

CHEMISTRY**PAPER - I**
SECTION A

1. Answer any four of the following:
- Explain the principle of ion selective electrodes. What are their applications? (10)
 - What is Born-Haber cycle? What is its use? (10)
 - What are quantum numbers? What are their significances? (10)
 - Write a note on liquefaction of gases. (10)
 - What are reverse reactions? Derive the rate equation for reverse reaction. (10)
2. (a) State phase rule and explain the term involved. Draw the phase diagram of a binary system of partially miscible liquids. (20)
- (b) Deduce a pressure-volume relationship in reversible adiabatic expansion of an ideal gas. (20)
3. (a) What are fuel cells? Describe the construction and working of a fuel cell (20)
- (b) Discuss the transition state theory of reaction rates. (20)
4. (a) Describe an experimental set up for the measurement of emf of a cell. (20)
- (b) What is an adsorption isotherm? How are Langmuir and BET isotherms obtained? What are their characteristics? (20)

SECTION B

5. Attempt any four of the following:
- Give an account of the red-ox and precipitation reactions in liquid ammonia. (10)
 - What is chelate effect? (10)

- (c) What are fluxional molecules? Give two examples. How are they characterized? (10)
- (d) Explain the variation of magnetic moments within the lanthanides. (10)
- (e) Identify the various physical pathways by which a photo excited molecule undergoes deactivation. (10)
6. (a) Discuss the structural aspects of metal-olefin and metal-alkyne complexes giving experimental evidences. (20)
- (b) Discuss the salient features of molecular orbital theory and discuss its use in explaining the bonding in N_2 , O_2 and HF molecule. (20)
7. (a) What are metal atom cluster?
Discuss the structure and bonding of two metal clusters with M-M single bond and M-M multiple bonds. (20)
- (b) Assign the observed electronic absorption bands of $[Ni(H_2O)_6]^{2+}$ and $[Cr(OX)_3]^{3-}$. Explain on the basis of crystal field theory. (20)
8. (a) Discuss in detail the mechanism of oxygen transport in biological system. (20)
- (b) Give an account of the linkage isomerism and the various factors stabilizing the isomers. Choose suitable example. (20)

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CHEMISTRY


PAPER - II SECTION A

1. Answer any four of the following:

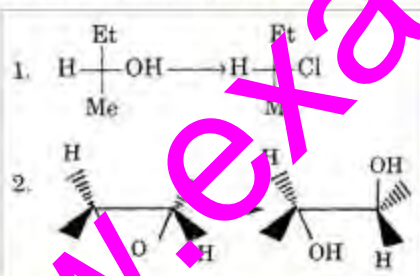
(About 150 words each)

(a) Draw the energy profile diagram for a two-step reaction of $A \rightarrow [B] \rightarrow C$, with the first step as rate determining. Indicate substrate, product, transition state, intermediate and activation energy. Offer a good example for such a reaction.

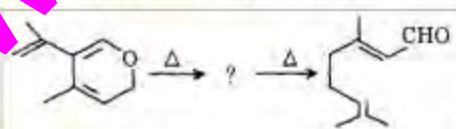
(b) Explain the reason for stability of the following species:

1. PhCH_2^-
2. $\text{CH}_2\text{COCH}_3^-$
3.  +
4. $\text{Ph}_3\text{P}^+ - \text{CHCH}_3^-$

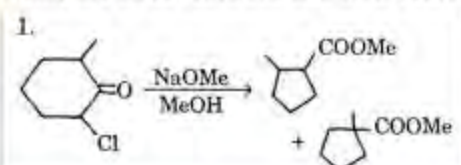
(c) Describe the conditions and reagents required for the two conversions; suggest mechanism:

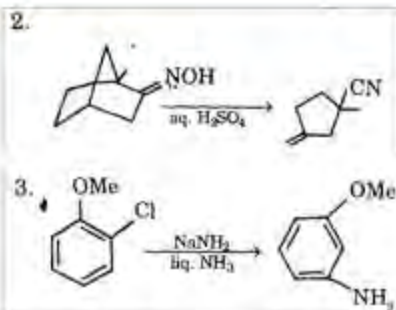


(d) In one of the syntheses of citral, a pericyclic reaction, symmetry allowed under thermal conditions, is involved twice; provide the name of the reaction and indicate mechanism drawing the intermediate product:



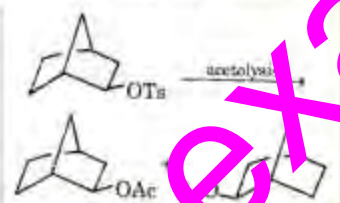
(e) Name the three reactions and offer reasonable mechanism:



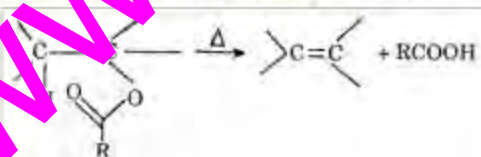


2. (a) Describe with appropriate examples, what is meant by kinetic control and thermodynamic control. Providing reasons and indicating conditions, draw structures of the enolate anion of 2Methylcyclohexanone under these conditions.
- (b) Explain why the bicyclo compound, 1-Bromobicyclo [2.2.1] heptane does not undergo substitution reaction.
- (c) Cyclopentadienone is very unstable, dimerising during preparation while Cycloheptatrienone is stable and easily prepared. Why?
- (d) Isotope effect is employed in the understanding of reaction mechanism. Explaining the principle briefly, account for:
1. Isotopes of H are frequently used, not isotopes of C.
 2. No isotopic effect observed in the study of the nitration of benzene/hexadeuterobenzene. (10 x 4 = 40)

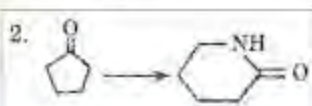
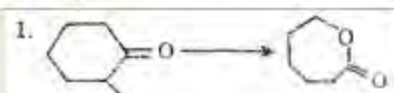
3. (a) Provide electronic structures for the singlet and triplet carbenes. Give an example of a carbene with ground state singlet. How will you determine whether RCH carbene is singlet/triplet using cis-2-butene?
- (b) Offer suitable mechanism for the reaction, indicating stereochemical aspect, if any/



- (c) Suggest name and mechanism for the reaction below. What evidence do you provide for your answer? How will you compare this reaction with Chugaev reaction?

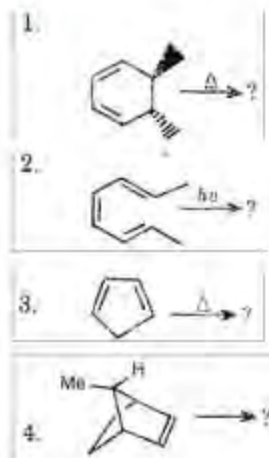


4. Suggesting suitable reagents, reaction conditions and mechanism, explain how you will accomplish:



4. Naming the below shown pericyclic reactions, draw stereo-structures (s) for the product (s):

(10 x 4 = 40)



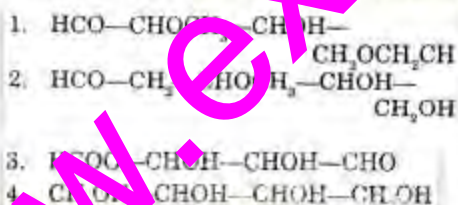
SECTION B

5. Answer any four of the following:

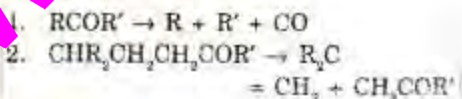
(About 150 words each)

(10 x 4)

- (a) Provide names and structures of the bases of DNA. Explain why base pairing in nucleic acid is favoured between fixed partners.
- (b) How will you employ reaction with HIO_4 in differentiating the four compounds (1- 4)? Indicate the products and HIO_4 consumed in each case:



- (c) Name the reactions and explain the mechanism for the below given two photochemical transformations:



- (d) In the absence of an ESR spectrometer, used to study radicals, CIDNP spectrum, recorded by an NMR instrument is employed. How will you employ this in study whether the exchange reaction, $\text{EtI} + \text{EtLi} \rightarrow \text{EtLi} + \text{EtI}$, is proceeding through radical intermediate?

- (e) How will you distinguish the following pairs (1—3) by the indicated spectroscopic method?

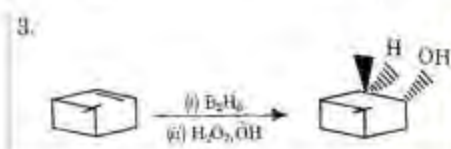
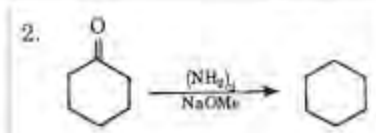
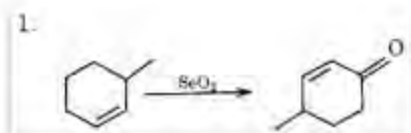
- Ethyl benzoate and Phenyl propanoate by IR
- 1, 4-Dimethylbenzene and 1, 2-Dimethylbenzene by NMR
- 2-Pentanone and 3-Pentanone by ESIMS

6. (a) What is meant by directed aldol condensation? Suggest a method for the preparation of $\text{CHOCH}_2\text{CHOH}(\text{CH}_3)_2$ employing propanone and a suitable aldehyde equivalent.
- (b) How will you accomplish benzoin condensation? Provide detailed mechanism highlighting the different roles of CN^- ion in the reaction.

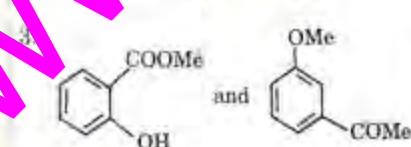
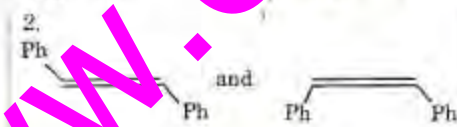
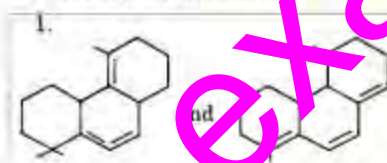
(20 x 2 = 40)

7. (a) Explain the formation of the products, including stereo-chemical aspects, if any, with mechanism:

(10 x 4 = 40)



8. (a) Apply Woodward-Fieser rule and differentiate the three pairs of compounds by their principal UV absorption maximum:



- (b) An organic cyclic compound, C_5H_{10} , on treatment with NaOMe/MeOH gave an acyclic product, $\text{C}_6\text{H}_{14}\text{O}$, whose $^1\text{H-NMR}$ spectrum exhibited three singlets at δ : 3.9(2H), 3.6(3H) and 0.8 (9H). Identify the substrate and product. Justify your answer.

(20 x 2 = 40)