BIRLA INSTITUTE OF TECHNOLOGY, MESRA, RANCHI
(END SEMESTER EXAMINATION)

CLASS: MSC/IMSC/PRE-PHD **SEMESTER : III/IX/NA**
BRANCH: CHEMISTRY **SESSION : MO/2022**

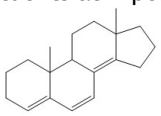
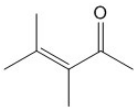
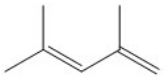
SUBJECT: CH501 SPECTROSCOPIC ELUCIDATION OF MOLECULAR STRUCTURE
TIME: 3:00 Hours **FULL MARKS: 50**

INSTRUCTIONS:
1. The question paper contains 5 questions each of 10 marks and total 50 marks.
2. Attempt all questions.
3. The missing data, if any, may be assumed suitably.
***4*. Before attempting the question paper, be sure that you have got the correct question paper.**
5. Tables/Data hand book/Graph paper etc. to be supplied to the candidates in the examination hall.

Q.1(a) How to detect by IR spectroscopy, the presence of: 2(1+1)
(i) intramolecular hydrogen bonding in a hydroxyl compound
(ii)highly hindered hydroxyl group

Q.1(b) Discuss the major intramolecular factors effecting carbonyl frequency. 3

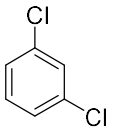
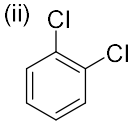
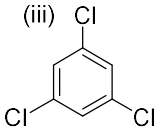
Q.1(c) Using Woodward - Fieser rule calculate λmax for following: 3
Core- α,β-unsaturated ketone =+ 215 nm, Substituents at α-position-= + 10 nm
Substituents at β-position = 12 nm

(i)  (ii)  (iii) 

Q.1(d) Explain the effect of solvent polarity on the λmax of π to π* and n to π* electronic transition with the help of example. 2

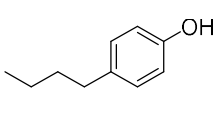
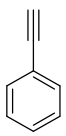
Q.2(a) Answer the following questions question (Either 2(A) or 2(B) 3+2+2+3=10
2(A) (i) Draw a clean diagram for the ^{1}H-NMR spectrum of $CH_3CH_2CH_2Br$ mention the multiplicities of different signals.
(ii) Explain the multiplicities based on Spin-spin coupling.
(iii) Draw a COSY NMR spectrum for the above-mentioned compound.
(iv)And correlate with ^{1}H NMR spectra.

Q.2(b)
2(B) (i) How can you distinguish the following molecules by ^{1}H NMR spectroscopy?

(i)  (ii)  (iii) 

(ii) Why TMS is used as reference compound for ^{1}H NMR spectrum?
(iii)Arrange the following compounds in order of increasing chemical shifts (δ- value) of the α -protons with explanation.
(a)$CH_3CH_2CH_2F$, (b) $CH_3CH_2CH_2I$, (c) $CH_3CH_2CH_2Br$, (d) $CH_3CH_2CH_2Cl$
(iv) Draw ^{1}H NMR spectrum of p-chloronitrobenzene. Explain the relative chemical shifts of different aromatic protons and splitting pattern.

Q.3(a) Outline the fragmentation pattern in MS of the following compounds and indicate the base peak. 2.5+2.5=5

(i)  (ii) 

Q.3(b) The base peak of most methyl ketones is at m/z 43. Explain the reason with suitable example. 2

Q.3(c) Compare and contrast the MS fragmentation pathways of alkyl fluorides, chlorides, bromides and iodides. 3

Q.4(a) Outline how Mossbauer spectroscopy can be applied to determine the oxidation state on 'Sn' in an organotin compound? 2

Q.4(b) Give the ESR spectrum (lines) of the following: 2
(i) $[Ti(H_2O)_6]^{+3}$, I_{Ti}= 3/2 (ii) $*CH_2D$ radical , I_D= 1, I_C=1/2 (iii) $[Cu(NH_3)_4]^{+2}$, I_N = 1, I_{Cu} = 3/2
(iv) $^{13}*CF_2H$ radical , I_C, I_F & I_H =1/2

Q.4(c) Diagrammatically show ESR peaks, electronic transitions and give their intensity ratio for Na atom (I=3/2) and *NH3 radical (I_N=1). Give Kramer's doublet for Cr^{+3} and Ti^{+2}. 4

Q.4(d) Explain the instrumentation of ESR Spectrometer with the help of block diagram and also mention any two applications. 2

Q.5 An organic compound 'A' $C_6H_{12}O_2$ on heating with Na/xylene produce another compound 'B', $C_6H_{12}O_2$ along with an alcohol C_3H_8O which does not give iodoform test. Oxidation of compound 'B' with Bi_2O_3/ ACOH generates compound 'C', $C_6H_{10}O_2$ which shows one quartet and one triplet signals in ^{1}H-NMR spectrum and a characteristic IR band at 1730 CM^{-1}. Treatment of compound 'C' with excess C_2H_5MgBr followed by usual workup gives compound 'D', $C_{10}H_{22}O_2$ which shows one quartet (8H), one triplet (12H) and a broad peak(2H) in ^{1}H-NMR spectrum and broad IR band at 3350 cm^{-1}. Heating the compound 'D' with dil. H_2SO_4 (1:1) affords 'E' $C_{10}H_{20}O$ containing two types of ethyl groups and showing an IR band at 1710 cm ^{1}. Write down all the reaction involved and identify the compound A, B, C, D and E. 5 x 2=10

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