2008 TJC H2 Prelim P2 Answers

For Examiner's Use

1 (a) For decades, scientists were puzzled by why dinosaurs suddenly became extinct 65 million years ago. In studying core samples of rock dating back to that period, scientists found an unusual high level of iridium. This possibly came from an iridium-rich asteroid that struck the Earth's surface and the mystery to dinosaurs' extinction was solved.

Iridium exists as two naturally occurring isotopes, iridium-191 and iridium-193.

(i) Define the term *relative atomic mass*.

- ***Relative atomic mass*** **is the average mass of one atom of an element on a scale in which one atom of ^{12}C isotope of carbon has a mass of 12 units.**

(ii) The relative atomic mass of iridium is 192.2. Calculate the natural abundance, in percentage, of each isotope.

Let y be the percentage of iridium-191

- **191 x** $\frac{y}{100} + \frac{193 \times (100 - y)}{100}$ **= 192.2**

$$191y + 19300 - 193y = 19220$$

$$y = 40$$

[3]

- **Iridium-191 (40%) ,**
  Iridium-193 (60%)

(b) Aqua regia (a mixture of 75% nitric acid and 25% hydrochloric acid by volume) is highly corrosive. Only noble metals like iridium are inert to this solution. A 5 g sample of platinum-iridium alloy required 24.6 cm^3 of aqua regia for complete reaction. Platinum was completely oxidised to platinum(IV) ions by nitric acid and 0.5 g of metal was recovered.

(i) Find the percentage of each metal in the alloy.

- **Since 0.5 g of iridium metal was recovered,**

Percentage of iridium = $\frac{0.5}{5} \times 100$ **= 10 %**

Percentage of platinum = 90%

(ii) The concentration of nitric acid used to make aqua regia is 5.0 mol dm^{-3}. Assuming that the reaction between the sample and aqua regia is complete, construct the balanced equation for the reaction.

- **No. of moles of platinum = $\frac{5-0.5}{195}$ = 0.0231 mol**

No. of moles of nitrate = $\frac{24.6\times\frac{3}{4}}{1000}\times 5$ = 0.0923 mol

- **(1 mark – working for construction of balanced equation)**

$Pt \equiv 4e^- \equiv Pt^{4+}$

No. of moles of electrons transferred = 0.0231 x 4 = 0.0924 mol

No. of moles of electrons transferred per mole of nitrate
= 0.0924 / 0.0923 = 1

NO_3^- is reduced to NO_2
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$
$Pt \rightarrow Pt^{4+} + 4e^-$

- **$Pt + 4NO_3^- + 8H^+ \rightarrow Pt^{4+} + 4NO_2 + 4H_2O$** [4]

[Total: 7]

For Examiner's Use

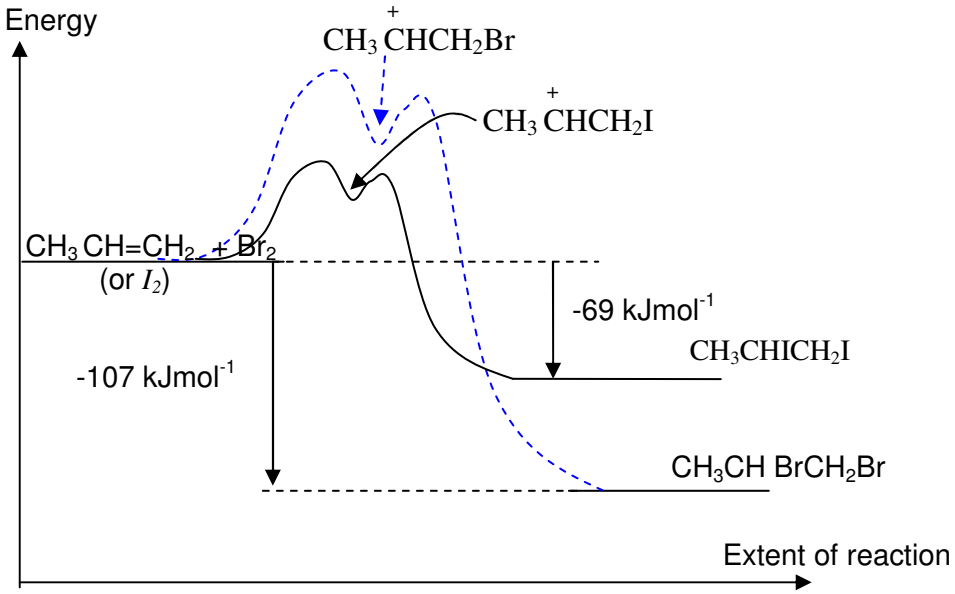
2 Propene readily undergoes electrophilic addition of bromine to give 1,2-dibromopropane.

(a) (i) Calculate the enthalpy change for this reaction

$H_3CCH=CH_2$ + Br-Br → H_3C-CHBrCH_2Br
Bonds broken are C=C and Br-Br, bonds formed are C-C and 2 C-Br

- **ΔH = Bonds broken – Bonds formed**
  = + 610 + 193 – 350 – 2(280)
- **= -107 kJmol^{-1} of propene**

(ii) By referring to the electrophilic addition mechanism, sketch the reaction pathway diagram for this reaction. Label your graph, showing clearly the intermediate formed and the enthalpy change of the reaction.



- **first step is slow step therefore higher E_A than second step and an intermediate is formed**
- **the reaction is exothermic (labels)**

(iii) Bromine adds to propene readily under normal conditions whereas iodine adds only at low temperatures; the 1,2-diiodopropane that results is unstable, decomposing back to propene and iodine at room temperature. The enthalpy change for this addition reaction is – 69 kJ mol^{-1}.

Sketch the reaction pathway diagram for iodine addition on the same diagram above labeling your curve clearly.

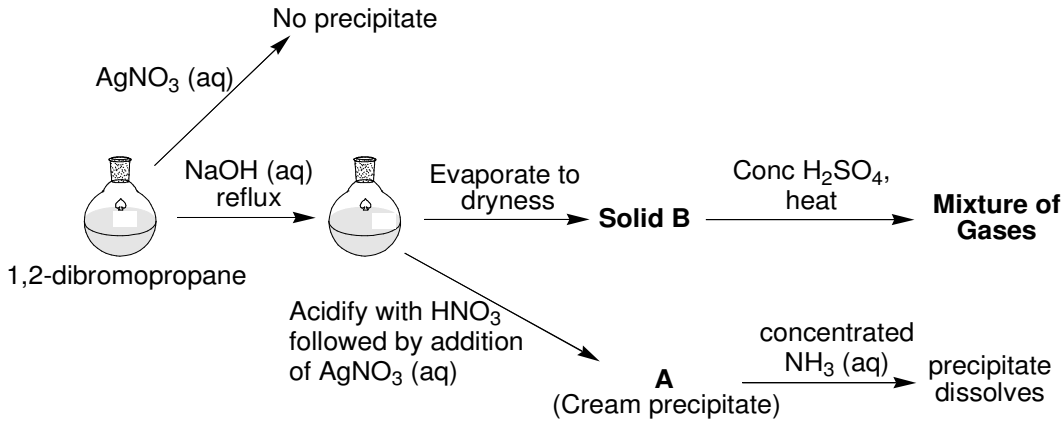
- **1 mark for curve which is less exothermic and show intermediate formed**
  The reaction is reversible thus the addition of iodine should have a lower E_a

[5]

[Turn over

For Examiner's Use

(b) 1,2-dibromopropane formed from electrophilic addition of bromine to propene undergoes a series of reactions as shown in the flow chart below.



(i) Identify the compounds A and B

- **A : AgBr**
- **B : NaBr**

(ii) Explain why no precipitate is formed when aqueous silver nitrate was added to 1,2-dibromopropane while a cream precipitate is formed when 1,2-dibromopropane was first heated with sodium hydroxide then acidified, followed by the addition of aqueous silver nitrate.

- **1,2-dibromopropane undergoes nucleophilic substitution to form 1,2-propandiol giving Br^-. $AgNO_3$ reacts with "free" Br^- to give a cream ppt, AgBr.**

  ($BrCH_2CH(Br)CH_3 + OH^- \rightarrow HOCH_2CH(OH)CH_3 + Br^-$

  $Ag^+ + Br^- \rightarrow AgBr$).

- **No precipitate is formed with unhydrolysed 1,2-dibromopropane as no "free" Br^- is released.**

(iii) Explain why the cream precipitate dissolves upon the addition of concentrated aqueous ammonia.

- **When NH_3(aq) is added, it reacts with the silver ions in solution to from diamminesilver(I) complex ion as shown in equation (1)**

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \quad \text{------ (1)}$$

$$Ag^+(aq) + Br^-(aq) \rightleftharpoons AgBr(s) \quad \text{---------- (2)}$$

- **This lowers the concentration of free silver ion in water causing the ionic product of the silver bromide, $[Ag^+][Br^-]$, to decrease.**
- **By LCP, the position of equilibrium in the equation (2) shifts left. In this instance, the ionic product, [Ag][Br] will decrease to a value lower than the K_{sp} of AgBr and the precipitate of AgBr will dissolve.**

(iv) Write balanced equation(s) of the reaction between solid **B** and concentrated H_2SO_4.

- **$2NaBr + 2H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O + Na_2SO_4$**

OR

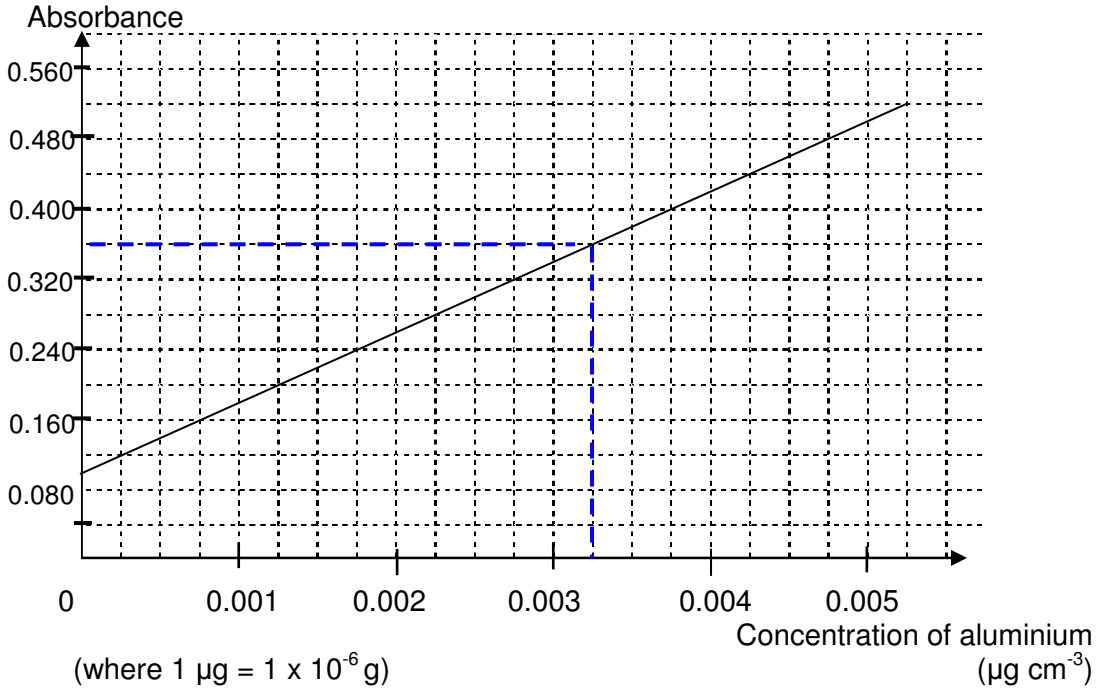
- **$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$**
- **$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$**

[9]

[Total: 14]

For Examiner's Use

3 (a) Trace amounts of elements in a sample can be determined by spectroscopy.In atomic spectroscopy, the concentration of an element in a solution can be determined by its absorbance. The relationship between concentration of aluminium in a solution and its absorbance is given in the graph below.



0.1g of a soil sample was made up to 10 cm^3 of solution for the analysis of the amount of aluminium present.

(i) From the graph, determine the concentration of aluminium in the soil given that it has an absorbance of 0.360.

- **0.00325 μg cm^{-3}**

(ii) Hence, determine the amount of aluminium in the soil in parts per million.

- **Mass of aluminium in 10 cm^3 sample = 0.00325 x 10 = 0.0325 μg**
- **Amount of aluminium in sample = (0.0325 x 10^{-6} / 0.1) x 10^6 = 0.325 ppm** [3]

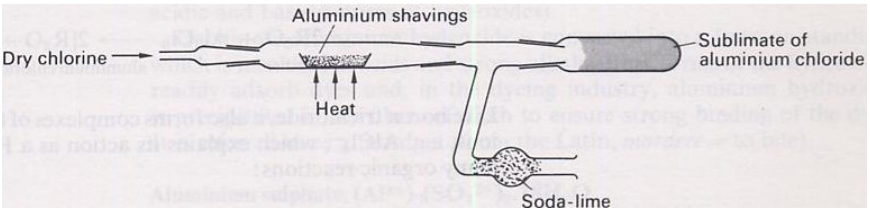
(b) Aluminium is the most abundant metallic element in the earth's crust and is often present in bauxite, as aluminium oxide. Bauxite also contains silica (SiO_2) as an impurity. The aluminium oxide is freed from silica (SiO_2) impurities by using aqueous sodium hydroxide.
Explain, with the aid of relevant equation(s) how the addition of aqueous sodium hydroxide separates aluminium oxide from silica.

- **Al_2O_3 is amphoteric and reacts with sodium hydroxide (soluble in NaOH).**
- **$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH_4)^-$**
- **Silica does not dissolve in NaOH hence it can be removed from Al_2O_3.** [3]

[Turn over

For Examiner's Use

(c) Aluminium chloride can be made by passing hydrogen chloride or chlorine over heated aluminium. This must be prepared under anhydrous conditions using soda lime to keep out moisture as well as to absorb excess chlorine.



(i) Suggest why the preparation of aluminium chloride must be done under anhydrous conditions.

- **Aluminium chloride readily dissolves in the presence of water to give hydrated aluminium ions and chloride ions.**
  ($AlCl_3 + 6H_2O \rightarrow Al(H_2O)_6^{3+} + 3Cl^-$)

(ii) At 200°C, aluminium oxide exist as a solid while aluminium chloride exist as a gas. Explain the observation in terms of structure and bonding.

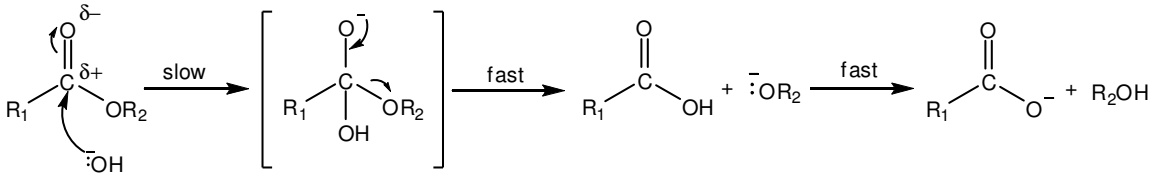
- **Al_2O_3 has giant ionic structure while $AlCl_3$ has a simple molecular structure.**
- **More energy is required to break the stronger ionic bonds in Al_2O_3 than the weaker van der Waals forces of attraction between $AlCl_3$ molecules. Hence Al_2O_3 has a higher melting point than $AlCl_3$. Thus, Al_2O_3 exist as a solid while $AlCl_3$ exist as a gas at 200 °C.**

[3]

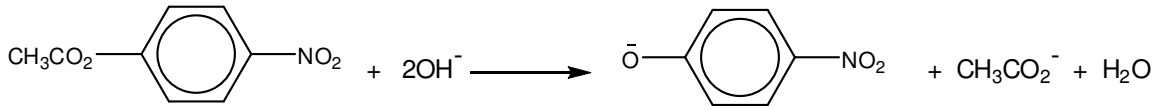
[Total: 9]

For Examiner's Use

4 In general, esters undergo alkaline hydrolysis by the following mechanism.



The ester 4-nitrophenyl ethanoate hydrolyses in alkaline solution according to the following equation.



4-nitrophenyl ethanoate

4-nitrophenoxide

To study the kinetics of this reaction, 0.001 mol dm^{-3} of ester was reacted with an excess of 0.2 mol dm^{-3} sodium hydroxide. The initial rate was found to be 3.6 x 10^{-5} mol dm^{-3} min^{-1}.

(a) (i) Determine the rate constant, stating its units. Show clearly how you arrive at the answer.

- **Since one molecule of ester reacts with one molecule of hydroxide in the rate-determining step, order of reaction w.r.t hydroxide and ester is 1 respectively.**

  rate = k[ester][hydroxide]
- **k = (3.6 x 10^{-5}) / (0.001 x 0.2) = 0.18 mol^{-1} dm^3 min^{-1}**

(ii) Calculate the time taken for the concentration of 4-nitrophenoxide to increase to 0.0005 mol dm^{-3}.

The time taken for concentration of 4-nitrophenoxide to increase to 0.0005 mol dm^{-3} equal time taken for the concentration of ester to be halved

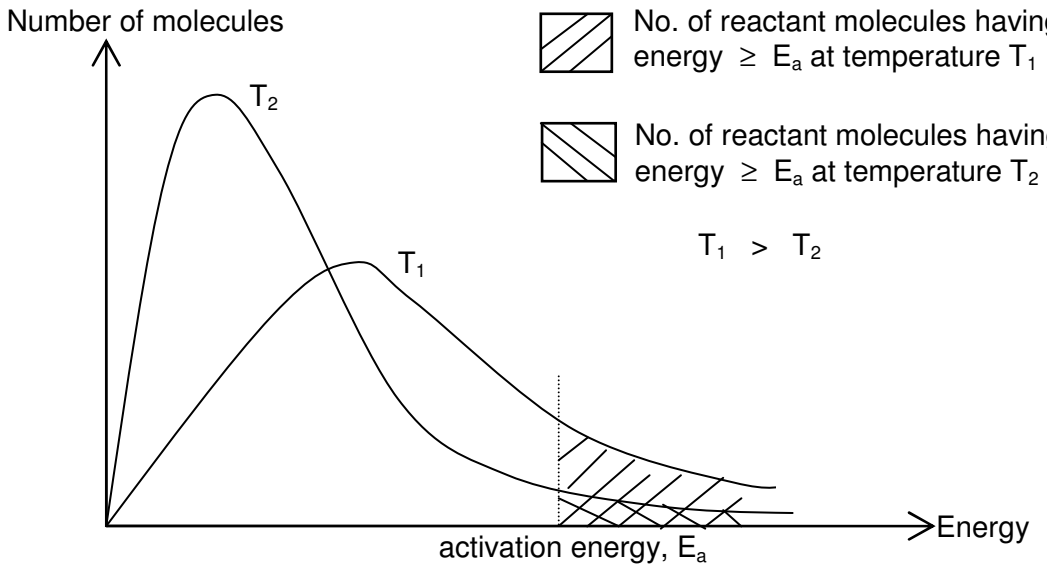
rate = k[ester][hydroxide]

- **rate = k'[ester], where k' = k[hydroxide] since hydroxide is used in large excess**
- **k' = 0.18 x 0.2 = 0.036 min^{-1}**
- **$t_{½}$ = (ln 2)/ 0.036 = 19.3 min**

[5]

(b) With the aid of an appropriate labelled diagram, explain how a decrease in temperature affects the rate of hydrolysis.

- **A decrease in temperature decreases the average kinetic energy of the reacting molecules, resulting in a decrease in the frequency of collision between the molecules. The fraction of molecules having energy ≥ activation energy, E_a (which is the minimum energy required for reaction to occur), is significantly decreased.**
- **Hence, this decreases the frequency of effective collisions leading to a decrease in reaction rate.**

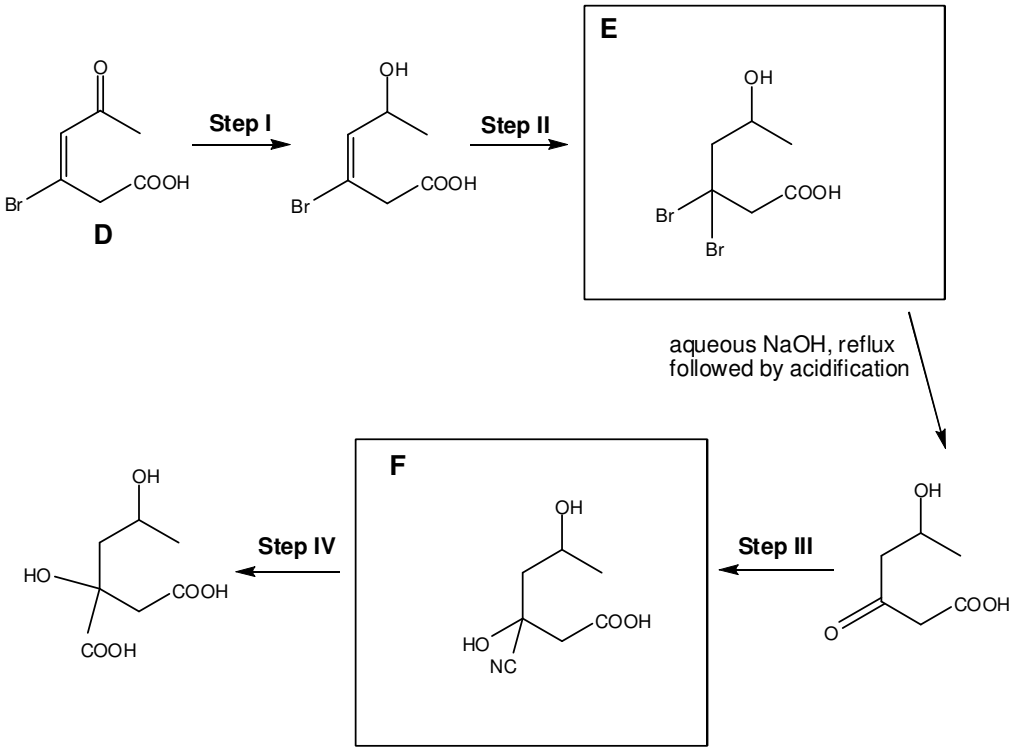


[3]

[Total: 8]

5 (a) (i) For the reaction scheme below, give the reagents and conditions for steps **I** to **IV** in the spaces provided, and draw the structures of the organic compounds **E** & **F** in the boxes provided.

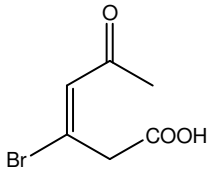
For Examiner's Use



Step	Reagents and conditions
I	$NaBH_4$ in alcohol, room temperature / Zn in dilute HC*l*
II	HBr(g), room temperature
III	NaCN in dilute H_2SO_4, 10-20°C
IV	dilute HC*l*, reflux

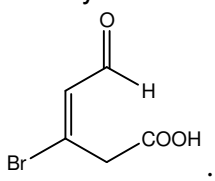
For Examiner's Use

(ii) Describe one simple chemical test you could carry out to distinguish



D

from



G

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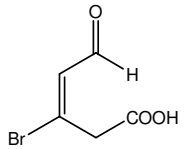
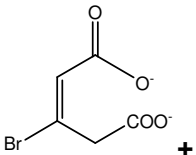
State clearly how **each** compound behaves in the test and write an equation for the reaction involved.

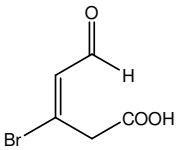
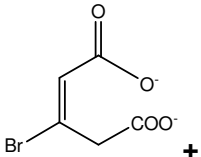
Reagent(s) & conditions:
- **Tollen's reagent, heat**

Observations:
- **Silver mirror formed for G but not D**

Equation :
- **$2Ag(NH_3)_2^+$ +**  **+ $4OH^-$ → 2Ag +**  **+ $4NH_3$ + $3H_2O$**

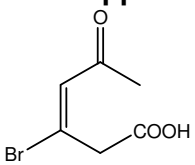
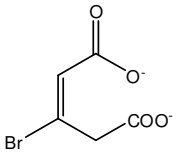
OR Reagent(s) & conditions:
- **Fehling's solution, heat**

Observations:
- **Reddish brown ppt formed with G but not with D**

Equation :
- **$2\ Cu^{2+}$ +**  **+ $6OH^-$ → Cu_2O +**  **+ $4H_2O$**

OR Reagent(s) & conditions:
- **aqueous alkaline iodine, heat**

Observations:
- **Yellow ppt formed for D but not with G**

Equation :
-  **+ $3\ I_2$ + $5OH^-$ → CHI_3 + $3I^-$ + $4H_2O$ +** 

(b) Most organic reactions occur in either an aqueous medium or an organic solvent. Tetrachloromethane (CCl_4) was a commonly used organic solvent.

Explain the difference in the reaction of CCl_4 and $SiCl_4$ with water respectively. Write equations for any reactions that occur.

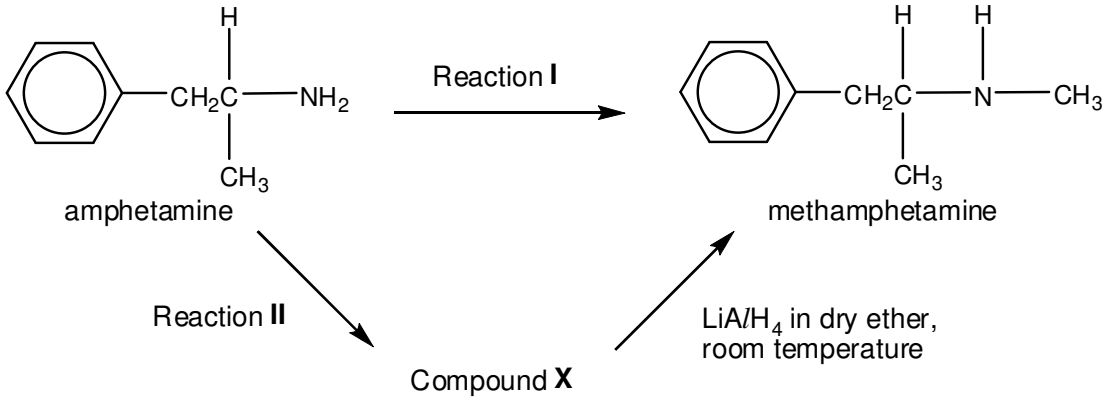
- **CCl_4 does not react with water as C which is in Period 2 cannot expand its octet configuration due to a lack of energetically accessible vacant d orbitals.**
- **$SiCl_4$ is hydrolysed by water because of the availability of energetically accessible vacant d orbitals in Si for dative bonding with water.**
- **$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$**

[3]

[Total: 9]

For Examiner's Use

6 Methamphetamine, commonly known as 'Ice', is a strong stimulant which is odourless and colourless. It usually comes in crystallized form known as methamphetamine hydrochloride. The reaction scheme below illustrated two possible pathways to synthesize methamphetamine from amphetamine.

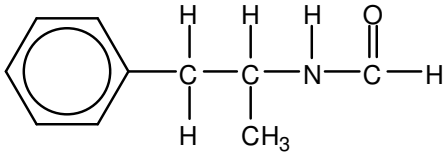


(a) (i) For each reaction, give the reagent(s) and conditions.

Reaction **I**: **CH_3Br in ethanolic solution, heat**

Reaction **II**: **HCOC*l*, cold**

(ii) What is the structural formula of the compound **X** formed in Reaction **II**?



(iii) Explain why Reaction **I** is not a good method to synthesize methamphetamine.

A mixture of amines arises because methamphetamine is a better nucleophile than amphetamine thus it will undergo further alkylation to give a tertiary amine.

[4]

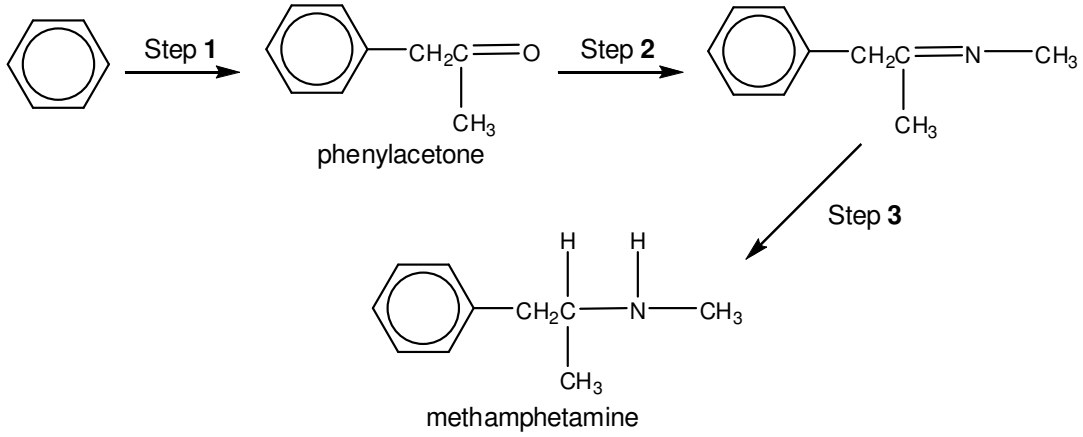
(b) Arrange methamphetamine, amphetamine and phenylamine in order of increasing basicity. Give reasons for your answer.

- **phenylamine < amphetamine < methamphetamine**
- **Phenylamine is the weakest base because the lone pair of electron from the N atom is delocalised into the benzene ring, thus making it less available for bonding to a proton.**
- **Methamphetamine is a stronger base than amphetamine because it has one more alkyl group attached to the N atom. The electron releasing effect of the alkyl group increases the electron density on the N atom hence makes the lone pair more available for bonding to a proton.**

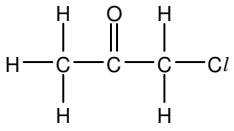
[3]

(c) Illegal production of methamphetamine involves the following process.

For Examiner's Use



(i) Give the reagent(s) and condition(s) required in Step **1**.



in the presence of anhydrous $AlCl_3$, room temperature

(ii) Phenylacetone reacts with 2,4-dinitrophenylhydrazine in a condensation reaction to give an orange precipitate. In Step **2**, phenylacetone will react in a similar manner. Give the structural formula of the reagent used.

CH_3NH_2

(iii) Name the type of reaction in Step **3**.

Reduction

[3]

[Total: 10]