Third Semester M.Sc. PHARMACEUTICAL CHEMISTRY

PH3C09 SYNTHETIC AND BIOORGANIC CHEMISTRY

MODEL QUESTION PAPER

Time: Three hours Total Weight: 30

Section A

*(Answer any **10** questions. Each question carries a weight of **1**)*

01. Give examples of chromium and silver based oxidation of alcohols to carbonyl compounds.
02. Discuss any two methods for the synthesis of diols from alkenes using Osmium.
03. What is Tebbe olefination?
04. What is Baylis-Hilman reaction? Explain its mechanism.
05. What is DIBAL-H? Give any two applications of DIBAL-H.
06. Explain Noyori asymmetric hydrogenation.
07. What is Nef reaction? Explain its mechanism.
08. Discuss Birch reduction.
09. Give two examples of metal based reductions using Li in ammonia.
10. Explain aza-Cope rearrangement.
11. How are alkaloids classified?
12. What is MPV reduction? Give one example.
13. Give the synthesis of beta carotene.

(10×1=10 weights)

Section B

*(Answer any **5** questions. Each question carries a weight of **2**)*

14. Discuss the method of synthesis of epoxide from alkenes. Explain the mechanism of Sharpless asymmetric epoxidation.
15. Discuss the photochemical approaches for the synthesis of oxetanes.
16. Explain the method of construction of macrocyclic rings by ring closing metathesis.
17. Discuss the mechanism and applications of inter and intra molecular ketene cycloaddition.
18. How will you synthesize esters and lactones from ketones? Explain Baeyer-Villiger oxidation.
19. Write note on synthesis of progesterone.
20. Explain the mechanism of host-guest complex formation. Comment on the forces involved in molecular recognition.

21. Discuss the green alternatives of organic synthesis with special reference to electrophilic aromatic substitution reactions.

(5×2=10 weights)

Section C

*(Answer any **2** questions. Each question carries a weight of **5**)*

22. Discuss the structure elucidation and synthesis of papaverine.
23. Write an essay on metal mediated C-C and C-X coupling reactions with special reference to
    (a) Suzuki coupling, (b) Heck reaction, (c) Ullmann reaction, (d) Nozaki-Hiyama reaction.
24. Discuss the stereoselective synthesis of tri and tetra substituted olefins.
25. What are molecular receptors? Explain the structure, functions, and applications of the following as receptors.
    (a) cyclodextrins, (b) crown ethers, (c) cryptands, (d) tweezers, (e) crown ethers

(2×5=10 weights)

PH3C10/PO3C10 PHYSICAL CHEMISTRY

(common to Pharmaceutical Chemistry and Polymer Chemistry)

MODEL QUESTION PAPER

Time : 3 Hrs Max. Weight: 30

Section A

*(Answer any **10** questions. Each question carries a weight of **1**)*

01. Define steric factor. Explain how it is related to entropy of activation.
02. Explain with an example how NMR can be used in the study of fast reactions.
03. Compare transition state theory with collision theory.
04. Discuss primary kinetic salt effect.
05. What is cage effect?
06. Differentiate between sedimentation potential and streaming potential.
07. Discuss the effects of pH and temperature on catalysis.
08. Distinguish between excimers and exciplexes.
09. What is meant by photostationary state? Discuss with reference to formation of ozone in the atmosphere.
10. What is immunogold labelling?
11. What is Donnan membrane equilibrium?
12. Define zeta potential.
13. Explain the application of green chemistry in ibuprofen manufacture.

(10 x 1 =10 weights)

Section B

*(Answer any **5** questions by attempting not more than **3** questions from each bunch. Each question carries a weight of **2**)*

Bunch 1 (Short Essay Type)

14. What are explosive reactions? Explain the mechanism with a suitable example.
15. What are the principles of green chemistry?
16. Derive the Michaelis-Menten equation.
17. Discuss the kinetics of enzyme inhibition.

Bunch 2 (Problem Type)

18. A second order reaction has a rate constant k = 2.5 x 10^{-3} L mol^{-1} S^{-1} at 25°C. Its energy of activation is 48 kJ mol^{-1}. Calculate $\Delta S^{\neq}$ for the reaction, assuming that the reaction takes place in solution.
19. For a homogeneous gaseous reaction the rate constants are 3.0 x 10^{-5} L mol^{-1} S^{-1} and 1.2 x 10^{-3} L mol^{-1} S^{-1} at 629K and 700K respectively. Calculate the energy of activation and frequency parameter.
20. In a photochemical reaction $A \rightarrow 2B + C$ the quantum efficiency with 500 nm light is 2.1 x 10^{2} mol $Einstein^{-1}$. After exposure of 300 m mol of A to the light 2.28 m mol of B was formed. How many photons were absorbed by A?
21. In an experiment to measure quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100W source for 45 minutes. The intensity of transmitted light was 40% of the intensity of the incident light. As a result of irradiation, 0.344 mol of the absorbing substance decomposed. Determine the quantum efficiency.

(5 x 2 =10 weights)

Section C

*(Answer any **2** questions. Each question carries a weight of **5**)*

22. a) Explain the BET theory of adsorption.
    b) Discuss the use of Langmuir and BET isotherms for surface area determination.
23. a) Explain the principles of ESCA and Auger electron spectroscopy.
    b) Discuss the applications of SEM and TEM in the study of surfaces.
24. a) Distinguish between E-type and P-type delayed fluorescence.
    b) Discuss the working of solar cells.
    c) Discuss the applications of LASER in the study of photochemical kinetics.
25. Give an account of the different types of nanomaterials and their applications.

(2 x 5 =10 weights)

PH3C11 DRUG DESIGN AND PHARMACOLOGY

MODEL QUESTION PAPER

Time : 3 Hrs Max. Weight: 30

Section A

*(Answer any **10** questions. Each question carries a weight of **1**)*

01. Stereoisomerism and biological activity are related. Illustrate by taking ephedrine as an example.
02. State Ferguson's principle.
03. What are analeptics? Write down the synthesis of nikethamide.
04. What do you mean by bioisosterism?
05. Give two examples for centrally acting muscle relaxants with structure.
06. Explain the role of cytochrome P450 in drug biotransformation.
07. What are monooxygenases? What are their significances?
08. What is a sympathomimetic agent ? Give two examples.
09. Name a synthetic narcotic analgesic and give its structure.
10. Differentiate between drug dependence and drug tolerance.
11. Give the retrosynthetic analysis of ketoprofen and name the synthons.
12. What is the principle involved in the assay of yellow mercuric oxide?
13. Give any two non-barbiturate hypnotics with structures.

(10 x 1 =10 weights)

Section B

*(Answer any **5** questions. Each question carries a weight of **2**)*

14. What is Hansch Analysis? How is it useful in the design of drugs?
15. Give the method of preparation, uses and limit tests for the following:
    a) aluminium hydroxide gel b) calcium lactate
16. What are the types of epilepsy? Give the synthesis of a hydantoin derivative.
17. Outline the role of benzodiazepines as antianxiety agents.
18. Discuss dose response relationship graphically.
19. Discuss SAR of barbituric acid derivatives for hypnotic and sedative action.
20. Discuss the structurally specific and non-specific activity of drugs with examples.
21. Write a note on metal toxicity.

(5×2=10 weights)

Section C

*(Answer any **2** questions. Each question carries a weight of **5**)*

22. Discuss the following compounds with synthesis of any one from each:
    a) Arylacetic acid derivatives used as analgesics.
    b) Intravenous anaesthetics.
    c) Salicylic acid derivatives used as antipyretics.

23. a) Discuss various factors affecting drug design.
    b) Explain the phase I metabolic reactions with suitable examples.
    c) Explain any two types of molecular graphics in drug modeling.

24. Illustrate the synthesis and therapeutic uses of the following drugs:
    a) Diazepam b) Levodopa c) besiperidine

25. a) What is Parkinsonism? What are the disorders associated?
    b) Discuss various agents used for the management of Parkinsonism.
    c) Cholinergic agonists for the management of Alzheimer's disease.

(2 x 5 =10 weights)

AN3C12/AP3C12/ CH3C12/ PH3C12/ PO3C12

SPECTROSCOPIC METHODS IN CHEMISTRY

(common to all branches of Chemistry)

MODEL QUESTION PAPER

Time: Three hours Total Weight: 30

Section A

*(Answer any **10** questions. Each question carries a weight of **1**)*

01. How would the fluorine NMR spectrum for F-CH_2-CO-CH_2-CH_3 appear?
02. How will you distinguish between $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions? Apply the effect of solvation to illustrate this.
03. Predict the signal pattern in DEPT-90 and DEPT- 135 spectra of phenyl acetic acid.
04. A trisubstituted benzene possessing one bromine and two methoxy substituents exhibits three aromatic resonance bands at 6.40, 6.46 and 7.41 ppm in its proton NMR spectrum. What is the substitution pattern?
05. Explain ORD with example.
06. What is meant by finger printing in IR spectroscopy?
07. How will you confirm the conversion of benzene to cyclohexane with ^{1}H NMR and ^{13}C NMR spectroscopy?
08. What is MALDI? Explain with example.
09. Comment on the differences between the scales in ^{1}H and ^{13}C NMR spectroscopy.
10. How will you estimate ring strain using IR and UV-Visible spectra.
11. Predict the proton and deuterium NMR spectra of D-CH_2-O-CH_3 (for D, I=1).
12. What are the applications of 2D- COSY spectra?
13. Sketch Karplus curve. Explain its characteristic features.

(10×1=10 weights)

Section B

*(Answer **5** questions. Each question carries a weight of **2**)*

14. Explain how IR spectroscopy can be applied to predict the product formation at each step in the following reaction series.

Benzaldehyde → Benzoin → Benzil → Benzilic acid.

15. Apply ^{1}H NMR and ^{13}C NMR spectroscopic techniques and explain how will you confirm the following conversions. Explain all characteristic features of the ^{1}H NMR and ^{13}C NMR of the substrates and the products.

a) $CH_3\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{[O]} CH_3\text{-}CH_2\text{-}CHO$

b) $CH_3\text{-}CH(OH)\text{-}CH_3 \xrightarrow{[O]} CH_3\text{-}CO\text{-}CH_3$

16. Sketch the H-H HOMOCOSY of (a) 2- chloro propane and (b) ethanol.
17. Write a note on (a) axial halo ketone rule and (b) Cotton effect.
18. Discuss the applications of HRMS and MS-MS techniques in structure analysis.
19. Define NOE. Explain Nuclear Overhauser Enhancement based on cross polarization theory.
20. Predict the structure of the compound with the following spectral characteristics:
    UV: 290 nm
    IR : 2980, 1718, 1440 cm^{-1}
    ^{1}H NMR : 2.3ppm (q), 2.15ppm(s), 1.1ppm(t)
    Mass (m/z) : 72(M^{+}), 43 (base peak), 29
21. Sketch the approximate ^{1}H NMR and ^{13}C NMR and mass spectra of 2-butenone. Explain the spectral features.

(5×2=10 weights)

Section C

*(Answer any **2** questions. Each question carries a weight of **5**)*

22. Define and explain spin-spin coupling. Using tree diagram method explain AX, AX_2, AX_3, A_2X_3, AB and ABC type coupling.
23. Write an essay on the application of DEPT, INEPT, and RINEPT in the structural elucidation of organic compounds. Illustrate the application of DEPT with examples.
24. (a) Predict the structure of the compound (commercial sample) with the following spectral characteristics and justify your answer.

    MF: $C_4H_{10}O$; IR: 3450 (broad), 2980, 1450, 1200, 1050cm^{-1}.

    ^{1}HNMR: 1.5 (3H, t), 2.8 (2H, dq), 3.4 (1H, m), 4.5 (1H, s), 2.1 (3H, d).

    ^{13}C NMR: 22.6, 68.7, 32.0, 9.9 ppm.

    DEPT 45: 4 signals, DEPT 90 : 1 signal, DEPT 135: 3 +ve and 1 –ve signals.

    (b) Discuss the theory and applications of MRI.

25. (a) An ester $C_5H_8O_2$ shows the following ^{13}C spectral results (off-resonance decoupled).

20 ppm (q), 50 ppm (q), 126 ppm (t), 130 ppm (s) and 160 ppm (s).

Predict the structure.

(b) Determine the structure of the compound with the following spectral characteristics.

MF: $C_5H_9NO_4$; IR: 1750, 1562, 1320$cm^{-1.}$

^{1}HNMR: 5.2 (q), 4.2 (q), 1.8 (d), 1.3 (t).

^{13}C (ppm)	PT 135	PT 90
		peak
		peak
		peak
	peak	peak

(2×5=10 weights)