Sem IV 2024

Paper / Subject Code: 69111 / Pharmaceutical Organic Chemistry- III

Duration: 3 Hours **Total Marks: 75**

N.B: 1. All questions are compulsory.

2. Figures to the right indicate full marks.

Q1. Answer the following multiple choice questions: **(20)**

Q1. Which of the following asymmetric carbon has (R) configuration?

A. I B. II C. III D. IV

Q2. Choose the appropriate statements to describe following molecules.

A. Both molecules are chiral
B. Molecule 1 is achiral due to axis of symmetry while molecule 2 is chiral
C. Molecule 1 is achiral due to plane of symmetry while molecule 2 is chiral
D. Both molecules are achiral

Q3. The given molecule is:

A. L-Threonine B. D- Threonine C. 2R, 3R-Threonine D. 2S, 3S- Threonine

Q4. Identify the percent of major enantiomer if the optical purity is found to be 20%?

A. 80% B. 20% C. 40% D. 60%

Q5. Assign R/S or E/Z notation (Whichever relevant) to the given molecule

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A. 2S,3E B. 2R,3Z C. 2E,4R D. 2Z,4S

Q6. Which is the most stable conformer of n-butane?

A. Anti, staggered conformation B. Gauche, eclipsed C. Skewed, eclipsed D. Butterfly

Q7. Which of the following compounds does not exhibit geometrical isomerism?

A. 1-Butene B. 2-Butene C. 3-Pentene D.4-Heptene

Q8. Which of the following structure is achiral?

A B C D

Q9. Which of the following agents are used in absolute asymmetric synthesis?

A. BINAP B. D-Mannitol C. $NaBH_4$ D. L-(+)Tartaric acid

Q10. The nomenclature of following molecule is.....

A. 7-Methylazepine B. 2-Methylazepine C. 7-Methyl-1H-azepine D. 2-Methyl-2H-azepine

Q11. Identify the reagent for sulphonation of thiazole:

A. Pyridine sulphur trioxide
B. 95% H_2SO_4
C. Oleum, 250°C, Mercury sulfate
D. Oleum at 160°C

Q12. Identify the correct order of reactivity:

A. Benzene < Thiophene < Furan < Pyrrole
B. Thiophene < Benzene < Furan < Pyrrole
C. Furan < Pyrrole < Thiophene < Benzene
D. Pyrrole < Furan < Thiophene < Benzene

Q13. Select appropriate IUPAC name for the following Structure.

A. 5-methyl-2H-1,2-thiazine
B. 3-methyl-6H-1,2-thiazine
C. 2-methyl-5H-1,2-thiazine
D. 6-methyl-3H-1,2-thiazine

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Q14. Identify which heterocycle is present in given molecule and also mention the use of following molecule.

A. Pyridine, Antihistaminic
B. Isoquinoline, Antimalarial
C. Quinoline, Antimalarial
D. Acridine, Anti-HIV

Q15. Cyclization of α-acyl amino ketone followed by dehydration in presence of $POCl_3$ is the _____.

A. Radiszewskii synthesis of imidazole
B. Van-Leusen reaction of oxazole
C. Robinson-Gabriel synthesis of oxazole
D. Gabriel synthesis of thiazole

Q16. Which of the following statements are true?
1. Pyridine is more basic than pyrimidine
2. Pyrimidine is more basic than pyridine
3. Electrophilic substitution of pyrimidine is less facile than pyridine.
4. Electrophilic substitution of pyridine is less facile than pyrimidine.

A. 1, 3 B. 2, 4 C. 1, 4 D. 2, 3

Q17. Which of the following reagents are used in Skraup synthesis?
A. β-phenylethylamine, acetyl chloride, phosphoryl chloride
B. Aniline, ethyl acetoacetate
C. Aniline, glycerol, conc. sulfuric acid, nitrobenzene
D. o-Aminobenzaldehyde acetaldehyde, alcohol, NaOH

Q18. Select appropriate reagent to carry out following conversion.

A. $NaBH_4$ B. $LiAlH_4$ C. Na, Liq. ammonia and alcohol D. NH_2NH_2, KOH

Q19. The conversion aromatic ketoxime to N-substituted amide under the influence of PCl_5 is _____.

A. Birch Reduction Reaction B. Beckmann rearrangement C. Schmidt rearrangement D. Dakin

Q20. What is the medicinal use of Clonidine?
A. Antihypertensive B. Anti-inflammatory C. Antimalarial D. Antihistaminic

QII. Attempt **any two** from the following questions: **(20)**

1. (i) Arrange the following heterocycles in increasing order of basicity: Imidazole, Oxazole, Pyrazole. Explain how the presence of another heteroatom influences the basicity of the molecule.

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(ii) Complete the following reactions. Give the detailed mechanism for any one of the reaction.

a) o-Toluidine $\xrightarrow{HCOCl}$ A $\xrightarrow[\Delta]{\text{Stong Base}}$ B

b) o-Chlorobenzoic acid + Aniline $\xrightarrow{\text{Base}}$ C $\xrightarrow{H_2SO_4}$ D $\xrightarrow[\text{Na, AmOH}]{\text{Na}}$ E $\xrightarrow{\text{Oxidation}}$ F

(iii) Depict the mechanism of formation of a diol of 2-butene by reaction with $KMnO_4$. Is this reaction stereospecific &/or stereoselective?

2. (i) Give the mechanism for **any two** of the following:

a) Reaction of pyrimidine with hydrazine
b) Reaction of oxazole with ammonia
c) Reimer Tiemann reaction of pyrrole.

(ii) Give the product for the following reaction and answer the given questions.

a) Identify the chiral centre/s in the product.
b) Assign R/S notation to the asymmetric carbon in the reactant.
c) How many product/s will be formed in the reaction and what will be the relation between the products formed?
d) Suggest a suitable method of separation of the isomeric products formed.

3. (i) Depict the mechanism for the for Claisen-Schmidt condensation and Schmidt rearrangement.

(ii) Suggest suitable reducing agent for the following reactions.

QIII Answer **any seven** questions from the following: **(35)**

Q1. Explain the term asymmetric synthesis. Explain any one method in detail.

Q2. (i) Enlist any four methods of resolution of a racemic mixture. Explain biochemical method of resolution of racemic mixture.

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(ii) Comment on the chirality of **any two** of the given molecules:

Q3. Depict the energy profile diagram for conformations of cyclohexane. Discuss the stability of cis-1,2-Dimethylcyclohexane.

Q4. Discuss optical isomerism in ortho substituted biphenyls. What are the necessary conditions for biphenyls to exhibit atropisomerism?

Q5. Depict the mechanism for the following synthesis **(any two).**

a. Gabriel synthesis of thiazole
b. Hantzsch synthesis of pyridine
c. Bischler Napieralski synthesis of isoquinoline

Q6. Discuss the following reactions using various reagents for:

a. Nitration of pyrrole
b. Oxidation of quinoline
c. Bromination of pyrazole

Q7. (i) Nomenclate **any three** of the following molecules using Hantzsch-Widman rules:

(ii) Give the therapeutic use of pyrantel pamoate and celecoxib.

Q8. Depict the reaction conditions and reagents for **any five** of the following conversions:

a. Diethylmalonate to pyrimidine
b. Salicylaldehyde to catechol
c. 2-Butene to 2S,3S-2,3-Dibromobutane
d. Benzil to imidazole
e. Butanedial to furan
f. 6-Aminopyrimidine to purine

Q9. Depict resonance in thiophene. Predict the most favorable position for electrophilic aromatic substitution in pyridine.

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