

## Table of Contents

|  |           |
|--|-----------|
| About the Authors .....                                | i         |
| Acknowledgements and Dedication .....                  | ii        |
| Introduction.....                                      | iii       |
| <b>Chapter 1: Structure of Organic Compounds .....</b> | <b>1</b>  |
| <b>1.1 Theory .....</b>                                | <b>1</b>  |
| 1) Hydrocarbons .....                                  | 1         |
| 2) Alcohols .....                                      | 2         |
| 3) Amines .....  | 3         |
| 4) Quarternary Ammonium Compounds .....                | 3         |
| 5) Aldehydes .....                                     | 3         |
| 6) Ketones .....                                       | 3         |
| 7) Esters .....  | 4         |
| 8) Fatty Carboxylic Acids .....                        | 5         |
| 9) Anhydrides .....                                    | 6         |
| 10) Ethers .....                                       | 6         |
| 11) Epoxides .....                                     | 7         |
| 12) Alkyl Halides .....                                | 7         |
| 13) Acyl Halides .....                                 | 7         |
| 14) Aromatics .....                                    | 7         |
| 15) Mercaptans .....                                   | 8         |
| 16) Lactones .....                                     | 8         |
| 17) Lactams .....                                      | 8         |
| 18) Amides .....                                       | 9         |
| <b>1.2 Practice .....</b>                              | <b>9</b>  |
| 1) Exercises .....                                     | 9         |
| 2) Exercise Solutions .....                            | 10        |
| <b>Chapter 2: Raw Materials .....</b>                  | <b>13</b> |
| Background .....                                       | 13        |
| 1) Triglycerides .....                                 | 16        |
| 2) Methyl Esters .....                                 | 22        |

|   |    |
|---|----|
| 3) Fatty Acids . . . . .                                      | 22 |
| A. Natural Acids . . . . .                                    | 22 |
| B. Synthetic Linear Acids . . . . .                           | 23 |
| C. Synthetic Branched Acids . . . . .                         | 24 |
| D. Ozone Acids . . . . .                                      | 25 |
| 4) Fatty Alcohols . . . . .                                   | 25 |
| A. Oxo Alcohols . . . . .                                     | 26 |
| B. Ziegler Alcohols . . . . .                                 | 26 |
| C. Natural Alcohols . . . . .                                 | 27 |
| 5) Reppe Chemistry . . . . .                                  | 28 |
| A. Acetylene Chemistry . . . . .                              | 28 |
| B. Reactions of Alcohols and Acetylene-Vinyl Ethers . . . . . | 29 |
| C. Phenol-Acetylene Reaction . . . . .                        | 29 |
| D. Mercaptan Reactions . . . . .                              | 30 |
| E. Reactions of Aldehydes with Acetylene . . . . .            | 31 |
| F. Tetrahydrofuran . . . . .                                  | 31 |
| G. Lactams . . . . .  | 32 |
| H. Propargyl Alcohol and Derivatives . . . . .                | 32 |
| I. Acrylic Acid . . . . .                                     | 33 |
| 6) Alkanolamines . . . . .                                    | 34 |
| A. Ethanolamines . . . . .                                    | 34 |
| B. Isopropanolamines . . . . .                                | 34 |
| C. Mixed Alkanolamines . . . . .                              | 35 |

**Chapter 3: Synthesis Approach . . . . . 37**

3.1 Analogues and Homologues . . . . . 39

3.2 Specificity and Selectivity . . . . . 40

**Chapter 4: Nucleophilic Substitution . . . . . 43**

4.1 Theory . . . . . 43

    1)  $S_N1$  . . . . . 44

    2)  $S_N2$  . . . . . 44

4.2 Practice . . . . . 45

    1) Esters . . . . . 45

        A. Direct Esterification . . . . . 47

            1. Esterification Reaction from Methyl Ester . . . . . 47

            2. Esterification Reaction from Fatty Acid . . . . . 50

        B. Trans esterification . . . . . 53

|  |     |
|--|-----|
| 2) Amides  | 56  |
| A. Amidification from Methyl Ester               | 57  |
| B. Amidification from Fatty Acids                | 60  |
| C. Amidification from Triglycerides              | 63  |
| 3) Carboxylates                                  | 65  |
| A. Carboxylation with Anhydrides                 | 65  |
| B. Soap from Methyl Ester                        | 68  |
| C. Soap from Fatty Acid                          | 71  |
| D. Soap from Triglyceride                        | 73  |
| E. Carboxylates                                  | 76  |
| 4) Amphoterics                                   | 78  |
| A. Amido Betaines                                | 78  |
| B. Alkyl Betaines                                | 81  |
| C. Amino Propionates                             | 84  |
| D. Sulfobetaines                                 | 88  |
| E. Phosphobetaines                               | 91  |
| 5) Quats   | 95  |
| A. Alkyl Quat—Benzyl Chloride                    | 95  |
| B. Alkyl Quat—Dimethyl Sulfate                   | 99  |
| 6) Monoalkyl Phosphate                           | 101 |
| A. Phosphation Reaction with Polyphosphoric Acid | 101 |
| 7) Sarcosinates                                  | 104 |
| 8) Taurates                                      | 106 |
| A. Schotten-Baumann Taurates                     | 106 |
| 9) Isoethionates                                 | 109 |

## **Chapter 5: Sulfation/Sulfonation** . . . . . 113

|  |     |
|--|-----|
| 5.1 Theory                               | 113 |
| 1) Sulfonation                           | 113 |
| 2) Sulfonation                           | 113 |
| 5.2 Practice                             | 115 |
| 1) Sulfonation—SO <sub>3</sub>           | 116 |
| 2) Chlorosulfonic Sulfation              | 119 |
| 3) Sulfamic Acid Sulfation               | 123 |
| 4) Sulfonation of Alpha Olefin Sulfonate | 125 |

## **Chapter 6: Fatty Tertiary Amine Oxidation** . . . . . 131

|                        |     |
|------------------------|-----|
| 6.1 Theory             | 131 |
| 1) Surfactant Activity | 132 |

|  |     |
|--|-----|
| 2) Antimicrobial Activity .....  | 132 |
| 6.2 Practice .....   | 133 |
| 1) Amine Oxides .....  | 133 |
| A. Peroxide Oxidation of Tertiary Amine .....  | 133 |
| <b>Chapter 7: Reduction</b> .....  | 137 |
| 7.1 Theory .....   | 137 |
| 1) Hydrogenation .....   | 137 |
| 2) Dehydrogenation .....   | 137 |
| 3) Reduction .....   | 138 |
| 4) Oxidation .....   | 138 |
| 5) Catalysts .....   | 140 |
| 7.2 Practice .....   | 140 |
| 1) Hydrogenation .....   | 140 |
| 2) Hydrogenolysis .....  | 142 |
| 3) Group Specific Hydrogenolysis .....   | 143 |
| <b>Chapter 8: Radical Polymers</b> .....   | 145 |
| 8.1 Theory .....   | 145 |
| 1) Conventional Radical Polymerization .....   | 145 |
| 2) Kinetics .....  | 146 |
| 3) Controlled “Pseudo-living” Radical Polymerization .....                           | 146 |
| 4) Atom Transfer Radical Polymerization (ATRP) .....                                 | 147 |
| 5) Reversible Addition-Fragmentation Transfer (RAFT) .....                           | 148 |
| 6) Nitroxi-Mediated Radical Polymerization (NMRP) .....                              | 148 |
| 8.2 Practice .....   | 150 |
| 1) Non-Living Polymerization .....   | 150 |
| A. Nonionic .....  | 151 |
| B. Cationic .....  | 156 |
| C. Anionic .....   | 162 |
| 2) Living Radical Polymerization .....   | 166 |
| A. Reversible-Addition Fragmentation Transfer Radical<br>Polymerization (RAFT) ..... | 166 |
| B. Nitroxide-Mediated Radical Polymerization (NMRP) .....                            | 170 |
| C. Atom Transfer Radical Polymerization (ATRP) .....                                 | 170 |
| <b>Chapter 9: Other Polymers</b> .....   | 173 |
| 9.1 Theory .....   | 173 |
| 1) Polyesters .....  | 173 |

|  |            |
|--|------------|
| 2) Polyamides.....                             | 174        |
| 3) Polyurethanes.....                          | 176        |
| 9.2 Practice.....                              | 178        |
| 1) Polyesters.....                             | 178        |
| 2) Polyamides.....                             | 181        |
| 3) Polyurethanes.....                          | 183        |
| <b>Chapter 10: Aldol Condensation.....</b>     | <b>187</b> |
| 10.1 Theory.....                               | 187        |
| 10.2 Practice.....                             | 187        |
| 1) Guerbet Alcohol.....                        | 187        |
| <b>Chapter 11: Diels-Alder Reactions.....</b>  | <b>193</b> |
| 11.1 Theory.....                               | 193        |
| 11.2 Practice.....                             | 194        |
| 1) Dimer Acid.....                             | 194        |
| A. Tall Oil ( <i>Tallol</i> ).....             | 194        |
| <b>Chapter 12: Ring Opening Reactions.....</b> | <b>199</b> |
| 12.1 Theory.....                               | 199        |
| 12.2 Practice.....                             | 199        |
| 1) Alkoxylation.....                           | 199        |
| 2) Ethenification.....                         | 205        |
| 3) Carboxylates.....                           | 207        |
| A. Reaction with Anhydrides.....               | 207        |
| 4) Butyrolactone Ring Opening.....             | 210        |
| A. Reaction to Make Carboxy.....               | 210        |
| <b>Chapter 13: Ring Closing Reactions.....</b> | <b>213</b> |
| 13.1 Theory.....                               | 213        |
| 1) Ring-Containing Components.....             | 213        |
| A. 3-Membered Rings.....                       | 213        |
| B. 4-Membered Rings.....                       | 213        |
| C. 5-Membered Rings.....                       | 214        |
| D. 6-Membered Rings.....                       | 215        |
| 13.2 Practice.....                             | 216        |
| 1) Imidazoline.....                            | 216        |

|   |            |
|---|------------|
| 2) Sorbitan Esters.....                     | 220        |
| 3) Lactams .....                            | 224        |
| 4) Alkylpolyglucoside .....                 | 227        |
| <b>Chapter 14: Analytical .....</b>         | <b>233</b> |
| 14.1 The mg KOH/gm System .....             | 233        |
| 1) Alkali Value .....                       | 234        |
| 2) Acid Value .....                         | 234        |
| 3) Hydroxyl Value .....                     | 235        |
| 4) Saponification Value.....                | 236        |
| 5) Summary .....                            | 236        |
| <b>Chapter 15: Analytical Methods .....</b> | <b>237</b> |
| <b>Index .....</b>                          | <b>285</b> |