

**UNIVERSITY OF SWAZILAND
MAIN EXAMINATION 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.

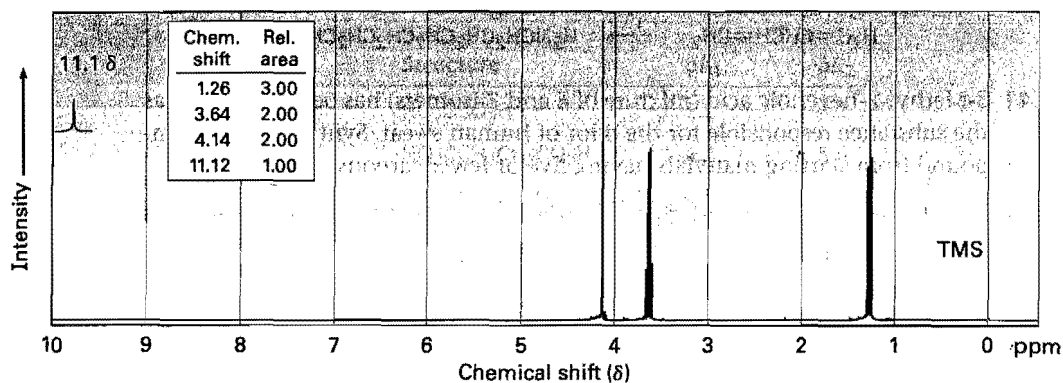
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SECTION A

SPECTROSCOPY AND STRUCTURE DETERMINATION

Question 1

- (a) Compound A, $C_4H_8O_3$, has infra red absorption at 1710 and 2500 to 3100 cm^{-1} and has 1H NMR spectrum shown. Propose a structure for A. (8 marks)



- (b) The integrated 1H 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. (8 marks)

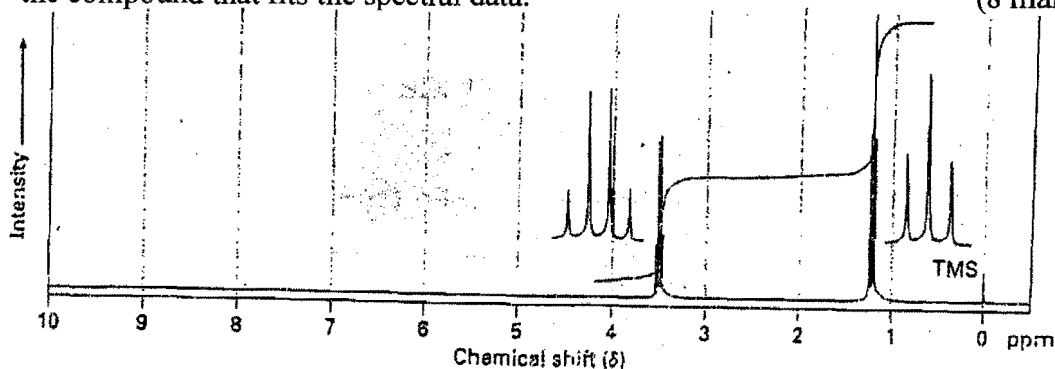


Figure 1. An integrated 1H NMR spectrum for $C_4H_{10}O$

- (c) Propose a structure for an aromatic hydrocarbon $C_{11}H_{16}$, that has the following ^{13}C NMR data. (9 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

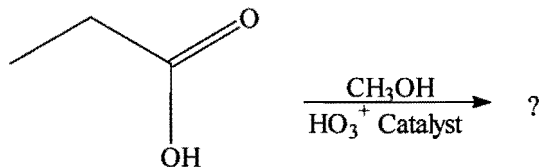
DEPT - 135 : Positive Peaks at 29.5, 125.5, 127.5, 130.3 δ Negative Peak at 50

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 carbon absorb if the spectrometer used to measure this absorption were operating at 200 MHz? (8 marks)
- (c) An ester is suspected of being either $(\text{CH}_3)_3\text{CCOOCH}_3$ or $\text{CH}_3\text{COOC}(\text{CH}_3)_3$. Its ^1H NMR spectrum consists of two peaks at δ 0.9 and δ 3.6 (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 ($\text{R}'\text{OH}$) 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 this product.? (8 Marks)



MS $M^+ = 88$

IR 1735 cm^{-1}

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

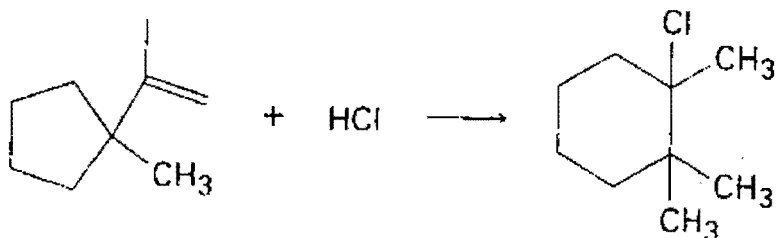
Broadband – decoupled ^{13}C NMR: 9.3, 27.6, 51.4, 174 δ

- (b) Propose a structure for a compound $\text{C}_5\text{H}_{12}\text{O}$ that fits the following: (3H, triplet $J = 7 \text{ Hz}$); 1.2 δ (6 H, singlet); 1.50 * (2H, quartet $J = 7 \text{ Hz}$); 1.64 δ (1 H, broad singlet) (9 marks)
- (c) Propose a structure for the alcohol $\text{C}_4\text{H}_{10}\text{O}$ 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 δ .
 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)



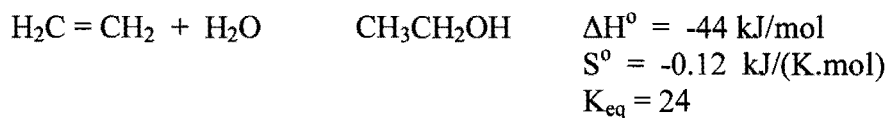
- (ii) Draw an energy diagram for the reaction, labeling all points of interest and making sure that the relative energy levels on the diagram are consistent with the information given. (6 marks)
- (b) (i) The reaction of hydroxide ion with chloromethane to yield methanol and chloride ion is an example of a general reaction type called nucleophilic substitution reaction:



The value of ΔH° for the reaction is -75 kJ/mol , and the value of ΔS° is $+54 \text{ J/(K.mol)}$. 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:



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

(7 marks)