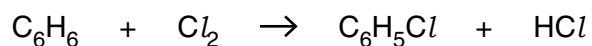


Answer **all** the questions.

- 1** Benzene and other arenes can be chlorinated to produce chloroarenes which are used in the manufacture of pesticides, drugs and dyes.
- (a)** Chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$, is formed by the reaction of benzene and chlorine in the presence of a suitable catalyst, such as AlCl_3 .

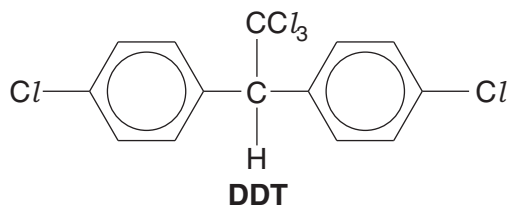


Outline the mechanism for the formation of chlorobenzene from benzene.

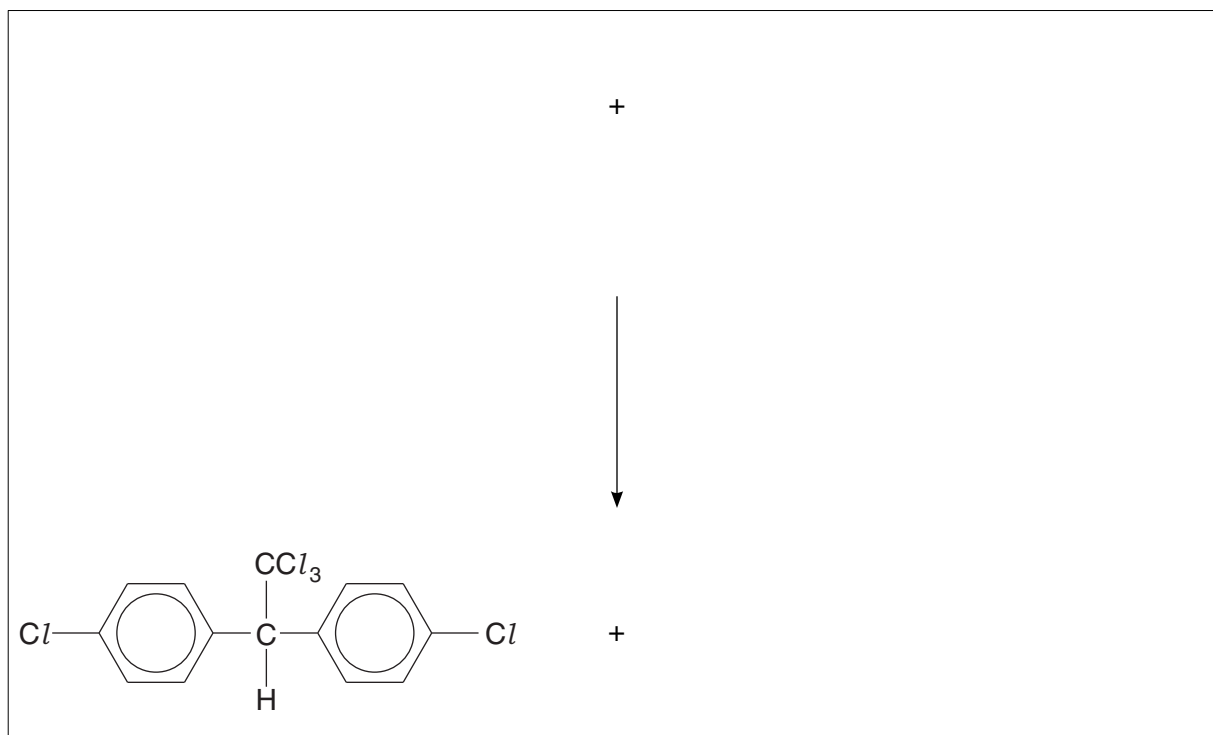
Show how AlCl_3 behaves as a catalyst.

[6]

- (b) Chlorobenzene reacts with trichloroethanal, Cl_3CCHO , to produce the pesticide DDT.



- (i) Construct an equation for the reaction of chlorobenzene with trichloroethanal to form DDT.



[2]

- (ii) Predict the number of peaks in the ^{13}C NMR spectrum of DDT.

..... [1]

- (c) Chlorobenzene can be nitrated to form a mixture of products.

Suggest why the reaction forms a mixture of products.

.....

.....

..... [1]

Turn over

[illegible]

3

2 A student was investigating the reactions and uses of organic amines.

(a) The student found that amines such as ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, and phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, both behave as bases.

(i) Explain why amines can behave as bases.

.....
 [1]

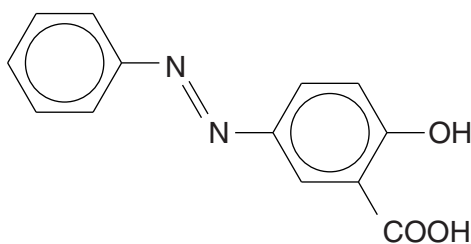
(ii) The student reacted an excess of $\text{C}_2\text{H}_5\text{NH}_2$ with two different acids.

Write the formulae of the salts that would be formed when an **excess** of $\text{C}_2\text{H}_5\text{NH}_2$ reacts with:

sulfuric acid,

ethanoic acid. [2]

(b) The student reacted phenylamine with a mixture of $\text{NaNO}_2(\text{aq})$ and $\text{HCl}(\text{aq})$ whilst keeping the temperature below 10°C . A diazonium ion was formed. The student then reacted the diazonium ion with compound **B**. After neutralisation, compound **A** was formed.



compound **A**

(i) Draw the structures of the diazonium **ion** and compound **B**.

Display the functional group in the diazonium ion.

| | |
|----------------------|-------------------|
| diazonium ion | compound B |
|----------------------|-------------------|

[2]

(ii) State the conditions required for the reaction of the diazonium ion with compound **B** and state a possible use for compound **A**.

conditions

possible use for compound **A**. [1]

- (iii) The student added Na_2CO_3 to a solution of compound **A**.

Draw the structure of the organic product and state the formulae of any other products from this reaction.

[2]

- (c) The student repeated the experiment in part (b) but allowed the temperature to rise above 10°C .

Under these conditions, the diazonium **ion** in (b)(i) reacts with water to produce phenol. A gas with molar mass of 28.0 g mol^{-1} and one other product are also formed.

Construct an equation for this reaction.

[1]

[Total: 9]

Turn over

- 3 Mandelic acid (2-phenyl-2-hydroxyethanoic acid), $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$, is used in some skin creams and can be converted into a condensation polymer.

The addition polymer of ethyl methacrylate (ethyl 2-methyl-2-propenoate), $\text{CH}_2\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_5$, is used to make some artificial fingernails.

- (a) Explain what is meant by the term *condensation polymerisation*.



Your answer should use appropriate technical terms, spelled correctly.

.....

.....

..... [1]

- (b) Draw **two** repeat units of a polymer that is formed when,

(i) mandelic acid, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$, polymerises

[2]

(ii) ethyl methacrylate, $\text{CH}_2\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_5$, polymerises.

[1]

- (c) When ethyl methacrylate, $\text{CH}_2\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_5$, is heated under reflux with aqueous dilute acid, a hydrolysis reaction takes place forming compound **C** and ethanol.

When compound **C** is heated with steam in the presence of an acid catalyst, an addition reaction takes place forming two organic products **D** and **E**.

Compounds **D** and **E** are structural isomers with the molecular formula $\text{C}_4\text{H}_8\text{O}_3$.

Draw the structures of compounds **C**, **D** and **E**.

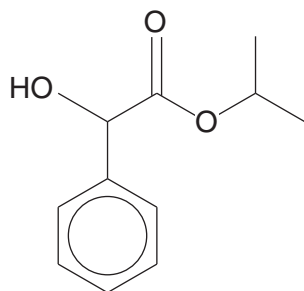
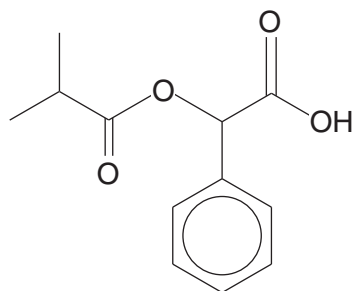
| |
|-------------------|
| |
| compound C |
| |
| compound D |
| |
| compound E |

[3]

TURN OVER FOR PART (d)

Turn over

- (d) Mandelic acid has anti-bacterial properties and is used in some skin creams. A cosmetic chemist used mandelic acid to prepare two different esters that might be suitable for new skin creams. The structures of the two esters are shown below.

**ester 1****ester 2**

- (i) Draw the structure of an organic compound that could react with mandelic acid, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$, to produce **ester 1**.

[1]

- (ii) Identify an organic compound that could react with mandelic acid to produce **ester 2**.

[1]

- (iii) **Ester 1** is less soluble in water than mandelic acid, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$.

Explain the difference in water solubility of mandelic acid and **ester 1**.

You may use a labelled diagram in your answer.

.....

.....

.....

.....

.....

..... [3]

- (iv) Before any skin cream can be sold to the public, it must be tested to ensure it is safe to use.

Suggest why.

.....

..... [1]

[Total: 13]

Turn over

- 4** 'Methylglyoxal', CH_3COCHO , is formed in the body during metabolism.

Describe **one** reduction reaction and **one** oxidation reaction of methylglyoxal that could be carried out in the laboratory.

Your answer should include reagents, equations and observations, if any.

..... [5]

[Total: 5]

- 5 Forest fires release a large number of organic compounds into the atmosphere, many in very small quantities.

(a) Compounds in the smoke from forest fires can be analysed using GC-MS.
Explain how GC-MS enables the compounds to be identified.

.....

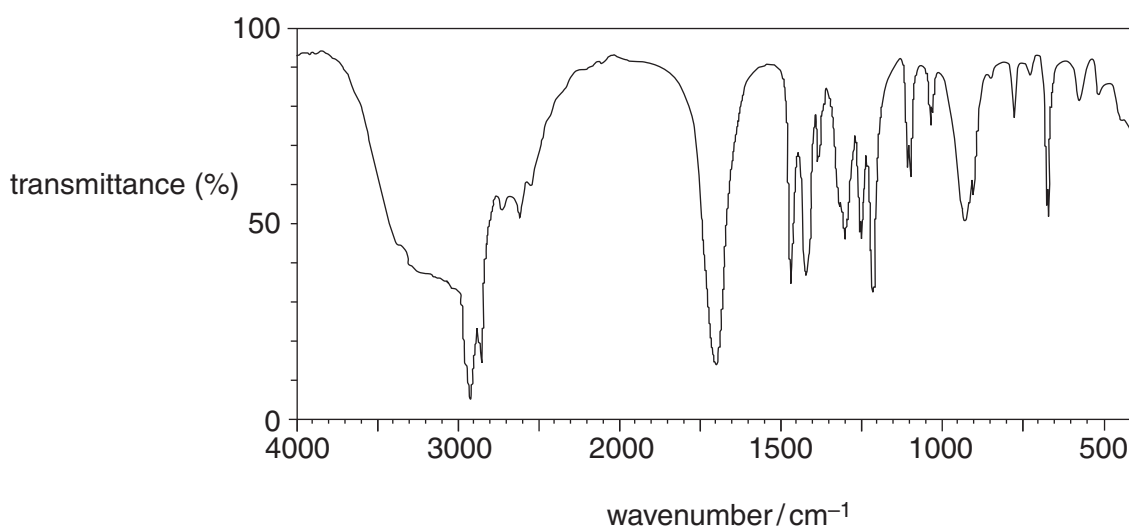
 [2]

(b) Compound **F** was found to be present in the smoke.
Compound **F** contains C, H and O only and contains 54.2% oxygen by mass.
The molar mass of compound **F** is 118.0 g mol^{-1} .

- (i) Using the information, show that the molecular formula of compound **F** is $\text{C}_4\text{H}_6\text{O}_4$.
Show all of your working.

[2]

(ii) The infrared spectrum of compound **F** is shown below.

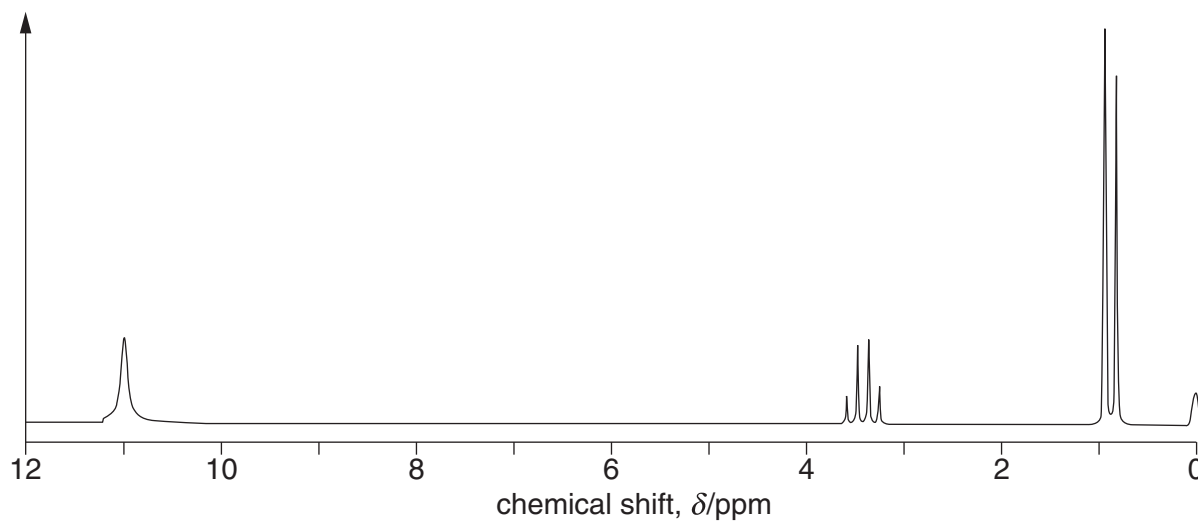


Using this spectrum, name the functional group present in compound **F**.

..... [1]

Turn over

- (c) Compound **F**, $\text{C}_4\text{H}_6\text{O}_4$, was dissolved in deuterated dimethylsulfoxide, $(\text{CD}_3)_2\text{SO}$, and some tetramethylsilane, TMS, was added. The proton NMR spectrum of compound **F** is shown below.



The peak centred at $\delta = 3.4 \text{ ppm}$ would normally be expected at a chemical shift value about 1 ppm to the right, i.e. 2.4 ppm.

- (i) Using the chemical shifts and splitting patterns, deduce the structural formula of compound **F**.

Explain your reasoning.

.....

.....

.....

.....

.....

.....

.....

.....

..... [4]

- (ii) Explain why deuterated dimethylsulfoxide, $(\text{CD}_3)_2\text{SO}$, is used as the solvent rather than $(\text{CH}_3)_2\text{SO}$.

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

- (iii) State why TMS was added.

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

- (iv) A second proton NMR spectrum of compound **F** was obtained after adding a few drops of D_2O .

What difference would you expect to see between the proton NMR spectra of compound **F** obtained with and without D_2O ?

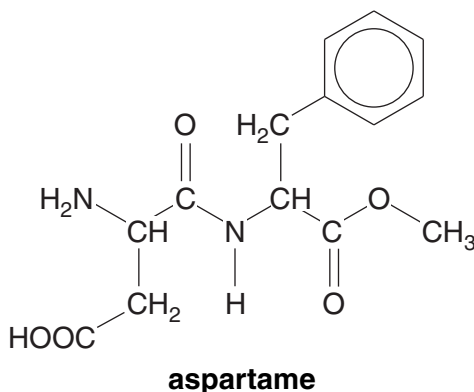
.....
.....
..... [1]

[Total: 12]

Turn over

- 6 The addition of sucrose, table sugar, to food and drink has been linked to the increased risk of obesity and insulin resistance. Aspartame is used as an alternative to sugar.

The structure of aspartame is shown below.



- (a) Aspartame contains five functional groups including the benzene ring, and has two chiral carbon atoms.

(i) Circle the **two** chiral carbon atoms on the structure above. [1]

(ii) **Name** the **four** functional groups, other than the benzene ring, in aspartame.

.....

..... [2]

- (b) Aspartame consumed in food or drink might be hydrolysed by the acid in the stomach. This acid consists mainly of hydrochloric acid.

Draw the structures of the **three** organic products formed by the **complete** acid hydrolysis of aspartame.

[4]

- (c) Some artificial sweeteners commonly available many years ago have now been withdrawn from use.

Suggest why.

.....

..... [1]

[Total: 8]

END OF QUESTION PAPER