Inorganic and Organic Chemistry: Concepts and Applications (CYL120)
Semester-II (2014-2015), Department of Chemistry, IIT Delhi

Exam: Major **Time: 6 to 8 pm**

Date and Day: 02-05-2015 and Saturday **Maximum Marks: 43**

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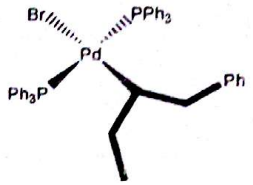
1 Starting from ferrocene, how will you prepare (a) ethynylferrocene and (b) bis(hydroxymethyl)ferrocene? (4 marks) **(OR)**

Show through equation(s), the Fischer-Hafner method for the synthesis of dibenzenechromium **I**. Further, draw the structures/write the formulae of the main products formed when **I** reacts with $Cr(CO)_6$ and PF_6. (4 marks)

2. (a) The reaction of RX and $R'SnBu_3$ to give $R-R'$ and $XSnBu_3$ is catalyzed by $L_2Pd(0)$. Propose a suitable catalytic loop/cycle for this reaction by taking into account the following hint. ***Hint:*** Apart from the other reaction(s), the catalytic loop/cycle has cis/trans isomerization and transmetalation (which is the reaction of Pd–X bond with R′–Sn bond to give Pd–R′ bond and X–Sn bond) reactions.

(b) The metal-alkane intermediate on the right is unstable. It undergoes a rearrangement and results in arylalkene palladium complex(es) with the general formula $Pd(PPh_3)_2(Br)(H)(\eta^2$-alkene). Draw the correct structure(s) of the arylalkene palladium complex(es).



(c) Compound $(Cp)_2Fe_2(CO)_4$ **Y** reacts with one equivalent of iodine and results in two equivalents of compound **X**. Suppose that the compounds **Y** and **X** are stable and show carbonyl stretching band(s) in the regions 2104-1760 cm^{-1} and 2020-1890 cm^{-1}, draw the precise structures of these compounds, respectively. Hint: During this reaction no gas was formed. (7 marks)

3. (a) Through a cartoon/simplified diagram (as mentioned in the class), show the product(s) formed when dioxygen reacts with (a) heme and (b) hemoglobin. Further, comment on the oxidation state(s), coordination number(s), and coordination environment(s) (by mentioning the symbols of all the atoms directly attached to the metal(s)) of the metal center(s) in the product(s).

(b) Mention the metal center(s) with their coordination environment(s) (by mentioning the symbols of all the atoms directly attached to the metal(s)) present in chlorophyll and carbonic anhydrase. (5.5 marks)

4. (a) Arrange the following compounds in the decreasing order of their molar extinction coefficient values. Also, give a very brief and suitable explanation for the trend that you have predicted. (i) $[Co(H_2O)_6]Cl_2$, (ii) $K_2Cr_2O_7$, (iii) $Co[CoCl_4]$

(b) In $Cs_2K[TiCl_6]$, two Ti–Cl bond lengths are different than the rest. Draw a suitable metal d-orbital splitting diagram with orbital labels. Also, fill the electron(s) in these orbitals. (3 marks)

5. Mention whether the following statements are true or false? (2 marks)

(i) Nephelauxetic effect supports the assumptions of CFT.

(ii) Temperature dependence of magnetic moment is explained by VBT.

(iii) 18-electron rule is more convenient to use than the EAN rule.

(iv) The ν_{CO} values of $Mo(CO)_3(P(OMe)_3)_3$ are higher than the same values found for $Mo(CO)_3(Py)_3$.

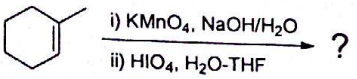
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

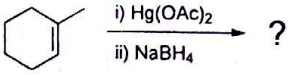
6. (a) Define a meso compound? Write the meso structure of tartaric acid in Fischer projection? (b) Discuss about the Simmons-Smith reaction. (c) Write the structure of the natural product Carvone that present in spearmint leaves. (3 Marks).

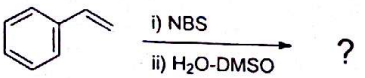
7. (a) Define a pro-chiral compound? Give two examples of pro-chiral compounds one having sp^2 and sp^3 carbon. Identify Pro-R and Pro-S hydrogen's in the benzyl alcohol. (1.5 Marks)

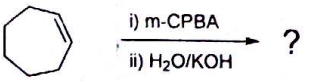
(b) What is the structure and stereochemistry of the product formed in the reduction of acetophenone with $NaBH_4$, where the hydride attacks from the Si face? (1 Mark)

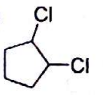
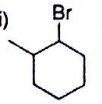
8. (a) Write the structures of the products formed in the following reactions. (4 Marks)

(a) 

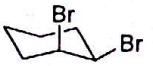
(b) 

(c) 

(d) 

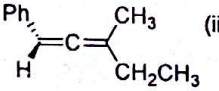
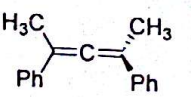
(b) Draw all the possible stereoisomers for each compound given below. Label the pairs of enantiomers and diastereomers. (2 Marks) (i)  (ii) 

(c) Write the names of the compounds below with their absolute configuration

(i)  (ii) 

9. (a) Calculate the relative proportion of (+)-2-butanol, $[\alpha]_D = +13.5\ °$, and (−)-2-butanol, $[\alpha]_D = -13.5\ °$, required to give a specific rotation of + 2.43 °. (1 Mark)

(b) Through a sequence of steps, show how will you resolve the racemic α-bromo-phenylacetic acid in to its pure enantiomers. (2 Marks)

(c) Classify the following in to chiral or achiral compounds and assign the R/S configurations. (1 Mark) (i)  (ii) 

10. **(A)** (i) Arrange the following groups with the increasing order of their leaving group ability in the carbonyl substitution reaction: (2 Marks)

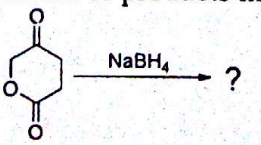
i) $CH_3CH_2O^-$ ii) $PhCH_2NH^-$ iii) $iPrCH_2COO^-$ iv) nBu^-

(ii) Write a stepwise mechanism for the formation of mixed anhydride from formic acid chloride and sodium acetate. (2 Marks) **OR**

(B) (i) Write a stepwise mechanism for the hydrolysis of trimethyl orthoacetate? (2 Marks)
(ii) Prepare a stable Grignard reagent from 4-bromo-2-butanone. (2 Marks) **OR**

(C) (i) How Grignard reagents are made? Write a stepwise mechanism for the addition of benzyl magnesium chloride to the benzaldehyde? (2 Marks)

(ii) Write the structures of products in the following reactions. (2 Marks)

(i) 

(ii)