

of configuration;<sup>17</sup> and second, reduction of neophyl-(tri-*n*-butylphosphine)copper(I) under similar conditions leads to *t*-butylbenzene, with no observable rearrangement to isobutylbenzene.

The detailed nature of the C-H bond forming step in these reductions has not been established, although it could plausibly proceed by intramolecular reaction of hydrido and alkyl ligands coordinated to a common cluster of copper(I) atoms.<sup>17,18</sup> Studies of the mechanism of this and related reactions, and of the role of copper hydride in the thermal decomposition of alkyl-copper(I) reagents, will be discussed in later papers.

(17) For a discussion of the stereochemical consequences expected from a free 2-butenyl radical in the related thermal decomposition of these compounds, see G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966).

(18) A. Cairncross and W. A. Sheppard, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, ORGN 118.

(19) (a) National Institutes of Health Predoctoral Fellow, 1966-1969; (b) National Institutes of Health Predoctoral Fellow, 1967-1968; (c) National Science Foundation Predoctoral Fellow, 1963-1967.

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### Mass Spectral Rearrangements of Siliconium Ions. Migration of Electronegative Groups from Carbon to Silicon

Sir:

Mass spectroscopy of organosilicon compounds is potentially a most valuable tool for the study of the properties of siliconium ions, since these are not easily produced in solution.<sup>1-4</sup> In the mass spectrum of

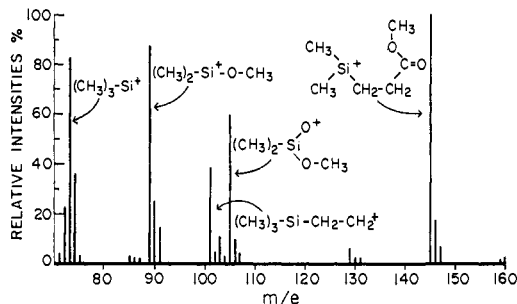


Figure 1. Methyl 3-trimethylsilylpropionate.

methyl 3-trimethylsilylpropionate<sup>5</sup> we have observed a novel intramolecular migration of a methoxy group

(1) R. West in "Organosilicon Chemistry," International Symposium at Prague, Butterworths, London, 1965, pp 1-9.

(2) L. H. Sommer and F. J. Evans, *J. Am. Chem. Soc.*, **76**, 1186 (1954).

(3) L. H. Sommer, *et al.*, *ibid.*, **76**, 801 (1954).

(4) F. C. Whitmore, *et al.*, *ibid.*, **69**, 1976 (1947).

(5) Methyl 3-trimethylsilylpropionate<sup>6</sup> and the other compounds discussed were prepared from trimethylallylsilane. Hydroboration, followed by oxidation, yielded 3-trimethylsilylpropanol.<sup>7</sup> This was oxidized with Jones reagent to yield 3-trimethylsilylpropionic acid.<sup>8,9</sup> This acid was converted to the acid chloride by treatment with thionyl chloride.<sup>8</sup> The methyl esters were prepared by reaction of the acid chloride with methanol.<sup>8</sup> The compounds so obtained agreed in physical properties with literature values and had satisfactory infrared and nmr spectra. All compounds were purified by gas chromatography on a 0.25 in. × 15 ft Carbowax 20M column before use, and were at least 99% pure. All mass spectra were run on a Varian M-66 mass spectrometer at an ionizing voltage of 70 eV.

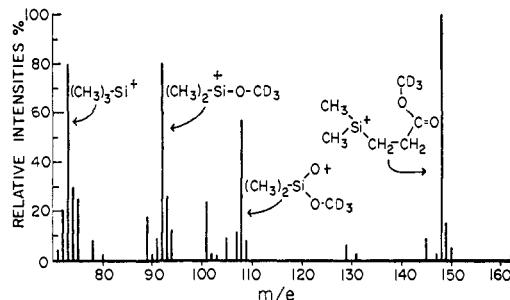
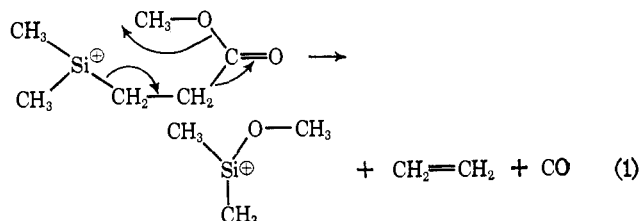


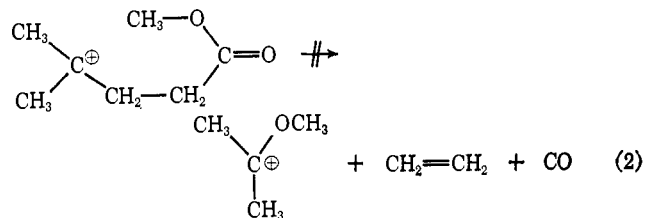
Figure 2. Methyl-*d*<sub>3</sub> 3-trimethylsilylpropionate.

from the ester carbon to a positively charged silicon center.

The base peak *m/e* 145 in the mass spectrum of methyl 3-trimethylsilylpropionate<sup>6</sup> results from loss of a methyl group from silicon (Figure 1). Fragmentation at such a highly branched center is the expected process.<sup>10,11</sup> Furthermore, the next most intense peak, *m/e* 89, is due to the dimethylmethoxysiliconium ion. This ion results from migration of a methoxy group from the ester carbon to the siliconium ion center with simultaneous loss of C<sub>3</sub>H<sub>4</sub>O, most likely as ethylene and carbon monoxide (eq 1). In order to verify this interpretation,



the mass spectrum of the corresponding methyl-*d*<sub>3</sub> ester was examined (Figure 2). The intense peak at *m/e* 92 is due to the dimethylmethoxy-*d*<sub>3</sub>-siliconium ion (Figure 2). In the case of similar carbonium ions, such rearrangements of methoxy groups are not observed (eq 2).<sup>12</sup>



The peak at *m/e* 73 is due to the trimethylsiliconium ion. The fourth most intense peak occurs at *m/e* 105. This fragment may be due to a rearrangement of the *m/e* 145 ion as indicated (eq 3), with loss of C<sub>3</sub>H<sub>4</sub> presumably as allene.<sup>13</sup>

This rearrangement of the electronegative group from

(6) A. D. Petrov, *Zh. Obshch. Khim.*, **29**, 2936 (1959).

(7) J. L. Speier, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

(8) L. H. Sommer, *et al.*, *ibid.*, **72**, 1935 (1950).

(9) L. H. Sommer, *et al.*, *ibid.*, **76**, 1609 (1954).

(10) N. Ya. Chernyak, *et al.*, *Zh. Obshch. Khim.*, **36**, 96 (1966).

(11) N. Ya. Chernyak, *et al.*, *ibid.*, **36**, 89 (1966).

(12) R. Ryhage and E. Stenhagen, *Ark. Kemi*, **15**, 333 (1959); see spectrum of methyl-4,4-dimethyldocosanoate.

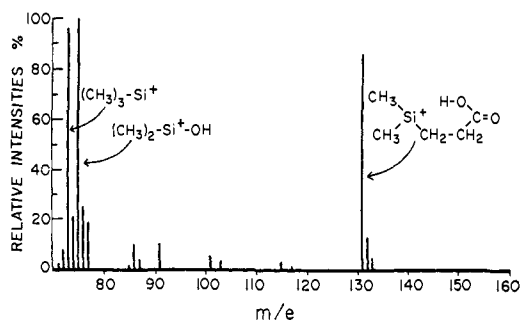
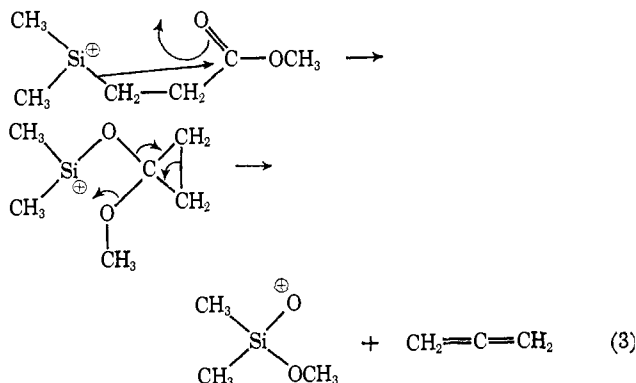


Figure 3. 3-Trimethylsilylpropionic acid.

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  $\text{C}_2\text{H}_4$ , presumably as ethylene.

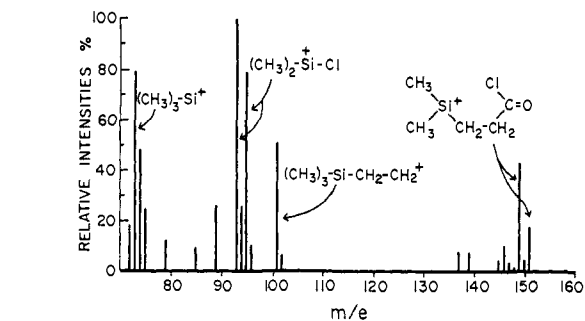
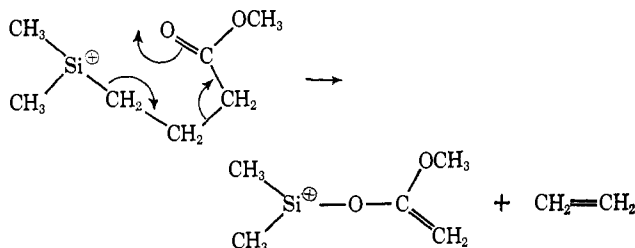


Figure 4. 3-Trimethylsilylpropionyl chloride.

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

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.<sup>14</sup> 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.

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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