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End Semester Examination of Semester-II, 2016

Subject: CHEMISTRY (PG)
Paper: CEMPG-201

Full Marks: 40
Time: 2 Hrs

The figures in the margin indicate the marks corresponding to the question

Candidates are requested to give their answers in their own word as far as practicable.

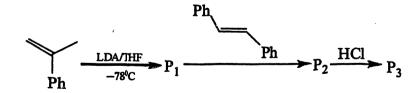
Illustrate the answers wheeever necessary.

Unit I

Answer any one questions

10x1=10

1. a) Predict the product with mechanistic details and mention the stereochemistry wherever it is applicable 4



b) The photoisomerization of optically active compound (A) to compound (B) in the following reaction proceeds with ~85% retention and 15% inversion of configuration at the migrating centre.

$$H_3C$$
 CN
 $h\nu$
 H_2C
 CN
 H
 CN
 H
 CH_3
 CN
 H
 CH_3
 CN
 H
 CH_3
 CN
 H
 CH_3
 CN
 CN
 H
 CH_3
 CN
 CN
 CN
 H
 CH_3

However the thermal reversion of the reaction (i.e. $B \xrightarrow{\Delta} A$) occurs with 90% retention of configuration at migrating centre. Suggest concerted symmetry allowed pathways for each reaction and comment on feasibility by energetically and sterically.

c) Explain the reaction by applying F.M.O. approach: 2

2. a) How would you explain the following observation

Relative rate R = p-NMe₂, p-oMe, H, p-Cl, m-NO₂, p-NO₂ (Kx10⁶mol⁻¹s⁻¹) 338 102 73 78 79 88

b) Account for the regioselectivity of the following reaction:

c) Carry out the following conversion by using at least one pericyclic reaction:

d) Synthesize any one of the following compound by applying pericyclic reaction 2

OHI II

Answer any one questions

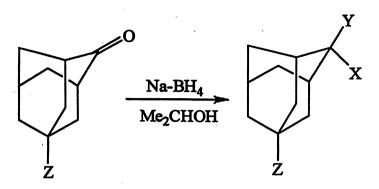
10x1=10

- a) Write all the stereoisomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexane. Identify the chiral and achiral ones. Upon base treatment under bimolecular conditions all the isomers undergo -1, 2-elimination at rates within a factor of 200 but the one, called β-isomer, does not react at all practically. Identify the β-isomer giving reasons.
 - b) w hen <u>cis-2-bromo-trans-4-phenyl</u> cyclohexan-r-1-ol is separately treated with moist silver oxide or alkali same product (4-phenyl cyclohexane) is formed but when cis-2-bromo-cis-4-phenylcyclohexan-r-1-ol is so treated with those two reagents different products are obtained. Explain these results.
- 4. a) Show the major product of the following reaction and explain with the help of Felkin-Anh model.

OLi | CH=O +
$$H_2C=C-C(CH_3)_3$$
 ?

How the anti-Cram product can be obtained as major in the same reaction. Explain your answer. 4

b) Explain with the help of Cieplak model, giving orbital interpretation, the diastereomeric composition of the products in the following reactions when substituent (Z) is varied as shown:



 $P_1 + P_2$

<u>Z</u>	Percentage of alcohol		
	P ₁ (E-isomer)	P ₂ (Z-isomers)	
-C1	59	41	
4ClC ₂ H ₄	60	40	
4-OH-C ₅ H ₄	44	56	4

c) What happens when trans-2-chloro cyclohexanol is treated with a base?

Unit III

Answer any one questions 10x1=10

5. a) From the following two starting materials same alkene is obtained. Identify the alkene and explain its formation mechanistically.

$$R^1$$
 R^2 & R^1
 R^2 R^2
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 R^2
 R^2
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 R^2

b) Predict the product of the following reaction and explain mechanistically its formation.

c) Complete the following reaction sequences and show that the mechanism in each step 3

 a) Draw the catalytic cycle for the following cross coupling reaction and hence explain the role of organoboron and solvents.

n-Bu
$$\begin{array}{c} B - O \\ O \\ \hline \\ Pd(O) \\ \hline \\ C_6H_6/NaOEt \\ 80^0C, 4h \end{array}$$

$$\begin{array}{c} Bu-n \\ \\ 98\% \end{array}$$

b) Write down the product(s) with proper mechanistic details: 2+2

c) Synthesize the following compound using Pd-catalyzed cross coupling reaction.

$$MeO - C = C - COOCH_2Ph$$

Unit IV

Answer any one questions

10x1=10

7. a) Carryout the following synthesis using retrosynthetic analysis (any two): $2\frac{1}{2}x^2=5$

ii)

iv)



b) Explain the formation of the following conversions (any two): $2\frac{1}{2}x^2$

ii)
$$NH_2$$
 aq. HCHO c. HCl

iii)
$$\frac{\text{HCl, Br}_2}{\text{Ph-NO}_2}$$

iv)
$$N$$
 NH_{2} NH_{3} NH_{2} NH_{2} NH_{2} NH_{3} NH_{2} NH_{3} NH

8. a) How do you convert the following (any two): $2x2\frac{1}{2}$

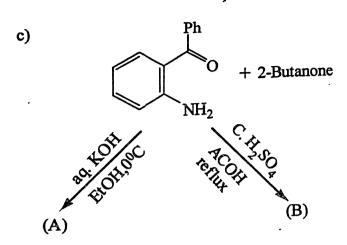
$$i) \quad \bigcap_{N} Br \quad \bigcap_{N}$$

$$ii) \bigcirc N$$

iii) Indole _____ Tryptophan

 NO_2

- b) Outline the synthesis of following (any one): 3
 - i) γ-Fagarine
 - ii) Pyridoxine



Identify (A) and (B) with reasons.

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