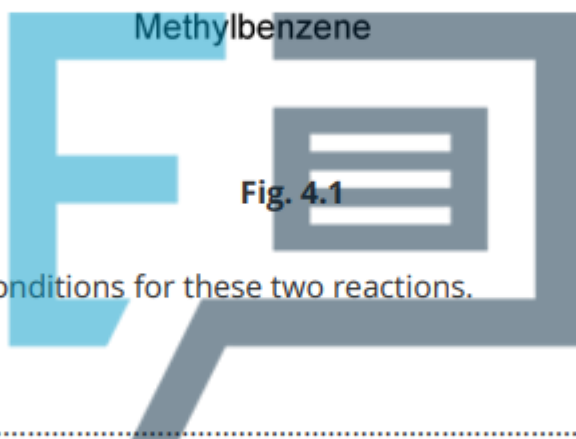
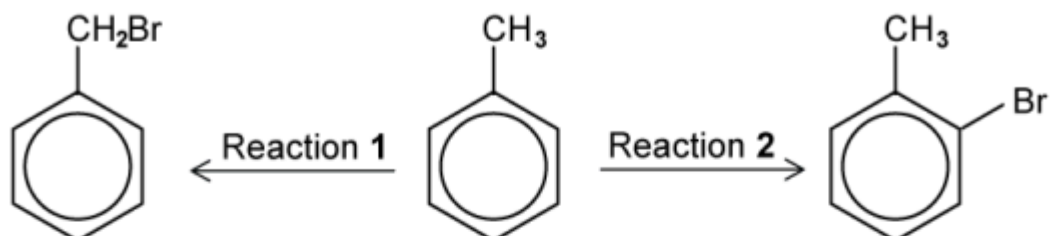
- (d) Using your answer to (a), write the equation for the formation of the electrophile in step 1.

(1 mark)



Question 8.

(a) Methylbenzene can undergo different reactions to form the products shown in Fig. 4.1.



Give the reagents and conditions for these two reactions.

reaction 1

reaction 2



(b) i) Name the mechanism of reaction **1** in part (a)

[1]

ii) Draw the structure of the product obtained if reaction **1** is carried out using an excess of bromine.

[1]

(2 marks)

(c) Draw the reaction mechanism for reaction 2.

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(3 marks)

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(d) Nitrobenzene reacts in the same conditions as reaction **2** in part (a). Draw and name the product of this reaction.

(2 marks)



Question 9.

(a) The nitration of benzene is the first important step in manufacturing dyes and explosives.

i) Write the equation for the generation of the electrophile.

[1]

ii) State which reactant acting as a Brønsted-Lowry base and justify your answer.

[1]

iii) Identify the conjugate acid in the reaction.

[1]

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(3 marks)

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(b) Compound **B** is produced in two steps as outlined in Fig. 1.1.

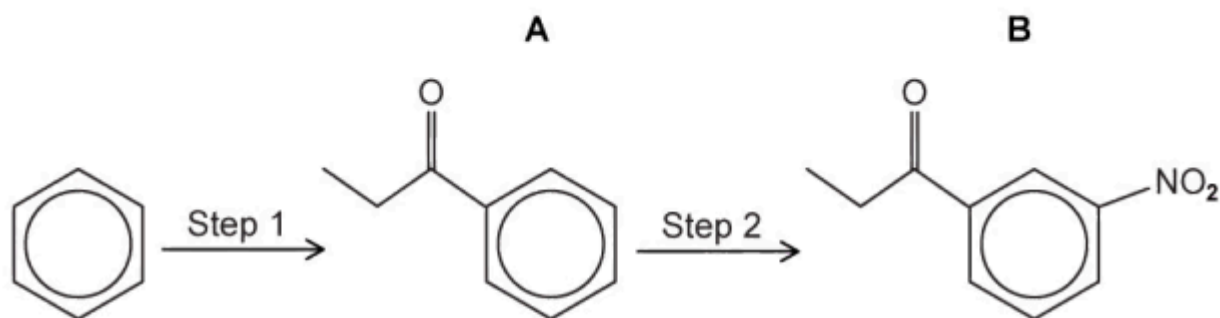


Fig. 1.1

- i) Outline the reagents and conditions required for the production of compound **A** drawn in Fig. 1.1.

[2]

- ii) Using curly arrows, describe the mechanism for step 1.

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[3]

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(5 marks)



- (c) Draw the dot-and-cross diagram for the structure of the catalyst, once the electrophile has been generated in part (b).

(2 marks)

- (d) Explain why benzene can generally only undergo substitution reactions.



(4 marks)

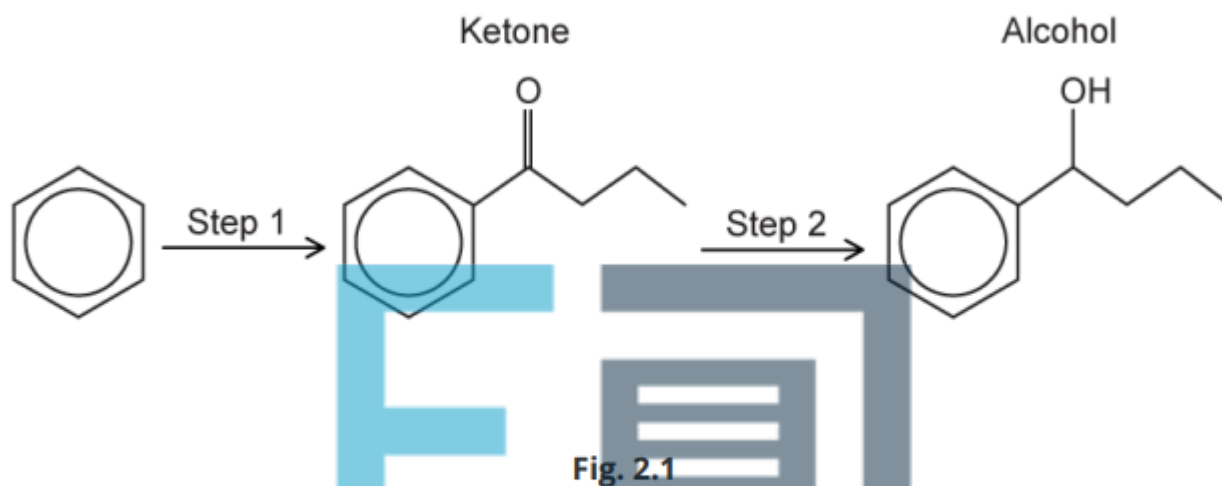
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Question 10.

(a) Fig. 2.1 shows the formation of a ketone followed by an alcohol.



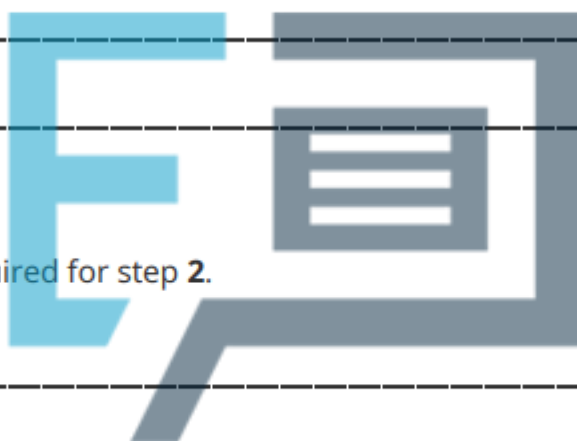
Draw the mechanism to show the formation of the catalyst responsible for step 1.

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- (b) Draw the mechanism for the formation of the ketone, including the regeneration of the catalyst required.



(5 marks)

- (c) State the reagents required for step 2.

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Question 11.

(a) Benzene can be converted into cyclohexane as shown in Fig. 3.1.

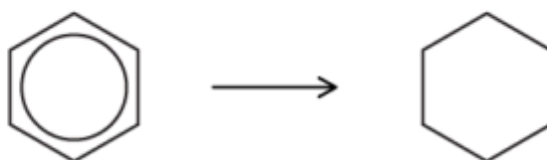


Fig. 3.1

i) For this reaction, name the type of reaction and identify the reagent and conditions needed.

type of reaction

reagent and conditions

[2]

ii) State the bond angles in benzene and cyclohexane.

bond angle in benzene

bond angle in cyclohexane

Explain your answers.

[2]

(4 marks)

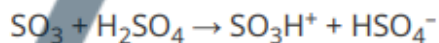


(b) When benzene reacts with SO_3 , as shown in Fig. 3.2, benzenesulfonic acid is produced.



Fig. 3.2

The mechanism of this reaction is similar to that of the nitration of benzene. Concentrated H_2SO_4 is used in an initial step to generate the SO_3H^+ electrophile as shown.



i) Draw a mechanism for the reaction of benzene with SO_3H^+ ions in Fig. 3.3. Include all necessary curly arrows and charges.

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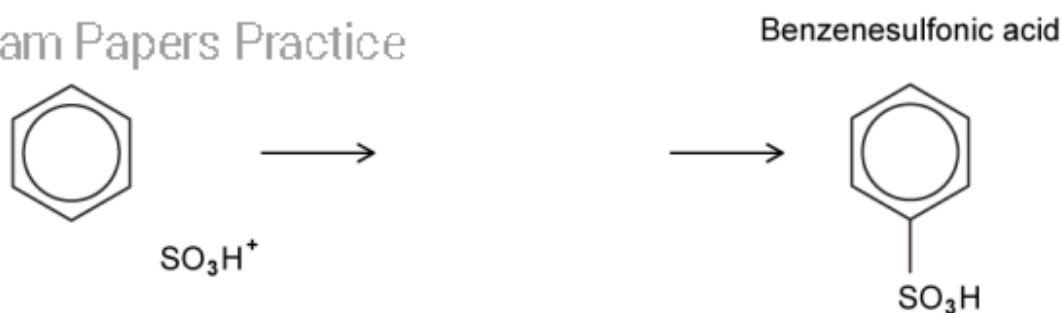


Fig. 3.3

[3]



ii) Write an equation to show how the H_2SO_4 catalyst is reformed.

[1]

(4 marks)

(c) 3-aminobenzoic acid can be synthesised from methylbenzene in three steps as shown in Fig. 3.4.

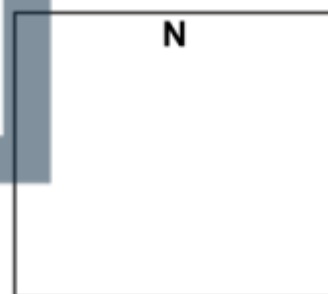
Methylbenzene



Step 1

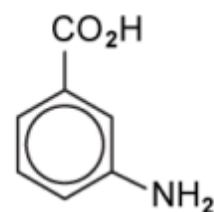


Step 2



Step 3

3-aminobenzoic acid



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Fig. 3.4

i) Draw the structures of **M** and **N** in the boxes.

[2]



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ii) Suggest reagents and conditions for each step of the synthesis.

step 1

step 2

step 3

[3]



(5 marks)

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