Surname	StemUp Model Solution	Centre Number	Candidate Number
Other Names			2

GCE A LEVEL

1410U40-1

S18-1410U40-1

CHEMISTRY – A2 unit 4
Organic Chemistry and Analysis

TUESDAY, 12 JUNE 2018 – AFTERNOON

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 5.**	**10**	
Section B	**6.**	**14**	
	7.	**14**	
	8.	**14**	
	9.	**14**	
	10.	**14**	
	Total	**80**	

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01

ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:
- calculator;
- **Data Booklet** supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen. Do not use gel pen or correction fluid.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **all** questions in the spaces provided.

Candidates are advised to allocate their time appropriately between **Section A (10 marks)** and **Section B (70 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q.9***(a)*.

If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

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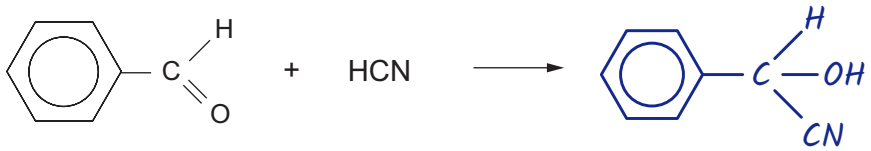
SECTION A

Answer **all** *questions in the spaces provided.*

1. *(a)* Complete the equation below, which shows the reaction of benzaldehyde with hydrogen cyanide. [1]



(b) Give the **formula** of the nucleophile that takes part in the reaction shown in part *(a)*. [1]

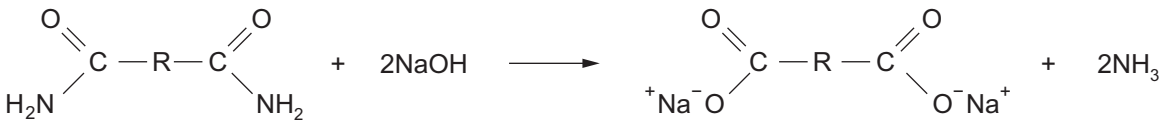
^{-}CN (cyanide ion)

2. Decarboxylation occurs when a carboxylic acid is heated with sodalime.

State the name of the carboxylic acid that will produce propane when strongly heated with sodalime. [1]

butanoic acid

3. Ammonia is produced when an amide is heated with aqueous sodium hydroxide.



amide **T**

In an experiment 3.90 g of the aliphatic amide **T** gave 0.060 mol of ammonia.
Use this information to find the formula of the hydrocarbon group R, present in the amide **T**. [2]

1 mol of amide T gives 2 mol NH_3

$n(T) = 0.060 \div 2 = 0.030$ mol

M_r of T = $3.90 \div 0.030 = 130$

M_r of $2 \times CONH_2 = 88$, so M_r of R = $130 - 88 = 42$

Formula C_3H_6 $(-CH_2CH_2CH_2-)$

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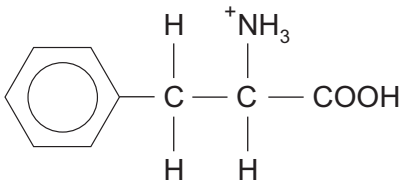
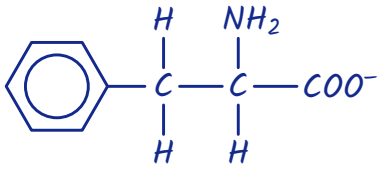
4. *(a)* In acid solution the formula of the ion formed from phenylalanine is



Give the formula of the ion formed from phenylalanine in basic solution. [1]



(b) The melting temperatures of four compounds are shown in the table.

Compound	Melting temperature / °C
CH_3CH_2COOH	–21
$CH_3CH(OH)COOH$	18
$CH_3CHBrCOOH$	26
$CH_3CH(NH_2)COOH$	289

Explain why the melting temperature of 2-aminopropanoic acid is very much higher than the other acids in the table. [2]

It exists as zwitterions, $CH_3CH(NH_3^+)COO^-$, so it has strong ionic character, giving much stronger forces between molecules than in the other acids.

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5. On detonation, the explosive RDX produces carbon monoxide, steam and nitrogen.

$$C_3H_6N_6O_6(s) \longrightarrow 3CO(g) + 3H_2O(g) + 3N_2(g)$$

RDX
M_r 222

Calculate the mass of RDX that would give 1.00 m^3 of gaseous products measured at 100 °C and at 1 atm. Give your answer to an **appropriate** number of significant figures. [2]

(1 mol of any gas occupies a volume of 30.6 dm^3 under these conditions)

1 mol RDX gives 3 + 3 + 3 = 9 mol of gas

9 × 30.6 = 275.4 dm^3 of gas from 222 g of RDX

1.00 m^3 = 1000 dm^3

mass = 222 × 1000 ÷ 275.4 = 806 g (3 sig figs)

Mass of RDX = 806 g

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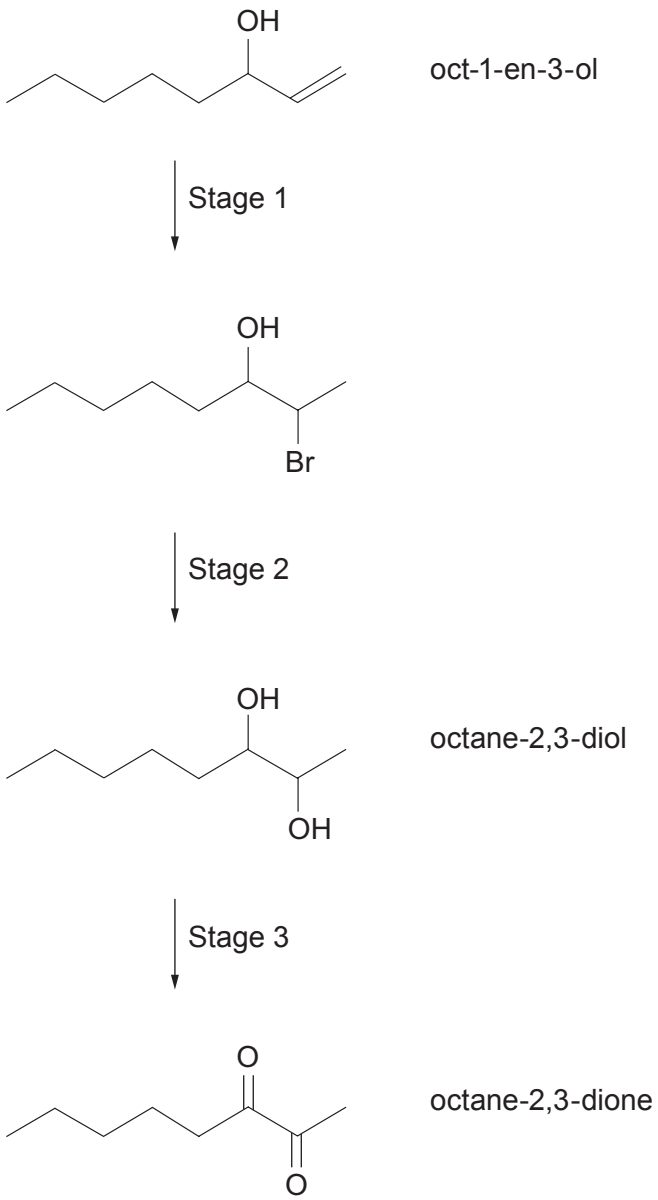
SECTION B

Answer **all** *questions in the spaces provided.*

6. *(a)* Oct-1-en-3-ol is a compound that attracts biting insects such as mosquitoes. It is contained in human breath and sweat and is also produced by some mushrooms.

A sequence of reactions starting with oct-1-en-3-ol is shown below.



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(i) Give the molecular formula of oct-1-en-3-ol. [1]

$C_8H_{16}O$

(ii) State a reagent that can be used for Stage 2 and name the type of reaction mechanism taking place. [2]

Reagent(s) NaOH(aq), aqueous sodium hydroxide

Type of reaction mechanism nucleophilic substitution

(iii) State a reagent that can be used for Stage 3. [1]

acidified potassium dichromate(VI), H^+ / $Cr_2O_7^{2-}$

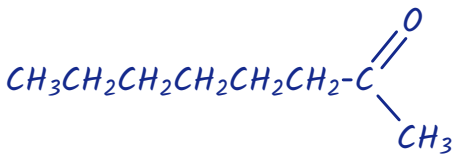
(b) An isomer of oct-1-en-3-ol was reacted with alkaline iodine and produced a yellow precipitate.

(i) Give the formula of the yellow precipitate. [1]

CHI_3

(ii) Suggest a structural formula for this isomer and identify the group that enables it to produce this yellow precipitate. [2]

Structural formula



(octan-2-one)

Group methyl ketone group, $CH_3C{=}O$

(c) Octane-2,3-dione is a pale yellow liquid and octane-2,3-diol is a colourless material.

(i) State a reagent that can be used to produce octane-2,3-diol from octane-2,3-dione. [1]

$NaBH_4$, sodium tetrahydridoborate(III)

(ii) Suggest how the rate of the reaction in part (i) could be studied. [1]

By following the disappearance of the pale yellow colour of the dione over time using a colorimeter.

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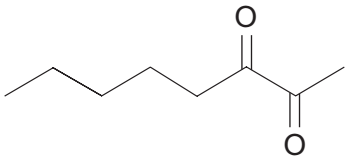
(d) The mass spectrum of octane-2,3-dione (M_r 142) shows fragmentation peaks at m/z 99, 71 and 43.



octane-2,3-dione

Identify the species responsible for these peaks. [2]

m/z 99: $CH_3CH_2CH_2CH_2CH_2CO^+$ ($C_5H_{11}CO^+$)

m/z 71: CH_3COCO^+

m/z 43: CH_3CO^+

(e) Oct-1-en-3-ol is formed biochemically by the breakdown of linoleic acid.

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$$

linoleic acid

The carbon to carbon double bonds in linoleic acid are reduced by hydrogen and the resulting product can then be reduced by another suitable reducing agent to give a compound of formula $C_{18}H_{38}O$.

(i) Write the **skeletal** formula of this compound. [2]

(ii) State the name of the reducing agent used in the second stage of the reduction. [1]

lithium tetrahydridoaluminate(III), $LiAlH_4$

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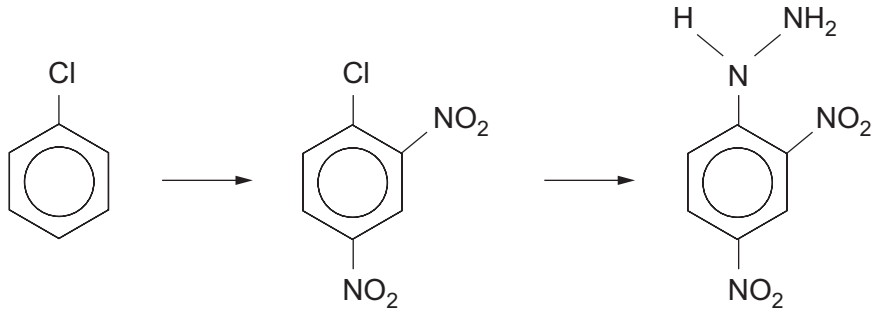
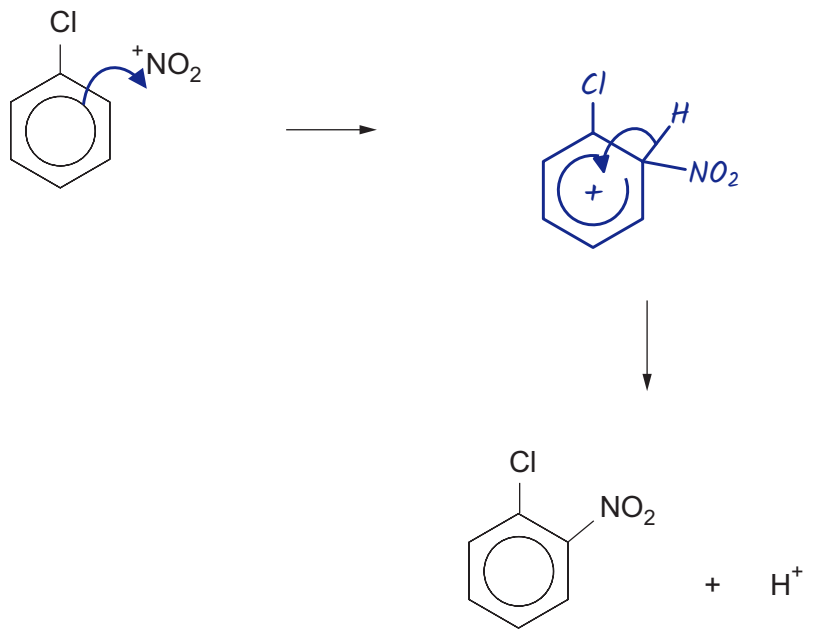
7. *(a)* 2,4-Dinitrophenylhydrazine (2,4-DNPH) can be made by the following route.



(i) Complete the mechanism for this reaction, which shows the nitration of chlorobenzene. You should use curly arrows and also show the structure of the intermediate. [2]



(ii) State the type of mechanism occurring in this nitration. [1]

electrophilic substitution

(b) State the feature of 2,4-DNPH that enables it to react as a base. [1]

The lone pair of electrons on the nitrogen atom (of the $-NH_2$ group).

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(c) 2,4-DNPH can be used as a reagent to identify aldehydes and ketones.

(i) State what is seen when 2,4-DNPH is used to identify an aldehyde or a ketone. [1]

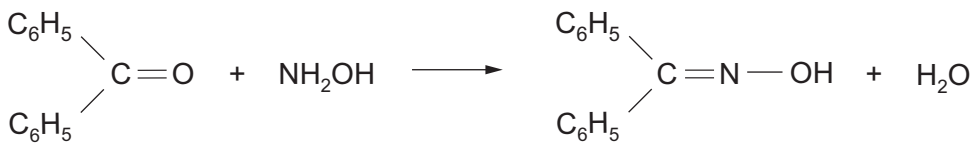
An orange / red solid (precipitate) forms.

(ii) Explain why 2,4-DNPH is an appropriate reagent to use in their identification. [1]

The 2,4-DNPH derivatives are solids with precise, sharp melting temperatures, so after recrystallisation their melting temperatures can be compared with data values to identify the compound.

(d) Alternative reagents can be used for this identification. One of them is hydroxylamine, NH_2OH, which produces a white crystalline solid when it reacts with an aldehyde or ketone.

For example with diphenylmethanone



diphenylmethanone oxime
melting temperature 143 °C

In an experiment, impure diphenylmethanone oxime was recrystallised from flammable methanol (boiling temperature 65 °C).

Outline a **safe** procedure to obtain pure dry crystals of diphenylmethanone oxime using methanol as the solvent. You should assume that all the material present in the crude oxime is soluble in methanol. [5]

Dissolve the impure oxime in the minimum volume of hot (warm) methanol.
Heat the methanol using a hot water bath or an electrical heater, never a naked flame, as methanol is flammable.
Allow the solution to cool (then in ice) so pure oxime crystallises; impurities stay in solution.
Filter off the crystals by suction filtration, wash with a little cold methanol, and dry them between filter papers or in a desiccator.

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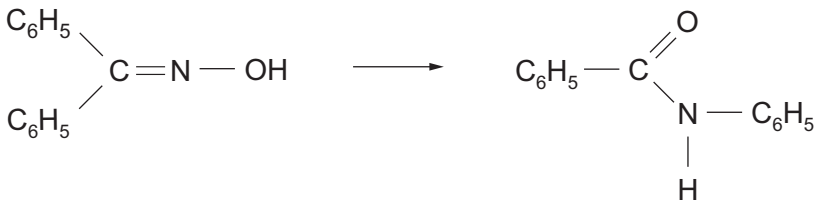
(e) Under suitable conditions diphenylmethanone oxime undergoes a rearrangement.



diphenylmethanone oxime N-phenylbenzamide

Describe how the infrared absorption spectra of these two compounds would differ, giving the relevant bonds and their wavenumbers. You should comment on **both** compounds when considering differences. [3]

Broad O–H peak at 3200 to 3550 cm^{-1}: present in the oxime only, not the amide.

C=O peak at 1650 to 1750 cm^{-1}: present in the amide only, not the oxime.

N–H peak at 3300 to 3500 cm^{-1}: present in the amide only, not the oxime.

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8. *(a)* For a number of years CFCs were used in refrigeration and in air conditioning. The use of these compounds is in decline as they damage the ozone layer. A typical CFC is chlorotrifluoromethane.

Give an equation that shows the formation of a chlorine radical from chlorotrifluoromethane. [1]

$F_3CCl \rightarrow F_3C\cdot + Cl\cdot$ (UV light)

(b) CFCs are being replaced by hydrofluorocarbons (HFCs) such as difluoromethane, which can be made by the reaction of dichloromethane with hydrogen fluoride in the presence of a catalyst.

$$CH_2Cl_2 + 2HF \longrightarrow CH_2F_2 + 2HCl$$

One problem with this reaction is that chlorofluoromethane is also produced.

The table below shows the percentage of the organic products formed (and unreacted dichloromethane) for various starting ratios of the reactants.

Mole ratio HF : CH_2Cl_2	Percentage composition of mixture / %		
	CH_2Cl_2	CH_2ClF	CH_2F_2
26 : 1	1.5	6.5	92.0
22 : 1	1.8	10.2	88.0
19 : 1	3.0	11.0	86.0
16 : 1	4.5	11.5	84.0

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(i) Write a statement that links the mole ratio of HF : CH_2Cl_2 with the yield of difluoromethane. [1]

The higher the mole ratio of HF : CH_2Cl_2, the higher the yield of difluoromethane, CH_2F_2.

(ii) In an experiment using 0.040 mol of CH_2Cl_2, the yield of CH_2F_2 was 89.0 %. Calculate the mass of difluoromethane produced. [2]

$n(CH_2F_2) = 0.040 \times 89.0 \div 100 = 0.0356$ mol

$M_r(CH_2F_2) = 12.0 + 2(1.0) + 2(19.0) = 52.0$

mass $= 0.0356 \times 52.0 = 1.85$ g

Mass = 1.85 g

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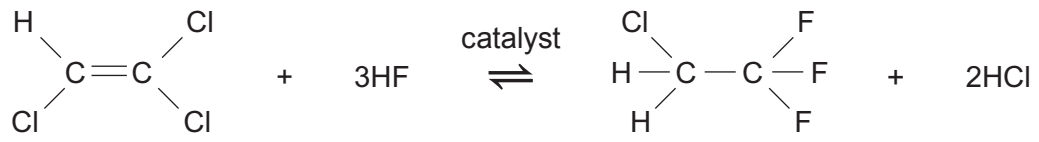
(c) 1,1,1,2-Tetrafluoroethane is an HFC that is made from trichloroethene and hydrogen fluoride in a two-stage vapour phase process.

Stage 1 – an exothermic process



Stage 2 – an endothermic process

(i) Suggest, giving a reason, whether a high or low pressure should be used in **stage 1**. [1]

High pressure, because there are more moles of gas on the left (4) than on the right (3).

(ii) Suggest, giving a reason, whether a high or low temperature should be used in **stage 2**. [1]

High temperature, as the forward reaction is endothermic, so heat moves the position of equilibrium to the right.

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(iii) The boiling temperatures of the organic products formed after each stage are shown below.

Compound	Boiling temperature / °C
1,1,1-trifluoro-2-chloroethane	7
1,1,1,2-tetrafluoroethane	–26

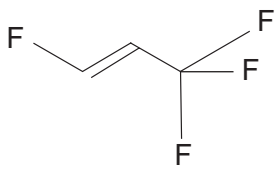
The final product tends to be contaminated with some of the chlorocompound formed in the first stage.

State the name of the method that can be used to separate these two compounds and suggest how this could be carried out in practice. [2]

Fractional distillation.

Cool the mixture to below −30 °C, then let it warm up slowly: CF_3CH_2F (−26 °C) distils off first and is condensed in a cold trap.

(d) The use of HFCs is now declining as these compounds are contributing to global warming. Compounds such as HFOs (hydrofluoroolefins) are under development as suitable replacements. One such HFO is 1,3,3,3-tetrafluoropropene.



(i) Explain why 1,3,3,3-tetrafluoropropene exists as *E/Z* isomers. [1]

Each carbon atom of the C=C double bond has two different groups bonded to it (and there is no rotation about C=C).

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(ii) The addition of hydrogen bromide to 1,3,3,3-tetrafluoropropene results in two structural isomers, each of molecular formula $C_3H_3BrF_4$.

I. State the type of mechanism occurring in this reaction. [1]

electrophilic addition

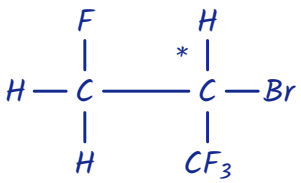
II. These two compounds are formed in **approximately equal amounts** in this reaction.

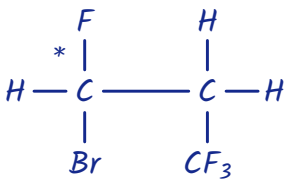
Suggest why this ratio is different to that found in the reactions of other alkenes. [1]

The two possible intermediate carbocations have similar stabilities (similar activation energies), so they form at similar rates, whereas with other alkenes the more stable carbocation forms preferentially.

(iii) Both the compounds formed in part (ii) will rotate the plane of plane polarised light.

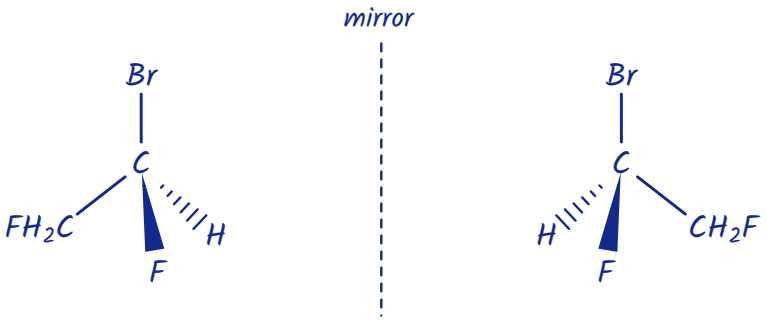
Give the formula of **both** compounds indicating the chiral centre in both. [2]





* = chiral centre

(iv) Draw the two mirror image forms of the compound 1-bromo-1,2-difluoroethane, $CHBrFCH_2F$. [1]



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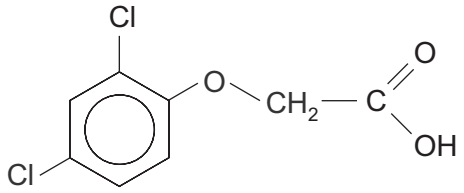
9. *(a)* A solid compound is believed to be the herbicide 2,4-dichlorophenoxyethanoic acid (2,4-D).



The following results were obtained when this compound was analysed.

- The percentage by mass of chlorine present was 32.1
- A solution of the compound reacted with sodium hydrogencarbonate to give a colourless gas
- 4.09 g of the compound was dissolved in a suitable solvent and the solution made up to 250 cm^3. A 25.0 cm^3 sample of this solution reacted with 24.70 cm^3 of aqueous sodium hydroxide of concentration 0.0750 mol dm^{-3}
- Refluxing a sample of the compound with aqueous sodium hydroxide did **not** show the presence of chloride ions in the resulting mixture
- The compound did **not** react with aqueous bromine to give a white precipitate or to decolourise the bromine
- The simplified ^1H NMR spectrum of the compound showed three separate peaks having the area ratio 1 : 2 : 3
- The ^{13}C NMR spectrum of the compound showed eight peaks

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Use **all** the information to confirm that the compound is likely to be 2,4-D and suggest a simple laboratory method that would help to confirm that it is 2,4-D. [6 QER]

M_r of 2,4-D, $C_8H_6Cl_2O_3$, is 221.0, so %Cl = 71.0 ÷ 221.0 × 100 = 32.1 %, consistent with the result.

A colourless gas (CO_2) with $NaHCO_3$ shows the compound is a carboxylic acid (COOH group).

n(NaOH) = 24.70 × 0.0750 ÷ 1000 = 1.85×10^{-3} mol. The mole ratio is 1:1 (only one COOH group), so n(acid) in 25.0 cm^3 = 1.85×10^{-3} mol and in 250 cm^3 = 1.85×10^{-2} mol. M_r = 4.09 ÷ 0.0185 = 221, consistent with 2,4-D.

No chloride ions after reflux with NaOH, so the Cl atoms are bonded directly to the benzene ring, not in an alkyl side chain.

No white precipitate with aqueous bromine, so it is not a phenol; bromine is not decolourised, so there are no C=C double bonds.

^1H NMR: three peaks in ratio 1 : 2 : 3 fit the O–H of COOH (1), the $-CH_2-$ (2) and the three aromatic ring protons (3).

^{13}C NMR: eight peaks, as 2,4-D has 8 different carbon environments (6 ring C, CH_2 and COOH).

To confirm: purify the solid, measure its melting temperature and compare it with the data book value for 2,4-D. Then mix a sample with pure 2,4-D and take the melting temperature again: if it is unchanged (not lowered), the compound is 2,4-D.

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(b) An ester can be hydrolysed by heating it with aqueous sodium hydroxide solution.

(i) Give the equation for the hydrolysis of methyl ethanoate. [1]

$CH_3COOCH_3 + NaOH \rightarrow CH_3COO^-Na^+ + CH_3OH$

(ii) The hydrolysis reaction can be used in a quantitative way to find the relative molecular mass of an ester.

A known mass of an ester is refluxed with a known volume of sodium hydroxide solution of concentration 1.0 mol dm^{-3} and the excess sodium hydroxide remaining after hydrolysis is determined by an acid-base titration.

The following results were obtained.

Mass of ester used = 1.76 g

Volume of aqueous sodium hydroxide added = 50.0 cm^3 (V_2)

Volume of aqueous sodium hydroxide remaining after hydrolysis = 30.0 cm^3 (V_1)

I. Use the formula below to calculate the M_r of the ester. [1]

$$\text{mass of ester} = \frac{M_r \text{ of the ester} \times (V_2 - V_1)}{1000}$$

$1.76 = M_r \times (50.0 - 30.0) \div 1000$

$M_r = 1.76 \times 1000 \div 20.0 = 88$

M_r = 88

II. The ester reacts with Tollens' reagent to give a silver mirror. Use this information and the M_r of the ester found in part I to suggest a formula for the ester. Give a reason for your answer. [2]

$HCOOCH_2CH_2CH_3$ (or $HCOOCH(CH_3)_2$), M_r 88.

The ester must contain the H–C=O group (a methanoate ester) for it to reduce Tollens' reagent.

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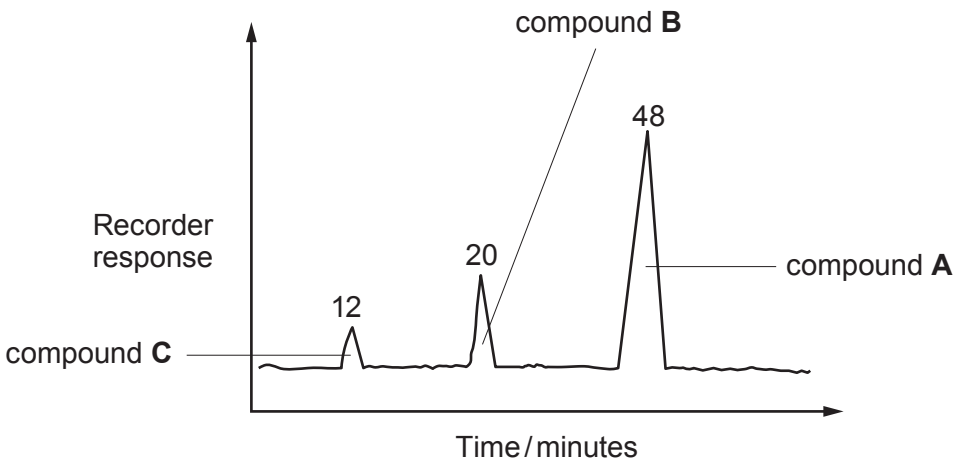
(iii) Esters of ethanoic acid with the formula $CH_3COOC_5H_{11}$ are used to give fruity flavours to confectionery.

I. The material used for this flavouring is often a mixture of esters having the formula above.

The diagram shows a gas chromatogram of a typical mixture.



Use the peak area data to calculate the percentage of compound **A** that is present in the mixture. [1]

% A = 48 ÷ (12 + 20 + 48) × 100 = 60

Percentage = 60 %

II. The peak areas shown give the molar percentage and in this case also the percentage by mass of each component present in the mixture.

Explain why the molar percentage of each compound **cannot** be used to find the percentage by mass of each component if the relative molecular mass of each component differs. [1]

If the M_r values are different, the number of moles shown on the chromatogram is not directly related to the mass of each component.

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(iv) The boiling temperatures of compounds **A**, **B** and **C** in part (iii) are shown in the table.

Compound	Name	R in $CH_3-C(=O)-O-R$	Boiling temperature / °C
A	2-methylbutyl ethanoate	$-CH_2CH(CH_3)CH_2CH_3$	134
B	3-methylbutyl ethanoate	$-CH_2CH_2CH(CH_3)CH_3$	142
C	pentyl ethanoate	$-CH_2CH_2CH_2CH_2CH_3$	147

Suggest a reason for the difference in boiling temperatures between compounds **A** and **C**. [1]

A is branched so its molecules have less surface contact, giving weaker intermolecular (van der Waals) forces than in C; less energy is needed to overcome them, so A has a lower boiling temperature.

(v) Compound **A** is made by heating 2-methylbutan-1-ol and ethanoic acid in the presence of concentrated sulfuric acid.

State the name of another organic compound that could be formed if concentrated sulfuric acid reacted with 2-methylbutan-1-ol. [1]

2-methylbut-1-ene

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10. *(a)* Butylamine can be made from propan-1-ol in a three-stage process.

Give the reagent used and the structural formula of the product for each stage. [3]

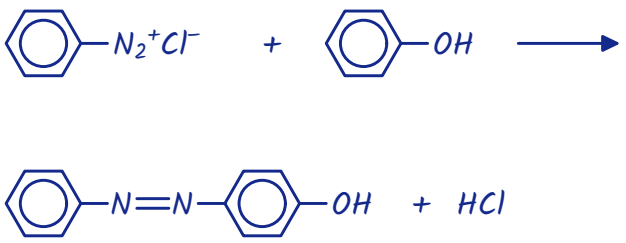
Stage	Reagent used	Structural formula of product
1	KBr / conc. H_2SO_4	$CH_3CH_2CH_2Br$
2	KCN (in ethanol)	$CH_3CH_2CH_2CN$
3	$LiAlH_4$	$CH_3CH_2CH_2CH_2NH_2$

(b) Below 10 °C, phenylamine reacts with nitric(III) acid, HNO_2, to give a benzenediazonium compound, which can react with phenol to give an azo dye.

(i) State how nitric(III) acid is prepared for use in this reaction. [1]

Mix sodium nitrate(III) (sodium nitrite, $NaNO_2$) with dilute hydrochloric acid below 10 °C.

(ii) Give the equation for the reaction of benzenediazonium chloride with phenol to produce an azo dye. [1]



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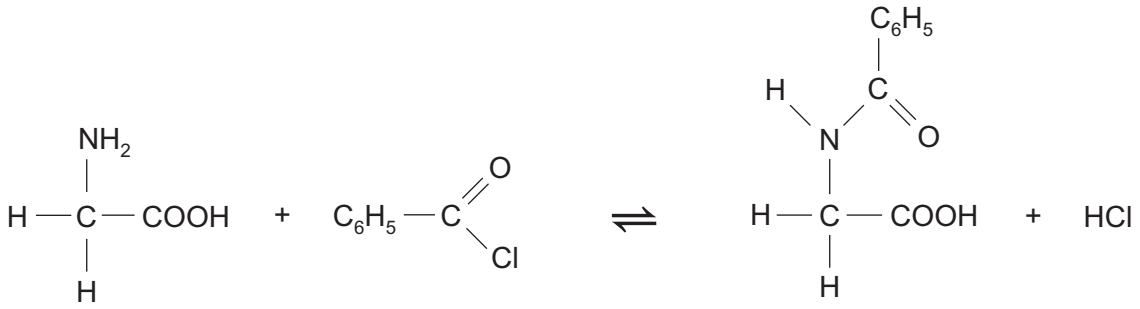
(c) Hippuric acid, so called because it is found in the urine of horses, can be made by reacting aminoethanoic acid and benzoyl chloride.



benzoyl chloride hippuric acid

In an experiment the percentage yield was 90 %.

Benzoyl chloride is only slowly hydrolysed by alkalis. A teacher suggested the following idea for increasing the percentage yield.

'The experiment could be carried out in the presence of aqueous sodium hydroxide.'

Comment on the validity of this suggestion and any effect it may have on the yield. Explain your answer. [1]

Valid: NaOH removes the HCl as it is formed, moving the position of equilibrium to the right, so the yield increases.

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(d) A straight chain α-amino acid of general formula R—CH(NH_2)COOH reacts with nitric(III) acid to give nitrogen gas.

$$R{-}CH(NH_2)COOH \xrightarrow{HNO_2} R{-}CH(OH)COOH + N_2 + H_2O$$

In an experiment 7.87 g of the amino acid was dissolved in water and the solution made up to 500 cm^3. A 25.0 cm^3 sample of this solution was reacted with an excess of nitric(III) acid and gave 73.5 cm^3 of nitrogen measured at 298 K and 1 atm pressure.

Calculate the molar mass of the amino acid and hence its structural formula. [4]

volume of N_2 from 500 cm^3 = 73.5 × 500 ÷ 25.0 = 1470 cm^3

$n(N_2)$ = 1470 ÷ 24 500 = 0.0600 mol

1 mol amino acid gives 1 mol N_2, so n(amino acid) = 0.0600 mol

molar mass = 7.87 ÷ 0.0600 = 131 g mol^{-1}

Molar mass = 131 g mol^{-1}

Structural formula

$CH(NH_2)COOH$ = 74, so R = 131 − 74 = 57 = C_4H_9

straight chain, so R = $CH_3CH_2CH_2CH_2$–

$CH_3CH_2CH_2CH_2CH(NH_2)COOH$

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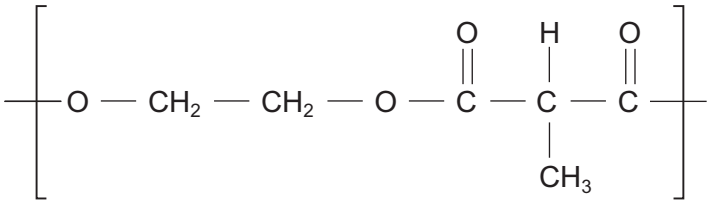
(e) Polyesters can be made from a dicarboxylic acid and a diol, such as ethane-1,2-diol.



polyester **E**

(i) State the name of the dicarboxylic acid that reacts with ethane-1,2-diol to give polyester **E**. [1]

2-methylpropanedioic acid

(ii) Complete the table to describe the high resolution ^{1}H NMR spectrum of polyester **E**. [3]

Protons	Splitting pattern	Relative peak area
—CH_2—CH_2—	*singlet*	4
—CH—	*quartet*	1
—CH_3	*doublet*	3

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