

30 ARENES

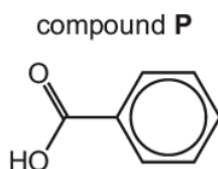
Learning outcomes

Candidates should be able to:

- describe the chemistry of arenes as exemplified by the following reactions of benzene and methylbenzene:
 - substitution reactions with Cl_2 and with Br_2 in the presence of a catalyst, AlCl_3 or AlBr_3 , to form halogenoarenes (aryl halides)
 - nitration with a mixture of concentrated HNO_3 and concentrated H_2SO_4 at a temperature between 25°C and 60°C
 - Friedel–Crafts alkylation by CH_3Cl and AlCl_3 and heat
 - Friedel–Crafts acylation by CH_3COCl and AlCl_3 and heat
 - complete oxidation of the side-chain using hot alkaline KMnO_4 and then dilute acid to give a benzoic acid
 - hydrogenation of the benzene ring using H_2 and Pt/Ni catalyst and heat to form a cyclohexane ring
- describe the mechanism of electrophilic substitution in arenes:
 - as exemplified by the formation of nitrobenzene and bromobenzene
 - with regards to the effect of delocalisation (aromatic stabilisation) of electrons in arenes to explain the predomination of substitution over addition
- predict whether halogenation will occur in the side-chain or in the aromatic ring in arenes depending on reaction conditions
- describe that in the electrophilic substitution of arenes, different substituents direct to different ring positions (limited to the directing effects of $-\text{NH}_2$, $-\text{OH}$, $-\text{R}$, $-\text{NO}_2$, $-\text{COOH}$ and $-\text{COR}$)

Introduction

1. Name compound P.



..... [1]

Substitution with Br_2 and Cl_2

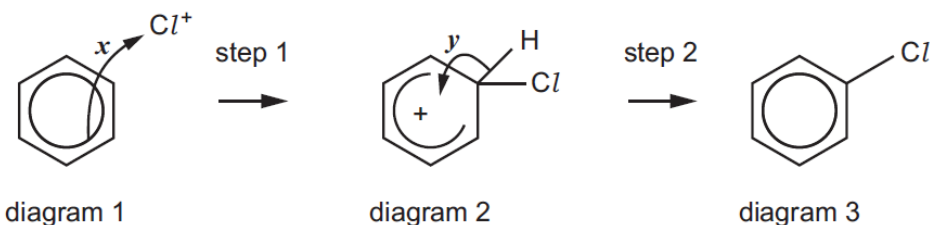
Electrophilic substitution: the replacement of an atom by another atom or group of atoms after initial attack by an electron-deficient species.

2. 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.



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]

(iii) There are six carbon atoms in diagram 2.

State how many of these carbon atoms are sp hybridised, sp^2 hybridised, and sp^3 hybridised.

sp hybridised

sp^2 hybridised

sp^3 hybridised

[1]

3. 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.

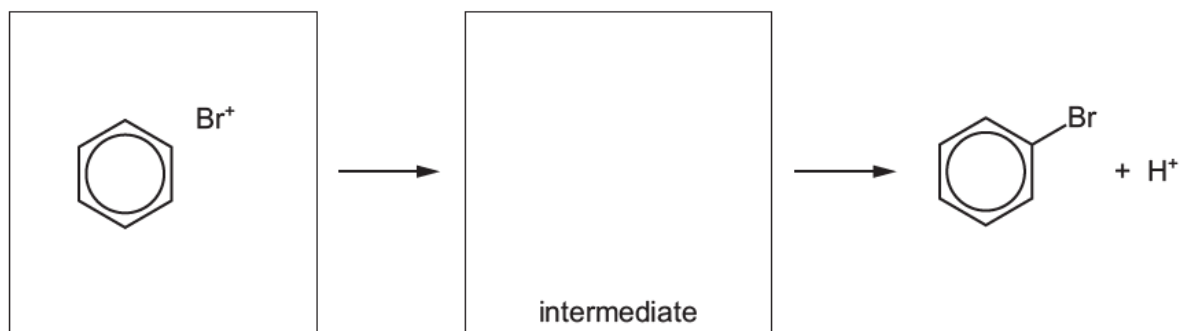
(i) Give the name or formula of the other product of this reaction.

..... [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]

4. 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]

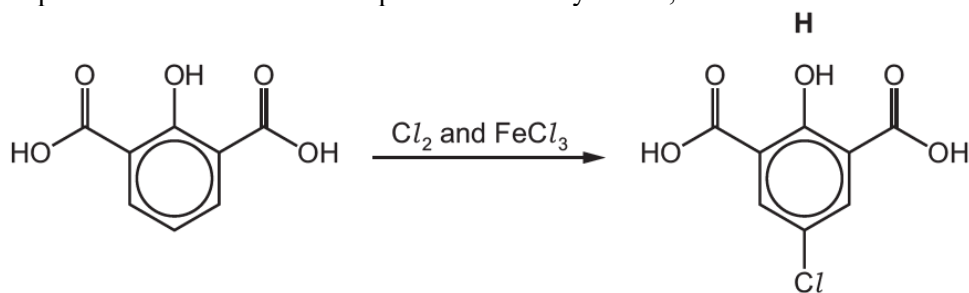
$AlBr_3$ reacts with bromine to generate an electrophile, Br^+ .

(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]

5. Compound H is formed in one step of a different synthesis, as shown.



- (i) State the role of FeCl_3 in this step.

..... [1]

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

$\text{C}_6\text{H}_6 + \dots\dots\dots + \dots\dots\dots$ [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. In a synthesis of tulobuterol, the first step involves the formation of chlorobenzene. Benzene reacts with Cl_2 in the presence of an AlCl_3 catalyst.

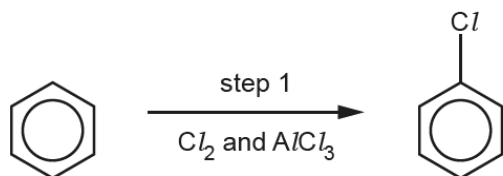


Fig. 5.2

- (i) Write an equation to show how Cl_2 reacts with AlCl_3 to generate an electrophile.

..... [1]

- (ii) Complete the mechanism in Fig. 5.3 for the reaction of benzene with the electrophile generated in (b)(i).

Include all relevant curly arrows and charges.

Draw the structure of the intermediate.

[3]

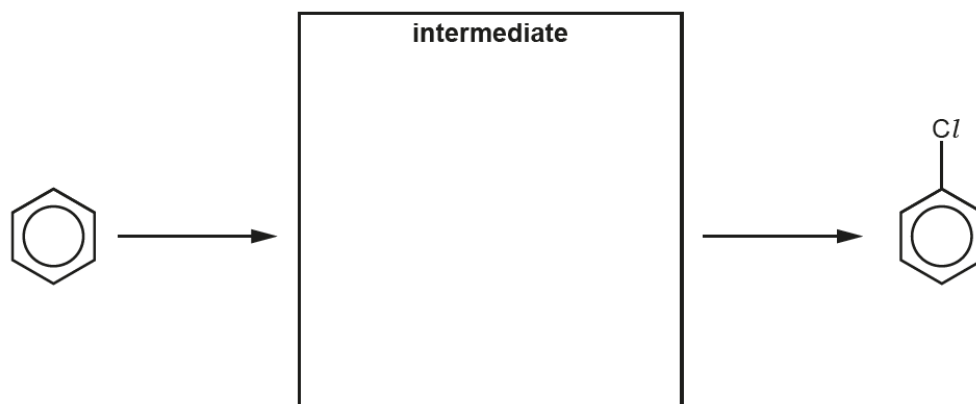


Fig. 5.3

7. Benzene reacts with bromine in the presence of an aluminium bromide catalyst, Al/Br_3 , to form bromobenzene. This is a substitution reaction. No addition reaction takes place.

(i) Explain why no addition reaction takes place.

..... [1]

A/Br_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.

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

..... [1]

8. Pyridine reacts with Cl_2 in the presence of AlCl_3 as shown in Fig. 4.3.

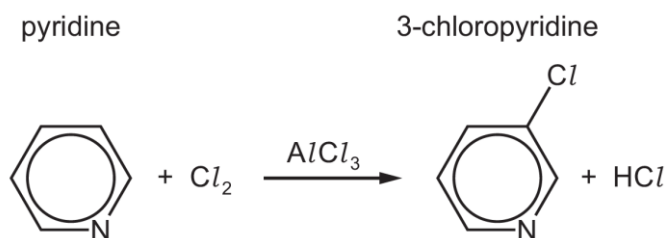
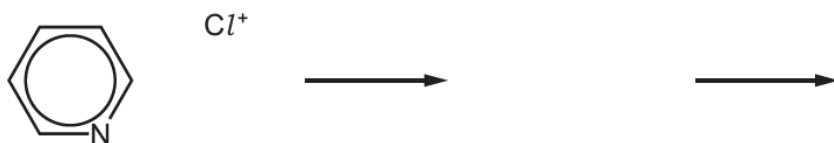


Fig. 4.3

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]

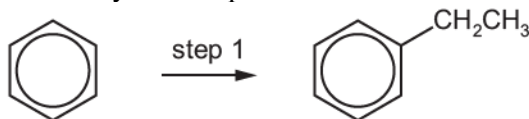
9. Iodine monobromide, I-Br, reacts with benzene in the presence of an AlBr_3 catalyst.

Predict whether the organic product will be bromobenzene or iodobenzene.

Explain your answer.

..... [1]

10. Identify a suitable reagent and a suitable catalyst for step 1.

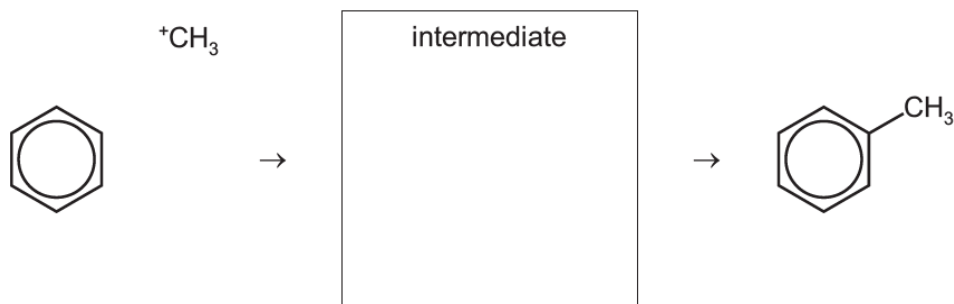


reagent

catalyst [2]

11. Draw the mechanism of the reaction between benzene and $^+\text{CH}_3$. Include all relevant curly arrows, charges and the structure of the intermediate.

[3]



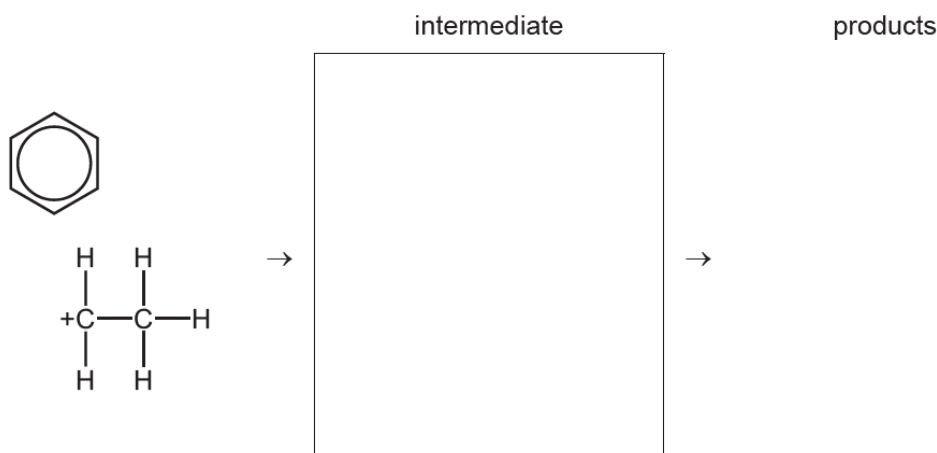
12. Benzene reacts with chloroethane in the presence of a catalyst. The reaction mechanism is called electrophilic substitution.

(i) The first step in the reaction is the generation of the $^+\text{CH}_2\text{CH}_3$ electrophile. Write an equation for the reaction that generates this electrophile.

..... [1]

(ii) Describe the mechanism for the reaction between benzene and the $^+\text{CH}_2\text{CH}_3$ electrophile. Include all relevant curly arrows and charges.

[3]



13. Phenylethanoic acid can be synthesised using benzene as the starting material.

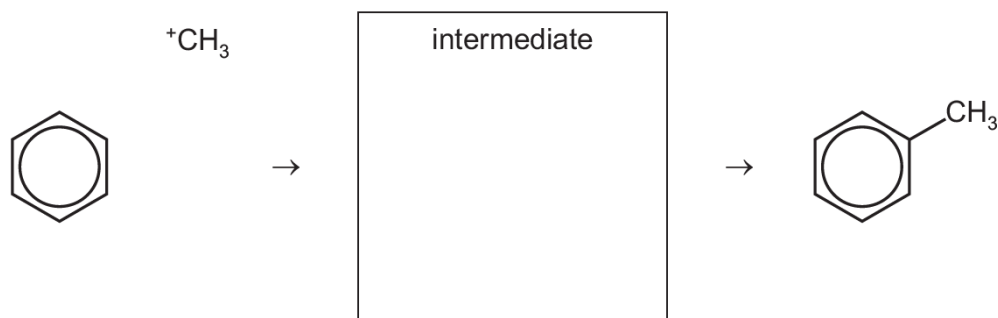
In the first stage of this synthesis, benzene reacts with chloromethane in the presence of an AlCl_3 catalyst to form methylbenzene.

Chloromethane reacts with AlCl_3 to form two ions. One of these is the carbocation $^+\text{CH}_3$.

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

..... [1]

(ii) Draw the mechanism of the reaction between benzene and $^+\text{CH}_3$. Include all relevant curly arrows, charges, and the structure of the intermediate.



14. Methylbenzene, $\text{C}_6\text{H}_5\text{CH}_3$, 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.

.....

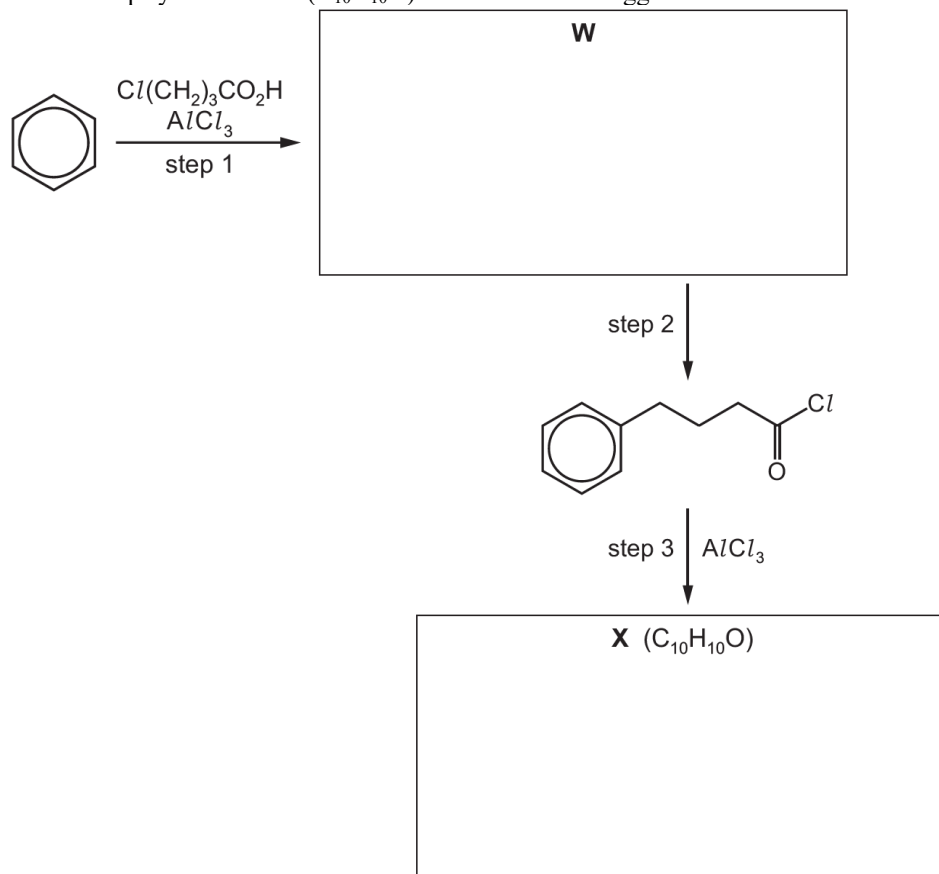
[1]

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

[3]



15. A three-step synthesis of X ($\text{C}_{10}\text{H}_{10}\text{O}$) from benzene is suggested as shown.

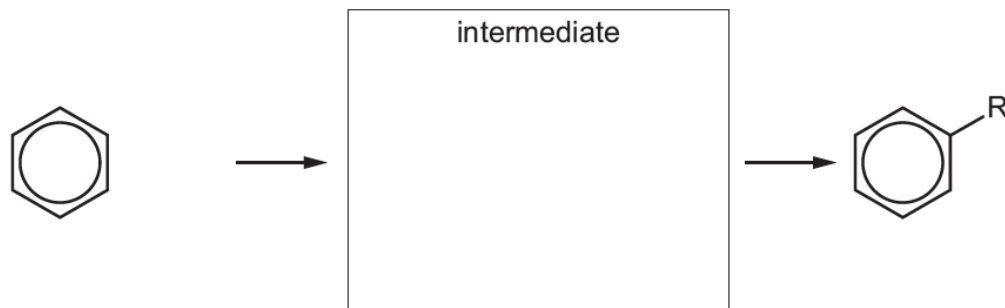


(i) Step 1 is the alkylation of benzene by electrophilic substitution.
 Use R–Cl to represent $\text{Cl}(\text{CH}_2)_3\text{CO}_2\text{H}$.
 Write an equation for the formation of an electrophile from R–Cl and AlCl_3 .

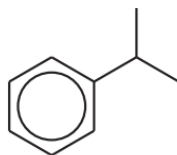
..... [1]

(ii) Complete the mechanism for the reaction of benzene with the electrophile formed in (i).
 Include all relevant charges and curly arrows showing the movement of electron pairs.
 Draw the structure of the intermediate.

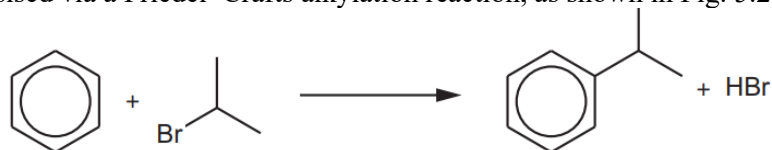
[3]



16. Cumene is an aromatic hydrocarbon used in the synthesis of other useful chemicals.
 cumene



(b) Cumene can be synthesised via a Friedel–Crafts alkylation reaction, as shown in Fig. 5.2.



(i) Name the mechanism involved in the Friedel–Crafts alkylation shown in Fig. 5.2.

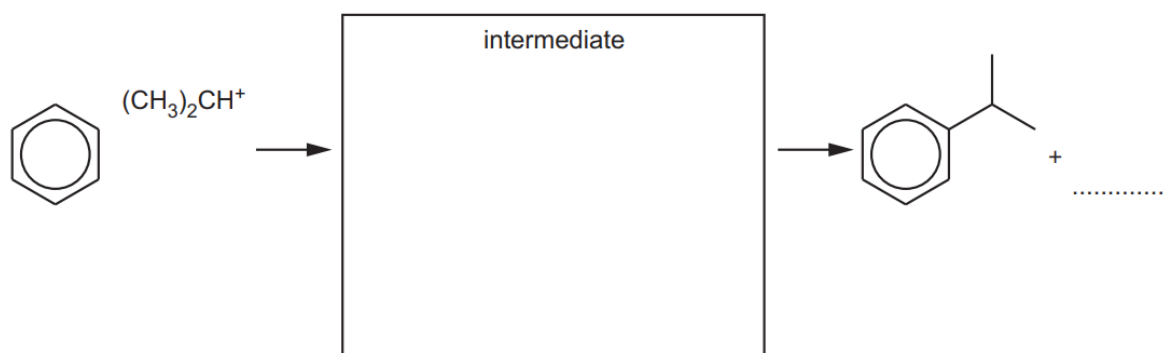
..... [1]

(ii) The first step of the reaction forms the $(\text{CH}_3)_2\text{CH}^+$ cation.
 Identify a suitable reagent for the formation of this cation from 2-bromopropane, $(\text{CH}_3)_2\text{CHBr}$.

..... [1]

(iv) Complete Fig. 5.3 to show the mechanism for the reaction of benzene with the $(\text{CH}_3)_2\text{CH}^+$ cation.
 Include all relevant curly arrows and charges

[3]

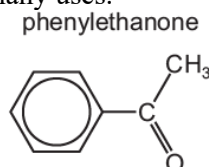


(iv) The Friedel–Crafts alkylation of benzene by 1-bromopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, also produces cumene as the major product.

The $\text{CH}_3\text{CH}_2\text{CH}_2^+$ cation formed in the first step quickly rearranges to form the $(\text{CH}_3)_2\text{CH}^+$ cation. Suggest why this is the case. Explain your answer.

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

17. Phenylethanone is an important chemical with many uses.



Phenylethanone can be synthesised using benzene as one of the starting materials. Identify the other reagents used and describe any essential reaction conditions.

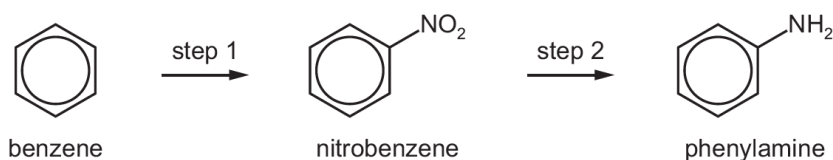
.....
..... [2]

Nitration

<https://www.youtube.com/watch?v=7tsHis091IM>

<https://www.chemtube3d.com/electrophilic-aromatic-substitution-nitration-of-benzene/>

18. Benzene can be used as a starting material to produce phenylamine by a two-step synthesis.

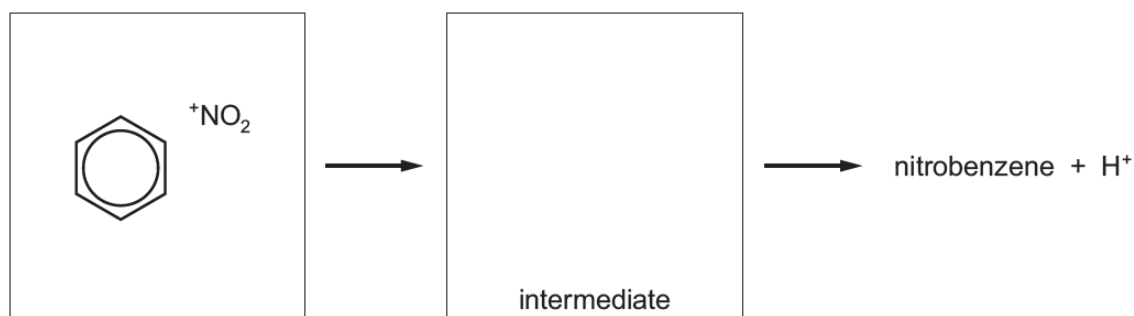


(i) Step 1 is the reaction of benzene with NO_2^+ ions.

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 (i).

..... [1]

(iii) Identify the reagents needed to produce NO_2^+ ions.
Write an equation to explain how these reagents produce NO_2^+ ions.

.....
.....
.....

[2]

(iv) 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]

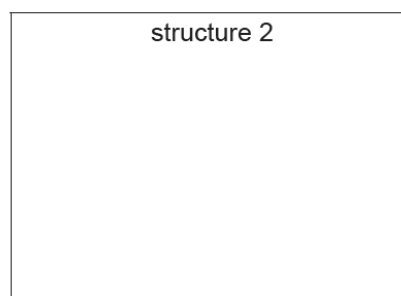
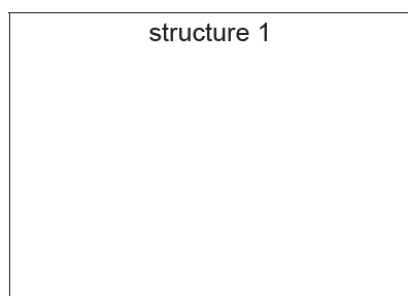
19. Naphthalene, C_{10}H_8 , is an arene hydrocarbon.

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.

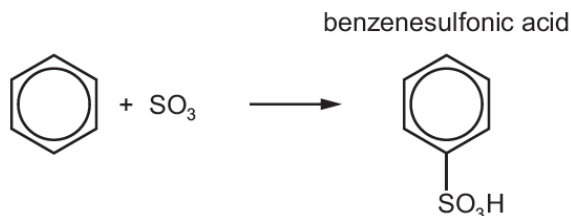
[1]



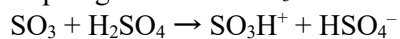
20. Naphthalene can be oxidised under certain conditions to phthalic anhydride, $\text{C}_8\text{H}_4\text{O}_3$, carbon dioxide and water.
Construct an equation for this reaction. Use [O] to represent an atom of oxygen from the oxidising agent.

..... [1]

21. When benzene reacts with SO_3 , benzenesulfonic acid is produced.



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.



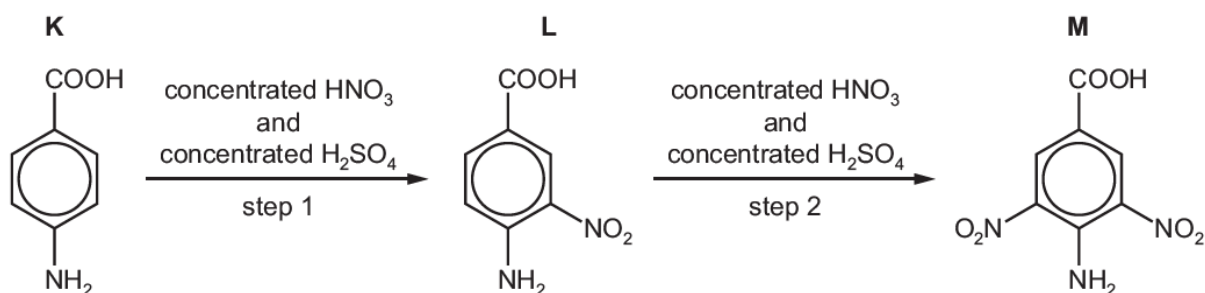
- (i) Draw a mechanism for the reaction of benzene with SO_3H^+ ions. Include all necessary curly arrows and charges. [3]



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

..... [1]

- 1 Compound **K** is used as the starting material in a synthesis of gallic acid. A student suggested the first two steps of the synthesis could be as shown.



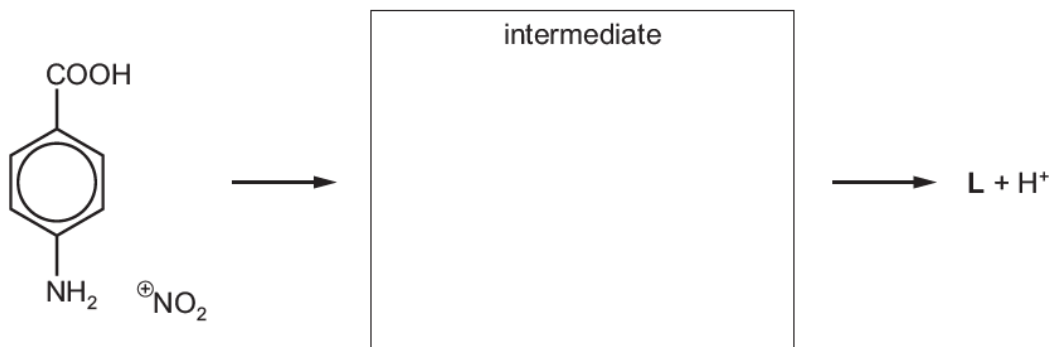
Nitronium ions, NO_2^+ , are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

- (i) Construct an equation for the formation of NO_2^+ by this method.

..... [1]

- (ii) Complete the mechanism and draw the intermediate of step 1.

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



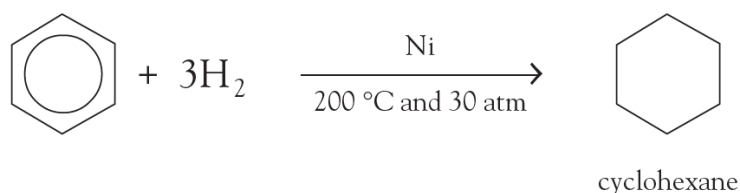
[2]

- (iii) State the name of the mechanism in (c)(ii).

..... [1]

Hydrogenation

Under certain conditions, it can be forced to undergo addition reactions. One of these is the addition of hydrogen. Ethene adds on hydrogen over a nickel catalyst readily at room temperature and slight pressure. Benzene, being more stable, requires an elevated temperature and pressure:



22. Benzene can be converted into cyclohexane.

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

type of reaction

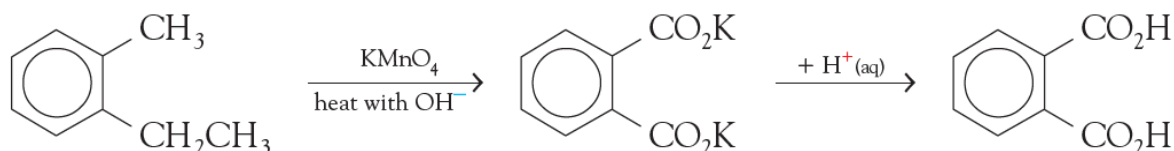
reagent and conditions

[2]

Complete Oxidation of the Side-chain

The presence of the benzene ring in an alkylarene, such as methylbenzene, can affect the characteristic reactions of its alkyl side-chain. For example, alkanes are not usually oxidised by a chemical oxidising agent such as potassium manganate(VII).

However, in alkylarenes, the alkane side-chain is oxidised to form a carboxylic acid. For example, methylbenzene produces benzoic acid when *refluxed* with alkaline potassium manganate(VII), and then acidified with dilute sulfuric acid:



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

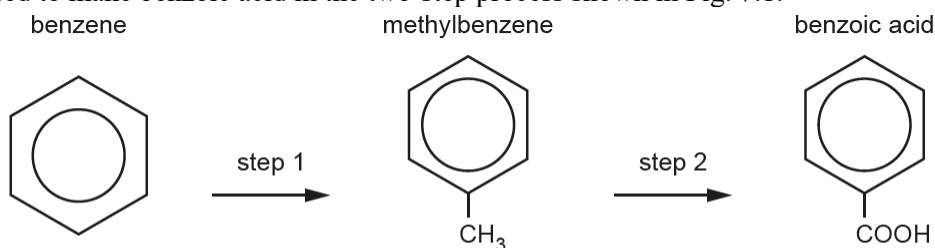


Fig. 7.1

Give the reagents and conditions for step 1 and step 2.

step 1

step 2

[2]

24. Identify a suitable reagent to oxidise methylbenzene to benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$.
Write an equation for this reaction using $[\text{O}]$ to represent one atom of oxygen from the oxidising agent.

reagent

equation [2]

25. Benzene-1,4-dicarboxylic acid, $\text{HOOC-C}_6\text{H}_4\text{-COOH}$, can be made from benzene, C_6H_6 , in two steps as shown in Fig. 6.2.

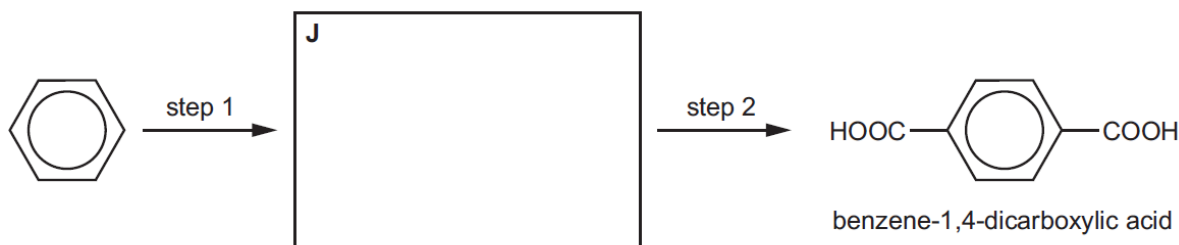


Fig. 6.2

Suggest the identity of J by drawing its structure in the box in Fig. 6.2.

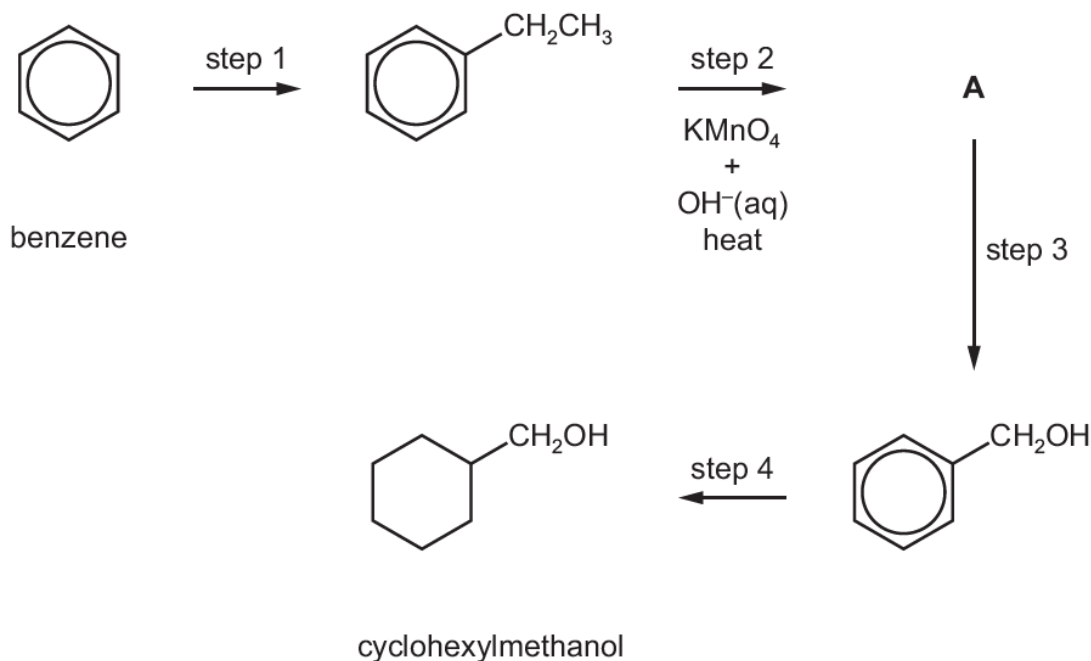
[1]

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

step 1

step 2 [2]

26. Benzene can be used as a starting material in the synthesis of cyclohexylmethanol, $\text{C}_6\text{H}_{11}\text{CH}_2\text{OH}$, as outlined below.



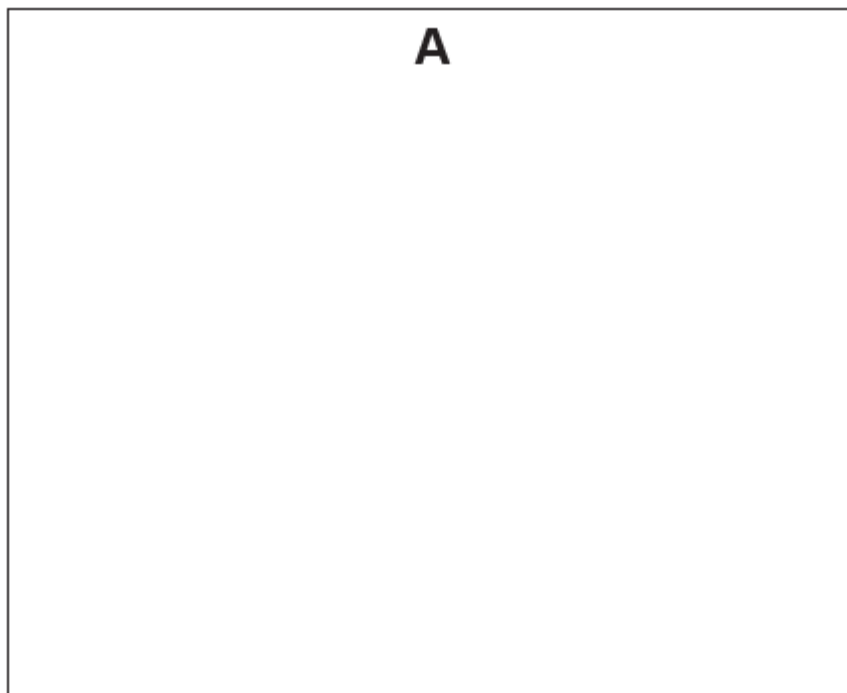
(i) Identify a suitable reagent and a suitable catalyst for step 1.

reagent

catalyst [2]

(ii) Draw the structure of A.

[2]



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

step 3

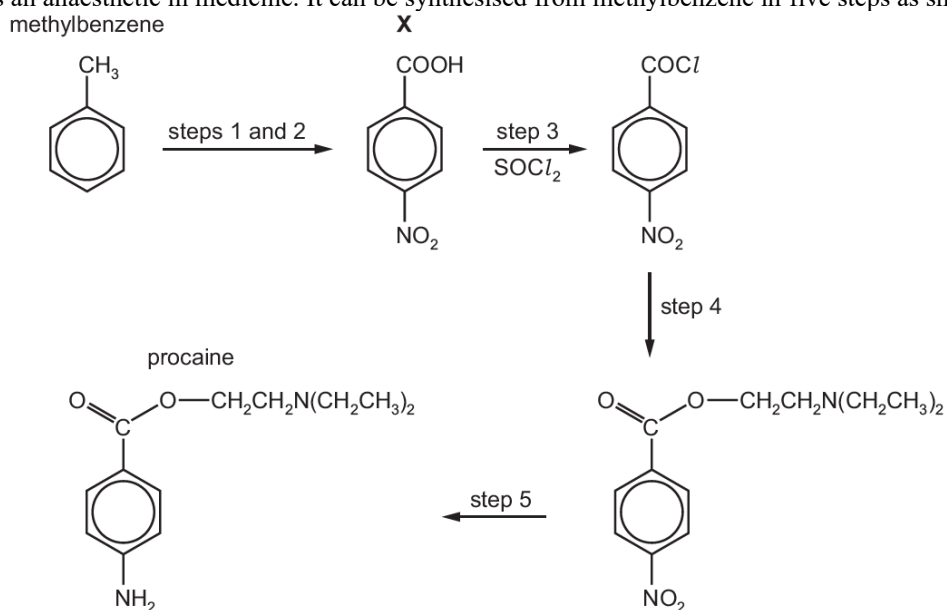
step 4 [2]

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

..... [1]

Reactions of methylbenzene

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



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

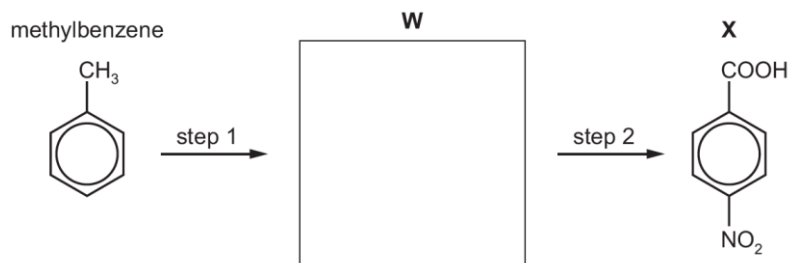


Fig. 7.2

(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]

28. Bromine reacts with methylbenzene in the dark in the presence of a suitable catalyst to form HBr and compound L, C_7H_7Br . L is one of three isomers that can form in this reaction.

(a) (i) The mechanism for the reaction involves methylbenzene reacting with a Br^+ ion. This ion is produced when bromine reacts with the catalyst.

Complete the equation for the reaction of Br_2 with the catalyst.

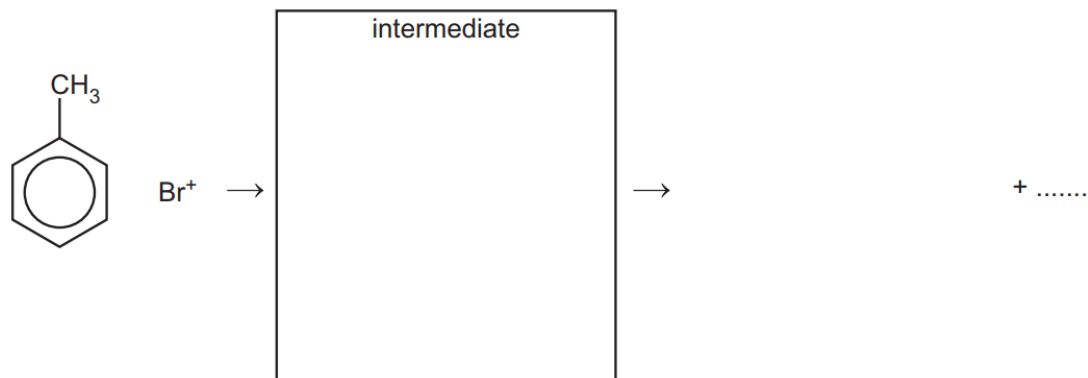
$Br_2 + \dots Br^+ + \dots$ [1]

(ii) One of the isomers of L forms in much smaller amounts than the other two isomers. Draw the structure of this isomer and explain why it forms in the smallest amount.

.....

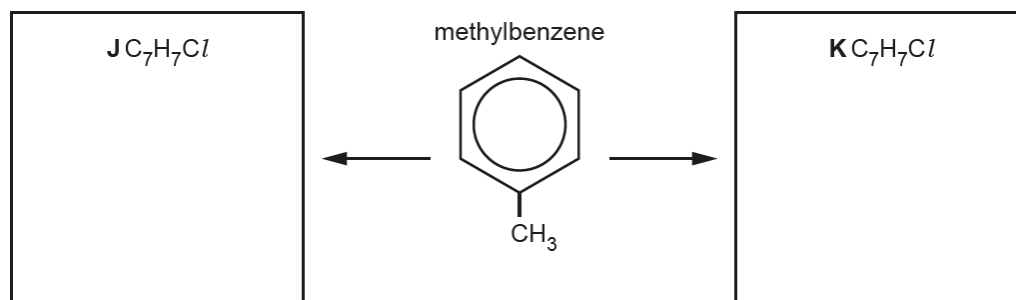
..... [2]

(iii) Complete the mechanism in Fig. 8.1 for the reaction between methylbenzene and the Br^+ ion. Include all relevant curly arrows and charges. [3]



Halogenation of the side chain

29. 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.



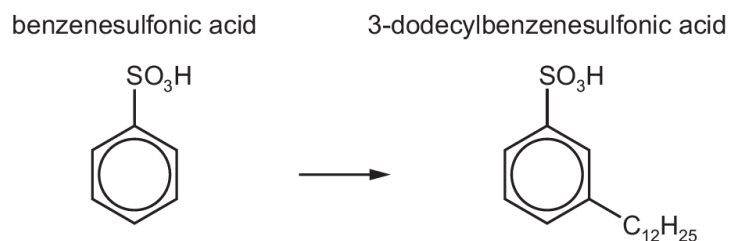
State the reagents and conditions required to form each product.

to form compound J

to form compound K [4]

Electrophilic substitution in substituted arenes

30. 3-dodecylbenzenesulfonic acid can be prepared from benzenesulfonic acid.



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

reagents and conditions

mechanism [2]

31.

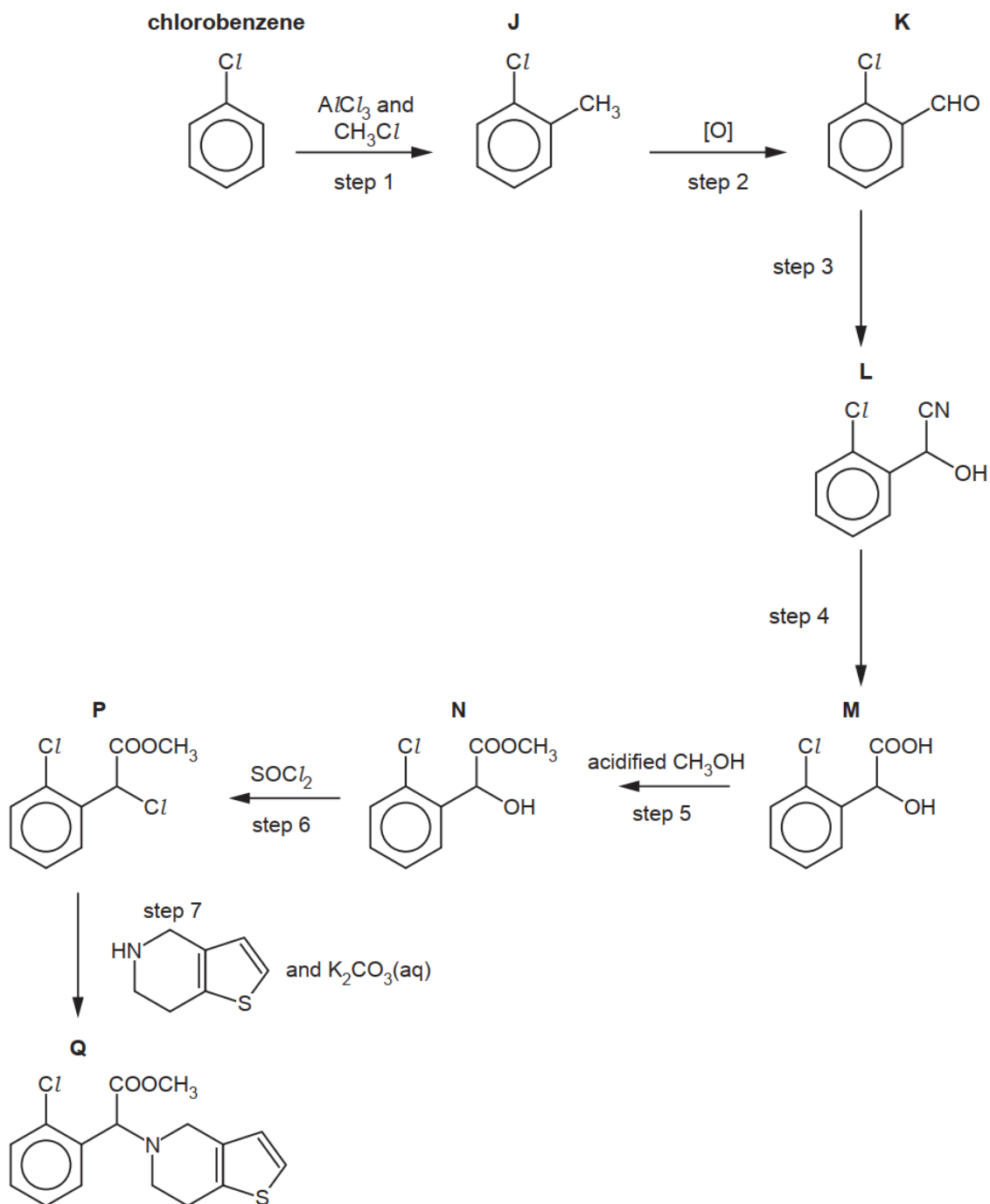


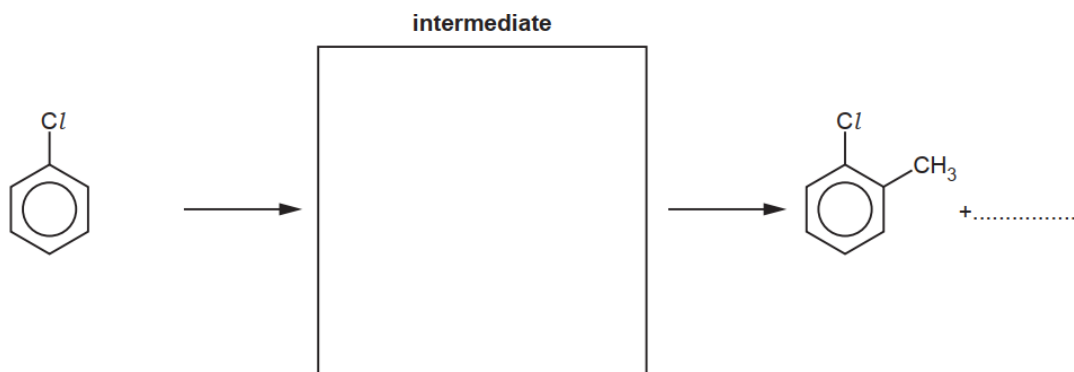
Fig. 5.1

(a) (i) Write an equation for the formation of the electrophile for step 1.

..... [1]

(ii) Complete the mechanism in Fig. 5.2 for step 1, the alkylation of chlorobenzene. Include all relevant curly arrows and charges. Draw the structure of the intermediate

[3]



(iii) Step 2 is an oxidation reaction.

Construct an equation for the reaction in step 2.

Use [O] to represent an atom of oxygen from an oxidising agent.

..... [1]

(iv) Suggest reagents for the conversion of K to M in steps 3 and 4.

step 3

step 4 [2]

(v) Identify the type of reaction that occurs in step 5.

..... [1]

2- and 4-directing substituents	3-directing substituents
$\text{CH}_3 \rightarrow \text{Ar}$	
$\text{H}-\text{O} \rightarrow \text{Ar}$	
$\text{H}_2\text{N} \rightarrow \text{Ar}$	

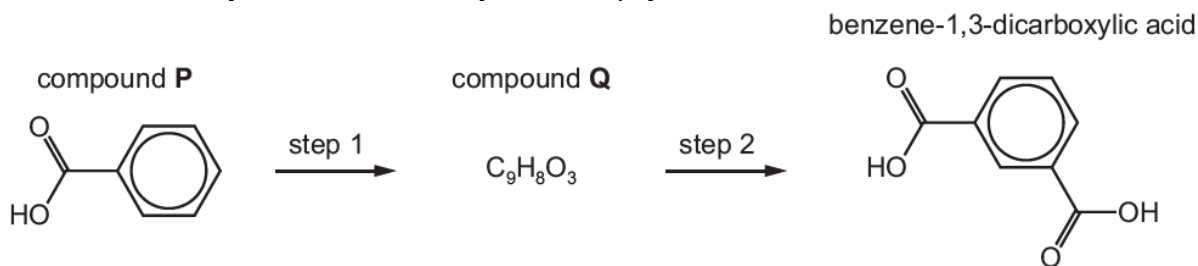
▲ Table 27.6 Substituents and their effects on the benzene ring

32. 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 $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2$ and $\text{HOCC}_6\text{H}_4\text{NO}_2$, respectively.

Draw the structures of these two products.

[1]

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



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

.....
 [1]

(ii) The reagents used for step 1 are CH_3COCl and AlCl_3 . These reagents give rise to $\text{CH}_3\text{C}=\text{O}^+$ ions which react with compound **P**.
 Name the mechanism of this reaction.

..... [1]

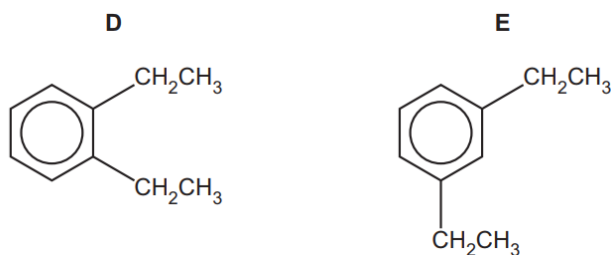
(iii) Draw the mechanism of the reaction of $\text{CH}_3\text{C}=\text{O}^+$ ions with compound **P**. Include all relevant curly arrows and charges, the structure of the intermediate and the structure of compound **Q**. [3]



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

..... [1]

34. A hydrocarbon is known to be either compound **D** or compound **E**.



Give the systematic name of **E**.

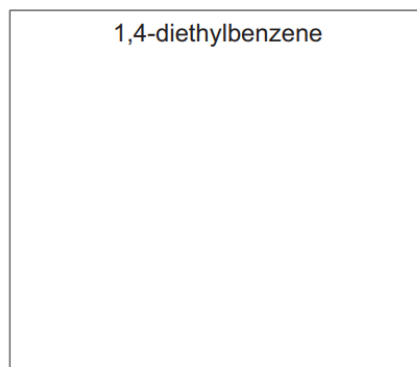
..... [1]

35. Benzene, C_6H_6 , reacts with chloroethane, $\text{C}_2\text{H}_5\text{Cl}$, in the presence of a suitable catalyst to form ethylbenzene, $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$. In the presence of the catalyst, the ion C_2H_5^+ is formed. This ion reacts with benzene.
 (a) Complete the equation for the reaction of $\text{C}_2\text{H}_5\text{Cl}$ with this catalyst to form C_2H_5^+ as one product.

$\text{C}_2\text{H}_5\text{Cl} + \dots\dots\dots \text{C}_2\text{H}_5^+ + \dots\dots\dots$ [1]

(b) Ethylbenzene reacts with more $\text{C}_2\text{H}_5\text{Cl}$, forming a mixture containing 1,2-diethylbenzene and 1,4-diethylbenzene.

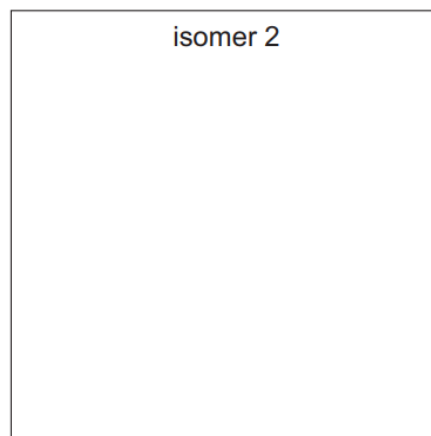
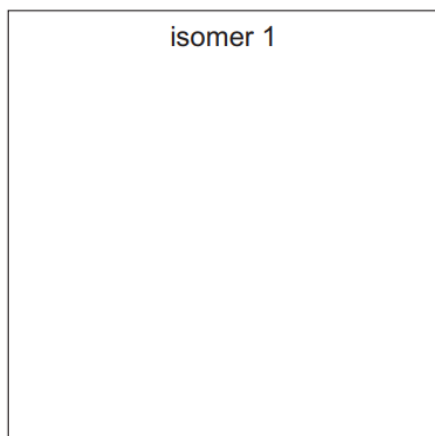
(i) Draw the structures of 1,2-diethylbenzene and 1,4-diethylbenzene.



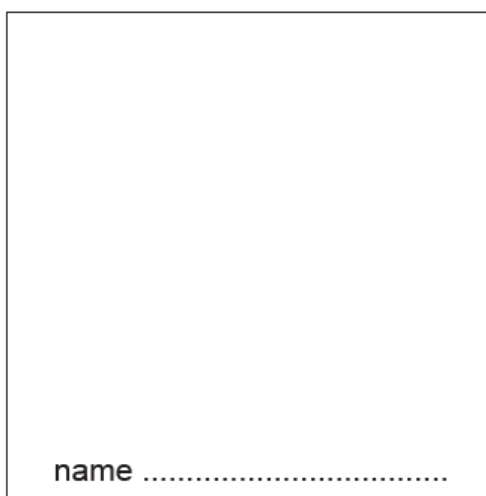
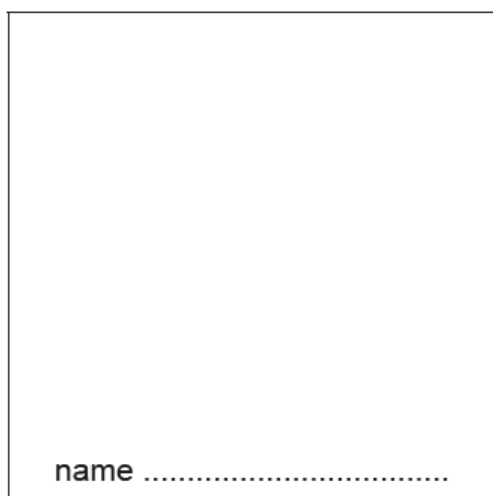
- (i) Explain why there is very little 1,3-diethylbenzene in the product mixture.

.....
 [1]

36. The reaction of phenol with HNO_3 produces a mixture of isomers with molecular formula $\text{C}_6\text{H}_5\text{NO}_3$. Identify the two isomers that are produced in the largest quantities. Explain your answer.



37. Phenol reacts with dilute aqueous nitric acid under room conditions to give a mixture of two isomeric products with molecular formula $\text{C}_6\text{H}_5\text{NO}_3$. Write the structural formulae of these two products in the boxes and name each product.



[2]

38. Draw the structure of the organic product, **R**, formed when phenol reacts with an excess of $\text{Br}_2(\text{aq})$. [1]

38.39.

The second step of a synthesis involves the reaction of chlorobenzene with ClCOCH_2Cl , also in the presence of an AlCl_3 catalyst, forming compound **Q**.

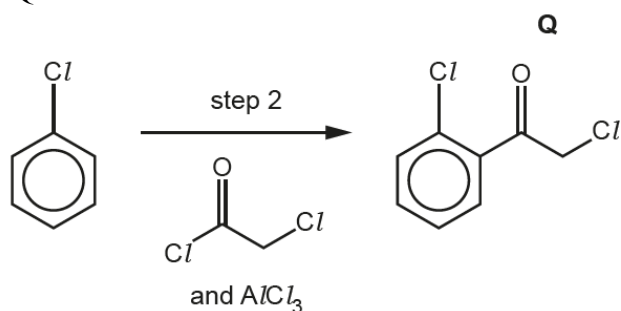


Fig. 5.4

(i) Name the mechanism of the reaction in step 2.

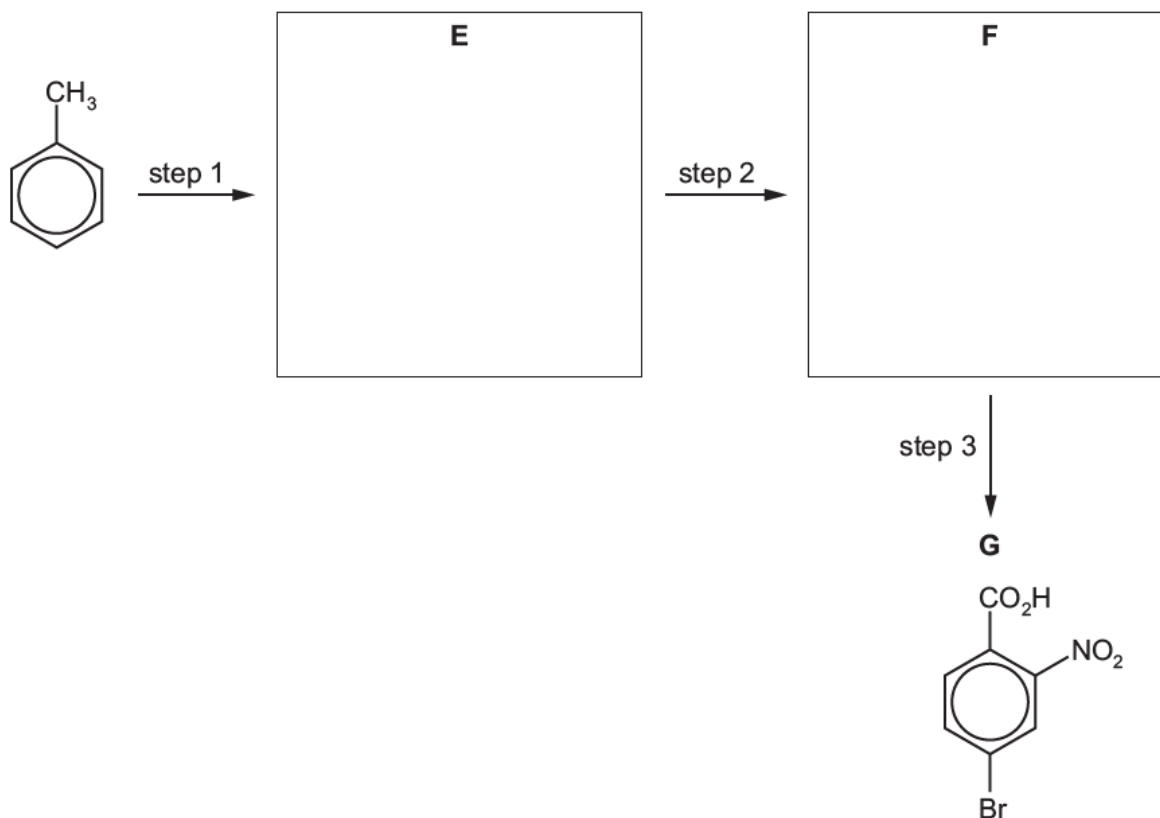
..... [1]

(ii) Draw the structure of an isomer of **Q** that forms as an organic by-product of the reaction in step 2. [1]

39.40.

Compound **G** can be synthesised from methylbenzene in three steps.

C



(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]

40-41.

An excess of $\text{Br}_2(\text{aq})$ is added to separate samples of $\text{C}_6\text{H}_5\text{NH}_2$ and benzene, C_6H_6 .

(i) $\text{C}_6\text{H}_5\text{NH}_2$ reacts readily with $\text{Br}_2(\text{aq})$ to form organic product **M**.

State the expected observations for this reaction. Draw the structure of **M**.

observations

structure of **M**

[2]

(ii) C_6H_6 does not react with $\text{Br}_2(\text{aq})$.

Suggest why $\text{Br}_2(\text{aq})$ reacts with $\text{C}_6\text{H}_5\text{NH}_2$ but not with C_6H_6 .

[2]

41.42.

C

Compound Z can be synthesised from benzene in three steps by the route shown in Fig. 4.1.

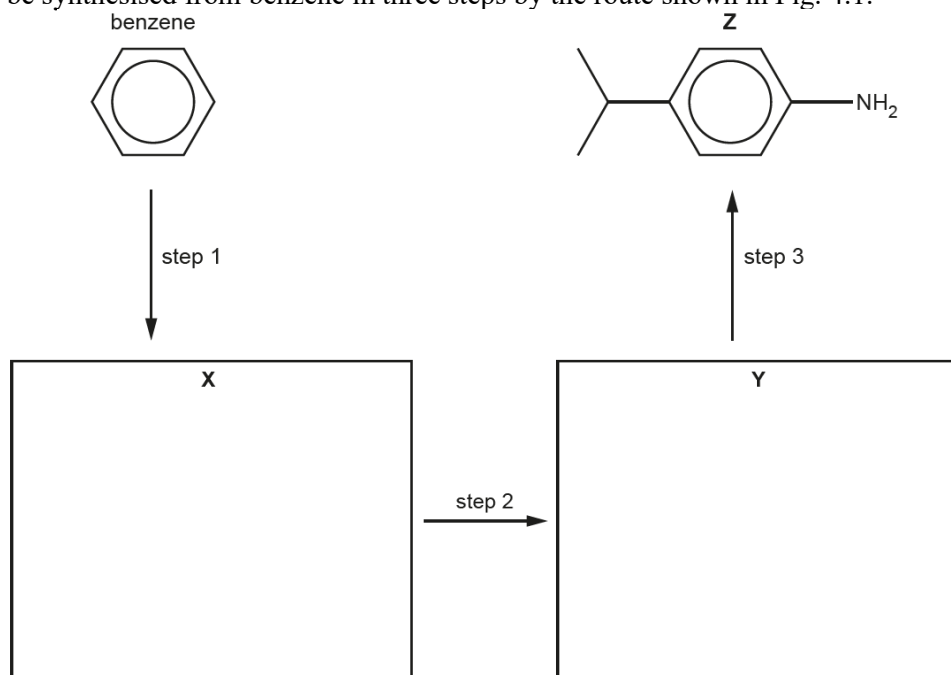


Fig. 4.1

(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

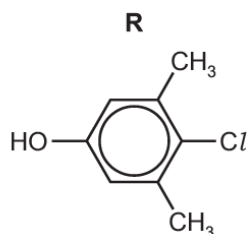
step 3

[3]

42.43.

C

Compound R is shown.



State the systematic name of compound R.

[1]

43.44.

(a

The reagents 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 ₂ SO ₄ catalyst

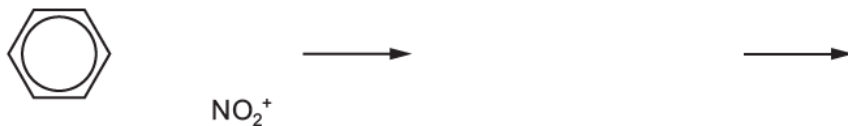
benzoic acid	concentrated HNO_3 , 100°C , concentrated H_2SO_4 catalyst
phenol	dilute $\text{HNO}_3(\text{aq})$, 20°C

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.

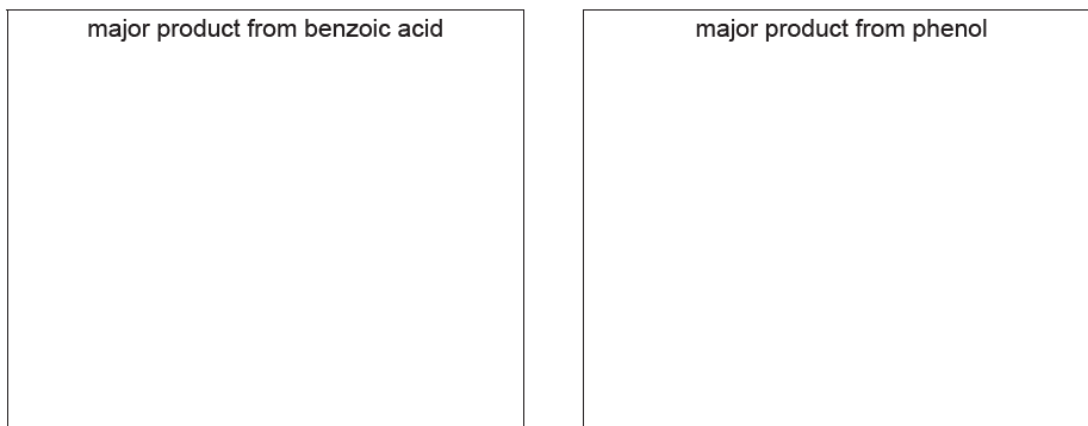
[3]



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

..... [1]

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



(iv) 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

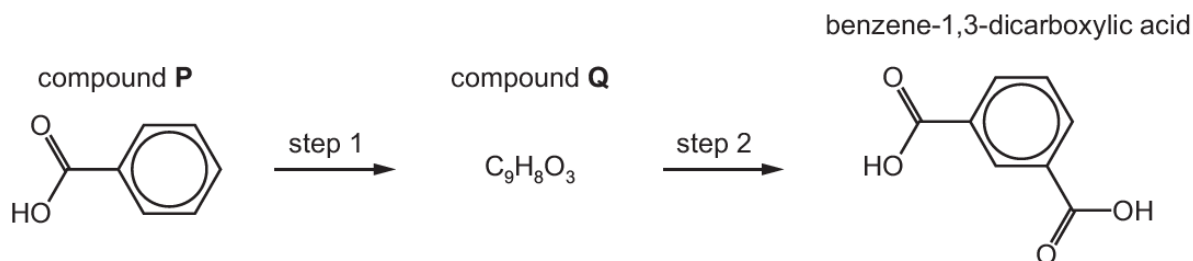
.....
.....
.....
.....
.....
.....

[4]

44.45.

benzene-1,3-dicarboxylic acid can be made by the two-step synthesis shown below.

B



(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.

.....

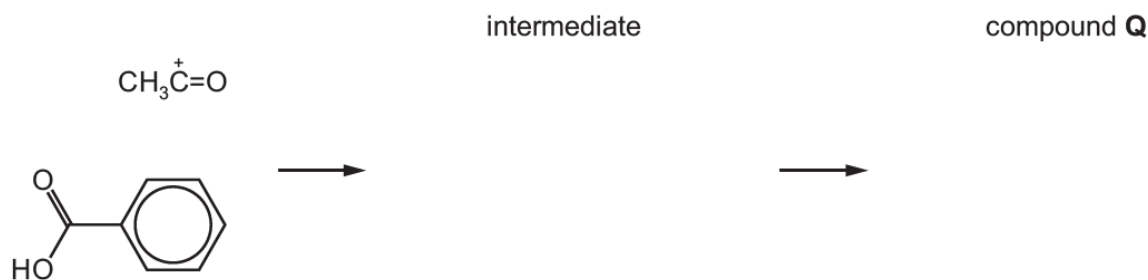
..... [1]

(iii) The reagents used for step 1 are CH_3COCl and AlCl_3 . These reagents give rise to $\text{CH}_3\text{C}=\text{O}^+$ ions, which react with compound P.

Name the mechanism of this reaction.

..... [1]

(iv) Draw the mechanism of the reaction of $\text{CH}_3\text{C}=\text{O}^+$ ions with compound P. Include all relevant curly arrows and charges, the structure of the intermediate, and the structure of compound Q.



[3]

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

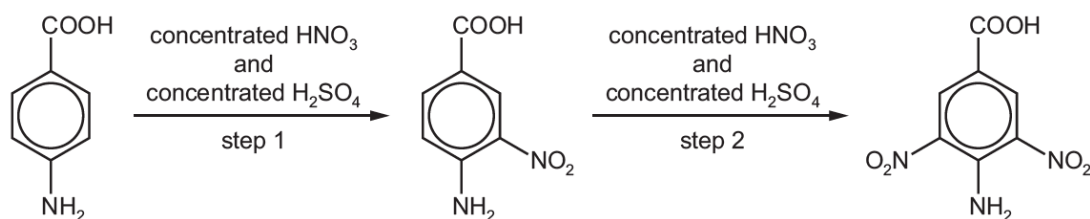
..... [1]

45.46.

C

Compound **K** is used as the starting material in a synthesis of gallic acid.

A student suggested the first two steps of the synthesis could be as shown.



Nitronium ions, NO_2^+ , are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

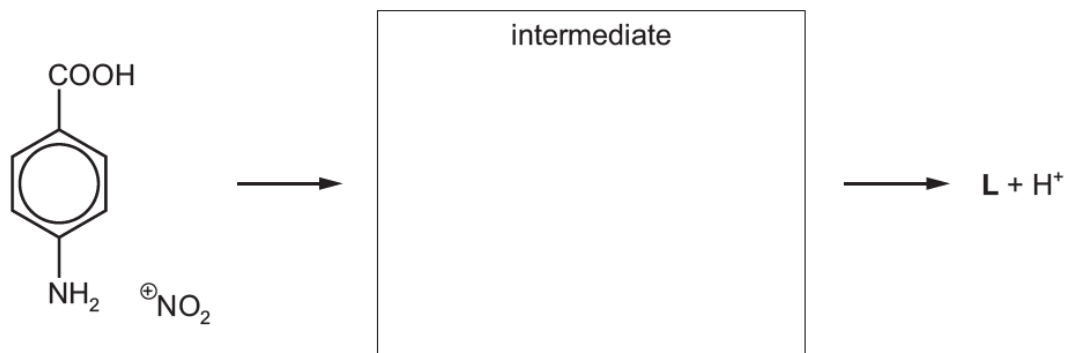
(i) Construct an equation for the formation of NO_2^+ by this method.

..... [1]

(ii) 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]



(iii) State the name of the mechanism in (ii).

..... [1]

46.47.

M

ethylbenzene can undergo different reactions, as shown in Fig. 5.1.

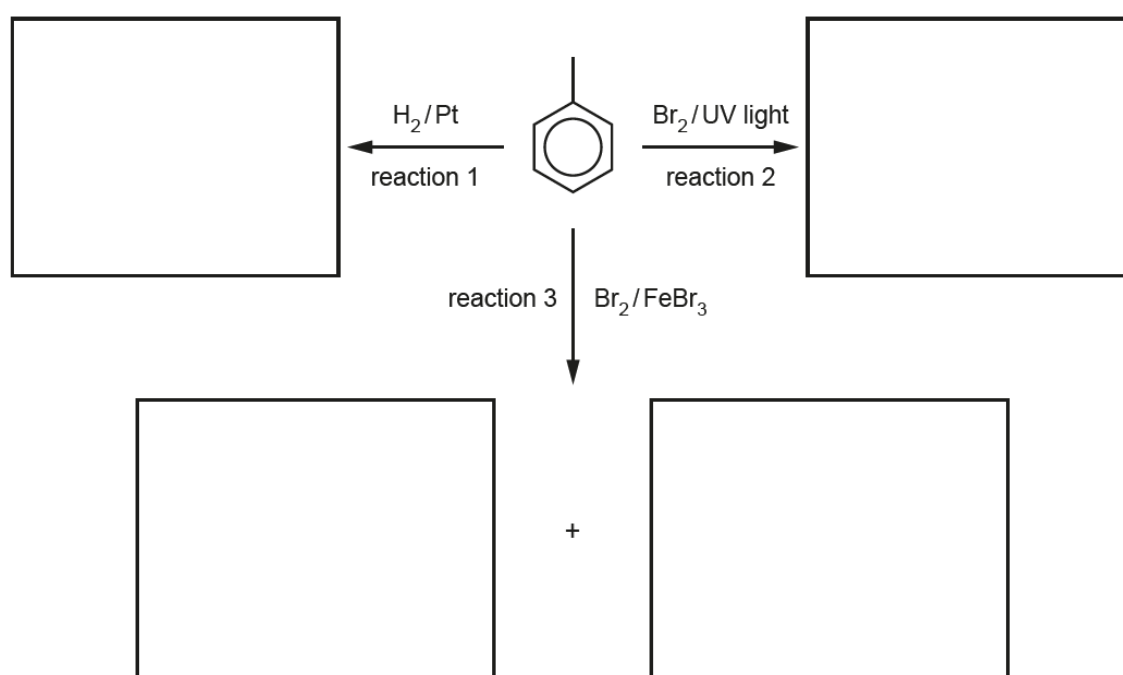


Fig. 5.1

(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.

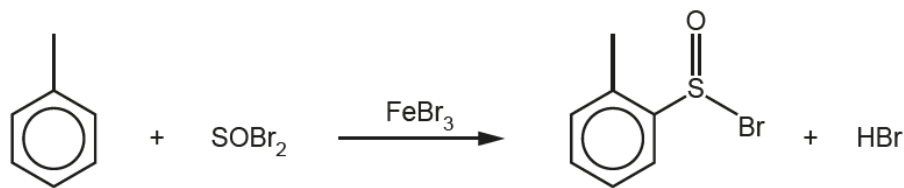
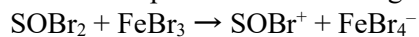


Fig. 5.2

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.



(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.

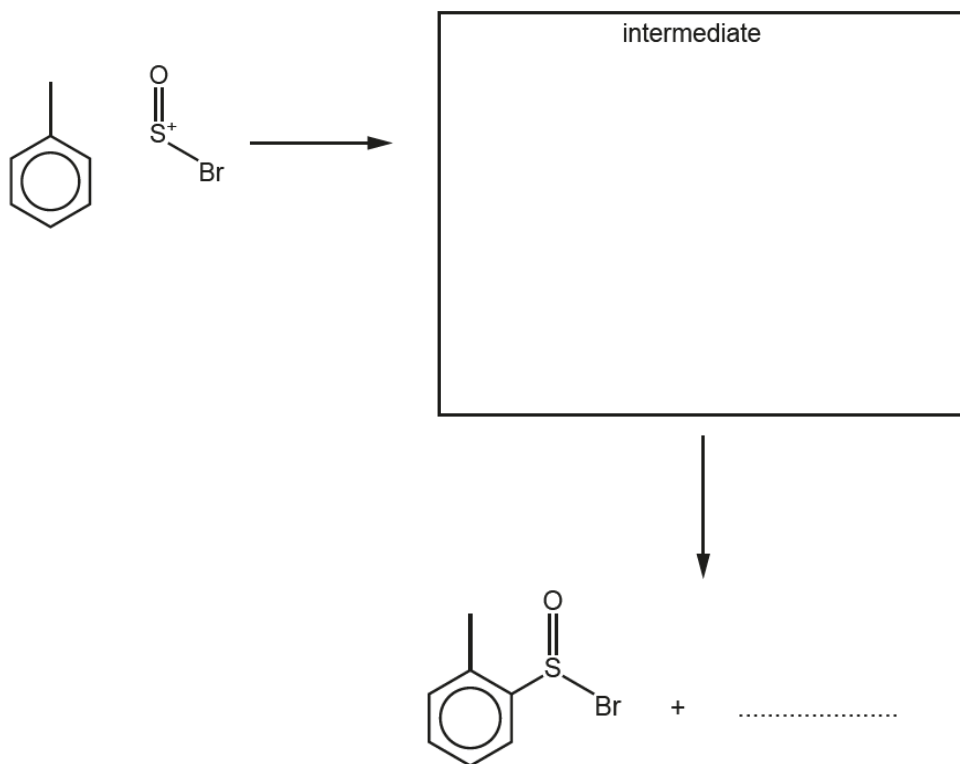


Fig. 5.3

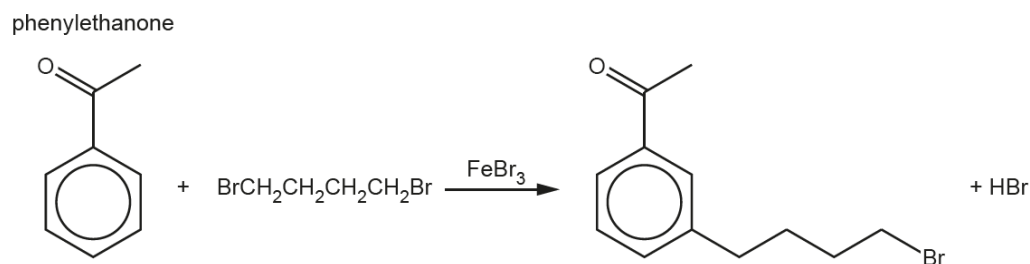
[3]

(ii) The reaction shown in Fig. 5.2 produces a small amount of a by-product, P, with the molecular formula $\text{C}_{14}\text{H}_{14}\text{OS}$.

Suggest a structure for by-product P.

[1]

he reaction of phenylethanone with 1,4-dibromobutane, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, in the presence of FeBr_3 is shown in 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, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$.

..... [1]

(ii) Complete the mechanism in Fig. 6.3 for the reaction of phenylethanone with $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$ ions. Include all relevant curly arrows and charges. Draw the structure of the organic intermediate.

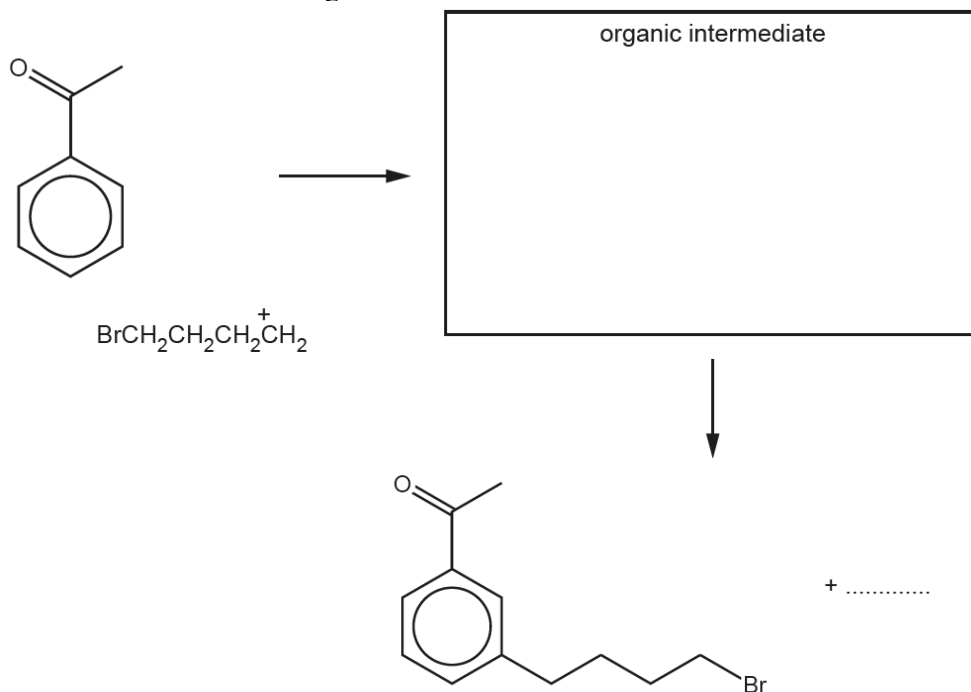


Fig. 6.3

[3]

(iii) The reaction shown in Fig. 6.2 forms small amounts of two by-products, Y ($\text{C}_{20}\text{H}_{22}\text{O}_2$) and Z ($\text{C}_{12}\text{H}_{14}\text{O}$). Suggest structures for Y and Z in the boxes in Fig. 6.4.

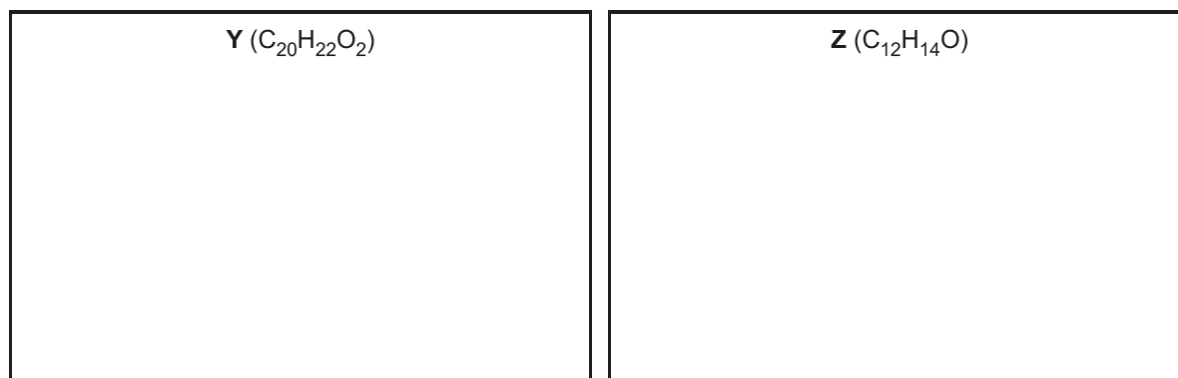


Fig. 6.4

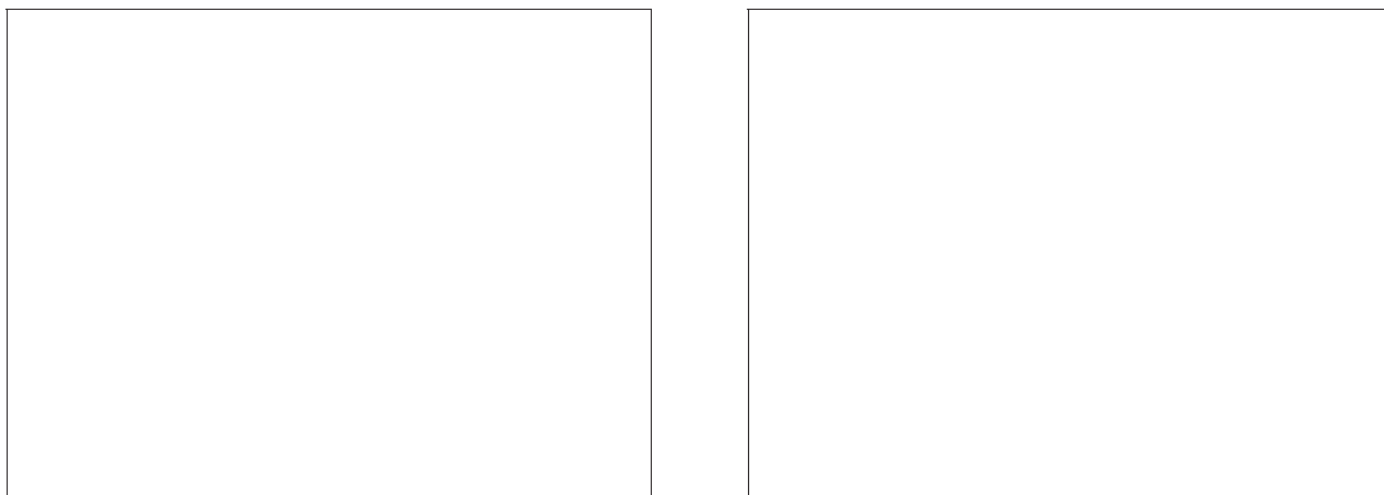
[2]

48.49. _____ (i)

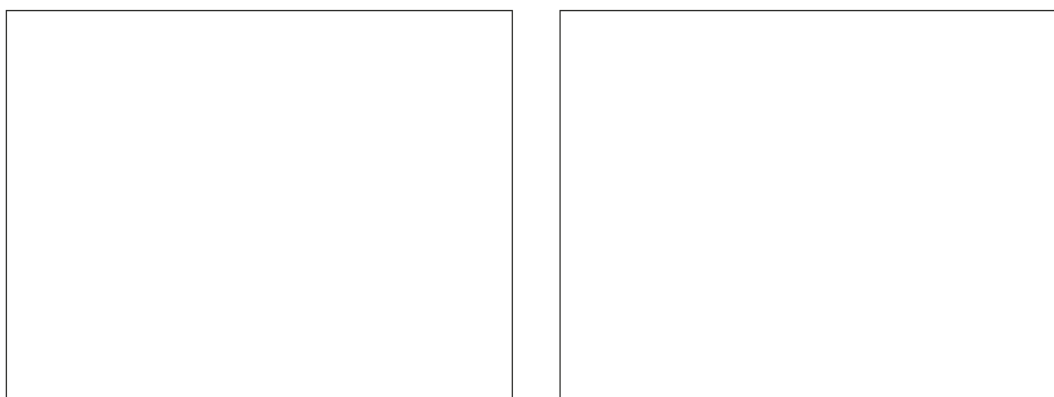
) Name the two products formed when phenol reacts with an excess of $Br_2(aq)$.

..... and [1]

(ii) Draw the structures of the two isomeric organic products, with $Mr = 139$, that are formed when phenol reacts with $HNO_3(aq)$ at room temperature.



49. Draw the structures of the **two** major isomeric organic products formed in the reaction of
50. phenol with dilute HNO_3 .



[1]

(ii) In a second multi-step synthesis, the student changes the order in which the reagents and conditions are used.

The reaction scheme is shown in Fig. 4.2.

G is the major product of this synthesis.

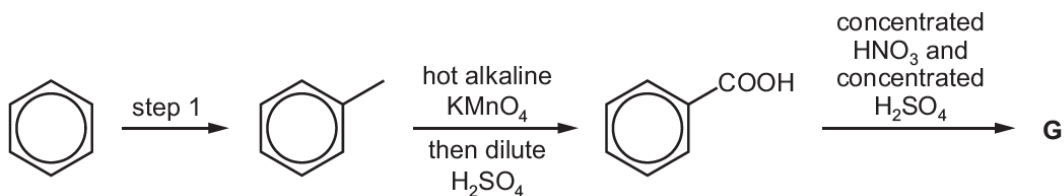
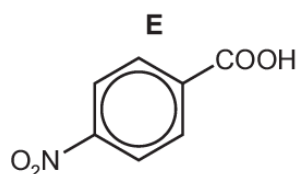


Fig. 4.2

Draw the structure of G.

Explain why G is the major product of the synthesis rather than E.

.....



.....

.....

.....

[2]

51. Phenylamine reacts with Br₂(aq).

(i) Write an equation for this reaction. You may use structural or displayed formulae.

..... [1]

(ii) Name the organic product of this reaction.

..... [1]

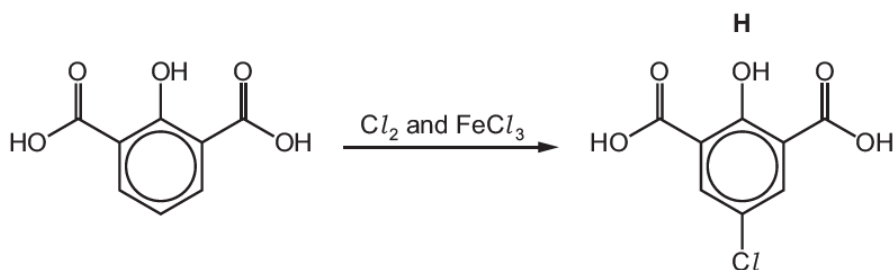
(iii) Describe two observations that can be seen when phenylamine reacts with Br₂(aq).

observation 1

observation 2

[1]

52. Compound **H** is formed in one step of a different synthesis, as shown.



(i) State the role of FeCl_3 in this step.

..... [1]

(ii) Suggest **two** reasons why the chlorine atom in compound **H** substitutes into the ring at the position shown, instead of the other positions in the ring.

2

.....

3

.....

[2]

Ease of Electrophilic Substitution

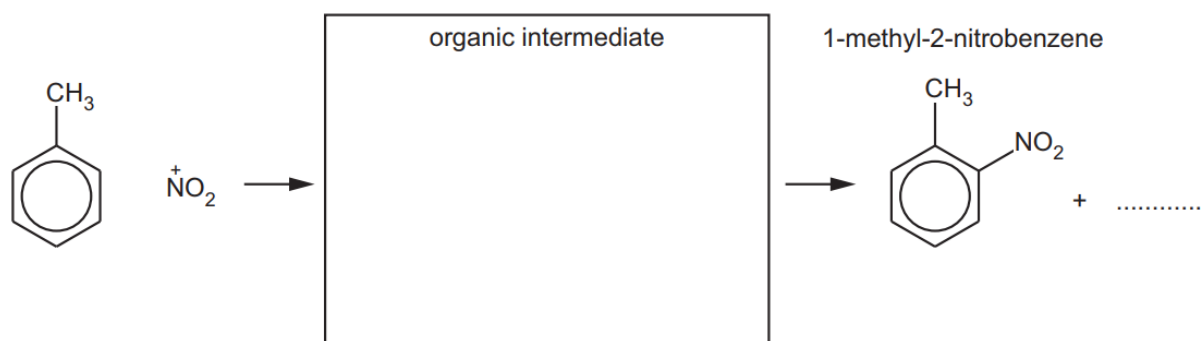


Fig. 6.1

[3]

53. In the electrophilic substitution of arenes, different substituents can direct to different ring positions.

(i) Describe the directing effect of the $-\text{NO}_2$ group. Explain your answer.

.....

..... [1]

(ii) The nitration of arenes uses a mixture of concentrated HNO_3 and concentrated H_2SO_4 to generate the NO_2^+ + electrophile.

Write an equation for the formation of the NO_2^+ electrophile.

..... [1]

54. Carbon-carbon bond formation is an important reaction in organic synthesis.

Fig. 8.1 shows the synthesis of compound Q from benzene in two reaction steps.

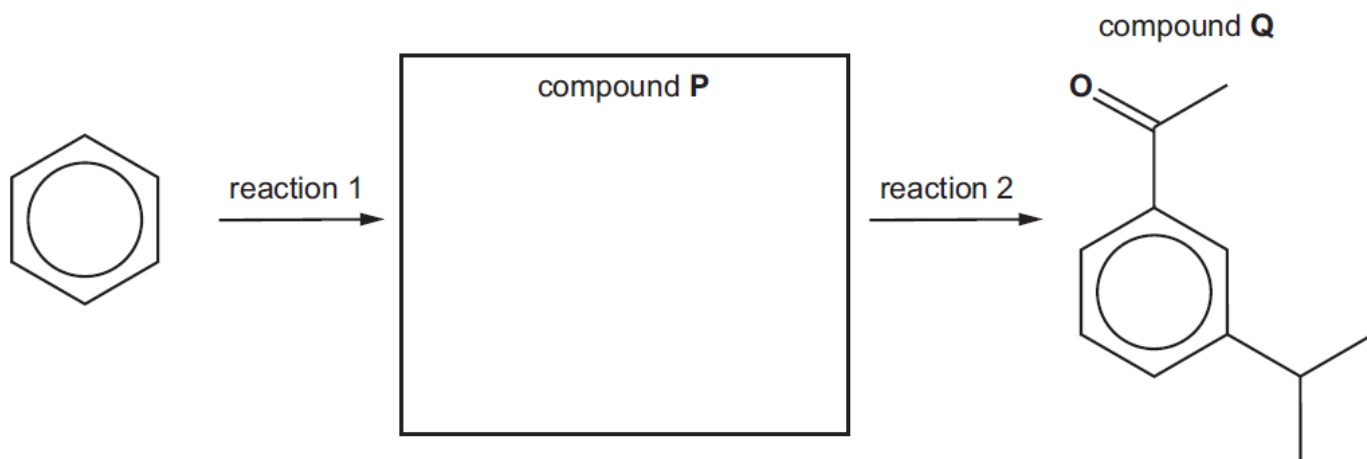


Fig. 8.1

- (i) Draw the structure of compound P in the box in Fig. 8.1. [1]
 (ii) Suggest reagents and conditions for reactions 1 and 2 in Fig. 8.1.

reaction 1

reaction 2 [2]

55. Fig. 5.1 shows two reactions of benzoic acid.

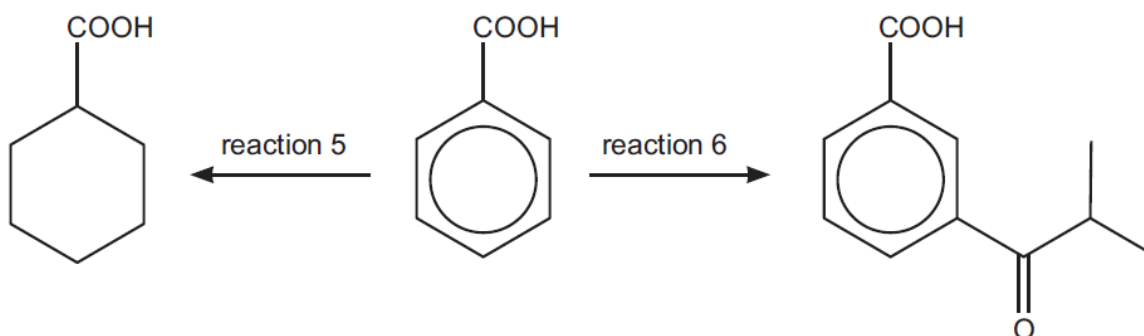


Fig. 5.1

- (i) Suggest reagents and conditions for reaction 5 and for reaction 6 in Fig. 5.1.

reaction 5

reaction 6 [2]

- (ii) State the type of reaction for reaction 5 in Fig. 5.1.

..... [1]

- (c) In the electrophilic substitution of arenes, different substituents can direct to different ring positions.

- (i) Describe the directing effect of the $-\text{CH}_2\text{CH}_3$ group.

Explain your answer.

.....

..... [1]

- (ii) The alkylation of arenes uses a mixture of $\text{CH}_3\text{CH}_2\text{Br}$ and FeBr_3 to generate the CH_3CH_2^+ electrophile. Write an equation for the formation of the CH_3CH_2^+ electrophile.

..... [1]

(iii) Complete the mechanism in Fig. 5.2.

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

[3]

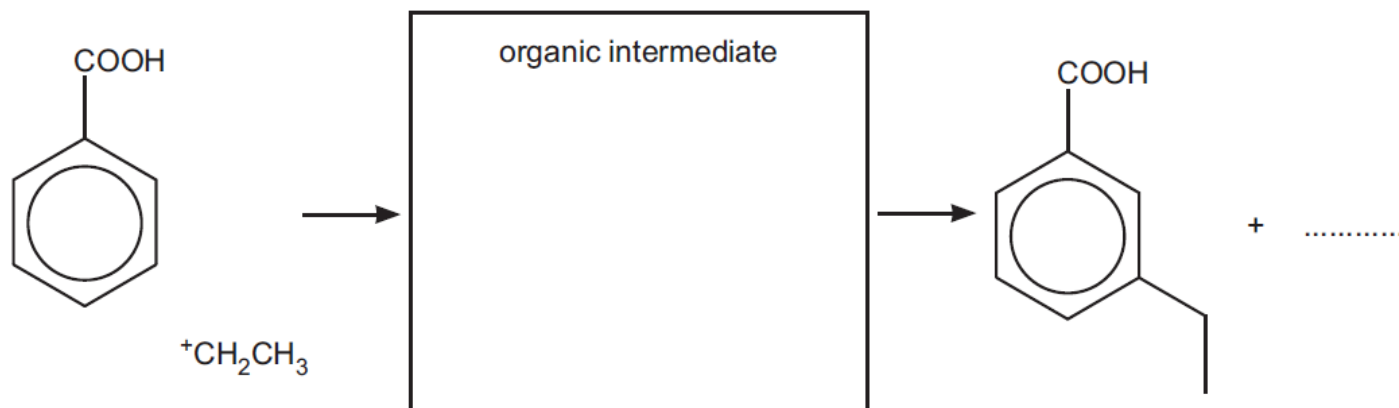


Fig. 5.2

(iv) Write an equation to show how FeBr_3 is regenerated after the reaction in Fig. 5.2.

[3]

..... [1]

*****This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****