JAMES COOK UNIVERSITY

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SCHOOL OF PHARMACY AND MOLECULAR SCIENCES
Chemistry Department

STUDY PERIOD 1 EXAMINATIONS 2008
CAMPUS: Cairns

No of pages including front page, exam paper and any attachments: 13
This paper must be handed in at the end of the Examination: Yes
Release to Library: No

STUDENT NAME:
(*block letters*)

STUDENT NUMBER:

SUBJECT CODE: CH1012:03

SUBJECT NAME: MOLECULAR CHEMISTRY

EXAMINER: Dr Michael Liddell **PHONE NO:** (07) 4042 1275

EXAMINER/CONTACT PERSON FOR ENQUIRIES ON DAY OF EXAM: **EXT. WORK:** 1275
Dr Michael Liddell

DURATION OF EXAMINATION (hours): TWO (2) HOURS

PERUSAL TIME (minutes): FIFTEEN (15) MINUTES

TOTAL NUMBER OF QUESTIONS: 27

INSTRUCTIONS TO STUDENTS:
The exam is composed of two sections:

Section A - Multiple choice	-	22 questions - 33%
Section B - Short answer	-	5 questions - 67%

Total marks for paper = 100
Answer **ALL** questions. All questions are **not** of equal value.
Timings are indicated to allow approximately 15 minutes of check-over time.

MATERIALS TO BE SUPPLIED BY EXAMINATION SECTION:
Examination Booklets required (Yes/No) Yes
Scanner Sheets required (Yes/No) Yes: a - e ☒

STANDARD MATERIALS PERMITTED IN AN EXAMINATION ROOM ARE:
Pencils, pens, erasers, white-out, rulers

ADDITIONAL MATERIALS STUDENTS MAY USE:
Scientific calculator with no text storage facilities.

Access to a dictionary:

- **English** **Yes ☒** **or** **No ☐**
- **Bilingual English translation** **Yes ☒** **or** **No ☐**

SECTION A

MULTIPLE CHOICE QUESTIONS (EACH QUESTION IS WORTH 1.5 MARKS). ANSWER ALL QUESTIONS – SHADE WITH A PENCIL THE MOST CORRECT ANSWER ON THE MULTICHOICE SCANNER SHEET.
Timing: you should complete the multi-choice section in 32 minutes (≈ 1.5 minutes per question).

SECTION B

SHORT ANSWER QUESTIONS. (MARKS FOR EACH QUESTION ARE AS INDICATED) ANSWER EACH OF THE FIVE (5) QUESTIONS.

Question 1

Timing: you should complete this question in 7 minutes.

(a) The **acid/base properties** of the oxides of elements **Groups 1A** to **4A** in Period 3 vary in a systematic manner traversing from sodium to silicon.

- Describe the **trend in the acid/base properties** using examples to illustrate your answer.
- Illustrate why sodium peroxide is **basic** in solution.
- What is an **amphoteric** oxide?

(6 marks)

Question 2

Timing: you should complete this question in 14 minutes.

(a) $[PdCl_2(NH_3)_2]$ is a palladium analogue of the anti-cancer drug *cis*-Platin.

- What is the **coordination number** and **geometry** at the palladium centre in $[PdCl_2(NH_3)_2]$.
- How many **ligands** and **donor atoms** does $[PdCl_2(NH_3)_2]$ have?
- Provide an example of a neutral **bidentate ligand** which could replace the two amine groups in $[PdCl_2(NH_3)_2]$ and **draw the resultant complex**.

(4 marks)

(b) Give **systematic names** for the following compounds:

- $[Mo(NH_3)_4(CN)Cl]I$
- $Na[AgCl_2]$

Provide a **molecular formula** for the following complex:

- diaquatriamminenitritocobalt(III) bromide

(4 marks)

(c) For the following complex **identify** and **draw** examples of each of the following types of isomers, if they are valid possibilities for the complex:
coordination isomers, linkage isomers, geometric isomers, optical isomers
.

- $[Fe(NH_3)_4(H_2O)SCN]Br$

(4 marks)

Question 3

Timing: you should complete this question in 21 minutes.

(a) Why is **steam distillation** used for distilling many natural oils rather than standard **fractional distillation**? In your answer explain the characteristics of both types of distillation

(3 marks)

(b) At 30°C benzene and toluene have vapour pressures in the pure state of 119.6 torr and 36.7 torr, respectively.

- What are the partial vapour pressures of each of these compounds and the total pressure over a solution consisting of equal weights of these two components at 30°C?
- What is a **supercritical fluid**?

(5 marks)

(c) Briefly describe the **metallurgical processes** involved in the transformation of hematite (Fe_2O_3) into iron metal.

- Why is expensive electricity used for smelting aluminium rather than using a simple blast furnace operation such as that is used for producing pig-iron?

(4 marks)

(d) (i) **Molecular orbital (MO) theory** is the area of quantum mechanics that is concerned with the description of the electronic structure of molecules.

- What are the four **quantum numbers** that are required to define an individual electron in an atom.
- Draw a complete **molecular orbital diagram** for the diatomic molecule Li_2^+
- Indicate on your diagram where the **HOMO** and the **LUMO** are.

(ii) Band theory is the extension of MO theory to solids. Use **band theory** to discuss the main differences between **p-type** and **n-type semiconductors**?

(5 marks)

Question 4

Timing: you should complete this question in 14 minutes.

(a) A colourless organic solid gave the following microanalytical results:

C 59.98 % H 10.06 %

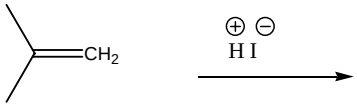
¤ In an **IR spectru**m of the sample strong bands were found at 3510 and 1702 cm^{-1}.
¤ A **EI mass spectrum** of the compound displayed a molecular ion at m/z 160.
¤ **^{1}H NMR** δ ($CDCl_3$/C: 0.75 (t, 3H), 1.2 – 1.5 (m, 8H), 1.60 (m, 2H), 3.75 (s, 1H), 4.1 (t, 1H), 10.02 (s, 1H)
¤ When the ^{1}H NMR was re-run after the addition of a drop of **D_2O** the peaks at 3.75and 10.02 ppm were absent from the spectrum.

- Provide the **molecular formula**, **IUPAC name** and **condensed** structure for this compound.
- Explain clearly **how you arrived at the structure of the compound** using <u>all</u> the information provided.
- What **chemical test** could you use to help verify the identity of this compound?

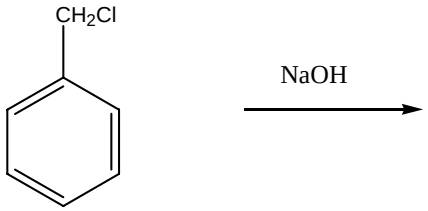
(8 marks)

(b) Predict the **major organic product(s)** from **two** of the following reactions and name the **type of reaction**. (N.B. you are <u>not required</u> to provide a detailed mechanism)

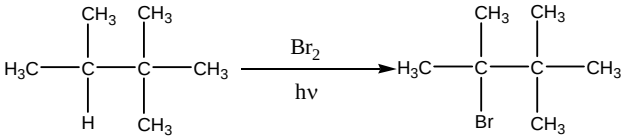
(i)



(ii)



(ii)



(4 marks)

Question 5

Timing: you should complete this question in 23 minutes.

(a) Describe in detail the **radical chain mechanism** for the mono-chlorination of methane in the presence of ultraviolet light.

- How would you **separate** the multi-substituted products from the mono-substituted products?

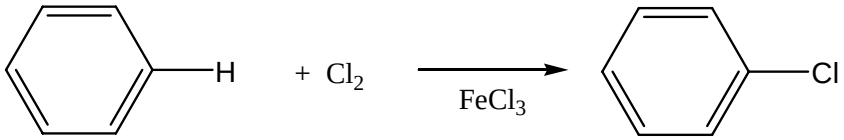
(5 marks)

(b) Draw the structure of (S)-2-bromobutane, indicating clearly the **S-configuration** at the stereocentre.

- Provide a detailed mechanism for the **S_N2 substitution reaction** between this reagent and sodium hydroxide.
- What does **S_N2** mean?

(5 marks)

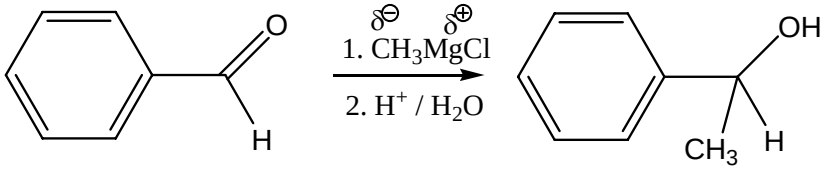
(c) The chlorination of benzene shown below illustrates a typical reaction of **aromatic compounds** with **electrophilic reagents.**



- Provide a **detailed mechanism** for this reaction.
- Explain in detail why **substitution** occurs rather than **addition**.
- What is the function of the $FeCl_3$ in the reaction?

(5 marks)

(d) The **Grignard reaction** is a particularly useful tool for synthetic organic chemists. The reaction between benzaldehyde and methylmagnesium chloride proceeds as below.



- Provide a **detailed mechanism** for the above reaction
- What **solvent** would you use for step 1 in the reaction – justify your answer?

(5 marks)

EQUATION LIST

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\ln p = \frac{-\Delta H}{RT} + \text{constant}$$

$$\ell n\left(\frac{p_2}{p_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$p_i = p_i^{O} x_i$

$p_{Total} = \Sigma p_i$

$[i] = K_H p_i$

$p_i = p_T x_i$

$p_i = (\%_i / 100)\, p_{atm}$

$\%_i = ppmv_i \times 10^{-4}$

$K_{sp} = [cation]^c[anion]^d$

$$\frac{m_O}{m_w} = \frac{p_O^o M_O}{p_w^o M_w}$$

$A = \varepsilon l [i]$

1 mole ideal gas = 22.41 dm^3 at STP

$$E = \frac{hc}{\lambda} = h\nu$$

$h = 6.63 \times 10^{-34}$ J s^{-1}

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/k_B T}$$

$k_B = 1.38 \times 10^{-23}$ J K^{-1}

$c = 3.00 \times 10^8$ m s^{-1}

$T(K) = T(^oC) + 273.15$

$R = 8.314$ J mol^{-1} K^{-1}

1 atm. $= 1.013 \times 10^5$ Pa = 760 torr

TABLE 1

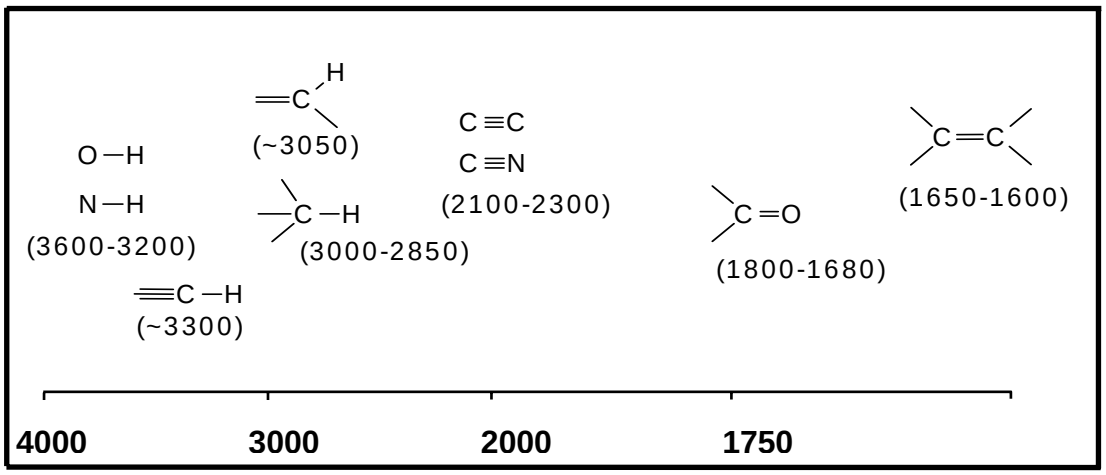
Physical Quantity	Name of Unit	Symbol for Unit
Length	metre	m
Mass	kilogram	kg
Time	second	s
Electric Current	Ampere	a
Thermodynamic Temperature	Kelvin	K
Amount of Substance	mole	mol

TABLE 2

Physical Quantity	Name of S.I. Unit	Symbol for S.I. Unit
Volume	cubic metre	m^3
Frequency	Hertz	Hz
Velocity	metre per second	$m\ s^{-1}$
Acceleration	metre per second squared	$m\ s^{-2}$
Density	kilogram per cubic metre	$kg\ m^{-3}$
Molar Mass	kilogram per mole	$kg\ mol^{-1}$
Concentration	mole per cubic metre	$mol\ m^{-3}$
Molality	mole per kilogram	$mol\ kg^{-1}$
Force	Newton	N
Pressure	Pascal	Pa
Energy	Joule	J
Electric Charge	Coulomb	C
Electron Potential Difference	Volt	V

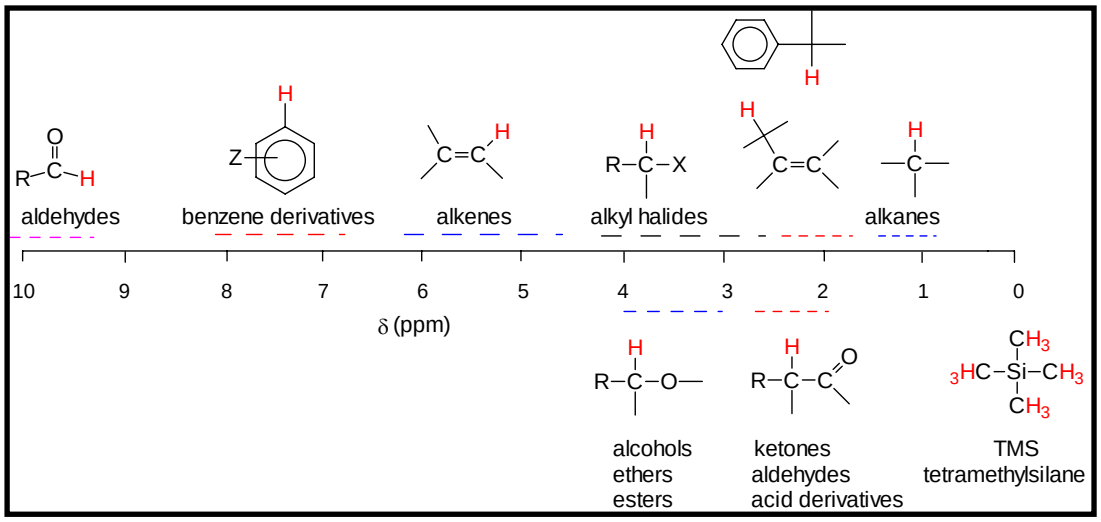
Spectroscopy Tables

Typical Infrared (IR) frequencies of common functional groups

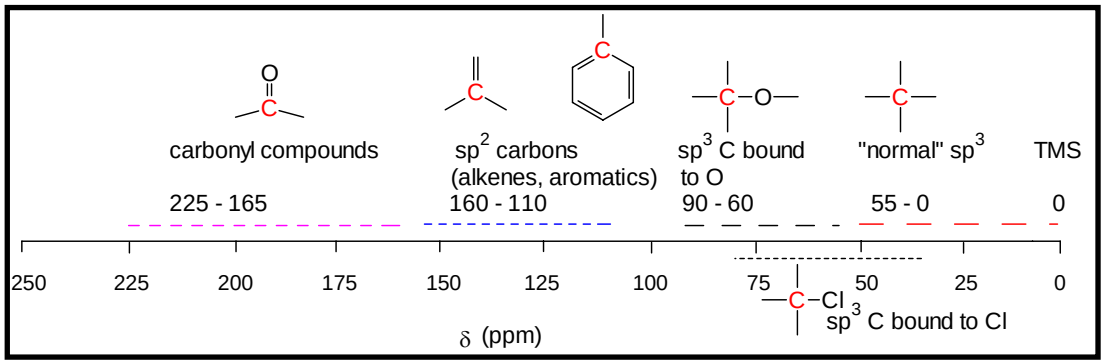


Carbonyl Absorptions ν (cm^{-1}) **Acid chlorides** ~ 1790**; Esters** ~ 1740**;**
Aldehydes ~ 1720**;** **Ketones** ~ 1710**;** **Acids** ~ 1700; **Amides** ~ 1650

Approximate ^{1}H NMR shifts of protons bound to C in organic compounds



Approximate ^{13}C NMR shifts for groups in organic compounds



PERIODIC TABLE
CH1012:03