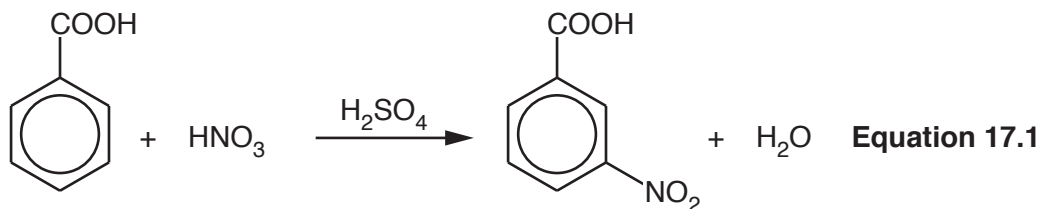


1 This question is about the chemistry of aromatic compounds.

- (a) Benzoic acid can be nitrated by concentrated nitric acid in the presence of concentrated sulfuric acid as a catalyst, as shown in **Equation 17.1**.

The organic product of this reaction is 3-nitrobenzoic acid.



benzoic acid

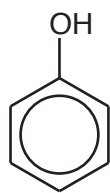
3-nitrobenzoic acid

- (i) Outline the mechanism for this nitration of benzoic acid.

Show how H_2SO_4 behaves as a catalyst.

[5]

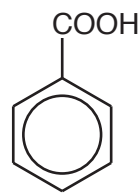
- 2 A student investigates the relative ease of nitration of phenol, benzene, and benzoic acid.



phenol



benzene



benzoic acid

The student finds that the conditions required for the nitration of each compound are different, as shown in **Table 17.1**.

Compound	phenol	benzene	benzoic acid
Conditions required for nitration	Dilute HNO_3 20°C No catalyst	Concentrated HNO_3 55°C H_2SO_4 catalyst	Concentrated HNO_3 100°C H_2SO_4 catalyst

Table 17.1

- (i) State the trend in the relative ease of nitration of phenol, benzene, and benzoic acid.

.....
.....
..... [1]

- (ii) Apply your knowledge of the bonding in arenes to explain the trend in part (b)(i).

.....
.....
.....
.....
.....
.....
..... [3]

- 3 A student synthesises 3-bromophenylamine, shown below, starting from nitrobenzene.

Another student attempts the same synthesis but carries out reduction **before** bromination. The student was surprised to find that two structural isomers of 3-bromophenylamine had been formed instead of the desired organic product.

Explain this result and suggest the structures of the two isomers that formed.

Explanation

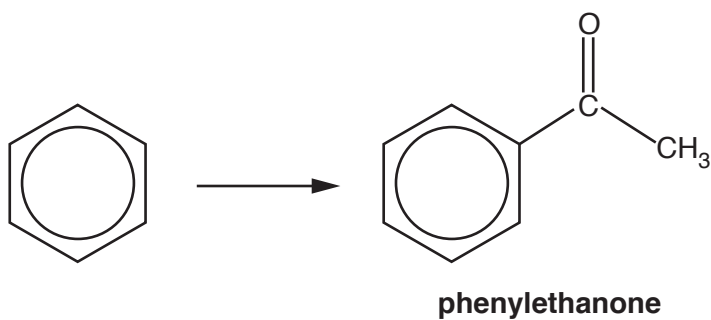
.....

.....

Structures

[3]

- 4 Benzene reacts with an organic reagent in the presence of a halogen carrier to form phenylethanone.



Which organic reagent is required?

- A** $\text{CH}_3\text{CH}_2\text{OH}$
- B** CH_3CHO
- C** CH_3COCl
- D** CH_3COOH

Your answer

[1]

- 5 Which statement(s) support(s) the delocalised model for the structure of benzene?
- 1 All carbon–carbon bonds have the same length.
 - 2 The enthalpy change of hydrogenation of benzene is less exothermic than expected.
 - 3 Bromine reacts with benzene less readily than with cyclohexene.
- A** 1, 2 and 3
- B** Only 1 and 2
- C** Only 2 and 3
- D** Only 1

Your answer

[1]

6 Explain why phenol is nitrated more readily than benzene.

.....

.....

.....

.....

.....

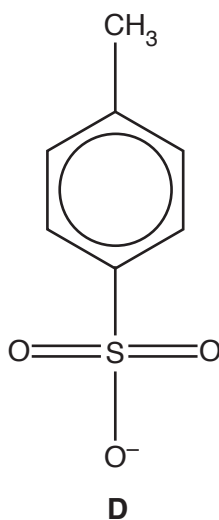
.....

.....

.....

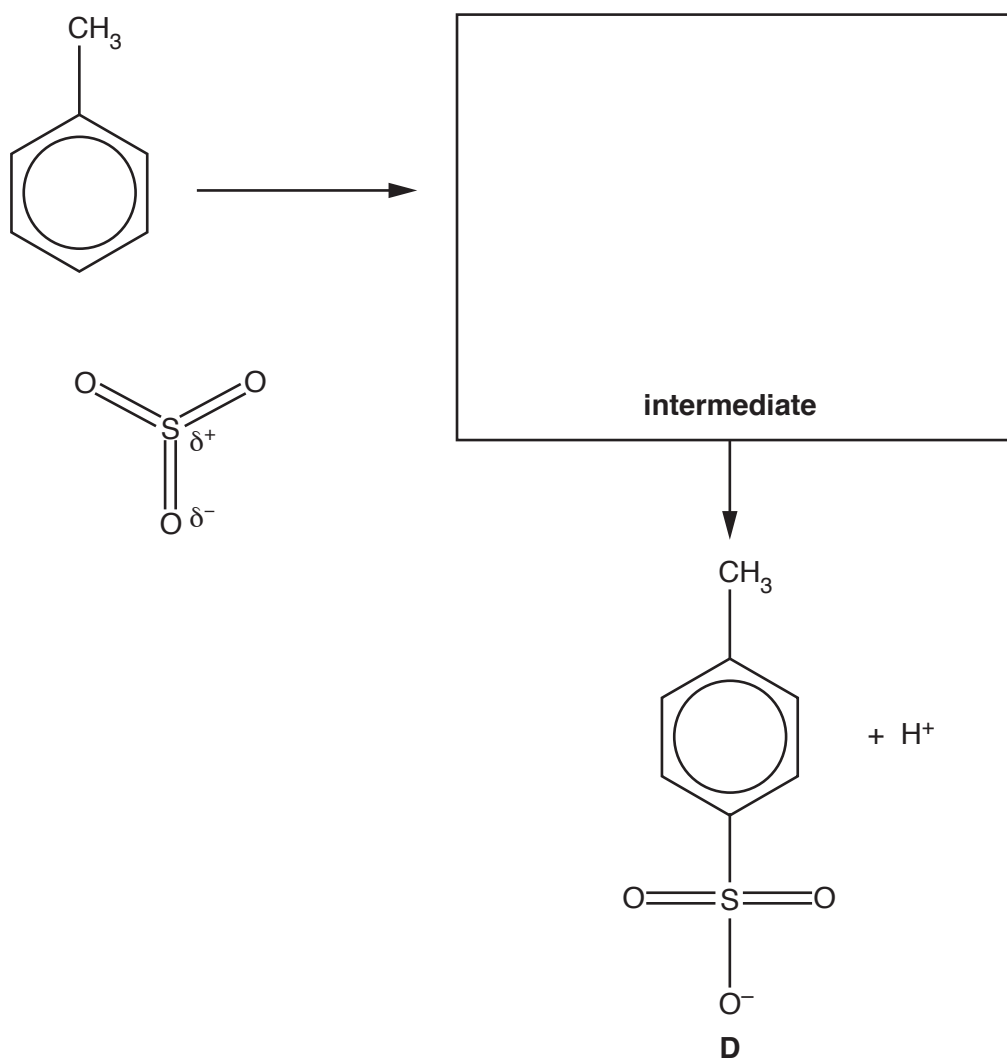
..... [3]

- 7 Methylbenzene reacts with sulfur trioxide, SO_3 , to form **D**, shown below.



The electrophile in this reaction is SO_3 .

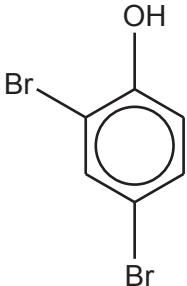
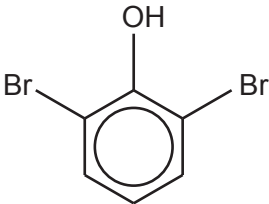
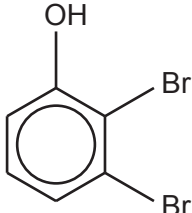
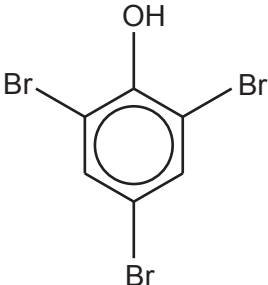
Complete the mechanism for the formation of **D**.
Show curly arrows and the structure of the intermediate.



[3]

8 Phenol reacts with bromine.

Which is the **least** likely organic product?

A	
B	
C	
D	

Your answer

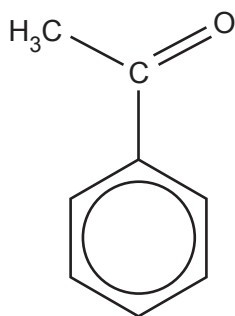
[1]

..... [3]

- Describe **two** pieces of evidence to support the delocalised model of benzene.

..... [2]

- 10 In the synthesis of compounds **D** and **E**, benzene is first reacted with ethanoyl chloride, CH_3COCl , to form phenylethanone, shown below.



phenylethanone

The reaction takes place in the presence of aluminium chloride, AlCl_3 , which acts as a catalyst.

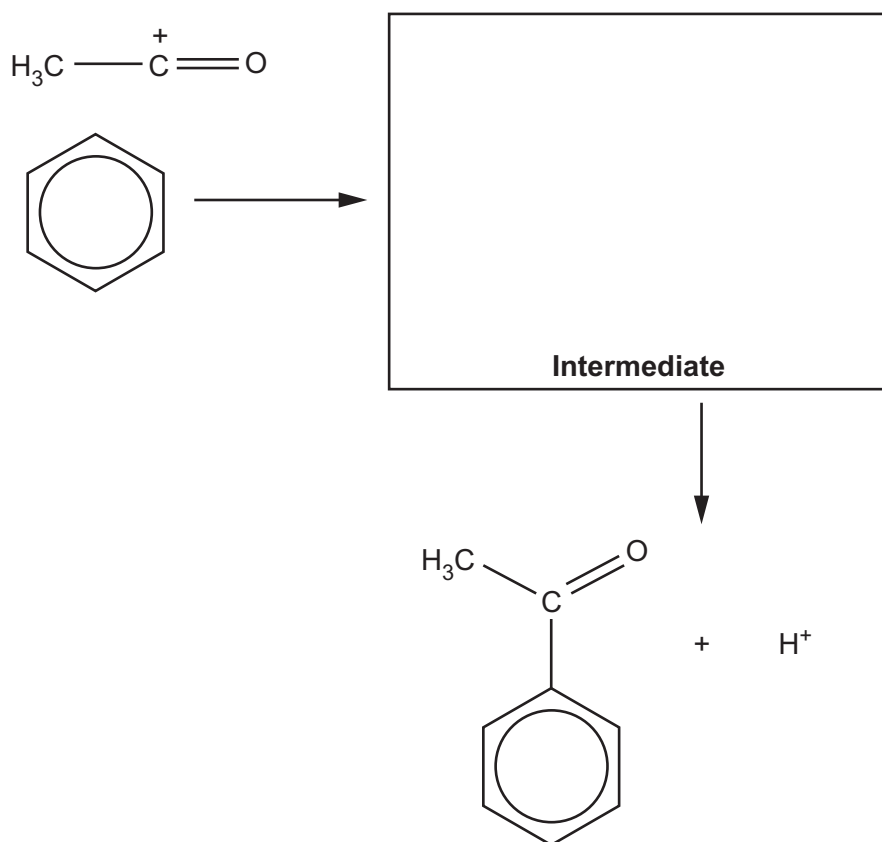
In the mechanism for this reaction,

- ethanoyl chloride first reacts with aluminium chloride to form the $\text{CH}_3\text{-C}^+=\text{O}$ cation
- the $\text{CH}_3\text{-C}^+=\text{O}$ cation then behaves as an electrophile.

Complete the mechanism for the reaction.

Include equations to show the role of the AlCl_3 catalyst, relevant curly arrows and the structure of the intermediate.

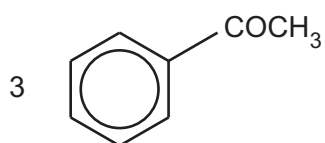
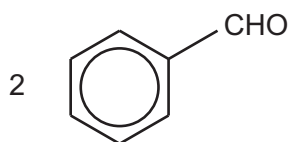
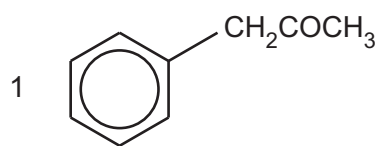
Formation of electrophile



Regeneration of catalyst

[5]

- 11 Which compound(s) could be prepared by reacting benzene with an acyl chloride in the presence of a halogen carrier?



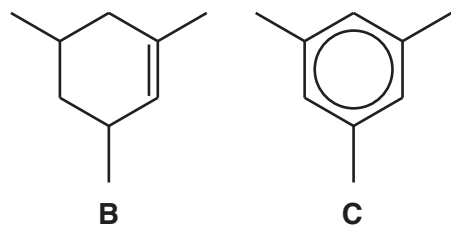
- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

☐

[1]

- 12 Compounds **B** and **C**, shown below, are unsaturated hydrocarbons containing nine carbon atoms.



- (a) Compound **B** reacts with chlorine at room temperature, but compound **C** requires the presence of a halogen carrier.

In both reactions, the organic compound reacts with chlorine in a 1:1 molar ratio.

- (i) Draw the structures of the organic product of each reaction.

Organic product with B	Organic product with C

[2]

- (ii) Explain the relative resistance to chlorination of compound **C** compared with compound **B**.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[3]

(iii) Outline the mechanism for the reaction of compound **C** with chlorine.

Show the role of the halogen carrier.

[5]

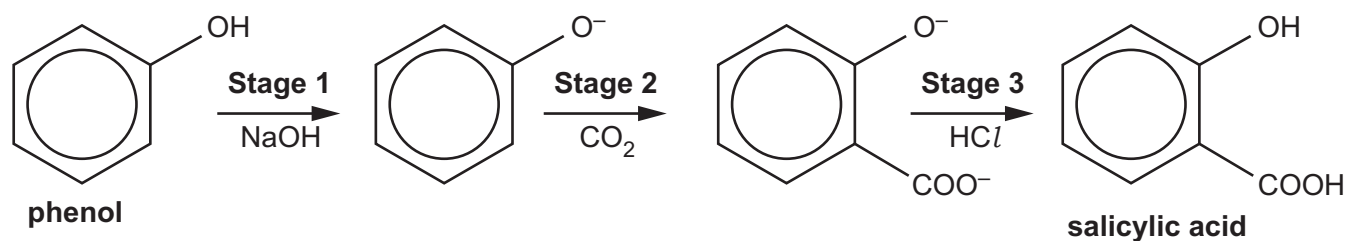
- 13 Which of the following statement(s) provide(s) evidence for the delocalised model of benzene rather than the Kekulé model?
- 1 The enthalpy change of hydrogenation is more exothermic than expected.
 - 2 Benzene only reacts with bromine in the presence of a halogen carrier.
 - 3 The carbon-carbon bonds all have the same length.
- A** 1, 2 and 3
- B** Only 1 and 2
- C** Only 2 and 3
- D** Only 1

Your answer

[1]

14 This question is about reactions of phenol.

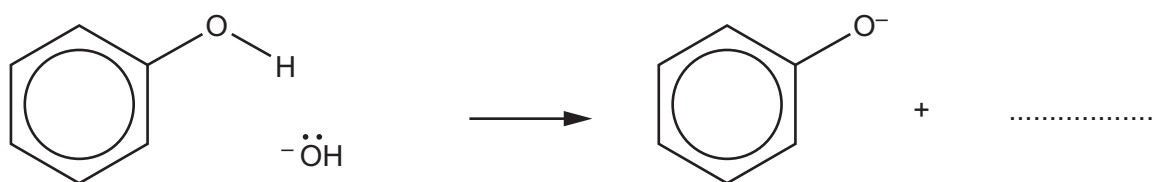
(a) Salicylic acid can be prepared from phenol as shown below.



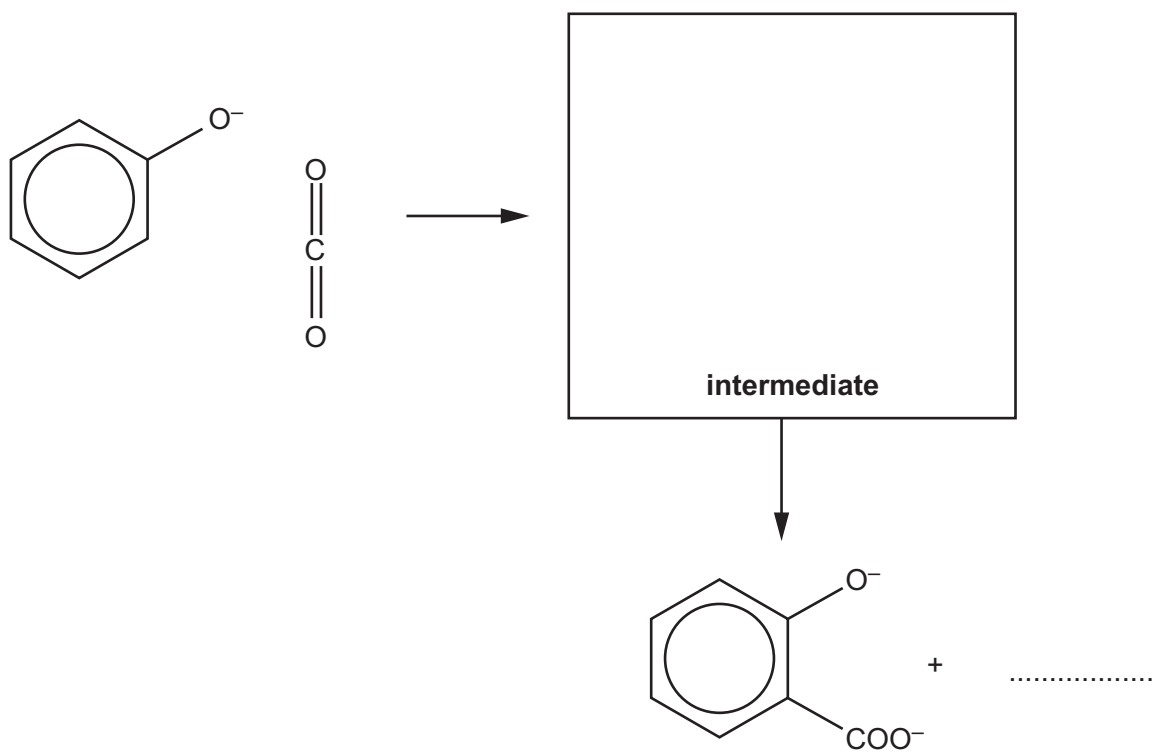
(i) Complete the mechanism below for **Stage 1** and **Stage 2**.

Show curly arrows, the structure of the intermediate and the missing formulae on the dotted lines.

Stage 1



Stage 2



[6]

(ii) What are the roles of ^-OH and CO_2 in the mechanism?

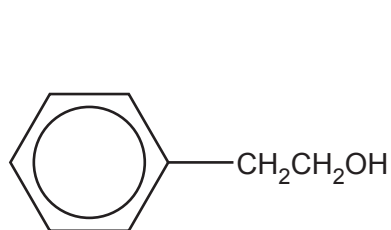
^-OH

CO_2

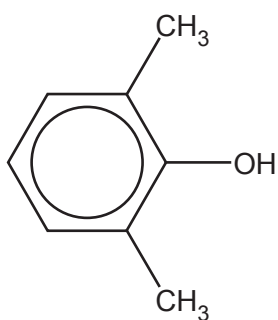
[2]

15 This question is about the chemistry of aromatic compounds.

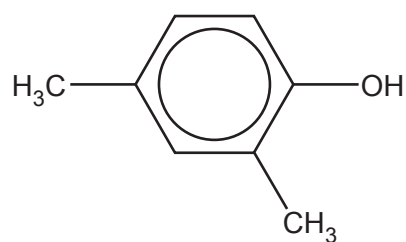
(a) Compounds **J**, **K** and **L**, shown below, are structural isomers.



Compound J



Compound K



Compound L

(i) What chemical test(s) could be used to confirm the presence of the phenol group in compounds **K** and **L**?

.....
.....
..... [1]

- (ii) Compound **J** is substituted at the 2- and 4- positions by chlorine in the presence of a catalyst.

Outline the mechanism for the 4 substitution of compound **J** by chlorine in the presence of a catalyst.

Show the role of the catalyst.

[4]

- (b) Compounds **K** and **L** react with chlorine much more readily than compound **J**.

Explain why.

.....

.....

.....

.....

.....

..... [3]

- 16 Which statement supports the delocalised model of benzene and **not** the Kekulé model?
- A** Sigma bonds overlap to form a π -system.
 - B** The carbon-carbon bond lengths are all the same.
 - C** The enthalpy change of hydrogenation is more exothermic than expected.
 - D** Benzene is more reactive than alkenes with bromine.

Your answer

[1]

- 17 1,3-dinitrobenzene is a solid at room temperature.

A chemist prepares 1,3-dinitrobenzene as outlined below.

Step 1 12.5 cm³ of nitrobenzene (density = 1.20 g cm⁻³) is refluxed with concentrated nitric acid in the presence of concentrated sulfuric acid as a catalyst.

Step 2 The mixture is cooled. Impure crystals of 1,3-dinitrobenzene appear.

Step 3 The impure crystals are purified to obtain pure 1,3-dinitrobenzene.

The chemist obtains 15.0 g of pure 1,3-dinitrobenzene.

(a) Outline the mechanism for this reaction, including the role of H₂SO₄ as a catalyst.

[5]

(b) Determine the percentage yield of 1,3-dinitrobenzene.

Give your answer to **3** significant figures.

percentage yield = ... % **[3]**

(c) Describe how to purify the impure crystals in **Step 3**.

.....

.....

.....

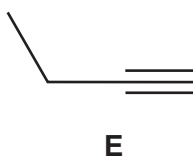
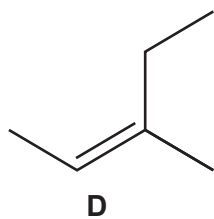
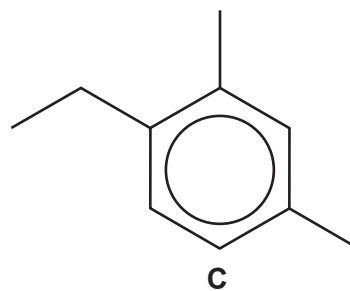
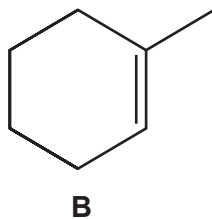
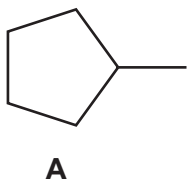
.....

.....

..... **[3]**

18 This question is about hydrocarbons.

The structures of hydrocarbons **A–E** are shown below.

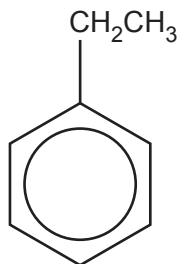


What is the systematic name of hydrocarbon **C**?

..... [1]

19 This question is about aromatic compounds.

- (a) Ethylbenzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$, can be prepared by reacting benzene with chloroethane, $\text{CH}_3\text{CH}_2\text{Cl}$, in the presence of AlCl_3 . The AlCl_3 acts as a halogen carrier.



Ethylbenzene

In the mechanism, chloroethane reacts with the halogen carrier to form a carbocation, which acts as the electrophile.

- (i) What is meant by the term **electrophile**?

.....
..... [1]

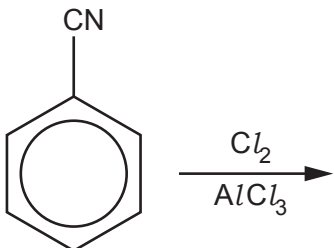
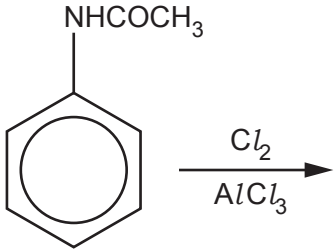
- (ii) Outline the mechanism for this reaction, including the role of AlCl_3 as a halogen carrier.

[5]

- 20 The table shows directing effects for different groups in the electrophilic substitution of aromatic compounds.

Directing effect	2- and 4- directing	3-directing
Group	-OH	-NO ₂
	-NH ₂	-COCH ₃
	-NHCOCH ₃	-CN

- (i) Draw all organic products formed from monosubstitution reactions of the substituted benzene compounds shown below.

Reaction	Monosubstituted Product(s)
 Reaction of benzonitrile (a benzene ring with a -CN group) with Cl_2 and AlCl_3 catalyst.	
 Reaction of N-ethanbenzamide (a benzene ring with an -NHCOCH₃ group) with Cl_2 and AlCl_3 catalyst.	

[3]

(ii) The reactions of $\text{C}_6\text{H}_5\text{NH}_2$ are similar to the reactions of phenol.

Write an equation for the tri-substitution of $\text{C}_6\text{H}_5\text{NH}_2$ with chlorine.

[2]

(iii) Explain why chlorine reacts much more readily with $\text{C}_6\text{H}_5\text{NH}_2$ than with benzene.

.....

.....

.....

.....

.....

.....

.....

.....

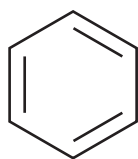
.....

.....

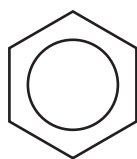
..... [3]

21 This question is about aromatic compounds.

(a) The diagrams show the Kekulé and delocalised models of benzene.



Kekulé



Delocalised

One piece of evidence for the delocalised model is that benzene does **not** decolourise aqueous bromine.

Suggest **two other** pieces of evidence which support the delocalised model of benzene.

.....

.....

.....

.....

.....

..... [2]

- (b) A student investigates the reactions of benzene and phenol with excess bromine.

The student's observations are given in **Table 20.1**.

Table 20.1

Compound	Benzene	Phenol
Observation with excess bromine	no change	decolourises and forms a white precipitate

- (i) Explain the difference in the relative reactivities of benzene and phenol with bromine.

.....

.....

.....

.....

.....

.....

.....

.....

.....

..... [3]

- (ii) The white precipitate has a relative molecular mass of 330.7.

Construct an equation for the reaction of phenol with excess bromine shown in **Table 20.1**.

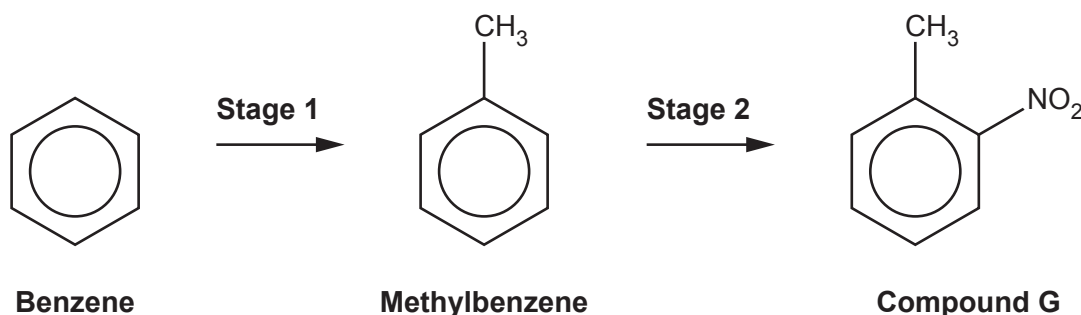
Show the structure of the organic species.

[2]

- (c) Compound **G** is an organic compound used in the production of pesticides.

Compound **G** can be synthesised from benzene in the two-stage process shown.

Synthesis 1



- (i) Suggest a reagent and halogen carrier that could be used in **Stage 1** of **Synthesis 1**.

..... [1]

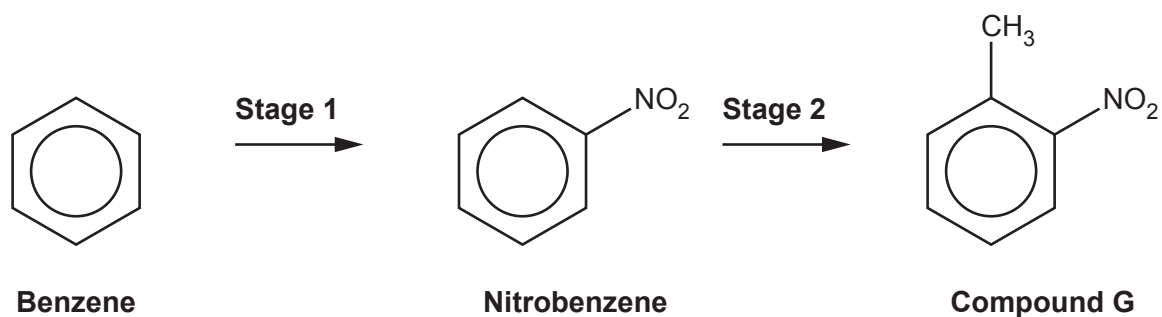
- (ii) **Stage 2** of **Synthesis 1** is the conversion of methylbenzene to compound **G**.

Outline the mechanism for the reaction in **Stage 2**.

Show the role of H_2SO_4 as a catalyst.

(iii) A student suggested an alternative two-stage synthesis of compound **G** from benzene.

Synthesis 2



When **Synthesis 2** is attempted, the synthesis is **not** successful and a different organic compound from compound **G** is produced.

- Suggest why **Synthesis 1** is successful but **Synthesis 2** is **not** successful.
- Suggest the structure of the different organic compound that is formed in **Synthesis 2**.

.....
.....

[2]