

CONTENTS

| | |
|--|----|
| Publisher's Note | v |
| Oxidations with Lead Tetraacetate and Periodic Acid. <i>by R. CRIEGEE.</i> | |
| <i>Translated and revised by CHARLES O. EDENS, JR., AND BRUCE GRAHAM</i> | 1 |
| I. Preparation of Lead Tetraacetate..... | 1 |
| II. Reactions of Lead Tetraacetate..... | 2 |
| III. Dehydrogenation with Lead Tetraacetate..... | 3 |
| IV. Substitution of H— by —OCOCH ₃ | 5 |
| V. Addition of Two Acetylated OH— Groups to Double Bonds..... | 9 |
| VI. Glycol Cleavage by Means of Lead Tetraacetate..... | 12 |
| VII. Oxidations with Periodic Acid..... | 17 |
| Dehydrogenation with Sulfur, Selenium, and Platinum Metals, <i>by P. A. PLATTNER.</i> | |
| <i>Translated and revised by E. C. ARMSTRONG</i> | 21 |
| I. Scope of Dehydrogenation Methods..... | 22 |
| II. Various Dehydrogenation Methods and Reagents..... | 23 |
| III. Reaction Mechanisms..... | 24 |
| IV. Behavior of Functional Groups..... | 25 |
| V. Hydrogenation Effects..... | 33 |
| VI. Normal Dehydrogenation..... | 34 |
| VII. Dehydrogenation Accompanied by Change in Carbon Skeleton..... | 36 |
| Migration of Side Chains..... | 39 |
| Elimination of Side Chains..... | 41 |
| Expansion of Rings..... | 43 |
| Contraction of Rings..... | 45 |
| Cleavage of Rings..... | 46 |
| Formation of New Rings..... | 48 |
| Other Rearrangements..... | 51 |
| VIII. Partial Dehydrogenation..... | 51 |
| IX. Disproportionation..... | 52 |
| X. Heterocyclic Compounds..... | 53 |
| XI. Secondary Reactions..... | 54 |
| XII. Dehydrogenation Techniques..... | 55 |
| 1. Sulfur..... | 55 |
| 2. Selenium..... | 55 |
| 3. Catalytic Methods..... | 56 |
| 4. Solvents..... | 57 |
| 5. Development and Identification of Dehydrogenation Products..... | 58 |
| XIII. Conclusion..... | 58 |
| Reductions with Raney Nickel Catalysts, <i>by R. SCHRÖTER.</i> | |
| <i>Translated and revised by I. SALMINEN</i> | 61 |
| I. Introduction..... | 61 |
| II. Preparation of Raney Catalysts..... | 62 |
| 1. Fusion of Alloy..... | 62 |
| 2. Pulverization..... | 63 |
| 3. Decomposition of Alloy and Washing of Active Metal..... | 64 |
| 4. Specific Procedures..... | 65 |
| A. Nickel..... | 65 |
| B. Cobalt..... | 66 |
| C. Copper..... | 67 |
| D. Iron..... | 67 |

| | |
|---|-----|
| III. Properties of Raney Metals..... | 68 |
| 1. Reducing Properties..... | 69 |
| 2. Raney Nickel as Oxidation and Oxidation-Reduction Catalyst..... | 70 |
| 3. Raney Nickel as Dehydrogenation Catalyst..... | 70 |
| 4. Special Reactions of Raney Nickel..... | 72 |
| IV. Reductions with Raney Catalysts..... | 74 |
| 1. Raney Iron..... | 75 |
| 2. Raney Copper..... | 75 |
| 3. Raney Cobalt..... | 76 |
| 4. Raney Nickel..... | 77 |
| 5. Reduction of Ethylene Bonds..... | 78 |
| 6. Reduction of Acetylene Bonds..... | 82 |
| 7. Reduction of Carbonyl Groups..... | 83 |
| 8. Introduction of Amino Groups..... | 86 |
| 9. Reduction of Carboxyl Groups..... | 91 |
| 10. Reduction of Compounds Containing Halogen..... | 92 |
| 11. Reduction of Aromatic Compounds..... | 93 |
| 12. Reduction of Heterocyclic Compounds..... | 96 |
| Hydrogenation with Copper Chromite Catalysts, by CH. GRUNDMANN. Translated by DONALD M. BURNES..... | 103 |
| I. Introduction..... | 103 |
| II. Properties and Experimental Conditions for Use of Copper Chromite Catalysts..... | 104 |
| III. Preparation of Catalyst..... | 107 |
| IV. Hydrogenation of Functional Groups..... | 109 |
| 1. Reduction of Carbon-Carbon Double Bond, and of Aromatic and Heterocyclic Nuclei..... | 109 |
| 2. Replacement of Alcoholic Hydroxyl, Carbonyl, and Carbalkoxy Groups by Hydrogen..... | 111 |
| 3. Reduction of Aldehydes and Ketones to Alcohols..... | 112 |
| 4. Reduction of Carboxylic Esters to Alcohols..... | 114 |
| Hexamethylene Glycol..... | 115 |
| 5. Reduction of Amides to Amines..... | 118 |
| 6. Reduction of Other Nitrogen-Containing Compounds..... | 120 |
| V. Selective Hydrogenation..... | 120 |
| Meerwein-Ponndorf Reduction and Oppenauer Oxidation, by THEODOR BERSIN. Translated and revised by ELEANOR R. WEBSTER AND JEAN V. CRAWFORD..... | 125 |
| I. Introduction..... | 125 |
| II. Meerwein-Ponndorf Reduction of Carbonyl Compounds..... | 127 |
| 1. General Considerations..... | 127 |
| 2. Preparation of Reagents..... | 131 |
| A. Anhydrous Alcohols..... | 131 |
| B. Aluminum Isopropoxide, $Al(i-OC_3H_7)_3$ | 132 |
| C. Aluminum Ethoxide, $Al(OC_2H_5)_3$ | 132 |
| D. Aluminum tert-Butoxide, $Al(tert-OC_4H_9)_3$ | 133 |
| 3. Examples of Experimental Procedures..... | 133 |
| A. Reduction of Butyl Chloral..... | 133 |
| B. Reduction of Ketones..... | 134 |
| C. Reduction of Dihydrorhodoxanthine..... | 134 |
| III. Oppenauer Oxidation of Hydroxyl Compounds..... | 143 |
| 1. General Considerations..... | 143 |
| 2. Examples of This Oxidation..... | 146 |
| 3. Examples of Experimental Procedures..... | 152 |
| A. Cholesterol to Cholestenone..... | 152 |
| B. Methyl 3(β),17(α)-dihydroxy-5-etiocolenate to Methyl 3-Keto-17-(α)-hydroxy-4-etiocolenate..... | 152 |
| C. Dimethyl Acetal of 5-Pregnen-3-01-20-one-214 to Dimethyl Acetal of 4-Pregnene-3,20-dion-21-al..... | 153 |
| D. 17-Ethynyl-5-androstene-3,17-diol to 17-Ethynyl-4-androsten-17-01-3-one..... | 153 |

| | |
|---|-----|
| The Use of Biochemical Oxidations and Reductions for Preparative Purposes. by F. G. FISCHER. <i>Translated and revised by</i> JEAN V. CRAWFORD AND ELEANOR R. WEBSTER. | 159 |
| I. Introduction. | 159 |
| II. Survey of Reaction Types. | 160 |
| III. Oxidation and Reduction of Hydroxyl and Carbonyl Compounds. | 162 |
| 1. General Considerations. | 162 |
| 2. Zymochemical Reduction of Aldehydes and Ketones. | 164 |
| 3. Dehydrogenation of Alcohols. | 166 |
| A. Monohydroxy Alcohols. | 166 |
| B. Polyhydroxy Alcohols. | 166 |
| Oxidation of Sorbitol to Sorbose I. | 168 |
| Oxidation of Sorbitol to Sorbose II. | 169 |
| Oxidation of Glycerol to Dihydroxyacetone. | 170 |
| IV. Oxidation of Aldehydes to Acids. | 170 |
| V. Hydrogenation of Ethylenic Compounds. | 172 |
| 1. General Considerations. | 172 |
| 2. Hydrogenations with Yeast. | 174 |
| A. Primary Alcohols. | 174 |
| B. Aldehydes. | 176 |
| C. Ketones. | 176 |
| D. Keto Acids. | 179 |
| 3. Hydrogenations with Bacteria. | 180 |
| 4. Hydrogenations in the Animal Organism. | 181 |
| VI. Hydrogenations and Dehydrogenations in the Steroid Series. | 182 |
| 1. Sterols and Bile Acids. | 182 |
| 2. Steroid Hormones. | 186 |
| A. Reduction of Keto Steroids. | 186 |
| Reduction of Estrone to a-Estradiol by Yeast. | 188 |
| Reduction of Androstene-3,17-dione to Etiocholan-17-01-3-one and Etiocholan-3,17-diol. | 190 |
| B. Dehydrogenation of Hydroxy Steroids. | 190 |
| Oxidation of Acetoxypregnenolone to Desoxycorticosterone. | 191 |
| C. Hydrogenation of Unsaturated Steroids. | 192 |
| Reduction of Androstenedione to Etiocholanedione. | 193 |
| VII. Oxidation of Methyl Groups | 194 |
| 1. General Considerations. | 194 |
| 2. General Experimental Procedure. | 195 |
| VIII. Conclusion. | 196 |
| Substitution Reactions of Aliphatic Compounds, by JOHANNES NELLES. <i>Translated and revised by</i> G. BRYANT BACHMAN. | 197 |
| I. Introduction. | 197 |
| II. Halogenation. | 198 |
| III. Nitration. | 203 |
| IV. Sulfonation. | 205 |
| V. Alcohols. | 208 |
| VI. Ethers. | 211 |
| VII. Amines. | 211 |
| VIII. Aldehydes and Ketones. | 216 |
| IX. Carboxylic Acids. | 223 |
| X. Carbonylation. | 226 |
| XI. Vinylation and Ethnylation. | 227 |
| Organic Fluorine Compounds, by WILHELM BOCKEMÜLLER. <i>Translated and revised by</i> CHARLES J. KIBLER. | 229 |
| I. Risks Involved in Work with Fluorine and Hydrogen Fluoride. | 229 |
| II. Materials for Reaction Vessels. | 230 |
| III. Addition of Fluorine to Double Bonds. | 230 |
| IV. Addition of Hydrogen Fluoride to Double Bonds. | 232 |
| A. Preparation of Ethyl Fluoride. | 233 |
| B. Cyclohexyl Fluoride. | 233 |

| | |
|---|-----|
| V. Exchange Reactions between Halogens and Fluorine..... | 235 |
| 1. Reactions with Hydrogen Fluoride | 235 |
| Preparation of Benzotrifluoride | 236 |
| 2. Reactions with Antimony Trifluoride..... | 238 |
| A. Preparation of p-Chlorobenzotrifluoride..... | 238 |
| B. Preparation of 2,2-Difluoropropane | 239 |
| 3. Reactions with Silver Fluoride..... | 241 |
| 4. Reactions with Mercurous Fluoride..... | 242 |
| Preparation of Fluoroform..... | 242 |
| 5. Reactions with Mercuric Fluoride..... | 242 |
| YI. Use of Diazonium Salts for Introduction of Fluorine in Aromatic Compounds | 245 |
| 1. Preparation of Fluorobenzene..... | 245 |
| 2. Preparation of Fluorobenzoic Acid..... | 245 |
| Catalysis of Organic Reactions by Boron Fluoride , by D. KÄSTNER. <i>Translated and revised by J. ELMORE JONES</i> | 249 |
| I. Introduction..... | 249 |
| II. Preparation of Boron Fluoride and Methods for Its Use..... | 250 |
| III. Synthesis of Esters, Alcohols, Nitriles, and Substituted Amides..... | 251 |
| IV. Reactions of Unsaturated Aliphatic Compounds..... | 256 |
| 1. Synthesis of Acetals by Alcoholysis of Acetylenes..... | 256 |
| 2. Reactions of Vinylacetylenes..... | 260 |
| 3. Preparation of Vinyl (Enol) Esters..... | 263 |
| 4. Polymerization, Isomerization, and Cyclization of Olefins | 264 |
| V. Reactions of Aromatic Compounds..... | 270 |
| 1. Nuclear Alkylation..... | 270 |
| A. Alkylation of Hydrocarbons..... | 270 |
| B. Alkylation of Phenolic Derivatives and Amines | 275 |
| 2. Introduction of Negative Substituents..... | 280 |
| A. Acylation, Nitration, and Sulfonation Reactions..... | 280 |
| B. Fries Rearrangement..... | 284 |
| C. Halogen Shifts in Aromatic Ethers..... | 290 |
| D. Decomposition of Diazonium Borofluorides..... | 291 |
| 3. Fischer Indole Synthesis..... | 293 |
| VI. Syntheses of β-Diketo Compounds. Condensations Involving Reactive Hydrogen Atoms..... | 295 |
| VII. Cleavage of Ethers..... | 301 |
| VIII. Tertiary Oxonium Salts..... | 305 |
| IX. Factors Limiting Industrial Use of Boron Fluoride..... | 312 |
| Use of Hydrogen Fluoride in Organic Reactions , by KURT WIECHERT. <i>Translated and revised by J. ELMORE JONES</i> | 315 |
| I. Introduction..... | 315 |
| II. Preparation, Purification, and Method of Handling Hydrogen Fluoride..... | 316 |
| III. Preparation of Fluorine Compounds by Use of Hydrogen Fluoride..... | 320 |
| 1. Addition of Hydrogen Fluoride to Unsaturated Compounds..... | 320 |
| A. Addition to Olefins | 320 |
| B. Addition to Acetylenes..... | 324 |
| C. Addition to Other Unsaturated Systems..... | 326 |
| 2. Preparation of Fluorides from Halides..... | 327 |
| A. In Presence of Catalysts..... | 327 |
| B. In Absence of Catalysts..... | 332 |
| 3. Preparation of Fluorides from Amino Compounds..... | 335 |
| 4. Preparation of Fluorides by Replacement of Hydroxyl and Certain Sulfur-Containing Groups..... | 336 |
| IV. Use of Liquid Hydrogen Fluoride as Solvent..... | 338 |
| 1. Solubility Characteristics of Organic Compounds..... | 338 |
| 2. Fluorination..... | 339 |
| 3. Nitration and Sulfonation..... | 340 |
| 1. Nitration of Benzoic Acid..... | 341 |
| 2. Nitration of Aniline..... | 341 |
| 4. Molecular Rearrangements..... | 343 |

| | |
|---|-----|
| V. Degradative Reactions Effected by Hydrogen Fluoride..... | 344 |
| 1. Alkyl Halides..... | 344 |
| 2. Derivatives of Acids..... | 345 |
| 3. Glucosides..... | 346 |
| 4. Wood Sugar Process..... | 348 |
| VI. Use of Hydrogen Fluoride for Catalysis of Organic Reactions..... | 349 |
| 1. Polymerization..... | 349 |
| 2. Formation of Esters and Ethers..... | 351 |
| 3. Acylation..... | 352 |
| 4. Alkylation of Aromatic Compounds..... | 354 |
| 5. Alkylation of Paraffin Hydrocarbons..... | 359 |
| 6. Ring Closure..... | 362 |
| Methods for the Thiocyanation of Organic Compounds. <i>by H. P. KAUF-</i> <i>MANN. Translated and revised by ROGER J. TULL.....</i> | 369 |
| I. Old Methods of Thiocyanation..... | 369 |
| II. Thiocyanation with Free Thiocyanogen..... | 371 |
| 1. Thiocyanation with Free Thiocyanogen in Solution..... | 371 |
| Examples..... | 373 |
| 2. Thiocyanation with Nascent Thiocyanogen..... | 374 |
| 3. Thiocyanation with Free Thiocyanogen Prepared from Inorganic Thio- cyanates and Compounds Containing Labile Halogen..... | 376 |
| III. Copper Thiocyanate Method..... | 377 |
| IV. Electrolytic Thiocyanation..... | 379 |
| The Diene Synthesis. <i>by K. ALDER. Translated and revised by C. V. WILSON</i> <i>AND J. A. VANALLAN.....</i> | 381 |
| I. Limits of Reaction and Its Practical Application..... | 381 |
| 1. Diene Component..... | 382 |
| 2. Enynes, Dienynes, and Ψ -Dienes as Diene Components..... | 389 |
| 3. Dienophile Partner..... | 399 |
| 4. Practical Application of Diene Synthesis..... | 401 |
| II. Types of Compounds Obtainable by Diene Synthesis..... | 404 |
| 1. Carbocyclic Ring Systems..... | 404 |
| A. Mononuclear Ring Systems..... | 404 |
| (1) Hydrobenzaldehydes and Hydrobenzoic Acids..... | 408 |
| (2) Phthalic Acids and Their Hydrogenated Derivatives..... | 408 |
| (3) Alicyclic Malonic Esters and Acetoacetic Esters..... | 410 |
| (4) Diene Syntheses with Higher Fatty Acids..... | 412 |
| B. Polynuclear Systems..... | 414 |
| (1) Uncondensed Types..... | 414 |
| (a) Di-, Ter-, and Quaterphenyl Series; Highly Arylated Compounds..... | 415 |
| (b) Diphenylmethane Series..... | 420 |
| (2) Spirocyclic Types..... | 421 |
| (3) Condensed Types..... | 422 |
| (a) Indene and Fluorene Series..... | 422 |
| (b) Naphthalene Series..... | 424 |
| (c) Anthracene and Naphthacene Series..... | 430 |
| (d) Phenanthrene, Chrysene, Picene, and Cyclopentenophen- anthrene Series; Synthesis of Steroids..... | 435 |
| (e) Benzanthrone Series..... | 442 |
| (f) Pyrene 1,12-Benzoperylene, Coronene, and Dibenzocoronene Series..... | 444 |
| C. Bridged Ring Systems..... | 446 |
| (1) Bicyclo-[2.2.1]-Heptane Series..... | 446 |
| (a) Cyclopentadiene and Its Derivatives as Diene Components | 448 |
| (b) Synthesis of Norcamphor and Camphor Group..... | 452 |
| (c) Condensed Ring Systems with Bridges..... | 455 |
| (d) Transition into Bicyclo-[3.2.1]-Octane Series..... | 456 |
| (e) Cyclopentadienone Type as Diene Components..... | 457 |
| (f) Fulvene and Fulvenecarboxylic Acids..... | 464 |

| | |
|---|------------|
| (2) Bicyclo-[2.2.2]-Octane Series..... | 465 |
| (a) Cyclohexadiene and Its Homologues as Components..... | 466 |
| (b) Cantharidin and Cantharic Acid..... | 469 |
| (c) Cyclohexadiene Derivatives and Esters of Acetylenedi-carboxylic Acid..... | 470 |
| (d) Cyclic Terpenes and Resin Acids..... | 473 |
| (e) Sterol Series. Additions to Ergosterol Type..... | 477 |
| (f) Anthracene and Other Polynuclear Aromatic Compounds... .. | 485 |
| (g) Nitrogen-Containing Hexacyclic Dienes..... | 491 |
| (3) Bicyclo-[3.2.2]-Nonane Series..... | 492 |
| (4) Compounds with Oxygen as Bridge..... | 493 |
| (a) Furans as Diene Components..... | 493 |
| (b) Cumalins (a-Pyrones)..... | 500 |
| 2. Heterocyclic Ring Systems..... | 501 |
| A. Pyran and Chroman Series..... | 501 |
| B. Pyridine Series..... | 503 |
| C. o-Diazine Series..... | 505 |
| D. p-Diazine Series..... | 506 |
| III. Cyclooctatetrene in Diene Synthesis..... | 507 |
| Syntheses with Diazomethane, by BERND EISTERT. Translated and revised by FRED W. SPANGLER..... | 513 |
| I. Introduction..... | 513 |
| II. Constitution of Diazomethane..... | 513 |
| III. Preparation..... | 515 |
| IV. Properties..... | 517 |
| V. Reactions with Acidic Hydrogen..... | 518 |
| VI. Reactions with Carbonyl Compounds..... | 521 |
| 1. Aldehydes..... | 521 |
| 2. Ketones..... | 527 |
| 3. Indirect Methylation..... | 535 |
| 4. Thiocarbonyl Compounds..... | 536 |
| VII. Reactions with Acid Halides..... | 537 |
| VIII. Reactions with Unsaturated Carbon Bonds..... | 551 |
| IX. Reactions with Free Radicals..... | 556 |
| X. Other Reactions..... | 558 |
| 1. Reduction of Diazo Groups..... | 558 |
| 2. Reactions with Organometallic Compounds..... | 558 |
| 3. Rearrangement Reactions..... | 559 |
| 4. Other Reactions..... | 560 |
| XI. Experimental Procedures..... | 561 |
| 1. Preparation of Nitrosomethylurea..... | 561 |
| 2. Preparation of Nitrosomethylurethan..... | 562 |
| 3. Preparation of Nitroso- β -methylaminoisobutyl Methyl Ketone..... | 562 |
| 4. Preparation of Gaseous Diazomethane..... | 563 |
| 5. Preparation of Diazomethane Solutions..... | 564 |
| 6. Reaction of Carbonyl Compounds with Nascent Diazomethane in Methanol..... | 565 |
| Conversion of Cyclohexanone into Cycloheptanone..... | 565 |
| Conversion of 3,3,5-Trimethylcyclohexanone into 3,3,5- and 3,5,5-Trimethylcycloheptanones..... | 566 |
| 7. Reaction of Carbonyl Compounds with Diazomethane in Absence of Methanol..... | 566 |
| 8. Preparation of Diazo Ketones..... | 567 |
| 9. Preparation of Chloromethyl Ketones..... | 567 |
| 10. Preparation of Methyl Ketones..... | 567 |
| 11. Preparation of Hydroxymethyl Ketones..... | 567 |
| 12. Preparation of Esters of Hydroxymethyl Ketones..... | 568 |
| Preparation of 4-Pregnen-21-ol-3,20-dione p-Toluenesulfonate..... | 568 |
| 13. Preparation of Aldehydes..... | 568 |
| Conversion of Stearic Acid into Stearaldehyde..... | 568 |
| 14. Preparation of Homologous Acids..... | 569 |
| Conversion of 1-Naphthoic Acid into 1-Naphthylacetic Acid..... | 569 |

| | |
|---|------------|
| 15. Preparation of Esters of Homologous Acids..... | 569 |
| Conversion of 1-Naphthoic Acid into Ethyl 1-Naphthylacetate..... | 569 |
| 16. Preparation of Amides of Homologous Acids..... | 570 |
| Conversion of 1-Naphthoic Acid into 1-Naphthylacetamide..... | 570 |
| Conversion of 1-Naphthoic Acid into 1-Naphthylacetanilide..... | 570 |
| Syntheses with Organolithium Compounds, by GEORG WITTIG. Translated and revised by JOHN R. THIRTLE. | 571 |
| I. Introduction..... | 571 |
| II. Preparation of Organolithium Compounds..... | 572 |
| 1. n-Butyllithium..... | 575 |
| A. In Ether Solution..... | 575 |
| B. In Benzene Solution..... | 575 |
| 2. Phenyllithium..... | 576 |
| III. Interconversion Reactions with Organolithium Compounds..... | 577 |
| 1. Hydrogen-Metal Interconversion (Metalation)..... | 577 |
| Dimethylallylacetoneitrile..... | 580 |
| N,N'-Dimethylhydrazobenzene..... | 581 |
| N,N'-Diphenylpyrazolidine..... | 581 |
| 2. Metal-Metal Interconversion..... | 582 |
| 3. Halogen-Metal Interconversion..... | 582 |
| 4. Coupling Reactions..... | 583 |
| Bibenzyl..... | 584 |
| IV. Addition Reactions of Organolithium Compounds..... | 584 |
| 1. Addition to C=C..... | 585 |
| 2. Addition to C=O..... | 586 |
| o-Bis(diphenylhydroxymethyl)benzene..... | 586 |
| 3. Addition to C=N..... | 590 |
| α -n-Butylpyridine from Pyridine..... | 590 |
| Addendum to "Organic Fluorine Compounds"..... | 593 |
| Subject Index..... | 597 |
| Compound Index..... | 623 |