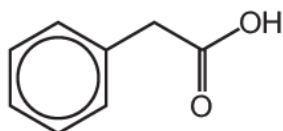


1. Nov/2021/Paper_41/No.7

The structure of phenylethanoic acid is shown.



- (a) Give the number of different peaks in the carbon-13 (^{13}C) NMR spectrum of phenylethanoic acid.

number of peaks = [1]

- (b) Phenylethanoic acid, ethanol and phenol can all behave as acids.

Compare and explain the relative acidities of these three compounds.

..... > >

most acidic least acidic

.....

.....

.....

.....

..... [4]

- (c) Phenylethanoic acid can be synthesised using benzene as the starting material.

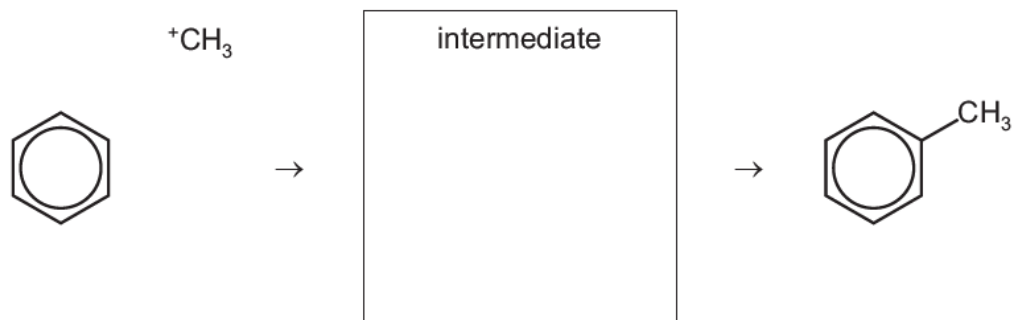
In the first stage of this synthesis, benzene reacts with chloromethane in the presence of an AlCl_3 catalyst to form methylbenzene.

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.



[3]

- (d) A three-step synthesis of phenylethanoic acid from methylbenzene is shown.



- (i) State reagents and conditions for step 1.

[1]

- (ii) Suggest the structure of compound **Q**.

[1]

- (iii) State reagents and conditions for steps 2 and 3.

step 2

step 3

[2]

- (iv) Draw the structure of an organic by-product that forms in step 1.

[1]

[Total: 14]

2. Nov/2021/Paper_41/No.8

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]

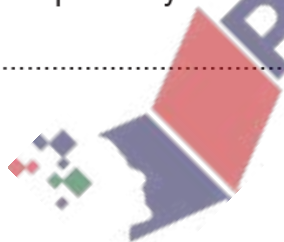
(c) Draw the structure of the organic product formed when an excess of aqueous bromine is added to phenylamine.

[1]

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

..... [1]

[Total: 5]

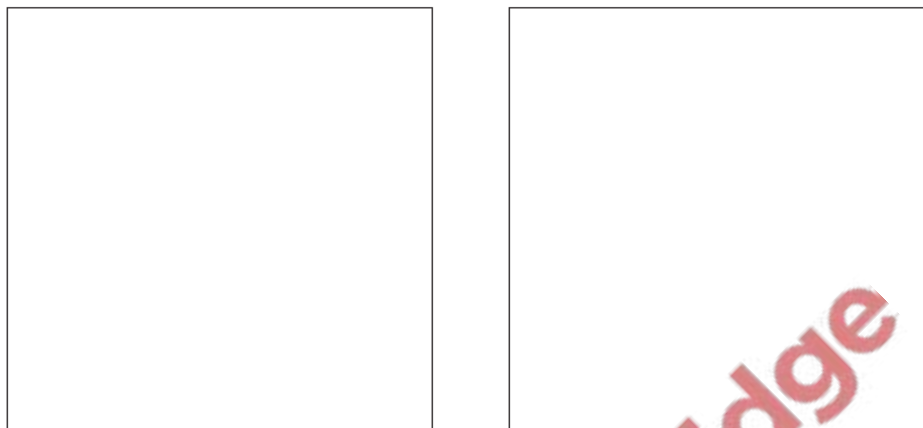


3. Nov/2021/Paper_42/No.8a,8d

Alanine, $\text{H}_2\text{NCH}(\text{CH}_3)\text{CO}_2\text{H}$, and glutamic acid, $\text{H}_2\text{NCH}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{CO}_2\text{H}$, are two naturally occurring amino acids.

(a) $\text{H}_2\text{NCH}(\text{CH}_3)\text{CO}_2\text{H}$ exists as two optical isomers.

Draw three-dimensional structures of these two optical isomers.



[2]

(d) At pH 11 alanine exists as $\text{H}_2\text{NCH}(\text{CH}_3)\text{CO}_2^-$ ions and glutamic acid exists as $\text{H}_2\text{NCH}(\text{CH}_2\text{CH}_2\text{CO}_2^-)\text{CO}_2^-$ ions. A mixture of alanine and glutamic acid at pH 11 is subjected to electrophoresis.

(i) State how the mixture can be maintained at pH 11 during electrophoresis.

..... [1]

(ii) Draw a fully labelled diagram for the apparatus that would be used to carry out this electrophoresis. Your diagram should include the position of the mixture of alanine and glutamic acid at the start of the electrophoresis experiment.



[2]

(iii) Identify the electrode that each amino acid travels towards during electrophoresis at pH 11.

alanine

glutamic acid

[1]

(iv) In a particular electrophoresis experiment at pH 11, the glutamic acid travels 3.4 cm. Alanine travels a shorter distance.

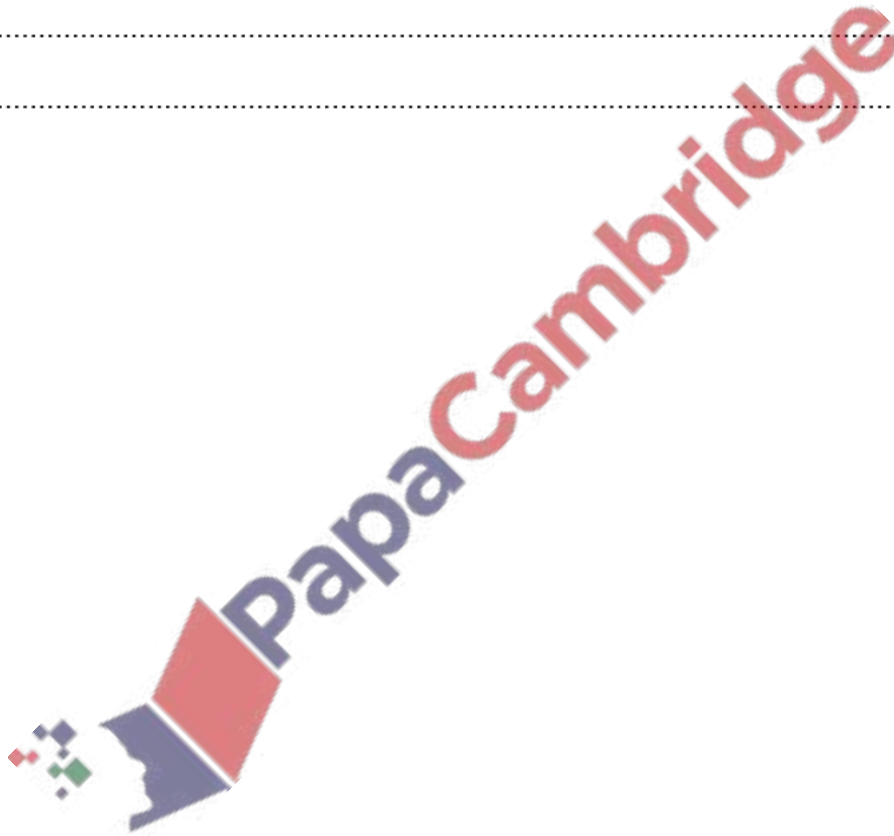
Explain the factors that account for the difference in the distances travelled.

.....

.....

.....

..... [2]



4. Nov/2021/Paper_42/No.9

Butylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, can be synthesised from different organic compounds by using suitable reagents. Each reaction involves one step.

(a) Complete the table to describe three different syntheses.

- One of the three syntheses should involve a nucleophilic substitution reaction.
- The starting organic compound for each synthesis should contain a different functional group.
- A different reagent should be used for each synthesis.

starting organic compound	reagent and conditions

[6]

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

..... > >

most basic least basic

.....

.....

.....

.....

.....

.....

.....

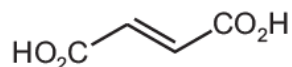
.....

..... [4]

[Total: 10]

Fumaric acid is a naturally occurring dicarboxylic acid.

fumaric acid



- (a) Identify the products of the reaction between fumaric acid and an excess of hot, concentrated, acidified manganate(VII).

..... [1]

- (b) Fumaric acid can form addition and condensation polymers.

- (i) Draw the repeat unit of the addition polymer poly(fumaric acid).

[1]

- (ii) Draw the repeat unit of the polyester formed when fumaric acid reacts with ethane-1,2-diol, (CH₂OH)₂.

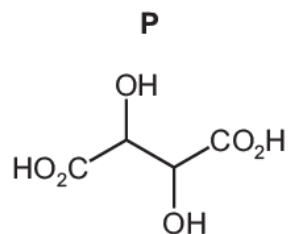
The ester bond should be shown fully displayed.

[2]

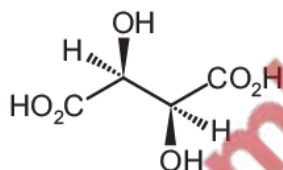
(iii) Explain why polyesters normally biodegrade more readily than polyalkenes.

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

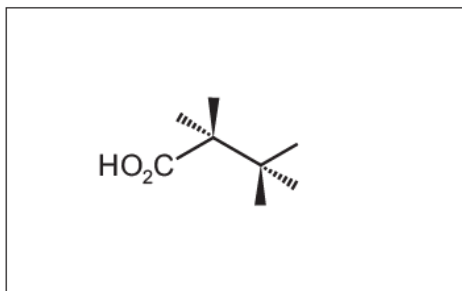
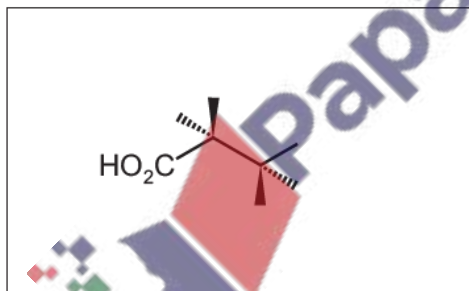
(c) Fumaric acid reacts with cold, dilute, acidified manganate(VII) to form compound **P**.



Only three stereoisomers of **P** exist. One of the stereoisomers is shown.

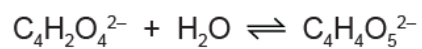


Complete the three-dimensional diagrams in the boxes to show the **other** two stereoisomers of **P**.



[2]

- (d) The enzyme fumarase catalyses the reaction of fumarate ions, $C_4H_2O_4^{2-}$, with water to form malate ions, $C_4H_4O_5^{2-}$.



Describe, with the aid of a suitably labelled diagram, how an enzyme such as fumarase can catalyse a reaction.

.....

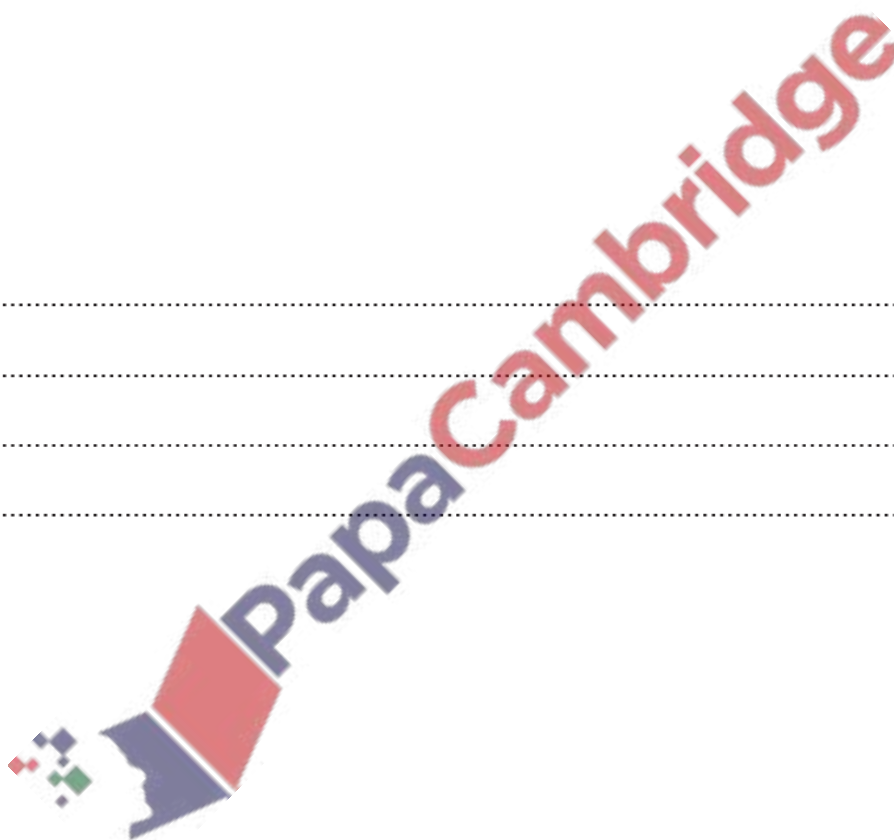
.....

.....

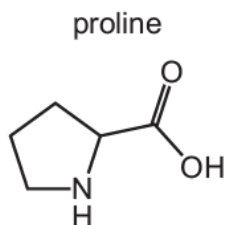
.....

[3]

[Total: 10]



Proline (Pro) is a naturally occurring amino acid.



(a) Proline is often found bonded to glycine (Gly) in a protein.

(i) Draw the dipeptide Pro-Gly.

The peptide bond must be shown fully displayed.

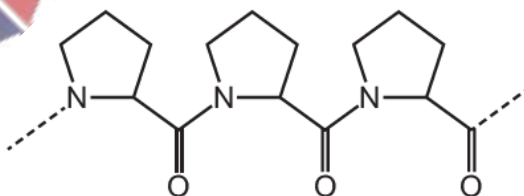
[2]

(ii) Name the type of reaction that forms a dipeptide from two amino acids.

[1]

(iii) Proline is able to form a poly(proline) peptide chain.

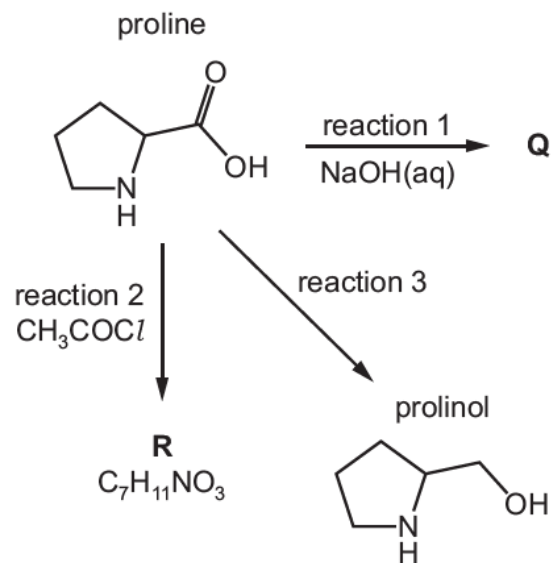
A section of a poly(proline) chain is shown.



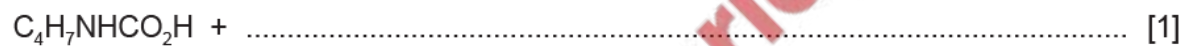
Suggest why the secondary structure of poly(proline) **cannot** be stabilised by hydrogen bonding.

[1]

(b) The reaction scheme shows several reactions of proline.

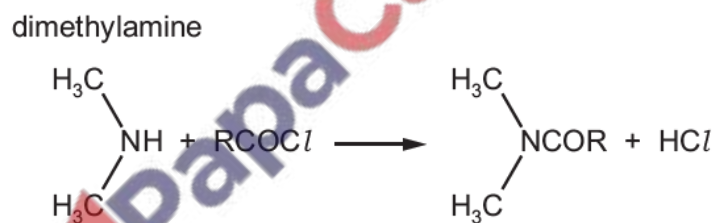


(i) Write an equation for the reaction of proline with NaOH(aq) in reaction 1.



(ii) Proline has a secondary amine functional group.

Secondary amines react with acyl chlorides. For example, dimethylamine reacts with RCOCl according to the following equation.



Suggest the skeletal structure of **R**, $\text{C}_7\text{H}_{11}\text{NO}_3$, the product of reaction 2.

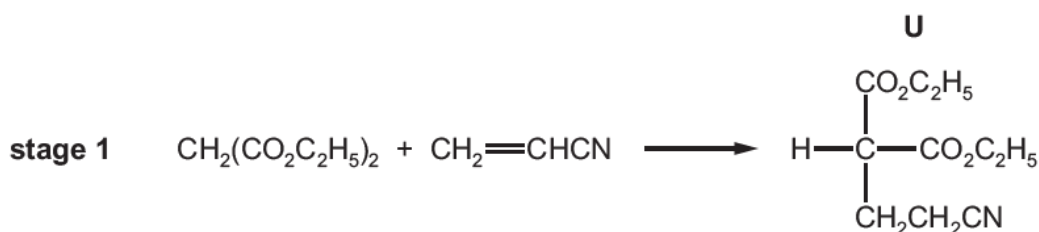
[1]

(iii) Suggest the reagent required for reaction 3.

..... [1]

(c) Proline was first synthesised in the laboratory using a multi-stage synthetic route.

In stage 1, $\text{CH}_2(\text{CO}_2\text{C}_2\text{H}_5)_2$ and $\text{CH}_2=\text{CHCN}$ react to form a single product **U**.



(i) Name **all** the functional groups present in the reactants of stage 1.

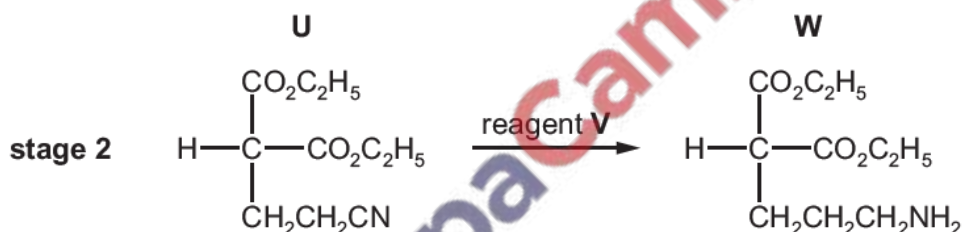
$\text{CH}_2(\text{CO}_2\text{C}_2\text{H}_5)_2$

$\text{CH}_2=\text{CHCN}$ [2]

(ii) Suggest the type of reaction that occurs in stage 1.

..... [1]

In stage 2, **U** reacts with reagent **V** to form **W**.

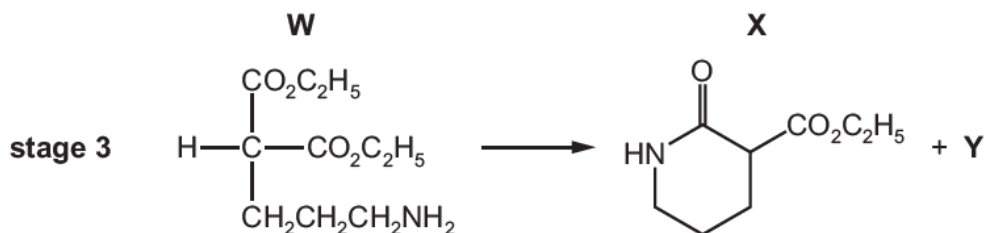


(iii) Suggest a suitable reagent **V**.

..... [1]

Stage 3 takes place in the presence of an acid catalyst.

X and **Y** are the only products of the reaction.



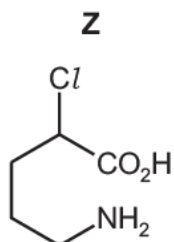
(iv) Suggest the type of reaction that occurs in stage 3.

..... [1]

(v) Deduce the identity of Y.

..... [1]

After several further stages, Z is produced.



In the final stage of the synthesis, Z reacts via a nucleophilic substitution mechanism to form proline.

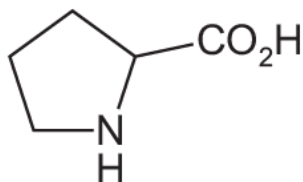
(vi) Complete the diagram to describe the reaction mechanism of the final stage. Draw curly arrows, ions and charges, partial charges and lone pairs of electrons, as appropriate.

Draw the structure of any organic intermediate ion.



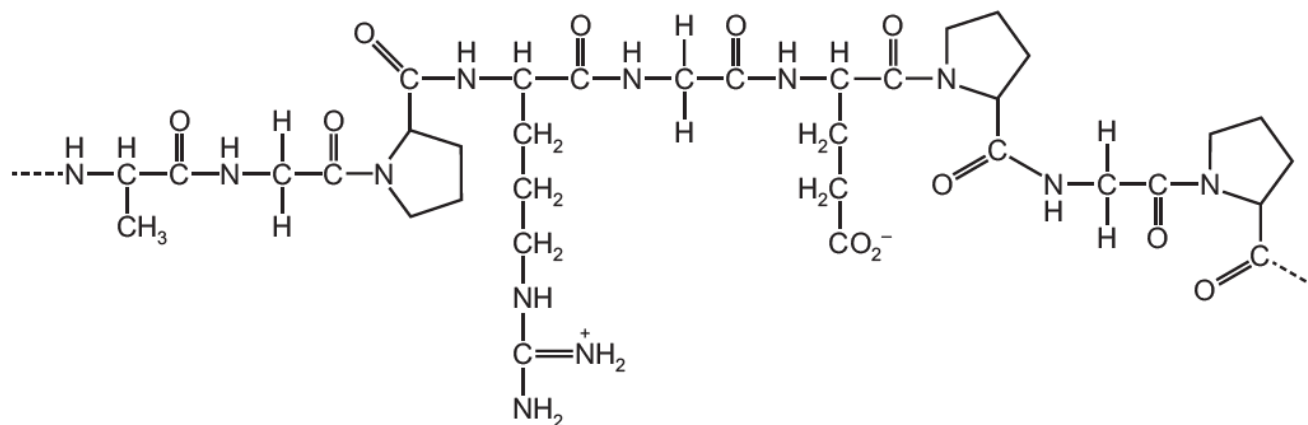
[3]

(vii) Identify with an asterisk (*) the chiral centre in proline.



[1]

(d) Part of the structure of gelatin is shown.



Identify the number of amino acid units in the structure shown.

..... [1]

(e) (i) At pH 6.5, proline exists in aqueous solution as a zwitterion.

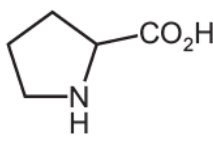
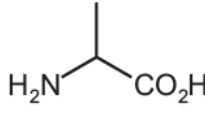
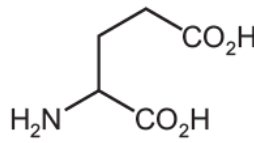
Draw the structure of the zwitterion of proline.

Explain how the zwitterion of proline forms.

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

(ii) The isoelectric point of an amino acid is the pH at which it exists as a zwitterion.

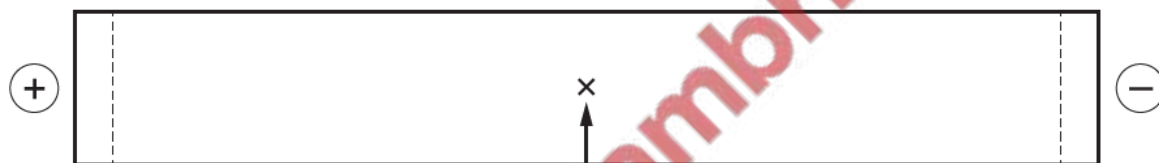
Three of the amino acids in gelatin are proline, alanine and glutamic acid. Their isoelectric points are shown.

	proline	alanine	glutamic acid
amino acid			
isoelectric point	6.5	6.0	3.1

A mixture of these amino acids was analysed by electrophoresis using a buffer solution at pH 4.0.

Draw and label three spots on the diagram of the electropherogram to indicate the likely position of each of these three species after electrophoresis.

Explain your answer.



mixture applied here

.....

.....

.....

.....

.....

.....

.....

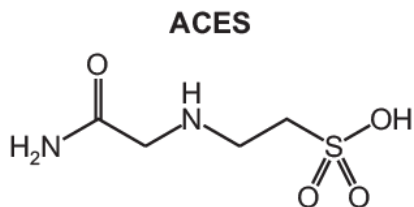
.....

.....

.....

[4]

- (f) The weak acid **ACES** is a compound that can be used to make a buffer solution for electrophoresis experiments.



The anion of the sodium salt of **ACES**, $C_4H_9N_2O_4SNa$, is a strong base.

A buffer solution is prepared by the following steps.

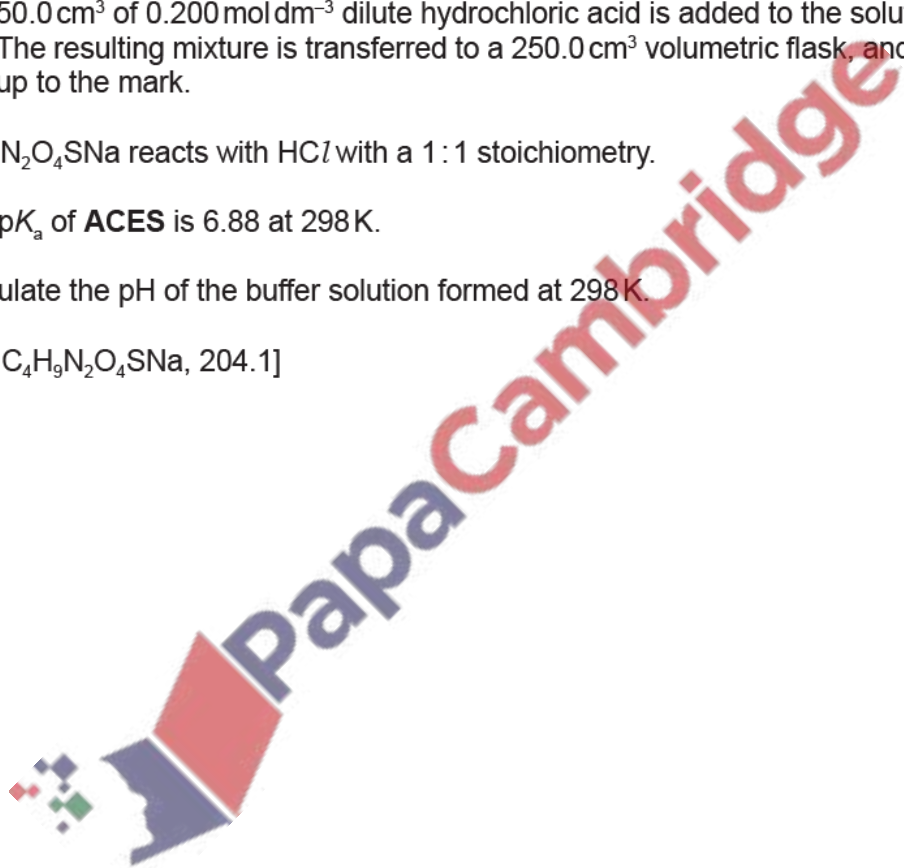
- 3.50 g of $C_4H_9N_2O_4SNa$ is dissolved in 100 cm^3 of distilled water.
- 50.0 cm^3 of 0.200 mol dm^{-3} dilute hydrochloric acid is added to the solution.
- The resulting mixture is transferred to a 250.0 cm^3 volumetric flask, and the solution made up to the mark.

$C_4H_9N_2O_4SNa$ reacts with HCl with a 1 : 1 stoichiometry.

The pK_a of **ACES** is 6.88 at 298 K.

Calculate the pH of the buffer solution formed at 298 K.

[M_r : $C_4H_9N_2O_4SNa$, 204.1]



pH = [4]

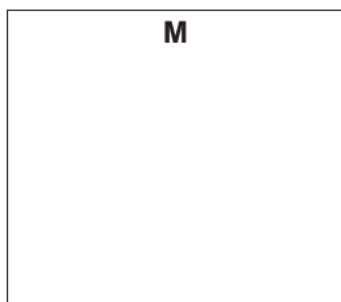
[Total: 28]

(a) 3-aminobenzoic acid can be synthesised from methylbenzene in three steps.

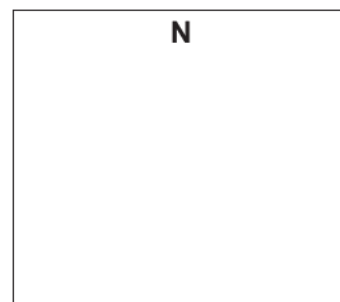
methylbenzene



step 1 →

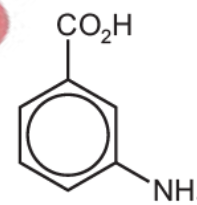


step 2 →



step 3 ↓

3-aminobenzoic acid



(i) Draw the structures of **M** and **N** in the boxes. [2]

(ii) Suggest reagents and conditions for each step of the synthesis.

step 1

step 2

step 3

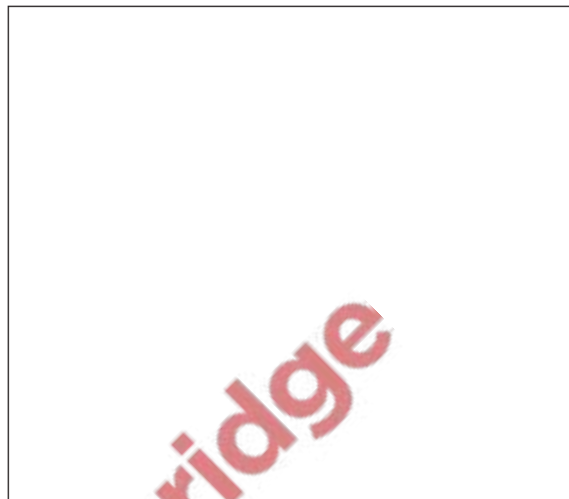
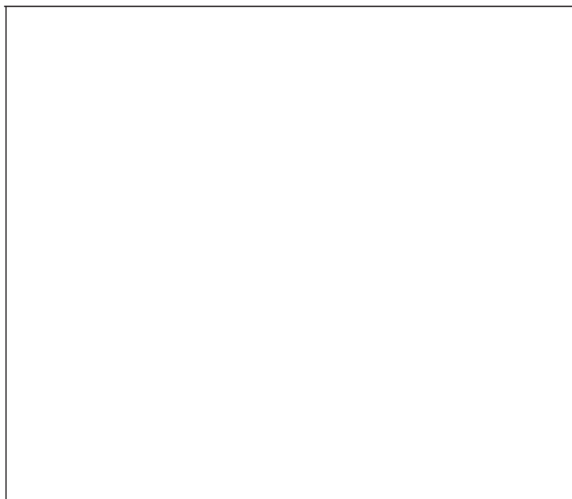
[3]



(b) A mixture of serine, $\text{HOCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, and lysine, $\text{H}_2\text{N}(\text{CH}_2)_4\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, reacts to form several different products.

(i) Draw the structures of the two structural isomers with the molecular formula $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_5$ that could be present in the product mixture.

The functional group formed in each case should be displayed.



[3]

(ii) Predict the number of different structural isomers with the molecular formula $\text{C}_9\text{H}_{19}\text{N}_3\text{O}_4$ that could be present in the product mixture.

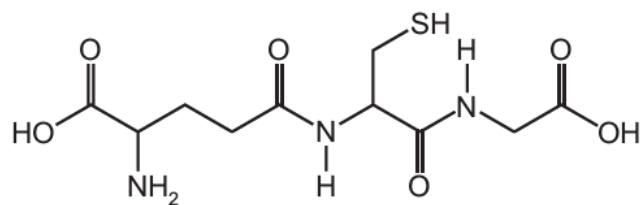
molecular formula	number of structural isomers formed
$\text{C}_9\text{H}_{19}\text{N}_3\text{O}_4$	

[1]

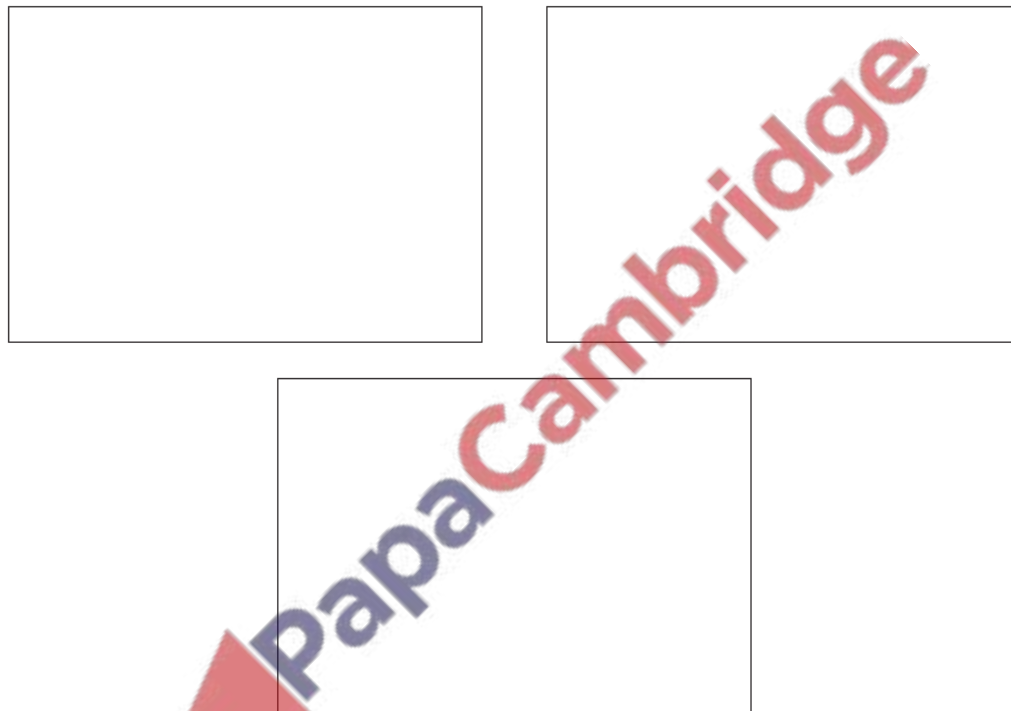


(c) Glutathione is a naturally occurring compound found in plants.

glutathione



- (i) On the diagram of glutathione, label each chiral centre with an asterisk (*). [1]
- (ii) Draw the structures of the three products formed after complete acid hydrolysis of glutathione. Assume the thiol group, $-SH$, does not react.



- (iii) Glutathione is soluble in water.

By referring to the structure of glutathione, explain why glutathione is soluble in water.

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

[Total: 13]

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

..... > >

most basic least basic

.....

.....

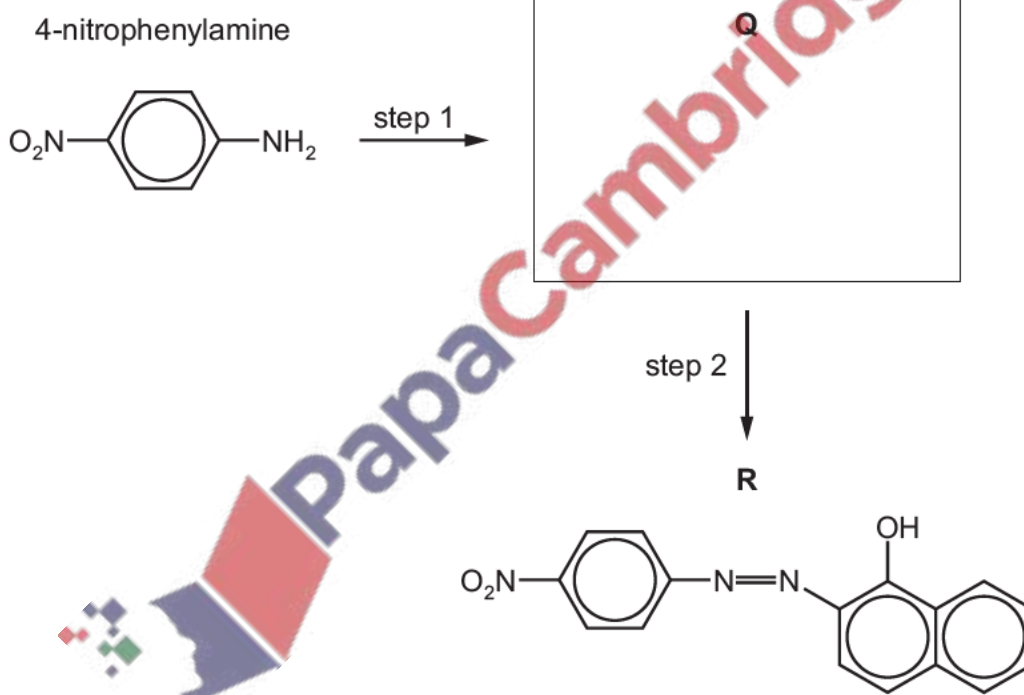
.....

.....

.....

..... [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]

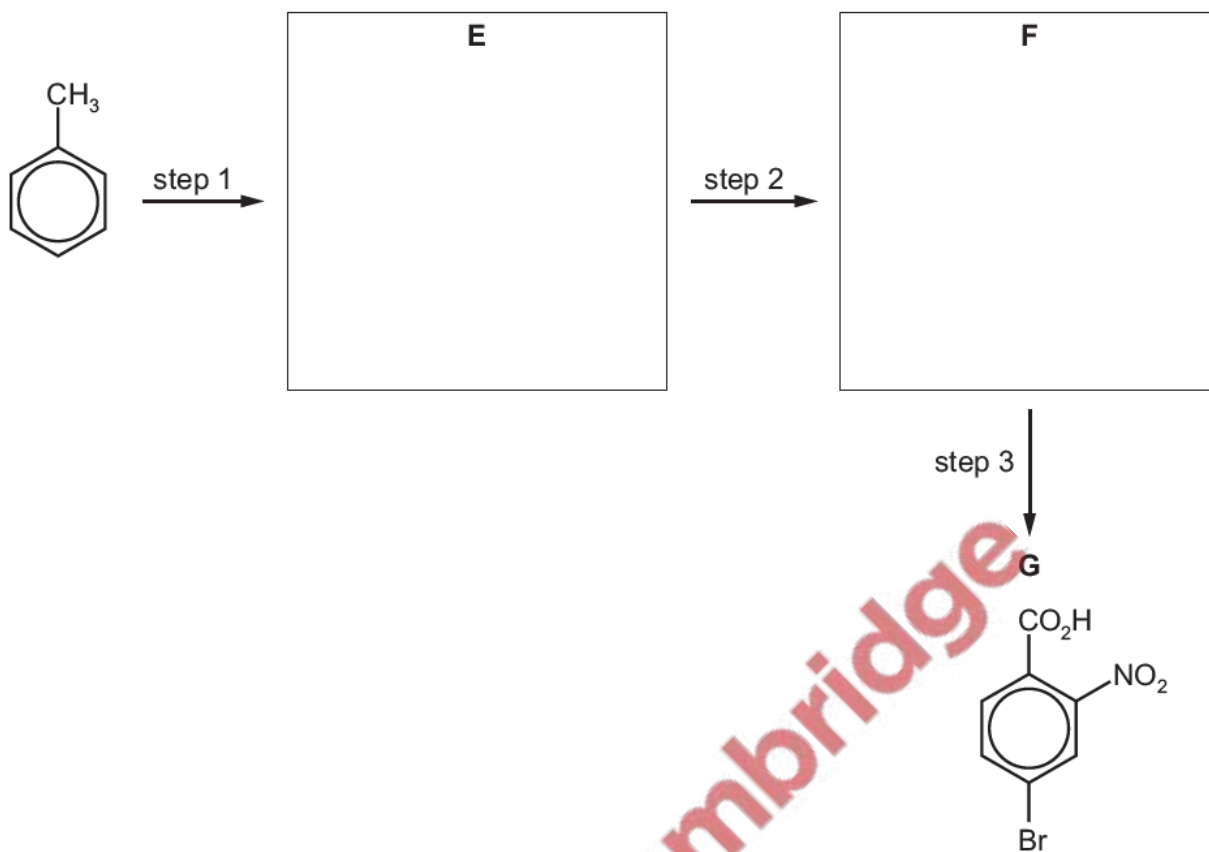
(ii) Suggest reagents and conditions for step 1 and 2 in (b).

step 1

step 2

[2]

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



(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]

[Total: 13]

(a) There are four possible structural isomers of C_8H_{10} that contain a benzene ring.

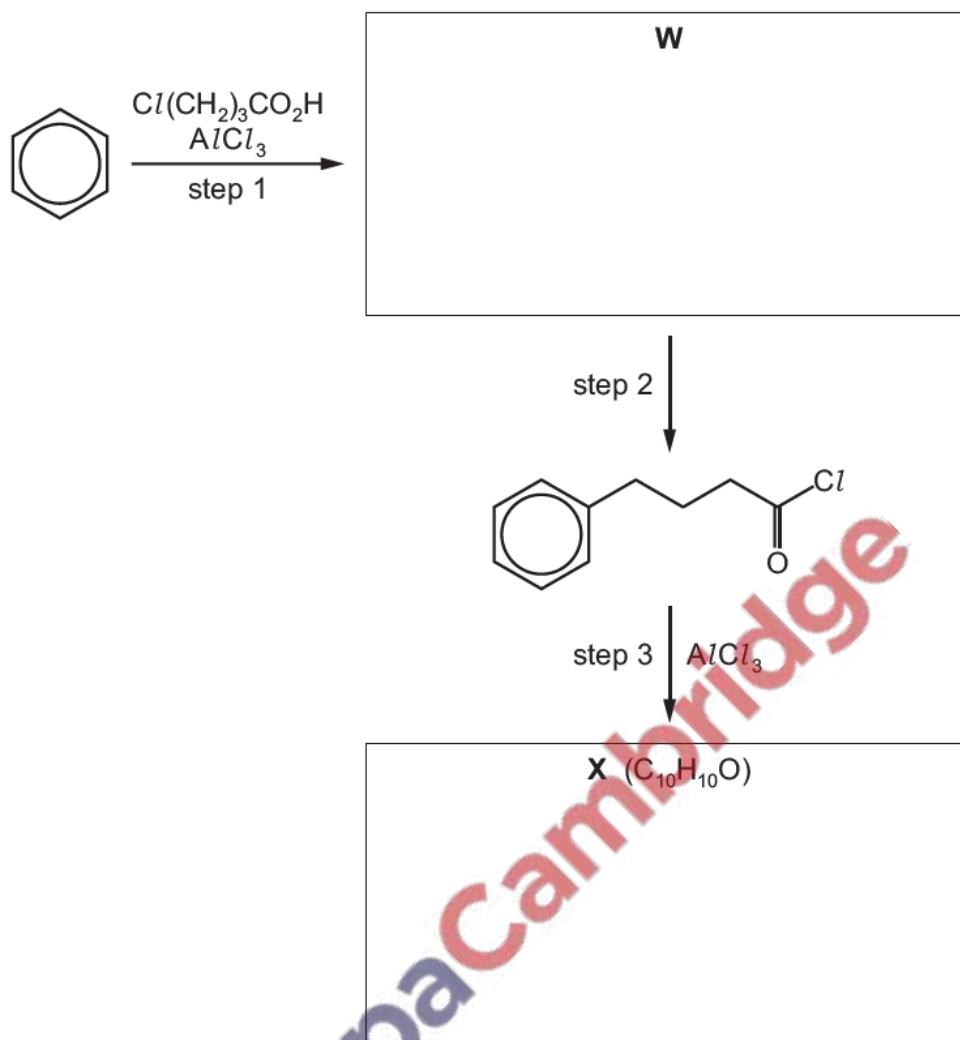
Draw the **skeletal** formulae of the four structural isomers in the appropriate boxes. The number of peaks observed in the carbon-13 (^{13}C) NMR spectrum of each compound is given.

<p>isomer 1</p> <p>three peaks in ^{13}C NMR</p>	<p>isomer 2</p> <p>four peaks in ^{13}C NMR</p>
<p>isomer 3</p> <p>five peaks in ^{13}C NMR</p>	<p>isomer 4</p> <p>six peaks in ^{13}C NMR</p>

[4]



(b) A three-step synthesis of **X** ($C_{10}H_{10}O$) from benzene is suggested as shown.



- (i) Step 1 is the alkylation of benzene by electrophilic substitution. Use $R-Cl$ to represent $Cl(CH_2)_3CO_2H$.

Write an equation for the formation of an electrophile from $R-Cl$ and $AlCl_3$.

..... [1]

- (ii) Deduce and draw the structures of **W** and **X** in the boxes. [2]

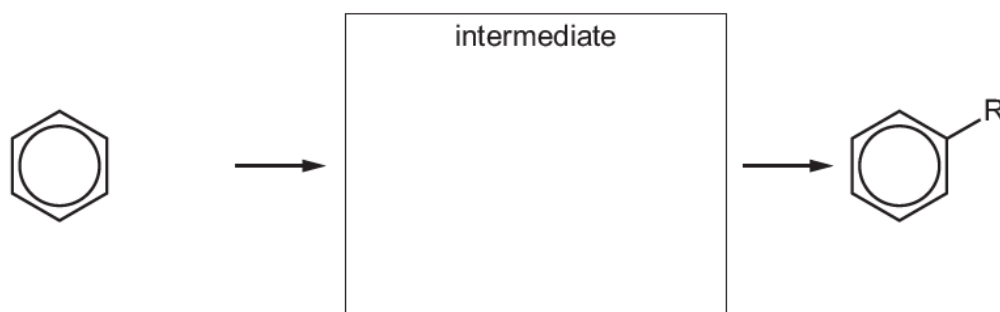
- (iii) Suggest the reagents and conditions for step 2.

..... [1]

(iv) Complete the mechanism for the reaction of benzene with the electrophile formed in (b)(i).

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

Draw the structure of the intermediate.



[3]

[Total: 11]

