M. SC. (Analytical Chemistry) / M. SC. (Organic Chemistry) /M. SC. (Inorganic Chemistry) Sem-II (Choice Based Credit & Grade System) : SUMMER - 2019

SUBJECT: ORGANIC CHEMISTRY - II

Day : Saturday
Date : 13/04/2019

S-2019-1174

Time : 03.00 PM TO 06.00 PM
Max. Marks : 60

N.B.:

1) All questions are **COMPULSORY**.
2) Figures to the right indicate **FULL** marks.
3) Answers to both the sections should be written in **SEPARATE** answer books.

SECTION – I

Q.1 Attempt **ANY THREE** of the following: **[15]**

a) Discuss the mechanism and applications of Dakin's reaction.

b) Explain the preparation of organo-lithium compounds. How are they useful for the preparation of alcohols, aldehydes and ketones?

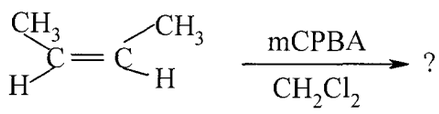
c) Discuss the mechanism and applications of Stobbe condensation.

d) Explain reduction of carbonyl compounds by $LiAlH_4$.

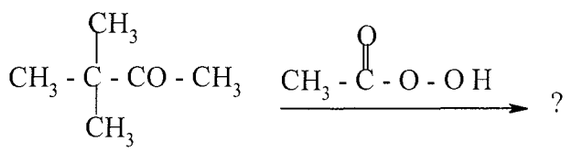
e) Write a note on : Oppenauer oxidation.

Q.2 Predict the product/s in **ANY THREE** of the following reactions by giving mechanism. Justify your answer: **[15]**

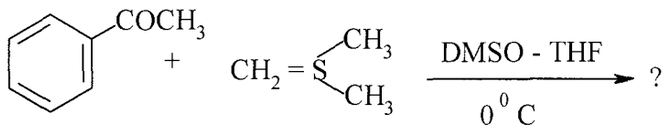
a)



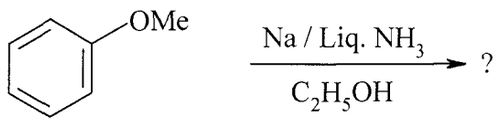
b)



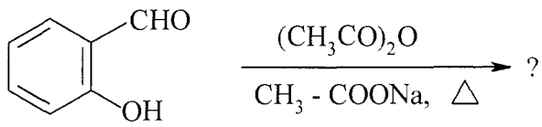
c)



d)



e)



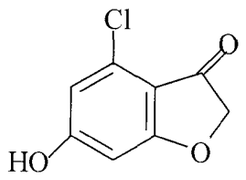
P.T.O.

SECTION – II

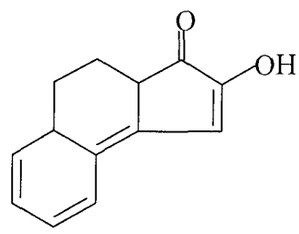
Q.3 Attempt **ANY THREE** of the following: **[15]**

a) Calculate λ_{max} for the following:

i)



ii)



b) On the basis of the data given below suggest the probable structures to the compounds:

i) MF : $C_8H_{14}O$, Iodoform test positive, IR : 1690 cm^{-1} and λ_{max} 250 nm.

ii) MF : $C_6H_{10}O$, Iodoform test negative, IR : 2720, 1700 cm^{-1} and λ_{max} 240 nm.

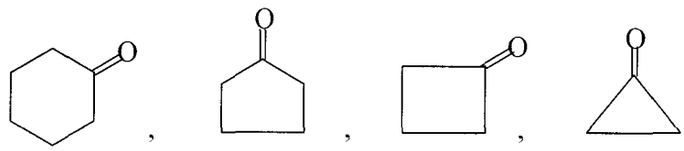
c) **i)** What are base peaks and molecular ion peaks in MS?

ii) Explain with suitable example Mac-Lafferty rearrangement.

d) **i)** Explain the effect of solvent on chemical shift of hydrocyl proton in alcohol.

ii) Use of Deuteration technique in PMR spectroscopy.

e) Carbonyl stretching frequency increases in the following order. Explain



Q.4 Assign the structure to **ANY THREE** of the following: **[15]**

a) MF : $C_9H_{10}O_3$
UV : λ_{max} 220 nm
IR : 2500 - 3000, 1715, 795 cm^{-1}
PMR : δ 3.57 (2H, s)
: δ 3.90 (3H, s)
: δ 6.95 (2H, d, J = 8Hz)
: δ 7.26 (2H, d, J = 8Hz)
: δ 11.8 (1H, bs, Exchangable)

b) MF : C_5H_8O
UV : Featureless
IR : 1649, 1242, 690cm^{-1}
PMR : δ 1.8 (quin, J = 6Hz, 2H)
: δ 1.95 (m, 2H)
: δ 3.9 (t, J = 6Hz, 2H)
: δ 4.62 (m, 1H)
: δ 6.3(m, 1H)

...2

c) MF : C_5H_6O
IR : 1600, 1500cm^{-1}
PMR : δ 2.3 (s, 3H)
: δ 5.85(d, J = 2Hz, 1H)
: δ 6.2 (dd, J = 1.5 and 2Hz, 1H)
: δ 7.2 (d, J = 1.5 Hz, 1H)

d) MF : C_9H_9N
IR : 2240, 1600, 1500 cm^{-1}
PMR : δ 2.3 (t, J = 7Hz, 2H)
: δ 2.5 (t, J = 7Hz, 2H)
: δ 7.2 (m, 5H)

e) MW : 92
m/e : 91, 65
IR : 1600, 1505 cm^{-1}
UV : 255 nm
PMR : δ 7.3 (s, 5H)
: δ 2.3 (s, 3H)

* * * *

Table 1 :

Some characteristic IR data in cm^{-1}. Only approximate values are listed.

≡ C–H 3300,	= C–H 3050
O = C – H 2800,	N–H 3300
O – H 3600 (free),	C ≡ N 2250
C ≡ C 2200,	C = C 1620 – 1680
Aromatic (C = C) 1600 to 1500,	– C = N 1660
Saturated ketone 1720,	Saturated ester 1750
Saturated acids 1720,	Saturated aldehydes 1730,
Saturated amides 1650	$CH = CH_2$ 900 and 910
CH = CH (trans) 960,	CH = CH – (cis) 690
$C = CH_2$ 890	C = CH 790 – 840
NO_2 1530 and 1050	

Bands for aromatic compounds depends on the number of adjacent free aromatic hydrogens :

5 free – 690 – 710 and 730 – 770

1 free 850 – 900,	4 free 735 – 770
3 free 750 – 810	2 free 770, 800 – 860

Table 2 :

Approximate chemical shifts on methyl, methylene and methine protons, in δ values TMS as internal reference.

$C – CH_3$ 0.9,	$O – C – CH_3$ 1.4
$C = C – CH_3$ 1.6,	$Ar – CH_3$ 2.3,
$O = C – CH_3$ 2.2,	$N – CH_3$ 2.3,
$S – CH_3$ 2.1,	$O - CH_3$ 3.3
C–H in cyclopropane 0.7,	$C = CH_2$ exocyclic 4.6,
$C = CH_2$ open chain 5.3	C – CH 5.1