M. SC. (ANALYTICAL CHEMISTRY) / M. SC. (ORGANIC CHEMISTRY) /M. SC. (INORGANIC CHEMISTRY) SEM-II (CHOICE BASED CREDIT & GRADE SYSTEM) : WINTER -2017

SUBJECT : ORGANIC CHEMISTRY-II

Day : Friday
Date : 27/10/2017

W-2017-0772

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

N.B.:

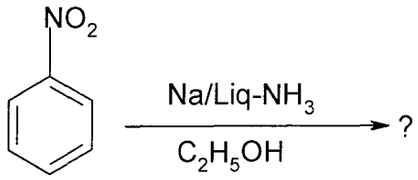
1) All questions are **COMPULSORY.**
2) Answers to both the sections should be written in **SEPARATE** answer books.
3) Figures to the **RIGHT** indicate full marks.

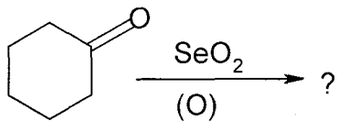
SECTION-I

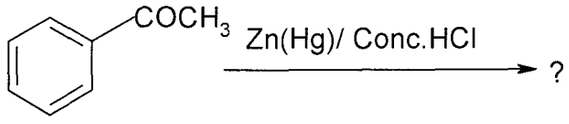
Q.1 Attempt any **THREE** of the following: **(15)**

a) What are sulphur ylides? How are they prepared? Discuss their applications.
b) What is Mannich reaction? Discuss its mechanism and applications.
c) Discuss the preparation of organolithium compounds. How are they useful for the preparation of alcohols, amines and cyanides?
d) Discuss the reduction of carbonyl compounds by $LiAlH_4$.
e) Write a note on : Oppenauer oxidation.

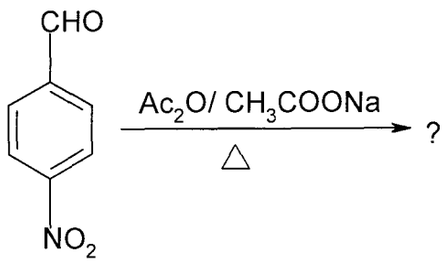
Q.2 Predict the products in any **THREE** of the following reactions by giving mechanism: Justify your answer. **(15)**

a) 

b) 

c) 

d) $H_5C_2OOC(CH_2)_4COOC_2H_5$ (I) C_2H_5ONa → ? (i) H_2O (ii) △

e) 

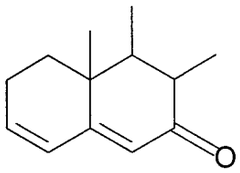
P.T.O.

SECTION-II

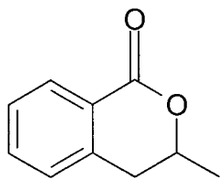
Q.3 Attempt any **THREE** of the following: **(15)**

a) Calculate λ_{max} for the following:

i)

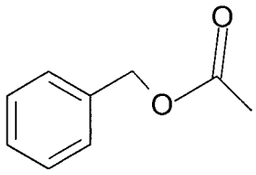


ii)



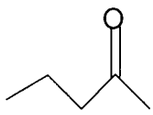
b) Explain genesis of the following ions:

(i)



m/e = 108, 91, 77, 43

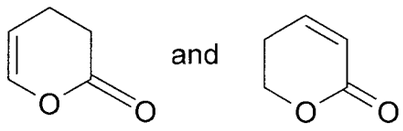
(ii)



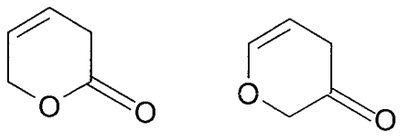
m/e = 86, 71, 58, 57, 43, 29

c) Distinguish between the following pairs by using IR spectroscopy.

i)

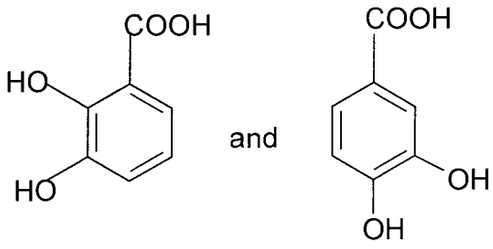


ii)

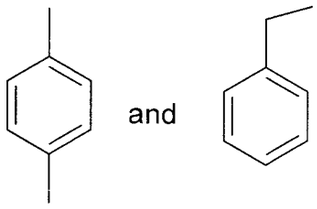


d) Distinguish between the following pairs by PMR spectroscopy.

i)



ii)



e) Write a note on: Spin-spin splitting.

Q.4 Assign the structure to any **THREE** of the following: **(15)**

a) MW: 122
m/e:122, 105, 77, 51
UV: λ_{max} 272 nm
IR: 2500 – 3000(br) 1690, 1602, 1504, 1486, 1285, 750 690 cm^{-1}
PMR: 7.6 δ (m, 2H)
8.2 δ (m, 2H)
12.7 δ (s, 1H)

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
C ≡ CH cyclic 5.3,	Ar – H 7 to 9

b) MF: C_8H_7N
IR: 2220, 1600, 1520 cm^{-1}
UV: 235 nm
PMR : 7.5 δ (d, J = 8Hz, 10 mm)
7.2 δ (d, J = 8Hz, 10 mm)
2.4 δ (s, 15 mm)

c) MF : C_4H_8O
UV : 290 nm
IR : 1715 cm^{-1}
PMR: 1.07 δ (t, J = 6Hz, 3H)
2.12 δ (s, 3H)
2.48 δ (q, J = 6Hz, 2H)

d) MF : $C_6H_{12}O_2Cl_2$
IR: 1150, 1240, 670 cm^{-1}
PMR : 1.2 δ (t, 6H)
3.7 δ (q, 4H)
4.2 δ (d, 1H)
4.6 δ (d, 1H)

e) MF: $C_5H_{10}O$
m/e: 85, 56, 29 amu
UV: 285 nm
IR: 1720 cm^{-1}
PMR: 1.05 δ (t, 30 mm)
2.40 δ (q, 20 mm)

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