**Birla Institute of Technology & Science Pilani, Pilani Campus**

**First Semester, 2023-2024**

**Date: December 15, 2023** | **CHEM F111: General Chemistry** | **Comprehensive Examination**

**Duration: 60 min.** | **CLOSED BOOK (PART A)** | **Total Marks: 40**

**ID No.:** **Name:**

| Q1 Marks | Q2 Marks | Total | Recheck request, if any |
|---|---|---|---|
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**Instructions to the students:**

- **This part (PART A) should be answered in the space provided below each question.**
- **Rough work can be done in the blank space provided at the end of the questions or at the back side of the answer sheet provided for solving PART B.**
- **Rough work should not be done in the question/answer area. Do not use pencil.**
- **As soon as you submit this answer script (PART A), you can collect the Open Book (PART B) materials.**

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**Q1**. **(a).** Consider the three species $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[NiCl_4]^{2-}$. Write separately for each one of the species, whether their structures are distorted or regular. Identify the species that will have maximum distortion. Justify your answer briefly. [Element (Atomic Number): Fe (26), Co (27), Ni (28)] **[3+1=4]**

**Q1**. **(b).** What kind of spinel structure (normal/inverse) will be adopted by $CoFe_2O_4$? Justify your answer with calculations. Write all the cations present in this solid and their corresponding site geometry (octahedral, tetrahedral *etc.*). [Element (Atomic Number): Fe (26), Co (27)] **[4+1=5]**

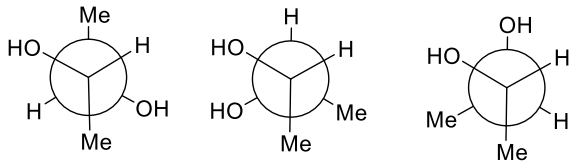
**Q1**. **(c).** The high resolution electronic spectrum of aqueous solution of $TiCl_3$ shows a broad absorption peak at around 20300 $cm^{-1}$ with a shoulder (the absorptions are of low intensity). Mention the transitions in terms of initial and final orbitals through an energy level diagram and explain. [Element (Atomic Number): Ti (22)] **[4]**

**Q1**. **(d).** Consider the $^1H$ NMR spectrum of benzyl alcohol ($C_6H_5CH_2OH$). The spectrum was recorded using $CCl_4$ as solvent and TMS as the reference compound. The absorption occurs at $\delta = 2.4$ for the OH proton; **(i)**. Calculate the difference in the frequency of absorption in Hz between OH and TMS signals in a 60 MHz spectrometer, and **(ii).** if the resonance frequency difference between $CH_2$ and TMS signals in a 300 MHz spectrometer is 1380 Hz, what will be the $\delta$ value for $CH_2$ proton? **[2+2=4]**

**Q1**. **(e).** How many signals are expected in the proton decoupled $^{13}C$ NMR spectra of methyl *ortho*-, *meta*- and *para*-chlorobenzoate (*o*-, *m*- & *p*- Cl-$C_6H_4$-$COOCH_3$)? **[3]**

**Rough Work**

**Q2. (a).** If viewing through C2-C3 bond, the following three staggered conformers (**I-III**) of a specific stereoisomer of 2,3-butanediol are possible, then



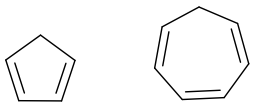

***Conformer I*** ***Conformer II*** ***Conformer III***

**(i).** Determine the absolute configuration at the two chiral centres (C2 & C3) for the given stereoisomer. **[1+1]**

**(ii).** *Given that a gauche OH-OH interaction energy is 1.6 kJ/mol, a gauche Me-Me interaction energy is 3.6 kJ/mol, and a gauche Me-OH interaction energy is 2.0 kJ/mol.* Using these given interaction energy values only, and ignoring all other effects, determine which one of the above three conformers (**I, II** or **III**) is more stable by individually calculating energies of all the conformers (in *kJ/mol*). **[1+1+1+1]**

**Q2. (b**). A pure sample of the (+) enantiomer of a compound **X** shows a specific rotation $[\alpha]_D$ of 42º. What would be the observed rotation $\alpha$ if a solution of this sample is made by dissolving 0.250 g in 2.0 mL of acetontirile and is placed in a 5 cm cell of a polarimeter? **[2]**

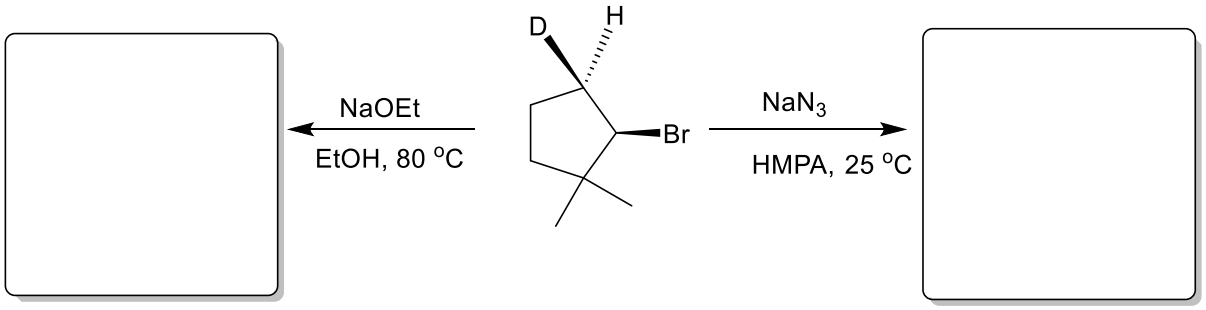
**Q2. (c).** From the two compounds (**Y-Z**) given below, which one of the them will undergo faster base-mediated deprotonation from the available $sp^3$-hydridized carbon. Explain the rejection and acceptance in no more than two sentences with the help of supporting structures. **[3]**



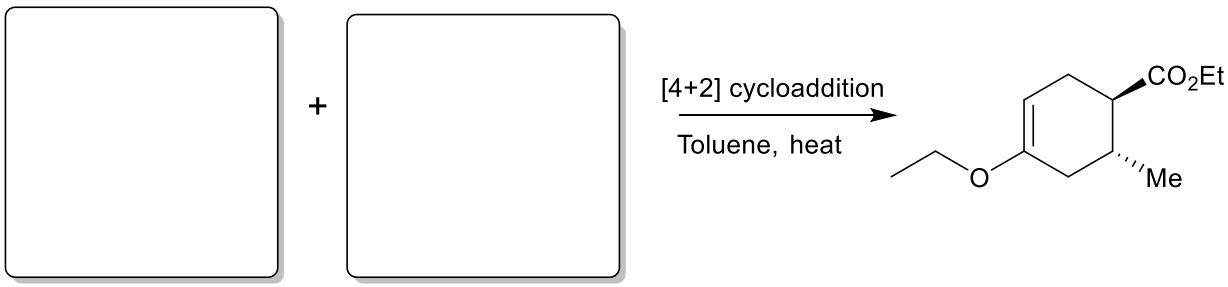
Y Z

**Q2. (d).** Draw the missing structures of major product/reactants *(with correct stereochemistry, wherever applicable)* in the boxes provided for the following chemical reactions. (*No partial marks will be granted if the stereochemistry is incorrect)* **[6x1.5=9]**

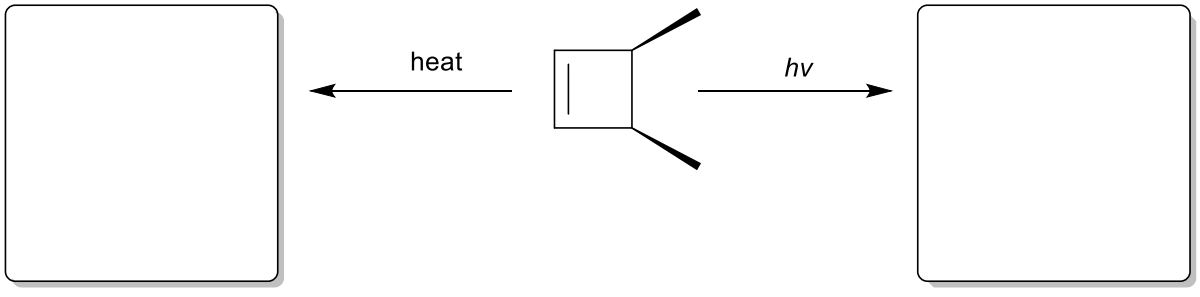
**(a).**




**(b).**




**(c).**




**Rough Work**