M. SC. (Analytical Chemistry) / M. SC. (Organic Chemistry) /M. SC. (Inorganic Chemistry) Sem-II (Choice Based Credit & Grade System) : WINTER - 2018

SUBJECT : ORGANIC CHEMISTRY - II

Day : Friday
Date : 12/10/2018

W-2018-0985

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 Perkin's reaction.

b) What are phosphorus ylides? How are they prepared? Discuss their applications.

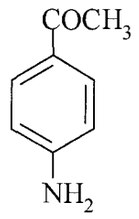
c) Explain regiospecific nature of organo-thallium compounds.

d) Discuss the mechanism and applications of Dieckmann condensation.

e) Write a note on : Birch reduction.

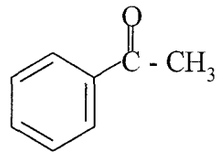
Q.2 Predict the product/s in **ANY THREE** of the following reactions by giving mechanism. Justify your answer: **[15]**

a)



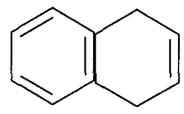
$\xrightarrow{H_2O_2 / \bar{O}H}$?

b)



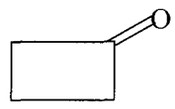
$\xrightarrow[(O)]{SeO_2}$?

c)



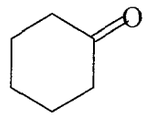
$\xrightarrow[ii)\ H_2O / H^+]{i)\ OsO_4 / Pyridine}$?

d)



$\xrightarrow[ii)\ H_2O / H^+]{i)\ LiAlH_4 / Ether}$?

e)



$\xrightarrow{Zn\ (Hg) / Conc.\ HCl}$?

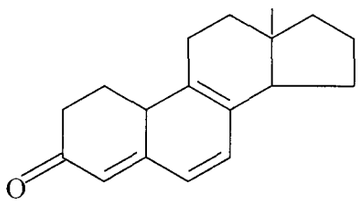
P.T.O.

SECTION – II

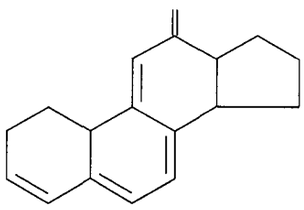
Q.3 Attempt **ANY THREE** of the following: **[15]**

a) Calculate λ_{max} for the following:

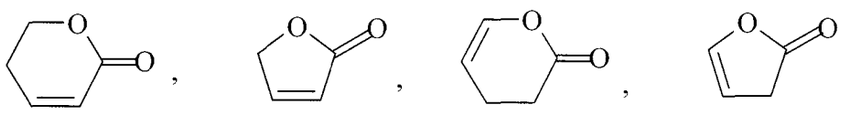
i)



ii)



b) Arrange the following compounds with their increasing order of IR streaching frequencies. Justify your answer.



c) **i)** PMR spectrum of acetonitrile shows shielded protons as compared to that of chloromethane. Explain.

ii) TMS is used as internal standard in PMR. Explain.

d) **i)** Explain molecular ion and base peak with suitable example.

ii) Explain double focusing technique in MS.

e) Explain o-Hydroxy acetophenone on methylation shows a blue shift while p-hydroxyacetophenone on methylation shows a red shift.

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

a) MF : $C_5H_6O_3$
UV : featureless above 210 nm
IR : 1820, 1770 cm^{-1}
PMR : δ 1.95 (quin J = 6Hz, 12 mm)
: δ 2.70 (t, J = 6Hz, 24 mm)

b) MF : $C_{10}H_{10}O_6$
UV : 206, 245, 251, 257, 263 nm (∈ 8300, 90, 120, 180, 140)
IR : 3600, 2220, 1600, 1490, 700 cm^{-1}
PMR : δ 1.7 s, 13 mm
: δ 2.5 s, 4.5 mm
: δ 2.9 s, 4.5 mm
: δ 7.2 m, 13 mm
: δ 7.55 m, 9 mm

c) MF : $C_{10}H_{15}N$
IR : 1510, 1610 cm^{-1}
PMR : δ 2.48 (s, 6H)
: δ 2.89 (s, 6H)
: δ 6.38 (bs, 2H)
: δ 7.27 (t, 1H)

...2

d) MF : $C_6H_{10}O_2$
IR : 1195, 1630, 1720 cm^{-1}
PMR : δ 1.3 (t, J = 7Hz, 3H)
: δ 2.0 (d, J = 7Hz, 3H)
: δ 4.2 (q, J) = 7Hz, 2H)
: δ 5.8 (d, J = 16Hz, 1H)
: δ 6.9 (dq J = 7 and 16 Hz, 1H)

e) MW : 122
m/e : 123, 122, 105, 77, 51
IR : 2500 – 3300 (br), 1690, 1504, 1485, 1285, 750, 690 cm^{-1}
UV : 272 nm
PMR : δ 12.69 (s, 1H)
: δ 8.20 (m, 2H)
: δ 7.60 (m, 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