[This question paper contains 6 printed pages]

Your Roll No

7645 **J**

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

Answer **all** *questions. Do not discuss mechanisms unless asked for State the principle and/or concept involved in the reactions*

Write neat perspective structural diagrams

1 (a) How is Wilkinson's catalyst prepared?

(b) When an alkene (RCH=CHR) is hydrogenated using a mixture of D_2 and H_2, the product (RCH_2CH_2R) contains molecules RCHD CHD R and RCH_2CH_2R only? There are no molecules containing D and H (RCHD CH_2R) Account

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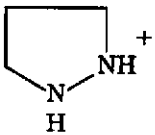
(c) How is borane prepared from sodium borohydride?

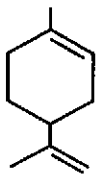
(d) Compare alkyl boranes and Grignard reagents in their chemical reactivity

2 (a) Select a hydride transfering agent which can be used to convert a carbonyl to methylene Write all the steps

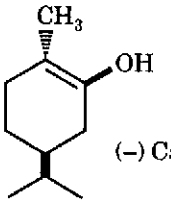
(b) Compare the reactivity of sodium borohydride and LAH towards a conjugated ketone

(c) Solve any ***two***

(i)  $+ OCH(CH_2)_2CHO \xrightarrow[CH_3CN-H_2O]{NaCNBH_3} ?$

(ii)  $\xrightarrow{THXBH_2} \xrightarrow[1\ mole\ \Delta]{CH_3COOH}$

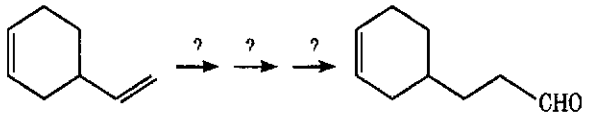
D-limonene

$\xrightarrow{H_2O_2\text{-}NaOH}$ 

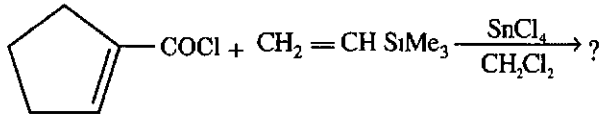
(–) Carvomenthol

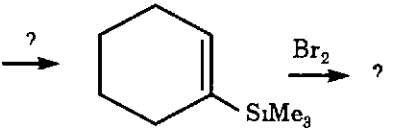
(iii) $9-BBN + PhLi \rightarrow ? \xrightarrow{CH_3SO_3H} ?$

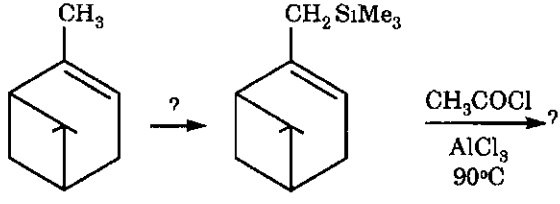
$\xrightarrow[Bu^tOH + Bu^tOK]{PhCOCH_2Br} ?$

(iv) 

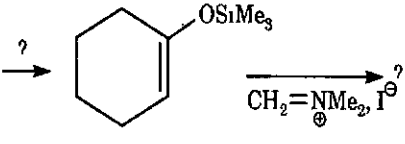
3 (a) Solve the following problems based on the concepts of vinyl silanes and allyl silanes

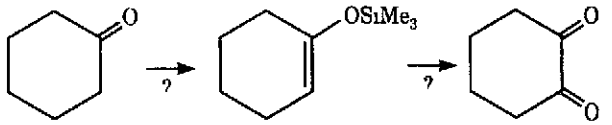
(i) 

(ii) Cyclohexanone 

(iii) 

(b) Recall the chemistry of enol silyl ethers, work out the following

(i) Cyclohexanone 

(ii) 

4 Annotate the following, choose any ***two***

(i) Peterson Reaction

(ii) Wacker Oxidation

(iii) Heck Reaction

(iv) Suzuki Cross coupling

(v) Trialkyl silyl halides (Cl, Br, I) in organic synthesis

SECTION-B

*Attempt any **five** questions*

1 Explain the term Umpolung synthesis Give the synthesis of 4-methylpent-3-ene involving acyl anion equivalent of 1,3-dithiane 2+5

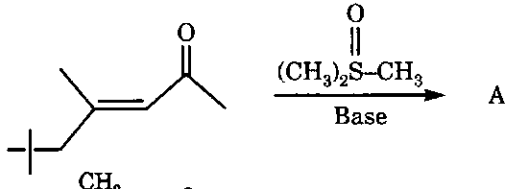
2 Write the mechanism of any two of the following reactions 3 5+3 5

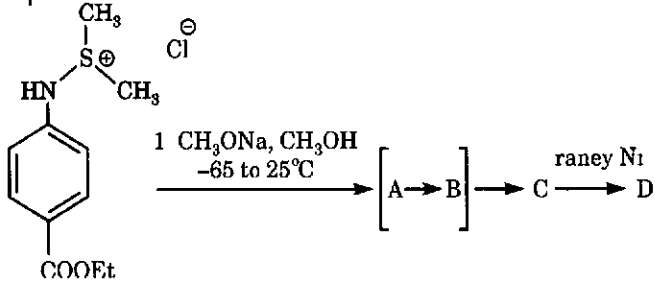
(i) Arbuzov rearrangement

(ii) Mukaiyama-Johnson aldol reaction

(iii) Horner-Wadsworth-Emmons reaction or Wittig reaction of stabilized yields

3 Predict the products(s) formed in each of the following reactions 2+5

(i) 

(ii) 

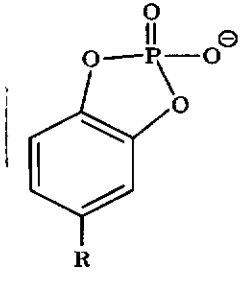
4 Explain any two 3.5 + 3.5

(i) Why enamines are nucleophilic? Give one example

(ii) Why clay-supported PTC is better than polymer-supported PTC?

(iii) Why Z-enolates give syn-aldol products and E-enolates give anti-aldol products? Explain on the basis of Zimmerman-Traxler model

5 Explain the action of the mimic of Ribonuclease A system in the hydrolysis of the phosphates 7



R = CH_3 or $C(CH_3)_3$

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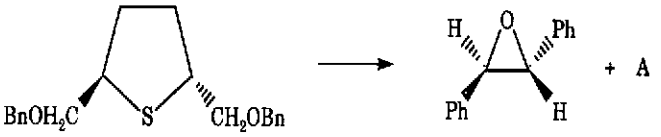
6 Predict the product formed by the reaction of acrylamide (a weak Michael acceptor) and aromatic aldehydes such as 2-formylthiazole at room temperature in an aqueous medium (1,4-dioxanel/H_2O) (1 1) in the presence of a stoichiometric amount of DABCO Write the name of reaction involved and its mechanism 3+1+3

7 (a) The sulphonium salt [B] formation was carried out by treating the precursor thiol [A] with C_7H_7Br [C], followed by addition of $AgClO_4$ The reaction of B with D (aldehyde) gives the compound E and recovered compound A Complete the reactions involved in this synthesis



A E

(b) Write structures for the following compounds

(i) DBU

(ii) Common ammonium or phosphonium salts used as PTC

(iii) Dicyclohexano-18-crown-6 4+3