A2 Level Organic Chemistry Topical Work Book



Fahad H. Ahmad Complete Video Course and Notes

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Introduction & Structure of Benzene

7 (a) Benzene can be converted into cyclohexane.



(i)	For this reaction name the type of reaction and identify the reagent and conditions need	ded.
	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]

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

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

Complete the three-dimensional diagrams in the boxes to show the ${\it other}$ two stereoisomers of ${\it P}$.

[2]

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

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 the results.	wo experiments,	stating the	similarities and	differences of
				[2]

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(c) Cortisone, $C_{21}H_{28}O_5$, is a naturally occurring chemical that contains chiral carbon atoms.

cortisone

Fig. 7.1

(1)	Deduce the number of chiral carbon atoms in one molecule of contisone.	
		[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]
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7 Procaine is used as an anaesthetic in medicine. It can be synthesised from methylbenzene in five steps as shown in Fig. 7.1.

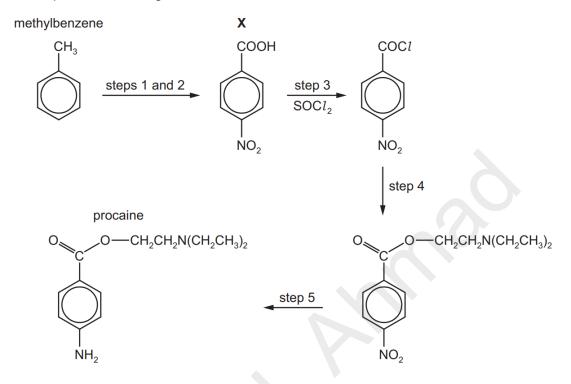


Fig. 7.1

(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, sp² and sp³ hybridised in procaine.

sp carbons = sp^2 carbons = sp^3 carbons = [1]

(d)	The ligand bipyridine consists of two pyridine rings.
	Pyridine, C ₅ H ₅ N, and benzene, C ₆ H ₆ , have similar planar, cyclic structures.
	pyridine
	Fig. 4.2
	By reference to the hybridisation of the carbon atoms and the nitrogen atom, and orbitation overlap, suggest how the σ and π bonds are formed in a pyridine molecule.

4 Compounds F and J are shown in Fig. 4.1.

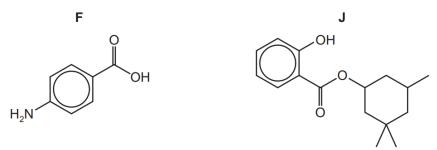


Fig. 4.1

- (a) F and J both contain the arene functional group.
 - (i) Identify the other functional groups in **F** and **J**.

(ii) State the number of chiral centres in a molecule of F and in a molecule of J.

number of chiral centres in: $\mathbf{F} = \dots \mathbf{J} = \dots \mathbf{J}$ [1]

(c) J reacts under suitable conditions with NaOH(aq).

After acidification of the reaction mixture, compounds K and L form.

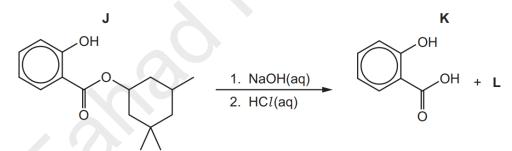


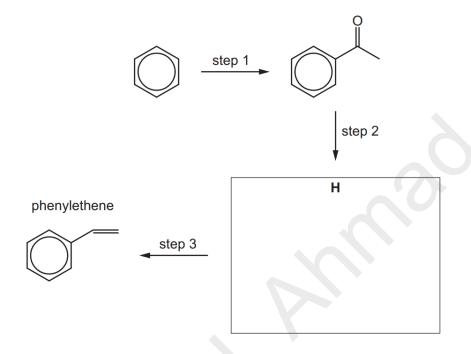
Fig. 4.3

(i) Give the molecular formula of L.

......[1]

Electrophilic Substitution

(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	
- des	
step 3	
	[3]

(b) When benzene reacts with SO₃, benzenesulfonic acid is produced.

benzenesulfonic acid

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 SO₃H⁺ ions. Include all necessary curly arrows and charges.

SO₃H⁺

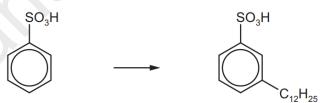
[3]

(ii) Write an equation to show how the H₂SO₄ catalyst is reformed.

_____[1]

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

benzenesulfonic acid 3-dodecylbenzenesulfonic acid



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

reagents and conditions

mechanism

[2]

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5	(a)	Benzene reacts with bromine in the presence of an aluminium bromide catalyst, $AlBr_3$, to form bromobenzene. This is a substitution reaction. No addition reaction takes place.			
		(i)	Explain why no addition reaction takes place.		
				[1]	
		ΑlΕ	gr₃ 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.	ant	
				[3]	
		(iii)	Write an equation to show how the AlBr ₃ catalyst is reformed.		
				[1]	
(l	o) (Sugg	gest why bromination of phenol occurs more readily than bromination of benzene.		
				[O	

(c) (i) There are four different carbocations with the same formula, $C_4H_9^+$. One structure is given in the table.

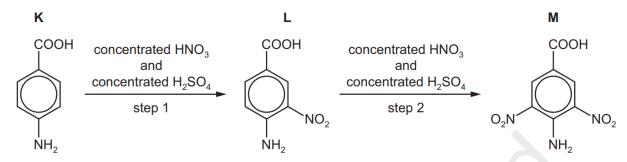
Suggest the structural formulae of the three other carbocations.

structure 1	structure 2	structure 3	structure 4
CH ₃ CH ₂ CH ₂ CH ₂ ⁺			

[3]

(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, NO₂⁺, are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

(i) Construct an equation for the formation of NO₂⁺ 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.

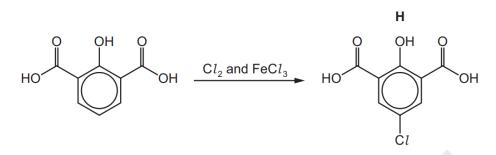


(iii) State the name of the mechanism in (c)(ii).

______[1]

[2]

(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]

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8		enylamine, $C_6H_5NH_2$, and ethylamine, $C_2H_5NH_2$, can be distinguished by adding aqueous mine.
	(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).
'01/	40.10	[1]

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

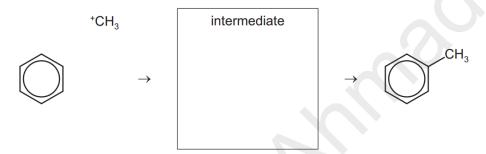
In the first stage of this synthesis, benzene reacts with chloromethane in the presence of an $AlCl_3$ catalyst to form methylbenzene.

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 ⁺CH₃. 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]

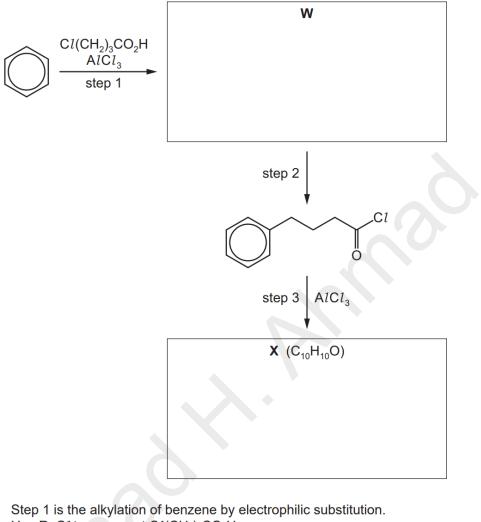
(ii) Suggest the structure of compound Q.

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

[1]

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



(1)	Use R–C l to represent $Cl(CH_2)_3CO_2H$.	
	Write an equation for the formation of an electrophile from R–C l and A l C l_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.	

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

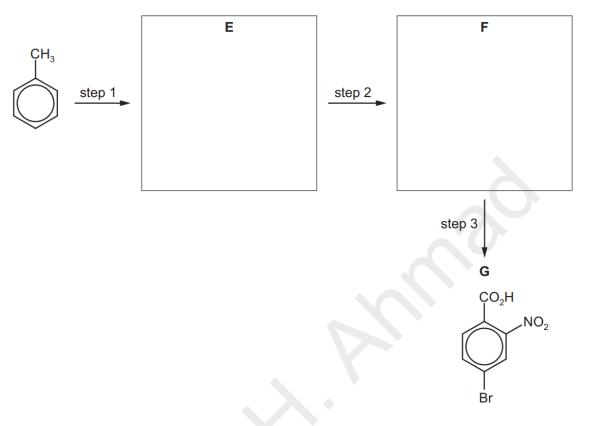
Include all relevant charges and curly arrows showing the movement of electron pairs.

[3]

Draw the structure of the intermediate.

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



(i) Give the systematic name of compound G.

 [1	ij

- (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]

9701/42/M/J/21

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

methylbenzene

M

step 2

step 3

3-aminobenzoic acid

CO₂H

NH₂

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

1,3-dimethylbenzene L
$$\frac{1}{Step 1}$$
 $C_8H_6O_4$ $\frac{step 2}{Cl}$ C_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 ${\rm COC}\,l_2$ as shown.

reaction 1
$$COCl_2 + AlCl_3 \rightarrow AlCl_4 + Cl - C=O$$

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

Reaction 2 is the electrophilic substitution of Cl - C = O for H^+ in benzene.

Suggest a mechanism for reaction 2.

[3]

9 Tyrosine and lysine, shown in Fig. 9.1, are naturally occurring amino acids found in proteins.

Fig. 9.1

(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 -CH₂CHNH₂COOH substituent.

Table 9.1

reagent	structure
an excess of Br₂(aq)	
an excess of NaOH(aq)	
an excess of HNO ₃ (aq)	

[3]

9701/42/O/N/22

(b)	Met	thylbenzene, C ₆ H ₅ CH ₃ , can be made from benzene by an electrophilic substitution reaction	on.
	(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 ${\rm CH_3}^+$ electroph Include all relevant curly arrows and charges.	ile.
		$\bigcirc \hspace{1cm} \rightarrow \hspace{1cm} \rightarrow$	
		CH ₃ ⁺	
			[3]

(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 CH₃C₆H₄NO₂ and HOOCC₆H₄NO₂ respectively.

Draw the structures of these two products.

[1]

9701/42/O/N/22

- **8** Benzene, C₆H₆, 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 *CH₂CH₃ electrophile.

Write an equation for the reaction that generates this electrophile.

......[1]

(ii) Describe the mechanism for the reaction between benzene and the ⁺CH₂CH₃ electrophile. Include all relevant curly arrows and charges.

 $\begin{array}{c|c} & & \text{intermediate} \\ \hline \\ H & H & \rightarrow \\ +C -C -H \\ H & H \end{array} \rightarrow$

products

[3]

9701/41/O/N/22

(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.

(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
HNO₂(aq) at 4°C	
an excess of Br₂(aq) at room temperature	

[2]

9701/41/O/N/22

6 (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 ₂ SO ₄ catalyst
benzoic acid	concentrated HNO ₃ , 100 °C, concentrated H ₂ SO ₄ catalyst
phenol	dilute HNO ₃ (aq), 20 °C

Concentrated HNO₃ reacts with concentrated H₂SO₄ to generate the electrophile NO₂⁺.

(i) Complete Fig. 6.1 to show the mechanism of the reaction between benzene and NO₂⁺. Include all relevant curly arrows and charges.



Fig. 6.1

[3]

(ii) Write an equation to show how H₂SO₄ is regenerated.

|--|

(b) Draw the major products from the mononitration of benzoic acid and of phenol.

major product from benzoic acid	major product from phenol

[2]

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9701/42/M/J/22

(d) Compound X can be synthesised in two steps from methylbenzene.

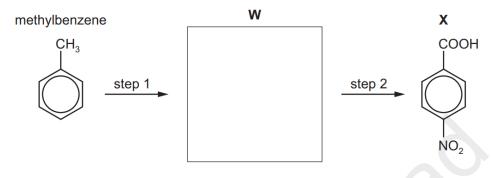


Fig. 7.2

- (i) Draw the structure of compound **W** in the box provided. [1]
- (ii) State the reagents and conditions for step 1 and step 2.

(e) Pyridine reacts with Cl_2 in the presence of $AlCl_3$ as shown in Fig. 4.3.

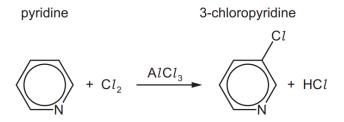
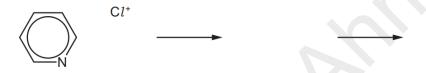


Fig. 4.3

The mechanism of this reaction is similar to that of the chlorination of benzene. A lCl_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]

(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.

- (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 ₂ SO ₄	D
3	D	hot alkaline KMnO ₄ then dilute H ₂ SO ₄	E COOH
4	O ₂ N COOH		F COOH

[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]

(d) K can also be synthesised from phenol, C₆H₅OH.

Fig. 4.4 shows several reactions of phenol.

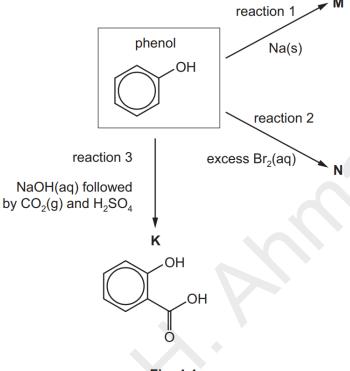


Fig. 4.4

(i) Write an equation for the formation of **M** in reaction 1.

.....[1]

(ii) Draw N, the product of reaction 2.

[1]

Hydrolysis

(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

$$H_2N - (CH_2)_5 - C$$

(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 (\checkmark) 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]

9701/41/M/J/19

9 (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 ₃ CH ₂ C1	CH₃COC <i>l</i>	C ₆ H ₅ Cl	
	·			
(,'0'				
				[31

8 (a)	State and explain the relative rate of hyaryl chlorides.	drolysis of acyl chlorides, alkyl chlorides and	
	fastest	slowest	
9701/42/M	1/.1/21		
(c) C		ifferent reactivities in nucleophilic substitution	
	(i) Identify a suitable reagent to illustrate this difference in reactivity.		
		ibly different results with chlorobenzene and	
(ii		s that occur.	
		[1]	
(iii	Explain the difference in the reactivities of substitution reactions.	of chlorobenzene and chloroethane in nucleophilic	
		[1]	

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(b) Cyclohexylamine reacts with ethanoyl chloride to form the corresponding amide, L.

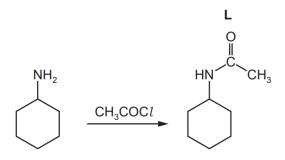


Fig. 9.2

(i) Name the mechanism for the reaction shown in Fig. 9.2.

.....[1]

(ii) Complete the mechanism of the reaction between cyclohexylamine and CH₃COC*l*.

R-NH₂ is used to represent cyclohexylamine.

Include all relevant lone pairs of electrons, curly arrows, charges and partial charges.



 $R-NH_2$

[4]

(iii) The reaction between cyclohexylamine and an excess of CH_3COC_l forms compound **M**. Compound **M** has the molecular formula $C_{10}H_{17}NO_2$.

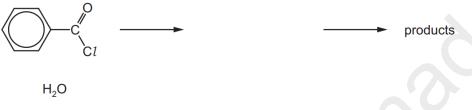
Suggest and draw the structure of M.

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- (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]

(c)	The reaction of ${\bf W}$ with ${\bf X}$, reaction 1, follows an addition–elimination mechanism.	
	Complete the mechanism for the reaction of $\bf W$ with $\bf X$. Include all relevant curly arrows, lone pairs of electrons, charges and partial charges. Use $Ar-NH_2$ to represent $\bf X$.	
	c_l	
	Ar—NH ₂	
		[4]
(d)	$(C_2H_5)_2$ NH reacts with Y in reaction 2.	
	Explain why $(C_2H_5)_2NH$ can act as a nucleophile.	
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Acids and Bases

(b) Epibatidine is a naturally occurring organochlorine compound.

epibatidine

(i) Epibatidine is a weak base.

State what is meant by the term weak base.

[4]	

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]

6	(a)	and propanoic acid. Explain your answer.		acidities of 2-chloropropanoic acid, 3-chloropropanoic acid, answer.
			most acidic	least acidic
		exp	olanation	
		••••		[3]
970	1/41/	M/J	/20	
4	(a)	The	e molecular formulae of three	nitrogen-containing compounds are given.
		S	C ₆ H ₅ CONH ₂	
		Т	$C_6H_5NH_2$	
		U	$C_6H_5CH_2NH_2$	
		Des	scribe and explain the relative	basicities of S , T and U .
			most basic	least basic
			*	
				[3]

5 Gallic acid, C₇H₆O₅, is a naturally occurring aromatic molecule.

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

State and explain the relative acid strength of t	hese two functional groups.
	[2]

9701/42/F/M/20

- **9** Compound **T** is made by a three-stage synthesis.
 - (a) In stage 1, phenylethanoic acid reacts with a suitable reagent to form compound R.

Suggest a suitable reagent for stage 1.

......[1]

9701/43/O/N/21

7 The	e structure of phenylethanoic acid	d is shown.
		OH
(b) Phenylethanoic acid, ethanol and	d phenol can all behave as acids.
	Compare and explain the relative	e acidities of these three compounds.
	most acidic	least acidic
		[4]
9701/43	/O/N/21	
5 (a)	Describe and explain the relative	e basicities of phenylamine, ethylamine and 4-nitrophenylamine
	most basic	least basic
		[4
9701/42	/M/J/21	

most acidic				least acidio
1/M/J/21 The reaction scher	ne shows several reacti	ons of proline.		
	ne shows several reacti proline	ons of proline.		
		N		
		reaction 1 NaOH(aq)	Q	
	proline	reaction 1 NaOH(aq)	Q	
	proline OH H reaction 2	reaction 1	Q	
	proline O N OH	reaction 1 NaOH(aq)	Q	

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

 $C_4H_7NHCO_2H +$ [1]

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

1,3-dimethylbenzene L M $\underbrace{\text{step 1}}_{C_8H_6O_4} \underbrace{\text{step 2}}_{C_l}$

(i) Draw the structure of L.

[1]

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

step 1step 2

[2]

(iii) Write an equation for step 2.

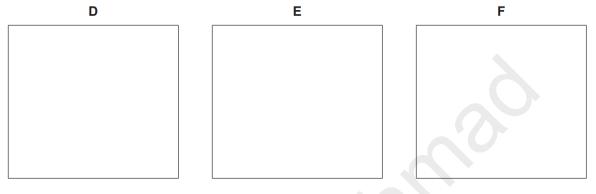
.....[1]

(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.



[3]

9701/42/O/N/22

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

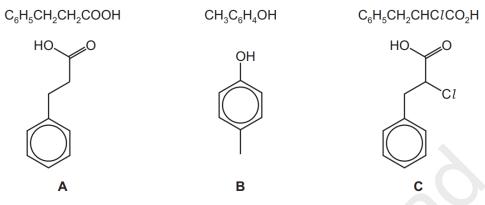


Fig. 7.1

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

most acidic	least acidic
Explain your answer.	
	[3]

9701/42/O/N/22

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

Fig. 7.1

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

[3]

9701/41/O/N/22

(a)	Compare the relative acidities of ethanol, ethanoic acid, chloroethanoic a Explain your reasoning.	cid and phenol.
	most acidic	least acidic
9701/	42/M/J/22	[4]
(0	Compare the relative ease of nitration of benzene, benzoic acid and plexplain your reasoning; include reference to the structures of the thranswer.	
	easiest >>	least easy
		[4]
		[4]

9701/42/M/J/22

7 Procaine is used as an anaesthetic in medicine. It can be synthesised from methylbenzene in five steps as shown in Fig. 7.1.

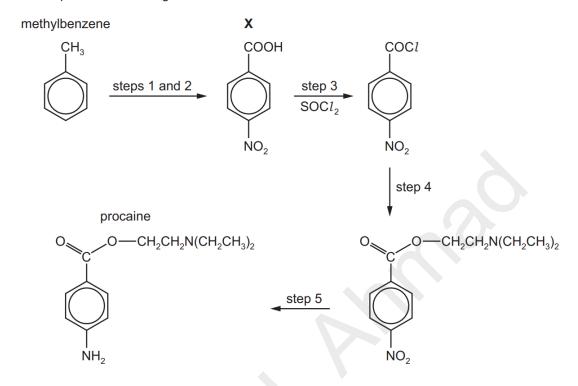


Fig. 7.1

(c) State why	procaine can act as a base.	
		[1]
***************************************		[1]

(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 (\checkmark) in the relevant box if a reaction occurs. Place a cross (x) in the box if no reaction occurs.

Table 5.1

	benzoic acid	phenylmethanol	phenol
Na(s)			
NaOH(aq)			
Na ₂ CO ₃ (aq)			

[3]

(c)	/i)	Bonzovi oblo	pride, C_6H_5COCl , can be synthesised by the reaction of benzoic acid v	with		
(0)	(i)	either PCl_5		WILII		
		Complete the	e equations for these reactions.			
		reaction 1	$C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl + \dots + \dots$			
		reaction 2	$C_6H_5COOH + SOCl_2 \rightarrow C_6H_5COCl + \dots + \dots + \dots$	 [1]		
	(ii)	from reaction	swer to (c)(i) to suggest why it is easier to isolate, in a pure form, the C_6H_5CC in 2 compared to reaction 1.	ЭC		
				[1]		
9701/4	11/M	/J/22				
(c)	A stu	udent studies hanism.	the reaction of CH ₃ CHC <i>l</i> COOH with aqueous NH ₃ to determine the reacti	ion		
	The student finds that when CH_3CHC_1COOH and NH_3 are added in a 1:1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.					
		reaction 1	$\text{CH}_3\text{CHC}l\text{COOH} + \text{NH}_3 \rightarrow \text{CH}_3\text{CHC}l\text{COO}^- + \text{NH}_4^+$			
	(i)	Identify the co	onjugate acid–base pairs in reaction 1.			
		conjugate aci	d–base pair I and			
		conjugate aci	d–base pair II and			
				[1]		
9701/4	12/F/	M/22				

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5	2-C	hlor	opropanoic acid, CH_3CHC_1COOH , is used in many chemical syntheses.
	(a)	(i)	An equilibrium is set up when CH ₃ CHC1COOH is added to water.
			Write the equation for this equilibrium.
			[1]
		(ii)	$0.150\mathrm{mol}$ of $\mathrm{CH_3CHC}\mathit{l}\mathrm{COOH}$ dissolves in $250\mathrm{cm^3}$ of distilled water to produce a solution of pH 1.51.
			Calculate the p K_a of CH $_3$ CHC $_1$ COOH.
			$pK_a =$ [2]
		(iii)	An equal concentration of aqueous propanoic acid has pH 2.55.
			Explain the difference in the pH of solutions of equal concentration of ${\rm CH_3CHC}{\it l}{\rm COOH}$ and propanoic acid.
			[2]
9701	1/42/	F/M	/22

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Fig. 4.4

(iii)	Explain why phenol is a weaker acid than K .						
	[2]						
9701/42/F/M	1/22						

(c) J reacts under suitable conditions with NaOH(aq).

After acidification of the reaction mixture, compounds K and L form.

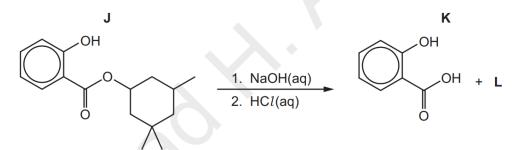


Fig. 4.3

(i) Give the molecular formula of L.

į,		
	41	
· · · · · · · · · · · · · · · · · · ·	ш	

(ii) State the **two** types of reaction that occur when **J** reacts with NaOH(aq).

1		
2		
	[2]	

Redox Reactions

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

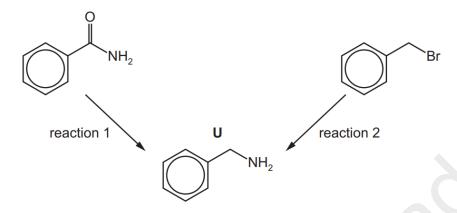
√ = observed change

x = no observed reaction

test	reagent(s) and conditions	HCO₂H	CH ₃ COCO ₂ H	HO ₂ CCO ₂ H	observed change
1		✓	x	x	6
2		x	√	X	
3		√	X	✓	

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]

(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]

[2]

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

valine

O H CH₃ H

C C C C C H

reaction 1

$$HO$$
 HO
 HO

- (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]

9701/42/F/M/20

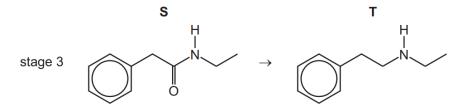
Compound **M** is converted into compound **P** as shown.

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

......[2]

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



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

......[1]

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

______[1]

9701/43/O/N/21

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

methylbenzene

M

Step 2

Step 3

3-aminobenzoic acid

CO₂H

NH₂

(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

(b) Three carboxylic acids, methanoic acid, HCO₂H, ethanedioic acid, HO₂CCO₂H, and butanedioic acid, HO₂CCH₂CH₂CO₂H, are compared. Two tests were carried out on separate samples of each organic acid, as shown.

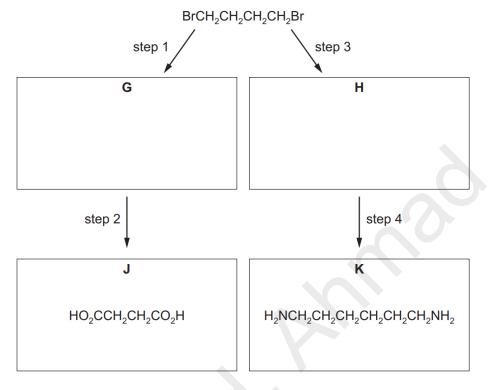
The following results were obtained. \checkmark = observed change x = no observed reaction

test	reagents and conditions	HCO₂H	HO ₂ CCO ₂ H	HO ₂ CCH ₂ CH ₂ CO ₂ H	observed change
1		✓	X	x	
2		1	1	х	30

(i)	Complete th	ne table	with the	e reagents	and	conditions	and	the	observed	change	for	ć
	positive test											

Assume these organic acids all have a similar acid strength. [3]

(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]
,	Bratt the directarde of G and H in the boxes.	19

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

step 1	
step 2	
siep 2	•••••
step 3	
step 4	
	[4]
	ניין

(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

$$HO_2C$$
 CO_2H CO_2H

reagent	structure of organic product	type of reaction
an excess of LiAℓH₄		
an excess of CH ₃ COC <i>l</i>		

[3]

[2]

9701/41/M/J/21

(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

9701/42/O/N/22

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

(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 $\bf Q$ is treated with an **excess** of LiA lH_4 in dry ether.

[3]

(c) ${\bf P}$ can be used to make compound ${\bf R}$ 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]

9701/41/O/N/22

(b)	An excess of ethanedioic acid, HOOCCOOH(aq), is reacted with warm acid	fied KMnO ₄ (a	q).
	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		
	oquation		[2]

9701/42/M/J/22

(d) Compound X can be synthesised in two steps from methylbenzene.

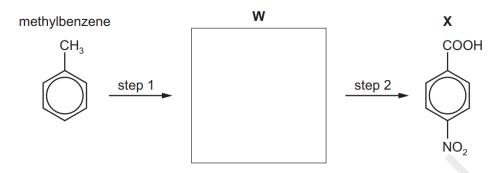


Fig. 7.2

- Draw the structure of compound **W** in the box provided.
- (ii) State the reagents and conditions for step 1 and step 2.

step 1 step 2 [2]

[1]

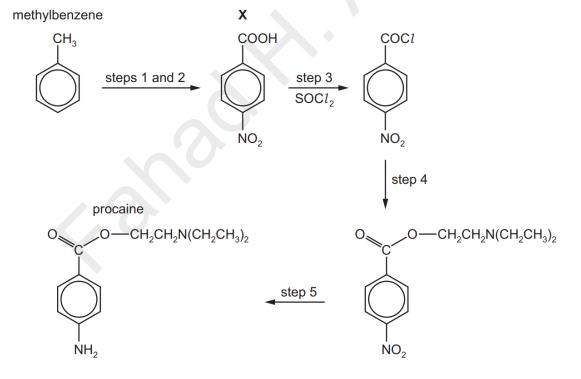


Fig. 7.1

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(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	
		ĮO.

- (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 ₂ SO ₄	D
3	D	hot alkaline KMnO ₄ then dilute H ₂ SO ₄	E COOH
4	O ₂ N COOH		F COOH

(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]

Nitrogen Compounds and Esters

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

(b) Valine and glycine, H₂NCH₂COOH, form the tripeptide Gly–Val–Gly.

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

[2]

r_1

P reacts with an excess of sodium nitrite, NaNO₂, and dilute HCl at 5 °C to form compound **Q**, C₉H₇N₆O₂C l_3 .

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

Q $C_9H_7N_6O_2Cl_3$

gallic acid
HO
HO
OH

step 6

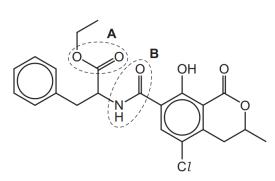
[2]

- (v) Suggest the structure of compound **Q** in the box provided.
- (vi) State the reagents and conditions for step 6.

.....[1]

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

F



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

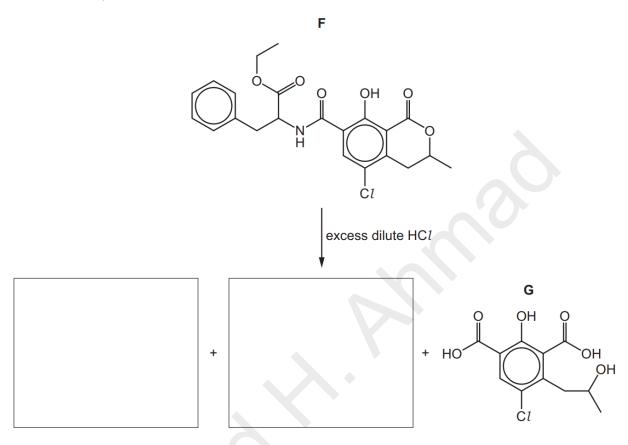
Α	
В	
	[2]

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

т.	47
- 11	11

(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]

10	Valine (Val) and lysine (Lys) ar the <i>Data Booklet</i> .	re amino acids. The structures of t	hese amino acids can be found in
	The isoelectric point of an am point of valine is 6.0. The isoel	nino acid is the pH at which it exis lectric point of lysine is 9.7.	ts as a zwitterion. The isoelectric
	(a) Draw the structure of valir	ne at pH 6.0.	
			[1]
		duced with pH 9.7. Dilute sulfuric a lfuric acid reacts with lysine to proc concentrations at pH 9.7.	
		ee of the organic ions that form du nic ion present at pH 1.0 in box C.	ring the addition of sulfuric acid in
	A	В	C (pH 1.0)
			[3]
(с) Draw the structure of the dip	peptide Val-Lys. The peptide bor	nd should be shown fully displayed.
			[2]

9701/43/O/N/21

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

stage 2
$$Cl$$
 + $C_2H_5NH_2 \rightarrow O$

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

.....[1]

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

.....[1]

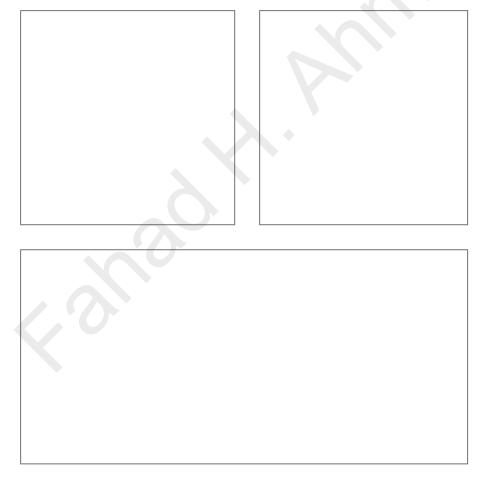
9701/43/O/N/21

(b) The drug remifentanil is shown.

remifentanil

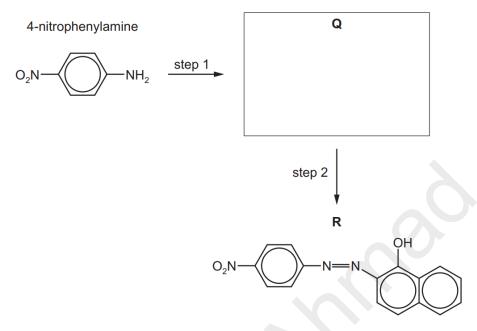
Remifentanil is **completely** hydrolysed under acidic conditions. Three different organic compounds are formed.

Draw the structures for these organic compounds in the boxes.



[3]

(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).

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tartaric acid

$$OH$$
 CO_2H
 OH

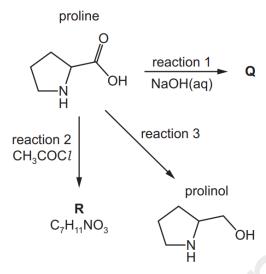
(ii) Tartaric acid reacts with the amine 1-phenylethylamine, $C_6H_5CH(NH_2)CH_3$, to form an ionic salt.

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

[1]

9701/41/M/J/21

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



(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.

dimethylamine

$$H_3C$$
 $NH + RCOC1$
 H_3C
 H_3C
 H_3C

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

(iii) Suggest the reagent required for reaction 3.

[1]

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(c)	Proline was first synthesised in the laboratory using a multi-stage synthetic route.
	In stage 1 CH (CO C H) and CH =CHCN react to form a single product II

stage 1 $CH_2(CO_2C_2H_5)_2 + CH_2$ =CHCN \longrightarrow H—C— $CO_2C_2H_5$ | CH_2CH_2CN

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

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

.....[1]

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

(iii) Suggest a suitable reagent V.

.....[1]

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

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

- (iv) Suggest the type of reaction that occurs in stage 3.
 -[1]
- (v) Deduce the identity of Y.
 -[1]

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

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

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

Draw the structure of any organic intermediate ion.

$$\begin{array}{c} \mathbf{Z} & \text{proline} \\ \hline \\ \mathbf{CO_2H} & \\ \hline \\ \mathbf{NH_2} & \\ \end{array}$$

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

[1]

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

identity the number	of affiling acid utilits in the structure's	HOWH.

(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]

9701/42/F/M/21

7 Proline (Pro) is a naturally occurring amino acid.

proline O N H

- (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.

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

[1]

[2]

9 Tyrosine and lysine, shown in Fig. 9.1, are naturally occurring amino acids found in proteins.

Fig. 9.1

/- \	T1		4		- 6 1			0 47
(a)	ıne	isoele	ectric	point	OT I	vsine	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

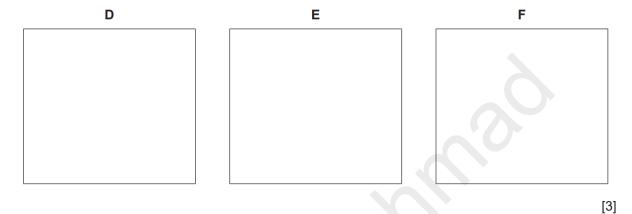
[2]

(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.



9701/42/O/N/22

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

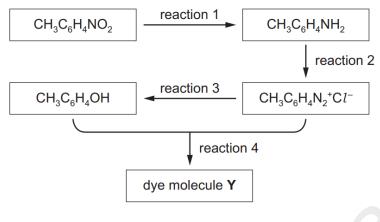


	Fig. 7.2
(i)	Describe the reagents and conditions to produce $CH_3C_6H_4N_2^+Cl^-$ from $CH_3C_6H_4NH_2$ in reaction 2.
	reagents
	conditions
	[1]
(ii)	Describe how $CH_3C_6H_4OH$ can be produced from $CH_3C_6H_4N_2^+Cl^-$ in reaction 3.
	[1]
(iii)	Draw the structure of the dye molecule Y formed when $CH_3C_6H_4N_2^+Cl^-$ and $CH_3C_6H_4OH$ react together in reaction 4. Describe the conditions for this reaction.
	structure

conditions	
	[2]

9701/42/O/N/22

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

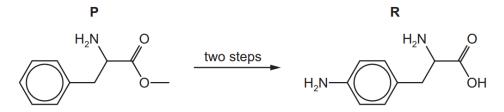


Fig. 7.2

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

(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
HNO₂(aq) at 4°C	
an excess of Br₂(aq) at room temperature	

[2]

9701/41/O/N/22

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

Fig. 7.1

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

Q HN

(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]

9701/41/O/N/22

9 The structure of cyclohexylamine is shown in Fig. 9.1.

cyclohexylamine



Fig. 9.1

(a)	Compare the relative basicities of ammonia Explain your reasoning.	nenylamine.
	most basic	least basic

9701/42/M/J/22

(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.

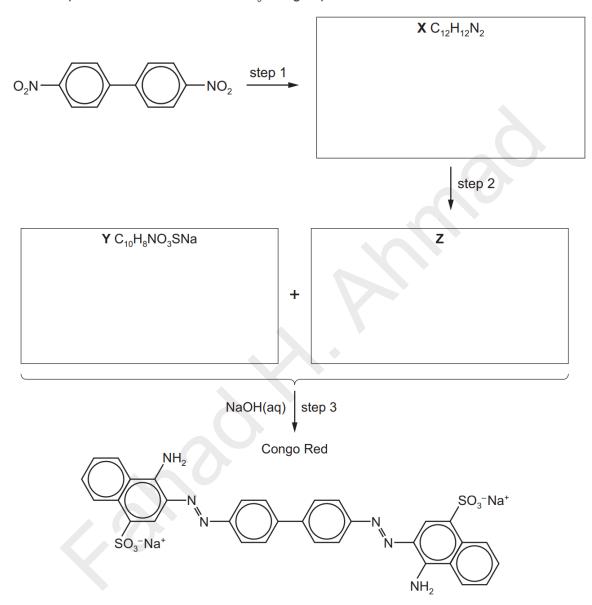


Fig. 6.2

(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]

9701/42/M/J/22

Fig. 6.1

- (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]

(e) The isoelectric point of lysine, lys, is at pH 9.8.

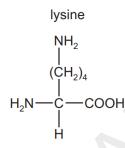


Fig. 6.2

A mixture of the dipeptide lys-asn and its two constituent amino acids, asparagine and lysine, is analysed by electrophoresis using a buffer at pH 5.0. The results obtained are shown in Fig. 6.3.

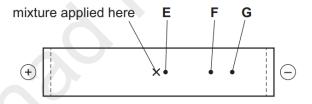


Fig. 6.3

Suggest identities for the species responsible for spots **E**, **F** and **G**. Explain your answers.

spot	identity
E	
F	
G	

	 		ΓO
			3

9701/41/M/J/22

6 Lidocaine is used as an anaesthetic. A synthesis of lidocaine is shown in Fig. 6.1.

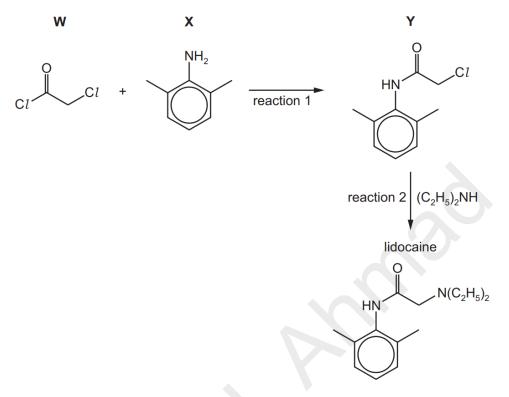


Fig. 6.1

(a)	W can be formed by reacting HOCH $_2$ COOH with an excess of SOC l_2 .
	Write an equation for this reaction.
	[1]
(b)	After ${\bf W}$ and ${\bf X}$ have reacted together, an excess of ${\rm CH_3COONa(aq)}$ is added to the reaction mixture.
	Suggest why.
	[1]

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(b) When CH₃CHC*l*COOH reacts with aqueous NH₃, alanine forms.

alanine

Fig. 5.1

Alanine is an amino acid. Its isoelectric point is 6.1.

(٥	State	what i	s	meant	bv	isoe	lectric	point.
٦	•	01010	***	_	11100111	\sim			P 0 11 1 t.

[41	

(ii) Give the structural formula of alanine at pH 2.

(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.

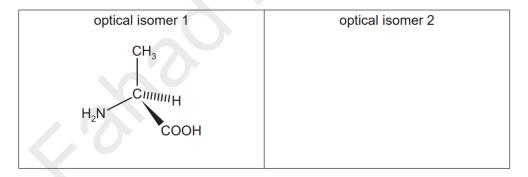


Fig. 5.2

[1]

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Polymers

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

$$HO_2C$$
 CO_2H H_2N OH OH

(i) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **F** and **G**.

	number of peaks
F	
G	

[2]

(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** (\checkmark) 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, CH₃CH=CH₂, with phenylethene, C₆H₅CH=CH₂, 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]

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(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

$$H_2N$$
— $(CH_2)_5$ — C

(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 (\checkmark) 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			

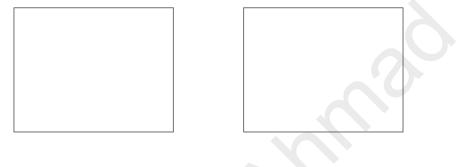
[1]

(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.

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- **(b)** A mixture of serine, HOCH₂CH(NH₂)CO₂H, and lysine, H₂N(CH₂)₄CH(NH₂)CO₂H, 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.



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

glutathione

$$HO$$
 NH_2
 HO
 NH_2
 HO
 NH_2
 HO
 NH_2
 HO
 NH_2
 HO
 NH_2
 HO

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



[2]

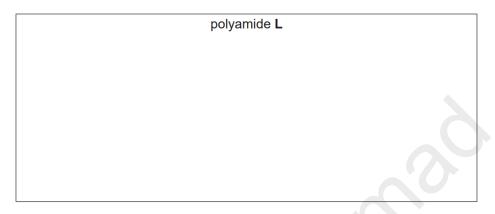
(iii) Glutathione is soluble in water.

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

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(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.



[2]

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6 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]

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(ii)	Draw the repeat unit of the polyester formed when fumaric acid reacts with ethane-1,2 $(CH_2OH)_2$.	-diol,
	The ester bond should be shown fully displayed.	
		[2]
(iii)	Explain why polyesters normally biodegrade more readily than polyalkenes.	[-]
		[1]
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(d) P can be used to produce compound 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]

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(c) A section of a polyester is shown.

Fig. 8.1

Draw the structures of the two monomers that form this polyester.



(d) Serine can polymerise to form two different types of condensation polymer; a polyester and a polypeptide.

serine
OH
H₂C
O
H₂N
C
O
O
O

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]
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(e) Acyl chlorides react with sodium carboxylates to form acid anhydrides as shown in Fig. 5.1.

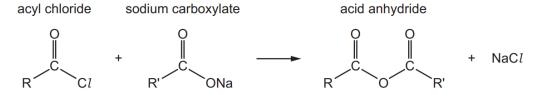


Fig. 5.1

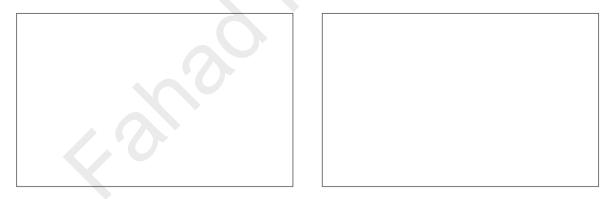
The condensation polymers, polyanhydride and polyester, are formed by similar methods.

The repeat unit for a polyanhydride is shown in Fig. 5.2.

polyanhydride

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.



[2]

(ii) Polyanhydrides are biodegradable polymers.

Suggest how this polyanhydride can be degraded.

......[1

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(b) When CH₃CHC*l*COOH reacts with aqueous NH₃, alanine forms.

 $\begin{array}{c} \text{alanine} \\ \text{CH}_3 \\ \\ \\ \text{H}_2 \text{N} \longrightarrow \text{C} \longrightarrow \text{COOH} \\ \\ \\ \\ \text{H} \end{array}$

Fig. 5.1

(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]

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