1. 9701/41/O/N/16 Q1e

(ii) Write an equation for the reaction of ethane-1,2-diamine with an excess of hydrochloric acid.

.... [1]

(f) **(i)** Under certain conditions, ethane-1,2-diamine reacts with ethanedioic acid, HO_2CCO_2H, to form the polymer **Z**.

Draw the structure of this polymer, **Z**, showing **two** repeat units.

[2]

(ii) Name the *type of reaction* occurring during this polymerisation.

.... [1]

(iii) Polymer **Z** is an example of a biodegradable polymer.

Name a polymer that is non-biodegradable.

.... [1]

2. 9701/41/O/N/16 Q5d

(d) Molecules of cycloheptadiene, C_7H_{10}, consist of a seven-membered ring with two carbon-carbon double bonds.

(i) Complete the skeletal formulae of two isomers of cycloheptadiene.

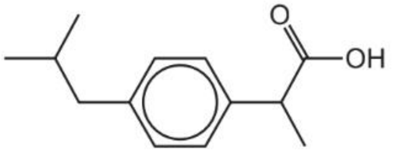
P

Q

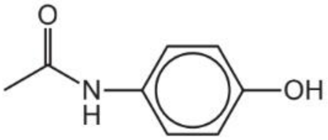
[1]

3. 9701/41/O/N/16 Q6

Ibuprofen and paracetamol are pain-relief drugs.



ibuprofen



paracetamol

(a) Ibuprofen and paracetamol both contain the aryl (benzene) functional group.

Name the **other** functional groups present in each molecule.

ibuprofen ....

paracetamol .... [2]

(b) Ibuprofen contains a chiral centre and shows stereoisomerism.

(i) State what is meant by the term *chiral centre*.

....

.... [1]

(ii) Draw the two stereoisomers of ibuprofen.

[2]

(c) Draw the structures of the organic products when ibuprofen and paracetamol react separately with $LiAlH_4$.

product with ibuprofen

product with paracetamol

[2]

(d) A student carried out some reactions with solutions of ibuprofen and paracetamol using reagents **D** and **E** and the following results were obtained.
(✓ means a reaction took place.)

reagent	ibuprofen	paracetamol
D	✓	✗
E	✗	✓

(i) Suggest a possible identity for each reagent **D** and **E**.

D ....

E ....

[2]

(ii) Give the structure of the organic product formed when reagent **D** reacted with ibuprofen.

product with ibuprofen

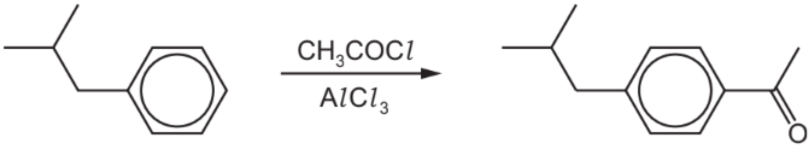
[1]

(iii) Give the structure of the organic product formed when reagent **E** reacted with paracetamol.

product with paracetamol

[1]

(e) One of the steps in the manufacture of ibuprofen is shown.

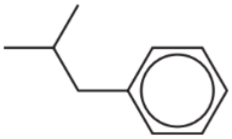


X **Y**

(i) Write an equation for the reaction between CH_3COCl and $AlCl_3$.

.... [1]

(ii) Complete the mechanism for the conversion of **X** into **Y**. Include all necessary curly arrows, any relevant dipoles and charges.



X

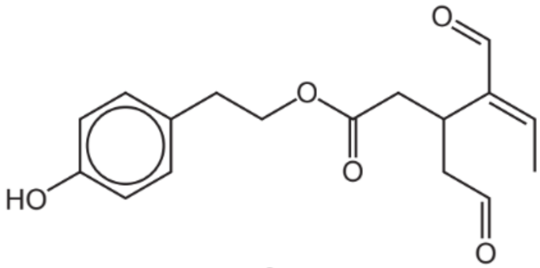
[3]

(iii) Name the mechanism in **(ii)**.

.... [1]

4. 9701/42/O/N/16 Q6a

Oleocanthal, **Q**, is a natural compound found in olive oil. It has antioxidant and anti-inflammatory properties and is thought to have a protective effect against Alzheimer's disease.



Q

(a) **Q** shows optical and cis-trans isomerism.

On the structure of **Q** above, **circle** the functional group that shows cis-trans isomerism and indicate with an **asterisk** (*) the chiral carbon atom. [1]

(c) Complete the following table to show the structures of the products formed when **Q** reacts with the three reagents.

<table>
<tr><th>reagent</th><th colspan="2">structure of product(s)</th><th>type of reaction</th></tr>
<tr><td>excess $Br_2(aq)$</td><td colspan="2"></td><td></td></tr>
<tr><td>$NaBH_4$</td><td colspan="2"></td><td></td></tr>
<tr><td>excess hot NaOH(aq)</td><td></td><td></td><td></td></tr>
</table>

[6]

(d) When a sample of **Q** synthesised in a laboratory was compared to a natural sample from olive oil, it was found that the therapeutic activity of the synthetic sample was lower.

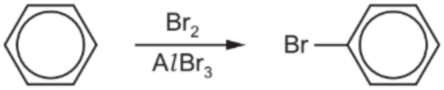
Suggest a reason for this.

....

.... [1]

5. 9701/42/O/N/16 Q7

(a) Bromobenzene can be prepared from benzene as shown.



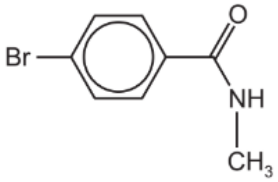
(i) Name the mechanism of this reaction.

.... [1]

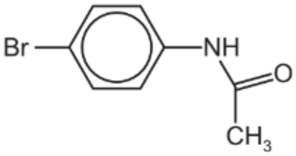
(ii) Draw the mechanism of this reaction. Include all relevant curly arrows, any dipoles and charges.

[4]

(b) Two isomeric aromatic compounds, **V** and **W**, each contain three functional groups, two of which are shown in the table.



V



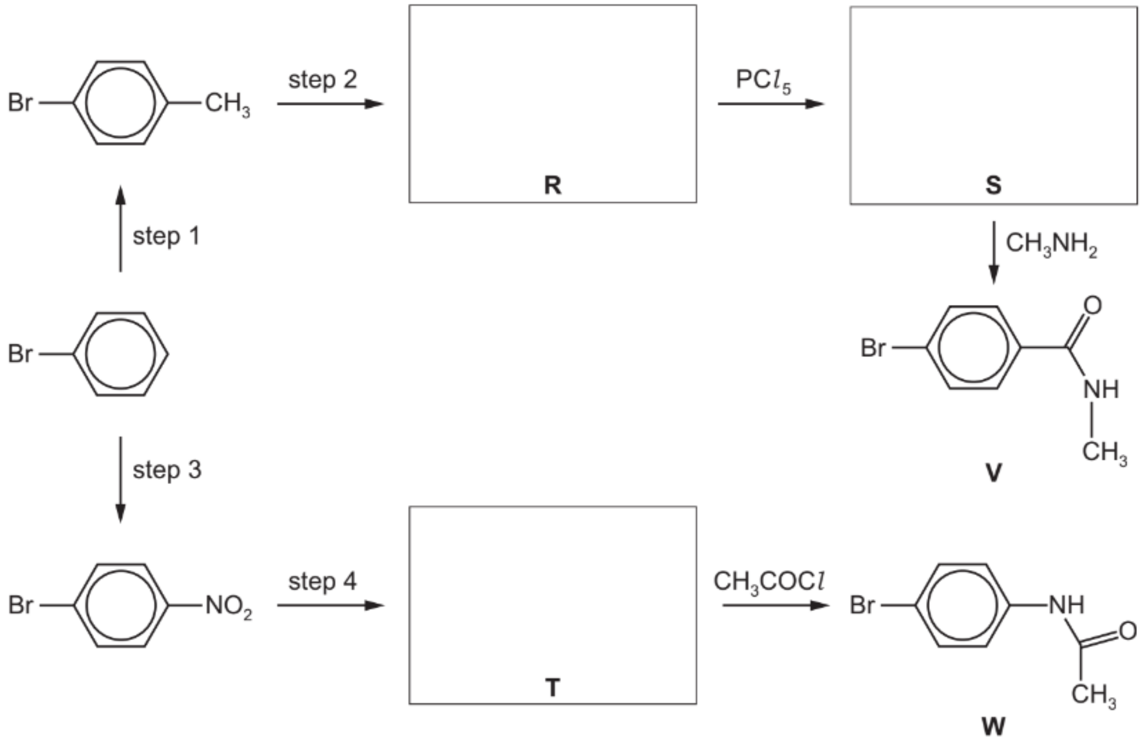
W

Complete the table with the **other** functional groups present in **V** and **W**.

substance	functional groups present		
V	bromo group	aryl (benzene) group	....
W	bromo group	aryl (benzene) group	....

[1]

(c) Compounds **V** and **W** can be synthesised from bromobenzene by the following routes.



(i) Suggest reagents for each of the steps 1–4.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

[4]

(ii) Deduce structures for **R**, **S** and **T** and draw their structural formulae in the boxes. [3]

(d) **(i)** Draw the structures of the two organic products from the reaction of **V** and **W** with $LiAlH_4$.

product from **V**

product from **W**

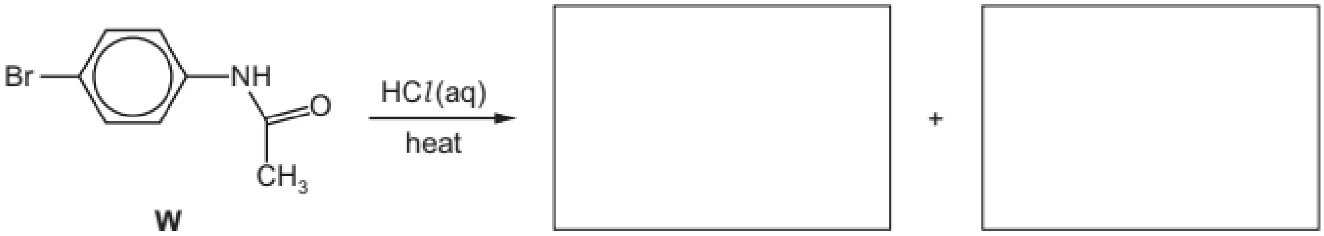
[2]

(ii) Name the *type of reaction* occurring between $LiAlH_4$ and **V** or **W**.

.... [1]

(e) **V** and **W** can be hydrolysed using hot HCl(aq).

(i) Draw the structures of the two organic products of the hydrolysis of **W**.



[2]

(ii) The products formed from the hydrolysis of **W** are soluble in aqueous acid, whereas a precipitate, **X**, is formed on hydrolysing **V**.

Draw the structure of compound **X**.

X

[1]

(iii) Suggest why **X** is insoluble in water.

....

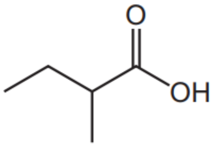
.... [1]

6. 9701/42/O/N/16 Q8b

(b) There are **four** possible structural isomers of $C_5H_{10}O_2$ that are carboxylic acids.

(i) The first isomer has been drawn.

Draw the skeletal formulae of the three **other** structural isomers.



isomer 1

isomer 2

isomer 3

isomer 4

[2]

(ii) State the systematic name of isomer 1.

.... [1]

7. 9701/41/M/J/16 Q6d

Nitrobenzene, $C_6H_5NO_2$, can be reduced to phenylamine, $C_6H_5NH_2$, in acid solution in a two step process.

(a) **(i)** Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.

$C_6H_5NO_2$ + ...e^- + ...H^+ → $C_6H_5NH_2$ + ...H_2O [1]

(ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to **(i)** useful.

......$C_6H_5NO_2$ + ...HCl + ...Sn → ......$C_6H_5NH_3Cl$ + ...$SnCl_4$ + ...H_2O [2]

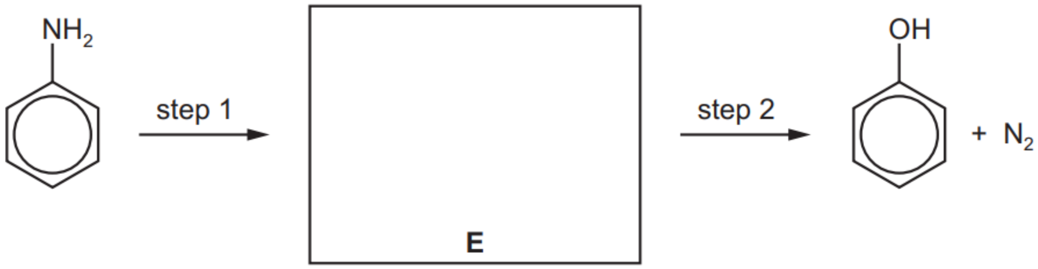
(d) How does the basicity of phenylamine compare to that of ethylamine? Explain your answer.

....

....

.... [2]

(e) Phenol can be synthesised from phenylamine in two steps.



(i) State the reagents and conditions for steps 1 and 2.

step 1 ....

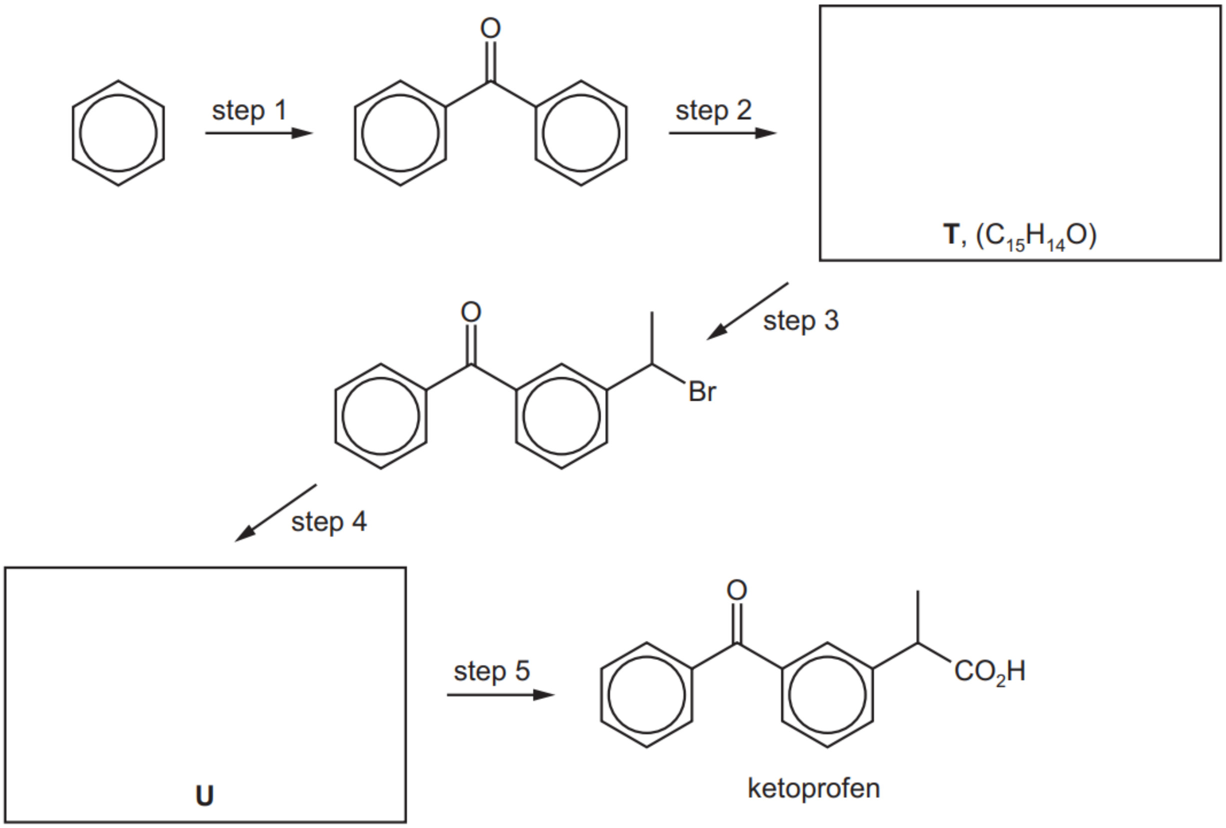
step 2 ....

[2]

(ii) Draw the structure of the intermediate compound **E** in the box above. [1]

8. 9701/41/M/J/16 Q9

The anti-inflammatory drug ketoprofen can be synthesised from benzene via the following five steps.



(a) Suggest the structures of compounds **T** and **U** and draw them in the boxes above.

(b) Suggest reagents and conditions for steps 1-5.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

step 5 ....

[5]

(c) What *types of reaction* are steps 1 and 5?

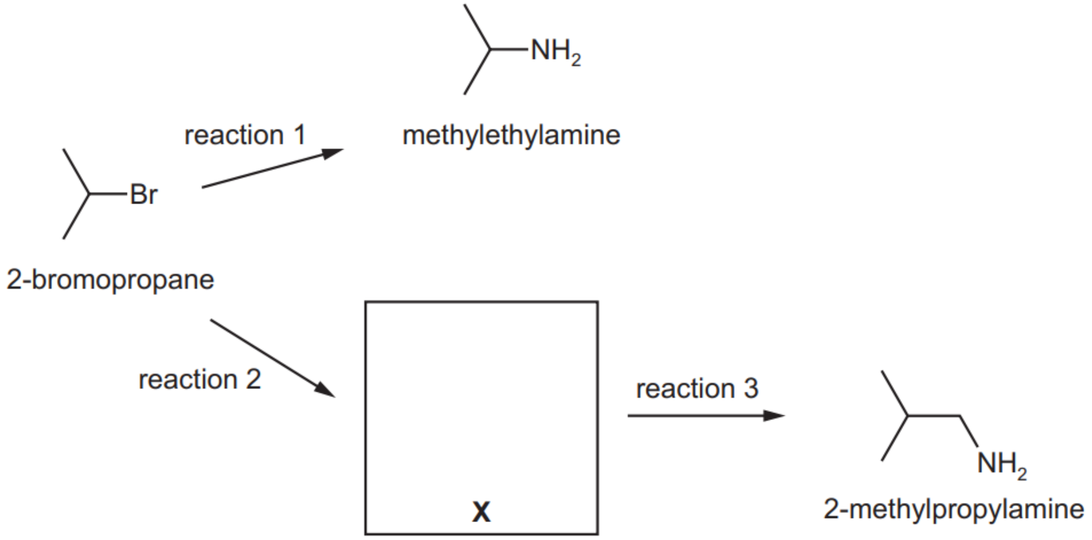
step 1 ....

step 5 ....

[2]

9. 9701/42/M/J/16 Q3

(a) 2-bromopropane can be used to synthesise methylethylamine and 2-methylpropylamine.



(i) Draw the structure of the intermediate **X** in the box above. [1]

(ii) Suggest reagents and conditions for

- reaction 1, ...
- reaction 2, ...
- reaction 3. ....

[3]

(b) (i) Write an equation showing why aqueous solutions of ethylamine are alkaline.

.... [1]

(ii) Compare the basicities of ethylamine and ammonia. Explain your answer.

....

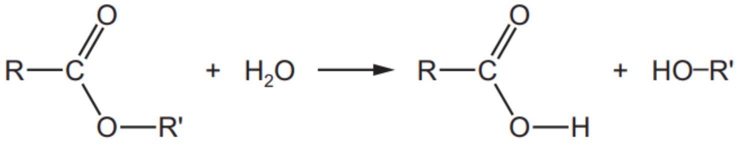
....

....

.... [2]

10. 9701/42/M/J/16 Q6a

Esterases are enzymes that hydrolyse esters.



Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould *Aspergillus niger* will hydrolyse phenyl ethanoate, $CH_3CO_2C_6H_5$, but not its isomer methyl benzoate, $C_6H_5CO_2CH_3$.

Use diagrams in your answer where appropriate.

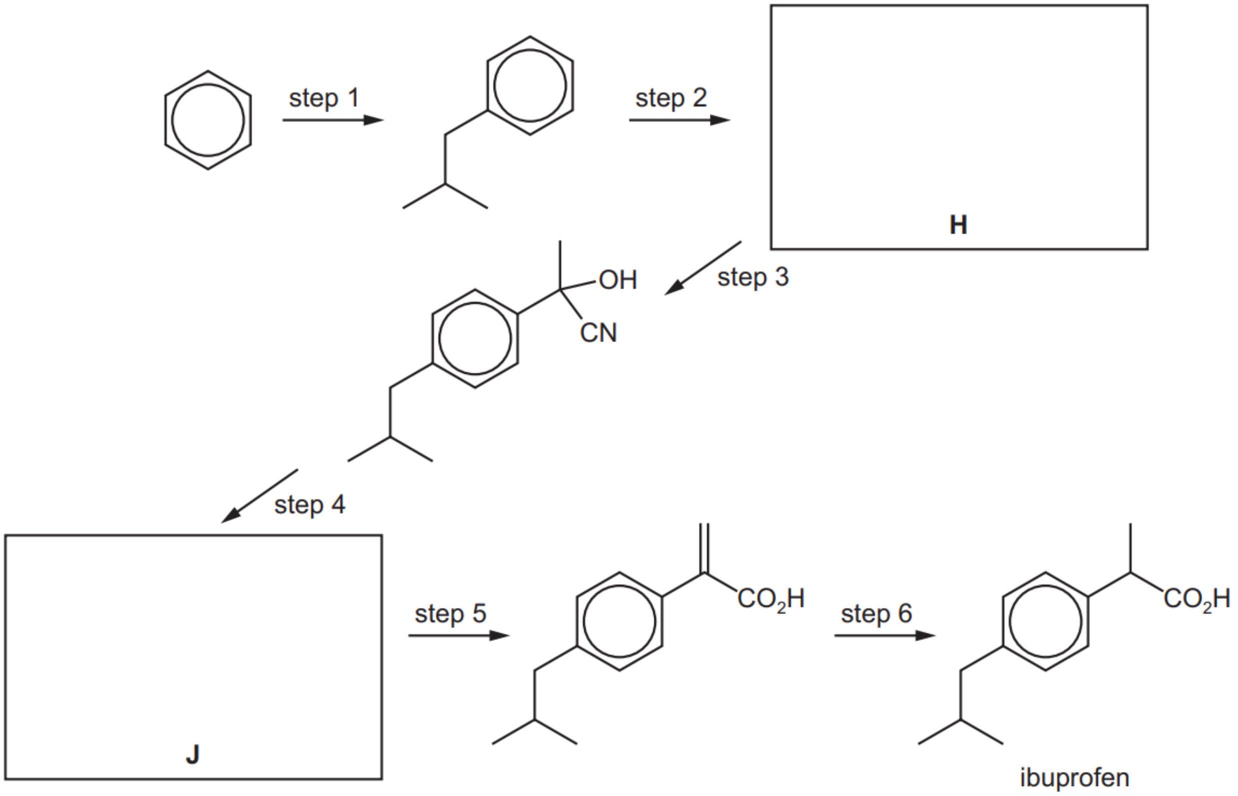
....

....

.... [3]

11. 9701/42/M/J/16 Q9

9 The anti-inflammatory drug ibuprofen can be synthesised from benzene via the following six steps.



(a) Draw circles around any chiral carbon atoms in the above five formulae. [1]

(b) Suggest the structures of compounds **H** and **J** and draw them in the boxes above. [2]

(c) Suggest reagents and conditions for steps 1-6.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

step 5 ....

step 6 ....

[6]

(d) Name the mechanism of step 1 and state the *type of reaction* for step 6.

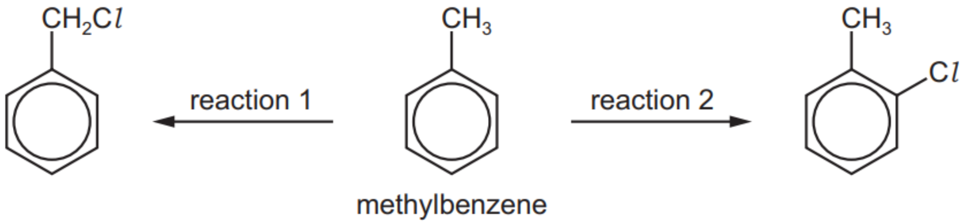
step 1 ....

step 6 ....

[2]

12. 9701/42/F/M/16 Q1c

(c) Methylbenzene can undergo different reactions to form the products shown below.



(i) Give the reagents and conditions for these two reactions.

reaction 1 ....

reaction 2 ....
[2]

(ii) Name the mechanism of reaction 1.

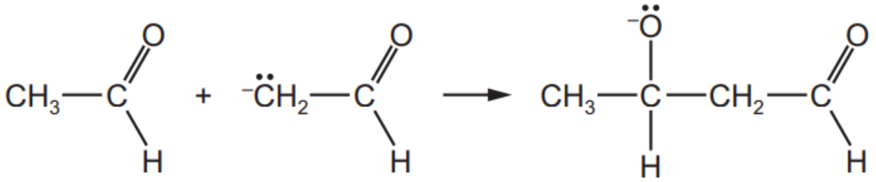
.... [1]

(iii) Draw the structure of the product obtained if reaction 1 is carried out using an excess of chlorine.

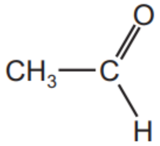
[1]

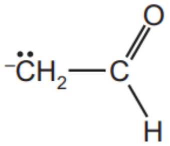
13. 9701/42/F/M/16 Q4d

step 2



(d) Using the diagram below, show the mechanism for step 2 showing the relevant curly arrows and dipoles.





[2]

14. 9701/42/F/M/16 Q7

(a) **(i)** State and explain the relative acidities of ethanol and phenol.

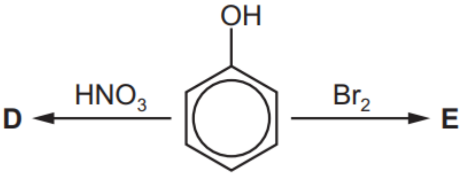
....

....

....

.... [2]

(ii) In the table below, give the reaction conditions for the formation of organic products **D** and **E** and draw their structures.



phenol

reagent	conditions	structure
HNO$_3$	dilute, 5 °C	**D**
Br$_2$		**E**

[3]

(iii) Name the mechanism of the reaction forming compound **E**.

.... [1]

(b) **(i)** Phenylamine reacts with aqueous bromine to give compound **F**.

Describe the appearance of compound **F**.

.... [1]

(ii) Phenylamine reacts with nitrous acid to form a diazonium salt.

State the conditions for this reaction.

.... [1]

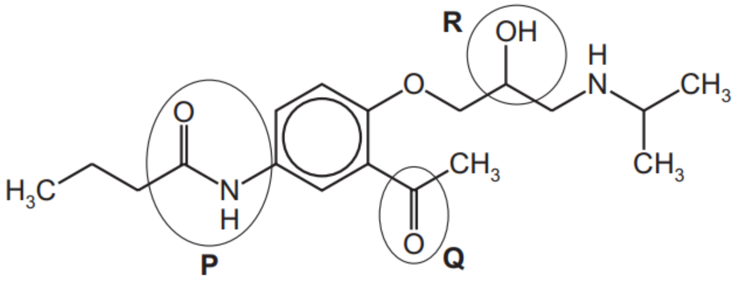
(iii) The diazonium salt in **(ii)** reacts with an alkaline solution of phenol to produce a coloured compound, **G**.

Draw the structure of **G**.

[2]

15. 9701/42/F/M/16 Q8

Acebutolol is a drug that can be used to lower blood pressure.



acebutolol

(a) Give the **full name** of the circled functional groups labelled **P**, **Q** and **R** in acebutolol.

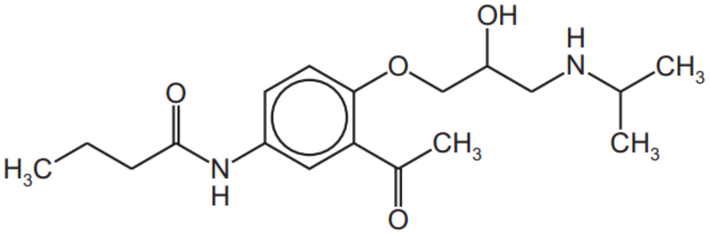
P ....

Q ....

R ....

[3]

(b) On the diagram of acebutolol below, draw a **circle** around any chiral carbon atoms.



[1]

(c) On warming with dilute hydrochloric acid, acebutolol splits to form two molecules.

(i) Draw a line through the bond broken by heating with dilute hydrochloric acid. [1]

(ii) Draw the structure of the **smaller** molecule produced by this reaction.

[1]

(d) Suggest what would be observed when acebutolol reacts with the following reagents. If no reaction would take place, write 'none' in the table below.

reagent	observation
alkaline iodine solution	
universal indicator solution	
2,4-dinitrophenylhydrazine	
Tollens' reagent	

[3]

(e) Butanoic acid can be reduced to form compound **N**. Compound **N** reacts with sodium.

(i) Suggest a suitable reducing agent for this reaction.

.... [1]

(ii) Draw the **skeletal** formula of the isomer of **N** that exists as a pair of optical isomers.

[1]

(iii) Another isomer of **N** does **not** react with acidified dichromate(VI) solution but does react with sodium.

Draw the structure of this isomer.

[1]

16. 9701/42/F/M/16 Q9

(a) **(i)** Name an example of a synthetic polyester and a synthetic polyamide.

polyester ....

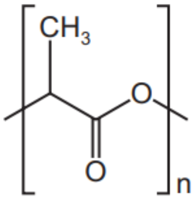
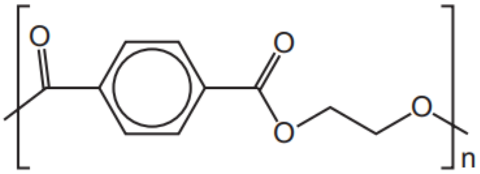
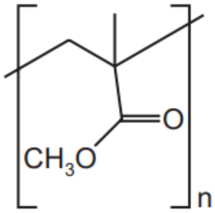
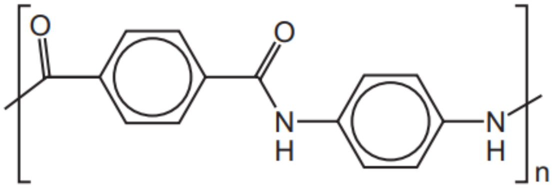
polyamide ....
[1]

(ii) Polyesters and polyamides are formed by condensation reactions.

Name a molecule which is commonly eliminated in such reactions.

.... [1]

(b) **(i)** The table shows the repeat units of a number of polymers. Place a tick (✓) against the ones which are biodegradable.

polymer	repeat unit	biodegradable
A		
B		
C		
D		

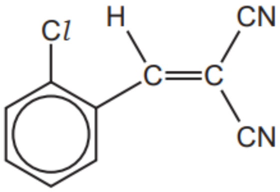
[2]

(ii) Draw the structures of two monomers used to form polymer **B**.

[2]

17. 9701/41/O/N/17 Q5

Compound **P** contains several functional groups.



P

(a) Name the functional groups present in **P**.

....

.... [2]

(b) Compound **P** can be polymerised.

Draw a section of the polymer of **P** showing **two** repeat units.
Name the type of polymerisation.

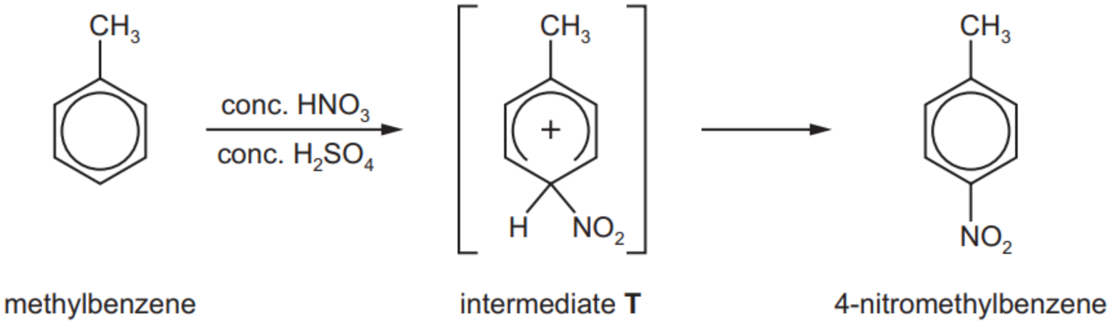
type of polymerisation ....
[2]

(c) Complete the following table to show the structures of the products formed and the *type of organic reaction* when **P** reacts with the four reagents.

reagent	structure(s) of product(s)		*type of organic reaction*
excess Br_2(aq)			
excess hot, concentrated, acidified MnO_4^-(aq)			
excess hot HC*l*(aq)			
excess H_2/Pt catalyst			

18. 9701/41/O/N/17 Q6

(a) 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown.



(i) This reaction also forms an isomer of 4-nitromethylbenzene as a by-product.

Draw the structure of this by-product.

[1]

(ii) Write an equation for the reaction between HNO_3 and H_2SO_4 that forms the electrophile for this reaction.

.... [1]

(iii) Describe how the **structure and bonding** of the six-membered ring in intermediate **T** differs from that in methylbenzene.

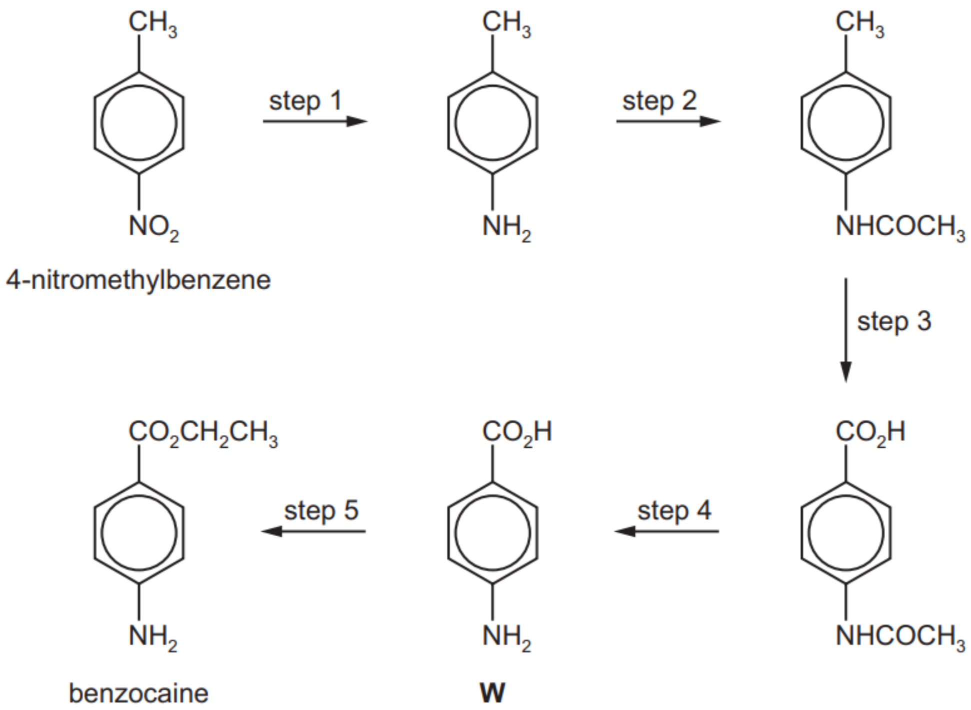
....

....

....

.... [3]

(b) Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown.



(i) Give the systematic name of compound **W**.

.... [1]

(ii) Suggest the reagents and conditions for steps 1–5.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

step 5 ....

[6]

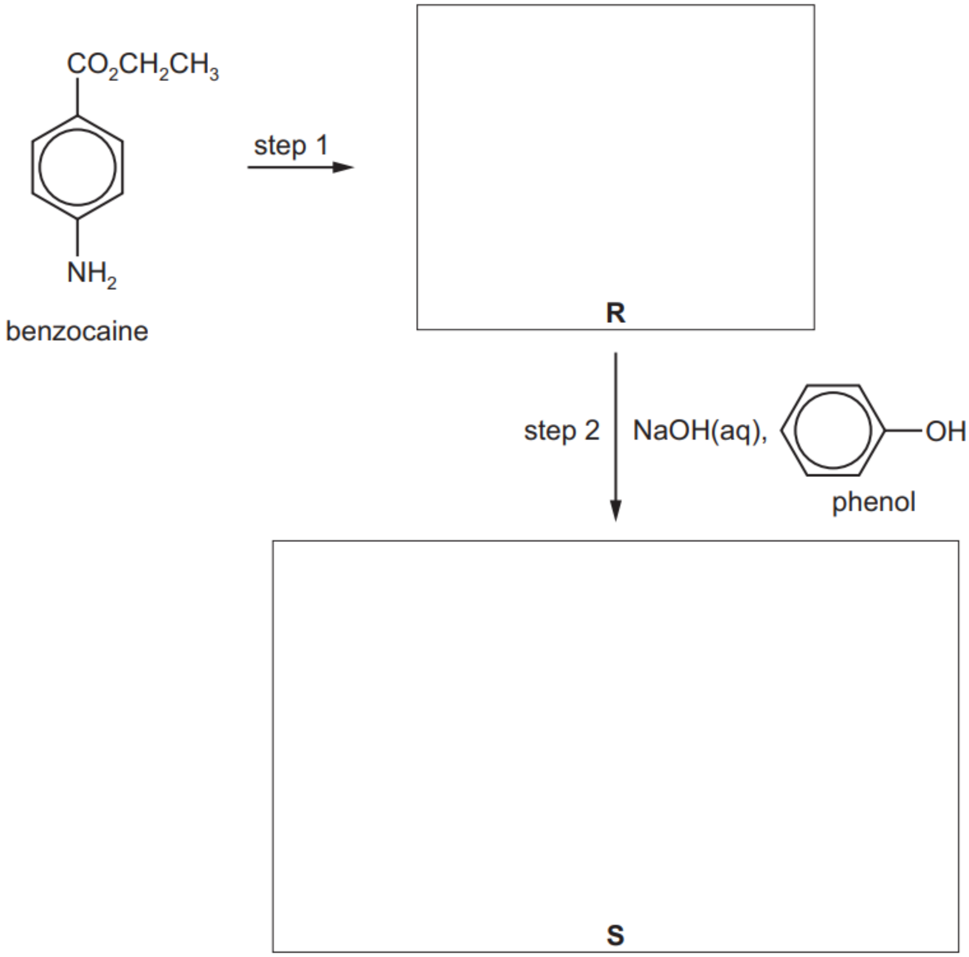
(c) Suggest how the basicity of benzocaine would compare to that of ethylamine.
Explain your answer.

....

....

.... [2]

(e) Benzocaine can also be used to synthesise the dyestuff **S** by the following route.



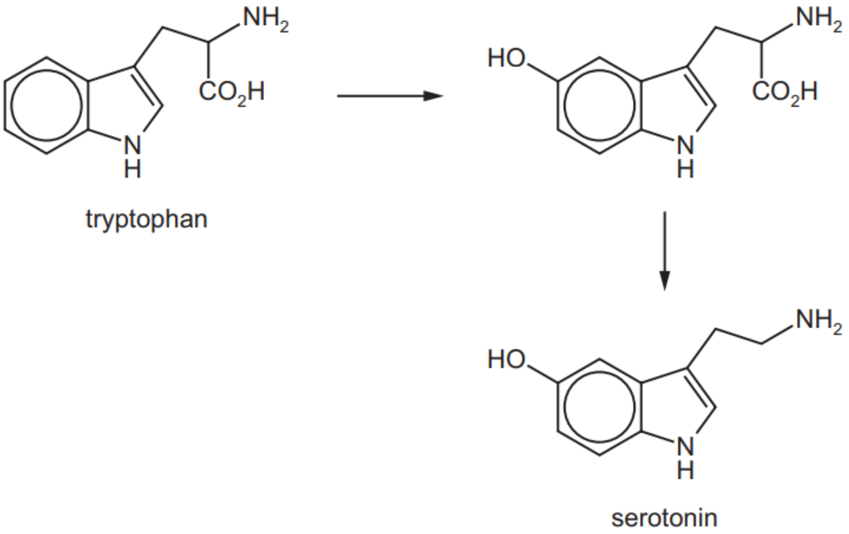
(i) Suggest the reagents used for step 1.

.... [1]

(ii) Suggest structures for compounds **R** and **S** and draw them in the boxes. [2]

19. 9701/42/O/N/17 Q3

Serotonin can be synthesised from the amino acid tryptophan in two steps.



reagent	structure of product	*type of reaction*
Na		
excess Br_2(aq)		
excess CH_3COCl		
excess H_2/Pt catalyst		

[8]

20. 9701/42/O/N/17 Q7b

(b) Ethyne is the simplest member of the alkyne homologous series.

$$H-C\equiv C-H$$

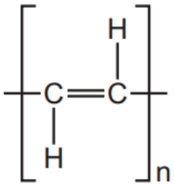
ethyne

Propyne, C_3H_4, and butyne, C_4H_6, are the next two members of the series.

Deduce the general formula for the alkynes.

.... [1]

(c) Ethyne can be polymerised into poly(acetylene), which is a conducting polymer.



$$\left[-\underset{\displaystyle H}{\underset{|}{C}}=\overset{\displaystyle H}{\overset{|}{C}}- \right]_n$$

poly(acetylene)

(i) Suggest why this polymer conducts electricity.

....

.... [1]

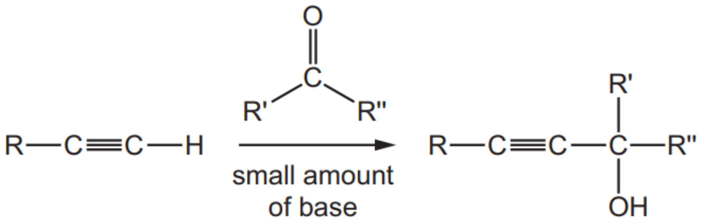
(ii) State the empirical formula of poly(acetylene).

.... [1]

(iii) By reference to a physical or chemical property, suggest **one** advantage of a conducting polymer when compared with metals.

.... [1]

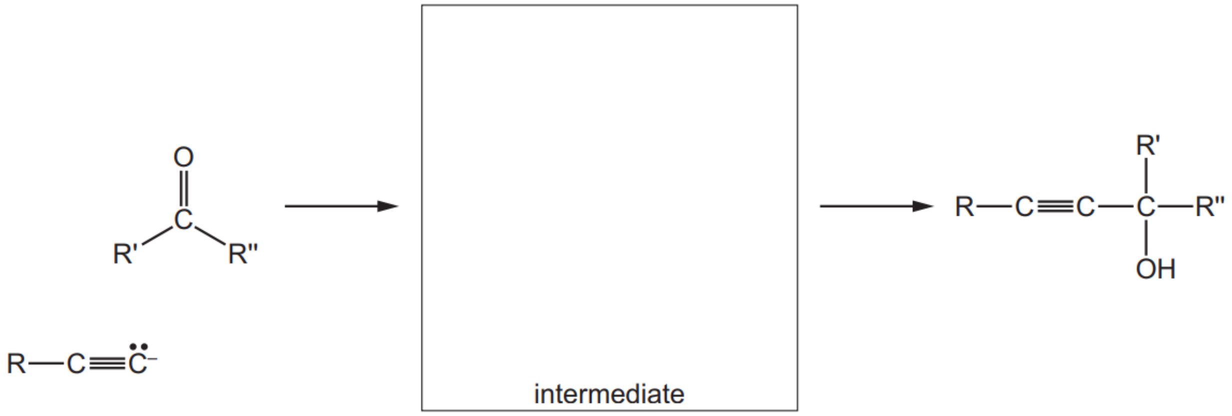
(d) Alkynes can react with carbonyl compounds under basic conditions as shown in reaction 1.



reaction 1

(i) The first step of the mechanism of reaction 1 involves the alkyne anion reacting with the carbonyl compound.

Complete the first step of the mechanism and draw the intermediate for this reaction. Include all relevant dipoles, charges and curly arrows.

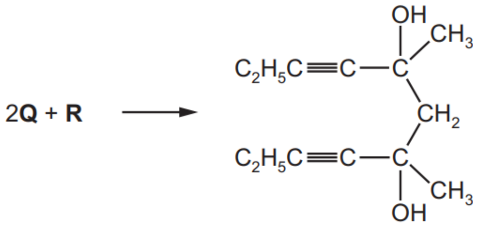


[3]

(ii) Suggest the name of the mechanism in reaction 1.

.... [1]

(iii) An alkyne, **Q**, and a carbonyl compound, **R**, react together to form compound **P** as shown.



P

Use reaction 1 to suggest the structures of **Q** and **R**.

Q

R

[2]

(e) A series of twelve separate experiments is carried out as shown in the table.

Complete the table by writing in **each** box a tick (✓) if a reaction occurs, or a cross (✗) if no reaction occurs.

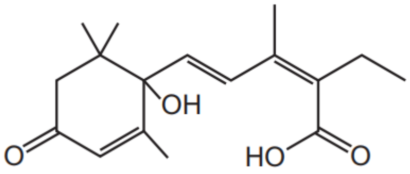
	CH_3CHO	HCO_2H	CH_3COCH_3	HO_2CCO_2H
hot, acidified MnO_4^-(aq)				
alkaline I_2(aq)				
warm Tollens' reagent				

[4]

21. 9701/42/O/N/17 Q8

(a) Compound **A** can be produced from a plant hormone.

A



(i) Compound **A** shows optical and geometrical isomerism.

On the structure of **A** above,

- draw a **line** through the bond(s) that give rise to geometrical isomerism,
- **circle** all chiral carbon atoms.

[2]

(ii) Give the **names** of four functional groups present in **A**.

....

.... [2]

(iii) A molecule of **A** has 17 carbon atoms.

State the number of carbon atoms that are sp, sp^2 and sp^3 hybridised in **A**.

sp carbons = ... sp^2 carbons = ... sp^3 carbons = ...

[1]

(iv) When **A** is reacted with an excess of hot, concentrated manganate(VII) ions, a mixture of three organic compounds is formed.

$$\mathbf{A} \rightarrow \underset{(C_{10}H_{14}O_7)}{\mathbf{X}} \text{ and } \underset{(C_3H_4O_3)}{\mathbf{Y}} \text{ and } \underset{(C_4H_6O_3)}{\mathbf{Z}}$$

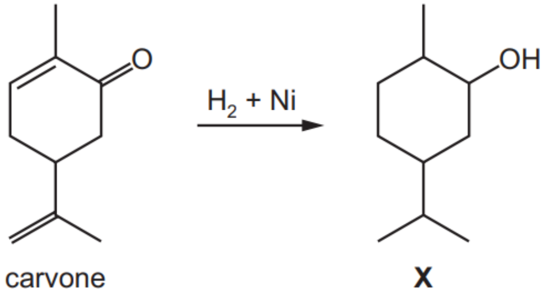
Suggest the structures of **Y** and **Z**.

Y ($C_3H_4O_3$)	**Z** ($C_4H_6O_3$)

[2]

22. 9701/41/M/J/17 Q4

Carvone occurs in spearmint and a stereoisomer of carvone occurs in caraway seeds. Treating either isomer with hydrogen over a nickel catalyst produces a mixture of isomers with the structural formula **X**.



(a) **(i)** State the type of stereoisomerism carvone can show. Explain your answer.

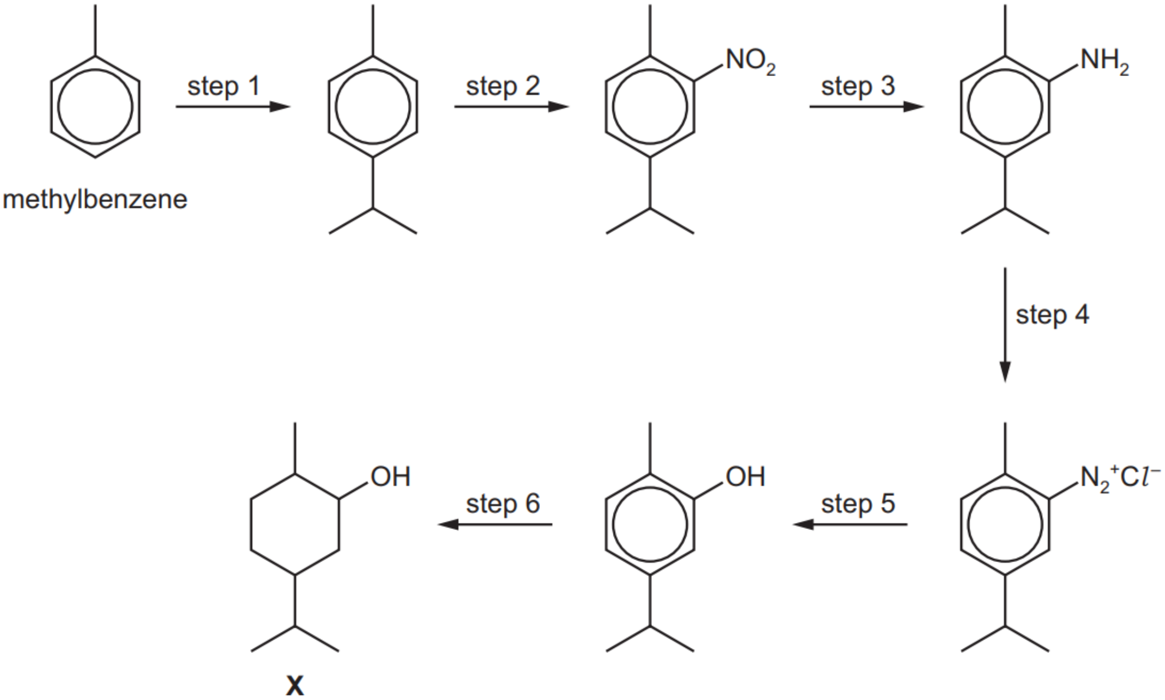
....

.... [1]

(ii) Write an equation, using molecular formulae, for this conversion of carvone to **X**.

.... [2]

X can be synthesised from methylbenzene by the following route.



(b) **(i)** Name the mechanism in step 1.

.... [1]

(ii) What type of reaction is occuring in the following steps?

step 3 ....

step 5 ....
[2]

(iii) Suggest reagents and conditions for each of the following steps.

step 1 ....

step 2 ....

step 3 ....

step 4 ....
[6]

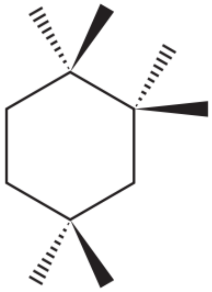
(c) During step 6, hydrogen is added to the benzene ring to produce the cyclohexane ring in **X**. The six hydrogen atoms are all added to the **same side** of the benzene ring.

(i) State the reagents and conditions needed for this reaction.

.... [1]

(ii) Complete the part structure to show the structure of the isomer of **X** that would most likely be obtained during this reaction.

X



[2]

23. 9701/41/M/J/17 Q5

5 Compounds **J**, **K**, **L** and **M** are isomers of each other with the molecular formula $C_9H_{11}NO$.
All four isomers contain a benzene ring.
Two of the isomers contain a chiral centre.
The results of six tests carried out on **J**, **K**, **L** and **M** are shown in the table.

test		observations with each isomer			
		J	**K**	**L**	**M**
1	add cold HC*l*(aq)	soluble	soluble	soluble	insoluble
2	add 2,4-DNPH reagent	orange ppt.	orange ppt.	orange ppt.	no reaction
3	add NaOH(aq) + I_2(aq)	pale yellow ppt.	no reaction	pale yellow ppt.	no reaction
4	warm with Fehling's solution	no reaction	red ppt.	no reaction	no reaction
5	heat with NaOH(aq)	no reaction	no reaction	no reaction	**P**(C_6H_7N) and **Q**($C_3H_5O_2Na$) produced
6	diazotization and addition of alkaline phenol	no dye produced	orange dye produced	no dye produced	no dye produced

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in each of the four isomers **J**, **K**, **L** and **M**.
Complete the table below, identifying the group(s) present in each isomer.

group(s) in compound			
J	**K**	**L**	**M**
....	....	....	....

[5]

(b) (i) Name the *type of reaction* occurring in test 5 that converts **M** into **P** + **Q**.

.... [1]

(ii) Suggest structures for compounds **P** and **Q**.

P (C_6H_7N)

Q ($C_3H_5O_2Na$)

[2]

(c) Isomers **J**, **K**, **L** and **M** all have the molecular formula $C_9H_{11}NO$.

Use the information in **(a)** to suggest a structure for each of these isomers and draw these in the boxes. Draw **circles** around all chiral centres in **K** and **L**.

J

K

L

M

[5]

(d) Compound **N** is another isomer which has the same molecular formula $C_9H_{11}NO$ and also contains a benzene ring.
N contains the same functional group as **M**.
When heated with NaOH(aq), **N** produces ethylamine and a sodium salt **W**.
Suggest the structure of **W**.

W

[1]

24. 9701/41/M/J/17 Q6c

The reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol is:

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

draw the mechanism for the reaction of :

c(i) 1-chloro-1-phenylethane with hydroxide ions, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structures of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

....

.... [1]

25. 9701/42/M/J/17 Q2d

Important information for this question

- In this question (pr) means 'a solution in propanone'.
- Sodium iodide is soluble in propanone giving $Na^+(pr)$ and $I^-(pr)$.
- Sodium chloride is insoluble in propanone.

The reaction between 2-chlorobutane and sodium iodide in propanone is shown.

$$CH_3CH_2CHClCH_3(pr) + Na^+(pr) + I^-(pr) \rightarrow CH_3CH_2CHICH_3(pr) + NaCl(s)$$

(d) **(i)** Suggest the mechanism for the reaction of 2-chlorobutane with iodide ions. Draw out the steps involved, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structure of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 2-chlorobutane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

....

.... [1]

26. 9701/42/M/J/17 Q3c

(c) The following synthetic route shows how a carboxylic acid can be converted into an amine.

$$CH_3CO_2H \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{\text{step 3}} CH_3CH_2NH_2$$

(i) Suggest a reagent for step 3.

.... [1]

Angelic acid, $C_5H_8O_2$, is a natural product isolated from the roots of the angelica plant.

- Angelic acid reacts with H_2 + Ni to form **T**, $C_5H_{10}O_2$.
- **T** undergoes the above synthetic route to form the amine **U**, $C_5H_{13}N$.
- **U** can also be made by reacting 1-bromo-2-methylbutane with ammonia.

Both angelic acid and **T** exist as stereoisomers.

(ii) Suggest structures for angelic acid, **T** and **U**.

angelic acid	**T**	**U**

[3]

(iii) State the type of stereoisomerism shown by angelic acid and **T**.

angelic acid ....

compound **T** ....
[1]

27. 9701/42/M/J/17 Q7

7 Compounds **W**, **X**, **Y** and **Z** are isomers of each other with the molecular formula C_8H_7ClO.
All four isomers contain a benzene ring.
Only **one** of the isomers contains a chiral centre.
The results of six tests carried out on **W**, **X**, **Y** and **Z** are shown in the table.

test		observations with each isomer			
		W	**X**	**Y**	**Z**
1	add cold $AgNO_3(aq)$	white ppt. forms immediately	none	white ppt. forms very slowly	none
2	heat with NaOH(aq), then add dilute HNO_3 + $AgNO_3(aq)$	white ppt.	none	white ppt.	none
3	add NaOH(aq) + $I_2(aq)$	none	pale yellow ppt.	none	none
4	warm with Fehling's solution	none	none	red ppt.	none
5	add cold, dilute, acidified $KMnO_4(aq)$	no change	no change	no change	decolourises
6	add $Br_2(aq)$	no change	no change	no change	decolourises and forms white ppt.

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in the four isomers **W**, **X**, **Y** and **Z**.

Complete the table below, identifying the group(s) present in each isomer.

group(s) in compound			
W	**X**	**Y**	**Z**
....	....	....	....
....	....	....	....
....	....	....	....

[5]

(b) Isomers **W**, **X**, **Y** and **Z** all have the molecular formula $C_8H_7C\mathit{l}O$.

(i) Use the information in **(a)** to suggest a structure for each of these isomers and draw these in the boxes.

W

X

Y

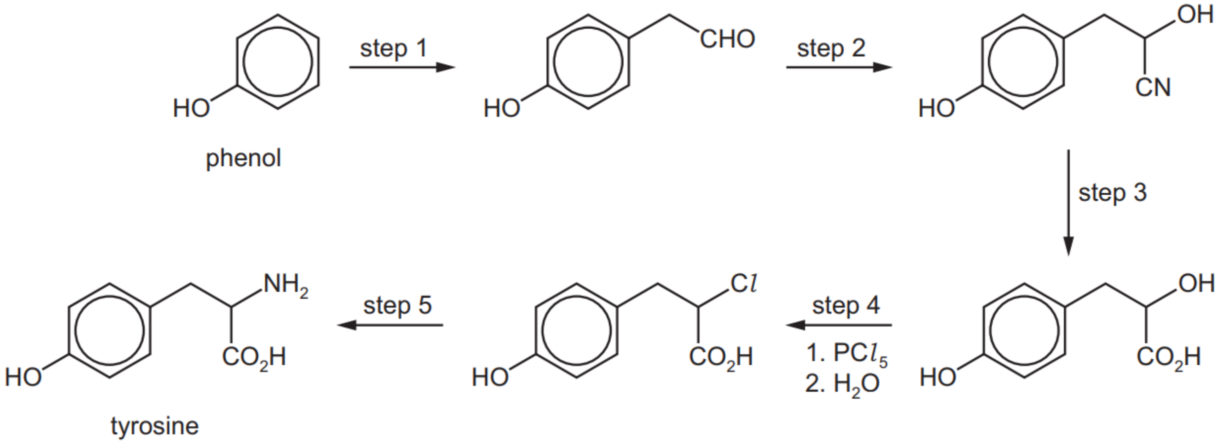
Z

[4]

(ii) Draw a **circle** around the chiral centre in **one** of the above structures. [1]

28. 9701/42/M/J/17 Q8

8 **(a)** The amino acid tyrosine can be synthesised from phenol by the route shown.



(i) Name the mechanism occurring in the following steps.

step 1 ....

step 2 .... [2]

(ii) What *type of reaction* is occurring in step 3?

.... [1]

(iii) Suggest reagents and conditions for each of the following steps.

step 1 ....

step 2 ....

step 3 ....

step 5 .... [5]

(iv) Draw the structures of the products of the reactions of tyrosine with an **excess** of each of the following reagents.

with NaOH(aq)

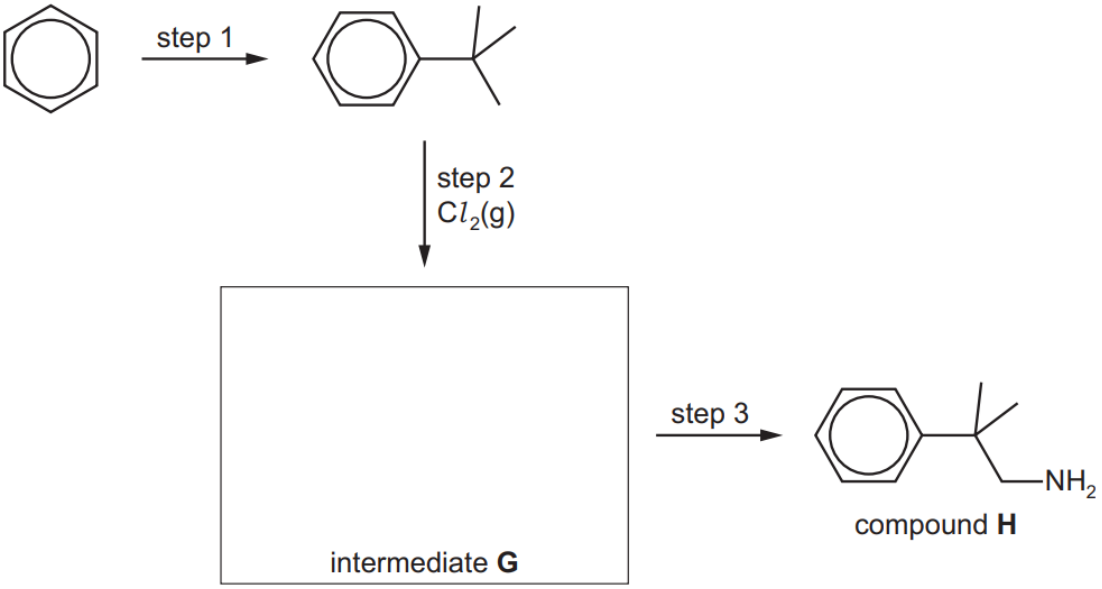
with HC*l*(aq)

with Br_2(aq)

[4]

29. 9701/42/F/M/17 Q5

(a) Compound **H** can be synthesised from benzene as shown.



(i) State the reagents and conditions needed for step 1.

reagents ....

conditions ....
[2]

(ii) Step 2 takes place in the presence of chlorine gas.

State the conditions for this reaction.

.... [1]

(iii) Draw the structure of intermediate **G** in the box. [1]

(iv) State the reagents and conditions needed for step 3.

reagents ....

conditions ....
[2]

(b) Write an equation to show how compound **H**, $C_{10}H_{13}NH_2$, behaves as a base.

.... [1]

(c) Compare the relative basicities of ammonia, phenylamine and compound **H**. Explain your answer.

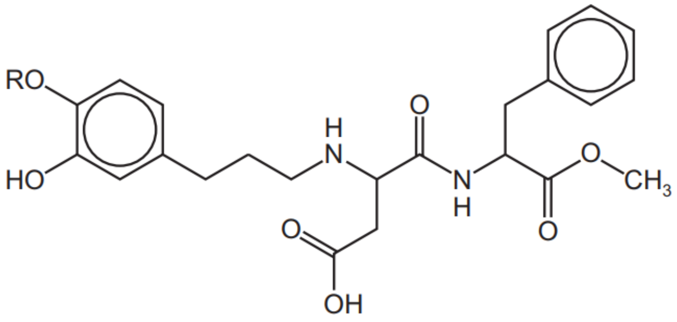
....

....

.... [2]

30. 9701/42/F/M/17 Q7

The compound *Advantame* is a sweetener that tastes approximately 25 000 times sweeter than sucrose.

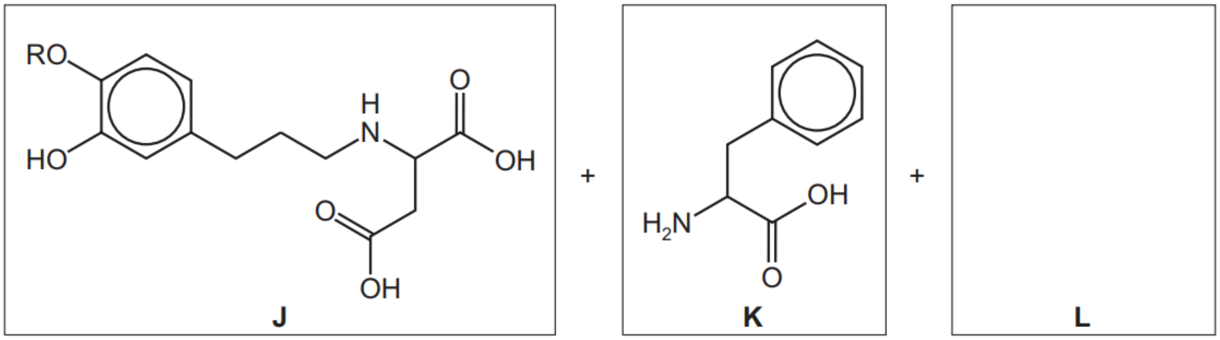


Advantame

(a) *Advantame* is optically active.

On the diagram of *Advantame*, circle all the chiral carbon atoms. [1]

(b) The decomposition of *Advantame* produces three molecules, **J**, **K** and **L**. The RO– group in *Advantame* is unreactive.



(i) Suggest possible reagents and conditions for this decomposition.

.... [1]

(ii) Name the *type of reaction* occurring.

.... [1]

(iii) Draw the structure of **L** in the box above. [1]

(c) **(i)** Aqueous bromine was added dropwise to a solution of **J** until the bromine was in excess.

State what you would observe.

....

.... [1]

(ii) **J** has the molecular formula $C_{14}H_{19}O_6N$.

Use this formula to write an equation for the reaction of excess aqueous sodium hydroxide with **one** mole of **J**.

.... [2]

(d) **(i)** State what you would observe when an excess of aqueous bromine is added to a solution of **K**.

.... [1]

(ii) **K** can be polymerised.

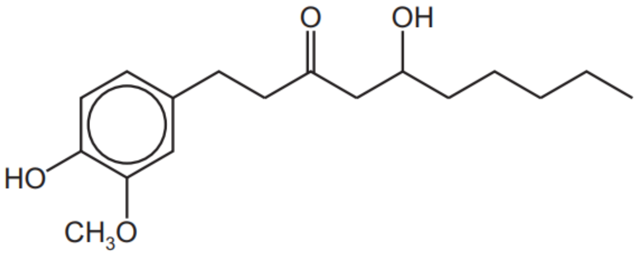
Draw the structure of the polymer showing **two** repeat units. The linkage between the monomer units should be fully displayed.

[2]

31. 9701/42/F/M/17 Q8

The root of the ginger plant contains compounds with medicinal and flavouring properties. Three of the more important compounds are gingerol, shogaol and zingerone.

(a) The structure of gingerol is shown. The CH_3O– group in gingerol is unreactive.



gingerol

Gingerol reacts with acidified potassium dichromate(VI).

State the *type of reaction* and the functional group change which occurs during this reaction.

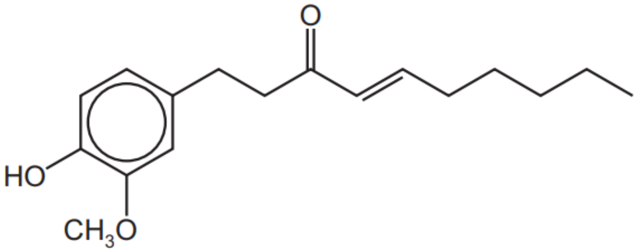
type of reaction ....

functional group change

from .... to ....

[1]

(b) The structure of shogaol is shown.



shogaol

(i) State the *type of reaction* needed to convert gingerol into shogaol.

.... [1]

(ii) State the reagents and conditions needed to convert gingerol into shogaol.

reagents ....

conditions ....

[1]

(iii) Shogaol reacts with hot, concentrated acidified manganate(VII) ions to form two organic products, **Q** and **R**.

Draw the structures of **Q** and **R**.

Q

R

[2]

(c) Zingerone is formed from gingerol.

Some reactions of zingerone are shown.

Complete the table to identify the functional groups in zingerone.

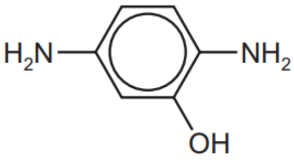
reagent and conditions	observation	functional group in zingerone indicated by the observation
benzenediazonium chloride, 5 °C, alkaline solution	red ppt.	
2,4-dinitrophenylhydrazine	orange ppt.	
warm with Tollens' reagent	no change	

[2]

32. 9701/41/O/N/18 Q5

(a) Polyhydroxyamide is a fire-resistant polyamide which is formed from the two monomers, **F** and **G**.

F



G

(ii) Draw the repeat unit of polyhydroxyamide. The amide bond should be shown displayed.

[2]

(b) When poly(ethene) is formed from ethene, many bonds are broken and formed.

Place **one tick** (✓) in **each row** of the table to indicate the types of bonds broken and formed in this process.

	σ-bonds only	π-bonds only	both σ- and π-bonds
bonds broken			
bonds formed			

[2]

(c) Addition polymers can be classified into two types.

- homopolymer - a polymer made up of the same monomer unit
- copolymer - a polymer made up of two or more different monomer units

The reaction of propene, $CH_3CH{=}CH_2$, with phenylethene, $C_6H_5CH{=}CH_2$, gives a copolymer.

Draw a length of the chain of this copolymer that contains one molecule of **each** monomer.

[2]

(d) (i) Polyalkenes biodegrade very slowly.

Explain why by referring to the structures of the polymers.

....

....

.... [1]

(ii) Some polymers will degrade in the environment.

Describe **two** processes by which this occurs.

1 ....

2 ....

[2]

33. 9701/41/O/N/18 Q7

(a) Chlorobenzene and phenol both show a lack of reactivity towards reactants that cause the breaking of the C–X bond (X = C*l* or OH).

Explain why.

....

....

....

....

.... [3]

(b) When phenol is reacted with bromine dissolved in an inert solvent, two isomeric bromophenols, C_6H_4BrOH, are formed.

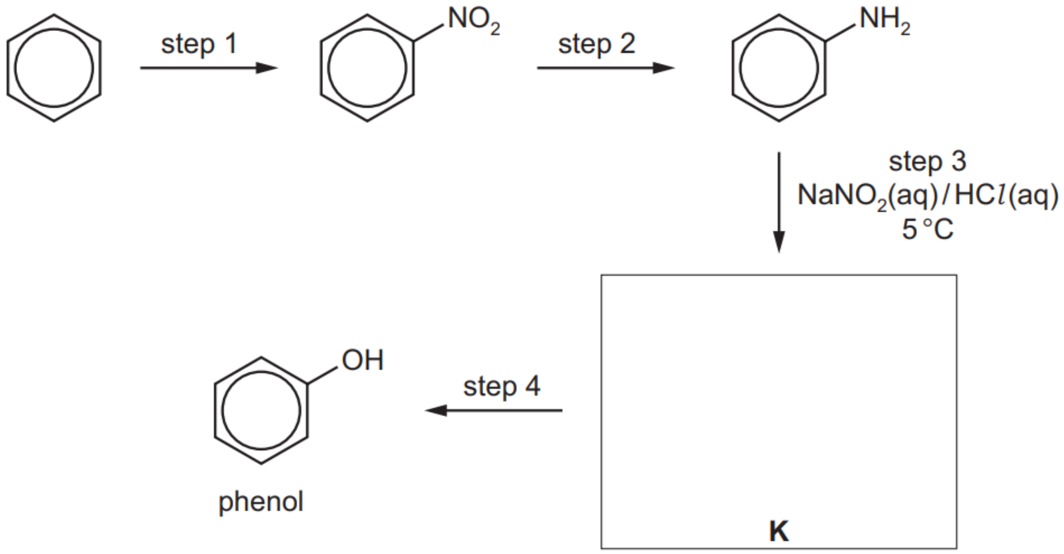
Suggest structures for these products. Name each compound.

name: ....

name: ....

[2]

(c) A student suggested that phenol can be prepared from benzene by the method shown.



(i) Suggest reagents and conditions for each of the following steps.

step 1 ....

step 2 ....

step 4 ....
[3]

(ii) Deduce the structure for **K** and draw its structural formula in the box. [1]

(iii) Name the mechanism for step 1.

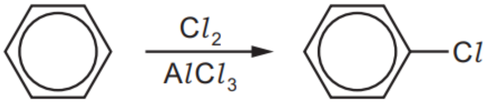
.... [1]

(iv) Write an equation for step 2. Use [H] for the reducing agent in this equation.

[1]

34. 9701/42/O/N/18 Q1b

(b) Chlorobenzene can be prepared from benzene as shown.



Aluminium chloride, $AlCl_3$, catalyses this reaction.

(i) Write an equation to show how $AlCl_3$ generates the electrophile needed in this reaction.

.... [1]

(ii) Draw the mechanism of the reaction between this electrophile and benzene to form chlorobenzene. Include all relevant curly arrows and charges.

[4]

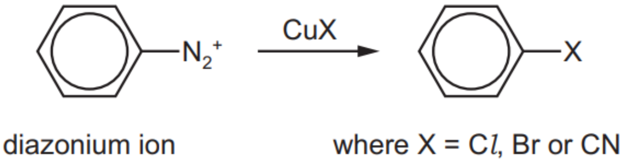
(iii) Write an equation to show how the catalyst is regenerated.

.... [1]

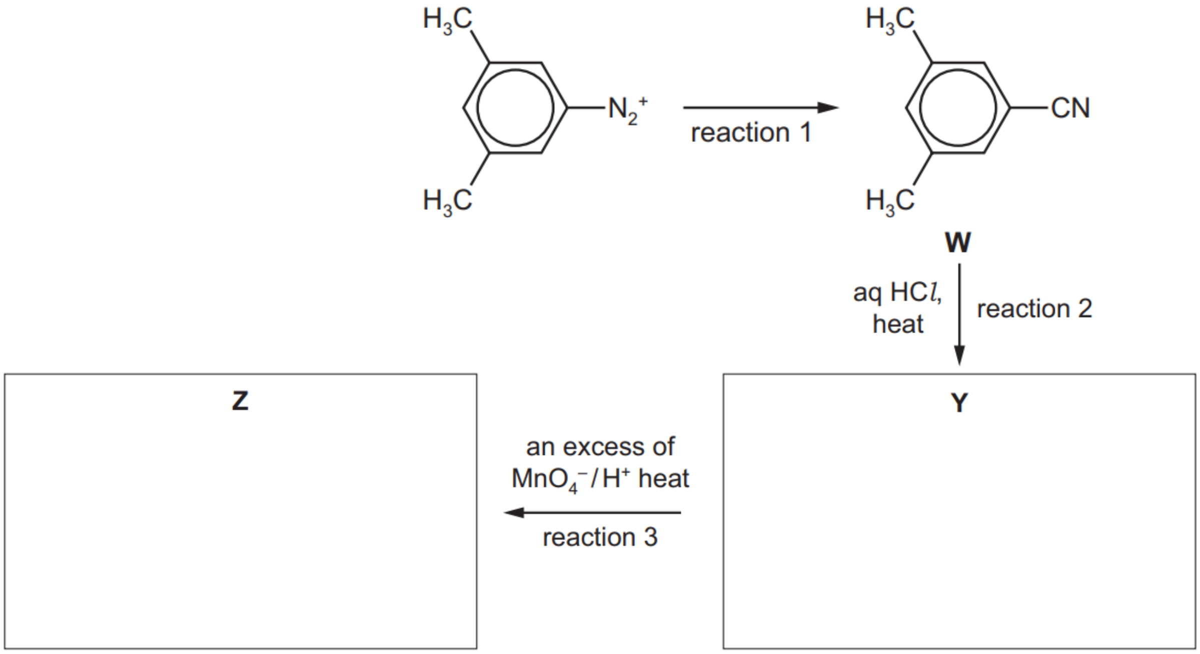
35. 9701/42/O/N/18 Q5f

(f) Nitrous acid is used in the preparation of diazonium salts. The –N_2^+ group in the diazonium ion can be replaced with C*l*, Br or CN as shown.

The reagent used is a copper(I) salt, CuX.



This reaction can be used in the synthesis of compound **Z** as shown.



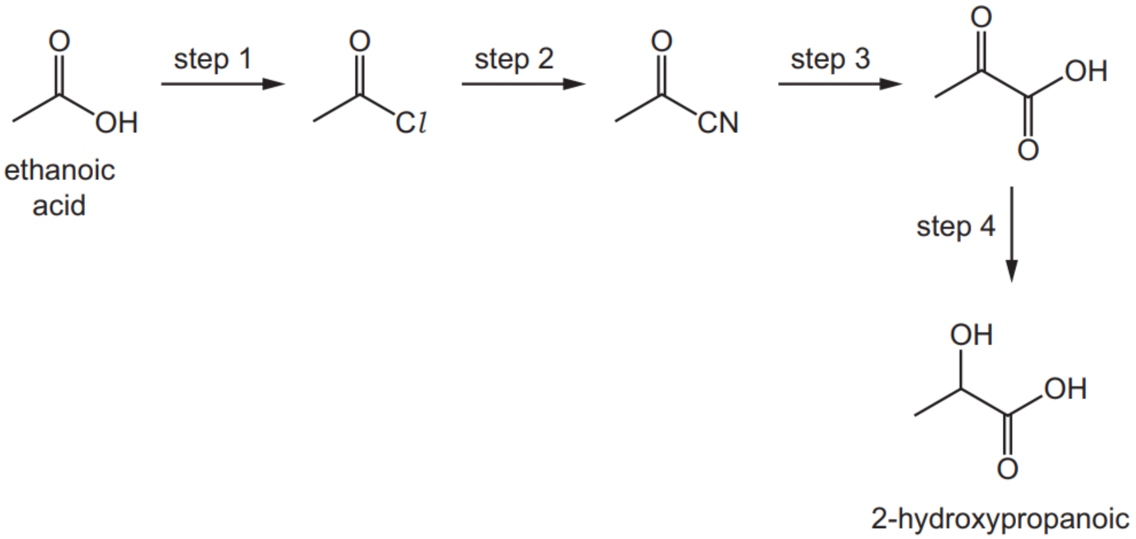
(i) Suggest the reagent used in reaction 1.

.... [1]

(ii) Suggest structures of compounds **Y** and **Z** and draw them in the boxes above. [2]

36. 9701/42/O/N/18 Q6

2-hydroxypropanoic acid can be synthesised in four steps from ethanoic acid.



2-hydroxypropanoic acid

(a) **(i)** Suggest a reagent for step 2.

.... [1]

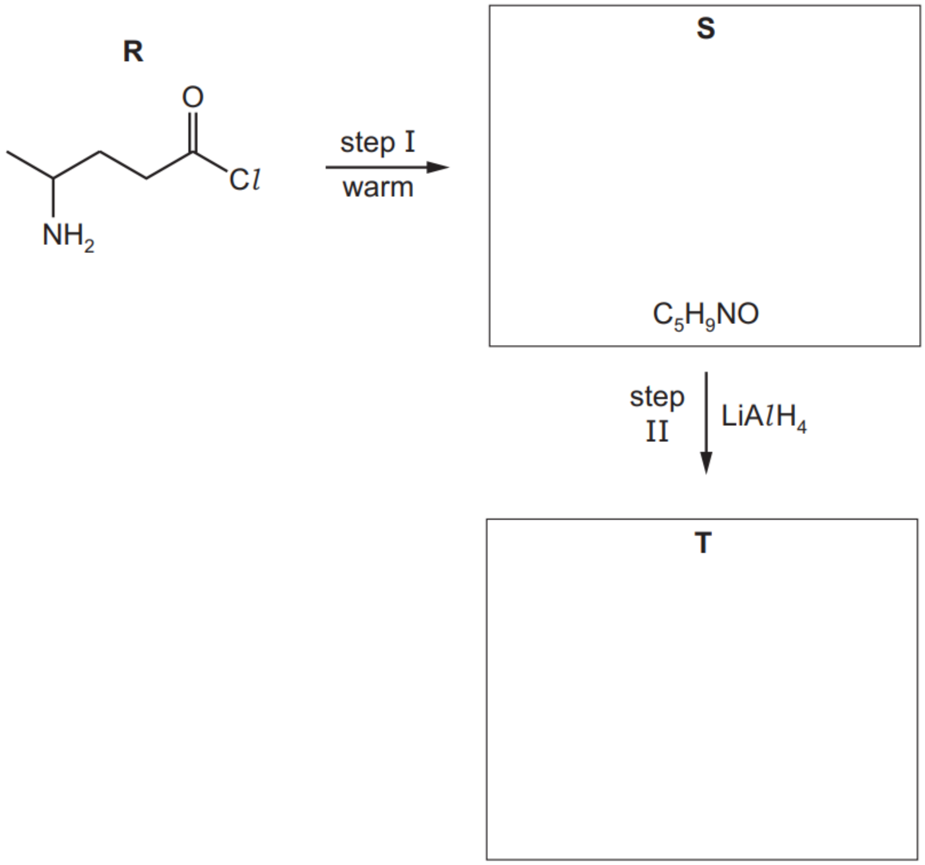
(ii) Suggest reagents and conditions for steps 1 and 4.

step 1 ....

step 4 ....

[2]

(b) Compound **R** can be used in the synthesis of compound **T** as shown.



(i) Suggest the structures of **S** and **T** and draw them in the boxes. [2]

(ii) Name the *type of reaction* for step I and step II.

step I ....

step II ....
[2]

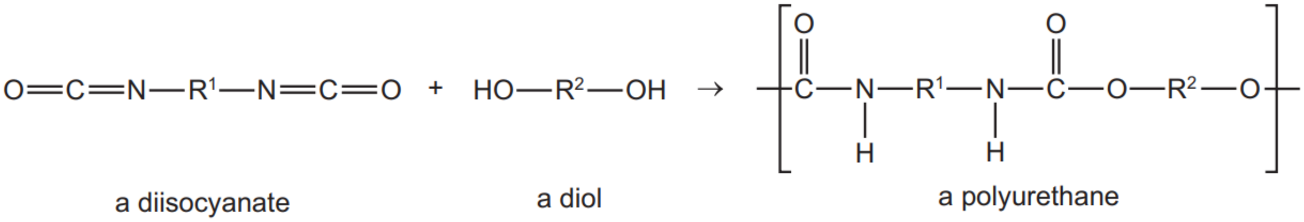
(c) Compound **R** can be polymerised.

Draw a section of this polymer showing **two** repeat units.

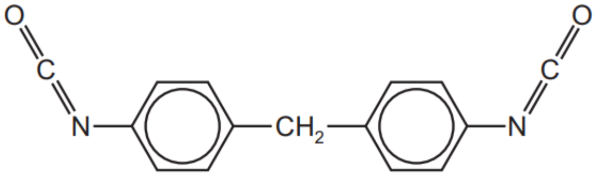
[2]

37. 9701/42/O/N/18 Q7

(a) Polyurethanes are polymers made by the reaction of a diisocyanate with a diol as shown. R^1 and R^2 are hydrocarbon groups.



Lycra® is a polyurethane formed from the diisocyanate **P** and $HOCH_2CH_2OH$.



P

(i) Give the molecular formula for **P**.

.... [1]

(ii) Draw the repeat unit of Lycra®.

[2]

(iii) Fibres of Lycra® are strong due to the intermolecular forces between the polymer chains.

Complete the table to identify two intermolecular forces responsible for this property and the group(s) involved.

intermolecular force	group(s) involved

[2]

(b) Name **one** example of each of the following types of polymer.

type of polymer	example
synthetic polyamide	
synthetic polyester	
conducting polymer	
non-solvent based adhesive	

[3]

38. 9701/42/O/N/18 Q8

(a) Chloramine, NH_2Cl, can be used in the treatment of drinking water to kill bacteria. Excess chloramine in water is destroyed using UV light. The mechanism for this involves free radicals.

The initiation step in this process is shown.

$$NH_2Cl \xrightarrow{UV} \bullet NH_2 + \bullet Cl$$

(i) What is meant by the term *free radical*?

....

.... [1]

The equation for a possible propagation step in the process is shown.

$$NH_2Cl + \bullet Cl \rightarrow \bullet NHCl + HCl$$

(ii) Suggest an equation for a possible termination step in this process.

.... [1]

(b) **(i)** Draw the 'dot-and-cross' diagram of NH_2Cl. Show outer electrons only.

[1]

(ii) State the hybridisation of the nitrogen atom and suggest the H–N–Cl bond angle in the NH_2Cl molecule.

hybridisation of N ....

H–N–Cl bond angle ....

[1]

(d) Compare and explain the basicities of ammonia, ethylamine and phenylamine.

....

....

....

....

....

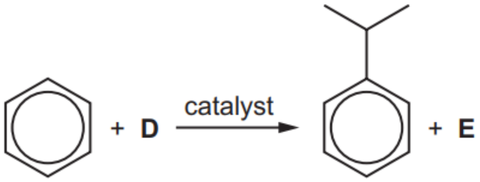
....

....

.... [4]

39. 9701/41/M/J/18 Q6

(a) Benzene reacts with **D** in the presence of a suitable catalyst to give cumene and non-organic product **E**. This is an electrophilic substitution reaction.



cumene

(i) Name the reactant **D** and the non-organic product **E**.

D ....

E ....

[2]

(ii) Give the name of the type of aromatic electrophilic substitution reaction taking place.

.... [1]

(b) Cumene undergoes substitution reactions with chlorine to give several different isomeric products with the formula $C_9H_{11}Cl$. The substitution can occur in the aromatic ring or in the side-chain of cumene.

(i) Describe the conditions that are used to ensure substitution takes place only in the **aromatic ring**.

.... [1]

(ii) Draw the structures of the **two** major isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the aromatic ring.

[1]

(iii) Describe the conditions that are used to ensure substitution takes place only in the **side-chain**.

.... [1]

(iv) Draw the structures of **two** isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the side-chain.

[1]

(c) Complete the following table to show the structures of the organic products formed when cumene reacts with each reagent.

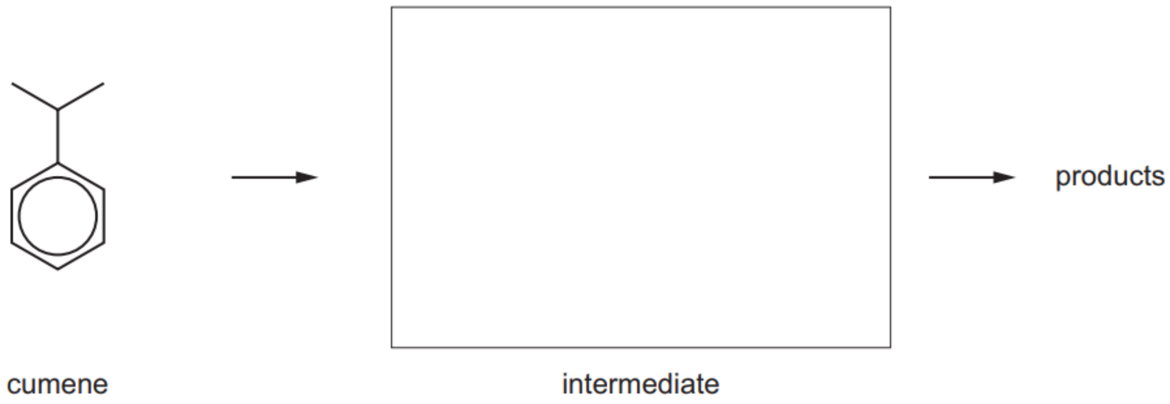
reagent	structure of organic product
hot $KMnO_4(aq)$	
H_2 + Ni, high pressure	

[2]

(d) Cumene can be nitrated using a mixture of concentrated nitric and sulfuric acids. The mechanism for this reaction is similar to the mechanism for the nitration of benzene.

Complete the mechanism for this reaction.

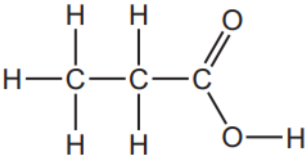
- Include all relevant charges and curly arrows showing the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.

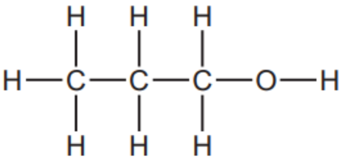


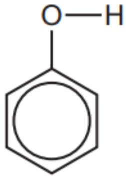
[4]

40. 9701/41/M/J/18 Q7

The three substances shown all have some acidic properties.


propanoic acid


propan-1-ol


phenol

(a) Write an equation for the reaction between propan-1-ol and sodium metal.

.... [1]

(b) **(i)** Give the order of the relative acidities of propanoic acid, propan-1-ol and phenol, stating the most acidic first.

.... [1]

(ii) Explain your answer to **(i)**.

....

....

....

....

....

.... [2]

(c) Methanoic acid, HCO_2H, has a similar acid strength to propanoic acid.

Describe a chemical test to distinguish between these two acids. Name the acid which gives a positive result in this test and describe the observations that would be made.

....

....

....

.... [2]

(d) The ester phenyl propanoate, $C_2H_5CO_2C_6H_5$, can be made from phenol and propanoic acid in a **two-step** synthesis. The first step produces an acyl chloride.

For this **two-step** synthesis,

- draw the structure of the product of the first step,
- state the reagents and conditions needed for each step of the synthesis.

....

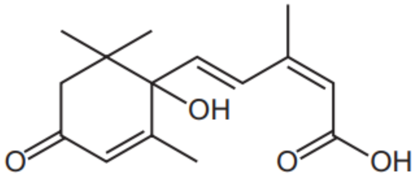
....

....

.... [3]

41. 9701/41/M/J/18 Q8

Abscisic acid, $C_{15}H_{20}O_4$, is a plant hormone.



abscisic acid, $C_{15}H_{20}O_4$

(a) On the diagram of abscisic acid, use an asterisk (*) to label each chiral carbon atom. [1]

(b) Abscisic acid is reacted with an excess of $NaBH_4$.

Give the molecular formula of the organic product formed.

.... [1]

(c) If abscisic acid is treated with an excess of hot, concentrated, acidified $KMnO_4$, three different carbon-containing products are formed.

(i) Draw the skeletal formula of the carbon-containing product with the **largest** molecular mass.

[1]

(ii) Identify the carbon-containing product with the **smallest** molecular mass. Explain how this product arises.

....

....

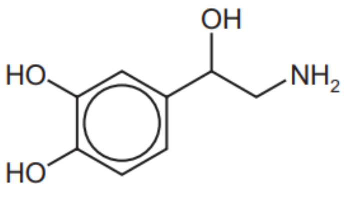
.... [2]

(iii) Identify the third carbon-containing product of this reaction by giving its displayed or structural formula.

[1]

42. 9701/41/M/J/18 Q9

Noradrenaline is a hormone found in humans.



noradrenaline

(a) Give the molecular formula of noradrenaline.

.... [1]

(b) State whether or not noradrenaline shows stereoisomerism. Explain your answer.

....

.... [1]

(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.

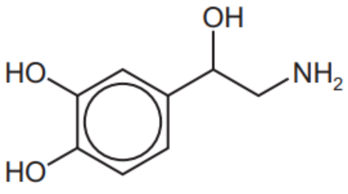
(i) Suggest why the diazonium ion produced with phenylamine is stable.

....

.... [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.



+ HNO_2 → + ... + H_2O

[2]

43. 9701/42/M/J/18 Q6

Phenol is an important industrial chemical used in the manufacture of dyestuff and other substances.

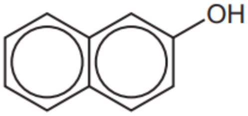
(a) Suggest **two** different substances that react with phenol to produce potassium phenoxide, $C_6H_5O^-K^+$. Identify the second product formed in each case.

substance .... second product ....

substance .... second product ....

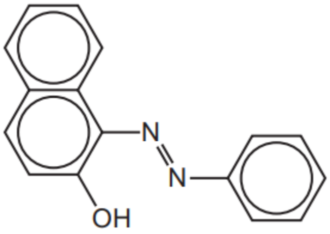
[3]

(b)



2-naphthol

2-naphthol can show similar properties to phenol. It can be used to produce Sudan I, an orange coloured dyestuff.



Sudan I

(i) On the diagram of Sudan I above **circle** the bond or bonds that make this substance a dyestuff. [1]

(ii) Describe how Sudan I can be made using phenylamine and 2-naphthol as the organic starting materials.

....

....

....

....

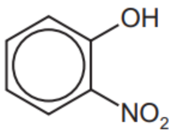
....

....

....

.... [3]

(c) Phenol can be used to make 2-nitrophenol.



2-nitrophenol

The nitration reaction of phenol to form 2-nitrophenol shows that phenol is more reactive than benzene.

(i) Describe the conditions used for the nitration of phenol.

Explain how these conditions show phenol to be more reactive than benzene.

conditions ....

explanation ....

....

.... [2]

(ii) Suggest why phenol is more reactive than benzene.

....

....

.... [1]

(iii) Complete the mechanism for the nitration of phenol to form 2-nitrophenol. You should assume that the mechanism is the same as that for the nitration of benzene.

- Include all relevant charges and curly arrows to show the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.

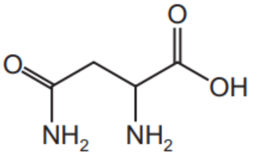
[3]

(iv) Name the isomer of 2-nitrophenol which is also a major product of this reaction.

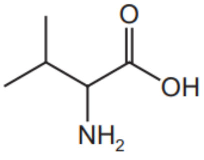
.... [1]

44. 9701/42/M/J/18 Q7

Asparagine and valine are two naturally occurring amino acids.



asparagine



valine

(a) Give the molecular formula of asparagine.

.... [1]

(b) Name **all** of the functional groups in an asparagine molecule.

.... [2]

(c) Draw the structure of the dipeptide formed by valine and asparagine.

The peptide bond should be shown displayed and should be clearly labelled.

[2]

(e) Each valine molecule has one chiral carbon atom.

Draw three-dimensional diagrams to show the two optical isomers of valine.
The $(CH_3)_2CH$ group can be represented as R.

[2]

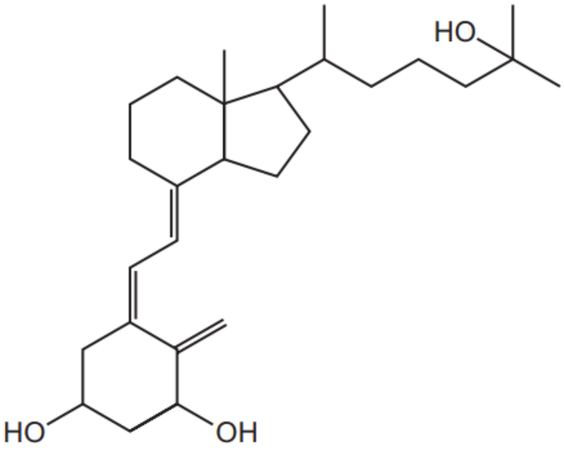
(f) Asparagine is hydrolysed when heated with aqueous sulfuric acid.

Write an equation for this reaction.

.... [2]

45. 9701/42/M/J/18 Q8

Calcitriol is a steroid hormone found in human blood.



calcitriol

(a) Give the number of primary, secondary and tertiary alcohol groups in one molecule of calcitriol.

primary .... secondary .... tertiary ....
[1]

(b) Give the number of chiral carbon atoms in one molecule of calcitriol.

.... [1]

(c) Calcitriol shows geometrical isomerism.

Give the number of geometrical isomers of calcitriol, including calcitriol.

.... [1]

46. 9701/42/F/M/18 Q7

(a) **(i)** Complete the equations to show the **two** types of polymerisation. Draw **one** repeat unit for each polymer. Include any other products.

- addition polymerisation

$n\,CH_2{=}CHCH_3(g) \rightarrow$

- condensation polymerisation

$n\,HO_2CCH_2CO_2H(s)$ + $n\,HOCH_2CH_2OH(l) \rightarrow$

[3]

(ii) Suggest the sign of the entropy changes, $\Delta S^{\ominus}$, for each of the **two** types of polymerisation. Explain your answers.

- $\Delta S^{\ominus}$ for addition polymerisation

....

....

....

- $\Delta S^{\ominus}$ for condensation polymerisation

....

....

....

[2]

(b) An amide bond forms when a carboxylic acid reacts with an amine.

(i) Complete the equation by writing the products in the box.

$R–CO_2H + H_2N–R' \rightarrow \boxed{\qquad\qquad\qquad + \qquad\qquad}$

[1]

(ii) Use your answer to **(i)** to work out the bonds that are broken and the bonds that are formed during the reaction between a carboxylic acid and an amine.

- bonds that are broken

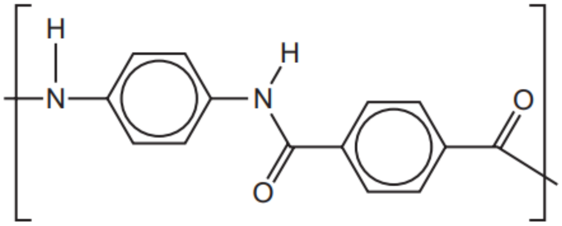
....

- bonds that are formed

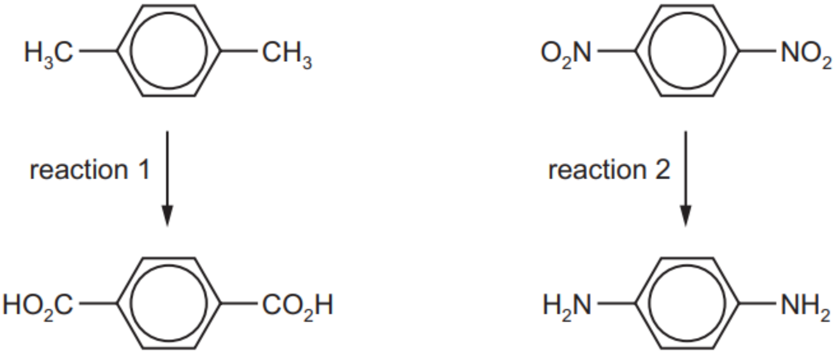
....

[2]

The repeat unit of the polyamide *Kevlar* is shown.



(d) The monomers of *Kevlar*, benzene-1,4-dioic acid and 1,4-diaminobenzene, can be synthesised as follows.



benzene-1,4-dioic acid

1,4-diaminobenzene

State the reagents and conditions needed for:

(i) reaction 1

.... [1]

(ii) reaction 2

....

.... [2]

(e) *Kevlar* is both strong and rigid.

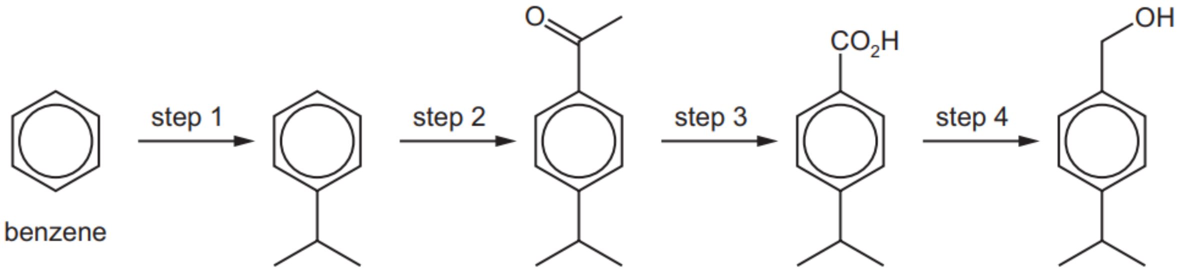
Complete the table to identify **two** intermolecular forces and the groups involved which are responsible for these properties of *Kevlar*.

intermolecular force	group(s) involved

[2]

47. 9701/42/F/M/18 Q8b

(b) Cuminyl alcohol can be synthesised from benzene by the following route.



cuminyl alcohol

(i) Suggest reagents and conditions for steps 1–4.

step 1 ....

step 2 ....

step 3 ....

step 4 ....
[4]

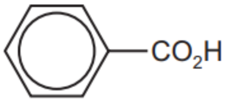
(ii) Name the mechanism of step 2 and state the type of reaction in step 4.

mechanism of step 2 ....

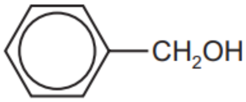
type of reaction in step 4 ....
[2]

48. 9701/42/F/M/18 Q9b

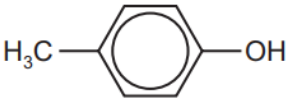
(b) Describe and explain the relative acidities of benzoic acid, phenylmethanol and 4-methylphenol.



benzoic acid



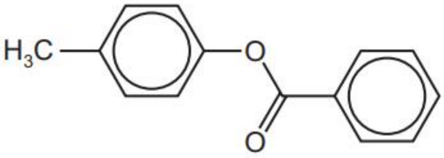
phenylmethanol



4-methylphenol

[3]

(c) The ester 4-methylphenyl benzoate is used in the manufacture of perfumes.



4-methylphenyl benzoate

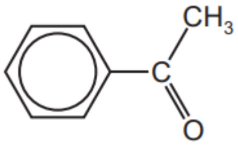
Suggest a **two**-step route for the synthesis of 4-methylphenyl benzoate from 4-methylphenol and benzoic acid.
Include reagents and conditions for each step, and the structure of the intermediate compound.

[3]

49. 9701/41/O/N/19 Q4

Phenylethanone is an important chemical with many uses.

phenylethanone



(a) Phenylethanone can be synthesised using benzene as one of the starting materials.

Identify the other reagents used and describe any essential reaction conditions.

....

.... [2]

(b) Phenylethanone is treated separately with three reagents.

Complete the table, for each reagent, to give the structural formula of one organic product formed and the name of the mechanism involved. If there is no reaction you should write 'no reaction'.

reagent	organic product	name of mechanism
chlorine gas at 10 °C in the presence of ultra-violet light		
a mixture of concentrated nitric and sulfuric acids at 50 °C		
bromine water		

[5]

(c) Phenylethanone reacts with HCN in the presence of a small amount of NaCN.

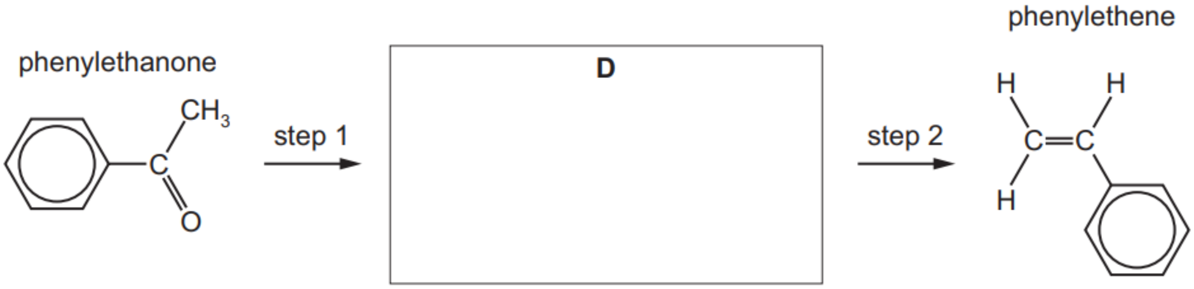
(i) Name the mechanism of this reaction.

.... [1]

(ii) Draw the mechanism of this reaction below. Include all relevant charges, dipoles, lone pairs and curly arrows. Your mechanism should show the catalytic role of CN^- ions.

[4]

(d) Phenylethanone can be used as a starting material to make phenylethene in a two-step synthesis.



(i) Draw the structure of compound **D** in the box. [1]

(ii) Identify a suitable reagent for step 1.

.... [1]

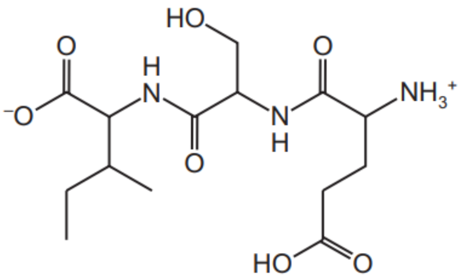
(iii) Identify a suitable reagent for step 2.

.... [1]

50. 9701/41/O/N/19 Q8

Proteins are natural polymers. When one particular protein is partially hydrolysed the product mixture includes tripeptide **E**.

tripeptide **E**



(a) **(i)** Describe the conditions that could be used to hydrolyse **E** to produce a mixture of three amino acids.

.... [1]

(ii) Draw the structures of the three amino acids produced by this hydrolysis reaction.

The three amino acids should be shown in the correct form for the conditions you have chosen in **(a)(i)**.

[2]

(b) If a pure sample of **E** is obtained in aqueous solution, several different types of intermolecular forces are possible between pairs of **E** molecules.

Name three different types of intermolecular force that exist between pairs of **E** molecules, stating the groups on the molecules where the forces are acting.

type of force/bond	pair of groups responsible

[3]

(c) Polyesters and polyamides are two important types of condensation polymer.

(i) Draw the structure of a compound that can polymerise to produce a polyamide, without the need for a second monomer.

[1]

(ii) Draw the structures of two different compounds that can polymerise together to produce a polyester with **four** carbon atoms per repeat unit. Name the two compounds.

name ....

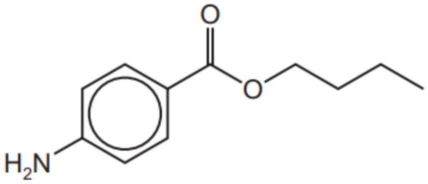
name ....

[4]

51. 9701/41/O/N/19 Q9

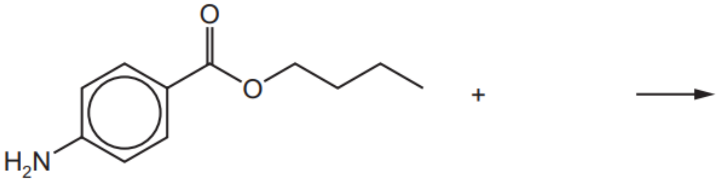
9 The structure of butamben is shown.

butamben



(a) Butamben can act as a base.

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



[1]

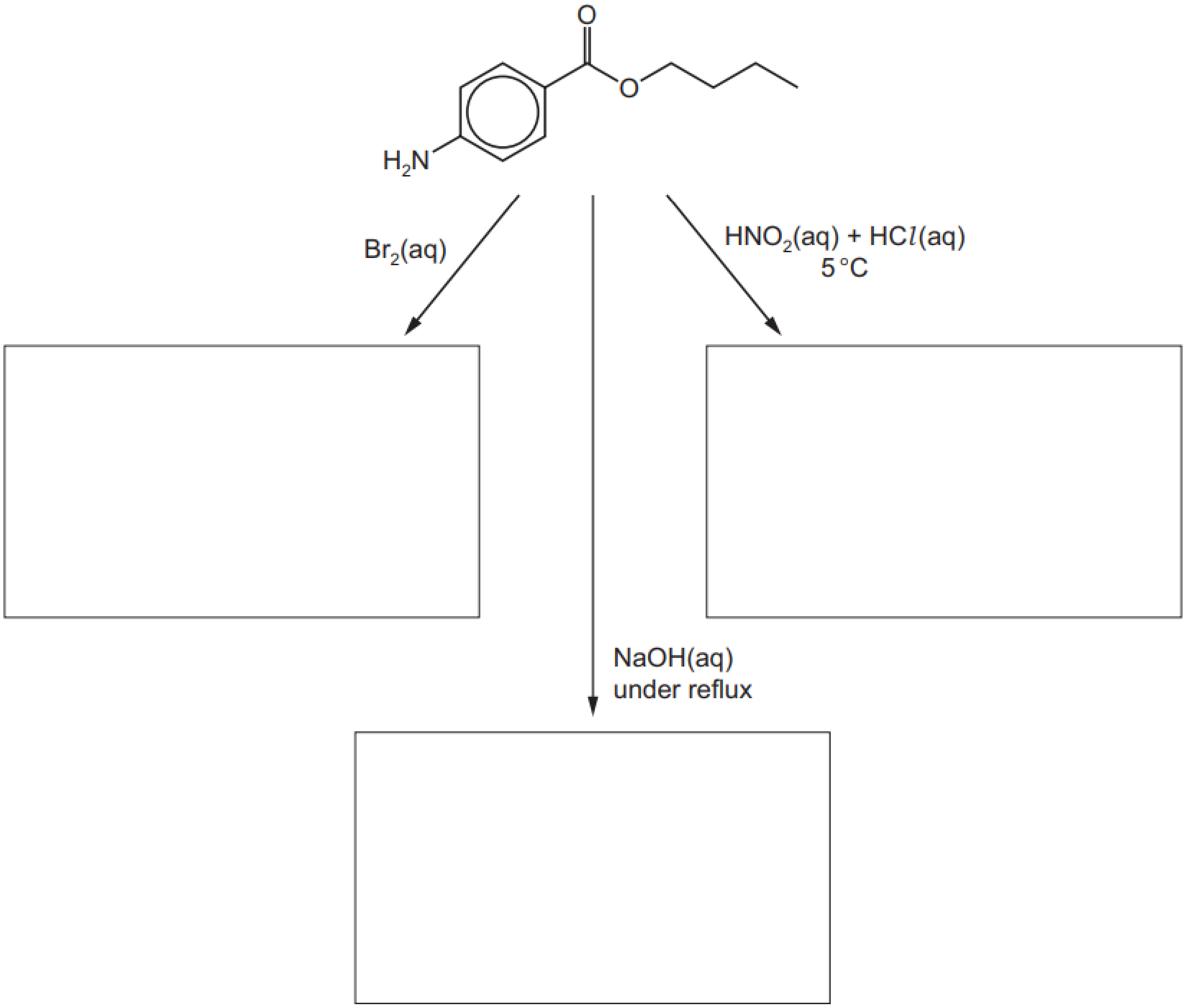
(ii) Predict whether butamben is a stronger or weaker base than ammonia. Give a reason for your answer.

....

....

.... [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.

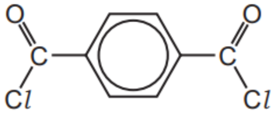


[3]

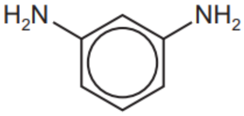
52. 9701/42/O/N/19 Q7

(a) A polymer, **P**, can be made from the monomers benzene-1,4-dioyl chloride and benzene-1,3-diamine.

benzene-1,4-dioyl chloride



benzene-1,3-diamine



(i) Draw a section of the polymer chain of **P**. Your structure should include two repeat units.

P

[2]

(ii) Place **one** tick in the table to describe polymer **P** and its method of polymerisation.

type of polymer	type of polymerisation	
	addition	condensation
polyalkene		
polyamide		
polyester		

[1]

(iii) State whether or not polymer **P** is biodegradable. Give a reason for your answer.

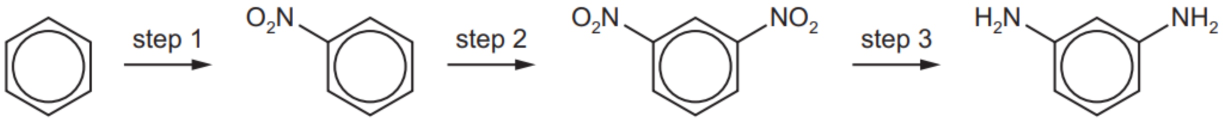
....

.... [1]

(iv) State a suitable reagent to produce benzene-1,4-dioyl chloride from benzene-1,4-dicarboxylic acid.

.... [1]

(v) Benzene-1,3-diamine can be made from benzene using the reaction sequence shown.



State the reagents used for steps 1 and 3.

step 1 ....

step 3 ....
[2]

(b) Proteins are natural polymers. A protein is said to have a primary, secondary and tertiary structure.

(i) Describe what is meant by each of these terms.

primary structure ....

....

secondary structure ....

....

tertiary structure ....

....
[3]

(ii) Name the forces or bonds responsible for holding together the primary structure of a protein molecule.

.... [1]

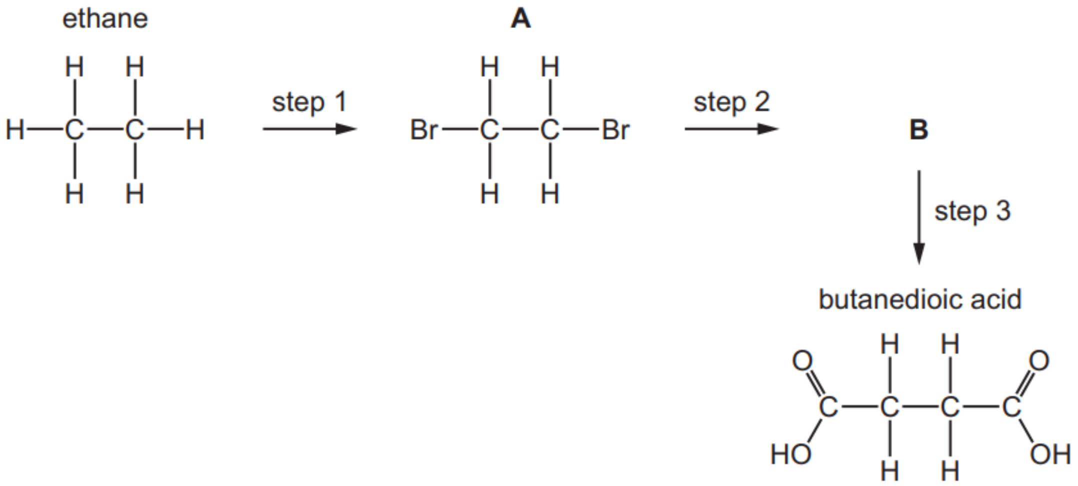
(iii) Name the forces or bonds responsible for the stabilisation of the secondary structure of a protein molecule, and identify the groups of atoms within the protein molecule that are held together by these forces or bonds.

....

.... [2]

53. 9701/42/O/N/19 Q8

Butanedioic acid can be made in a three-step synthesis using ethane as the starting material.



(a) Describe the reagents and conditions needed for step 1.

.... [1]

(b) Name the other product also formed in step 1 which is an isomer of **A**.

.... [1]

(c) Give the structural formula of **B**.

[1]

(d) State the reagents and conditions needed for step 2.

.... [2]

(e) Butanedioic acid cannot be oxidised by a warm, aqueous solution of any commonly used oxidising agents but ethanedioic acid can.

(i) Identify the oxidising agent that could be used to oxidise ethanedioic acid.

.... [1]

(ii) State the product(s) of the reaction in **(e)(i)**.

.... [1]

(f) Compare and explain the relative acidities of hexanoic acid, hexan-1-ol and phenol.

....

....

....

....

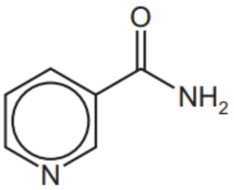
....

.... [3]

54. 9701/42/O/N/19 Q9

The structure of nicotinamide is shown.

nicotinamide



(a) The nitrogen atom in the six-membered ring has one electron in an unhybridised p-orbital. This electron becomes delocalised, becoming part of a single delocalised system of electrons. This delocalised system also includes:

- electrons from the carbon atoms in the six-membered ring
- the two electrons in the π bond of the C=O group
- the two electrons in the lone pair on the nitrogen atom of the amide group.

(i) State the number of delocalised electrons in one nicotinamide molecule.

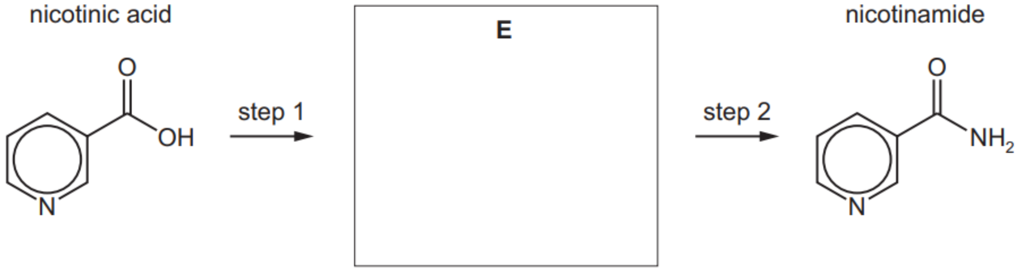
.... [1]

(ii) Predict the H–N–H bond angle in the NH_2 group in nicotinamide.

.... [1]

(b) Nicotinamide can be synthesised from nicotinic acid.

The synthesis involves two steps.



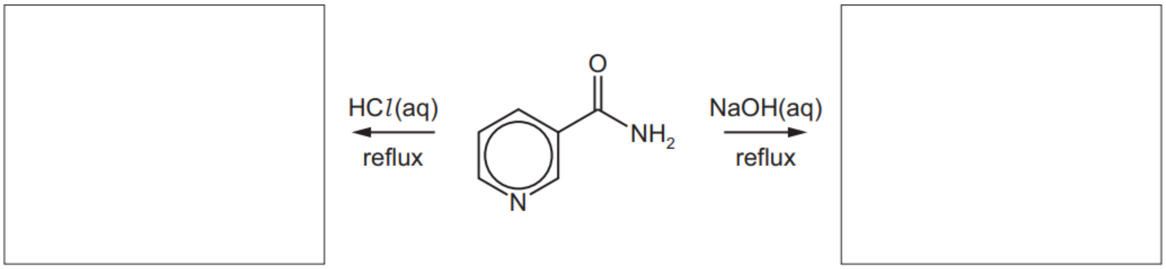
(i) Draw the structural formula of **E** in the box. [1]

(ii) Give the name or formula of a suitable reagent for step 2.

.... [1]

(c) Nicotinamide reacts separately with aqueous acid and aqueous alkali. The six-membered ring remains unchanged in these reactions.

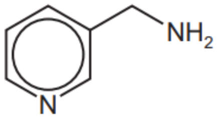
Complete the reaction scheme below to give the structural formula of the organic product of each reaction.



[2]

(d) Nicotinamide can be reduced to compound **X**.

X



(i) Identify a suitable reducing agent for this reaction.

.... [1]

(ii) Predict and explain the relative basicities of the NH_2 groups in phenylamine, $C_6H_5NH_2$, nicotinamide and compound **X**.

....

....

....

.... [3]

55. 9701/41/M/J/19 Q7

(a) Benzene can be converted into cyclohexane.

(i) For this reaction name the type of reaction and identify the reagent and conditions needed.

type of reaction ....

reagent and conditions .... [2]

(ii) State the bond angles in benzene and cyclohexane.

bond angle in benzene .... bond angle in cyclohexane ....

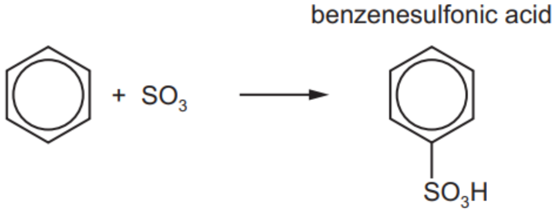
Explain your answers.

....

....

.... [2]

(b) When benzene reacts with SO_3, benzenesulfonic acid is produced.



The mechanism of this reaction is similar to that of the nitration of benzene. Concentrated H_2SO_4 is used in an initial step to generate the SO_3H^+ electrophile as shown.

$$SO_3 + H_2SO_4 \rightarrow SO_3H^+ + HSO_4^-$$

(i) Draw a mechanism for the reaction of benzene with SO_3H^+ ions. Include all necessary curly arrows and charges.

[3]

(ii) Write an equation to show how the H_2SO_4 catalyst is reformed.

.... [1]

(c) 3-dodecylbenzenesulfonic acid can be prepared from benzenesulfonic acid.

Suggest the reagents and conditions and name the mechanism for this reaction.

reagents and conditions ....

mechanism ....
[2]

56. 9701/41/M/J/19 Q9

(a) Organochlorine compounds can undergo hydrolysis.

$$R–Cl + H_2O \rightarrow R–OH + HCl$$

State and explain the relative rates of hydrolysis of the following compounds.

CH_3CH_2Cl CH_3COCl C_6H_5Cl

....

....

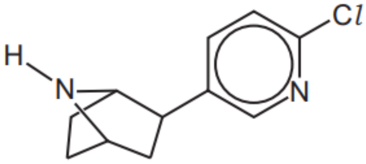
....

....

.... [3]

(b) Epibatidine is a naturally occurring organochlorine compound.

epibatidine



(i) Epibatidine is a weak base.

State what is meant by the term *weak base*.

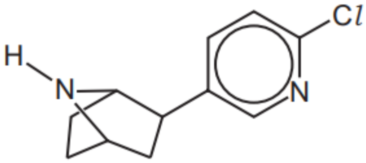
....

.... [1]

A molecule of epibatidine contains two nitrogen atoms, both of which can act as a base.

(ii) Epibatidine reacts with HCl(aq).

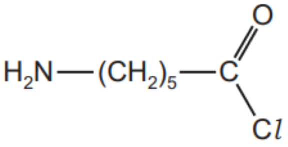
Complete the structure to suggest the product formed in this reaction.



[1]

(c) Polyamides, such as nylon-6, can be prepared from a monomer that contains both an amine and an acyl chloride functional group.

nylon-6 monomer



(i) When the nylon-6 monomer is hydrolysed, bonds are broken and formed.

By considering the two steps in the mechanism of the reaction, complete the table by placing **one** tick (✓) in each row to indicate the types of bonds broken and formed during the mechanism.

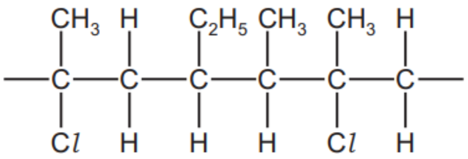
	σ bonds only	π bonds only	both σ and π bonds
bonds broken			
bonds formed			

[1]

(ii) Draw **two** repeat units of nylon-6. The amide bond should be shown fully displayed.

[2]

(d) An addition polymer made from two different alkene monomers is called a co-polymer. A section of a polyalkene co-polymer is shown.



Draw the structure of the **two** alkene monomers which produce this co-polymer.

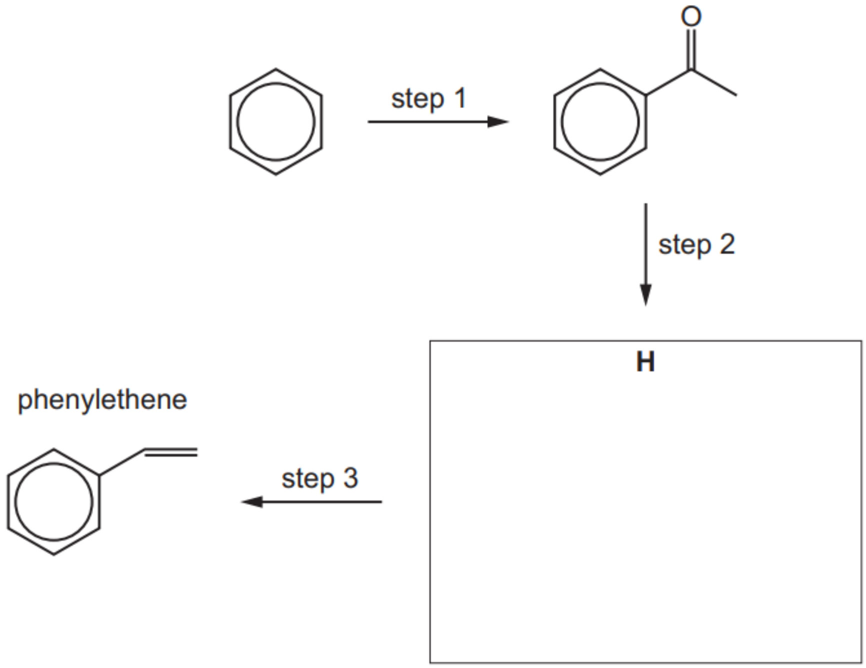
[2]

(e) Explain why polyamides normally biodegrade more readily than polyalkenes.

....

.... [1]

(f) The alkene phenylethene can be prepared from benzene in three steps.



(i) Deduce the identity of compound **H** and draw its structure in the box. [1]

(ii) Suggest reagents and conditions for each of the steps 1–3.

step 1 ....

step 2 ....

step 3 ....

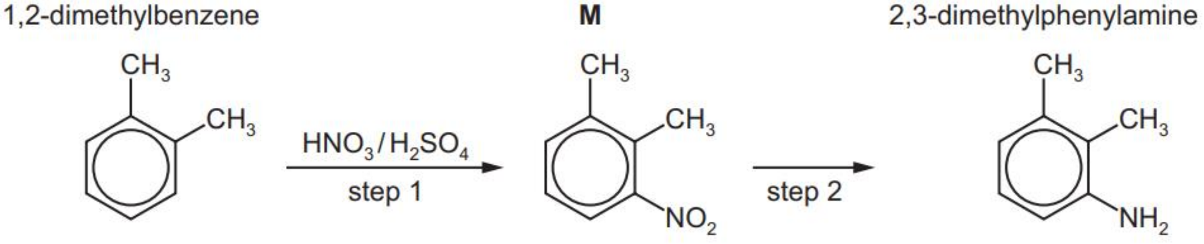
[3]

57. 9701/42/M/J/19 Q6

(a) By reference to the formation of σ and π bonds, describe and explain the shape of a benzene molecule, C_6H_6.

.... [3]

(b) 2,3-dimethylphenylamine can be prepared from 1,2-dimethylbenzene in two steps as shown.

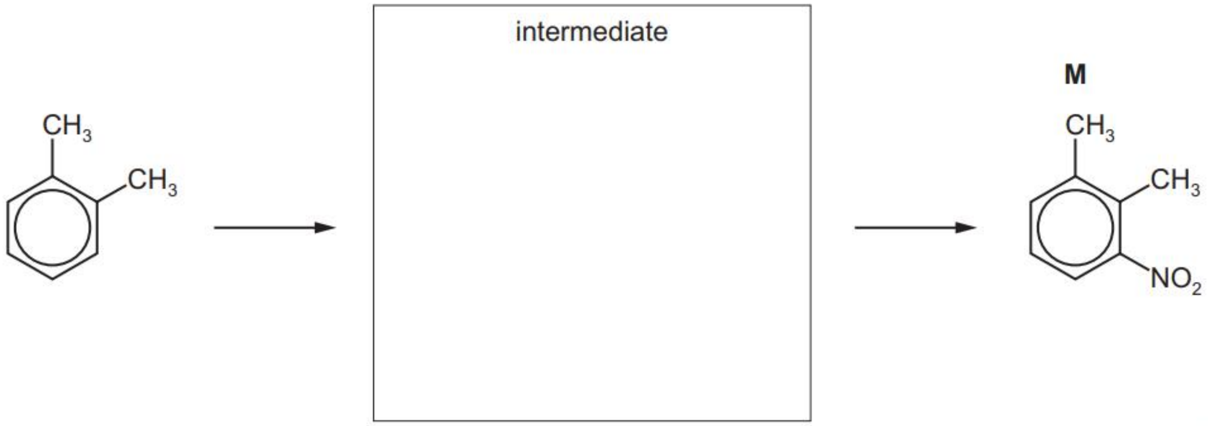


Step 1 is catalysed by H_2SO_4.

(i) Write an equation to show how H_2SO_4 generates the electrophile during step 1.

.... [1]

(ii) Draw the mechanism of the reaction between this electrophile and 1,2-dimethylbenzene to form **M**. Include all relevant curly arrows and charges.



[3]

(iii) Write an equation to show how the H_2SO_4 catalyst is reformed.

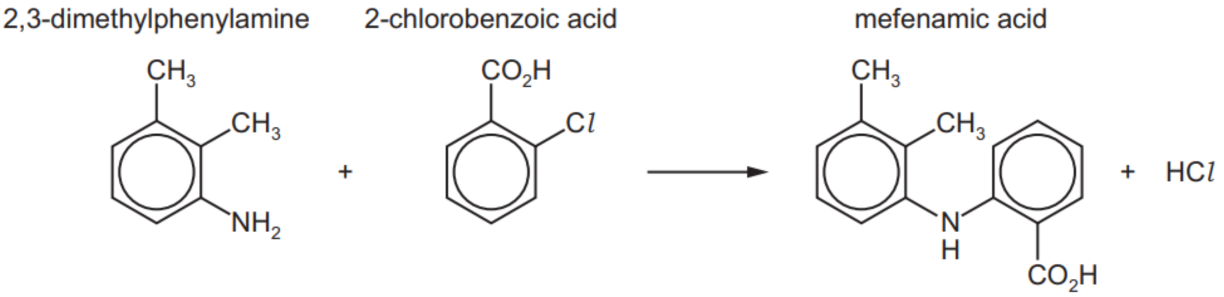
.... [1]

(iv) For step 2, suggest the reagents and conditions and name the *type of reaction*.

- reagents and conditions ....
- type of reaction ....

[2]

(c) The drug mefenamic acid can be made using 2,3-dimethylphenylamine in an excess of 2-chlorobenzoic acid.



(i) Deduce the molecular formula of mefenamic acid.

.... [1]

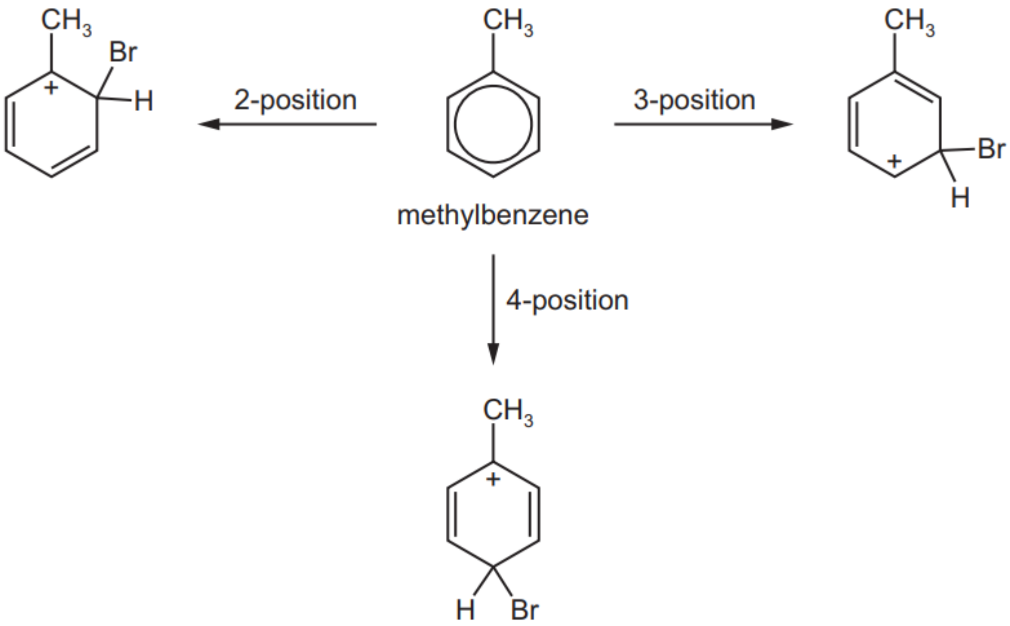
(ii) Name the functional groups, apart from the benzene ring, in mefenamic acid.

.... [1]

(iii) Calculate the maximum mass of mefenamic acid that could be formed from 5.00 g of 2,3-dimethylphenylamine in this reaction. Give your answer to **three** significant figures.

mass of mefenamic acid = ... g [2]

(d) The position of substitution in the electrophilic substitution of arenes can be explained based on the stability of the intermediate cations formed in the first step. The example given involves the bromination of methylbenzene.



Use this information and your knowledge about the stability of cations to suggest why the CH_3 group directs incoming electrophiles to the 2- and 4-positions in preference to the 3-position.

....

....

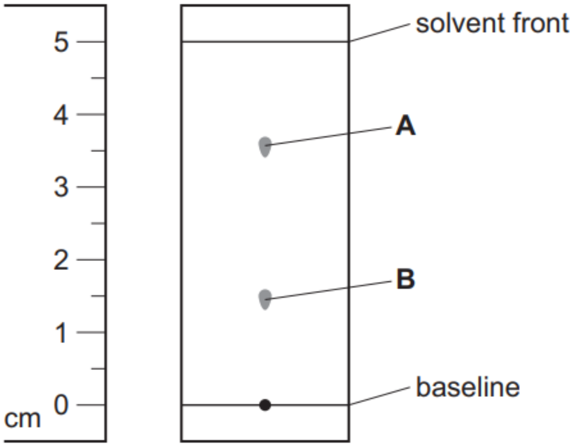
....

.... [2]

58. 9701/42/M/J/19 Q7

(a) Amino acids can be separated by thin-layer chromatography. A mixture of amino acids is analysed using this technique.

The chromatogram obtained is shown, drawn to scale. The table shows some R_f values for different amino acids in the solvent used.



amino acid	R_f value
alanine	0.40
glutamic acid	0.29
leucine	0.71
valine	0.61

(i) Use the chromatogram and the R_f values to deduce the amino acid responsible for spot **A** and spot **B**.

amino acid responsible for spot **A** ....

amino acid responsible for spot **B** ....
[1]

(ii) A second chromatogram of the same mixture is taken using a **more polar** solvent.

Predict the effect on the R_f values of the amino acids. Explain your reasoning.

....

....

....

.... [1]

(b) Glycine, $H_2NCH_2CO_2H$, is the simplest amino acid.

(i) Complete the equations to show the acid-base properties of glycine.

$H_2NCH_2CO_2H(aq) + HCl(aq) \rightarrow$ ....

$H_2NCH_2CO_2H(aq) + NaOH(aq) \rightarrow$ ....
[2]

(ii) In aqueous solution, amino acids exist as zwitterions.

Draw the zwitterionic structure of glycine. Explain how the zwitterion for glycine is formed.

....

....

.... [2]

(c) Apart from glycine, all naturally occurring amino acids have a chiral centre and exhibit stereoisomerism.

Draw the two stereoisomers of alanine, $CH_3CH(NH_2)CO_2H$.

[1]

(d) The amino acid alanine can be synthesised from 2-chloropropanoic acid, $CH_3CHClCO_2H$.

(i) State the reagents and conditions and name the mechanism for this reaction.

reagents and conditions ....

name of mechanism .... [2]

(ii) State and explain the relative acidities of trichloroethanoic acid, chloroethanoic acid and ethanoic acid.

....

....

....

....

.... [3]

(e) Serine, $HOCH_2CH(NH_2)CO_2H$, can react with alanine, $CH_3CH(NH_2)CO_2H$, to form three different **structural** isomers, each with the molecular formula $C_6H_{12}N_2O_4$.

Draw the structures of these three structural isomers.

isomer 1 ($C_6H_{12}N_2O_4$)

isomer 2 ($C_6H_{12}N_2O_4$)

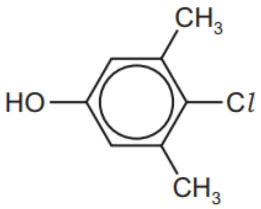
isomer 3 ($C_6H_{12}N_2O_4$)

[3]

59. 9701/42/M/J/19 Q8

Compound **R** is shown.

R

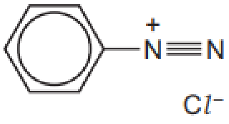


(a) State the systematic name of compound **R**.

.... [1]

(c) Compound **R** reacts separately with the four reagents shown in the table.

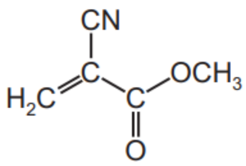
Complete the table by
- drawing the structures of the organic products formed,
- stating the type of reaction.

reagent	organic product structure	type of reaction
Na		
CH_3COCl		
$Br_2(aq)$		
		

60. 9701/42/F/M/19 Q5

(a) Methyl 2-cyanoprop-2-enoate, **W**, is the major component of *Super Glue*, a rapid-setting adhesive.
As the adhesive sets, the monomer **W** polymerises.

W



(i) Draw a section of the polymer showing **two** repeat units.

[2]

(ii) Name the type of polymerisation occurring.

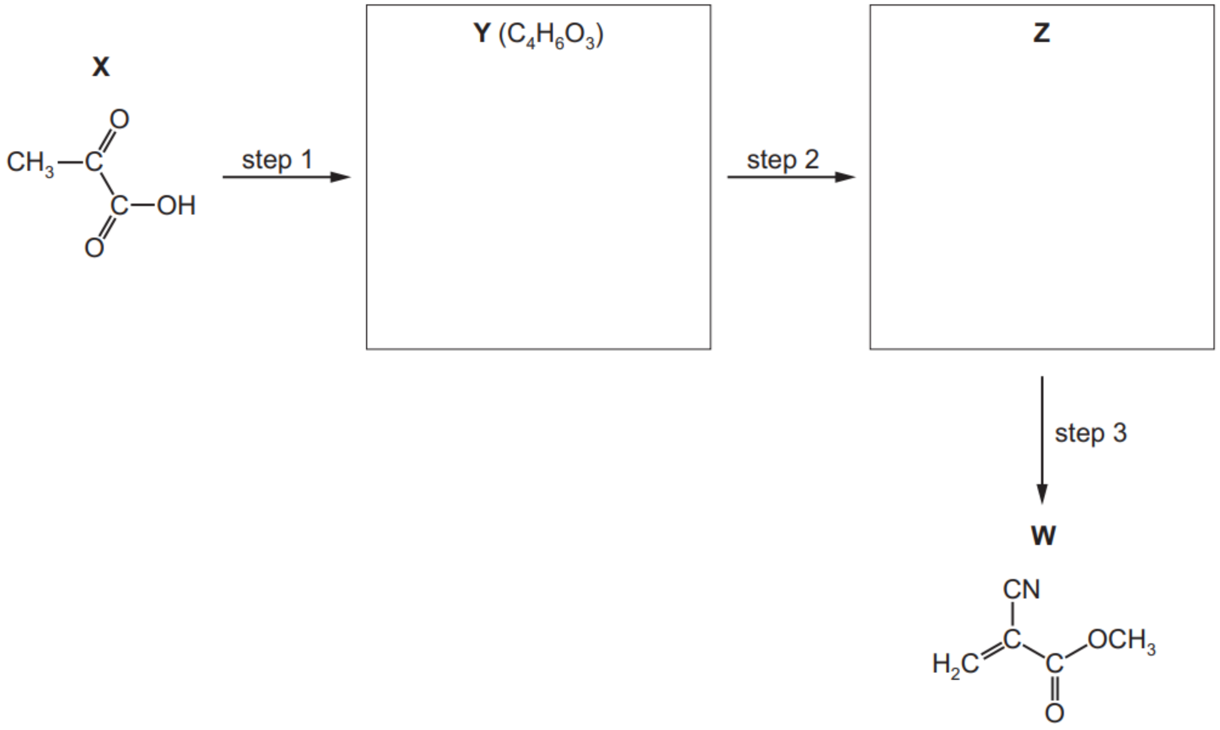
.... [1]

(iii) Suggest **two** types of intermolecular force that could occur between the *Super Glue* polymer and the objects glued together. For each type of intermolecular force, refer to the atoms/groups in the *Super Glue* polymer involved in the attraction.

type of intermolecular force	atoms/groups in the *Super Glue* polymer

[2]

(b) **W** can be synthesised in three steps, starting from 2-oxopropanoic acid, **X**.



(i) Suggest the identities of compounds **Y** and **Z** by drawing their structures in the boxes. [2]

(ii) Suggest suitable reagents and conditions for each of the steps 1–3.

step 1 ....

step 2 ....

step 3 ....

[4]

61. 9701/42/F/M/19 Q6

The names of many drugs used in medicine often include parts of the names of the functional groups their molecules contain.

(a) Suggest **two** functional groups present in a molecule of the drug named chloramphenicol.

1 ....

2 ....
[1]

(b) The drug named ketamine readily reacts with protons as shown.

$$\text{ketamine} + H^+ \rightarrow [\text{ketamine-H}]^+$$

(i) State the role of ketamine in this reaction.

.... [1]

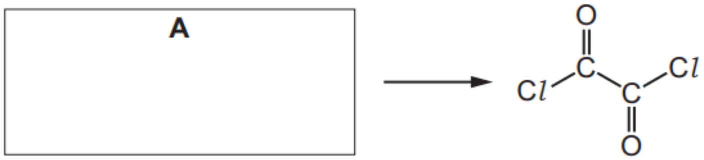
Ketamine gives an orange precipitate with 2,4-dinitrophenylhydrazine (2,4-DNPH).

(ii) Suggest the functional group in the ketamine molecule responsible for this observation.

.... [1]

62. 9701/42/F/M/19 Q7

Ethanedioyl dichloride, $ClCOCOCl$, is a useful reagent in organic synthesis. It can be made from compound **A** in one step.

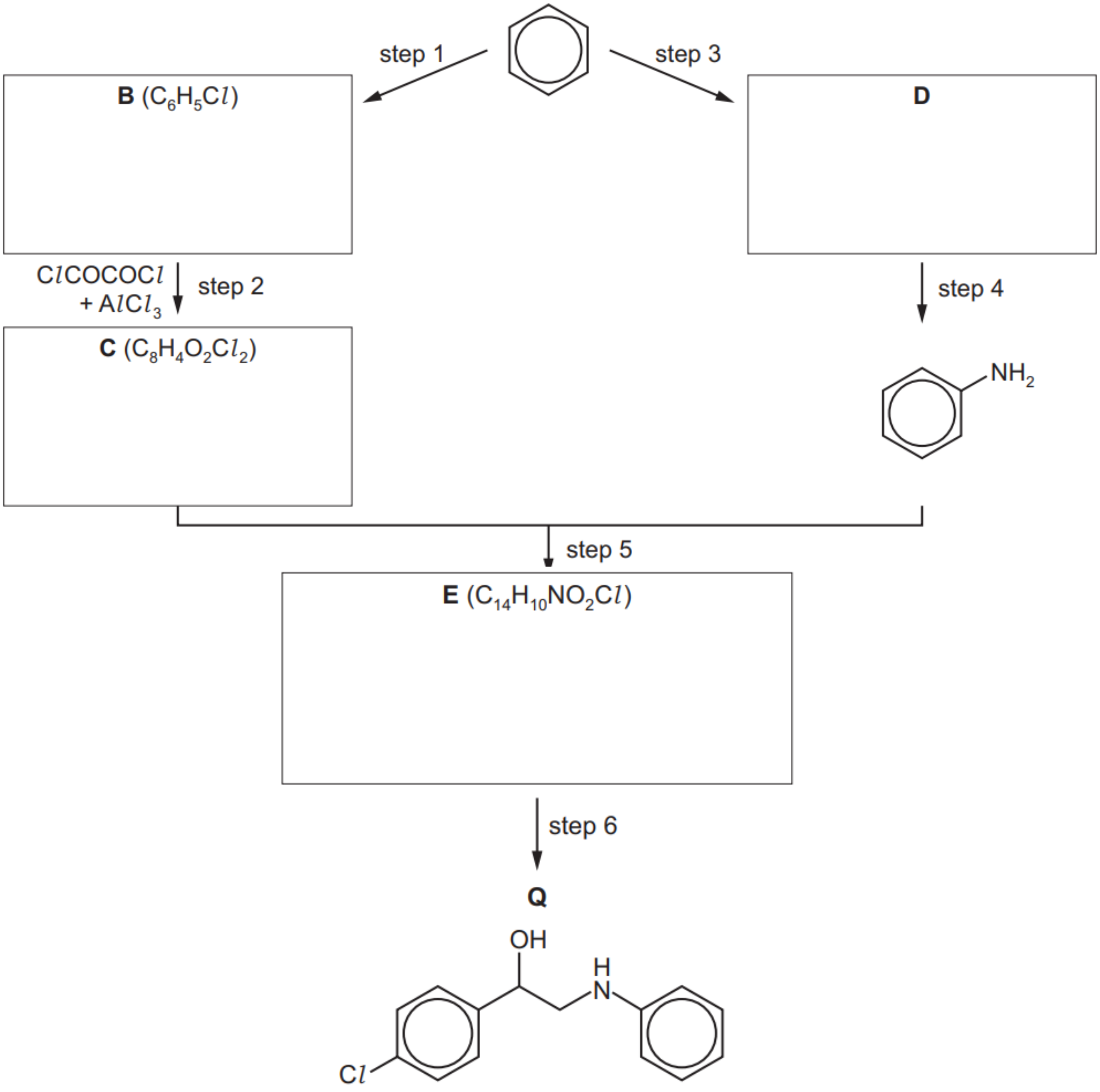


(a) **(i)** Suggest the identity of compound **A** by drawing its structure in the box. [1]

(ii) State the reagents and conditions needed to convert **A** into $ClCOCOCl$.

.... [1]

Ethanedioyl dichloride is used in the following synthesis of compound **Q**. It is used in a 1:1 stoichiometric ratio with **B** in step 2.



(b) **(i)** Suggest the identities of the compounds **B**–**E** by drawing their structures in the boxes. [4]

(ii) State the reagents and conditions for the following steps.

step 1 ....

step 3 ....

step 4 ....

step 6 ....
[5]

If the amount of $ClCOCOCl$ used in step 2 is decreased, another compound is formed in step 2 with the molecular formula $C_{14}H_8O_2Cl_2$.

(iii) Suggest the structure of this compound.

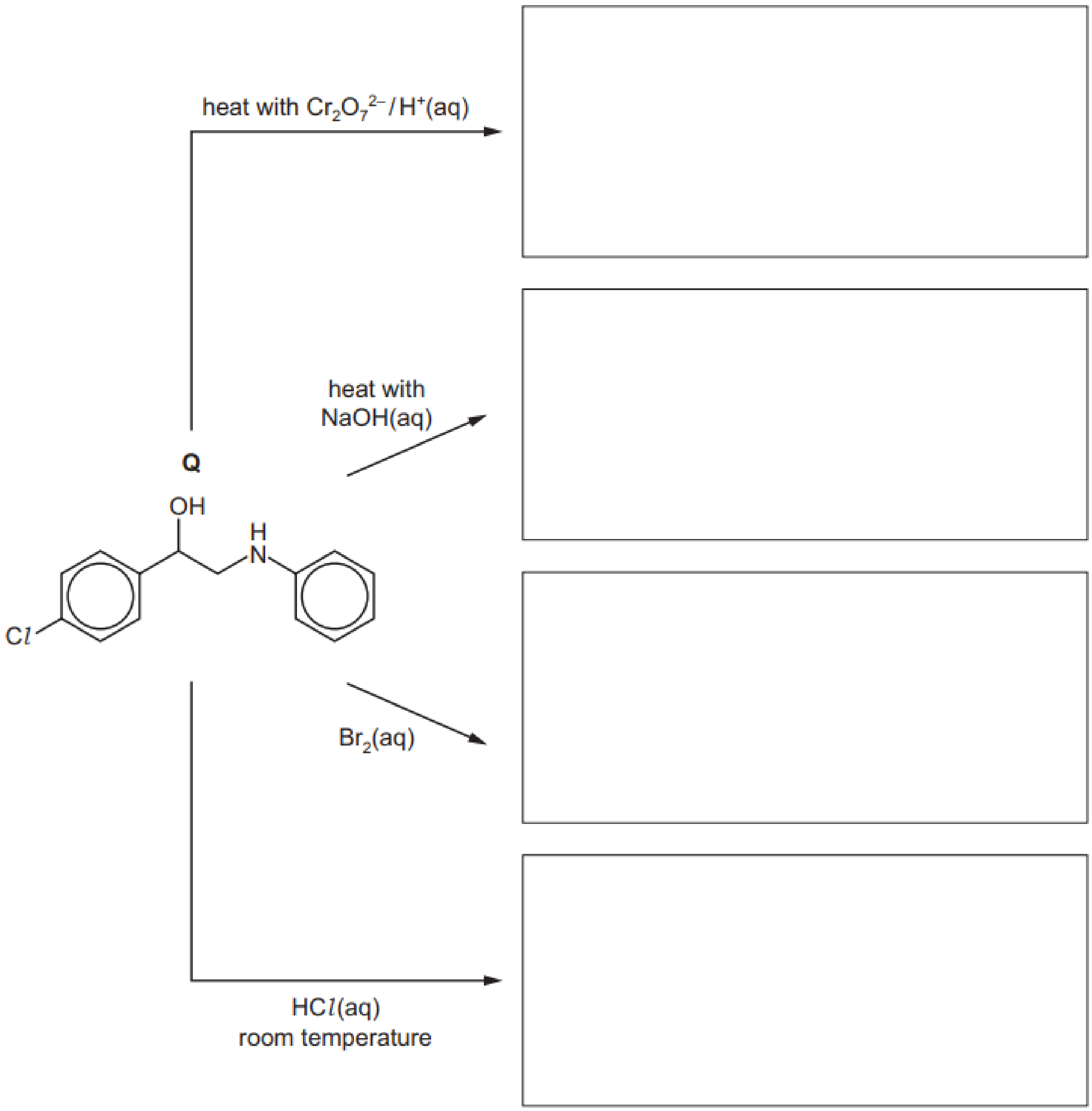
$C_{14}H_8O_2Cl_2$

[1]

(iv) Identify **all** the steps in the synthesis of **Q** from benzene that are electrophilic substitution reactions.

.... [1]

(c) Draw structures of the compounds formed when **Q** is treated with the following reagents. If there is no reaction, write 'no reaction' in the box.



[4]

63. 9701/41/O/N/20 Q7

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]

64. 9701/41/O/N/20 Q8

Benzene, C_6H_6, can be obtained from crude oil.

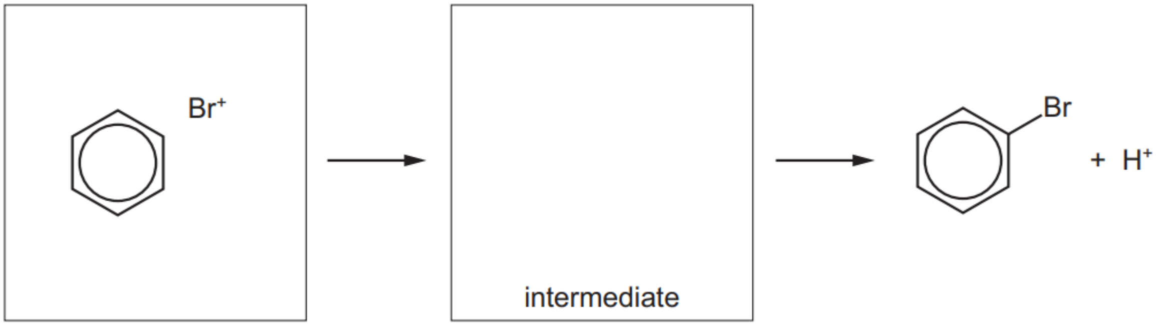
(a) Benzene reacts with bromine, in the presence of a suitable catalyst, forming bromobenzene as one product.

(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.

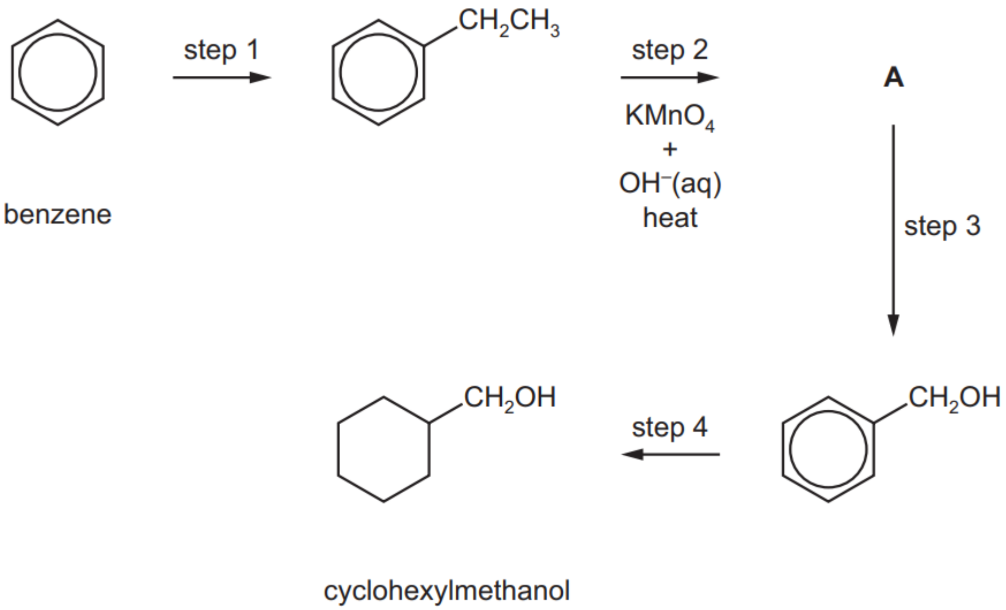


[2]

(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]

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

reagent ....

catalyst ....
[2]

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

A

[1]

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

step 3 ....

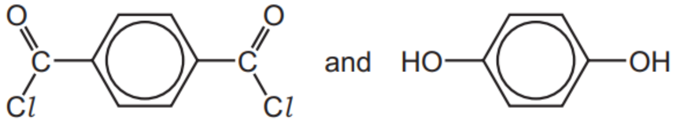
step 4 ....

[2]

65. 9701/41/O/N/20 Q10

(a) The table shows three pairs of monomers that are capable of polymerisation.

Complete the table by identifying each type of polymerisation.

pair of monomers	type of polymerisation
$HOCH_2CH_2OH$ and $HO_2CCH_2CO_2H$	
	
CH_3CHCF_2 and CH_3CHCH_2	

[1]

(b) 2-aminopropanoic acid, $CH_3CH(NH_2)CO_2H$, can polymerise under suitable conditions. No other monomer is involved in this reaction.

(i) Draw a section of the polymer chain formed including **three** monomer residues. Clearly identify **one** repeat unit on your diagram.

[3]

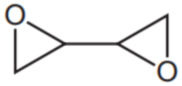
(ii) 2-aminopropanoic acid, $CH_3CH(NH_2)CO_2H$, exists as two stereoisomers.

Draw three-dimensional diagrams to show the two stereoisomers of 2-aminopropanoic acid. State the type of stereoisomerism shown.

type of stereoisomerism ....

[2]

(c) The skeletal formula of compound **W** is shown.



When **W** is mixed with a second compound, called a hardener, a polymerisation reaction occurs, producing a non-solvent-based adhesive.

(i) Give the name of this type of non-solvent-based adhesive.

.... [1]

(ii) The hardener is a diamine. A diamine has an alkyl chain with two amine groups which are not bonded to the same carbon atom.

Draw the structural formula of a compound that would make a suitable hardener.

[1]

66. 9701/42/O/N/20 Q6

(a) Ethanoic acid, CH_3CO_2H and trichloroethanoic acid, CCl_3CO_2H, are both carboxylic acids. Ethanoic acid can be used to make ethanamide, CH_3CONH_2.

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

.... < .... < ....
least acidic most acidic

....

....

....

....

.... [3]

(b) Methanoic acid, HCO_2H, and ethanedioic acid, HO_2CCO_2H, are two other carboxylic acids.

(i) State which, if any, of ethanoic acid, methanoic acid and ethanedioic acid will react with Fehling's reagent.

.... [1]

(ii) State which, if any, of ethanoic acid, methanoic acid and ethanedioic acid will react with warm acidified manganate(VII) ions.

.... [1]

(c) Ethanamide can be made from ethanoic acid in a two-step synthesis.

$$\text{ethanoic acid} \xrightarrow{\text{step 1}} \textbf{A} \xrightarrow{\text{step 2}} \text{ethanamide}$$

(i) Compound **A** contains chlorine.

Give the structural formula and name of **A**.

structural formula ....

name .... [2]

(ii) Suggest suitable reagents for steps 1 and 2.

step 1 ....

step 2 .... [2]

67. 9701/42/O/N/20 Q7

(a) Describe the structure of a benzene molecule, C_6H_6.

Your answer should include:

- the shape of the molecule
- the relative lengths of the C–C bonds
- bond angles
- the hybridisation of the carbon atoms
- the overlap between orbitals that produces each type of bond present.

....

....

....

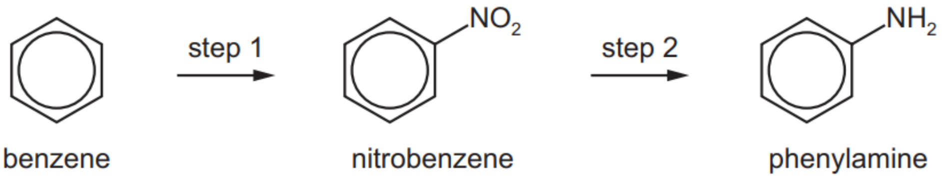
....

....

....

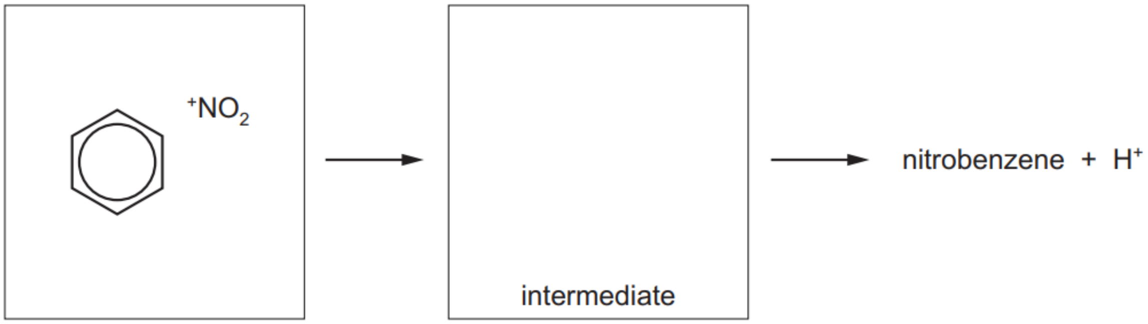
.... [4]

(b) Benzene can be used as a starting material to produce phenylamine by a two-step synthesis.



(i) Step 1 is the reaction of benzene with NO_2^+ ions.

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]

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

.... [1]

(iii) Identify the reagents needed to produce NO_2^+ ions.

Write an equation to explain how these reagents produce NO_2^+ ions.

....

....

.... [2]

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

....

.... [2]

(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]

(e) 1,3-diaminopropane, $H_2NCH_2CH_2CH_2NH_2$, 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]

68. 9701/41/M/J/20 Q4

(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

....

....

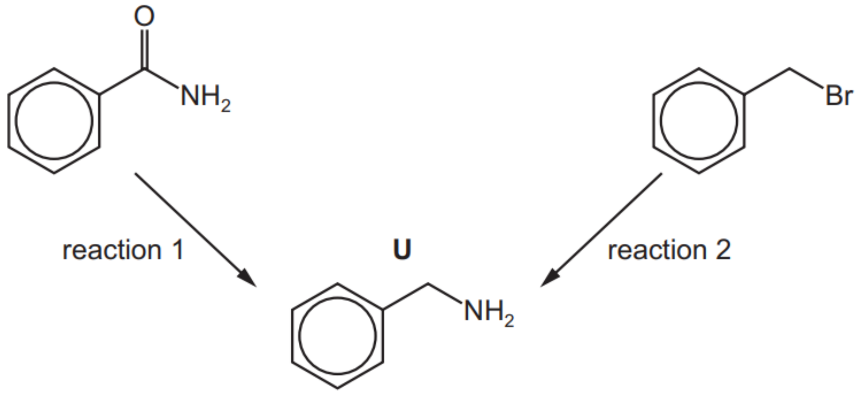
....

....

....

.... [3]

(b) Compound **U** can be prepared by two different methods as shown.



(i) Suggest reagents and conditions for reaction 1 and for reaction 2.

reaction 1 ....

reaction 2 .... [2]

(ii) State the type of reaction in reaction 1 and name the mechanism in reaction 2.

type of reaction in reaction 1 ....

mechanism of reaction 2 .... [2]

69. 9701/41/M/J/20 Q5

(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.

[3]

(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]

70. 9701/41/M/J/20 Q6

(a) Compare and explain the relative acidities of 2-chloropropanoic acid, 3-chloropropanoic acid, and propanoic acid. Explain your answer.

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

most acidic least acidic

explanation ....

....

....

....

....

.... [3]

(c) Three tests were carried out on separate samples of the organic acids shown in the table. The following results were obtained.

✓ = observed change

✗ = no observed reaction

test	reagent(s) and conditions	HCO_2H	CH_3COCO_2H	HO_2CCO_2H	observed change
1	....	✓	✗	✗	
2	....	✗	✓	✗	
3	....	✓	✗	✓	

Complete the table with the reagent(s) and conditions and the observed change for each test. Assume these organic acids all have a similar acid strength. [5]

71. 9701/42/M/J/20 Q4

(a) **(i)** When benzene undergoes nitration a nitro group substitutes at a carbon atom.

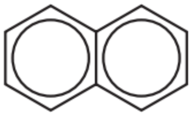
State the shape (geometry) around the substituted carbon atom

- 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

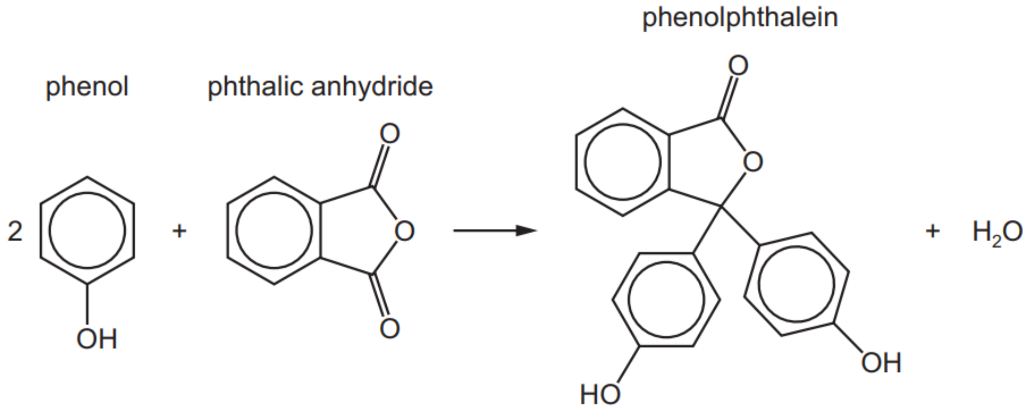
[1]

(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]

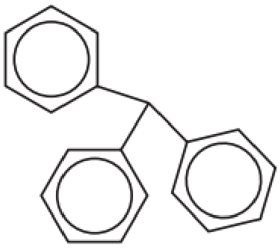
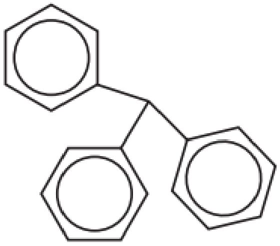
(d) (i) Name the functional groups, in addition to the benzene ring, present in a phenolphthalein molecule.

.... [1]

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

Complete the table by:

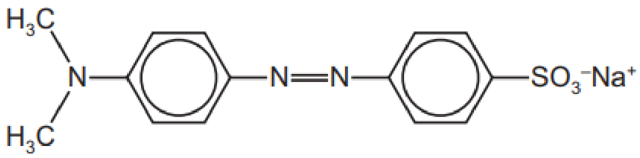
- drawing the structures of the organic products formed (part of the structure has been given for you)
- stating the types of reaction.

reagent	organic product structure	type of reaction
an **excess** of hot NaOH(aq)		
an **excess** of Br_2(aq)		

[4]

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

methyl orange



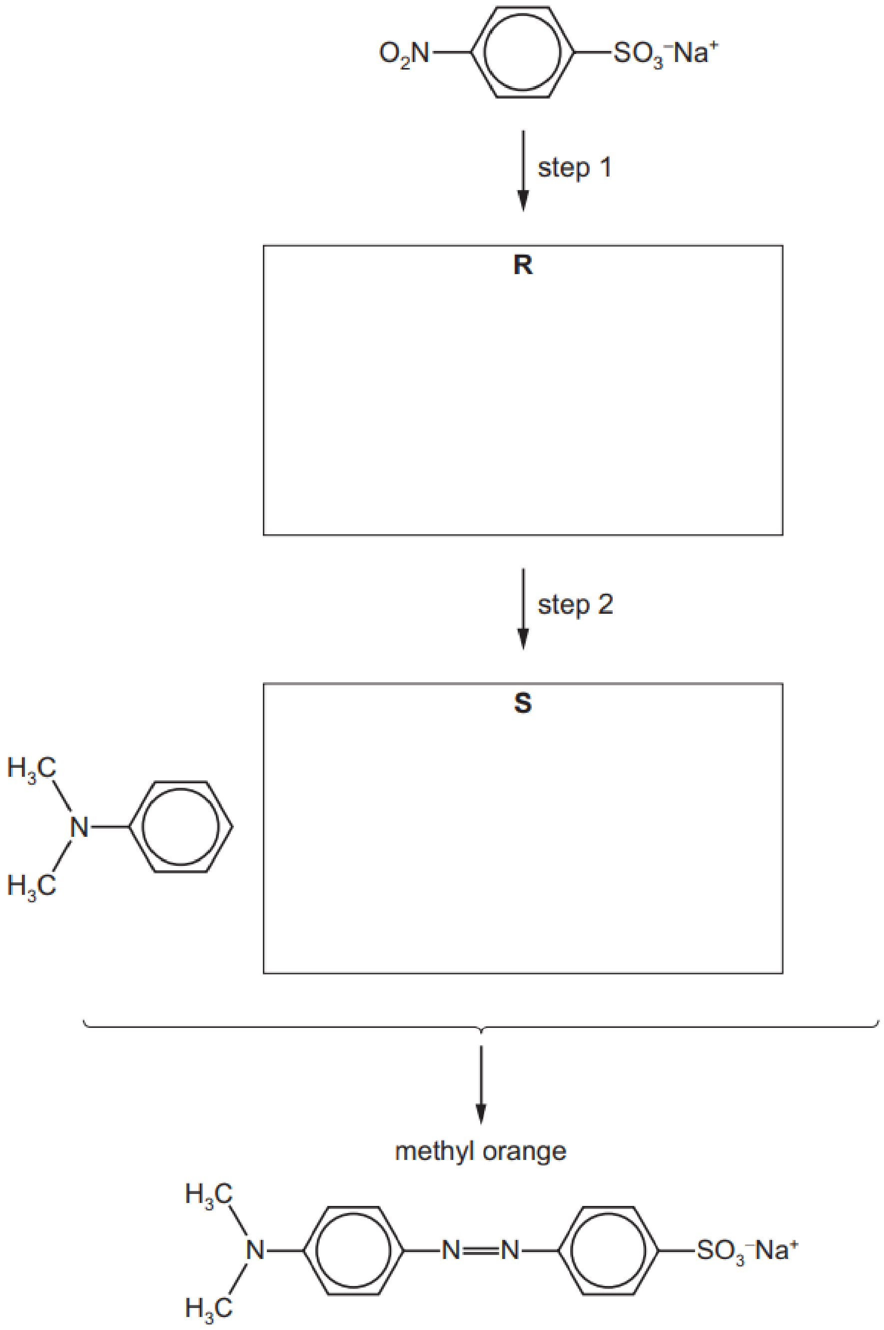
(i) On the structure of methyl orange, **circle** the bond or bonds that make this compound a dye. [1]

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 ....

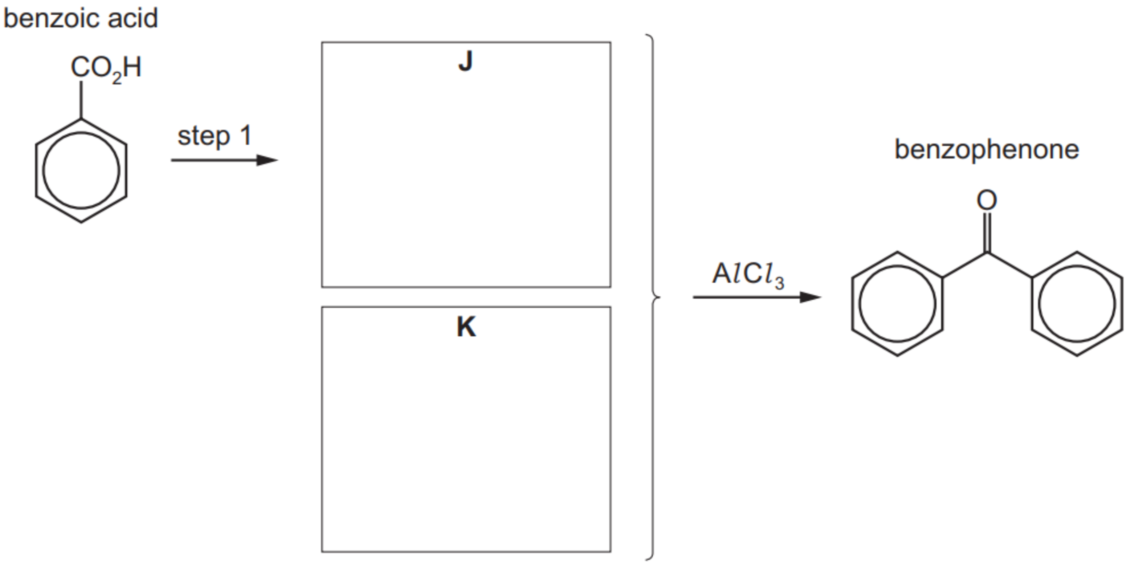
[3]

72. 9701/42/M/J/20 Q5c

(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.

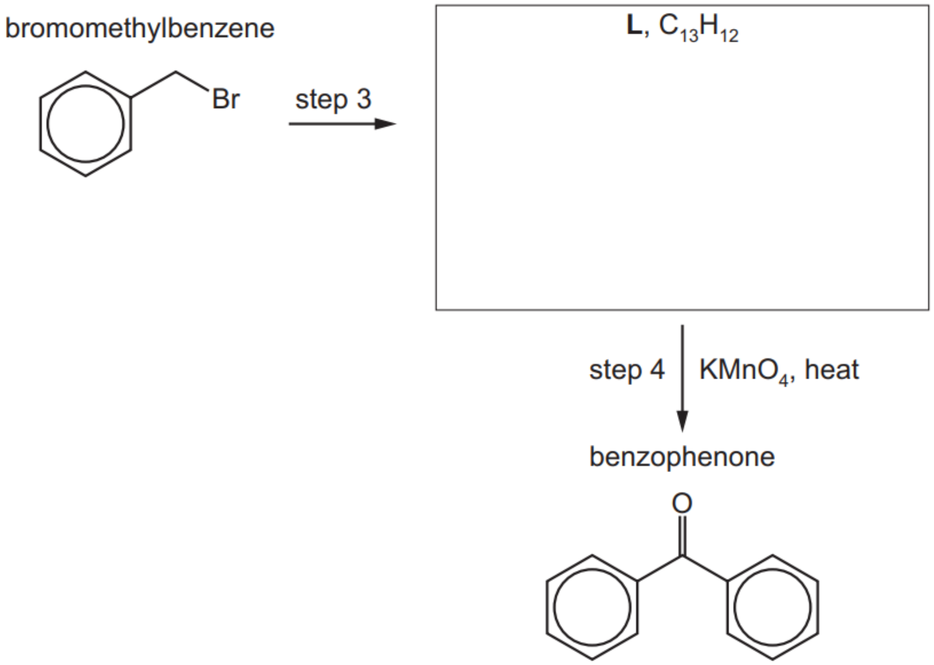


(i) Deduce the identities of organic compounds **J** and **K** and draw their structures in the boxes. [2]

(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 ....

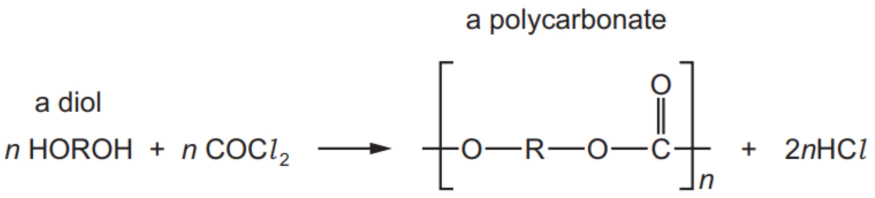
reagents and conditions ....
[2]

(iii) Deduce the *type of reaction* in step 4.

.... [1]

73. 9701/42/M/J/20 Q6

The class of polymers called polycarbonates are made by the reaction of carbonyl dichloride, $COCl_2$, with a diol.

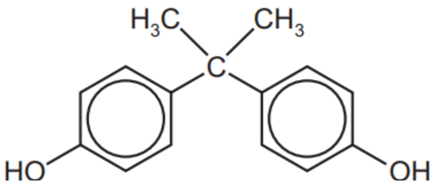


(a) **(i)** Deduce the *type of polymerisation* shown here.

.... [1]

Nalgene® is a polycarbonate formed from the diol **P** and $COCl_2$.

P



(ii) Draw **one** repeat unit of Nalgene®.

[1]

(iii) Nalgene® is a strong and tough polymer.

Identify **two** types of intermolecular force that are responsible for these properties of Nalgene®.

1 ....

2 ....

[1]

(b) Proteins are polymers of amino acids.

Complete the table to show how the secondary and tertiary structures of proteins are stabilised.

	one intermolecular force responsible	groups involved
secondary structure		
tertiary structure		

(c) Explain the significance of hydrogen bonding in DNA in relation to the accurate replication of genetic information.

....

....

.... [2]

(d) Many polymers are degradable.

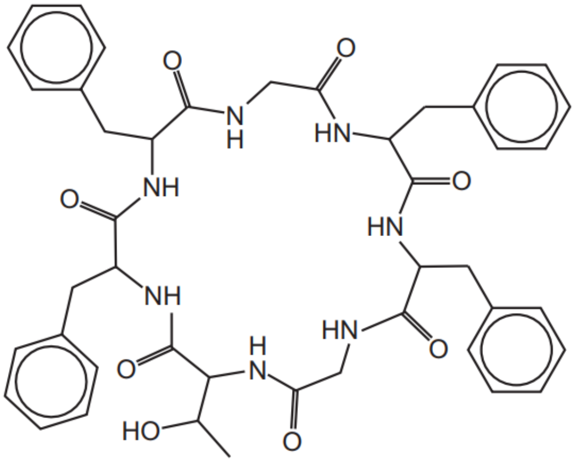
State **two** different processes by which some polymers can be degraded.

....

.... [1]

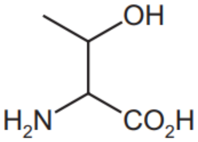
(e) The cyclic peptide **B** is shown.

B



Cyclic peptide **B** is broken into its monomers by heating under reflux with dilute hydrochloric acid. The amino acid threonine, Thr, and two other organic products are formed.

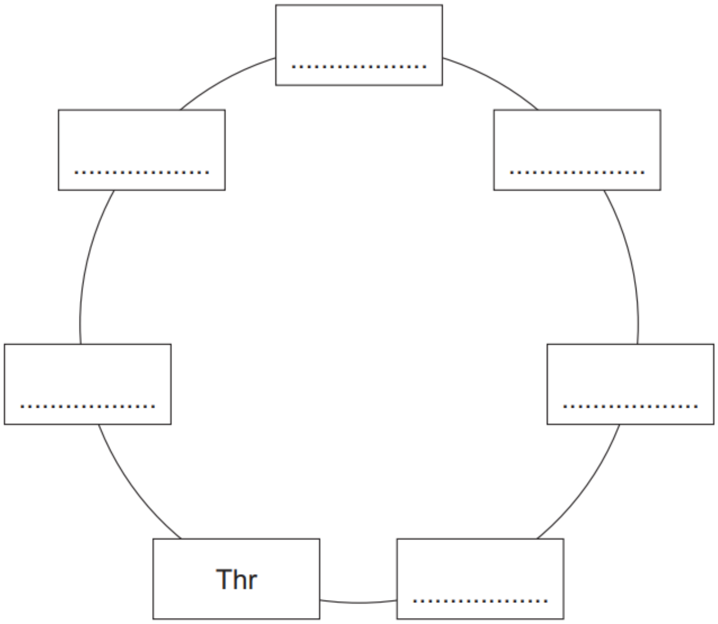
threonine



(i) Draw the structures of the two other organic products formed.

[2]

(ii) Using the 3-letter abbreviations for the amino acids as given in the *Data Booklet*, complete the sequence for the cyclic peptide, **B**.



[1]

(iii) Name **two** analytical techniques that could be used to separate these amino acids.

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

74. 9701/42/F/M/20 Q1c (iii)

Complete the table to show any observations for the reactions of HO_2CCO_2H with the named reagents.

Where no change is observed, write 'none'.

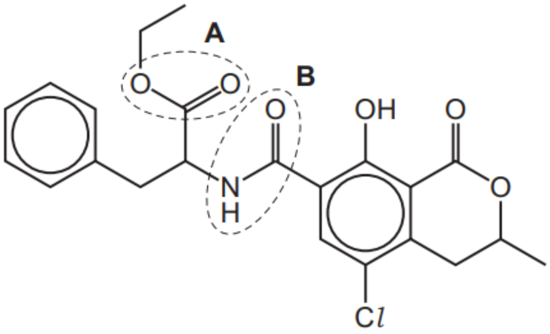
reagent	observations with HO_2CCO_2H
warm acidified manganate(VII)	
2,4-dinitrophenylhydrazine	
warm Tollens' reagent	

[2]

75. 9701/42/F/M/20 Q4

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 ....

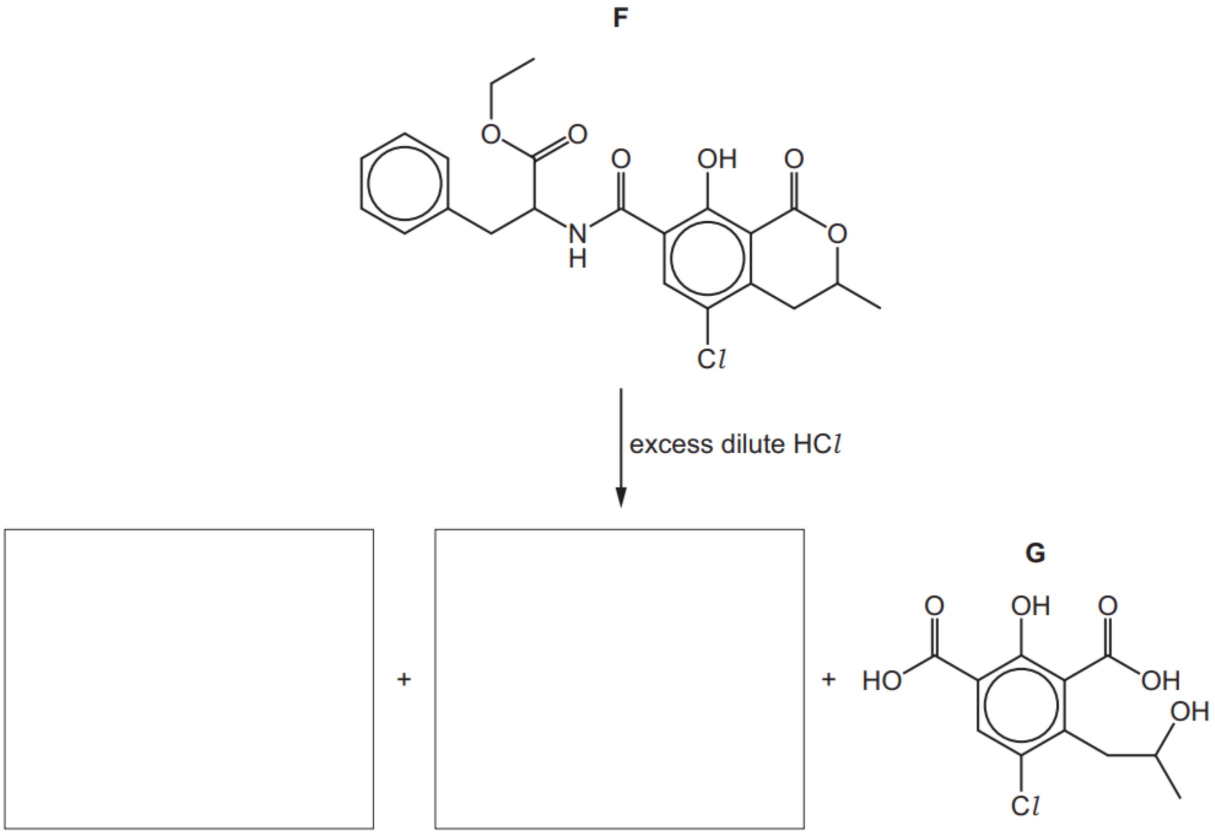
[2]

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

.... [1]

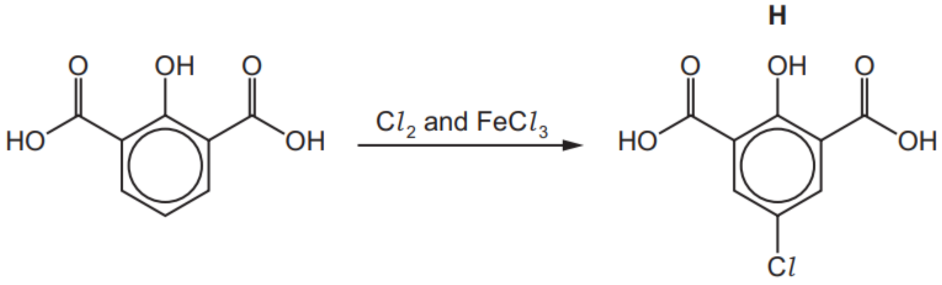
(b) **F** can be hydrolysed by heating with an excess of dilute hydrochloric acid, as shown.

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



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 ....

....

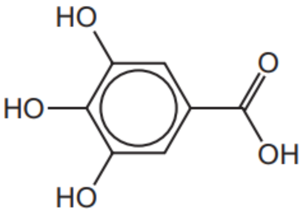
2 ....

.... [2]

76. 9701/42/F/M/20 Q5

Gallic acid, $C_7H_6O_5$, is a naturally occurring aromatic molecule.

gallic acid



(a) Gallic acid contains the carboxylic acid and phenol functional groups.

State and explain the relative acid strength of these two functional groups.

....

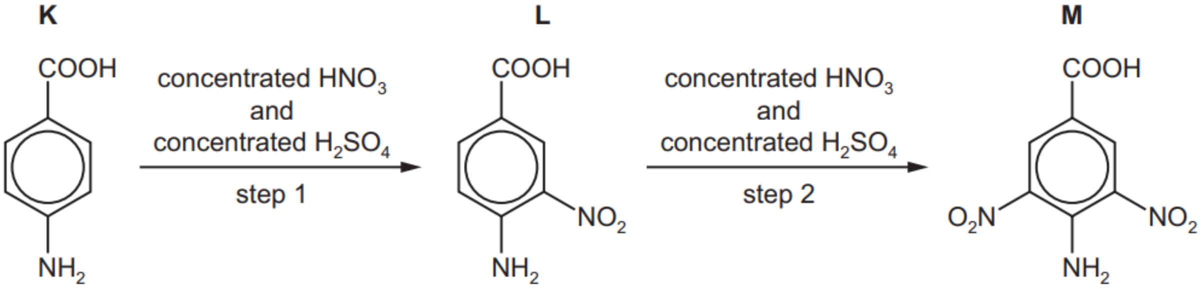
....

....

.... [2]

(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.



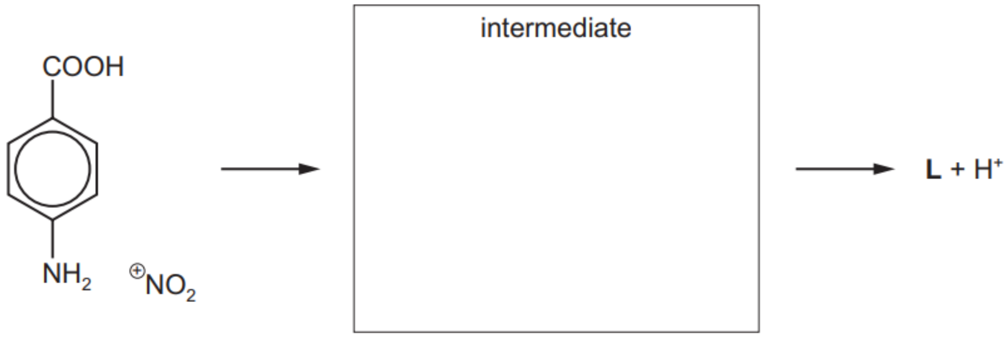
Nitronium ions, NO_2^+, are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

(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.

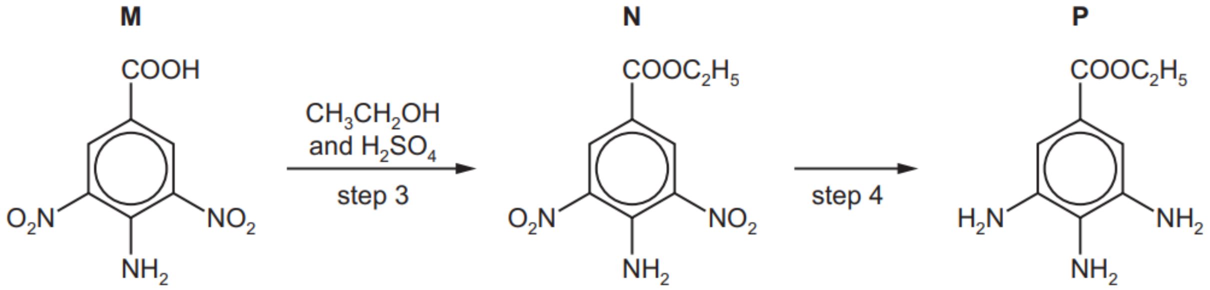


[2]

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

.... [1]

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

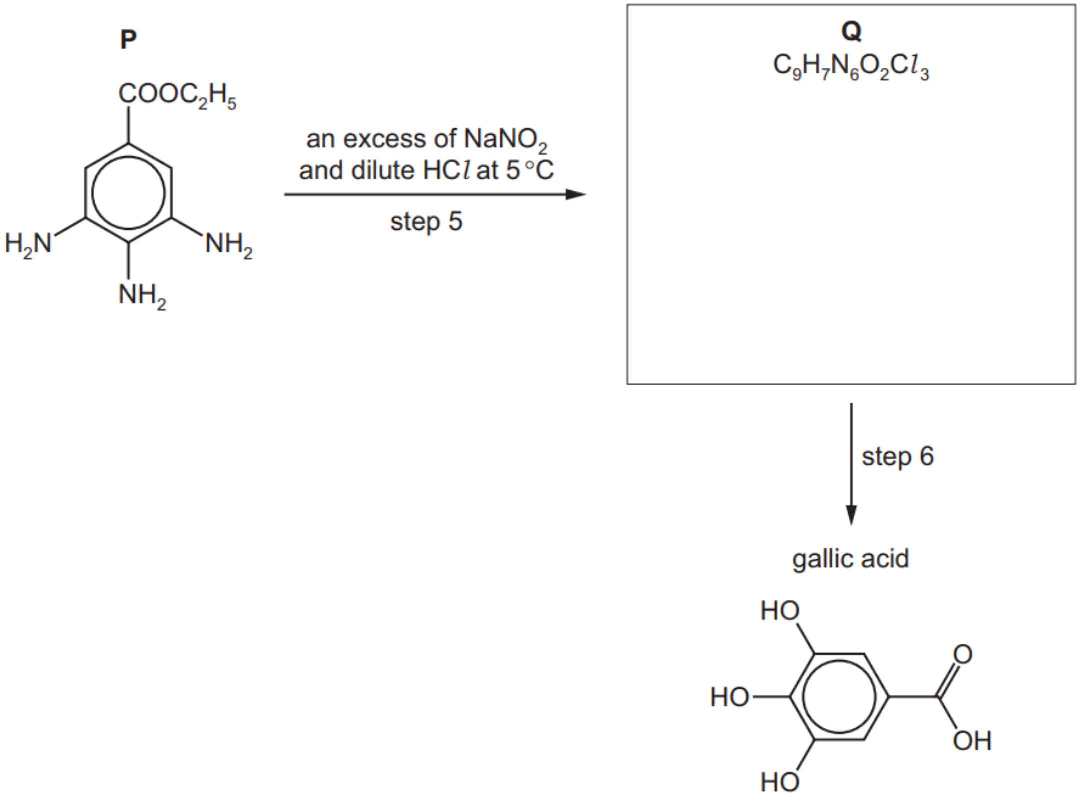


(iv) State the reagents and conditions for step 4.

.... [2]

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

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



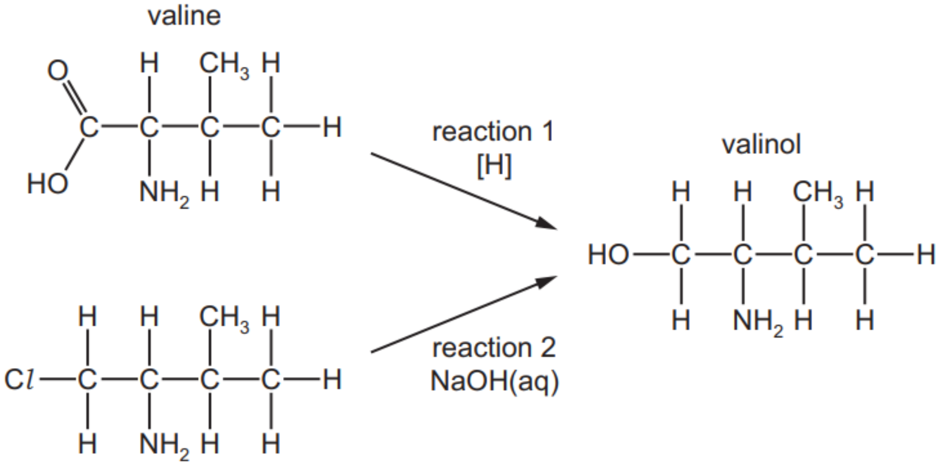
(v) Suggest the structure of compound **Q** in the box provided. [2]

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

.... [1]

77. 9701/42/F/M/20 Q6

Valinol can be synthesised by the following reactions. Reaction 1 uses valine as the starting material.



(a) **(i)** Write an equation for reaction 1, using [H] to represent the reducing agent.

.... [1]

(ii) Suggest a suitable reagent for reaction 1.

.... [1]

(iii) Name the mechanism for reaction 2.

.... [1]

(b) Valine and glycine, H_2NCH_2COOH, form the tripeptide Gly–Val–Gly.

Draw the structure of this tripeptide. Show the peptide bonds fully displayed.

[2]

(c) **(i)** Valine exists as two stereoisomers.

Draw three-dimensional diagrams to show the two stereoisomers of valine. In your diagrams, the $–CH(CH_3)_2$ group can be represented by –R.

State the type of stereoisomerism shown.

type of stereoisomerism ....
[2]

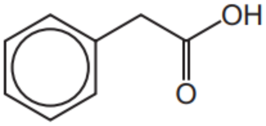
(ii) Valine is an amino acid.

Draw the zwitterion of valine.

[1]

78. 9701/41/O/N/21 Q7b

The structure of phenylethanoic acid is shown.



(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.

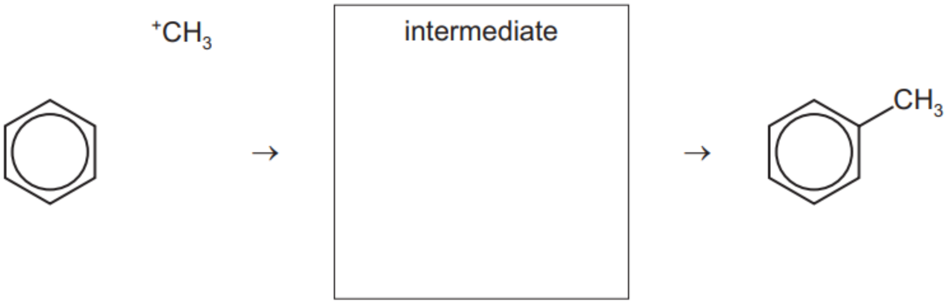
In the first stage of this synthesis, benzene reacts with chloromethane in the presence of an $AlCl_3$ catalyst to form methylbenzene.

Chloromethane reacts with $AlCl_3$ to form two ions. One of these is the carbocation $^+CH_3$.

(i) Write an equation for the reaction between chloromethane and $AlCl_3$.

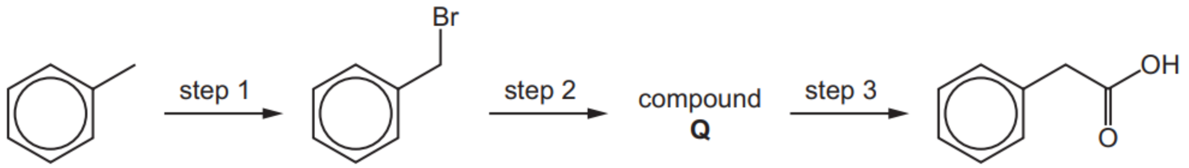
.... [1]

(ii) Draw the mechanism of the reaction between benzene and $^+CH_3$. 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]

79. 9701/41/O/N/21 Q8

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)**.

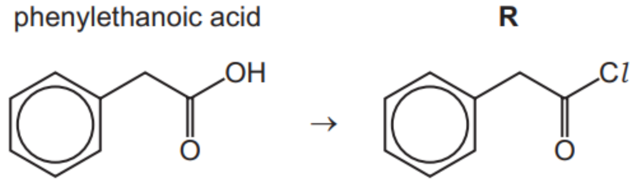
.... [1]

80. 9701/41/O/N/21 Q9

Compound **T** is made by a three-stage synthesis.

(a) In stage 1, phenylethanoic acid reacts with a suitable reagent to form compound **R**.

stage 1

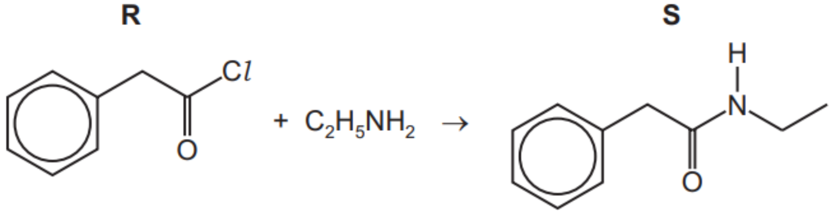


Suggest a suitable reagent for stage 1.

.... [1]

(b) In stage 2, compound **R** reacts with ethylamine to form compound **S**.

stage 2



+ $C_2H_5NH_2$ →

(i) Name the functional group formed in stage 2.

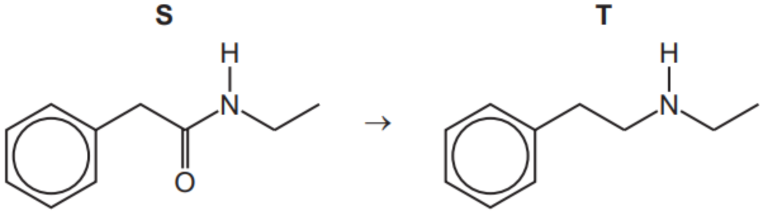
.... [1]

(ii) Identify the other product formed in stage 2.

.... [1]

(c) In stage 3, compound **S** reacts with a suitable reagent to form compound **T**.

stage 3



(i) State the formula of a suitable reagent for stage 3.

.... [1]

(ii) Name the type of reaction that occurs in stage 3.

.... [1]

81. 9701/41/O/N/21 Q10

Valine (Val) and lysine (Lys) are amino acids. The structures of these amino acids can be found in the *Data Booklet*.

The isoelectric point of an amino acid is the pH at which it exists as a zwitterion. The isoelectric point of valine is 6.0. The isoelectric point of lysine is 9.7.

(a) Draw the structure of valine at pH 6.0.

[1]

(b) A solution of lysine is produced with pH 9.7. Dilute sulfuric acid is added slowly until the pH of the solution is 1.0. The sulfuric acid reacts with lysine to produce different organic ions that are not present in significant concentrations at pH 9.7.

Draw the structures of three of the organic ions that form during the addition of sulfuric acid in the boxes. Draw the organic ion present at pH 1.0 in box C.

A	B	C (pH 1.0)

[3]

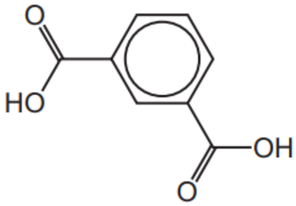
(c) Draw the structure of the dipeptide Val-Lys. The peptide bond should be shown fully displayed.

[2]

82. 9701/42/O/N/21 Q7a,c

The structure of benzene-1,3-dicarboxylic acid is shown.

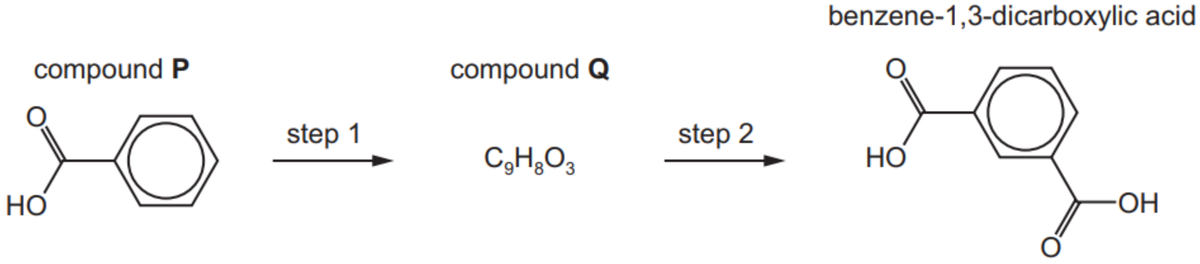
benzene-1,3-dicarboxylic acid



(a) State the empirical formula of benzene-1,3-dicarboxylic acid.

.... [1]

(c) Benzene-1,3-dicarboxylic acid can be made by the two-step synthesis shown below.



(i) Name compound **P**.

.... [1]

(ii) Explain why the major product of this two-step synthesis is benzene-1,3-dicarboxylic acid and **not** benzene-1,4-dicarboxylic acid.

....

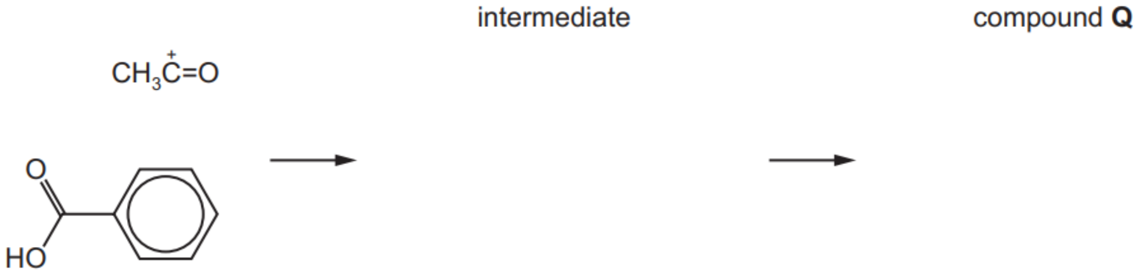
.... [1]

(iii) The reagents used for step 1 are CH_3COCl and $AlCl_3$. These reagents give rise to $CH_3\overset{+}{C}{=}O$ ions which react with compound **P**.

Name the mechanism of this reaction.

.... [1]

(iv) Draw the mechanism of the reaction of $CH_3\overset{+}{C}{=}O$ ions with compound **P**. Include all relevant curly arrows and charges, the structure of the intermediate and the structure of compound **Q**.



[3]

(v) Suggest a reagent and conditions to convert compound **Q** into benzene-1,3-dicarboxylic acid, in step 2.

.... [1]

83. 9701/42/O/N/21 Q8a

Alanine, $H_2NCH(CH_3)CO_2H$, and glutamic acid, $H_2NCH(CH_2CH_2CO_2H)CO_2H$, are two naturally occurring amino acids.

(a) $H_2NCH(CH_3)CO_2H$ exists as two optical isomers.

Draw three-dimensional structures of these two optical isomers.

[2]

(d) At pH 11 alanine exists as $H_2NCH(CH_3)CO_2^-$ ions and glutamic acid exists as $H_2NCH(CH_2CH_2CO_2^-)CO_2^-$ 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]

84. 9701/42/O/N/21 Q9

Butylamine, $CH_3CH_2CH_2CH_2NH_2$, 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

....

....

....

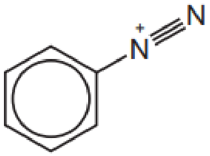
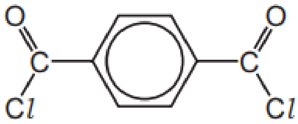
....

....

.... [4]

85. 9701/42/O/N/21 Q10

(a) Complete the table to show the structure of the organic product from each reaction of phenol, C_6H_5OH.

reaction	reaction mixture	structure of organic product
1	phenol + NaOH(aq)	
2	phenol + Na(s)	
3	phenol +  (aq) + NaOH, at 4 °C	
4	an excess of phenol + 	

[4]

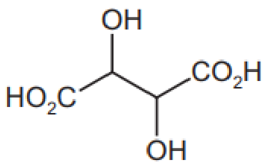
(b) Identify **two** reactions from the table in which ethanol would behave in a similar way to phenol.

.... [1]

86. 9701/41/M/J/21 Q3e

(e) **(i)** Complete the following table to show the structures of the organic products formed when tartaric acid reacts separately with each reagent. Identify each type of reaction.

tartaric acid



reagent	structure of organic product	type of reaction
an excess of $LiAlH_4$		
an excess of CH_3COCl		

[3]

(ii) Tartaric acid reacts with the amine 1-phenylethylamine, $C_6H_5CH(NH_2)CH_3$, to form an ionic salt.

Draw the structure of the salt formed in this reaction. Include the charges on the ions.

[1]

87. 9701/41/M/J/21 Q6

(a) Compare and explain the relative acidities of butanoic acid, ethanol, ethanoic acid and water.

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

most acidic least acidic

....

....

....

....

....

.... [4]

(b) Three carboxylic acids, methanoic acid, HCO_2H, ethanedioic acid, HO_2CCO_2H, and butanedioic acid, $HO_2CCH_2CH_2CO_2H$, are compared. Two tests were carried out on separate samples of each organic acid, as shown.

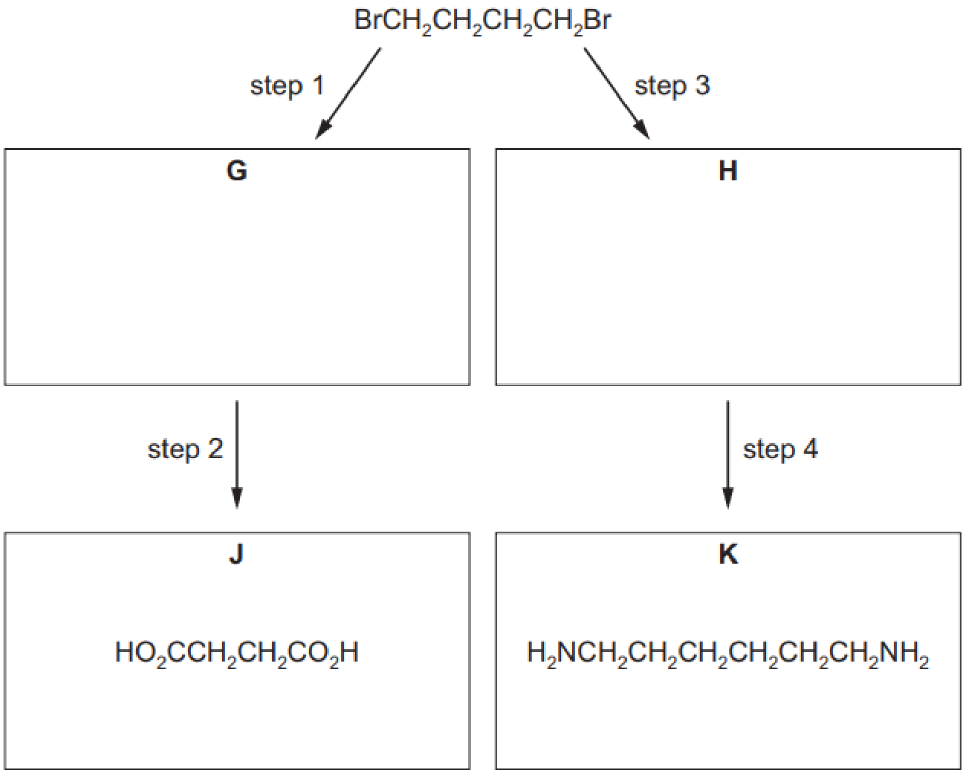
The following results were obtained. ✓ = observed change ✗ = no observed reaction

test	reagents and conditions	HCO_2H	HO_2CCO_2H	$HO_2CCH_2CH_2CO_2H$	observed change
1		✓	✗	✗	
2		✓	✓	✗	

(i) Complete the table with the reagents and conditions and the observed change for a positive test.
Assume these organic acids all have a similar acid strength. [3]

88. 9701/41/M/J/21 Q6c,d

(c) 1,4-dibromobutane, $Br(CH_2)_4Br$, is used in the synthesis of the dicarboxylic acid **J** and diamine **K** as shown.



(i) Draw the structures of **G** and **H** in the boxes. [2]

(ii) Suggest reagents and conditions for each of steps 1 to 4.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

[4]

(d) Polyamide **L** can be synthesised from dicarboxylic acid **J**, $HO_2C(CH_2)_2CO_2H$, and diamine **K**, $H_2N(CH_2)_6NH_2$.

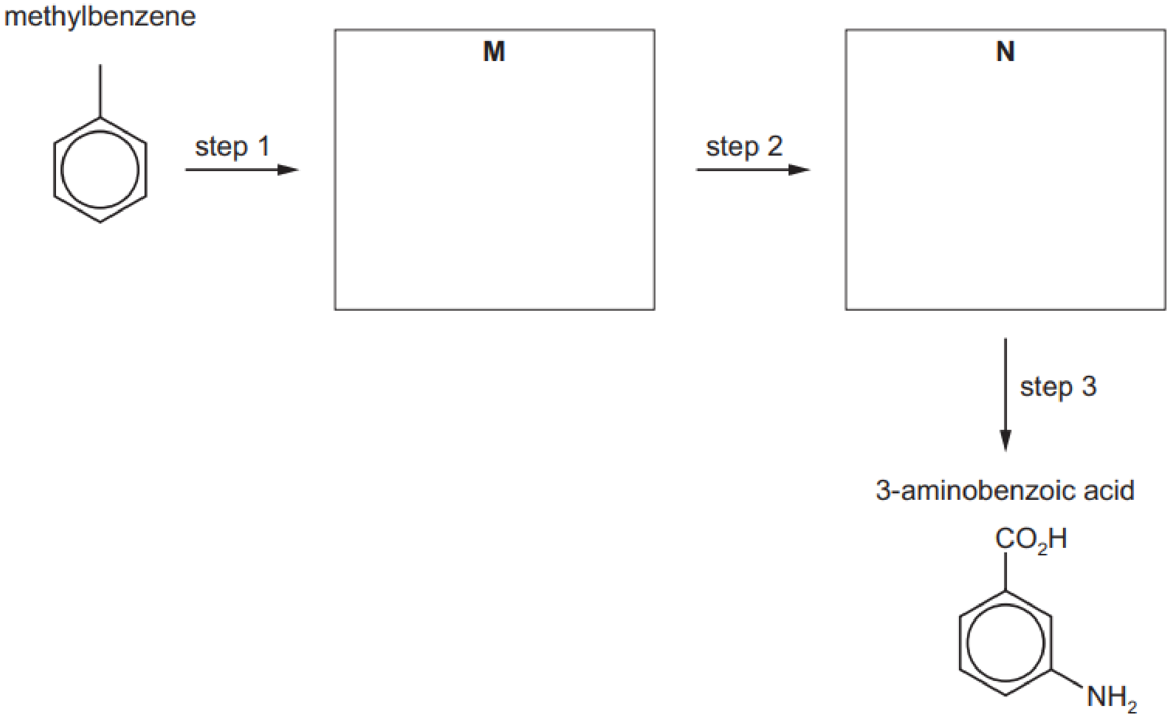
Draw the repeat unit of the polymer formed in the box. Any functional groups should be shown displayed.

polyamide **L**

[2]

89. 9701/41/M/J/21 Q7

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



(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, $HOCH_2CH(NH_2)CO_2H$, and lysine, $H_2N(CH_2)_4CH(NH_2)CO_2H$, reacts to form several different products.

(i) Draw the structures of the two structural isomers with the molecular formula $C_6H_{12}N_2O_5$ that could be present in the product mixture.

The functional group formed in each case should be displayed.

[3]

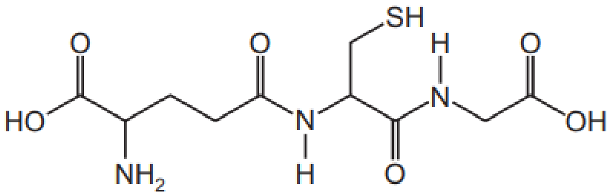
(ii) Predict the number of different structural isomers with the molecular formula $C_9H_{19}N_3O_4$ that could be present in the product mixture.

molecular formula	number of structural isomers formed
$C_9H_{19}N_3O_4$	

[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.

[2]

(iii) Glutathione is soluble in water.

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

....

....

.... [1]

90. 9701/41/M/J/21 Q9

9 The carbon-13 (^{13}C) NMR spectrum of compound **A**, $C_8H_8O_2$, contains six peaks.

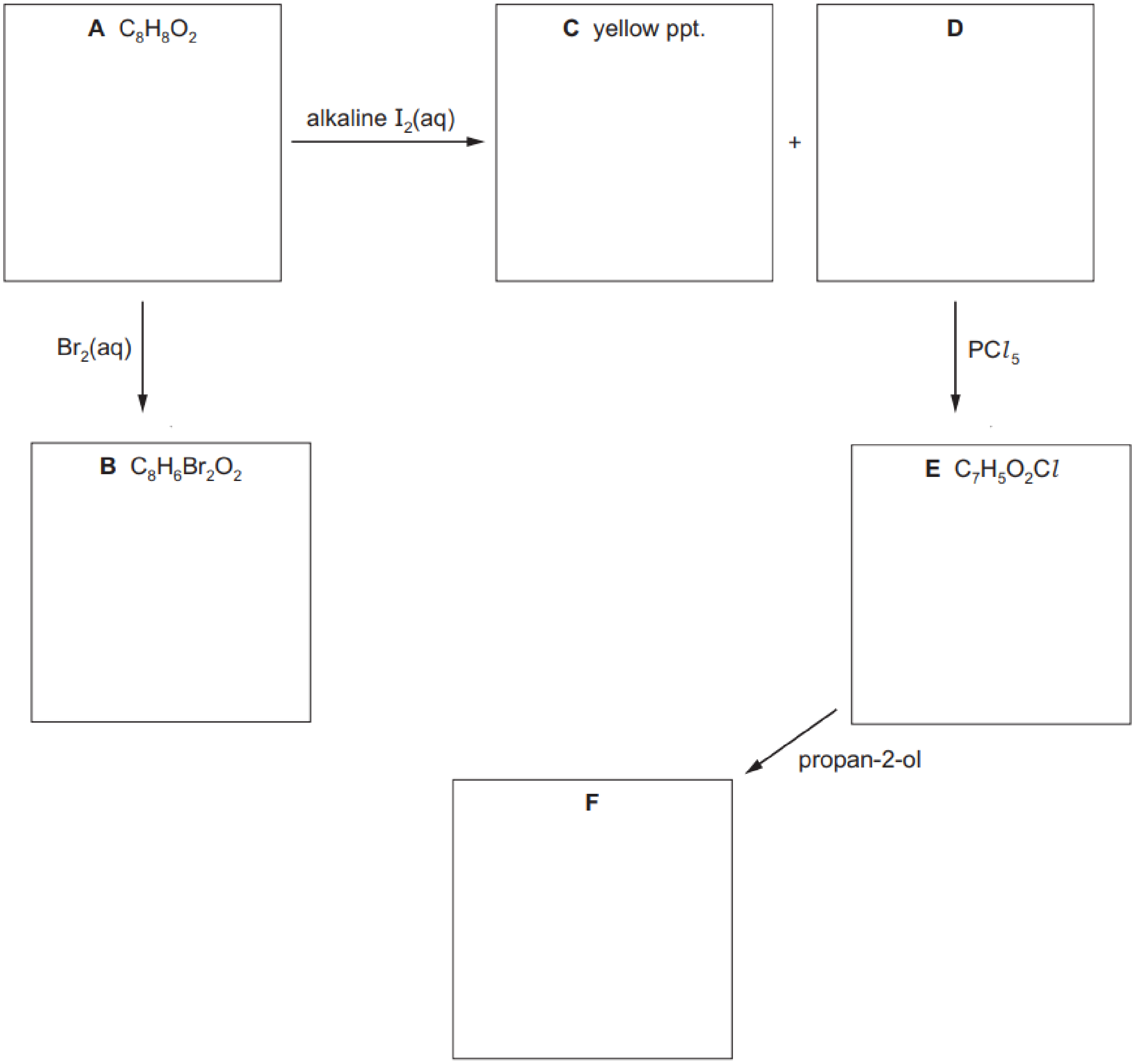
Compound **A** reacts with an excess of bromine water to give compound **B**, $C_8H_6Br_2O_2$.

Compound **A** reacts with alkaline aqueous iodine to form a yellow precipitate **C** and compound **D**.

Compound **D** reacts with PCl_5 to form compound **E**, $C_7H_5O_2Cl$.

Compound **E** reacts with propan-2-ol to form compound **F**.

Draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F** in the boxes.



[6]

91. 9701/42/M/J/21 Q5

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

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

most basic least basic

....

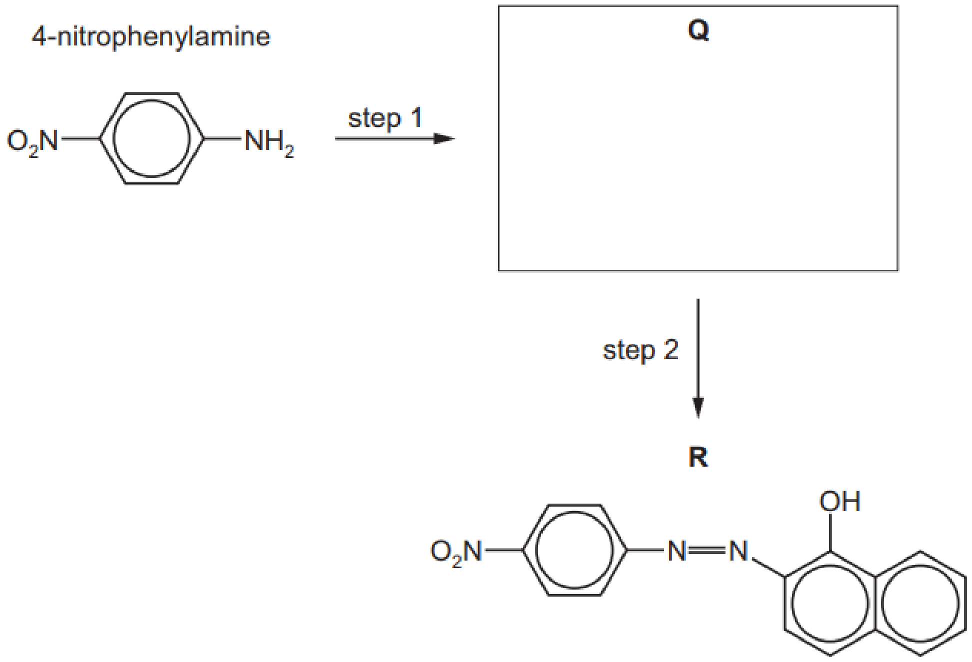
....

....

....

.... [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]

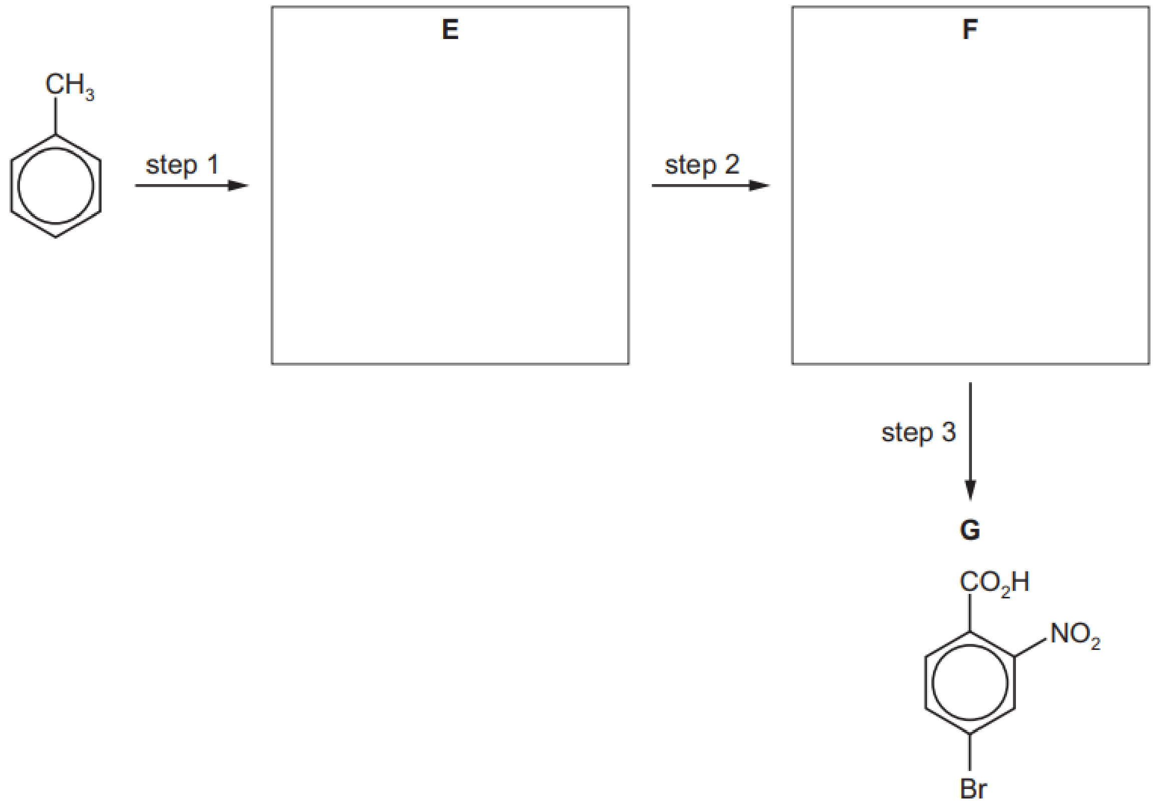
(ii) Suggest reagents and conditions for step 1 and 2 in **(b)**.

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)**.

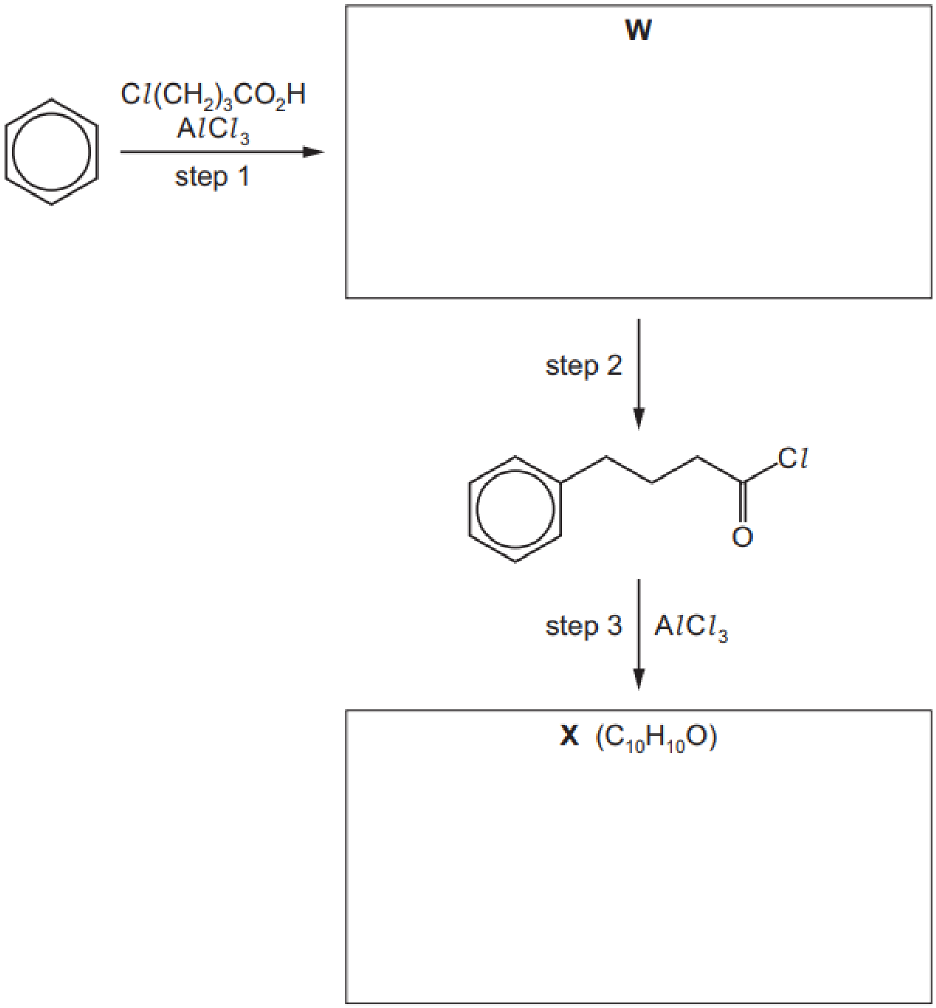
step 1 ....

step 2 ....

step 3 ....
[3]

92. 9701/42/M/J/21 Q6b

(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]

93. 9701/42/M/J/21 Q8

(a) State and explain the relative rate of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.

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

fastest slowest

....

....

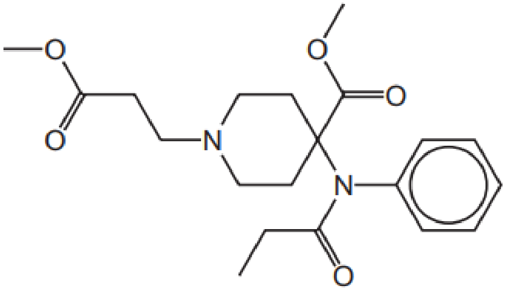
....

....

.... [3]

(b) The drug remifentanil is shown.

remifentanil



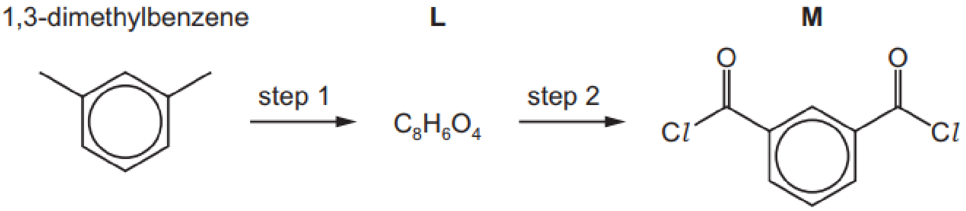
Remifentanil is **completely** hydrolysed under acidic conditions. Three different organic compounds are formed.

Draw the structures for these organic compounds in the boxes.

[3]

94. 9701/42/F/M/21 Q5b

(b) Compound **M** is made from 1,3-dimethylbenzene in a two-step synthesis.



(i) Draw the structure of **L**.

[1]

(ii) Suggest reactants and conditions for each step of this synthesis.

step 1 ....

step 2 ....
[2]

(iii) Write an equation for step 2.

.... [1]

(iv) A student investigates a possible synthesis of **M** directly from benzene using $COCl_2$ in the presence of an $AlCl_3$ catalyst.

Benzene initially reacts with $COCl_2$ as shown.

reaction 1 $COCl_2 + AlCl_3 \rightarrow AlCl_4^- + Cl{-}\overset{+}{C}{=}O$

reaction 2 $C_6H_6 + Cl{-}\overset{+}{C}{=}O \rightarrow C_6H_5COCl + H^+$

Reaction 2 is the electrophilic substitution of $Cl{-}\overset{+}{C}{=}O$ for H^+ in benzene.

Suggest a mechanism for reaction 2.

[3]

95. 9701/42/F/M/21 Q6

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, $(CH_2OH)_2$.

The ester bond should be shown fully displayed.

[2]

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

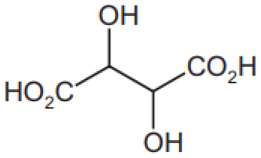
....

....

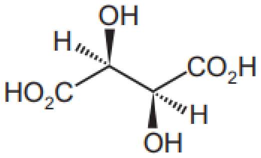
.... [1]

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

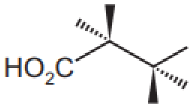
P

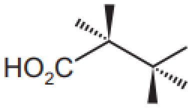


Only three stereoisomers of **P** exist. One of the stereoisomers is shown.



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, $C_4H_4O_5^{2-}$.

$$C_4H_2O_4^{2-} + H_2O \rightleftharpoons C_4H_4O_5^{2-}$$

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

....

....

....

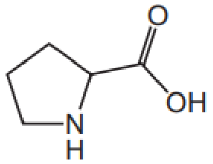
....

[3]

96. 9701/42/F/M/21 Q7

Proline (Pro) is a naturally occurring amino acid.

proline



(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.

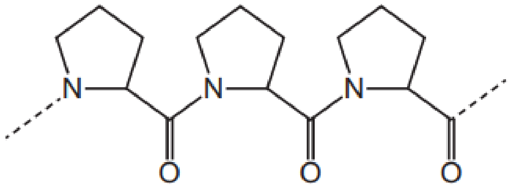
[2]

(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.

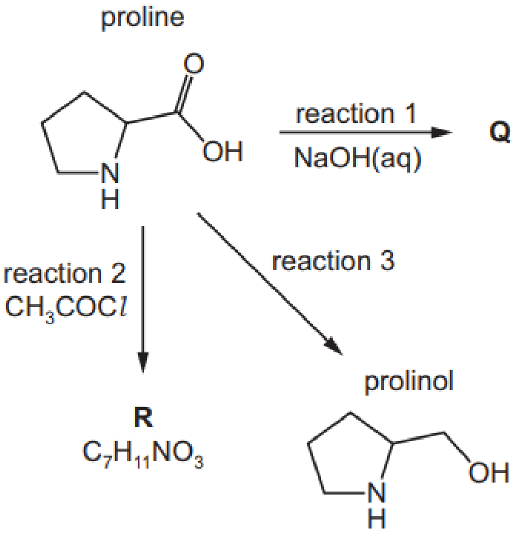


Suggest why the secondary structure of poly(proline) **cannot** be stabilised by hydrogen bonding.

....

.... [1]

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

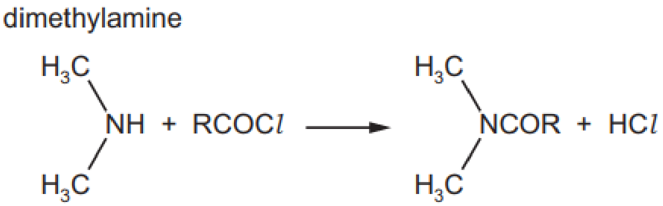


(i) Write an equation for the reaction of proline with NaOH(aq) in reaction 1.

$C_4H_7NHCO_2H$ + ... [1]

(ii) Proline has a secondary amine functional group.

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



Suggest the skeletal structure of **R**, $C_7H_{11}NO_3$, the product of reaction 2.

[1]

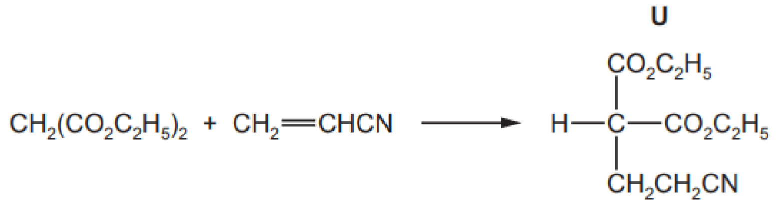
(iii) Suggest the reagent required for reaction 3.

.... [1]

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

In stage 1, $CH_2(CO_2C_2H_5)_2$ and $CH_2{=}CHCN$ react to form a single product **U**.

stage 1



$$CH_2(CO_2C_2H_5)_2 + CH_2{=}CHCN \longrightarrow \begin{array}{c} \textbf{U} \\ \begin{array}{ccl} & CO_2C_2H_5 & \\ & | & \\ H- & C & -CO_2C_2H_5 \\ & | & \\ & CH_2CH_2CN & \end{array} \end{array}$$

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

$CH_2(CO_2C_2H_5)_2$ ....

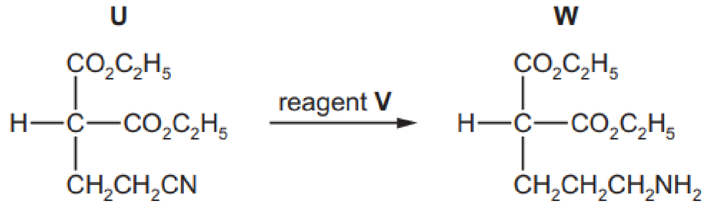
$CH_2{=}CHCN$ .... [2]

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

.... [1]

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

stage 2



$$\begin{array}{c} \textbf{U} \\ \begin{array}{ccl} & CO_2C_2H_5 & \\ & | & \\ H- & C & -CO_2C_2H_5 \\ & | & \\ & CH_2CH_2CN & \end{array} \end{array} \xrightarrow{\text{reagent } \mathbf{V}} \begin{array}{c} \textbf{W} \\ \begin{array}{ccl} & CO_2C_2H_5 & \\ & | & \\ H- & C & -CO_2C_2H_5 \\ & | & \\ & CH_2CH_2CH_2NH_2 & \end{array} \end{array}$$

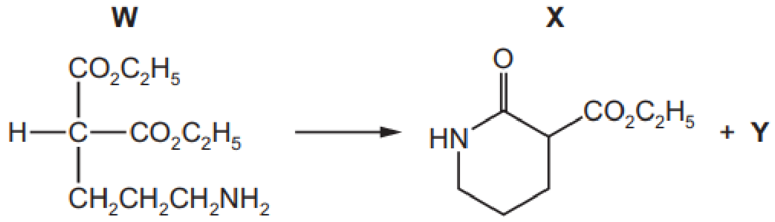
(iii) Suggest a suitable reagent **V**.

.... [1]

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

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

stage 3



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

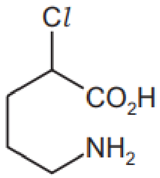
.... [1]

(v) Deduce the identity of **Y**.

.... [1]

After several further stages, **Z** is produced.

Z



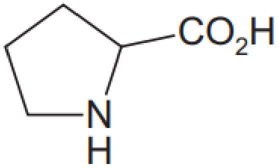
In the final stage of the synthesis, **Z** reacts via a nucleophilic substitution mechanism to form proline.

(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.

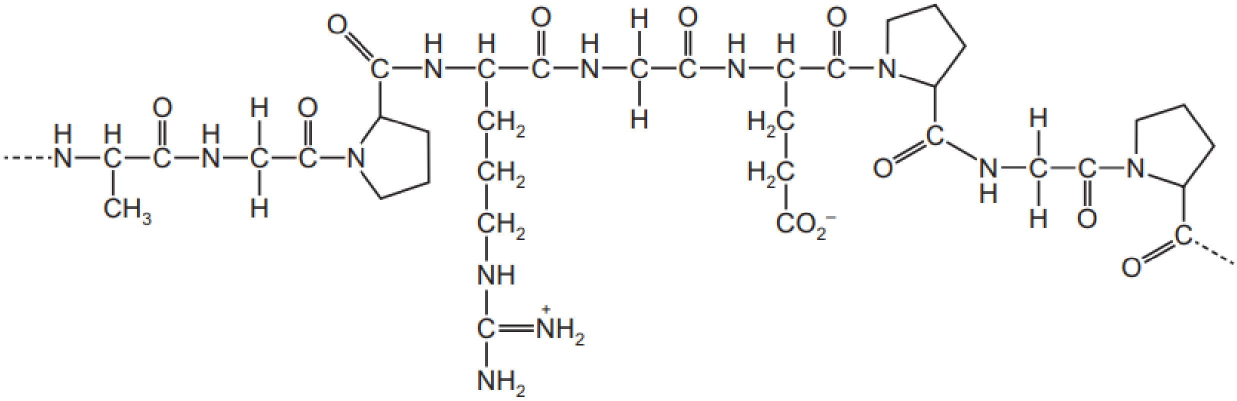
[3]

(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.

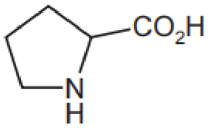
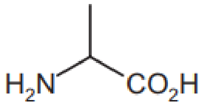
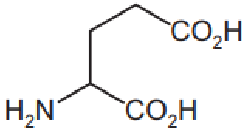
....

....

.... [2]

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

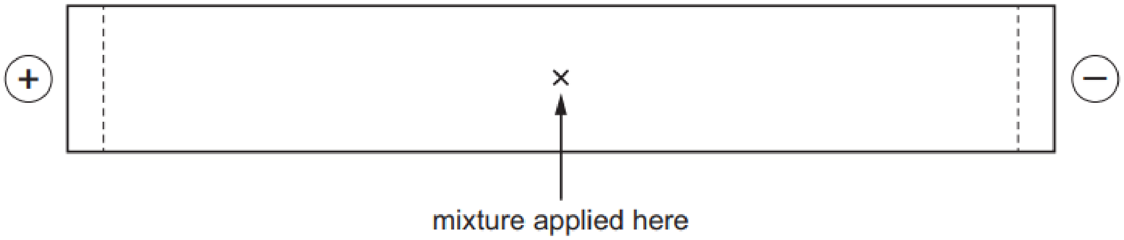
Three of the amino acids in gelatin are proline, alanine and glutamic acid. Their isoelectric points are shown.

amino acid	proline 	alanine 	glutamic 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.



[4]

97. 9701/41/O/N/22 Q7

(a) The structure of compound **P** is shown in Fig. 7.1.

P

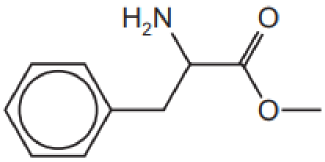


Fig. 7.1

(i) **P** is optically active.

Use an asterisk (*) to identify all chiral carbon atoms on the structure of **P** in Fig. 7.1. [1]

(ii) Plane polarised light is passed through a pure sample of one enantiomer of **P**. This is then repeated with a pure sample of the other enantiomer of **P**.

Describe the results of these two experiments, stating the similarities and differences of the results.

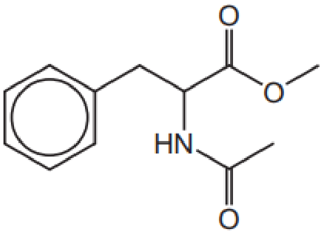
....

....

.... [2]

(b) **P** can be used to make compound **Q** in a single step reaction.

Q



(i) Give the structural formula of the compound that is added to **P** to make **Q** and give the formula of the other product of this reaction.

compound added to **P** ....

other product ....

[1]

(ii) When an ester is treated with $LiAlH_4$ in dry ether the ester linkage is cleaved by the addition of four hydrogen atoms and two alcohols are produced.

Draw the structures of the compounds formed when **Q** is treated with an **excess** of $LiAlH_4$ in dry ether.

[3]

(iii) Compare the relative basicities of compound **P**, compound **Q** and phenylamine.

.... < .... < ....

least basic most basic

Explain your answer.

....

....

....

....

[3]

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

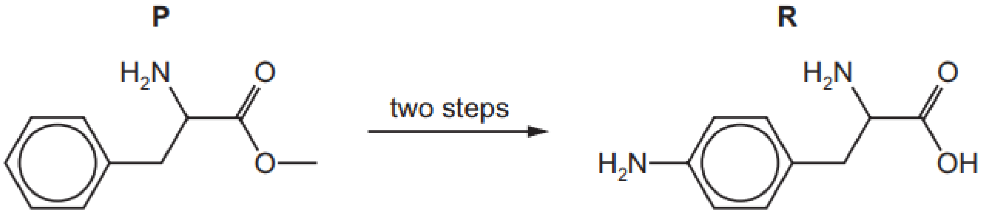


Fig. 7.2

(i) Identify the reagents and conditions used for the two steps of the reaction.

step 1 ....

step 2 ....

[2]

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

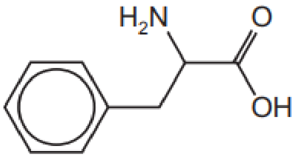
Table 7.1

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

[2]

(d) **P** can be used to produce compound **T**.

T



(i) In aqueous solution, **T** has a property called an isoelectric point.

Explain what is meant by isoelectric point.

....

.... [1]

(ii) **T** can polymerise under suitable conditions. No other monomer is involved in this reaction.

Draw a section of the polymer chain formed that includes three **T** monomers. Identify the repeat unit on your diagram.

[2]

98. 9701/41/O/N/22 Q8

Benzene, C_6H_6, is an aromatic molecule.

(a) State the C–C–C bond angle and the hybridisation shown by the carbon atoms in benzene.

bond angle ....

hybridisation .... [1]

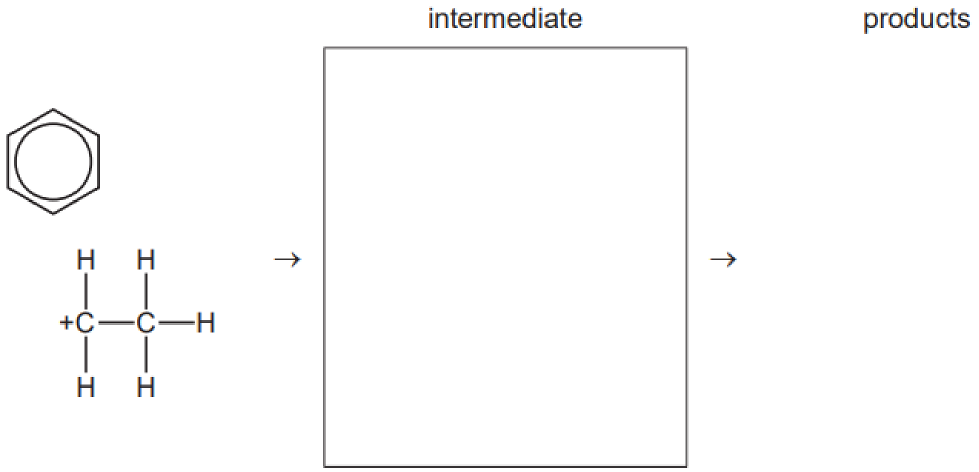
(b) Benzene reacts with chloroethane in the presence of a catalyst. The reaction mechanism is called electrophilic substitution.

(i) The first step in the reaction is the generation of the $^+CH_2CH_3$ electrophile.

Write an equation for the reaction that generates this electrophile.

.... [1]

(ii) Describe the mechanism for the reaction between benzene and the $^+CH_2CH_3$ electrophile. Include all relevant curly arrows and charges.



[3]

(c) Chlorobenzene and chloroethane have different reactivities in nucleophilic substitution reactions.

(i) Identify a suitable reagent to illustrate this difference in reactivity.

The reagent chosen should give **visibly** different results with chlorobenzene and chloroethane.

.... [1]

(ii) Write equations to describe any reactions that occur.

[1]

(iii) Explain the difference in the reactivities of chlorobenzene and chloroethane in nucleophilic substitution reactions.

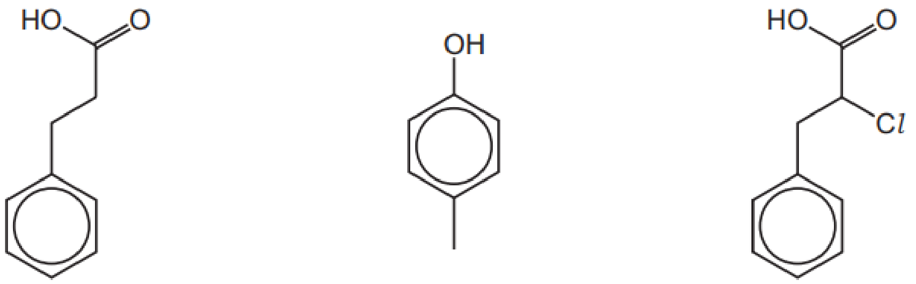
....

.... [1]

99. 9701/42/O/N/22 Q7

(a) The structural and displayed formulae of three aromatic compounds, **A**, **B** and **C**, are shown in Fig. 7.1.

$C_6H_5CH_2CH_2COOH$ $CH_3C_6H_4OH$ $C_6H_5CH_2CHC\mathit{l}CO_2H$



A **B** **C**

Fig. 7.1

Compare the relative acidities of **A**, **B** and **C**.

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

most acidic least acidic

Explain your answer.

....

....

....

.... [3]

(b) Methylbenzene, $C_6H_5CH_3$, can be made from benzene by an electrophilic substitution reaction.

(i) Identify a compound that reacts with benzene to form methylbenzene.
Identify the catalyst used.

compound ....

catalyst ....

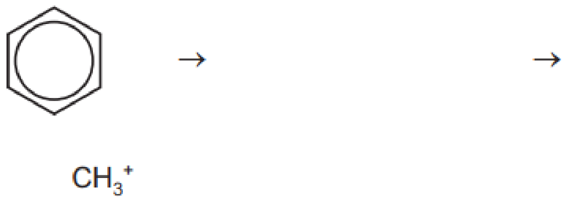
[1]

(ii) The first step in the reaction is the generation of the CH_3^+ electrophile.

Write an equation for the reaction that generates this electrophile.

.... [1]

(iii) Describe the mechanism for the reaction between benzene and the CH_3^+ electrophile. Include all relevant curly arrows and charges.



[3]

(iv) Identify a suitable reagent to oxidise methylbenzene to benzoic acid, C_6H_5COOH.

Write an equation for this reaction using [O] to represent one atom of oxygen from the oxidising agent.

reagent ....

equation ....

[2]

(v) Methylbenzene and benzoic acid are both nitrated with a mixture of concentrated nitric acid and sulfuric acid to give mononitrated products. The structural formulae of these products are $CH_3C_6H_4NO_2$ and $HOOCC_6H_4NO_2$ respectively.

Draw the structures of these two products.

[1]

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

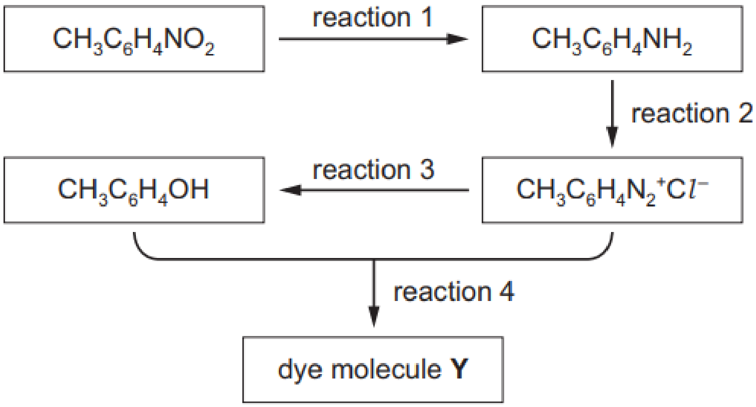


Fig. 7.2

(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]

100. 9701/42/O/N/22 Q9

Tyrosine and lysine, shown in Fig. 9.1, are naturally occurring amino acids found in proteins.

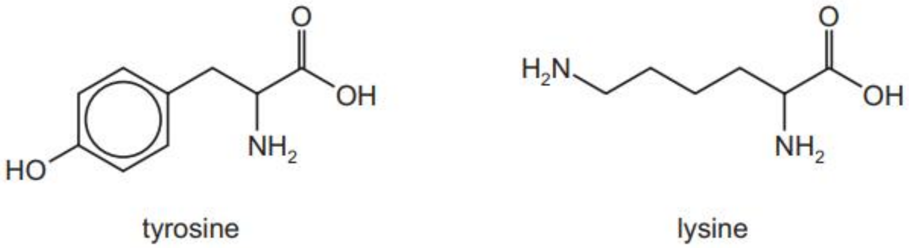


Fig. 9.1

(a) The isoelectric point of lysine is 9.47.

Draw the structure of lysine at the stated pH in the boxes below.

lysine at pH 7.00	lysine at pH 9.47	lysine at pH 12.00

[2]

(b) When ethanoic acid is treated with PCl_5 product **D** is formed.

When **D** is added to tyrosine two different isomeric products, **E** and **F**, are formed.

E has an ester linkage, **F** does not.

Draw the structures of **D**, **E** and **F** in the boxes below.

D	**E**	**F**

[3]

(c) Complete Table 9.1 by drawing the structure of the organic product formed when tyrosine reacts with each named reagent.

Ignore the directing effect of the $-CH_2CHNH_2COOH$ substituent.

Table 9.1

reagent	structure
an excess of $Br_2(aq)$	
an excess of NaOH(aq)	
an excess of $HNO_3(aq)$	

[3]

101. 9701/41/M/J/22 Q4d

(d) The ligand bipyridine consists of two pyridine rings.

Pyridine, C_5H_5N, and benzene, C_6H_6, have similar planar, cyclic structures.

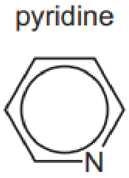


Fig. 4.2

By reference to the hybridisation of the carbon atoms and the nitrogen atom, and orbital overlap, suggest how the σ and π bonds are formed in a pyridine molecule.

....

....

....

....

.... [3]

(e) Pyridine reacts with Cl_2 in the presence of $AlCl_3$ as shown in Fig. 4.3.

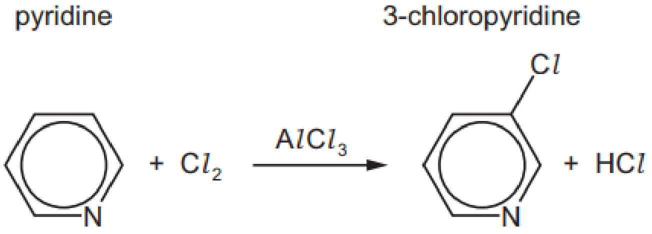
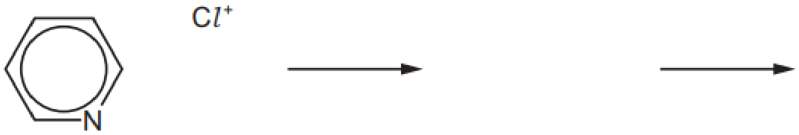


Fig. 4.3

The mechanism of this reaction is similar to that of the chlorination of benzene. $AlCl_3$ reacts with chlorine to generate an electrophile, Cl^+.

Complete the diagram to show the mechanism for the reaction of pyridine with Cl^+. Include all relevant charges, dipoles, lone pairs of electrons and curly arrows as appropriate.



[3]

102. 9701/41/M/J/22 Q5

(a) Compare the relative acidities of benzoic acid (C_6H_5COOH), phenylmethanol ($C_6H_5CH_2OH$), and phenol (C_6H_5OH).
Explain your reasoning.

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

....

....

....

....

....
[3]

(b) A series of nine separate experiments is carried out as shown in Table 5.1.

Complete the table by placing a tick (✓) in the relevant box if a reaction occurs. Place a cross (✗) in the box if no reaction occurs.

Table 5.1

	benzoic acid	phenylmethanol	phenol
Na(s)			
NaOH(aq)			
Na_2CO_3(aq)			

[3]

(c) **(i)** Benzoyl chloride, C_6H_5COCl, can be synthesised by the reaction of benzoic acid with either PCl_5 or $SOCl_2$.

Complete the equations for these reactions.

reaction 1 $C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl +$ .... + ...

reaction 2 $C_6H_5COOH + SOCl_2 \rightarrow C_6H_5COCl +$ .... + ...
[1]

(ii) Use your answer to **(c)(i)** to suggest why it is easier to isolate, in a pure form, the C_6H_5COCl from reaction 2 compared to reaction 1.

....

.... [1]

(d) Benzoyl chloride is hydrolysed by water at room temperature to form benzoic acid.

(i) Complete the diagram to show the mechanism for the reaction between C_6H_5COCl and H_2O.

Include charges, dipoles, lone pairs of electrons and curly arrows as appropriate.

[4]

(ii) Name the type of mechanism you showed in **(d)(i)**.

.... [1]

(e) Acyl chlorides react with sodium carboxylates to form acid anhydrides as shown in Fig. 5.1.

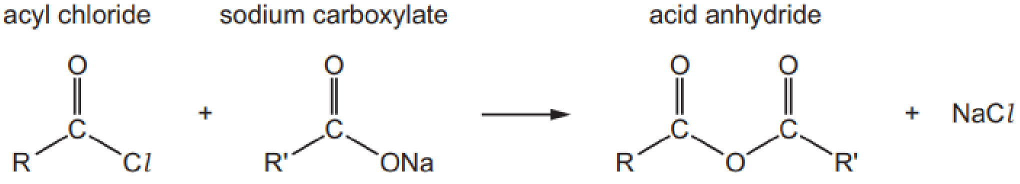


Fig. 5.1

The condensation polymers, polyanhydride and polyester, are formed by similar methods.

The repeat unit for a polyanhydride is shown in Fig. 5.2.

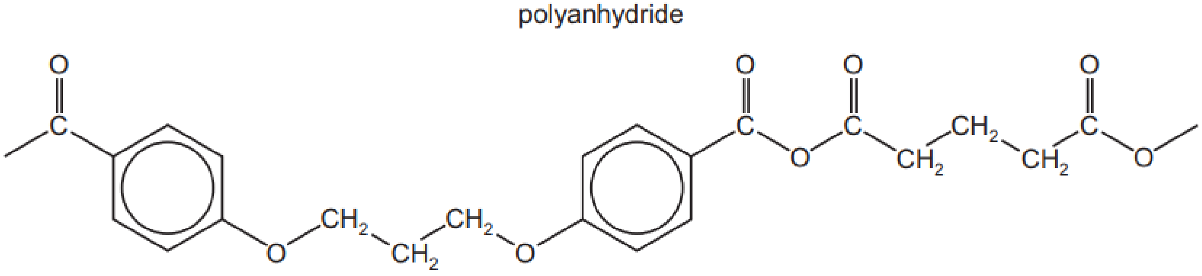


Fig. 5.2

(i) Use Fig. 5.1 and Fig. 5.2 to suggest the structures of the two monomers used to make this polyanhydride.

(ii) Polyanhydrides are biodegradable polymers.

Suggest how this polyanhydride can be degraded.

....

.... [1]

103. 9701/41/M/J/22 Q6

(a) Describe what is meant by a racemic mixture.

....

.... [1]

(c) The isoelectric point of asparagine, asn, is at pH 5.4.

(i) Describe the meaning of the term isoelectric point.

....

.... [1]

(ii) Draw the structure of asparagine at pH 1.0.

[1]

(d) Asparagine can polymerise to form poly(asparagine).

Draw the structure of poly(asparagine), showing **two** repeat units. The peptide linkage should be shown displayed.

[2]

104. 9701/41/M/J/22 Q7

Procaine is used as an anaesthetic in medicine. It can be synthesised from methylbenzene in five steps as shown in Fig. 7.1.

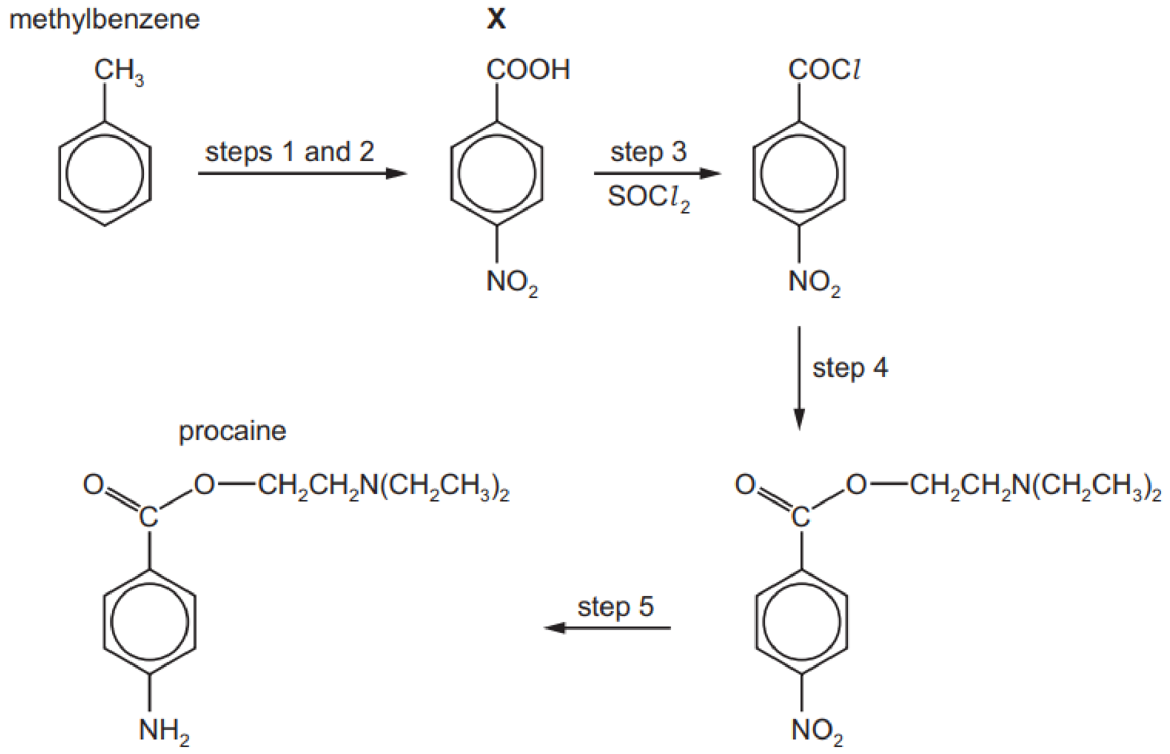


Fig. 7.1

(a) **(i)** Name all the functional groups present in procaine.

.... [1]

(ii) A molecule of procaine has 13 carbon atoms.

State the number of carbon atoms that are sp, sp^2 and sp^3 hybridised in procaine.

sp carbons = ... sp^2 carbons = ... sp^3 carbons = ... [1]

(b) The proton (^1H) NMR spectrum of procaine dissolved in D_2O is recorded.

Predict the number of peaks observed.

.... [1]

(c) State why procaine can act as a base.

....

.... [1]

(d) Compound **X** can be synthesised in two steps from methylbenzene.

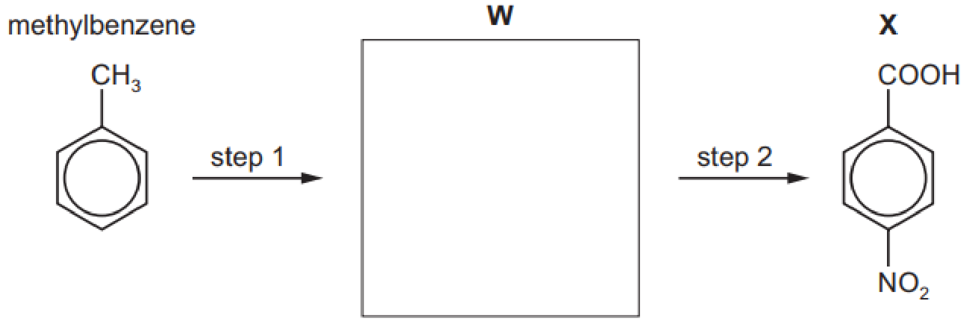


Fig. 7.2

(i) Draw the structure of compound **W** in the box provided. [1]

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

step 1 ....

step 2 ....
[2]

(e) Procaine is synthesised in three steps from **X**.

Suggest the reagents and conditions for step 4 and for step 5 in Fig. 7.1.

step 4 ....

step 5 ....
[3]

105. 9701/42/M/J/22 Q6

(a) The reagent and conditions required for the nitration of benzene, benzoic acid and phenol are shown in Table 6.1.

Table 6.1

compound	reagents and conditions for nitration
benzene	concentrated HNO_3, 50 °C, concentrated H_2SO_4 catalyst
benzoic acid	concentrated HNO_3, 100 °C, concentrated H_2SO_4 catalyst
phenol	dilute $HNO_3(aq)$, 20 °C

Concentrated HNO_3 reacts with concentrated H_2SO_4 to generate the electrophile NO_2^+.

(i) Complete Fig. 6.1 to show the mechanism of the reaction between benzene and NO_2^+. Include all relevant curly arrows and charges.

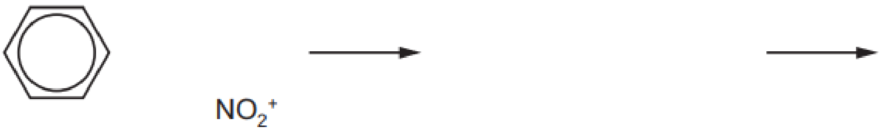


Fig. 6.1

[3]

(ii) Write an equation to show how H_2SO_4 is regenerated.

.... [1]

(b) Draw the major products from the mononitration of benzoic acid and of phenol.

major product from benzoic acid	major product from phenol

[2]

(c) Compare the relative ease of nitration of benzene, benzoic acid and phenol.
Explain your reasoning; include reference to the structures of the three compounds in your answer.

.... > .... > ....
easiest least easy

....

....

....

....

....
[4]

(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.

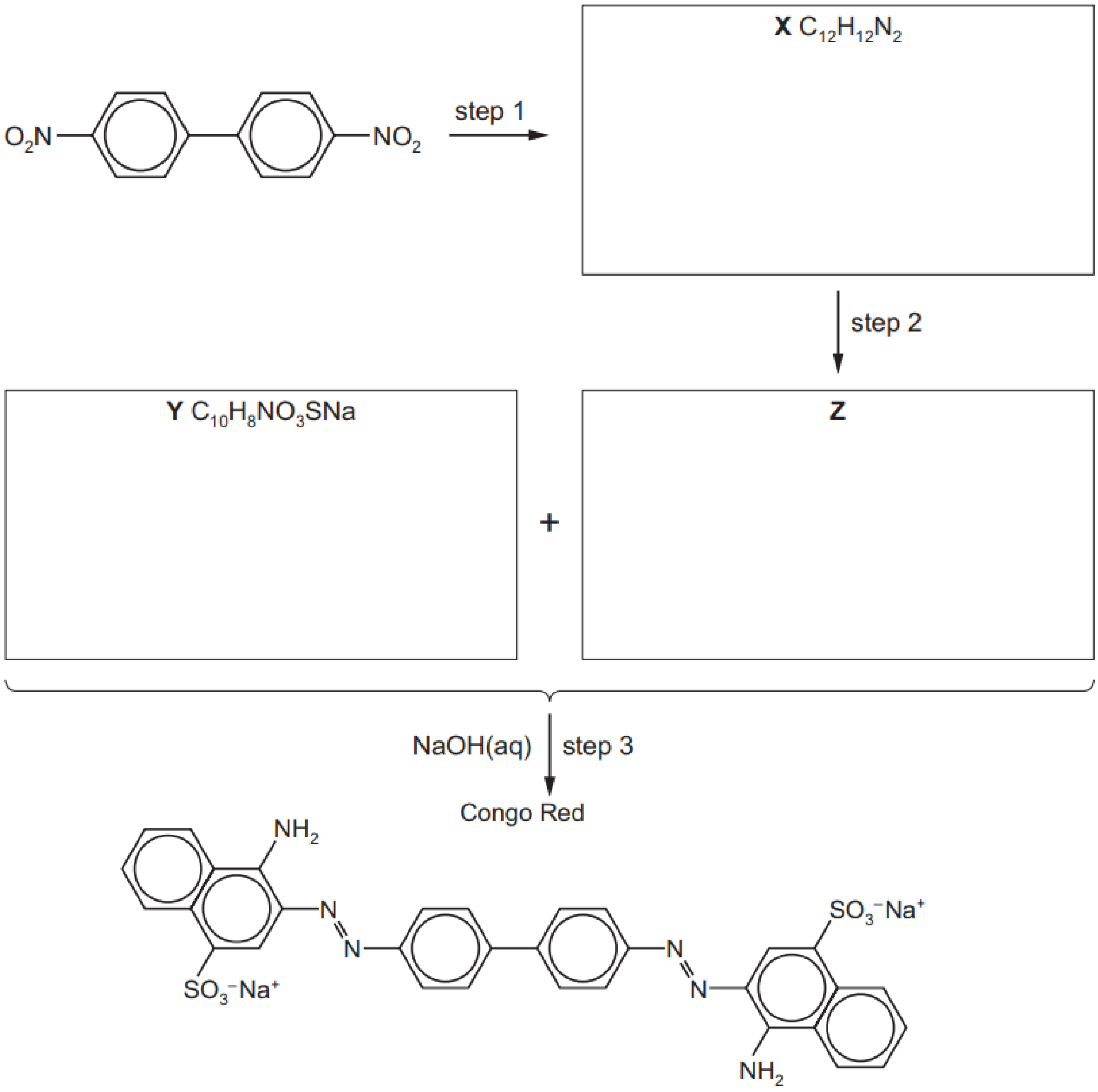


Fig. 6.2

(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]

106. 9701/42/M/J/22 Q7c

(c) Cortisone, $C_{21}H_{28}O_5$, is a naturally occurring chemical that contains chiral carbon atoms.

cortisone

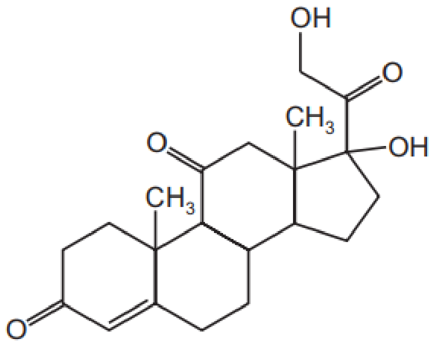


Fig. 7.1

(i) Deduce the number of chiral carbon atoms in one molecule of cortisone.

.... [1]

(ii) Cortisone is reacted with an excess of $NaBH_4$.

State the molecular formula of the organic compound formed.

.... [1]

(iii) Cortisone is an optically active molecule.

Explain what is meant by optically active.

....

....

.... [1]

107. 9701/42/M/J/22 Q8

(a) Compare the relative acidities of ethanol, ethanoic acid, chloroethanoic acid and phenol. Explain your reasoning.

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

....

....

....

....

....

.... [4]

(b) An excess of ethanedioic acid, HOOCCOOH(aq), is reacted with warm acidified $KMnO_4$(aq).

State the type of reaction undergone by ethanedioic acid.
Describe what you would observe.
Write an equation for this reaction.

Your equation can use [O] or [H] as necessary.

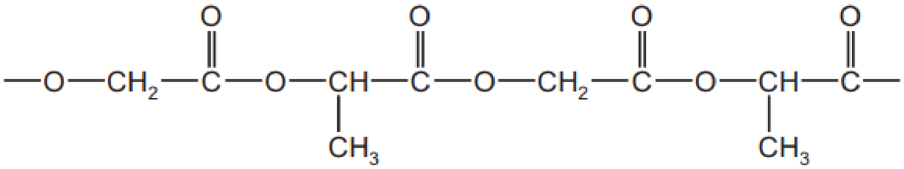
type of reaction ....

observations ....

equation .... [2]

(c) A section of a polyester is shown.

polyester



$$-O-CH_2-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-$$

Fig. 8.1

Draw the structures of the two monomers that form this polyester.

[2]

(d) Serine can polymerise to form two different types of condensation polymer; a polyester and a polypeptide.

serine

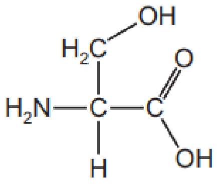


Fig. 8.2

Draw the structure of the polypeptide showing **two** repeat units. The peptide linkage should be shown displayed.

[2]

(e) Explain why condensation polymers normally biodegrade more readily than addition polymers.

....

.... [1]

108. 9701/42/M/J/22 Q9

The structure of cyclohexylamine is shown in Fig. 9.1.

cyclohexylamine

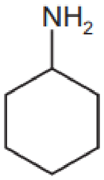


Fig. 9.1

(a) Compare the relative basicities of ammonia, cyclohexylamine and phenylamine. Explain your reasoning.

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

most basic least basic

....

....

....

....

....

[3]

(b) Cyclohexylamine reacts with ethanoyl chloride to form the corresponding amide, **L**.

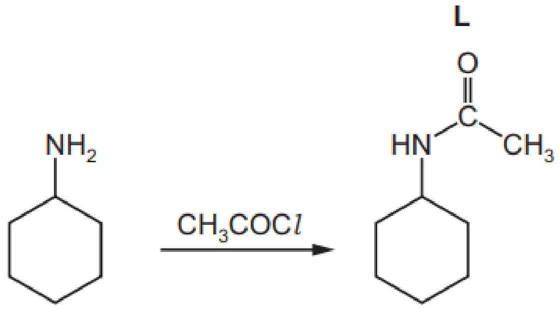


Fig. 9.2

(i) Name the mechanism for the reaction shown in Fig. 9.2.

.... [1]

(ii) Complete the mechanism of the reaction between cyclohexylamine and CH_3COCl.

R–NH_2 is used to represent cyclohexylamine.

Include all relevant lone pairs of electrons, curly arrows, charges and partial charges.

[4]

(iii) The reaction between cyclohexylamine and an excess of CH_3COCl forms compound **M**. Compound **M** has the molecular formula $C_{10}H_{17}NO_2$.

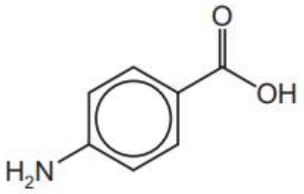
Suggest and draw the structure of **M**.

[1]

109. 9701/42/F/M/22 Q4

Compounds **F** and **J** are shown in Fig. 4.1.

F



J

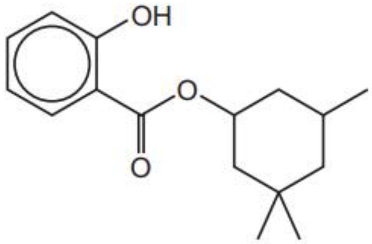


Fig. 4.1

(a) **F** and **J** both contain the arene functional group.

(i) Identify the other functional groups in **F** and **J**.

F: ....

J: .... [2]

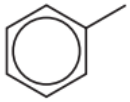
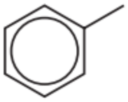
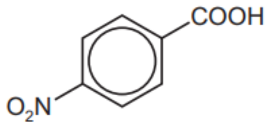
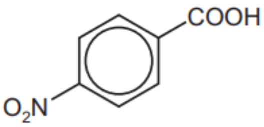
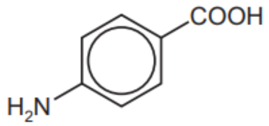
(ii) State the number of chiral centres in a molecule of **F** and in a molecule of **J**.

number of chiral centres in: **F** = ... **J** = ... [1]

(b) A student proposes a multi-step synthesis of **F** from benzene, as shown in Table 4.1.

(i) Complete Table 4.1 by providing relevant details of the reagents and conditions for steps 1 and 4, and the structure of product **D**.

Table 4.1

step	organic reactant	reagent(s) and conditions	organic product
1		....	
2		concentrated HNO_3 and concentrated H_2SO_4	**D**
3	**D**	hot alkaline $KMnO_4$ then dilute H_2SO_4	**E** 
4		....	**F** 

[3]

(ii) In a second multi-step synthesis, the student changes the order in which the reagents and conditions are used.
The reaction scheme is shown in Fig. 4.2.
G is the major product of this synthesis.

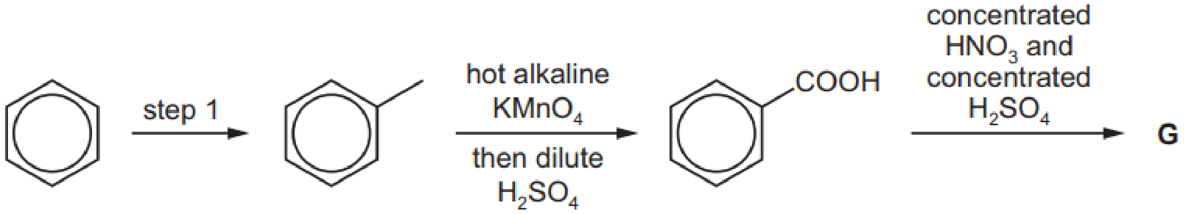


Fig. 4.2

Draw the structure of **G**.
Explain why **G** is the major product of the synthesis rather than **E**.

....

....

.... [2]

(c) **J** reacts under suitable conditions with NaOH(aq).
After acidification of the reaction mixture, compounds **K** and **L** form.

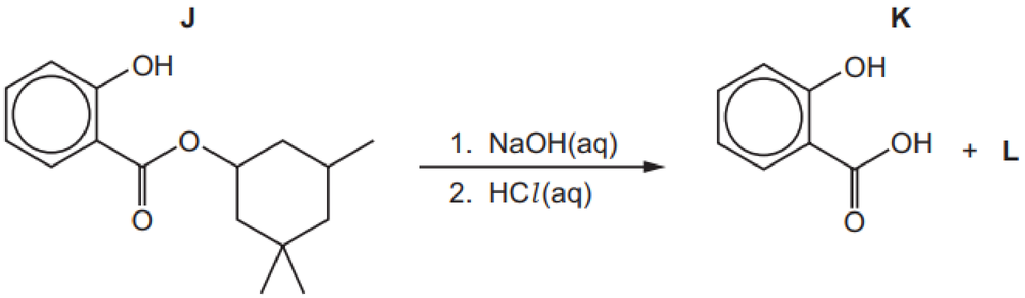


Fig. 4.3

(i) Give the molecular formula of **L**.

.... [1]

(ii) State the **two** types of reaction that occur when **J** reacts with NaOH(aq).

1 ....

2 ....

[2]

(d) **K** can also be synthesised from phenol, C_6H_5OH.

Fig. 4.4 shows several reactions of phenol.

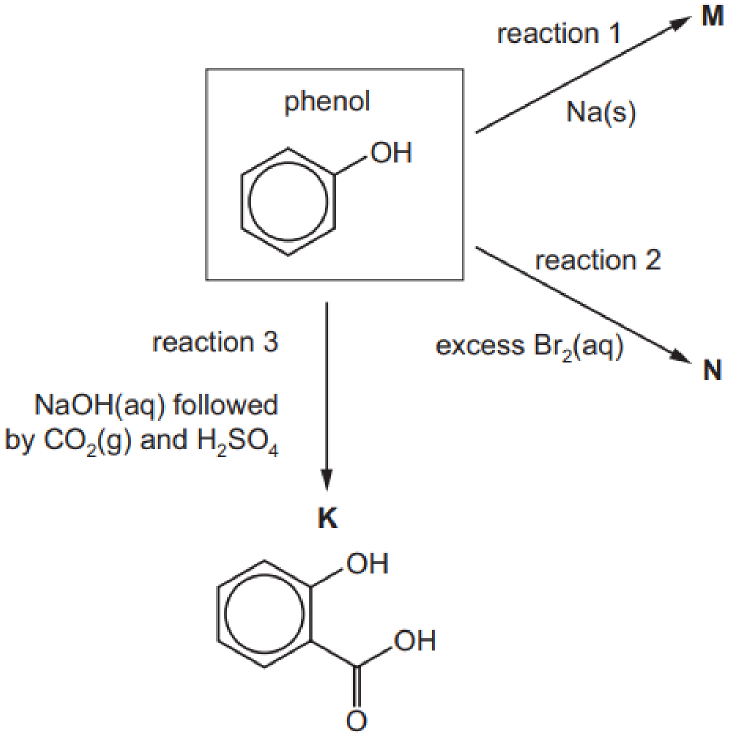


Fig. 4.4

(i) Write an equation for the formation of **M** in reaction 1.

.... [1]

(ii) Draw **N**, the product of reaction 2.

[1]

(iii) Explain why phenol is a weaker acid than **K**.

....

....

....

.... [2]

(e) Phenol and benzene both react with nitric acid, as shown in Fig. 4.5.

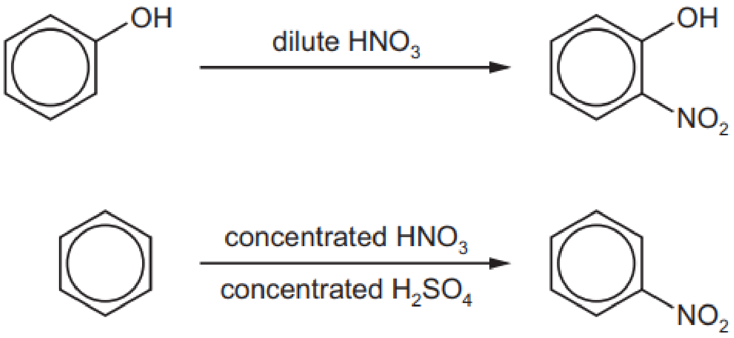


Fig. 4.5

Explain why the reagents and conditions for these two reactions are different.

....

....

....

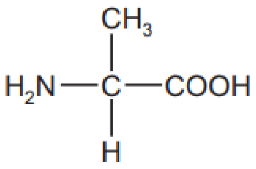
....

.... [3]

110. 9701/42/F/M/22 Q5b

(b) When $CH_3CHClCOOH$ reacts with aqueous NH_3, alanine forms.

alanine



$$H_2N-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-COOH$$

Fig. 5.1

Alanine is an amino acid. Its isoelectric point is 6.1.

(i) State what is meant by isoelectric point.

....

.... [1]

(ii) Give the structural formula of alanine at pH 2.

.... [1]

(iii) Alanine exists as a pair of optical isomers. The structure of one optical isomer is shown in Fig. 5.2.

Draw the three-dimensional structure of the other optical isomer of alanine.

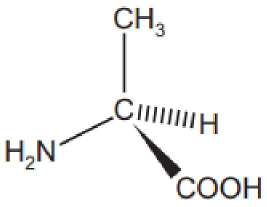
optical isomer 1	optical isomer 2
	

Fig. 5.2

[1]

(iv) Polymer **C** forms from the reaction between alanine and 4-aminobutanoic acid, $H_2N(CH_2)_3COOH$.

Draw a repeat unit of **C**. The functional group formed should be displayed.

[2]

(v) State the type of polymerisation shown in **(b)(iv)**.

.... [1]

(vi) Scientists are investigating **C** as a replacement for poly(propene) in packaging.

Suggest an advantage of using **C** instead of poly(propene).

....

.... [1]

111. 9701/42/F/M/22 Q6

Lidocaine is used as an anaesthetic. A synthesis of lidocaine is shown in Fig. 6.1.

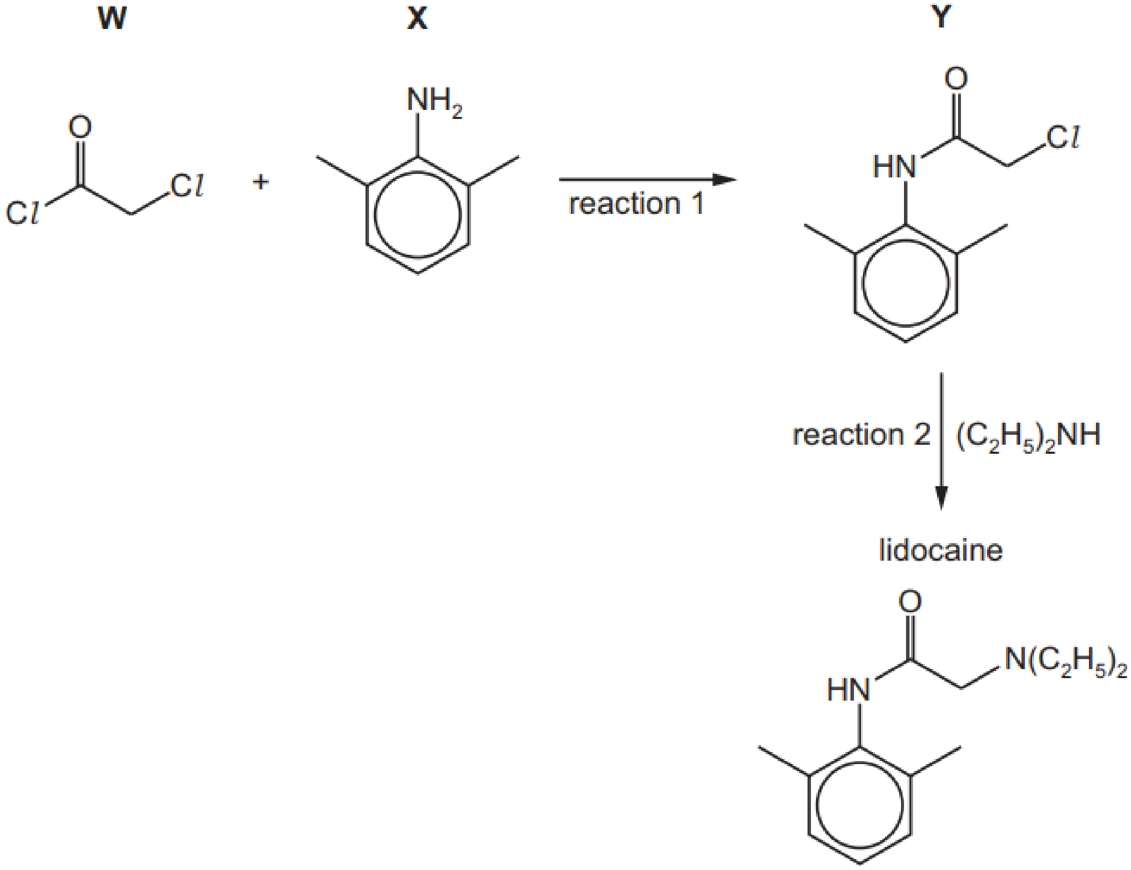


Fig. 6.1

(a) **W** can be formed by reacting $HOCH_2COOH$ with an excess of $SOCl_2$.

Write an equation for this reaction.

.... [1]

(b) After **W** and **X** have reacted together, an excess of $CH_3COONa(aq)$ is added to the reaction mixture.

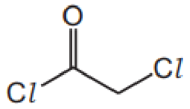
Suggest why.

....

.... [1]

(c) The reaction of **W** with **X**, reaction 1, follows an addition–elimination mechanism.

Complete the mechanism for the reaction of **W** with **X**.
Include all relevant curly arrows, lone pairs of electrons, charges and partial charges.
Use Ar–NH_2 to represent **X**.



Ar—NH_2

[4]

(d) $(C_2H_5)_2NH$ reacts with **Y** in reaction 2.

Explain why $(C_2H_5)_2NH$ can act as a nucleophile.

....

.... [1]