UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2011/2012

TITLE OF PAPER: **INTRODUCTORY ORGANIC CHEMISTRY**

COURSE NUMBER: **C203**

TIME ALLOWED: **THREE (3) HOURS**

INSTRUCTIONS: **THERE ARE SIX (6) QUESTIONS. ANSWER ANY FOUR (4) QUESTIONS. EACH QUESTION IS WORTH 25 MARKS.**

A PERIODIC TABLE AND A TABLE OF CONSTANTS HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

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Question One

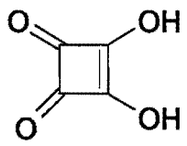
a) Consider the substances shown in the following acid-base reactions. Complete each equation and expand the structural formulas to show all the unshared electron pairs. Identify the acid, base, conjugate acid and conjugate base.

i) $(CH_3)_3CO^- + CH_3SH \rightleftharpoons$

ii) $CH_3CO_2H + CH_3CH_2NH_2 \rightleftharpoons$

[6]

b) Squaric acid is unusually acidic for a compound containing only C, H and O atoms. The structure of the molecule is sketched below. The molecule has two acidic protons so that it has two dissociation constants, K_{a1} and K_{a2}. Consequently in the presence of a base, the ions $[C_4O_4H]^-$ and $[C_4O_4]^{2-}$ are formed.

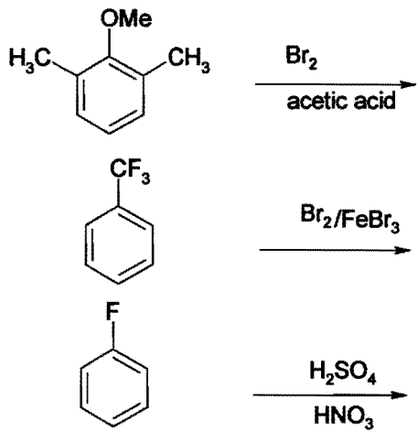


i) Write a dot structure for each of the two ions

ii) Using curved arrows, write two resonance structures to show how each of the two ions is resonance stabilized

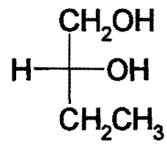
[8]

b) Complete the following reactions:



[6]

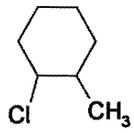
Q.1. d) What is the absolute configuration (R or S) of the compound represented by the Fisher projection shown below.



[5]

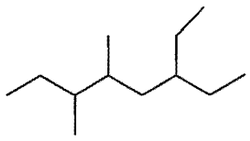
Question Two

a) Name each of the following:

i) 

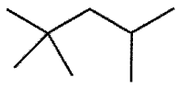
ii) $CH_3CH_2CH(CH_3)CH_2CH(CH_2CH_3)_2$

iii) $CH_3C(Br_2)CH_2CH_2CH_2C(Br_2)CH_3$

iv) 

[8]

b) Photochemical chlorination of 2,2,4-trimethylpentane (whose structure is sketched below) gives four isomeric monochlorides. Write structural formulas for these four isomers.



[6]

c) Cyclopropyl chloride has been prepared by the free radical chlorination of cyclopropane. The structure of cyclopropane is sketched below. Write a stepwise mechanism for this reaction. Your answer should include initiation, propagation and **two** termination reactions.

[6]

d) Sight down the C-2-C-3 bond and draw Newman projection formulas for the

i) most stable conformation of 2,2-dimethylbutane

ii) two most stable conformations of 2,3-dimethylbutane

[5]

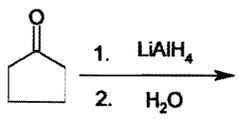
Question Three

a) Write structural formulas for six of the isomeric aldehydes and ketones that have the molecular formula $C_5H_{10}O$. For structures, you may use any one of line, condensed, or dash formulas.

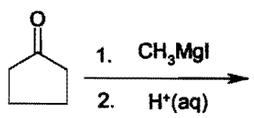
[9]

b) Predict the product of the reaction of cyclopentanone with each of the following:

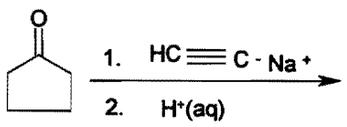
i) Lithium aluminium hydride followed by water



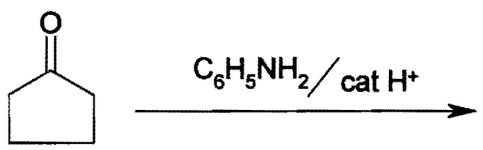
ii) CH_3MgI, followed by dilute acid



iii) $HC{\equiv}C^-Na^+$, followed by dilute acid



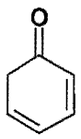
iv) Aniline, $C_6H_5NH_2$, in the presence of a little acid



[8]

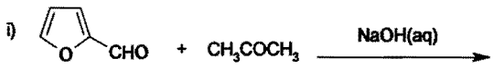
c) Write enol form of each of the following:

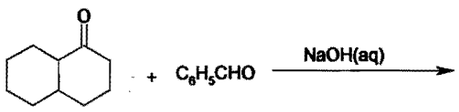
i) $(CH_3)_2CHCHO$

ii) 

[4]

d) Write the structure of the major product formed in each of the following reactions:

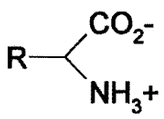
i) 

ii) 

[4]

Question Four

a) Structures of amino acids are represented by the general structure shown below.



Write line structures for the following alpha amino acids:

i) Valine, R = isopropyl
ii) Leucine, R = isobutyl
iii) Isoleucine, R = sec-butyl
iv) Aspartic acid, R = CH_2X, where X is the carboxylic group.

[6]

b) Write a stepwise mechanism for the formation of oxane (whose structure is shown below) from 1,5-pentanediol, $HOCH_2(CH_2)_3CH_2OH$. The reaction is aci-catalysed.

Oxane

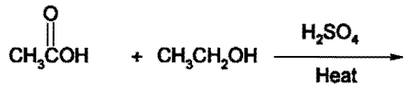
[6]

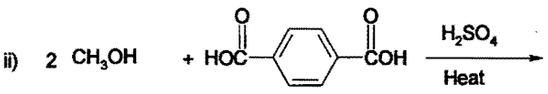
c) Write equations showing how 1-phenylethanol, $C_6H_5CH(OH)CH_3$ could be prepared from each of the following starting materials:

i) Bromobenzene
ii) Benzaldehyde

[7]

d) Write the structure of the ester from each of the following:

i) 

ii) 

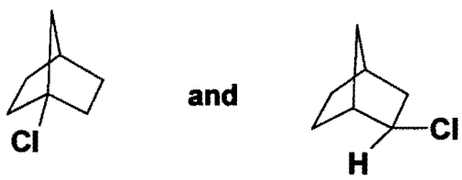
[6]

Question Five

a) In each of the following pairs of compounds, one is chiral and the other one is achiral. Identify each compound as chiral or achiral,

i) 

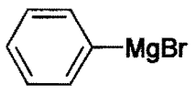
ii) $CH_3CH{=}CHCH_2Br$ and $CH_3CH(Br)CH{=}CH_2$

iii) 

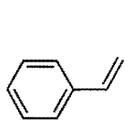
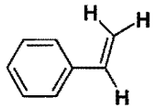
[6]

b) Write equations (not necessarily balanced) showing how 2-phenyl, $C_6H_5CH_2CH_2OH$, could be prepared from each of the following materials:

i) Phenylmagnesium bromide



ii) Styrene

 or 

[5]

c) Give a dash formula for the carbocation intermediate that leads to the major product in the reaction of hydrogen chloride with each of the compounds given below. Briefly explain your answer.

i) 2-methyl-2-butene, $(CH_3)_2C{=}CHCH_2CH_3$

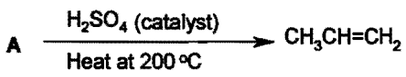
ii) 2-methyl-1-butene, $CH_2{=}C(CH_3)CHCH_2CH_3$

iii) Cis-2-butene, $CH_3CH{=}CHCH_3$

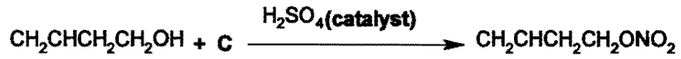
iv) $CH_3CH{=}C(C_6H_5)_2$

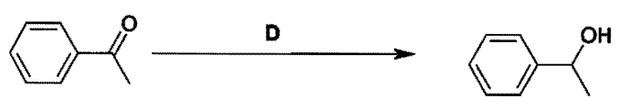
[8]

d) For each of the following reactions, identify the missing substances **A**, **B**, **B** and **C** and write its formula.

i) 

ii) 

iii) 

iv) 

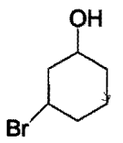
[6]

Question Six

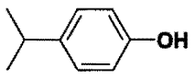
a) Give the IUPAC name for each of the following

i) $CH_3CH{=}CHCH_2CH_2CH(CH_3)_2$

ii) The cyclic alcohol,



iii) A phenol of structure,



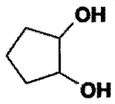
[6]

b) Write chemical equations for a reaction that takes place between each of the following pairs of reactants.

i) 2-butanol, $CH_3CH(OH)CH_2CH_3$, and potassium dichromate, $K_2Cr_2O_7$

ii) 1-butene, $CH_2{=}CHCH_2CH_3$ and water, H_2O, in the presence of a catalytic amount of acid

iii) 1,2-cyclopentanediol,



and periodic acid, HIO_4.

[6]

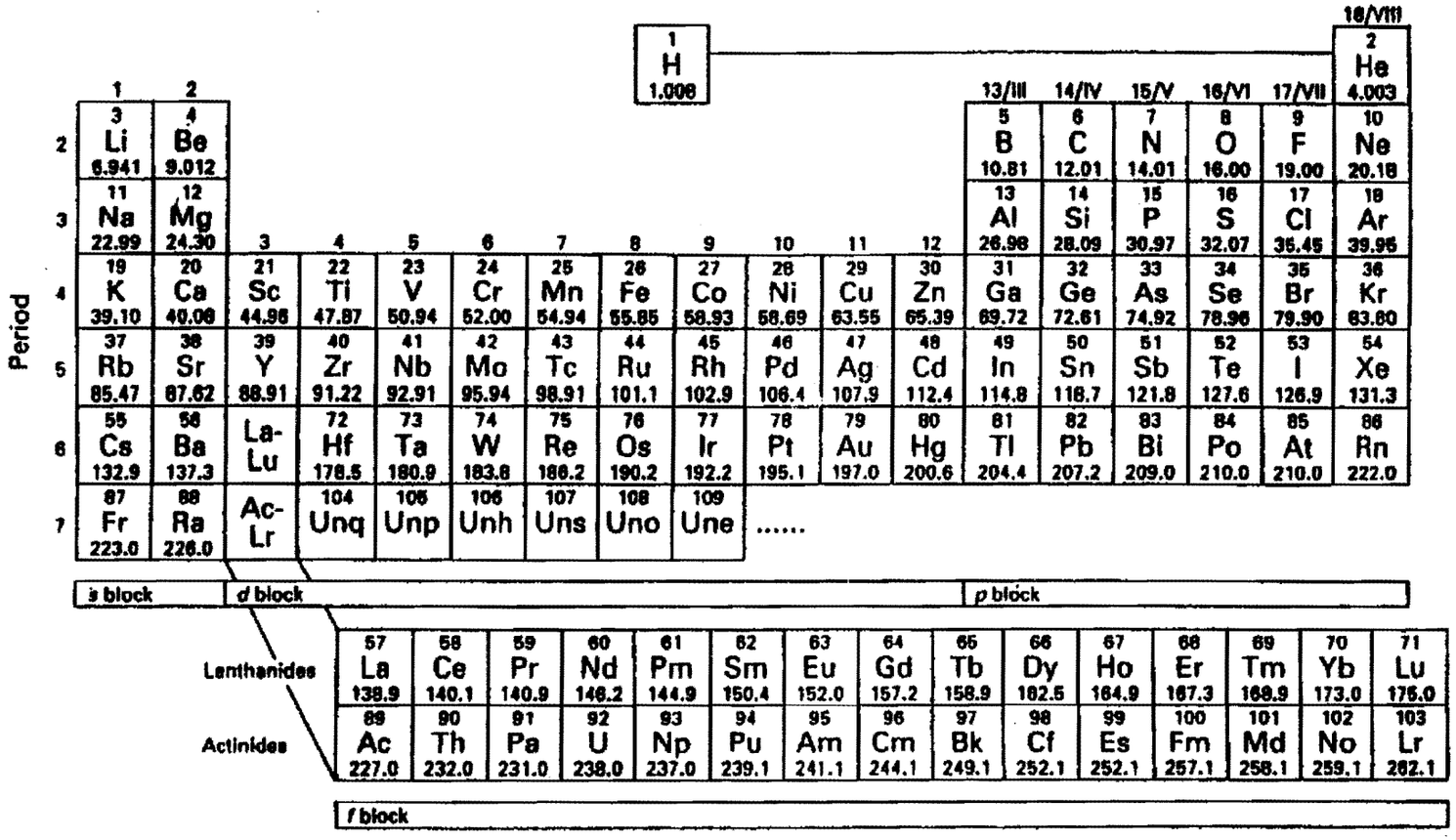
c) Consider the reaction of cyclohexanol, $C_6H_{11}OH$, with hydrogen bromide, HBr, to form bromocyclohexane, $C_6H_{11}Br$ and water. Write chemical equations for the steps involved in the reaction.

[8]

d) Which one of the two species, $(CH_3)_3C^+$ or $(CF_3)_3C^+$ would you expect to be more stable? Explain your answer.

[5]

The Periodic Table



Useful relations

At 298.15 K, $RT = 2.4790$ kJ mol^{-1} and $RT/F = 25.693$ mV

1 atm = 101.325 kPa = 760 Torr (exactly)

1 bar = 10^5 Pa

1 eV = $1.602\,18 \times 10^{-19}$ J = 96.485 kJ mol^{-1} = 8065.5 cm^{-1}

1 cm^{-1} = 1.986×10^{-23} J = 11.96 J mol^{-1} = 0.1240 meV

1 cal = 4.184 J (exactly)

1 D (debye) = $3.335\,64 \times 10^{-30}$ C m

1 T = 10^4 G

1 Å (ångström) = 100 pm

1 M = 1 mol dm^{-3}

General data and fundamental constants

	Quantity	Symbol	Value
*	Speed of light	c	$2.997\,925 \times 10^8$ m s^{-1}
*	Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
	Faraday constant	$F = eN_A$	9.6485×10^4 C mol^{-1}
	Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1} 8.6174×10^{-5} eV K^{-1}
*	Gas constant	$R = kN_A$	8.314 51 J K^{-1} mol^{-1} $8.205\,78 \times 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
*	Planck constant	h $\hbar = h/2\pi$	$6.626\,08 \times 10^{-34}$ J s $1.054\,57 \times 10^{-34}$ J s
*	Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
	Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ kg
*	Mass of electron	m_e	$9.109\,39 \times 10^{-31}$ kg
*	Vacuum permittivity	ε_0 $4\pi\varepsilon_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^2 m^{-1} $1.112\,65 \times 10^{-10}$ J^{-1} C^2 m^{-1}
	Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
*	Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
*	Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	$1.097\,37 \times 10^5$ cm^{-1} = 1.09737×10^7 m^{-1}

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^3	10^6	10^9