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PG Even Semester (CBCS) Exam., May—2019

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)* How can metal-alkene complex be synthesized from nickelocena? Explain the bonding in metal-olefin complex. Discuss the dependence of backbonding on the—
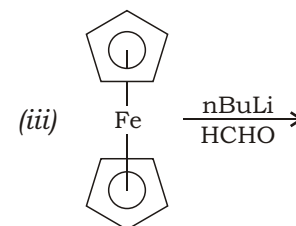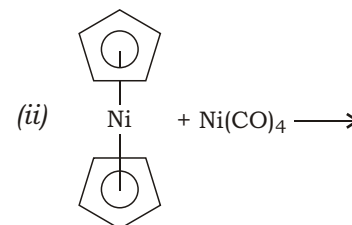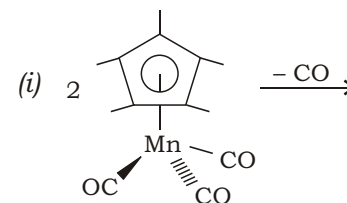
    (i) nature of olefin;

    (ii) nature of metal;

(Turn Over)

    (iii) donor capacity of occupied ML_n frontier orbital fragments. 1+1+5=7

(b) Write the products (give structures) : 1×3=3

    (i)

    (ii)

    (iii)

(c) Write short notes on the following : 2×2=4

    (i) Multidecker compounds

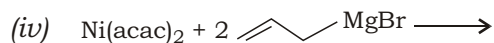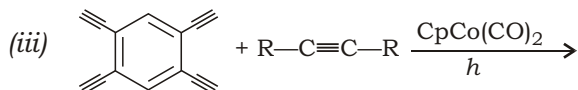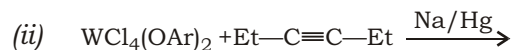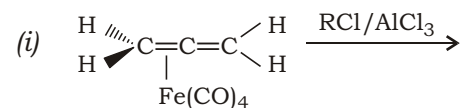   *(ii)* Arene half-sandwich complexes

2. *(a)* Give one method of synthesis of ferrocene. Explain the structure and bonding of ferrocene. 1+4=5

(Continued)

(3)

(b) Mention one application of bent metallocene in alkene polymerization reaction. 2

(c) "Coordinated olefin in metal-olefin complexes is susceptible towards nucleophilic attack." Explain citing an example. 2

(d) Complete the following reactions (give structures) : 1×5=5

(i)

$$H \overset{\text{\tiny///}}{\underset{H}{}} C=C=C \overset{H}{\underset{H}{}} \quad \overset{RCl/AlCl_3}{\xrightarrow{\hspace{1.5cm}}}$$

Fe(CO)$_4$

(ii) $WCl_4(OAr)_2 + Et\text{—}C\equiv C\text{—}Et \xrightarrow{Na/Hg}$

(iii) [structure] $+ R\text{—}C\equiv C\text{—}R \xrightarrow[h]{CpCo(CO)_2}$

(iv) $Ni(acac)_2 + 2$ [allyl] MgBr $\longrightarrow$

(v) $\underset{Cp^*}{\overset{Cp^*}{\diagdown}} Ti\text{—}|| + H_3C\text{—}C\equiv N \longrightarrow$
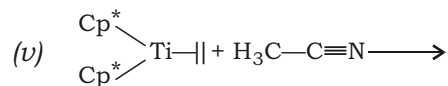
UNIT—II

3. (a) Explain the role of charge-transfer excited state in inorganic photochemical reaction citing suitable example(s). 5

(4)

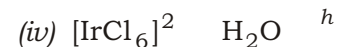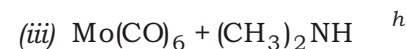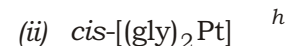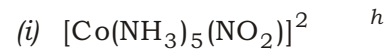(b) Furnish the products and comment : 2+2=4

(i) $[Co(NH_3)_5 N_3]^2 \quad \xrightarrow[h \text{ (LF)}]{H_2O}$

(ii) $trans\text{-}[CrCl(en)_2] \quad \xrightarrow[h \text{ (LF)}]{H_2O}$

(c) Give a brief account of chemiluminescence. How does the phenomenon differ from fluorescence? 5

4. (a) Give an account of 'chemical actinometry'. Furnish three examples to elucidate. 3+3=6

(b) "Thermal reactions are quite different from photochemical reactions." Rationalize with suitable example. 4

(c) Mention the products and give one line justification : 4

(i) $[Co(NH_3)_5(NO_2)]^2 \xrightarrow{h}$

(ii) $cis\text{-}[(gly)_2 Pt] \xrightarrow{h}$

(iii) $Mo(CO)_6 + (CH_3)_2 NH \xrightarrow{h}$

(iv) $[IrCl_6]^2 \quad H_2O \xrightarrow{h}$

UNIT—III

5. (a) Explain the use of tracer technique in chemical reaction mechanism study and chemical analysis. 7

(b) Describe isotope dilution technique for the separation of isotopes from a mixture.   7

6. (a) Render a brief account on 'hot atom' chemistry.   7

(b) Explain radiocarbon dating by ^{14}C.   7

UNIT—IV

7. (a) What is superoxide dismutase (SOD)? Discuss the structure and mechanism of the action of bovine erythrocyte superoxide dismutase (BSOD).   2+5=7

(b) What is calmodulin? Explain its function as Ca^2 ion carrier protein.   4

(c) Write a short note on metallothionein.   3

8. (a) Discuss the structural properties of catalase and peroxidase. How do they function? Suggest a model compound that mimic the activity of catalase.   4+4=8

(b) Comment on the different oxidation states of cobalt in vitamin B_{12} to explain its reactivity.   6

UNIT—V

9. (a) Define supramolecular synthon and secondary building unit. Give examples.   2

(b) Draw the crystal packing of acridone and 1 : 1 cocrystal of hydroquinone and 1,4-benzoquinone and show the different types of intermolecular interactions present in their structures.   5

(c) What is crystallization? Describe the major events in crystallization process.   2+5=7

10. (a) What are polymorphs? Discuss the different polymorphic forms and properties of 2-(4-anisyl)-1, 4-benzoquinone and pyrazine-2-carboxamide.   1+4=5

(b) What are coordination polymers? Give the design strategies for the synthesis of coordination polymer. Classify different types of porous coordination polymer and discuss about their application.   1+4+4=9

OPTION—B

Course No. : CHMCC–403 B

(Organic Chemistry—IV)

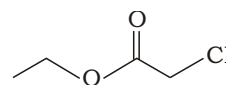Answer **five** questions, taking **one** from each Unit

UNIT—I

1. *(a)* Explain why trimethylsilylchloride follows S_N2 mechanism whereas *t*-butylchloride follows S_N1 mechanism on treatment with aqueous sodium hydroxide. 3

(b) Predict the reagent(s) and reaction conditions in support of the product formed for the following reactions with supportive mechanism : 2+3+2+2=9
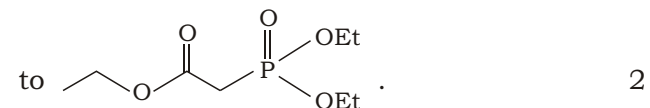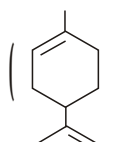
(i)

(ii)

(iii)
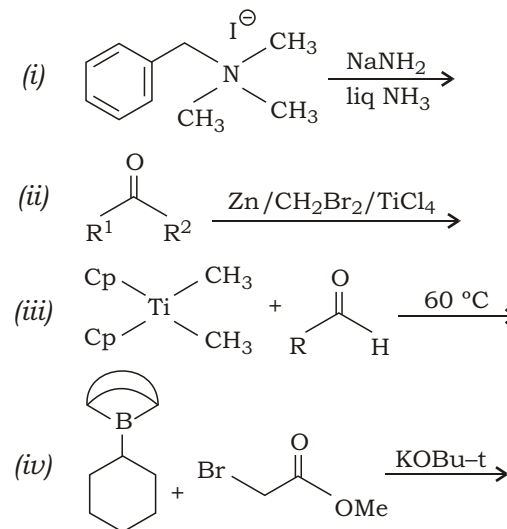
(iv)
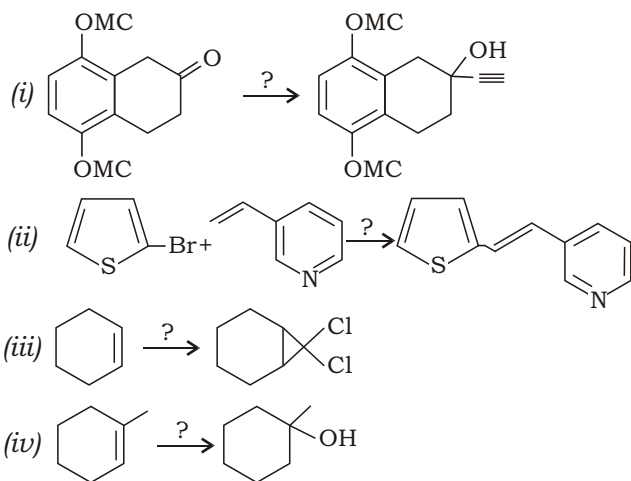
(Turn Over)

(c) How can be converted

to . 2

2. *(a)* How can Limonene be prepared from 1-(4-methylcyclohex-3-enyl) ethanone and triphenylphosphine ylide? Suggest mechanism. 3

(b) Designate the product(s) and suggest mechanism for the following : 2+2+2+2=8

(i)
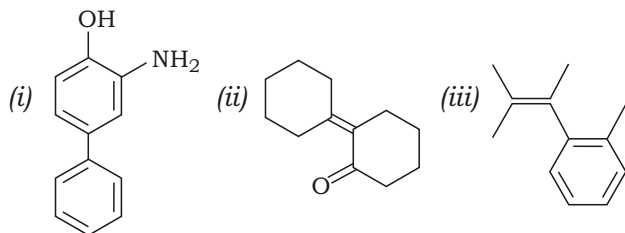
(ii)

(iii)

(iv)

(Continued)

(9)

(c) Dimethyl sulphonium methylide provides epoxide whereas dimethyl sulphoxonium methylide provides cyclopropane, on treatment with , -unsaturated ketones. On the contrary gives same products with simple ketones. 3

UNIT—II

3. (a) Provide retrosynthesis and the corresponding forward reaction for the following compounds : 3+2+3=8

(i) (ii) (iii)

(b) Two possible alternative sites of disconnection are indicated for the following compound : (1½+1½)+(1+1)+1=6
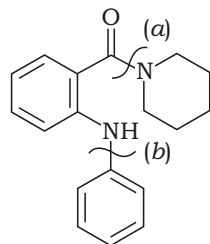
(i) Perform retrosynthesis of the compound following the starting disconnections at (a) and (b) separately.
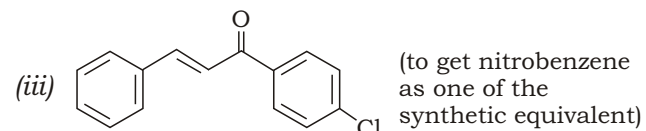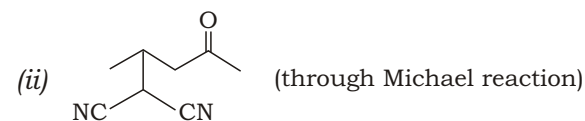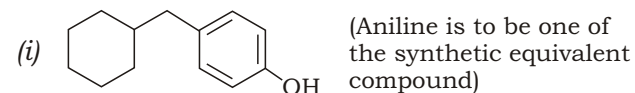
(10)

(ii) Which pathway is better in your opinion and why?

(iii) Provide forward synthesis of the compound (mechanism not required).

4. (a) Carry out retrosynthesis of the following compounds with forward synthesis as per the instruction : (2+1)×3=9

(i) (Aniline is to be one of the synthetic equivalent compound)

(ii) (through Michael reaction)

(iii) (to get nitrobenzene as one of the synthetic equivalent)

(b) Illustrate the retrosynthesis of 1, 2 and 1,3-difunctional compounds through two groups disconnection with a suitable example. 2+2=4
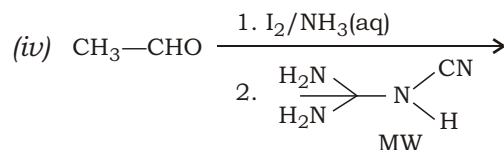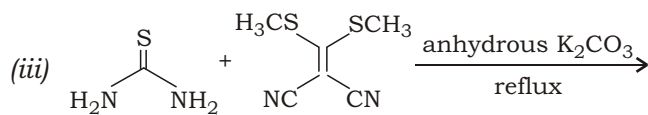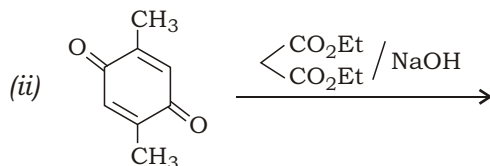
(c) What is synthon? 1

UNIT—III

5. *(a)* Predict the major product for the following reactions and suggest mechanism : 2½×4=10

(i)

1. $\diagup\!\!\!\diagup$ MgBr

2. H_3O

(ii)

$\langle{}^{CO_2Et}_{CO_2Et}$ / NaOH

(iii)

anhydrous K_2CO_3

reflux

(iv) CH_3—CHO

1. I_2/NH_3(aq)

2.

MW

(b) Complete the following reactions : 2+2=4

(i)

H_3C—$\overset{\displaystyle O}{C}$—$CH_3$ / H

D

Br_2/Dioxane → A

B

C

(ii)

Ph_2C=O/nBnLi

THF, –95 °C → E

PhCHO/LDA

Et_2O, –10 °C → F
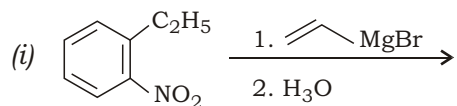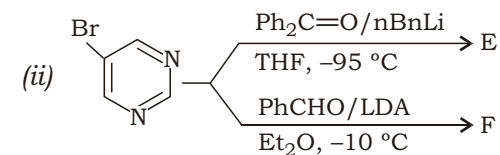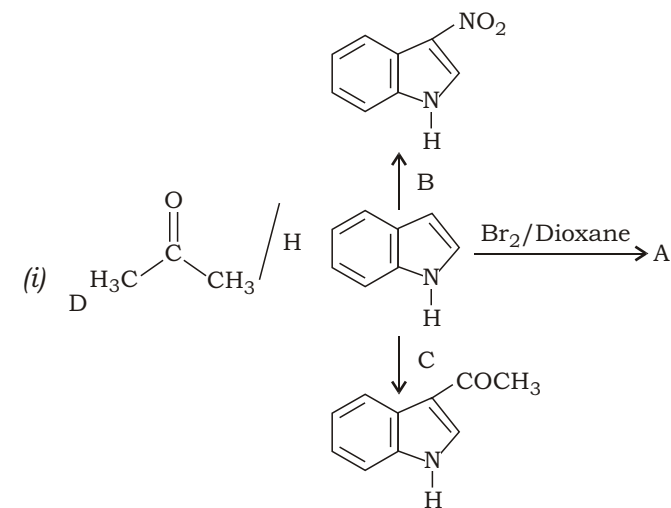
6. *(a)* Carry out synthesis of 2-methyl indole from aniline using *t*-butyl hypochloride and appropriate -ketosulfide. Provide other reagents, reaction condition and mechanism. 3

(13)

(b) Carry out the following conversions with plausible mechanism. Mention the reagents and reaction conditions : 7

(i)

 from

(ii)

 from

(iii)

 from and
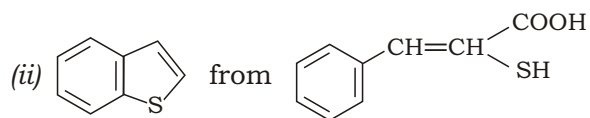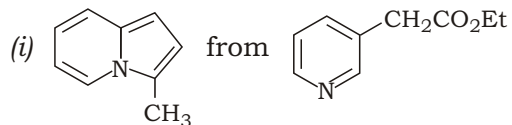
(c) Predict the product(s) and provide plausible mechanism. 2+2=4

(i)

 $\xrightarrow{\text{1. Tf}_2\text{O/0 °C}}{\text{2. Pb—CN/65 °C}}$
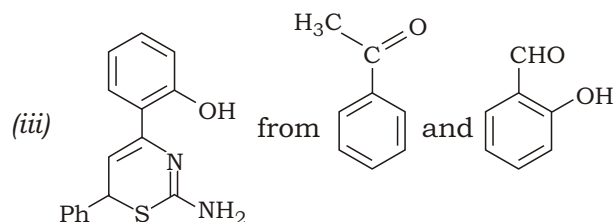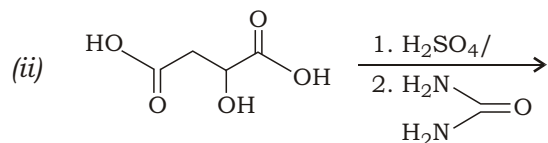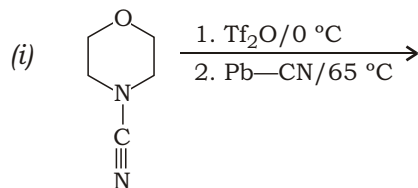
(ii)

 $\xrightarrow{\text{1. H}_2\text{SO}_4/}{\text{2. H}_2\text{N}}$

(14)

UNIT—IV

7. (a) Discuss the drug-receptor interaction with necessary illustration. 4

(b) Explain the theories of drug activity. 3×2=6

(c) What is QSAR? Explain QSAR with two examples. 1+(1½×2)=4

8. (a) Discuss structure-based drug design strategy considering complementary interaction and space. 4

(b) What is pro-drug? How is it classified (with example). 1+3=4

(c) What is enzyme therapy? State briefly the techniques of enzyme therapy. 2+2=4

(d) What is LD_{50}? 2

UNIT—V

9. (a) Emphasize the necessity for treating cancer patient with multiple types of chemotherapeutic drugs simultaneously. A combination of via-cristine and cyclophosphanide are administered together. Provide the mode of drug action for each. 2+(3+3)=8

(15)

(b) Highlight the basic modes of treatment of cancer through chemotherapy in brief.   2

(c) How can combined therapy aid in the treatment of cancer? Explain how both chemotherapy and PDI can be achieved together. Suggest strategies.   4

10. (a) Delineate an apoptosis initiated sequence of post-PDI activity in detail. How can photosensitizers be manipulated to promote apoptosis?   8+3=11

(b) Explain the actions of certain pyrinidine analogues as antimetabolites in cancer chemotherapy.   3

(16)

OPTION—C

Course No. : CHMCC–403 C

(Physical Chemistry—IV)

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

UNIT—I

1. (a) Explain different types of photophysical pathway mentioning both radiative and non-radiative transition with the help of Jablonski diagram.   8

(b) What is fluorescence quenching? Explain collisional quenching by using Jablonski diagram.   1+5=6

2. (a) Derive Stern-Volmer equation.   5

(b) Write short notes on :   3×3=9

  (i) Fluorescence resonance energy transfer

  (ii) Sphere of effective quenching

  (iii) Excimer and exciplex formations

UNIT—II

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

(b) Explain the effect of solvent mixture on emission spectra taking one specific example. 4

(c) Write short notes on : 3×2=6

 (i) Probe-probe interaction

 (ii) Biochemical application of environment sensitive fluorophores

4. (a) Derive Lippert equation and discuss one application of Lippert equation. 10

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

UNIT—III

5. (a) What is thermoelectric effect? Discuss Thomson effect, Seebeck effect and Peltier effect. 1+9=10

(b) Discuss the effect of dielectric materials in the presence of electric field. 4

6. (a) Write short notes on : 3×2=6

 (i) Ferroelectricity

 (ii) Electrically conducting polymers

(b) What are the characteristics of dielectric materials? 2

(c) What are pyso- and piezo-electricity? Discuss one example of each. 3+3=6

UNIT—IV

7. (a) Discuss the salient features of partition function method to derive an expression of energy of liquid molecules. 9

(b) What are meant by 'communal free energy' and 'communal entropy'? 3+2=5

8. (a) Discuss the salient features of dipole-induced dipole and induced dipole-induced dipole interactions. 5+5=10

(b) Calculate the potential energy of attraction between an Ar-atom and a CH_3OH molecule arising from dipole-induced dipole interaction at a spacing of 10 Å. [Given, CH_3OH 1 7D, $_d$ (Ar) 1 63 10^{24} c.c]. 4

(**19**)

UNIT—V

9. *(a)* Write down the postulates of Lindeman theory of unimolecular reaction. Obtain a rate expression of unimolecular reaction and discuss the order of unimolecular reaction at two extremes of concentration. What are the difficulties of Lindeman theory of unimolecular reaction?   2+3+2+3=10

(b) Discuss the mechanism of photo-chemical decomposition of ozone.   4

10. *(a)* Write short notes on :   4×2=8

  (i) Hinshelwood theory

  (ii) RRK theory

(b) Obtain the rate expression of thermal decomposition of N_2O_5.   6

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