

This question paper contains 8 printed pages.]

Your Roll No.

4340

A

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

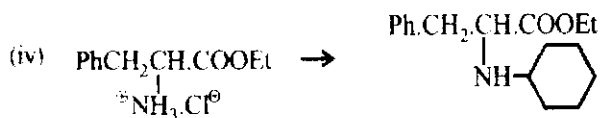
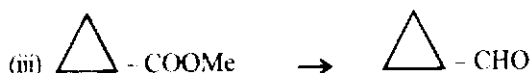
Time : 1½ Hours

Maximum Marks : 35

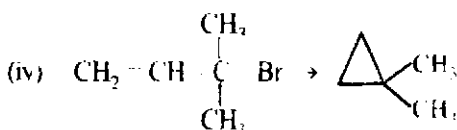
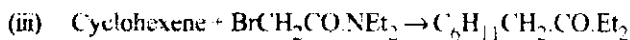
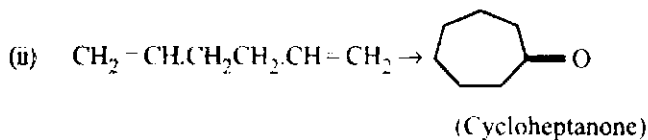
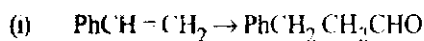
Answer any four questions.

- 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) $\text{HOOC}\cdot\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5 \rightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{COOEt}$
- (ii) $\text{PhCH}=\text{CH}\cdot\text{CHO} \rightarrow \text{PhCH}=\text{CH}\cdot\text{CH}_2\text{OH}$

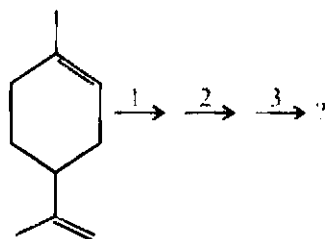
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2. (a) Workout the following transformations using Hydroboration methodology (Reagents, steps, general conditions etc.) Any **three** :

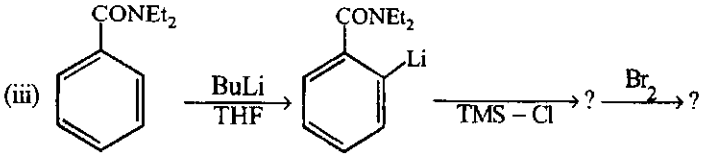
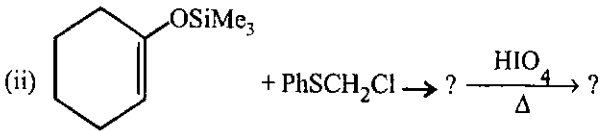
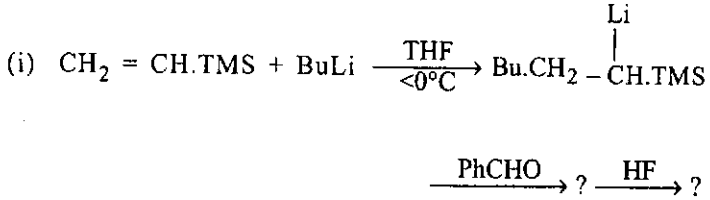


- (b) Rationalise :



Reagents : 1. $\text{THF} + \text{BH}_3$ 2. $\text{AcOH} \Delta$ 3. $\text{H}_2\text{O}_2 - \text{NaOH}$.

3. Workout the following transformations using the concepts of organosilicon chemistry :



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).

(A)	(B)
(1) Pd/C - N ₂ - BaSO ₄	(a) Desulphurisation
(2) (Me ₃ Si) ₂ NLi	(b) Desilylation reagent
(3) Trimethyl silyliodide	(c) Protection of Hydroxyl
(4) Dichlorodimethylsilane	(d) Ar-Ar coupling
(5) DDQ	(e) MPV reduction
(6) K-triethyl borohydride	(f) Powerful Hindered base
(7) Suzuki reaction	(g) Silylation process
(8) N, O-bis (trimethylsilyl) acetamide (BSA)	(h) Prepn of silicon polymers
(9) Raney Nickel -H ₂	(i) Acid chloride to aldehyde
(10) Tetrabutyl ammonium fluoride	(j) Oxidising agent
(11) Aluminium isopropoxide	(k) Selectride
(12) TBDMSCl	(l) Cleavage of ether

SECTION-B

Time : 1½ Hours

Maximum Marks : 35

Answer any five questions.

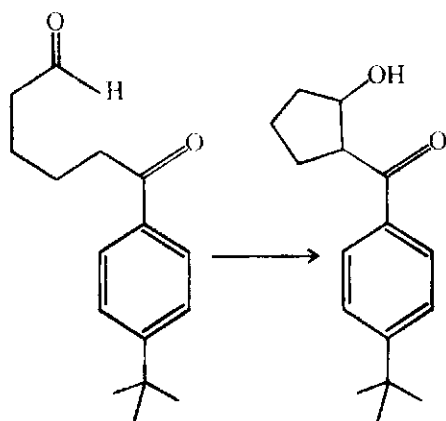
1. (a) Cyclic ketone, cyclohexanone, on reaction with secondary amine, pyrrolidin in presence of PTSA gives a product A. Compound A then act as nucleophile in a nucleophilic acyl substitution reaction with acetic anhydride. The final product B will be obtained following a hydrolysis reaction. Write the 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. 3.5+3.5

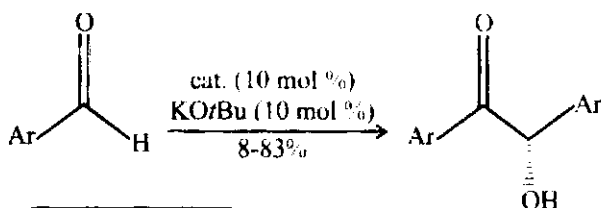
2. (a) Define the term artificial enzymes.

- (b) Explain the intramolecular cyclisation of given aldehyde to hydroxyl ketone by using cyclodextrin derivative as artificial enzyme. 2+5

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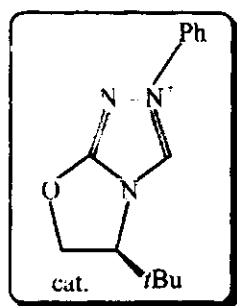
3. (A) Define the term umpolung.
 (B) Write the mechanism of the following reaction :



ce = 80-95%

Ar = Ph, *m*-Me-Ph,
p-Me-Ph, *p*-MeO-Ph,
m-Cl-Ph, *p*-F-Ph,
p-Cl-Ph, *p*-Br-Ph,
o-Furyl, *o*-Naphthyl

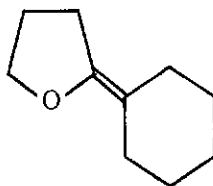
Or



Triazolium salt

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 a least three nucleophiles which can be used in Baylis Hillamn 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. 3.5 + 3.5
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) (C_4H_7OBr) and (b) $(C_6H_{10}O)$. 3.5 + 3.5



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6. Predict the products (A-E) formed in the following reactions : 7

