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

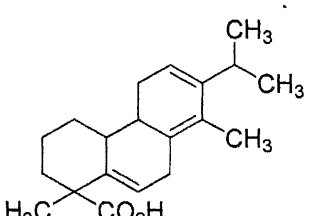
THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme and Stand Alone Courses in Science - 2012/2013
CMU2221/CME4221 - Organic Chemistry 1

CONTINUOUS ASSESSMENT TEST 1

Ques. No.	Max.	Marks
1	12	
2	30	
3	24	
4	16	
5	18	
Total	100	

Date: Saturday, 23rd February 2013 **Time:** 11.00 a.m.– 12.30 p.m.

1. Predict the λ_{max} of the following compound **A**, using Woodward-Fieser rules for dienes.



A

Basic value for Heteroannular diene Basic value for Homoannular diene	= 214 nm = 253 nm	
Increments for, Double bond extending conjugation	= +30 nm	
Alkyl substituent or ring residue	= +05 nm	
Exocyclic double bond	= +05 nm	
	λ_{max}	

(12 Marks)

2. The compound **B** with the molecular formula $C_9H_{10}O$, gave an orange coloured precipitate with Brady's reagent. It showed a strong IR absorption at ν_{max} 1725 cm^{-1}. Its ^1H NMR spectrum showed following signals.

   δ ppm 1.2 triplet (3H) 2.2 quartet (2H) 7.4 two doublets (2H each) 10.2 singlet (IH)

   Elucidate the structure of **B** and assign δ values to the protons in it.

Structure elucidation of **B**:

Structure and assignment of δ values:

(30 marks)

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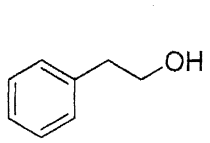
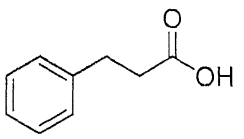
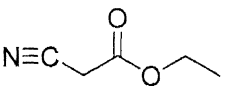
3. IR spectra given in the table belong to **THREE** of the following compounds labelled as **C, D, E** and **F**. Giving reasons select the correct compound responsible for each spectrum.



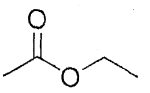
C



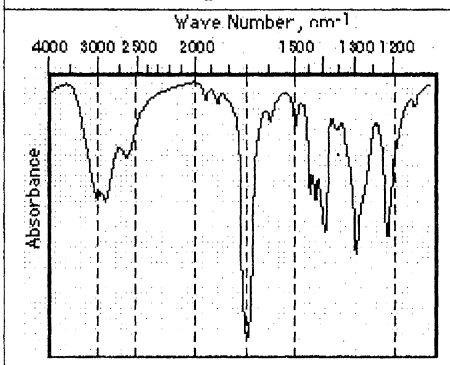
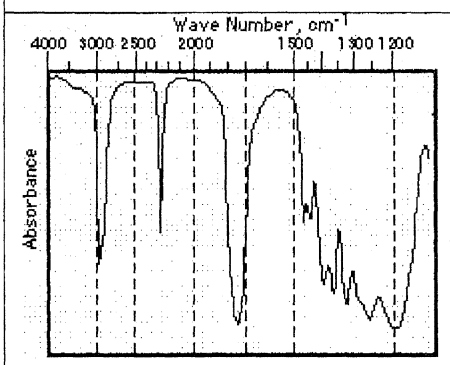
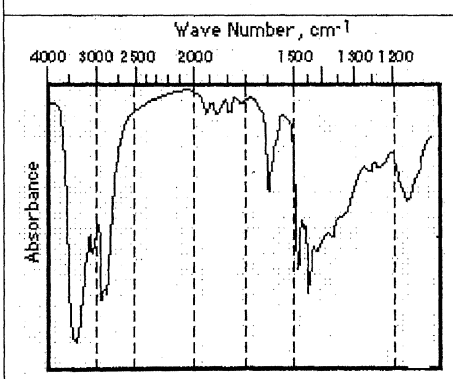
D



E

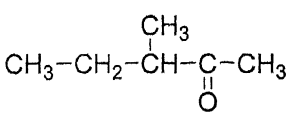


F

IR spectrum	Compound	Reasons
		....
		....
		....

(24 marks)

4. Draw the fragmentation pattern and the structures of ions responsible for the peaks at m/z 43 and 72 in the EI mass spectrum of compound **G**.



G

(16 marks)

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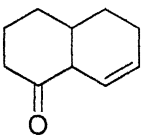
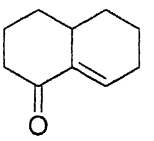
5. Give **ONE** major difference that you could observe in the **spectra** of each pair of compounds listed below.

(i) IR spectra of



and



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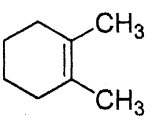
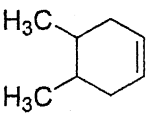
(ii) ^{1}H NMR spectra of



and



....

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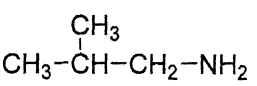
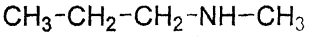
(iii) Mass spectra of



and



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....

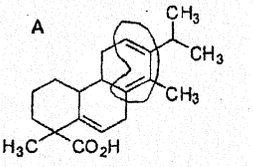
(18 marks)

THE OPEN UNIVERSITY OF SRI LANKA
B.Sc Degree Programme and Stand Alone Courses in Science - 2012/2013
CMU2221/CME 4221 - Organic Chemistry 1 CAT I - Answer guide

1.

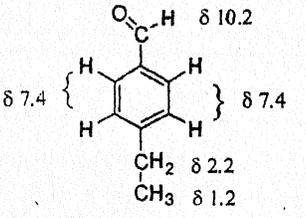
Basic value for Homoannular diene		= 253 nm
Alkyl substituent or ring residue	x 5	= +25 nm
Exocyclic double bond		= +05 nm
λ_{max}		283 nm

A



2.

IR absorption at ν_{max} 1725 cm^{-1} → carbonyl or aliphatic C=C group
Positive Brady's Test → aldehyde or ketone (confirms presence of carbonyl group)
^{1}HNMR signals
δ 1.2 → methyl group region; $-CH_3$ group
δ 2.2 → $-CH_2$ group
3H triplet- 2H quartet splitting pattern → CH_2 and CH_3 attached to each other $-CH_2CH_3$ group
δ 7.4 → aromatic region; to get two doublets of 2H each, benzene ring should be *para* di-substituted.
δ 10.2→ singlet due to one H; since it is deshielded it can be attached to the carbonyl group. –CHO group

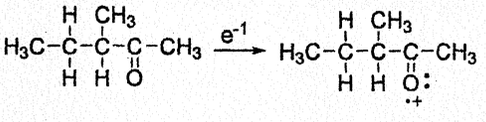


3.

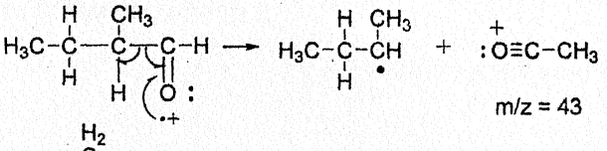
D	• peak at ~1700 cm^{-1} indicating a carbonyl (-C=O) group and a broad –O-H absorption at ~2500 – 3500 cm^{-1} overlapping with –C-H absorptions indicates a carboxyl (-COOH) group • Peak for aromatic C=C bond at 1450 cm^{-1} – 1600 cm^{-1} range
E	• Peak at ~ 2200 cm^{-1} – 2300 cm^{-1}(triple bond region) indicates a cyanide group (-C≡N) • Peak at ~ 1750 cm^{-1} indicates carbonyl group (-C=O), higher absorption frequency due to ester carbonyl
C	• Absence of peak ~1700 cm^{-1} : No carbonyl group • absorption above 3000 cm^{-1} due to O-H stretching

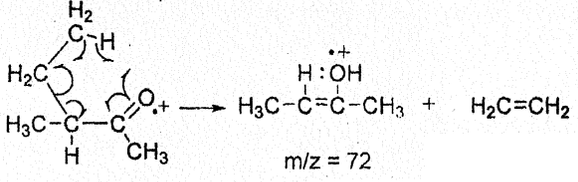
4.

Molecular ion [M^+] formation



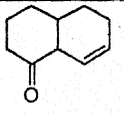
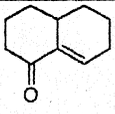
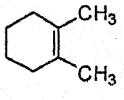
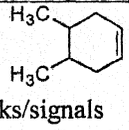
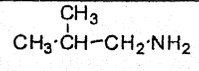
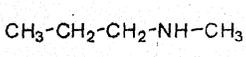
Fragmentation of the molecular ion





McLafferty Rearrangement

5.

(i) IR spectra of  and 	
• ketone is unconjugated. ∴ carbonyl absorption at ~ 1700 -1800 cm^{-1}	• ketone is conjugated. ∴ absorption is comparatively at a lower frequency.
(ii) ^{1}H NMR spectra of  and 	
• 3 peaks/signals • No vinyl proton signal • 6H singlet for CH_3	• 4 peaks/signals • 2H quartet for vinylic protons / 2H quartet for CH=CH • 6H doublet for CH_3
(iii) Mass spectra of  and 	
• Peaks at m/e 57 and 16 • No peaks at m/e 64 and 29	• No peaks at m/e 57 and 16 • Peak at m/e 64 and 29