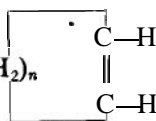
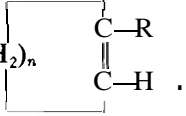
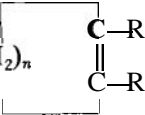


Contents

| | | |
|----------|--|-----------|
| 1 | Introduction and Survey | 3 |
| | Early History | 4 |
| | Chemistry of Organoboranes | 4 |
| | Isomerization of Organoboranes | 7 |
| | Displacement Reactions of Organoboranes | 8 |
| | Borohydride Chemistry | 10 |
| | Hydroboration Procedures | 10 |
| | Scope of the Hydroboration Reaction | 11 |
| | Directive Effects | 12 |
| | Stereochemistry of Hydroboration | 14 |
| | Hydroboration of Hindered Olefins | 16 |
| | Alkylboranes | 18 |
| | Selective Hydroborations with Disiamylborane | 20 |
| | Asymmetric Hydroborations with Diisopinocampheylborane | 23 |
| | Hydroboration of Dienes | 24 |
| | Hydroboration of Acetylenes | 27 |
| | Diborane as a Reducing Agent | 29 |
| | Disiamylborane as a Reducing Agent | 30 |
| | Hydroboration of Functional Derivatives | 31 |
| | Related Reactions | 33 |
| | Conclusion | 38 |
| 2 | Early History | 39 |
| 3 | Chemistry of Organoboranes | 45 |
| | Synthesis of Organoboranes via Organometallics | 46 |
| | Physical Properties | 50 |

| | |
|---|------------|
| Thermal Behavior | 50 |
| Behavior as Lewis Acids | 55 |
| Redistribution Reactions | 59 |
| Protonolysis | 62 |
| Hydrogenation | 66 |
| Halogenation | 67 |
| Oxidation — Oxygen | 67 |
| Oxidation — Alkaline Hydrogen Peroxide | 69 |
| Oxidation — Chromic Acid | 72 |
| Grignard-like Reactions — Metalation | 74 |
| Grignard-like Reactions — Cyclization | 75 |
| Coupling | 77 |
| Conclusion | 80 |
| 4 Borohydride Chemistry | 81 |
| Early Studies | 81 |
| Recent Studies | 84 |
| Amine-Boranes | 91 |
| Conclusion | 92 |
| 5 Hydroboration Procedures | 93 |
| Lithium Borohydride | 96 |
| Sodium Borohydride | 97 |
| Potassium Borohydride | 99 |
| Lithium Aluminum Hydride | 99 |
| Alkali Metal Hydrides | 99 |
| Amine-Boranes | 100 |
| Conclusion | 101 |
| 6 Scope | 102 |
| Monosubstituted Terminal Olefins, $RCH=CH_2$ | 102 |
| Disubstituted Terminal Olefins, $R_2C=CH_2$ | 103 |
| Disubstituted Internal Olefins, $RCH=CHR$ | 104 |
| Tri- and Tetrasubstituted Olefins, $R_2C=CHR$ and $R_2C=CR_2$ | 105 |
| Phenyl-Substituted Ethylenes | 105 |
| Simple Cyclic Olefins, $(CH_2)_n$ | 106 |



| | | |
|--|---|-----|
| Substituted Cyclic Olefins, $(\text{CH}_2)_n$ |  | |
| and $(\text{CH}_2)_n$ |  | 107 |
| Bicyclic Olefins | | 108 |
| Steroids | | 110 |
| Olefins Containing Substituent Groups | | 111 |
| 7 Directive Effects | | 113 |
| Monosubstituted Terminal Olefins, $\text{RCH}=\text{CH}_2$ | | 114 |
| Disubstituted Terminal Olefins, $\text{R}_2\text{C}=\text{CH}_2$ | | 115 |
| Disubstituted Internal Olefins, $\text{RCH}=\text{CHR}'$ | | 115 |
| Trisubstituted Olefins, $\text{R}_2\text{C}=\text{CHR}$ | | 117 |
| p-Substituted Styrenes | | 118 |
| Theoretical Considerations | | 118 |
| 8 Stereochemistry | | 123 |
| Monocyclic Systems | | 124 |
| Bicyclic Systems | | 126 |
| Stereochemistry of the Hydroboration Reaction | | 130 |
| Applications | | 132 |
| 9 Isomerization | | 136 |
| Organoboranes from Straight-Chain Olefins | | 139 |
| Organoboranes from Branched-Chain Olefins | | 140 |
| Organoboranes from Cyclic Olefins | | 144 |
| Organoboranes from Dienes | | 145 |
| Mechanism | | 145 |
| Cyclization | | 147 |
| Conclusion | | 149 |
| 10 Displacement Reactions | | 150 |
| Monosubstituted Terminal Olefins, $\text{RCH}=\text{CH}_2$ | | 153 |
| Disubstituted Terminal Olefins, $\text{R}_2\text{C}=\text{CH}_2$ | | 154 |
| Disubstituted Internal Olefins, $\text{RCH}=\text{CHR}'$ | | 155 |
| Trisubstituted Olefins, $\text{R}_2\text{C}=\text{CHR}$ | | 155 |
| Cyclic Olefins | | 156 |

| | |
|---|------------|
| Bicyclic Olefins | 157 |
| The Displacing Olefin | 157 |
| Mechanism | 158 |
| Conrathermodynamic Isomerization of Olefins | 158 |
| 11 Hydroboration of Hindered Olefins | 161 |
| Cyclic Olefins | 162 |
| Acyclic Olefins | 164 |
| Substituted Cyclic Olefins | 167 |
| Bicyclic Olefins | 168 |
| Disubstituted Terminal Olefins | 170 |
| Hydroboration Mechanism | 170 |
| Conclusion | 172 |
| 12 Alkylboranes | 173 |
| Alternative Syntheses | 174 |
| Infrared Spectra | 178 |
| sym-Tetrasiamyldiborane | 181 |
| sym-Dithexyldiborane | 183 |
| <i>sym</i> -Bis-(2,4,4-trimethyl-3-pentyl)-diborane | 187 |
| sym-Tetracyclohexyldiborane | 187 |
| sym-Tetrakis-(trans-2-methylcyclohexyl)-diborane | 189 |
| sym-Tetraisopinocampheyldiborane | 189 |
| The Dimerization Phenomenon | 189 |
| 13 Selective Hydroboration with Disiamylborane | 191 |
| Directive Effects | 192 |
| Relative Reactivities | 193 |
| Kinetics | 195 |
| Structure and Reactivity | 198 |
| Selective Hydroborations | 202 |
| 14 Asymmetric Hydroboration with Diisopinocampheylborane | 205 |
| 15 Hydroboration of Dienes | 209 |
| Dihydroboration of 1,3-Butadiene | 209 |
| Dihydroboration with Diborane | 214 |
| Dihydroboration with Disiamylborane | 216 |
| Dihydroboration with Trimethylamine- <i>t</i> -butylborane | 216 |
| Isomerization of Organoboranes from Dienes | 217 |
| Monohydroboration with Diborane | 218 |

| | |
|--|------------|
| Monohydroboration with Disiamylborane | 220 |
| Conclusion | 226 |
| 16 Hydroboration of Acetylenes | 227 |
| Monohydroboration of Acetylenes , | 228 |
| Protonolysis of the Vinyl Organoboranes | 230 |
| Stereochemistry of the Hydroboration-Protonolysis Reaction | 232 |
| Oxidation of the Vinyl Organoboranes | 233 |
| Dihydroboration of Acetylenes | 234 |
| 17 Diborane as a Reducing Agent | 238 |
| Lithium Aluminum Hydride as a Reducing Agent | 239 |
| Sodium Borohydride as a Reducing Agent | 242 |
| Diborane as a Reducing Agent | 247 |
| Theoretical Considerations | 250 |
| 18 Disiamylborane as a Reducing Agent | 255 |
| Scope | 256 |
| Rates of Reduction | 259 |
| Comparison of Disiamylborane and Diborane | 261 |
| Selective Reductions and Hydroborations | 263 |
| 19 Hydroboration of Functional Derivatives | 265 |
| Derivatives with Inert Substituents | 266 |
| Derivatives with Vinylic and Allylic Halogen | 268 |
| Derivatives with Reducible Groups | 271 |
| Scope | 274 |
| 20 Epilog | 277 |
| About B. C. Subba Rao | 280 |
| About George Zweifel | 280 |
| About the Author | 283 |
| Index | 285 |