Indian Association for the Cultivation of Science
(Deemed to be University under *de novo* Category)
Integrated Bachelor's-Master's Program
End-Semester Examination-Autumn 2024

Subject: **Chemical Reactivity** ***Subject Code(s): CHS 2101***
Full Marks: 50 ***Time Allotted: 3 h***

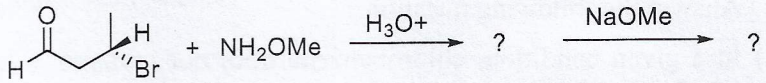
Section-A

(There are FIVE questions in this section. Q1 is COMPULSORY. Answer any THREE from Q2-Q5)

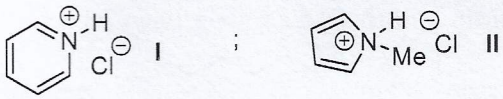
1. Answer *any four* of the following questions. [2.5x4]

(a) Predict the ^{1}H NMR spectrum of propyl acetate.

(b) Predict the major products of the reactions given below with proper stereochemistry.

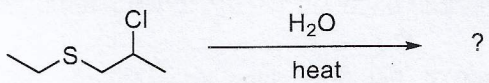


(c) Among the salts **I** and **II**, which one would react at a faster rate with benzylamine? Provide a suitable explanation.

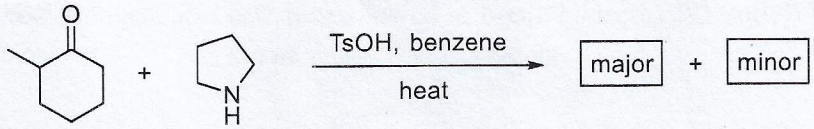


(d) Draw the most stable conformer of all *cis* and *trans* hexachlorocyclohexane and predict which one would undergo base-mediated E2 elimination faster.

(e) Predict all possible products of the reaction given below. What conclusion can you draw about the reaction mechanism based on the reaction outcome?

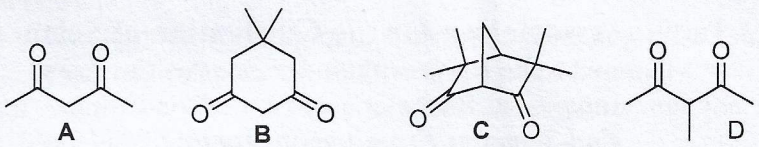


(f) Complete the following reaction and justify your answer.



2. Answer the following questions:

(a) Arrange the following di-ketones in increasing rate of enolization in water. Justify your answers. [3]

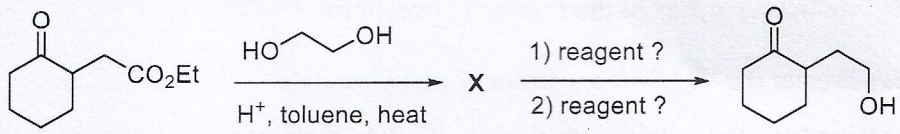


(b) Explain homoaromaticity with a proper example. [2]

3. Answer the following questions:

(a) Propose a shorted synthetic route for the selective conversion of benzene to *n*-propyl benzene with proper explanation and the reaction mechanism. [3]

(b) Complete the following transformations indicating the structure of **X** and suitable reagents for the subsequent steps. [2]

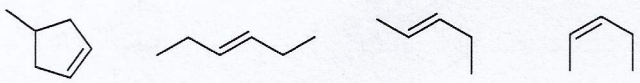


(over two steps)

4. Answer the following questions:

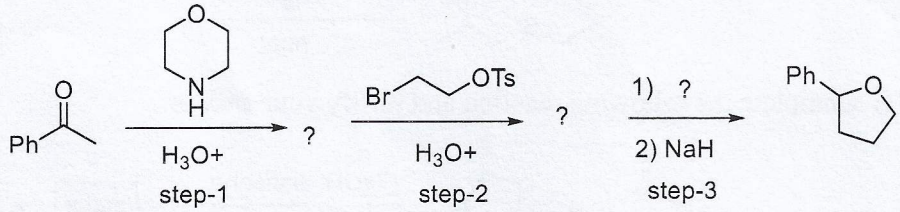
(a) In a given condition, chlorobenzene does not undergo a reaction with PhSK in DMF solvent, but para-nitro chlorobenzene delivers the desired product. Draw the product expected for the later reaction and explain the observation. [2]

(b) Predict the number of signals expected in ^{1}H NMR spectra of the following alkenes. [2]



(c) How can you distinguish between vinyl chloride and ethyl chloride using a single reagent? [1]

5. Complete the following transformation predicting the structure of products and suitable reagents. Provide reaction mechanism for steps 2 and 3. [5]



Section-B

(There are FIVE questions in this section. Q6 is compulsory. Answer any THREE from Q7-Q10)

6. Consider the Latimer diagram below for Iodine in an acidic solution (pH =0).

$$H_5IO_6 \xrightarrow{1.589} IO_3^- \xrightarrow{1.154} HOI \xrightarrow{1.430} I_2 \xrightarrow{0.535} I^-$$

(i) Show the formation of H_5IO_6 in the hydration-hydrolysis of I ion in its appropriate oxidation state. [2]
(ii) Draw the Lewis structure of IO_3^-. What would be the electron pair and molecular geometry of the molecule? [1.5]
(iii) What would be expected *p*Ka of the oxo acids, H_5IO_6 and HIO_3? [2]
(iv) Why is IO_3^- anionic whereas H_5IO_6 is protonated in the diagram? [1.5]
(v) Calculate the skipped reduction potential for IO_3^- to I_2. [1.5]
(vi) Write the balanced reaction for the reduction of IO_3^- to IO^-. [1.5]

7. (i) Construct the Frost diagram for iodine in aqueous acidic solution. [3]
(ii) From the Frost diagram that you have drawn, indicate the most stable species of iodine? [1]
(iii) Identify any species that are unstable to disproportionation. What would happen if IO_3^- and I^- were mixed? [1]

8. (i) What are the symmetry elements present in PCl_3? What is its point group? [1.5]
(ii) Explain why BF_3 possesses an S_3 axis, but NF_3 does not. [1.5]
(iii) Schematically show how the molecular orbitals would 'look' like when a sigma MO from *p* orbitals (p_z) and a sigma MO from *s* orbitals mixed as shown below: [2]

in-phase out-of-phase

9. (i) Consider the molecule NF and the ions NF^+ and NF^-. Write the molecular orbital description of the ground state for each species. Determine which of the three species would be paramagnetic. Predict the bond orders for all three species. [2.5]
(ii) For the following reaction, indicate with an explanation whether the equilibrium will favor the reactants or the products. [1.5]

$$TiF_4 + 2TiI_2 \rightarrow TiI_4 + 2TiF_2$$

(iii) What is the strongest acid and base allowed in liquid hydrofluoric acid?[1]

10. (i) For the complex, [Cr(acetylacetonate)$_3$], indicate the primary and secondary valency of the metal center. Does the complex display stereoisomerism? If so, draw the isomers. [2]

(ii) Draw the *d*-orbital splitting of the complex assuming an octahedral field at the metal center and calculate the $10Dq$ value. (CFSE in terms of 10Dq) [1.5]

(iii) What would be the spin-only magnetic moment value for a tetrahedral cobalt(II) complex? [1.5]

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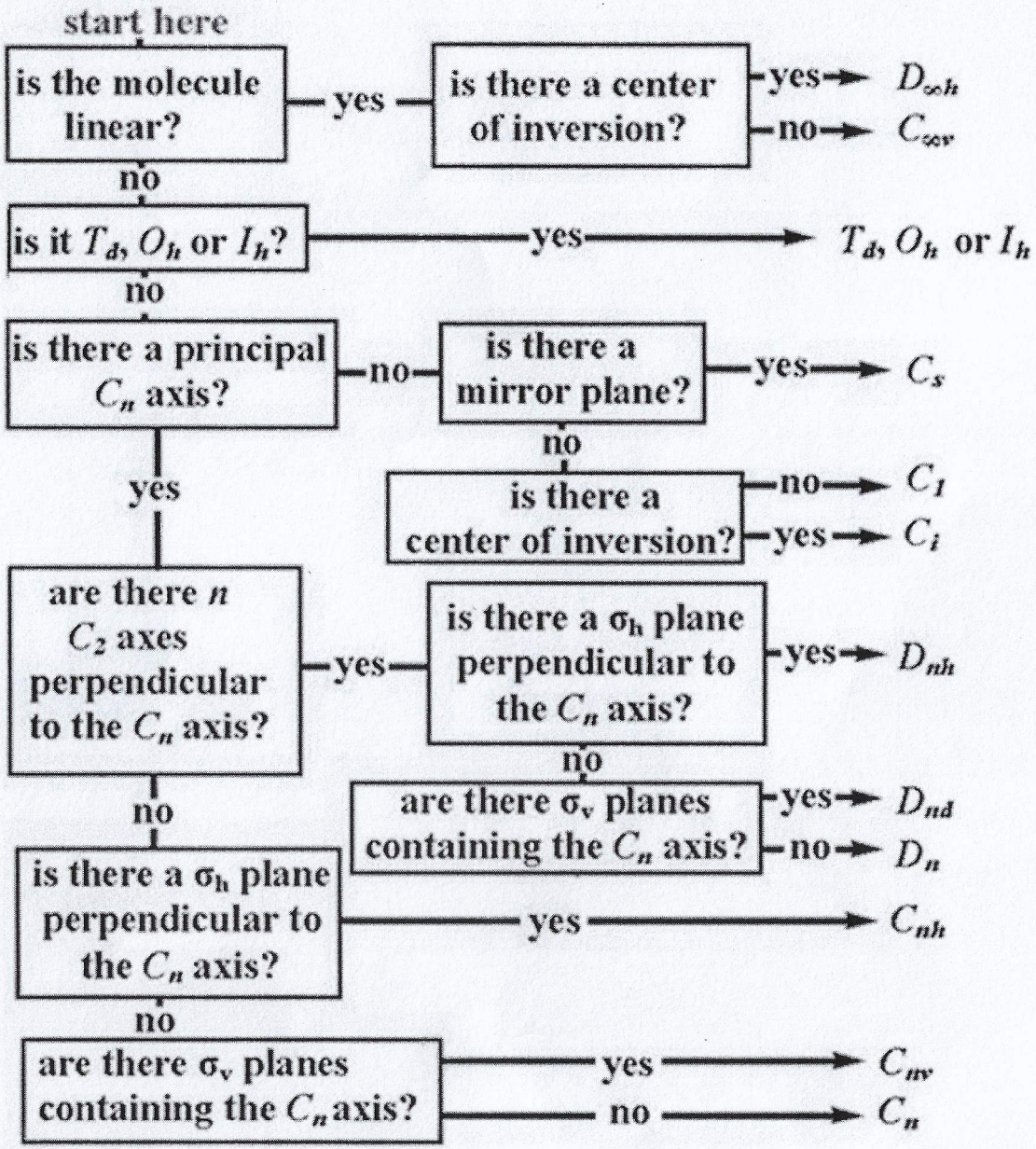
start here
is the molecule linear?
yes
is there a center of inversion?
yes
$D_{\infty h}$
no
$C_{\infty v}$
no
is it T_d, O_h or I_h?
yes
T_d, O_h or I_h
no
is there a principal C_n axis?
no
is there a mirror plane?
yes
C_s
no
yes
is there a center of inversion?
no
C_1
yes
C_i
are there n C_2 axes perpendicular to the C_n axis?
yes
is there a σ_h plane perpendicular to the C_n axis?
yes
D_{nh}
no
no
are there σ_v planes containing the C_n axis?
yes
D_{nd}
no
D_n
is there a σ_h plane perpendicular to the C_n axis?
yes
C_{nh}
no
are there σ_v planes containing the C_n axis?
yes
C_{nv}
no
C_n