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TEMASEK JUNIOR COLLEGE

2024 JC2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME										
CENTRE NUMBER	S					INDEX NUMBER				

Chemistry **9729/03**

Paper 3 Free Response Questions **11 September 2024**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, 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.

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 Examiner's Use		
Paper 3	**Q1**	**/18**
	Q2	**/20**
	Q3	**/22**
	Q4	**/20**
	Q5	**/20**
	Total	**/80**

This document consists of **23** printed pages and **1** blank page.

[Turn over

Section A

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

1 **(a)** In Periodic Table, Group 14 consists of 5 elements. The elements at the top of the group, carbon to germanium, have very different properties from those at the bottom, tin and lead. For instance, carbon to germanium tend to adopt oxidation states of +4, whereas the heavier elements, such as tin and lead, exhibit the +2 oxidation state due to the inert pair effect.

(i) Table 1.1 shows the melting points of the elements of Group 14.

Table 1.1

element	C	Si	Ge	Sn	Pb
melting point / °C	>3550	1410	937	232	327

Carbon, silicon and germanium each forms a solid with the same type of structure. Using structure and bonding and the information from the *Data Booklet*, suggest why the melting points of these elements decrease from carbon to germanium.

Carbon, silicon and germanium have √ **giant molecular structure**.

Melting involves breaking √ **numerous strong covalent bonds between atoms.**

	Atomic radius nm
C	0.077
Si	0.117
Ge	0.122

√ The atomic radius increases from C to Ge, leading to less effective overlap of the orbitals.

√**Bond strength decreases** and hence less energy is required for melting.

2 √ : 1 mark

[2]

Carbon forms many allotropes such as graphite and diamond. Recent scientific research has found that replacing the graphite electrodes with graphene in lithium-ion batteries can extend battery life. Graphene is a **single, one atom thick** layer of graphite.

(ii) Explain why graphene can conduct electricity along the plane.

The remaining **2p electron on each carbon atom can delocalise along the plane** when a potential difference is applied. **[1]**

[1]

(iii) State and explain how you would expect the bond strength of carbon-carbon bonds in graphene to differ when compared with that in diamond.

The carbon-carbon bond in graphene is **stronger** than that in diamond. **[1]**

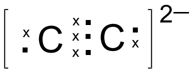
- This is due to the √ **presence of both** σ **and** π **bonds / partial double bond character in the C–C bond in graphene,**

√while there are only σ bonds present in diamond
OR
greater s character / smaller p character of the sp^2–sp^2 overlap in graphene as compared to the **sp^3–sp^3 overlap in diamond**.

[2]

(b) Carbon forms carbide anion, C_2^{2-} in calcium carbide while silicon mostly forms Si^{4+} ions. Calcium carbide is a crystalline solid with a melting point of approximately 2160 °C.

(i) Draw the dot-and-cross diagram of C_2^{2-}.



Anion:
Accept additional electrons of opposite symbol/ third symbol
do not accept dative bonds

[1]

(ii) When some calcium carbide is added to excess water with a drop of Universal Indicator, ethyne gas, C_2H_2, is produced. The solution changes from green to blue after the reaction is complete.

Write an equation, with state symbols, for this reaction.

$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$ [1]
[1] state symbols

[2]

(iii) In a particular experimental set-up, a beam of $^{12}C_2^{2-}$ ions was deflected by an angle of -2.45°. Assuming an identical set of conditions, calculate the angle of deflection for $^{28}Si^{4+}$ ions.

$^{12}C_2^{2-}$ whose $\frac{q}{m} = \frac{-2}{24} = +\frac{1}{12}$ gives an angle of deflection, θ, of -2.45°

$$\theta = k\left(\frac{q}{m}\right) \Rightarrow -2.45° = k\left(+\frac{1}{12}\right) \Rightarrow k = 29.4$$

For $^{28}Si^{4+}$ whose $\frac{q}{m} = \frac{+4}{28} = +\frac{1}{7}$,

angle of deflection, $\theta = 29.4 \times \left(+\frac{1}{7}\right) = \underline{+\mathbf{4}.2°}$

[2]

[Turn over

(c) Using the data from *Data Booklet*, describe and explain the reducing strength of Group 2 elements from magnesium to strontium.

Group 2 element	**Standard electrode potential / V**
Magnesium	-2.38
Calcium	-2.87

[1]

√ **The standard electrode potential values become more negative down the group. This is due to√ increasing atomic radius down the group,**
√the attraction of nucleus for the valence electrons decreases.

Hence the electrons can be removed more easily through ionisation. √Reducing strength increases down the group.
2√, 1 mark

[3]

(d) Aluminium chloride is used as a catalyst for the reaction between methylbenzene and 2-chloropropane to form two constitutional isomers **L** and **M** with the formula $C_{10}H_{14}$.

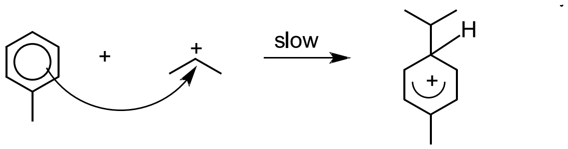
(i) Suggest the mechanism for this reaction to form the major product, **L**. Show all charges and relevant lone pairs and show the movement of electron pairs using curly arrows.

Type of reaction: Electrophilic Substitution **[1]**

Step 1: Generating the electrophile, $CH_3\overset{+}{C}HCH_3$

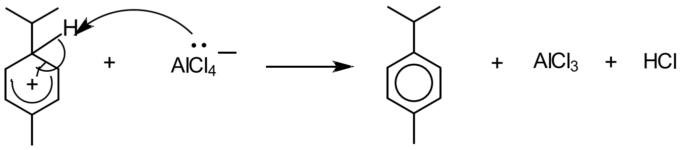
$$AlCl_3 + CH_3CHClCH_3 \rightleftharpoons AlCl_4^{-} + CH_3\overset{+}{C}HCH_3$$

Step 2: Electron-rich methylbenzene attacks the $CH_3\overset{+}{C}HCH_3$ electrophile



[1]

Step 3: Abstraction of proton followed by regeneration of the catalyst



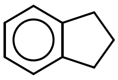
[1]

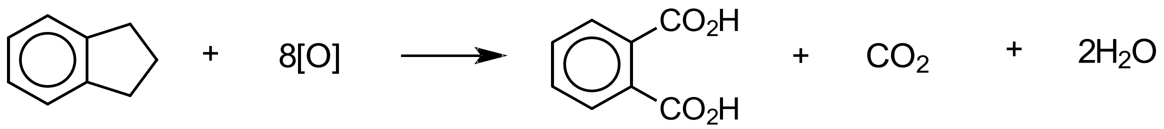
[3]

(ii) **L** and **M** are formed in a 60:40 ratio. Suggest why **L** is the major product.

The *ortho*-positions are adjacent to the substituent which cause steric effects and block the path of incoming electrophile. The *para*-position is more accessible for the incoming electrophile to attack.

[1]

(e) **(i)** Write an equation for the reaction of  with acidified $KMnO_4$. [1]



[1]

(ii) Name the oxidised product formed in **(e)(i)**. [1]

benzene-1,2-dicarboxylic acid **[1]**

[Total: 19]

2 Many chemical processes release waste products into the atmosphere. Scientists are developing new catalysts to convert these emissions into useful products, such as methanol which can be used as a fuel.

An equation for the synthesis of methanol is given below.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g) \qquad \Delta H = -49\ kJ\ mol^{-1}$$

(a) **(i)** State and explain the effect on the position of equilibrium when the temperature is increased. [2]

By LCP, the position of equilibrium shifts left [✓] to favour the endothermic [✓] reaction to absorb heat [✓] and decrease temperature of the system. [✓]

(ii) State and explain the effect on the position of equilibrium when the pressure is increased. [1]

By Le Chatelier's Principle, the position of equilibrium shifts to the right to decrease the number of moles of gases to decrease the pressure. [1]

(iii) Write an expression for K_p of the reaction. [1]

$$K_p = \frac{(P_{CH_3OH})(P_{H_2O})}{(P_{CO_2})(P_{H_2})^3}$$ **[1]**

[Turn over

1.0 mol of carbon dioxide and 3.0 mol of hydrogen were sealed in a container. After the mixture had reached equilibrium, at a pressure of 500 kPa, the amount of methanol produced was 0.86 mol.

(iv) Determine the mole fraction of methanol when the system reached equilibrium. [2]

	$CO_2(g)$ +	$3H_2(g)$ ⇌	$CH_3OH(g)$ +	$H_2O(g)$
Initial amount/ mol	**1**	**3**	**0**	**0**
Change in amount/ mol	**-0.86**	**-3(0.86)**	**+0.86**	**+0.86**
Eqm amount/ mol	**0.14**	**0.42**	**0.86**	**0.86 [1]**

Total number of moles of gases = 2.28 mol

Mole fraction of CH_3OH = 0.86/2.28 = 0.377 [1]

(v) Hence, calculate the K_p value, stating its units. [2]

$$P_{CH_3OH} = P_{H_2O} = \frac{0.86}{2.28} \times 500 = 188.60\text{kPa}$$

$$P_{CO_2} = \frac{0.14}{2.28} \times 500 = 30.70\text{kPa}$$

$$P_{H_2} = \frac{0.42}{2.28} \times 500 = 92.1\text{ kPa}$$

[1] All partial pressure values, or correct working shown in working of K_p

$$K_p = \frac{(188.6)(188.6)}{(30.7)(92.1)^3} = 0.00148\ (\text{kPa})^{-2}$$

[1] value and units

(vi) Suggest one possible environmental advantage of this reaction. Explain your answer. [1]

The reaction removes CO_2, which causes greenhouse effect/ global warming. [1]

(b) The standard enthalpy change of formation of some species are given in table 2.1.

Table 2.1

compound	ΔH_f^{θ}/ kJ mol^{-1}
$CO_2(g)$	–394
$H_2O(g)$	–242

(i) Define standard enthalpy change of formation. [1]

The enthalpy change when 1 mole of substance is formed from its constituent elements in their standard states under standard conditions of 298 K and 1 bar. [1]

(ii) Write an equation to represent the standard enthalpy change of formation of $CH_3OH(g)$. [1]

$C(s) + 2H_2(g) + \frac{1}{2} O_2(g) \rightarrow CH_3OH(g)$ [1]

(iii) Use the enthalpy change of reaction for the synthesis of methanol and data provided in table 2.1 to calculate the standard enthalpy change of formation of $CH_3OH(g)$. [1]

$\Delta H_r = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$

$-49 = (\Delta H_f\ CH_3OH - 242) - (-394)$

$\Delta H_f\ CH_3OH(g) = -201\ \text{kJ mol}^{-1}$ [1]

(c) **(i)** State two assumptions of ideal gas behaviour. [1]

Negligible intermolecular forces of attraction between the gas particles.

Gas particles have negligible volume compared to the volume of the container the gas occupies. [1]

(ii) Fig. 2.1 shows the graphical plot of pV = nRT for $CO_2(g)$ at 500K as a function of pressure. On the same axes provided in Fig 2.1, sketch the graph for $H_2O(g)$ at 500K. [1]

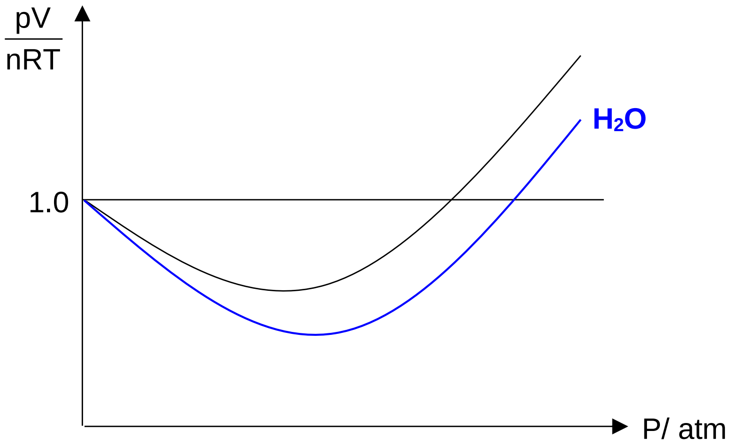


Fig. 2.1

(d) Carbon dioxide can be formed by thermal decomposition of carbonates and hydrogen carbonates. The thermal decomposition of potassium hydrocarbonate, $KHCO_3$, proceeds according to reaction 1.

Reaction 1: $2KHCO_3(s) \rightarrow K_2CO_3(s) + CO_2(g) + H_2O(l)$ ΔH_1

The enthalpy change of this reaction cannot be measured directly. It is calculated from the enthalpy changes of other reactions, as shown in reactions 2 and 3.

Reaction 2: $K_2CO_3(s) + 2HCl(aq) \rightarrow 2KCl(aq) + CO_2(g) + H_2O(l)$ $\Delta H_2 = -34.0\ \text{kJ mol}^{-1}$

Reaction 3: $KHCO_3(s) + HCl(aq) \rightarrow KCl(aq) + CO_2(g) + H_2O(l)$ $\Delta H_3 = +32.8\ \text{kJ mol}^{-1}$

(i) Suggest why it is not possible to measure ΔH_1 for the decomposition reaction directly. [1]

It is not possible to measure a temperature when heating. [1]

(ii) Construct a suitable energy cycle to determine the enthalpy change of reaction 1. [2]

$$\begin{tikzcd}
2KHCO_3(s) + 2HCl(aq) \arrow[rr, "\Delta H_1"] \arrow[dr, "2\Delta H_3"'] & & K_2CO_3(s) + CO_2(g) + H_2O(l) + 2HCl(aq) \arrow[dl, "\Delta H_2"] \\
& 2KCl(aq) + 2CO_2(g) + 2H_2O(l) &
\end{tikzcd}$$

[1] balanced cycle with state symbols

By Hess' Law,

$$\Delta H_1 = 2\Delta H_3 - \Delta H_2$$
$$= 2(+32.8) - (-34.0)$$
$$= +99.6\ \text{kJ mol}^{-1}$$ **[1]**

(iii) State and explain the sign of entropy change of reaction 2. [1]

Positive entropy change. [✓]

There is an increase in number of moles of gases, hence degree of disorder increases. [✓]

(iv) Hence, state and explain whether reaction 2 is spontaneous at all temperatures. [1]

$$\Delta G = \Delta H - T\Delta S$$

Since ΔH is negative and ΔS is positive, ΔG is negative and reaction is spontaneous for all temperatures. [1]

[Total: 19]

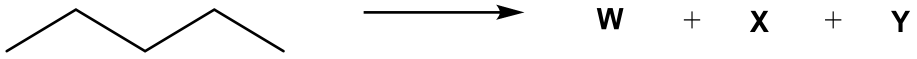
3 **(a)** Singapore is one of 197 countries that signed the Montreal Protocol, a treaty to reduce the production and consumption of chlorofluorocarbons (CFCs).

Outline the environmental consequence of releasing chlorofluorocarbons into the atmosphere. [1]

Chlorofluorocarbons produce free C*l* radical in the presence of UV light in the atmosphere which can destroy the ozone layer. [1]

(b) Pentane has many applications, including acting as a replacement for CFCs.

When pentane is reacted with chlorine in the presence of *uv* light, three mono-chlorinated compounds, **W**, **X** and **Y** are formed.



Compounds **W** is not chiral while compound **Y** is produced as a racemic mixture.

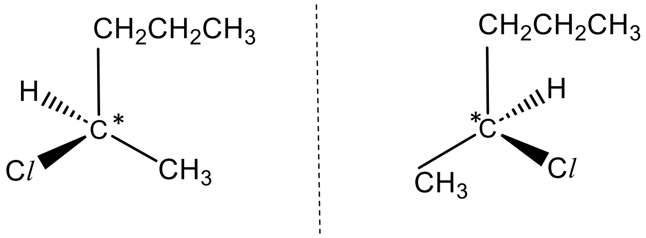
(i) Compound **W** only forms pent-1-ene in an elimination reaction.

Deduce the structure of **W** and state the reagent and condition for the elimination reaction. [2]

W: $CH_3CH_2CH_2CH_2CH_2Cl$ [1]

Alcoholic NaOH, heat [1]

(ii) Draw three-dimensional structures for the enantiomers of compound **Y** and suggest why a racemic mixture is formed. [2]



[1]

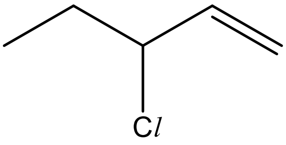
$CH_3\dot{C}HCH_2CH_2CH_3$ radical has a trigonal planar arrangement around the C with the lone electron. This radical can react with chlorine on either top or bottom of the plane with equal probability. Since equal quantity of each enantiomer is formed, a racemic mixture is obtained. [1]

(iii) Suggest how the pair of enantiomers differ in their physical properties. [1]

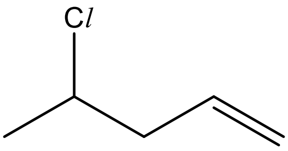
Enantiomers differ in the direction in which they rotate plane-polarised light.

[1]

(c) Pent-1-ene also reacts with chlorine in the presence of *uv* light. Two of the products are 3-chloropent-1-ene and 4-chloropent-1-ene.

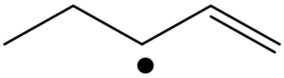


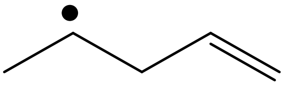
3-chloropent-1-ene



4-chloropent-1-ene

(i) Draw the structures of the organic radical intermediates leading to the formation of 3-chloropent-1-ene and 4-chloropent-1-ene. [1]





[1] both correct structures

(ii) Hence, suggest why 3-chloropent-1-ene is formed in larger quantity. [1]

The radical forming 3-chloropent-1-ene is more stable due to resonance stabilisation / delocalisation of lone / unpaired electron with the adjacent C=C. [1]

(iii) 1-chloropent-1-ene is an isomer of 3-chloropent-1-ene.

Suggest an identification test to distinguish 1-chloropent-1-ene from 3-chloropent-1-ene. State the positive observation for this test. [2]

NaOH(aq), heat followed by HNO_3 and $AgNO_3$ / ethanolic $AgNO_3$, heat [1]

3-chloropent-1-ene: white precipitate [1]

1-chloropent-1-ene: no (white) ppt

(d) In biological systems, oxygen accepts an electron to form superoxide. An enzyme regulates the level of superoxide by catalysing its decomposition to hydrogen peroxide and oxygen.

Explain how the **rate** of this enzyme-catalysed reaction varies with [superoxide]. [2]

At low [superoxide], [✓] rate of reaction is directly proportional to [superoxide] since active sites are not fully occupied → 1st order reaction

As [superoxide] increases, [✓] rate increases to a lesser extent and is no longer proportional to [superoxide] since more active sites are occupied → mixed order reaction / between 1st and 0th order

At high [superoxide], [✓] rate becomes constant as active sites of enzyme are fully occupied / saturated → 0th order reaction

[✓]: correct order of reaction

2[✓] = [1]

(e) Benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes in water as shown in the following equation.

$$C_6H_5N_2Cl\,(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

A solution of 0.0750 mol dm^{-3} of $C_6H_5N_2Cl(aq)$ decomposes at a constant temperature of 50 °C.

The volume of nitrogen gas, $N_2(g)$, collected is recorded every 5 minutes for 45 minutes as shown in the graph in Fig. 3.1

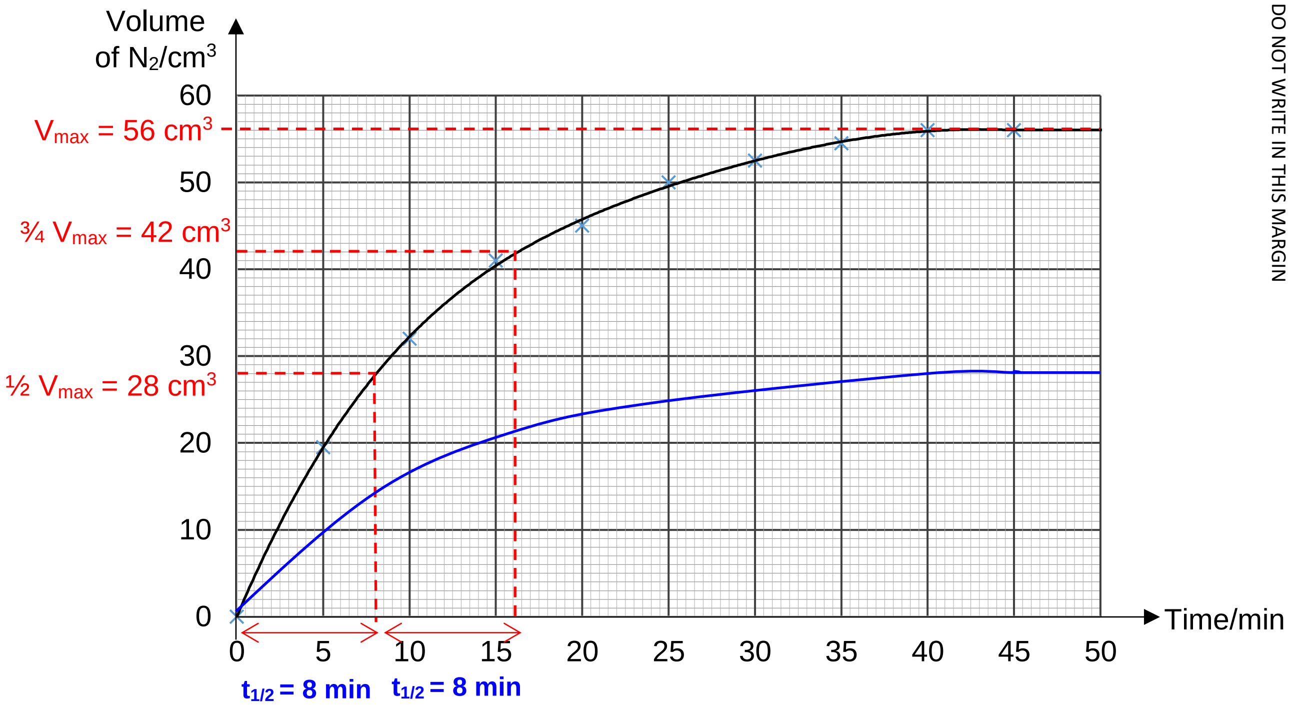


Fig. 3.1

(i) Determine the order of reaction with respect to [$C_6H_5N_2Cl$]. [2]

Max volume of N_2 = 56 cm^3

Since half-life is constant at 8 min, reaction is 1st order respect to benzoyl peroxide. [1]

Clear construction lines on graph, with $t_{1/2}$ labelled or mentioned in explanation [1]

(ii) Hence, calculate the concentration of $C_6H_5N_2Cl$ (aq) at 32 min. [1]

At 32 min, 4 half-lives have passed.

remaining [benzene diazonium chloride]

$= 0.075 \times (\frac{1}{2})^4 = 4.69 \times 10^{-3}$ mol dm^{-3} [1]

(iii) Calculate the rate constant for the reaction and include its units. [1]

$k = \frac{In\ 2}{8} = 0.0866$ min^{-1} [1] ecf from (i)

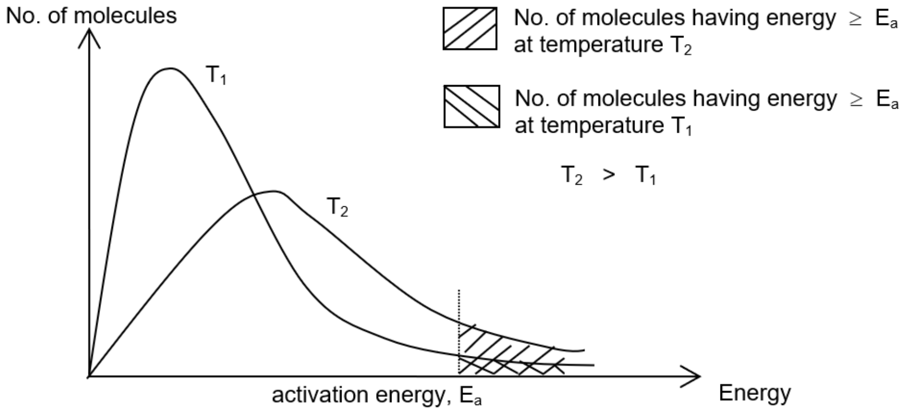
(iv) On Fig. 3.1, draw the graph produced if the same volume of half the concentration of $C_6H_5N_2Cl$(aq) decomposes at a constant temperature of 50 °C. All other conditions remained unchanged. [1]

[1] Key points on graph

- curve starts at 0
- grad of graph gentler than at 50 °C, reaching max volume of 28 cm^3 (56 cm^3 / 2)

(v) The reaction was repeated at 20 °C.

Sketch the Boltzmann distribution and explain how a decrease in temperature affects the rate. [3]



[✓] decrease in the average kinetic energy of molecules leads to a decrease in collision frequency.

[✓] number of reactant molecules having energy greater than or equal to activation energy, E$_a$, is decreased.

[✓] frequency of effective collisions decreases

[✓] rate constant decreases + rate decreases

[1] correct Boltzmann curve + legends + labels

2 [✓] = [1]

(vi) The effect of temperature on the rate of the reaction is given by the Arrhenius equation:

$$\mathrm{k} = \mathrm{A}e^{-\frac{\mathrm{E_a}}{\mathrm{RT}}}$$

where k = rate constant, E_a = activation energy, R = molar gas constant,

T = temperature in Kelvin and A = Arrhenius constant

The value of the rate constant at 20 °C is 2.58 x 10^{-3}. Using your answer to **(iii)**, calculate the activation energy of this reaction. [2]

If you were unable to obtain an answer in **(e)(iii)**, use the value of 0.06.

Note: Arrhenius constant is NOT rate constant

Analysis: converts both temperatures to K and substitute to the Arrhenius equation

$$\mathbf{k_{293K} = 2.58 \times 10^{-3} = Ae^{-\frac{E_a}{293R}}} \quad \text{------ (1)}$$

$$\mathbf{k_{323K} = 0.0866 = Ae^{-\frac{E_a}{323R}}} \quad \text{------ (2)}$$

(1) divided by (2):

$$\frac{0.00258}{0.0866} = e^{-\frac{E_a}{R}\left(\frac{1}{293}-\frac{1}{323}\right)}$$

$$-\frac{E_a}{8.31}\left(\frac{1}{293}-\frac{1}{323}\right) = \ln(0.0298)$$

[1] E_a = +92.1 kJ mol^{-1} / +82.5 kJ mol^{-1} (when 0.06 is used)

[1] working

Section B

Answer **one** question from this section.

4 **(a)** Barium meals are given to patients prior to receiving an X-ray imaging. The main component in barium meals is barium sulfate.

At 30°C, 0.285 mg of barium sulfate is found to dissolve in 100 cm^3 water to form a saturated solution.

(i) Calculate the solubility product, K_{sp}, of barium sulfate at 30°C. [2]

M_r of $BaSO_4$ = 233.4

Amt of $BaSO_4$ dissolved in 1 dm^3 = $(0.285 \times 10^{-3}) / 233.4 \times 10 = 1.22 \times 10^{-5}$ mol [1]

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (1.22 \times 10^{-5})^2 = 1.49 \times 10^{-10}$ $mol^2\ dm^{-6}$ [1]

(ii) A small amount of sodium sulfate is added to the saturated solution in **(a)**.

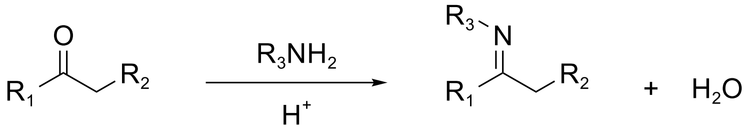
Explain how the solubility of barium sulfate would change. [1]

$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

When sodium sulfate is added, [SO_4^{2-}] increases. By Le Chatelier's Principle, position of equilibrium shifts to left to decrease [SO_4^{2-}]. More $BaSO_4$ is formed, so solubility drops. [1]

(b) Imines are a group of organic molecules which are common intermediates in many biological reactions, where they are often referred to as Schiff bases.

Imines can be synthesised from the reaction between carbonyl compounds and primary amines, in the presence of acid catalyst.



imine

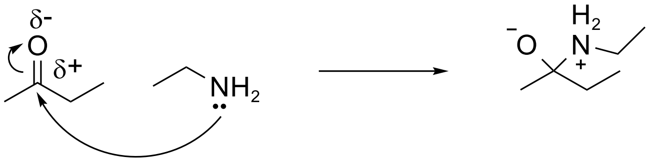
where R_1, R_2 and R_3 are H, alkyl or aryl groups

The mechanism for the formation of imines follows a 3-step reaction.

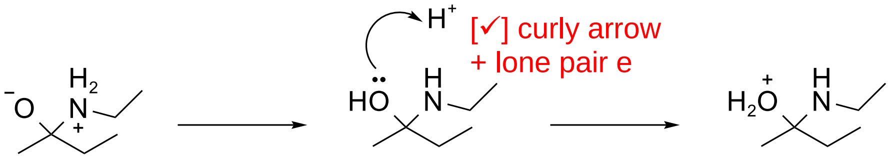
Step 1	Nucleophilic addition between the carbonyl compound and primary amine occurs, producing a dipolar intermediate.
Step 2	The dipolar intermediate undergoes proton transfer, forming a neutral molecule, followed by protonation of an oxygen atom
Step 3	Expulsion of water (a good leaving group) and forming of C=N bond, followed by regeneration of the acid catalyst to form the imine.

(i) Using appropriate curly arrows, illustrate the 3-step mechanism for the formation of the imine when butanone reacts with ethylamine.

Show clearly the charges and lone pair of electrons as well as structure of intermediate formed. [3]



[1] Step 1:

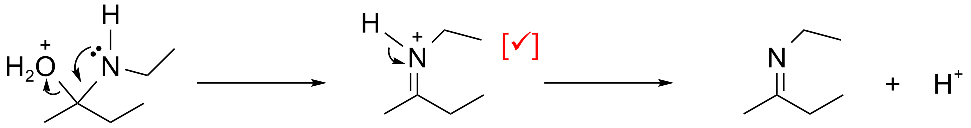


[✓] curly arrow + lone pair e

[✓]

Step 2:

[✓]



[✓]

Step 3:

[1] for each step with correct charges, lone pair electrons, curly arrows

2[✓] = [1]

(ii) The mechanism above is highly sensitive to pH of the reaction medium. Figure 4.1 below shows the rate of formation of imine at various pH.

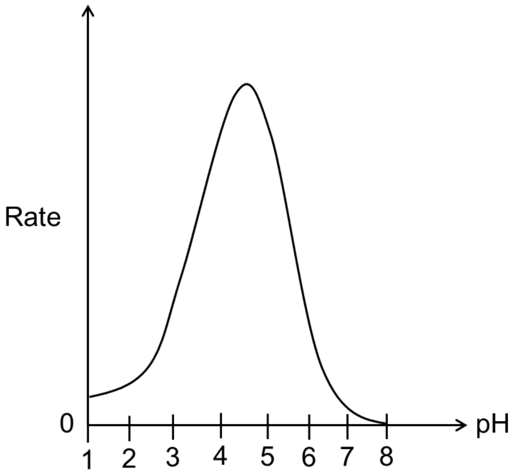


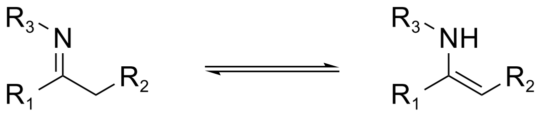
Fig 4.1

With reference to the mechanism and information above, suggest explanations why the rate of reaction is very slow at very low pH and at very high pH. [2]

[1] At very low pH, the amine will be fully protonated to form a salt, which can no longer function as a nucleophile for nucleophilic addition in step 1.

[1] At very high pH, there will be insufficient H^+ to protonate the OH group in step 2, preventing the formation of a good leaving group (water).

(c) Under certain conditions, an imine undergoes tautomerisation to form an enamine.

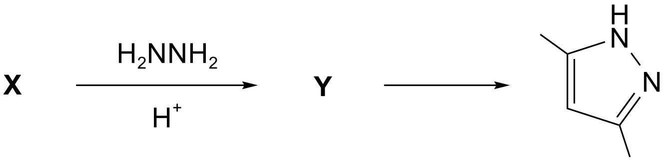


imine enamine

Imine and enamine are known as tautomers of each other.

In the presence of an acid catalyst, dicarbonyl compound **X** reacts with hydrazine, N_2H_4, in a similar reaction as **(b)** to form intermediate **Y**, which tautomerises to form **Z**.

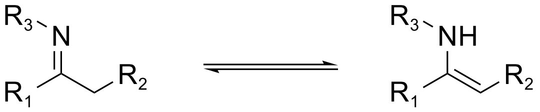
Y and **Z** are tautomers of each other.



Z

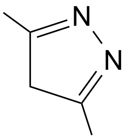
(i) Draw the structure of intermediate **Y**. [1]

Analysis:



imine enamine

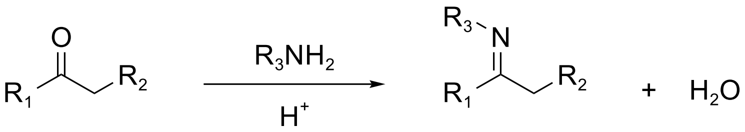
Working backwards from Z, remove H from -NH and change the C=C to C=N.



[1]

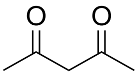
(ii) Hence, deduce the structure of dicarbonyl compound **X**. [1]

Analysis:



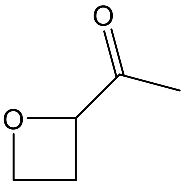
imine

Working backwards from Y, change C=N to C=O.

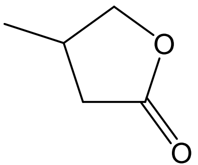


[1]

(iii) Compound **P** and **Q** are isomers of **X**.



P



Q

Suggest a simple chemical test which could be used to give a positive observation for **P**. [1]

	Add Brady's reagent to each sample	Add alkaline aqueous iodine and warm
P	orange ppt formed	yellow ppt formed
Q	no orange ppt formed	no yellow ppt formed

[1] correct reagent / condition + correct obs for both cpds

The 5-membered ring structure of **Z** behaves like a benzene ring.

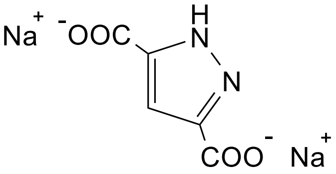
(iv) With reference to the structure of **Z**, suggest why **Z** is more likely to exist than its tautomer. [1]

[1] **Y** is more stable than its tautomer / resonance stabilised due to delocalisation of pi electrons over the 5 atoms in the ring, resulting in resonance stability.

(v) **Z** reacts with hot alkaline potassium manganate(VII) to form a single ionic product **V**, $C_5H_2N_2O_4Na_2$.

Draw the structure of product **V**. [1]

Analysis: Since Z behaves like benzene ring, the alkyl groups undergo side-chain oxidation.



(d) **A**, C_5H_8O, and **B**, $C_5H_6O_4$, are cyclic compounds. Both give **C**, $C_5H_6O_5$, upon heating with acidified potassium manganate(VII).

A and **B** each exists as a pair of enantiomers but not **C**. 1 mole of **A** and **B** each produces 0.5 mole of H_2 gas while 1 mole of **C** produces 1 mole of H_2 gas when excess sodium metal is added.

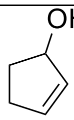
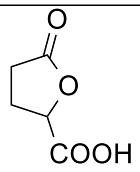
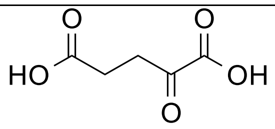
A decolourises aqueous bromine in the dark. **B** reacts with sodium carbonate to form $C_5H_5O_4Na$ and reacts with hot aqueous NaOH to form $C_5H_6O_5Na_2$. Only **C** gives orange solid with Brady's reagent.

Deduce the structures of **A**, **B** and **C** and explain your reasoning. [7]

Observation	**Type of reaction**	**Deduction**
A and **B** give **C**, $C_5H_6O_5$, upon heating with acidified potassium manganate(VII).	[✓] Oxidation [✓*] acidic hydrolysis	[✓] complete cleavage of 1 C=C in **A** (gain 4 O atoms) / **A** contains -OH [✓^] ester bond in **B** (gain 1 O atom)
A and **B** each exists as a pair of enantiomers but not **C**.	-	[✓] **A** and **B** each has 1 chiral center and **C** has no chiral center.
1 mole of **A** and **B** each produces 0.5 mole of H_2 gas while 1 mole of **C** produces 1 mole of H_2 gas when excess sodium metal is added.	[✓] Redox (note: not acid-metal reaction)	[✓] **A, B** and C contains -OH group [✓] **A** and **B** each has 1-OH group while **C** has 2-OH groups. (note: when the amount of the substance is given, use it to deduce the no. of functional group present.)
Only **C** gives orange solid with Brady's reagent	[✓] Condensation (Note: not oxidation)	[✓] **C** has a ketone group (note: C is an oxidised product, aldehyde cannot be be present in C.)
B reacts with sodium carbonate to form $C_5H_5O_4Na$ and reacts with hot aqueous NaOH to form $C_5H_6O_5Na_2$.	[✓] Acid-base reaction (note: not acid-carbonate reaction) [✓*] alkaline hydrolysis	[✓] **B** has 1 COOH group (since formula only has 1 Na). [✓^] ester bond in **B**
A decolourises aqueous bromine.	[✓] electrophilic addition	[✓] **A** has a C=C group

2✓: [1] max 6 marks

[✓*] & [✓^] credit once in either reaction.

A is  [1]	**B** is  [1]	**C** is  [1]

Overall max 7 marks

[Total: 20]

5 **(a)** The use of *Data Booklet* is relevant to this question.

When iron is heated with chlorine, $FeCl_3$ is produced. However, when heated with iodine, FeI_2 is produced instead.

(i) Explain why when iron is heated with iodine, FeI_2 is produced but not FeI_3. [2]

$I_2 + 2e^- \rightleftharpoons I^-$ $E^\ominus = +0.54$ V ---(1)

$Fe^{2+} + 2e^- \rightleftharpoons Fe$ $E^\ominus = -0.44$ V ----(2)

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77$ V ---(3)

(1) + (2): $Fe + I_2 \rightarrow FeI_2$

[1] $E^\ominus_{cell} = +0.54 - (-0.44) = +0.98$ V > 0, reaction is spontaneous.

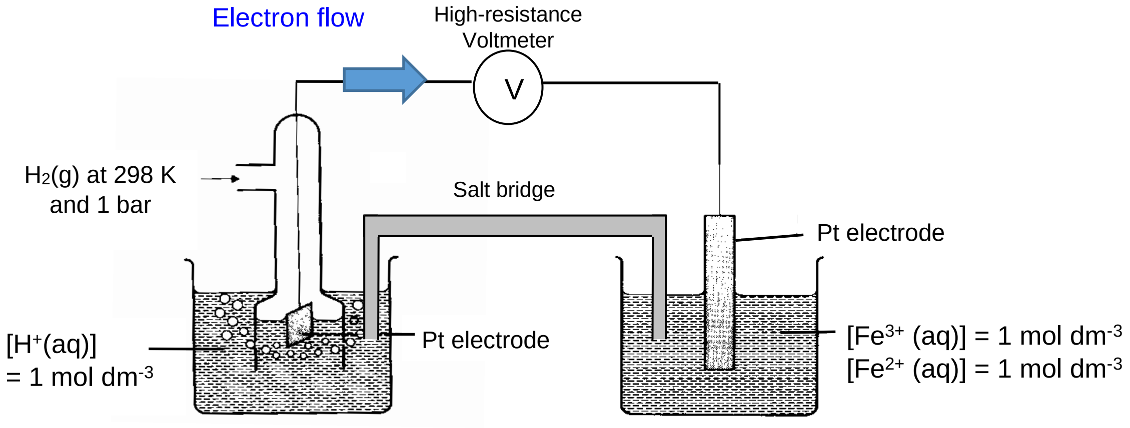
(1) + (3): $FeI_2 + \frac{1}{2} I_2 \rightarrow FeI_3$

[1] $E^\ominus_{cell} = +0.54 - 0.77 = -0.23$ V < 0, reaction is not spontaneous.

Iodine can only oxidise iron to Fe^{2+}, not Fe^{3+}.

Oxidation of Fe to Fe^{2+} by I_2 is a stepwise reaction. The Fe^{2+} formed is unable to oxidise by I_2 to Fe^{3+} by comparing $E^\ominus_{Fe3+/Fe2+} = +0.77$ V and $E^\ominus_{I2+/I=} = +0.54$ V.

(ii) Draw a fully labelled diagram to show how the standard electrode potential of the $Fe^{3+}(aq)/Fe^{2+}(aq)$ system could be measured. Show the direction of electron flow in the circuit. [3]



[1] Fully labelled S.H.E. with respective standard conditions and inert electrode

[1] Fully labelled Fe^{2+}/Fe^{3+}half-cell with respective standard conditions and inert electrode

[1] Direction of electron flow, voltmeter as V, salt bridge

$E^\ominus_{Fe3+/Fe2+} = +0.77$ V & $E^\ominus_{(H+/H2)} = 0$ V

Fe^{3+} is reduced & H_2 is oxidized. Electrons flow from S.H.E to iron compartment.

Inert Pt electrode should be used.

(iii) A few drops of acidified potassium manganate(VII) is added to the $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell. Predict and explain how the cell potential would change.

[2]

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^{\ominus} = +0.77\ V$ ------------- reaction (1)

$$\mathbf{E^{\ominus}_{cell} = E^{\ominus}(Fe^{3+}/Fe^{2+}) - E^{\ominus}(H^{+}/H_2)}$$

$$\mathbf{= +0.77V}$$

When H^{+}/MnO_4^{-} is added dropwise to the Fe^{2+}/Fe^{3+} half-cell, $[Fe^{2+}]$ decreases as Fe^{2+} is oxidised to Fe^{3+}. [✓]

By Le Chatelier's Principle, the position of equilibrium for reaction (1) shifts right to increase $[Fe^{2+}]$. [✓]

Hence E (Fe^{3+}/Fe^{2+}) becomes more positive [✓] and E_{cell} increases. [✓]

This is a redox reaction between $KMnO_4$ & Fe^{2+}. The change in $[Fe^{2+}]$ & $[Fe^{2+}]$ will affect $E(Fe^{3+}/Fe^{2+})$.

$FeCl_3$ is a dark brown solid which dissolves in water to give an acidic solution. This solution is often used, in the electronics industry, to dissolve the copper used in printed circuit boards.

(iv) Explain, with the aid of a chemical equation, why aqueous $FeCl_3$ is acidic.

[2]

[1] Fe^{3+} has a high charge density, which polarises the electron cloud of H_2O. This weakens the O–H bond, hence resulting in the breaking of the O−H bond to release a H^{+}.

[1] $[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^{+}$

(b) Chloroethane can be made by reacting PCl_3 with ethanol, via nucleophilic substitution mechanism.

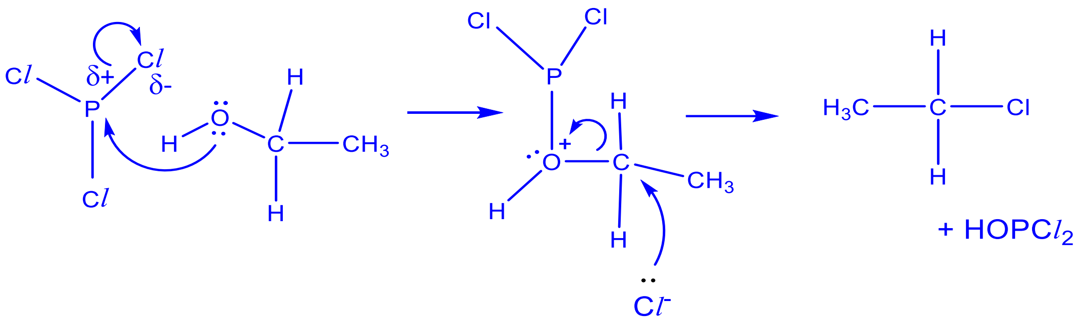
$$PCl_3 + CH_3CH_2OH \rightarrow CH_3CH_2Cl + HOPCl_2$$

(i) The mechanism is thought to involve these steps:

- The first step involves a nucleophilic attack on P by the oxygen atom of ethanol with simultaneous P-C*l* bond cleavage to form a positively charged intermediate.
- The second step involves a nucleophilic attack on a carbon atom by the Cl^{-} ion with simultaneous C-O bond cleavage to form the products.

Use the information given above to suggest a mechanism to show how chloroethane is formed. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs.

[3]



[1] arrows for first step, with lone pair and partial charges

[1] balanced equation and correct structure of intermediate

[1] arrows for second step, with lone pair

Common mistake: equation not balanced and putting + on P instead of oxygen.

(ii) Explain why chlorobenzene cannot be made in the same way using phenol and PCl_3. [1]

[1] The lone pair of electrons on O atom can delocalise into the benzene ring and resulting in strengthening of the C-O bond. Hence the bond does not break easily for nucleophilic substitution to take place.

Common mistake: explain the bond strength of C-Cl instead of C-O.

(c) Compound **X**, $C_9H_{11}NO_2$, rotates plane polarised light and reacts with the following reagents:

- aqueous bromine to give compound **Y**, $C_9H_9NO_2Br_2$
- sodium carbonate to give a salt
- PCl_5 to give a 5-membered cyclic compound **Z**

Compound **X** does not react with neutral $FeCl_3$.

Deduce the structural formulae of compounds **X**, **Y** and **Z**. [7]

- **The C:H ratio in X is almost 1:1 OR X has high C:H ratio ⇒ X contains a benzene ring [✓]**
- **X rotates plane polarised light ⇒ X contains a chiral carbon; has no plane of symmetry and a non-superimposable mirror image [✓]**
- **X undergoes electrophilic substitution with aq Br_2 to give compound Y [✓]**

  ⇒ X is phenylamine [✓]

  ⇒ one of the 2, 4, 6 positions relative to first substituent on benzene is occupied with another substituent [✓]
- **X undergoes acid-base reaction with sodium carbonate to give a salt [✓]**

  ⇒ X contains a –COOH group [✓]
- **X does not react with $FeCl_3$**

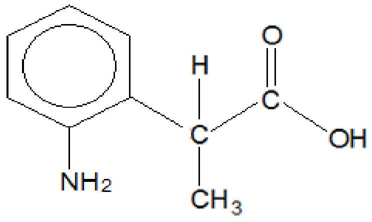
  ⇒ X cannot be phenol[✓]

- **–OH in –COOH undergoes <u>nucleophilic substitution</u> with PC*l*$_5$ [✓] to give –COC*l*, which subsequently undergoes <u>condensation</u> with the –NH$_2$ in phenylamine [✓] to form a 5-membered ring**

  ⇒ –NH$_2$ group & the other substituent on benzene ring are ortho to each other [✓]

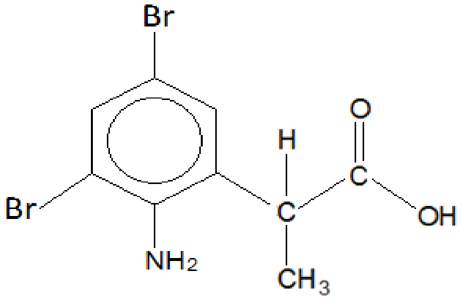
9-11✓ = 4m; 6-8✓ = 3m; 4-5✓ = 2m; 2-3✓ = 1m

X:



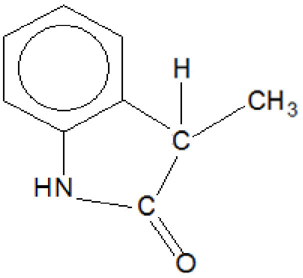
[1]

Y:



[1]

Z:



[1]

Common mistakes: relate reaction with aqueous Br$_2$ to alkene instead of phenylamine and forget to include a chiral carbon in structure X.

Also, reaction between X and Na$_2$CO$_3$ is classified s acid-base reaction and NOT acid-carbonate reaction!

[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.