Reg. No. | | | | | | | | | |

THE OPEN UNIVERSITY OF SRI LANKA

B.Sc Degree Programme and Stand Alone Courses in Science - 2011/2012

CMU2221/CME4221 - Organic Chemistry 1

CONTINUOUS ASSESSMENT TEST II

Ques No.	Max.	Marks
1	40	
2	60	
Total	100	

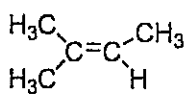
Date: Wednesday, 9th November 2011 Time: 4.00 p.m. – 5.30 p. m.

1. a) UV λ_{max} values of four compounds are given below. Indicate the type of electronic transition responsible for each of the absorptions.

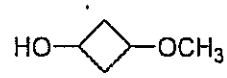
	(i)	(ii)	(iii)	(iv)
Compound	CH_3OH	$CH_3-\overset{\overset{O}{\|\|}}{C}-CH_3$	$CH_3CH=C(CH_3)_2$	CH_3NH_2
λ_{max}/**nm**	183	187 and 273	175	210
Electronic transition/s	.....	....	.....	.....

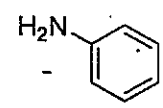
(10 marks)

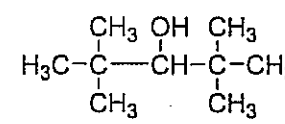
b) Predict the total number of signals in the ^1H NMR spectra of the following compounds.

(i) 

(ii) 

(iii) 

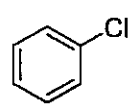
(iv) 

(v) 

....

(10 Marks)

c) Indicate the functional group responsible for the given IR absorptions of the following compounds.

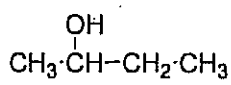
	Compound	ν/cm^{-1}	Group
(i)	$CH_3-O-CH_2CH_2-C\equiv CH$	2160	.....
(ii)	$Br-CH_2-CH_2-\overset{\overset{O}{\|\|}}{C}-CH_3$	1685	.....
(iii)	$CH_3-\overset{OH}{\overset{\|}{C}}H-CH_2-\overset{\overset{O}{\|\|}}{C}-CH_3$	3350	.....
(iv)	$CH_3-CH=CH-CH_2-C\equiv N$	1650	.....
(v)		~1500	.....

(10 marks)

Reg. No. | | | | | | | | | | |

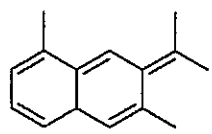
d) Giving fragmentation pathway, draw the fragment ions responsible for the peaks at m/e 74 (M^+), 59 and 45 in the EI mass spectrum of **X**.

(10 marks)



X

2. a) Calculate UV λ_{max} of **Y** according to the Woodward - Fieser rules by filling the cages using appropriate values.

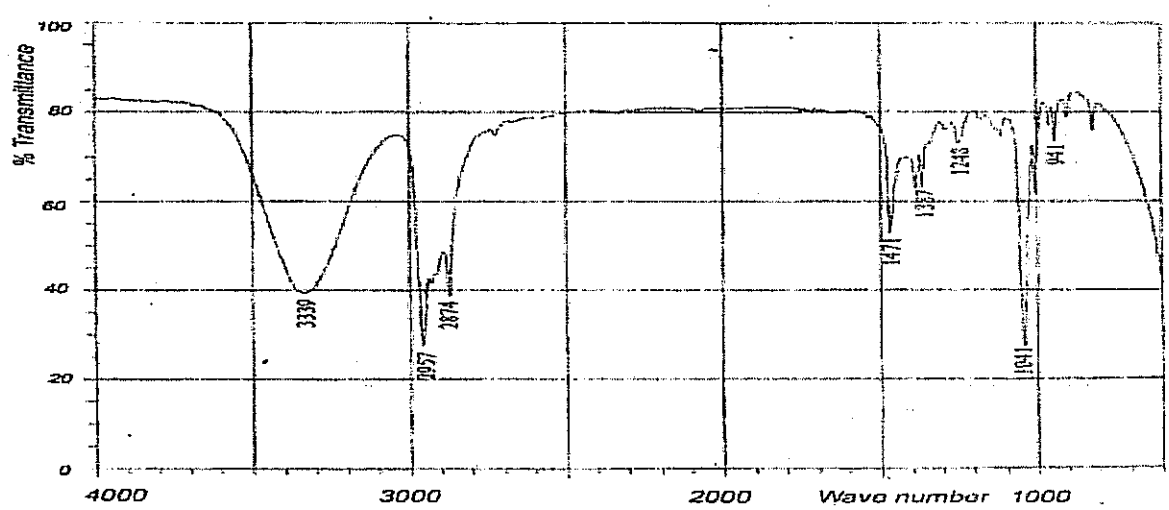


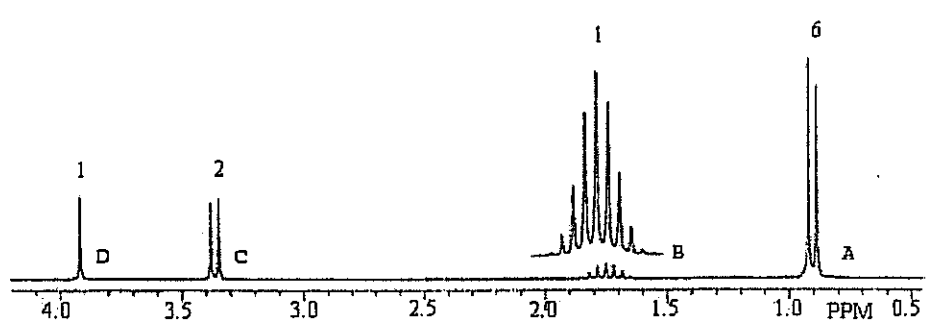
Y

Base value for homoannular or cis-oid diene	= 253 nm	
Base value for heteroannular or trans-oid diene	= 214 nm	
Double bond extending conjugation	=+30 nm	
Exocyclic double bond	=+05 nm	
Alkyl substituents or ring residues	=+05 nm	
Observed UV λ_{max} value of compound **Y**		

(10 marks)

b) IR and ^{1}H NMR spectra of compound **Z** (C_4H_8O) are given below.
(Integrals of ^{1}H NMR peaks are indicated above each peak)





Reg. No. | | | | | | | | | | |

Elucidate the structure of **Z**. Label the protons responsible for the peaks A, B, C and D in the structure correctly.

(40 marks)

c) A solution of an amine gave a proton signal due to $-NH_2$ group at δ 5.0 ppm. When the amine solution is diluted the same signal shifted to δ 1.0 ppm. Explain why?

.....

.....

.....

.....

.....

(10 marks)

CMU2221 ORGANIC CHEMISTRY I
Answer Guide for CAT II

1. a) (i) $n \longrightarrow \sigma^*$ (ii) $\pi \longrightarrow \pi^*$, $n \longrightarrow \pi^*$ (iii) $\pi \longrightarrow \pi^*$ (iv) $n \longrightarrow \sigma^*$

b) (i) 4 (ii) 1 (iii) 5 (iv) 2 (v) 3

c) (i) C≡C (ii) C=O (iii) OH (iv) C=C (v) aryl C=C

d) $CH_3-\overset{OH}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow{-e^-} CH_3-\overset{+\dot{O}H}{\underset{|}{CH}}-CH_2-CH_3$ m/e = 74 (M^+)

$H_3C-\overset{+\dot{O}H}{\underset{|}{CH}}-CH_2-CH_3 \longrightarrow \dot{C}H_3 + \overset{+\ddot{O}}{\underset{||}{CH}}-CH_2-CH_3$ m/e = 59

$H_3C-\overset{+\dot{O}H}{\underset{|}{CH}}-CH_2-CH_3 \longrightarrow \dot{C}H_3CH_4 + H_3C-\overset{+\ddot{O}}{\underset{||}{CH}}$ m/e = 45

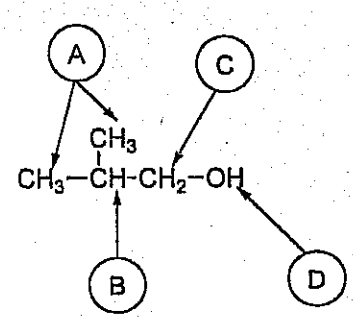
2. a)

Base value for homoannular or cis-oid diene	=	253 nm
Double bond extending conjugation (2)	=	60 nm
Exocyclic double bond (2)	=	10 nm
Ring residues (6)	=	30 nm
Observed UV λ_{max} value of compound Y	=	353 nm

b) IR band at 3339 cm^{-1} suggests a –OH group. ^1H NMR spectrum gives a detail about presence of 4 different types of Hydrogen's. δ ~ 1.0 signal due to 2 CH_3 groups. Doublet due to the presences of 1 H in the adjacent C atom. Therefore $CH_3-\overset{CH_3}{\underset{|}{CH}}-$ group present. δ ~ 3.5 signal due to 2 H's.(as $-CH_2$ group).

Doublet due to the presences of 1 H in the adjacent C atom. Therefore $-CH-CH_2-$ group present. δ ~ 1.5 – 2.0 signal due to 1H which shows multiplet. This implies presence of –CH- group and its neighboring C's have several H's. δ ~ 4.0 signal due to 1H which shows singlet may be due to OH group.By considering all these information and molecular formula,

The structure responsible for Z is



c) Amino protons are involved in H- bonding. In concentrated solution, more molecules can come into contact with one another and more hydrogen bonding takes place. So protons become more deshielded and absoption gives at δ 5.0 ppm. But in diluted solution amino protons are free and they become less deshielded. So same signal shifted to δ 1.0 ppm.