NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

12 September 2011

2 hours

Students answer on separate paper.

Additional Materials: Answer Paper
Graph Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together.

Answer any **four** questions.

1 This question is about the reactions of compounds containing the cyanide group.

(a) Cyanogen, $(CN)_2$ is called a pseudohalogen because several of its reactions are similar to those shown by halogens Cl_2, Br_2 and I_2. For example, it can be reduced to hydrogen cyanide, which is a weak acid.

$$\tfrac{1}{2}\,(CN)_2 + H^+ + e \rightleftharpoons HCN \qquad E^{\ominus} = +0.37\ V$$

(i) By analogy with the reactions of halogens or halides ions and by making use of the above data and information in the Data Booklet, predict the reactions, if any, that might occur when the following reagents are mixed.

I. $Cl_2 + HCN$
II. $Na_2S_2O_3 + (CN)_2$
III. $K_2Cr_2O_7 + (CN)_2$

(ii) Draw a dot-and-cross diagram of the cyanogen molecule, suggesting its shape.

[8]

(b) **(i)** When chiral 2-chloroheptane, $C_7H_{15}Cl$ reacts with ethanolic sodium cyanide, the optical isomerism of the product is reversed.

Explain, with the aid of structural formula, why the optical isomerism is reversed.

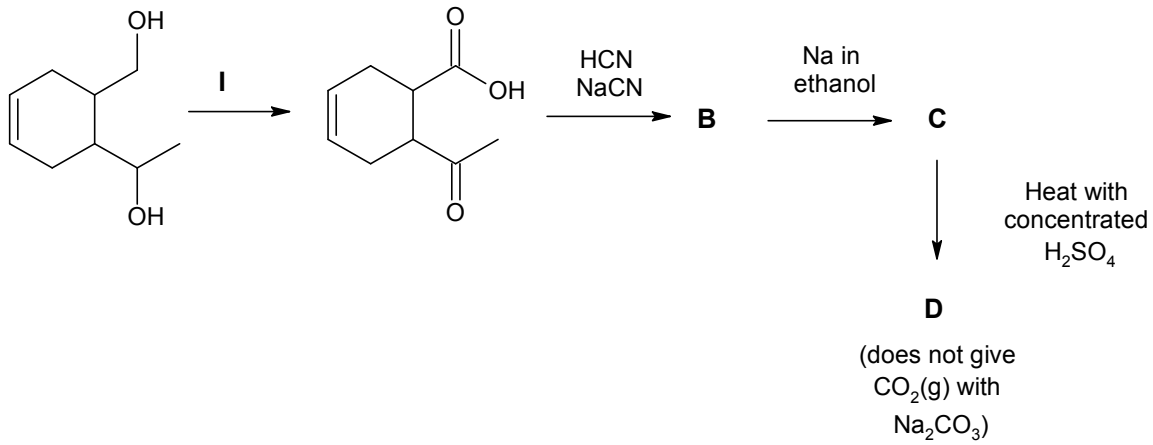
(ii) Another compound **A** with the same molecular formula $C_7H_{15}Cl$ also reacts with ethanolic sodium cyanide. **A**, which is optically active, eventually loses its optical activity after reaction with ethanolic sodium cyanide.

Give the structural formula of **A** and describe the mechanism of its reaction with ethanolic sodium cyanide.

(iii) Predict which reaction **b(i)** or **b(ii)** will proceed at a faster rate when the concentration of ethanolic sodium cyanide is increased. Explain your answer.

[8]

(c) Suggest the reagents and conditions required for stage **I** and the structural formula for **B**, **C** and **D** for the following scheme.

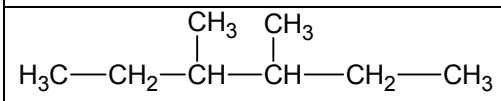


[4]

[Total: 20]

2(a) The term "octane rating" is often used in the petroleum industry for rating the ability of octane's various branched isomers in reducing engine knock in vehicles. Compounds **A**, **B**, **C** and **D** are isomers of the hydrocarbon octane, C_8H_{18}.

The table below shows the boiling points and data relating to the optical activity of the compounds.

Structure	Boiling Points / ^oC	Number of chiral centres	Optical Activity?
Isomer A	119	1	Yes
 **Isomer B**	118	2	No
Isomer C	110	1	Yes
Isomer D	107	0	No

(i) Suggest why Isomer **B** has no optical activity even though it has 2 chiral centres.

(ii) Draw the structural formula of each of the compounds **A**, **C** and **D**.

(iii) Explain in terms of structure and bonding, why isomers **A** to **D** have different boiling points.

(iv) Controlled chlorination of Isomer **B** in the presence of UV light produces 4 different isomers of formula $C_8H_{17}Cl$. Draw the structural formula of each of the 4 isomers and give the mole ratio in which they are formed.

(v) Monochlorination of Isomer **B** in part **(iv)** produces many by-products, one of which has the formula $C_{16}H_{34}$. Assuming that the carbon atoms in Isomer **B** do not rearrange themselves during the reaction, draw the structural formula of the isomer of $C_{16}H_{34}$ that has the lowest boiling point.

[11]

(b) Studies have shown that drinking water that contains high levels of dissolved barium compounds results in health effects such as difficulties in breathing, changes in heart rhythm, stomach irritation and even brain swelling. The Environmental Protection Agency has decreed that a concentration of more than 1.45×10^{-5} moldm^{-3} of barium in drinking water is considered harmful to humans.

A sample of water was obtained from a lake that is located near a paint manufacturing plant where barium sulfate which is the main component for white paint is discharged into the lake. The water sample obtained is also saturated with other compounds such as lead(II) hydroxide and lead(II) sulfate. The lake water has a pH of 7.4.

Calculate the concentration of Ba^{2+} in the lake water which is saturated with lead(II) sulfate, lead(II) hydroxide and barium sulfate and conclude whether the Ba^{2+} concentration lies within the safety limits.

[K_{sp} of $Pb(OH)_2 = 1.43 \times 10^{-20}$ mol^{3}dm^{-9}; K_{sp} of $PbSO_4 = 2.53 \times 10^{-8}$ mol^{2}dm^{-6}; K_{sp} of $BaSO_4 = 1.08 \times 10^{-10}$ mol^{2}dm^{-6}]

[3]

(c) The following statements involve the chemistry of Group I elements.

(i) "Lithium is only slowly attacked by water at 25^{o}C, whereas, with water, sodium reacts vigorously, potassium inflames, and rubidium and caesium reacts explosively". Explain the difference in reactivity of the Group I metals with water.

(ii) "Lithium and sodium metals are obtained by electrolysis of their molten salts. However this method is not suitable for obtaining potassium, rubidium and caesium". Explain this observation in terms of the structure and bonding of the different metals.

(iii) Lithium is the only Group I metal which produces the oxide, Li_2O, when heated in oxygen whereas sodium, potassium, and the other Group I metals produces peroxides as in Na_2O_2 and the superoxides such as KO_2 when heated in oxygen. Explain the difference in products formed.

[6]

[Total 20]

3 Bad news always seems to get more attention than good news. Newspaper headlines dwell on atmospheric pollutants, not the components of the atmosphere that are essential to life.

One of the major pollutants from the internal combustion engine of cars are the oxides of nitrogen. Many are highly toxic, contribute to acid rain and react with other compounds to form even more toxic pollutants. Consider the following questions on some of the oxides of nitrogen.

(a) The chemistry of nitrogen oxides is very versatile.

Given the following reactions and their standard enthalpy changes:

		ΔH_{rxn} / kJ
(1)	$NO(g) + NO_2(g) \rightarrow N_2O_3(g)$	– 39.8
(2)	$NO(g) + NO_2(g) + O_2(g) \rightarrow N_2O_5(g)$	–112.5
(3)	$2NO_2(g) \rightarrow N_2O_4(g)$	– 57.2
(4)	$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	– 114.2
(5)	$N_2O_5(g) \rightarrow N_2O_5(s)$	– 54.1

Calculate by means of an energy cycle or otherwise, the heat of reaction for

$$N_2O_3(g) + N_2O_5(s) \rightarrow 2N_2O_4(g)$$

[5]

(b) The decomposition of gaseous dinitrogen pentoxide is represented by

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The data for the decomposition of gaseous dinitrogen pentoxide at 333 K are shown below.

Pressure of $N_2O_5(g)$ remaining / Pa	**Rate of reaction / Pa s^{-1}**
1200	1.04
1000	0.88
800	0.69
400	0.34

(i) Plot these data on graph paper and determine the order of the reaction with respect to dinitrogen pentoxide.

(ii) Calculate the value of the rate constant at 333K, giving the appropriate unit.

(iii) Propose a mechanism for the decomposition in view of your results in **(i)**.

[6]

(c) The discovery of the Periodic Table was an essential requirement of the amazing growth in theoretical and practical chemistry in the 19th century. Today's version has the elements arranged in order of atomic number rather than atomic mass.

Write the formula of the compound formed from the following ionic interactions:

(i) The ions form from the largest and smallest ionizable atoms in Period 2.

(ii) The 2+ ion and the 2− ion are both isoelectronic with the Period 3 noble gas.

(iii) The 2+ ion is the smallest with a filled d subshell; the anion forms from the smallest halogen.

(iv) The 2+ ion and the 1− ion are both isoelectronic with the atoms of a chemically unreactive Period 4 element.

[2]

(d) **A** is a compound of a Group II element **M**. When **A** was treated with dilute hydrochloric acid, a colourless gas, **B** was evolved, which turned moist litmus paper red.
On bubbling **B** through lime water, a precipitate, **C** was formed, but passage of further gas resulted in a clear solution, **D**.
On strong heating, 1.9735 g of **A** decomposed, giving 1.5334 g of **E** its oxide, a white solid.
The sample of **E** was dissolved in water and made up to 250 cm^3 in a standard flask. 25.0 cm^3 aliquots were titrated with acid and required 20.30 cm^3 of 0.0985 mol dm^{-3} hydrochloric acid.

(i) Identify the compounds **B, C and D**.

(ii) Calculate the relative molecular mass of **A**.

(iii) Consider the identity of **A** and calculate the relative atomic mass of the Group II element **M** in **A**. Hence identify **M**.

[7]

[Total: 20]

4 The halogens refer to the series of nonmetallic elements in Group VII of the Periodic Table. Owning to their high reactivity, they are commonly found in the environment as part of organic or inorganic compounds. This question looks at the chemistry of halogen compounds.

(a) The halogens all form binary compounds with hydrogen known as hydrogen halides. State and explain how the thermal stability of hydrogen halides varies down the Group.

[2]

(b) Glass etching refers to the technique of creating art on glass surface. Out of all the hydrogen halides, only hydrogen fluoride can be used to etch glass. The following reaction takes place during the etching process:

$$4HF + SiO_2\ (glass) \rightarrow SiF_4 + 2H_2O$$

Suggest a reason why only hydrogen fluoride can be used to etch glass.

[1]

(c) Two unknown gases **X** and **Y** could be hydrogen fluoride or hydrogen chloride. In an experiment conducted at 1 atmospheric pressure, the volumes of separate samples containing equal amounts of gas **X** and **Y** were measured at different temperatures and the results are tabulated below.

Experiment No.	**T / K**	**Gas X**	**Gas Y**
		V / dm^3	**V / dm^3**
1	200	20 000	16 500
2	300	22 500	20 000
3	600	24 000	23 500

(i) Sketch and explain the expected variations of V/T with T for a given amount of an ideal gas at constant pressure.

(ii) Identify gas **X** and **Y**. Explain your reasoning.

[4]

(d) Interhalogen compounds are formed between different Group VII elements. The properties of interhalogen compounds tend to be intermediate between those of its parent halogens. The following properties, however, are found in neither parent halogens.

(i) Cl_2 and I_2 are soluble in non-polar solvent but ICl is insoluble. Explain why ICl is insoluble in non-polar solvent.

(ii) Cl_2 and I_2 exists as discrete molecules but ICl_3 dimerizes. Suggest a dot-cross diagram for the dimer, given that it exists as a planar molecule.

(iii) Br_2 and F_2 are non-conductors of electricity but BrF_3 is a good electrical conductor in the molten state. With the aid of an equation, suggest a possible reason why BrF_3 can conduct electricity.

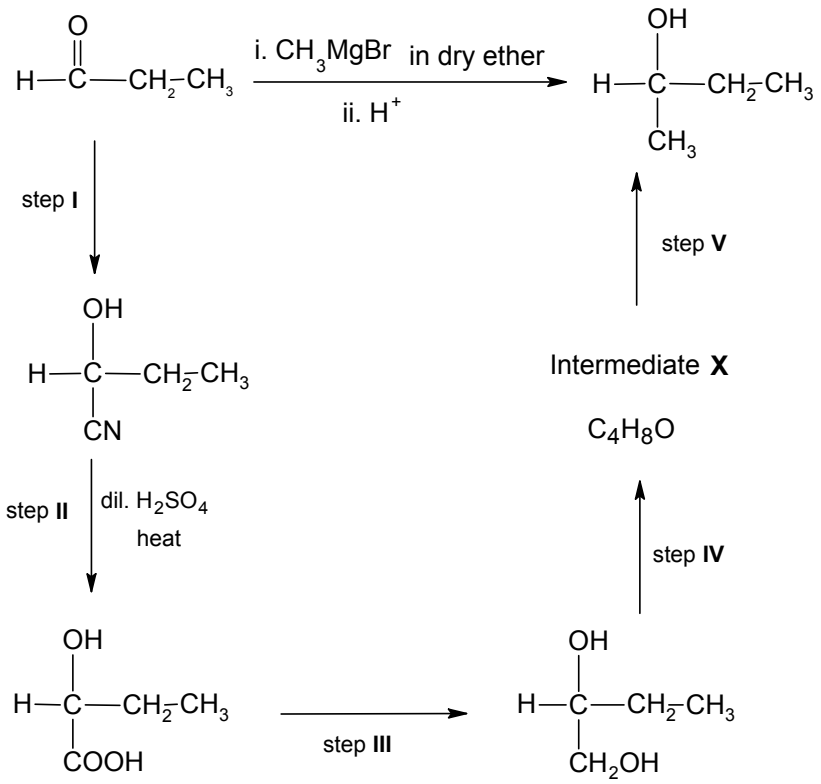
[3]

(e) Halogens are found in the Grignard reagent, RMgX, an important reagent in organic synthesis. Grignard reagents are prepared by the addition of activated magnesium on an alkyl halide in non-polar solvents such as diethyl ether Et_2O or Tetrahydrofuran, THF in anhydrous conditions.

$$RBr + Mg \xrightarrow[Et_2O \text{ or THF}]{\text{anhydrous}} RMgBr$$

The Grignard reagent is a useful organometallic reagent as it provides a convenient source of alkyl nucleophile (R^-) that can attack an electron deficient carbon in organic functional groups such as carbonyls and esters. This allows chemists to extend a carbon chain by almost any carbon length desired in a single-step synthesis.

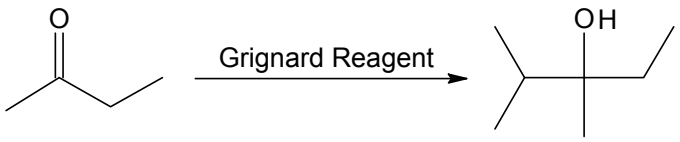
The synthetic scheme on the next page compares the addition of a methyl group to propanal via a 1-step Grignard synthesis and the alternative 5-step synthesis before Grignard reagents were introduced.



(i) Suggest the identity of the intermediate **X** and the reagents and conditions needed for steps **I** and **III**.

(ii) Apart from the multiple steps involved, the alternative synthesis is not favoured because of low yield. Identify the step which accounted for the low yield and state the total number of possible isomeric products.

(iii) Suggest the Grignard reagent required for the following conversion.



(iv) An unknown compound **X** $C_6H_{12}O$ was synthesized from an aldehyde and Grignard reagent CH_3MgBr. 1 mole of **X** evolves 0.5 mole of H_2 upon reaction with Na. 1 mole of **X** also produces 1 mole of CHI_3 precipitate upon warming with alkaline aqueous iodine. **X** reacts with hot, acidified $KMnO_4$ to form **Y** and **Z**. 1 mole of **Y** evolves 0.5 mole of H_2 upon reaction with Na. 1 mole of **Z** produces 2 moles of CHI_3 precipitate upon warming with alkaline aqueous iodine.

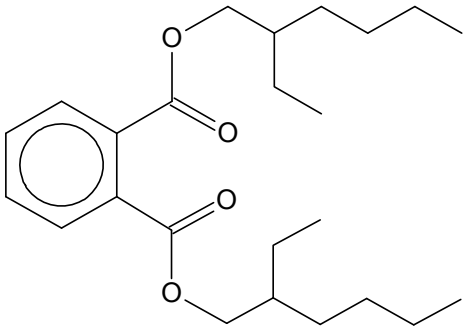
Deduce the structural formulae of **X, Y** and **Z**, explaining your reasoning.

[10]

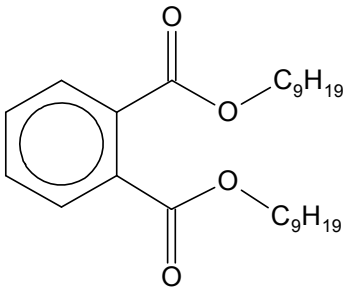
[Total: 20]

5(a) Plasticisers are additives that increase the fluidity of the material to which they are added and they are most commonly used in the manufacture of plastics. In May 2011, the illegal use of the plasticiser DEHP in food and beverages was reported in Taiwan. As more products were tested, inspectors found extensive use DEHP and DINP. This incident caused shock and panic among the citizens and had attracted international attention.

The structures of DEHP and DINP are given below.



2-ethylhexyl phthalate
DEHP



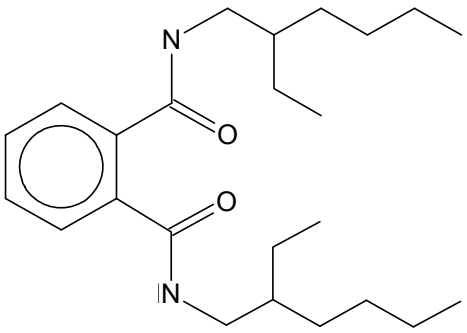
Diisononyl phthalate
DINP

(i) Name the functional group, other than phenyl, which is common to both DEHP and DINP.

(ii) Copy the structure of DEHP onto your writing paper, label clearly (with an *) the chiral carbon(s) in the structure and determine the total number of π electrons that are present in one molecule of DEHP.

(iii) Suggest a three–step reaction sequence to convert 1,2–dimethylbenzene to DEHP, giving structural formulae of the intermediates involved. State the reagents and conditions used in each step.

(iv) Compound **A** has a similar structure to DEHP.

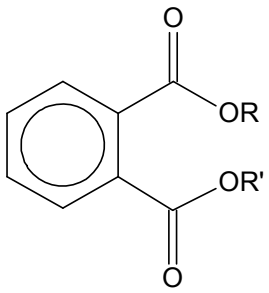


Compound A

Suggest one chemical test to distinguish between DEHP and Compound **A**.

[8]

(b) Both DEHP and DINP belong to the class of organic compounds called phthalates which are easily released into the environment when plastics break down. This release of phthalates is accelerated at higher air temperature.

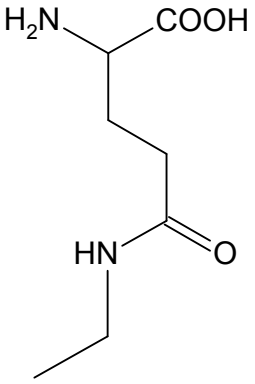


Phthalates

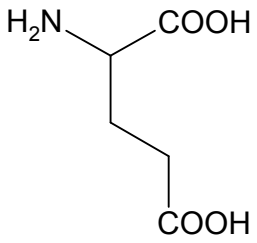
Use the concept of activation energy, together with an appropriate sketch of the Boltzmann distribution, to explain why the increase in air temperature accelerates the release of phthalates.

[3]

(c) In Singapore, the Agri–Food and Veterinary Authority (AVA) has suspended the import of "Jin Guo Wan" brand of fruit juice concentrates from Taiwan, which are used as ingredients for Bubble Tea. Theanine is an amino acid found in tea that produces a calming effect on the brain. There are about 20 different types of amino acids in tea. More than 60% of these amino acids consist of theanine, which is unique to green tea because the steaming process does not eliminate it. Theanine has a similar structure to glutamine providing an elegant taste and sweetness in green tea.



theanine



glutamine

(i) Draw the zwitterionic structure of theanine and suggest one reason why the steaming process does not eliminate the theanine in green tea.

(ii) Amino acids can act as buffers in solutions. By means of equations, show how glutamine can act a buffer when dilute hydrochloric acid and dilute sodium hydroxide is added separately into its solution.

(iii) Construct a displayed formula of a dipeptide formed from theanine and glutamine. Hence, calculate the M_r of the dipeptide formed.

(iv) Briefly describe the type of R–group interactions that give rise to the tertiary structure in proteins. Illustrate your answer using theanine and glutamine.

[9]

[Total: 20]

BLANK PAGE