STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86 (For candidates admitted during the academic year 2023-24)

M.Sc. DEGREE EXAMINATION, NOVEMBER 2024 BRANCH IV- CHEMISTRY THIRD SEMESTER

COURSE : CORE

PAPER : SYNTHETIC ORGANIC CHEMISTRY AND NATURAL

PRODUCTS

SUBJECT CODE : 23CH/PC/SO34

TIME : 3 HOURS MAX.MARKS :100

| Q. No. | SECTION A (10 x 1 = 10 marks) | CO | KL |
|--------|--|----|----|
| 1. | Papaverine belongs to the class of natural products called | 1 | 1 |
| | a) Alkaloids b) Terpenoids | | |
| | c) Steroids d) Natural Pigments | | |
| 2. | Umpolung means | 1 | 1 |
| | a) Reversal of polarity b) Same polarity | | |
| | c) reverse reaction d) Equilibrium | | |
| 3. | Ethylene glycol is used as a protecting group for | 1 | 1 |
| | a) Carbonyl group b) Amino group | | |
| | c) Hydroxyl group d) Carboxyl group The basic structural unit in anythocyanins is | | |
| 4. | | 1 | 1 |
| | a) γ-pyrone b) polyene c) benzpyran d) pyrrole | | |
| | c) benzpyran d) pyrrole | | |
| 5. | Palladium catalyst is widely used in | 1 | 1 |
| | a) Ziegler-Natta reaction b) Gilman reaction | | |
| | c) Simmons-Smith reaction d) Suzuki coupling | | |
| 6. | The reagent used to convert CH ₃ COCH ₃ into CH ₃ COOCH ₃ is | 1 | 1 |
| | a) DDQ b) DCC | | |
| | c) C ₆ H ₅ CO ₃ H d) OsO ₄ | | |
| 7. | The synthetic equivalent for CH ₃ | 1 | 1 |
| | a) CH ₃ MgBr b) CH ₃ CN c) CH ₃ SO ₂ H d) CH ₃ Br | | |
| 8. | What reagent converts a cyanide into a primary amine? | 1 | 1 |
| | a) H ₂ SO ₄ b) NaOEt c) LiAlH ₄ d) Perbenzoic acid | | |
| 9. | Enolates adding to α , β -unsaturated carbonyl compounds is called | 1 | 1 |
| | reaction. | | |
| | a) Claisen-Schmidt b) Knoevenagel | | |
| | c) Michael d) Perkin | 1 | |
| 10. | | | 1 |
| | hydroaromatic compounds. | | |
| | a) DCC b) DDQ c) Tosyl chloride d) SeO ₂ | | |

| Q. No. | SECTION B (10 x 1 = 10 marks) | | KL |
|--------|--|---|----|
| | Fill in the blanks | 2 | 2 |
| 11. | is the synthetic equivalent of O | 2 | 2 |
| 12. | Anthocyanidins are the part of anthocyanins. | 2 | 2 |

| 13. | NBS is used to brominate positions in a molecule. | 2 | 2 |
|-----|--|---|---|
| 14. | Gilman reagent is | 2 | 2 |
| 15. | Acetic anhydride is used to determine functional group in an alkaloid. | 2 | 2 |
| | Answer in a line or two. | 2 | 2 |
| 16. | Define FGI. | 2 | 2 |
| 17. | What is the isoprene rule? | 2 | 2 |
| 18. | What is the Kuhn-Roth method? | 2 | 2 |
| 19. | How can an alcoholic group be converted into a good leaving group? | 2 | 2 |
| 20. | What is the application of the Ziesel's method? | 2 | 2 |

| Q. No. | SECTION C $(4 \times 6 = 24 \text{ marks})$ | | KL |
|--------|--|---|----|
| | Answer any four questions. | | |
| 21. | Show how flavonoids can be distinguished by colour reactions. | 3 | 3 |
| 22. | Illustrate how the position of the hydroxyl group and the angular | 3 | 3 |
| | methyl group in cholesterol can be determined. | | |
| 23. | Complete the following reaction sequences. | 3 | 3 |
| | a. | | |
| | NH ₂ | | |
| | + Br Pd(PPh ₃) ₄ | | |
| | Br B(OH) ₂ KOH, solvent | | |
| | b. | | |
| | O 2 eq. Ti(O/Pr) ₄ (cat.) R OMe + XMg Ti(O/Pr) ₄ (cat.) | | |
| | R OMe THF, r.t. (3+3) | | |
| 24. | Discuss any two synthetic applications of dicyclohexylcarbodiimide | 3 | 3 |
| | and Perbenzoic acid. | | |
| 25. | Demonstrate with suitable examples how carbonyls and carboxylic | 3 | 3 |
| | acids can be protected and deprotected. | | |

| Answer any four questions. 26. Identify the synthetic route for the following two compounds using the retro method. a. b. 27. Outline the structural elucidation of daidzein. 4 4 28. Predict the products of the following reactions. a. DDQ, CeHe Reflux b. NBS CCL4 c. PBA, CHCl3 5 °C, 24 h d. (4x2=8 marks) | Q. No. | SECTION D $(4 \times 8 = 32 \text{ marks})$ | | KL |
|---|--------|--|---|----|
| the retro method. a. b. CH ₃ H ₃ C N Outline the structural elucidation of daidzein. 4 4 28. Predict the products of the following reactions. a. DDQ, C ₀ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| the retro method. a. b. CH ₃ H ₃ C N Outline the structural elucidation of daidzein. 4 4 28. Predict the products of the following reactions. a. DDQ, C ₀ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | 26. | | 4 | 4 |
| 27. Outline the structural elucidation of daidzein. 28. Predict the products of the following reactions. a. DDQ, C ₆ H ₆ Reflux b. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| 27. Outline the structural elucidation of daidzein. 28. Predict the products of the following reactions. a. DDQ, C ₆ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | a. b. | | |
| 27. Outline the structural elucidation of daidzein. 28. Predict the products of the following reactions. a. DDQ, C ₆ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| 27. Outline the structural elucidation of daidzein. 28. Predict the products of the following reactions. a. DDQ, C ₀ H ₀ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| 27. Outline the structural elucidation of daidzein. 28. Predict the products of the following reactions. a. DDQ, C ₆ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | CH ₃ | | |
| 27. Outline the structural elucidation of daidzein. 28. Predict the products of the following reactions. a. DDQ, C ₀ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | H_3C | | |
| 27. Outline the structural elucidation of daidzein. 28. Predict the products of the following reactions. a. DDQ, C ₀ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | \sim | | |
| 27. Outline the structural elucidation of daidzein. 28. Predict the products of the following reactions. a. DDQ, C ₀ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| 27. Outline the structural elucidation of daidzein. 28. Predict the products of the following reactions. a. DDQ, C ₀ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | (4+4) | | |
| 28. Predict the products of the following reactions. a. DDQ, C ₆ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | 27. | | 4 | 4 |
| a. DDQ, C ₆ H ₆ Reflux b. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| DDQ, CeHe Reflux b. NBS CCL4 c. PBA, CHCl3 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | 28. | Predict the products of the following reactions. | 4 | 4 |
| D. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | a. | | |
| D. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| D. NBS CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| b. NBS CCL C. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | DDQ, C _e H _e | | |
| DBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | Reflux | | |
| DBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | b. | | |
| CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| CCL ₄ c. PBA, CHCl ₃ 5 °C, 24 h d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | NDO | | |
| c. PBA, CHCl ₃ 5 °C, 24 h 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | NBS | | |
| c. PBA, CHCl ₃ 5 °C, 24 h 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | CCM | | |
| PBA, CHCl ₃ 5 °C, 24 h 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | DD 4 certical | | |
| d. 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | | | |
| 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | 3 °C, 24 II | | |
| 1. 9-BBN 2. HOOH, NaOH (4x2=8 marks) | | <i>((() ((((((((((</i> | | |
| 2. HOOH, NaOH (4x2=8 marks) | | d. | | |
| 2. HOOH, NaOH (4x2=8 marks) | | | | |
| 2. HOOH, NaOH (4x2=8 marks) | | | | |
| 2. HOOH, NaOH (4x2=8 marks) | | 1. 9-BBN | | |
| (4x2=8 marks) | | | | |
| | | | | |
| 29. Analyse the Nozaki-Hiyami reaction and explain with mechanism. 4 4 | 29 | | 4 | 4 |
| 30. Discuss the general methods for the synthesis of anthocyanins. 4 4 | | | | |

| Q. No. | SECTION E (2 x 12 = 24 marks) | | | CO | KL |
|--------|--------------------------------------|---|------|----|----|
| | Answer the following | g questions. | | | |
| 31. | a) Establish the struct | ure of Zingiberene. | (10) | | |
| | b) Predict the product | of the following reaction. | (2) | | |
| | Me, AHMe | TiCl ₄ , Zn, CH ₂ Br ₂ | | | |
| | Me H | CH₂Cl₂, THF -40 to 0 °C, 20 h, 98% | | | |

..4

| | (OR) | 5 | 5 |
|-----|---|---|---|
| 32. | a) Synthesise the following compound using Michael addition. (4) COOEt COOEt b) Assess the following reactions and predict the products. (8) | | |
| | i. MeCN LDA 1. 7 THF 2. TMSCI | | |
| | ==SiMe ₃ Pd(PPh ₃) ₂ Cl ₂ /Cul Et ₃ N, 50 °C 90% iii | | |
| | 0.1 - 0.5 mol-% catalyst 1.5 eq. KOfBu dioxane 100°C, 2 h (3+2+3) | | |

| 33. | a) Evaluate the use of sterically hindered bases to achieve the desired stereochemical outcome in the Aldol reaction. (7) b) Discuss the role of phenylisothiocyanate in the Edman degradation method with mechanism. (5) | 5 | 5 |
|-----|---|---|---|
| | (OR) | | |
| 34. | a) Propose a retrosynthetic analysis and synthesis for the following compounds. (8) i. ii. | | |
| | H ₃ C CH ₃ OH | | |
| | b) Identify the products obtained when the following compounds are fused with KOH. (4) i. Apigenin ii. Cyanidin chloride | | |