

Five Year Integrated M.Sc. Examination, 2017

Semester - VI

Course: CH-3-6-2

(Chemistry)

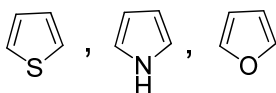
Time: Four Hours

Full Marks: 80

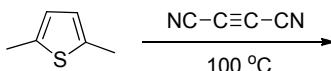
Questions are of value as indicated in the margin.

Group-A

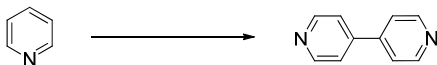
1. Answer **any ten** of the following: 10x2=20
- Write down general unit cell dimensions of monoclinic and hexagonal system.
 - Write down coordinates of lattice points of unit cell of hexagonal systems.
 - Calculate distance between two successive 111 planes of orthorhombic cell with $a = 3 \text{ \AA}$, $b = 4 \text{ \AA}$ and $c = 5 \text{ \AA}$.
 - Which of following lattices do not exist: C-centered tetragonal, Body centered orthorhombic, A-centered cubic, primitive hexagonal?
 - Arrange the following heterocycles in decreasing order of their dipole moment:



- Pyrrole-2-aldehyde does not undergo Cannizzaro reaction whereas furan-2-aldehyde does.
- Identify the products of the following reaction with proper explanation :



- Accomplish the following transformation indicating appropriate reagents. Give mechanism :



- The Landé splitting factor (g_N) is the characteristic property of the nucleus. Explain.
- Define the term “shielding constant”. What is its role in NMR spectroscopy?
- ESR spectra always record in derivative mode. Why?
- The benzene radical anion has $g = 2.0025$. At what field should you search for resonance to occur in a spectrometer operating at 9.302 GHz?

Group-B

Answer **any two** questions.

- Define the following terms: unit cell and lattice. 2
 - Describe the structure of spinel. Identify the types of spinel structures from the following compounds with proper explanations: Fe_3O_4 , Mn_3O_4 and Co_3O_4 . 2+6
- Discuss the diamond structure in terms of close packing (statement only). Calculate packing fraction of diamond system and mention coordinates of all the lattice points. 2+4
 - Describe and draw fluorite structure. Draw the conventional layer sequence of fluorite of structure. 2+2
- Compare between rock salt and zinc blende structure. 2
 - Describe and draw the ReO_3 structure and derive perovskite structure from this. 4
 - Calculate the effective number of octahedral and tetrahedral holes within a unit cell of FCC lattice. 2
 - Generally all metals at a very high temperature tend to adopt the bcc structure. Justify. 2

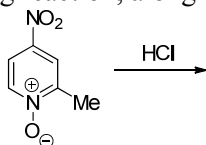
P.T.O.

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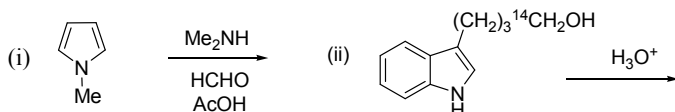
Group-C

Answer *any two* questions.

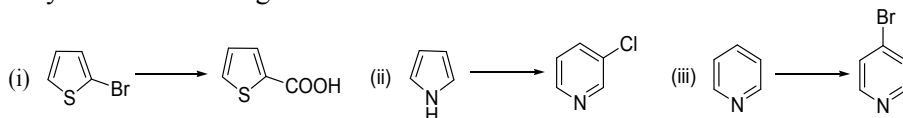
5. a) Write the product of the following reaction, along with the mechanism involved. 1.5



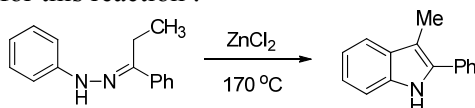
- b) Identify the product(s) of the following reactions with proper mechanism 4



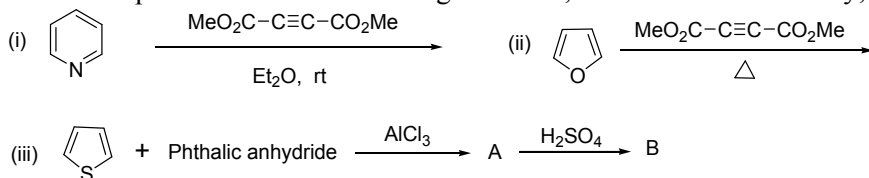
- c) Carry out the following conversions : 4.5



6. a) Suggest mechanisms for this reaction : 3

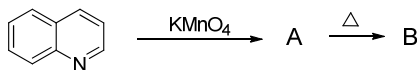


- b) Predict the product/s for the following reactions, include stereochemistry, if any: 2.5+2+2.5

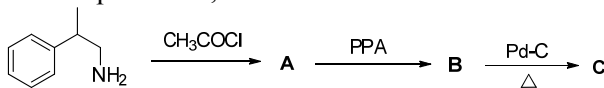


7. a) Give the synthesis of quinoline through Skraup reaction. 3

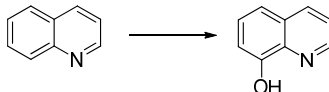
- b) Identify A and B: 2



- c) Draw structures for compounds A, B and C. 3



- d) Carry out the following conversion: 2



Group-D

Answer *any two* questions.

8. a) What is chemical shift (δ) in NMR spectra? Why does it appear in NMR spectra? Why do you need a reference material to report the chemical shift of a nucleus in NMR spectra? Name one of such reference material and discuss its advantages over the other material. 6

(3)

- b) A radical containing two equivalent protons shows a three-line spectrum with an intensity distribution 1:2:1. The lines occur at 330.2 mT, 332.5 mT and 334.8 mT. What is the hyperfine coupling constant for each proton? What is the g-value of the radical given that the spectrometer is operating at 9.332 GHz. 4
9. a) A molecule having two unpaired electrons shows two lines instead of one in ESR spectra. Explain with suitable diagram. 3
- b) Sketch a hyperfine spectrum of $^{\circ}\text{NH}_2$ radical, where, spin quantum number for ^{14}N and ^1H nucleuses are 1 and $\frac{1}{2}$, respectively. What are their intensities? 3+1
- c) A particular n.m.r. instrument operates at 60.512 MHz. What magnetic field is required to bring ^1H nucleus to resonance at this frequency?
[Given, $g_{\text{N}} = 5.585$ and $\beta_{\text{N}} = 5.05 \times 10^{-27} \text{ JT}^{-1}$]. 3
10. a) What do you mean by positive coupling and negative coupling? Do they make any changes in the pattern of NMR spectra? Discuss with suitable example and proper diagram. 2+1
- b) Write the McConnell's equation and explain the terms in it. How can you prove that the electron density over a nucleus should be replaced with the spin density of an electron? 1+2
- c) What is quadrupole moment? Why does it appear in a particular nucleus? Draw the NMR spectra of acidified methylamine molecule and explain the pattern if you find any abnormality. 1+1+2
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