

Anglo-Chinese Junior College
JC2 Preliminary Examination
Higher 2



A Methodist Institution
(Founded 1866)

CANDIDATE
NAME

Solutions

FORM
CLASS

TUTORIAL
CLASS

INDEX
NUMBER

CHEMISTRY

Paper 3 Free Response

9729/03

1 September 2025
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

Circle the number of the question you have attempted.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.

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

For Examiners' use only	
Section A	
1	/ 15
2	/ 24
3	/ 21
Section B	
4 / 5	/ 20
Presentation	
Total	/ 80

Section A

Answer **all** the questions in this section.

- 1 The Mars Curiosity rover's landing in August 2012 was achieved using hydrazine fuelled rocket thrusters. The rapid decomposition of hydrazine, N_2H_4 , over a suitable catalyst to produce hot gaseous elements as products provides the thrust. Ammonia can be formed as an intermediate during the decomposition.

- (a) Write a balanced equation for hydrazine decomposing to ammonia and nitrogen gas. [1]



- (b) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide as shown in equation 1.

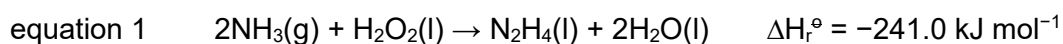


Table 1.1 shows the standard enthalpy change of formation, ΔH_f^\ominus , for some compounds in equation 1.

Table 1.1

compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
NH_3	-46.1
H_2O_2	-187.8
H_2O	-285.8

Calculate the standard enthalpy change for the decomposition of hydrazine to its elements. [2]

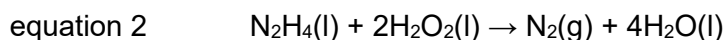
$$\Delta H_r^\ominus = -(2 \times -46.1) - (-187.8) + \Delta H_f^\ominus (\text{N}_2\text{H}_4) + (2 \times -285.8) = -241.0$$

$$\Delta H_f^\ominus (\text{N}_2\text{H}_4) = +50.6 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{decomp}}^\ominus (\text{N}_2\text{H}_4) = -50.6 \text{ kJ mol}^{-1}$$

- (c) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol fuel mixture, known as 'C-Stoff', and hydrogen peroxide, known as 'T-Stoff'.

- (i) Hydrazine reacts with hydrogen peroxide as shown in equation 2.



State the oxidation number of nitrogen and oxygen in the reactants and products. [1]

- (ii) Methanol reacts with hydrogen peroxide to form carbon dioxide and water.

Write a balanced equation for this reaction. [1]

- (iii) The fighter plane would hold 225 dm^3 of hydrazine and 862 dm^3 of methanol.

Table 1.2 shows the standard enthalpy change of combustion, ΔH_c^\ominus , and densities of hydrazine and methanol.

Table 1.2

compound	$\Delta H_c^\ominus / \text{kJ mol}^{-1}$	density / g cm^{-3}
N_2H_4	-622.2	1.021
CH_3OH	-726.0	0.7918

Use data in Table 1.2 to calculate the heat energy evolved during the combustion of this quantity of rocket fuel at standard conditions. Assume that hydrazine and methanol are fully combusted. [2]

.....
(i) N: -2 in N_2H_4 and 0 in N_2 ; O: -1 in H_2O_2 and -2 in H_2O
.....

(ii) $\text{CH}_3\text{OH} + 3\text{H}_2\text{O}_2 \rightarrow \text{CO}_2 + 5\text{H}_2\text{O}$
.....

(iii) Amount of hydrazine = $(225000 \times 1.021) / 32.0 = 7179 \text{ mol}$
.....

Amount of methanol = $(862000 \times 0.7918) / 32.0 = 21329 \text{ mol}$
.....

Heat energy evolved from hydrazine = $7179 \times 622.2 = 4.467 \times 10^6 \text{ kJ}$
.....

Heat energy evolved from methanol = $21329 \times 726.0 = 15.485 \times 10^6 \text{ kJ}$
.....

Total heat energy evolved from oxidation of rocket fuel = $19.9 \times 10^6 \text{ kJ}$
.....
.....
.....

(d) Hydrazine is also commonly combined with dinitrogen tetroxide, N_2O_4 , in rocket fuels.

(i) Reactions used in rocketry produce chemically stable gaseous products.

Suggest the products that are formed in the reaction between N_2H_4 and N_2O_4 . [1]

(ii) Pure N_2O_4 , when warmed, does not immediately decompose into its elements, but instead forms a brown gas.

Suggest the identity of this brown gas. [1]

(iii) N_2H_4 does not exhibit ideal gas behaviour.

State and explain two reasons for its deviation from ideal gas behaviour. [2]

(i) N_2 and H_2O

(ii) NO_2

(iii) There are significant intermolecular forces of attraction / hydrogen bonding between molecules and is not negligible.

The particles of N_2H_4 take up space relative to the volume of the gas and are not negligible.

Collisions are inelastic. 2 of 3

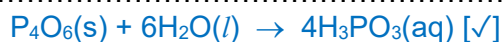
e) A derivative of hydrazine with formula $\text{C}_2\text{H}_8\text{N}_2$ was used as rocket fuel in the Apollo missions. Draw two isomers of $\text{C}_2\text{H}_8\text{N}_2$ containing an N–N bond. [1]

$(\text{CH}_3)_2\text{N}-\text{NH}_2$, $(\text{CH}_3)\text{NH}-\text{NH}(\text{CH}_3)$, or $\text{CH}_3\text{CH}_2\text{NH}-\text{NH}_2$. 2 of 3

- (f) Phosphorus is one element below nitrogen in the Periodic Table.

Describe the reactions of the oxide and chloride of phosphorus with water. Write equations where appropriate and suggest the pH of the solutions formed. [3]

P_4O_6 / P_4O_{10} is readily soluble in water to form an acidic solution. [✓]



pH 2 or 3 [✓]

PCl_3 / PCl_5 undergoes complete hydrolysis with water to give an acidic solution. [✓]



pH 1 or 2 [✓]

[Total: 15]

2 Cocoa trees have been used as a source of food for more than 5,000 years. In modern times, they are used to make chocolates.

- (a) Palmitic acid and stearic acid are saturated fatty acids, while oleic acid and linoleic acid are unsaturated fatty acids commonly found in chocolates.

An example of an unsaturated fatty acid is shown below in Fig. 2.1.

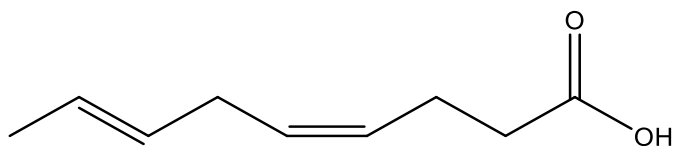


Fig. 2.1

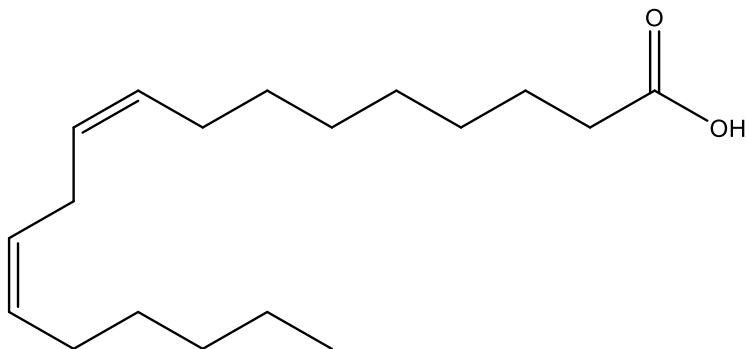
The systematic name of the unsaturated fatty acid in Fig. 2.1 is *cis,trans-4,7-nonadienoic acid*. The numbers indicate the positions of the alkene functional groups, and "dien" indicates that there are two alkenes in the chain.

Table 2.2 shows the percentage composition of fatty acids found in three different cocoa butter samples.

Table 2.2

fatty acid	% of fatty acids in cocoa butter samples		
	A	B	C
palmitic acid	28	25	35
stearic acid	35	40	40
oleic acid	31	28	21
linoleic acid	6	12	4

- (i) The structure of linoleic acid is shown below.



Given that 'octadeca' refers to an 18-carbon chain, write the systematic name for linoleic acid. [1]

- (ii) Using given information about the arrangement of atoms about the C=C bond of unsaturated fatty acids and data in Table 2.2, state and explain which cocoa butter sample is expected to have the highest melting point. [2]

(i) *cis,cis*-9,12-octadecadienoic acid (AOB)

(ii) Unsaturated fatty acids contain kinks / bends in the chain caused by the C=C double bonds which prevents them from packing as well as saturated fatty acids which generally have more linear structures allowing them to pack closer together. Saturated fatty acids have stronger intermolecular forces of attraction, leading to higher melting points as they are able to pack more closely together compared to unsaturated fatty acids. [1]

Hence, sample C is expected to have the highest melting point due to the highest percentage of saturated fatty acids, i.e. palmitic + stearic acids. [1]
(AOA+AOB)

- (b) A chocolatier investigated the quality of two varieties of cocoa beans from the same producer. Table 2.3 shows the results of the chemical analysis.

Table 2.3

chemicals	variety of cocoa beans	
	D	E
theobromine (mg / g)	12.5	15.2
epicatechin (mg / g)	4.8	6.1
ash content (% mass)	3.0	3.5
reducing sugars (% mass)	2.5	3.0

- (i) The ash content of cocoa beans is determined by burning the sample until all organic matters are combusted, leaving behind the inorganic residue, which is reported as the percentage mass of the original sample.

Suggest one use for determining the ash content.

[1]

- (ii) Chocolate is poisonous to dogs as they metabolise theobromine much more slowly compared to humans. The median lethal dose of theobromine for dogs is 120 mg per kg of body weight.

A 60 g of a dark chocolate bar contains 85% cocoa content of variety E.

Calculate the percentage of a chocolate bar, to 1 decimal place, that would be the median lethal dose for a small dog weighing 5.4 kg.

[2]

- (iii) Theobromine is metabolised more slowly than caffeine in the human body. Following a first-order kinetics, the half-life of theobromine is 8 hours.

The integrated rate law for a first-order reaction is given.

$$\ln [A]_t = -kt + \ln[A]_0$$

where k = rate constant

t = time

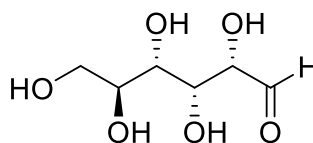
$[A]_t$ = concentration of A at time t

$[A]_0$ = initial concentration of A

A social media influencer consumed a large quantity of giant chocolate bars during a broadcast. An immediate blood test revealed a theobromine level of 15.5 mg dm^{-3} .

Calculate the time taken for his theobromine level to fall below 1.5 mg dm^{-3} . [2]

- (iv) D-glucose is one of the main reducing sugar molecules found in chocolates. The structure of D-glucose is shown below.



With reference to the changes in the reaction of D-glucose with Fehling's solution, explain why D-glucose is called a reducing sugar. [1]

- (i) It gives insights into the total mineral content / quality (such as iron and calcium) of the cocoa beans.

OR

It may help to detect adulteration or impurities if the ash content is different from that of pure cocoa beans.

- (ii) Mass of theobromine in a chocolate bar = $60 \times \frac{85}{100} \times 15.2$
 $= 775.2 \text{ mg}$

Median lethal dose for the dog = $5.4 \times 120 = 648 \text{ mg}$

Percentage of a chocolate bar = $648 / 775.2 \times 100\% = 83.6\%$

- (iii) $k = \ln 2 / t_{1/2} = 0.6931 / 8 = 0.08664 \text{ h}^{-1}$

$$\ln [A]_t = -kt + \ln [A]_0$$

$$\ln (1.5) = -0.08664t + \ln (15.5)$$

$$t = 26.95 \approx \underline{27.0 \text{ h}} \text{ (3 s.f.)}$$

OR

$$\text{proportion left} = 1.5 / 15.5 = 0.09677$$

let n = no. of half-lives

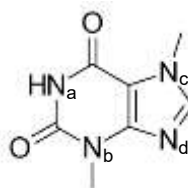
$$0.09677 = \left(\frac{1}{2}\right)^n$$

$$n = \log 0.09677 \div \log \frac{1}{2} = 3.369$$

$$t = 8 \times 3.369 = 26.95 \approx \underline{27.0 \text{ h}} \text{ (3 s.f.)}$$

- (iv) Glucose reduces the copper(II) complex in Fehling's solution to Cu_2O , while itself is oxidised from aldehyde to carboxylic acid.

- (c) Theobromine is the principal alkaloid in cocoa beans. In the structure below, four nitrogen atoms are labelled N_a, N_b, N_c and N_d.



Theobromine has a pK_b value of 4.1.

- (i) Theobromine is an aromatic compound. It is known that N_a, N_b and N_c are not basic, while N_d is basic in nature. All the nitrogen atoms are sp^2 hybridised and lie on the same plane.

With reference to the orbitals, explain why N_c is not basic while N_d is basic. [2]

- (ii) To study the effects of theobromine on certain biological systems, a buffer solution at a pH of 10.1 is prepared by adding 300 cm³ of 0.500 mol dm⁻³ of hydrochloric acid to 700 cm³ of theobromine solution, which is in excess.

Calculate the original concentration of the theobromine solution used to make the buffer solution. [3]

(i) In N_c, the three sp^2 hybrid orbitals are used to form sigma bonds with the neighbouring carbon atoms. As such, the lone pair of electrons occupies the unhybridised p orbital that delocalises into the pi electron cloud and thus is not available for accepting a proton.

In N_d, the unhybridised p orbital is used to form a pi bond with a neighbouring carbon atom. As such, the lone pair of electrons occupies one of the sp^2 hybrid orbital and is not part of the pi electron cloud, making it available for accepting a proton.

(ii) Let c be the original concentration of Tb



$$n(\text{TbH}^+) \text{ in buffer} = n(\text{HCl}) \text{ added} = 0.300 \times 0.500 = 0.150 \text{ mol}$$

$$n(\text{Tb}) \text{ in buffer} = n(\text{Tb}) \text{ original} - n(\text{HCl}) \text{ added} = 0.700c - 0.150 \text{ mol}$$

$$pOH = pK_b + \lg \frac{[\text{TbH}^+]}{[\text{Tb}]}$$

$$14.0 - 10.1 = 4.1 + \lg \frac{[0.15]}{[0.700c - 0.15]}$$

$$10^{-0.2} = \frac{[0.15]}{[0.700c - 0.15]}$$

$$c = 0.554 \text{ mol dm}^{-3}$$

- (d) Compared to other types of chocolate, dark chocolate is richer in epicatechin, which is an antioxidant.

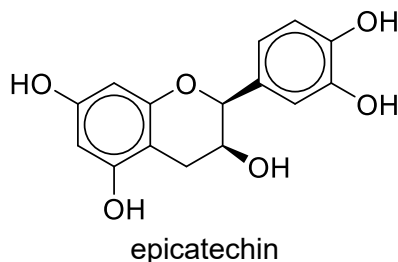


Fig 2.4 shows a possible synthetic pathway of epicatechin in the laboratory.

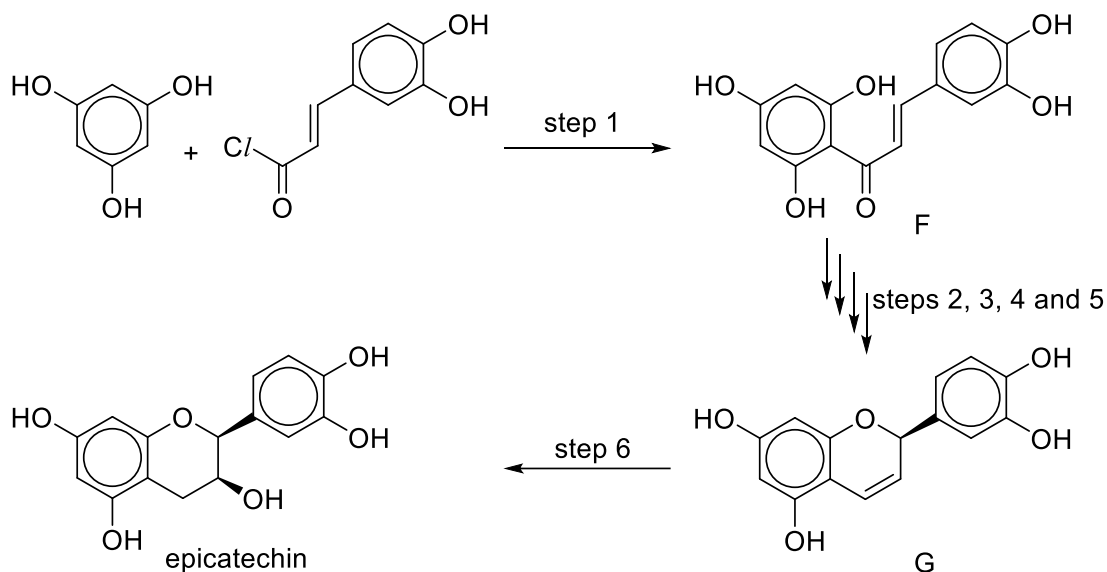


Fig. 2.4

- (i) In step 1, electrophilic substitution occurs to form F in the presence of AlCl_3 .

Draw the mechanism for step 1. Show the relevant curly arrows and charges, and all the products formed.

You may represent the non-reacting group with R. [3]

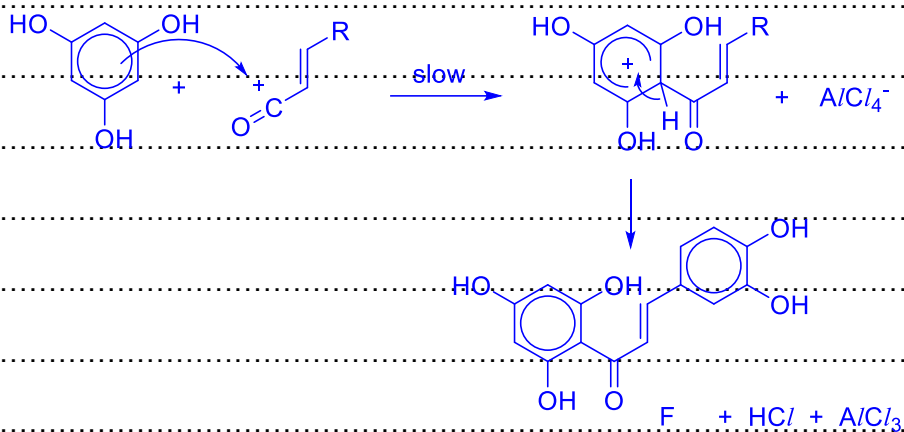
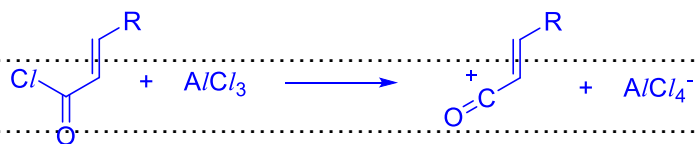
- (ii) Intermediate G can be formed from F in four steps. The reactions involved are:

- electrophilic addition,
- acid-base reaction and intramolecular nucleophilic substitution,
- reduction, and
- elimination.

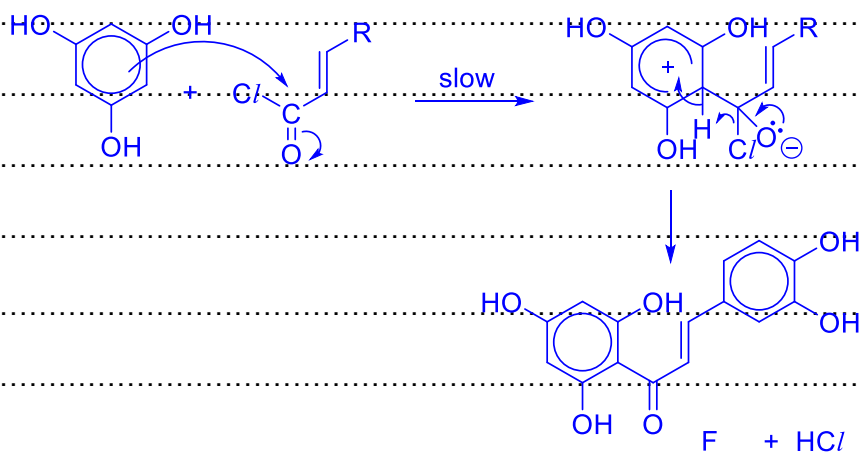
Suggest reagents and conditions for each step. Draw the structure of the intermediate compound formed after each step.

You may represent the non-reacting group with R. [7]

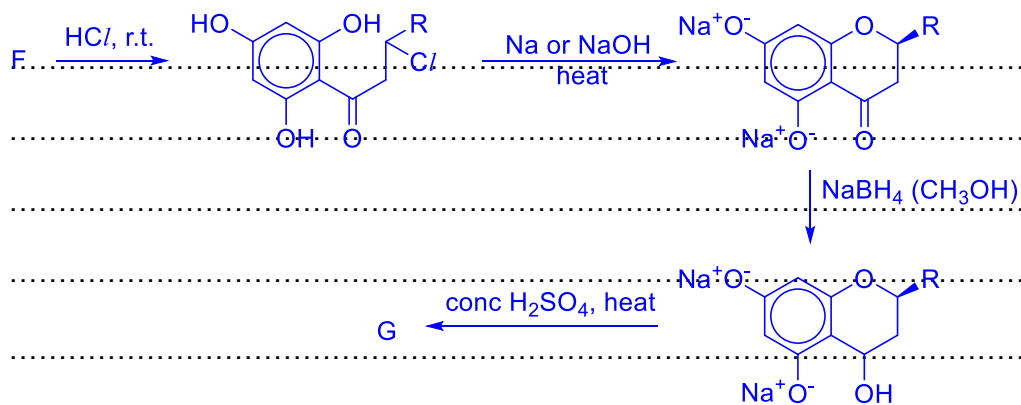
(i.)



OR



(ii.)

EA HCl, Na or NaOH to NS RCl, reduce ketone, eliminate H_2O [4x1m]

Accept alternative reagents/conditions.

Intermediate [3x1m]

[Total: 24]

- 3 Iron is the fourth most abundant element in the crust of the Earth, deposited mainly by meteorites in its metallic state.

- (a) Depending on the arrangement of the particles in the solid state, iron exists as a few allotropes, one of which is α -iron.

Paramagnetism and ferromagnetism are two types of magnetic behaviour found in materials. In ferromagnetic materials, the magnetic moments due to unpaired electrons in each particle align strongly in the same direction, resulting in them behaving as magnets. In paramagnetic materials, however, the magnetic moments are randomly oriented such that they can only behave as magnets when an external magnetic field is applied.

At room temperature, α -iron is ferromagnetic, but it becomes paramagnetic above 770 °C.

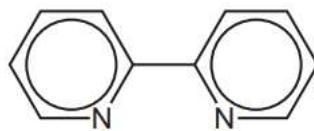
With reference to the electronic configuration of $_{26}\text{Fe}$, explain why this is so. [2]

$_{26}\text{Fe}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

At lower temperatures, due to the 4 unpaired electrons in the 3d subshell aligning in the same direction in each particle, α -iron is ferromagnetic.

However, at higher temperatures, the electrons gain significant (kinetic) energy, resulting in the disruption of the alignment of the magnetic moments / excitation of electrons to be randomly oriented, thus exhibiting paramagnetism instead.

- (b) Bipyridine, bipy, is a bidentate ligand.



bipy

- (i) A molecule with a conjugated system has multiple p orbitals overlapping with each other, resulting in delocalised electrons.

A compound is said to be aromatic when it has a conjugated, planar and cyclic structure with $[4n + 2]$ π electrons (where $n = 0$ or a positive integer 1, 2, 3, etc.).

Given that bipyridine is an aromatic compound, with each ring maintaining its own aromaticity, deduce the total number of π electrons present in the molecule.

Explain your answer.

[2]

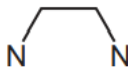
- (ii) Explain what is meant by the term *bidentate ligand*.

[1]

- (iii) The 3d orbitals in an isolated Fe^{2+} ion are degenerate.

Draw a diagram to show the relative energies of the 3d orbitals' energy levels in an isolated Fe^{2+} ion **and** when Fe^{2+} ion forms an octahedral complex. [2]

- (iv) The octahedral complex ion $[\text{Fe}(\text{bipy})_3]^{2+}$ exists as two stereoisomers.

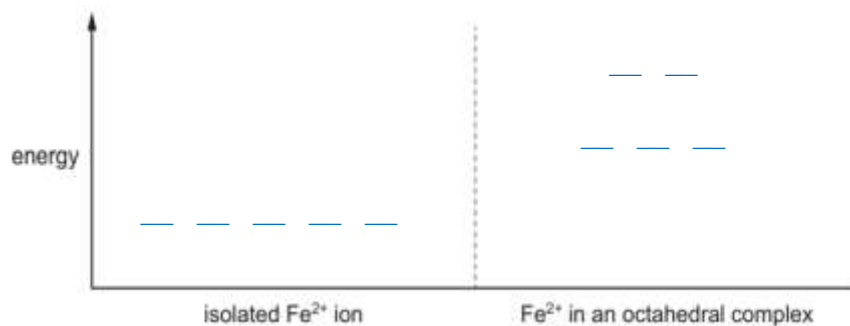
Using  to represent the structure of bipy, draw three-dimensional diagrams to show the two stereoisomers of $[\text{Fe}(\text{bipy})_3]^{2+}$. State the type of stereoisomerism shown. [3]

- (i) Each of the ten sp^2 hybridised carbon contributes one electron from the unhybridised p orbital, while each of the two sp^2 nitrogen atoms contributes one electron from the unhybridised p orbital into the π system.

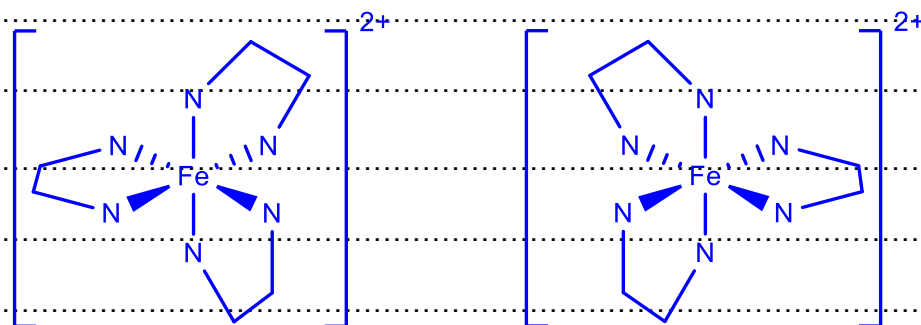
Hence, there are 12 π electrons present, with 6 from each ring.

(ii) It is a neutral or anionic species that donates two lone pairs of electrons to form dative covalent bonds to a metal atom or ion.

(iii)



(iv)



Enantiomerism

- (c) The relationship between the energy of a photon of light and its wavelength is shown.

$$E = \frac{hc}{\lambda}$$

E = energy of a photon, in J

h = Planck constant = 6.63×10^{-34} J s

c = speed of light in a vacuum = 3.00×10^8 m s $^{-1}$

λ = wavelength, in m

Fig. 3.1 shows the visible spectrum with the approximate range of wavelengths for each colour of light.

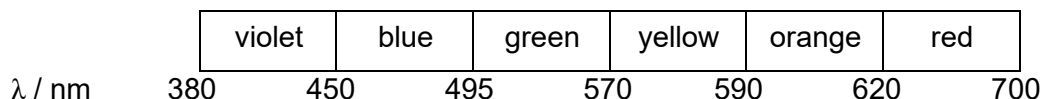


Fig. 3.1

- (i) Calculate the amount of energy, in J, in 1 photon of light that contains the maximum amount of energy in the visible spectrum. [2]
[1 nm = 1×10^{-9} m]
- (ii) Transition metal complexes are often coloured due to the absorption of photons of light at specific wavelengths. The colour observed is complementary to the colour absorbed.

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is green in colour, while $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ appears yellow.

With reference to Fig. 3.1 and the electronic configuration of the two complex ions, suggest why they exhibit different colours. [2]

(i) Shortest $\lambda = 380 \text{ nm} = 3.80 \times 10^{-7} \text{ m}$

$$E = hc / \lambda$$

$$= (6.63 \times 10^{-34})(3.00 \times 10^8) / (3.80 \times 10^{-7})$$

$$= \underline{5.23 \times 10^{-19} \text{ J}}$$

(ii) Fe^{3+} and Fe^{2+} have different number of electrons (OR electronic configurations), which results in the different extent of interactions with the H_2O ligands that causes the energy gap between the split 3d orbitals in both complexes to differ.

As $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ absorbs photons of light with shorter wavelengths compared to $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, the former appears yellow while the latter appears green.

(d) Prussian Blue is a deep blue solid. The word 'blueprint' was coined from the use of Prussian Blue on sensitised paper to lay out detailed plans for architectural and engineering projects in the 19th century.

- (i) Prussian Blue can be precipitated out by adding a solution of $\text{Fe}^{3+}(\text{aq})$ to a solution of $[\text{Fe}(\text{CN})_6]^{4-}(\text{aq})$.

Write a balanced chemical equation, with state symbols, for the formation of Prussian Blue. [1]

Standard electrode potentials can be used to compare the stability of different complex ions of a given transition element.

Table 3.2 lists electrode potentials for some electrode reactions of $\text{Fe}^{3+} / \text{Fe}^{2+}$ systems.

Table 3.2

electrode reaction	E^\ominus / V
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	+0.77
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	+0.36
$[\text{Fe}(\text{bipy})_3]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{bipy})_3]^{2+}$	+0.96

- (ii) State and explain which iron(II) complex is the most stable. [2]

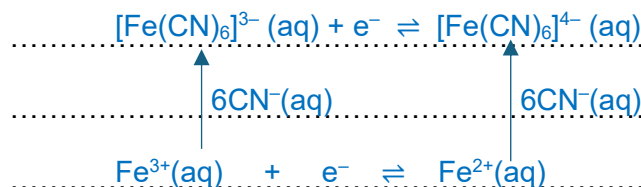
- (iii) Given, $\text{Fe}^{3+}(\text{aq}) + 6\text{CN}^-(\text{aq}) \rightleftharpoons [\text{Fe}(\text{CN})_6]^{3-}(\text{aq}) \quad \Delta G^\ominus = -250 \text{ kJ mol}^{-1}$
 $\text{Fe}^{2+}(\text{aq}) + 6\text{CN}^-(\text{aq}) \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}(\text{aq}) \quad \Delta G^\ominus = -210 \text{ kJ mol}^{-1}$

Calculate ΔG^\ominus for $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$, and hence construct an energy cycle to calculate the E^\ominus for, $[\text{Fe}(\text{CN})_6]^{3-}(\text{aq}) + \text{e}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}(\text{aq})$. [4]



(ii) The electrode potential of $[\text{Fe}(\text{bipy})_3]^{3+} / [\text{Fe}(\text{bipy})_3]^{2+}$ is the most positive, which means $[\text{Fe}(\text{bipy})_3]^{2+}$ has the lowest tendency to be oxidised ... Hence, $[\text{Fe}(\text{bipy})_3]^{2+}$ is the most stable.

(iii) $\Delta G^\ominus_{(\text{Fe}^{3+}/\text{Fe}^{2+})} = -(1 \times 96500 \times +0.77) = -74.3 \text{ kJ mol}^{-1}$



$$\Delta G^\ominus = -(-250) + (-74.3) + (-210) = -34.3 \text{ kJ mol}^{-1}$$

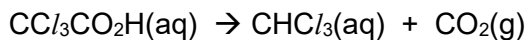
$$E^\ominus = -(-34300) / 96500 = \underline{+0.355 \text{ V}}$$

9729/03/Prelim/2025

Section B

Answer **one** question from this section.

- 4 (a) Trichloroethanoic acid decarboxylates steadily in aqueous solution at room temperature and pressure.



In an experiment, 100.0 cm³ of an aqueous trichloroethanoic acid was allowed to decarboxylate at room temperature and pressure, and the volume of CO₂ collected was tabulated against time. The results are as shown in Table 4.1.

Table 4.1

vol. of CO ₂ (V _t) / cm ³	9.5	17.0	22.5	32.5	35.5	37.5	40.0
time / s	500	1000	1500	3000	4000	5000	∞
V _∞ – V _t / cm ³	30.5	23.0	17.5	7.5	4.5	2.5	0.0

- (i) Calculate V_∞ – V_t and fill in the table accordingly. [1]

- (ii) Explain the significance of V_∞ – V_t. Make reference to V_∞ and V_t. [2]

.....
 (ii) V_∞ is the volume of CO₂ produced when decarboxylation is complete and hence it is directly proportional to the initial [CCl₃COOH]₀.

.....
 V_t is the volume of CO₂ produced in the given time and hence it is directly proportional to the change in [CCl₃COOH] based on the amount that reacted.

.....
 (V_∞ – V_t) is therefore directly proportional to the [CCl₃COOH]_t remaining at time t.

.....

- (iii) Plot a suitable graph on Fig. 4.2 on page 19 that will allow you to determine the rate equation for the decarboxylation reaction, ensuring it can be extrapolated to t = 0 s. [3]

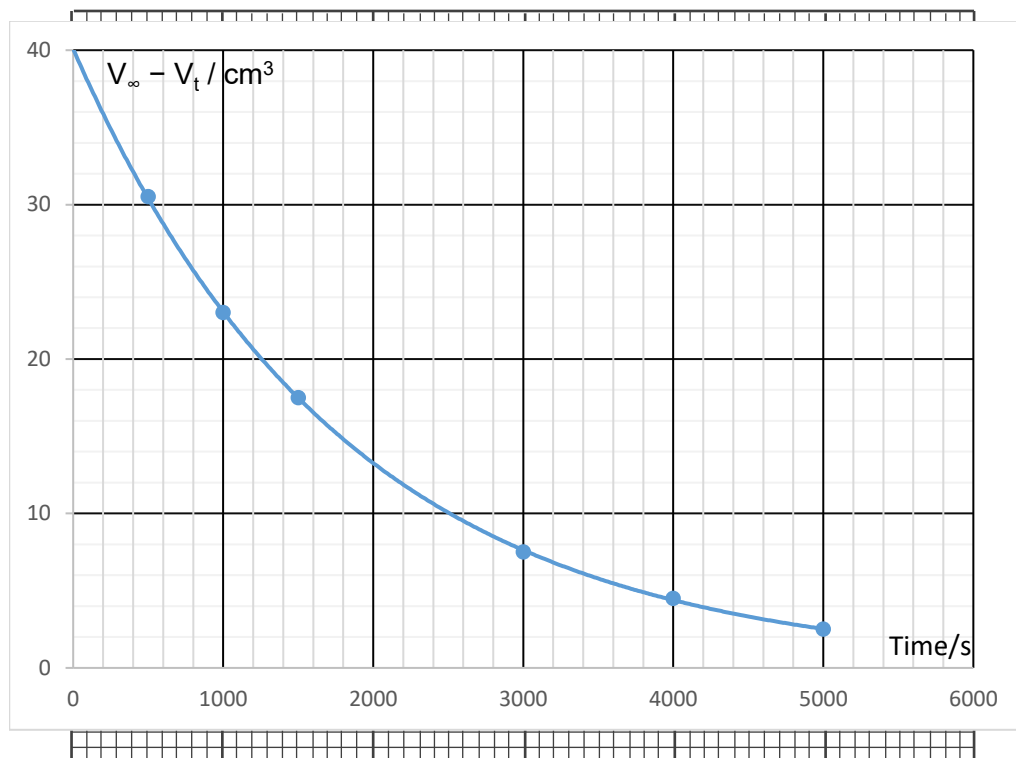


Fig. 4.2

- (iv) Calculate the initial concentration of the trichloroethanoic acid used in the experiment. [2]
- (v) Use your graph in Fig. 4.2 to deduce the order of reaction with respect to trichloroethanoic acid, calculate the value of the rate constant, and write an expression for the rate equation. Show how you obtained your answer. [3]
- (vi) Use the graph to estimate the time taken for the initial concentration of trichloroethanoic acid to fall by 10 %. [1]

(iv) $n(\text{CCl}_3\text{COOH}) = 40.0/24000 = 0.00167 \text{ mol}$

$[\text{CCl}_3\text{COOH}] = 0.00167/0.1 = 0.0167 \text{ mol dm}^{-3}$

(v) Constant $t_{1/2} = 1250 \text{ s}$

Hence, 1st order with respect to $[\text{CCl}_3\text{COOH}]$

$k = \ln 2 / t_{1/2} = 5.55 \times 10^{-4} \text{ s}^{-1}$

Rate = $k [\text{CCl}_3\text{COOH}]$

(vi) 200 s

- (b) (i) The pK_a of trichloroethanoic acid is 0.52 while that of ethanoic acid is 4.76. Explain why the pK_a of trichloroethanoic acid is smaller. [2]
- (ii) With reference to the pK_a value of trichloroethanoic acid, state an assumption about its dissociation and use it to estimate the pH of 0.05 mol dm^{-3} trichloroethanoic acid. [2]
- (iii) Suggest if partial neutralisation of trichloroethanoic acid can result in a buffer solution. [1]

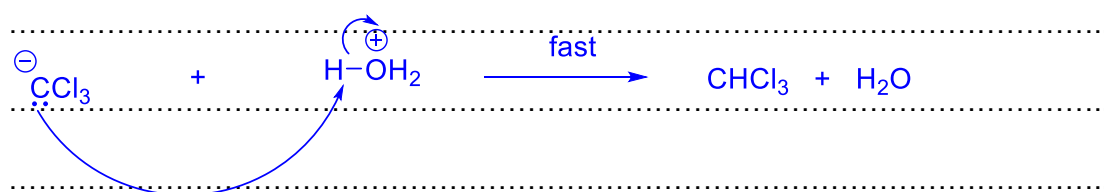
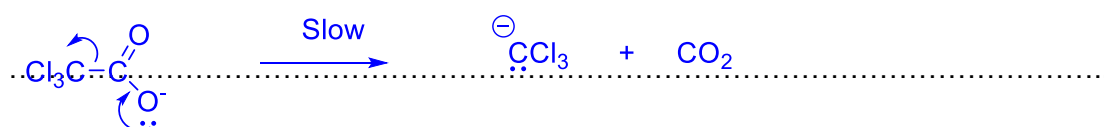
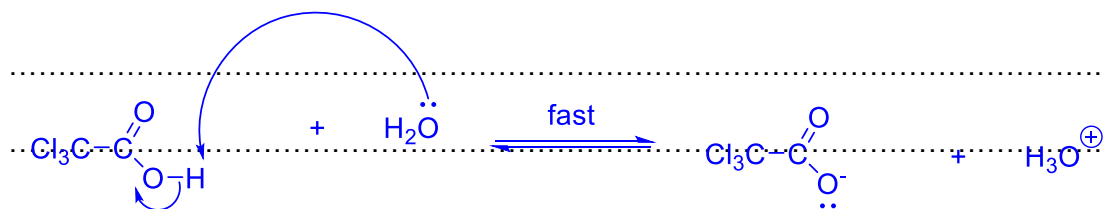
(i) The three chlorine atoms are very strongly electron withdrawing and hence help to disperse the negative charge on the conjugate base thereby stabilising it OR weakens O-H bond more. This leads to a stronger acid and smaller pK_a value.

(ii) $[H^+] = 0.05 \text{ mol dm}^{-3}$ as K_a is very large and hence can be assumed to be fully dissociated.

$$pH = -\lg 0.05 = 1.30$$

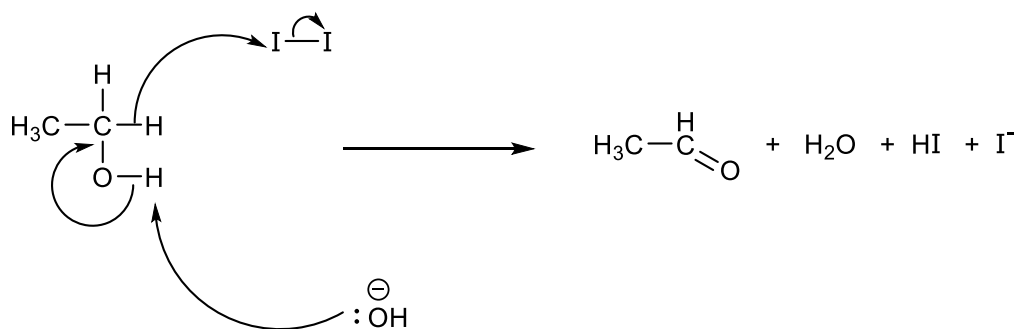
(iii) Since trichloroethanoic acid is a very strong acid which dissociates almost fully, it will not be able to form a buffer upon partial neutralisation.

- (c) Draw the mechanism for the decarboxylation of trichloroethanoic acid, showing all curly arrows, lone pairs and charges. The steps are as follows:
 Step 1: Water reacts with trichloroethanoic acid as a Brønsted-Lowry base.
 Step 2: Loss of CO_2 from the conjugate base from step 1.
 Step 3: Formation of CHCl_3 from the intermediates formed in steps 1 and 2. [3]



[Total: 20]

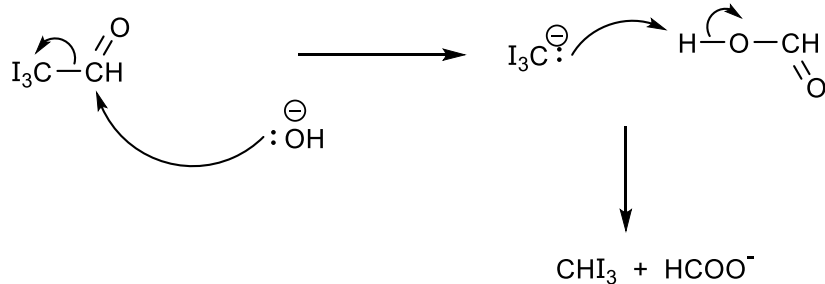
Step 1



Reaction mechanism for the iodination of acetaldehyde:

- Deprotonation of acetaldehyde by hydroxide ion (OH^-) to form the enolate ion ($\text{CH}_2=\text{CH}-\text{O}^-$).
- Reaction of the enolate ion with molecular iodine (I_2) to form an intermediate α -iodo enolate ($\text{CH}_2=\text{CH}(\text{O}^-)-\text{CH}_2\text{I}$).
- Proton transfer and tautomerization of the intermediate to yield iodoacetaldehyde (ICH_2CHO).

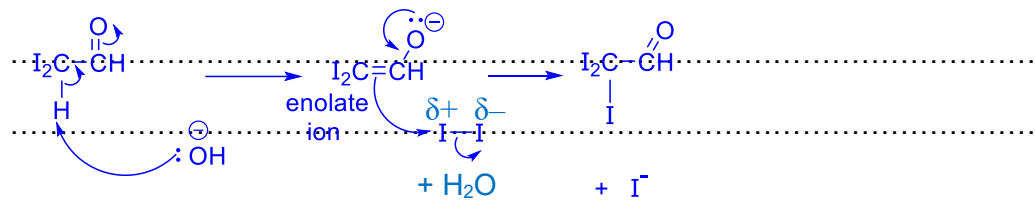
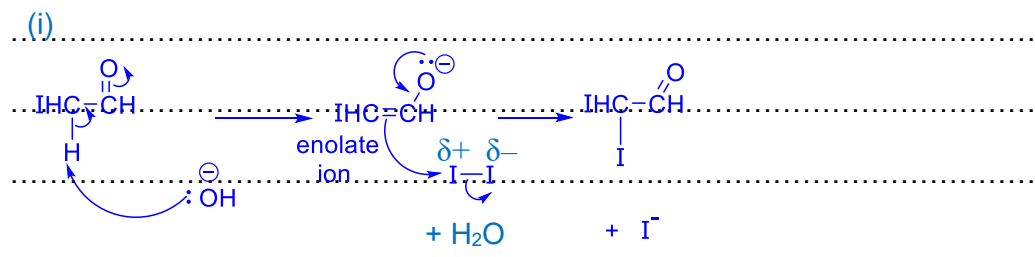
Step 3



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- (i) Outline the portion of step 2 in the mechanism for the repeated replacement of the remaining H atoms in CH_2ICHO to form CI_3CHO . Show all lone pairs, dipoles, charges and curly arrows. [4]
- (ii) The repeated replacement of the hydrogen atom is made possible by the repeated abstraction of the H^+ by OH^- from the α -methyl group. [2]

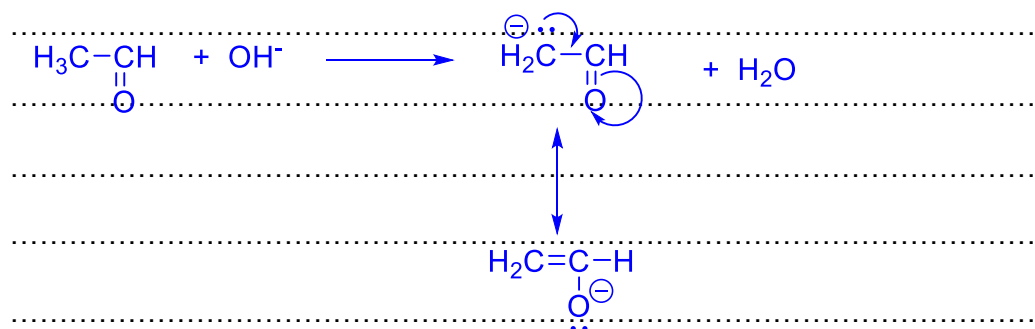
State the behaviour of the methyl ketone in this step and explain how it can give up the H^+ . [2]



(ii) Methyl ketone behaves as a proton donor or Brønsted-Lowry acid.

The strongly electron withdrawing carbonyl group stabilises the negative charge on the alpha carbon due to delocalisation forming the conjugate enolate ion OR weakens the C-H bond.

For illustration:



- (iii) Based on the mechanism, explain why only ketones with the α -methyl group can undergo the iodoform reaction while acids such as ethanoic acid or esters, such as, $\text{CH}_3\text{COOCH}_3$, which have the α -methyl group do not undergo a similar reaction. [2]
- (iv) In step 3, the triiodoethanal undergoes a substitution reaction instead of the expected addition reaction with the nucleophile, OH^- .

Suggest why this reaction occurs.

[2]

(iii) The reaction requires a structure that can form a stable conjugate base / enolate ion under basic conditions and ketones can do that.

Esters will undergo alkaline hydrolysis while carboxylic acids will undergo acid-base reactions respectively instead.

(iv) The $-\text{CI}_3$ group alpha to the ketone group is strongly electron withdrawing which weakens the bond between the CI_3 -group and the adjacent $\text{C}=\text{O}$ group and hence results in the bond breaking resulting in substitution. OR makes C more electron deficient and susceptible to nucleophilic attack.

- (b) Study the reaction scheme in Fig. 5.2. State the reagents and conditions for each step from steps 1 to 7, as well as the identities of U, V and W. [10]

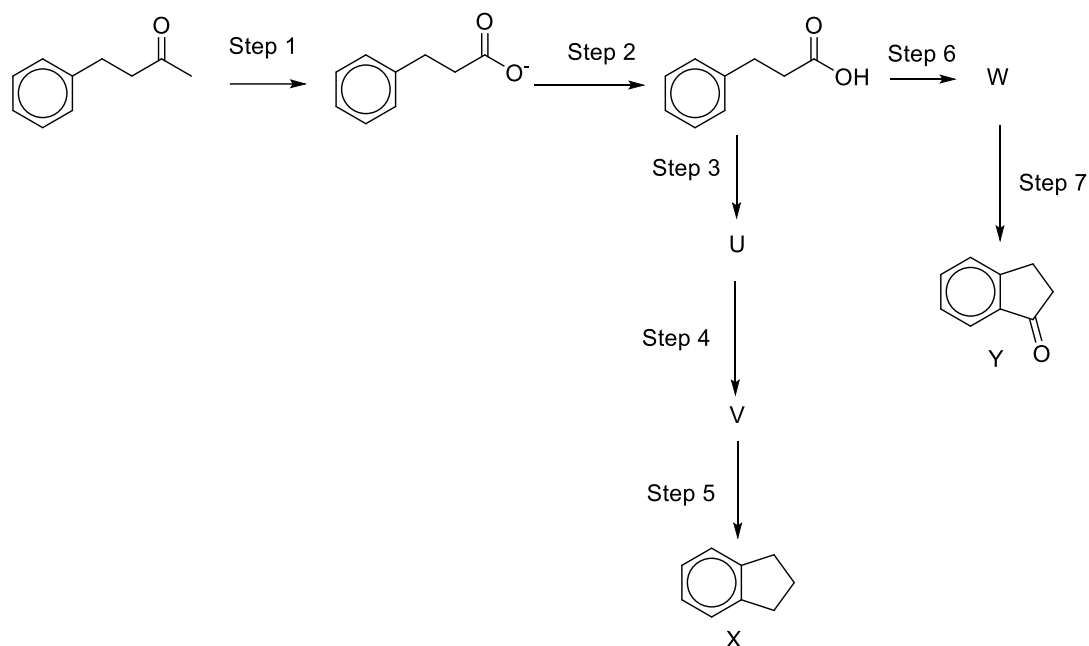


Fig. 5.2

Step 1 – I_2 , NaOH(aq) and r.t.p. / warm

Step 2 – aqueous HCl or H_2SO_4

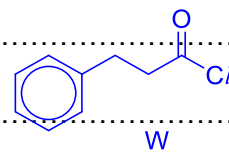
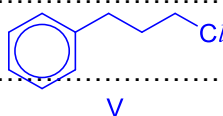
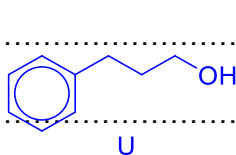
Step 3 – LiAlH₄ (dry ether), reflux

Step 4 – PCl_5 or PCl_3 or PBr_3 or $SOCl_2$ or conc HCl

Step 5 – $AlCl_3$, (heat optional)

Step 6 – PCl_5 or PCl_3 or PBr_3 or $SOCl_2$ or conc HCl

Step 7 – $AlCl_3$, (heat optional)



[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

This image shows a full page of white paper with horizontal dotted lines, typical of primary school writing paper. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.