2016/ODD/08/22/CHM-302/347

PG Odd Semester (CBCS) Exam., December—2016

CHEMISTRY

(3rd Semester)

Course No.: CHMCC-302

(Organic Chemistry—III)

Full Marks: 70
Pass Marks: 28

Time: 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, selecting **one** from each Unit

UNIT-I

1. (a) (i) Complete the following reactions and suggest mechanism. Mention the step where reversal of polarity is noticed:

OHC CHO SH
$$Br_3$$
-OEt₂ $[A]$ $BuLi$ Br_3 -OEt₂ $[B]$ $RaNi$ $[C]$ $RaNi$ $[C]$

(ii) Explain why ${\rm HgCl}_2$ is necessary for the hydrolysis of dithiane.

(2)

(b) Predict the product(s) of the following reaction with plausible mechanisms:

 $2\frac{1}{2}+2\frac{1}{2}+2=7$

(i)
$$\stackrel{\text{SiMe}_3}{\stackrel{\text{lime}_3}{\circ}} \xrightarrow{\text{H}_2\text{SO}_4}$$
 ? $\stackrel{\text{SiMe}_3}{\stackrel{\text{SiMe}_3}{\circ}} \xrightarrow{\text{KH}}$

$$(ii) \xrightarrow{\text{SiMe}_3} \xrightarrow{\text{KH}} ?$$

(iii) Me
$$\xrightarrow{\text{1) DIBAL-H}}$$
 ? $\xrightarrow{\text{hexane, -70 °C}}$?

2. (a) Predict the product(s) of the following reaction and suggest plausible mechanisms: 3+3+2=8

(i)
$$N \longrightarrow N$$
 $ODE (1) ODE (1) ODE (2) S% KOH, EtOH $ODE (2)$?$

(ii)
$$\xrightarrow{\text{OTf}}$$
 + BnSn $\xrightarrow{\text{Pd(PPh_3)_4(5 mol\%)}}$?

(iii)
$$CH_3$$
 CH_2OH DCC $DMAP$?

(b) Suggest a plausible mechanism for the following transformation:

(c) Explain with suggestive mechanism, BuLi undergoes addition with , -unsaturated ketones whereas Me₂CuLi undergoes 1,4-addition with the same.

UNIT—II

3. (a) Carry out the following transformations (with mechanisms of reactions involved): $1\frac{1}{2}\times2=3$

(ii)
$$\begin{array}{c} CH_3 \\ CH_3 \\ H_3C \end{array}$$
 from $\begin{array}{c} H_3C \\ H_3C \end{array}$ $\begin{array}{c} CH \\ N \\ H \end{array}$

(b) Predict the products of the following reactions and suggest the mechanisms of reactions involved: 2×3=6

(i)
$$H_3C$$
 O CH_3 $NH_3/$ CH_3

(ii)
$$\sim$$
 Ph POCl₃/DMF ?

(iii)
$$\stackrel{N}{\underset{Ph}{\bigvee}} + \stackrel{COCl}{\underset{OCH_3}{\longleftarrow}} \stackrel{Et_3\ddot{N}}{\longrightarrow} ?$$

(c) Complete the following reactions by suggesting the structures of (A) to (F): $\frac{1}{2} \times 6 = 3$

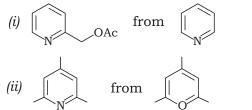
(i) Ph—CH=CH₂ + Ph—N—N=N—
$$(A)$$
 + (B) (major) (minor) /—N₂ \uparrow (C)

(ii)
$$R^1 \xrightarrow{R^2} R^3 \xrightarrow{PPh_3} (D) \xrightarrow{rt} (E)$$

(iii)
$$\longrightarrow$$
 COOEt \longrightarrow COOEt

(d) Describe the synthesis of olefin (G) from ketone (H) by using the Shapiro reaction:

4. (a) Provide the strategies employed to obtain the following (provide mechanisms): $2 \times 2 = 4$



(b) Delineate the outcome of the following reactions with supportive mechanisms:

 $(i) \qquad \qquad \text{NaNH}_2 \qquad \text{NaNH}_2 \qquad \text{NH}_3 \text{ (liq)} \qquad ?$ $(ii) \qquad + \text{Glycerol} \qquad \frac{\text{C.H}_2\text{SO}_4}{\text{PhNO}_2, 130 \text{ °C}} ? \qquad ? \qquad ?$ $(iii) \qquad \qquad \frac{\text{aq. CH}_2\text{O}}{\text{C.HCl/}} ?$ $(iv) \qquad \qquad \frac{1) \text{H}_2\text{O}_2/\text{AcOH/65 °C}}{2) \text{NO}_2\text{BF}_4} \qquad 3) \text{Ph}_3\text{P/280 °C}$

(c) Suggest a strategy to control the production of NO_2 from quinoline. Provide mechanism.

UNIT—III

- **5.** (a) Provide and compare the old and green methods of Ibuprofen synthesis. $2\frac{1}{2}+1\frac{1}{2}=4$
 - (b) What is the percentage atom economy for the reaction for making hydrogen by reacting coal with steam? 2
 - (c) Provide two advantages and two disadvantages of using water as solvent in synthesis.
 - (d) Conventional bromination of *trans*—Stilbene involves the use of molecular bromine. Depict the reaction and propose a green alternative to this process with justification. 1+2=3

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(e) Provide one environmentally benign alternative to the following conventional reaction schemes and state the major advantage of your proposed alternative:

(i) HO OH $+ H_3CCOCH_2COOC_2H_5 \xrightarrow{conc. H_2SO_4} \xrightarrow{0 \text{ °C}}$ (ii) CHO $+ H_3CCOCH_2COOC_2H_5 \xrightarrow{conc. H_2SO_4} \xrightarrow{0 \text{ °C}}$ (iii) $+ H_3CCOCH_2COOC_2H_5 \xrightarrow{CHO} \xrightarrow{NaOH} \xrightarrow{EtOH/} \xrightarrow{O}$

- **6.** (a) Illustrate (with example) the following principles of Green chemistry: $2 \times 2 = 4$
 - (i) Use renewable feedstock
 - (ii) Avoid derivatives
 - (b) Hydrazine (N_2H_4) is used for rocket fuel. Calculate the percentage atom economy for hydrazine production

2NH₃ NaOCl N₂H₄ NaCl H₂O 2

(c) How is ultrasound employed to energize chemical reactions?

(d) Compare the greenliness between the following two schemes:

OH

Ca(NO₃)₂

acetic acid
Scheme-I

NO₂

OH

OH

NaNO₃

H₂SO₄
Scheme-II

NO₂

(e) Explain the mechanism of phase-transfer catalysis.

UNIT—IV

7. (a) What is glycoside? Classify the glycosides depending on the atom involved in glycosidic bond formation. Give at least one example of each class of glycoside. Write a short note on 'Fischer glycosylation reaction' stating the reagents and reaction condition.

 $1+2\frac{1}{2}+1\frac{1}{2}=5$

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(b) Provide a synthetic scheme along with the reagents for the synthesis of L-glyceric acid from L-ascorbic acid. 2

(10)

- (c) Draw the structures of different optical isomers of ephedrine with their names. Discuss the synthesis of () pseudo-ephedrine from ${\rm H_3CCH_2CHO}$. 2+2=4
- (d) Provide the natural synthesis of cholesterol.
- 8. (a) Define heparin. Draw the structure of the most abundant disaccharide present in heparin oligosaccharides. Discuss the problem associated with the synthesis of heparin and heparin oligosaccharide. Provide a synthetic scheme stating reagent and condition for synthesis of monosaccharide acceptor (X) from glucose: 1+1+1½+3½=7

- (b) Provide a synthetic scheme stating reagent and condition for synthesis of testosterone from cholesterol.
- (c) Discuss the constitution and partial syntheses of () quinine from () quinotoxine.

UNIT-V

9. (a) (i) Explain the synthesis of mRNA from a DNA blueprint with illustrations and description of template strand and sense strand.

ii) "A gene is not necessarily a continuous sequence of bases." Explain the statement.

- (b) How many forms can naturally occurring DNA exist in? Explain how these forms are characterized. What properties of the functional groups determine the binding of DNA with anti-cancer agents? Explain. $1+2\frac{1}{2}+2=5\frac{1}{2}$
- (c) (i) How is the fluidity of cell membranes controlled by the fatty acid components? Explain with structural representations.
 - (ii) What types of phosphoacylglycerols are susceptible to oxidation and how can that be prevented? $3+1\frac{1}{2}=4\frac{1}{2}$
- **10.** (a) Provide one chemical method each for N-and C-terminal amino acid sequencing of protein. 2+2=4

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(Turn Over)

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(11)

(b)	Explain the role of Asp102, His57 and Ser195 present in the chymotrypsin on its activity.	5
(c)	Explain the important factors on which the activity of an enzyme largely depends on.	3
(d)	Why is uracil not present in the DNA?	2
