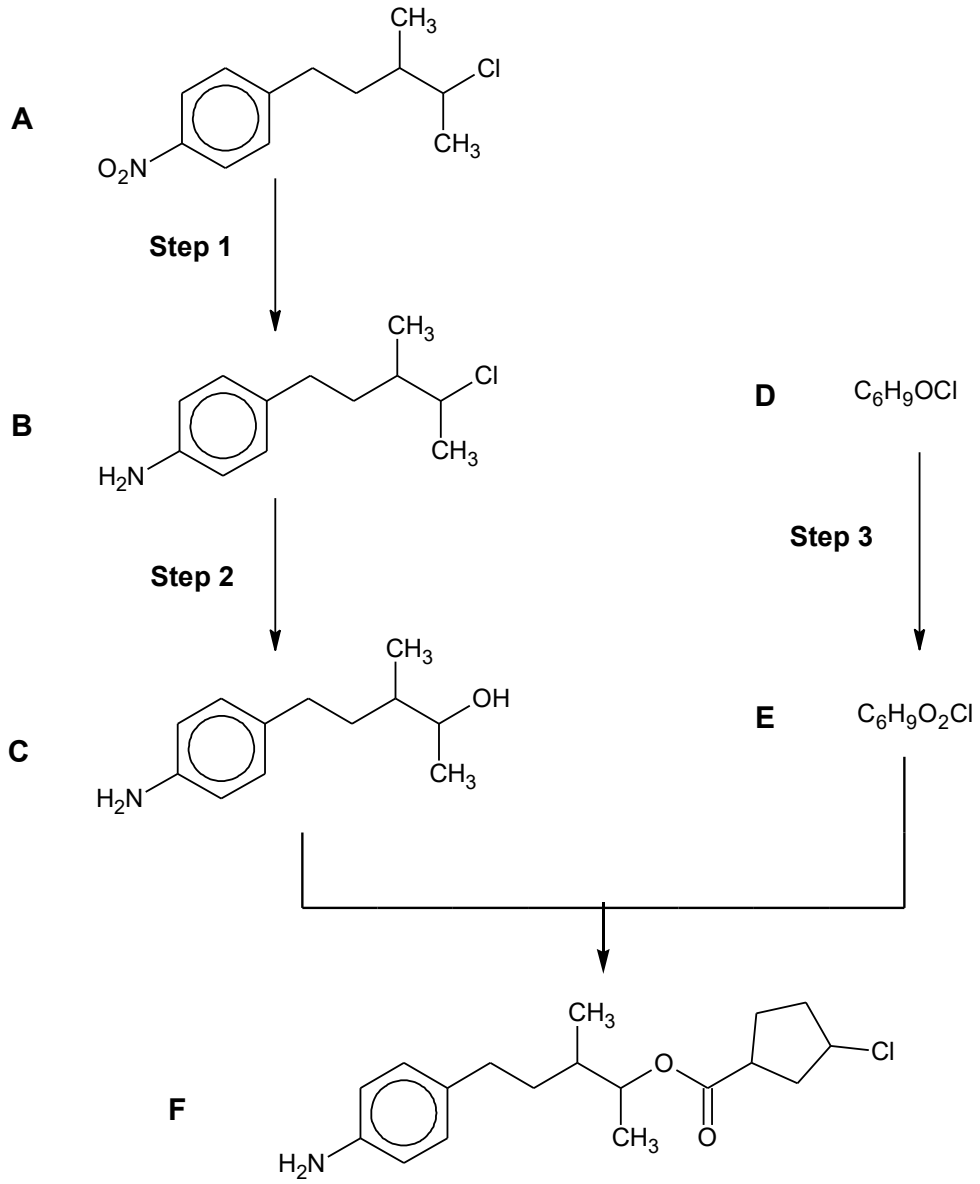
Name: _____ Class: _____

Organic Chemistry Revision Booklet (Structured Questions)

1) Organic Synthesis

1 The diagram below shows the synthetic pathway by which compound **F** may be prepared. The inorganic side product, which is produced together with compound **F**, is constantly removed from the reaction mixture.



(a) Give the structural formulae for compounds **D** and **E**.

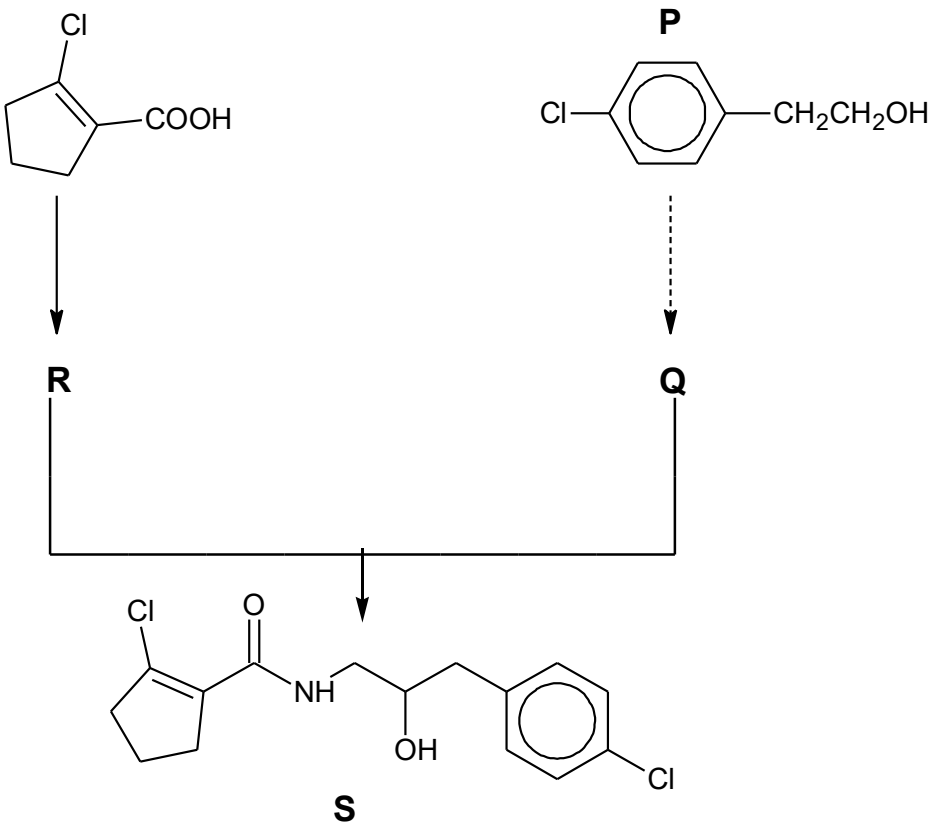
(b) Suggest the reagents and conditions for steps **2** and **3**.

(c) Draw the structures of the organic products formed when compound **F** is reacted with each of the following:

(i) $Br_2(aq)$

(ii) KOH(aq), heat

2 The reaction scheme below shows the final stages in the synthesis of compound **S**.



s

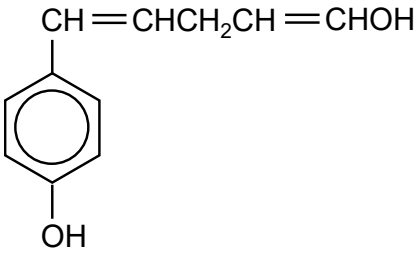
(a) Draw the displayed formulae of compounds **R** and **Q**.

(b) Give the synthetic route, involving *not more than three steps*, from **P** to **Q**. In your answer, suggest the reagent(s) and conditions involved in each step and draw the structural formulae of the intermediate organic products.

Name the type of reaction occurring at each step.

(c) In the reaction of **R** and **Q**, another organic compound can also possibly be formed. Draw the structural formula of the organic compound and explain how its formation may arise.

3 There are four stereoisomers of compound **P**.

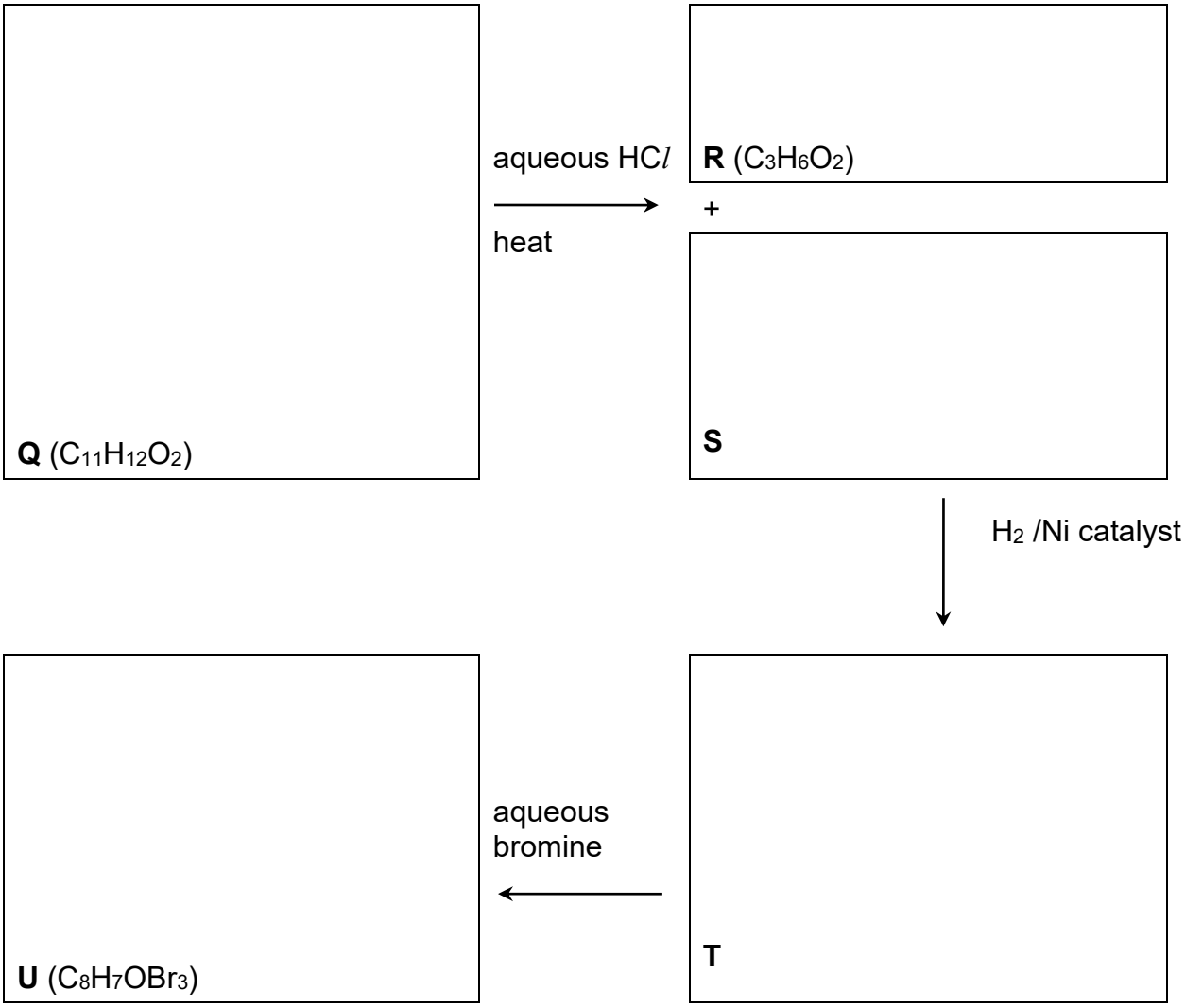


P

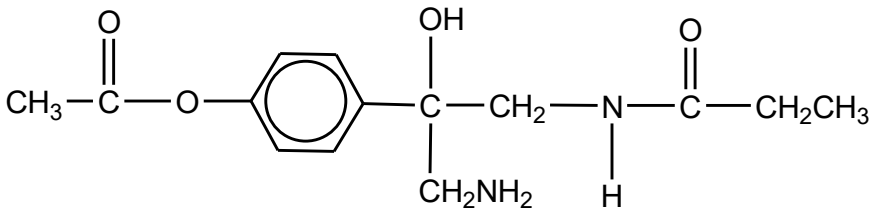
(a) What is the type of stereoisomerism exhibited by **P**? Draw the stereoisomers of **P**.

(b) **Q** is a structural isomer of **P** in **(a)**.

Suggest the structures of **Q**, **R**, **S**, **T** and **U** in the reaction scheme below.



4



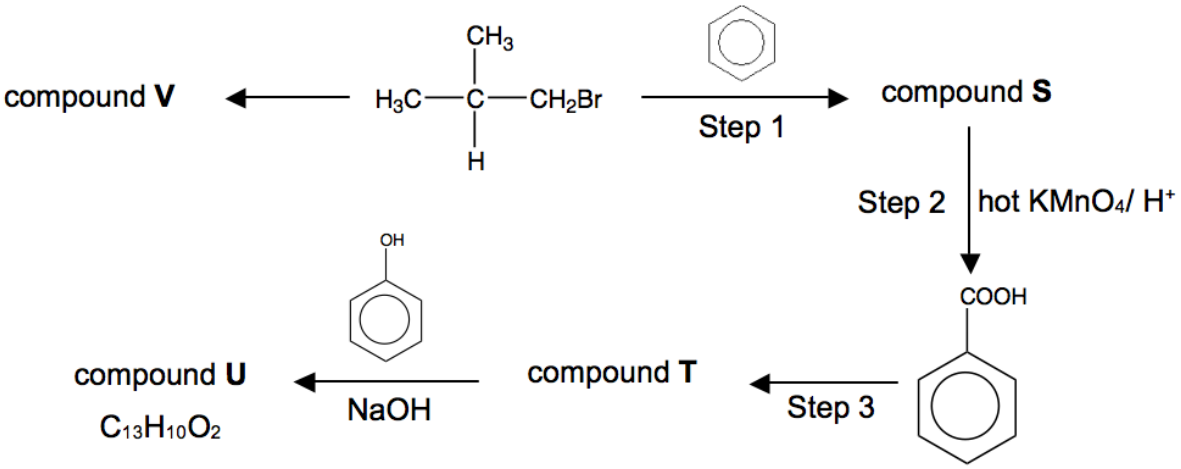
Q

(i) Name the four functional groups in compound **Q**, other than the phenyl group.

(ii) Draw the structural formulae of the compound(s) when compound **Q** is treated with

- cold HC*l*(aq)
- hot NaOH(aq)

5 1-bromo-2-methylpropane undergoes a series of reactions as shown by the given flow scheme.



(i) State the conditions needed for step 1.

(ii) Explain as fully as you can why the conditions you stated in **(i)** are required.

(iii) Draw the structures of compounds **S**, **T** and **U.**

(iv) When an alkaline solution of complexed Cu^{2+}(aq) is added to compound **V**, a reddish-brown precipitate is observed.

Propose a 2-step synthesis for compound **V** from 1-bromo-2-methylpropane.

6 Transesterification is the process of exchanging the organic group R' of an ester with the organic group R'' of an alcohol.

$RCO_2R' + R''OH \rightarrow RCO_2R'' + R'OH$

(a) State the type of reaction taking place in transesterification.

(b) Write an equation for the reaction between methyl ethanoate and ethanol.

(c) Suggest which is the limiting reagent for the reaction in **(b)** to give a high percentage conversion of esters.

Explain your answer.

(d) The boiling points of methanol, methyl ethanoate and ethyl ethanoate are shown below.

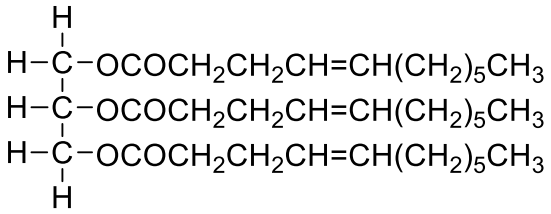
compound	**boiling point / °C**
methanol	65
methyl ethanoate	57
ethyl ethanoate	75

Account for the differences in the boiling point of methanol as compared to that of the esters

.

(e) Suggest a suitable method for separating a mixture of methyl ethanoate and ethyl ethanoate

(f) Transesterification has been used industrially to prepare biodiesel from recycled vegetable oil. Suggest the organic products formed when the following molecule undergoes transesterification in the presence of methanol.



(g) Similar methods can be used to synthesize amides by reacting esters with ethanolic ammonia.

$CH_3CO_2(CH_2)_xCH_3 + NH_3 \rightarrow CH_3CONH_2 + CH_3(CH_2)_xOH$

After 1.00 g of an ester, $CH_3CO_2(CH_2)_xCH_3$, is reacted completely with 25.0 cm^3 of 1.00 mol dm^{-3} ethanolic ammonia, the resultant mixture is titrated against 1.00 mol dm^{-3} dilute HC*l*. The titre value is 15.20 cm^3.

Determine the value of *x*.

7 To combat pollution and soaring fuel cost, car makers are experimenting with ethanol to help produce cars with lower carbon dioxide emissions and improve fuel economy. Ethanol is also often used in the synthesis of many organic compounds.

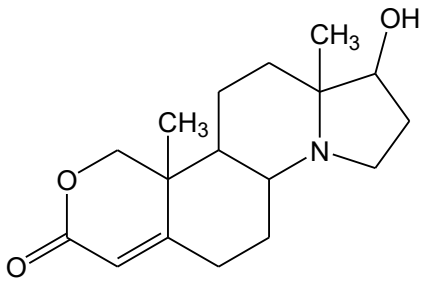
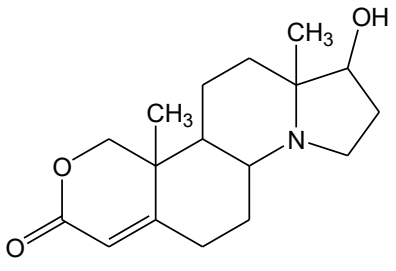
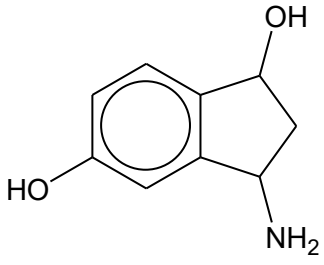
(i) Write an equation for the complete combustion of ethanol.

(ii) Write an equation for the synthesis of sodium methanoate from ethanol.

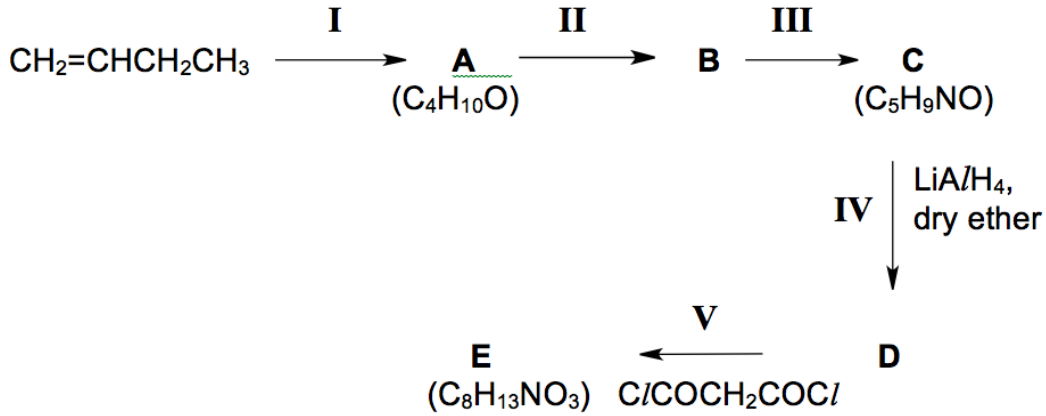
(iii) Draw a dot–and–cross diagram of sodium methanoate.

(iv) Suggest the structural formula of the organic compound formed when ethanol reacts with phosgene $COCl_2$. In phosgene, the carbon atom is in the centre of the molecule and is attached to both chlorine atoms and to the oxygen atom.

8 In the table below, draw the structures of the organic products formed when compounds **Y** and **Z** react with the reagents stated below.

compound	reagent(s)	organic product
 **Y**	$KMnO_4$, dilute H_2SO_4	
 **Y**	HBr(g), heat	
 **Z**	propanoyl bromide	

9 But-1-ene can be converted to compound **E** via the following series of reactions.



Both compounds **A** and **B** produce a yellow precipitate on warming separately with aqueous alkaline iodine.

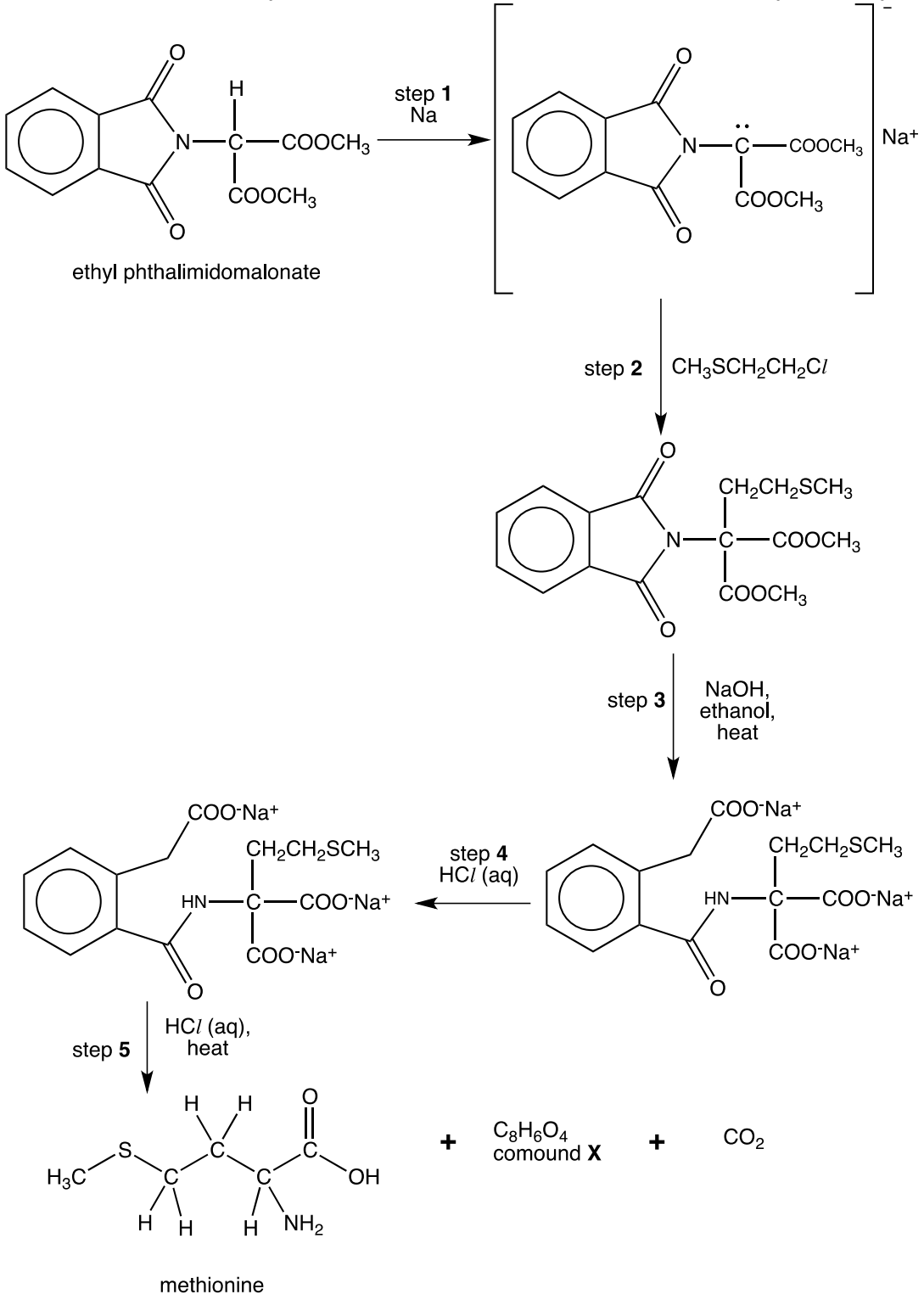
(i) State the reagents and conditions for steps **I** and **III**.

(ii) Draw the structural formulae of compounds **B**, **D** and **E**.

(iii) Explain why the reaction in Step **III** produces an equimolar mixture of two stereoisomers of compound **C.**

10 Methionine is an α-amino acid which is essential to humans and is also used by plants to synthesise ethene.

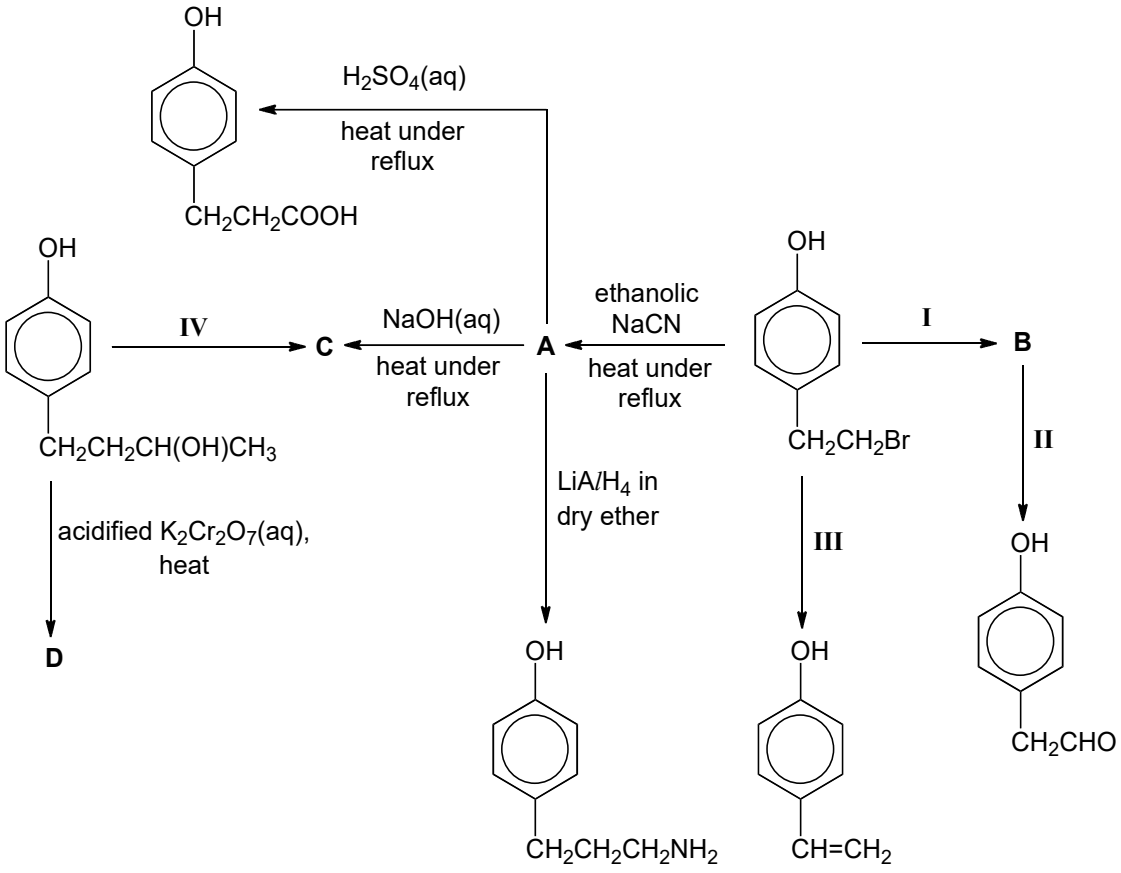
In the 1930s, Barger and Weichselbaum reported the synthesis of methionine using the sodium salt of ethyl phthalimidomalonate and 2-chloroethyl methyl sulfide.



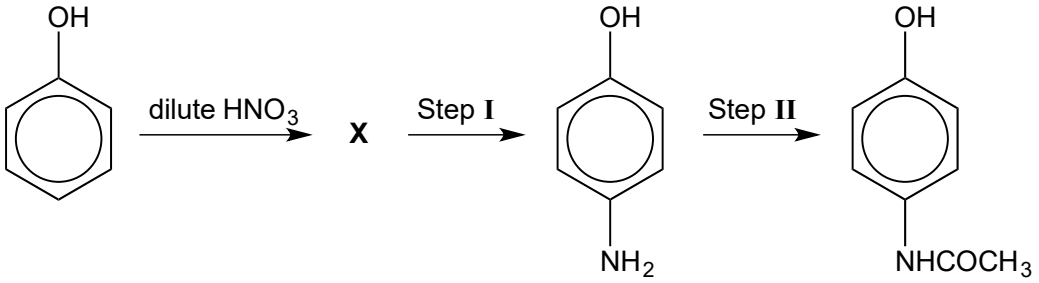
(i) What *types of reactions* are steps **1** and **3**?

(ii) Compound **X**, $C_8H_6O_4$, obtained as a by-product in step **5**, is sparingly soluble in water.
1 mol of **X** reacts with exactly 1 mol of sodium carbonate.
Give the structure of compound **X**.

11 Benzene is an aromatic hydrocarbon present in many compounds.
A reaction scheme involving benzene derivatives is given below. Draw the structures of **A** to **D** and give the reagents and conditions for steps **I** to **IV**.



12 Students often complain of headaches when faced with a tough problem they cannot solve. A very common over-the-counter drug to combat headaches is paracetamol. The synthesis of paracetamol is shown below:



Paracetamol

(a) Draw the structure of compound **X.**

(b) Step **I** is actually a two-stage process. State the reagents and conditions for the two stages.

(c) Step **II** involves a condensation reaction. An organic side-product, **Y**, can be formed along with paracetamol.

(i) State the reagent for this step.

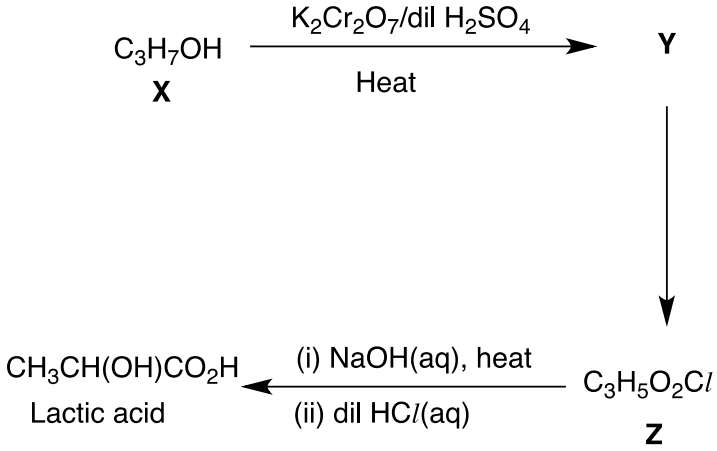
(ii) Suggest a structure for **Y.**

(d) Suggest the structures of all the organic products formed when paracetamol reacts with

(i) NaOH(aq) at room temperature

(ii) NaOH(aq) with heating

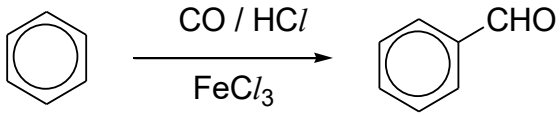
13 Lactic acid, $CH_3CH(OH)CO_2H$, can be prepared from **X**, C_3H_7OH, by the following series of reactions.



Write the structural formulae of organic compounds **X** to **Z** and state the reagents and conditions for the conversion of **Y** to **Z**.

14 Suggest a two-step synthesis to convert $BrCH_2CH_2OH$ to $H_2NCH_2CH_2CH_2OH$. State the reagents and conditions for each step and draw the structure of the intermediate compound.

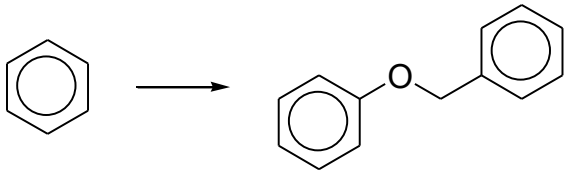
15 Iron(III) chloride is often used as a catalyst in the conversion of benzene to produce carbonyl compounds.



(a) **(i)** Write an equation to show the generation of the electrophile to form benzaldehyde.

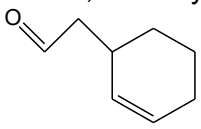
(ii) Explain why iron(III) chloride must be anhydrous in order to generate the electrophile.

(b) By making use of the reaction in **(a)** and suitable starting materials, suggest a synthetic pathway (in no more than 4 steps) to convert benzene into the following compound. State clearly the reagents and conditions for each stage, and draw the structural formulae of every intermediate formed.



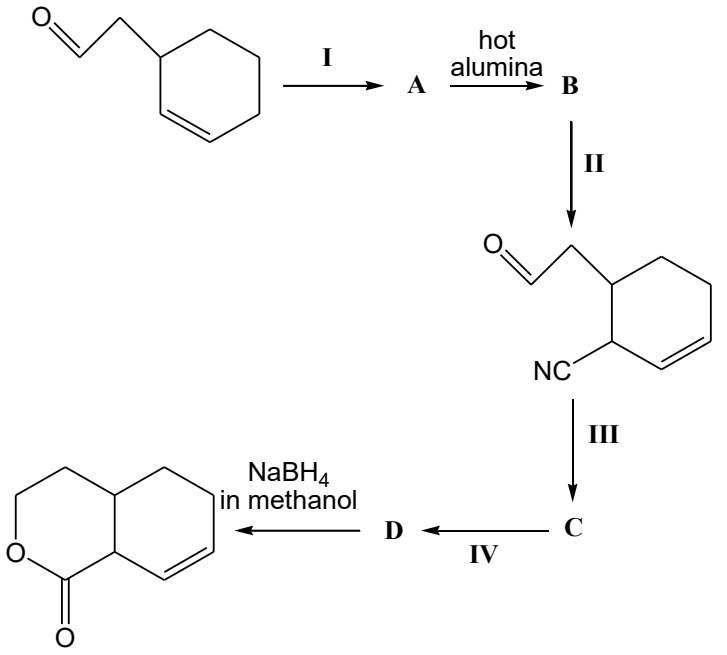
16

(a) **(i)** Predict the products formed when $BaCl_2$ reacts with concentrated H_2SO_4.

(ii) Hence, identify the structural formula for the organic product formed when  reacts with $BaCl_2$ and concentrated H_2SO_4.

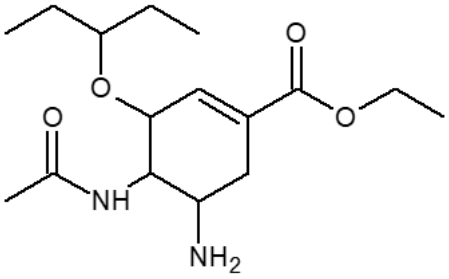
(b) The reaction scheme below shows how an ester is generated from.

Complete the reaction scheme below by writing the structural formulae of the organic products and the reagents and conditions.

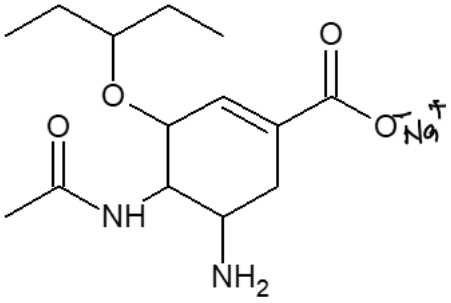


17

(a) *Oseltamivir* is an anti–influenza drug being used to treat the so called 'Bird–flu'. This anti–viral drug can be converted to its active form *GS 4071*, in the body after being administered. The structure of *Oseltamivir* is shown below:



Oseltamivir



GS 4071

You may assume that the ether (–O–) group in *Oseltamivir* is unreactive in any reactions in this question.

(i) Circle and name four different functional groups present in *Oseltamivir.*

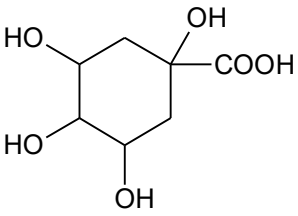
(ii) *Oseltamivir* is actually sold as the phosphate salt rather than in the form as shown above. Suggest why this is so.

(iii) What type of reaction is involved in the conversion of *Oseltamivir* into GS 4071?

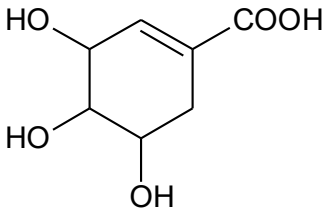
(iv) Draw the structural formula of all organic products formed when *Oseltamivir* is heated with excess sodium hydroxide.

(v) At room conditions, *Oseltamivir* reacts with HBr in 1:2 ratio. Draw the structure of the product formed.

(b) *Oseltamivir* can be produced from *Quinic acid*, found in coffee beans or *Shikimic acid*, found in star anise.



Quinic acid

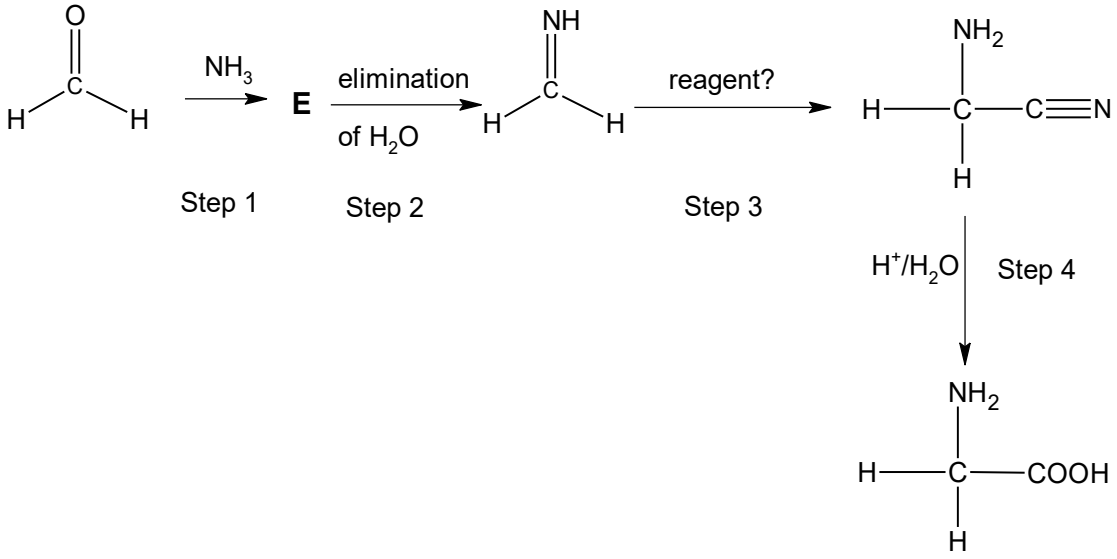


Shikimic acid

(i) Use the **table of characteristic values for infra–red absorption in the *Data Booklet***, identify an infra–red absorption range shown by *Shikimic* acid but not *Quinic* acid.

(ii) Give the structural formula of the organic product when *Shikimic* acid reacts with excess ethanoyl chloride.

18 The Strecker synthesis is a route to preparing amino acids. Glycine, 2–aminoethanoic acid, can be prepared from methanal, as a starting material. This is shown in the four–steps reaction scheme below:



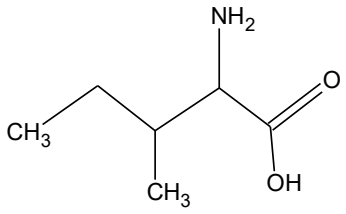
2-aminoethanoic acid

(i) State the role of ammonia used in Step 1.

(ii) Suggest a structure for compound **E.**

(iii) Suggest a suitable reagent used in Step 3.

(iv) A starting material, compound **Z**, can be used to prepare isoleucine, shown below using a Strecker synthesis.

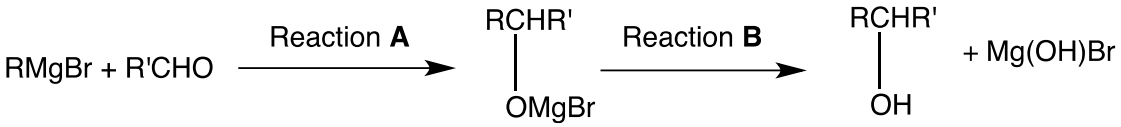


Isoleucine

Draw the structure of compound **Z**.

19 (*Advance Question*) In 1911, the French chemist F.A.V. Grignard reacted small pieces of magnesium with a warm solution of halogenoalkane, such as iodomethane or a haloarene, such as bromobenzene, in a dry, non-polar solvent and obtained a solution containing a Grignard reagent commonly written as RMgX. Grignard reagents with different alkyl or aryl groups have been prepared and are widely used in organic synthesis.

A typical example of the use of a Grignard reagent is the two-step reaction of RMgX with aldehydes to form alcohols.



(a) Suggest the type of reaction which occurs in Reaction **A** and **B.**

(b) A student wanted to prepare alcohol **W** using a similar two-step process as shown in (**a**).

He used pentan-2-one and a Grignard reagent.

The table shows the volatilities and hazards of the reagents and the alcohol **W**.

Substance	**Volatility**	**Hazard**
iodoethane	moderate	flammable; toxic; respiratory irritant
ethoxyethane $(C_2H_5)_2O$	high	flammable; harmful
magnesium turnings	non-volatile	flammable
pentan-2-one	low	flammable; harmful
alcohol **W**	very low	flammable; irritant

(i) Identify **one** potential safety hazard of using these materials and state how you would minimise this risk. You may assume that the experimenters are wearing gloves, eye protection and lab coats.

(ii) The day before the experiment, anhydrous calcium chloride is added to the iodoethane, sodium wire is added to the ethoxyethane and the glassware is left in an oven.

Suggest the **single purpose** of these three precautions.

Step I

1.50 g of magnesium turnings is added to a round-bottomed flask with an equimolar quantity of iodoethane and 20 cm^3 of ethoxyethane.

Table 1.2 gives some physical properties of the reagents and the organic product.

Substance	**Formula**	**Molar mass /g mol^{-1}**	**Density /g cm^{-3}**	**Solubility in water**	**Boiling point /°C**
iodoethane	C_2H_5I	156	1.93	slightly soluble	72
ethoxyethane	$(C_2H_5)_2O$	74	0.713	slightly soluble	35
Mg turnings	Mg	24.3	1.74	insoluble	1110
pentan-2-one	$C_5H_{10}O$	86	0.814	slightly soluble	102
alcohol **W**			0.823	slightly soluble	143

Table 1.2

(iii) Calculate the volume of iodoethane required to react with magnesium.

Step II

A crystal of iodine is added to the mixture from **Step I** to activate the magnesium, and this mixture is heated under reflux.

Step III

The mixture from Step II is allowed to cool and 6.0 cm^3 of pentan-2-one is added dropwise. The mixture is then gently heated under reflux.

(iv) Show with calculations that the Grignard reagent is in excess. Assume that the reaction between magnesium and iodoethane in **Step II** had 100% yield.

Step IV

The mixture from **Step III** is cooled using an ice bath, and then 25 cm^3 of dilute hydrochloric acid is slowly added.

(v) Draw the structure of alcohol **W** produced in **Step IV.**

(vi) Suggest the organic by-product produced in **Step IV.**

Step V

The mixture from **Step IV** is transferred into a separating funnel. The lower aqueous layer is separated and shaken successively with two 10 cm^3 portions of ethoxyethane, retaining the ethoxyethane extracts and combining them with the original ethoxyethane layer.

(vii) Explain why the ethoxyethane forms an *immiscible layer above the aqueous layer.*

Step VI

The combined ethoxyethane layer is treated successively with 20 cm^3 of

1. water,

2. saturated sodium hydrogencarbonate solution,

3. 1 mol dm^{-3} aqueous sodium thiosulfate,

4. saturated sodium chloride solution.

Step VII

The ethoxyethane layer is allowed to stand over anhydrous magnesium sulfate. After some time, the mixture is filtered. Pure alcohol **W** is collected using distillation.

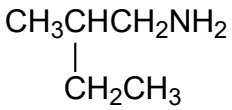
(viii) In **Step VI**, the water and the three aqueous solutions used to wash the ethoxyethane layer are each intended to remove a particular impurity.

Suggest the impurity removed in each step.

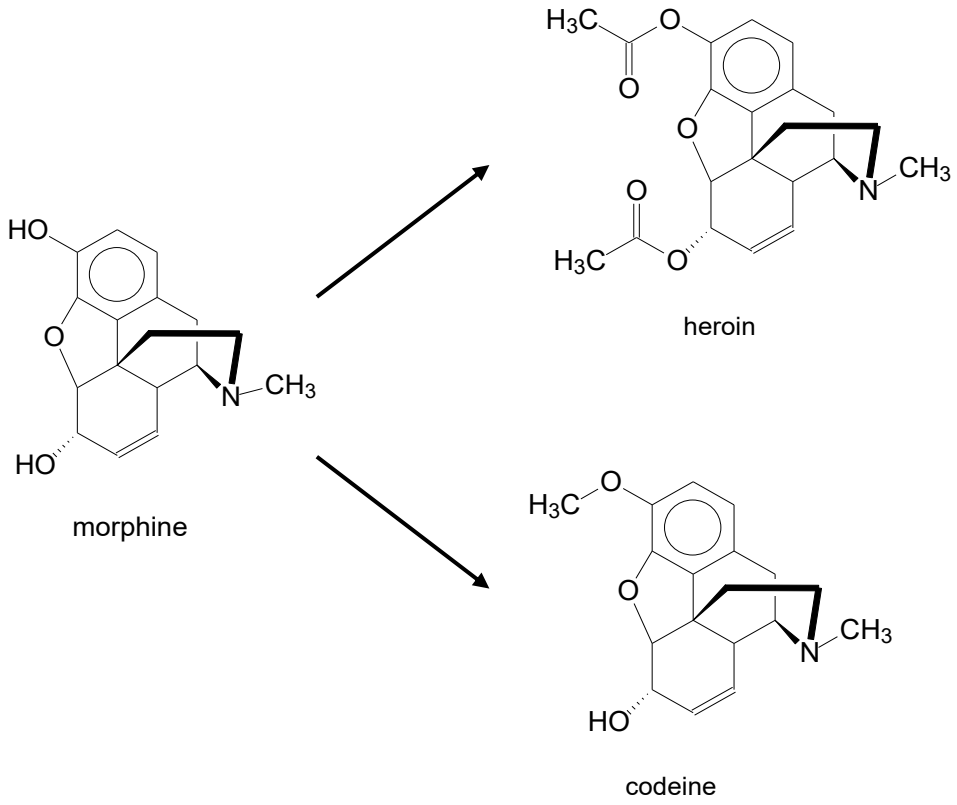
Chemicals added	Impurity removed
1. water	
2. saturated $NaHCO_3$	
3. sodium thiosulfate	
4. saturated sodium chloride	

(c) Alcohols obtained from such synthesis can be converted to other organic compounds.

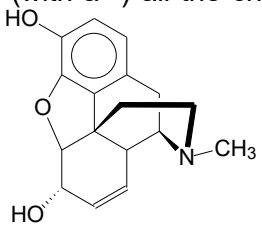
Suggest a synthetic route for the formation of the amine given below starting from butan-2-ol.



20 Heroin and codeine are derivatives of morphine. Heroin and morphine are often used to ease chronic pain caused by cancer or severe trauma injury, while codeine is used to treat mild to moderate pain and to relieve cough. [Assume –OR is inert.]

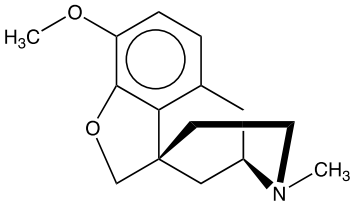


(i) On the structure below, label (with a *) all the chiral carbon centers present in morphine.



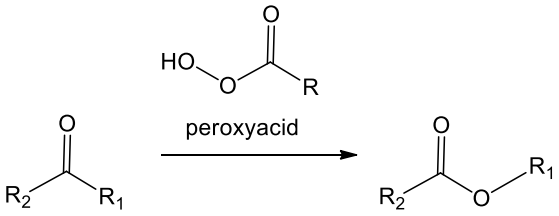
morphine

(ii) Give the structure of the organic species formed when $CH_3C\ell$ is added to codeine and heated, by **completing the partial structure below**.

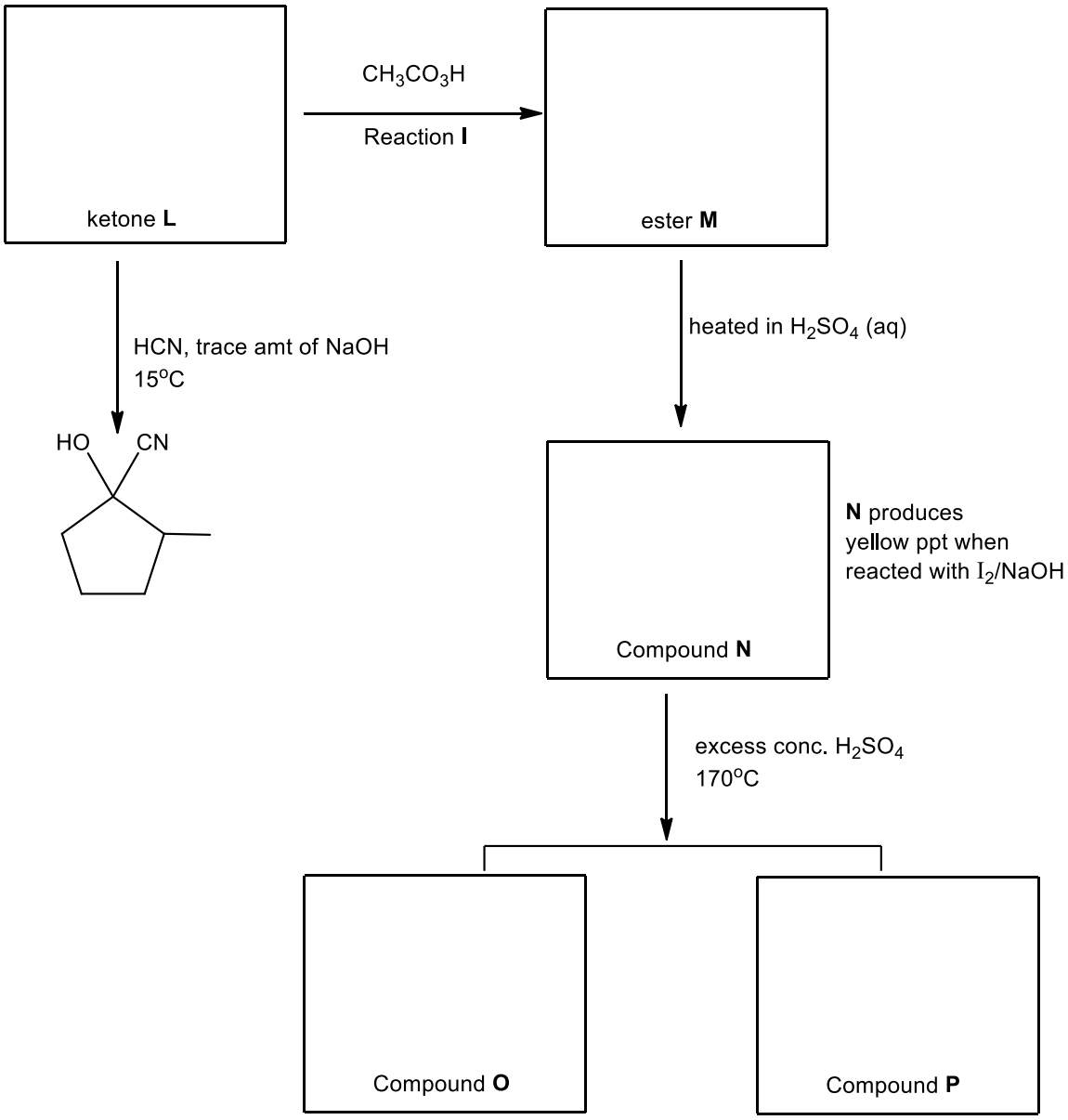


(iii) Give the structure(s) of the organic species formed when heroin is heated with aqueous NaOH for some time.

21 The Baeyer-Villiger oxidation is an organic reaction that converts ketones into esters using peroxyacids.

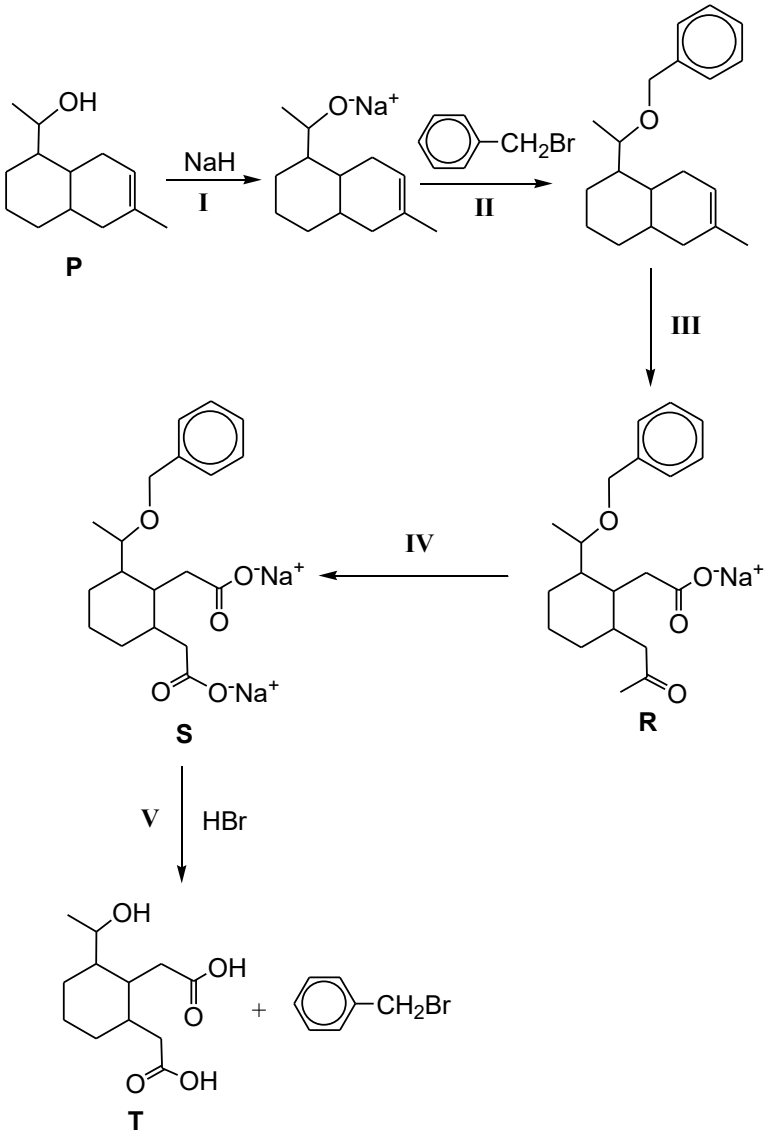


In the following reaction scheme, reaction **I** is a Baeyer-Villiger oxidation.
Give the structural formulae of compounds **L**, **M**, **N**, **O** and **P**.



22 Benzyl bromides are often used to form benzyl ethers ($C_6H_5CH_2$–O–R), which are known to be good protecting groups in multi-step organic syntheses. The benzyl ethers formed will protect reactive functional groups from further reactions. These protecting groups can subsequently be removed to recover the originally unprotected functional groups.

The following illustrates a synthetic scheme in which a benzyl ether is acting as the protecting group.



(i) Name the functional groups present in compound **P**.

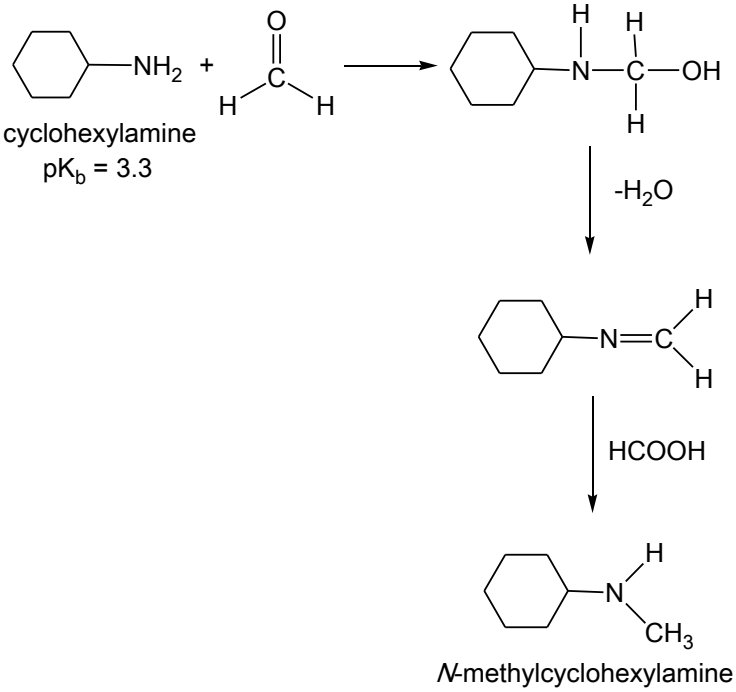
(ii) State the reagents and conditions needed for steps **III** and **IV**.

(iii) In this synthesis, benzyl bromide was added to protect a particular functional group in compound **P** from further reaction.
Identify this particular functional group in **P** and explain what would have happened instead in the reaction scheme if this functional group was not protected.

23 In the Leuckart reaction, a carbonyl compound reacts with primary amines to form substituted amines.

The first step of the reaction involves the nucleophilic addition of amines to a carbonyl compound, forming an intermediate that can be reduced by methanoic acid.

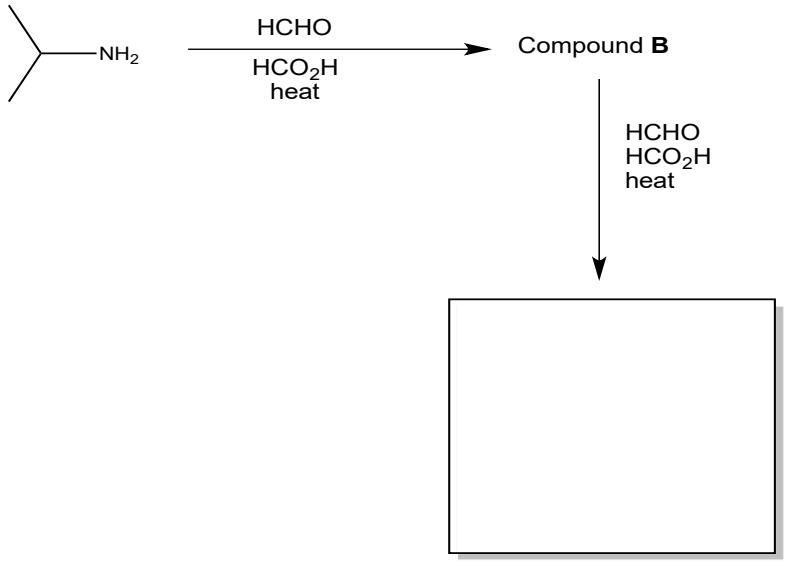
One example of the Leuckart reaction using methanal, HCHO, is shown as follows.



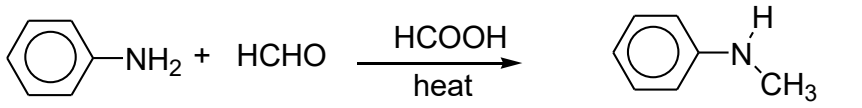
(i) Cyclohexylamine has a pK_b value of 3.3.

Explain why pK_b value for *N*-methylcyclohexylamine is lower than 3.3.

(ii) Draw the displayed formula of the organic product formed in the box when 1 mole of 2–propylamine reacts with 2 moles of methanal via the Leuckart reaction.



iii) When phenylamine undergoes the Leuckart reaction with methanal, the yield of the product,
N-methylphenylamine, is only 10.1%.



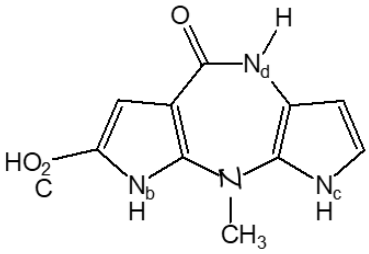
phenylamine

N-methylphenylamine

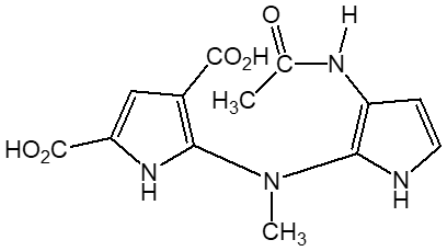
yield = 10.1%

Suggest a reason why the yield of *N*-methylphenylamine is poor.

24 Compound **A** can be synthesised from compound **B** via a 3-step synthesis route.



A

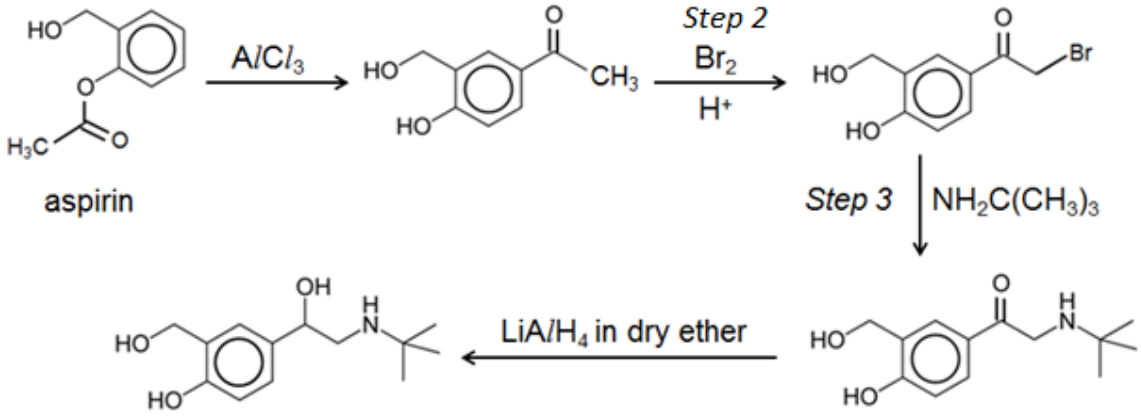


B

State the reagents and conditions needed for each step.

Step	Reagents and conditions
1	
2	
3	

25 (*Advance Question*) A 4-step synthesis route of salbutamol is shown as follows:



(a) An organic chemist suggested the use of bromine gas under ultraviolet light in *Step 2*. Explain why his choice of reagent and condition may not be appropriate for the conversion.

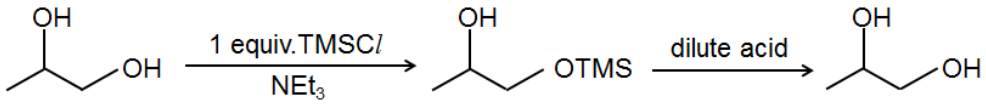
(b) Name the reaction in *Step 3* and outline the mechanism.

You may use **R** to denote bulky alkyl groups in your mechanism.

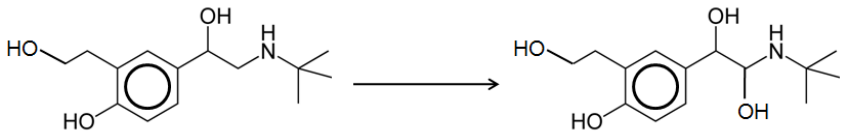
(c) Explain why $LiAlH_4$ must be used in dry ether during the final step.

(d) Chlorotrimethylsilane (TMS*Cl*) in the presence of triethylamine (NEt_3) is usually used as a protecting group for alcohols in organic synthesis. This allows the alcohol group to remain unreactive while the rest of the molecule undergoes reaction. To regenerate the alcohol group, dilute acid can be added.

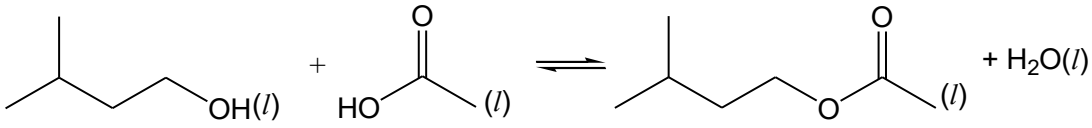
A representative equation is shown as follows:



Using the information provided, suggest a method to perform the following conversion.



26 Isopentyl acetate is also widely referred to as banana oil for its odour.



3-methylbutan-1-ol ethanoic acid isopentyl acetate

(a) Banana oil can be synthesised through a simple esterification method. The laboratory synthesis of banana oil is carried out as follows.

Step 1	15 cm^3 of 3-methylbutan-1-ol and 20 cm^3 of ethanoic acid are added to a 100 cm^3 round bottomed flask.
Step 2	4 cm^3 of 1.5 mol dm^{-3} sulfuric acid is added dropwise to the flask with constant swirling. The mixture was heated under reflux for 1 hour. During the heating, the top of the condenser was left open to the atmosphere. The mixture was then allowed to cool to room temperature.
Step 3	The cooled mixture was poured into a separating funnel and 55 cm^3 of cold water was added. The separating funnel was shaken several times and the mixture was allowed to stand before discarding the aqueous layer.
Step 4	Solid Na_2CO_3 was added to the organic layer and the mixture was swirled with the top of the separating funnel opened. Pure isopentyl acetate was finally obtained through distillation.

(i) Explain why isopentyl acetate can be separated from water using a separating funnel.

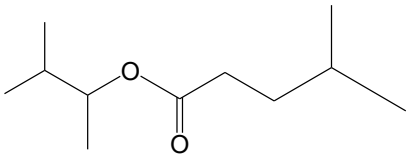
(ii) Isopentyl acetate has a higher boiling point than 3-methylbutan-1-ol. Explain.

(iii) With reference to **Step 2**, suggest why the reflux condenser was not stoppered open during the refluxing process to increase the yield of the ester.

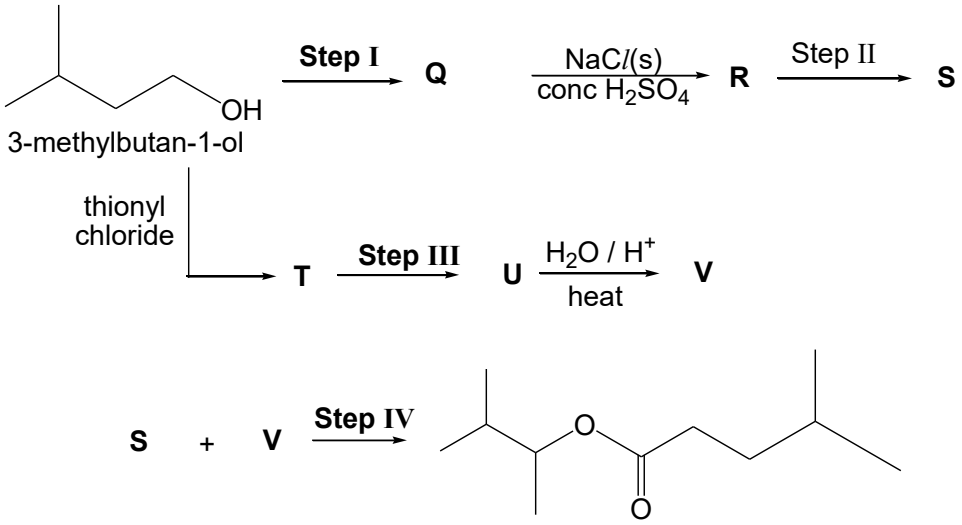
(iv) Suggest why Na_2CO_3 was added to the organic layer.

(v) Why was it necessary to ensure that the top of the separating funnel was opened while swirling in **Step 4**?

(b) The following ester can be formed using isopentyl alcohol as the only organic starting material.



The synthesis of the ester is as shown in the reaction sequence below.



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

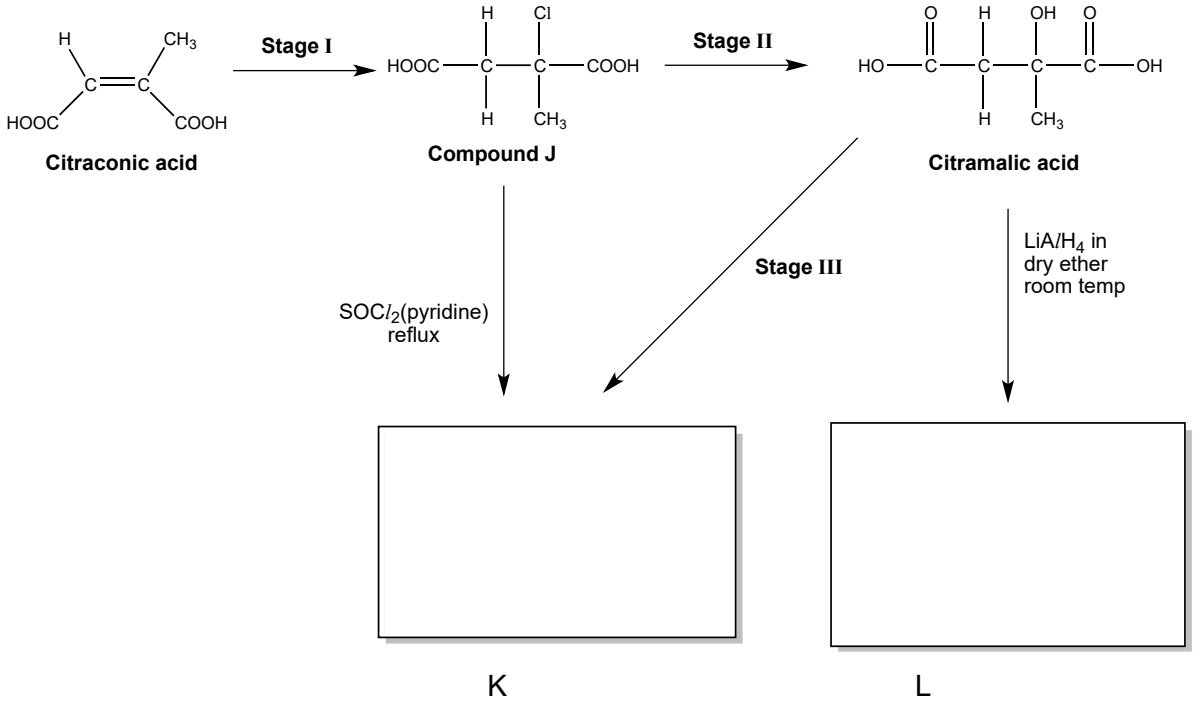
Step I	
Step II	
Step III	
Step IV	

(ii) Draw the structural formulae of compounds **Q**, **R**, **S**, **T**, **U** and **V**.

(iii) **W** is an isomer of 3-methylbutan-1-ol. **W** has a chiral centre and does **not** give yellow precipitate with alkaline aqueous iodine. Suggest the structural formula of **W** and indicate the chiral centre on **W** with an asterisk (*).

27 Citraconic acid is one of several isomeric carboxylic acids obtained from citric acid. Studies showed that citraconic acid was involved in vitamin B12 synthesis.

(a) Citraconic acid can be converted into citramalic acid by the following scheme:



(i) State the functional groups present in citramalic acid.

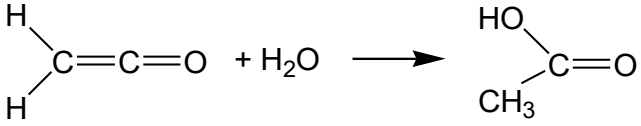
(ii) State the reagents and conditions needed for Stages **I**, **II** and **III**.

(iii) Draw the structures of the organic compounds **K** and **L.**

(iv) Name and describe the mechanism involved in Stage **II** given that the reaction is first order with respect to J.

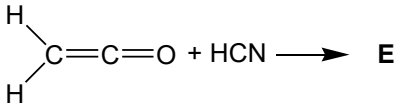
(v) In view of the mechanism describe in **(iv)**, explain if the citramalic acid formed in Stage **II** is optically active.

28 Ketene is a reactive compound that undergoes addition reaction as shown below.

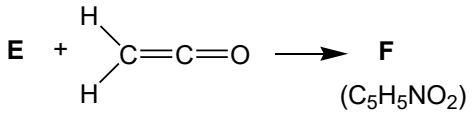


Compound **F** is an ester formed via a two-step process.

Step 1:



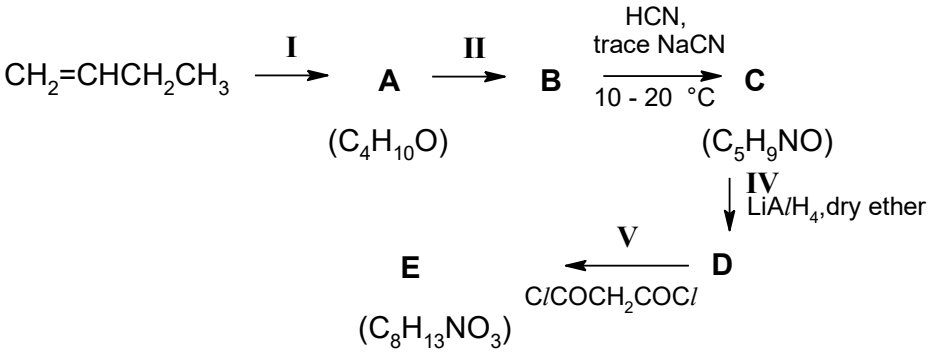
Step 2:



The first step involves an addition reaction to form the cyanohydrin intermediate.

Suggest the structure of compound **E** and **F**.

29 But–1–ene can be converted to compound **E** via the following series of reactions.



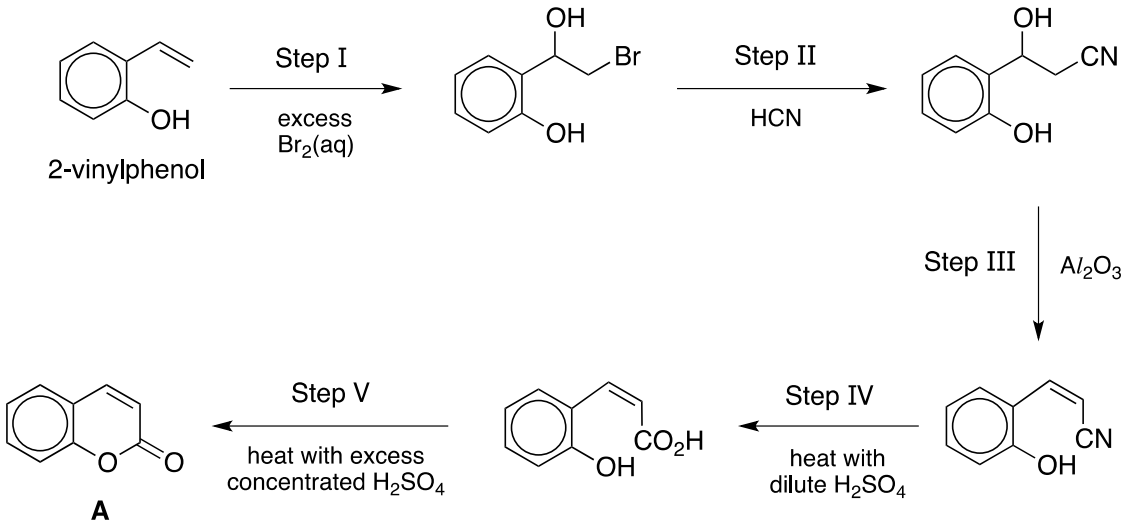
Both compounds **A** and **B** produce a yellow precipitate on warming separately with aqueous alkaline iodine.

(a) State the reagents and conditions for steps **I** and **II**.

(b) Draw the structural formulae of compounds **A**, **B**, **D** and **E**.

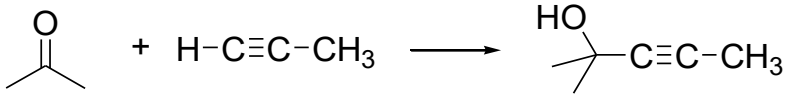
(c) Explain why the reaction in Step **III** produces an equimolar mixture of two stereoisomers of compound **C**.

30 A student was asked to prepare compound **A** using 2-vinylphenol as the starting material. He suggested the following synthetic scheme.

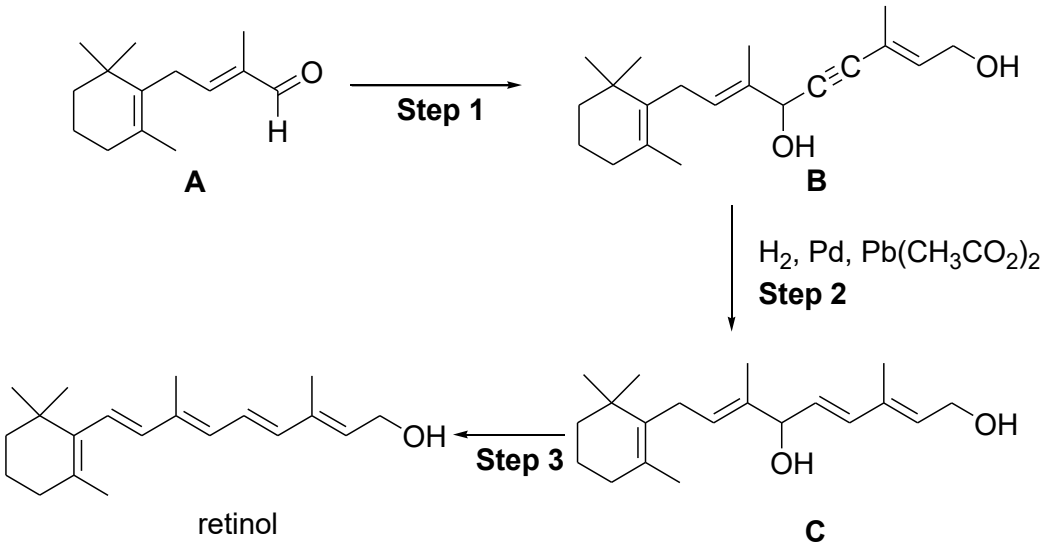


Steps I, II and V are unsatisfactory in his proposed synthesis. For each step that is unsatisfactory, explain why the reaction does not give a good yield of the desired product. Suggest an alternative method to obtain the desired product in steps II and V.

31 Alkynes are hydrocarbons with a carbon-carbon triple bond. When treated with a suitable strong base, alkynes with a hydrogen bonded to the carbon on the triple bond can act as a strong nucleophile that reacts with ketones or aldehydes. For example, propyne reacts with propanone as shown in the reaction below.



The following reaction scheme shows the final steps in the synthesis of retinol (a form of vitamin A).



(i) Draw the structure of the alkyne that is used in **Step 1**.

In **Step 2** of the reaction, compound **B** was heated with hydrogen gas in the presence of palladium and lead(II) ethanoate, $Pb(CH_3CO_2)_2$.

(ii) What type of reaction takes place in this step?

(iii) What is the role of palladium in this step? Explain what feature of palladium makes it suitable for its role.

(iv) Suggest why this step cannot be achieved using hydrogen gas and nickel.

32 In a laboratory, methanol can also be oxidised to other organic compounds using suitable chemicals.

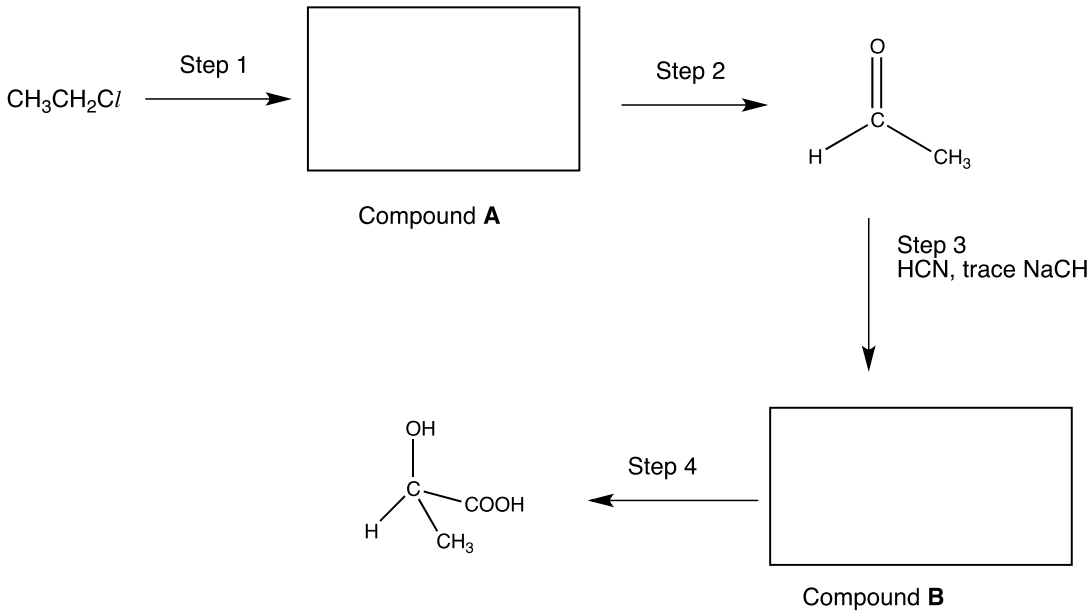
Give the appropriate reagents and conditions required for the following conversion.

I: Methanol $\rightarrow$ Methanal

II: Methanol $\rightarrow$ Methanoic acid

III: Methanol $\rightarrow$ Carbon dioxide

33 A student tries to synthesize lactic acid from chloroethane using a series of reactions as shown.



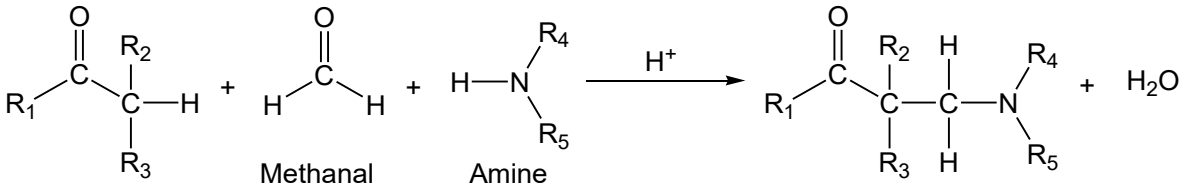
(i) Fill in the intermediate organic compounds **A** and **B**

(ii) State the reagents and conditions for Step 1.

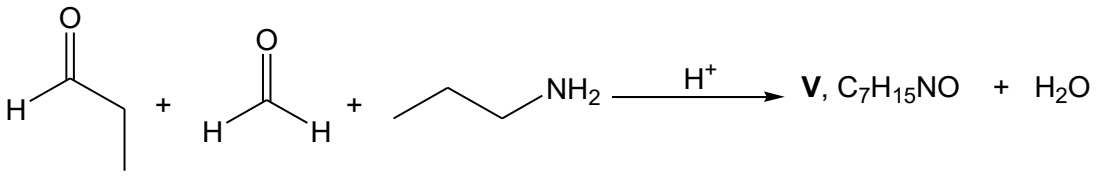
(iii) State the type of reaction for Step 4 and write a balanced equation for this step.

(iv) Lactic acid formed in the above flow scheme is a racemic mixture while lactic acid formed via bacteria fermentation contains only one optical isomer. Explain.

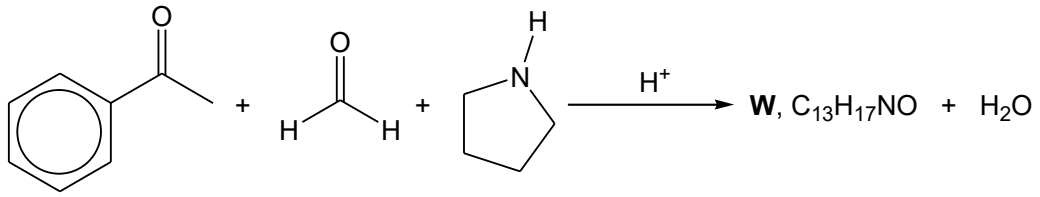
34 (*Advance Question*) Mannich reaction is an organic reaction which consists of an amino alkylation of the hydrogen atom adjacent to a carbonyl functional group, by methanal and a primary amine, secondary amine or ammonia, in the presence of acid.



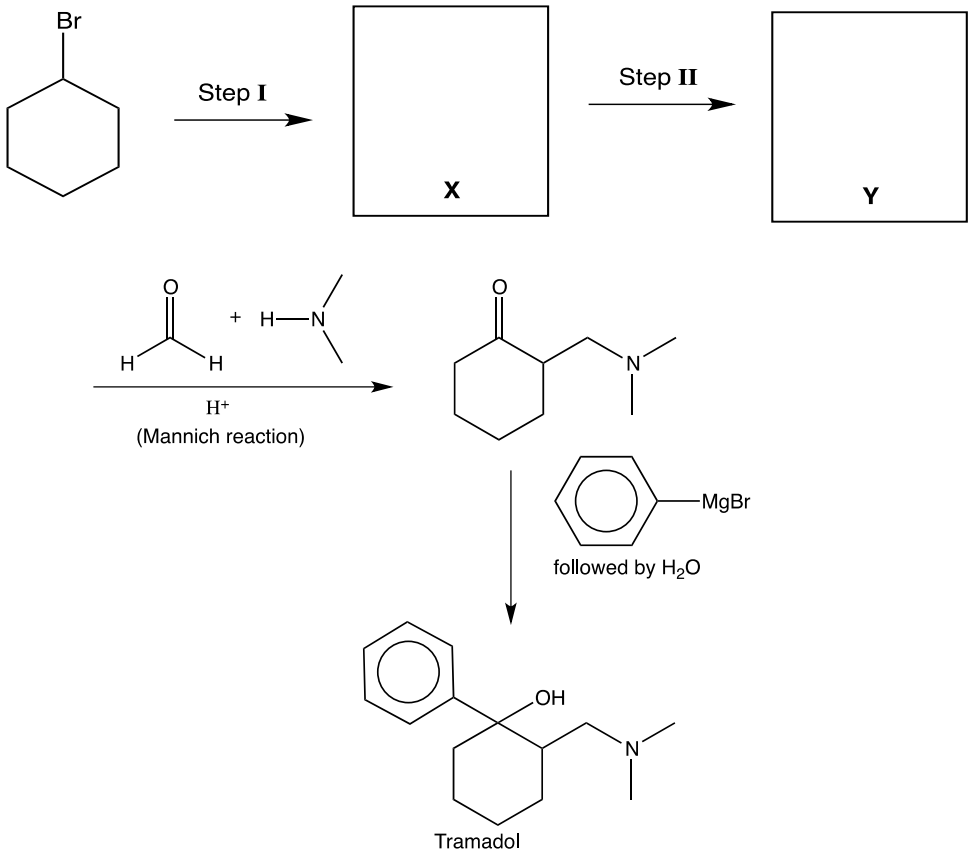
(a) Predict the structures of **V** and **W** for each of the following Mannich reactions.



(ii)



(b) Tramadol is a narcotic-like pain reliever. It could be synthesised from bromocyclohexane via a four step synthetic route. The third step of the reaction scheme involves a Mannich reaction.



(i) Draw the structures of **X** and **Y.**

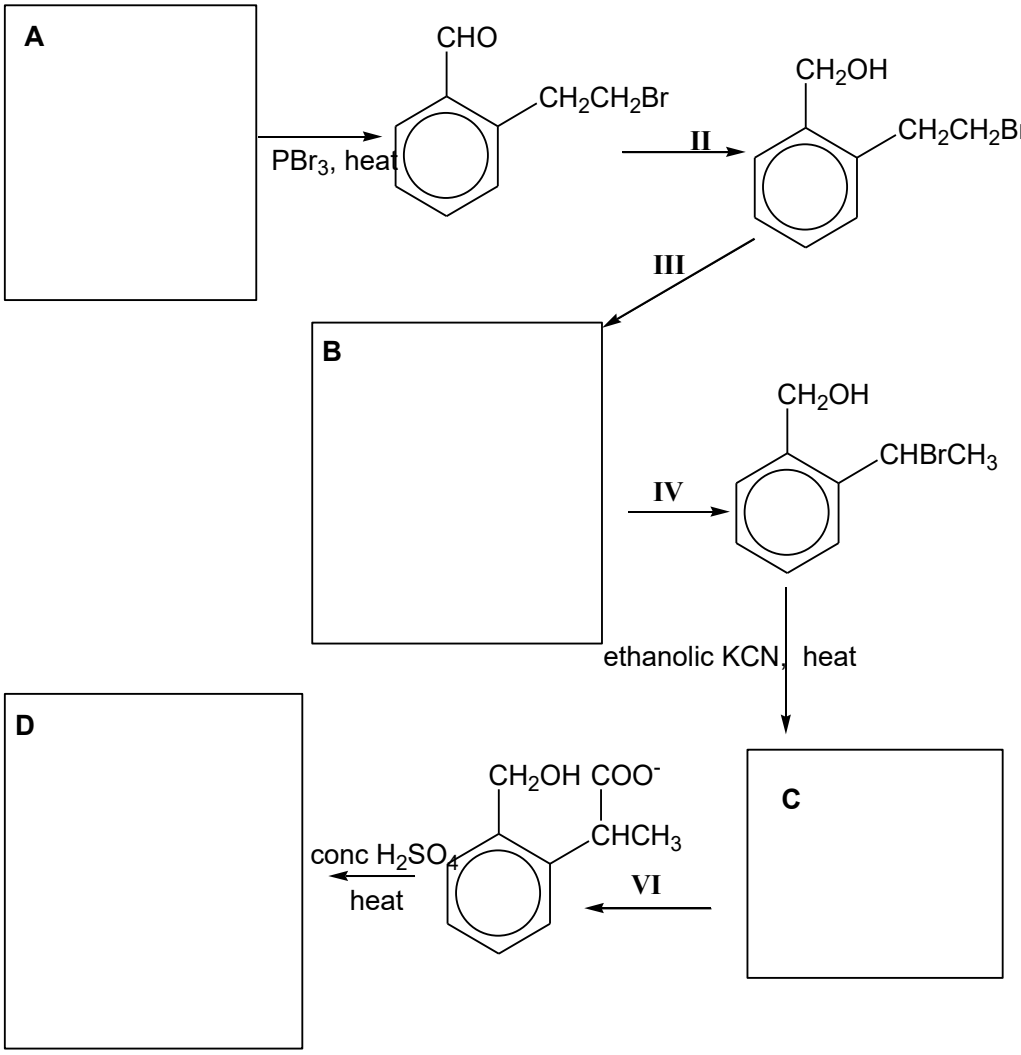
(ii) Suggest the reagents and conditions for **I** and **II.**

(c) When aqueous silver nitrate is added to a solution containing sodium chloride, a white precipitate is formed. When excess aqueous ammonia is added to the resulting solution, the white precipitate dissolves to give solution **Z**.

(i) Suggest the identity of the white precipitate and complex ion found in solution **Z**.

(ii) Solution **Z** is added separately to compounds **V** and **W** from **(a)** and warmed. State the observation and write equations for any reactions that occur.

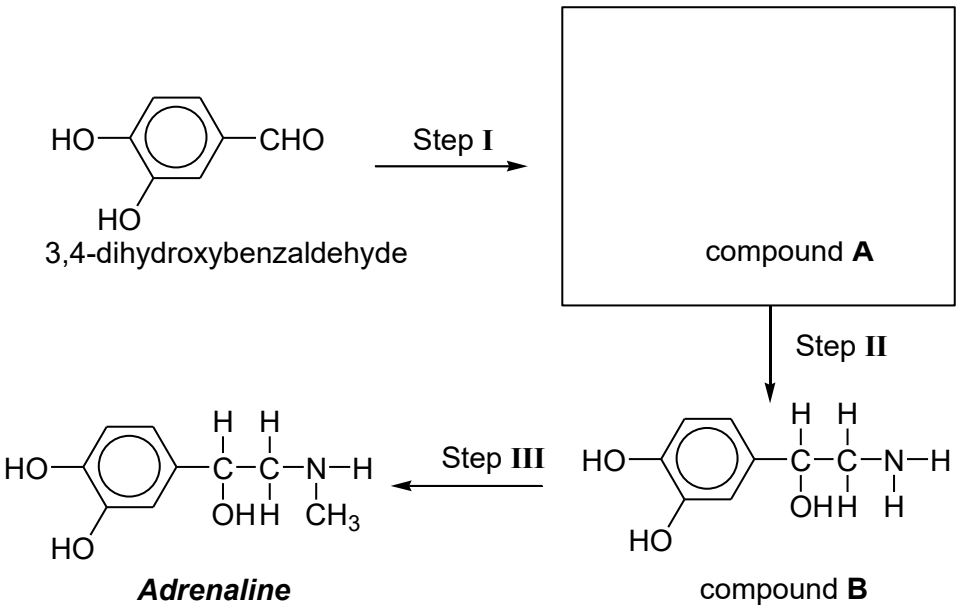
35 PBr_3 is used in the following reaction scheme to produce a sweet-smelling compound **D**.



(i) Draw the structures of **A** to **D** in the spaces provided above.

(ii) Give the reagents and conditions for Steps **II**, **III**, **IV** and **VI**.

36 Adrenaline can be synthesised from 3,4-dihydroxybenzaldehyde via the following reaction pathway with a hydroxynitrile being the intermediate.

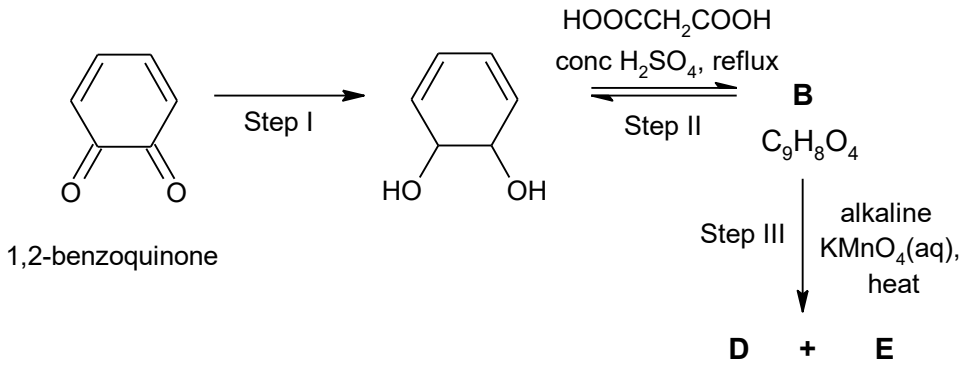


(i) Draw the structural formula of compound **A.**

(ii) State the reagents and conditions required for Steps **I** – **III.**

37 Quinones are used in photography as a reducing agent. Quinone compounds are multifunctional as they exhibit properties of both ketones and alkenes.

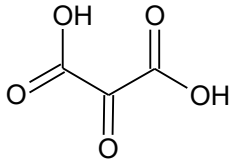
The following scheme involves 1,2-benzoquinone.



(i) State the reagents and conditions needed for Step I.

(ii) Suggest the structures of **B**, **D** and **E**.

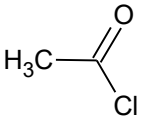
(iii)

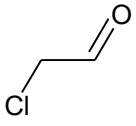


Suggest, in no more than 3 steps, how can be obtained from C*l*CH_2CHO.

Identify the reagents and conditions for each step, and draw the structural formulae of all the intermediates.

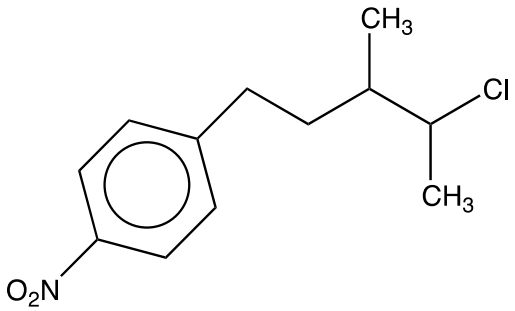
(iv)



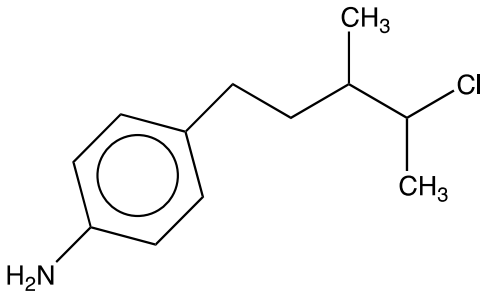
Describe and explain why undergoes hydrolysis more readily compared to  .

2) Distinguishing Test

1 Describe a chemical test that can be used to distinguish between compounds **A** and **B**.



A



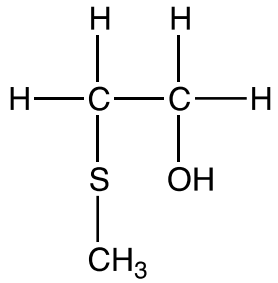
B

2 When the separation of two esters is not complete, one ester will be present as an impurity in a sample of the other ester. Suggest a chemical test that can confirm the presence of the impurity. In each case, state the reagents and conditions, and give the expected observations for each ester.

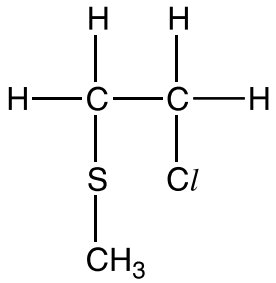
(i) methyl ethanoate in ethyl ethanoate

(ii) ethyl ethanoate in methyl ethanoate

3 Describe a simple chemical test to distinguish between $CH_3SCH_2CH_2OH$ and $CH_3SCH_2CH_2C\mathit{l}$, stating the expected observation for each compound.



$CH_3SCH_2CH_2OH$

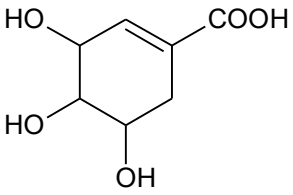


$CH_3SCH_2CH_2C\mathit{l}$

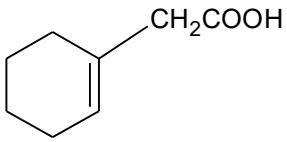
4 Describe a simple chemical test to distinguish between but-1-ene and but-2-ene. State clearly what would be observed with each compound.

5 Suggest a simple chemical test that can be used to distinguish $BrCH_2CH_2OH$ from $HOCH_2CH_2OH$. Give the reagents and conditions and state what would be seen for each compound.

6 Suggest the reagents and conditions for a reaction that could be used to distinguish between *Shikimic* acid and another compound **R.**



***Shikimic* acid**

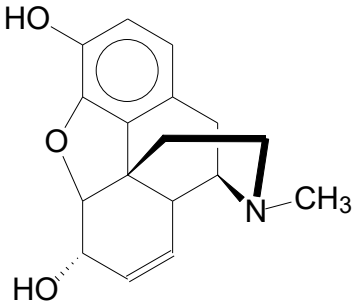


R

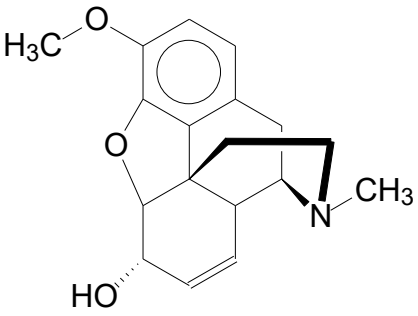
State the expected observation of the reaction on each compound.

7 Suggest how you would distinguish morphine and codeine from each other by means of a chemical test.

State the reagents and conditions you would use, and the observations you would make with **each** compound undergoing the test.

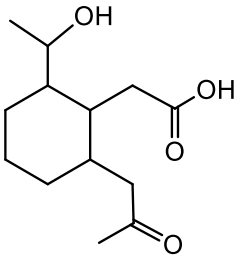


morphine

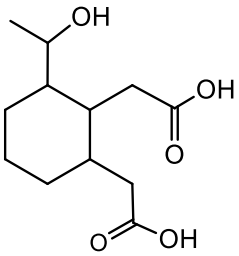


codeine

8 State how compound **U** can be distinguished from product **T** by a simple chemical test, and draw the structure of the organic product that would be produced during this test.

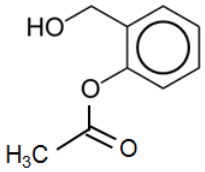


U

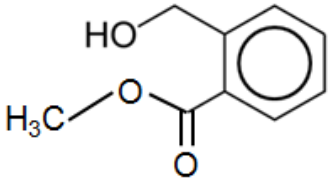


T

9 A laboratory technician realised that the labels to the bottles containing aspirin and another compound had fallen off.



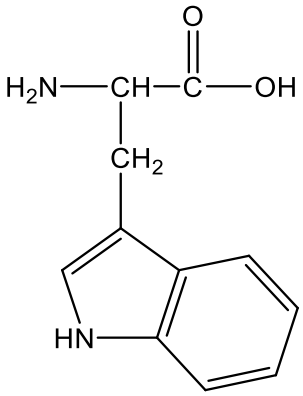
aspirin



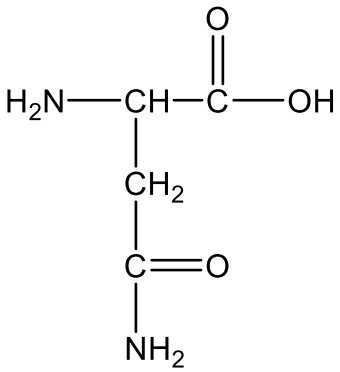
compound X

Suggest a simple chemical test to distinguish between these two compounds.

10 Describe a simple chemical test to distinguish between tryptophan and asparagine.



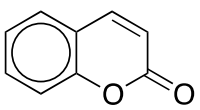
Tryptophan



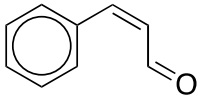
Asparagine

11 The spice cassia has been used in traditional Chinese medicine, where it is considered one of the 50 fundamental herbs.

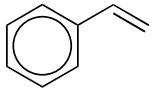
The following four compounds present in cassia are toxic to humans if consumed in large amounts.



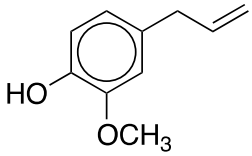
A



B



C



D

[The $-OCH_3$ group in **D** is to be regarded as inert].

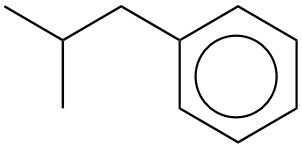
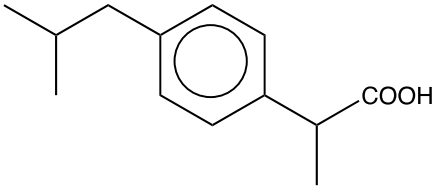
Only **one** of the compounds **A**, **B**, **C** or **D** will react with **each** of the following reagents. In **each** case identify the compound concerned and draw the structural formula of the organic product formed.

Each compound may be used once, more than once, or not at all.

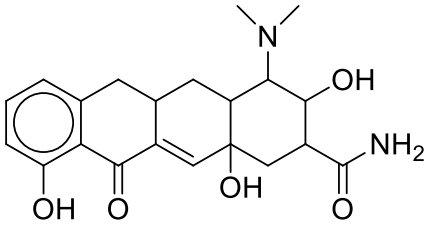
reagent	compound **A**, **B**, **C** or **D**	structural formula of the organic product
dilute HNO_3		
Na		
dilute H_2SO_4; heat		
Fehling's reagent, warm		

12 Describe a simple chemical test that can be used to distinguish between 2-methylpropylbenzene and ibuprofen.

State the observation for each compound.

 2-methylpropylbenzene	 Ibuprofen

13 Tetracycline is a broad–spectrum polyketide antibiotic indicated for use against many bacterial infections. It is commonly used to treat acne today. Compound **M**, a derivative of tetracycline, has the structure shown below.



compound **M**

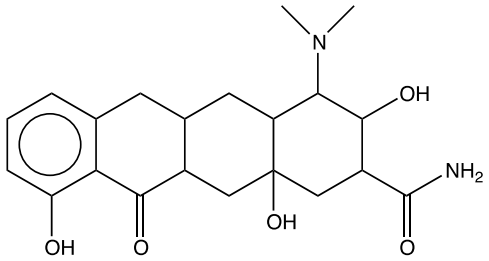
Draw the structures of the organic products formed when compound **M** is treated with

(i) $K_2Cr_2O_7$(aq), H_2SO_4(aq); heat

(ii) aqueous bromine, room temperature

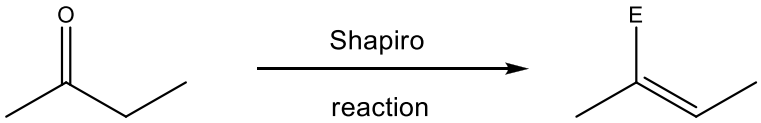
(iii) LiA/H_4 in dry ether, followed by addition of water

(iv) Suggest a simple chemical test to distinguish between **M** and **N**. You should state clearly the reagents and conditions used, and the observations you would expect for each compound.



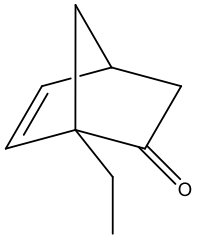
Compound **N**

14 In the Shapiro reaction, a carbonyl group reacts with an electrophile to form an alkene. A simplified example of the Shapiro reaction is shown below.



where E represents an electrophile

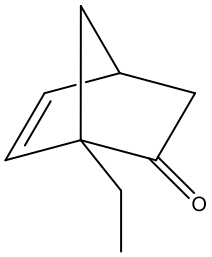
In this question, Shapiro reaction is used on **Q**.



Q

(i) State the number of chiral centers in **Q**

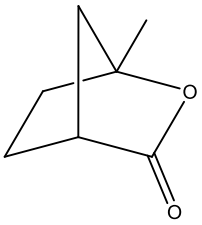
(ii) In the diagram below, circle the sp^2 hybridised carbons.



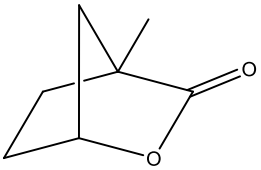
(iii) Draw the structures of the product formed when **Q** reacts with each of the following reagents in the Shapiro reaction.

(I) H_2O (II) Chloroethane

(iv) Cyclic esters **R** and **S** are possible products of the Shapiro reaction.



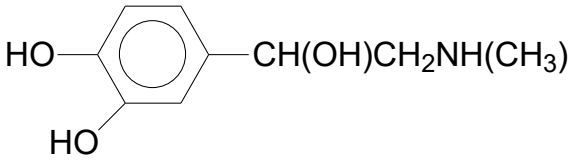
R



S

Suggest reagents and conditions to distinguish between esters **R** and **S**. State the observations for each ester.

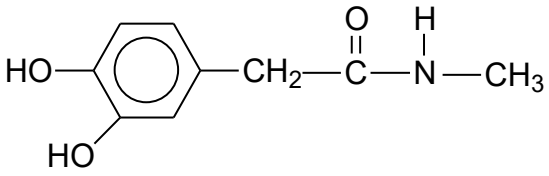
15 Adrenaline is an important hormone concerned with 'fight' and 'flight' situations.



(a) In the boxes below, give the structural formulae of the organic products formed when adrenaline reacts with each of the following reagents.

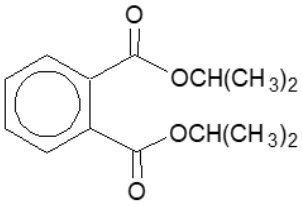
Reagents	**Organic product**
(i) $SOCl_2$	
(ii) Dilute hydrochloric acid	
(iii) Excess NaOH(aq)	

(b) Suggest a simple chemical test that can be used to distinguish between adrenaline and the following compound **Z**:

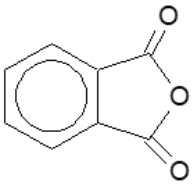


Z

16 Describe a simple chemical test that would allow you to distinguish between compounds **C** and **D.**



C



D

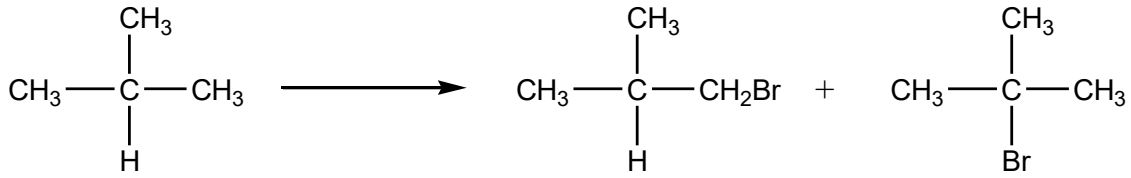
3) Reaction Mechanism

1 When methylbenzene is nitrated by a mixture of concentrated nitric acid and concentrated sulfuric acid, the product consists largely of two isomers, **V** and **W**, of formula $C_7H_7NO_2$. **V** has a plane of symmetry perpendicular to the plane of the benzene ring in its molecule, while **W** does not. The formation of **V** proceeds via an organic intermediate **X**.

(a) Draw the displayed formulae of **V** and **X**, showing clearly the geometry of the bonds around the carbon atom bonded to the nitrogen atom.

(b) What is the name of the mechanism of the reaction for the formation of **V**? Briefly outline the mechanism of this reaction using equations.

2 2-methylpropane reacts with Br_2 to give a mixture in which the major products are two monobrominated alkanes.



37% 63%

(i) State the conditions required for this reaction.

(ii) Outline the mechanism for the formation of 1-bromo-2-methylpropane from 2-methylpropane under the conditions stated in **(i).**

(iii) Discuss two factors which are responsible for the observed percentages of the two monobrominated alkanes.

3 $CH_2C\ell CH_2OH$ reacts with CH_3ONa to give compound **W**, C_2H_4O.

$$CH_2C\ell CH_2OH \xrightarrow{CH_3ONa} C_2H_4O$$

compound **W**

Compound **W** does not decolourise aqueous bromine and it does not react with 2,4-dinitrophenylhydrazine to form an orange precipitate.

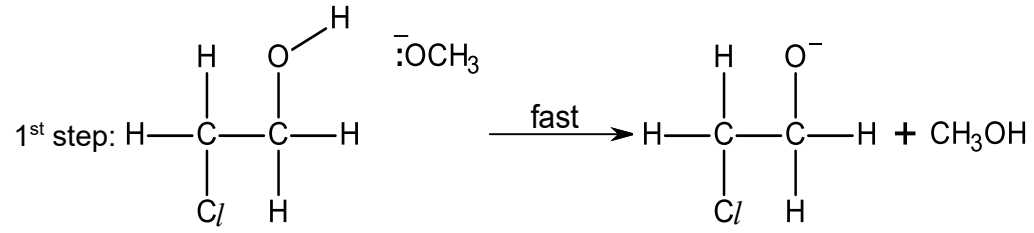
The reaction between CH_3ONa and $CH_2C\ell CH_2OH$ occurs in two steps.

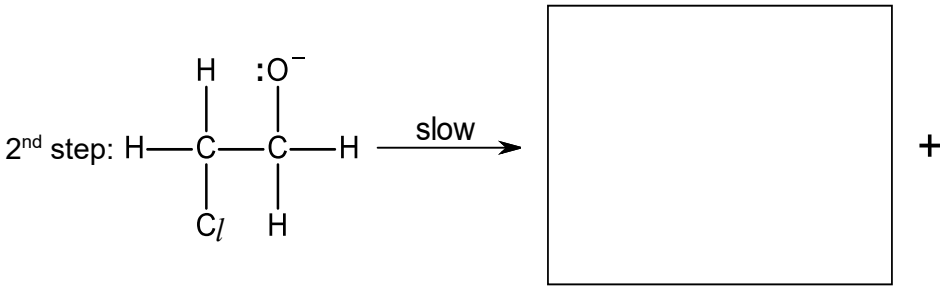
The first step involves an acid-base reaction.

The second step involves an intramolecular reaction and it is rate-determining.

In **each** step below,

label the partial charges on the reacting species, draw **two** curly arrows to show the flow of electrons during the reaction and draw the **displayed** formula of compound **W**.





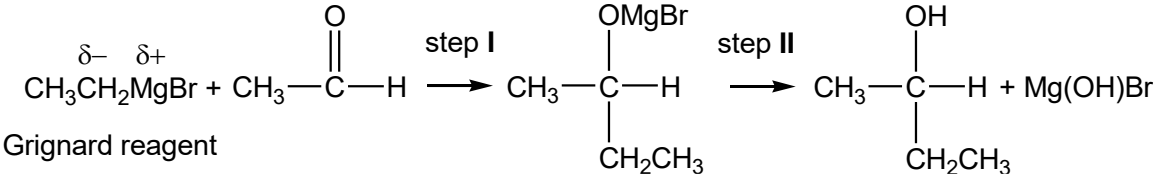
compound **W**

4 In 1911, Victor Grignard discovered that alkyl or aryl halides and magnesium metal turnings will react to produce the Grignard reagent using anhydrous ether as solvent.

$$R{-}X + Mg \xrightarrow{\text{Anhydrous ether}} R^{\delta-}{-}Mg^{\delta+}X$$

Grignard reagent
(R = alkyl or aryl)

Grignard reagents can be used to prepare alcohols from carbonyl compounds as illustrated by the reaction of a Grignard reagent, CH_3CH_2MgBr, with ethanal shown below.



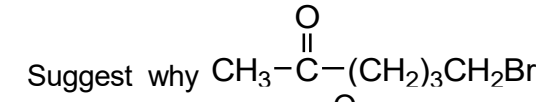
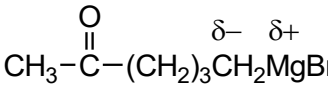
Grignard reagent

(a) **(i)** What type of reaction takes place in step **I**?

(ii) Suggest the type of reaction which occurs in step **II**.

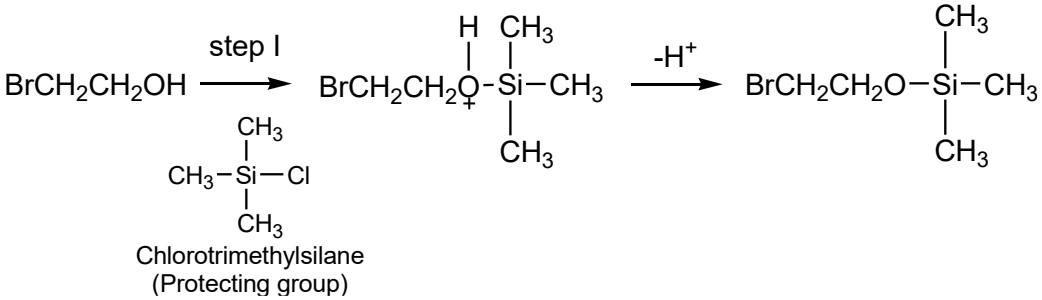
(iii) A racemic mixture of the final organic product was obtained. Account for this observation.

(iv) Suggest the structural formula of the final organic product formed when CH_3CH_2MgBr is reacted with propanone, CH_3COCH_3, in a similar two-step process.

(b) Suggest why  and magnesium cannot be used to prepare the Grignard reagent,  .

(c) $BrCH_2CH_2OH$ cannot be used to prepare the Grignard reagent as the Grignard reagent would react with the –OH group of $BrCH_2CH_2OH$.

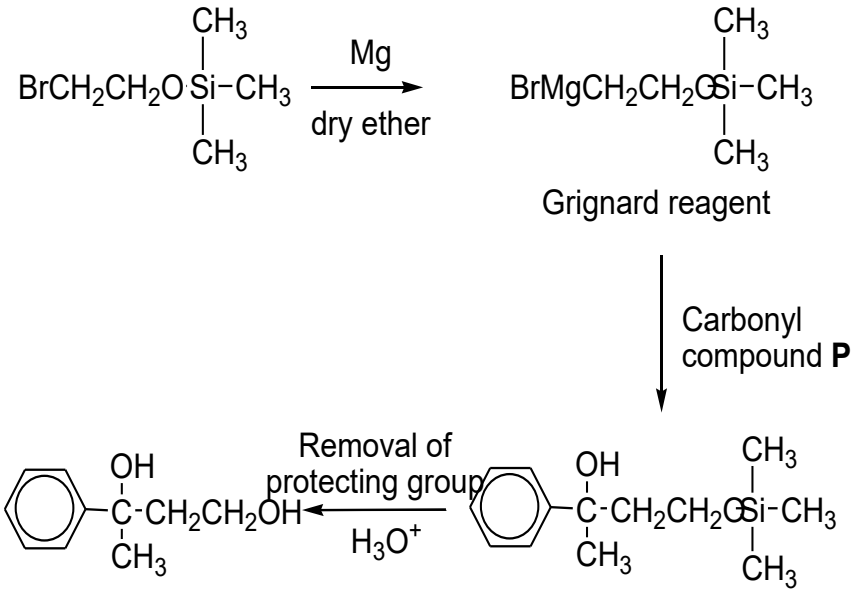
A *protecting group*, chlorotrimethylsilane, can be introduced on the –OH group as shown below to prevent the –OH group from reacting with the Grignard reagent.



(i) In step **I**, $BrCH_2CH_2OH$ acts as a nucleophile and reacts with chlorotrimethylsilane via a S_N2 mechanism. Describe the reaction mechanism in step **I**.

(ii) Silicon is in the same group as carbon. S_N2 mechanism is usually observed for primary alkyl halides. Suggest why a S_N2 reaction can occur at the tertiary trialkyl substituted silicon atom in step **I**.

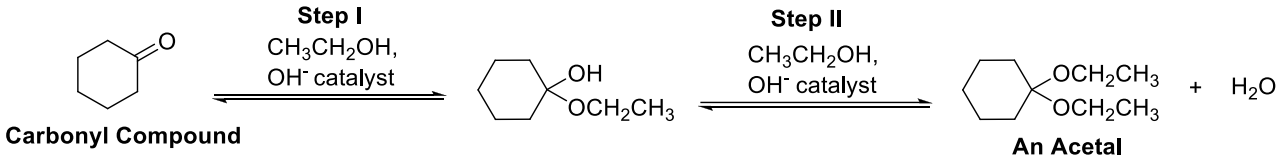
After the protection of the –OH group, the following reaction scheme is carried out between the Grignard reagent and carbonyl compound **P**.



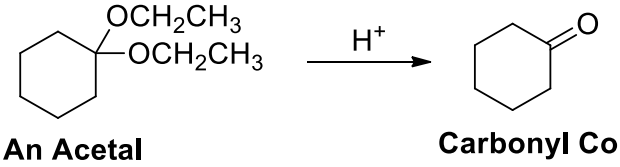
(iii) Draw the structure of the carbonyl compound **P**.

5 Acetal is relatively inert and can be made from a carbonyl compound. The carbonyl functional group may be restored by adding aqueous acid.

Formation of Acetal



Carbonyl functional group is restored by adding aqueous H^+



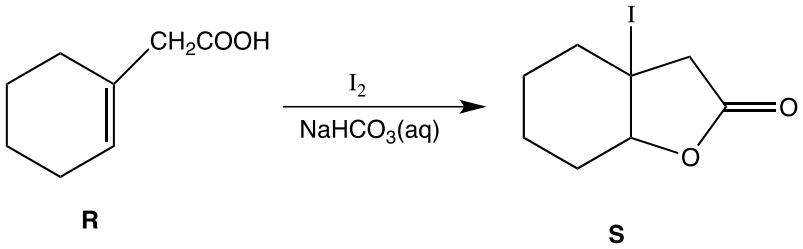
(a) Suggest the type of reaction which occurs in **Step I**.

(b) Suggest why OH^- catalyst is needed in **Step I**.

(c) Outline a mechanism for **Step I.** In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

(d) Explain why anhydrous calcium chloride is added after **Step II.**

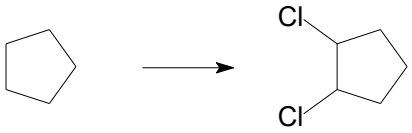
6 (Tutorial Question under Alkene) When compound **R** is reacted with iodine in the presence of aqueous sodium hydrogencarbonate, iodine does **not** add across the carbon–carbon double bond of compound **R** as might be expected. Instead, a compound **S**, which has a molecular formula, $C_8H_{11}O_2I$, is formed as shown:



R **S**

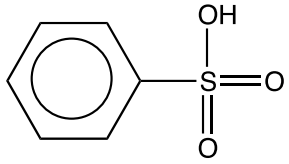
Suggest an explanation for the observation.

7 1,2−dichlorocyclopentane, $C_5H_8Cl_2$, can be produced from cyclopentane, C_5H_{10}, using chlorine gas in the presence of UV light.



Describe the mechanism for this reaction.

8 Aromatic sulfonic acid is an important precursor to industrial materials and has the following structure:



Aromatic sulfonic acid

Sulfonation of benzene is the reaction mechanism between benzene and sulfuric acid. The first step of the reaction mechanism is given by the following equation.

$$H_2SO_4 \rightleftharpoons H_2O + SO_3$$

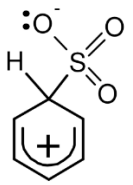
Sulfur trioxide is an important intermediate in the reaction mechanism.

(i) Draw a dot-and-cross diagram of sulfur trioxide.

(ii) With reference to the structure of the molecule, state and explain the function of sulfur trioxide in the mechanism.

(iii) The final step of the mechanism is different from other benzene reactions because the hydrogen atom is not removed from the ring by a separate negative ion. Instead it is removed by a lone pair of electrons on a negative oxygen atom in the sigma complex.

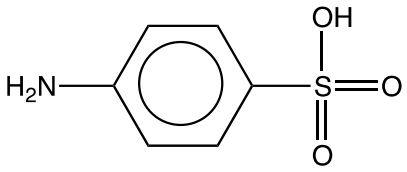
The sigma complex formed has the following structure:



Sigma complex

With the above information, complete the mechanism for the reaction between benzene and sulfuric acid.

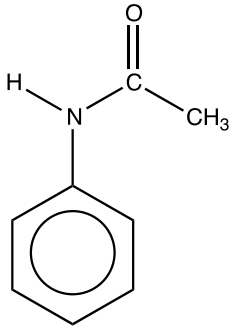
(iv) Sulfonation of aniline produces sulfanic acid compounds with an unusually high melting point. With reference to the structure of sulfanic acid, suggest why this is so.



Sulfanic acid

9 (Advanced Question) Some chemistry students were doing an organic chemistry practical.

(a) Student X heated compound **F** with hydrochloric acid to form two organic products. In order to isolate both products, the reaction mixture was placed in a separating funnel and shaken with water.



Compound **F**

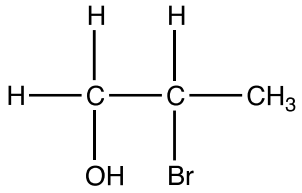
(i) Draw the products of the above reaction.

(ii) Explain why the separation will not be successful.

(iii) Describe the correct procedure to separate the hydrolysis products.

(b) Under acidic conditions, Student Y treated ethylamine with excess iodomethane in an attempt to form a quaternary amine salt. Explain why this synthesis will not be successful.

(c) Student Z predicted that compound **G** was formed from the reaction of propene and aqueous bromine in the presence of concentrated sodium chloride.



Compound **G**

(i) Explain why his prediction is wrong.

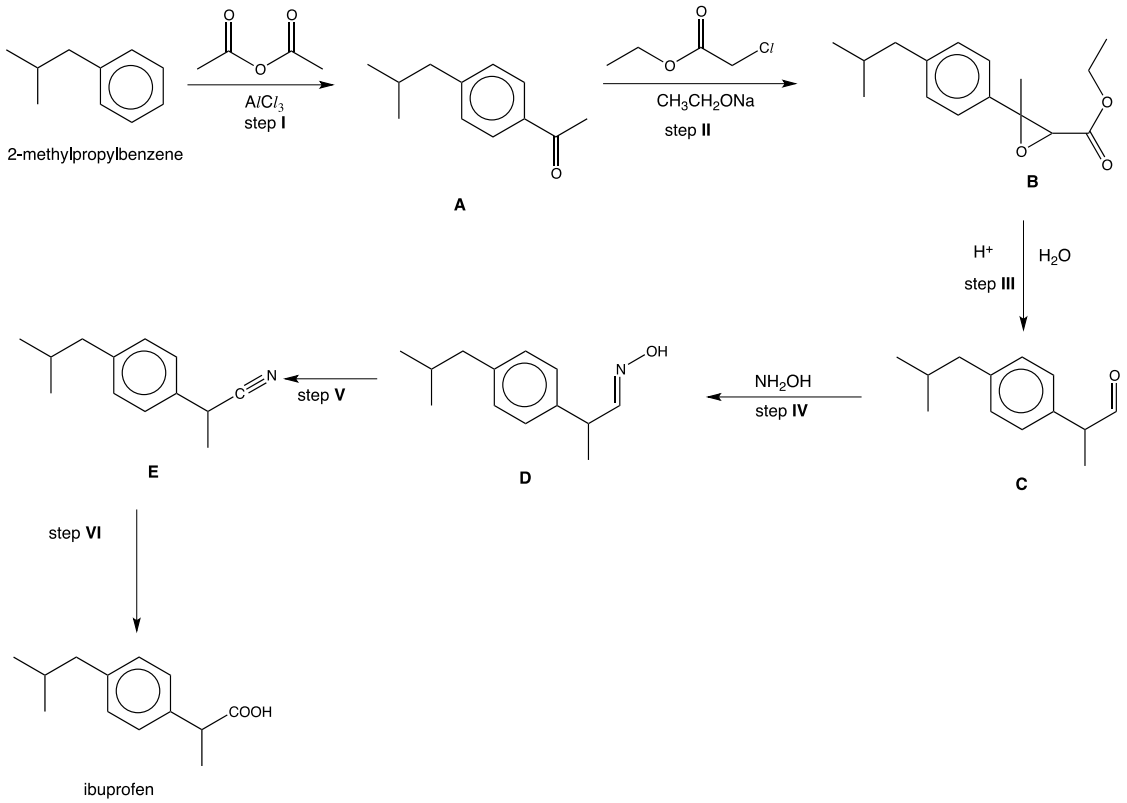
(ii) Hence, suggest the structure of the major product formed.

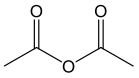
10 Benzyl iodide is converted to its alcohol readily by heating with aqueous sodium hydroxide.
$C_6H_5CH_2I + NaOH \longrightarrow C_6H_5CH_2OH + NaI$
The rate equation is rate = k [$C_6H_5CH_2I$].

(i) Describe the mechanism of this reaction. In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.

(ii) Explain why benzyl iodide undergoes a unimolecular reaction with NaOH(aq) whereas (2–iodoethyl)benzene, $C_6H_5CH_2CH_2I$, undergoes a bimolecular reaction with NaOH(aq).

11 Ibuprofen is an over-the-counter remedy for mild to moderate pain and is sold under the brand name Nurofen. In the United Kingdom, ibuprofen was originally synthesised and first patented in 1961 by the research team in Boots Company. The starting material for the synthesis of ibuprofen is 2-methylpropylbenzene, which has a similar carbon skeleton to that of ibuprofen. The reaction scheme below shows Boots' synthesis of ibuprofen:



(a) Step **I** proceeds via an electrophilic substitution mechanism where the aluminium chloride acts as a Lewis acid catalyst. The aluminium atom is electron deficient, allowing it to accept a lone pair of electrons from the oxygen on the  molecule. The C–O bond breaks, generating the electrophile and another singly-charged anion as the only products.

(i) Draw the structure of the electrophile.

(ii) From the information given and your answer in **(i)**, suggest a balanced equation to illustrate the step involving the generation of the electrophile.

(iii) Describe the mechanism for the formation of intermediate **A** from 2-methylpropylbenzene, including curly arrows showing the movement of electrons, and all charges.

(b) The three-membered ring in intermediate **B** is known as an epoxide functional group.

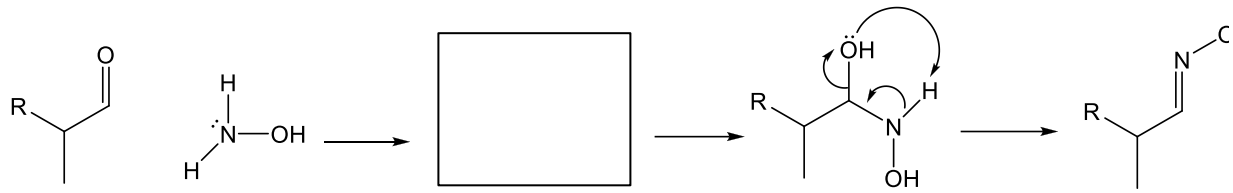
State the hybridisation of the carbon atom in the epoxide ring and suggest why epoxides are highly reactive.

(c) The conversion of intermediate **C** to **D** in step **IV** involves the following sub-steps:

1. nucleophilic addition of NH_2OH to the carbonyl group in **C** to form a zwitterion

2. intramolecular transfer of proton, forming an O–H bond and breaking an N–H bond in the zwitterion to give intermediate **X**

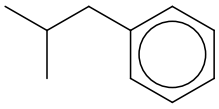
Draw the zwitterion formed from the nucleophilic addition step in the box. Complete the reaction scheme below for sub-steps 1 and 2, using curly arrows to show movement of electrons and label all charges.



C **X**

D

where R =



(d) (Advanced Question) A dose of Nurofen contains more than just ibuprofen, the active ingredient. The science of blending other ingredients into the dose is known as formulation and Nurofen is available in a number of formulations. They include tablets to be taken orally or gels to be applied onto the skin. The oral variant is often formulated as the free acid or a lysine salt while the gel variant is often formulated with propan-2-ol.

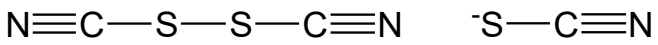
(i) The ibuprofen in the lysine salt variant is found to be absorbed by the body nearly twice as quickly as the free acid variant.

Suggest why this is so.

(ii) The gel variant is rubbed into painful parts of the body so that the active ingredient is applied directly to the site of pain. The inner layer of the skin consists mainly of polar molecules.

With reference to the polarities of ibuprofen and propan-2-ol, explain why ibuprofen is formulated with propan-2-ol instead of being applied directly on the skin as the free acid.

12 Pseudohalogens are a class of compounds that show chemical reactivity similar to halogens. An example of a pseudohalogen and its anion is $(SCN)_2$ and SCN^- respectively.



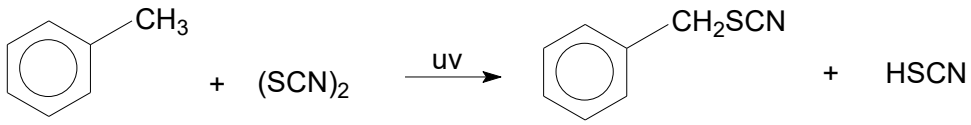
thiocyanogen thiocyanate

(a) **(i)** Draw the shape of the hybrid orbitals around one of the carbon atoms in thiocyanogen.

(ii) Draw a diagram to illustrate the shape of thiocyanogen, indicating clearly the covalent bonds and lone pairs of electrons.

(iii) Thiocyanogen can be synthesised by reacting sodium thiocyanate, NaSCN, with chlorine gas. Write an equation for the formation of thiocyanogen.

(b) Thiocyanogen can react with hydrocarbons such as methylbenzene via free radical substitution.



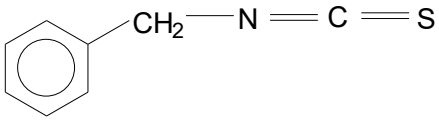
(i) Write equations that describe the following steps.

Initiation:

Propagation:

Termination: (write all the possible termination steps)

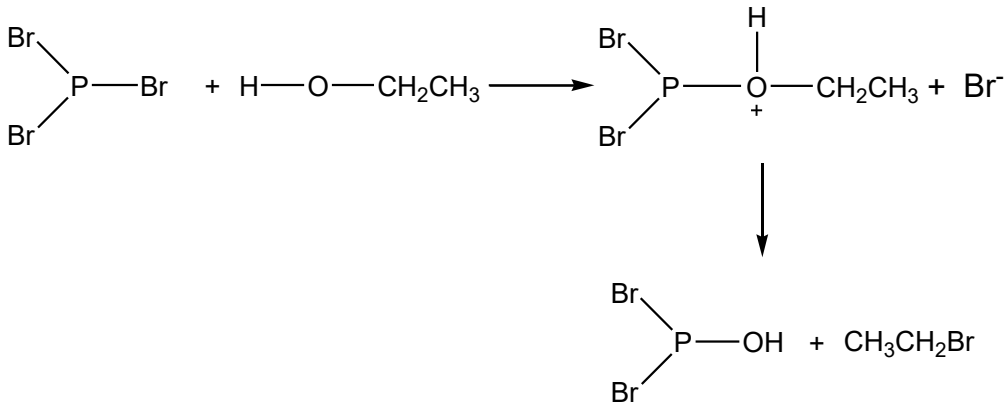
(ii) An isomer of the product shown below was also isolated. Suggest a reason for the formation of this isomer.



13 The general equation for the formation of alkyl bromide from alcohols using phosphorus tribromide is:

$PBr_3 + 3ROH \rightarrow 3RBr + H_3PO_3$

The reaction mechanism for the above reaction using ethanol and phosphorus tribromide is shown below.



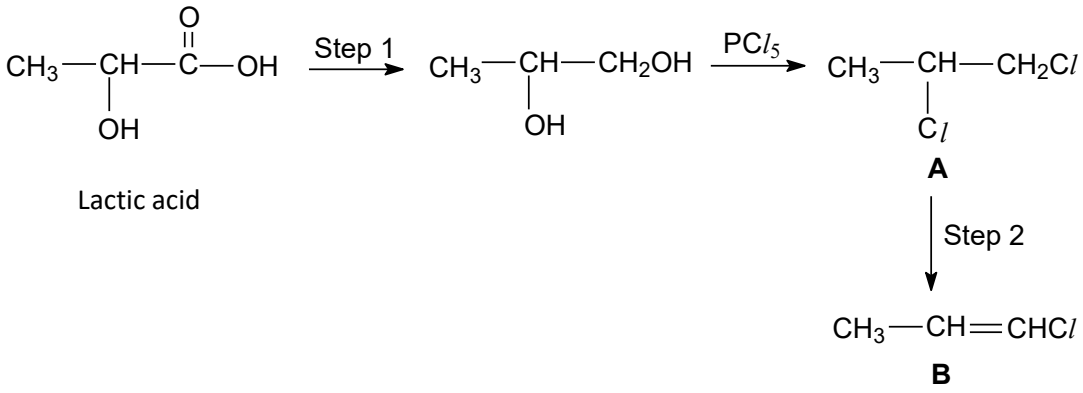
(i) State the type of reaction for the overall reaction

(ii) Complete the mechanism above by using partial charges, lone pairs and curly arrows to represent the electron flow.

(iii) Suggest a reason why this reaction method cannot be used to prepare $C(CH_3)_3Br$.

(iv) Using the above mechanism in **(ii)**, suggest the organic compound formed when *ethanoic acid* is reacted with phosphorus tribromide.

14 Lactic acid can undergo a series of reactions as shown below.



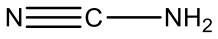
Lactic acid

(i) What reagents and conditions are required for step 1 and 2?

(ii) Arrange the two compounds **A** and **B** in order of increasing ease of hydrolysis, giving your explanations clearly.

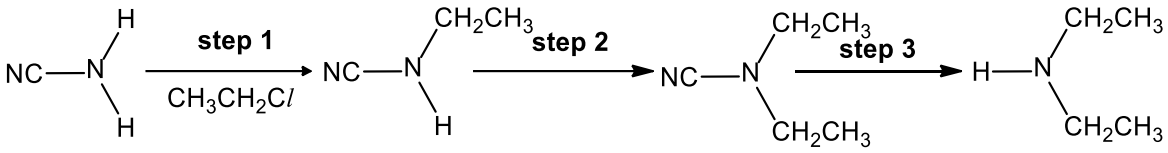
15 (a)

Cyanamide, CH_2N_2, is a compound commonly used in fertilisers that could also cause eutrophication, which deplete the water's oxygen supply through excessive growth and decomposition of algae and water plants.



cyanamide

Cyanamide is a useful precursor for the synthesis of secondary amines with a relatively high yield. Below is the sequence of steps for the synthesis of N-ethylethylamine.



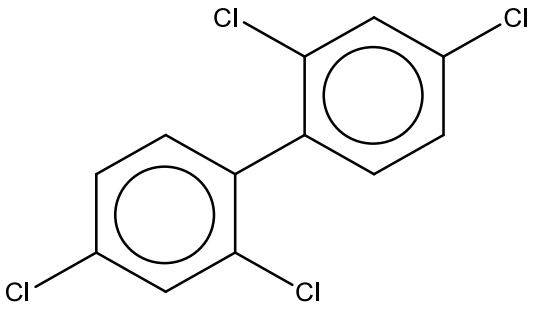
N-ethylethylamine

(i) Describe the mechanism for the reaction in **step 1**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

(ii) Identify the two roles of cynnamide in your mechanism.

(iii) Besides using a specific catalyst and heating under reflux for steps 1 and 2, suggest another condition which would allow a high yield of the intermediate formed in step 2.

(b) 2,2',4,4'-tetrachlorobiphenyl is a common organic pollutant that is immiscible in water.

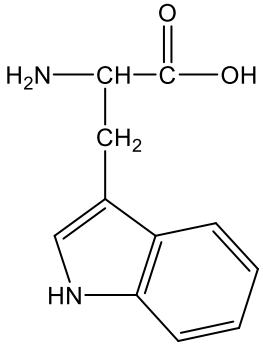


2,2',4,4'-tetrachlorobiphenyl

Suggest two reasons why 2,2',4,4'-tetrachlorobiphenyl is typically inert and chemically unreactive to nucleophilic reagents.

4) Amino Acids & Proteins

1. Isopentyl alcohol is one of the main ingredients for Kovac's reagent. Kovac's reagent is used to determine the ability of an organism to split the bicylic structure from the amino acid tryptophan.

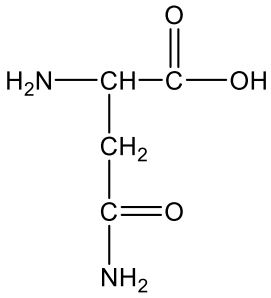


Tryptophan

(i) Explain why tryptophan is a crystalline solid at room temperature.

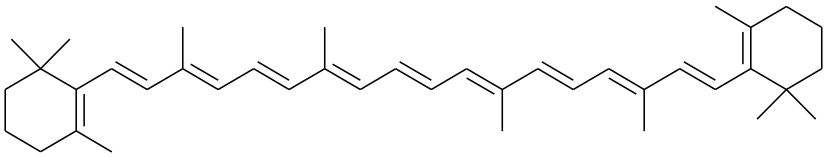
(ii) With the aid of a diagram, explain why tryptophan is soluble in water.

(iii) Draw the dipeptide formed between tryptophan and asparagine.



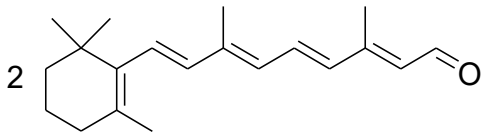
Asparagine

2 *β*-carotene, a red-orange pigment found in carrots and papayas, is converted in our body by the enzyme beta-carotene monooxygenase (BCO) to retinal, which is a precursor of retinol.



β-carotene

BCO



retinal

A student attempts to carry out the same conversion in the laboratory using hot acidified potassium manganate(VII), but finds that different products are obtained

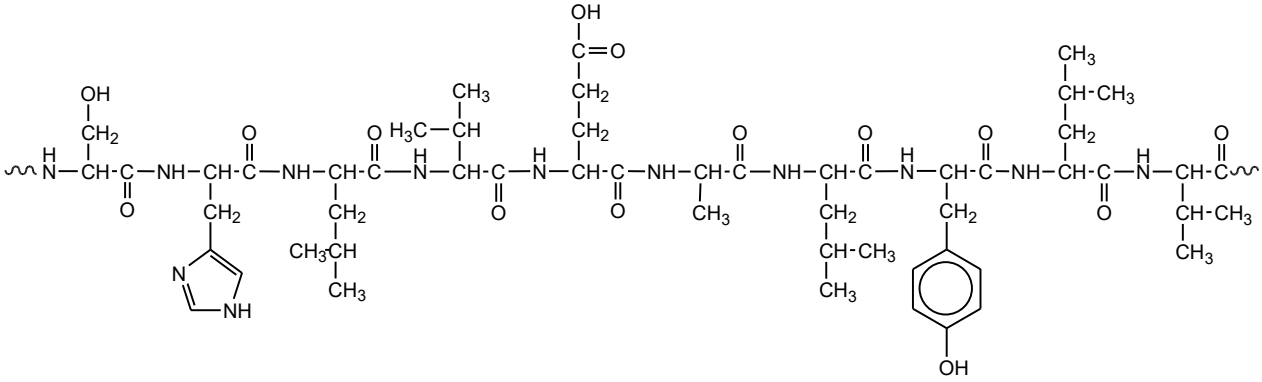
(i) Draw the structures of the two organic products formed when *β*-carotene is treated with an excess of hot acidified potassium manganate(VII).

(ii) Suggest why the enzyme BCO is able to convert *β*-carotene to retinal, but this conversion cannot be achieved in the laboratory using excess hot acidified potassium manganate(VII).

3 (Advanced Question)

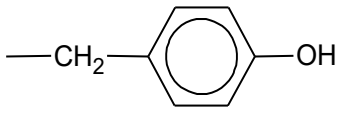
a Insulin is a peptide hormone that is essential in regulating carbohydrates and fat metabolism in the body. It is composed of two peptide chains (e.g. chain A and chain B). Both the chains are joined together by two disulfide linkages, and another disulfide linkage is formed within chain A. In most species, the insulin is composed of 51 amino acids, where chain A consists of 21 amino acids while chain B consists of 30 amino acids.

The structure of a portion of chain B is shown below.



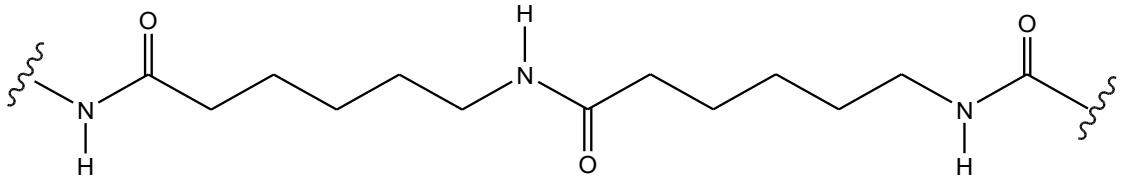
How many different amino acid residues are present in this portion of chain B?

b A nonapeptide **P** was analysed and it contained the following amino acids:

amino acid	*abbreviation*	*formula of R-group*	*number of residues*
Aspartic acid	Asp	$-CH_2CO_2H$	3
Lysine	Lys	$-(CH_2)_4NH_2$	2
Tyrosine	Tyr		3
Valine	Val	$-CH(CH_3)_2$	1

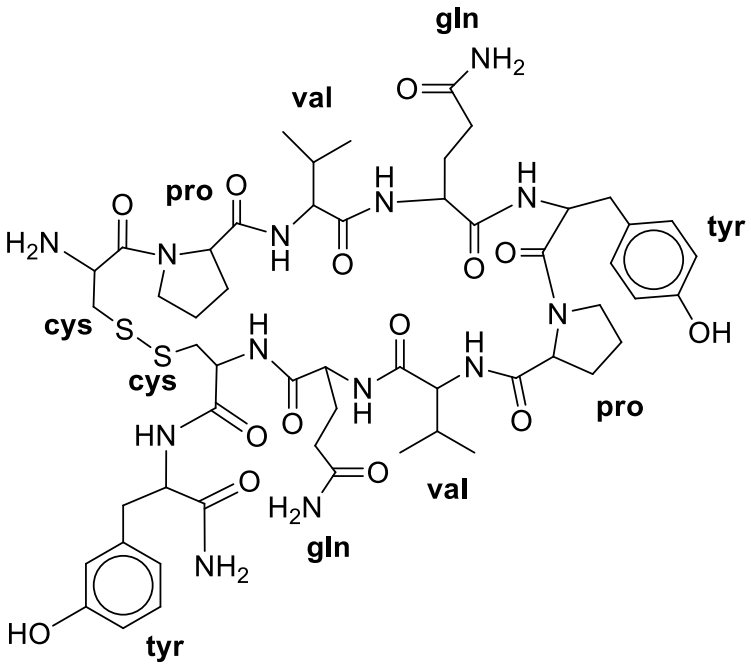
Draw the displayed formula of the Lys-Asp-Tyr tripeptide at pH 11.

(c) Nylon 6 is synthesised by ring opening polymerisation of caprolactam molecules. When caprolactam molecule polymerises, the ring breaks and the molecules join up in a continuous chain as shown below.



Suggest the structure of caprolactam.

4 The structure of a small protein is given below, along with the abbreviated names of its constituent amino acids: **val**, **gln** etc.



(i) This protein is ionised at pH 7. Identify **one** functional group that could be ionised at pH 7 by circling it on the structure above.

(ii) The activity of the above protein is destroyed by heating it under reflux with 6 mol dm^{-3} sulfuric acid for several hours.

Draw the structures of the organic products formed under these conditions from the part of the above protein containing the amino acids: **val-gln**.

5) Kinetics of Organic Reactions

1 The kinetics of the reaction below was studied.

$CH_3SNa + CH_2C\mathit{l}CH_2OH \xrightarrow[\text{heat}]{\text{ethanol,}} CH_3SCH_2CH_2OH + NaC\mathit{l}$

The experimental results are given in the table below.

experiment number	$[CH_3SNa]$ / mol dm^{-3}	$[CH_2C\mathit{l}CH_2OH]$ / mol dm^{-3}	relative rate
1	0.100	0.150	6
2	0.150	0.150	9
3	0.200	0.200	16

(i) Use the data to determine the order of reaction with respect to both CH_3SNa and $CH_2C\mathit{l}CH_2OH$.

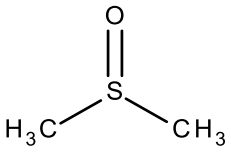
Hence, write a rate equation for the reaction.

(Advanced Question)

In organic syntheses, the choice of solvent can affect the rate of a reaction.

The process of forming ion-dipole interactions between ions and solvent molecules is called solvation. Polar protic solvents such as ethanol, CH_3CH_2OH, contain at least one hydrogen atom directly bonded to an electronegative atom. These solvents solvate both cations and anions.

Polar aprotic solvents contain no hydrogen atom directly bonded to an electronegative atom. These solvents solvate cations well, but not anions. Dimethyl sulfoxide (DMSO) is an example of a polar aprotic solvent.



DMSO

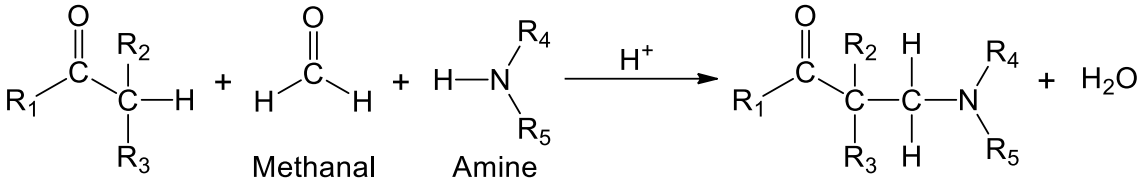
(ii) State the ion which acts as the nucleophile in the reaction

$CH_3SNa + CH_2C\mathit{l}CH_2OH \xrightarrow[\text{heat}]{\text{ethanol,}} CH_3SCH_2CH_2OH + NaC\mathit{l}$

(iii) Explain why DMSO does not solvate anions effectively.

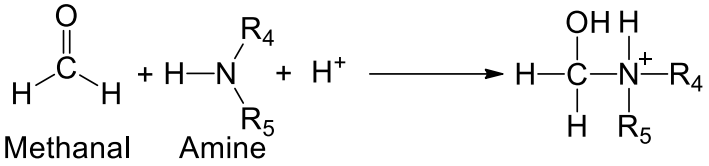
(iv) With reference to your answers to **(i)** and **(iii)**, explain why the rate of reaction is 1000 times faster when the reaction in step **II** is carried out in DMSO instead of ethanol.

2 Mannich reaction is an organic reaction which consists of an amino alkylation of the hydrogen atom adjacent to a carbonyl functional group, by methanal and a primary amine, secondary amine or ammonia, in the presence of acid.

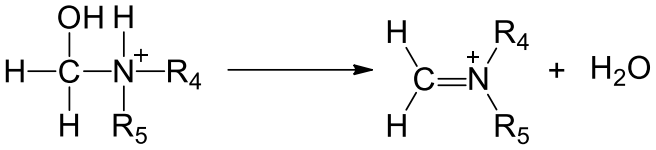


The proposed mechanism for Mannich reaction:

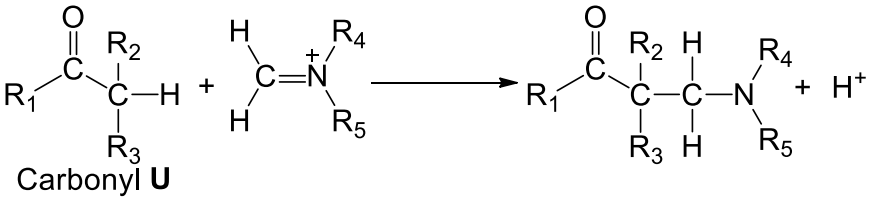
Step 1:



Step 2:



Step 3:

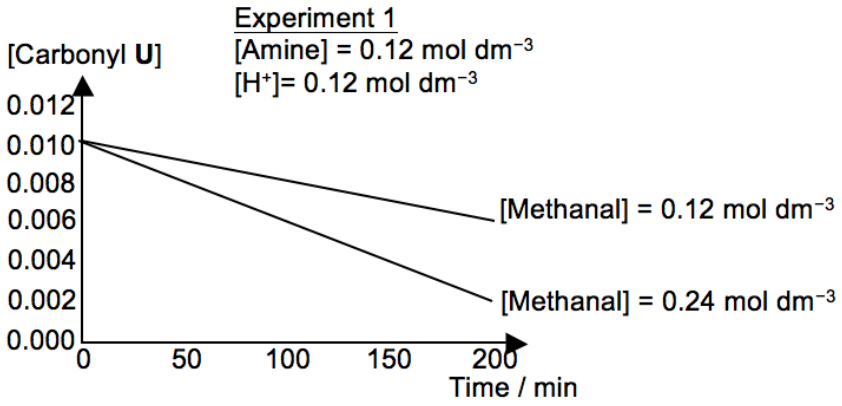


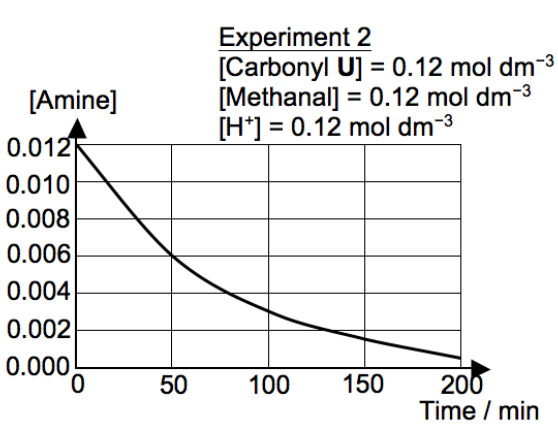
(a) Suggest the types of reaction that occurred in steps 1 and 2.

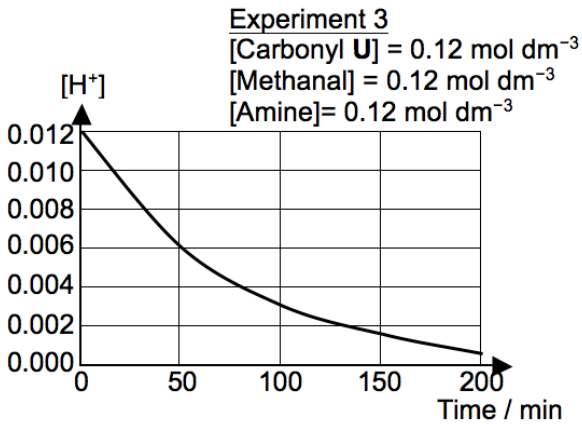
(b) The rate equation for the Mannich reaction can be expressed as

rate = k [Carbonyl **U**]^p [Methanal]^q [Amine]^r [H$^+$]^s

A chemist carried out a series of experiments to investigate the order of reaction with respect to each of the reactants.







(i) Determine the values of p, q, r and s.

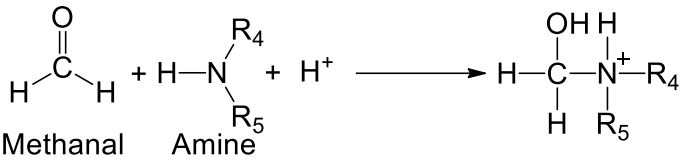
(ii) State and explain which step of the mechanism is the rate-determining step

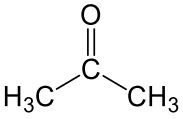
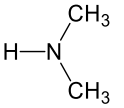
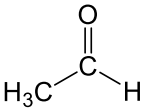
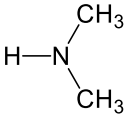
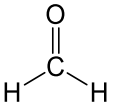
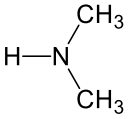
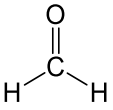
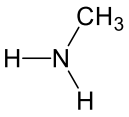
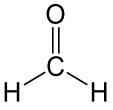
(iii) Suggest why such a reaction is unusual.

(iv) Using data from experiment 2, calculate the rate constant k, stating its units.

(c) The chemist decides to further investigate step 1 of the mechanism by replacing methanal with other carbonyl compounds, and using different amines. The concentrations of all the reactants are kept constant for all experiments.

Step 1:



experiment	*carbonyl compound*	*amine*	*initial rate / $\times 10^{-4}$ mol dm^{-3} min^{-1}*
4			0.55
5			1.02
6			1.98
7			1.01
8		NH_3	0.33

Suggest an explanation of the trend in the initial rate for

(i) Experiments 4, 5 and 6

(ii) Experiments 6, 7 and 8

6) Acidity and Basicity of Organic Compounds

1 Sodium methanethiolate, CH_3SNa, can be made from methanethiol, CH_3SH.

Although methanethiol is structurally similar to methanol, the two compounds have significantly different pK_a values at 298 K.

compound	**formula**	**pK_a**
methanol	CH_3OH	15.5
methanethiol	CH_3SH	10.4

Explain briefly why methanethiol has a smaller pK_a value than methanol.

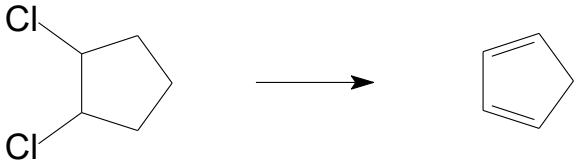
2 An aqueous solution of lactic acid, $CH_3CH(OH)CO_2H$, of concentration 0.100 mol dm^{-3} has a pH value of 2.04.

(a) Calculate the value of the dissociation constant, K_a, for lactic acid (to be covered under acid-base equilibrium)

(b) Suggest with reasoning, whether lactic acid or propanoic acid would result in a less exothermic reaction with 0.100 mol dm^{-3} NaOH solution.

(K_a of propanoic acid =1.3 x 10^{-5} mol dm^{-3})

3 1,2−dichlorocyclopentane can be converted to cyclopentadiene.



(a) Identify the type of reaction and give the reagents and conditions required for this conversion.

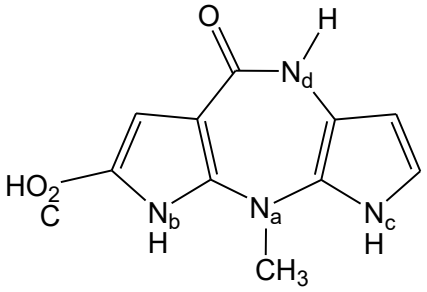
(b) Unlike the normal alkenes, cyclopentadiene is unusually acidic with a pK_a of 16. It can react with sodium metal to produce hydrogen gas.

$C_5H_6 + Na \rightarrow C_5H_5Na + ½\ H_2$

Draw the structure of the anion of cyclopentadiene formed in the above reaction and hence explain the acidic nature of cyclopentadiene.

4 (Advanced Question)

A derivative of an anti-viral drug, nevirapine (compound **A**), is recently found to be effective in treatment against AIDS and AIDS-related opportunistic infections. Compound **A** has 4 nitrogen atoms labelled N_a to N_d.



compound **A**

(a) Name all the functional groups present in compound **A**.

(b) **(i)** The nitrogen atoms labelled, N_b and N_c, are part of two planar aromatic rings. State the type of hybridisation exhibited by N_b and N_c.

(ii) The nitrogen labelled, N_a, is the most basic among the 4 nitrogen atoms. Rank the basicity of the other 3 nitrogen atoms from the most basic to the least basic. Explain the order of the basicity of the 3 nitrogen atoms you have ranked.

(c) Compound **A** exists mainly as zwitterions. Two physical properties of compound **A** are described as follows. Account for the physical properties using equation(s) when appropriate.

(i) Compound **A** has high melting point and exists as a crystalline solid at room temperature and pressure.

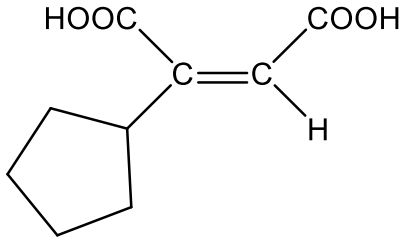
(ii) The pH remains relatively constant when a small amount of base is added to a solution of compound **A**.

5 Lactic acid is a carboxylic acid with the formula $CH_3CH(OH)CO_2H$.

In solution, lactic acid can lose a proton from the carboxyl group, producing the lactate ion $CH_3CH(OH)CO_2^-$. Compared to ethanoic acid, lactic acid is more acidic as it deprotonates ten times more easily than ethanoic acid.

Other than the electron withdrawing effect of –OH group, suggest **another** factor which explains the additional stability of the lactate ion. Illustrate your answer with a diagram.

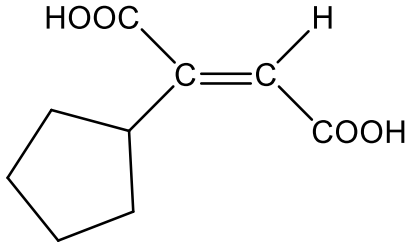
6 The structure of a dicarboxylic acid **J** is shown below.



J

i The pK_a values of the two acidic groups in **J** are 2.2 and 6.4. In the diagram above, circle the acidic group which has a pK_a value of 2.2. Explain your answer.

K is an isomer of **J.**

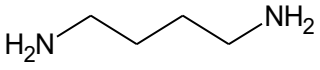


K

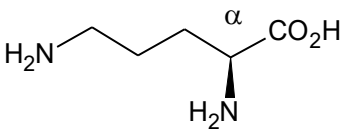
(ii) State the type of isomerism exhibited in **J** and **K.**

(iii) Draw a diagram of the anion formed for **J** to explain the large difference between the two pK_a values in **J**.

7 A polyamine, butane-1,4-diamine, can be prepared from the decarboxylation of the α-COOH of an amino acid, L-ornithine, under suitable conditions.



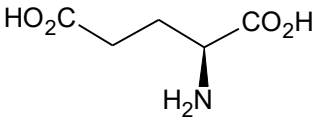
butane-1,4-diamine



L-ornithine

(i) Deduce the identity of the gaseous by-product of the reaction and hence write an equation for the formation of butane-1,4-diamine from L-ornithine.

(ii) Draw and name the organic product formed when L-glutamic acid undergoes decarboxylation in a similar manner.



L-glutamic acid

(iii) α-NH_2 and R-NH_2 of L-ornithine have different base dissociation constants, K_b.

Explain what is meant by the term K_b as applied to a weak base, **B**.

(iv) State and explain how the K_b values of α-NH_2 and R-NH_2 of L-ornithine would differ.

7) Isomerism

1 But-2-ene is able to exist as 2 isomers.

(i) State the type of isomerism exhibited by but-2-ene.

(ii) Draw the displayed structural formulae for the 2 isomers of but-2-ene.

2 Trioxanes are structures made up of three carbon atoms and three oxygen atoms in a six-membered ring.

Compound **A**, of molecular formula $C_3H_6O_3$, can form only **one** mono-bromo derivative when reacted with Br_2 under uv light.

(i) Draw the structural formula of trioxane, **A**.

There are three possible structural isomers of trioxane.

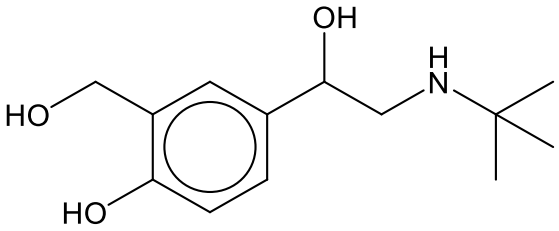
The other two trioxane structural isomers are known to be hypothetical structures and cannot be isolated.

(ii) Draw the structural formulae of the other two "trioxane" isomers.

(iii) Suggest a reason why the above two "trioxane" isomers cannot be isolated.

3 Haze levels in Singapore hit a record high of PSI 401 on 21 June this year, as a consequence of widespread forest fires in Indonesia. Many hospitals and clinics reported a spike in the number of patients seeking medical attention for respiratory problems, such as asthma and rhinitis.

To provide quick relief from asthma symptoms, the drug salbutamol is commonly prescribed.



salbutamol

(a) Identify two functional groups, other than phenyl, that are present in salbutamol.

(b) Salbutamol is sold in pharmacies as a racemic mixture, mainly because the (*S*)-enantiomer blocks metabolism pathways while the (*R*)-enantiomer shows activity.

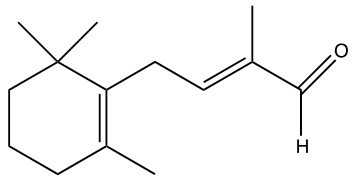
Identify the type of stereoisomerism salbutamol exhibits and draw two structures to illustrate this.

4 In order to study the mechanism of organic reactions, tracer studies using isotopes can be used. ^{18}O in water can be used to understand the hydrolysis of esters.

(i) Draw the structures of the two products formed when methylpropanoate is hydrolysed with $H_2{}^{18}O$ in an acidic medium. Label the ^{18}O isotope clearly.

(ii) Draw all the possible structural isomers of esters with the same molecular formula as methylpropanoate.

5 State the type of stereoisomerism that compound **A** can exhibit and describe how such stereoisomerism can arise.



Compound A

6 Lactic acid is a carboxylic acid with the formula $CH_3CH(OH)CO_2H$.

State the type of stereoisomerism exhibited by lactic acid. Draw appropriate structures to illustrate your answer.

7 Sorbic acid (hex-2,4-dienoic acid) is a natural organic compound used as a food preservative. It has the following structure:

1 2 3 4 5 6
$CH_3CH=CH-CH=CH-COOH$

(i) Although both **C1**–**C2** and **C3**–**C4** bonds are single bonds, they have different bond strengths. Suggest which bond is stronger and explain your answer.

(ii) Draw diagrams to illustrate all the geometrical isomers of sorbic acid.

(iii) On oxidation of sorbic acid with hot acidified $KMnO_4(aq)$, an organic compound **R** is obtained.

Draw the full displayed formula of compound **R.**

8) Organic Structural Elucidation

1 **A**, C_nH_{2n}, readily decolourises aq bromine at room temperature. (Identify the functional group present)

2 **B**, C_nH_{2n}, does not readily decolourise aq bromine at room temperature. (Identify the functional group present)

3 **C**, C_4H_8, reacts with hydrogen in the presence of nickel to give $CH_3CH_2CH_2CH_3$. With hot acidified potassium manganate(VII), only one organic product is obtained and no gas is detected.

Draw the structures of all the stereoisomers of **C**.

4 **D**, C_4H_8, reacts with hot, acidified potassium manganate(VII) to give an acidic gas and a compound **E** which turns moist blue litmus paper red.

5 **F**, C_4H_8, reacts with hot, acidified potassium manganate(VII) to give an acidic gas and a compound **G** which does not turn moist blue litmus paper red.

6 Two alkenes with the molecular formula C_5H_{10} were oxidised by hot, concentrated $KMnO_4$. Alkene **H** gave **K**, $C_3H_6O_2$, and **L**, $C_2H_4O_2$, as oxidation products, whereas alkene **J** gave **L** and **M**, C_3H_6O.

7 **N**, C_6H_{10}, reacts with hot, acidified potassium manganate(VII) to give $HO_2HC(CH_2)_4CO_2H$. One mole of **N** reacts with one mole of Br_2 in tetrachloromethane.

8 **P**, C_6H_{10}, exists as 3 geometric isomers. One mole of **P** reacts with 2 moles of bromine in an organic solvent. When **P** is warmed with acidified potassium manganate(VII), the only organic product obtained is ethanoic acid, CH_3CO_2H. Draw the structures of all the geometric isomers of **P**.

9 **Q**, C_6H_{10}, does not exhibit stereoisomerism. One mole of **Q** reacts with 2 moles of bromine in an organic solvent. When **Q** is warmed with acidified potassium manganate(VII), an acidic gas is evolved and the only other product obtained is $HO_2CCH(CH_3)CO_2H$.

10 **R,** C_8H_9Cl, is inert towards NaOH(aq) but is oxidised by aqueous potassium manganate(VII) to an acid **S**, $C_7H_5ClO_2$. **T**, an isomer of **R**, reacts with NaOH(aq) to form a secondary alcohol, **U**, $C_8H_{10}O$. **T** also reacts with hot concentrated alcoholic sodium hydroxide to give **V**, C_8H_8. Suggest why **T** is optically active but **U** does not rotate plane-polarised light.

11 Compound **L**, C_8H_7OCl, gives an orange precipitate with 2,4–dinitrophenylhydrazine and a silver mirror with Tollen's' reagent.

On heating **L** under reflux with aqueous acidified potassium manganate(VII), **M**, $C_8H_6O_4$, is formed.

On warming with aqueous sodium hydroxide, **L** gives **N**. Upon acidifying with nitric acid, and then adding aqueous silver nitrate, white precipitate is formed.

Suggest possible identity for each of the organic compounds **L**, **M** and **N**.

12 Suggest possible identities for each of the organic compounds **A** to **F** below. Explain your reasoning and give equations where appropriate.

(a) Compound **A**, C_4H_7Cl, is optically active. 1 mole of **A** reacts with 1 mole of HBr gas to form **B**. **A** reacts with hot concentrated potassium manganate(VII) to form an acid **C** as well as a gas that produces a white precipitate with limewater.

(b) An organic compound **D** has the following composition by mass: C, 60.8%; H, 9.3%; C*l*, 29.9%. **D** does not decolourise bromine, but reacts with hot concentrated ethanolic KOH to form compound **E**. **E** reacts with hot hydrogen gas in the presence of a nickel catalyst to form **F**, C_6H_{12}.

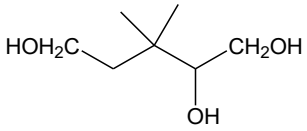
13 Substitution reaction of 3–chloropropene with phenyllithium (C_6H_5Li) produces an aromatic compound **B**, C_9H_{10}.

- **B** decolourises bromine in an inert organic solvent in the absence of UV light.
- **B** reacts with hot acidified concentrated $KMnO_4$ to produce a gas which gives a white precipitate with limewater.
- On reacting with steam using H_3PO_4 as catalyst, **B** gives an alcohol **C**, C $C_9H_{12}O$, which consists of an equimolar (1 : 1) mixture of two isomers.

  Heating **C** over hot Al_2O_3 produces **D**, C_9H_{10}, which is a structural isomer of **B**. Vigorous oxidation of **D** produces CH_3CO_2H and **E**, $C_7H_6O_2$, which reacts in NaOH(aq) to form a salt.

  Deduce the structures of compounds **B**, **C**, **D** and **E** and explain the chemistry of the reactions described. [There is no need to comment on the chemistry of the formation of **B** from 3-chloropropene.

14 When bromine in CCl_4 is added to an organic dye stuff **P**, $C_{10}H_{14}O$, bromine is decolourised and compound **Q**, $C_{10}H_{14}OBr_4$, is formed. **P** is insoluble in aqueous NaOH. Both **P** and **Q** give silver precipitates when reacted with Tollen's reagent. When **P** is treated with hot acidified potassium manganate(VII), two organic products, **R**, $C_3H_4O_3$, and **S**, $C_7H_{10}O_5$, are formed. **R** gives a pale yellow precipitate when warmed with alkaline aqueous iodine. Treatment of **S** with $LiAlH_4$ produces a compound with the structure below.



Suggest the structures of **P**, **Q**, **R** and **S**, giving your reasoning.

15 Compound **A**, $C_9H_{10}NOCl$, is a basic compound. It reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate **B**, but does not react with Tollen's' reagent. **A** does not react with aqueous bromine. When **A** was heated with bromine and iron(III) bromide, it was found that **A** reacts with 2 moles of bromine. Compound **C**, $C_9H_{11}NO_2$, is formed when **A** is heated under reflux with aqueous sodium hydroxide. **C** reacts with acidified potassium dichromate(VI) to produce **D**. 0.10 mole of **D** reacts completely in the presence of 0.05 moles of sodium carbonate. Upon heating **A** with ethanol in a sealed tube, a single organic compound **E**, C_9H_9NO, is obtained.

Deduce the structures of compounds **A**, **B**, **C**, **D** and **E**, giving reasons for your answer.

16 A neutral liquid **A**, $C_{10}H_{12}O_2$, when heated with aqueous hydrochloric acid gave two products, **B** and **C**.

B, $C_8H_{10}O$, gave a yellow precipitate when warmed with aqueous alkaline iodine. When heated with acidified sodium dichromate(VI) (VI), **B** gave **D**, C_8H_8O.

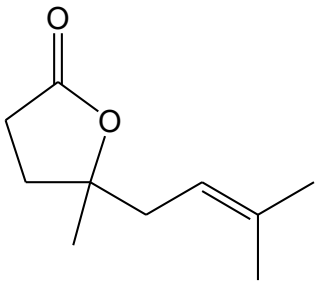
D reacts with 2,4-dinitrophenylhydrazine to give orange crystals, **E**.

Deduce the possible structures of compounds **A** to **E**. Explain the chemistry of the reactions involved. Write an equation for **A** when it is heated with aqueous hydrochloric acid.

17 One of the essential oils found in lemon grass is *Nerol*, $C_{10}H_{18}O$. Its isomer **A** is made in the laboratory. When a piece of sodium metal is added to a pure sample of **A**, immediate effervescence is observed. **A** can be oxidised to **B**, $C_{10}H_{16}O_2$, using acidified potassium dichromate(VI).

1 mole of **A** readily decolourises 2 moles of bromine dissolved in a suitable organic solvent. With oxidation of **A** using hot acidified potassium manganate(VII) solution, **C**, C_3H_6O and **D**, $C_5H_8O_3$ are formed together with effervescence. Both **C** and **D** result in the formation of a yellow precipitate when treated with alkaline aqueous iodine.

On treatment of **B** with steam in the presence of the H_3PO_4 catalyst at high temperature and pressure, followed by excess concentrated H_2SO_4, a cyclic ester **F** as shown below is formed as one of the major products.

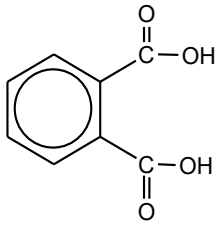


Deduce the structures of **A**, **B**, and **D**, explaining how you arrive at your answers and the chemistry of the reactions involved.

18 When an optically active bromo-compound **W** is treated with hot concentrated alcoholic sodium hydroxide, it produces three isomeric compounds **X**, **Y** and **Z**. Only a small quantity of **Z** is produced. When reacted with bromine, both **X** and **Y** give 1,2-dibromo-1-phenylpropane while **Z** gives 2,3-dibromo-1-phenylpropane.

Deduce the structures for the compounds **W**, **X**, **Y** and **Z**.

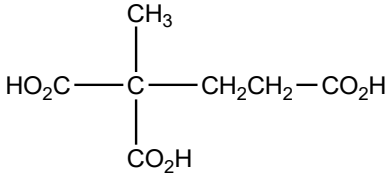
19 A compound **J**, $C_{11}H_{14}$, exhibits cis-trans isomerism but does not possess any chiral carbon. Oxidation of **J** with hot acidified potassium manganate(VII) gives **K**, $C_9H_8O_3$, which has only one carboxylic acid group. Under suitable conditions, **K** undergoes a stepping-down reaction that results in the formation of benzene-1,2-dicarboxylic acid:



J reacts with steam in the presence of concentrated phosphoric acid to give **L**, $C_{11}H_{16}O$, which has a chiral carbon.

Deduce the structures of **J**, **K** and **L** based on these observations.

20 Organic compound **A**, C_8H_{12}, reacts with hot, concentrated acidified $KMnO_4$ to form the following organic product.



Draw a possible structure of **A**, given that **A** is optically active.

21 An organic compound **P** has a molecular formula $C_{18}H_{20}$ and exists in 2 isomeric forms. 1 mol of **P** only reacts with 1 mol $Br_2(g)$ at room temperature in the absence of light. When treated with hot, acidified $KMnO_4$, **P** forms **Q**, $C_8H_6O_4$, and CO_2 as the only carbon-containing products. 1 mol of **Q** reacts with 2 mol of NaOH for complete neutralization. When **Q** is heated with concentrated HNO_3 and concentrated H_2SO_4, only one monosubstituted product is formed. Deduce the structures of **P** and **Q**, explain your reason clearly.

22 On complete combustion, 0.00754 mol of a hydrocarbon **L** gave 2.654 g of CO_2 and 1.086 g of H_2O. 1 mole of **L** reacts with 1 mole of $Br_2(g)$ in the dark. When **L** is treated with acidified $KMnO_4$ and heated under reflux, carbon dioxide and 3, 4-dimethylpentanoic acid are obtained. When **L** reacts with HBr(g), it produces an optically active product, **M**. On treating **M** with suitable reagents and conditions, product **N**, $C_8H_{18}O$, is formed.

(a) Determine the molecular formula of **L**.

(b) Draw the structural formula of **L**.

(c) Draw all the possible optical isomers of **M**.

(d) State the reagents and conditions for the conversion of **M** to **N**. Draw the structural formula of **N**.

23 Compound **A** has molecular formula, C_4H_8O. Reaction of **A** with hot acidified potassium manganate(VII) produces compound **B**, $C_3H_4O_4$, and effervescence is observed. One mole of **B** requires two moles of NaOH for complete neutralization. **A** decolourises aqueous bromine rapidly to form compound **C**, $C_4H_9O_2Br$, as the major product. Both **A** and **C** turn hot orange acidified potassium dichromate(VI) green. When treated with phosphorus pentachloride, **A** gives white fumes and compound **D**, C_4H_7Cl, is formed.

Suggest a possible structure for each of the compounds, **A** to **D**. Explain the chemistry of the reactions described.

24 An organic compound **B**, $C_{10}H_{13}I$, on boiling with aqueous potassium hydroxide gave a compound **C**, $C_{10}H_{14}O$. With acidified sodium dichromate(VI) compound **C** yielded **D**, $C_{10}H_{12}O$. With hot acidified potassium manganate(VII) compound **C** yielded **E**, $C_7H_6O_2$. Both compounds **C** and **D** when warmed with potassium hydroxide and iodine are able to produce a yellow precipitate.

(a) Give the structures of **B** to **E** and explain the chemistry of the reactions with appropriate equations.

(b) When **B** was treated with hot ethanolic sodium hydroxide, a mixture of isomers, **H**, $C_{10}H_{12}$ was isolated. Draw the structures and three possible isomers of **H**.

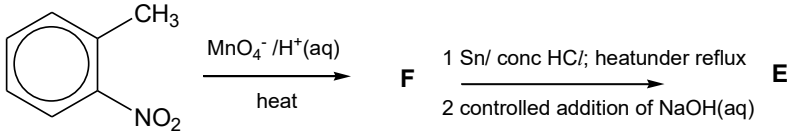
25 Compound **A** ($C_{10}H_{12}O_2$), which is optically active, gives a positive test with Tollen's reagent and alkaline aqueous iodine. Compound **B** is produced together with steamy fumes when **A** reacts with phosphorus pentachloride. **A** reacts with hot concentrated phosphoric acid to give two compounds **C** and **D**. When hot acidified potassium manganate(VII) is added to **A**, **B, C** or **D** separately, **E** ($C_8H_6O_4$) is formed.

Deduce structures of **A**, **B**, **C**, **D** and **E** and explain each type of reaction that has taken place. (Balanced equations are **NOT** required.)

26 This question is about compound **B,** $C_9H_9NO_2$ **,** which forms zwitterions in aqueous solution.

- On warming **B** with aqueous Na_2CO_3, a colourless gas gives white ppt with limewater is evolved.
- With bromine water, **B** gives white precipitates, **C,** $C_9H_7Br_4NO_2$**,** and **D**, $C_9H_8Br_3NO_3$.
- Treatment of 1 mole of **B** with hot acidified potassium manganate(VII) gives a colourless solution and 2 moles of carbon dioxide gas. Controlled neutralisation of the colourless solution gives a white precipitate, **E**, $C_7H_7O_2N$.

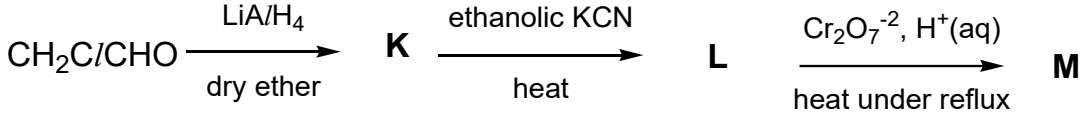
  E, dissolves in both NaOH(aq) and HC*l*(aq). **E** can also be synthesised as indicated in the following reaction sequence.



Deduce the structures of compounds **B** to **F**. Explain the chemistry of the reactions described, with the aid of equations where appropriate.

27 This question is about compound **H**, $C_5H_{10}O_2$, which is quite soluble in water and neutral to litmus.

- **H** readily forms **I**, $C_5H_6O_4$**,** when heated under reflux with acidified potassium dichromate(VI). **I** forms a di-ester when warmed with 2 moles of ethanol in the presence of a little concentrated sulfuric acid.
- On reaction with aqueous bromine, **H** produced **J,** $C_5H_{11}O_3Br$ which also decolourised bromine water.
- Strong oxidation of **H**, $C_5H_{10}O_2$, by hot acidified potassium manganate(VII) causes it to form only one organic product **M**, $C_3H_4O_4$.
- **M** can be synthesised as indicated in the following reaction scheme.



Deduce the structures of compounds **H** to **M.** Explain the chemistry of the reactions described, with the aid of equations where appropriate.

28 Compound **P** ($C_5H_{10}Cl_2$) reacts with NaOH(aq) to give **Q**. **Q** gives a yellow precipitate with alkaline aqueous iodine. **R** ($C_5H_{10}O_2$) is formed when hot acidified $K_2Cr_2O_7$ is added to **Q**. When HCN with trace amounts of dilute NaOH is added to **R**, **S** is obtained. Upon reduction of **S**, **T** is formed. **U** ($C_7H_{17}O_2N$) is formed when chloromethane is added to **T**.

Deduce structures of compounds **P**, **Q**, **R**, **S**, **T** and **U** and explain each type of reaction that has taken place. (Balanced equations are **NOT** required.)

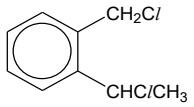
29(a) An organic compound **A**, $C_9H_{11}Br$, on treatment with hot aqueous potassium hydroxide gave a compound **B**, $C_9H_{12}O$. B responded to oxidation in three different ways. With acidified potassium dichromate(VI) it yielded **C**, $C_9H_{10}O$. With sodium hydroxide and iodine it yielded **D**, $C_8H_7O_2Na$ and a yellow precipitate. With hot, acidic potassium manganate(VII) it yielded **E**, $C_7H_6O_2$.

Identify compounds **A** to **E** and explain the above reactions.

(b) Benzoic acid reacts with NaOH(aq), but phenylmethanol does not react with NaOH. With reference to the above observation, explain why there is a difference in the acidities of benzoic acid and phenylmethanol.

30 This question is about compound **P**, $C_9H_8O_2$.

- Warming **P** with Tollen's reagent produces a silver mirror.
- With alkaline aqueous iodine, **P** gives a yellow precipitate.
- Treating **P** with lithium aluminium hydride yields compound **Q**, $C_9H_{12}O_2$.
- **Q** is inert to aqueous sodium carbonate
- **Q** reacts with sodium metal to form compound **R**, $C_9H_{10}O_2Na_2$, with strong effervescence.
- **Q** can be obtained by reacting compound **Y** (shown below) with hot NaOH(aq).



Y

- **P** decolourises acidified potassium manganate(VII) to produce a compound **S**, $C_9H_8O_3$.

(a) Deduce the structures of compounds **P**, **Q**, **R** and **S**. Explain the chemistry of the reactions described.

(b) For the reaction **Y** → **Q**, suggest the structure of the product obtained if ethanolic sodium hydroxide was used instead of NaOH(aq).

31 An optically active compound **A**, $C_8H_{13}Cl$, is heated under reflux with NaOH(aq) to form **B**, $C_8H_{14}O$. **B** decolorizes two moles of liquid bromine. On warming with alkaline aqueous iodine, **B** gives yellow crystals and another compound **C**, $C_7H_{10}O_2$, upon acidification. Treatment of **B** with hot acidified $KMnO_4$ gives a mixture of 2 organic compounds **D**, $C_3H_4O_4$ and $CH_3COCH_2CO_2H$, together with a colourless and odourless gas.

(a) Identify the yellow crystals formed upon warming **B** with alkaline aqueous iodine.

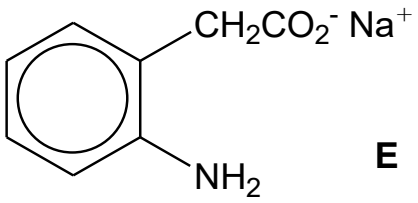
(b) Account for all these observations and identify compounds **A** to **D**.

32(a) Compound **A**, C_6H_6O, was first used as a surgical antiseptic till it was later found to be carcinogenic. Reaction of **A** with 3-chloropropene in the presence of anhydrous aluminium chloride yields **B**, $C_9H_{10}O$. Both **A** and **B** are found to decolourise aqueous bromine to form white precipitates **C** and **D**, respectively. Both **C** and **D** contain the same number of bromine atoms per molecule and **D** is found to be optically active.

(i) Identify **A** and write equations to illustrate the mechanism for the reaction of **A** with 3-chloropropene and anhydrous aluminium chloride.

(ii) Give the structural formulae of **C** and **D**.

(b) Show how benzene and 2-chloroethanoic acid can be used to synthesize compound **E** shown below. Indicate the reagents, conditions and all intermediate products in your answer.



E

33 A neutral compound **T** contains 46.2% carbon, 7.7% hydrogen and 46.1% oxygen by mass. When heated with NaOH(aq), **T** gives **U**, $C_2H_6O_2$ and sodium ethanoate. When one mole of **U** reacts with only one mole of hydrogen chloride, **V**, C_2H_5OCl, is formed, **V** gives **W**, C_3H_5ON, on heating with ethanolic potassium cyanide. When **W** is heated with dilute sulfuric acid, an optically inactive liquid **X**, $C_3H_6O_3$, is obtained. On heating **X** alone, a sweet smelling liquid **Y**, $C_3H_4O_2$, is formed. Oxidation of **X** gives solid **Z**, $C_3H_4O_4$, which is soluble in water.

Deduce the structural formulae of compounds **T** to **Z**, giving your reasoning.

34 Compound **P**, $C_{16}H_{30}O_4$, is believed to be an anti-cancer drug found in one medicinal plant extract in the Amazon forest. On analysis, it was found that:

- **P** is insoluble in both water and dilute NaOH(aq)
- Upon heating with dilute HC*l*, **P** gives two compounds: **Q**, $C_6H_{14}O$ and **R**, $C_4H_6O_4$.
- **Q** can rotate the plane of plane-polarised light and reaction of **Q** with hot acidified potassium manganate(VII) produces **S**, $C_6H_{12}O$, which give a yellow precipitate with iodine in NaOH(aq).
- Heating **Q** over Al_2O_3 produces **T**, C_6H_{12}, and vigorous oxidation of **T** produces butanone as one of the products.
- **R** can be synthesised by reacting 1, 2-di-iodoethane with hot ethanolic NaCN followed by warming with dilute sulfuric acid.

Deduce the structures of compounds **P**, **Q, R**, **S** and **T**. Explain the chemistry of the reactions described, writing equations where appropriate.

35 A mono-substituted aromatic organic compound, **P**, was heated under reflux with NaOH(aq) for several hours. The resulting mixture, containing **Q** and **R**, was acidified with aqueous hydrochloric acid and a white solid, **S**, $C_7H_6O_2$, was formed which was filtered off. The subsequent distillation of the filtrate yielded a liquid containing a neutral organic compound, **R**. **R** reacts with sodium and formed ethanoic acid when heated with acidified potassium dichromate(VI).

Give the structural formulae of compounds **P**, **Q**, **R** and **S**. Explain the chemistry involved and write balanced equations where possible.

36 A neutral compound **C**, $C_{10}H_9NO$, is not very soluble in water. When **C** is heated under reflux with dilute sulfuric acid, a compound **D** which is soluble in both NaOH(aq) and aqueous sodium carbonate is obtained. **C** is obtained from **E**, C_9H_9ClO by refluxing **E** with alcoholic potassium cyanide. **E** does not react with Tollen's' reagent, but it reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate, **F**. **E** also reacts with warm iodine in NaOH(aq) to give a pale yellow precipitate and **G**. When **G** is heated under reflux with acidified potassium manganate(VII), **H** is obtained. **H** reacts with 2 mol of PCl_5 to give **I**, $C_8H_4Cl_2O_2$.

Deduce the possible structures of the compounds **C**, **D**, **E**, **F**, **G**, **H** and **I**. Explain the chemistry of the reactions described, writing equations where appropriate.

37 Compound **A** ($C_{10}H_{14}O_2$) is optically active and does not react with aqueous sodium carbonate. However, it reacts slowly with NaOH(aq) to form a soluble substance **B**. **A** reacts with hydrogen bromide but will not change colour of acidified potassium dichromate(VI). **A** decolourises aqueous bromine to form white precipitate **C** ($C_{10}H_{12}O_2Br_2$) together with dense white fumes. Upon treatment with hot concentrated phosphoric acid, **A** gives **D** ($C_{10}H_{12}O$) which exists as a pair of geometric isomers. **D** gives **E** ($C_{10}H_{14}O_3$) on addition of cold, dilute aqueous alkaline manganate(VII). **E** reacts with phosphorous pentachloride to give copious fumes and **F** ($C_{10}H_{12}OCl_2$).

Suggest a structure for each lettered compound and explain the reactions involved.

38 In boiling with concentrated ethanolic sodium hydroxide, compound **A**, $C_{10}H_{13}Br$, gives only one product **B**, $C_{10}H_{12}$.

B undergoes oxidation under certain conditions to give benzaldehyde and **C**, C_3H_6O.

C reacts with hydrogen cyanide to give **D**, C_4H_7NO, which is optically active.

On treating **D** with lithium aluminium hydride, **E**, $C_4H_{11}NO$, is produced.

One mole of **E** reacts with two moles of ethanoyl chloride to give **F**, $C_8H_{15}NO_3$.

Deduce the structures of the compounds **A** to **F**. Explain the chemistry of the reactions described. (There is no need to comment on the chemistry of the oxidation of **B**.)

39 An organic compound **G**, $C_{10}H_{11}O_2Br$, does not react with aqueous sodium carbonate solution but reacts slowly on heating in sodium hydroxide to form phenyl methanol and a water soluble substance, **H**, $C_3H_5O_3Na$. **H** produces hydrogen with sodium and reacts with warm alkaline aqueous iodine to form a yellow precipitate. On acidification of **H** with dilute hydrochloric acid, **I**, $C_3H_6O_3$, is formed and separated out by distillation. **I** reacts with phosphorus pentachloride to give **J**, $C_3H_4Cl_2O$, and white fumes. **J** reacts with ammonia at room temperature to give **K**, C_3H_6ONCl.

Deduce the structures of the compounds **G** to **K**. Explain the chemistry of the reactions described.

40 Compound **X**, a diacid found in apples and citrus fruits, has the following percentage composition by mass:

C, 35.8% H, 4.50% O, 59.7%

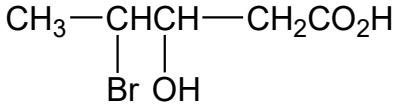
When heated under reflux with ethanol in the presence of concentrated sulfuric acid, **X** forms compound **Y**, $C_8H_{14}O_5$. Compound **Y** liberates hydrogen gas when treated with sodium metal and reacts with acidified potassium dichromate(VI) to give compound **Z**. **Z** produces an orange precipitate with 2,4-dinitrophenylhydrazine, but has no reaction with Fehling's and Tollen's reagents.

(a) Find the empirical formula of **X**.

(b) Suggest structures for **X**, **Y** and **Z**. Explain the reactions they have undergone and write balanced equations for all the reactions that have occurred.

(c) State the type of isomerism exhibited by **X** and draw the isomers.

41 This question is about compound **P**, $C_5H_9Cl O_2$, which is sparingly soluble in water but readily soluble in NaOH(aq). Heating compound **P** in NaOH(aq) and adding excess acid to the product yields compound **Q**, $C_5H_{10}O_3$, which reacts with warm aqueous alkaline iodine when warmed to give a yellow precipitate. Compound **Q** forms isomers, **R** and **S**, $C_5H_8O_2$, when it is heated under reflux with concentrated sulfuric acid and hot phosphoric acid respectively. **R** is a sweet smelling liquid and **S** can exhibit *cis-trans* isomerism. **S** also reacts with aqueous bromine to give a number of products, one of which is shown below:



S undergoes reaction with acidified potassium manganate(VII) to give **T**, $C_3H_4O_4$, and ethanoic acid. 1 mole of **T** liberates one mole of carbon dioxide on reaction with aqueous sodium carbonate.

Deduce the structure of compounds **P**, **Q**, **R**, **S** and **T**, explaining the chemistry of the reactions described. Write equations for the reactions that occurred.

42 An optically active compound **T**, with molecular formula $C_3H_7O_2N$, reacts with PCl_5 to give white fumes and a compound **U**.

When a solution containing **U** is warmed with NaOH(aq), a pungent gas is evolved and compound **V** is obtained. Upon acidification of **V**, compound **W**, $C_3H_6O_3$, can be isolated. When **W** is warmed with concentrated sulfuric acid, a cyclic compound **X**, $C_6H_8O_4$, is formed.

Compound **Y** is a structural isomer of **W** and is not optically active. When **Y** is warmed with concentrated phosphoric acid, a non-cyclic compound **Z**, $C_3H_4O_2$, is produced.

Deduce the structures of compounds **T**, **U**, **V**, **W**, **X**, **Y** and **Z** . Explain the chemistry of the reactions described.

43 An organic compound **A**, of relative molecular mass 136.5, has the following composition by mass: C, 44.0%; H, 6.6%; C*l*, 26.0%; O, 23.4%. This compound readily dissolves in NaOH(aq) at room temperature. When **A** is heated with NaOH(aq), followed by addition of dilute hydrochloric acid, **B**, $C_5H_{10}O_3$, is obtained. **B** reacts with warm aqueous alkaline iodine to give a yellow ppt, **C**. When **B** is heated under reflux with conc sulfuric acid, 2 isomers, **D** and **E**, $C_5H_8O_2$, are formed. **D** is a sweet-smelling liquid and **E** exhibits cis-trans isomerism. One mole of **E** reacts with one mole of bromine in organic solvent. When **E** reacts with hot, acidified potassium manganate(VII), one of the products formed is **F**, $C_3H_4O_4$.

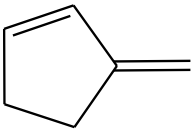
Identify the compounds **A** to **F** and explain e reactions described.

44 Linalo-ol, **G**, $C_{10}H_{18}O$, is a common constituent of the scent given by flowers.

G does not react with 2,4-dinitrophenylhydrazine reagent, but reacts with hydrogen in the presence of palladium to give **H**, $C_{10}H_{22}O$. **G** reacts with ethanoyl chloride to give **J**, $C_{12}H_{20}O_2$, but is not oxidised by warm acidified $K_2Cr_2O_7$.

With cold acidified $KMnO_4$, **G** gives **K**, $C_{10}H_{22}O_5$. **G** reacts with warm concentrated phosphoric acid to give a mixture of **L** and **M**, both $C_{10}H_{16}$. **L** reacts with hot concentrated acidified $KMnO_4$ to give **N**, $C_3H_4O_3$, **P**, $C_3H_4O_4$, and **Q**, C_3H_6O. **N** and **Q** both give a yellow precipitate with alkaline aqueous iodine. A 0.104 g sample of **P** requires 20.00 cm^3 of 0.10 mol dm^{-3} NaOH for neutralisation. **M** reacts with hot concentrated acidified $KMnO_4$ to give **Q** and **R**, $C_5H_6O_5$. **R** can be obtained from **S** by careful oxidation with hot concentrated acidified $KMnO_4$.

S



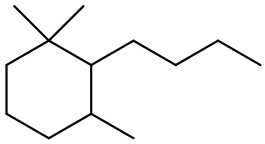
Explain each step in this sequence; suggest structures for **G** to **R**.

45 **C** and **D** have the same molecular formula, $C_{13}H_{22}$, while **E** has molecular formula, $C_{13}H_{20}$. **C** can exist as a pair of enantiomers, but **D** and **E** do not show any optical activity.

1 mol of **C** and **D** each reacts with 2 mol of liquid bromine at room temperature.

1 mol of **E**, however, reacts with 3 mol of liquid bromine.

C, **D** and **E** react with hydrogen in the presence of nickel to give the same compound, $C_{13}H_{26}$:



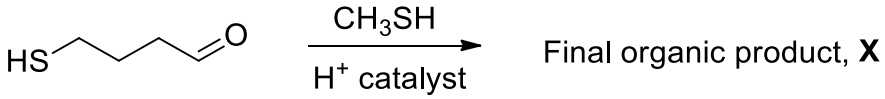
C and **D** each undergo oxidative cleavage with acidified $KMnO_4$ to give ethanoic acid as one of the two organic products. In addition, **C** also gives compound **F,** $C_{10}H_{16}O_3$, while **D** gives compound **G**, $C_{11}H_{18}O_4$, respectively. Both **F** and **G** react with NaOH in a 1 : 1 ratio. **E**, on the other hand, gives three organic products on reaction with $KMnO_4$: ethanoic acid, CH_3COCO_2H and compound **H**, $C_8H_{12}O_5$. 1 mol of **H** is completely neutralised by 2 mol of NaOH.

Deduce the structures of compounds **C**, **D**, **E**, **F,** G, and **H**, giving explanations of the reactions that occurred.

46 0.050 mol of liquid ketone **Q**, $C_nH_{2n}O$, underwent complete combustion in excess oxygen. The remaining gases occupied 8.2 dm^3. After shaking these gases with aqueous sodium hydroxide, the final volume of gas remaining is 3.4 dm^3. All gaseous volumes were measured at room temperature and pressure.

Deduce the structural formula of **Q**, showing your working clearly.

47 Thiols (RSH) are sulfur analogs of alcohols.



(a) Compound **X** has the following composition by mass.

C: 51.2%; H: 7.7%; S: 27.4%; O:13.7%

Using the given data, calculate the empirical formula of the final organic product **X.**

(b) When a sample of 0.219 g of compound **X** was vaporised using a suitable apparatus, the vapour occupied 38.2 cm^3 at 95 ^0C and 150 kPa.

Calculate the Mr of compound **X.**

48 Compound **C** is a specialty product for proteomics research. Refluxing **C** in dilute sulfuric acid produces **D** and ethanoic acid.

Elemental analysis of compound **D** gives the following results:

Elemental Analysis (% by mass)		
C	**H**	**O**
60.8	4.4	34.8

Some reactions of **D** are given below:

Reaction 1 : **D** + $Br_2(aq) \rightarrow$ White solid, **E** (M_r = 374.7)

Reaction 2 : **D** + $Na_2CO_3(aq) \rightarrow$ Effervescence of gas.

(i) When vaporised in a suitable vessel, 1g of **D** occupies a volume of 282 cm^3 at 200 ^oC and a pressure of 101 kPa. Calculate the M_r of **D**.

(ii) Using the elemental analysis results and your answer in **(c)(i)** , deduce the molecular formula of **D**.

(iii) Name the functional groups present in **D**.

(iv) State the molecular formula of **E** in reaction **1**.

(v) Draw the structure of **D**.

(vi) Hence deduce the structure of compound **C**.

49 Hot, concentrated potassium manganate (VII) oxidises several classes of organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds can be determined. Some compounds are easily oxidised, while others require longer heating.

The following describes some reactions of compounds **F** and **K**, and of their oxidation products.

F, $C_8H_{12}O$ reacts with excess potassium manganate (VII) to produce single organic products, **G,** $C_4H_6O_5$ while **K,** $C_{12}H_{12}$**,** reacts with the same reagent to produce **H,** $C_{10}H_{10}O_3$. Carbon dioxide is produced in both reactions in a mole ratio of 2 : 1 respectively. During oxidation of **F**, four moles of carbon dioxide were liberated.

Although **F** reacts with potassium manganate (VII), it gives no reaction with potassium dichromate (VI). When 0.10 mol of **F** is reacted with an excess of sodium metal, 1.2 dm^3 of hydrogen is formed, measured at room temperature and pressure.

G reacts with concentrated phosphoric acid to give **I**, $C_4H_4O_4$. Upon further oxidation, **I** is found to give **J,** $C_3H_2O_5$, and an inorganic by-product.

H gives a positive iodoform test and dissolves in aqueous sodium hydroxide. Upon further oxidation of **H**, **L,** $C_9H_6O_6$, and a similar inorganic by-product formed from **I** is also produced.

(i) Deduce the structure of compounds **F** to **L**, explaining the chemistry of the reactions described.

(ii) State the type(s) of stereoisomerism shown by compound **F** and give one further piece of relevant information about it.

(iii) Hence, predict the total number of isomers shown by **F**.

50 (a) Aside from the common oxides, carbon forms a series of reactive oxocarbons. One such compound is tricarbon monoxide, C_3O, a reactive molecule found in space

(i) Suggest a structure of tricarbon monoxide. Indicate clearly any lone pairs present.

Tricarbon monoxide is isoelectronic to cyanogen, $(CN)_2$. The molecule of cyanogen contains a C–C single bond.

(ii) Draw the dot-and-cross diagram of cyanogen. In your diagram, you should distinguish the electrons originating from each of the two carbon atoms and those from the two nitrogen atoms.

(b) Another oxycarbon is pentacarbon dioxide, C_5O_2. It can be obtained by heating compound **X**, $C_6H_6O_3$, at a high temperature. **X** exists in equilibrium with its isomer, **Y**.

X does not react with aqueous bromine. **X** also gives an orange precipitate with 2,4-DNPH but does not give a silver mirror with Tollens' reagent. When reacted with limited bromine under ultraviolet light, **X** produced **only one** mono-brominated compound.

Y reacts with dilute nitric acid to form **only one** mono-nitrated compound, **Z**.

Suggest the structures of compounds **X**, **Y** and **Z**. Explain your reasoning.