182002

COMBINED COMPETITIVE EXAMINATION (MAIN)

CHEMISTRY

Paper–II

Time : 3 Hours *Full Marks* : 200

Note : *(1) The figures in the right-hand margin indicate full marks for the questions.*

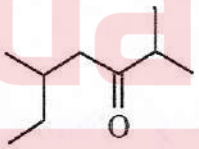
*(2) Attempt **five** questions in all.*

(3) Question No. 1 is compulsory.

1. Answer any ***ten*** questions from the following : 4×10=40

(a) Out of *cis*-1,2-dichloroethylene and *trans*-1,2-dichloroethylene, which one will have more dipole moment and why?

(b) Write the IUPAC names of the compounds represented by

(i)  and *(ii)* C_6H_5COCl.

(c) Differentiate between linear, branched and cross-lined polymers.

(d) Write the Woodward-Hoffmann rules for [2+2] cycloaddition reactions.

(e) Explain why CH_3OCH_2Cl undergoes substitution by the S_N1 mechanism even though it has a 1°-substrate carbon.

(f) How is electronegativity going to influence the chemical shift value?

(g) Why is Et_4N^+ neither an electrophile nor a nucleophile?

(h) Why do the peaks in a UV spectrum appear as broad? Explain with the help of an energy diagram.

(i) How will you distinguish between CH_3COSH and CH_3CSOH by IR technique?

(j) Which of the following will not show ESR spectra? Give explanation.

(i) O_2 (ii) C_2H_5 (iii) N_2 and (iv) Cu^{2+}

(k) What are hot bands?

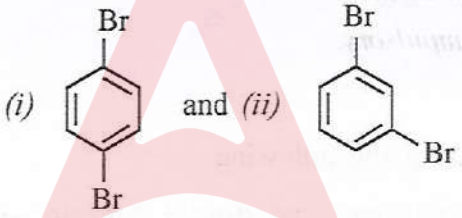
(l) Which one is more acidic— *o*-nitrophenol or *m*-nitrophenol? Give reason.

2. Answer any ***eight*** questions from the following : 5×8=40

(a) Suggest the mechanism of CO loss from phenol molecular ion.

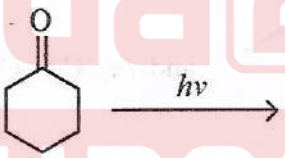
(b) Justify that the population in the ground state vibrational level of a diatomic molecule is more than an excited state.

(c) What will be the multiplicities of the protons in 1H NMR spectra of the following compounds?



(d) What are metastable ions in a mass spectrometric experiment?

(e) Write the product of the following reaction :



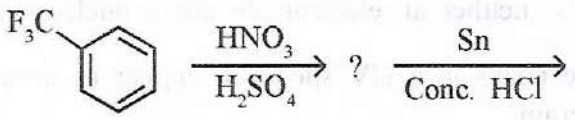
Norrish type I reaction

(f) For a solution, calculate the absorbance *(A)* at 50% transmittance *(T)*

(g) Describe the role of $AlCl_3$ in Friedel-Crafts alkylation reaction from mechanistic point of view.

(h) What is the relationship between relaxation and line broadening in NMR spectroscopy?

(i) Write the product(s) in the following reaction :

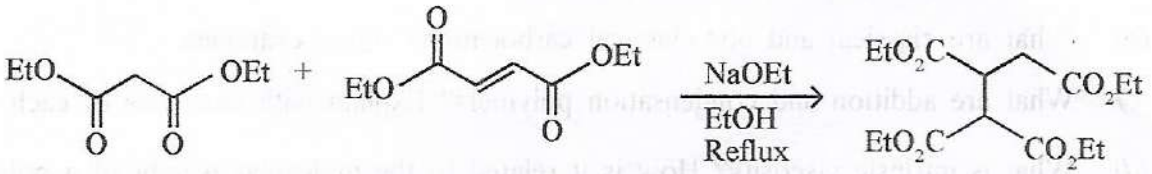


(j) With a schematic diagram describe the bonding in acetylene.

3. Answer any ***five*** questions from the following : 8×5=40

(a) With suitable examples, elaborate the stereochemical outcome of addition of bromine to an alkene.

(b) Write the mechanism of the following reaction :



(c) Sketch the potential energy function of an harmonic oscillator and indicate the energy levels.

(d) Describe McLafferty rearrangement taking a suitable example.

(e) What is sedimentation? How is sedimentation method applied for the determination of molecular weight of polymers?

(f) Write a short note on Fermi resonance.

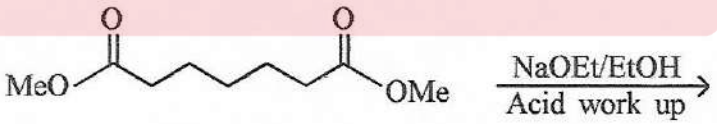
(g) Describe the magnetic anisotrophy in aromatic compounds and its influence over chemical shift values.

4. Answer any ***four*** questions from the following : 10×4=40

(a) What is terylene? How will you synthesize terylene starting from ethylene and *p*-xylene? Describe with all reaction steps.

(b) Suggest the relative stability of the carbonium ions CH_3^+, $C_2H_5^+$, $(CH_3)_2CH^+$ and $(CH_3)_3C^+$ with logic.

(c) Suggest a suitable mechanism to rationalise the following reaction :



(d) Describe the uses of Na/Liq. NH_3 as a reducing agent in organic synthesis.

(e) How can you synthesise caprolactam via Beckmann rearrangement reaction?

(f) What do you understand by Larmor precession? Explain.

5. Answer any ***two*** questions from the following : 20×2=40

(a) Show the importance of diborane in synthesis.

(b) Discuss the mechanism, utility and limitations of Aldol reaction.

(c) Describe the determination of molecular weight of polymer by light scattering method.

6. Answer any ***four*** questions from the following : 10×4=40

(a) Comment on the structure of benzynes.

(b) What are classical and non-classical carbocations? Give examples.

(c) What are addition and condensation polymers? Explain with examples of each.

(d) What is intrinsic viscosity? How is it related to the molecular weight of a polymer? When does the viscosity average molecular weight become equal to weight average molecular weight?

(e) How many normal modes of vibrations does the H_2O molecule possess? Show all of them.

7. Answer any ***two*** questions from the following : 20×2=40

(a) With a suitable example, describe Walden inversion.

(b) Draw and explain the correlation diagram for disrotatory interconversion of cyclobutene-butadiene system.

(c) Discuss the geometry of singlet and triplet carbenes.

8. Describe the Jablonski diagram. 40

9. Explain catalytic cycle for ethylene polymerization by the Ziegler catalyst with the help of a suitable mechanism. 40

10. "Substitution reactions are accompanied by elimination reactions." Explain this statement from mechanistic point of view. 40

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