

EASTERN UNIVERSITY, SRI LANKA*

FOURTH EXAMINATION IN SCIENCE-2019/201127 OCT 2017

SPECIAL DEGREE IN CHEMISTRY

CHS 06 Organic Chemistry II

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Time Allowed: Two hours

enswer all the parts (a), (b) and (c).

- Define the following terms used in retrosynthetic analysis:
 - i) Disconnection
 - ii) Synthon
 - iii) Functional Group Interconversion
- Give three criteria for a good disconnection in retrosynthetic analysis.

Using retrosynthetic analysis, devise synthetic strategies for the following target molecules and show how the syntheses could be effected from the suggested starting materials:

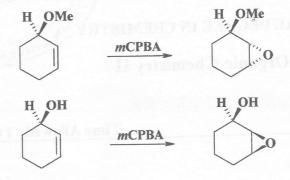
swer all the parts (a), (b) and (c).

Briefly explain how kinetic resolution could be achieved in the Sharpless Asymmetric Epoxidation given below:

$${}^{1}R \qquad {}^{1}R \qquad {}^{1}R \qquad {}^{2}R \qquad {}^{$$

Contd...

- b) Considering 'Felkin-Ahn' model, how you would predict the stereoselection nucleophilic addition to a carbonyl group having an adjacent stereogenic Briefly explain.
- c) Explain the following observations:



- 3) Answer **Both** parts (a) and (b).
 - (a) Two possible disconnection approaches are suggested for the synthesis of ear following molecules. Giving reasons, select the preferred approach in each care

- (b) Explain any five of the following:
 - (i) Chemical shift δ in NMR spectroscopy
 - (ii) Coupling constant J in NMR spectroscopy
 - (iii) Spin-lattice relaxation in NMR spectroscopy
 - (iv) Double resonance or spin decoupling in NMR spectroscopy
 - (v) Proton noise decoupled spectrum in ¹³C-NMR spectroscopy
 - (vi) Symmetric stretching vibration in IR spectroscopy.
 - (vii) Bending vibrations (scissoring and twisting) in IR spectroscopy

Answer all the parts (a), (b) and (c).

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- (a) What is/are the information obtained from the following 2-D NMR methods for a particular organic compound?
 - i) ¹H-¹H COSY ii) HMQC iii) HETCOR iv) HMBC
 - (b) Two isomeric compounds $\underline{\mathbf{A}}$ and $\underline{\mathbf{B}}$ with molecular formula $C_5H_{10}O$ have the following 1H and ^{13}C NMR data. Both compounds have a strong IR absorption band in the region 1710-1740 cm⁻¹. Elucidate the structures of $\underline{\mathbf{A}}$ and $\underline{\mathbf{B}}$ and interpret the spectral data.

Compound $\underline{\mathbf{A}}$: ¹H NMR (δ in ppm): 2.55 (septet,1H), 2.10 (s,3H) and 1.05 (d,6H)

¹³C NMR (δ in ppm): 212.6, 41.5, 27.2 and 17.8

Compound $\underline{\mathbf{B}}$: ¹H NMR (δ in ppm): 2.38 (t,2H), 2.10 (s,3H) and 1.57 (m,2H) and 0.88 (t,3H)

¹³C NMR (δ in ppm): 209.0, 45.5, 29.5, 17.0 and 13.2

- (c) A compound $\underline{\mathbf{C}}$ showed three singlets with area ratio 9:2:1 in its ¹H-NMR spectrum. The weakest singlet disappeared with the addition of D_2O . On treatment with concentrated H_2SO_4 at 180 °C, $\underline{\mathbf{C}}$ gave an olefin $\underline{\mathbf{D}}$ which when ozonolised under reducing conditions gave acetone and acetaldehyde as the products.
 - (i) Deduce the structures of $\underline{\mathbf{C}}$ and $\underline{\mathbf{D}}$.
 - (ii) Write the mechanism for the formation of compound $\underline{\mathbf{D}}$ from compound $\underline{\mathbf{C}}$.
 - (iii) Draw a rough sketch of the ¹H-¹H COSY spectrum of compound <u>C</u>.