M. SC. (Analytical Chemistry) / M. SC. (Organic Chemistry) / M. SC. (Inorganic Chemistry) Sem-II (CBCS – 2018 Course) : SUMMER - 2019

SUBJECT : ORGANIC CHEMISTRY – II

Day : Tuesday
Date : 16/04/2019

S-2019-1167

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 book.

SECTION – I

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

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

b) Discuss the preparation and applications of organo magnesium compounds.

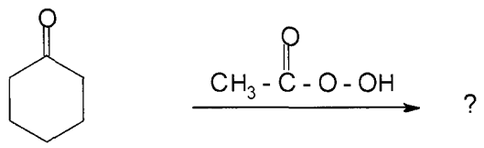
c) Discuss the reduction of carbonyl group by $NaBH_4$.

d) Explain the oxidation of olefins by peracids.

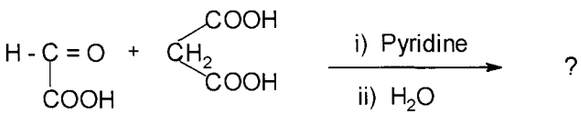
e) Write a note on : Phosphorous ylides.

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

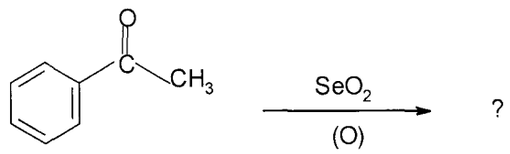
a)



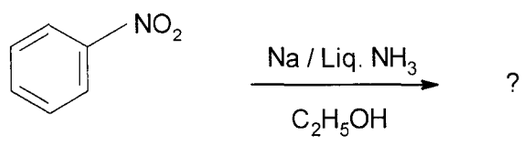
b)



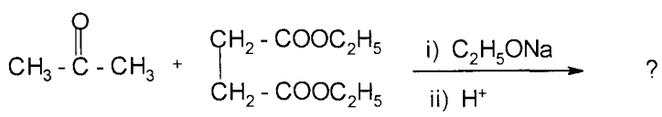
c)



d)



e)



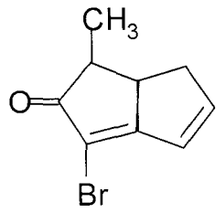
P.T.O.

SECTION – II

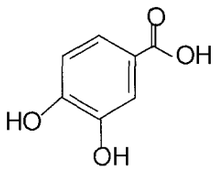
Q.3 Attempt **ANY THREE** of the following: **[15]**

a) Calculate λ_{max} for the following compound:

i)

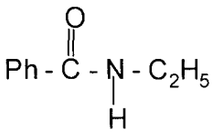


ii)

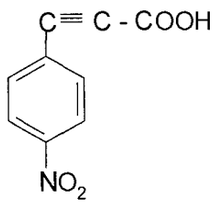


b) What information regarding the structure of the compound you can get from the IR spectrum of the following compounds?

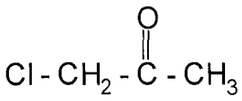
i)



iii)



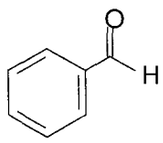
ii)



c) Hydrogenation of Ph – C ≡ C – COOH gives two isomeric products. How will you differentiate these two by NMR spectroscopy?

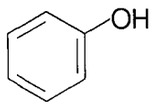
d) Explain the genesis of ions in the following compounds:

i)



106, 105, 77, 51

ii)



94, 66, 65

e) **i)** Explain why ethylacetoacetate shows IR bands at 3300, 1750, 1720, 1660 and 1620 cm^{-1}.

ii) PMR spectrum of acetonitrite shows shielded protons as compared to that of chloromethane.

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

a) MF : C_3H_6O
IR : 1200 – 1280 cm^{-1}
PMR : 1.32 δ (3H, d, J = 6 Hz)
: 2.42 δ (1H, dd, J = 3.5 and 2.5 Hz)
: 2.72 δ (1H, dd, J = 3.5 and 3.00 Hz)
: 2.98 δ (1H, ddq, J = 2.5, 3.00, 6.00 Hz)

b) MF : $C_7H_{12}O_4$
IR : 1742 cm^{-1}
PMR : 2.6 δ (2H, s)
: 1.3 δ (6H, t, J = 6.5 Hz)
: 4.6 δ (4H, q, J = 6.5 Hz)

c) MF : $C_{10}H_{10}O$
IR : 3600, 3320, 2210, 1600, 1490 cm^{-1}
PMR : 1.7 δ (3H, s)
: 2.5 δ (1H, s)
: 2.9 δ (1H, s, D_2O exchange)
: 7.2 δ (3H, m)
: 7.55 δ (2H, m)

d) MF : $C_5H_4O_2$
IR : 2700, 1670 cm^{-1}
PMR : 6.03 δ (1H, dd, J = 5Hz and 2 Hz)
: 7.27 δ (1H, d, J = 5 Hz)
: 7.72 δ (1H, d, J = 2 Hz)
: 9.07 δ (1H, s)

e) MW : 122
m/e : 122, 105, 77, 51
IR : 2500 – 3300 (br), 1690, 1602, 1504, 1485, 750, 690 cm^{-1}
PMR : 12.69 δ (1H, s)
: 8.20 δ (2H, m)
: 7.60 δ (3H, m)

* * * *

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