IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2016, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

1A PAPER TWO

Tuesday 12th January 2016, 14:00-16:15

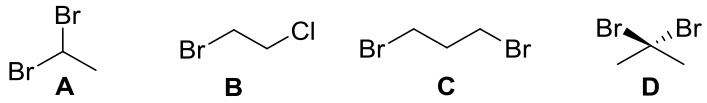
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

1.I9 – Spectroscopy and Characterisation

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Sketch the ^{1}H NMR spectra of the molecules **A**-**D**. Pay attention to the peaks' chemical shifts, integration values and multiplicities.

[Assume that: ^{1}H, I=½, 100% abundant; all other nuclei are NMR silent; where relevant, coupling occurs through 3 bonds or fewer]



(15 marks)

b) Answer **ALL** parts of this question.

i) Three gases (**E**-**G**) were analysed using IR spectroscopy. The table shows the measured IR absorptions.

Vibrational Mode	**E**	**F**	**G**
Symmetric stretch	Not observed	Not observed	859 cm^{-1}
Asymmetric Stretch	1533 cm^{-1}	2349 cm^{-1}	2062 cm^{-1}
Bend	397 cm^{-1}	667 cm^{-1}	527 cm^{-1}

Compounds **E**-**G** are samples of CO_2, CS_2 and COS (not necessarily in the order given). Rationalize which sample corresponds to **E**-**G** and include explanations for the number and frequencies for the observed vibrations.

(6 marks)

ii) Fluoroacetylene (FCCH) shows an absorption in its IR spectrum at 3335 cm^{-1} which is assigned to a C-H bond vibration. Calculate the analogous absorption wavenumber, in cm^{-1}, for FCCD. State clearly any assumptions you make.

[D = ^{2}H]

(4 marks)

c) Compound **H** shows strong absorptions in the IR spectrum, in the regions 3300-2800, 1711 and 1239 cm^{-1}. Its ^{1}H NMR spectrum shows a septet at 2.59 ppm, with a relative integral of 1, and a doublet at 1.20 ppm, with a relative integral of 6. The mass spectrum shows a molecular ion at *m/z* 88 and fragmentation peaks at *m/z* 73, 71 and 43 amu.

Identify compound **H**. Your answer should include a full assignment of all the spectroscopic data and a sketch of the structure of molecule **H**.

(10 marks)

1.O1 – Structure, Mechanism and Reactivity

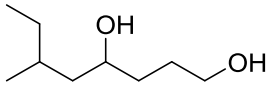
NB. 'Half a question' (out of 12.5 marks).

This is a multiple choice question. A correct answer will be given full marks. An incorrect answer will be given zero. Please only mark *one* answer per question.

Answer **ALL** of the following:

1) What is the systematic name for the compound with structure **1**?

(2 marks)



1

A) 6-Methyl-1,4-octanediol

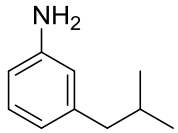
B) 6-Ethyl-4-hydroxyheptanol

C) 3-Methyl-5,8-octanediol

D) 6-Ethyl-1,4-heptanediol

2) Which of the following represents a reasonable name for compound **2**?

(2 marks)



2

A) *meta*-*iso*-Butylaniline

B) 3-*sec*-Butylaniline

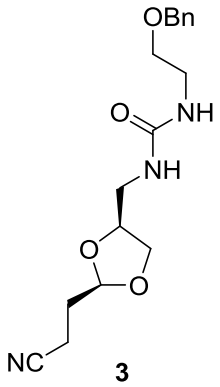
C) 3-*iso*-Butylphenol

D) *meta*-*sec*-Butylphenol

QUESTION CONTINUED OVERLEAF

3) Which of the following sets of functional groups is present, amongst others, in compound **3**?

(2 marks)



3

A) Amide, acetal, nitrile

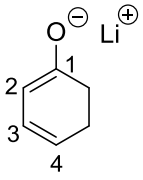
B) Urea, ester, nitro group

C) Nitrile, urea, acetal

D) Amine, ether, acetal

4) Which statement is correct with regards to the predominant reactivity of compound **4**?

(3 marks)



4

A) Compound **4** is likely to act as a nucleophile. The oxygen atom and the carbons labelled 1 and 2 are the only nucleophilic centres.

B) Compound **4** is likely to act as an electrophile, because of the presence of the lithium cation.

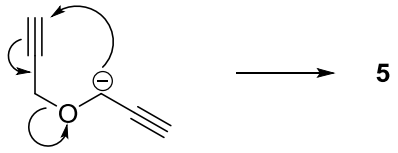
C) Compound **4** is likely to act as a nucleophile. The oxygen atom is the only nucleophilic centre.

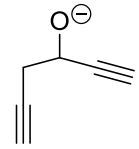
D) Compound **4** is likely to act as a nucleophile. The oxygen atom and the carbons labelled 2 and 4 are nucleophilic centres.

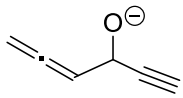
QUESTION CONTINUED OVERLEAF

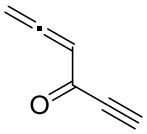
5) Which of the following structures correctly represents the product **5** from the reaction mechanism drawn below?

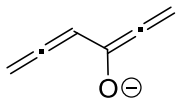
(3.5 marks)



A) 

B) 

C) 

D) 

1.O6 – Stereochemistry

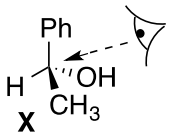
NB. 'Half a question' (out of 12.5 marks).

This is a multiple choice question. A correct answer will be given full marks. An incorrect answer will be given zero. Please only mark *one* answer per question.

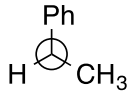
Answer **ALL** of the following:

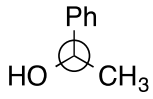
1) Based on diagram **X**, which is the correct projection?

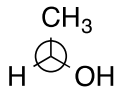
(2 marks)

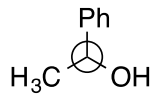


X

A) 

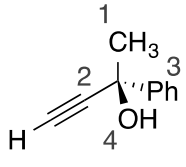
B) 

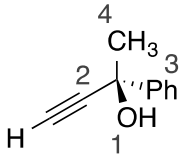
C) 

D) 

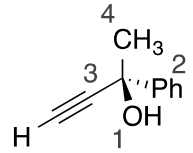
2) For which one of the molecules below has the correct order of priority been assigned?

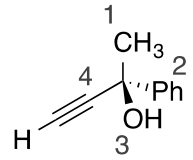
(2 marks)

A) 

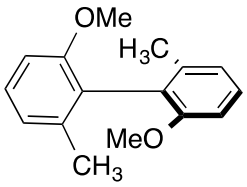
B) 

QUESTION CONTINUED OVERLEAF

C) 

D) 

3) What is the correct stereochemical assignment of the molecule below? (3.5 marks)



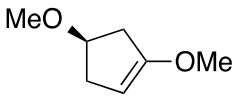
A) *meso*

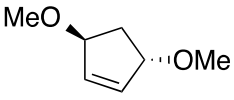
B) achiral

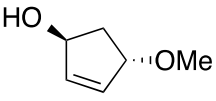
C) *S*

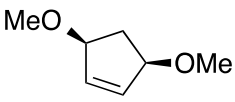
D) *R*

4) Which of the following molecules is chiral and dissymmetric? (2.5 marks)

A) 

B) 

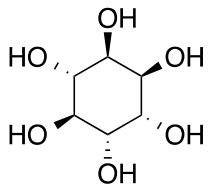
C) 

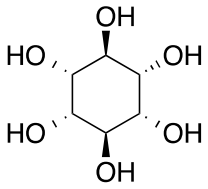
D) 

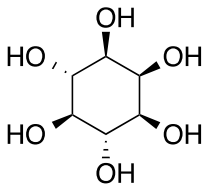
QUESTION CONTINUED OVERLEAF

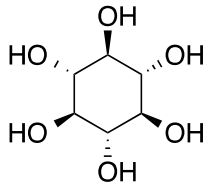
5) Which of the following molecules is chiral?

(2.5 marks)

A) 

B) 

C) 

D) 

1.P5 – Thermodynamics 1: Chemical Equilibria

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Answer **ALL** parts of this question.

i) Explain why the uniform mixing of two ideal gases in a sealed container is a spontaneous process. State all assumptions made.

(4 marks)

ii) Explain what is meant by a closed system. Why is the concept of a closed system useful when considering chemical reactions?

(3 marks)

iii) Butane is a commonly used fuel for portable gas cookers. Using the thermodynamic data below, calculate the mass of butane that would need to be burned to boil 350 ml of water which is initially at 18 °C. State all assumptions made.

c_P (H_2O) = 4.18 $kJ.kg^{-1}.K^{-1}$

$\Delta_f H^{\ominus}$ (C_4H_{10}) = -125.6 $kJ.mol^{-1}$

$\Delta_f H^{\ominus}$ (CO_2) = -393.5 $kJ.mol^{-1}$

$\Delta_f H^{\ominus}$ (H_2O) = -285.8 $kJ.mol^{-1}$

(6 marks)

b) Answer **ALL** parts of this question.

i) With reference to the entropy of the system and entropy of the surroundings, describe why water boils above a critical temperature.

(3 marks)

ii) Describe with the use of a diagram what is meant by the activity of a species in solution. Under what circumstances is it important to consider activities rather than concentration, and how are concentration and activity related?

(4 marks)

QUESTION CONTINUED OVERLEAF

iii) The chemical equation and thermodynamic data for binding of ammonia to a silver ion is shown below.

$$\mathbf{Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+}$$

$\Delta_r H^\ominus = -21.4$ kJ.mol^{-1}

$\Delta_r S^\ominus = 8.66$ J.K^{-1}.mol^{-1}

If the activity of Ag^+ is 0.02 mol.dm^{-3} and the activity of NH_3 is 0.01 mol.dm^{-3} at equilibrium at 80 °C, calculate the activity of $[Ag(NH_3)]^+$.

(5 marks)

c) Answer **BOTH** parts of this question.

i) At 25 °C the pH of a 0.5 mol.dm^{-3} solution of citric acid is 1.72. What would the pH be at 60 °C?

The standard enthalpy of dissociation ($\Delta H^\ominus$) for citric acid is 4.07 kJ.mol^{-1}.

(7 marks)

ii) 100 ml of the solution in (i) above is mixed with 100 ml of 0.25 mol.dm^{-3} sodium hydroxide solution. What is the pH of the resulting solution at 25 °C?

(5 marks)