

CONTENTS

| | |
|--|-----------|
| <i>Preface</i> | <i>v</i> |
| <i>Syllabus Course—BP301T, BP305P and BP401T</i> | <i>x</i> |
| PART III | |
| 3(I)-1 Introduction to Structure of Benzene | 1 |
| Kekule Structure of Benzene | 1 |
| Resonance Structure of Benzene | 2 |
| Unusual Stability of Benzene | 3 |
| Orbital Structure of Benzene | 3 |
| Aromaticity or Aromatic Character | 5 |
| 3(I)-2 Electrophilic Reactions of Benzene | 7 |
| Electrophilic Aromatic Substitution | 7 |
| 3(I)-3 Electrophilic Aromatic Substitution Reactions | 14 |
| Effect of Substituent on Reactivity Towards EAS Reaction | 14 |
| Effect of Substituent on Orientation in Monosubstituted Benzene | 15 |
| 3(I)-4 DDT, Saccharin, BHC and Chloramine-T: Structure and Uses | 22 |
| DDT | 22 |
| Saccharin | 22 |
| BHT | 23 |
| Chloramine-T | 23 |
| Questions | 25 |
| 3(II)-1 Phenols | 28 |
| Qualitative Tests for Phenols | 29 |
| Preparation of Phenols | 30 |
| Properties | 31 |
| Uses of Phenols | 35 |
| 3(II)-2 Aromatic Amines | 37 |
| Preparation of Aromatic Amines | 37 |
| Basicity of Aromatic Amines | 38 |
| Effects of Substituents on Basicity | 39 |
| 3(II)-3 Aromatic Acids | 45 |
| Questions | 52 |
| 3(III)-1 Oils and Fats | 55 |
| Triglycerides | 55 |
| 3(III)-2 Oils and Fats: Analytical Constants | 64 |
| Acid Value | 64 |
| Saponification Value | 65 |
| Ester Value | 66 |
| Iodine Value | 66 |
| Reichert-Meissl (RM) Value | 69 |
| Acetyl Value or Acetyl Number | 71 |
| Peroxide Value | 72 |
| Questions | 73 |
| 3(IV)-1 Polynuclear Aromatic Hydrocarbons | 75 |
| Naphthalene | 76 |
| Anthracene | 81 |
| Phenanthrene | 84 |

| | |
|---|------------|
| Diphenylmethane 87 | |
| Triphenylmethane 88 | |
| Questions 89 | |
| 3(V)-1 Cycloalkanes | 91 |
| Cyclopropane 92 | |
| Cyclobutane 94 | |
| 3(V)-2 Stabilities in Cycloalkanes | 96 |
| Baeyer's Angle Strain Theory 96 | |
| Coulson-Moffitt Model or Concept of Maximum Overlap of Carbon Orbitals 98 | |
| Sachse-Mohr Theory 99 | |
| Questions 100 | |
| Practicals (BP305P) | 102 |
| Experiments Involving Laboratory Techniques 102 | |
| A. Crystallization Technique 102 | |
| Experiment 3.A: To prepare crystals of pure benzoic acid from an impure sample of benzoic acid 105 | |
| B. Steam Distillation 104 | |
| Experiment 3.B: Isolation of orange oil by steam distillation 105 | |
| Determination of Analytical Constants 106 | |
| Synthetic Organic Chemistry 110 | |
| Experiment 3.1: Synthesis of acetanilide by acetylation of aniline 110 | |
| Experiment 3.2: Synthesis of benzanilide from aniline by benzylation 113 | |
| Experiment 3.3: Synthesis of <i>p</i> -bromoacetanilide from aniline (bromination reaction) 114 | |
| Experiment 3.4: Synthesis of 2,4,6-tribromophenol from phenol 115 | |
| Experiment 3.5: Synthesis of phenyl benzoate from phenol 117 | |
| Experiment 3.6: Synthesis of <i>m</i> -dinitrobenzene from nitrobenzene 118 | |
| Experiment 3.7: Synthesis of 2-naphthol aniline or aniline yellow dye 120 | |
| Experiment 3.8: Synthesis of 5-nitro salicylic acid from salicylic acid 122 | |
| Experiment 3.9: Synthesis of benzil (dibenzoyl) from benzoin by oxidation with nitric acid 123 | |
| Experiment 3.10: Synthesis of dibenzalacetone from acetone 125 | |
| Experiment 3.11: Synthesis of cinnamic acid from benzaldehyde 126 | |
| Experiment 3.12: Preparation of benzoic acid from alkyl benzoate (ethyl benzoate) 128 | |
| Experiment 3.13: Preparation of benzoic acid from benzyl chloride 129 | |
| Experiment 3.14: Preparation of salicylic acid from alkyl salicylate (methyl salicylate) 131 | |
| Experiment 3.15: Preparation of para-iodo benzoic acid from para-amino benzoic acid 132 | |

PART IV

| | |
|---|------------|
| 4(I)-1 Optical Isomerism | 135 |
| Structural Isomerism 135 | |
| Stereoisomerism 135 | |
| Optical Isomerism 135 | |
| 4(I)-2 Racemic Modification and Resolution of Racemic Mixture, Reactions of Chiral Molecules | 143 |
| Racemic Modification 143 | |
| Formation of Racemic Modification 143 | |
| Resolution of Racemic Mixture 145 | |
| 4(I)-3 Asymmetric Synthesis: Partial and Absolute | 148 |
| Questions 150 | |
| 4(II)-1 Geometrical Isomerism | 153 |
| Geometrical Isomerism 153 | |

| Contents | ix |
|---|------------|
| 4(II)-2 Conformational Isomerism in Ethane, <i>n</i>-Butane and Cyclohexane | 159 |
| Conformations of Ethane 160 | |
| Conformations of Butane 160 | |
| Conformations of Cyclohexane 161 | |
| 4(II)-3 Stereoisomerism in Biphenyl Compounds | 164 |
| 4(II)-4 Stereospecific and Stereoselective Reactions | 166 |
| Questions 168 | |
| 4(III)-1 Heterocyclic Compounds: Nomenclature and Classification | 171 |
| 4(III)-2 Synthesis, Reactions and Medicinal Uses of Pyrrole, Furan and Thiophene | 178 |
| Pyrrole 178 | |
| Furan 185 | |
| Thiophene 188 | |
| Relative Aromaticity of Pyrrole, Furan and Thiophene 194 | |
| Relative Reactivity of Pyrrole, Furan and Thiophene 195 | |
| Questions 196 | |
| 4(IV)-1 Azoles | 199 |
| Pyrazole 199 | |
| Imidazole 203 | |
| Oxazole 210 | |
| Thiazole 212 | |
| 4(IV)-2 Pyridine | 215 |
| Pyridine 215 | |
| Synthesis of Pyridines 215 | |
| Basicity of Pyridine 217 | |
| Reactions of Pyridine 218 | |
| Medicinal Uses 225 | |
| 4(IV)-3 Benzfused Heterocyclic Compounds | 226 |
| Heterocycles with Fused Five-membered Ring 226 | |
| Indole 226 | |
| Heterocycles with Fused Six-membered Ring 231 | |
| Acridine 237 | |
| 4(IV)-4 Synthesis and Medicinal Uses of Pyrimidine, Purine, Azepines and their Derivatives | 241 |
| Pyrimidine 241 | |
| Azepines 243 | |
| Purine 244 | |
| Questions 247 | |
| 4(V)-1 Reactions of Synthetic Importance | 251 |
| Metal Hydride Reduction 251 | |
| Lithium Aluminium Hydride (LAH) 251 | |
| Sodium Borohydride 254 | |
| Clemmensen Reduction 255 | |
| Wolff-Kishner Reduction 256 | |
| Birch Reduction 257 | |
| Oppenauer Oxidation 258 | |
| Dakin Reaction 259 | |
| Backmann Rearrangement 260 | |
| Schmidt Rearrangement 261 | |
| Claisen-Schmidt Condensation 262 | |
| Questions 263 | |
| Index | 265 |