

Figure 3. 3-Trimethylsilylpropionic acid.

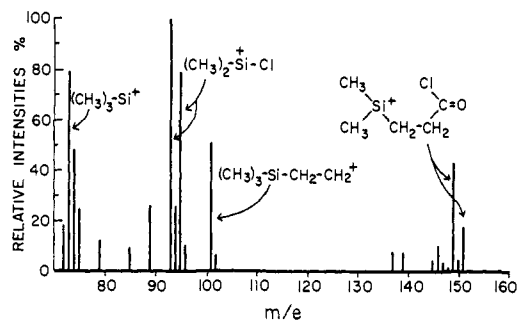
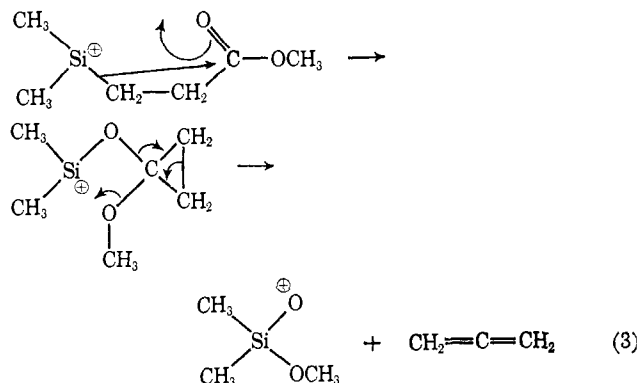
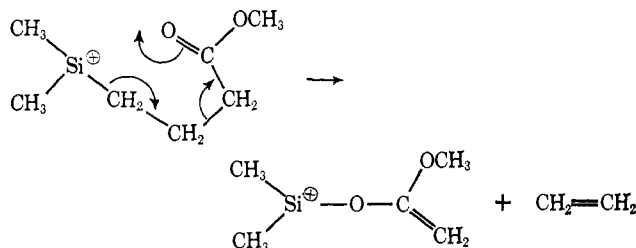


Figure 4. 3-Trimethylsilylpropionyl chloride.

carbon to the positively charged siliconium center in



(13) Additional evidence in support of this fragmentation mechanism is found in the mass spectrum of methyl 4-trimethylsilylbutyrate. The peak at m/e 131 may be due to rearrangement of the m/e 159 ion with loss of C_2H_4 , presumably as ethylene.



this system is not unique for the methoxy substituent. We also found that the hydroxy group of the corresponding 3-trimethylsilylpropionic acid^{8,9} will migrate to the siliconium ion center (Figure 3). Similarly a chlorine of the corresponding acid chloride rearranges (Figure 4).⁸

A possible driving force for this extremely facile rearrangement of electronegative groups is the considerably greater strengths of the silicon-oxygen and silicon-chlorine bonds compared to those of the corresponding carbon-oxygen and carbon-chlorine bonds.¹⁴ Both the ring size of the transition state for migration and the stability of the neutral products eliminated may effect the facility of this rearrangement. Further studies are in progress to determine the generality of this rearrangement and factors which may limit its occurrence.

Acknowledgment. We wish to acknowledge a National Science Foundation grant for purchase of the mass spectrometer. This work was also supported in part by the Research Corporation.

(14) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p 90: Si-O 108 kcal/mol, Si-Cl 91 kcal/mol, C-O 85.5 kcal/mol, C-Cl 81 kcal/mol.

William P. Weber, Raymond A. Felix, Alvin K. Willard
Department of Chemistry, University of Southern California
Los Angeles, California 90007
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Book Reviews

Aromatic Nucleophilic Substitution. By J. MILLER, Superintendent, Organic Chemistry Division, Defence Standards Laboratories, Melbourne, Australia. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1968. xi + 408 pp. 15 × 22 cm. \$23.50.

The author of this book has been engaged in research in its field for nearly 20 years. His chief interests have been in the determination of reaction rates as affected by substituents, leaving groups, reagents, and solvents, and in a thermochemical scheme for calculation of the energy profiles of reactions.

The emphasis in this book reflects the author's interests. The chapter on substituent effects constitutes 19% of the book; the two chapters on the reactivity of nucleophiles and the mobility of leaving groups are heavily oriented toward Miller's thermochemical scheme, and together represent 25% of the total. Another chapter (18%)

concerns substitutions in heterocyclic and other nonbenzenoid systems, with emphasis on factors affecting reactivity. Important topics that are dealt with rather briefly or even superficially include synthetic applications, side reactions, catalytic effects, the basic experimental evidence in support of various mechanisms, and the chemistry of Jackson-Meisenheimer complexes.

This book contains a good deal of information, but its manner of presentation sometimes impedes ready access to it. Numerous tables summarize data on reactivity in various systems and are perhaps the book's most useful feature. However, the tables are awkward to read, largely because of a cumbersome cross-keying system between wordy table titles and the main body of the table. (One table title fills more than a third of a page.)

In general, the presentation tends to emphasize the rationalization of observations, and frequently it does not succeed in distinguishing

well-supported explanations from those which are speculative. Sometimes factual information gets lost among the rationalizations.

The style of writing also puts much emphasis on *who* made observations, even those of straightforward character, and on *who* suggested interpretations and *who* criticized them. Unfortunately this emphasis tends to divert attention from the facts and valid conclusions that would be of primary interest to most readers.

Writing of the manuscript appears to have started in 1965; it was completed in 1967. Although some publications as late as 1967 are cited, there are serious omissions in respect to 1966 and 1967, of which R. W. Hoffmann's book, "Dehydrobenzene and Cycloalkynes," the review of linear free energy correlations by Shein and Kozorez, and several papers of A. J. Parker (a former student of Miller's) are noteworthy. Papers which appeared in 1965 are mentioned as "recent," and in some cases they seem not to have been fully digested by the author.

Two faults of nomenclature warrant comment. One is of omission: no mention or use of systematic names for substitution reactions (such as methoxydechlorination for displacement of

chlorine by methoxide) could be found. The other is of commission, and is more serious: the symbol S_N2 is used for the common aromatic nucleophilic substitutions which occur by the intermediate complex mechanism (a mechanism fundamentally different from S_N2 at saturated carbon), and even for reactions which occur *via* benzyne intermediates. Such usage only serves to confuse. The symbol S_{NAr} , which Miller himself has used in the past, is much preferable for the intermediate complex mechanism of substitution at aromatic carbon.

Over-all, this reviewer has doubts as to how useful this book will be to chemists unfamiliar with the field. Although he differs from Miller in regard to some points of scientific interpretation, this judgment is based primarily on the uneven emphasis and oblique style of the book, which seriously limit its value.

Joseph F. Bunnett

University of California
Santa Cruz, California 95060