30. Hydrocarbons

30.1 Arenes

Paper 4

Question Paper

1 **(f)** The reaction of phenylethanone with 1,4-dibromobutane, $BrCH_2CH_2CH_2CH_2Br$, in the presence of $FeBr_3$ is shown in Fig. 6.2.

phenylethanone

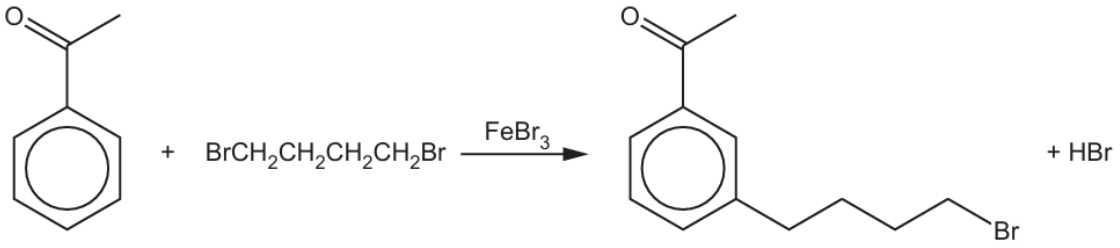


Fig. 6.2

The mechanism of this reaction is similar to that of the alkylation of benzene.

(i) Construct an equation for the formation of the electrophile, $BrCH_2CH_2CH_2CH_2^+$.

..... [1]

(ii) Complete the mechanism in Fig. 6.3 for the reaction of phenylethanone with $BrCH_2CH_2CH_2CH_2^+$ ions.

Include all relevant curly arrows and charges.
Draw the structure of the organic intermediate.

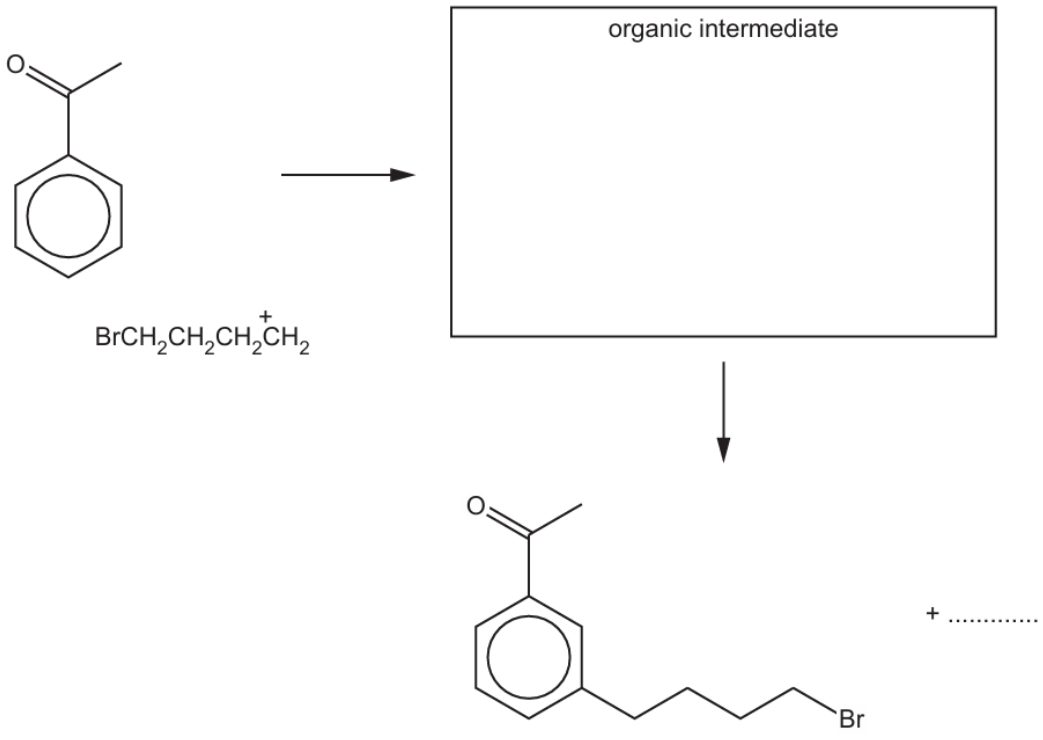


Fig. 6.3

[3]

(iii) The reaction shown in Fig. 6.2 forms small amounts of two by-products, **Y** ($C_{20}H_{22}O_2$) and **Z** ($C_{12}H_{14}O$).

Suggest structures for **Y** and **Z** in the boxes in Fig. 6.4.

Y ($C_{20}H_{22}O_2$)	**Z** ($C_{12}H_{14}O$)

Fig. 6.4

[2]

2 **(b)** Salicylic acid can be synthesised from phenol.

salicylic acid

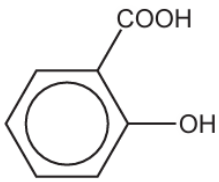


Fig. 9.2

One of the steps in this synthesis is the electrophilic substitution reaction of carbon dioxide with the phenoxide ion, $C_6H_5O^-$.

Complete the mechanism in Fig. 9.3 for the reaction of $C_6H_5O^-$ with CO_2.

Include all relevant curly arrows, dipoles and charges. Draw the structure of the organic intermediate.

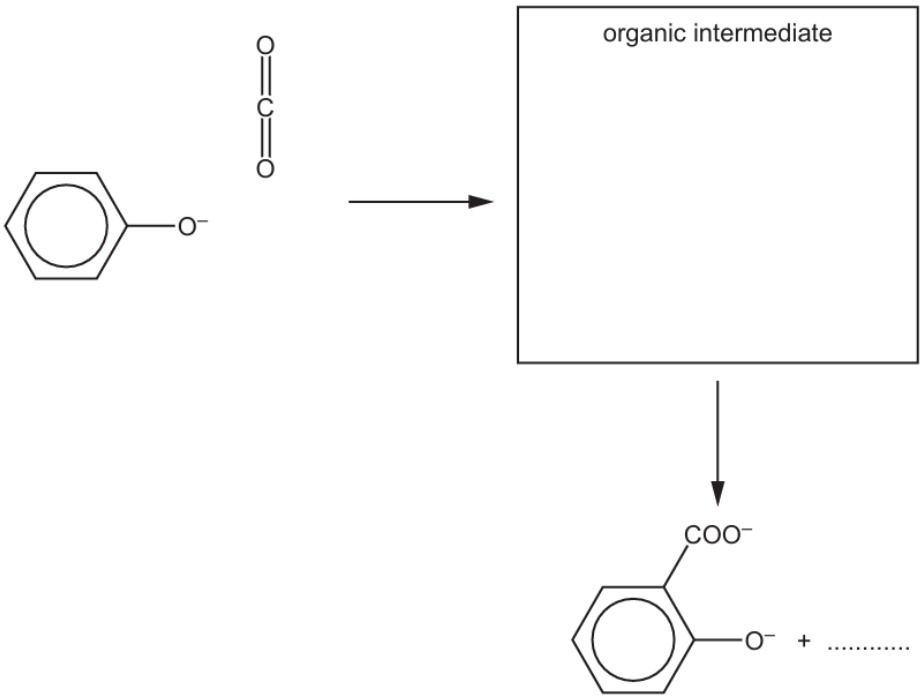


Fig. 9.3

[3]

3 Methyl red can be synthesised as shown in Fig. 7.1.

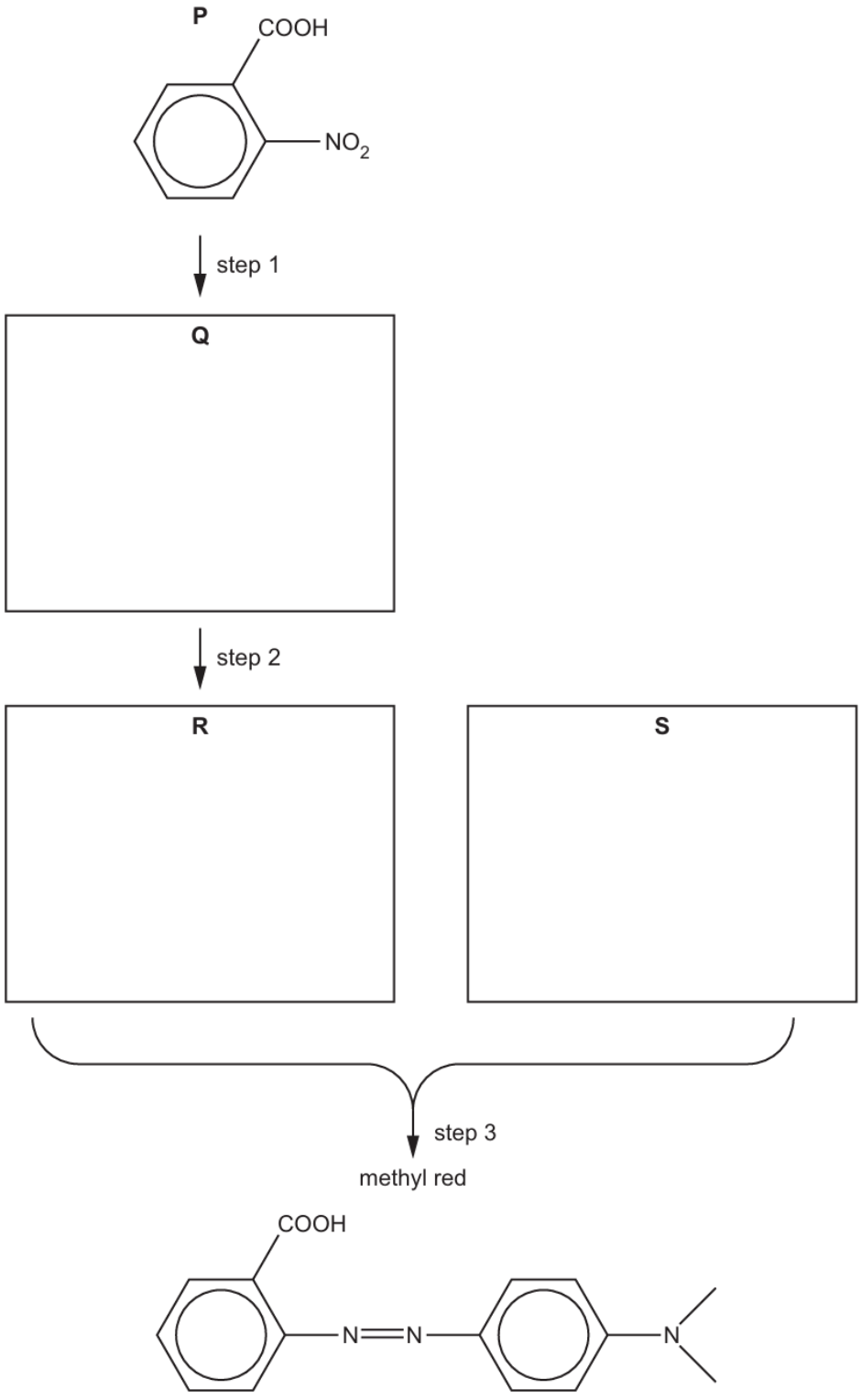


Fig. 7.1

(a) (i) Give the systematic name of **P**.

..... [1]

(ii) **P** can be synthesised as shown in Fig. 7.2.

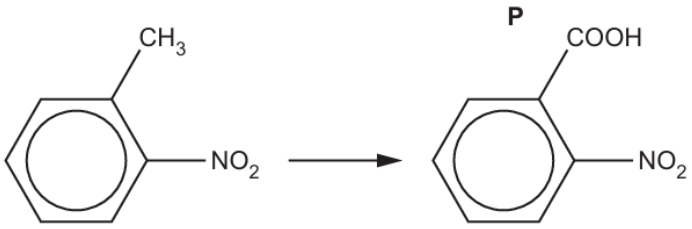


Fig. 7.2

Suggest reagents and conditions for this reaction.

..... [1]

(iii) A student attempts to synthesise **P** by an alternative route, as shown in Fig. 7.3.

Compound **T** is the major product in this reaction rather than **P**.

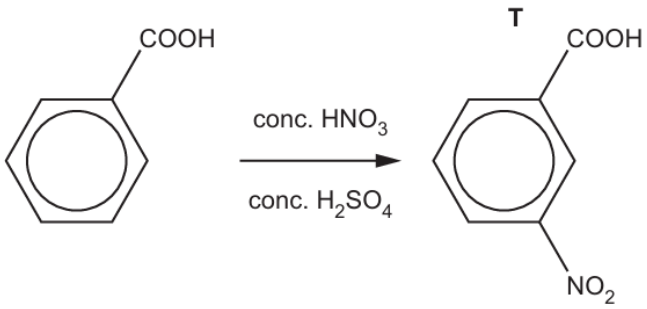


Fig. 7.3

Explain why **T** is the major product in this reaction.

.....

..... [1]

4 Fig. 6.1 shows two reactions of ethanedioic acid, HOOCCOOH.

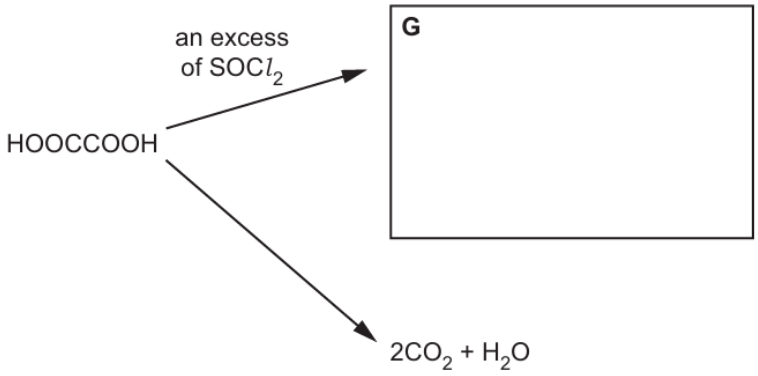


Fig. 6.1

(d) Benzene-1,4-dicarboxylic acid, $HOOCC_6H_4COOH$, can be made from benzene, C_6H_6, in two steps as shown in Fig. 6.2.

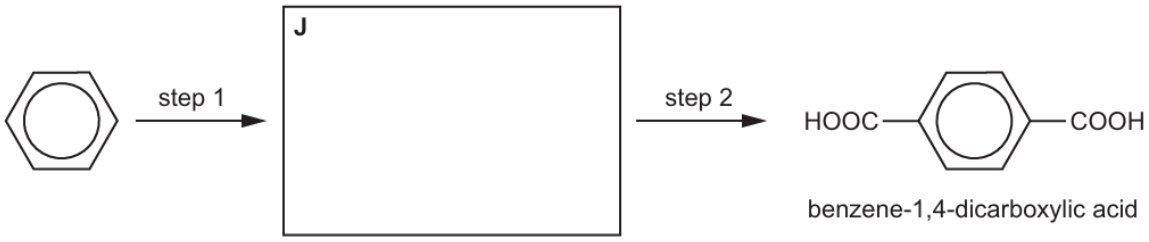


Fig. 6.2

(i) Suggest the identity of **J** by drawing its structure in the box in Fig. 6.2.

[1]

(ii) Identify the reagents and conditions for step 1 and step 2.

step 1 .....

step 2 .....

[2]

5 Benzene reacts with chlorine gas to form chlorobenzene. This reaction can be described as the reaction between benzene molecules and Cl^+ ions. The Cl^+ ions are formed by adding a suitable catalyst to the chlorine gas.

(a) Give the name or formula of a catalyst that can be used for this reaction.

..... [1]

(b) The mechanism for this reaction is shown.

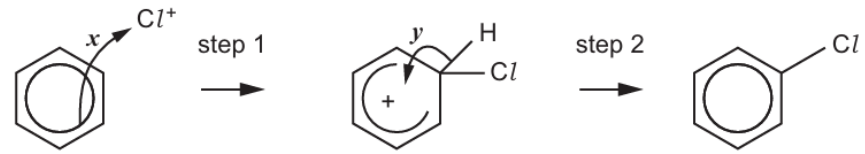


diagram 1 diagram 2 diagram 3

(i) The movement of a pair of electrons is represented by x in diagram 1.

- State where this pair of electrons is **before** step 1 takes place.

  .....

- State where this pair of electrons is **after** step 1 has taken place.

  .....

[2]

(ii) The movement of another pair of electrons is represented by y in diagram 2.

- State where this pair of electrons is **before** step 2 takes place.

  .....

- State where this pair of electrons is **after** step 2 has taken place.

  .....

[2]

(d) Complete the equation for this reaction between benzene and chlorine.

C_6H_6 + ... → ..... + ...

[1]

(e) The mechanism for this reaction is electrophilic substitution.

Complete the following sentence. Write formulae in the gaps provided.

During this reaction, the electrophile is ..... and a ..... atom in benzene is substituted by a ..... atom.

[1]

6 **(b)** Compound **Z** can be synthesised from benzene in three steps by the route shown in Fig. 4.1.

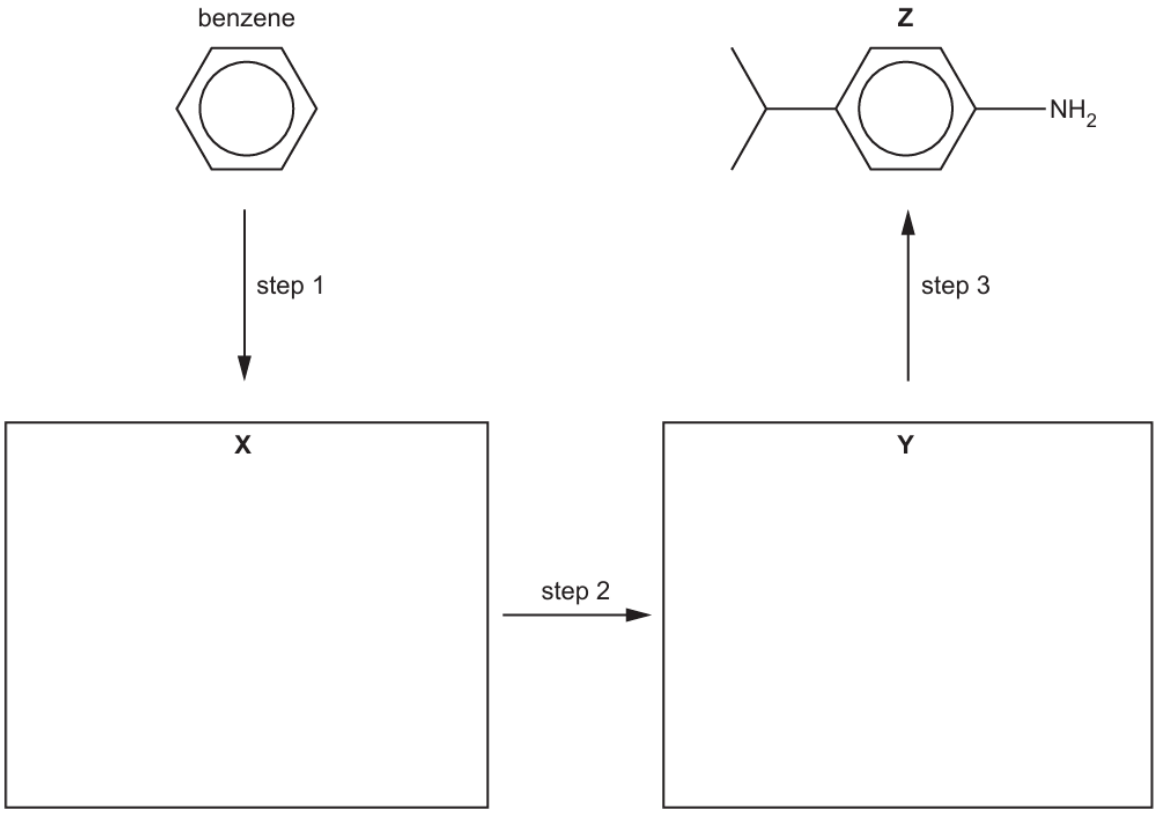


Fig. 4.1

(i) Draw structures for **X** and **Y** in Fig. 4.1. [2]

(ii) Give the reagents and conditions for steps 1, 2 and 3.

step 1 .....

step 2 .....

step 3 .....

[3]

7 **(a)** Methylbenzene can undergo different reactions, as shown in Fig. 5.1.

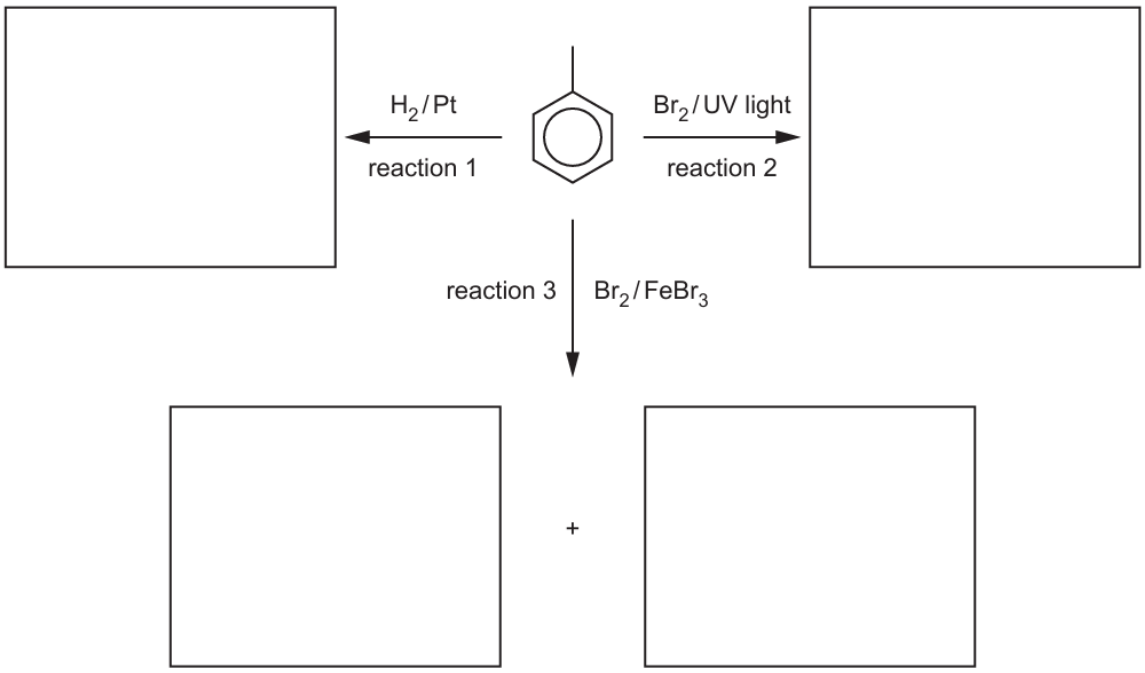


Fig. 5.1

(i) Draw structures in Fig. 5.1 for the possible organic products of the three reactions shown. [3]

(ii) Complete Table 5.1.

Table 5.1

	type of reaction	mechanism
reaction 1		
reaction 2		

[2]

(b) When methylbenzene reacts with an electrophile, a substitution reaction occurs. No addition reaction takes place under these conditions.

Explain why no addition reaction takes place.

.....

..... [1]

(c) The reaction of methylbenzene with thionyl bromide, $SOBr_2$, in the presence of an iron(III) bromide catalyst, $FeBr_3$, is shown in Fig. 5.2.

Fig. 5.2

The mechanism of this reaction is similar to that of the bromination of benzene.

The first step of the mechanism generates the $SOBr^+$ electrophile, as shown.

$$SOBr_2 + FeBr_3 \rightarrow SOBr^+ + FeBr_4^-$$

(i) The reaction of methylbenzene with $SOBr^+$ ions is shown in Fig. 5.3. Complete the mechanism in Fig. 5.3.

Include all relevant curly arrows and charges.

Draw the structure of the organic intermediate.

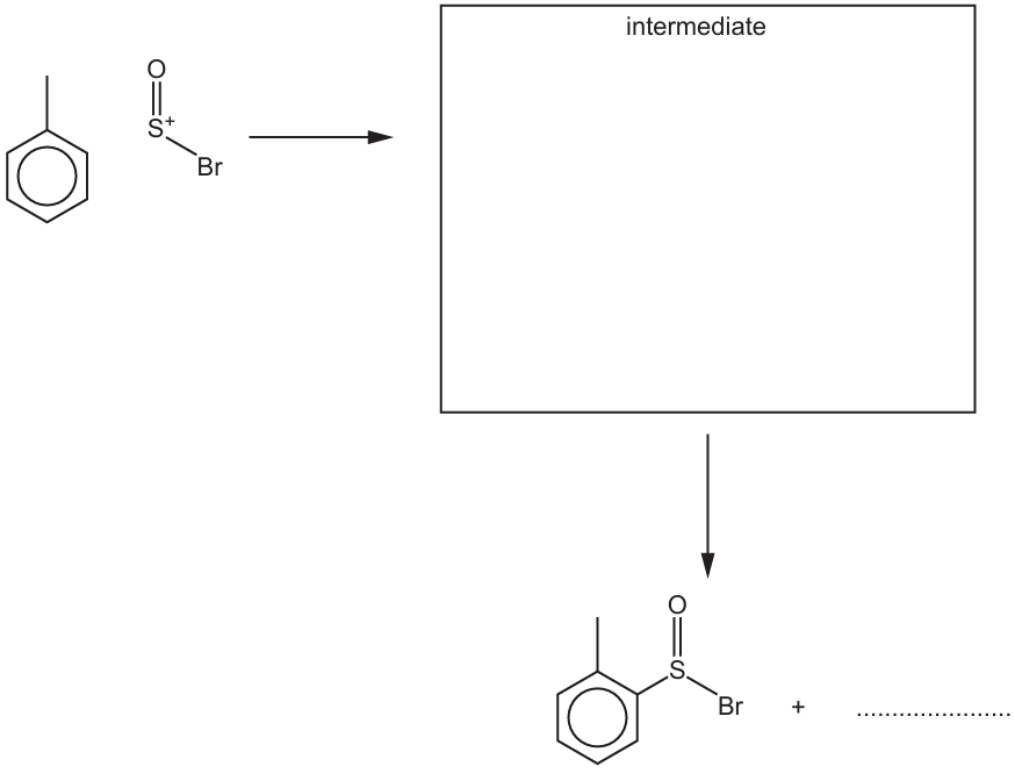


Fig. 5.3

[3]

(ii) The reaction shown in Fig. 5.2 produces a small amount of a by-product, **P**, with the molecular formula $C_{14}H_{14}OS$.

Suggest a structure for by-product **P**.

[1]

8 **(b)** **(i)** Name all the functional groups in perindopril.

.....

..... [2]

9 **(b)** Iodine monobromide, I–Br, reacts with benzene in the presence of an $AlBr_3$ catalyst.

Predict whether the organic product will be bromobenzene or iodobenzene.
Explain your answer.

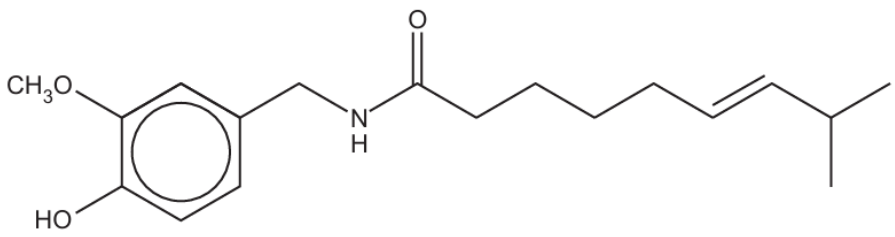
.....

.....

..... [1]

10 Capsaicin is found in chilli peppers.

capsaicin



You should assume the CH_3O group is unreactive in the reactions involved in this question.

(c) Capsaicin is heated with an excess of hydrogen gas in the presence of platinum metal.

The six-membered ring reacts in the same way as benzene under these conditions.

Draw the structure of the organic product formed.

[2]

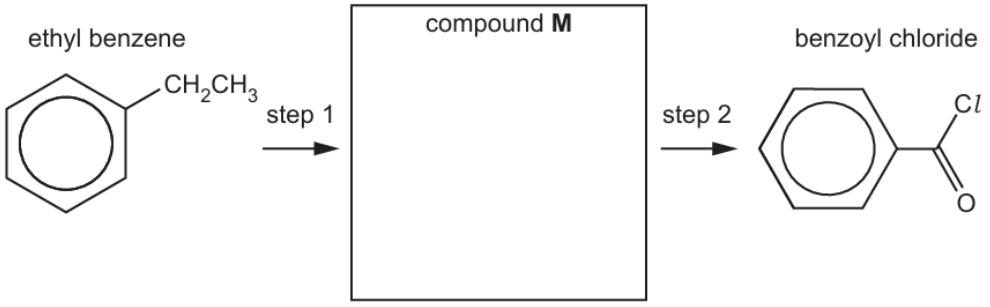
(d) When capsaicin is treated with reagent **J** under suitable conditions one of the products is methylpropanoic acid, $CH_3CH(CH_3)COOH$.

(i) Identify reagent **J** and any necessary conditions.

..... [1]

11 **(a)** Benzoyl chloride, C_6H_5COCl, can be made from ethyl benzene in a two-step process.

A reaction scheme is shown.



(i) Draw the intermediate organic compound **M** in the box. [1]

(ii) Suggest suitable reagents and conditions for step 1 and step 2.

step 1 .....

step 2 .....

[2]

(iii) Identify the type of reaction in step 1 and step 2.

step 1 .....

step 2 .....

[2]

12 Benzene can be used to make benzoic acid in the two-step process shown in Fig. 7.1.

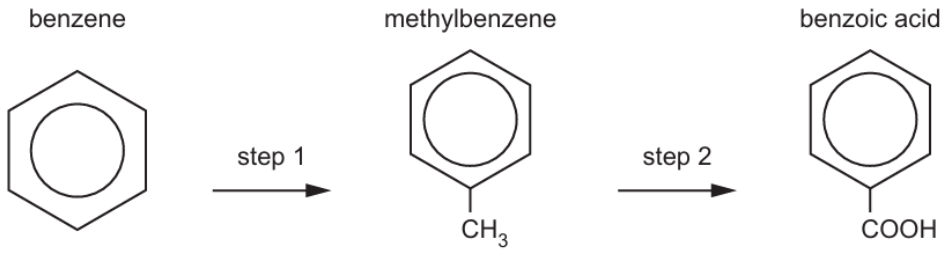


Fig. 7.1

(a) Give the reagents and conditions for step 1 and step 2.

step 1 .....

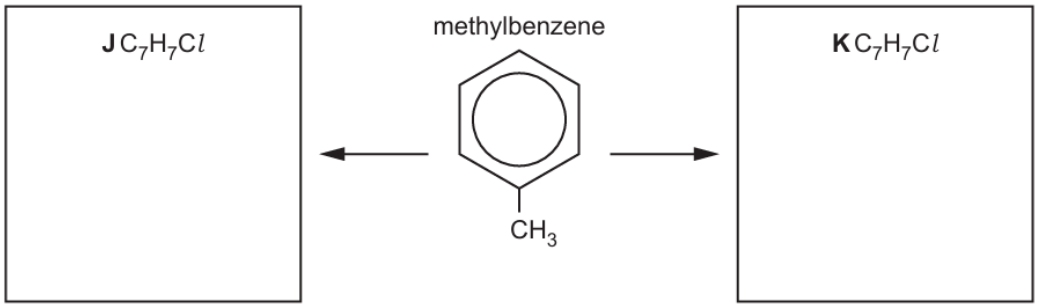
step 2 .....

[2]

(c) **(i)** When treated with Cl_2 under suitable conditions, methylbenzene forms compound **J**.

When treated with Cl_2 under **different** conditions with **different** reagents, methylbenzene forms compound **K**.

Suggest and draw structures of compounds **J** and **K** in the boxes. The molecular formula of each compound is given.



State the reagents and conditions required to form each product.

to form compound **J** .....

to form compound **K** .....

[4]

13 **(e)** Pyridine reacts with Cl_2 in the presence of $AlCl_3$ as shown in Fig. 4.3.

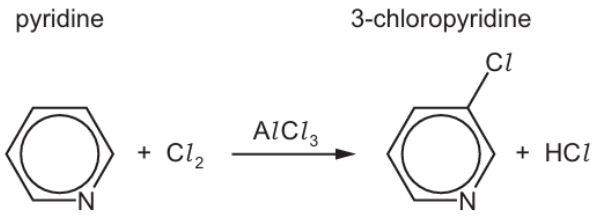


Fig. 4.3

The mechanism of this reaction is similar to that of the chlorination of benzene. $AlCl_3$ reacts with chlorine to generate an electrophile, Cl^+.

Complete the diagram to show the mechanism for the reaction of pyridine with Cl^+. Include all relevant charges, dipoles, lone pairs of electrons and curly arrows as appropriate.

[3]

14 Procaine is used as an anaesthetic in medicine. It can be synthesised from methylbenzene in five steps as shown in Fig. 7.1.

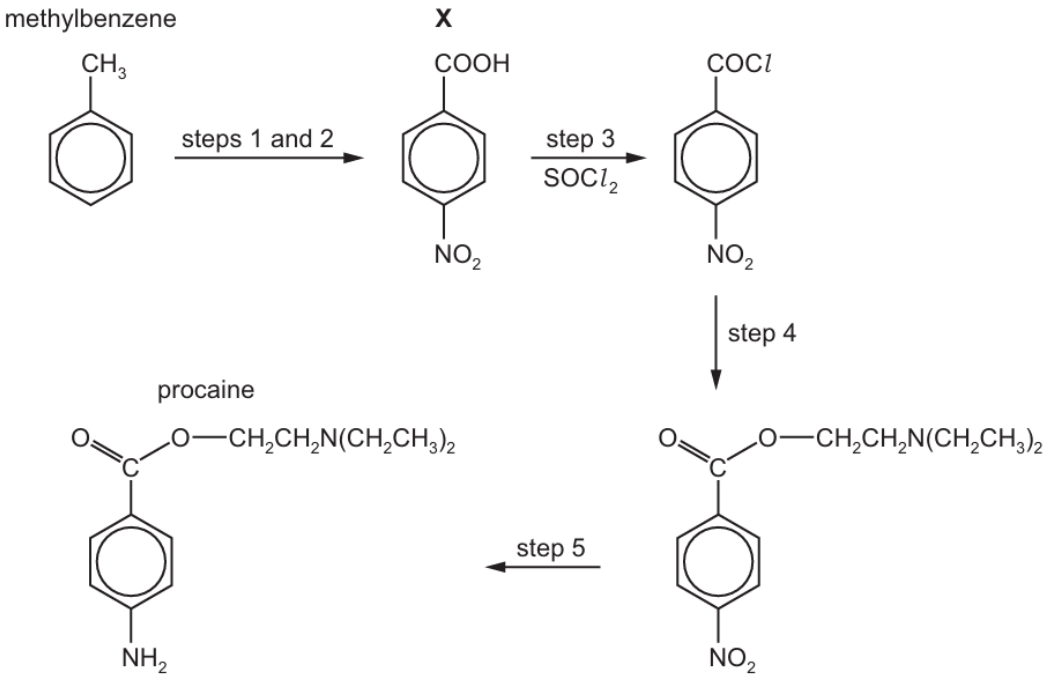


Fig. 7.1

(d) Compound **X** can be synthesised in two steps from methylbenzene.

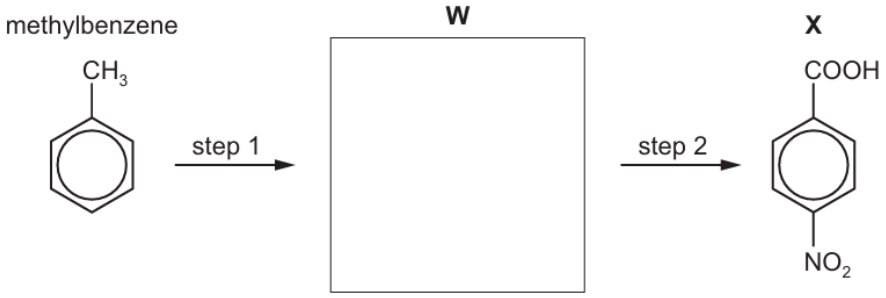


Fig. 7.2

(i) Draw the structure of compound **W** in the box provided. [1]

(ii) State the reagents and conditions for step 1 and step 2.

step 1 .....

step 2 .....

[2]

15 **(a)** The reagent and conditions required for the nitration of benzene, benzoic acid and phenol are shown in Table 6.1.

Table 6.1

compound	reagents and conditions for nitration
benzene	concentrated HNO_3, 50 °C, concentrated H_2SO_4 catalyst
benzoic acid	concentrated HNO_3, 100 °C, concentrated H_2SO_4 catalyst
phenol	dilute HNO_3(aq), 20 °C

Concentrated HNO_3 reacts with concentrated H_2SO_4 to generate the electrophile NO_2^+.

(i) Complete Fig. 6.1 to show the mechanism of the reaction between benzene and NO_2^+. Include all relevant curly arrows and charges.

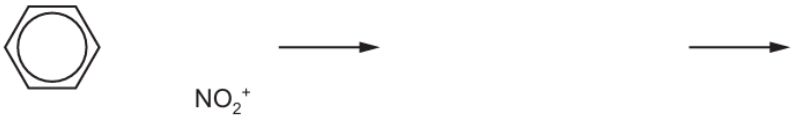


Fig. 6.1

[3]

(ii) Write an equation to show how H_2SO_4 is regenerated.

..... [1]

(b) Draw the major products from the mononitration of benzoic acid and of phenol.

major product from benzoic acid	major product from phenol

[2]

(c) Compare the relative ease of nitration of benzene, benzoic acid and phenol.
Explain your reasoning; include reference to the structures of the three compounds in your answer.

..... > ..... > .....
easiest least easy

.....

.....

.....

.....

.....

[4]

16 Benzene, C_6H_6, is an aromatic molecule.

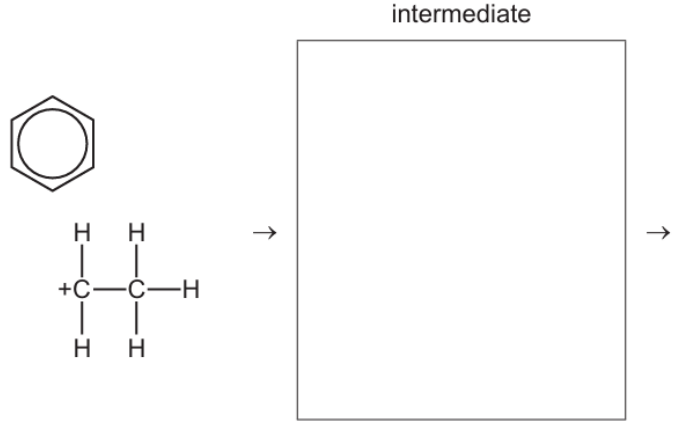
(b) Benzene reacts with chloroethane in the presence of a catalyst. The reaction mechanism is called electrophilic substitution.

(i) The first step in the reaction is the generation of the $^+CH_2CH_3$ electrophile.

Write an equation for the reaction that generates this electrophile.

..... [1]

(ii) Describe the mechanism for the reaction between benzene and the $^+CH_2CH_3$ electrophile.
Include all relevant curly arrows and charges.



[3]

17 **(b)** Methylbenzene, $C_6H_5CH_3$, can be made from benzene by an electrophilic substitution reaction.

(i) Identify a compound that reacts with benzene to form methylbenzene.
Identify the catalyst used.

compound .....

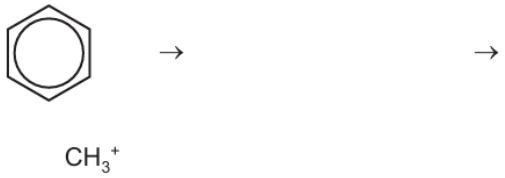
catalyst .....
[1]

(ii) The first step in the reaction is the generation of the CH_3^+ electrophile.

Write an equation for the reaction that generates this electrophile.

..... [1]

(iii) Describe the mechanism for the reaction between benzene and the CH_3^+ electrophile. Include all relevant curly arrows and charges.



[3]

(iv) Identify a suitable reagent to oxidise methylbenzene to benzoic acid, C_6H_5COOH.

Write an equation for this reaction using [O] to represent one atom of oxygen from the oxidising agent.

reagent .....

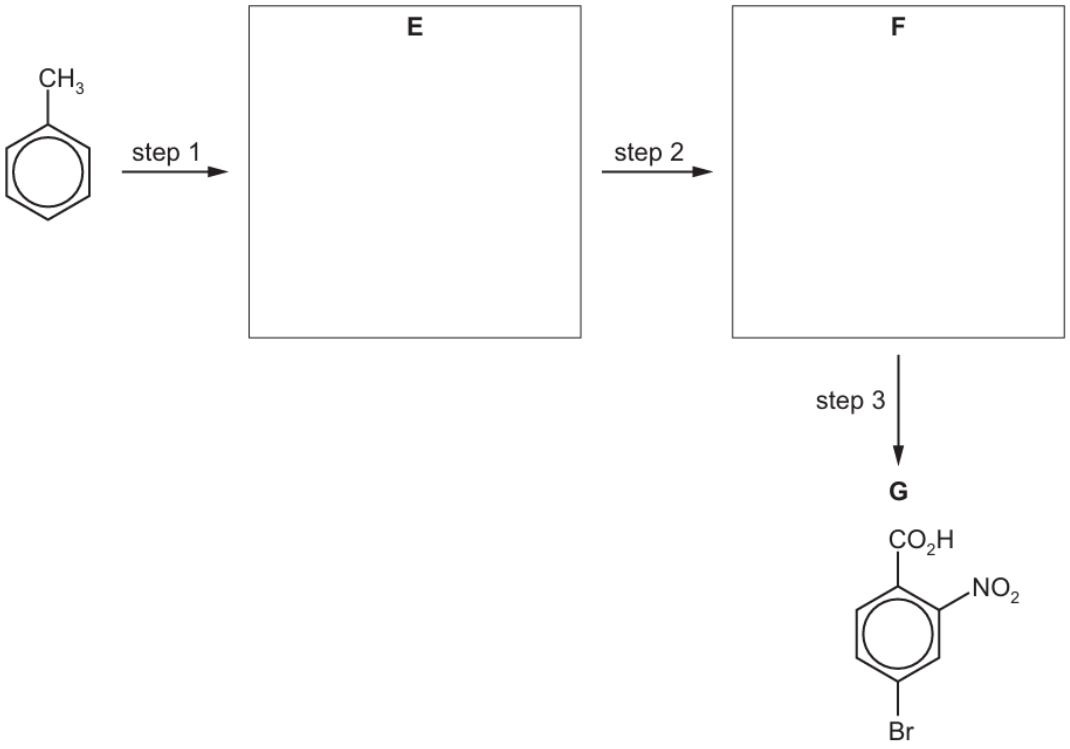
equation .....
[2]

(v) Methylbenzene and benzoic acid are both nitrated with a mixture of concentrated nitric acid and sulfuric acid to give mononitrated products. The structural formulae of these products are $CH_3C_6H_4NO_2$ and $HOOCC_6H_4NO_2$ respectively.

Draw the structures of these two products.

[1]

18 **(c)** Compound **G** can be synthesised from methylbenzene in three steps.



(i) Give the systematic name of compound **G**.

..... [1]

(ii) Deduce the identities of **E** and **F** and draw their structures in the boxes. [2]

(iii) Suggest reagents and conditions for each of steps 1 to 3 in **(c)**.

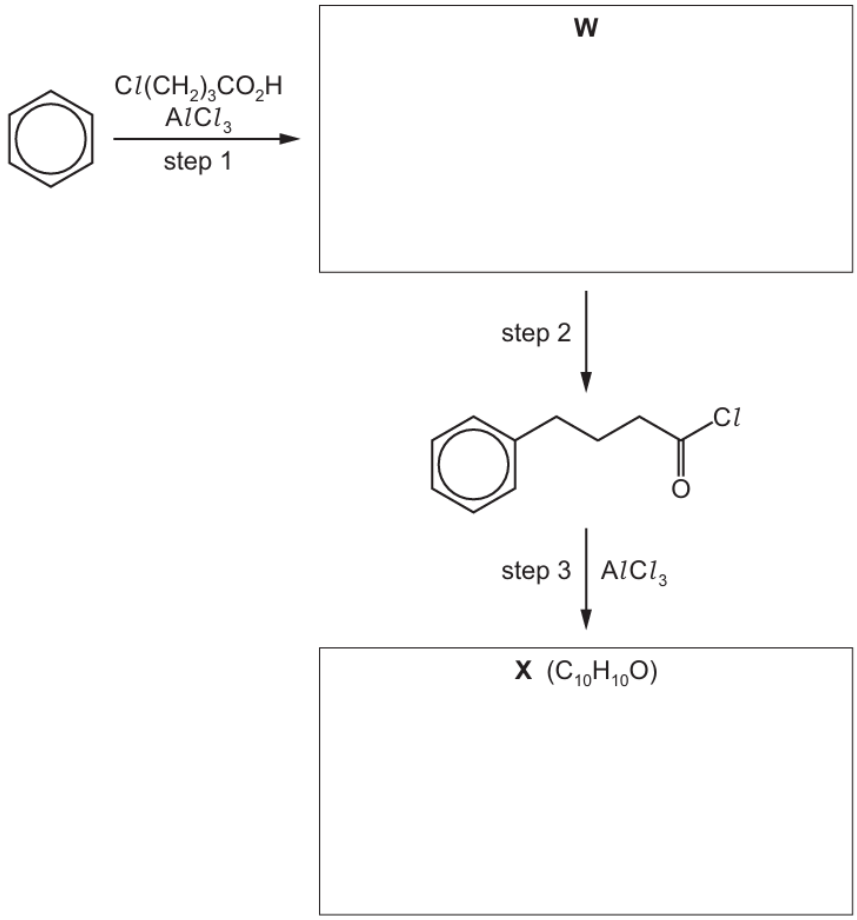
step 1 .....

step 2 .....

step 3 .....

[3]

19 **(b)** A three-step synthesis of **X** ($C_{10}H_{10}O$) from benzene is suggested as shown.



(i) Step 1 is the alkylation of benzene by electrophilic substitution.
Use R–Cl to represent $Cl(CH_2)_3CO_2H$.

Write an equation for the formation of an electrophile from R–Cl and $AlCl_3$.

..... [1]

(ii) Deduce and draw the structures of **W** and **X** in the boxes. [2]

(iii) Suggest the reagents and conditions for step 2.

..... [1]

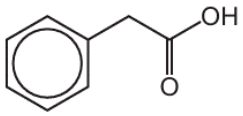
(iv) Complete the mechanism for the reaction of benzene with the electrophile formed in **(b)(i)**.

Include all relevant charges and curly arrows showing the movement of electron pairs.

Draw the structure of the intermediate.

[3]

20 The structure of phenylethanoic acid is shown.



(c) Phenylethanoic acid can be synthesised using benzene as the starting material.

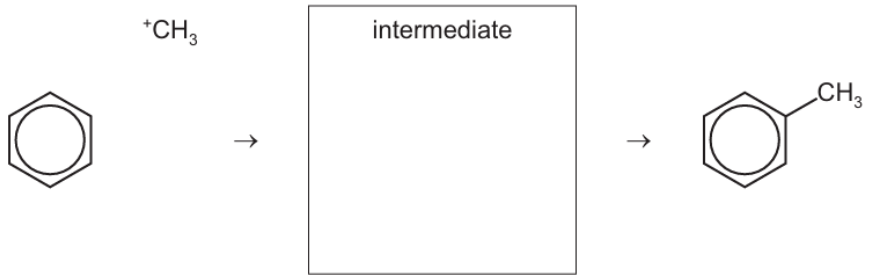
In the first stage of this synthesis, benzene reacts with chloromethane in the presence of an $AlCl_3$ catalyst to form methylbenzene.

Chloromethane reacts with $AlCl_3$ to form two ions. One of these is the carbocation $^+CH_3$.

(i) Write an equation for the reaction between chloromethane and $AlCl_3$.

..... [1]

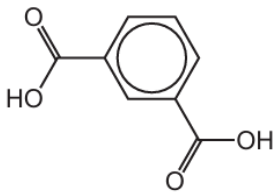
(ii) Draw the mechanism of the reaction between benzene and $^+CH_3$. Include all relevant curly arrows, charges and the structure of the intermediate.



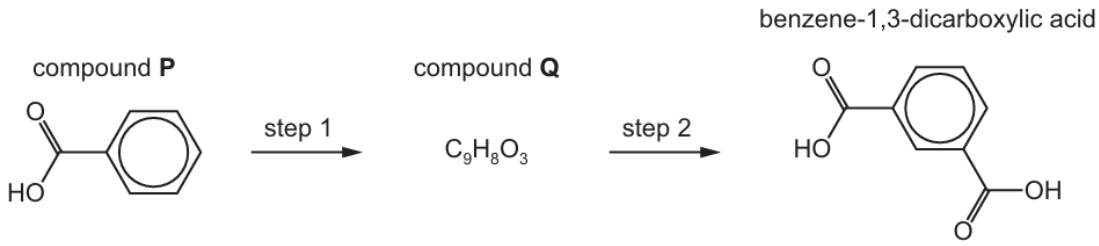
[3]

21 The structure of benzene-1,3-dicarboxylic acid is shown.

benzene-1,3-dicarboxylic acid



(c) Benzene-1,3-dicarboxylic acid can be made by the two-step synthesis shown below.



(i) Name compound **P**.

..... [1]

(ii) Explain why the major product of this two-step synthesis is benzene-1,3-dicarboxylic acid and **not** benzene-1,4-dicarboxylic acid.

.....

..... [1]

(iii) The reagents used for step 1 are CH_3COCl and $AlCl_3$. These reagents give rise to $CH_3\overset{+}{C}{=}O$ ions which react with compound **P**.

Name the mechanism of this reaction.

..... [1]

(iv) Draw the mechanism of the reaction of $CH_3\overset{+}{C}{=}O$ ions with compound **P**. Include all relevant curly arrows and charges, the structure of the intermediate and the structure of compound **Q**.

intermediate compound **Q**

$CH_3\overset{+}{C}{=}O$

[3]

(v) Suggest a reagent and conditions to convert compound **Q** into benzene-1,3-dicarboxylic acid, in step 2.

..... [1]

22 **(a)** Benzene reacts with bromine in the presence of an aluminium bromide catalyst, $AlBr_3$, to form bromobenzene. This is a substitution reaction. No addition reaction takes place.

(i) Explain why no addition reaction takes place.

.....

..... [1]

$AlBr_3$ reacts with bromine to generate an electrophile, Br^+.

(ii) Draw the mechanism of the reaction between benzene and Br^+ ions. Include all relevant arrows and charges.

[3]

(iii) Write an equation to show how the $AlBr_3$ catalyst is reformed.

..... [1]

(b) Suggest why bromination of phenol occurs more readily than bromination of benzene.

.....

.....

.....

.....

..... [2]

(c) (i) There are four different carbocations with the same formula, $C_4H_9^+$. One structure is given in the table.

Suggest the structural formulae of the three other carbocations.

structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[3]

23 (a) (i) When benzene undergoes nitration a nitro group substitutes at a carbon atom.

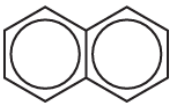
State the shape (geometry) around the substituted carbon atom

- in the benzene molecule, ...
- in the intermediate complex, ...
- in the nitrobenzene product. .....

[2]

(ii) Naphthalene, $C_{10}H_8$, is an arene hydrocarbon.

naphthalene



When naphthalene undergoes nitration, a mixture of two organic compounds is formed. Each compound contains **one** nitro group.

Suggest the structures of these compounds.

structure 1	structure 2

[1]

(b) Naphthalene can be oxidised under certain conditions to phthalic anhydride, $C_8H_4O_3$, carbon dioxide and water.

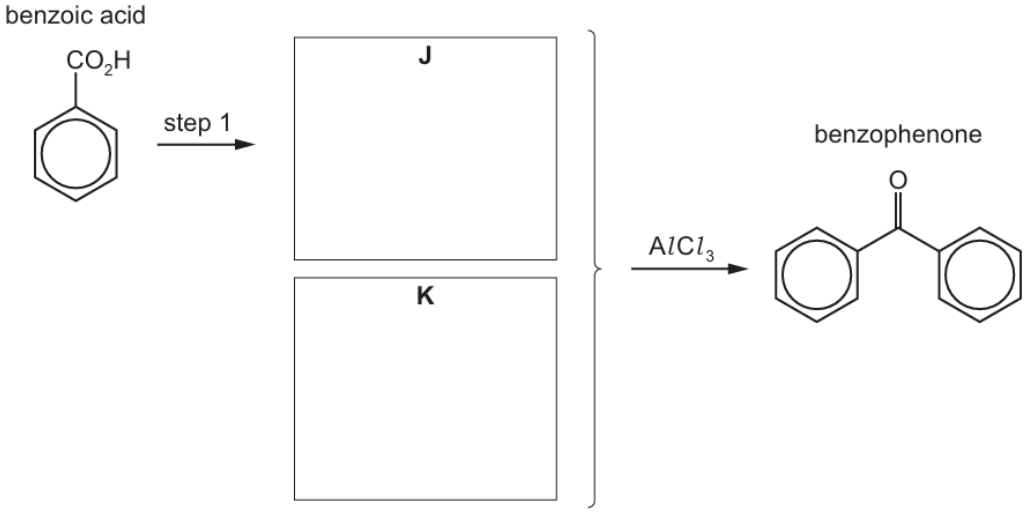
Construct an equation for this reaction. Use [O] to represent an atom of oxygen from the oxidising agent.

..... [1]

24 **(c)** Benzophenone can be synthesised from benzoic acid in two steps as shown.

In step 1 compound **J**, a reactive reaction intermediate, is formed.

Compound **J** then reacts with an organic compound, **K**, to form benzophenone.

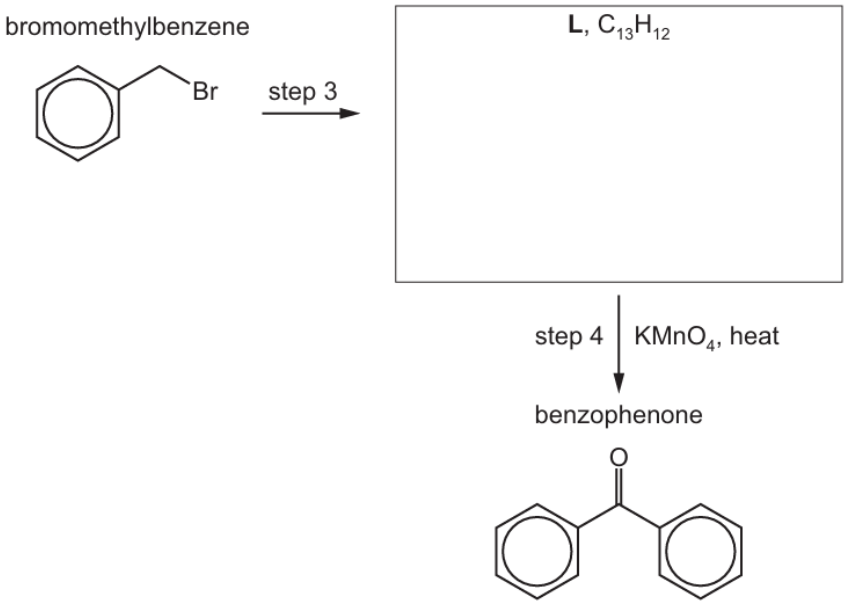


(i) Deduce the identities of organic compounds **J** and **K** and draw their structures in the boxes. [2]

(ii) Suggest reagents and conditions for step 1.

..... [1]

(d) Benzophenone can also be synthesised in two steps from bromomethylbenzene.



(i) Deduce the identity of compound **L** and draw its structure in the box. [1]

(ii) Name the mechanism of step 3 and suggest reagents and conditions for step 3.

mechanism of step 3 .....

reagents and conditions .....

[2]

(iii) Deduce the *type of reaction* in step 4.

..... [1]

25 Benzene, C_6H_6, can be obtained from crude oil.

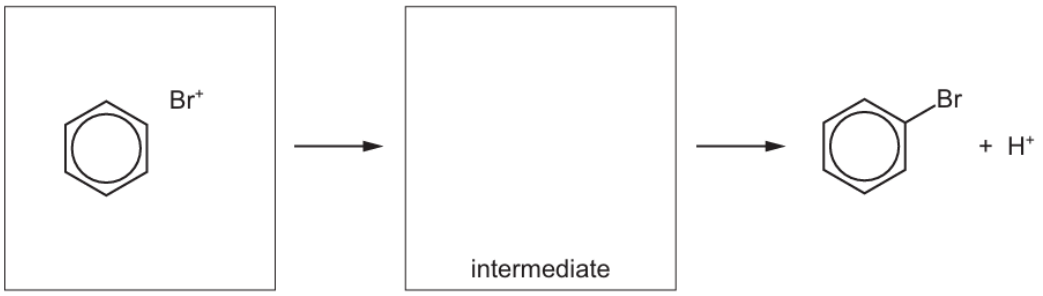
(a) Benzene reacts with bromine, in the presence of a suitable catalyst, forming bromobenzene as one product.

(i) Give the name or formula of the other product of this reaction.

..... [1]

(ii) In the presence of the catalyst, bromine can be considered to form the electrophile Br^+.

Complete the mechanism by which benzene reacts with Br^+, using curly arrows to show the movement of electron pairs.

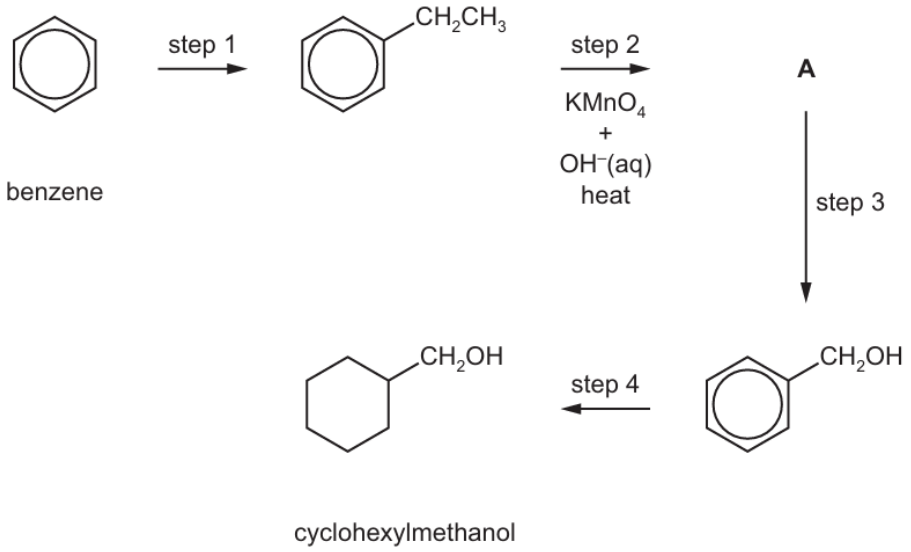


[2]

(iii) Name this mechanism.

..... [1]

(b) Benzene can be used as a starting material in the synthesis of cyclohexylmethanol, $C_6H_{11}CH_2OH$, as outlined below.



(i) Identify a suitable reagent and a suitable catalyst for step 1.

reagent .....

catalyst .....

[2]

(ii) Draw the structure of **A**.

A

[1]

(iii) Identify suitable reagents for steps 3 and 4.

step 3 .....

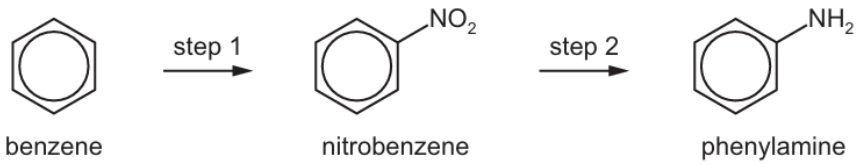
step 4 .....

[2]

(iv) Deduce the number of peaks in the carbon-13 NMR spectrum of cyclohexylmethanol.

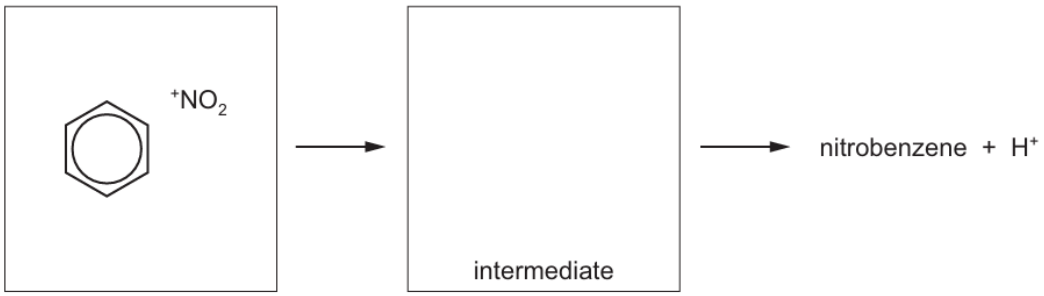
..... [1]

26 **(b)** Benzene can be used as a starting material to produce phenylamine by a two-step synthesis.



(i) Step 1 is the reaction of benzene with NO_2^+ ions.

Complete the mechanism and draw the intermediate of step 1.
Include all relevant charges and curly arrows to show the movement of electron pairs.



[2]

(ii) State the name of the mechanism in **(b)(i)**.

..... [1]

27 **(a)** Benzene can be converted into cyclohexane.

(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.

.....

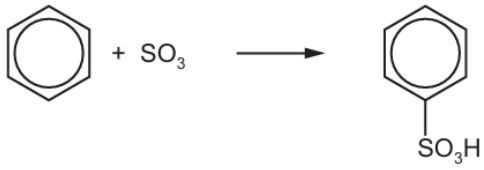
.....

.....

[2]

(b) When benzene reacts with SO_3, benzenesulfonic acid is produced.

benzenesulfonic acid



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.

$$SO_3 + H_2SO_4 \rightarrow SO_3H^+ + HSO_4^-$$

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

benzenesulfonic acid

[3]

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

..... [1]

(c) 3-dodecylbenzenesulfonic acid can be prepared from benzenesulfonic acid.

benzenesulfonic acid 3-dodecylbenzenesulfonic acid

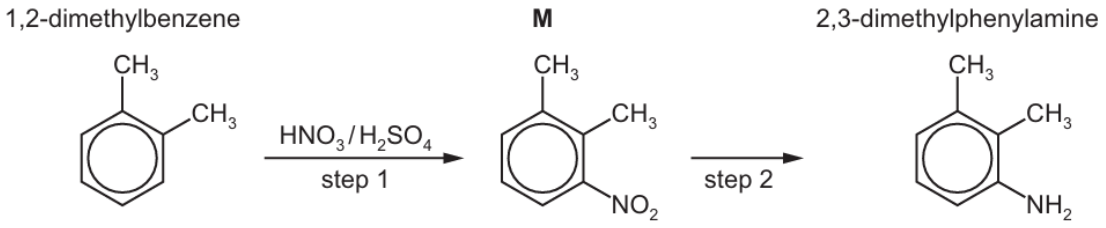
Suggest the reagents and conditions and name the mechanism for this reaction.

reagents and conditions .....

mechanism .....

[2]

28 **(b)** 2,3-dimethylphenylamine can be prepared from 1,2-dimethylbenzene in two steps as shown.

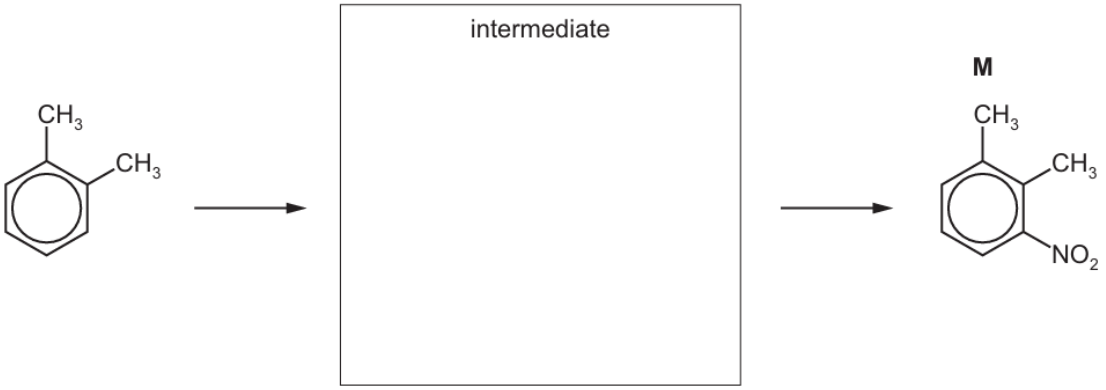


Step 1 is catalysed by H_2SO_4.

(i) Write an equation to show how H_2SO_4 generates the electrophile during step 1.

..... [1]

(ii) Draw the mechanism of the reaction between this electrophile and 1,2-dimethylbenzene to form **M**. Include all relevant curly arrows and charges.



[3]

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

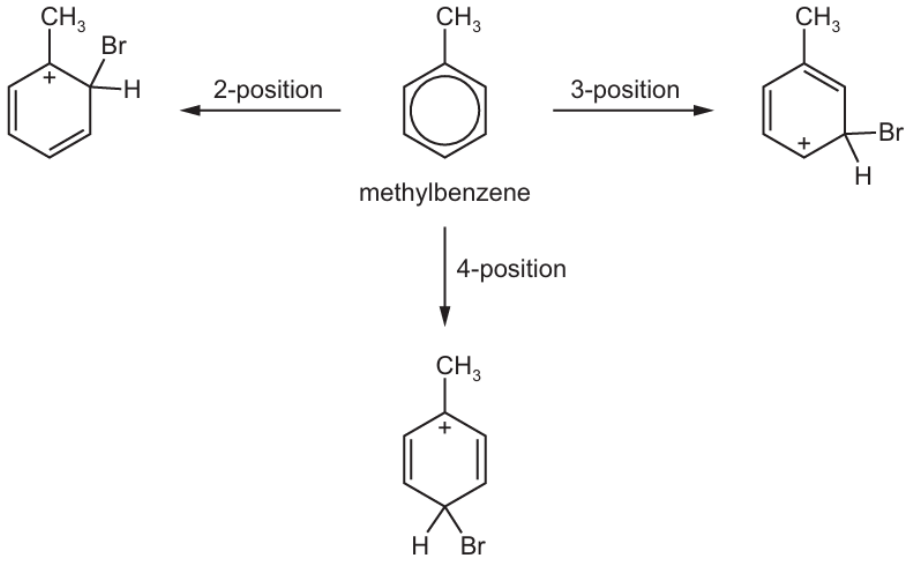
..... [1]

(iv) For step 2, suggest the reagents and conditions and name the *type of reaction*.

- reagents and conditions .....
- type of reaction .....

[2]

(d) The position of substitution in the electrophilic substitution of arenes can be explained based on the stability of the intermediate cations formed in the first step. The example given involves the bromination of methylbenzene.



Use this information and your knowledge about the stability of cations to suggest why the CH_3 group directs incoming electrophiles to the 2- and 4-positions in preference to the 3-position.

.....

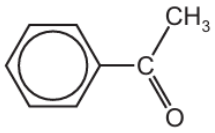
.....

.....

..... [2]

29 Phenylethanone is an important chemical with many uses.

phenylethanone



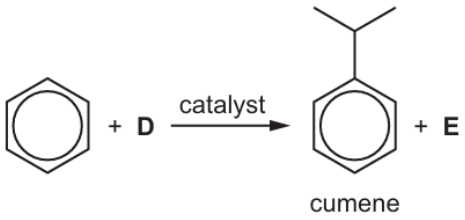
(a) Phenylethanone can be synthesised using benzene as one of the starting materials.

Identify the other reagents used and describe any essential reaction conditions.

.....

..... [2]

30 **(a)** Benzene reacts with **D** in the presence of a suitable catalyst to give cumene and non-organic product **E**. This is an electrophilic substitution reaction.



cumene

(i) Name the reactant **D** and the non-organic product **E**.

D .....

E .....

[2]

(ii) Give the name of the type of aromatic electrophilic substitution reaction taking place.

..... [1]

(b) Cumene undergoes substitution reactions with chlorine to give several different isomeric products with the formula $C_9H_{11}Cl$. The substitution can occur in the aromatic ring or in the side-chain of cumene.

(i) Describe the conditions that are used to ensure substitution takes place only in the **aromatic ring**.

..... [1]

(ii) Draw the structures of the **two** major isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the aromatic ring.

[1]

(iii) Describe the conditions that are used to ensure substitution takes place only in the **side-chain**.

..... [1]

(iv) Draw the structures of **two** isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the side-chain.

[1]

(c) Complete the following table to show the structures of the organic products formed when cumene reacts with each reagent.

reagent	structure of organic product
hot $KMnO_4(aq)$	
H_2 + Ni, high pressure	

[2]

(d) Cumene can be nitrated using a mixture of concentrated nitric and sulfuric acids. The mechanism for this reaction is similar to the mechanism for the nitration of benzene.

Complete the mechanism for this reaction.

- Include all relevant charges and curly arrows showing the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.

cumene intermediate

[4]