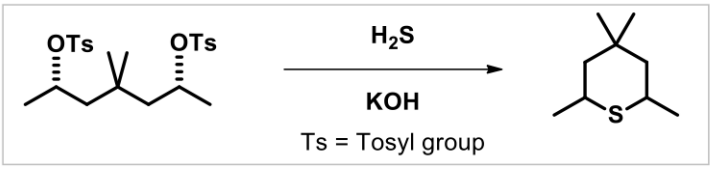
CML101 2020-21 **I semester Major**
Feb. 12, 2021
Important: **This is a** 140 **min. exam.**

Useful information:

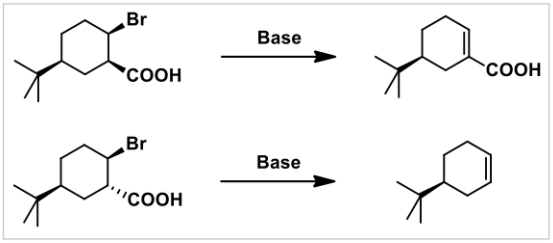
$$\nabla^2 = \left(\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2\theta}\frac{\partial}{\partial \phi^2} \right)$$

1. 28 mg of mandelic acid was dissolved in 1 cm^3 of ethanol and the solution placed in a 10 cm long polarimeter cell. An optical rotation of α of $-4.35°$ was measured at 20 °C with light of wave length 589 nm. What is the specific rotation of the acid? (1.5)

2. Predict the stereochemistry of the product with mechanism. Is this single diastereomer, enantiomerically pure, or something else? (1+1/2)

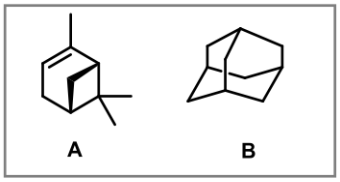


3. Account for the contrasting results in these two reactions with mechanism. (1+1)



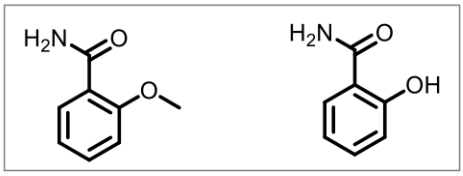
4. What will be the product structure when (2*R*, 3*R*)-2-bromo-3-methyl-pentane will react with NaOEt. Explain the mechanism with the help of any projection. (1+1)

5. How many types of chemically non-equivalent protons are present in the following two molecules (**A**, **B**)? (1/2+1/2)



6. The ^{1}H-NMR spectrum of a compound of molecular formula $C_5H_{10}O_2$ shows: 6H (d), 1 ppm; 1H (septet), 4.5 ppm; 3H (s), 2.1 ppm. It also shows an absorption band at 1740 cm^{-1} (strong) in the infrared spectrum. Find the possible structure of the compound with explanation. (1+1)

7. Among the following two molecules which one will have higher $\tilde{\nu}_{C=O}$ and why? (1)



8. Verify whether the steady state approximation is valid for O and O_3 at an altitude of 30 km in the atmosphere given that at this height the mechanism for ozone creation and destruction is

$$O_2(g) + h\nu \xrightarrow{j_1} O(g) + O(g)$$

$$O(g) + O_2(g) + M(g) \xrightarrow{k_2} O_3(g) + M(g)$$

$$O_3(g) + h\nu \xrightarrow{j_3} O(g) + O_2(g)$$

$$O(g) + O_3(g) \xrightarrow{k_4} O_2(g) + O_2(g).$$

Here j indicates a rate constant for a photochemical reaction (by light), and M is a species that does not take part in the reaction. It is known that $j_1 = 2.51 \times 10^{-12}\,s^{-1}$, $j_3 = 3.16 \times 10^{-4}\,s^{-1}$, $k_2 = 1.99 \times 10^{-33}\,cm^6\,molecule^{-2}\,s^{-1}$, $k_4 = 1.26 \times 10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$, $[O_2] = 3.16 \times 10^{17}\,molecule\,cm^{-3}$, and $[M] = 3.98 \times 10^{17}\,molecule\,cm^{-3}$.

9. Consider the hydrogen atom with the nucleus at the origin, and the electron orbiting it at a fixed radial distance in the $x - y$ plane.

   (a) Write the Schrödinger equation for this system in spherical coordinates.

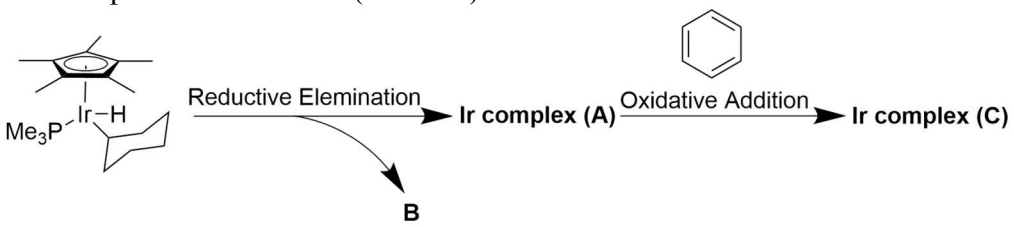
   (b) What are the solutions of the Schrödinger equation in question 9a? You are given that the solutions of $\frac{d^2y}{dx^2} + k^2y = 0$ is of the form $y =$ constant $e^{\pm ikx}$.

   (c) It is possible to obtain the Bohr quantization condition $pr = n\hbar$ from your solutions to question 9b. Explain how.

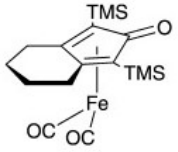
10. (a) From the following metal carbonyls identify that/those which react/reacts with metallic Na without the loss of CO. Write the formula of product. (**3** Marks)

$Fe(CO)_5$, $Mn_2(CO)_{10}$, $Cr(CO)_6$, $Co_2(CO)_8$, $V(CO)_6$

(b) Predict the products (**A**, **B** & **C**) of the following reaction. Mention oxidation state of Ir in the products **A** and **C**. (**2** Marks)



(c) The reaction of the following complex with H_2 results in a stable complex **A**. Draw the structure of compound **A** along with the electron count (for the metal and ligands). (**1** Mark)

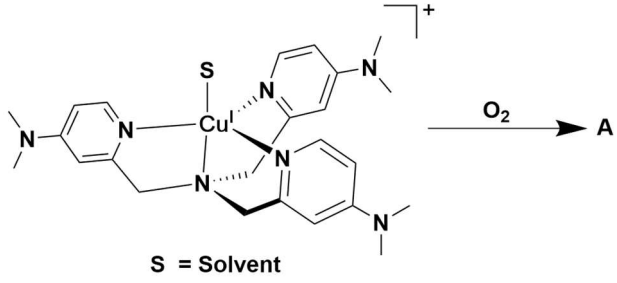


11. (a) Calculate CFSE for $[CoCl_4]^{2-}$ and $[Fe(CN)_6]^{3-}$ (**2** marks)

(b) The value of ϵ_{max} in the electronic spectra of $[CuCl_4]^{2-}$ and $[Cu(OH_2)_6]^{2+}$ differ by a factor of about 100. Comment on this observation and state which complex you expect to exhibit the larger value of ϵ_{max}. (**2** marks)

(c) The magnetic moment of $[CoL_6]SO_4$ is 3.8 BM. Choose correct ligands from water, cyanide, chloride and ammonia, and draw the crystal-field splitting diagram. (**2** marks)

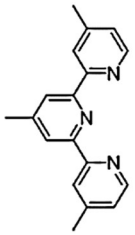
12. (a) The reaction of a copper(I) complex with molecular oxygen results in the formation of a new complex A, which shows O–O stretching vibration at 1120 cm^{-1}. Draw the structure of the species **A** (you can define the Ligand as L). How many number(s) of unpaired electron you would expect to be present in the complex **A**? (**2** Marks)



(b) $Cu(CH_3COO)_2 \cdot 2H_2O$ is present as a dimer in the solid state and the observed magnetic moment of the compound is close to zero. Explain the observation (**1** Mark)

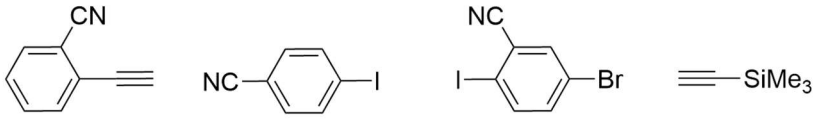
(c) In the solid-state structure of $CuCl_2 \cdot 2H_2O$, Cu was found coordinated octahedrally by four chloride ions and two water molecules, where two types of Cu–Cl bonds were observed (d_{Cu-Cl} = 2.28 & 2.91 Å; d_{Cu-OH2} = 1.93 Å). Explain why Cu–Cl bond distances are different in the molecule. (**2** Marks)

13. (a) The reaction of $(Br)Re(CO)_5$ with the following ligand at refluxing toluene for four hours affords product A with the evolution of a colorless gas. Heating compound A at 270 °C for six hours gave compound B and the evolution of a colorless gas. Compound B's reaction with pyridine and AgOTf in refluxing toluene gave an ionic rhenium compound C without a gas's evolution (OTf = $CF_3SO_3^-$; it is called as triflate). Considering that compounds A, B, and C are stable and they have two Re-N, three Re-N, and four Re-N bonds, respectively, draw the structures of these compounds. (**3** Marks)



(b) Using the following reagents, suggest a synthetic route with the minimum number of steps for the product formation shown below. Show the reagents at each step. (**3** Marks)

Reactants



Product