34. Nitrogen compounds

34.2 Phenylamine and azo compounds

Paper 4

Question Paper

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

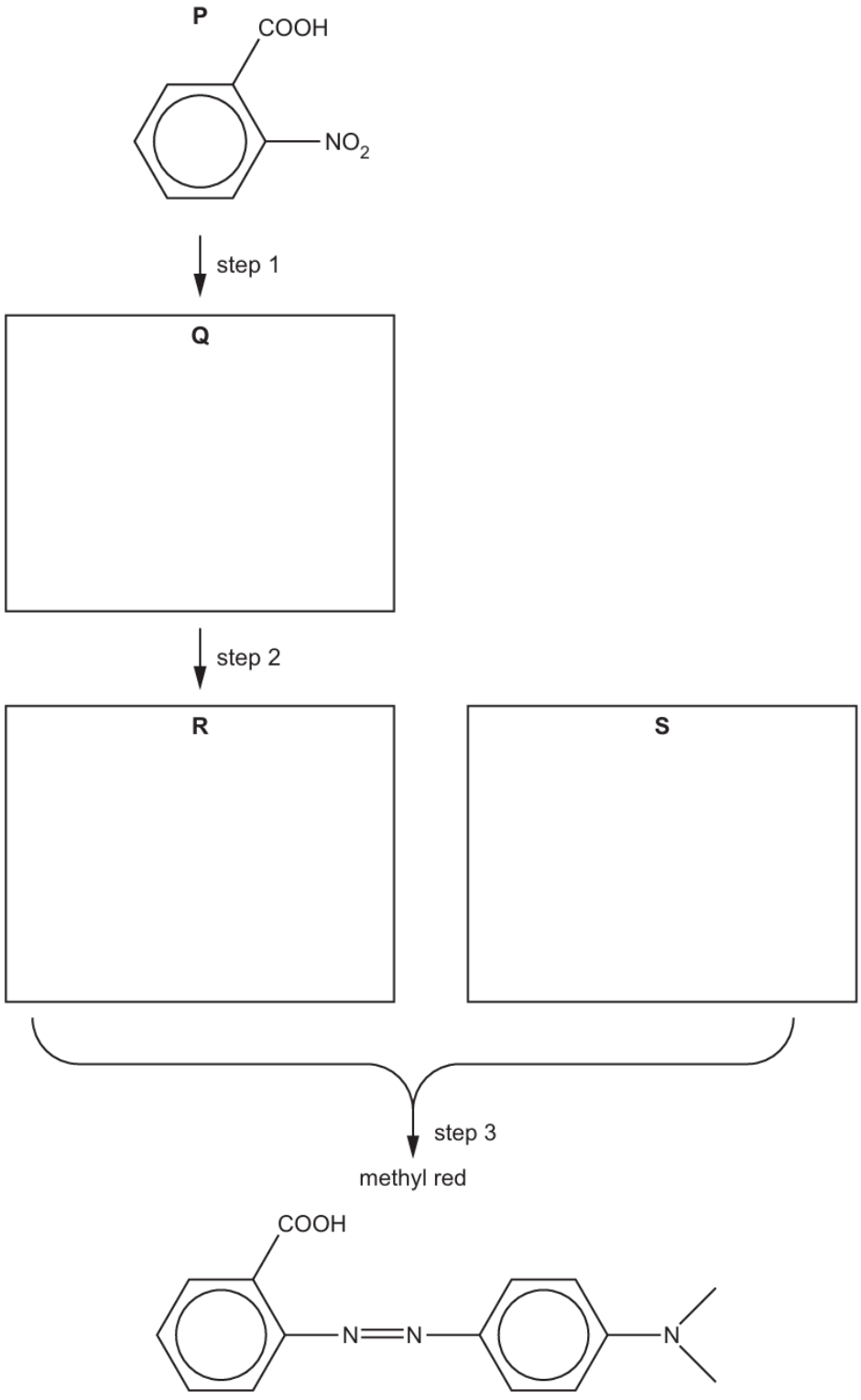


Fig. 7.1

(b) **S** reacts in a similar way to phenol in step 3.

(i) Draw the structures of **Q**, **R** and **S** in the boxes in Fig. 7.1. [3]

(ii) Suggest reagents and conditions for steps 1 and 2 in Fig. 7.1.

step 1 .....

step 2 .....

[3]

2 **(b)** An excess of $Br_2(aq)$ is added to separate samples of $C_6H_5NH_2$ and benzene, C_6H_6.

(i) $C_6H_5NH_2$ reacts readily with $Br_2(aq)$ 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 $Br_2(aq)$.

Suggest why $Br_2(aq)$ reacts with $C_6H_5NH_2$ but **not** with C_6H_6.

.....

.....

..... [2]

3 Sunset Yellow is an additive used for colouring foods.

A synthetic route for making Sunset Yellow is shown.

Molecules **E** and **G** each contain one $-SO_3^-$ group. These groups are unchanged in the formation of Sunset Yellow.

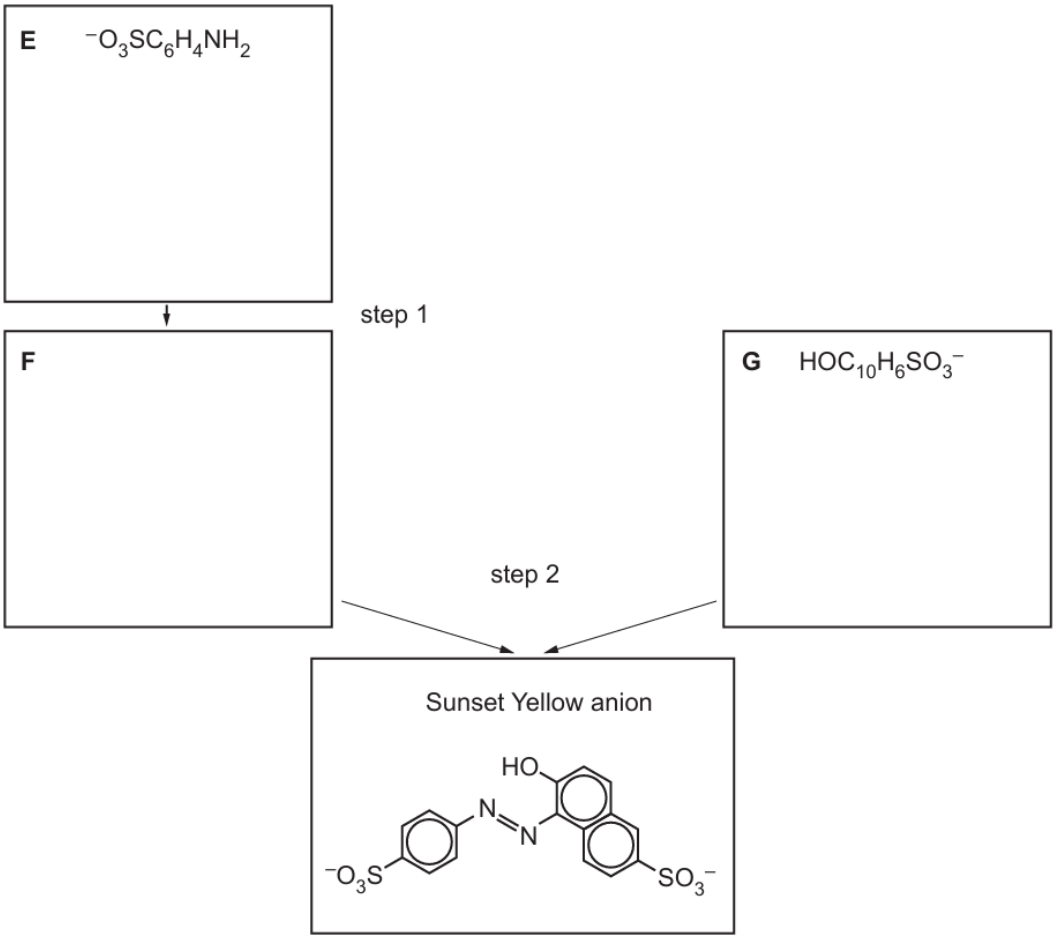


Fig. 7.1

(a) State the molecular formula of the Sunset Yellow anion.

..... [1]

(b) Deduce the structures of **E**, **F** and **G** and draw them in the boxes in Fig. 7.1. [3]

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

step 1 .....

step 2 .....

[3]

4 **(b)** Describe the relative basicities of diethylamine, phenylamine and ammonia in aqueous solution.

Explain your answer in terms of structure.

....
least basic most basic

explanation .....

.....

.....

.....

.....

[3]

(c) Phenylamine reacts with HNO_2(aq) at 4° C to form compound **P**. Compound **P** reacts with phenol under alkaline conditions at 4° C. The product of this reaction is acidified, forming azo compound **Q**.

Draw the structure of compound **Q**.

Circle the azo group on your structure.

State one use of an azo compound such as **Q**.

compound **Q**:

An azo compound can be used ..... .

[2]

5 **(d)** The azo compound Congo Red is used as an acid–base indicator and can be made by the route shown in Fig. 6.2.

In step 3 of this synthesis, compound **Y** reacts with compound **Z**. Compound **Z** is made from compound **X**. Assume that the $-SO_3^-Na^+$ groups do not react.

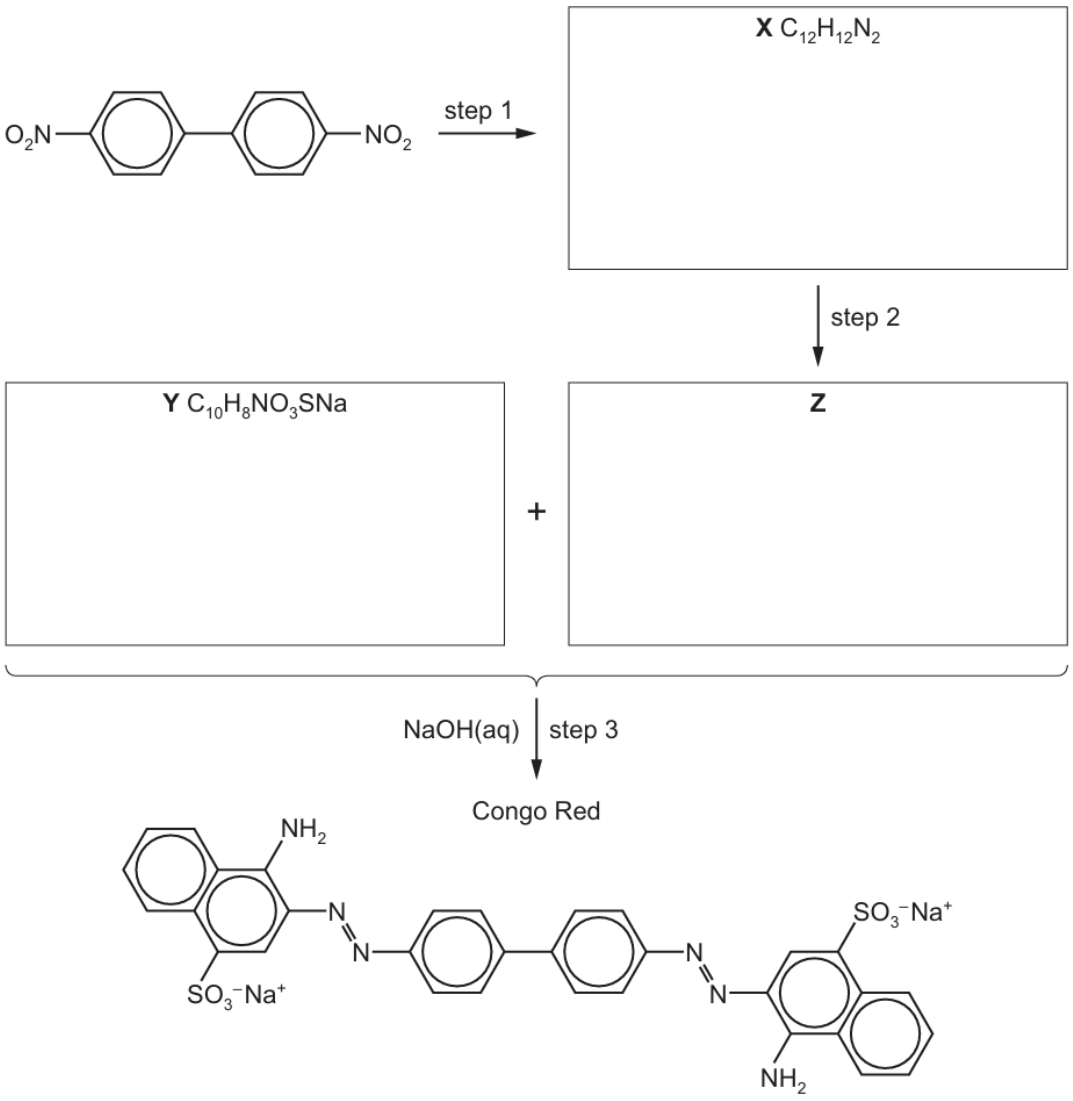


Fig. 6.2

(i) Suggest structures for compounds **X**, **Y** and **Z** and draw them in the boxes in Fig. 6.2. [3]

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

step 1 .....

step 2 .....

[3]

6 **(c)** **P** can be used to make compound **R** in a two-step reaction, shown in Fig. 7.2.

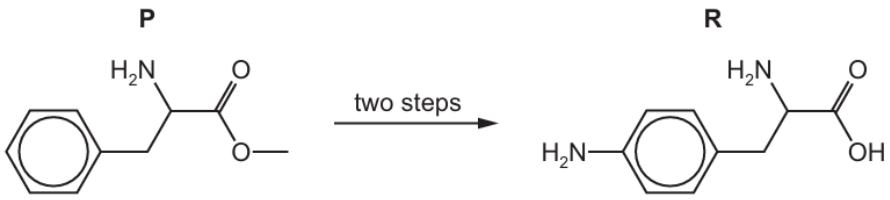


Fig. 7.2

(ii) Complete Table 7.1 by drawing the structures of the organic products formed when **R** is treated separately with the reagents given.

Table 7.1

reagent	product
HNO_2(aq) at 4 °C	
an excess of Br_2(aq) at room temperature	

[2]

7 **(c)** A reaction scheme is shown in Fig. 7.2.

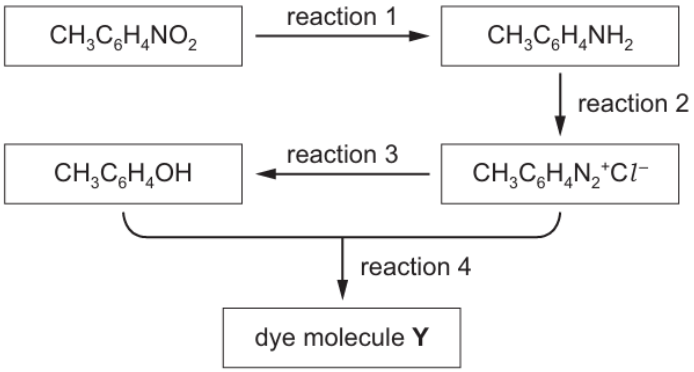


Fig. 7.2

(i) Describe the reagents and conditions to produce $CH_3C_6H_4N_2^+Cl^-$ from $CH_3C_6H_4NH_2$ in reaction 2.

reagents .....

conditions .....
[1]

(ii) Describe how $CH_3C_6H_4OH$ can be produced from $CH_3C_6H_4N_2^+Cl^-$ in reaction 3.

..... [1]

(iii) Draw the structure of the dye molecule **Y** formed when $CH_3C_6H_4N_2^+Cl^-$ and $CH_3C_6H_4OH$ react together in reaction 4. Describe the conditions for this reaction.

structure

conditions .....
[2]

8 **(a)** Describe and explain the relative basicities of phenylamine, ethylamine and 4-nitrophenylamine.

..... > ..... > .....

most basic least basic

.....

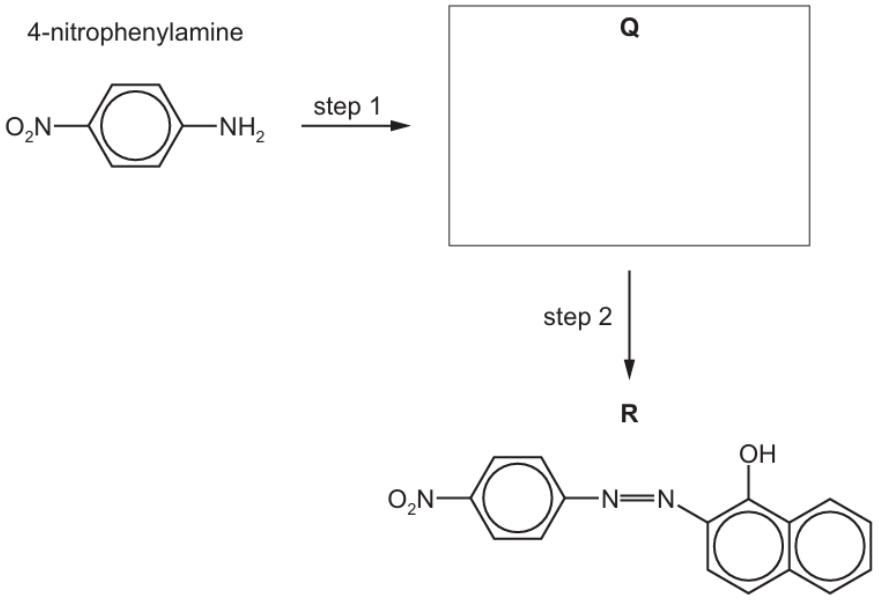
.....

.....

.....

..... [4]

(b) The dye **R** can be synthesised from 4-nitrophenylamine in two steps.



(i) Deduce and draw the structure of the organic salt **Q** in the box. [1]

(ii) Suggest reagents and conditions for step 1 and 2 in **(b)**.

step 1 .....

step 2 .....

[2]

9 Phenylamine, $C_6H_5NH_2$, and ethylamine, $C_2H_5NH_2$, can be distinguished by adding aqueous bromine.

(a) State what is seen when aqueous bromine is added to phenylamine.

.....

..... [2]

(b) Suggest what is seen when aqueous bromine is added to ethylamine.

..... [1]

(c) Draw the structure of the organic product formed when an excess of aqueous bromine is added to phenylamine.

[1]

(d) Name the product you have drawn in **(c)**.

..... [1]

10 Butylamine, $CH_3CH_2CH_2CH_2NH_2$, can be synthesised from different organic compounds by using suitable reagents. Each reaction involves one step.

(b) Compare and explain the relative basicities of ammonia, butylamine and phenylamine.

..... > ..... > .....
most basic least basic

.....

.....

.....

.....

.....

..... [4]

11 **(a)** The molecular formulae of three nitrogen-containing compounds are given.

S $C_6H_5CONH_2$

T $C_6H_5NH_2$

U $C_6H_5CH_2NH_2$

Describe and explain the relative basicities of **S**, **T** and **U**.

..... > ..... > .....
most basic least basic

.....

.....

.....

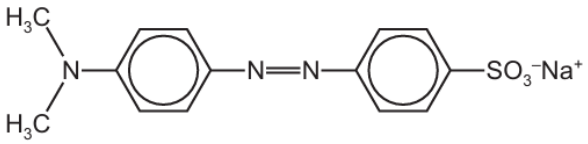
.....

.....

.....
[3]

12 **(f)** Methyl orange is another acid-base indicator. Its structure in aqueous solution at pH 4.4 is shown.

methyl orange



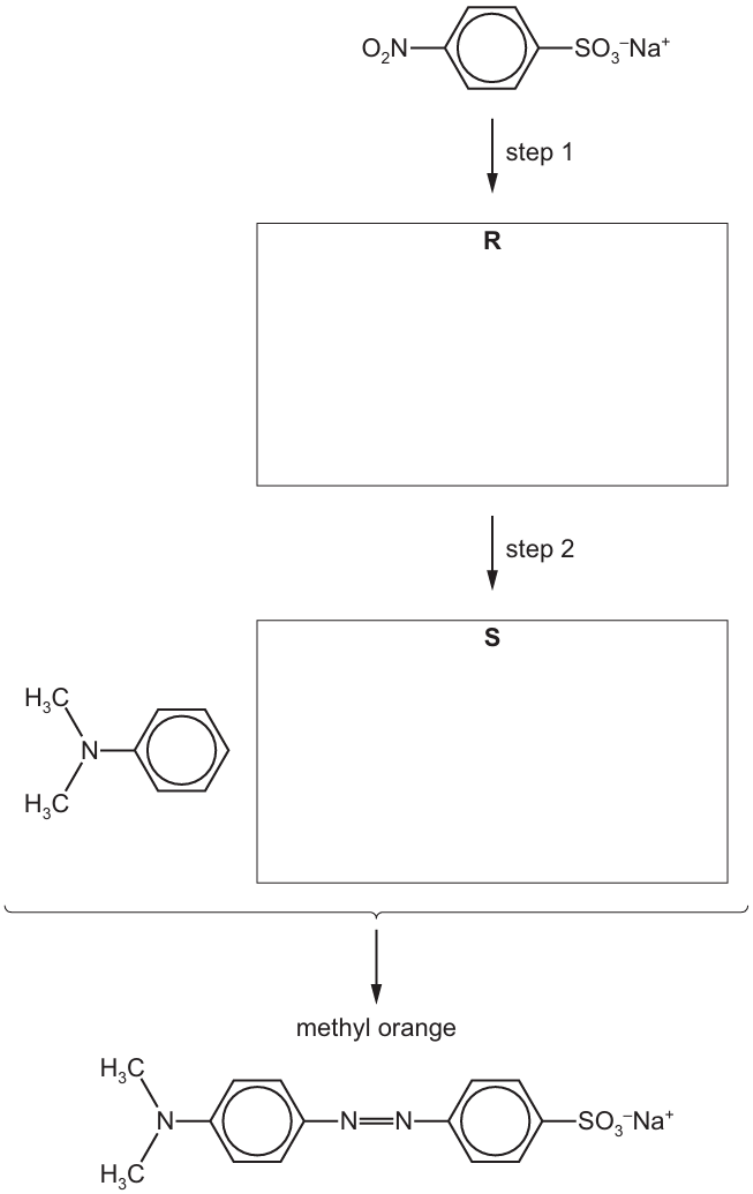
(i) On the structure of methyl orange, **circle** the bond or bonds that make this compound a dye. [1]

The colour of this indicator changes between pH 3.2 and pH 4.4.

(ii) Suggest the structure of methyl orange at pH 3.0. Assume the $-SO_3^-Na^+$ group is unreactive.

[1]

(g) Methyl orange can be synthesised as shown.



(i) Deduce the identities of compounds **R** and **S** and draw their structures in the boxes. [2]

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

step 1 .....

step 2 .....

[3]

13 **(c)** Phenylamine reacts with $Br_2(aq)$.

(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 $Br_2(aq)$.

observation 1 .....

observation 2 .....

[1]

(d) Describe the relative basicities of ammonia, ethylamine and phenylamine, starting with the **least** basic.
Explain your answer in terms of their structures.

..... < ..... < .....
least basic most basic

.....

.....

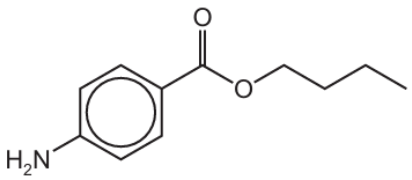
.....

.....

[3]

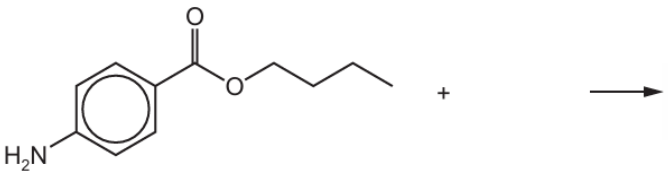
14 The structure of butamben is shown.

butamben



(a) Butamben can act as a base.

(i) Complete the equation for a reaction in which butamben acts as a base.



[1]

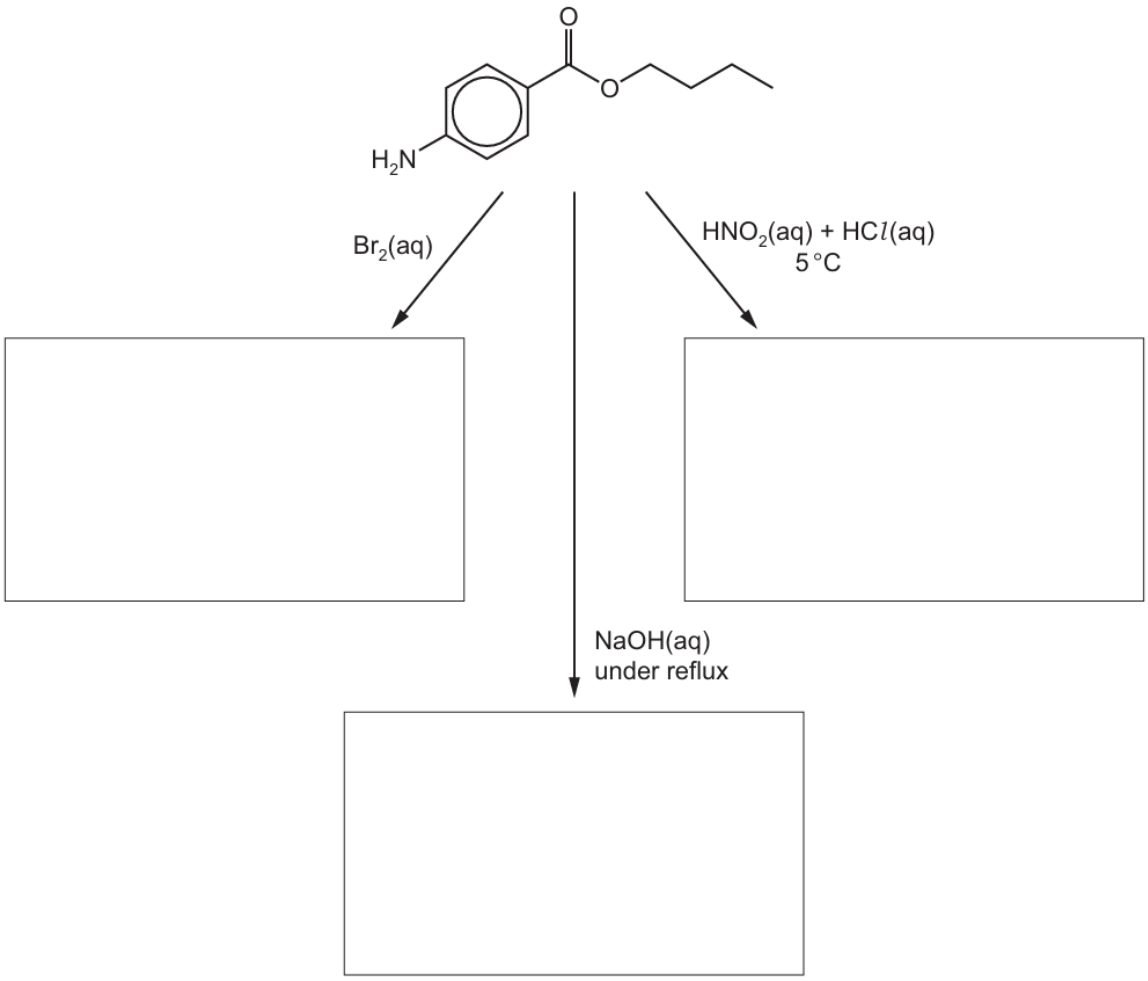
(ii) Predict whether butamben is a stronger or weaker base than ammonia. Give a reason for your answer.

.....

.....

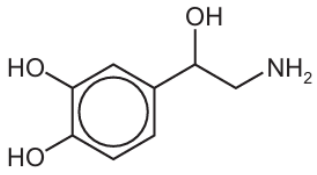
..... [1]

(b) Complete the reaction scheme below to show the structural formulae of the products formed when butamben is treated separately with the stated reagent.



[3]

15 Noradrenaline is a hormone found in humans.



noradrenaline

(c) HNO_2(aq) is reacted at 5 °C with separate samples of noradrenaline and phenylamine.
The reaction with phenylamine produces a stable diazonium ion.
The reaction with noradrenaline produces an unstable diazonium ion.

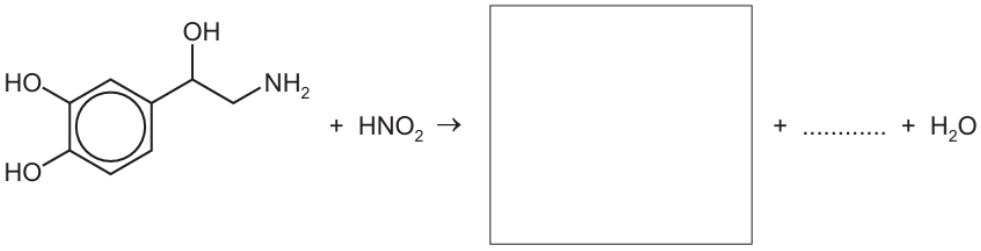
(i) Suggest why the diazonium ion produced with phenylamine is stable.

.....

..... [1]

(ii) When one noradrenaline molecule reacts with one HNO_2 molecule, the products are one water molecule, one molecule of an unreactive gas, and one molecule of an organic compound made up of carbon, hydrogen and oxygen only.

Complete the chemical equation for this reaction.



[2]