protons will be observed. When the lifetime is long compared to this quantity, the epr spectrum is that of one conformation. In the intermediate case, alternating line widths result. The fact that the metal hyperfine splitting remains unbroadened as the temperature is raised suggests that the exchange process is intramolecular rather than intermolecular.

An alternate explanation for the nonequivalency of the four methylene protons is that the four-membered ring is skewed. However, we have found that when BCB is reduced in dimethoxyethane (90%) and hexamethylphosphoramide (10%) or in dimethoxyethane with crown ether the four methylene protons are equivalent even at −95°. This evidence strongly supports the thesis that the four-membered ring is still intact after reduction and the nonequivalency is caused by ion pairing.

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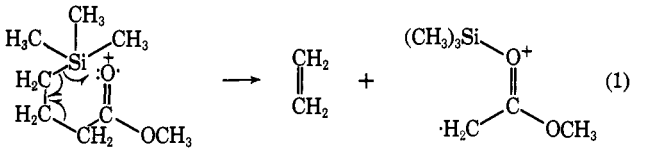
Mass Spectral Rearrangements. A Silyl McLafferty Rearrangement

Sir:

Volatile trimethylsilyl derivatives have been a popular choice for vapor phase chromatographic separation of nonvolatile materials. This has led to extensive study of the mass spectra of these derivatives for alcohols,[1,2] carboxylic acids,[3] and other functional groups.[4] The mass spectra of functionalized organosilicon compounds *per se* have only been slightly examined.[5] We have observed in the mass spectrum of methyl 4-trimethylsilylbutyrate[6] two novel intramolecular rearrangements involving the silyl center.

The peak at *m/e* 146 in the mass spectrum of methyl 4-trimethylsilylbutyrate results from migration of the trimethylsilyl group from the γ carbon of the alkyl chain to the positively charged carbonyl oxygen of the ester functionality with simultaneous loss of ethylene (eq 1).



(1)

This rearrangement is similar to the McLafferty rearrangement of methyl esters,[12] with the notable difference that a trimethylsilyl group is transferred rather than a hydrogen. By comparison, alkyl groups are not normally transferred from the γ carbon to the carbonyl oxygen *via* the McLafferty rearrangement. This rearrangement is particularly unusual in that a similar photochemical rearrangement of a trimethylsilyl group from carbon to oxygen does not occur on photolysis of 5-trimethylsilyl-2-pentanone.[13] Hence, although the normal mass spectral McLafferty rearrangement of esters is related to the photochemical Norrish type II cleavage of ketones, the silyl McLafferty rearrangement finds no analogy in a photochemical silyl Norrish type II cleavage[13] (eq 2).

The base peak in the mass spectrum of methyl 4-trimethylsilylbutyrate is at *m/e* 73. This is due to the trimethylsiliconium ion, while the peak at *m/e* 159 results from loss of a methyl group from the parent ion. Fragmentation at such a highly branched center producing these two ions is a highly favored process.[14,15] The second most intense peak occurs at *m/e* 89. This ion is the dimethylmethoxysiliconium ion which results from migration of a methoxy group from the ester functionality to the siliconium ion center with loss of C_4H_6O, probably as ethylene and ketene. The observation of the expected metastable ion at *m/e* 49.8 (calcd $89^2/159 = 49.8$) provides additional evidence for this rearrangement (eq 3). This rearrangement is unimportant in the case of a similar carbonium ion[16] (eq 4).

The final important rearrangement ion is the peak at *m/e* 131. This ion is most probably formed by loss of a methyl radical from the initially formed silyl McLafferty rearrangement ion *m/e* 146. The observation of the expected metastable ion at *m/e* 117.5 (calcd $131^2/$

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(6) Methyl 4-trimethylsilylbutyrate was prepared from 3-trimethylsilylpropanol.[7] This was converted to the corresponding tosylate. The tosylate was converted to 4-trimethylsilylbutyronitrile[8] by treatment with sodium cyanide in DMSO. The nitrile was hydrolyzed to the corresponding methyl ester by treatment with methanolic HCl. Ir, nmr, and analytical data were in agreement with this structure. Methyl 4-trimethylsilyl-2,2-dideuteriobutyrate was prepared by reduction of methyl 3-trimethylsilylpropionate[9] with $LiAlD_4$ in anhydrous ether yielding 1,1-dideuterio-3-trimethylsilylpropanol.[7] This alcohol was converted to the desired ester *via* the tosylate and nitrile as above. Methyl-d_3 4-trimethyl-silylbutyrate was prepared from 4-trimethylsilylbutyric acid[10] which was converted to the corresponding acid chloride[11] with thionyl chloride. The desired ester was prepared by treatment of the acid chloride with methanol-d_4. The compounds so obtained agreed in physical properties with literature values and had satisfactory ir and nmr spectra. All compounds were purified by gas chromatography on a 1/4 in. × 15 ft Carbowax 20M column before use, and were run on Varian M-66 and Perkin-Elmer Hitachi RMU-6E mass spectrometers at an ionizing voltage of 70 eV.
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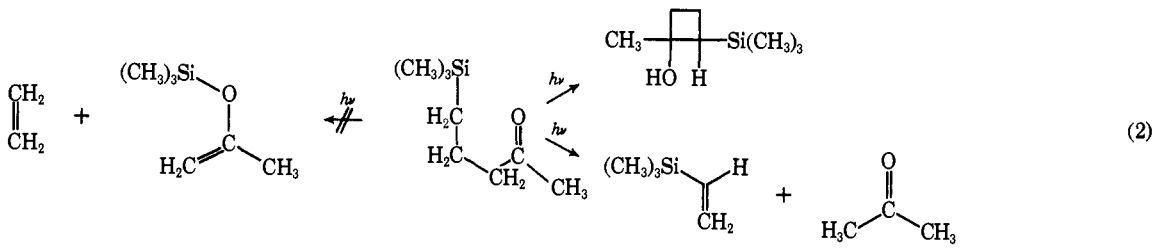
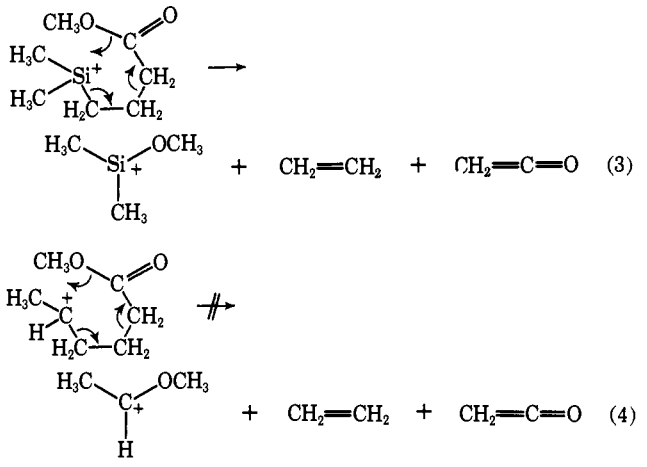


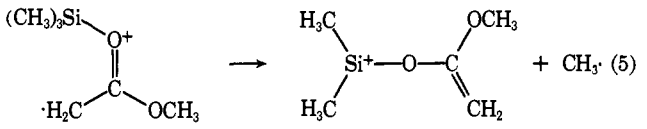
(2)



(3)

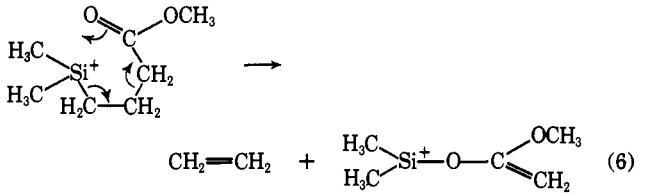
(4)

146 = 117.54) provides additional evidence in support of this process (eq 5).



(5)

An alternative fragmentation process which could have led to this same ion—previously favored by us[5]—involves attack of the carbonyl oxygen on the siliconium ion center of the ion *m/e* 159 with simultaneous loss of ethylene[17] (eq 6). While this rearrangement was attractive, it is *not* supported by the observation of a metastable ion at *m/e* 107.9 (calcd $131^2/159 = 107.9$). Hence, we must conclude that the ion *m/e* 131 arises by loss of a methyl radical from the silyl McLafferty rearrangement ion.



(6)

To verify the structures of these rearrangement ions, the mass spectra of the methyl-d_3 ester, as well as that of the methyl 4-trimethylsilyl-2,2-dideuteriobutyrate, were examined. They were completely in accord with the assigned structures.[18]

A possible driving force for the rearrangement of a methoxy group to the siliconium ion center is the high silicon–oxygen bond strength.[19] The greater strength of a silicon–oxygen bond compared to that of a hydrogen–oxygen or a carbon–oxygen bond must be important also in the silyl McLafferty rearrangement. The possibility that silicon can form a pentacoordinate transition state by use of its 3d orbitals may also favor this migration of the trimethylsilyl group.

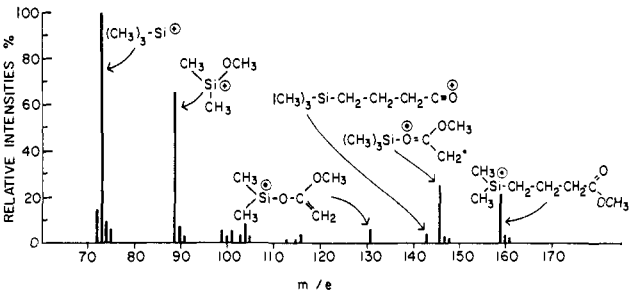


Figure 1. Methyl 4-trimethylsilylbutyrate.

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Enzymatic and Nonenzymatic Demethylation of Methylcobalamin and of Abiogenic Cobaloxime Model Substrates. Methane Biosynthesis by *Methanobacillus omelianskii*[1]

Sir:

Extracts of the methanogenic bacterium *Methanobacillus omelianskii* (MOH)[2] have recently been shown[3] to utilize methylcobalamin and, most surprisingly, the completely abiogenic methyl cobaloximes as substrates for methane evolution. Reaction 1 shows an absolute requirement for catalytic amounts of ATP and factor III ((Co) denotes the cobaloxime, [Co] the cobinamide moiety).[4]

(17) This observation places serious doubt on the rearrangement process we have previously discussed for the formation of the *m/e* 105 ion in the mass spectrum of methyl 3-trimethylsilylproprionate.[5] Studies to clarify the source of this ion are continuing.

(18) A similar silyl–McLafferty rearrangement has been observed in the mass spectrum of 4-trimethylsilylbutyronitrile.

(19) C. Eaborn, "Organosilicon Compounds," Butterworth & Co., Ltd., London, 1960, p 90: Si–O, 108 kcal/mol; C–O, 85.5 kcal/mol.

(1) This research was supported by Grant GP 12324 of the National Science Foundation.

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(4) Factor III is cobalt(III) 5-hydroxybenzimidazolylcobamide: J. M. Wood and R. S. Wolfe, *Biochemistry*, **5**, 3598 (1966), the natural cofactor. However, vitamin B_{12a}, the corresponding cobamide with