

Chemistry

Paper-II

Time Allowed: Three Hours

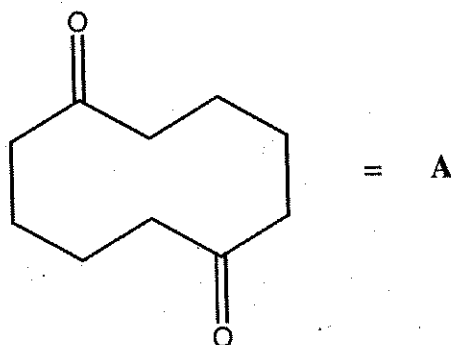
Maximum Marks: 300

Note: Candidate should answer questions No. 1 and 5 which are compulsory and any three of the remaining questions, selecting at least one from each section.

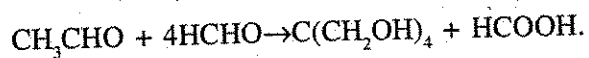
SECTION - A

1. Answer any **three** of the following: 20×3=60
- (a) State Huckel's rule of aromaticity. Which of the following compounds is aromatic? Explain.
- (i) Pyrrole
 - (ii) 1, 3, 5- hexatriene
 - (iii) 1, 3, 5- cycloheptatriene
 - (iv) 18- Annulene
- (b) pKa of cycloheptatriene is about 39 but that of cycloheptadiene is 16. Explain.

- (c) (i) When compound A is treated with alkali what product is formed? Show the mechanism of conversion.



- (ii) Electrophilic substitution in indole occurs at position-3. Explain.
- (d) (i) Using suitable reagents, how will you convert toluene into ethyl p-amino benzoate?
- (ii) Give mechanistic explanation for the following observed fact:



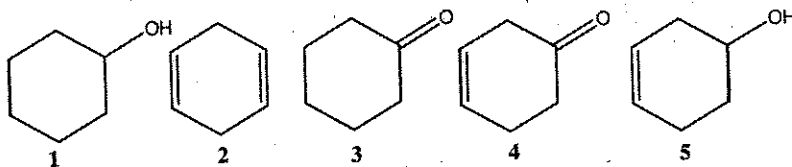
2. (a) Discuss the reaction with mechanism.

10×2=20

- (i) Cannizzaro Reaction
- (ii) Knoevenagel reaction

- (b) (i) Give two important methods of generation of free radicals and explain why allylic and benzylic radicals are both more stable than non-allylic radicals. 10

- (ii) One of the five compounds shown below was analysed by IR spectroscopy. Peaks were observed at 1639 cm^{-1} (weak) and 1714 cm^{-1} (strong). There was no signal between 3100 cm^{-1} to 3500 cm^{-1} . Which compound was analysed? 10



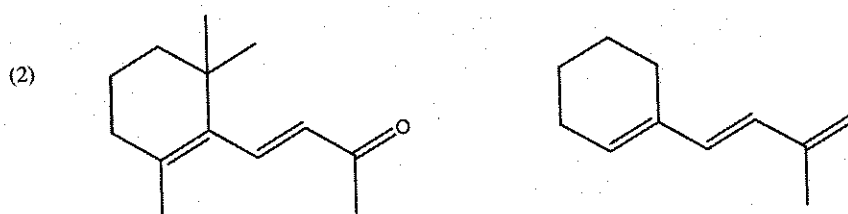
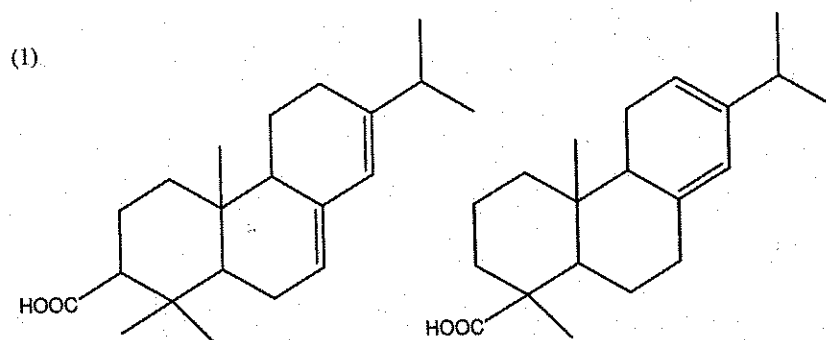
- (c) (i) Treatment of phthalic anhydride with urea yields phthalimide which with bromine in aq. NaOH gives anthranilic acid. Explain the reactions giving mechanisms. 15
- (ii) Give a brief account of structure, configuration and uses of proteins. 5
3. (a) An organic compound (X) gave the following spectral data: 20
- (i) Mass (m/z) : 73, 91, 149, 164
- (ii) IR (ν) : 1730 cm⁻¹
- (iii) ¹H-NMR = δ : 2.0 ppm (3H, s)
- δ : 2.93 ppm [2H, t (J = 7 Hz)]
- δ : 4.30 ppm [2H, t (J = 7 Hz)]
- δ : 7.3 ppm (5H, s)
- Deduce the structure of the compound.
- (b) (i) How will you use IR and NMR spectroscopy to distinguish o- and p-hydroxyacetophenones? 10
- (ii) Give major m/e peaks for 1-phenyl-1-butanone. Give mechanism involved in the formation of McLafferty rearrangement product for the same. 10
- (c) (i) Why does benzene undergo electrophilic substitution reactions rather than addition reactions? Discuss with the help of energy profile diagram. 10
- (ii) Why do we need Lewis acids as catalyst in electrophilic substitution reactions of benzene? 10
4. (a) (i) Draw the structure of repeating unit of following polymers: 10
Neoprene rubber, Gatta Percha, Polystyrene, Dacron, PET.
- (ii) Sketch the synthetic route for monomers of Nylon- 6 and Kevlar fibres. 10

- (b) (i) Explain with reasons the relative selectivity of acid derivatives towards nucleophilic substitution. 10
- (ii) Write essential conditions for resonance and aromaticity. 10
- (c) (i) Describe the steps and mechanism involved in the preparation of 1-methyl isoquinoline by Bischler- Napieralski procedure. 10
- (ii) What are kinetic methods to determine organic reaction mechanism? 10

SECTION – B

5. Answer any **three** of the following:

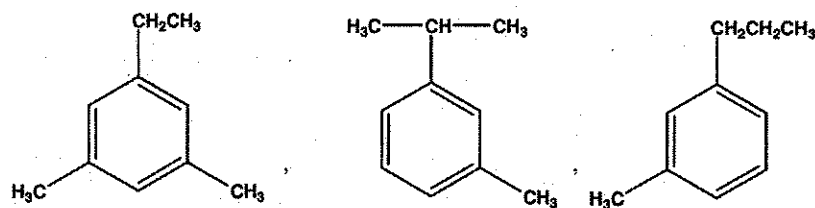
- (a) (i) Discuss electron spin resonance and its applications. 10
- (ii) Calculate λ_{\max} for a $\pi-\pi^*$ transition absorption band in UV spectra of the following compounds: 10



(b) Answer the following:

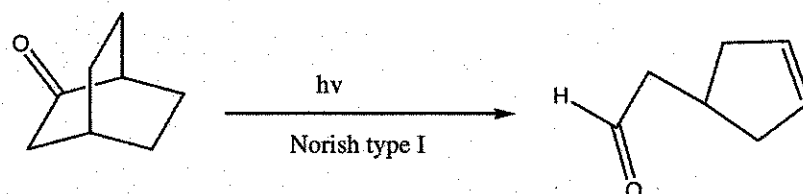
5×4=20

- (i) How acetone and ethanol are differentiated by IR spectrum?
- (ii) What do you understand by 'base peak' in mass spectrum? Which of the following compounds will exhibit a base peak at m/z 105?



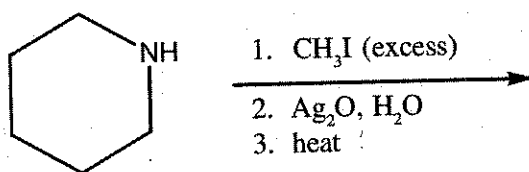
- (iii) Explain why a polar solvent usually shifts the $\pi - \pi^*$ transition to longer wavelength and $n - \pi^*$ transition to shorter wavelength?
 - (iv) Explain the ESR spectrum of isopropyl alcohol radical.
- (c) Discuss the effect of followings on the position of carbonyl stretching vibration in IR spectra. 20
- (i) Electronegativity (ii) α β -unsaturation (iii) Ring strain (iv) Hydrogen bonding
- (d) Discuss the fact that there is relationship between chemical shift and chemical structure by examples and explain the term shielding and deshielding. 20

6. (a) (i) Discuss the following reactions with mechanism. 10×2=20



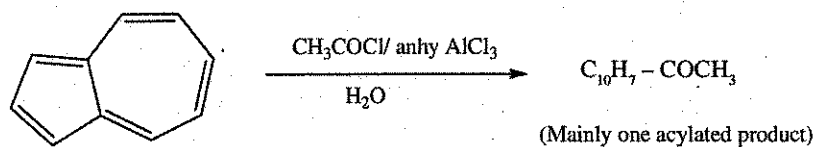
- (ii) How will you determine the relative viscosity and specific viscosity of a polymer solution using Ostwald viscometer?
- (b) How will you convert the following (Three steps) 5×4=20
- (i) Acetylene to Lactic acid
 - (ii) Toluene to 1, 3, 5-trinitrobenzene
 - (iii) Aniline to phenylhydrazine
 - (iv) 2-Propenal to 2, 3-dihydroxypropenal

- (c) (i) Dipole movements of pyrrole and furan are in opposite direction. Explain. 10
- (ii) Triplet carbene is more stable than singlet carbene. Why? 10
7. (a) (i) Outline the synthesis of cyclopentanone by Dickman condensation and explain the mechanism. 10
- (ii) What is quantum efficiency? Explain the photochemical reaction of ketones having a γ -hydrogen atom. 10
- (b) (i) What product would you expect from Hofmann elimination of a cyclic amine such as piperidine? Write all the steps involved in the elimination. 15



- (ii) What is the effect of denaturation on the structure of Proteins? 5
- (c) (i) 3-bromocyclohexane reacts with NaOH more rapidly than 4-bromocyclohexane which in turn reacts more rapidly than bromocyclohexane. Explain. 10
- (ii) Acid hydrolysis of Nylon 6 is faster than acid hydrolysis of polyester. Explain with mechanism. 10
8. (a) Explain the following: 4×5=20
- (i) Why radicals prefer to add at carbon 1 of isoprene rather than carbon 2, 3 and 4.
- (ii) In SBR (styrene- butadiene rubber) why do most double bonds have a trans configuration?
- (iii) P-nitroaniline exhibits pronounced red shift in the K- band, which is not observed in o or m- isomer.

- (iv) Pyrrole is a much weaker base compared to pyridine.
- (v) Why TMS is used as a reference standard in ^1H NMR spectroscopy.
- (b) (i) Using appropriate reagents, how will you transform thiophene into 5-nitrothiophene-2-aldehyde? Explain giving the mechanism. 10
- (ii) Friedel – Crafts acylation of azulene gives mainly one acylated product.



Which ring of azulene does undergo attack by CH_3CO^+ preferentially and why? Give the mechanism of the reaction. 10

- (c) (i) Give an example of Ribonucleic Acid (RNA) to show the basic bonds present in its primary and secondary structures. 10
- (ii) Write the mechanism of radical polymerization of ethylene leading to branching in the resultant polymer. 10