New Evidence for the Electron-impact Induced Migration of Trimethylsilyl Substituents

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SOME evidence for rearrangement of silyl groups has been reported for the formation of a fragment of mass 147 in the case of the tristrimethylsilyl derivative of pyridoxine.[1] Accurate mass determination established the empirical formula $C_5H_{15}OSi_2$. This composition indicated that two trimethylsilyl groups, originally separated by three carbon and two oxygen atoms, had become linked by a simple ether bridge, in a structure resulting from expulsion of the aromatic moiety:

$$Me_3Si\text{–}\overset{+}{O}{=}SiMe_2$$

m/e 147. Such ions have also been observed in other cases,[2–4] in part due to artifacts.[4]

More unexpectedly, a rearrangement of intact trimethylsilyl groups over larger molecular distances has been observed in the fragmentation of 1,10-bistrimethylsiloxydecane.[3] The same (*m/e* 147) fragment is produced in considerable abundance, although a macrocyclic transition state is required for a direct transfer.

We report new evidence for the operation of long-range transfer reactions of trimethylsilyl groups, which is derived mainly from the mass spectrum of methyl 12-trimethylsiloxyoctadecanoate (I) (Figure). A peak of moderate intensity at *m/e* 197 corresponds to a fragment a_1 (Scheme 1) which is related to a precursor *a* of mass 301 by a metastable peak (*m/e* 129·1).† The precursor ion represents the larger of the two expected products which result from α-cleavage, with respect to the trimethylsilyloxy-function. Its counterpart (*b*) which retains the smaller, unsubstituted alkyl chain, appears at *m/e* 187.

The composition of the eliminated moiety was established by accurate mass measurement to be $C_4H_{12}SiO$, indicating a migration of the remote trimethylsilyl group to the ester function prior to the metastable transition. That the trimethylsilyl group migrated intact is revealed by the absence of a mass shift for ion a_1 in the spectrum of the [$^2H_9$]trimethylsilyl derivative.‡ In principle, two

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† Similar data from a related hydroxyalkanoate methyl ether lending themselves to an analogous interpretation have been disclosed in a personal communication by Dr. W. Vetter, F. Hoffmann-La Roche & Co., Basel, Switzerland, to one of the authors.

‡ Prepared from methyl 12-hydroxyoctadecanoate and $(CD_3)_3SiCl$ in pyridine (see ref. 3).

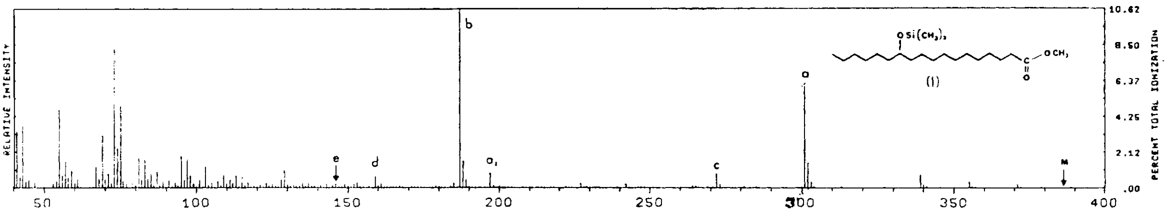


FIGURE. *Methyl 12-trimethylsiloxyoctadecanoate.*

mechanistic pathways may lead to a rearranged intermediate *a′* and hence to the fragment a_1 (Scheme 1):

(1) α-Cleavage as an initial step, followed by an ionic, S_Ni-like attack of the remote ester group at the silicon atom (pathway A), or

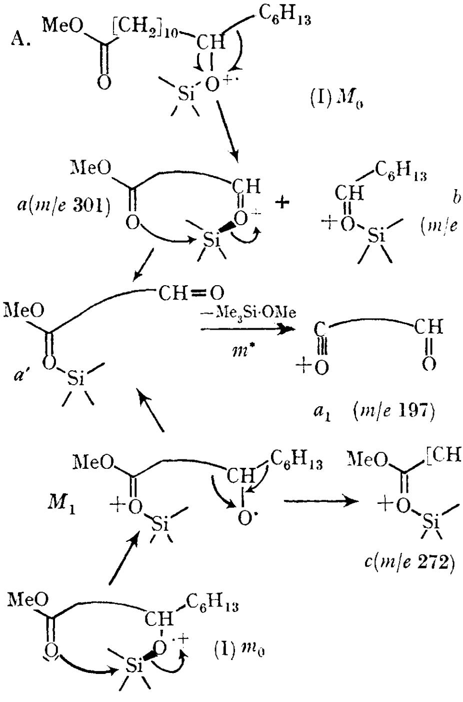
(2) A reverse sequence of similar steps, consisting of trimethylsilyl transfer in the initial phase, with subsequent (or possibly concomitant) α-cleavage, triggered by the alkoxy-radical thus generated (pathway B).

This would also, in contrast to A, account for the formation of ion *c* (*m/e* 272, Scheme 1), as an alternative product. The transfer step, which is again depicted as an ionic S_N2 displacement, could in this case be facilitated by the enhanced polarization of the silicon–oxygen bond in the charged species,[5] and would, of course, not be distinguishable from a radical-type transfer of the silyl group, upon attack of the septet of an ionized ester function.

A second piece of evidence for silyl migration in the spectrum of (I),§ is the observation of a fragment at *m/e* 159, of composition $C_7H_{15}SiO_2$ and displaced by 9 mass units to *m/e* 168 in the spectrum of the [$^2H_9$]analogue. This suggests a structure and origin similar to those of the *m/e* 87 fragments present in the mass spectra of methyl esters of long-chain fatty acids; more closely analogous is the formation of the same ion from the corresponding hydroxy-esters, *e.g.* methyl 12-hydroxyoctadecanoate. A hydrogen atom is abstracted from the δ- or ε-position in the first case,[6] effecting protonation of the basic ester function: in the second case a long-range abstraction of hydrogen with surprising specificity from the remote 12-hydroxy-group, comparable to the trimethylsilyl-transfer, is observed.[7] Subsequent hydrogen abstraction from the activated α-position yields a radical-ion with an extended resonance system, allowing β-cleavage to a conjugated ion (*d*, Scheme 2). For the protonated *m/e* 87 species, it is known that more than one transfer step occurs prior to cleavage, leading to partial loss of both labels in [2,2-$^2H_2$]-esters.[6] This suggests that the two events are not concerted.

Of additional mechanistic interest is an ion of mass **146** (*e*), the silylated analogue of the most prominent fragment formed by fatty-acid methyl esters, *m/e* 74 (McLafferty rearrangement). Ion *e* is only of low abundance in the spectrum of (I), but is identifiable by high-resolution techniques. It is more pronounced in the spectrum of methyl 16-trimethylsiloxyhexadecanoate and several related compounds.[8] The mechanism proposed for the formation of this ion (Scheme 2) assumes a γ-hydrogen abstraction by the remote alkoxy-radical,

SCHEME 1



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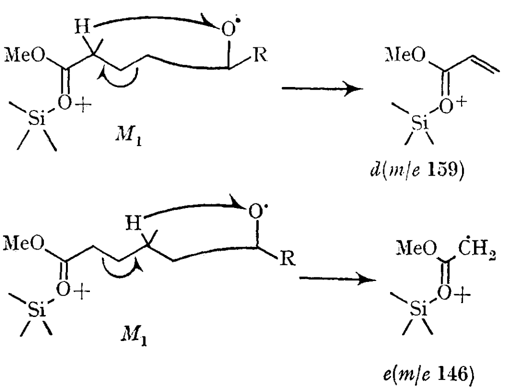
§ Data on dicarboxylic acid bis-trimethylsilyl esters, which reveal fragmentation processes which may be interpreted in a similar mechanistic fashion, have been recorded independently. Personal communication, September 1967: Professor J. A. McCloskey, Baylor University, Houston, Texas.

followed by cleavage of the β,γ-bond. For a concerted abstraction–cleavage process, the activation of the γ-position in contrast to other sites, would give a conjugated (and thus energetically favourable) transition state.

Besides the ready migration of trimethylsilyl substituents, these findings suggest a behaviour analogous to that of hydrogen-transfer processes. The protonation, or silylation, of the ester moiety in the resulting fragments (m/e 74 and 87, or 146 and 159, respectively), can be interpreted as consequences of acid–base reactions in which the transferred hydrogen atom functions as a Brønsted acid and the transferred silyl moiety as a Lewis acid. That silyl groups can also substitute for hydrogen in elimination reactions is suggested by the loss of methyl trimethylsilyl ether (m/e 301 → 197) from even-electron fragments. By analogy with the behaviour of the 12-hydroxy-ester, a loss of methanol might have been expected instead. Surprisingly, both transferred entities, hydrogen[7] as well as trimethylsilyl, which are finally lost in the elimination step, originate in the same remote position.

SCHEME 2



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[4] J. Diekman, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, 1967, **32**, 3911.
[5] This formulation is not intended to imply an entirely localized charge on the ether oxygen atom, but rather a certain presence of the charge during the time the reaction takes place. For example, see ref. 16 in P. Brown and C. Djerassi, *J. Amer. Chem. Soc.*, 1967, **89**, 2711.
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[8] The authors are indebted to Dr. G. Eglinton and Mr. D. H. Hunneman, The University of Bristol, for providing low resolution mass spectra prior to publication: *Phytochemistry*, 1968, **7**, 313.