NAME DATE STARTED TARGET END DATE

GCE A LEVEL — CHEMISTRY UNIT 4 QUESTION PACK

1095-01 (Legacy CH4) · New spec Unit 4 Topic 1 · A2 unit, first sat 2017, 80 marks, 1h 45min paper

REVISE.wales

CHEMISTRY — UNIT 4 · Arenes & Aromatic Substitution

Topic 4.2 — Aromaticity, benzene reactions and electrophilic aromatic substitution

Benzene's delocalised π system, the mechanism of electrophilic substitution, nitration, halogenation, sulfonation, Friedel-Crafts acylation and alkylation, side-chain oxidation, and activating/deactivating directing groups on the ring.

Legacy 2008 specification

Estimated time for entire question pack: ~12 h 24 min

Derived from the legacy CH4 paper's pace of ~1.3 min/mark, padded for long-prose and synthesis answers (465 marks over 28 questions).

*You are advised to **not** attempt to complete all of this in one sitting.*

ABOUT THIS QUESTION PACK

This is a **comprehensive practice question pack**, not a single mock paper. It contains every question from the legacy WJEC CH4 papers (2008 modular spec, Jan 2010 – Jun 2016) that maps onto the new-spec A2 Unit 4 Topic 4.2.

Questions are ordered by source paper date.

INSTRUCTIONS

Use black ink or black ball-point pen. Show all working — quality of written communication will affect marks. A calculator is allowed. You will need the WJEC Periodic Table / Data Booklet.

For Examiner's use only

Q	Source	Max	Mark
1	Jan 10 Q2	12	
2	Jan 10 Q4	20	
3	Jun 10 Q3	15	
4	Jun 10 Q5	20	
5	Jan 11 Q1	13	
6	Jan 11 Q2	12	
7	Jan 11 Q3	15	
8	Jan 11 Q4	20	
9	Jun 11 Q1	13	
10	Jun 11 Q5	20	
11	Jan 12 Q1	13	
12	Jan 12 Q3	15	
13	Jun 12 Q1	19	
14	Jun 12 Q3	11	
15	Jun 12 Q5	20	
16	Jan 13 Q4	20	
17	Jun 13 Q4	20	
18	Jun 13 Q5	20	
19	Jan 14 Q2	13	
20	Jan 14 Q3	14	
21	Jan 14 Q4	20	
22	Jan 14 Q5	20	
23	Jun 14 Q1	13	
24	Jun 14 Q3	15	
25	Jun 14 Q4	20	
26	Jun 15 Q1	12	
27	Jun 15 Q4	20	
28	Jun 16 Q5	20	
Total		**465**	

Arenes & Aromatic Substitution — what the new spec asks

WJEC GCE A Level Chemistry (from 2015) · Unit 4: Organic Chemistry & Analysis · Topic 4.2.

Benzene structure

- Planar 6-membered ring; each C is sp^2 hybridised.
- 6 p-orbitals overlap above and below ring ⇒ delocalised π system (6 e^-).
- All C–C bond lengths equal (139 pm), between single (154) and double (134).
- Enthalpy of hydrogenation evidence: −208 kJ vs predicted −360 kJ ⇒ extra stability ~152 kJ.

Electrophilic substitution mechanism

- Step 1: electrophile E^+ attacks π system → arenium ion intermediate (loss of aromaticity).
- Step 2: H^+ lost from sp^3 carbon → aromaticity restored.
- Substitution preferred over addition because addition would destroy aromatic stabilisation.
- Curly arrows from delocalised ring (semicircle) to E^+, then C–H to ring.

Nitration

- Reagents: conc. HNO_3 + conc. H_2SO_4, ~55 °C.
- Electrophile: NO_2^+ (nitronium ion).
- $H_2SO_4 + HNO_3 \rightarrow H_2NO_3^+ + HSO_4^- \rightarrow NO_2^+ + H_2O$.
- Above 55 °C, dinitration occurs; in industry, used to make TNT and dye precursors.

Halogenation & Friedel-Crafts

- Br_2 with $FeBr_3$ (or $AlBr_3$) catalyst → bromobenzene + HBr.
- Cl_2 with $AlCl_3$ → chlorobenzene + HCl.
- Friedel-Crafts alkylation: RCl + $AlCl_3$ → R^+ → substitutes H on ring.
- Friedel-Crafts acylation: RCOCl + $AlCl_3$ → RCO^+ → ketone product (preferred — no polysubstitution).

Directing & activating groups

- Activating (e^--donating, ortho/para): −OH, $-NH_2$, −OR, $-CH_3$.
- Deactivating (e^--withdrawing, meta): $-NO_2$, −COOH, −CHO, −CN, $-SO_3H$.
- Halogens: deactivating but still ortho/para directing.
- Phenol much more reactive than benzene; nitrobenzene much less reactive (further nitration needs harsher conditions).

Side-chain oxidation

- Alkyl side chain on benzene oxidised by hot conc. $KMnO_4$.
- Methylbenzene → benzoic acid (C_6H_5COOH).
- Any length side chain oxidises to single −COOH (C closest to ring).
- Benzene ring itself is resistant to oxidation.

Crib sheet »

Arenes & Aromatic Substitution in one page

Quick-reference notes — revisit before each question.

Why substitution > addition

Addition would destroy the delocalised π system worth ~152 kJ. Substitution preserves aromaticity, so it's thermodynamically favoured despite higher activation energy.

Nitration mechanism

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$.

NO_2^+ attacks ring → arenium ion → loss of H^+.

Friedel-Crafts

Alkylation: $RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$.

Acylation: $RCOCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$.

Acylation preferred (no polysubstitution).

Directing rules

Lone pair / +I donors (–OH, $–NH_2$, –OR, –R): activate, direct 2,4 (o/p).

–I/–M ($–NO_2$, –COOH, –CHO): deactivate, direct 3 (m).

Halogens: deactivate but o/p.

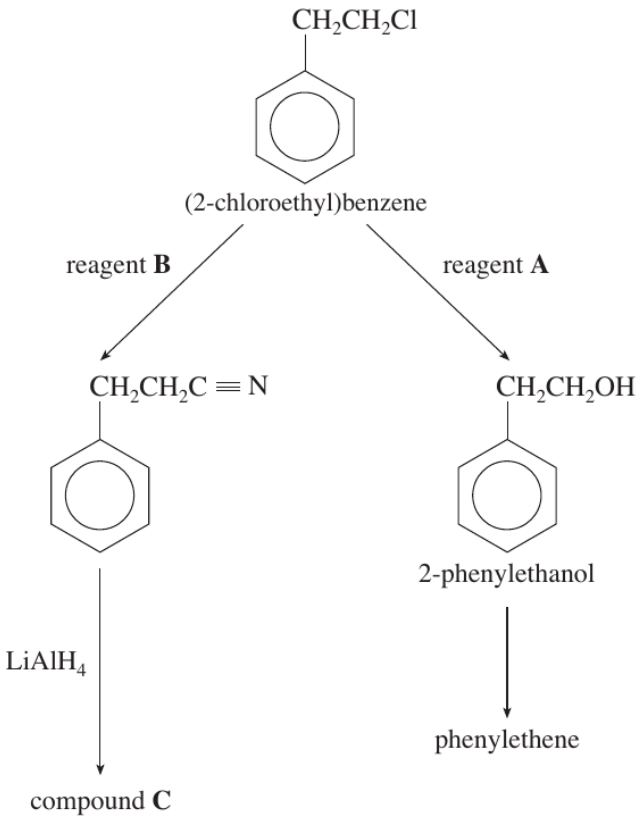
Phenol vs benzene

Phenol so reactive it brominates with Br_2(aq) at RT (no catalyst); white 2,4,6-tribromophenol precipitate.

Side-chain oxidation

Hot conc. $KMnO_4$ oxidises any alkyl side chain to –COOH (one C remains, attached to ring). e.g. propylbenzene → benzoic acid.

2. *(a)* (2-Chloroethyl)benzene is the starting material for the production of a number of other compounds.



(i) State the name of reagent **A**. ..... [1]

(ii) State the name of reagent **B**. ..... [1]

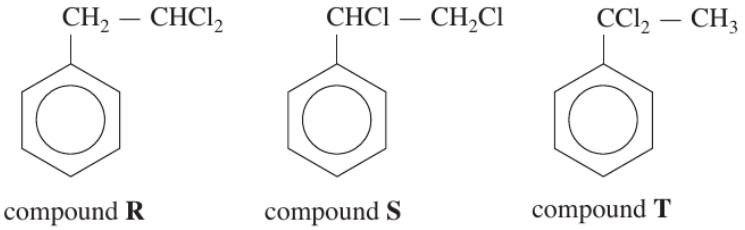
(iii) Name the type of reaction that occurs when phenylethene is produced from 2-phenylethanol. [1]

.....

(iv) Give the displayed formula of compound **C**. [1]

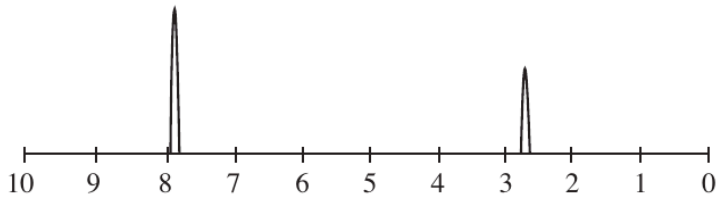
Examiner only

(b) (2-Chloroethyl)benzene can be made by reacting ethylbenzene with chlorine.
During this reaction a number of other compounds, including the following, are produced.



compound **R** compound **S** compound **T**

The low resolution NMR spectrum of one of these compounds is shown below.



State, giving a reason, which of the three compounds **R**, **S** or **T** will have the low resolution NMR spectrum shown. [2]

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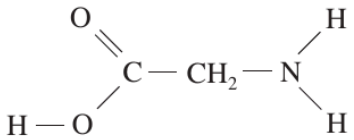
(c) (i) Aminoethanoic acid (glycine), whose displayed formula is shown below, reacts with ethanoyl chloride.



Give the equation for this reaction, showing the displayed formula of the organic product. [2]

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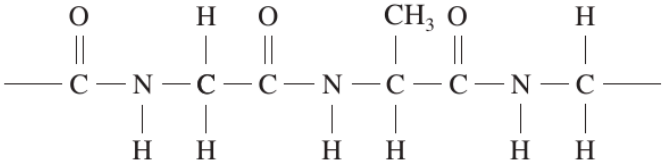
Examiner only

(ii) Draw the displayed formula of the zwitterion structure of aminoethanoic acid. [1]

(d) The formula of a section of a polypeptide is given below.



This formula represents the primary structure of a protein.

Briefly outline how the **secondary** structure of a protein arises from the primary structure. [2]

(QWC) [1]

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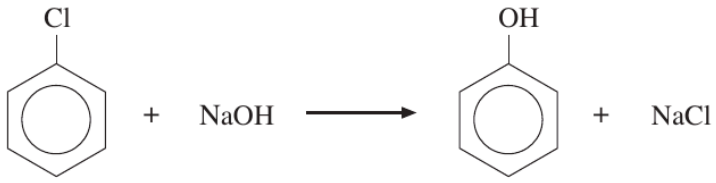
Total [12]

SECTION B

Answer **both** *questions in the separate answer book provided.*

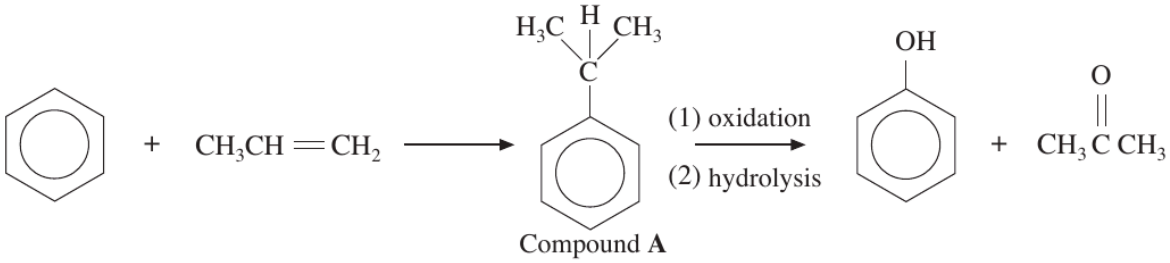
4. *(a)* Chlorobenzene, C_6H_5Cl, is an important industrial chemical. It can be made in the laboratory by reacting benzene and chlorine in the presence of an iron or iron(III) chloride catalyst.
Give the mechanism for this electrophilic substitution reaction. [4]

(b) One method for making phenol is by reacting chlorobenzene with aqueous sodium hydroxide, but at a pressure of 200 atmospheres.



Explain why it is difficult to react chlorobenzene with sodium hydroxide. [3]

(c) Most phenol is now produced from benzene and propene in a three-stage reaction.



(i) State the name of compound **A**. [1]

(ii) Explain why the atom economy of this reaction to make phenol is poor. [2]

(iii) Using the Data Sheet, describe how an infrared spectrum of a sample of phenol produced in this process would indicate that traces of propanone were also present. [2]

(iv) At room temperature phenol is a solid. A sample of phenol was dissolved in ethanol and then a few drops of the solution were added to some iron(III) chloride solution. State what was seen and why ethanol is a suitable solvent to use for this reaction. [2]

Turn over.

(v) Ketones, such as propanone, can be identified by using 2,4-dinitrophenylhydrazine.
In a test, a few drops of a compound suspected to be propanone were added to a solution of 2,4-dinitrophenylhydrazine.
Describe what was seen and how the product of this test could be used to positively identify the compound as propanone.

You should assume that any compound produced has been separated and purified. [3]

(vi) In analytical laboratories, compounds can be separated by gas chromatography and identified by mass spectroscopy.

An impure sample of propanone was obtained in this way and its mass spectrum showed the presence of another ketone, **T**, which showed a molecular ion peak, M^+, at m/z 86.
In addition, other significant peaks were seen at m/z values of 29 and 57.
Use this information to show that **T** could be pentan-3-one. [3]

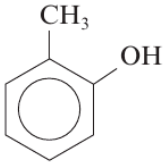
Total [20]

3. *Read the passage below and then answer the questions in the spaces provided.*

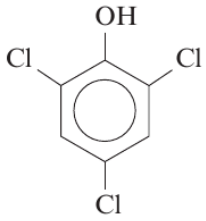
Phenol

Phenol, formula C_6H_5OH, has an hydroxyl group joined directly to an aromatic ring.

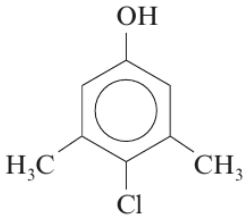
Phenol has many derivatives including 2-methylphenol.



Phenol was isolated from coal tar in 1835 and its original name was carbolic acid. It is a weak acid, between carboxylic acids and alcohols in strength. In 1865 the English surgeon Joseph Lister pioneered the use of phenol as the first surgical antiseptic and by the beginning of the 20th century phenol was commonly used as an antiseptic, but its use is not permitted today. Familiar pharmaceutical products such as TCP and Dettol are much more effective as antiseptics and disinfectants and do not have the toxicity of phenol itself.



TCP



Dettol

Nowadays most phenol is produced by the cumene process with less than 5% being made from coal tar. Recently a new process has been developed where phenol is made by the direct oxidation of benzene using nitrous oxide, N_2O, as the oxidising agent. This reaction could be of particular value since N_2O, a pollutant under strict control, is a by-product of the production of hexanedioic acid used to make nylon-6,6. The new process provides a very high yield of phenol and produces no significant aqueous waste products.

Phenol is very important since it is used in the production of

- epoxy and polycarbonate resins (e.g. as adhesives, in safety glasses and in drinking bottles),
- nylon,
- phenolic resins (e.g. as plywood adhesive, in fibreglass and in moulded electrical components),
- derivatives of ethanoic anhydride.

You would be unwise to handle phenol, but it is a key chemical in the manufacture of many everyday materials you do handle.

– End of passage –

Examiner only

(a) Describe a chemical test to show the presence of the –OH group in 2-methylphenol (line 4) by giving the reagent(s) and observation(s).

Reagent(s) ..... [1]

Observation(s) ..... [1]

(b) Explain why phenol is more acidic than alcohols but less acidic than carboxylic acids (line 6). [4]

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(c) Give the systematic name of Dettol (line 11). [1]

.....

(d) The new process for the production of phenol (line 13) can be represented by the following equation.

$$C_6H_6 + N_2O \longrightarrow C_6H_5OH + N_2$$

Calculate the atom economy of the reaction. [2]

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.....

Examiner only

(e) Draw the displayed formula of hexanedioic acid (line 16). [1]

(f) State the name of a compound that can react with hexanedioic acid to form nylon-6,6. [1]

.....

(g) Draw the repeating unit in nylon-6,6 (line 16). [1]

(h) Nylon-6,6 is a typical example of a condensation polymer. Explain the difference between condensation polymerisation and addition polymerisation. [2]

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(i) Give **one** important industrial use of ethanoic anhydride. [1]

.....

Total [15]

Total Section A [40]

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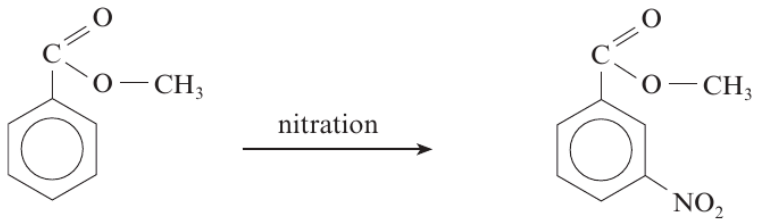
5. *(a)* Describe the structure of, and bonding in, benzene and explain why benzene is less ready to undergo addition reactions than alkenes. [6]

(QWC) [2]

(b) Frances wanted to prepare a nitro-aromatic compound in the laboratory, so her teacher told her to prepare methyl-3-nitrobenzoate by nitrating methyl benzoate using the following method.



methyl benzoate methyl-3-nitrobenzoate

- Prepare a nitrating mixture by mixing 2 cm^3 of concentrated nitric acid and 2 cm^3 of concentrated sulfuric acid in a test tube, cooling it in ice.
- Weigh 2.75 g of methyl benzoate in a small conical flask, place the flask in a beaker of ice and slowly add 5 cm^3 of concentrated sulfuric acid.
- Add the nitrating mixture a few drops at a time to the solution in the flask ensuring that the temperature stays below 10 °C.
- When the addition is complete, allow the mixture to stand at room temperature for 15 minutes.
- Pour the mixture onto crushed ice in a small beaker, stir and leave until all the ice has melted and crystals have formed.
- Filter the mixture, wash well with water and recrystallise it from ethanol.

At the end of the experiment Frances' yield was 2.70 g.

(i) Suggest why the teacher told her to nitrate methyl benzoate, not benzene. [1]

(ii) State why it is necessary to recrystallise the product before weighing it. [1]

(iii) Outline how Frances would recrystallise methyl-3-nitrobenzoate from ethanol. [3]

(iv) State how she could prove that the product was pure. [1]

(v) Methyl benzoate is a liquid at room temperature and has a density of 1.1 $g\,cm^{-3}$. Calculate the volume of 2.75 g of methyl benzoate. [1]

(vi) Calculate the percentage yield obtained by Frances. [3]

(vii) Methyl benzoate undergoes nitration by the same mechanism as benzene.

I. Classify the mechanism for the nitration of methyl benzoate. [1]

II. Give the formula of the species attacking the benzene ring. [1]

Total [20]

Section B Total [40]

Examiner only

SECTION A

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

1. *(a)* Complete the following passage by inserting suitable words or formulae where required. [3]

Nitrobenzene, an aromatic yellow oil, has the molecular formula ..... .

However, in blue light, this compound appears black because .....

..... .

The ^{1}H NMR spectrum of nitrobenzene is produced as a result of interactions between the spin of the nuclei and an applied magnetic field. This spectrum is seen as a number of peaks because the protons causing the spectrum are not ..... .

(b) Benzene reacts with chloromethane in the presence of a catalyst giving methylbenzene as the main organic product.

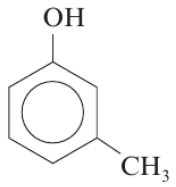
(i) Give the equation for this reaction. [1]

(ii) State the name of a catalyst that can be used. [1]

.....

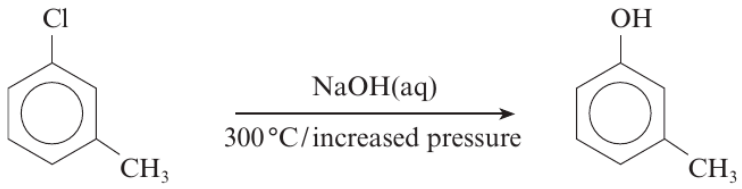
Examiner only

(c) Creosote was once the most widely used wood preservative in the world. However, the use of this material is now severely restricted because of its high toxicity.
It is a mixture of compounds, including cresols such as 3-methylphenol.



3-methylphenol

(i) 3-Methylphenol is obtained from coal tar but another method of preparing this compound is by heating 3-chloro-1-methylbenzene with aqueous sodium hydroxide.



Explain why these conditions are needed to obtain 3-methylphenol from the chloro-compound. [3]

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(ii) A number of safer wood preservatives have been developed to replace creosote. Suggest **two** factors that companies should take into account, apart from toxicity and cost, when considering an alternative material for use as a wood preservative. [2]

1. .....

.....

2. .....

.....

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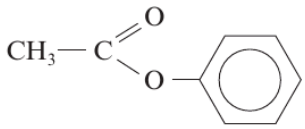
Examiner only

(d) The reaction between phenol and ethanoyl chloride gives the aromatic compound **W**.



compound **W**

(i) State the name of the group of compounds to which compound **W** belongs. [1]

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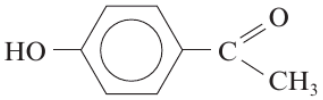
(ii) Using a suitable catalyst, compound **W** can rearrange to give compound **Y**.



compound **Y**

Compound **Y** gives a positive triiodomethane (iodoform) test.
State the reagents used for this test and what is observed. [2]

Reagents .....

Observation .....

Total [13]

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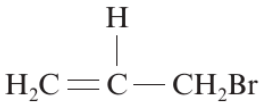
Examiner only

2. *(a)* Allyl bromide is the traditional name for the compound that has the following formula.



(i) Give the **systematic name** for this compound. [1]

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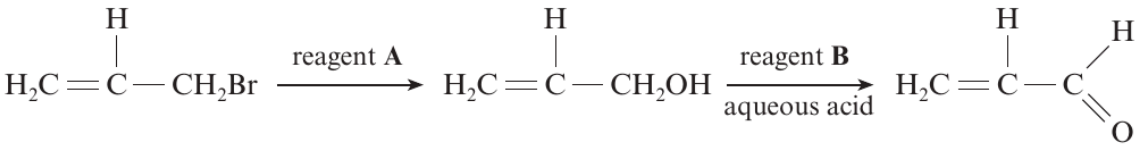
(ii) Allyl bromide can be converted to acraldehyde (prop-2-en-1-al) in a two-stage reaction.



State the names of reagent **A** and reagent **B**. [2]

Reagent **A** .....

Reagent **B** .....

(b) Acraldehyde reacts with 2,4-dinitrophenylhydrazine.

(i) State the type of reaction that occurs. [1]

.....

(ii) Describe the appearance of the organic product that is produced. [1]

.....

(iii) State how the purified organic product from (ii) is used to clearly identify the starting aldehyde as acraldehyde. [1]

.....

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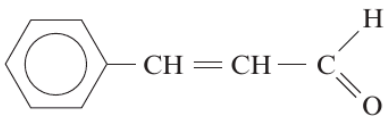
(iv) The infrared spectrum of an impurity present when acraldehyde is made by the method above, shows peaks at 1725 cm^{-1} and at 2500-3550 cm^{-1}.
Suggest the displayed formula of the impurity that is responsible for these peaks and the type of reaction that has produced it from acraldehyde. [2]

Displayed formula .....

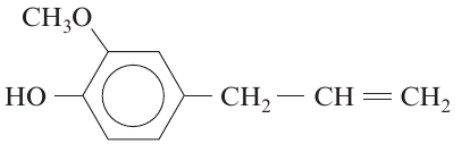
Type of reaction .....

Examiner only

(c) The smell and flavour of cinnamon oil is largely due to cinnamaldehyde (3-phenylpropenal) and, to a smaller extent, eugenol.



cinnamaldehyde



eugenol

(i) Explain why only cinnamaldehyde, and not eugenol, is able to have E-Z isomers. [1]

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(ii) Giving the reagent and an observation, state a chemical test that gives a positive result with eugenol but not with cinnamaldehyde. [2]

Reagent .....

Observation .....

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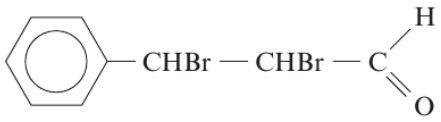
(iii) Cinnamaldehyde reacts with bromine to give the chiral compound **C**.



compound **C**

Both compound **C** and cinnamaldehyde can be used to illustrate stereoisomerism. State what is meant by *stereoisomerism.* [1]

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.....

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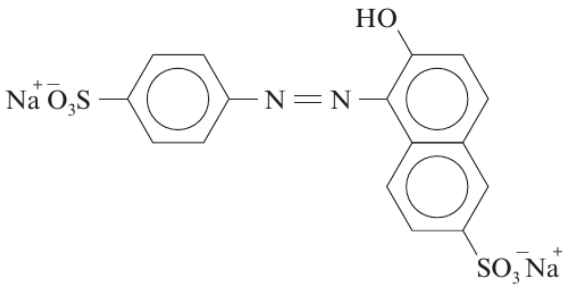
Total [12]

3. *Read the passage below and then answer the questions in the spaces provided.*

Food additives

Since 1986 manufacturers have been required, for most foods, to list their ingredients in descending proportions by mass. Food additives can be listed by their chemical names or by using an E-number. They are used for a number of reasons and as a result they are classified into different groups, some of which are discussed in this article.

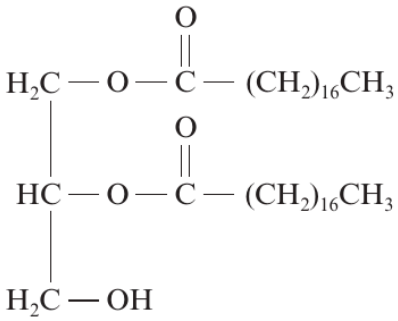
Colouring agents Consumers are probably most worried about compounds used to colour food. A number of permitted colours are synthetic azo-dyes and there are particular concerns about the effect that some of these compounds have on children. In recent years there has been a move towards safer naturally occurring dyes such as annatto and anthocyanins. However, azo-dyes such as Sunset Yellow FF (E110) continue to be used.



E110

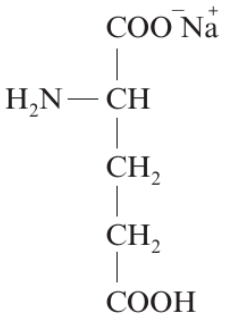
Preservatives With the move towards foods having longer shelf lives, there is a need to use preservatives to prevent spoilage. 2-Hydroxypropanoic acid (lactic acid), occurs naturally in sour milk and is used as a preservative in salad dressings. The salts of organic acids, for example sodium benzoate and sodium citrate, are used in fizzy drinks.
Calcium propanoate, $(CH_3CH_2COO)_2Ca$, is used as a preservative in bread, as it inhibits the growth of mould-producing microorganisms.

Emulsifiers These are used to enable oily substances and water to mix, so that separation into two layers does not occur. These compounds generally have water-'soluble' groups and a hydrocarbon chain that is fat-'soluble'. An example is the ester E477.



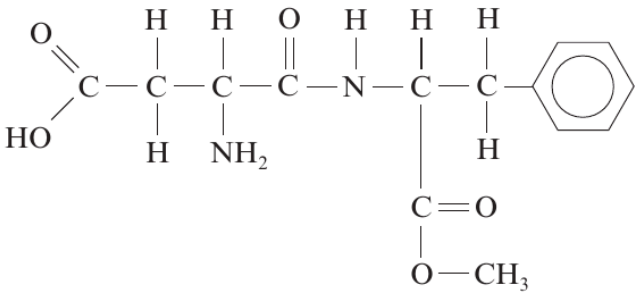
E477

Flavour enhancers Compounds such as monosodium glutamate (MSG) are added to food to increase its flavour. MSG occurs naturally in Parmesan cheese and tomatoes. Perhaps that is the reason why pizzas and soups are sometimes garnished with cheese and tomato.



MSG

Artificial sweeteners Many consumers are suspicious of food that has added sugar and manufacturers are naturally keen to label their products as containing 'no added sugar'. This may be true, but very often artificial sweetening agents are added in place of sugar to make the food more palatable. One of the commonest of these is aspartame, which is 200 times sweeter than sugar.



aspartame

The use (and misuse) of additives is an area of chemistry that has increasing importance as world population increases leading to a greater reliance on prepared, rather than fresh food.

– End of passage –

Examiner only

(a) (i) State the general name given to groups present in compounds such as Sunset Yellow FF that gives them their colour. [1]

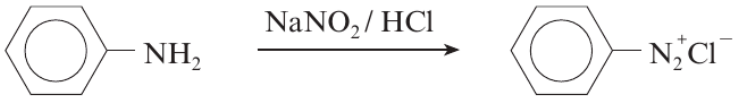
.....

(ii) Sunset Yellow FF is soluble in water. Like sodium chloride it contains sodium ions, Na^+. Explain how sodium ions interact with water molecules. [1]

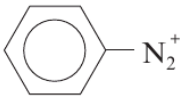
.....

.....

(iii) In the first stage of preparing an azo-dye, an aromatic amine reacts with sodium nitrate(III) (nitrite) and hydrochloric acid to give a diazonium compound.



I. State the temperature required for this reaction. ..... [1]

II. The benzenediazonium ion,  , then reacts with a phenol to produce an azo-dye.

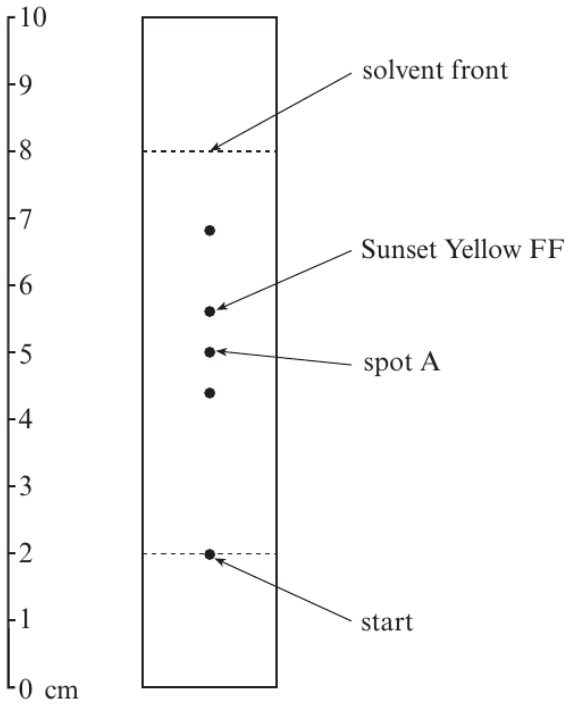
The benzenediazonium ion reacts as an electrophile.
State what is meant by the term *electrophile*. [1]

.....

.....

Examiner only

(b) A government chemist was using thin layer chromatography to identify the colours found in some imported sweets. She obtained the chromatogram below.



The R_f values for some of the expected colours are given in the following table.

Colour	R_f value
Sunset Yellow FF	0.60
Brilliant Blue FF	0.80
Fast Green FF	0.90

(i) Use the table of R_f values to state which other colour, apart from Sunset Yellow FF, is definitely present. Use the chromatogram to show how you arrived at your answer. [2]

.....

.....

(ii) The chemist suspected that spot A was due to amaranth or indigo carmine. This spot was removed from the plate and dissolved in a suitable solvent. Suggest **two** methods that she could then use to decide which of these two dyes was present. [2]

1. .....

.....

2. .....

.....

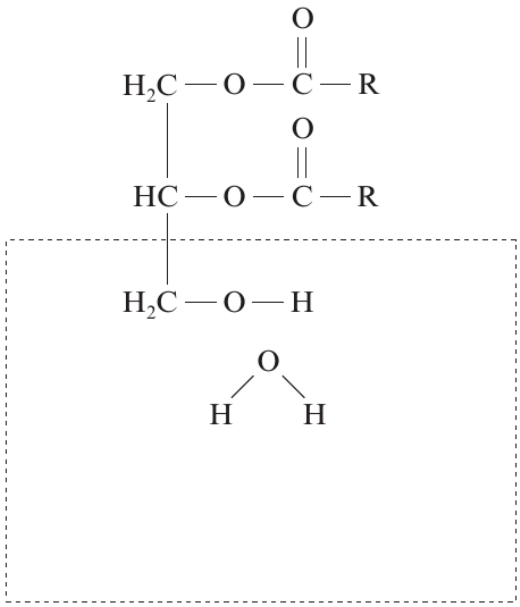
Examiner only

(c) Calcium propanoate *(line 14)* is used to inhibit mould growth in bread.
Salts of carboxylic acids, such as calcium propanoate, undergo decarboxylation when heated with calcium hydroxide or sodalime.
Complete the equation by giving the formula of the only organic product and balance the equation. [2]

$(CH_3CH_2COO)_2Ca + Ca(OH)_2 \rightarrow \square\ CaCO_3 + \square$ .....

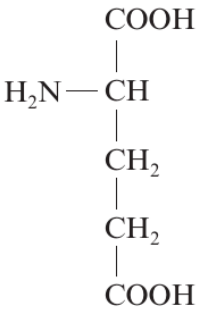
(d) E477 *(line 18)* forms hydrogen bonds with water molecules.

Working inside the box only, complete the diagram below by showing the polarity in E477 and the water molecule and the hydrogen bonds between them. For simplicity the hydrocarbon chain in E477 is shown as R. [2]



Examiner only

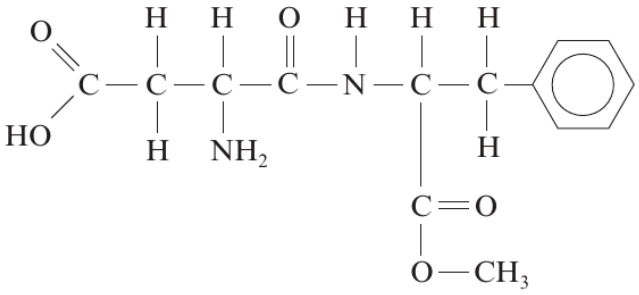
(e) MSG *(line 19)* is the monosodium salt of the α-amino acid glutamic acid.



glutamic acid

Give the **structural** formula of the organic species produced when glutamic acid is dissolved in excess alkali. [1]

(f) The artificial sweetener aspartame is a common sweetener in soft drinks. However, these should not be kept for any length of time as the **ester group** slowly hydrolyses.



aspartame

Give the structural formula of the two organic compounds produced from this hydrolysis of the ester group. [2]

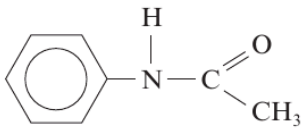
Total [15]

Section A Total [40]

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* Phenylamine reacts with ethanoyl chloride to produce N-phenylethanamide.



These two reactants are mixed together under suitable conditions and the products are poured into a large excess of cold water, when N-phenylethanamide is formed as impure white crystals. After filtering, N-phenylethanamide is recrystallised from hot water. The pure product melts at 113 °C.

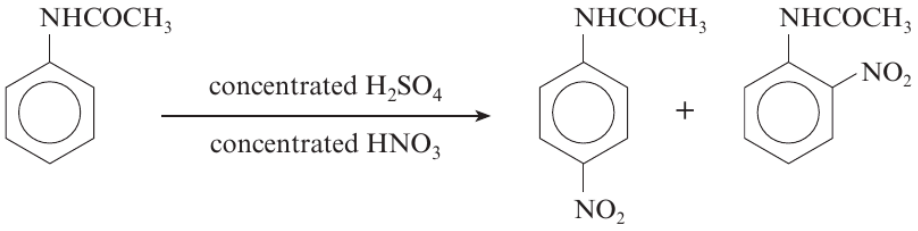
(i) Write the chemical equation for the reaction of phenylamine and ethanoyl chloride. [1]

(ii) When filtering the mixture containing impure N-phenylethanamide, the material in the filter paper is washed several times with cold water.
State why this is done. [1]

(iii) Use the account above to help you describe how you would obtain pure, dry crystals of N-phenylethanamide from the impure white crystals. [4]

(QWC) [1]

(b) N-phenylethanamide can be nitrated using a mixture of concentrated nitric and sulfuric acids, giving mainly 4-nitro-N-phenylethanamide as colourless crystals, together with small quantities of the yellow 2-nitro-N-phenylethanamide.



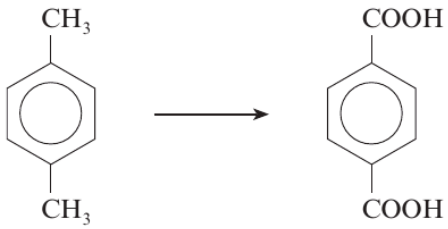
colourless solid yellow solid

(i) The mechanism for this reaction is similar to the nitration of benzene.
Give the reaction mechanism for the production of 4-nitro-N-phenylethanamide, starting from N-phenylethanamide and the nitronium ion (nitryl cation), NO_2^+.
Your answer should also state the type of reaction mechanism occurring. [4]

(ii) The two isomers are separated by recrystallisation from ethanol, in which the 2-isomer is much more soluble.
Use the information provided to state and explain how you would know when the 4-isomer is no longer contaminated with traces of the 2-isomer. [2]

(iii) In an experiment 8.10 g of N-phenylethanamide (M_r 135) produced 6.48 g of pure 4-nitro-N-phenylethanamide (M_r 180).
Calculate the percentage yield of 4-nitro-N-phenylethanamide. [3]

(c) One stage in the preparation of the polyester PET is the oxidation of 1,4-dimethylbenzene to benzene-1,4-dioic acid.



This is carried out in the laboratory by refluxing 1,4-dimethylbenzene and an alkaline solution (containing sodium hydroxide) of an oxidising agent **G**, giving an intermediate product, which is then acidified.

(i) State the name of oxidising agent **G**. [1]

(ii) Explain why it is then necessary to acidify the intermediate product to give the required acid. [1]

(d) The polyester PET is produced by reacting benzene-1,4-dioic acid and ethane-1,2-diol.
Draw the formula of the repeating unit found in PET and state why this reaction is described as condensation polymerisation. [2]

Total [20]

Examiner only

SECTION A

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

1. *(a)* Nitrobenzene, $C_6H_5NO_2$, is a yellow oily liquid.

(i) Give the general name of a group responsible for colour in organic compounds. [1]

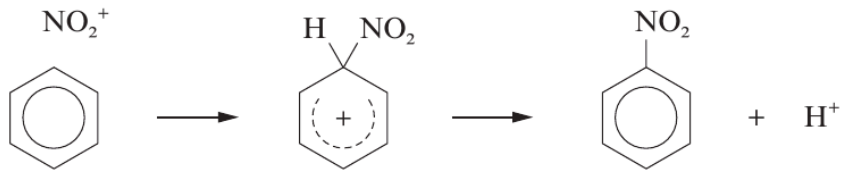
.....

(ii) State why nitrobenzene is yellow in white light. [1]

.....

(b) Nitrobenzene is produced from benzene by reaction with the nitronium ion (nitryl cation), NO_2^+.

(i) Complete the mechanism below by the use of the curly arrows (↷) [1]



(ii) During this reaction to produce nitrobenzene small quantities of 1,3-dinitrobenzene are produced.
Give the **empirical** formula of 1,3-dinitrobenzene. [1]

.....

(iii) In this reaction the nitronium ion is produced from nitric and sulfuric acids.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Use this equation to state why the sulfuric acid is acting as an acid. [1]

.....

.....

Examiner only

(c) Explain why benzene compounds tend to react by electrophilic **substitution** rather than undergo electrophilic addition. [2]

(QWC) [1]

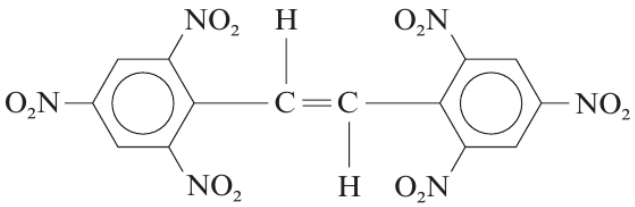
.....

.....

.....

.....

(d) Many explosives contain nitro-groups. The explosive hexanitrostilbene (HNS)



hexanitrostilbene

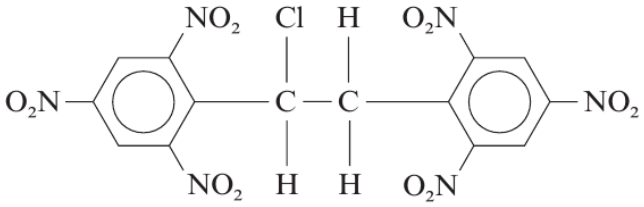
has been used to separate different sections in space rockets and for seismic experiments on the Moon.

(i) HNS is the E-isomer of a pair of E-Z isomers. State why HNS has both E- and Z-isomers. [1]

.....

.....

(ii) The manufacture of HNS is believed to proceed via compound **R**.



compound **R**

I Compound **R** contains a chiral centre. Identify the chiral centre in the formula of compound **R** by using an asterisk (*). [1]

Examiner only

II Compound **R** exists as two enantiomers. Explain what is meant by the term *enantiomers* and how these affect plane-polarised light. [2]

.....

.....

.....

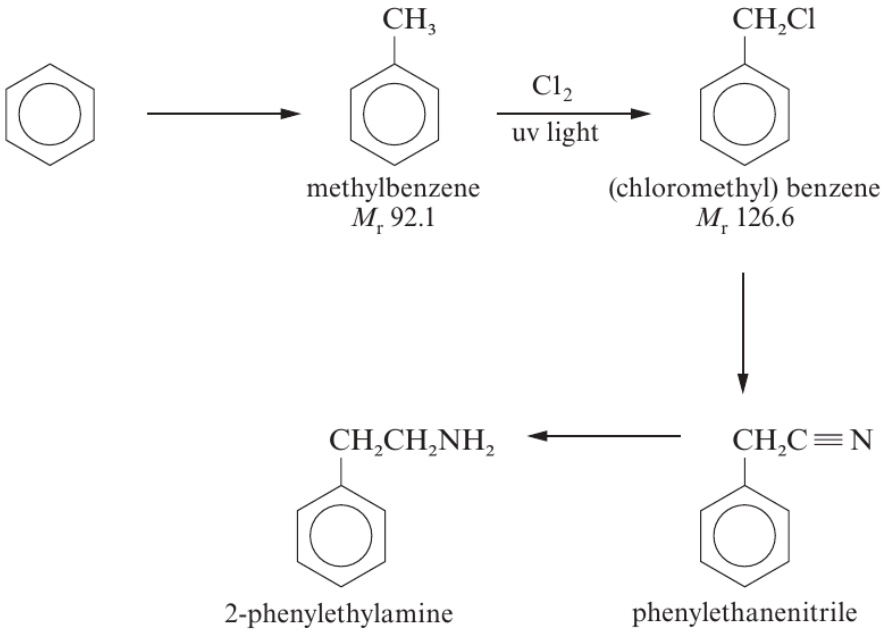
III State the type of reaction that occurs when compound **R** is converted to HNS by the use of a suitable base. [1]

.....

Total [13]

1094 010005

5. *(a)* 2-Phenylethylamine, present in chocolate, can be made from benzene in four stages.



(i) Give the equation, and the name of a suitable catalyst, for the Friedel-Crafts alkylation of benzene leading to methylbenzene. [2]

(ii) (Chloromethyl)benzene is produced by passing chlorine gas into methylbenzene in the presence of ultraviolet light. In practice the substitution by chlorine can proceed further giving (dichloromethyl)benzene and (trichloromethyl)benzene.
In order to prevent further chlorination the reaction is stopped when the increase in mass corresponds to (chloromethyl)benzene being produced.
You should assume that the other product, gaseous hydrogen chloride, is lost from the mixture.
In an experiment the following results were obtained.

Mass of flask	+	product	=	158.4 g
Mass of flask	+	methylbenzene	=	148.0 g
Mass of flask			=	120.4 g

Show that the increase in mass corresponds to the conversion of all the methylbenzene into (chloromethyl)benzene. [4]

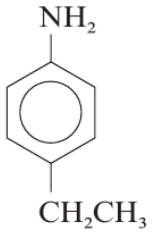
(iii) State the names of the reagents necessary to convert

I (chloromethyl)benzene to phenylethanenitrile, [1]

II phenylethanenitrile to 2-phenylethylamine. [1]

(b) Explain why 2-phenylethylamine is a base. [2]

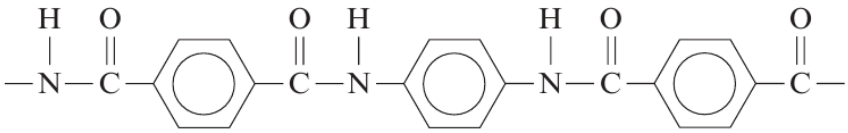
(c) State how both 2-phenylethylamine and its isomer 4-ethylphenylamine react with nitric(III) (nitrous) acid at 5°C.



4-ethylphenylamine

In **each** case you should state the type of compound produced and any relevant observations. [3]

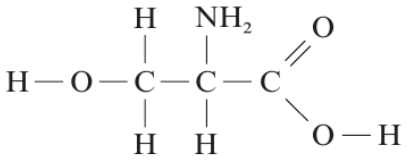
(d) Kevlar ® is a polyamide that is used in bullet-proof vests.



Kevlar ®

Give the formula of two starting materials that can be reacted together to give Kevlar ®. [2]

(e) Silk is a naturally occurring material composed of polymerised serine molecules. Serine is an α-amino acid.



serine

(i) Give the **systematic name** of serine, which is a derivative of propanoic acid. [1]

(ii) Hydrogen bonding is largely responsible for the solubility of serine in water. Explain what is meant by hydrogen bonding, using serine to illustrate your answer. [3]

(QWC) [1]

Total [20]

Section B Total [40]

WJEC CBAC

GCE A level

1094/01-A

CHEMISTRY CH4
DATA SHEET

P.M. WEDNESDAY, 15 June 2011

Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber/cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C=C	1620 to 1670
C=O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into n components indicates the presence of n–1 hydrogen atoms on the adjacent carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
$CH_3-C(=O)-$	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
$-O-CH_3$, $-OCH_2-R$, $-O-CH=C<$	3.5 to 4.0
$R-OH$	4.5 *
$CH_2=C<$	4.8
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

Examiner only

SECTION A

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

1. *(a)* The formulae of some compounds are shown below.

$CH_3CH_2NH_2$	$CH_3CH_2CONH_2$	$CH_3CHCHCHO$
A	**B**	**C**
$CH_3CH(OH)CH_2CH_3$	CH_2CHCH_3	$CH_3CH_2COCH_2CH_3$
D	**E**	**F**

Each letter may be used once, more than once or not at all, to answer the questions below.

Give the letter of the compound which

(i) is most basic, [1]

.....

(ii) forms yellow crystals when warmed with iodine in alkaline solution, [1]

.....

(iii) forms a silver mirror when warmed with Tollens' reagent, [1]

.....

(iv) exhibits E-Z isomerism. [1]

.....

(b) (i) Butylamine is one of the compounds responsible for the smell of rotting fish. It can be prepared in the laboratory from 1-chlorobutane.

Classify the reaction mechanism when butylamine is prepared in this way. [1]

.....

(ii) Explain why phenylamine, an aromatic amine, cannot be prepared from chlorobenzene using a similar reaction to that in part (i). [2]

.....

.....

.....

.....

Examiner only

(iii) Write a **balanced** equation for the reaction of butylamine with ethanoyl chloride, [1]

.....

(iv) Phenylamine is normally prepared from nitrobenzene.

I. Give the reagents used in this preparation and a technique to separate the product from the reaction mixture. [3]

.....

.....

.....

.....

II. When phenylamine reacts with cold nitric(III) acid (nitrous acid) a colourless solution of benzenediazonium chloride is formed. Write the formula for benzenediazonium chloride. [1]

1094 010003

III. State the type of organic substance formed when aqueous benzenediazonium chloride reacts with an alkaline aqueous solution of naphthalene-2-ol. [1]

.....

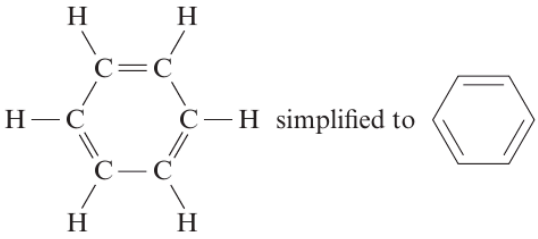
Total [13]

3. *Read the passage below and then answer the questions in the spaces provided.*

Benzene

Benzene, C_6H_6, is a colourless, highly flammable liquid with a sweet smell, but it is carcinogenic. The word "benzene" derives historically from "gum benzoin", an aromatic resin known to European pharmacists and perfumers since the 15th century.

Discovering the structure of benzene proved to be quite difficult. Benzene was first isolated and identified by Michael Faraday in 1825 from the oily residue derived from the production of illuminating gas. However, it was not until 1865 that Kekulé proposed this structure for benzene.



However this structure fails to explain why benzene does not react like an alkene. Ethene reacts readily with bromine as follows:

$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2Br\,CH_2Br$$

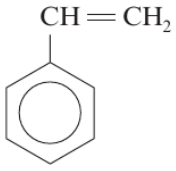
In contrast, benzene needs far more stringent conditions to react with bromine.

It was around 1930 that the structure of the benzene ring was finally confirmed using X-ray diffraction. It was shown that all the carbon-carbon bonds were of the same length. To account for this, it was proposed that three pairs of electrons were not localised in particular double bonds, but were shared equally amongst all six carbons. These electrons were said to be delocalised giving benzene great stability (delocalisation energy of benzene). The structure of benzene is therefore usually represented as:

An understanding of the structure of benzene was crucial to early chemists since benzene is the parent molecule of all arene or 'aromatic' compounds and a huge variety of compounds are derived from benzene. Simple benzene derivatives include:

phenol

phenylamine

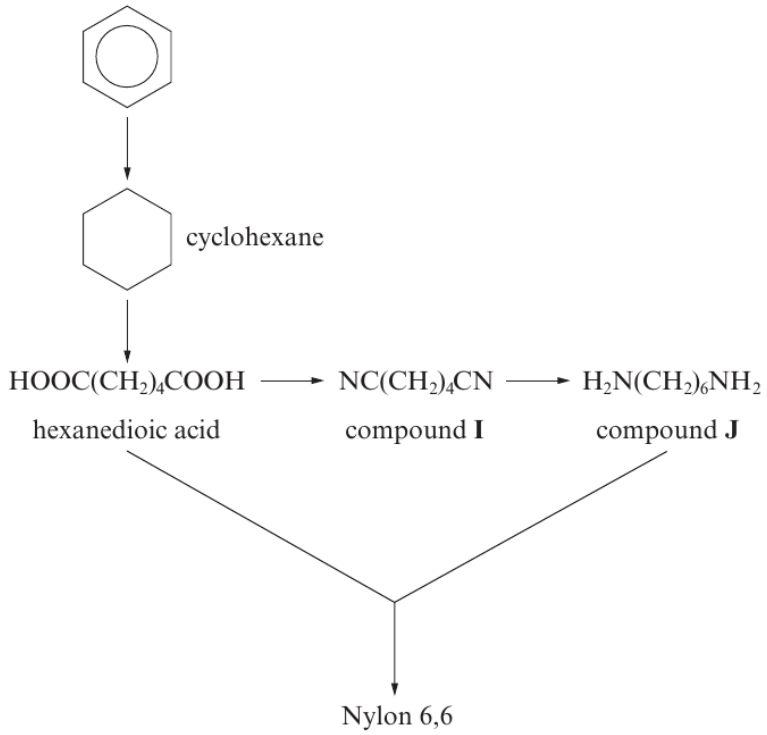


phenylethene

In the 19th and early 20th centuries, benzene was used as an after-shave lotion because of its pleasant smell, but today benzene is used to make other chemicals.

Examiner only

One of its most widely-produced derivatives is cyclohexane, which is used in the manufacture of Nylon 6,6 as shown in the scheme below:



28

– End of passage –

(a) Benzene reacts with bromine *(line 12)* in the presence of an iron(III) bromide catalyst to form bromobenzene.

(i) Classify the reaction mechanism. [1]

.....

(ii) Draw the mechanism for this reaction. [3]
(The mechanism is similar to that for the chlorination of benzene.)

Examiner only

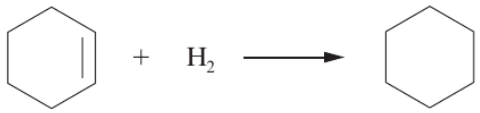
(b) (i) Explain what is meant by the *delocalisation energy* of benzene *(line 17)*. [1]

.....

.....

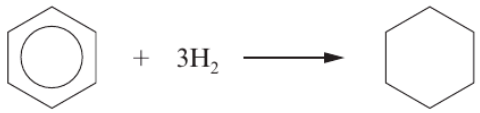
.....

(ii) Given that the enthalpy change of hydrogenation of cyclohexene is $-120\,kJ\,mol^{-1}$ and that the enthalpy change of hydrogenation of benzene is $-208\,kJ\,mol^{-1}$, calculate the delocalisation energy of benzene. [2]



$\Delta H^{\ominus} = -120\,kJ\,mol^{-1}$

cyclohexane



$\Delta H^{\ominus} = -208\,kJ\,mol^{-1}$

benzene

.....

.....

.....

$\Delta H^{\ominus} =$ ..... $kJ\,mol^{-1}$

(c) Use the information in the passage to give a reason why benzene is no longer used in after-shave lotion. [1]

.....

(d) In the production of Nylon 6,6 *(line 28)* each of the repeating units requires **two** molecules of benzene; one for the formation of hexanedioic acid and one for the formation of compound **J**.

(i) Draw the **skeletal** formula of hexanedioic acid. [1]

(ii) Name the type of reaction occurring when compound **I** is converted to compound **J**. [1]

.....

(iii) State the name of compound **J**. [1]

.....

Examiner only

(iv) Draw the repeating unit in Nylon 6,6. [1]

(v) What type of condensation polymer is Nylon 6,6? [1]

.....

(vi) A typical plant makes 800 tonnes of nylon per day. Given that the relative molecular mass of each repeating unit is 226 and assuming yields of 100% at each step, calculate the mass of benzene needed per day to produce this quantity of nylon. [2]

.....

.....

.....

Total [15]

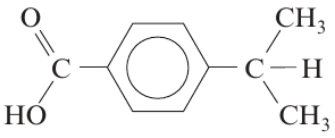
Total Section A [40]

Examiner only

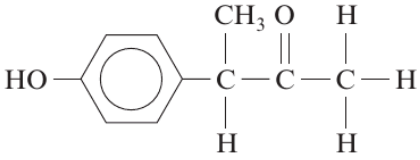
SECTION A

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

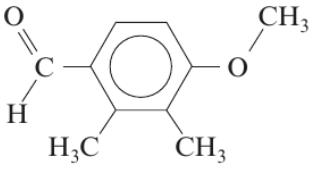
1. This question focuses on the chemistry of some of the many compounds which share the molecular formula $C_{10}H_{12}O_2$. Four compounds with this formula are shown below.



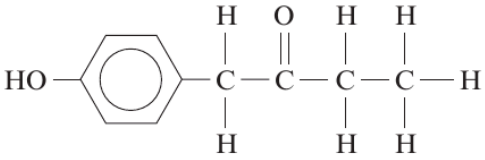
compound **W**



compound **X**



compound **Y**



compound **Z**

(a) Draw an **ester** which is an isomer of the compounds above. [1]

(b) Only one of the compounds shown can exhibit optical isomerism.

(i) Identify which compound can exhibit optical isomerism. ..... [1]

(ii) Indicate the chiral centre in this molecule by labelling it with an asterisk (*). [1]

(iii) State how the two enantiomers of this compound can be distinguished. [1]

.....

.....

.....

Examiner only

(c) The four compounds **W**, **X**, **Y** and **Z** were tested using a series of reagents. For each of the tests listed below, describe what would be expected to be observed in a positive test. Indicate which compounds would be expected to give a positive result. [6]

All the tests listed will give positive results with at least one compound.

Reagent(s)	*Observation if the test is positive*	*Compounds that would give a positive result*
I_2/NaOH(aq)	.....	.....
Na_2CO_3(aq)	.....	.....
$FeCl_3$(aq)	.....	.....

(d) Compound **W** can be oxidised to produce benzene-1,4-dioic acid *(terephthalic acid)*. This reaction can be undertaken in the same way as the oxidation of methylbenzene to form benzenecarboxylic acid.

compound **W**

benzene-1,4-dioic acid
(terephthalic acid)

(i) Give the reagent(s) and condition(s) required for this oxidation reaction. [2]

.....

.....

(ii) Almost all the benzene-1,4-dioic acid produced worldwide is used in the production of condensation polymers.

I. Give **two** differences between condensation polymerisation and addition polymerisation. [2]

.....

.....

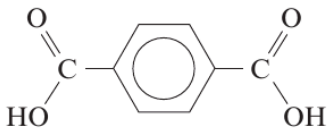
.....

1094 010003

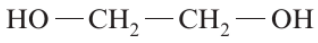
Turn over.

Examiner only

II. Draw the repeat unit for the polymer formed between benzene-1,4-dioic acid and ethane-1,2-diol. [1]

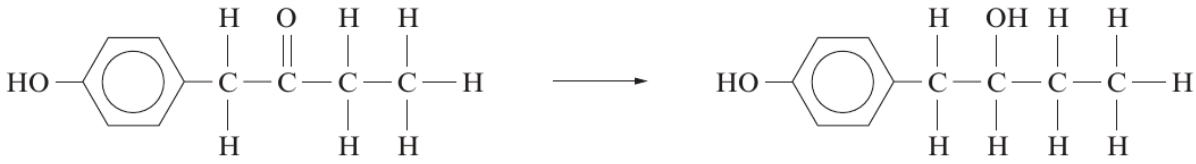


benzene-1,4-dioic acid
(terephthalic acid)



ethane-1,2-diol

(e) Compound **Z** may be converted into a secondary alcohol as shown below.



compound **Z** compound **V**

(i) Give a suitable reagent for this process and classify the reaction that occurs. [2]

Reagent .....

Classification of reaction .....

Examiner only

(ii) Compound **V** will react with ethanoyl chloride.
Give the structure of a carbon-containing product of this reaction. [1]

(iii) Compound **V** is insoluble in cold water, but reacts with sodium hydroxide solution and then dissolves.
Give the structure of the carbon-containing species present in the resulting solution. [1]

1094 010005

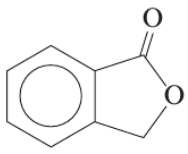
Total [19]

Turn over.

3. *Read the passage below and then answer the questions in the spaces provided.*

Phthalides

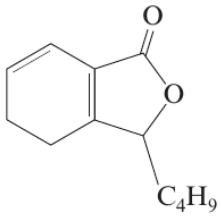
Phthalides are a family of compounds which are present in many plants, fungi and moulds. They are all based around the basic phthalide structure which has a benzene ring with a five-membered cyclic ester attached to it.



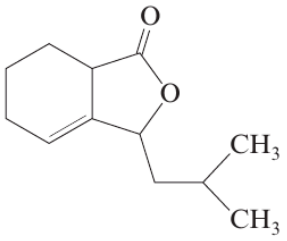
phthalide

Many phthalide-containing plants have been used worldwide as herbal remedies in traditional and folk medicines, and these have been found to affect many biological systems. 3-arylphthalides are also useful intermediates in the synthesis of anthracycline antibiotics.

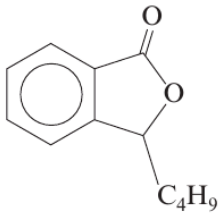
Some phthalides and their derivatives also act to enhance the flavour of food. In studies of celery, it was found that three particular compounds present in the plant had no flavour of their own, but enhanced the flavours of other foods when cooked together. These three were sedanenolide, sedanolide and 3-butylphthalide.



sedanenolide



sedanolide

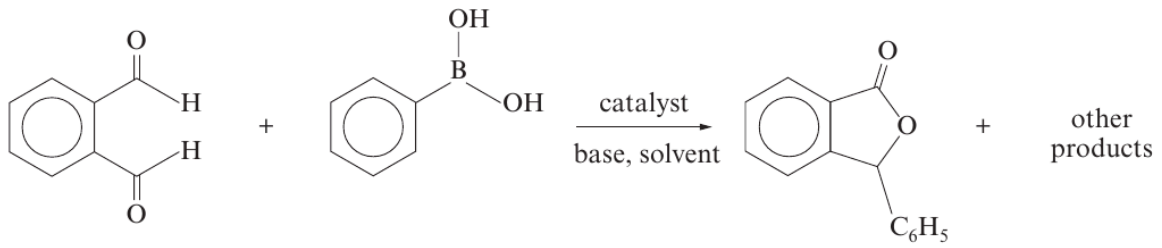


3-butylphthalide

These molecules, amongst many others, are present in substantial amounts in oil of celery seed. These compounds are usually liquids with different boiling temperatures.

Due to the phthalide structure being a key part of useful molecules, there have been many attempts at synthetic routes to produce this structure. Two successful methods to form 3-phenylphthalide are shown as route 1 and route 2 opposite. Route 1 was developed more recently than route 2, and is considered to be a significant improvement. One reason for considering route 1 to be the better approach is the greater variety of different phthalides that can be produced by this method, whilst route 2 is only useful for a limited number of phthalides.

Route 1

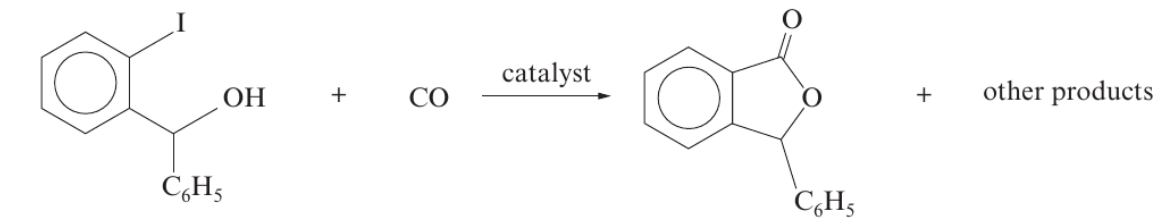


compound **Q** $M_r = 134$

$M_r = 122$

phthalide **P** $M_r = 210$

Route 2



compound **R** $M_r = 310$

carbon monoxide $M_r = 28.0$

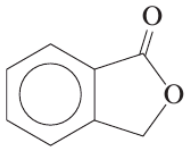
phthalide **P** $M_r = 210$

– End of passage –

Examiner only

(a) Phthalides are considered to be cyclic esters *(line 3)*.

(i) Indicate the ester group on the diagram of phthalide below by drawing a circle around it. [1]



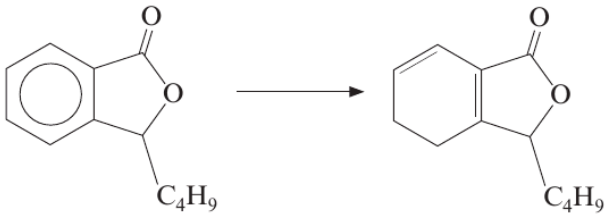
phthalide

(ii) Esters can be hydrolysed by heating with dilute sodium hydroxide solution. Draw the structure of the ion formed by hydrolysis of phthalide in this way. [1]

(b) Celery seed oil contains many different compounds *(lines 13-14)*. Suggest a method for obtaining pure samples of each different compound. [1]

.....

(c) It is possible to convert 3-butylphthalide into sedanenolide in a hydrogenation reaction.



3-butylphthalide sedanenolide

In this case the enthalpy change is +20 kJ mol^{-1}. The enthalpy change during hydrogenation of an alkene to form an alkane is typically –120 kJ mol^{-1}.
Explain this significant difference in enthalpy values for these two reactions. [2]

.....

.....

.....

Examiner only

(d) The atom economy for route 1 to produce phthalide **P** is 82.0%.
Calculate the atom economy for route 2 to produce **P**. [1]

.....

.....

(e) Route 1 is considered to be the better of the two methods for producing phthalides *(line 18)*.

(i) Give **one** reason stated in the passage for considering route 1 to be the better method. [1]

.....

.....

(ii) Give **one** reason not stated in the passage for considering route 1 to be the better method. [1]

.....

.....

(f) Give a chemical test that would distinguish between compound **Q** and compound **R** *(page 9)*. Include any reagent(s) required and state the observations expected for **each** compound. [3]

Reagent(s) .....

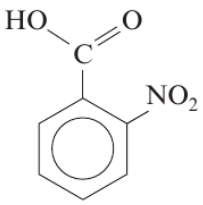
Observations .....

.....

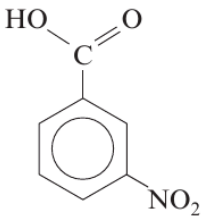
Total [11]

Total Section A [40]

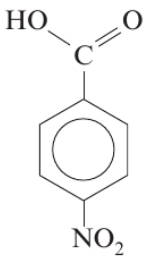
5. *(a)* Nitrobenzenecarboxylic acids *(nitrobenzoic acids)* are useful starting materials in the preparation of many dyes and can be prepared by nitration of benzenecarboxylic acid *(benzoic acid)*, C_6H_5COOH.
Many nitrobenzoic acids exist including those shown below:



2-nitrobenzoic acid



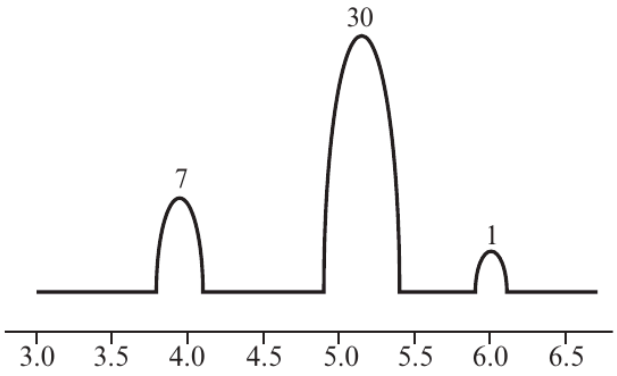
3-nitrobenzoic acid



4-nitrobenzoic acid

(i) Benzenecarboxylic acid can be nitrated under similar conditions to the nitration of benzene.
Give the reagent(s) and condition(s) required and classify the mechanism of this reaction. [3]

(ii) Nitration of benzenecarboxylic acid gives a mixture of products. These can be identified by gas chromatography followed by mass spectrometry *(GC-MS)*. The gas chromatograph for the products of this reaction is shown below, with the relative areas of each peak indicated.



Retention time/minutes

I. The main isomer produced is 3-nitrobenzenecarboxylic acid.
Calculate the percentage of this isomer produced. [2]

II. The mass spectrum of 3-nitrobenzenecarboxylic acid has main peaks at m/z 45, 46, 122 and 167. Suggest which species are responsible for **each** of these peaks. [2]

(iii) An impure sample of 3-nitrobenzenecarboxylic acid was obtained.

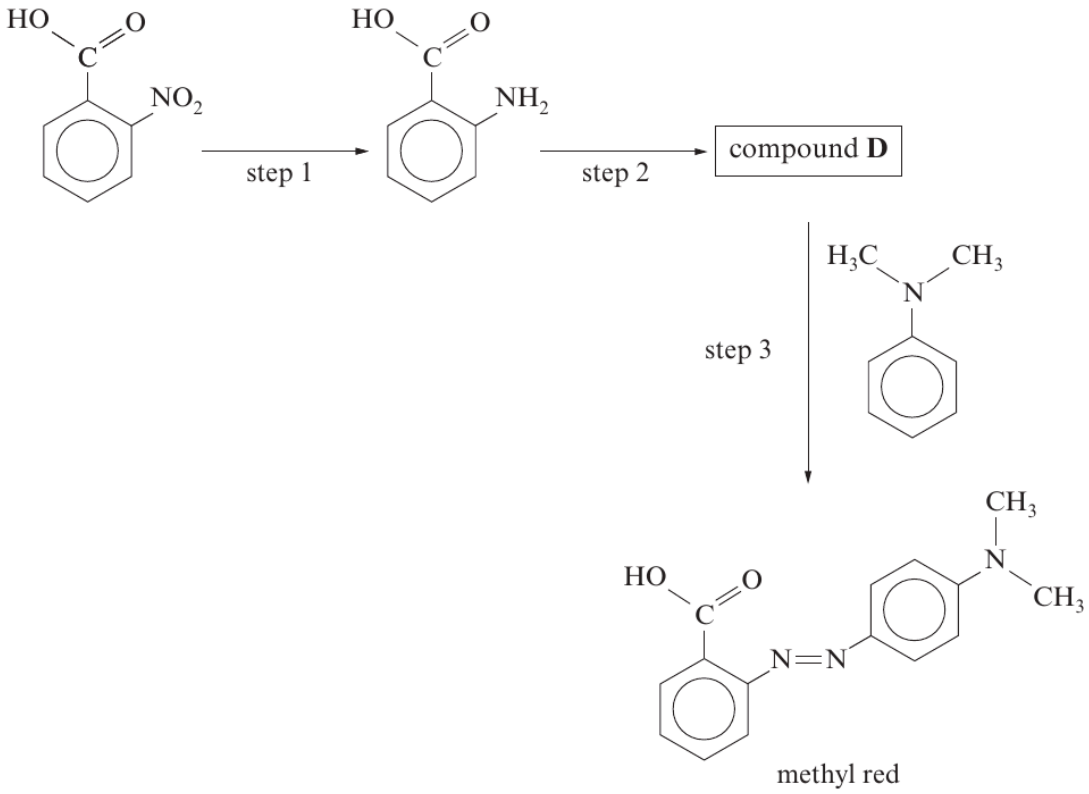
I. State how the melting temperature of the impure sample of 3-nitrobenzenecarboxylic acid would differ from that of pure 3-nitrobenzenecarboxylic acid, if at all. [1]

II. 3-nitrobenzenecarboxylic acid was found to be soluble in boiling water but not in cold water. It has a melting temperature of 142 °C.

Describe how impure 3-nitrobenzenecarboxylic acid could be purified by recrystallisation. Include full experimental details. [4]
(QWC) [1]

QUESTION 5 CONTINUES ON PAGE 16

(b) 2-nitrobenzenecarboxylic acid may be used as a starting material for the production of the indicator methyl red. A reaction scheme for this process is given below.



methyl red

(i) Give the reagent(s) necessary for step 1. [1]

(ii) Step 2 uses a mixture of sodium nitrate(III), $NaNO_2$, with dilute hydrochloric acid. Give the conditions required for this reaction and the structure of the product, compound **D**. [2]

(iii) Methyl red is red below pH 4. Explain the origin of this colour. [2]

(c) Methyl red is used to differentiate between acids and bases. Explain why amines such as ethylamine are bases. [2]

Total [20]

Total Section B [40]

WJEC CBAC

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

A.M. WEDNESDAY, 13 June 2012

Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber/cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C=C	1620 to 1670
C=O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift (ppm)
$-CH_3$	0.1 to 2.0
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$CH_3-C\equiv N$	2.0
$CH_3-C(=O)-$	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
$-O-CH_3$, $-OCH_2-R$, $-O-CH=C<$	3.5 to 4.0
R—OH	4.5 *
$CH_2=C<$	4.8
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* Today there are thousands of different polymers and they are used in a wide range of applications.

Describe the formation of **one** synthetic polymer and **one** natural polymer, both made by condensation polymerisation.

Your answer should include

- the names or structures of the starting materials required for both polymers,
- a structure which shows the repeating unit for the synthetic polymer,
- a structure which shows the relevant linkage in the natural polymer. [5]

QWC [1]

(b) **F** and **G** are two organohalogen compounds.

(chloromethyl) benzene

F **G**

Compound **F** is used in the manufacture of plasticizers and perfumes and behaves as a chloroalkane. Compound **G** is used as a pesticide and as a deodorant.

(i) Draw the displayed formula of compound **F**. [1]

(ii) Name compound **G**. [1]

(iii) State the reagent(s) and condition(s) needed to substitute a chlorine atom into a benzene ring. [2]

(iv) Describe how you could use a chemical test to distinguish between compounds **F** and **G**. Give the expected result for **each** compound and an explanation for any difference in their behaviour. [6]

QWC [1]

(c) Benzenediazonium chloride can be prepared as follows.
Phenylamine is dissolved in excess hydrochloric acid and the solution cooled to 5 °C.
Aqueous sodium nitrate(III), $NaNO_2$, is added gradually until in excess, keeping the temperature at approximately 5 °C.

(i) State why the temperature is kept under 10 °C. [1]

(ii) Give the displayed formula of the compound that forms when benzenediazonium chloride reacts with naphthalene-2-ol in alkaline conditions. [1]

(iii) State what is meant by the term *chromophore*. [1]

Total [20]

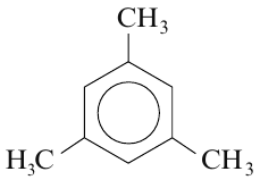
SECTION B

Answer **both** *questions in the separate answer book provided.*

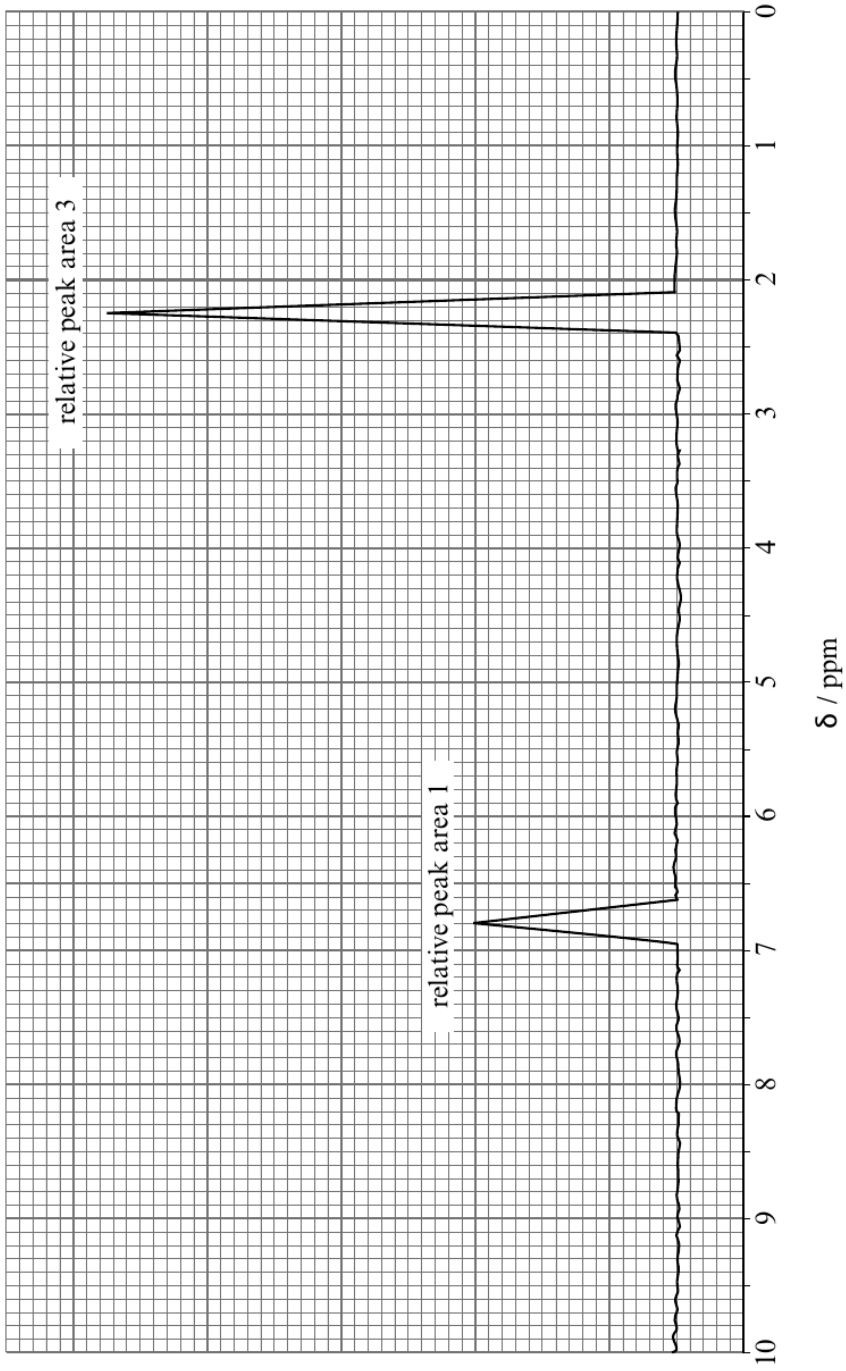
4. *(a)* Describe the structure and bonding in benzene and explain why it is susceptible to electrophilic substitution reactions. [6]
QWC [2]

(b) Methylbenzene can be made by the Friedel-Crafts alkylation of benzene.
Give the equation for this reaction and name a catalyst that can be used. [2]

(c) 1,3,5-Trimethylbenzene (mesitylene) is also an alkylbenzene.

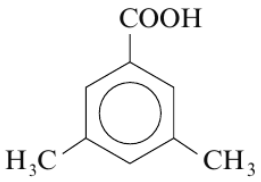


(i) The NMR spectrum of mesitylene is shown opposite.
Use the chemical formula to help you explain the peaks in this spectrum, including the relative peak areas and the absence of splitting. [3]



Turn over.

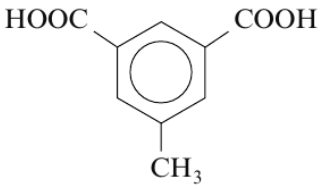
(ii) The presence of three methyl groups makes mesitylene a reactive compound. Mesitylene is oxidised by dilute nitric acid to give 3,5-dimethylbenzenecarboxylic acid.



melting temperature 172 °C

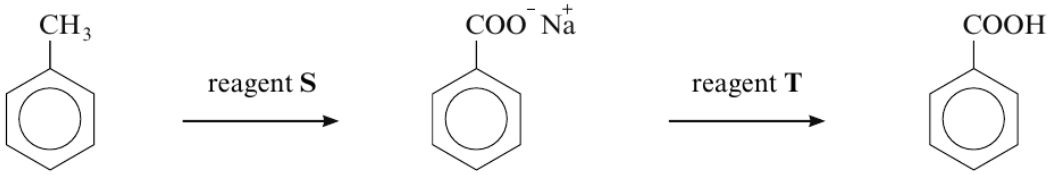
Describe how you would purify a sample of this acid by recrystallisation. The acid is fairly soluble in hot water but nearly insoluble in cold water. [4]

(iii) Further oxidation of mesitylene gives 5-methylbenzene-1,3-dicarboxylic acid.



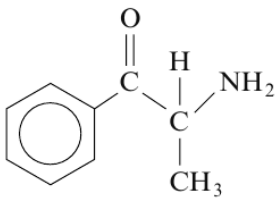
By analogy with the preparation of PET from benzene-1,4-dioic acid and ethane-1,2-diol, give the repeating unit of the polyester formed from 5-methylbenzene-1,3-dicarboxylic acid and ethane-1,2-diol. [1]

(iv) The oxidation of methylbenzene to benzenecarboxylic acid needs stronger oxidising conditions than are required for the oxidation of mesitylene. State the reagents **S** and **T** necessary for this reaction. [2]



Total [20]

5. *(a)* Cathinone, $C_9H_{11}NO$, is a naturally-occurring psycho-active drug.



(i) Explain why this molecule can act as a base. [1]

(ii) You are provided with some information about an **isomer** of cathinone, compound **L**.

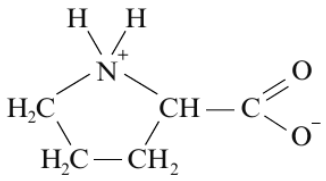
- It contains a peptide linkage.
- It can be hydrolysed by aqueous sodium hydroxide giving primary aromatic amine **M** as one of the products.
- Primary aromatic amine **M** reacts with nitric(III) acid (nitrous acid) to give a phenol with the molecular formula C_7H_8O.

Use **all** this information to suggest a **structural** formula for compound **L**, giving your reasons throughout. [6]

QWC [1]

QUESTION 5 CONTINUES ON PAGES 18 AND 19

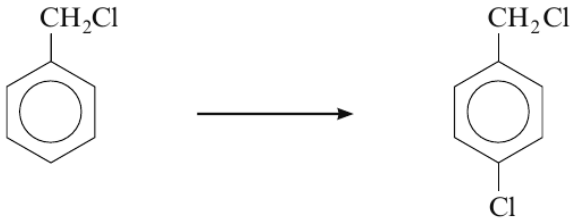
(b) Proline is a cyclic α-amino acid. In an aqueous solution of pH 6.3, proline exists largely as its zwitterion form.



(i) Write the structural formula of proline in its non-zwitterion form. [1]

(ii) Proline forms two different dipeptides when it reacts with aminoethanoic acid. Give the structural formula of **one** of these dipeptides. [1]

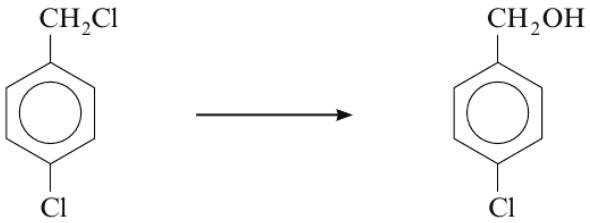
(c) (i) (Chloromethyl)benzene, $C_6H_5CH_2Cl$, reacts with chlorine in the presence of a catalyst to produce a mixture of isomers, **one** of which is 1-(chloromethyl)-4-chlorobenzene.



The mechanism of this electrophilic substitution reaction is similar to the reaction of benzene with chlorine. Give the mechanism for the reaction to produce the 4-isomer.

Your mechanism should show any necessary polarisation, curly arrows, the structure of the intermediate and how the catalyst is regenerated so that it can be used again. [4]

(ii) A student made (4-chlorophenyl)methanol by refluxing 1-(chloromethyl)-4-chlorobenzene (shown in (i)) with aqueous sodium hydroxide.
He obtained a 72% yield.

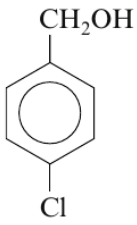


He wrote an outline of his method as follows.

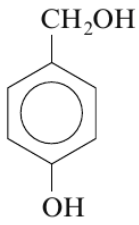
- Place 0.1 mol of the chloro-compound in a flask and add some sodium hydroxide solution of concentration 2 mol dm^{-3}.
- Reflux this mixture using an electrical heater.

Suggest **two** other details that you would need to know before you could test the reliability and validity of his method. [2]

(iii) Explain why the product of the reaction in (ii) is (4-chlorophenyl)methanol and not (4-hydroxyphenyl)methanol. [2]

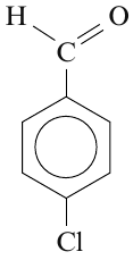


(4-chlorophenyl)methanol



(4-hydroxyphenyl)methanol

(iv) (4-Chlorophenyl)methanol was oxidised to give (4-chlorophenyl)methanal.



The mass spectrum of the product of this reaction showed traces of another compound with molecular ions, m/z, of 156 and 158 in a ratio of 3:1.
Suggest a structural formula for this compound and state why it has these two molecular ions. [2]

Total [20]

Total Section B [40]

END OF PAPER

WJEC CBAC

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. WEDNESDAY, 12 June 2013

Infrared Spectroscopy characteristic absorption values

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C≡N	2100 to 2250
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O—H	2500 to 3550
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Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

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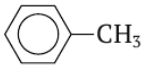
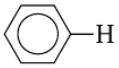
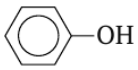
$CH_3-C\equiv N$	2.0
$CH_3-C(=O)-$	2.0 to 2.5
$-CH_2-C(=O)-$	2.0 to 3.0
	2.2 to 2.3
$R-CH_2-$Halogen	3.3 to 4.3
$-O-CH_3$, $-OCH_2-R$, $-O-CH=C<$	3.5 to 4.0
$R-OH$	4.5 *
$CH_2=C<$	4.8
	6.5 to 7.5
	7.0 *
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

Turn over.

Examiner only

2. Mauveine is a purple dye that was developed by Perkin in 1856 and was one of the first organic compounds to be synthesised on a large scale. He is credited with launching the synthetic chemical industry.

(a) Give the name for the part of a molecule that causes it to be coloured. [1]

.....

(b) The dye mauveine often contains a mixture of impurities. Iwan and Georgia wanted to confirm that a sample of the dye was impure.

(i) Iwan used the melting temperature of the sample to confirm that the sample was impure. Give **one** way that the melting temperature would show this. [1]

.....

.....

(ii) Georgia used gas chromatography to confirm that the sample was impure. State what information she obtained using this method that Iwan could not obtain from the melting temperature. [2]

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.....

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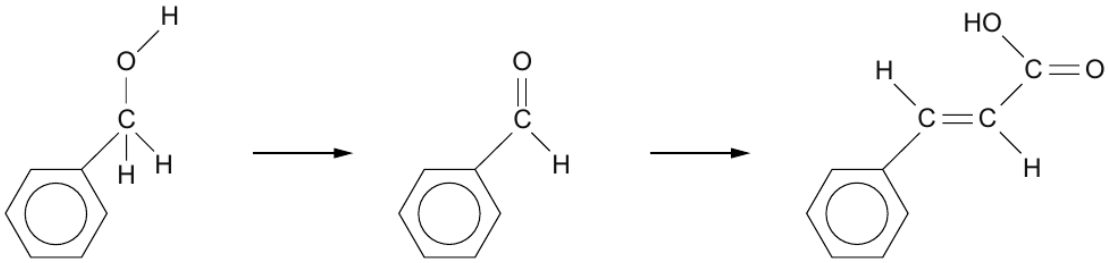
Examiner only

(c) Another compound synthesised by Perkin was cinnamic acid. Cinnamic acid can be produced in two steps from phenylmethanol as shown below.



phenylmethanol benzenecarbaldehyde cinnamic acid

(i) Give the reagent(s) and condition(s) required to obtain a sample of benzenecarbaldehyde from phenylmethanol. [2]

Reagent(s) .....

Condition(s) .....

(ii) The conversion of phenylmethanol to benzenecarbaldehyde has a yield of 86%. Calculate the mass of benzenecarbaldehyde that could be produced from 10.0 g of phenylmethanol. [3]

1094 010007

Mass = ... g

(iii) The ^{1}H NMR high resolution spectrum of cinnamic acid contains peaks in the area 7.0-7.5 with an area of 5 due to the benzene ring. Describe what other features you would expect to see in the spectrum. [4]

.....

.....

.....

.....

.....

Total [13]

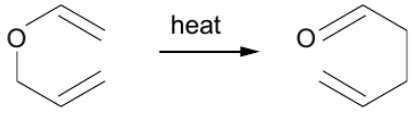
13

Turn over.

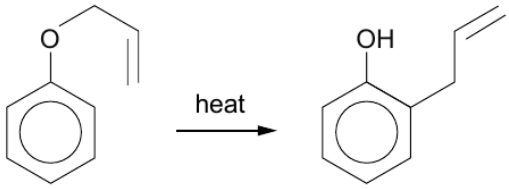
3. *Read the passage below and then answer the questions in the spaces provided.*

Rearrangement reactions

The many different chemical reactions that occur for organic compounds can be classified in different ways, and reaction types such as addition, substitution and elimination are familiar to all students of organic chemistry. A different group of organic reactions is the rearrangement reactions, where the product has the same molecular formula as the starting material. One of the first rearrangement reactions to be identified was the Claisen rearrangement and two examples of this are given below.



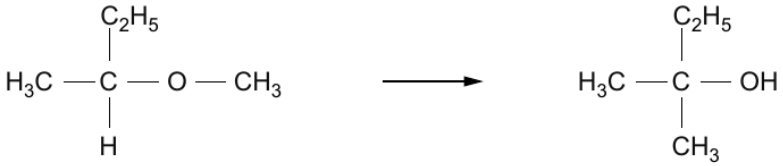
Claisen rearrangement



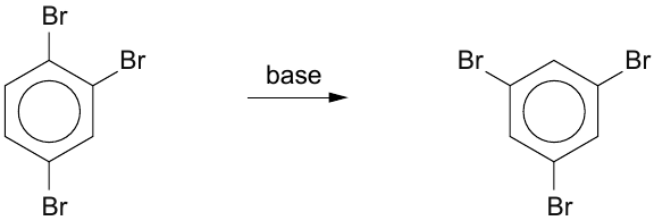
aromatic Claisen rearrangement

This rearrangement can occur in a wide range of molecules, and so it is used in the production of a number of biologically active molecules including *Pancratistatin* and *Halomon*, both of which have antitumour activity. The rates of these reactions are much higher in polar solvents, especially those that can form hydrogen bonds, and the rate can also be increased by using catalysts containing aluminium compounds.

Another group of rearrangement reactions is the 1,2-shift reactions where a side chain or a functional group moves from one atom to an adjacent carbon atom. An example is the 1,2-Wittig rearrangement where an alkoxy compound rearranges to form an alcohol. An alkyl lithium compound is used to initiate the reaction.



1,2-rearrangement reactions can also occur in benzene compounds, and one example is the halogen dance reaction which is shown below.



Rearrangement reactions are of great interest in modern chemistry as they meet the aims of green chemistry and provide an alternative to multistep processes where each part of a molecule is added in turn. They also provide a straightforward route to the formation of carbon-carbon covalent bonds.

– End of passage –

Examiner only

(a) The products of rearrangement reactions have the same molecular formulae as the reactants *(lines 3-4)*. State the term given to different molecules that share the same molecular formula. [1]

.....

(b) A chemist used infrared spectroscopy to study the factors that affect the rate of the aromatic Claisen rearrangement shown in *line 7*.

(i) Give the difference(s) between the infrared spectra of the reactant and product. [1]

.....

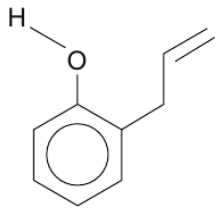
.....

(ii) Give the reagent(s) and observation(s) for a chemical test that would show that the product is a phenol. [2]

Reagent(s) .....

Observation(s) .....

(iii) The reaction is faster in solvents that can form hydrogen bonds, such as methanol or water *(lines 10-11)*. Draw the hydrogen bonding that can occur between the product shown and a molecule of water. [2]



(c) The products of the aromatic Claisen and 1,2-Wittig rearrangements shown *(lines 7* and *17)* both contain —OH groups. Explain why the acidity of the two molecules is very different. [3]

QWC [1]

.....

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Examiner only

(d) Many of these rearrangement reactions are useful as they create carbon-carbon covalent bonds *(lines 23-24)*. Another way of forming carbon-carbon covalent bonds is the reaction of hydrogen cyanide, HCN, with a carbonyl compound.

Draw the mechanism of the reaction of ethanal with hydrogen cyanide and classify the mechanism. [4]

Classification of mechanism .....

Total [14]

Total Section A [40]

14

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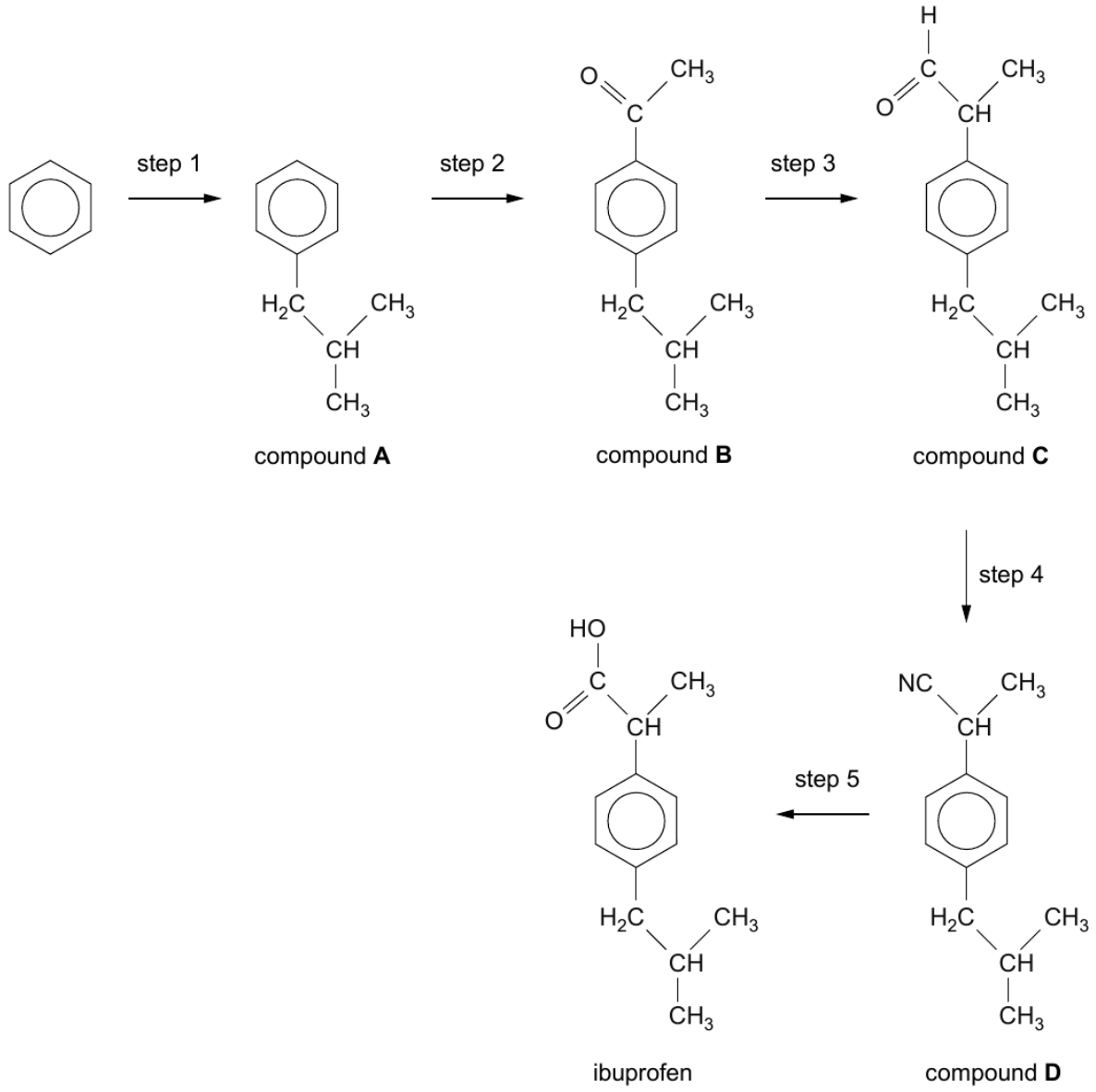
SECTION B

Answer **both** *questions in the separate answer book provided.*

4. Ibuprofen is a common drug taken as an analgesic and anti-inflammatory treatment.

A possible route to the synthesis of ibuprofen is shown below.



(a) Step 1 is a Friedel-Crafts alkylation reaction. Give the reagent(s) and condition(s) required for this step. [3]

(b) Compounds **B** and **C** can be analysed using chemical tests.

(i) Give a chemical test that would give a positive result for **both** compound **B** and compound **C**. Include reagent(s) and the observation(s) expected for a positive result. [2]

(ii) Give a chemical test that would give a positive result for compound **C** but **not** for compound **B**. Include reagent(s) and the observation(s) for both compounds. [2]

(c) Compound **C** shows optical isomerism. Discuss this statement.
Your answer should include:

- What is meant by optical isomerism.
- What feature of compound **C** allows it to exhibit optical isomerism.
- Diagrams to show the two optical isomers of compound **C**.
- How the two optical isomers of compound **C** can be distinguished. [4]

QWC [1]

(d) Give the reagent(s) and condition(s) required for step 5 and classify the reaction that occurs. [3]

(e) A student investigating alternative methods of producing ibuprofen suggests that it would be better to convert compound **C** into ibuprofen in a one-step process. Discuss whether this is correct.
Your answer should include:

- The reagent(s) and condition(s) for a reaction expected to convert compound **C** directly into ibuprofen.
- Why it is generally better to use one step rather than two or more steps when producing a desired compound.
- A suggestion of why a two-step process is chosen for the synthesis of ibuprofen from compound **C** rather than a one-step process. [4]

QWC [1]

Total [20]

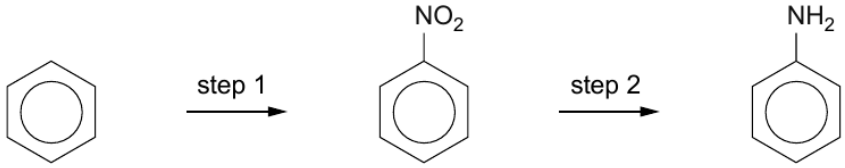
5. This question focuses on molecules that contain the —NH_2 group.

(a) Phenylamine and propylamine are both bases, with phenylamine being a weaker base than propylamine.

(i) Explain why both propylamine and phenylamine can act as bases. [2]

(ii) Give a reason why phenylamine is a weaker base than propylamine. [2]

(iii) Phenylamine can be prepared from benzene in a two-step process.



I. Step 1 uses a mixture of concentrated nitric and sulfuric acids to produce NO_2^+ during the reaction. Draw the mechanism of the reaction between NO_2^+ and benzene. [3]

II. During step 1, some dinitrobenzene is produced. Suggest a method of separating the different compounds in the product mixture. [1]

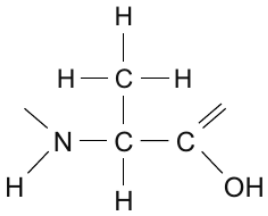
III. Give the reagent(s) required to produce phenylamine from nitrobenzene in step 2. [2]

(b) 1,6-diaminohexane is used to make Nylon-6,6, which is a polyamide.

(i) Draw the **skeletal** formula for the molecule that would be combined with 1,6-diaminohexane to make Nylon-6,6. [1]

(ii) Nylon is an example of a condensation polymer. Give **two** differences between condensation polymerisation and addition polymerisation. [2]

(c) Amino acids contain both — NH_2 and — COOH groups, such as in the molecule below.



alanine *(2-aminopropanoic acid)*

(i) Alanine dissolves in strong acid. Draw the carbon-containing species that would be present in this solution. [1]

(ii) When two molecules of alanine react together they make a dipeptide. Draw the structure of this dipeptide, circling the peptide link. [2]

(iii) Alanine has a melting temperature of 258 °C. This is much higher than compounds with molecules of a similar size such as butanoic acid, which has a melting temperature of −8 °C. Explain why the melting temperatures of these two compounds are so different. [2]

(iv) Alanine can undergo decarboxylation. Give the reagent(s) required for this reaction and identify the organic product formed. [2]

Total [20]

Total Section B [40]

END OF PAPER

WJEC CBAC

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. MONDAY, 13 January 2014

Infrared Spectroscopy characteristic absorption values

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Nuclear Magnetic Resonance Spectroscopy

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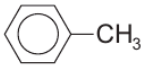
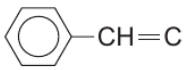
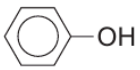
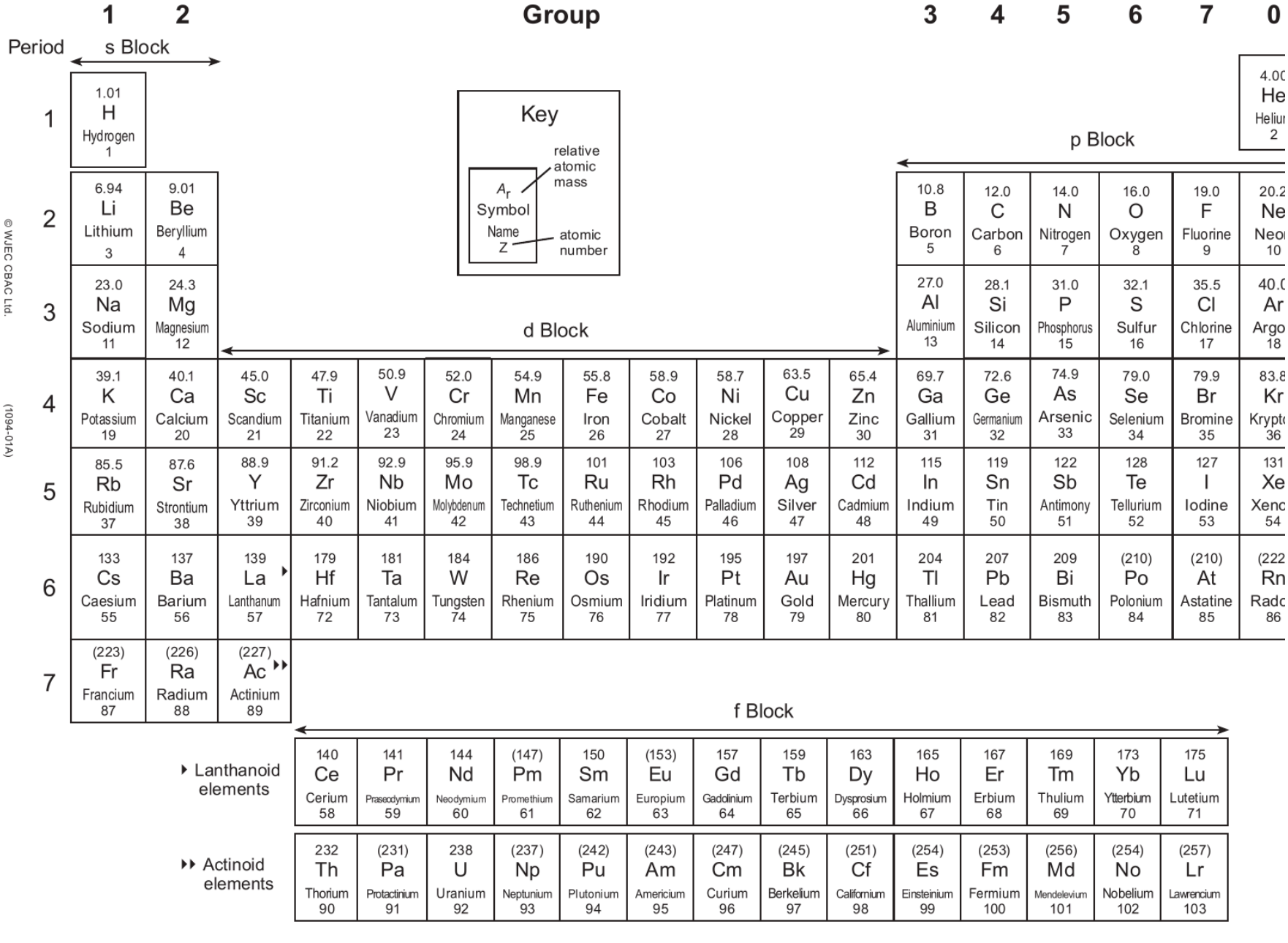
	2.2 to 2.3
$R-CH_2Cl$	3.3 to 4.3
$R-OH$	4.5 *
$-C=CH-CO$	5.8 to 6.5
	6.5 to 7.0
	7.0 *
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

Turn over.

THE PERIODIC TABLE



WJEC CBAC

GCE A level

1094/01-A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. MONDAY, 13 January 2014

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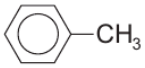
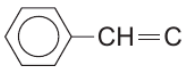
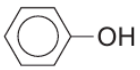
	2.2 to 2.3
$R-CH_2Cl$	3.3 to 4.3
$R-OH$	4.5 *
$-C=CH-CO$	5.8 to 6.5
	6.5 to 7.0
	7.0 *
$R-C(=O)-H$	9.8 *
$R-C(=O)-OH$	11.0 *

*variable figure dependent on concentration and solvent

Turn over.

Examiner only

SECTION A

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

1. *(a)* 1-Chloropentane can be made by the free radical chlorination of pentane, in a similar way to the reaction of methane with chlorine.

(i) Give the equation for the reaction of pentane with chlorine, showing the displayed formula of 1-chloropentane as part of your answer. [1]

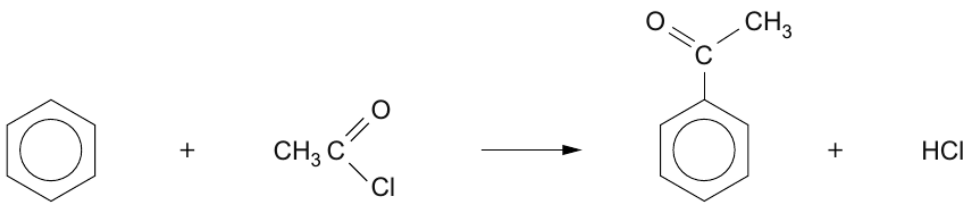
(ii) The free radical reaction of pentane with chlorine gives other chlorinated organic products. Give the structural formula of the carbon-containing free radical that leads to the formation of 2-chloropentane. [1]

.....

(b) Pentylbenzene can be produced by the reaction of 1-chloropentane and benzene in a Friedel-Crafts reaction. State the name of a catalyst that can be used in this reaction. [1]

.....

(c) A Friedel-Crafts reaction can be carried out with ethanoyl chloride in place of 1-chloropentane. This reaction gives phenylethanone as the main organic product.



phenylethanone

(i) State what is seen when a few drops of phenylethanone are added to a solution of 2,4-dinitrophenylhydrazine. [1]

.....

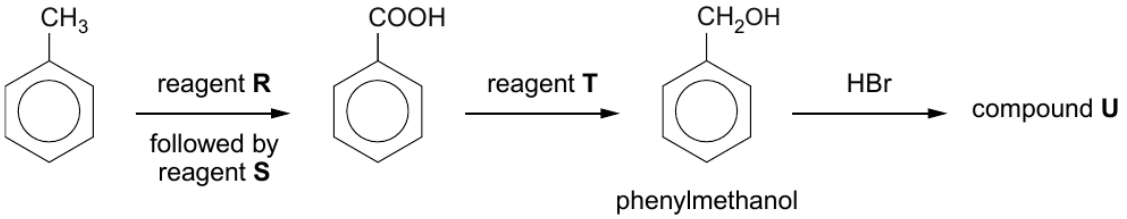
Examiner only

(ii) This preparation of phenylethanone also gives small traces of an impurity. This impurity has a molecular formula $C_{10}H_{10}O_2$ and reacts in a similar way to phenylethanone when it is treated with 2,4-dinitrophenylhydrazine. It does not react with Tollens' reagent. Suggest a displayed formula for this impurity, giving a reason for your choice. [2]

.....

.....

(d) Methylbenzene can be oxidised to benzoic acid by heating it strongly with an alkaline solution of reagent **R** followed by treatment with reagent **S**. The benzoic acid can then be used to produce a number of other compounds. A reaction sequence is shown below.



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(i) State the name of reagent **R**. ..... [1]

(ii) State the name of reagent **S**. ..... [1]

(iii) State the name of reagent **T**. ..... [1]

(iv) Give the displayed formula of the organic compound **U**. [1]

(e) State and explain how the infrared spectrum of benzoic acid would differ from that of phenylmethanol. [2]

.....

.....

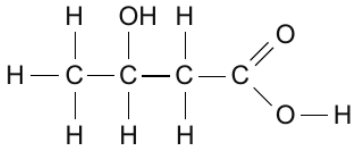
.....

Total [12]

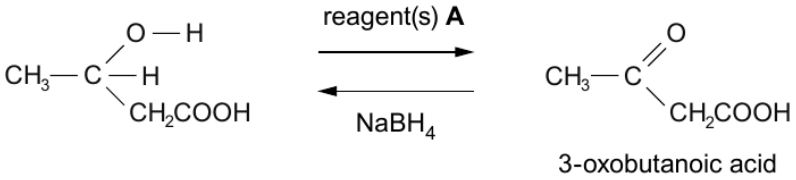
Examiner only

2. 3-Hydroxybutanoic acid is a white solid that can react as a carboxylic acid and an alcohol.

(a) Indicate the position of any chiral centre in the formula of 3-hydroxybutanoic acid by use of an asterisk (*). [1]



(b) The acid can be oxidised to an oxoacid by using reagent(s) **A**. This oxoacid can then be reduced back to the hydroxyacid by sodium tetrahydridoborate(III), $NaBH_4$.



3-oxobutanoic acid

(i) State the name(s) of reagent(s) **A**. [1]

.....

(ii) The reduction of the oxoacid gives 3-hydroxybutanoic acid, which is present as a racemic mixture.

I State what is meant by the term *racemic mixture*. [1]

.....

.....

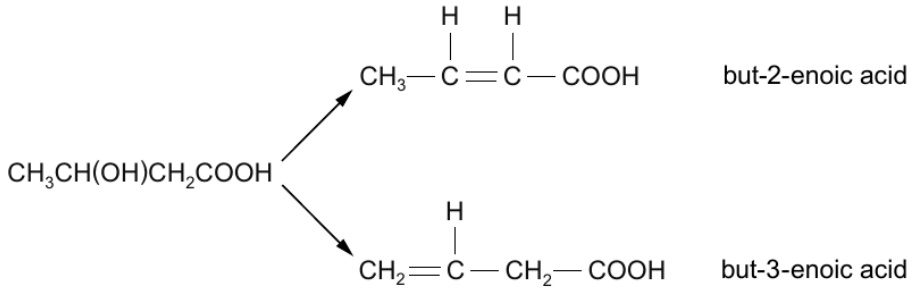
II State the effect (if any) that a racemic mixture has on the plane of polarised light. [1]

.....

.....

Examiner only

(c) 3-Hydroxybutanoic acid readily undergoes an elimination reaction to form a mixture of unsaturated acids.



(i) State which of these unsaturated acids exists as *E*-*Z* isomers, giving a reason for your answer. [1]

.....

.....

.....

(ii) A scientist reported that the yield of the products was

but-2-enoic acid	89 %
but-3-enoic acid	4 %
together with unreacted 3-hydroxybutanoic acid	7 %

State any additional information that another scientist would have to know so that the experiment could be repeated to confirm these yields. [2]

1 .....

2 .....

(d) Both 3-hydroxybutanoic acid and 3-oxobutanoic acid will undergo the triiodomethane (iodoform) reaction. State the reagent(s) used for this reaction and the observation made. [2]

Reagent(s) .....

Observation .....

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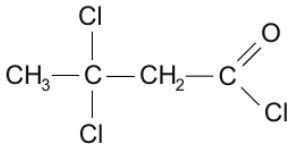
Examiner only

(e) 3-Oxobutanoic acid reacts with phosphorus(V) chloride to give 3,3-dichlorobutanoyl chloride.



Describe the NMR spectrum of this chloro-compound.
In your answer you should include the following points, **giving an explanation for each**.

- the number of peaks (and their approximate position in ppm)
- the relative peak areas
- any splitting pattern

[3]
QWC [1]

Total [13]

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010007

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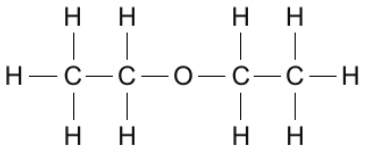
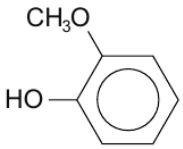
3. *Read the passage below and then answer the questions in the spaces provided.*

The chemistry of some compounds containing the ether (R–O–R) linkage

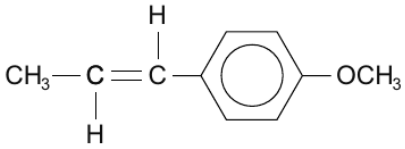
Organic compounds containing the R–O–R linkage, where R is alkyl or aryl are very common. This is due in part to the stability of the C—O bond. Some examples are shown below.



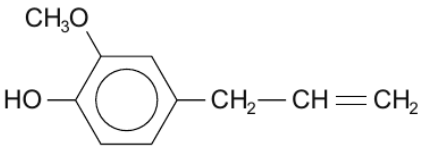
ethoxyethane



guaiacol



anethole



eugenol

Ethoxyethane (diethyl ether) is one of the most familiar compounds containing the ether linkage. It can be made by heating ethanol with an excess of concentrated sulfuric acid, which acts as a dehydrating agent.

$$2CH_3CH_2OH \xrightarrow{-H_2O} CH_3CH_2OCH_2CH_3$$

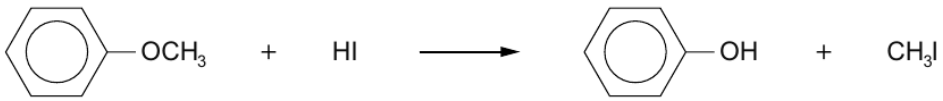
Another method is by reacting bromoethane with sodium ethoxide (a source of the ethoxide ion).

$$CH_3CH_2Br + {}^{-}OCH_2CH_3 \longrightarrow CH_3CH_2OCH_2CH_3 + Br^{-}$$

ethoxide ion

Ethoxyethane has a boiling temperature of 35 °C whereas ethanol, a smaller molecule, boils at 78 °C. The solubility of these two compounds in water also varies. Ethanol is completely miscible with water but ethoxyethane has a much reduced solubility.

The strong C—O bond means that compounds such as ethoxyethane and methoxybenzene have relatively few reactions. However, carbon–oxygen bond fission occurs when they are heated with concentrated hydrobromic (HBr) or hydriodic acid (HI).



methoxybenzene

Examiner only

20 Naturally occurring compounds that contain the ether linkage often owe their reactions to other functional groups present in the molecule. Both eugenol (found in cloves) and guaiacol (from wood) have medicinal uses. Anethole (occurring in aniseed) has a promising use as an insecticide and is also effective against some bacteria and fungi.

- End of passage -

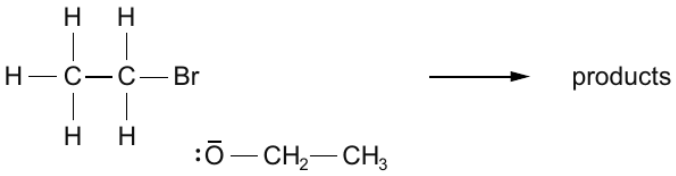
(a) (i) Bethan prepared some ethoxyethane *(line 6)* by reacting ethanol with concentrated sulfuric acid. She used 69 g of ethanol (M_r = 46) and obtained a 45 % yield of ethoxyethane (M_r = 74). Calculate the mass of ethoxyethane obtained. [3]

Mass = ... g

(ii) One of the reasons for only obtaining a 45 % yield of ethoxyethane was that sulfuric acid reacted with ethanol in a different reaction. State the organic product of this side reaction. [1]

.....

(iii) Bethan would have obtained a higher percentage yield of ethoxyethane if she had reacted bromoethane with sodium ethoxide *(line 10).* This reaction is an example of nucleophilic substitution. Complete the mechanism below by inserting curly arrows and appropriate partial charges (δ+, δ-). [2]



(iv) Ethoxyethane has a much lower boiling temperature than ethanol because its molecules are unable to hydrogen bond with each other. State the feature of a molecule that needs to be present for hydrogen bonding to occur. [1]

.....

.....

Examiner only

(b) Guaiacol *(line 4)* reacts with (aqueous) bromine.

(i) By analogy with the reaction of phenol with (aqueous) bromine, suggest a displayed formula for the organic product of the reaction between guaiacol and (aqueous) bromine. [1]

(ii) Describe what is seen during this reaction. [1]

.....

(c) The article shows the formulae of anethole and eugenol *(line 5)*. State a reagent that will react with eugenol but not with anethole, giving the observation. [2]

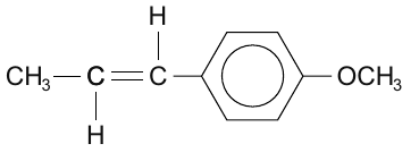
Reagent .....

Observation .....

(d) (i) State the molecular formula of anethole *(line 5)*. [1]

.....

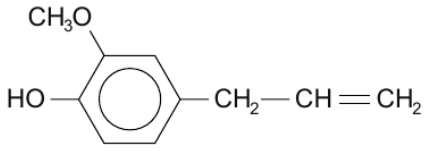
(ii) The article describes C—O bond fission of an ether linkage by hydrobromic acid *(lines 17-18)*. Suggest a displayed formula for the aromatic compound formed when **anethole** reacts with hydrobromic acid. [1]



anethole

displayed formula of product

(e) An isomer of eugenol *(line 5)*, compound **Y**, reacts with sodium carbonate giving carbon dioxide. Suggest a displayed formula for compound **Y** and state the name of the functional group present in the organic compound that produces carbon dioxide in this reaction. [2]



eugenol

displayed formula for compound **Y**

Functional group .....

Total [15]

Total Section A [40]

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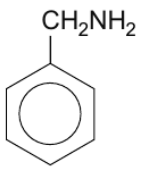
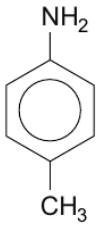
SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* The formulae of the isomers phenylmethylamine and 4-methylphenylamine are shown below.



phenylmethylamine



4-methylphenylamine

These compounds are colourless liquids with different boiling temperatures.

(i) Give the name of a technique that can be used to separate these two liquids. [1]

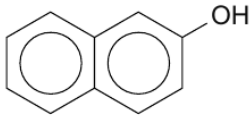
(ii) State and explain how the mass spectra of these two compounds would differ. [1]

(iii) Phenylmethylamine reacts with ethanoyl chloride to give a white solid, compound **G**.

I Give the equation for this reaction. [1]

II Compound **G** was purified by recrystallisation from ethanol. It has a melting temperature of 60 °C. Describe how you would recrystallise compound **G** from ethanol to obtain a pure dry product. You should assume that you are starting with cold ethanol and impure solid compound **G**. Washing of the purified solid product is unnecessary. [5]
QWC [1]

(iv) 4-Methylphenylamine can be used to make an azo dye by reaction of its diazonium compound with an alkaline solution of naphthalene-2-ol.

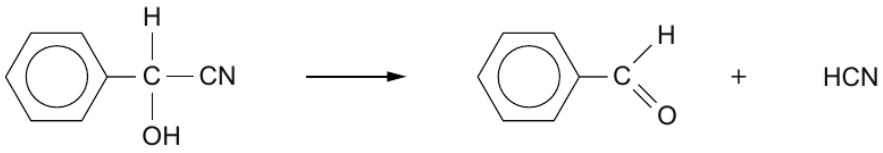


naphthalene-2-ol

I State how the diazonium compound can be made from 4-methylphenylamine, giving the reagents used and any essential conditions. [2]

II Give the structural formula of the azo dye produced. [1]

(b) A species of millipede can protect itself by producing hydrogen cyanide. This poisonous gas is produced from mandelonitrile by enzyme action.



2-phenyl-2-hydroxyethanenitrile (mandelonitrile) benzaldehyde

The reaction can be carried out in the reverse direction in the laboratory.

(i) Draw the mechanism for the reaction between benzaldehyde and the cyanide ion. State the type of mechanism occurring. [4]

(ii) Mandelonitrile is a yellow material. State the general name for groups that cause colour in organic compounds and give the appearance of mandelonitrile when viewed under blue light, giving a reason for your answer. [3]

(iii) Give the structural formula of the organic compound obtained when mandelonitrile is warmed with dilute hydrochloric or sulfuric acid. [1]

Total [20]

TURN OVER FOR QUESTION 5

Examiner only

SECTION A

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

1. *(a)* Complete the gaps in the following sentences choosing from the words: [3]

blue **yellow** **higher** **lower**

Each word can be used once, more than once or not at all.

Benzene is a colourless compound that absorbs energy in the ultraviolet region of the electromagnetic spectrum.

Nitrobenzene is a yellow compound that absorbs energy in the ..... region of the visible spectrum.

The absorption of energy for benzene occurs at a ..... energy and at a ..... frequency than for nitrobenzene.

(b) Methylbenzene can be produced from benzene using a Friedel-Crafts reaction.

(i) Give an equation for this reaction. [1]

(ii) State the role of the catalyst used in this reaction, apart from increasing the rate. [1]

.....

.....

Examiner only

(c) The Friedel-Crafts reaction can also be used to introduce more than one methyl group to the benzene ring giving, for example, 1,4-dimethylbenzene.

The low resolution proton NMR spectrum of this compound shows two peaks with a peak area ratio of 3:2.

Explain how 1,4-dimethylbenzene produces this spectrum. [2]

.....

.....

.....

.....

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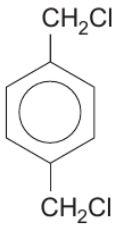
(d) 1,4-Dimethylbenzene reacts with chlorine in a free radical reaction to give the liquid 1,4-di(chloromethyl)benzene.



(i) State the names of **two** methods that could be used to show that a sample of this compound is pure. [2]

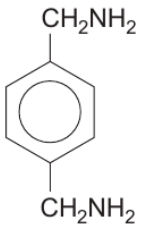
Method 1 .....

Method 2 .....

(ii) Give the displayed formula of the compound produced when 1,4-di(chloromethyl)benzene reacts with an excess of aqueous sodium hydroxide. [1]

Examiner only

(e) (i) 1,4-Di(chloromethyl)benzene reacts with ammonia to give the diamine below.



Draw the repeating section of the polymer obtained when this diamine reacts with benzene-1,4-dicarboxylic acid. [1]

(ii) The polymer obtained in *(e)*(i) above contains a peptide linkage.

State the name of a naturally occurring material that also contains a peptide linkage. [1]

.....

Total [12]

12

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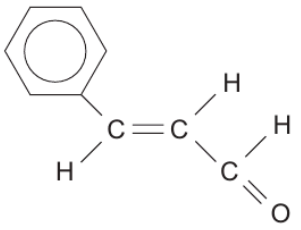
SECTION B

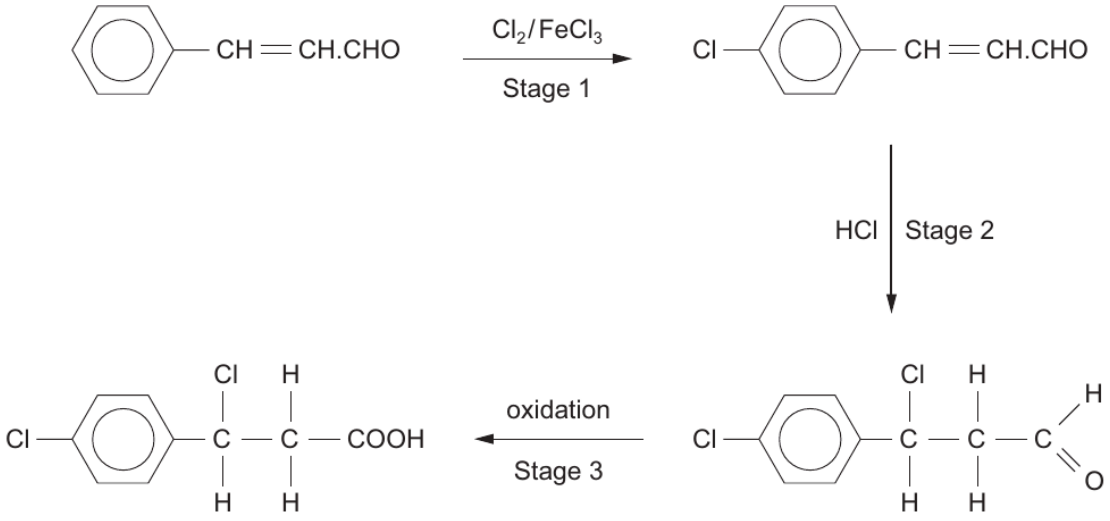
Answer **both** *questions in the separate answer book provided.*

4. *(a)* Cinnamaldehyde (3-phenylprop-2-enal) is a pale yellow liquid that occurs in the oil obtained from the bark of cinnamon trees.



cinnamaldehyde

An organic chemist suggested the following method for producing compound **M** from cinnamaldehyde.



compound **M**

(i) Suggest **two** reasons why the reaction of cinnamaldehyde with chlorine is **unlikely** to give only the compound shown and give the displayed formula of another possible product. [3]

(ii) Give the displayed formula of another product that may be formed when hydrogen chloride is added across the double bond in the second stage, explaining why this can occur. [2]

(iii) State the name of a suitable oxidising agent for stage 3. [1]

(iv) Explain why compound **M**, made in this way from cinnamaldehyde, has no effect on the plane of polarised light. [2]

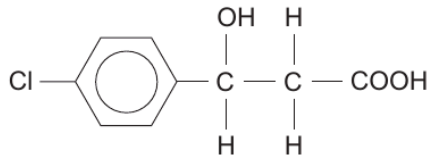
QWC [1]

(v) Bethan attempted to reverse stage 3 by using a reducing agent. Suggest a suitable reducing agent that she should use and give the displayed formula of a different product that could be an impurity in her product. [2]

(b) You are given a pure sample of compound **M** and asked to carry out some reactions with it.

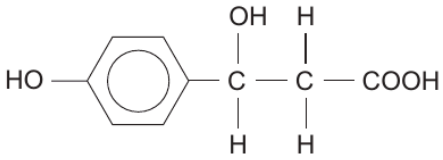
(i) A sample is added to aqueous sodium hydrogencarbonate. State what is seen during this reaction and name the functional group that has been confirmed. [2]

(ii) Compound **M** is heated under reflux with aqueous sodium hydroxide, followed by acidification. The organic product of this reaction is compound **N**.



compound **N**

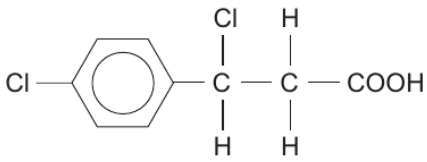
Explain why compound **N** is formed in preference to compound **P**.



compound **P**

[2]

(c) Compound **R** is an isomer of compound **M** (whose formula is shown below).

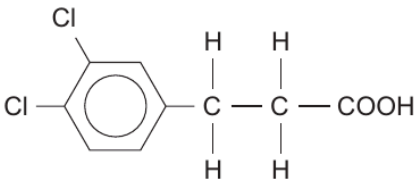


compound **M**

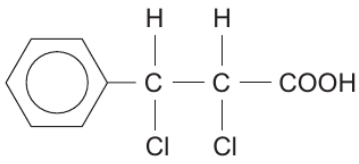
Tests on compound **R** show that it:

- does not contain a chiral centre;
- has an aromatic-containing fragment at m/z 77 in its mass spectrum;
- is not quickly hydrolysed by the addition of water.

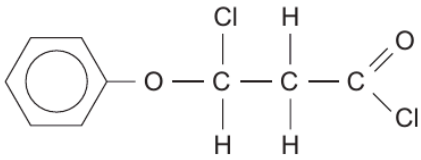
Three compounds that do **not** fit this information are shown below.



compound **1**



compound **2**



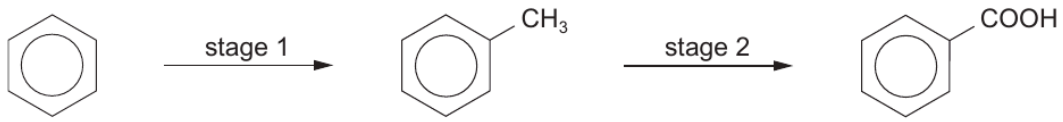
compound **3**

Discuss why **each** of these structures is **not** the formula for compound **R**, giving **one** reason for **each** compound. Give the displayed formula of a compound of your choice that **does fit** the information given for compound **R**. [4]

QWC [1]

Total [20]

5. Benzene can be made into benzenecarboxylic acid (benzoic acid) using a two-stage process.



(a) Stage 1 proceeds using a mechanism that is similar to that of the halogenation of benzene. Describe the reaction in stage 1. You should include

- the reagent(s) needed
- the type of reaction
- the conditions needed
- details of the mechanism. [7]

(b) Stage 2 involves refluxing methylbenzene with alkaline potassium manganate(VII), filtering the mixture whilst it is still hot and then adding hydrochloric acid. This produces a white precipitate of benzoic acid.

(i) Explain what is meant by *reflux*. [2]

(ii) Write the **balanced** equation for the reaction in stage 2 – the oxidation of methylbenzene to benzoic acid. Use [O] to represent alkaline potassium manganate(VII). [1]

(iii) Apart from neutralising any excess alkali, why is hydrochloric acid added after filtration? [1]

(iv) Benzoic acid is very much more soluble in hot water than it is in cold water. Use this fact to describe how you would purify the benzoic acid produced in stage 2. [3]

(v) Describe a method to show if the benzoic acid is now pure. [1]

(vi) A student used 10.0 g of benzene to prepare benzoic acid as described above. He obtained 3.8 g of pure benzoic acid. Calculate the percentage yield of this process. [3]

(vii) The percentage yield obtained in this particular preparation is usually low. Describe **two** reasons why this percentage yield is low, even if the reaction is carried out carefully. [2]

Total [20]

Total Section B [40]

END OF PAPER

wjec cbac

GCE A level

1094/01-A

S16-1094-01A

CHEMISTRY – DATA SHEET
FOR USE WITH CH4

P.M. TUESDAY, 14 June 2016

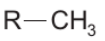
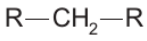
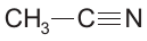
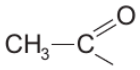
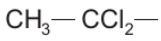
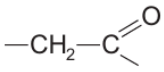
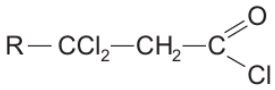
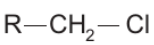
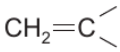
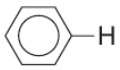
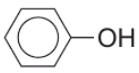
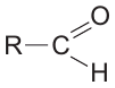
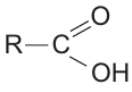
Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber / cm^{-1}
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C═C	1620 to 1670
C═O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n–1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift / ppm
	0.1 to 2.0
	0.9
	1.3
	2.0
	2.0 to 2.5
	2.0 to 2.5
	2.0 to 3.0
	2.5 to 3.0
	3.3 to 4.3
	4.5 *
	4.8
	6.5 to 7.5
	7.0 *
	9.8 *
	11.0 *

*variable figure dependent on concentration and solvent

Turn over.

END OF QUESTION PACK

28 questions · 465 marks · ~12 h 24 min
Source: WJEC CH4 (2008 modular spec, Jan 2010 – Jun 2016)
Curated for WJEC Chemistry 2015 spec A2 Unit 4 — Topic 1 (4.2)