UNIVERSITY OF SWAZILAND
SUPPLEMENTARY EXAMINATION 2014/2015

TITLE OF PAPER : Organic Chemistry

COURSE NUMBER : C303

TIME : Three Hours

INSTRUCTIONS : Answer any **Two Questions** from **Section A** and any **Two Questions** from **Section B**. Each Question carries 25 Marks.

This Paper contains five (5) pages.

You must not open this paper until the Chief Invigilator so has granted permission to do.

SECTION A

SPECTROSCOPY AND STRUCTURE DETERMINATION

Question 1

(a) Explain why all protons in a molecule do not absorb radio frequency (rf) energy at the same time. (8 marks)

(b) The integrated ^{1}H NMR spectrum of a compound of formula $C_4H_{10}O$ is shown in Figure 1. Examine the spectrum, interpret all the signals and propose a structure for the compound that fits the spectral data. (6 marks)
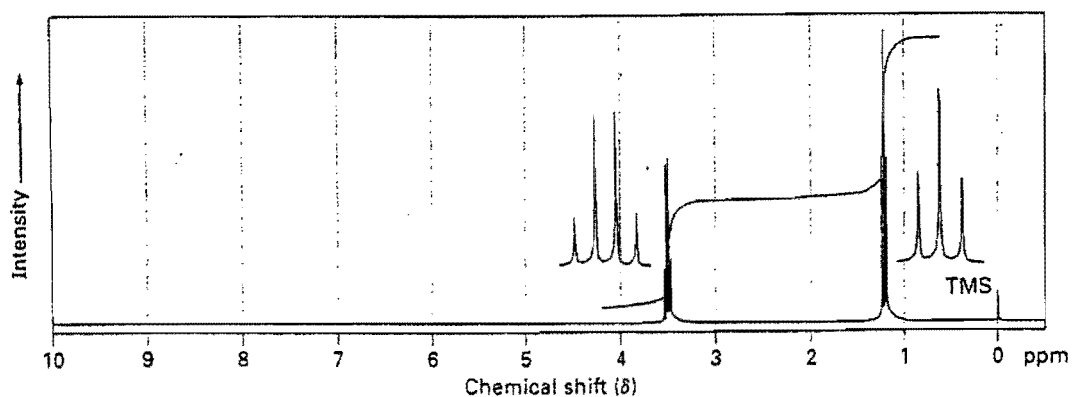

Figure 1. An integrated ^{1}H NMR spectrum for $C_4H_{10}O$

(c) Propose a structure for an aromatic hydrocarbon C11H16, that has the following ^{13}C NMR data. (6 marks)

Broadband decoupled ^{13}C NMR: 29.5, 31.8, 50.2, 125.5, 127.5, 130.3, 139.8 δ

DEPT - 90 : 125.5, 127.5, 130.3 δ
DEPT - 135 : Positive Peaks at 29.5, 125.5, 127.5, 130.3 δ Negative Peak at 50

(d) It is known that addition of HBr to a terminal alkyne leads to the Markovnikov addition product with the Br bonding to the more highly substituted carbon. How would you use ^{13}C NMR to identify the product of the addition of 1 equivalent of HBr to hex-1-yne. (5 marks)

Question 2

(a)   Explain the term Chemical Shift with reference to Carbon-13 and proton NMR Spectroscopy. .   (9 marks)

(b)   The carbonyl carbon resonance of 3-methyl-2-butanone occurs at 208.7 ppm downfield from TMS. How many hertz (Hz) downfield from TMS would this carbonyl absorb if the spectrometer used to measure this absorption were operating at 200 MHz?   (8 marks)

(c)   An ester is suspected of being either $(CH_3)_3CCOOCH_3$ or $CH_3COOC(CH_3)_3$. Its ^1HNMR spectrum consists of two peaks at δ 0.9 and δ3.6 (relative areas 3.1).

   (i)   Which compound is it? Explain your answer.   (4 marks)

   (ii)   Describe the spectrum that would be expected if it had been the other ester.   (4 marks)

Question 3

(a)   Carboxylic acids (RCOOH) react with alcohols (R^1OH) in the presence of an acid catalyst. The reaction product of propanoic acid with methanol has the following MS, IR, and NMR data. Propose a structure for the product.?   (8 Marks)
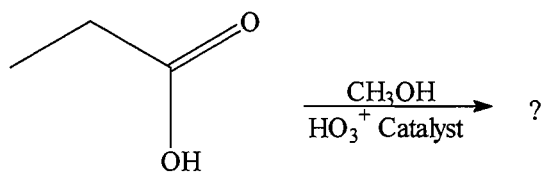
MS $M^+ = 88$

IR   1735 cm^{-1}

^1H 1011 δ (3H, triplet, J = 7 Hz); 2.32 δ (2H, quarted, J = 7 Hz); 3.65 δ (3 H, singlet)

Broadband – decoupled 13C NMR: 9.3, 27.6, 51.4, 174 δ

(b)   Propose a structure for a compound $C_5H_{12}O$ that fits the following: (3H, triplet J = 7 Hz); 1.2 δ (6 H, singlet); 1.50 * (2H, quartet J = 7 Hz); 1.64 δ (1 H, broad singlet)
                                                                    (9 marks)

(c)   Propose a structure for the alcohol C4H10O that has the following :

   ^{13}C NMR spectral data:

   Broadband – decoupled ^{13}C NMR
   19.0, 31.7, 69.5 δ
   Dept – 90: 31.7 delta.
   Dept – 135 positive peak at 19.0 δ, negative peak at 69.5 δ
                                                                    (8 marks)

SECTION B: REACTION AND SYNTHESIS OF ORGANIC COMPOUNDS

Question 4

(a)   (i)   Addition of HCl to 1-isopropenyl-1-methylcyclopentane yields 1-chloro-1,2,2-trimethylcyclohexane. Suggest a mechanism, showing the structures of the intermediate and using curved arrows to indicate electron flow.   (6 marks)
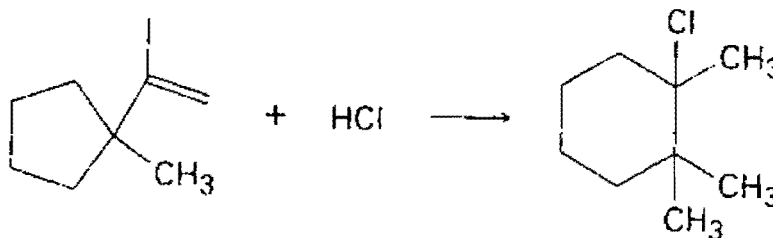
(ii)   Draw an energy diagram for the reaction, labeling all points of interest and making sure that the relative energy levels on the diagram are consistent with the information given.   (6 marks)
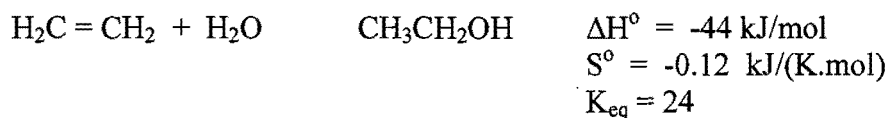
(b)   (i)   The reaction of hydroxide ion with chloromethane to yield methanol and chloride ion is an example of a general reaction type called nucleophilic substitution reaction:

$$HO^- + CH_3Cl \quad CH_3OH + Cl^-$$

The value of ΔH° for the reaction is -75 kJ/mol, and the value of ΔS° is +54 J/(K.mol). What is the value of ΔG° (in kJ/mol) at 298 K? Is the reaction exothermic or endothermic? Is it exergonic or endergonic?

(6 marks)

(ii)   The addition of water to ethylene to yield ethanol has the following thermodynamic parameters:

$$H_2C = CH_2 + H_2O \quad CH_3CH_2OH \qquad \begin{array}{l} \Delta H^\circ = -44 \text{ kJ/mol} \\ S^\circ = -0.12 \text{ kJ/(K.mol)} \\ K_{eq} = 24 \end{array}$$

(a)   Is the reaction exothermic or endothermic?
(b)   Is the reaction favorable (spontaneous) or unfavorable (nonspontaneous) at room temperature (298 K)?
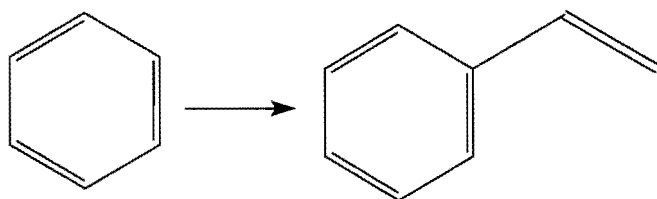
(7 marks)

Question 5

(a)   Identify reagents a – c in the following scheme.   (12 marks)
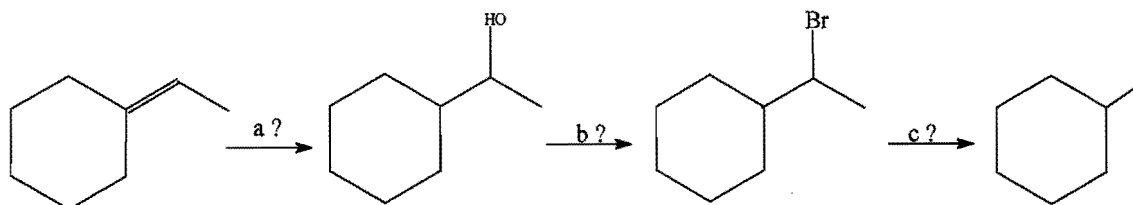
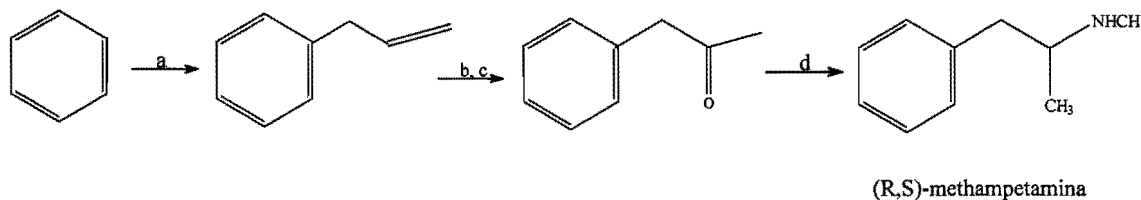(b)   Outline a sequence of reactions to carry out the following conversion.
                                                                (13 marks)

Question 6

(a)   Fill in the reagents a – d in the following synthesis of racemic methamphetamine from benzene.   (12 marks)

(R,S)-methampetamina

(b)   Using a malonic ester synthesis method, write a sequence of reactions for the synthesis of the following carboxylic acids

(i)   (6 marks)

(ii)   (7 marks)