

**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 2017, for Internal Students of the  
Imperial College of Science, Technology and Medicine**

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

**CHEM40001 Introduction to Chemistry**

**PAPER TWO**

**Friday 13<sup>th</sup> January 2017, 14:00-16:15**

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

## Q1: Spectroscopy & Characterisation

Answer part a) **AND** either part b) **OR** part c) of this question.

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

**A**, **B** and **C** are three isomers of an aromatic compound with the molecular formula  $C_6H_3Cl_3$ . They are distinguished by their  $^1H$  NMR spectra where **A** shows a singlet, **B** shows 2 multiplets and **C** shows 3 multiplets.

i) Rationalise the spectral observations and draw the structures of **A**, **B** and **C**. [ $^1H$ :  $I = \frac{1}{2}$ , 100%, all other nuclei are spin inactive and assume that coupling only occurs through 3 bonds or less].

(6 marks)

ii) Sketch the  $^1H$  NMR spectrum of the isomer **B**, paying attention to the chemical shifts, multiplicities and relative integrals of the peaks.

(3 marks)

iii) Sketch the molecular ion peaks observed in the EI mass spectrum [Assume isotopic abundance:  $^1H$ : 100%,  $^{12}C$ : 100%,  $^{35}Cl$ : 75 %,  $^{37}Cl$ : 25%].

(4 marks)

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

The IR spectrum of gaseous lithium hydride at 298 K shows a single peak at  $588\text{ cm}^{-1}$ .

i) Sketch the molecular motion responsible for this absorption. Use your sketch to explain why lithium hydride absorbs IR radiation, whereas hydrogen does not.

(2 marks)

ii) Calculate the energy and population difference between the excited and ground states of lithium hydride.

(4 marks)

iii) Lithium deuteride also shows a single peak in the IR spectrum. Calculate its expected wavenumber. For your calculations assume that  $^1H$ ,  $^2H$  (D) and  $^6Li$  are 100 % abundant. State any further assumptions that you make.

(6 marks)

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

i) Predict whether the nuclear spin of the following isotopes will have zero, half-integer or integer values:  $^{14}C$ ,  $^{36}Cl$ ,  $^{182}W$  and  $^{205}Tl$ .

(4 marks)

ii) Sketch (line diagram) the  $^1H$  NMR spectrum expected for triethyl phosphine  $P(C_2H_5)_3$ , taking into account chemical shift values, spin-spin coupling constants and relative integrals.

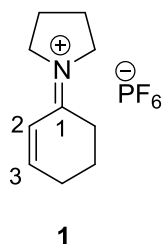
(8 marks)

## Q2: Structure, Mechanism, Reactivity and Stereochemistry

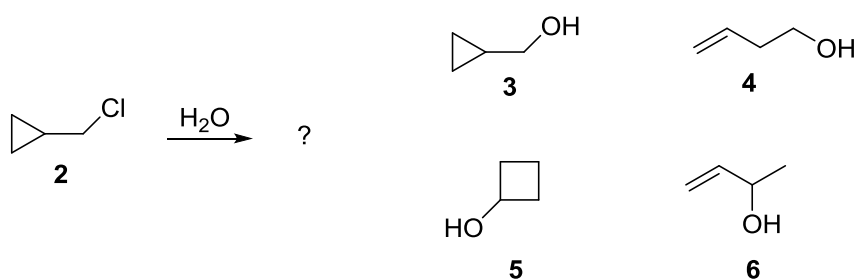
This is a multiple choice question. A correct answer will be given full marks. An incorrect answer will be given zero. Please only mark *one* answer per question.

Answer ALL of the following:

- 1) Which statement is correct with regards to the predominant reactivity of compound **1**? (3 marks)



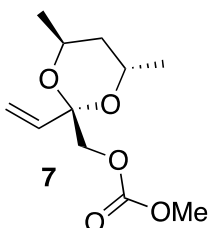
- A) Compound **1** is likely to act as either an electrophile or a nucleophile, because it consists of both positive and negative ions.
- B) Compound **1** is likely to act as an electrophile. The nitrogen atom and the carbons labelled 1 and 3 are electrophilic centres.
- C) Compound **1** is likely to act as an electrophile. The carbons labelled 1 and 3 are electrophilic centres.
- D) Compound **1** is likely to act as an electrophile. The carbons labelled 1, 2 and 3 are all electrophilic centres.
- 2) Considering possible curly arrow mechanisms, which of the products **3-6** are reasonable products from the hydrolysis of cyclopropylmethyl chloride **2**? (4 marks)



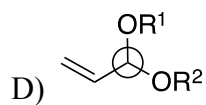
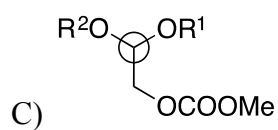
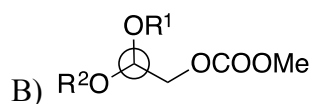
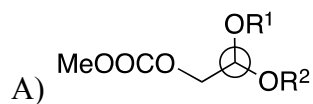
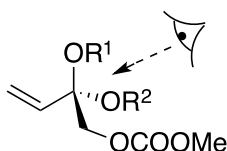
- A) Product **3** only.
- B) Products **3** and **5** only.
- C) Any of the products **3-6**.
- D) Products **3**, **4** and **5**.

QUESTION CONTINUED OVERLEAF

- 3) Which statement correctly describes the functional groups present in molecule 7?  
(2 marks)

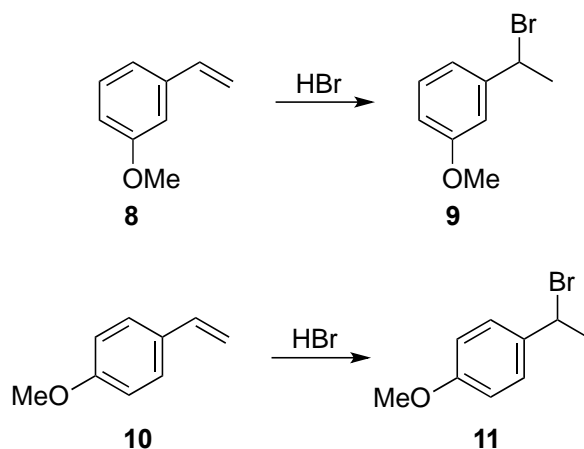


- A) Compound 7 contains ether, ester and alkene functional groups.
- B) Compound 7 contains carbonate, acetal and alkene functional groups.
- C) Compound 7 contains carbonate, ether and acetal functional groups.
- D) Compound 7 contains ether, urea and alkene functional groups.
- 4) Based on the simplified diagram of 7 below, which is the correct Newman projection?  
(2 marks)

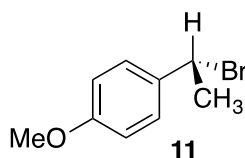


QUESTION CONTINUED OVERLEAF

- 5) Compound **8** reacts with HBr to give bromide **9**. Under the same conditions, alkene **10** affords bromide **11**. Which statement is correct with regards to these reactions? (4 marks)



- A) The reactions are electrophilic additions. Compound **8** would be expected to react faster than **10**, due to greater resonance stabilization of the intermediate carbocation.
- B) The reactions are electrophilic additions. Compound **10** would be expected to react faster than **8**, due to greater resonance stabilization of the intermediate carbocation.
- C) These are substitution reactions. Compound **8** would be expected to react faster than **10**, due to greater resonance stabilization of the intermediate carbocation.
- D) These are substitution reactions. Compound **10** would be expected to react faster than **8**, due to greater resonance stabilization of the intermediate carbocation.
- 6) One configuration of product **11** is depicted below. What is the correct stereochemical assignment of the molecule below? (4 marks)

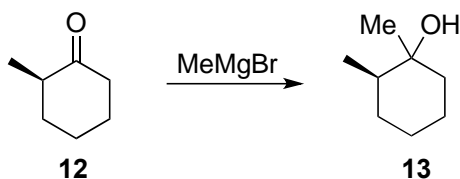


- A) dissymmetric
- B) *meso*
- C) *S*
- D) *R*

QUESTION CONTINUED OVERLEAF

- 7) Consider the reaction of enantiomerically pure ketone **12** with a Grignard reagent, MeMgBr, giving (after aqueous work-up) the alcohol product **13**. Which statement is correct?

(3 marks)



- A) Only one product stereoisomer is possible.  
B) Two diastereoisomeric products are possible, which may be formed in unequal amounts.  
C) Two enantiomeric products are possible, which must be formed in equal amounts.  
D) Two enantiomeric products are possible, which may be formed in unequal amounts.
- 8) Which of the following statements is correct concerning the characterisation of product **13**? You may assume this compound has never been made before and therefore there are no literature data for comparison.
- (3 marks)

- A) Product **13** contains stereoisomers that could be differentiated by NMR spectroscopy.  
B) The absolute configuration of the newly formed centre(s) could be established by optical rotation.  
C) Product **13** contains stereoisomers that could only be differentiated by separation of the isomers and anomalous dispersion X-ray crystallography.  
D) The absolute configuration of the newly formed centre(s) could be established by IR spectroscopy.

### Q3: Spectroscopy

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

**Remember to define any symbols or terms that you use. Marks will be lost if you use symbols which you do not define in your answers.**

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

i) An electromagnetic wave is defined by the following relationships

$$E(\vec{r}, t) = \hat{E} e^{-i(\omega t - \vec{k} \cdot \vec{r})} + c.c.$$

$$B(\vec{r}, t) = \hat{B} e^{-i(\omega t - \vec{k} \cdot \vec{r})} + c.c.$$

Define all of the symbols and terms in the above expressions.

(4 marks)

ii) Answer **ALL** parts.

a. The infrared linewidth of the C-H stretch in solvated tyrosine at  $1615 \text{ cm}^{-1}$  has a standard deviation of  $20 \text{ cm}^{-1}$ . Assuming that the lineshape is homogeneously broadened, what is the lifetime of the excited vibrational state?

b. The NMR linewidth of one of the ring protons in the same amino acid has a standard deviation of 70 Hz. Assuming homogeneous broadening, what is the dephasing time for this resonance?

(4 marks)

iii) Two tyrosine sidechains in a peptide have C-H stretches at  $1615 \text{ cm}^{-1}$  and  $1620 \text{ cm}^{-1}$  and both have widths at half maximum height of  $20 \text{ cm}^{-1}$ . Determine whether the two features are spectrally resolved or not. (hint: The formula for a Lorentzian lineshape is given below and the width at half maximum height is  $2\gamma$ )

$$f(x; x_0, \gamma, I) = I \left[ \frac{\gamma^2}{(x - x_0)^2 + \gamma^2} \right]$$

(4 marks)

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

i) By relating rates of transition at equilibrium between two states 'i' and 'j' derive a relationship between the Einstein Coefficients which takes into account the populations of the two states.

(4 marks)

QUESTION CONTINUED OVERLEAF

- ii) From the result above derive two relationships between the Einstein Coefficients which are independent of the number of states.

(hint: The Planck distribution is  $\rho(\nu) = \frac{8\pi h\nu^3/c^3}{e^{h\nu/kT} - 1}$ )

(6 marks)

- iii) Give an explanation for the relationship between the Einstein Coefficients which you derived in ii) above.

(3 marks)

- c) Answer **ALL** parts of this question

- i) The IR spectrum of a diatomic molecule in solution is found to have a strong absorption at  $1500\text{ cm}^{-1}$  and another much weaker absorption band at  $2950\text{ cm}^{-1}$ . Explain this observation

(4 marks)

- ii) Describe and sketch a typical Birge-Sponer plot and explain how it can be used to obtain the dissociation energy for a molecule.

(4 marks)

- iii) The IR spectrum of the molecule in part (i) above is now measured in the gaseous phase. Describe/sketch what is likely to be observed and explain why.

(5 marks)