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Nos. of printed pages : 4

SARDAR PATEL UNIVERSITY
B.Sc.(SEMESTER V) EXAMINATION
2013
Tuesday, 12th November
10.30 am to 1.30 pm
INDUSTRIAL CHEMISTRY
US05CICH01(ORGANIC CHEMISTRY – II)

Maximum marks : 70

Q. 1 MULTIPLE CHOICE QUESTION |10|

1. Pyridine reacts with a mixture of KNO_3 and H_2SO_4 at 300°C to give
   (a) 1-Nitropyridine (b) 2-Nitropyridine
   (c) 3-Nitropyridine (d) 4-Nitropyridine
2. One signal is observed in
   (a) CH_3COCH_3 (b) $CH_3CH_2COCH_3$
   (c) CH_3CH_2OH (d) $CH_3CH_2COOCH_3$
3. Naphthalene undergoes nitration with HNO_3 H_2SO_4 at 60°C to give mainly
   (a) 1-Nitronaphthalene (b) 1,2-Dinitronaphthalene
   (c) 2-Nitronaphthalene (d) 1,5-Dinitronaphthalene
4. Osmium Tetraoxide is used for...
   (a) Reduction (b) Oxidation
   (c) Hydroxylation (d) Methylation.
5. Pyrrole is less basic than pyridine because the lone-pair of electrons on N-atom in pyrrole
   (a) is part of the delocalised π molecular orbital.
   (b) is not part of the delocalised π molecular orbital
   (c) resides in sp^2 hybrid orbital
   (d) resides in sp hybrid orbital
6. The internal standard used in NMR spectra is
   (a) Tetramethyl silane (b) Trimethyl silane
   (c) Tetraethyl silane (d) Triethyl silane
7. In a base catalyzed reaction, α-diketones are converted to α-hydroxy acids are called _____reaction.
   (a) Diels–Alder Reaction. (b) Pinacol–Pinacolone Rearrangement
   (c) Benzilic Acid Rearrangement (d) Fries Rearrangement
8. _____ is a valuable reagent for brominating specifically allylic and benzylic positions.
   (a) $(Me_2CHO)_3Al$ (b) NBS
   (c) $LiAlH_4$ (d) OsO_4
9. Anthracene undergoes oxidation with $O_2 - V_2O_5$ at 500°C to give
   (a) Benzoic acid (b) Anthraquinone
   (c) Phthalic acid (d) Phenylacetic acid
10. How many NMR signals do you expect from Acetone and Ethanol?
    (a) 1 & 2 respectively (b) 1 & 3 respectively
    (c) 2 & 3 respectively (d) None of these

Q.2 ANSWER ANY TEN **[20]**

1. Give synthesis of α- and β-Naphthol from Naphthalene.
2. What happens when
   (a) Toluene + $[Pb(OAc)_4] \rightarrow ?$ (b) $CH_3(CH)_2CH_2CH{=}CHCH_3 + NBS \rightarrow ?$
3. Name the reaction which involves
   i. The reduction of aldehydes or ketones to alcohols by treatment with aluminum iso-propoxide in excess of isopropyl alcohol.
   ii. The 1,4 –addition of an alkene to a conjugated diene to form an adduct of six-membered ring.
4. Write two applications of N- bromosuccinimide.
5. Give rules for naming mono heterocyclic compound.
6. How many signals would you see in the NMR spectra of the following compounds?
   (a) Butanone (b) p-xylene
7. Which reagents will react with furan to form 2-furansulphonic acid ?
8. Give synthesis of Aluminum isopropoxide
9. Name the reagent which
   i. oxidises methylene group into carbonyl group.
   ii. reduces carbonyl compounds to alcohols without affecting other sensitive reducible groups.
10. Compare the basicity of Pyridine with that of Pyrrole.
11. Differentiate the term Reaction and Rearrangement.
12. Write the resonance structures of Anthracene and Naphthalene.

Q.3

1. "Pyridine undergoes nucleophilic substitution more readily at 2 or 4 position." justify **[5]**
2. Explain Chichibabin reaction. **[5]**

OR

Q.3

1. Discuss the important properties of Pyridine and discuss its constitution. **[5]**
2. Discuss the structure of Thiophene **[5]**

Q.4

1. Predict giving reasons, whether Anthracene is more likely to undergo electrophilic substitution at the 1, 2 or 9-position. **[5]**
2. Write notes on Buchere reaction. **[5]**

OR

Q.4

1. How will you arrive at the structure of Naphthalene? **[5]**
2. Give synthesis of Anthracene. **[5]**

Q.5

1. Explain Diels Alder and Benzilic Acid rearrangement reaction mechanism with suitable example. **[10]**

OR

Q.5

1. Write the preparation and uses of Lead tetra acetate and Selenium dioxide. **[10]**

Q.6

1. What is meant by multiplicity of peaks? How does it arise and what can it tell about molecular structure. **[5]**
2. From the following sets of N.M.R., IR and UV data, give a structure consistent with each of the following: **[5]**

   Molecular weight: 88 gm/mol; %age: C=54.54%, H=13.64%, N=31.82%; UV: λmax: 220nm; IR: 2860, 1120 cm^{-1}.; NMR: δ 3.6 (singlet, for all protons).

OR

Q.6

1. What is meant by the term Chemical Shift of a particular proton in NMR Spectroscopy? Draw the splitting patterns of protons in NMR spectrum of ethyl alcohol. **[5]**
2. From the following sets of N.M.R., IR and UV data, give a structure consistent with each of the following: **[5]**

   Molecular weight: 130gm/mol; %age: C=73.84%, H=13.84% and O=12.34%; UV: λmax: 200nm; NMR: δ 1.1 (singlet for all protons).

CHARACTERISTIC IR ABSORPTION FREQUENCY

Bond	Compound type	Frequency range cm^{-1}
C-H	Alkanes.	2850-2960, 1350-1470.
C-H	Alkenes.	3020-3080 (*m*), 675-1000.
C-H	Aromatic rings.	3000-3100 (*m*), 675-870.
C-H	Alkynes.	3300
C=C	Alkenes.	1640-1680 (*v*)
C≡C	Alkynes.	2100-2260 (*v*)
C=C	Aromatic rings.	1500, 1600 (*v*)
C-O	Alcohols, Ethers, Carboxylic acids, Esters.	1080-1300
C=O	Aldehyde, Ketones, Carboxylic acids, Esters.	1690-1760
O-H	Monomeric alcohols, Phenols	3610-3640 (*v*)
	Hydrogen bonded alcohols, Phenols.	3200-3600 (*broad*)
	Carboxylic acids.	2500-3000 (*broad*)
N-H	Amines.	3300-3500 (*m*)
C-N	Amines.	1180-1360.
C≡N	Nitriles.	2210-2260 (*v*)
$-NO_2$	Nitro compounds	1515-1560, 1345-1385

Characteristic Proton Chemical Shift

Double Bonds	
Structure unit	Frequency cm^{-1}
C=C	1620-1680
C=O	
Aldehydes and ketones	1710-1750
Carboxylic acids	1700-1725
Acid anhydrides	1800-1850 & 1740-1790
Acyl halides	1770-1815
Esters	1730-1750
Amides	1680-1700
Substituted derivatives of Benzene	
Mono substituted	730-770 & 690-710
Ortho-disubstituted	735-770
Meta-disubstituted	750-810 & 680-730
Para-disubstituted	790-840

Type of Proton		Chemical shift δ, ppm	Type of Proton		Chemical shift δ, ppm
zCyclopropane		0.2	Alcohols	H-C-OH	3.4 – 4
Primary	$R\text{-}CH_3$	0.9 -1.8	Ethers	H-C-OR	3.3 – 4
Secondary	R_2CH_2	1.3	Esters	RCOO-C-H	3.7 – 4.1
Tertiary	R_3CH	1.5	Esters	H-C-COOR	2 – 2.2
Vinylic	C=C-H	4.6 -5.9	Acids	H-C-COOH	2 – 2.6
Acetylenic	C≡C-H	2 - 3	Carbonyl compounds	H-C-C=O	2 – 2.7
Aromatic	Ar-H	6 - 8.5	Aldehydic	RCH=O	9 – 10
Benzylic	Ar-C-H	2.2 - 3	Hydroxylic	RO-H	1 – 5.5
Allylic	C=C-C-H	1.7	Phenolic	ArO-H	4 – 12
Fluorides	H-C-F	4 - 4.5	Enolic	C=C-O-H	15 – 17
Chlorides	H-C-Cl	3 - 4	Carboxylic	RCOO-H	10.5 – 12
Bromides	H-C-Br	2.5 - 4	Amino	$R\text{-}NH_2$	1 – 5
Iodides	H-C-I	2 - 4			

— XXX —