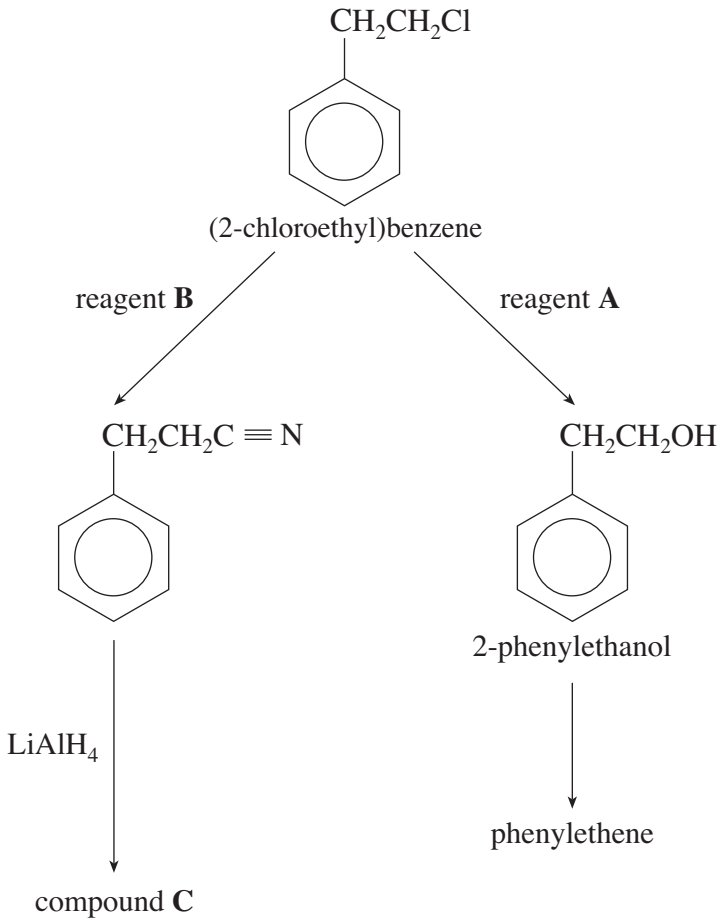
Examiner only

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]

.....

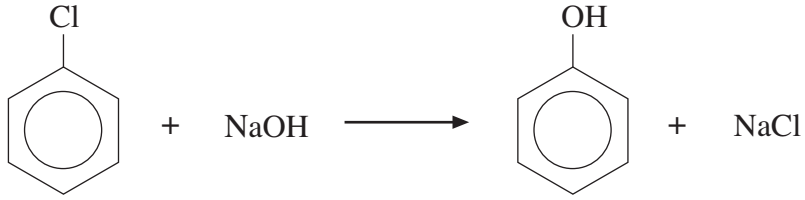
(iv) Give the displayed formula of compound **C**. [1]

SECTION B

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

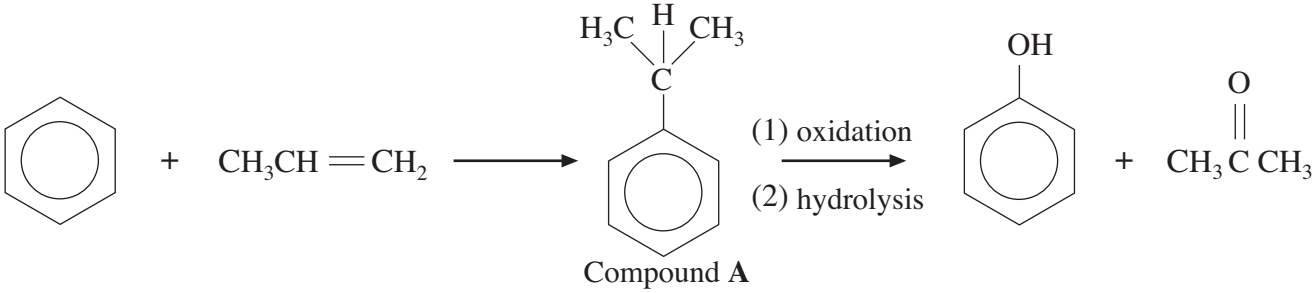
4. *(a)* Chlorobenzene, C_6H_5Cl, is an important industrial chemical. It can be made in the laboratory by reacting benzene and chlorine in the presence of an iron or iron(III) chloride catalyst.
Give the mechanism for this electrophilic substitution reaction. [4]

(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]

Examiner only

2. *(a)* Explain the difference in structure between *primary* and *secondary* alcohols. [1]

.....

.....

(b) Quantitative analysis of an alcohol shows that its percentage composition by mass is C 68.1%, H 13.7% and O 18.2%. It has a relative molecular mass of 88.1.

Calculate the empirical formula of the alcohol and show that its molecular formula is the same as the empirical formula. [3]

.....

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(c) The following compounds have the same molecular formula, $C_5H_{10}O$.

A $CH_3CH_2COCH_2CH_3$ **B** $CH_3CH_2CH_2CH_2CHO$

C $CH_3CH_2CHCHCH_2OH$ **D** $CH_2CHCH_2CH(OH)CH_3$

(i) Draw the structure of an isomer of **B** that is also an aldehyde. [1]

(ii) I. State which **one** of the compounds **A–D** exhibits E-Z (trans-cis) isomerism. [1]

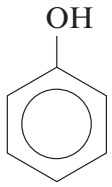
.....

II. Draw the structures of **both** isomers. [1]

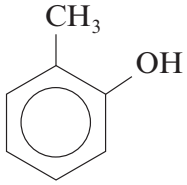
3. *Read the passage below and then answer the questions in the spaces provided.*

Phenol

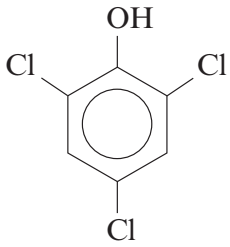
Phenol, formula C_6H_5OH, has an hydroxyl group joined directly to an aromatic ring.



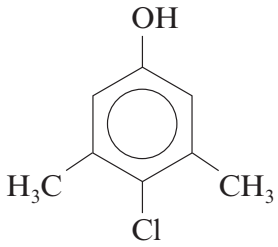
Phenol has many derivatives including 2-methylphenol.



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]

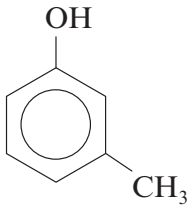
.....

.....

.....

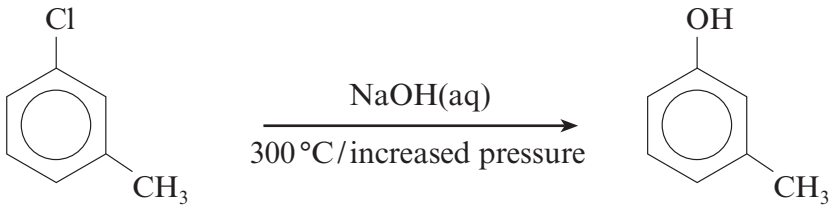
.....

(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]

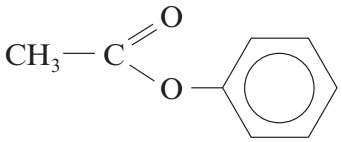
1. .....

.....

2. .....

.....

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

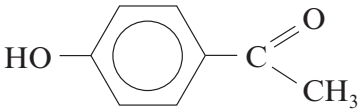


compound **W**

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

.....

(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 .....

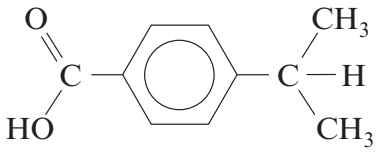
Total [13]

Examiner only

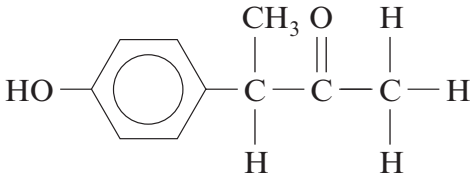
SECTION A

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

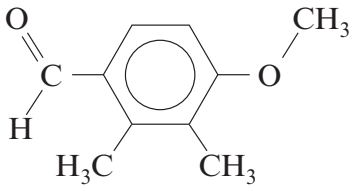
1. This question focuses on the chemistry of some of the many compounds which share the molecular formula $C_{10}H_{12}O_2$. Four compounds with this formula are shown below.



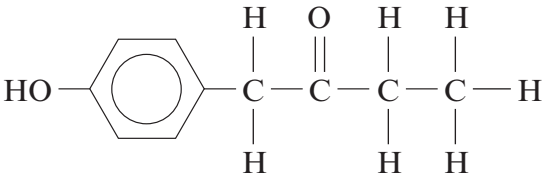
compound **W**



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]

.....

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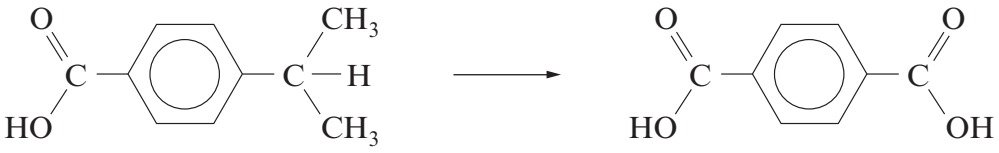
Examiner only

(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]

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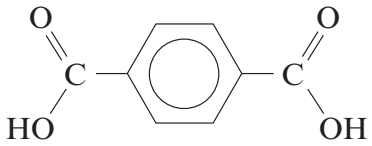
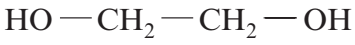
Examiner only

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

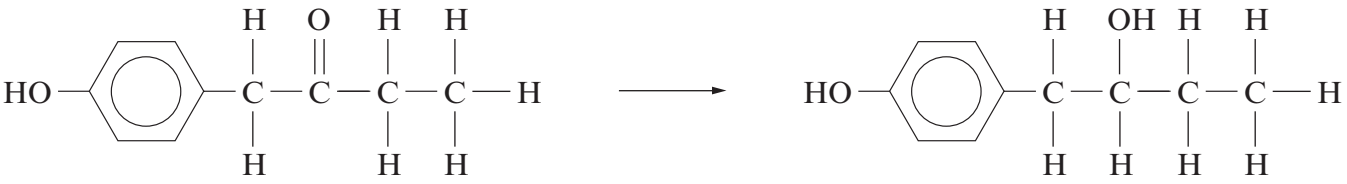


benzene-1,4-dioic acid
(terephthalic acid)



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]

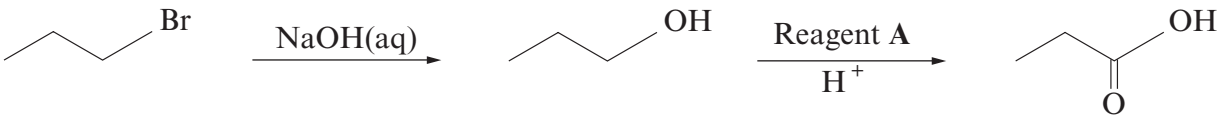
(iii) Compound **V** is insoluble in cold water, but reacts with sodium hydroxide solution and then dissolves.
Give the structure of the carbon-containing species present in the resulting solution. [1]

Total [19]

SECTION B

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

4. *(a)* 1-bromopropane can be used to prepare propanoic acid in a two-stage process shown below.



(i) Classify the reaction occurring in the first stage of this process. [1]

(ii) The first stage uses aqueous sodium hydroxide. Under alternative conditions, 1-bromopropane produces a different product when it reacts with sodium hydroxide.
Give the alternative conditions required, and the product that would be formed from 1-bromopropane under these conditions. [2]

(iii) For the second stage, state the **full name** of reagent **A** and classify the reaction occurring. [2]

(iv) Reagent **A** can also be used to produce propanal from propan-1-ol. State how you would isolate propanal from this reaction. [1]

(b) (i) 1-bromopropane can also be used to prepare butanoic acid in a different two-stage process. For **each** of these two stages, give reagents and conditions required, and draw the **displayed** formula (showing all bonds) of the intermediate. [3]

(ii) Butanoic acid is used to prepare esters used in the flavouring and perfume industries. It may be prepared from 1-bromopropane in a two-stage process as in *(b)*(i) above or from butan-1-ol or butanal in a one-stage process.

Suggest **two** factors that a scientist would consider in choosing between these different routes to produce butanoic acid on a bulk scale. [2]

(c) Compound **B** is an isomer of formula $C_4H_8O_2$ which exists as a sweet-smelling liquid at room temperature.

(i) Elemental analysis of compound **B** shows that it has a composition of 54.5% carbon, 9.1% hydrogen and 36.4% oxygen, by mass. Show that this composition is consistent with the formula above. [2]

(ii) Compound **B** shows three resonances in its $^{1}_{1}H$ nuclear magnetic resonance spectrum.

- A triplet at 1.0 ppm with an area of 3
- A singlet at 2.1 ppm with an area of 3
- A quartet at 4.0 ppm with an area of 2

The infrared spectrum of compound **B** shows absorptions at 2981 cm^{-1} and 1750 cm^{-1}.
These are the only significant absorptions above 1500 cm^{-1}.
Using **all** the information supplied, deduce the structure of compound **B**.
Give **reasons** in support of your answer. [5]

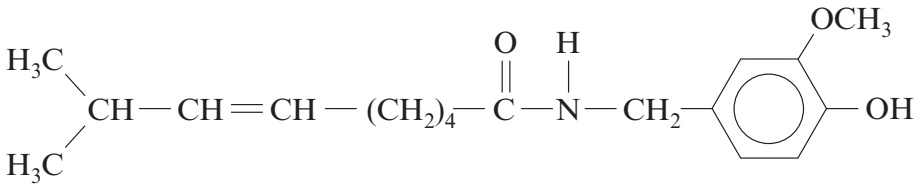
(QWC) [2]

Total [20]

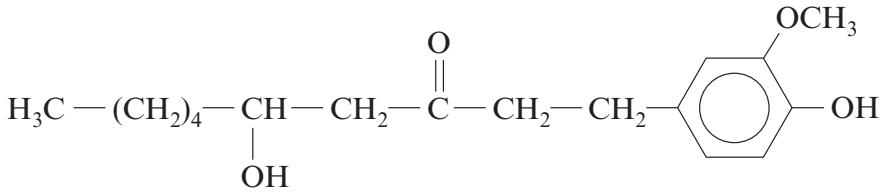
Examiner only

Pungency

One group of compounds that produce a sensation of pungency or heat contain an aromatic ring system carrying two oxygen atoms. This seems to be the key structure responsible for their
25 interaction with the taste buds. Two examples are shown below.



capsaicin (chilli peppers)



gingerol (ginger)

– End of passage –

(a) Describe what is meant by hydrogen bonding, using an example of your choice. [3]
QWC [1]

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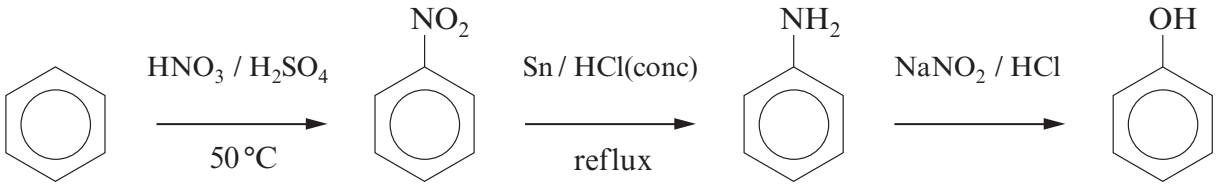
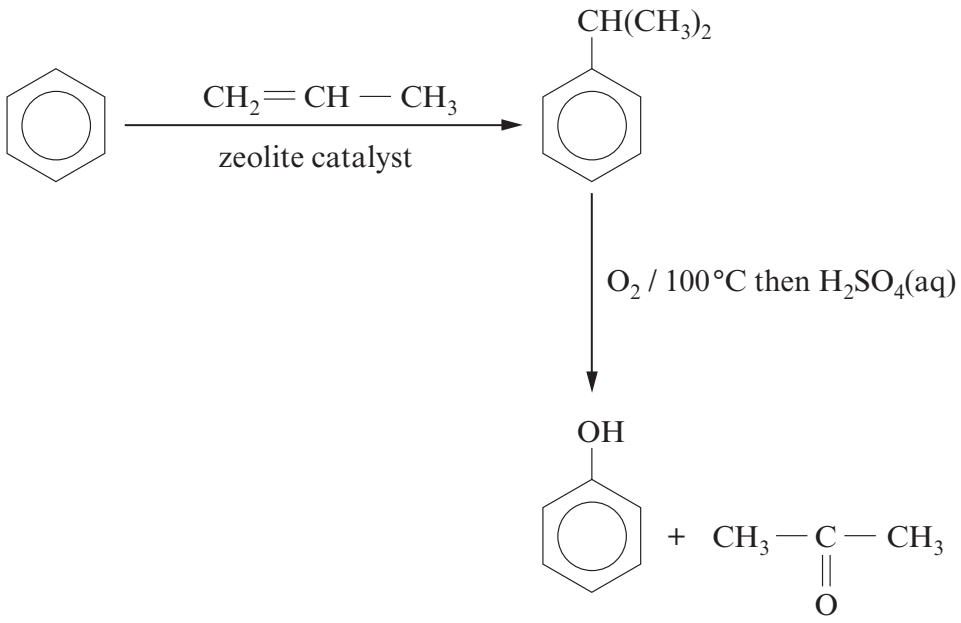
(c) Phenol can be made by the following three-step synthesis.



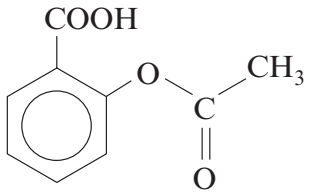
However, the industrial method of making phenol uses a different route as shown below.



(i) Give **two** possible advantages of the industrial route. [2]

(ii) Until 1995 solid phosphoric acid was used as the catalyst for the first stage of the industrial route. Suggest a reason, apart from an increased reaction rate, why this was changed to a zeolite catalyst. [1]

(d) Phenol can be converted into aspirin.



aspirin

When 58.75 g of phenol was reacted with the appropriate chemicals, the yield of aspirin was 65%. Calculate the mass of aspirin produced in this process. [3]

Total [20]

Section B Total [40]

END OF PAPER

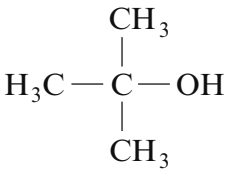
Examiner only

SECTION A

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

1. *(a)* In 2012 an off-licence in Derby was prosecuted for selling fake vodka.

(i) A report in the local paper stated that this 'vodka' was contaminated by 'tertiary butanol', the formula of which is shown below.



State the **systematic** name of this compound. [1]

.....

(ii) Analysis showed that the total alcohol content of a bottle of the fake vodka was 35%.
A gas-liquid chromatogram showed a mixture of alcohols to be present in the following proportions:

tertiary butanol	6 parts
methanol	8 parts
ethanol	86 parts

Calculate the percentage of ethanol by volume in the fake vodka. [1]

..... %

(iii) Tertiary butanol can be dehydrated in an elimination reaction to produce 2-methylpropene. Suggest a suitable dehydrating agent for this reaction. [1]

.....

Examiner only

(iv) 2-Methylpropene can be polymerised to give poly(2-methylpropene). Draw the repeating unit of the polymer. [1]

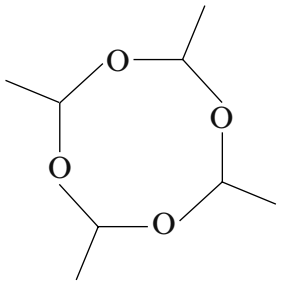
(v) Write the displayed formula of any isomer of tertiary butanol that contains a chiral centre. Identify the chiral centre by an asterisk (*). [2]

(vi) The main alcoholic compound of the fake vodka is ethanol. This can be oxidised to give ethanal.

I State the reagent(s) used to oxidise ethanol to ethanal in the laboratory. [1]

.....

II Ethanal can be polymerised to 'metaldehyde', $(CH_3CHO)_4$, which is used to kill slugs.



Use the Data Sheet to describe how the infrared spectrum of 'metaldehyde' will differ from the infrared spectrum of its monomer, ethanal, giving the absorption values and the bonds involved. Reference to C—H bonds is not required. [2]

.....

.....

.....

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Examiner only

2. *(a)* You are given two aqueous solutions in unlabelled bottles. One is methyl propenoate, $CH_2 = CHCOOCH_3$, and the other is phenol, C_6H_5OH.

Give a chemical test, other than the use of an acid-base indicator, which you could use to distinguish between these two compounds, giving the result of the test for **each** compound. [2]

.....

.....

.....

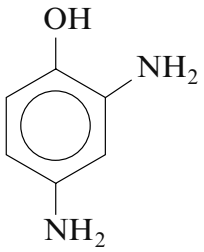
(b) 2,4-Dinitrophenol is a yellow solid that is an inhibitor of ATP production in cells. As a result it has been sold as an aid to slimming, in spite of it being a dangerous and unlicensed product.

(i) State why this compound is seen as yellow in white light. [1]

.....

.....

(ii) Reduction of 2,4-dinitrophenol, using the same reducing agent that is used for the reduction of nitrobenzene, gives the photographic developer 'amidol'.



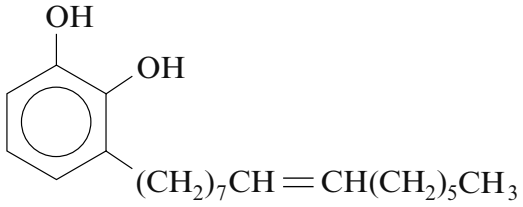
amidol

State the reagent(s) used for this reduction. [1]

.....

Examiner only

(d) 'Urushiol' is a yellow liquid that is found in the plant poison ivy. It causes an allergic skin rash. Urushiol is not a single compound but a mixture of phenolic compounds that have long saturated or unsaturated alkyl groups bonded to the benzene ring.
It contains, for example, the following compound.



(i) Suggest a catalyst that could be used in the hydrogenation of the unsaturated alkyl side chain. [1]

.....

(ii) By analogy with carboxylic acids, explain why 1,2-dihydroxybenzene is soluble in water but urushiol is not. [2]

.....

.....

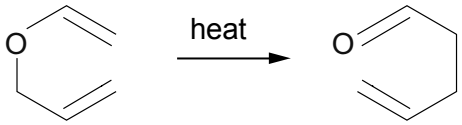
.....

Total [12]

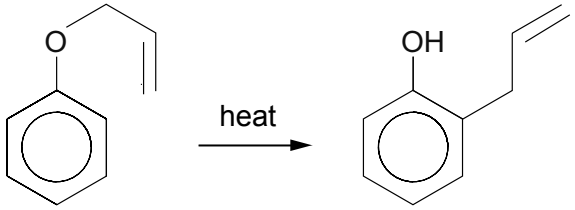
3. *Read the passage below and then answer the questions in the spaces provided.*

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.



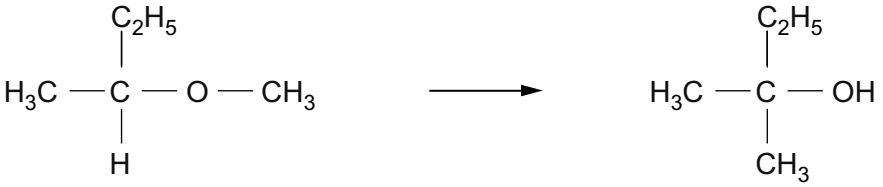
Claisen rearrangement



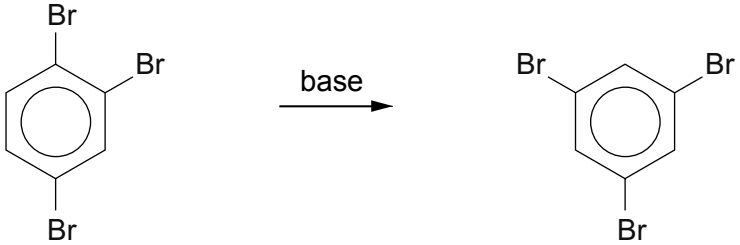
aromatic Claisen rearrangement

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]

.....

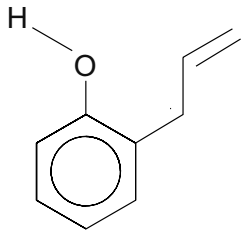
.....

(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]

.....

.....

.....

.....

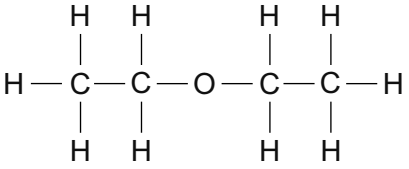
.....

.....

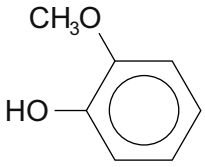
3. *Read the passage below and then answer the questions in the spaces provided.*

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

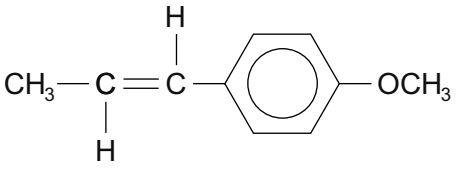
Organic compounds containing the R–O–R linkage, where R is alkyl or aryl are very common. This is due in part to the stability of the C—O bond. Some examples are shown below.



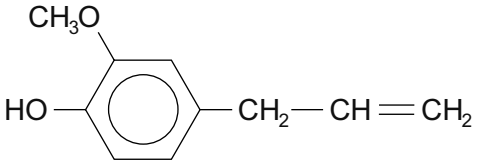
ethoxyethane



guaiacol

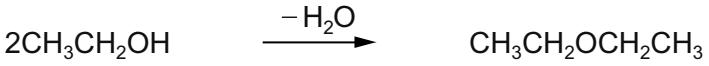


anethole

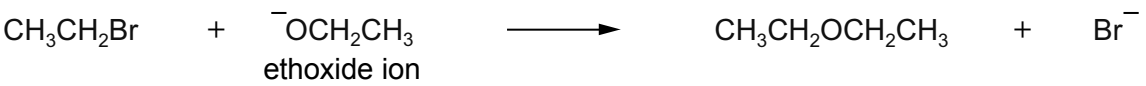


eugenol

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.



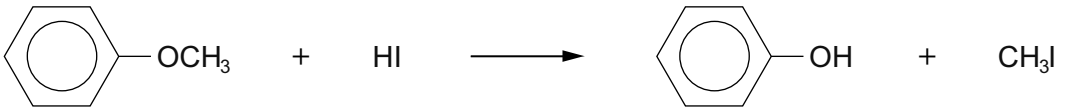
Another method is by reacting bromoethane with sodium ethoxide (a source of the ethoxide ion).



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 -

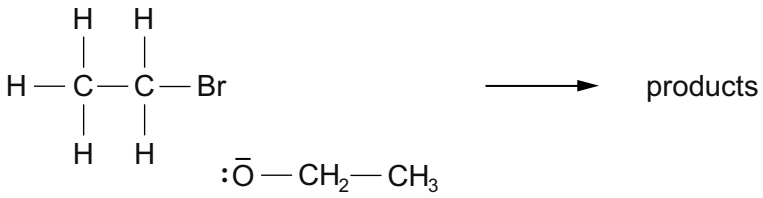
(a) (i) Bethan prepared some ethoxyethane *(line 6)* by reacting ethanol with concentrated sulfuric acid. She used 69 g of ethanol (M_r = 46) and obtained a 45 % yield of ethoxyethane (M_r = 74). Calculate the mass of ethoxyethane obtained. [3]

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]

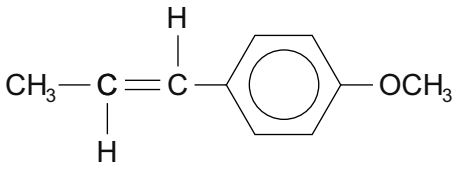
Reagent .....

Observation .....

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

.....

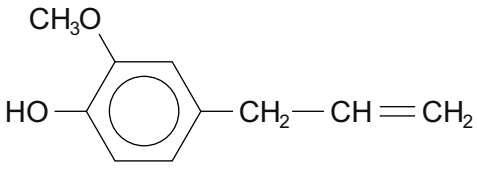
(ii) The article describes C—O bond fission of an ether linkage by hydrobromic acid *(lines 17-18)*. Suggest a displayed formula for the aromatic compound formed when **anethole** reacts with hydrobromic acid. [1]



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]

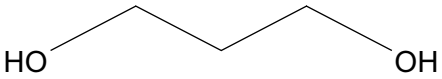
Total Section A [40]

5. *(a)* An Australian cockroach protects itself from attack by spraying predators with an unpleasant unsaturated compound **E**. Analysis of this unsaturated compound, which is not cyclic, gave the following information.

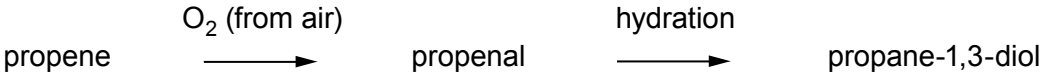
- It contains C, 71.3 % and H, 9.6 % by mass. The remainder is oxygen.
- Only one oxygen atom is present in each molecule.
- It gives a silver mirror with Tollens' reagent (ammoniacal silver nitrate solution).
- The mass spectrum shows a fragmentation ion, containing only carbon and hydrogen, at m/z 29.

Use **each** piece of information to help you deduce a possible displayed formula for compound **E**. [6]

(b) Propane-1,3-diol is a starting compound for the manufacture of some economically important materials.



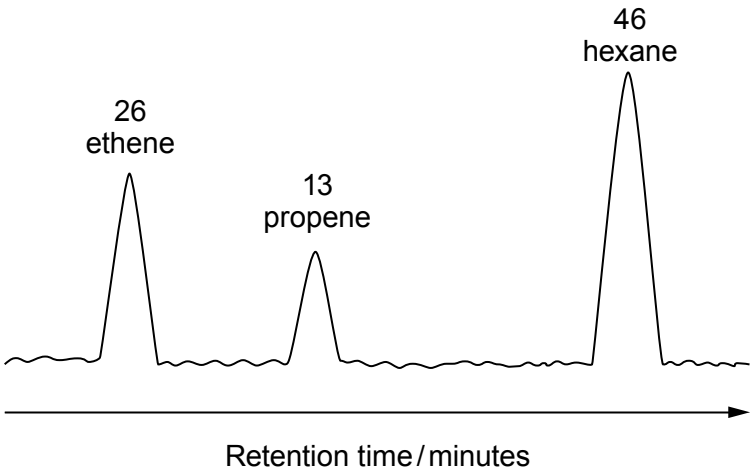
One method of its production is a two-stage process starting from propene. This process is dependent on the supply of crude oil (petroleum) as a source of propene.



A newer method uses a strain of the bacterium *E. coli* to obtain propane-1,3-diol directly from maize.

(i) Give the equation for the cracking of undecane, $C_{11}H_{24}$, into hexane, ethene and propene. [1]

(ii) A simplified gas chromatogram for the cracking of undecane is shown below.



The peak areas indicate the relative volumes of each compound.
Use the chromatogram to calculate the percentage by volume of propene present. [1]