22MIS10083

INDIAN INSTITUTE OF TECHNOLOGY KHARAGPUR

End-Autumn Semester Examination 2022-23

Date of Examination: _____ **Session: (FN/AN)** _____ **Duration: 3 hrs.**

Full Marks: 75 Marks _____

Subject No.: CY11003 _____ _____

Department/Center/School: Chemistry _____

Specific charts, graph paper, log book etc., required NO

Special Instructions (if any): given below _____

Special Instructions:

1) The question paper contains two parts: **Part A** and **Part B**

2) Two answer scripts which are tied together will be given to you.

3) Label one of the answer scripts as **Part A** and the other as **Part B**

4) Write your name, roll number and section no. on both the answer scripts.

5) Answer the questions of **Part A** in the answer book marked as **Part A**

6) Answer the questions of **Part B** on the answer book marked as **Part B**

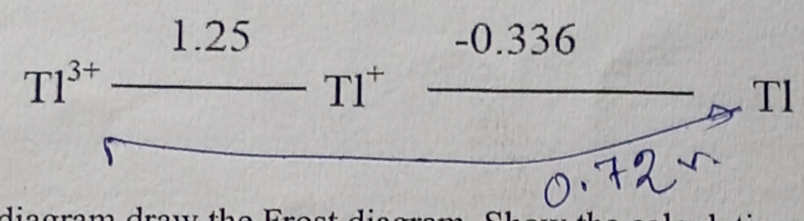
7) Write the answers in sequence; otherwise they would not be checked.

8) If the additional sheets are used, please mark on the sheets as **Part A** or **Part B.**

PART-A (Inorganic Chemistry)

Instruction: Answer all questions

Q1. (a) Calculate the E^0 value for the reduction of Tl^{3+} to Tl in aqueous acidic solution using the Latimer diagram.



(b) Using the Latimer diagram draw the Frost diagram. Show the calculations. **(2 + 2)**

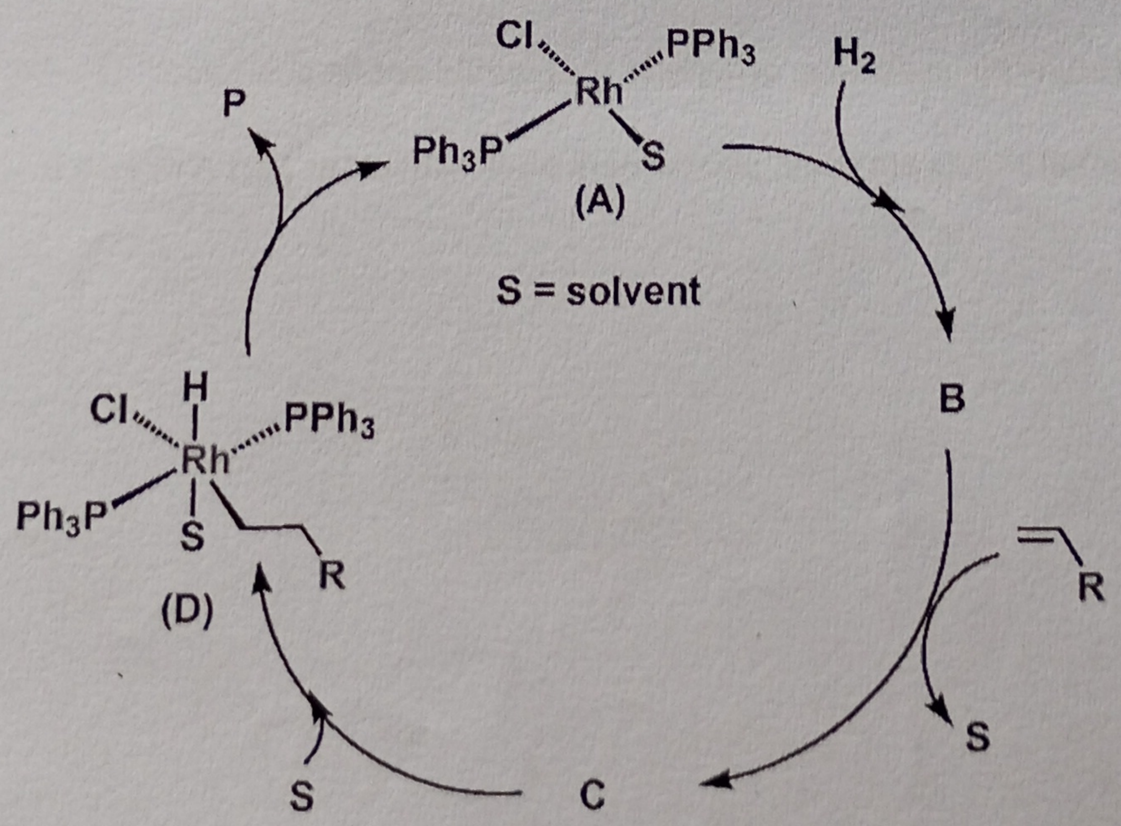
Q2. Draw the molecular orbital diagram of the following species and identify the species with highest bond order? **(3)**

a) F_2 b) O_2^- c) B_2^{2+}

Q3. From the given catalytic cycle, **(3+3)**

(i) draw the structure of B, C and P.

(ii) identify the oxidative addition, reductive elimination and migratory insertion steps.



Q4. (a) Draw the d-orbital splitting diagrams for *z*-in and *z*-out distortions in a high-spin d^6 octahedral complex of $[ML_6]$ type. (2+2)

(b) The absorption band for the electronic transition from $e \rightarrow t_2$ of complex $[VCl_4]$ appears at 8000 cm^{-1}. Where would the $t_{2g} \rightarrow e_g$ transition occur for $[VCl_6]^{2-}$ complex? (2)

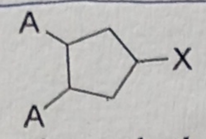
(c) $[Fe(H_2O)]^{2+}$ is paramagnetic, but its magnetic moment decreases when a significant excess of cyanide ions is added. Explain. (2)

Q5. Assume $[Cu(NH_3)_4]^{2+}$ is formed by stepwise reactions with $K_1 = 10^{2.65}$, $K_2 = 10^{2.10}$, $K_3 = 10^{1.44}$ and $K_4 = 10^{1.25}$ at 25°C. The overall enthalpy change ($\Delta H°$) for formation of $[Cu(NH_3)_4]^{2+}$ is -53.2 $kJ \cdot mol^{-1}$. Calculate the entropy change ($\Delta S°$) at 25°C. (Given, R = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$) (4)

Part B : Organic Chemistry

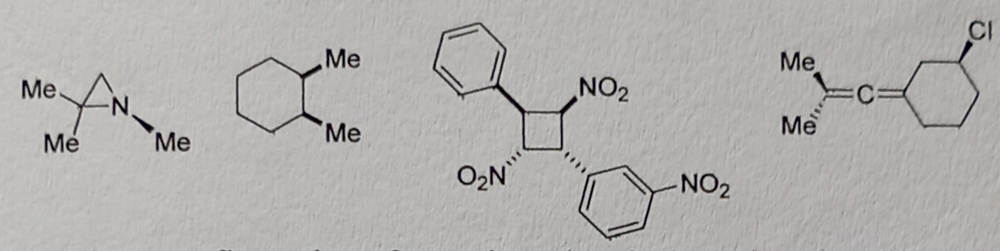
Answer all the questions (Total Marks 50)

Q.6 a) Draw all the probable stereoisomers for the given molecule. Indicate the meso-isomers and enantiomers in your drawing. [assume the cyclopentane ring is planar] [2]

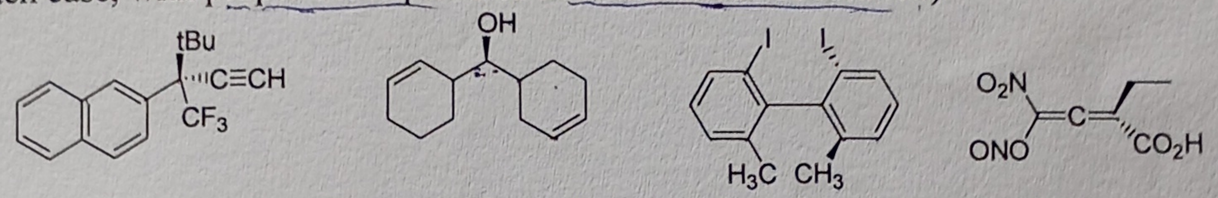


A and X are non hydrogen;
A and X are atom(s) or ligands (without any stereogenic element)

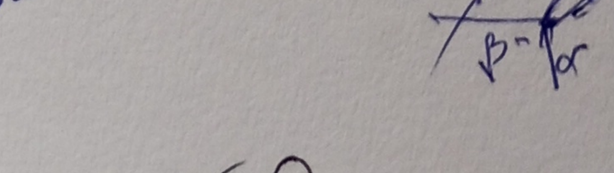
b) Mention whether the following compounds are (i) chiral but non-resolvable; (ii) chiral and resolvable; (iii) achiral or meso. [assume the cyclobutane ring is planar] [4]



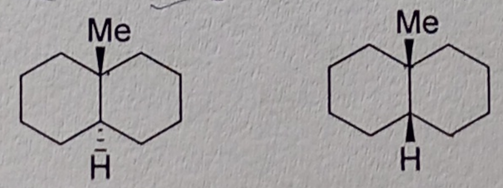
c) Write the absolute configurations for each molecule (mention the CIP notation in each case, with proper descriptor and show the mode of rotation) [4]



Q.7 a) Explain the following observation with the help of conformational analysis. [2]



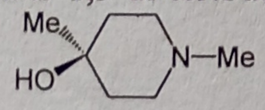
b) Compare the stability of the given two decalin derivatives with the help of conformational analysis (Identify the gauche-butane (GB) interactions. The GB interactions with in the cyclohexane ring can be omitted). [4]



A B

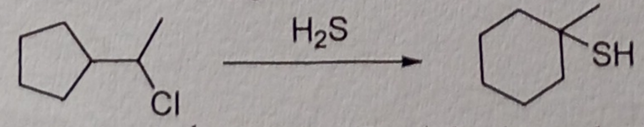
c) Draw the most stable conformation of the following and justify your answer. [4]

(a) *trans*-1,3-di-tertbutyl-cyclohexane; (b) *cis*-1,3-dihydroxycyclohexane

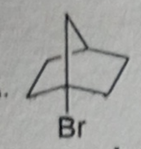
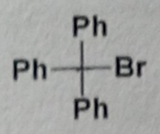
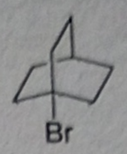
(c) 

(d) 1-ethyl-cyclopentane

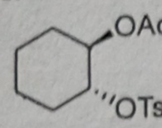
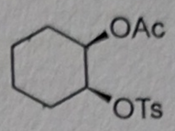
Q.8 a) Give the possible mechanism for the given reaction [2]



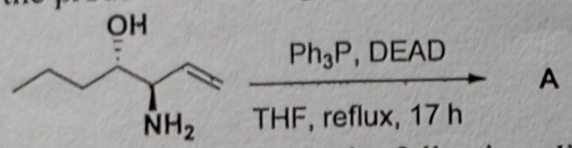
b) Predict the reactivity order for S_N1 reaction. Explain the carbocation stability. [2]

A.  B.  C. $(CH_3CH_2CH_2)_3CBr$ D. 

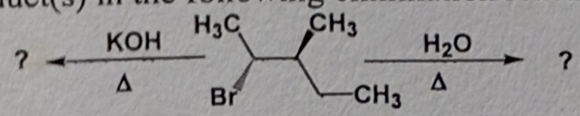
c) Suggest the mechanism for the reactions and comment on stereochemistry of the products. [3]

 reacts with acetic acid 670 time faster than 

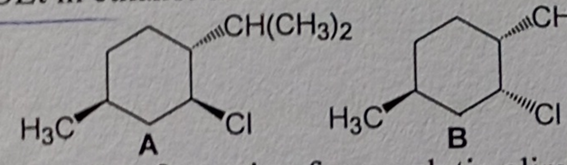
d) Predict the product A and suggest the suitable mechanism for this reaction. [3]



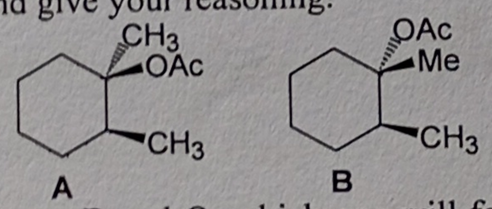
Q.9 a) Predict the major product(s) in the following elimination reactions. [2]



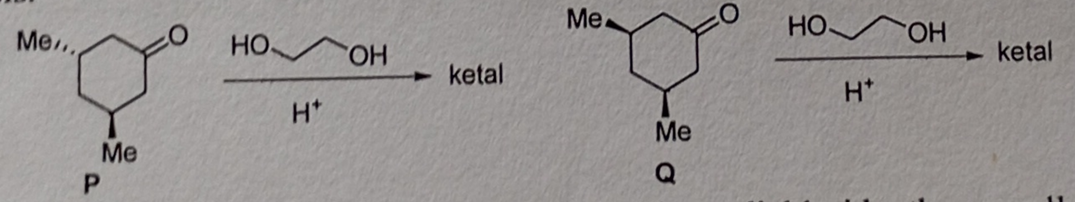
b) One of the following steterojsomers undergo elimination much more readily upon treatment with NaOEt in ethanol than the other. Which one reacts faster and why? [4]



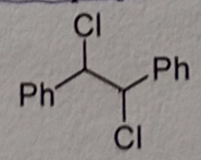
c) Predict the possible product formation for pyrolytic elimination from the following stereo isomers A and B and give your reasoning. [4]



Q.10 a) Among the following ketones **P** and **Q**, which one will form ketal faster under the given conditions? Justify your answer through mechanism and conformational analysis. [3]



b) Among the optically active and meso forms of stilbene dichloride, the overall dipole moment is lower in the meso form than the optically active form. Justify with conformational stability using Newman projection. [3]



c) Draw the most stable conformations of the following compounds **M** and **N**. Predict with justification the relative rates of chromic acid oxidation of the following alcohols. [4]