

D 93388

(Pages : 2)

Name.....

Reg. No.....

**FIRST SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY)
EXAMINATION, NOVEMBER 2020**

(CBCSS)

Chemistry

CHE 1C 03—STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

(2019 Admissions)

Time : Three Hours

Maximum : 30 Weightage

General Instructions

1. *In cases where choices are provided, students can attend **all** questions in each section.*
2. *The minimum number of questions to be attended from the Section / Part shall remain the same.*
3. *There will be an overall ceiling for each Section / Part that is equivalent to the maximum weightage of the Section / Part.*

Section A

*Answer any **eight** questions.*

Each question carries a weight of 1.

1. Cyclopentadiene has a pka value 15 which is quite high (for a H bonded to sp³ carbon). Account for this observation.
2. Instead of adopting a planar structure assisting complete overlap of its *p* orbitals, cyclooctatetraene exists as a tub shaped molecule. Explain.
3. Differentiate between classical and non-classical carbocations.
4. What are conformationally biased molecules? Give examples.
5. Draw the preferred conformation of *trans*- and *cis*-1-methyl-3-isopropylcyclohexane.
6. What are the destabilizing interactions present in axially substituted cyclohexanes ?
7. Write down the structure of a prochiral compound and assign the stereodescriptor for the prochiral center.
8. Draw all 1, 3-dimethyl cyclohexanes. Which of these are chiral ?
9. What are chiral auxiliaries ? Give an example of one used in asymmetric Diels-Alder reactions.
10. Illustrate Sharpless asymmetric epoxidation reaction and specify the reagents and conditions employed.

(8 × 1 = 8 weightage)

Turn over

Section B

Answer any **six** questions.

Each question carries a weight of 2.

11. Discuss the effect of resonance on the acidity of carboxylic acids. Give examples.
12. Explain the aromaticity of cyclopentadienyl anion and [18] annulene, based on Huckel's rule.
13. State Hammond postulate and apply it to predict the relative rates of solvolysis of 2-bromopropane and 2-methyl-2-bromopropane.
14. Illustrate the terms kinetic and thermodynamic control with appropriate examples.
15. Explain the origin of optical isomerism in certain cummulenes and biphenyls.
16. What is the basic principle involved in resolution of racemates ? Explain the application of S-brucine in resolution ?
17. Explain the stereochemistry of reduction with CBS reagent with any suitable example.
18. With a suitable example, explain an asymmetric aldol reaction by Zimmerman-Traxler model.

(6 × 2 = 12 weightage)

Section C

Answer any **two** questions.

Each question carries a weight of 5.

19. Discuss the effect of hydrogen bonding on the physical and chemical properties (including reactivity) of organic compounds. How does hydrogen bonding affect conformation of 1, 2-, 1, 3- and 1, 4-cyclohexanediols ?
20. (a) Write a detailed note on the application of isotope effects in the study of reactions mechanisms. Discuss with suitable examples.
(b) Write a brief note on Bredt's rule.
21. Discuss the effect of conformation on the course and rate of reactions in cyclohexane systems citing sufficient example.
22. (a) Explain the concept of asymmetric induction and illustrate the prediction of stereochemical outcome with Felkin-Ahn model, in an appropriate example.
(b) Write a note on symmetric hydroboration reactions.

(2 × 5 = 10 weightage)

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9. What are chiral auxiliaries ? Give an example of one used in asymmetric Diels-Alder reactions.
10. Illustrate Sharpless asymmetric epoxidation reaction and specify the reagents and conditions employed.

(8 × 1 = 8 weightage)

Turn over

Section B

*Answer any six questions.
Each question carries a weight of 2.*

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17. Explain the stereochemistry of reduction with CBS reagent with any suitable example.
18. With a suitable example, explain an asymmetric aldol reaction by Zimmerman-Traxler model.

(6 × 2 = 12 weightage)

Section C

*Answer any two questions.
Each question carries a weight of 5.*

19. Discuss the effect of hydrogen bonding on the physical and chemical properties (including reactivity) of organic compounds. How does hydrogen bonding affect conformation of 1, 2-, 1, 3- and 1, 4-cyclohexanediols ?
20. (a) Write a detailed note on the application of isotope effects in the study of reactions mechanisms. Discuss with suitable examples.
(b) Write a brief note on Bredt's rule.
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(b) Write a note on symmetric hydroboration reactions.

(2 × 5 = 10 weightage)

D 13104

(Pages : 2)

Name.....

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**FIRST SEMESTER M.Sc. DEGREE (REGULAR/SUPPLEMENTARY)
EXAMINATION, NOVEMBER 2021**

(CBCSS)

Chemistry

CHE 1C 03—STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

(2019 Admission onwards)

Time : Three Hours

Maximum : 30 Weightage

General Instructions

1. *In cases where choices are provided, students can attend all questions in each section.*
2. *The minimum number of questions to be attended from the Section / Part shall remain the same.*
3. *The instruction if any, to attend a minimum number of questions from each sub section / sub part / sub division may be ignored.*
4. *There will be an overall ceiling for each Section / Part that is equivalent to the maximum weightage of the Section / Part.*

Section A*Answer any eight questions.**Each question carries a weightage of 1.*

1. In which of the following solvents benzoic acid is expected to exist as a hydrogen bonded dimer ? Benzene or methanol. Justify.
2. What are cyclodextrins ? Give any two applications.
3. Comment on the stability of benzylic carbocations and radicals.
4. *exo*-Halonorbornene reacts faster than its *endo* isomer. Explain.
5. *trans*-Decalin is a conformationally rigid system. Explain.
6. Illustrate bond opposition strain and bond angle strain with appropriate examples, in simple cyclic systems.
7. Define the term enantiomeric excess. How is it determined ?
8. What are prochiral centers ? Predict whether the-CH₂-hydrogens of ethanol are homotopic, enantiotopic or diastereotopic.

Turn over

9. Illustrate substrate controlled asymmetric synthesis with any suitable example.
10. Give an example of an asymmetric hydrogenation reaction with BINAL-H.
- (8 × 1 = 8 weightage)

Section B

Answer any six questions.

Each question carries a weightage of 2.

11. Write down the structures of cyclopropyl, cyclopentadienyl, and cyclohexadienyl cations. Classify the compounds into aromatic, non-aromatic or anti-aromatic.
12. Comment on the acidity of benzoic acid, 4-nitrobenzoic acid and 4-methoxy benzoic acid. Identify the strongest acid. Justify.
13. Consider the chromic acid oxidation of *cis*- and *trans*-4-*tert*-butylcyclohexanols. Which of these is expected to undergo the reaction faster? Why?
14. Draw the stable conformations of all 2-*tert*-butylcyclohexanols and 3-*tert*-butylcyclohexanols.
15. Explain the stereochemical outcome in pyrolytic elimination of esters.
16. Explain the origin of chirality in organic compounds containing nitrogen and sulfur. Give examples.
17. What are the advantages and disadvantages of chiral pool strategy of asymmetric synthesis?
18. What is 1, 2-asymmetric induction? Predict the stereochemical outcome in an appropriate example.
- (6 × 2 = 12 weightage)

Section C

Answer any two questions.

Each question carries a weightage of 5.

19. Discuss the stability of various cyclic conjugated pi-systems in organic compounds, based on the concepts of aromaticity and anti-aromaticity.
20. With appropriate examples, describe the terms kinetic and thermodynamic control. Draw structures of the enolate anion of 2-methylcyclohexanone generated under these conditions. Highlight the reagents and conditions used in each case.
21. Discuss the effect of conformation on the course and rate of E1, E2 eliminations illustrated by the following compounds, (i) 4-*t*-butylcyclohexyl tosylate (*cis* and *trans*), (ii) menthyl and neomenthyl chlorides.
22. State and explain the Taft's equation and its application in the mechanistic study of organic reactions with appropriate examples.
23. Differentiate between chiral reagent controlled and chiral catalyst controlled asymmetric synthesis. Give examples. Discuss the advantages and disadvantages of each.
- (2 × 5 = 10 weightage)

D 32673

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**FIRST SEMESTER M.Sc. (CBCSS) [REGULAR/SUPPLEMENTARY] DEGREE
EXAMINATION, NOVEMBER 2022**

Chemistry

CHE 1C 03—STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

(2019 Admission onwards)

Time : Three Hours

Maximum Weightage : 30

Section A*Answer any **eight** questions.**Each question carries a weightage of 1.*

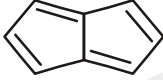
1. Depict the molecular orbitals of ethylene molecule.
2. Illustrate the tautomerism exhibited by nitro compounds.
3. Construct a reaction energy diagram for a slow endothermic reaction.
4. Draw the most stable conformer for ethylene glycol.
5. Arrange the following in increasing order of acidity : 4-nitro benzoic acid, 4-methoxy benzoic acid, benzoic acid, phthalic acid.
6. Draw the Newman projection of the least stable conformer of 2, 3-dimethylbutane.
7. Will 1-bromo bicyclo [2.2.1] heptane undergo elimination ? Justify your answer with suitable illustration.
8. Depict the structures of (2Z, 4Z)-2, 4-hexadiene and (2E, 4Z, 6E)-2, 4, 6-octatriene.
9. (1R, 2S, 5R)-2-isopropyl-5-methylcyclohexanol is natural menthol. Depict its structure.
10. Illustrate the hydroboration reaction with an example.

(8 × 1 = 8 weightage)

Section B*Answer any **six** questions.**Each question carries a weightage of 2.*

11. 2-Bromo fumaric acid undergoes dehydrohalogenation 50 times faster than 2-bromo maleic acid. Justify with illustration showing the elimination product also.
12. Specific rotation of a mixture of 2-bromobutanes is -9.2° . (R)-bromobutane has a specific rotation of -23.1° . How much % R and % S enantiomer is there in the mixture ?

Turn over

13. Pentalane  has not been isolated, but its dianion is known and stable. Explain.
14. Illustrate the product formed when (S)-2-butanol reacts with SOCl_2 .
15. Predict the product formed when meso-2,3-dibromobutane is treated with magnesium.
16. Explain the peculiar bonding in cyclopropanes.
17. Illustrate the Sharpless asymmetric epoxidation reaction.
18. Depict the structure of CBS catalyst and mention one application. (6 × 2 = 12 weightage)

Section C

Answer any **two** questions.

Each question carries a weightage of 5.

19. Trans-2-amino cyclohexanol on treatment with nitrous acid yields cyclopentane carbaldehyde alone while the cis isomer yields cyclohexanone as well. Illustrate with mechanism.
20. (-) Lactic acid has a specific rotation of -3.8° . What is the specific rotation of a solution containing 7.5 g. of (-)-lactic acid and 2.5 g. of (+)-lactic acid.
21. Acetolysis of threo-3-phenyl-2-butyl tosylate gives the threo racemic product while erythro isomer proceeds largely with retention of configuration. Illustrate and explain.
22. Depict examples of (i) non-carbon chiral centred molecule ; (ii) axially chiral molecule ; (iii) atropisomers. Also give R/S designations of the chiral molecules that you have depicted. (2 × 5 = 10 weightage)

D 52780

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Chemistry

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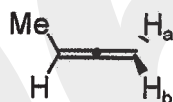
(2019 Admission onwards)

Time : Three Hours

Maximum : 30 Weightage

Section A*Answer any **eight** questions.**Each question carries 1 weightage.*

1. To which category does cyclopentadienyl radical belong - aromatic, anti-aromatic, homo-aromatic or non-aromatic ?
2. Which has a larger pK_a value - cyclopentadiene or cycloheptatriene ?
3. Illustrate a reaction where a hydroxyl group acts as a neighbouring group to produce an epoxide.
4. Arrange in the order of increasing stability for the conformational isomers of cyclohexane - boat, chair and twist boat.
5. Cis-4-t-Bu-cyclohexanol undergoes oxidation faster than trans-4-t-Bu-cyclohexanol. Why ?
6. Predict the product formed when 1-bromo-1-methyl cyclopentane is reacted with tert-butoxide anion in DMF solvent ?
7. Designate the topicity of H_a and H_b in :



8. Depict the Fischer projection of R-alanine [Alanine is $CH(CH_3)(NH_2)(CO_2H)$].

Turn over

9. What product is formed when 2(R)-hydroxy pentane is treated with thionyl chloride ?
10. Depict the structure of IPC_2BH .

(8 × 1 = 8)

Section B

Answer any **six** questions.

Each question carries 2 weightage.

11. Illustrate the substitution and elimination product obtained by action of methanol on 1-chloro-1-phenyl cyclopentane.
12. Which has higher dipole moment and why - 2, 3-diphenyl cyclopropanone or 2, 3-diphenyl cyclobut-2-enone.
13. Arrange the following in increasing order of basicity : pyrrole, indole, pyridine and piperidine.
14. Give an example of a molecule possessing diastereotopic hydrogens.
15. Specific rotation of a mixture of 2-bromobutanes is -9.2° (R)-bromobutane has a specific rotation of -23.1° . How much % R and % S enantiomer is there in the mixture ?
16. What product is formed when trans-2-chlorocyclohexanol is treated with a base ?
17. Illustrate the Sharpless asymmetric epoxidation reaction.
18. Illustrate the structure of a catalyst which can do asymmetric reductions.

(6 × 2 = 12)

Section C

Answer any **two** questions.

Each question carries 5 weightage.

19. Predict the major and minor products formed by the reaction of α -phenyl propionaldehyde with methyl magnesium bromide.
20. Considering the base hydrolysis of esters as an example, explain the Hammett equation, and the significance of reaction constant and substitution constant.
21. Give the structures of : (i) Cis-decalin ; (ii) (1R, 2S, 5R)-2-Isopropyl-5-methylcyclohexanol ; and (iii) Bicyclo[2.2.2]octane ; (iv) A R-allene ; and (v) A chiral biphenyl compound.
22. How are asymmetric reactions classified ? Give examples of any *two* classes.

(2 × 5 = 10)