

Contents

PART ONE

Techniques of Organic Analysis

1. *Introduction* 3
 - Identification, 3 The Systematic Approach, 3 Physical Methods, 4
 - Microscopic Methods, 5 Sample Size, 6 References, 6

2. *Equipment and Procedures for Small-Scale Work* 8
 - Weighing, 9 Measuring Volumes, 12 Heating, 19 Handling, 19
 - Stirring and Grinding, 24 Separating of Immiscible Solvents, 29
 - Filtering, 30 Drying, 31 Evaporating, 31 Heating under Reflux, 34
 - Reaction Vessels, 35 High Vacuum Line, 39 Apparatus and Procedure for Microhydrogenation, 40
 - Apparatus and Procedure for Preparation of Grignard Reagents, 45 References, 48

- Fractionation Procedures* 54
 - Crystallization*: Selection of Solvents, 55 Determination of Solubility, 60
 - Preparation of Solutions for Crystallization, 61 Filtration of the Hot Solution and Formation of Crystals, 63
 - Other Apparatus for Crystallization, 74 Drying of Crystals, 75
 - Distillation*: Simple Distillation at Atmospheric Pressure, 83 Fractional Distillation at Atmospheric Pressure, 87
 - Distillation under Reduced Pressure, 90 Distillation of Small Quantities at Atmospheric or Reduced Pressures, 96
 - Steam Distillation, 99 *Sublimation*: Fractional Sublimation under Reduced Pressure, 105
 - Extraction*, 109 References, 111

4. *Fractionation Procedures* 117
 - Chromatographic Procedures*: Principles of the Chromatographic Separation, 117
 - Paper Chromatography, 120 Column Chromatography, 131
 - Thin-Layer Chromatography, 145 Ion-Exchange Chromatography, 152
 - Gas Chromatography, 157 *Other Methods of Fractionation*, 159 References, 162

5. *Physical Properties of Organic Compounds* 171
 - Melting Point, 172 Boiling Point, 202 Refractive Index, 213
 - Density, 219 Optical Rotation, 225 Molecular Weight, 228
 - Molar Refraction and Dispersion, 234 References, 237

6. <i>The Separation of Mixtures</i>	244
<p><i>Mixtures: General Principles, 246 Preliminary Tests for a General Mixture, 246 A General Procedure for the Separation of Mixtures, 251 Suggestions for Separating Intraclass Mixtures, 257 Alternate Methods for the Separation of Mixtures, 260 The Use of Other Methods of Separation, 261 References, 264</i></p>	
<p>PART TWO Procedures for Tentative Identification of an Unknown</p>	
7. <i>Preliminary Examination of the Pure Compound</i>	275
<p><i>Ignition and Preliminary Tests with Reagents, 276 Observations During Fusion and Cooling, 277 Analysis for Elements: Detection of Carbon and Hydrogen, 282 Decomposition of Organic Compounds, 286 Detection of the Elements in the Sodium Fusion Filtrate, 291 References, 299</i></p>	
8. <i>Classification by Solubility</i>	303
<p><i>The Classification of Solvents, 306 Comparison of Water and Ether as Solvents, 307 Solubility in Water, 308 Solubility in Ethyl Ether, 312 Solubility in Dilute Hydrochloric Acid, 313 Solubility in Dilute Sodium Hydroxide, 315 Solubility in Dilute Sodium Bicarbonate, 317 Solubility in Concentrated Sulfuric Acid, 318 Solubility Determinations, 320 Designation for the Solubility Divisions, 322 Table of Solubility Classifications, 324 References, 326</i></p>	
9. <i>Classification by the Indicator Method</i>	328
<p><i>Indicator Method of Classifying Acids and Bases, 335 Procedures for Testing, 337 Table of Indicator Classifications, 338 References, 341</i></p>	
10. <i>Tests for the Classification of an Unknown</i>	343
<p><i>Part I: An Inventory and a Forward Look: P-1 Gross Observations, 347 P-2 The Ignition Test, 348 P-3 Tests for Salts, 349 P-4 Tests for Aromatic Structure, 350 P-5 Tests for Active Unsaturation, 352 P-6 Tests by Selected Oxidizing Agents, 355 P-7 Detection of Acidic Substances, 359 P-8 Test for Compounds that have Nitrogen and Oxygen in the Same Group, 360 P-9 Iodoform Formation Test, 361</i></p> <p><i>Part II: Tests for Special Classes: 10.01 Acids, 363 10.02 Acid Anhydrides, 366 10.03 Acid Halides, 366 10.04 Alcohols, 367 10.05 Alkyl and Aryl Halides, 372 10.06 Unsubstituted Amides, 373</i></p>	

10.07 Substituted Amides, 376 10.08 Amines, 378 10.09 Carbo-
hydrates, 388 10.10 Carbonyl Compounds, 392 10.11 Esters, 397
10.12 Ethers, 398 10.13 Hydrazines, 399 10.14 Hydrocarbons, 400
10.15 Nitrates and Nitrites, 401 10.16 Nitriles, 402 10.17 Nitro
Compounds, 402 10.18 Nitroso Compounds, 405 10.19 Oximes,
Hydrazones, and Semicarbazones, 406 10.20 Phenols, 406 10.21
Sulfides, Disulfides, and Sulfones, 410 10.22 Thiols (Mercaptans
and Thiophenols), 411 Coordination of Data, 413 References, 414

PART THREE

Procedures for Final Characterization of an Unknown

Index to Preparation of Derivatives, 427

11. *Problems in the Derivatization of Organic Compounds* 429

Selection of Derivatives, 430 General Procedure for Preparation
of Small Quantities of Derivatives, 434 Evaluation of the Melting
Points of Derivatives, 436

12. *Derivatives of Carboxylic Acids and Acid Derivatives* 437

Carboxylic Acids: Amides, *p*-Toluidides, Anilides, *p*-Bromoanilides,
and Other Substituted Amides of Carboxylic Acids, 439 Solid
Esters of Carboxylic Acids, 447 Salts and Other Derivatives of
Carboxylic Acids, 449 *Amino Acids:* N-Acyl and N-Aroyl Deriva-
tives of Amino Acids, 452 α -Naphthylureido Derivatives and
Hydantoin of Amino Acids, 455 Salts of Amino Acids, 456
Chromatographic Detection of Amino Acids, 457 *Acid Halides*, 458
Acid Anhydrides, 459 References, 459

13. *Derivatives of Alcohols and Phenols (Monohydric and Polyhydric)* 465

Alcohols: 3,5-Dinitrobenzoates and *p*-Nitrobenzoates, 467 3-
Nitrophthalates, 473 α -Naphthylurethans, 474 Other Substi-
tuted Urethans, 479 Other Derivatives, 480 Chromatographic
Detection of Small Amounts of Alcohols, 482 *Phenols:* 3,5-
Dinitrobenzoates, *p*-Nitrobenzoates, Benzoates, and Acetates, 485
Urethans, 487 Aryloxyacetic Acids, 489 Other Derivatives, 490
Chromatography of Phenols, 491 References, 492

14. *Derivatives of Aldehydes, Ketones, and Acetals* 496

Aldehydes: Phenylhydrazones, 497 2,4-Dinitrophenylhydrazones
and *p*-Nitrophenylhydrazones, 499 Semicarbazones and Thio-
semicarbazones, 502 Dimethone Derivatives, 504 Other Deriva-
tives, 506 Chromatographic Identification and Separation of

- Aldehydes, 509 *Ketones*: Substituted Hydrazones, 510 Semi-carbazones and Thiosemicarbazones, 511 Oximes, 512 Other Derivatives, 513 *Acetals*: Hydrolysis of Acetals, 514 References, 515
15. *Derivatives of Carbohydrates* 519
 Substituted Phenylhydrazones, Osazones, and Osotriazoles, 520
 Other Derivatives, 525 Specific Rotation of Carbohydrates and Their Derivatives, 528 Chromatography of Sugars, 528 References, 530
16. *Derivatives of Esters and Ethers* 532
Esters: Derivatization of the Acidic Part of an Ester, 534 Derivatization of the Acidic and Alcoholic Components after Hydrolysis, 537
 Derivatization of the Alcoholic Component, 538 Examples of Complete Characterization of Esters, 538 Derivatization of Lactones and Esters of Inorganic Acids, 540 *Ethers*: Derivatives from Aliphatic Ethers, 542 Derivatives from Aromatic Ethers, 544
 References, 547
17. *Derivatives of Halogen Compounds* 548
Alkyl and Cycloalkyl Halides: S-Alkylthiuronium Picrates, 549
 Picrates of β -Naphthyl Ethers, 551 Anilides, *p*-Toluidides, α -Naphthalides, and Alkylmercuric Salts, 551 3,5-Dinitrobenzoates, 555
 Other Derivatives of Alkyl and Cycloalkyl Halides, 555 *Aryl Halides*: Nitro Derivatives of Aryl Halides, 559 Sulfonamides of Aryl Halides, 564 *Fluorine Compounds*: Identification and Characterization of Fluorocarbons, 565 Specific Class Tests for Fluorine Compounds, 567 Derivatization of Fluorine Compounds, 567
 References, 569
18. *Derivatives of Hydrocarbons* 571
Alkanes and Cycloalkanes: Characterization by Means of Physical Constants, 572 Oxidation of a Cycloalkane to a Dicarboxylic Acid, 573 *Alkenes and Cycloalkenes, Alkynes, Dienes*, 574 *Aromatic Hydrocarbons*: Nitration of Aromatic Hydrocarbons, 578
 Acetamido Derivatives of Aromatic Hydrocarbons, 581 Picrates and 2,4,7-Trinitrofluorenone Adducts of Aromatic Hydrocarbons, 582
 Aroylbenzoic Acids from Aromatic Hydrocarbons, 583 Preparation of Derivatives of Aromatic Hydrocarbons with 2,4-Dinitrobenzenesulfenyl Chloride, 585 Oxidation of Side Chains, 585 References, 586
19. *Derivatives of Amino-Nitrogen Functions* 589
Amines: Acetamides and Benzamides of Amines, 589 Sulfonamides and Sulfenamides of Amines, 595 Substituted Ureas and Thioureas

of Amines, 598 General Method for Preparation, 599 Quaternary Ammonium Salts of Amines, 601 Other Derivatives of Amines, 604 Chromatographic Detection of Amines, 606 *Hydrazines*, 607 *Amides, Imides, and Ureas*: Characterization by Hydrolysis, 608 Xanthyl Derivatives of Amides, 609 Mercuric Salts and Other Derivatives of Amides, 610 References, 611

20. *Derivatives of Other Nitrogen Functions*

Azo Compounds, 615 *Azoxy and Hydrazo Compounds*, 617 *Iso-cyanates and Isocyanides*, 617 *Nitriles*: Hydrolysis of Nitriles to Carboxylic Acids and Amides, 618 Reduction of Nitriles to Amines and Their Characterization by Preparation of Substituted Thioureas, 621 Other Derivatives of Nitriles, 622 *Nitro Compounds*: Derivatization of Nitro Compounds by Reduction to Amines, 625 Other Derivatives of Nitro Compounds, 626 *Nitroso Compounds*, 628 References, 629

21. *Derivatives of Sulfur Functions*

Sulfonamides, 631 *Sulfonyl Chlorides*, 634 *Sulfonic Acids*: S-Benzylthiuronium Derivatives of Sulfonic Acids, 635 Arylamine Salts of Sulfonic Acids, 636 Preparation of Sulfonyl Chlorides from Sulfonic Acids and Conversion to Sulfonamides and N- α -Naphthylsulfonamides, 637 *Thiocyanates and Isothiocyanates*, 640 *Thioethers*, 641 *Thiols (Mercaptans and Thiophenols)*: Thioethers, 642 Thioesters, 643 References, 644

22. *Instrumental Methods*

Advantages of the Instrumental Methods, 646 Types of Information Obtained, 647 Sample Handling, 648 Special Procedures for Reducing the Size of the Sample, 649 References, 651

646

PART FOUR

Tables of Organic Compounds with Their Constants and Derivatives 657

Preface to Tables: Nomenclature, 659 General References, 661 General Comments, 663 Abbreviations, 664 *List of Tables*, 665

Appendix, 969

Subject Index of Text, 981

Compound Index of Tables, 995