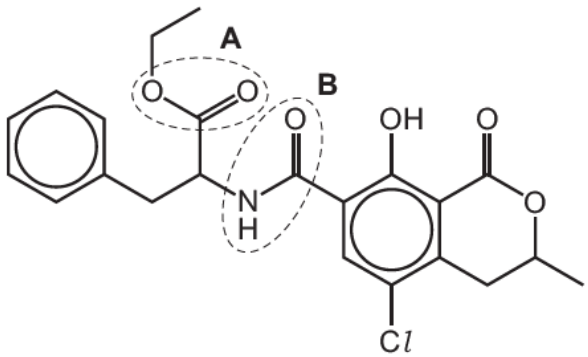
Organic synthesis - 2021

1. March/2020/Paper_42/No.4

Compound **F** has been found in small quantities in some cereals and dried fruit.

F



(a) (i) Give the name of the functional groups labelled **A** and **B**.

A .....

B .....

[2]

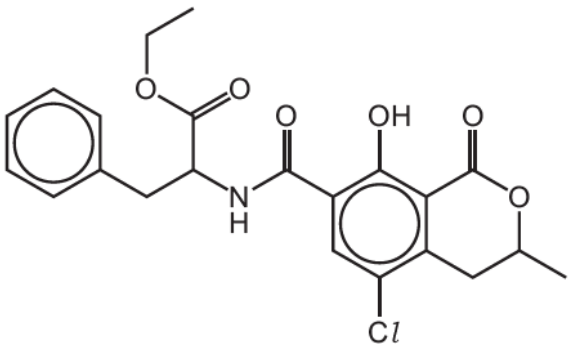
(ii) State the number of chiral carbon atoms in one molecule of **F**.

..... [1]

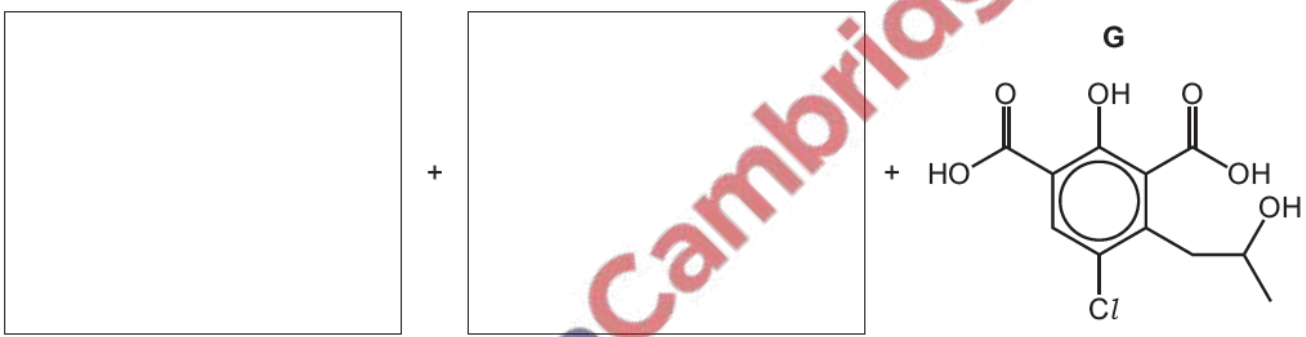
(b) **F** can be hydrolysed by heating with an excess of dilute hydrochloric acid, as shown.

Three products are formed: **G** and two others.

F

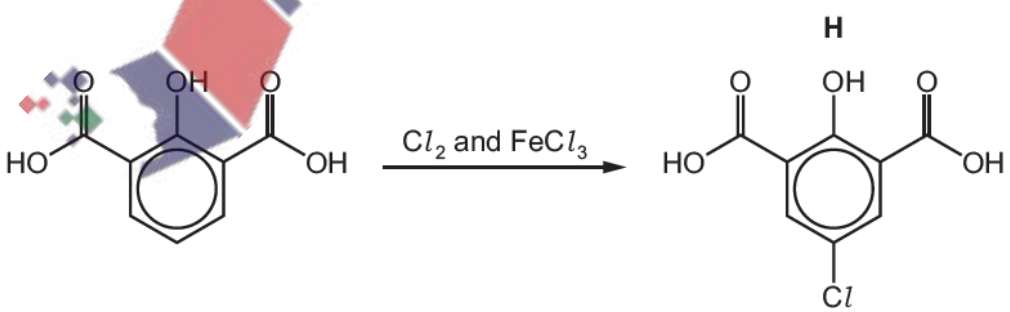


excess dilute HC*l*



Draw the structures of the other products of the reaction in the boxes provided. [3]

(c) 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) Use the *Data Booklet* to 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.

1 .....

.....

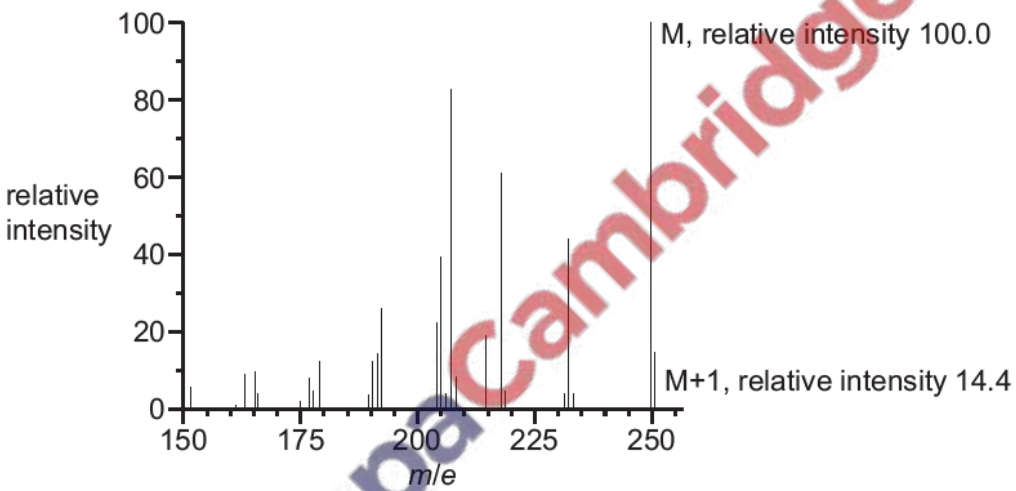
2 .....

.....

[2]

(d) Compound **J**, $C_xH_yO_z$, is also found in some cereals.

Part of the mass spectrum of **J** is shown. The M and M+1 peaks are labelled, along with their relative intensities.



(i) Calculate the number of carbon atoms, *x*, present in **J**.

x = ... [2]

(ii) The mass spectrum has a peak at *m*/*e* = 205.

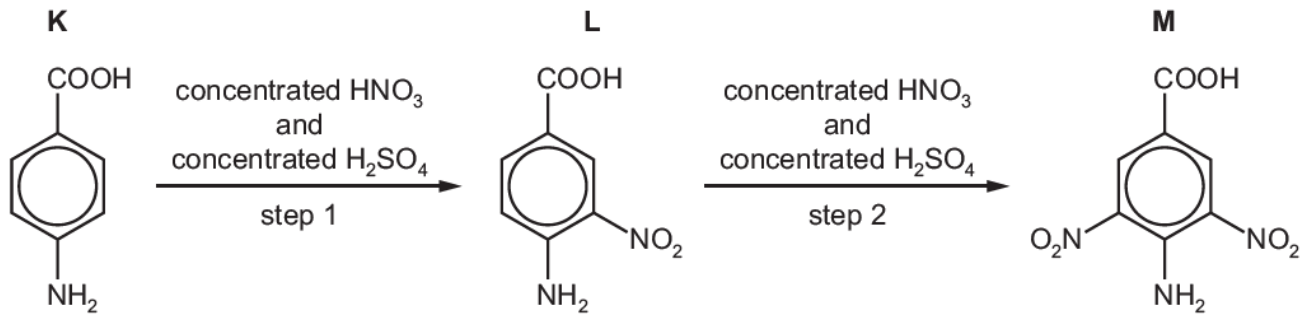
Suggest the identity of the fragment lost from **J** to form this peak.

..... [1]

[Total: 12]

(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.

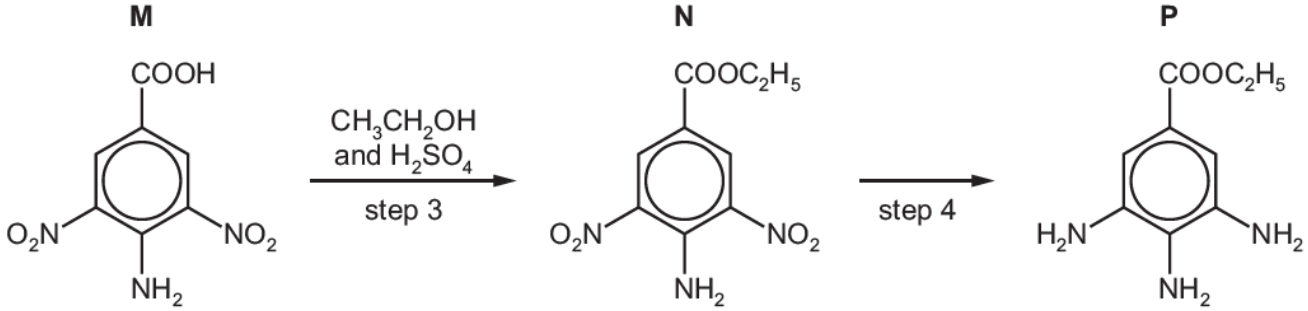
Include all relevant charges and curly arrows to show the movement of electron pairs.

[2]

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

..... [1]

Compound **M** is converted into compound **P** as shown.

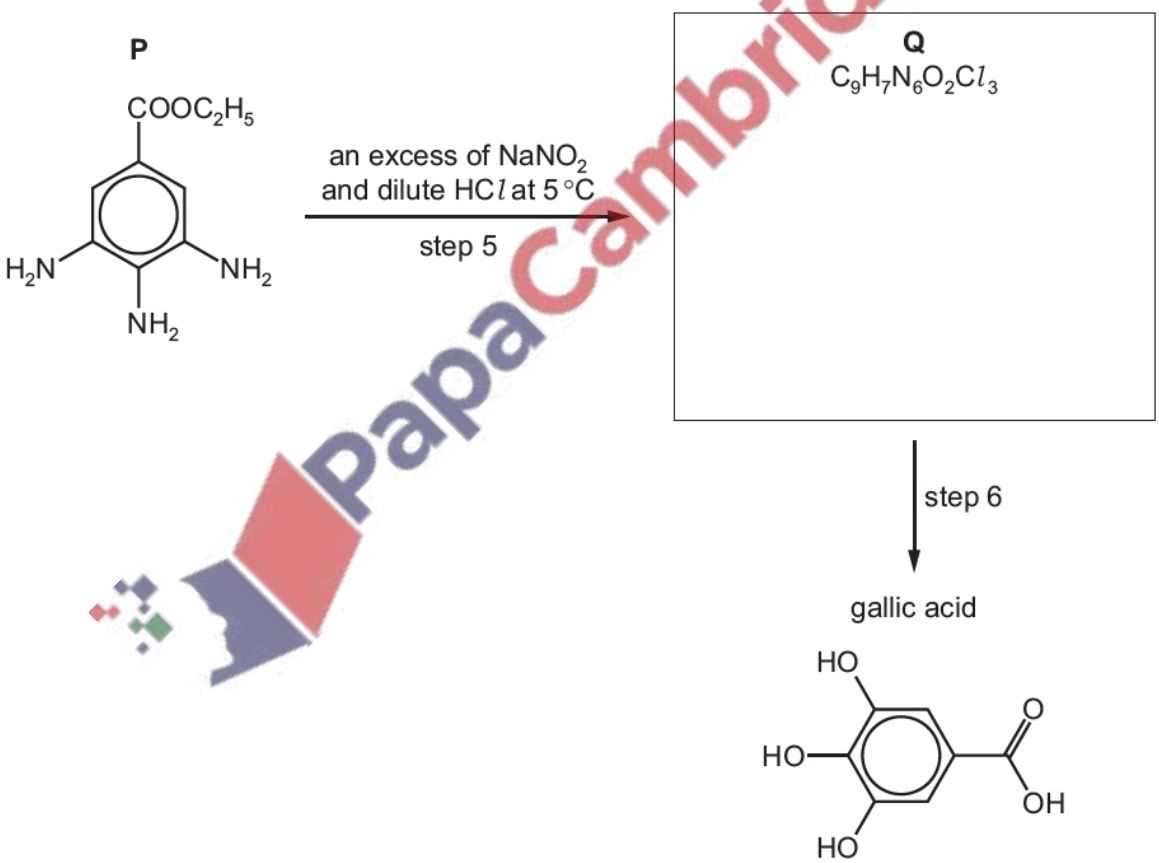


(iv) State the reagents and conditions for step 4.

..... [2]

P reacts with an excess of sodium nitrite, $NaNO_2$, and dilute HCl at 5 °C to form compound **Q**, $C_9H_7N_6O_2Cl_3$.

Compound **Q** is then converted into gallic acid.



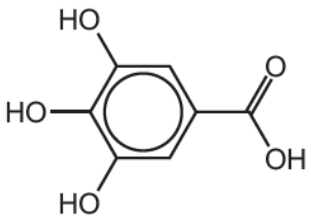
(v) Suggest the structure of compound **Q** in the box provided. [2]

(vi) State the reagents and conditions for step 6.

..... [1]

(d) (i) State the number of peaks that would be observed in the ^{13}C NMR spectrum of gallic acid.

gallic acid



..... [1]

(ii) The proton NMR spectrum of gallic acid dissolved in D_2O is recorded.

- Predict the number of peaks observed and any expected splitting pattern.
- State the expected chemical shift range (δ) of each peak predicted.

.....

.....

..... [2]

3. June/2020/Paper_42/No.5

(a) Define the term *partition coefficient*, K_{pc}.

.....

.....

..... [2]

(b) K_{pc} of benzoic acid between octan-1-ol and water is 79.4.

(i) A solution of 0.400 g of benzoic acid in 25.0 cm^3 octan-1-ol is shaken with 125 cm^3 of water.

Calculate the mass of benzoic acid extracted into the water layer.

mass of benzoic acid extracted = ... g [2]

(ii) K_{pc} of benzophenone, $C_6H_5COC_6H_5$, between octan-1-ol and water is different from the value of K_{pc} of benzoic acid given in **(b)(i)**.

Explain why.

.....

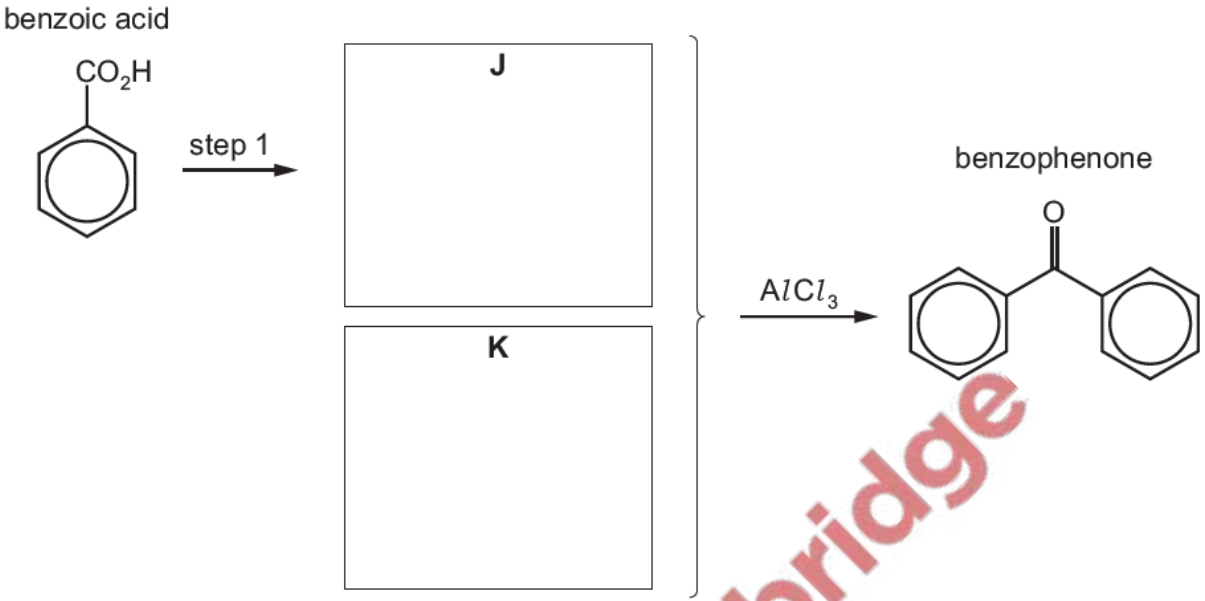
.....

..... [1]

(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.

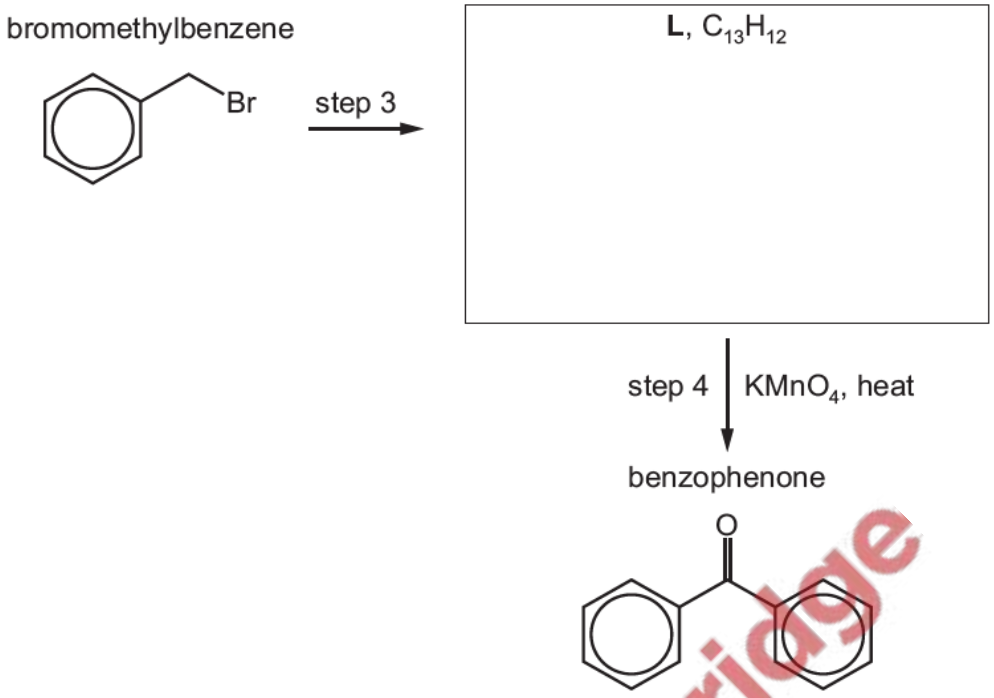


(i) Deduce the identities of organic compounds **J** and **K** and draw their structures in the boxes. [2]

(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]

(e) (i) Deduce the number of peaks that would be present in the carbon-13 NMR spectrum of benzophenone.

number of peaks ..... [1]

(ii) Identify **two** different environments of carbon atom that would result in different chemical shift ranges in this carbon-13 NMR spectrum of benzophenone.

environment of carbon atom	chemical shift range (δ)

[2]

[Total: 15]