Q.P. Code: 60787

## Fourth Semester M.Sc. Degree Examination, September/October 2020

(CBCS Scheme)

#### Chemistry

# Paper C401-OC - ORGANOMETALLIC AND HETEROCYCLIC CHEMISTRY

Time: 3 Hours]

[Max. Marks: 70

Instructions to Candidates: Answer Q.No. 1 and any five of the remaining.

1. Answer any **TEN** of the following questions:

 $(10 \times 2 = 20)$ 

- (a) What is Felkin's reaction? Illustrate with an example.
- (b) Several of the catalytically important organometallic compounds are 16-electron, 4-coordinate square planar species. Comment on this statement.
- (c) What is the catalytic species used in Wacker's process and how is it generated?
- (d) Formulate the product(s) in the following with suitable mechanism:

Ph - CHO + Br - CH<sub>2</sub> - CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub> 
$$\xrightarrow{Zn}$$
 ?

(e) Give the products of the following reactions:

- (f) What is hydrocyanation reaction? Mention its commercial importance.
- (g) Give any two general methods of synthesis of organocerates.

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(h) Predict the product and outline the mechanism :

$$rac{\text{n-Bu}_3\text{SnH}}{\text{AIRN, } \Delta}$$
 ?

- (i) What is the product formed when 2, 2 dimethyloxirane is treated with dimethyloxosulfonium methylide?
- (i) Write the product(s) in the following:

$$\begin{array}{c|c}
Ph-N & \bigcirc \\
\hline
 & \bigcirc \\
N & \bigcirc \\
\end{array} + DMAD \longrightarrow ?$$

(k) Draw the structures of the products formed in the following reactions:

? 
$$\leftarrow$$
 CH<sub>3</sub> CN CN CN  $\rightarrow$  CH<sub>3</sub> CN  $\rightarrow$  CN  $\rightarrow$  CN  $\rightarrow$  CH<sub>3</sub>  $\rightarrow$  CN  $\rightarrow$  CH<sub>3</sub>  $\rightarrow$  CH<sub>3</sub>

- (l) Outline one method each for the synthesis of 5- and 6- membered Reterocyclic compound containing phosphorous.
- (a) Give two examples each to illustrate nucleophilic and electrophilic cleavage of metal-carbon sigmal bond.
  - (b) Write the catalytic cycle for hydrogenation of ethylene catalysed by (Ph<sub>3</sub>P)<sub>3</sub>RhCl. Indicate the rate determining step in the reaction.
  - (c) What is Heck reaction? Explain the mechanism using a suitable example.

    (4 + 3 + 3)
- 3. (a) How is propene converted into butyraldehyde? Describe the catalytic cycle.
  - (b) Explain the mechanism of alkene isomerisation via metal allyl intermediate
  - (c) How does cyclobutadiene complex with metals? Comment on its reactivity.

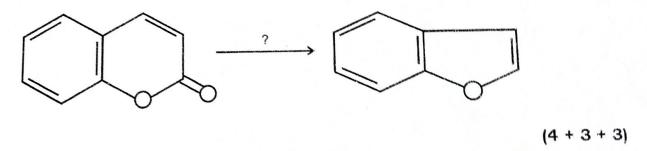
(4 + 3 + 3)

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- 4. (a) Discuss the utility of organo-selenium compounds in the synthesis of alkenes and  $\alpha$ ,  $\beta$  unsaturated carbonyl compounds.
  - (b) Predict the product and discuss the mechanism of the following reactions:

(i) Ph 
$$\xrightarrow{i)} \xrightarrow{\text{BuLi}} ?$$
(ii)  $\xrightarrow{\text{CH}_2 I_2 / Z_n(\text{Cu})} ?$ 
(iii)  $\xrightarrow{\text{CH}_2 I_2 / Z_n(\text{Cu})} ?$ 

- (a) Discuss with mechanism the Peterson olefination reaction for the stereospecific synthesis of E- and Z- alkenes.
  - (b) Explain the mechanism of Barton decarboxylation.
  - (c) How do you bring about the following conversion :

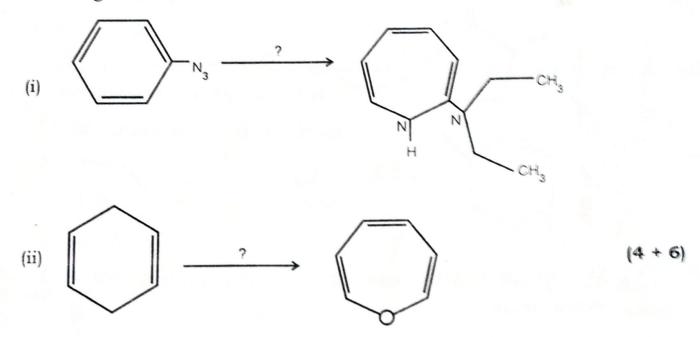


- 6. (a) Discuss the preparation and reactions of organomercury compounds.
  - (b) Identify the product in the following reaction and suggest the suitable mechanism:

(c) Enumerate the steps involved in the synthesis of benzimidazoles. (4+3+3)

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- (a) Explain the synthesis of pyrimidine and with the help of resonance structure show the preferred position for electrophilic reactions.
  - (b) Write the reagents/conditions and propose suitable mechanism for the following conversions:



- (a) Formulate the reactions of Gilman reagent with epoxides and α, β unsaturated carbonyl compounds.
  - (b) Give an account of solvomercuration-de-mercuration reaction.
  - (c) Outline a method for the synthesis of dithiocines and give any one reaction of them.
    (4 + 3 + 3)