

## Benzene and compounds - 2021

### 1. Nov/2020/Paper\_41/No.7

Phenol,  $C_6H_5OH$ , is a weak acid.

(a) Phenol can be made from phenylamine,  $C_6H_5NH_2$ .

Give the reagents and conditions for this reaction.

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

(b) Phenol reacts with dilute aqueous nitric acid under room conditions to give a mixture of two isomeric products with molecular formula  $C_6H_5NO_3$ .

Use the *Data Booklet* to draw the structural formulae of these two products in the boxes and name each product.

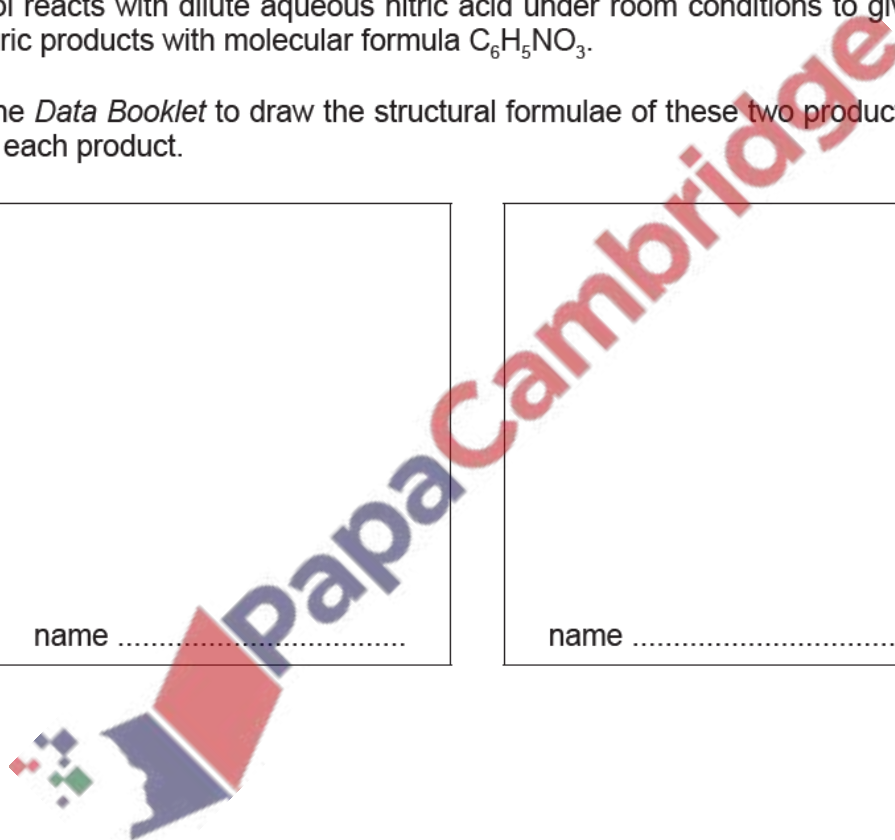
.....  
.....

name .....

.....  
.....

name .....

[2]

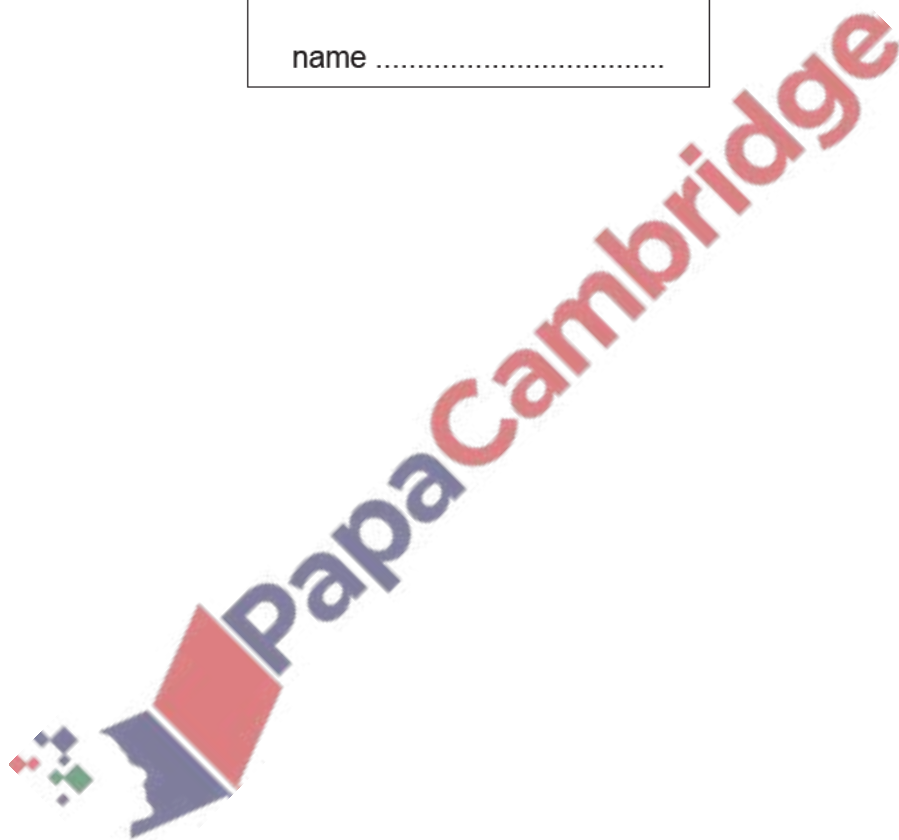


(c) Phenol reacts with an excess of aqueous bromine.

(i) Draw and name the organic product of this reaction in the box.

name .....

[2]



(ii) Describe **two** visual observations that can be made when phenol reacts with an excess of aqueous bromine.

observation 1 .....

observation 2 .....

[1]

(d) Write an equation for a neutralisation reaction in which phenol behaves as an acid.

..... [1]

(e) Water, phenol and ethanol can all behave as acids.

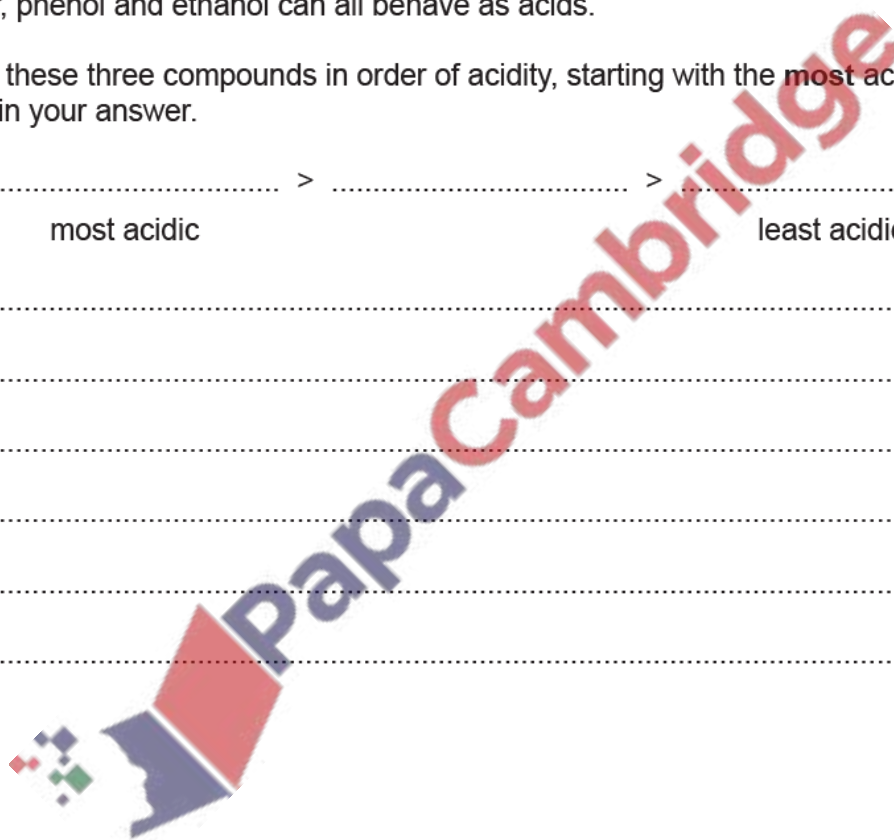
Place these three compounds in order of acidity, starting with the **most acidic**.  
Explain your answer.

..... > ..... > .....  
most acidic least acidic

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

[3]

[Total: 11]



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  $Br^+$ .

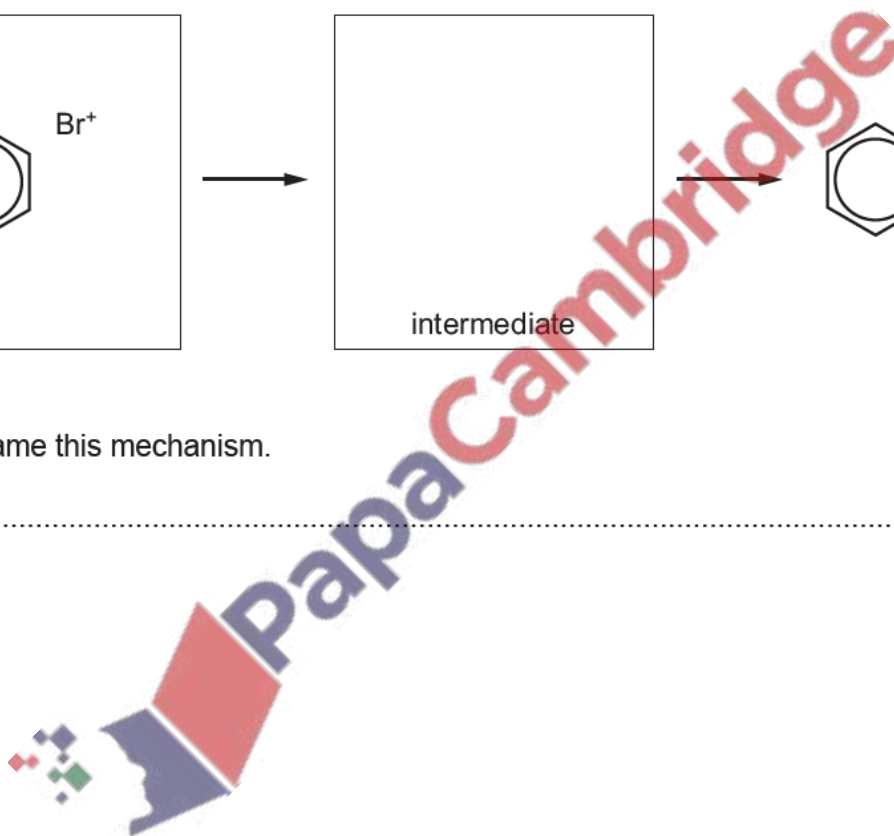
Complete the mechanism by which benzene reacts with  $Br^+$ , using curly arrows to show the movement of electron pairs.



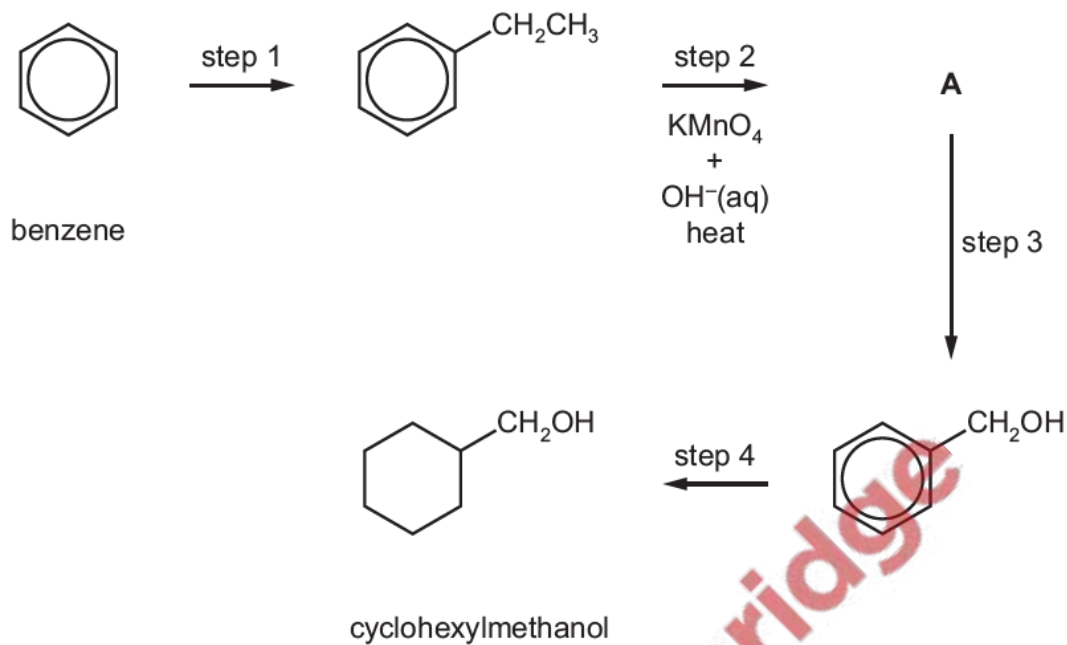
[2]

(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.



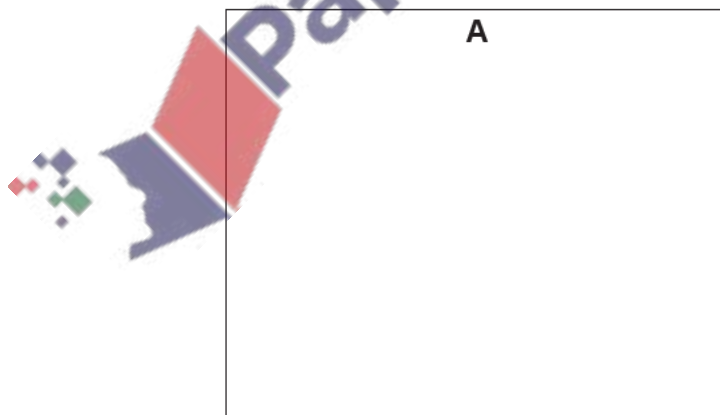
(i) Identify a suitable reagent and a suitable catalyst for step 1.

reagent .....

catalyst .....

[2]

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



[1]

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

step 3 .....

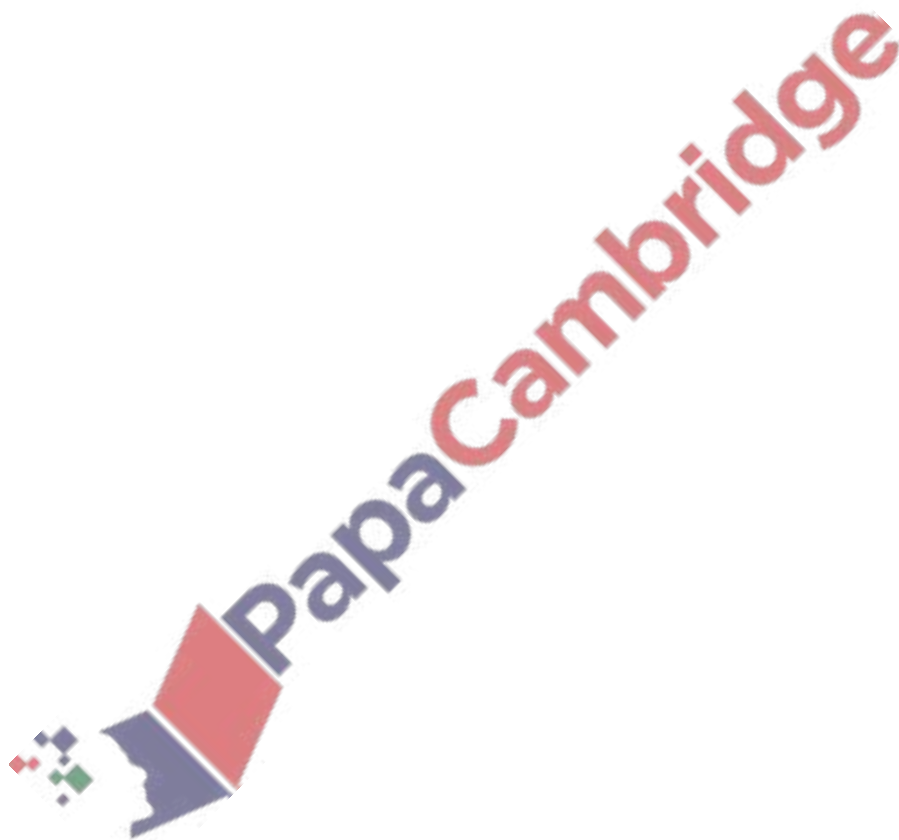
step 4 .....

[2]

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

..... [1]

[Total: 10]





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

..... [1]

(iii) Identify the reagents needed to produce  $\text{NO}_2^+$  ions.

Write an equation to explain how these reagents produce  $\text{NO}_2^+$  ions.

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

(iv) Give reagents and conditions for the production of phenylamine from nitrobenzene in step 2.

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

(c) Phenylamine reacts with  $\text{Br}_2(\text{aq})$ .

(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  $\text{Br}_2(\text{aq})$ .

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]

- (e) 1,3-diaminopropane,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , can be used to make polyamides.

- (i) Identify **one** compound that would react with 1,3-diaminopropane to form a polyamide.

..... [1]

- (ii) Draw a section of the polymer chain formed from 1,3-diaminopropane and the compound you chose in (e)(i).

Your answer should:

- include four monomer residues (two of each type of monomer)
- show the amide link fully displayed
- clearly identify **one** repeat unit of this polymer.



[2]

[Total: 20]

4. June/2020/Paper\_41/No.5

(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.

(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.

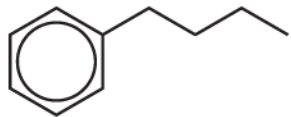

structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[3]

- (ii) Benzene reacts with each of these carbocations in separate Friedel-Crafts alkylation reactions.

In each reaction an organic compound with formula  $C_{10}H_{14}$  is formed. The number of peaks observed in the carbon-13 NMR spectrum of each compound is given.

Suggest the structures for the three other compounds.

	
number of peaks in carbon-13 NMR = 8	number of peaks in carbon-13 NMR = 6
	
number of peaks in carbon-13 NMR = 7	number of peaks in carbon-13 NMR = 8

[4]

[Total: 14]

(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
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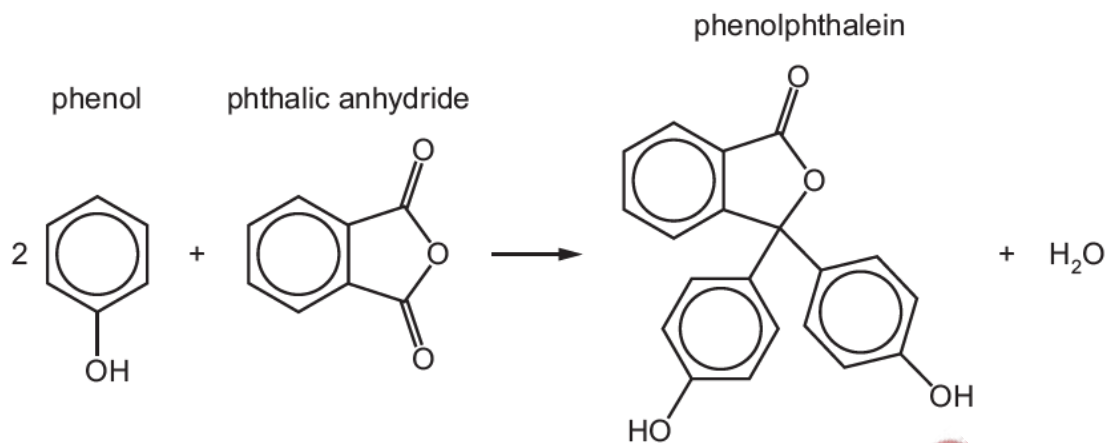
[1]

(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.

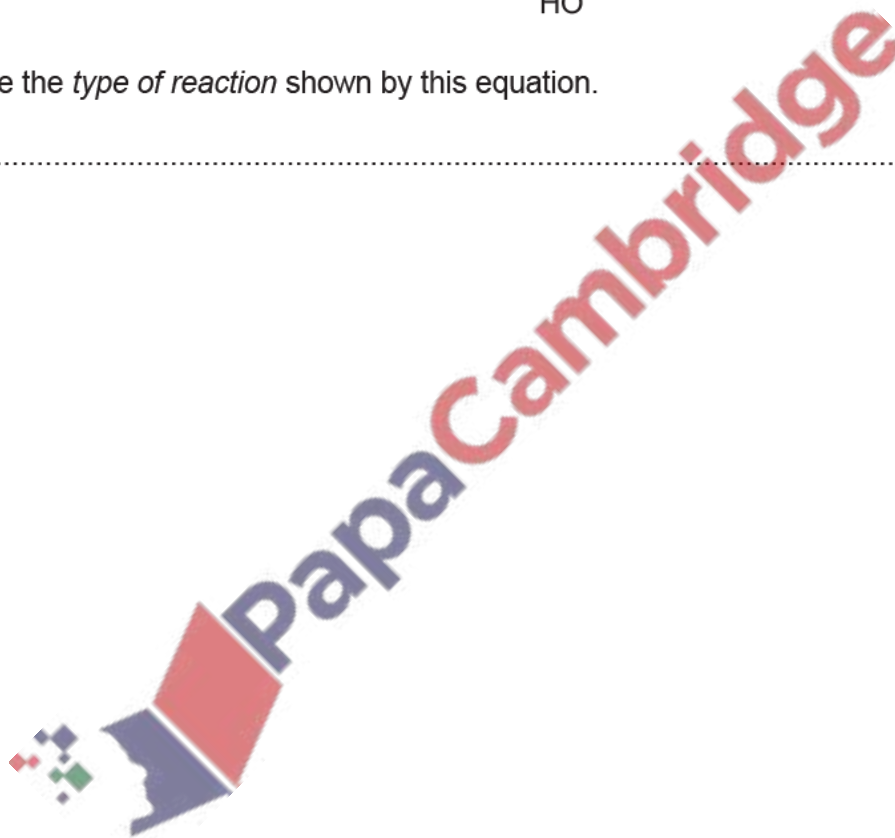
..... [1]

(c) The indicator, phenolphthalein, can be synthesised from phthalic anhydride and phenol under certain conditions.



Deduce the *type of reaction* shown by this equation.

..... [1]



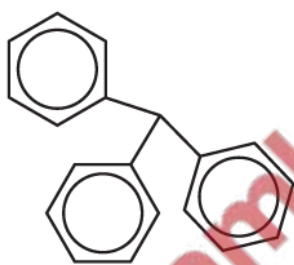
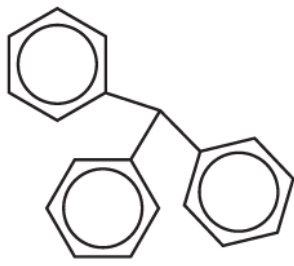
(d) (i) Name the functional groups, in addition to the benzene ring, present in a phenolphthalein molecule.

..... [1]

(ii) Phenolphthalein reacts separately with the two reagents shown in the table.

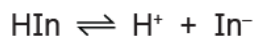
Complete the table by:

- drawing the structures of the organic products formed (part of the structure has been given for you)
- stating the types of reaction.

reagent	organic product structure	type of reaction
an excess of hot NaOH(aq)		
an excess of Br <sub>2</sub> (aq)		

[4]

- (e) Phenolphthalein is an indicator and is represented by the formula HIn. Phenolphthalein, HIn, is a weak acid.

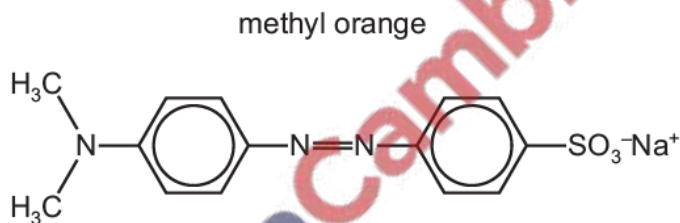


The  $K_a$  value for phenolphthalein is  $5.0 \times 10^{-10} \text{ mol dm}^{-3}$  at 298 K. This indicator changes colour at a pH of approximately 8.8.

Calculate the ratio  $\frac{[\text{In}^-]}{[\text{HIn}]}$  at pH 8.8.

ratio  $\frac{[\text{In}^-]}{[\text{HIn}]} = \dots\dots\dots$  [2]

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



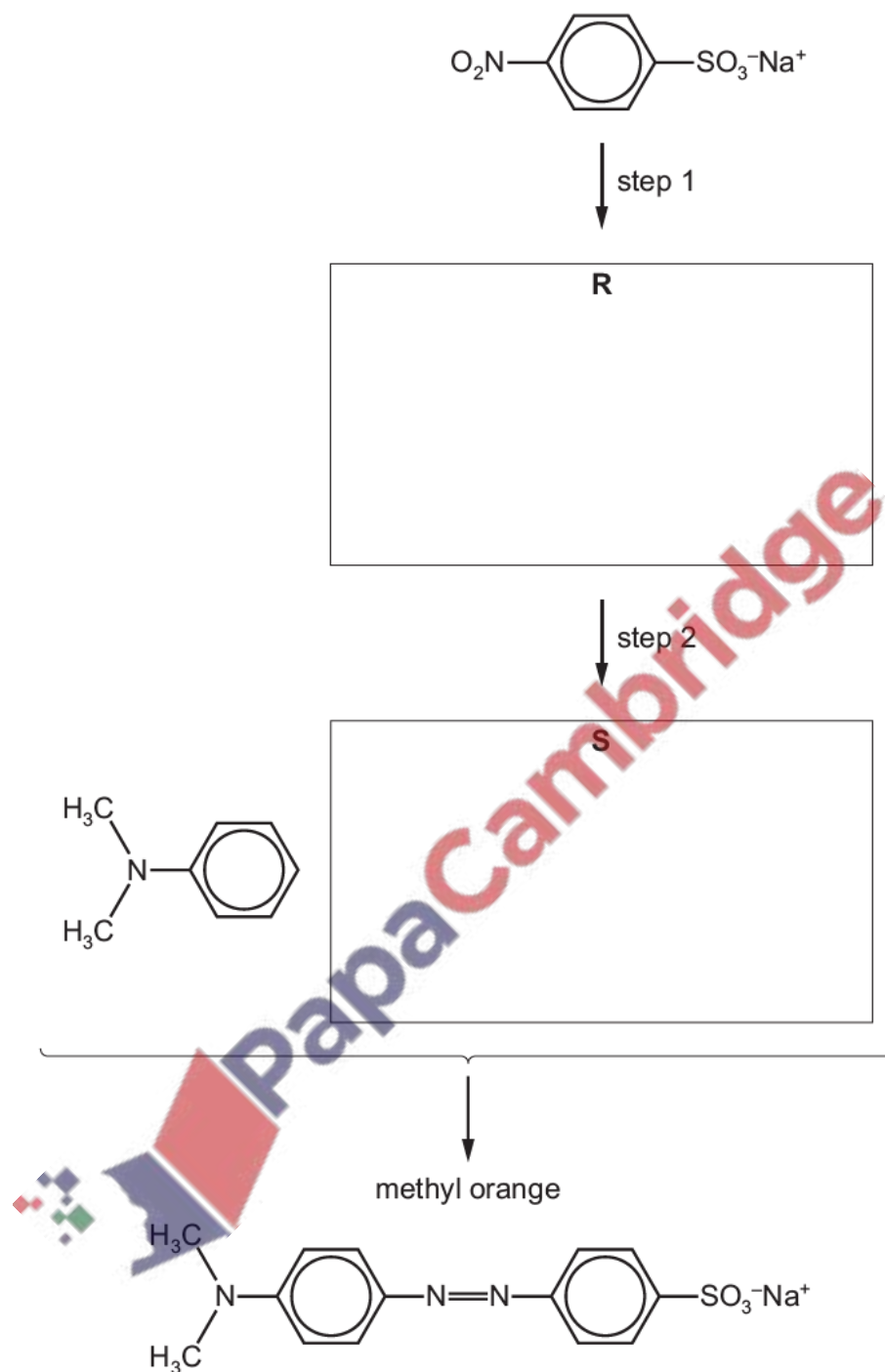
- (i) On the structure of methyl orange, circle the bond or bonds that make this compound a dye. [1]

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  $-\text{SO}_3^- \text{Na}^+$  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]

[Total: 19]