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Book reviews

Carbon-Functional Organosilicon Compounds; edited by V. Chvalovský and J.M. Bellama. Plenum, New York and London, 1984, xiii + 303 pages, \$45.00.

This book does not, as one might expect from its title, present a comprehensive account of the preparation, properties, and reactions of organosilicon compounds containing functional organic centres. Instead it provides four essays on special aspects of the chemistry of such compounds.

The first chapter (33 pages), by V. Chvalovský, presents a brief outline of the uses of organofunctional silicon compounds for making derivatives of natural products, as stationary phases in GLC, and in surface treatment of inorganic materials. The second chapter (86 pages), by J. Pola is concerned with the influence of intramolecular interactions on the chemical behaviour of carbon-functional silicon compounds, the interactions considered being inductive and conjugative effects, anchimeric assistance, and steric effects. The reactions dealt with include both those at the carbon-functional centres under the influence of the organosilicon substituent and those at the silicon centres under the influence of the organic functional group, and thus the review provides a fairly wide-ranging guide to mechanisms of reactions of organosilicon compounds. Much interesting information is clearly presented. (I should say, however, that I am not aware of any convincing experimental evidence for stabilization of carbanions by conjugative delocalization in systems of the type $R_3Si-\overset{\overset{|}{|}}{C}-\overset{\overset{|}{|}}{C}$,

such as is mentioned on page 36.) The third and longest chapter (112 pages) by J. Schraml, is a very helpful summary of the use of 1H , and ^{13}C , and ^{29}Si NMR spectroscopy in the study of carbon-functional organosilicon compounds; the account of the use of ^{29}Si NMR is especially valuable, and understandably so since the author has himself contributed substantially to the subject.

The final chapter (66 pages) is concerned with theoretical aspects of bonding in organosilicon chemistry; again the writing is by someone who has made valuable contributions to the subject, but in this case this has not led to a satisfactory presentation. To my mind the review confuses rather than clarifies, and most readers will, I believe, be left with the impression that all attempts to rationalize the behaviour of organosilicon compounds in terms of conventional electronic effects, even if only to provide a temporary working framework, are pointless, and that any example of the influence of silicon must simply be accepted as an isolated fact and attributed to polarizability. (There is no clear differentiation between electron-releasing and electron-withdrawing effects of silicon in specific locations.) The account of the history of the concept of hyperconjugation in organosilicon chemistry is totally misleading. For example, it is asserted that after Nesmeyanov's initial interpretation of spectroscopic data (for mercury compounds) in 1984 in terms of resonance contributions which correspond to hyperconjugation, the concept was used only by Russian

authors (in 1956–1961, to interpret spectroscopic data) until the early seventies, when C.G. Pitt published his very important theoretical analysis. In fact I myself (unaware of Nesmeyanov's suggestion for mercury compounds) first used hyperconjugation in 1954 to interpret spectroscopic properties of organosilicon compounds, and in 1956 to account for the effects of Me_3Si groups on reactivity (and I discussed both aspects in my book on Organosilicon Compounds in 1960). Completely ignored is the all-important work by T.G. Traylor in the 1960's on charge transfer complexes, which was the most powerful factor in the acceptance of the importance of hyperconjugation in organometallic chemistry. His work preceded, and was certainly more influential than that on photoelectron spectroscopy which Dr. Ponec believes to have provided the first experimental evidence for such hyperconjugation; indeed, the authors of the earlier of the cited papers dealing with photoelectron spectroscopy actually used their results to argue in favour of inductive rather than conjugative effects. Again, contrary to the impression given in the review, I myself clearly attributed the reactivity of Ar-SiMe_3 bonds to powerful electron-release from Me_3Si groups β - to a carbonium ion centre as early as 1964, and specifically attributed this to hyperconjugation from 1969. I fear that similar inadequacies apply to other parts of the review.

The book has been printed by photoreproduction of typescript, with the reduction in readability which that entails. However, in this case the procedure is justified by the impressively low price, a pleasing feature of many Plenum publications.

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Electron Deficient Aromatic- and Heteroaromatic-Base Interactions; by E. Buncl, M.R. Crampton, M.J. Strauss, and F. Terrier, Elsevier, Amsterdam etc., 1984, vii + 499 pages, Dfl. 300. ISBN 0-444-42305-2.

The sub-title of this book, "The Chemistry of Anionic Sigma Complexes", gives a much clearer indication than of the content than does the main title. It is concerned with the carbanions ("Meisenheimer adducts" or σ -complexes) produced when appropriate aromatic compounds are treated with bases, and which are best known as intermediates in common nucleophilic aromatic substitutions. Such carbanions are usually associated, more or less closely, with metal cations, and that is why the book is reviewed in this journal.

The emphasis is on the properties of the complexes themselves, although their role in the mechanism of $\text{S}_{\text{N}}\text{Ar}$ reactions is also well described. The chapters are: Introduction (14 pages), Spectroscopic studies (109 pages); Theoretical studies (17 pages); Structure and reactivity (110 pages); Kinetics and mechanisms of sigma complex formation and decomposition reactions (76 pages); Role of sigma complexes in $\text{S}_{\text{N}}\text{Ar}$ processes (40 pages); Role of electron transfer and proton transfer processes (25 pages); Reactions of anionic sigma complexes (73 pages). There is an adequate subject index. There are a