This question paper contains 8 printed pages.]

Your Roll No. ......................

4340

M.Tech./II Sem.
CHEMICAL SYNTHESIS AND PROCESS TECHNOLOGIES
Paper-201—Reagents in Organic Synthesis, Newer Synthetic Reactions and Methodologies

Time : 3 Hours

Maximum Marks : 70

(Write your Roll No. on the top immediately on receipt of this question paper.)
Use separate answer script for section A and B.

SECTION—A

Time : 1½ Hours

Maximum Marks : 35

Answer any four questions.

I.  (a) (i) How is Wilkinson’s catalyst prepared?

(ii) Name functional groups which are unreactive towards Wilkinson’s Catalyst + Hydrogen.

(iii) Write a very brief note on the concept of ‘Asymmetric Hydrogenation’.

(b) Suggest the most suitable reagent(s) (formulae, names) and general reaction conditions for the following. Outline the general course of the reactions:

(i) $\text{HOOC.CH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \rightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{COOEt}$

(ii) $\text{PhCH} = \text{CH.CH}_2\text{CHO} \rightarrow \text{PhCH} = \text{CH.CH}_2\text{OH}$

[P.T.O.]
2. (a) Work out the following transformations using Hydroboration methodology (Reagents, steps, general conditions etc.) Any three:

(i) PhCH - CH₂ → PhCH₂CH₂CHO

(ii) CH₂ - CH₂CH₂CH₂CH - CH₂ → O

(Cycloheptanone)

(iii) Cyclohexene + BrCH₂CO₂NaEt₂ → C₆H₉CH₂CO₂Et₂

(iv) CH₂ - CH C Br → CH₃

CH₃

(b) Rationalise:

Reagents: 1. TH + BH₃ 2. AC·OH Δ 3. H₂O₂· NaOH.
3. Workout the following transformations using the concepts of organosilicon chemistry:

(i) \( \text{CH}_2 = \text{CH} \cdot \text{TMS} + \text{BuLi} \xrightarrow{\text{THF, } <0^\circ\text{C}} \text{Bu.CH}_2 \cdot \text{CH} \cdot \text{TMS} \xrightarrow{\text{PhCHO}} \text{?} \xrightarrow{\text{HF}} \text{?} \)

(ii) \( \text{O} \text{SiMe}_3 \xrightarrow{+ \text{PhSCH}_2\text{Cl}} \text{?} \xrightarrow{\text{HIO}_4, \Delta} \text{?} \)

(iii) \( \text{CONEt}_2 \xrightarrow{\text{BuLi, THF}} \text{?} \xrightarrow{\text{TMS - Cl}} \text{?} \xrightarrow{\text{Br}_2} \text{?} \)

4. Write short notes on any two:

(1) Heck Reaction

(2) Wacker Oxidation

(3) CBS-Reduction

(4) Peterson Reaction

(5) Hydrosilylation.
Match the item under (A) with the most appropriate item under (B).

*Example*: 1. Pd/C - H₂ (a) Debenzylation. Answer as 1(a).

<table>
<thead>
<tr>
<th>(A)</th>
<th>(B)</th>
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<tbody>
<tr>
<td>1. Pd C                  N₂  BaSO₄</td>
<td>(a) Desulphurisation</td>
</tr>
<tr>
<td>2. (Me₂Si)₂ NLi</td>
<td>(b) Desilylation reagent</td>
</tr>
<tr>
<td>3. Trimethyl silyliodide</td>
<td>(c) Protection of Hydroxyl</td>
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<tr>
<td>4. Dichlorodimethylsilane</td>
<td>(d) Ar·Ar coupling</td>
</tr>
<tr>
<td>5. DDQ</td>
<td>(e) MPV reduction</td>
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<tr>
<td>6. K-triethyl borohydride</td>
<td>(f) Powerful Hindered base</td>
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<tr>
<td>7. Suzuki reaction</td>
<td>(g) Silylation process</td>
</tr>
<tr>
<td>8. N, O-bis(trimethylsilyl) acetamide (BSA)</td>
<td>(h) Prepn of silicon polymers</td>
</tr>
<tr>
<td>9. Raney Nickel - H₂</td>
<td>(i) Acid chloride to aldehyde</td>
</tr>
<tr>
<td>10. Tetrabutylammonium fluoride</td>
<td>(j) Oxidising agent</td>
</tr>
<tr>
<td>11. Aluminium isopropoxide</td>
<td>(k) Selectride</td>
</tr>
<tr>
<td>12. TBDMSCl - Chloride</td>
<td>(l) Cleavage of ether</td>
</tr>
</tbody>
</table>
SECTION-B

Time : 1½ Hours

Maximum Marks : 35

Answer any five questions.

1. (a) Cyclic ketone, cyclohexanone, on reaction with secondary amine, pyrrolidin in presence of PTSA gives a product A. Compound A then act as nucleophile in a nucleophilic acyl substitution reaction with acetic anhydride. The final product B will be obtained following a hydrolysis reaction. Write the complete mechanism involved in the reaction and the structures of compounds A and B.

(b) Explain, by drawing only scheme, the principle of PTC for the nucleophilic displacement reaction of an alkyl chloride RCl, benzylchloride with sodium cyanide NaCN, in the presence of a quaternary chloride QCl, (1-Hexadecyl) trimethyl ammonium chloride.

2. (a) Define the term artificial enzymes.

(b) Explain the intramolecular cyclisation of given aldehyde to hydroxy ketone by using cyclodextrin derivative as artificial enzyme.
3. (A) Define the term umpolung.

(B) Write the mechanism of the following reaction:

Starting from the lithiated 1,3-dithiane of benzaldehyde, which can be viewed as an masked acyl anion, prepare the following compounds: α-hydroxy ketone and β-hydroxy ketone.
4. (a) Write the names and structures of at least three nucleophiles which can be used in Baylis Hillsman reaction.

(b) Predict the product formed by the reaction of vinyl methyl ketone (a Michael acceptor) and 2-formylfuran in the presence of a stoichiometric amount of DABCO. Write the mechanism involved in this reaction.

5. Attempt any two:

(i) Explain Corey-Chaykovsky reaction by taking at least one example.

(ii) Explain: Reactive ylides will predominantly afford $E$-alkenes if equilibration of the erythro and threo betaines can be accelerated. However, it has been shown that addition of another equivalent of the organolithium reagent into the reaction mixture leads to the formation of $E$-alkenes in a selective fashion.

(iii) Prepare the compound given below stating from Compounds (a) $\text{(C}_4\text{H}_7\text{OBr)}$ and (b) $\text{(C}_6\text{H}_{10}\text{O)}$. 

[Diagram of the compound]

3.5 + 3.5
6. Predict the products (A-E) formed in the following reactions:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{Pb} & \quad 1. \text{LiN(SiMe)}_2 \quad 1. \text{H}_2\text{O}_2, \text{NaOH} \\
& \quad 2. \text{CH}_2=\text{CHCH}_3 \quad 2. \text{LiAlH}_4 \\
\text{A} & \quad \text{B} \\
& \quad \text{D} \quad \text{C} \\
\text{E} & \quad \text{D} \\
\downarrow & \quad \downarrow \\
\text{Pumiliotoxin B} & \quad \text{Pumiliotoxin B}
\end{align*}
\]