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PG Even Semester (CBCS) Exam., May—2018

CHEMISTRY

(4th Semester)

Course No. : CHMCC–403

Full Marks : 70
Pass Marks : 28

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

Candidates are to answer *either* OPTION—A *or*
OPTION—B *or* OPTION—C
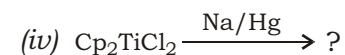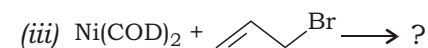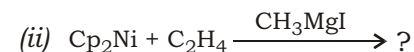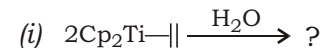
OPTION—A

Course No. : CHMCC–403 (A)

(Inorganic Chemistry—IV)

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

UNIT—I

1. *(a)* Suggest two strategies for the synthesis of transition metal-butadiene organometallic complexes. Discuss the bonding in metal-butadiene complex taking suitable example. 2+4=6
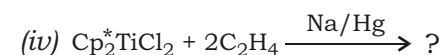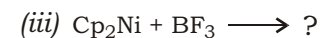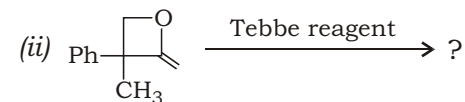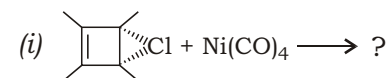
(b) Predict the products (give structures) : 4

(i) $2Cp_2Ti\!\!-\!\!\| \xrightarrow{H_2O}$?

(ii) $Cp_2Ni + C_2H_4 \xrightarrow{CH_3MgI}$?

(iii) $Ni(COD)_2 + \diagup\!\!\!\!\diagdown\!\!\!\diagdown^{Br} \longrightarrow$?

(iv) $Cp_2TiCl_2 \xrightarrow{Na/Hg}$?

(c) Furnish synthesis of a bent metallocene. Explain the bonding and reactivity in Cp_2MoCl_2. 4

2. *(a)* Write the characteristic difference in the bonding of alkynes to metals compared to alkenes. 3

(b) Give two methods for the synthesis of transition metal-alkyne complexes. 2

(c) Suggest the products with probable structures for the following reactions : 1½×4=6

(i) $\square\!\!\!\!\Vert^{\cdots Cl} + Ni(CO)_4 \longrightarrow$?

(ii) $Ph\!-\!\square^{O}_{CH_3} \xrightarrow{\text{Tebbe reagent}}$?

(iii) $Cp_2Ni + BF_3 \longrightarrow$?

(iv) $Cp_2^*TiCl_2 + 2C_2H_4 \xrightarrow{Na/Hg}$?

(3)

(d) Write a short note on stereospecific polymerization of 1-alkenes. 3

UNIT—II

3. (a) Briefly discuss the ligand field excited state and its relevance in relation to inorganic photochemistry. 5

(b) How does inter-system crossing (ISC) occur? Why is a triplet electronic excited state considered as a slowly leaking energy reservoir? 5

(c) Write and comment on the products formed : 4

   (i) $[Mo(CN)_8]^{4-} \xrightarrow[OH^-]{h\nu \ (LF \simeq 365 \ nm)} ?$

   (ii) $[CrCl(NH_3)_5]^{2+} \xrightarrow{H_2O, \ h\nu} ?$

4. (a) Give an account of 'thexi' state and explain DOSENCO state in relation to inorganic photochemistry. 4+2=6

(b) "*trans*-$[Cr(NCS)_4(NH_3)_2]^-$ is a very good actinometer." Elaborate. 4

(4)

(c) Furnish the product :

   $[IrCl_6]^{2-} \xrightarrow{H_2O, \ h\nu} ?$

Explain the formation of the product. Which type of excited states is responsible for such reaction? 4

UNIT—III

5. (a) Deduce the rate of a chemical exchange reaction using trace technique for the following reaction : 8

   $AX + BX^* \rightleftharpoons AX^* + BX$

(where X^* is the radioactive atom of X)

(b) What are meant by evaporation residue and heavy residue? Discuss one radio-chemical technique for the collection of recoiling heavy products of a nuclear reaction. 2+4=6

6. (a) Explain the radiochemical separation of lanthanides using ion-exchange method. 8

(b) Write short notes on : 3×2=6

   (i) Precipitation

   (ii) Solvent extraction

(5)

UNIT—IV

7. *(a)* Briefly discuss the classification of cytochromes with appropriate examples. Explain the mechanism of dioxygen reduction by cytochrome C oxidase.   4+4=8

(b) Outline the mechanism of isomerase reaction through 1,2-shift mediated by B_{12} coenzyme.   6

8. *(a)* Discuss the role of the metal ion and the protein chain in relation to the activity of carboxypeptidase (CPA).   7

(b) Briefly discuss the biological function of carbonic anhydrase (CA). How are CA classified? Highlight the role of the metal ion in CA.   7

UNIT—V

9. *(a)* "A crystal structure is a combination of different kinds of intermolecular interactions." Explain taking suitable example.   3

(b) What is supramolecular synthon? Illustrate with suitable example, its importance in crystal engineering.   1+2+1=4

(6)

(c) What are polymorphs? How are they characterized? Briefly discuss the crystal packing and color of two polymorphs of 2-(4-anisyl)-1,4-benzoquinone.   1+1+3=5

(d) Discuss crystal growth process with schematic representation.   2

10. *(a)* Define nucleation in crystallization process. What are meant by primary and secondary nucleations?   1+2=3

(b) "Higher the supersaturation, higher the probability of having nucleation in a given system." Justify the statement.   3

(c) What are coordination polymers? Classify them based on their dimensionality. Briefly discuss the topologies of three-dimensional structure.   1+1+6=8
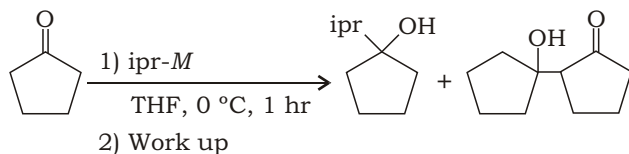
OPTION—B

Course No. : CHMCC–403 (B)

(Organic Chemistry—IV)

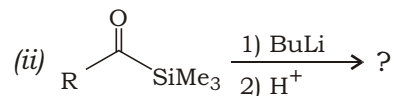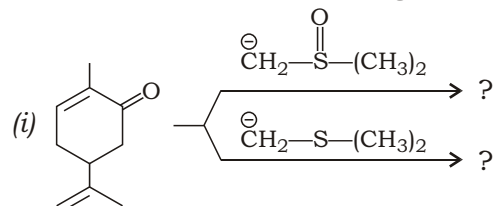Answer **five** questions, taking **one** from each Unit

UNIT—I

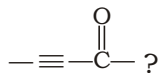**1.** *(a)* Suggest plausible mechanism for the following conversion : 5

| M = Mg | iprMgBr | 3% | 88% |
| M = Ce | iprCeCl$_2$ | 80% | trace |

(b) Designate the products and suggest mechanisms for the following : 4+2=6

(i)

(ii)

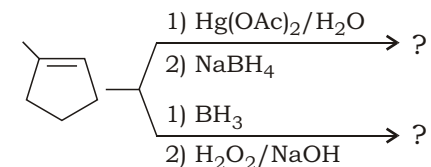*(c)* How can $-\equiv-H$ be converted to

$-\equiv-\overset{O}{\underset{}{C}}-$? 3

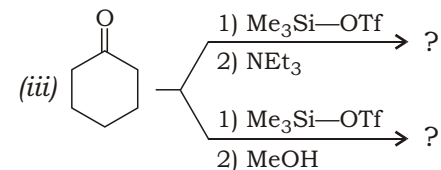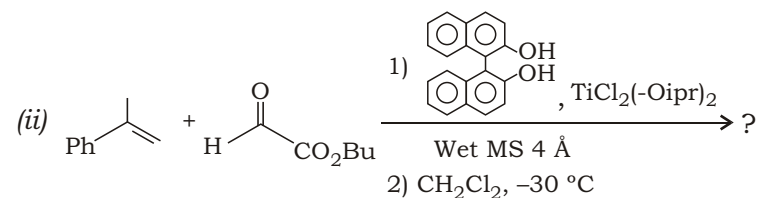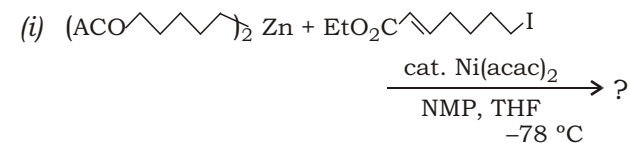**2.** *(a)* Complete the following reactions and provide mechanism : 2+2=4

(b) Write the products and provide mechanisms for the following : 3+3+4=10

(i) $(ACO\diagdown\diagup\diagdown\diagup)_2$ Zn + EtO$_2$C$\diagdown\diagup\diagdown\diagup$I

$\xrightarrow[\substack{\text{NMP, THF} \\ -78\ ^\circ\text{C}}]{\text{cat. Ni(acac)}_2}$?

(ii)

(iii)

UNIT—II

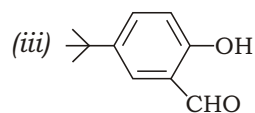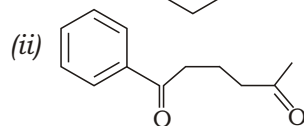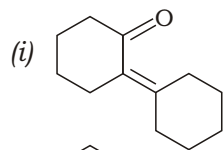**3.** *(a)* What do you mean by synthons and synthetic equivalents? 1+1=2

(b) With proper reasoning, provide the retrosynthesis and forward synthesis for the following compounds : (1+2+1)×3=12

(i)

(ii)

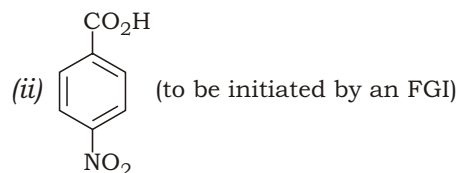*(iii)*

4. *(a)* Give the expansions and explain the following terms used in retrosynthetic descriptions using suitable examples : 3

  (i) FGA

  (ii) FGR

  (iii) FGI

(b) Provide the retrosynthesis along with forward reaction for the following compounds as directed : (2+1)×2=6
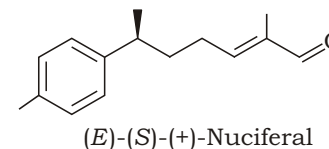
(i) (employing Robinson annulation)

(ii) (to be initiated by an FGI)

(c) Nuciferal is a sesquiterpene component of the essential oil obtained from the wood *Torreya nucifera.* Provide the retrosynthesis along with forward reaction for nuciferal (stereochemistry may be ignored) : 3

(*E*)-(*S*)-(+)-Nuciferal

(d) Explain the importance of the 'order of events' in organic synthesis. 2

UNIT—III

5. *(a)* Carry out the following conversions with suitable reagents, reaction conditions and provide mechanisms : 2½×2=5
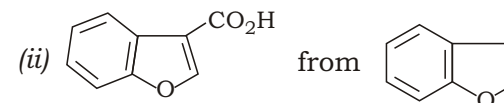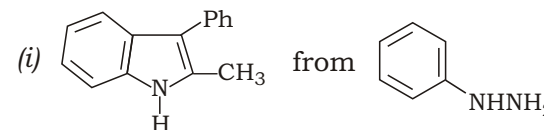
(i)

from

(ii)

from

(b) Predict the products of the following reactions and provide mechanisms : 3+2+2+2=9

(i)

(ii)

MeO— + H₃COOC—C≡C—COOCH₃

$$\xrightarrow{CH_3COOH}$$?

(with SH group on benzene ring)

(iii)

Ph-triazine + Me₂N—CH=CH—NO₂ $\xrightarrow[\text{reflux}]{\text{dioxane}}$?
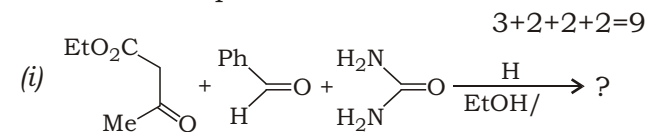
(iv)

benzonitrile (CN)

1) 5 mol% Ni(OH)₂
   H₂N—NH₂, 60 °C
2) NaNO₂/HCl

$$\longrightarrow$$?

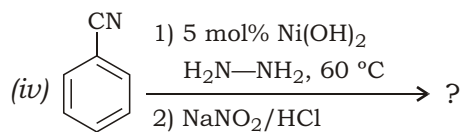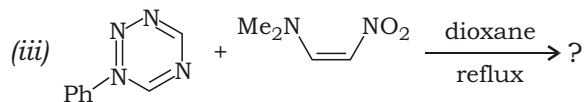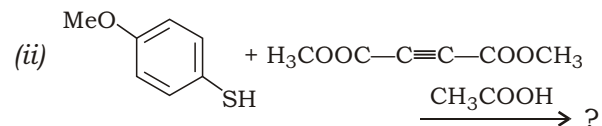**6.** *(a)* Predict the products of the following reactions and provide mechanisms : 2+3+2=7
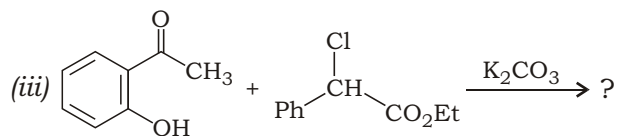
(i)

4-OCH₃-benzaldehyde (CHO) + C₆H₅ + thiourea $\begin{pmatrix} S \\ \| \\ H_2N \quad NH_2 \end{pmatrix}$ $\xrightarrow{TFA/CH_3OH}$?

(ii)

3-CH₃-indole

NBS/CH₃COOH (dry) $\longrightarrow$?

NBS/CH₃COOH (aq) $\longrightarrow$?

(iii)

2-OH-acetophenone (CH₃) + Ph—CH(Cl)—CO₂Et $\xrightarrow{K_2CO_3}$?
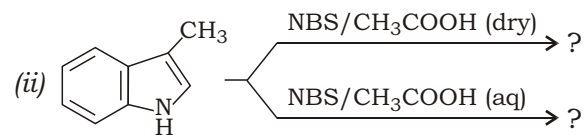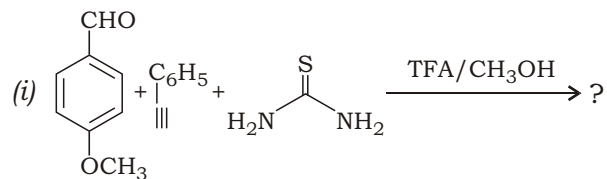
(b) Carry out the following conversions with suitable reagents and reaction conditions : 2½×2=5

(i) pyridazine from maleic anhydride

(ii) 1-Ph-isoquinoline from 2-(CH₂Br)benzoic acid (COOH)

(c) Complete the following reactions : 2

indolizine-2-CH₃ with COC₆H₅ $\xrightarrow{CH_2O/Me_2NH}$ A

$\xrightarrow{CH_3I}$ B $\xrightarrow[\text{KOH,}]{CN^{\ominus}}$ C
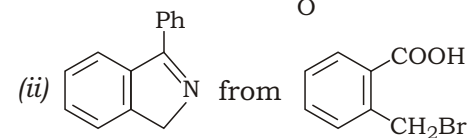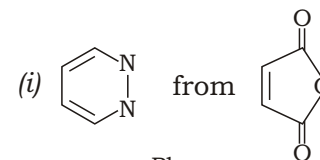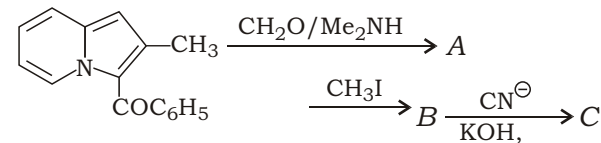
UNIT—IV

7. *(a)* What are prodrugs? How are prodrugs classified? Provide suitable example of each class. 1+2+2=5

(b) Explain the important three theories of drug activity. 2+1½+1½=5

(c) What is allosteric binding? Describe allosteric inhibition of an enzyme. 1+3=4

(13)

8. *(a)* What is agonist? How is an agonist for a target designed? Explain with suitable examples. 1+2+4=7

(b) Illustrate the induced fit model enzyme-substrate binding. 3

(c) What do you mean by the half-life and steady-state concentration of a drug? 1+1=2

(d) What is lipophilicity of a drug? 2

UNIT—V

9. *(a)* Delineate the immunological effects of photodynamic therapy. 4

(b) What is the role of microtubules in mitosis? How does vincristine contribute to the cell cycle arrest of cancer cells? Explain. 2+3=5

(c) How does alkylating antineoplastic agent contribute to chemotherapy? Suggest mechanism. 3

(d) Provide the structures of uramustine and melphalan. 1+1=2

(14)

10. *(a)* How are malignant neoplastic cells/tissues different from normal cells/tissues? What is the role of apoptosis in the treatment of cancer? Explain. 2+3=5

(b) Illustrate the role of phosphoramide mustard as chemotherapeutic agent. Depict the formation of phosphoramide from its prodrug through structural representation. 1+3=4

(c) Which phase of cell growth is disrupted by antimetabolites? Explain how methotrexate functions as folate antagonist. 1+2=3

(d) Provide two different advantages of PDT over chemotherapy. 2

OPTION—C

Course No. : CHMCC–403 (C)

(Physical Chemistry—IV)

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

UNIT—I

1. *(a)* Derive Stern-Volmer equation.   5

   (b) Write short notes on :   3×3=9

       (i) Photoinduced electron transfer

       (ii) Fluorescence quenching

       (iii) Fluorescence resonance energy transfer

2. *(a)* Explain different types of photophysical pathways using Jablonski diagram.   8

   (b) Write short notes on :   3×2=6

       (i) Excimer and Exciplex formations

       (ii) Excitation energy transfer

UNIT—II

3. *(a)* Derive Lippert equation and discuss one application of Lippert equation.   11

   (b) Write short notes on specific and non-specific interactions.   3

4. *(a)* Explain the effect of solvent polarity on emission spectra with the help of Jablonski diagram.   6

   (b) Write a short note on the effect of temperature on solvent relaxation.   4

   (c) Explain the effect of viscosity on the emission intensity of fluorophores.   4

UNIT—III

5. *(a)* What are the characteristic properties of dielectric material?   4

   (b) What is dielectric constant? Discuss the effect of an applied electric field on the dielectric material.   1+4=5

   (c) Using the concept of band theory, discuss Peltier effect.   5

6. *(a)* What are the properties of organic metals? Give one example of organic metal. How can organic metal be synthesized? Discuss the effect of dopant on the conductivity of organic metals.   2+1+1+4=8

   (b) Write short notes on :   3×2=6

       (i) Pyroelectricity

       (ii) Piezoelectricity

UNIT—IV

7. *(a)* Clearly stating the essential conditions, give a brief account of induced dipole-induced dipole interaction potential for a pair of He atoms. 8

(b) Give an expression for the total energy of liquid molecules and graphically explain the variation of Lennard-Jones potential as a function of internuclear distance. 3

(c) One mole of substance occupied 20 mL when it is a liquid and 22·4 L as a gas. Calculate the ratio of dipole-dipole interaction at the boiling point of the materials (assuming the molecules to be spherical in nature). 3

8. Discuss the salient features of 'Clausius virial theorem' and hence obtain an equation of state for liquid molecules. 7+7=14

UNIT—V

9. *(a)* Discuss the salient features of kinetics of thermal decomposition of hydrocarbon. 6

(b) Discuss the salient features of Lindemann theory of unimolecular reaction. Obtain a rate expression of unimolecular reaction by considering the reaction

$$A + M \xrightarrow{k_1} A^*$$
$$A^* \xrightarrow{k_2} \text{Product} + M$$
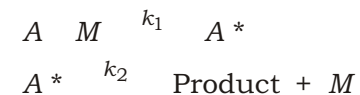
Discuss the effect of concentration or pressure on the order of a reaction.

2+3+3=8

10. *(a)* Discuss the criticism of Lindemann theory of unimolecular reaction. 5

(b) Discuss the Ogg's mechanism for the decomposition of N_2O_5. Show that the rate of decomposition of N_2O_5 explains first-order kinetics. 3+6=9

★★★