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Investigation of Group Migration in the Fragmentation of *Bis*(trimethylsilyl) Ethers of Diols Separated by Rigid Groups

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Two fragmentations of $(CH_3)_3SiO\text{-}CR_2\text{-}X\text{-}CR_2\text{-}OSi(CH_3)_3$, where X is a rigid group such as a triple bond or an aromatic ring, are losses of a methyl or R group (where R is H or alkyl). The metastable-ion dissociations of $[M-R]^+$ and $[M-CH_3]^+$ ions include the rearrangement of a trimethylsilyl (TMS) cation and a $(CH_3)_2Si{=}O$ neutral species through an ion–neutral complex. On the basis of tandem mass spectrometry (MS/MS), exact mass measurement and isotopic labeling experiments, it has been established that the two trimethylsilyloxy groups in the TMS ethers interact across a wide range of distances via an ion–neutral complex. The migration of a TMS cation occurs when the group that is bound to carbon is expelled as a radical by an oxygen-directed cleavage to give a trimethylsilylated oxonium ion. If, on the other hand, a methyl radical is lost from the silicon atom, then $(CH_3)_2Si{=}O$ migrates. The mobilities of the TMS cation and the neutral $(CH_3)_2Si{=}O$ are governed by the capability of the rigid group to delocalize charge.

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INTRODUCTION

The trimethylsilylation of diols reduces hydrogen-bonding interactions and polarity and also increases thermal stability and volatility, thereby making the derivatized diols suitable for determination by gas chromatography/mass spectrometry.[1] The formation of the ion of *m/z* 147 $[(CH_3)_3Si{-}O^+{=}Si(CH_3)_2]$ and related ions from ionized *bis*(trimethylsilyl) ethers of terminal diols that have the general structure $HO{-}(CH_2)_n{-}OH$ was reported previously.[2–5] A McLafferty-type rearrangement of the trimethylsilyl (TMS) group produces predominant odd-electron ions from TMS derivatives of hydroxy dicarboxylic acids.[6,7] For TMS ether derivatives of some steroid compounds, the predominant fragment ions are produced by the migration of the TMS cation or a related group to an oxygen located elsewhere on the semi-rigid steroid ring system.[5,8–11]

In addition, TMS cations from tetramethylsilane have been used as a reagent gas in chemical ionization (CI) mass spectrometry because these cations bind well with a variety of compounds that have atoms with non-bonding electron pairs (e.g. N, O).[12–18] Many studies of the TMS cation as a CI reagent gas have provided important information with regard to fragmentation mechanisms and thermodynamic data. Moreover, the strong Si—O bond is a driving force for the CI reaction.[19]

The capability of the TMS cation group to migrate over a wide range of distances in semi-rigid or rigid molecules was demonstrated not only for metastable-ion decompositions of radical cations that are produced by electron impact (EI) ionization, but also for bimolecular reactions.[10,11,20,21] Although the mechanisms were not proved, these migrations may take place by means of ion–neutral complexes. Metastable dissociations that take place through a weakly bonded complex were recognized as intermediates in the fragmentation of closed-shell ions by Bowen and coworkers[22,23] in 1978 and were termed ion–neutral complexes by Morton[24] in his classic review article in 1982. In recent reviews, the binding forces, transition states for decomposition of complexes and the distinction between ion–neutral complexes and other reaction intermediates were described.[25,26] An additional interesting and significant observation made in numerous

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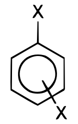
studies is that in EI-induced metastable-ion decompositions of TMS ethers, the TMS cation is likely to transfer to electron-rich sites at a remote position.[3,6,7,20,21,27–29]

The migration of Me_3Si^+ in the systems reported in this paper may occur by either σ or π complexes. In the former, the bonding between Si and C is stronger and the positive charge is delocalized onto the carbon skeleton. In the latter, the binding between the Si and the π-center is weak and there is considerable positive charge on Si. The distinction between these two pictures was recently the subject of intense debate in the literature.[30–33]

The primary goal of this study was to determine whether two trimethylsilyloxy groups separated by a rigid function (e.g. benzene ring or triple bond) interact with each other via an ion–neutral complex. The metastable-ion and collisionally activated dissociation (CAD) mass spectra of $[M-R]^+$ ($R = H$, CH_3 or C_2H_5) and $[M-CH_3]^+$ produced from the molecular ions containing aromatic, **I–III** and aliphatic, **IV–VI**, groups were examined. The first-generation fragment ions were chosen for study because molecular ions are of low relative abundance or are non-detectable.

The secondary goal was to identify the fragmentation pathways of the selected TMS ethers and determine the structure of fragment ions from specific precursors (e.g. $[M-R]^+$ and $[M-CH_3]^+$). Fragmentation pathways and structures for fragment ions of *m/z* 119 or 147, which form from various precursors in metastable-ion processes, were determined on the basis of exact mass measurement, tandem mass spectrometry (MS/MS) and isotopic labeling experiments.

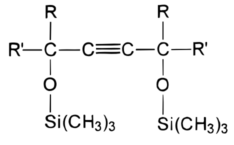


where $X = CH_2\text{-}O\text{-}Si(CH_3)_3$

(I) 1,4-*bis*(trimethylsilyloxymethyl)-benzene

(II) 1,3-*bis*(trimethylsilyloxymethyl)-benzene

(III) 1,2-*bis*(trimethylsilyloxymethyl)-benzene



(IV) R = R' = H: 1,4-*bis*(trimethysilyloxy)-but-2-yne

(V) R = R' = CH_3: 2,5-dimethyl-2,5-*bis*(trimethysilyloxy)-hex-3-yne

(VI) R = CH_3, R' = C_2H_5: 3,6-dimethyl-3,6-*bis*(trimethysilyloxy)-oct-4-yne

EXPERIMENTAL SECTION

Reagents

Benzenedimethanol isomers, but-2-yne-1,4-diol, but-2-ene-1,4-diol, butane-1,4-diol, lithium aluminum deuteride, 1-(trimethylsilane)imidazole dimethyl phthalate and dimethyl fumarate were purchased from Aldrich Chemical (Milwaukee, WI, USA). Chlorotrimethylsilane-d_9 was purchased from MSD Isotopes (Pointe Claire, Canada). 2,5-Dimethylhex-3-yne-2,5-diol and 3,6-dimethyloct-4-yne-3,6-diol were provided by Air Products and Chemicals (Allentown, PA, USA).

Synthesis

TMS ether derivatives were synthesized by dissolving 3 mmol of the diol in distilled dichloromethane followed by adding 6.3 mmol of 1-(trimethylsilyl)imidazole. The reaction mixture was stirred for 2 h at room temperature. Argon was used to provide an oxygen-free and moisture-free atmosphere because most TMS ether derivatives investigated in this study were sensitive to moisture. The final TMS ether was isolated by removing the solvent at 30 °C under vacuum. Thin-layer chromatography and NMR spectrometry of all the TMS ether derivatives showed that the purity of the product was greater than 98%.

To prepare the isotopically labeled compound, 20 ml of a solution of distilled diethyl ether containing 0.01 mol of dimethyl phthalate was added to 100 ml of distilled diethyl ether containing 0.04 mol of lithium aluminum deuteride. The mixture was stirred overnight and the reaction was quenched by adding water until the remaining $LiAlD_4$ and the water formed a gray paste. After drying with magnesium sulfate and filtering the salts, the solvent was evaporated and the liquid residue was used to synthesize the TMS ether of d_4-1,2-benzenedimethanol. The TMS-d_4 ether was synthesized by using the same procedure except benzenedimethanol was substituted for d_4-1,2-benzenedimethanol. A 10 ml volume of a solution of dried CH_2Cl_2, 2 mmol of chloromethylsilane-d_9, 1 mmol of the diol and 2.1 mmol of imidazole were mixed and then stirred for 12 h. The TMS-d_{18} ether was isolated as a slightly yellow liquid by evaporating the solvent.

NMR spectroscopy

^1H NMR spectra were acquired in $CDCl_3$ at 25 °C on a Nicolet 360 MHz spectrometer. Chemical shifts are reported relative to tetramethylsilane (internal reference).

1,4-*Bis*(trimethylsilyloxymethyl)benzene: ^1H NMR, δ 0.34 (s, 18H, 6 CH_3 on the Si), 4.86 (s, 4H, 2 benzylic CH_2) and 7.37 (s, 4 ring H).

1,3-*Bis*(trimethylsilyloxymethyl)benzene: ^1H NMR, δ 0.40 (s, 18H, 6 CH_3 on the Si), 4.94 (s, 4H, 2 benzylic CH_2), 7.24 (s, H, 2-H on the benzene), 7.45 (d, 1H, 5-H on the benzene) and 7.52 (d, 2H, 4-H and 6-H on the benzene).

1,2-*Bis*(trimethylsilyloxymethyl)benzene: ^1H NMR, δ 0.26 (s, 18H, 6 CH_3 on the Si), 4.85 (s, 4H, 2 benzylic CH_2), 7.35 (m, 2H, 4-H and 5-H on the benzene) and 7.49 (m, 2H, 3-H and 6-H on the benzene).

1,4-*Bis*(trimethylsilyloxy)-but-2-yne: ^1H NMR, δ 0.16 (s, 18H, on the Si) and 4.30 (s, 4H, 2CH_2 of the C-1 and C-4).

2,5-Dimethyl-2,5-*bis*(trimethylsilyloxy)-hex-3-yne: ^1H NMR, δ 0.16 (s, 18H, on the Si) and 1.47 (s, 12H, 4CH_3 on the C-2 and C-5).

3,6-Dimethyl-3,6-*bis*(trimethylsilyloxy)-oct-4-yne: ^1H NMR, δ 0.17 (s, 18H, on the Si), 1.43 (s, 6H, 2 CH_3 on the C-3 and C-6), 0.96 (t, 6H, 2 CH_3 of the C-1 and C-8) and 1.63 (q, 4H, 2 CH_2 of the C-2 and C-7).

Instrumentation and procedures

A Kratos MS-50 tandem mass spectrometer was used to acquire the tandem mass spectra.[34] The first-stage mass spectrometer was a high-resolution, double-focusing instrument of normal geometry; the second stage was an electrostatic analyzer. An ion accelerating voltage of 8 kV and an electron energy of 70 eV were used for these experiments. All samples were introduced into the source through a room temperature liquid inlet. For MS/MS experiments, precursor ions were selected at a resolving power of 1500 with MS-1 and product-ion mass spectra were obtained by scanning the electric field of the second electrostatic analyzer (ESA). Helium was employed as a collision gas for activating ions for collisionally activated decomposition (CAD), and its pressure was increased until the intensity of the selected ion beam was reduced by 50%. For metastable-ion experiments, the same procedure was employed in acquiring tandem mass spectra except that no collision gas was used. In MS/MS/MS experiments, the ions produced in the source were activated in the first collision cell, which is located between the source and the first ESA. A specific fragment ion was chosen by adjusting the first ESA and the magnetic sector to the appropriate values, and the ion of interest was transmitted at a resolving power that was sufficient to separate ions that are one mass unit apart to the second collision cell; the CAD spectrum was then obtained by scanning the second ESA. A more detailed explanation of the tandem mass spectrometric experimental procedures was published previously.[35]

RESULTS AND DISCUSSION

The molecular ions of aliphatic and aromatic compounds **I** – **VI** are of low abundance or are not detectable. For the aromatic TMS ethers, **I** – **III**, the ions that are generated by the loss of a hydrogen radical from the CH_2 group or by the loss of a methyl radical that is bound to the silicon atom are more abundant than are the molecular radical cations.

For aliphatic TMS ethers, the $[M - R]^+$ ion, which is generated by the loss of a hydrogen, methyl or ethyl radical from the carbon backbone, is barely observable. The ion $[M - CH_3]^+$, produced by the loss of a methyl group from the silicon atom, however, is of higher abundance. For the hexyne TMS ether V, one cannot determine the origin of the expelled methyl group without isotopic labeling experiments, which will be described later.

$[M - H]^+$ ions from aromatic TMS ethers

The significant fragment ions produced from the $[M - H]^+$ species and their relative abundances in the EI-induced metastable-ion mass spectra are summarized in Table 1. The three principal fragments are of *m/z* 147, 119 and 73. The formation of the ion of *m/z* 119 from the $[M - H]^+$ ion is the major metastable-ion decomposition process and may occur via an ion–neutral complex. Details of the fragmentation pathways will be presented later. The relative abundances of the ion of *m/z* 73 vary depending on substitution positions between the two trimethylsilyloxy groups. A possible explanation of this dependence is that major fragments from the ion of **I** and **II** are produced via an ion–neutral complex as an intermediate. Substitution at the ortho position (**III**), however, allows the two TMS groups to interact directly en route to producing fragments.

The decompositions of metastable $[M - H]^+$ ions from 1,4-*bis*(trimethylsilyloxymethyl)benzene, **I**, produce a number of fragment ions (see Fig. 1). The ion of *m/z* 251 is generated by the loss of CH_2O. The ions of *m/z* 207 and 193 are produced by a hydride and methide group abstraction by a TMS cation, leading to the losses of $HSi(CH_3)_3$ and $Si(CH_3)_4$, respectively. A TMS cation is also formed by simple cleavage of the Si—C bond. The dissociation of metastable $[M - H]^+$ ions from the meta, **II** and ortho, **III**, isomers also produces an ion of *m/z* 119 as the major fragment. The formation of the fragment ions of *m/z* 119 and 147, which occur in the mass spectra of the aromatic ethers, **I**, **II** and **III**,

Table 1. Fragment ions and their relative abundances produced from $[M - H]^+$ and $[M - CH_3]^+$ ions from aromatic TMS ethers during the EI-induced metastable-ion process

			$[M - H]^+$ [a]			$[M - CH_3]^+$ [b]	
Compound	Molecular ion *m/z*	*m/z* 147	*m/z* 119	*m/z* 73	*m/z* 237	*m/z* 147	*m/z* 119
I	282	3	100	25	100	17	3
II	282	5	100	8	43	7	100
III	282	2	100	ND[c]	5	30	100
III-d_4	286		100[d]			27	100[e]
III-d_{18}	300					32[f]	100[g]

[a] $[M - D]^+$ in **III**-d_4.
[b] $[M - CD_3]^+$ in **III**-d_{18}.
[c] Not detected.
[d] *m/z* 122 in **III**-d_4.
[e] *m/z* 123 in **III**-d_4.
[f] *m/z* 162 in **III**-d_{18}.
[g] *m/z* 122 in **III**-d_{18}.

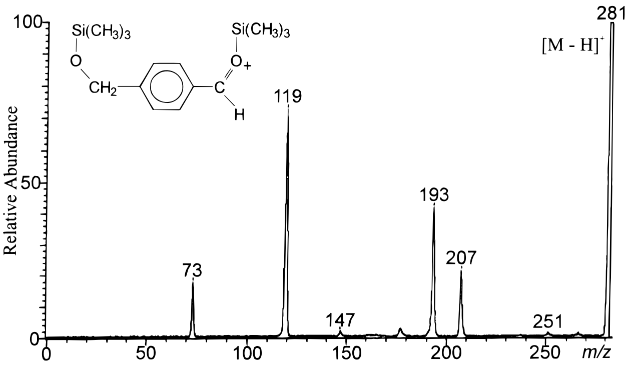


Figure 1. Metastable ion spectrum of the $[M-H]^+$ ion obtained from 1,4-*bis*(trimethylsilyloxymethyl)benzene (magnified 1000 times with respect to the precursor relative abundance of 100%).

must involve shifts of the rearranging group over the rigid spacer. If an intermediate ion–neutral complex is involved, the reactivity of the $[M-H]^+$ ion is governed by the charge delocalization capability of the benzene ring and the ion–dipole interaction. High-resolution peak matching of the source-produced *m*/*z* 119 ions revealed that there are two isobaric ions, $C_8H_7O^+$ and $C_9H_{11}^+$ and that the ion of *m*/*z* 147 has the formula $C_5H_{15}Si_2O$. The atom combination for the *m*/*z* 147 ion must result by long-range interaction of two trimethylsilyloxy groups.

An MS/MS/MS experiment was performed to determine the formula of the ion of *m*/*z* 119 that is produced in the metastable-ion and collisionally activated decompositions. The ion of *m*/*z* 281, $[M-H]^+$, produced in the source, was allowed to undergo metastable-ion decomposition in the first field-free region. The product ion of *m*/*z* 119 was transmitted by adjusting the first ESA and magnetic sector to the third field-free region for activation in the second collision cell. The CAD mass spectrum was obtained by scanning the second ESA. The CAD spectrum of the source-produced $C_8H_7O^+$ ion (mass selected at a resolving power of 10 000) [Fig. 2(A)] and that of the metastably produced ion of *m*/*z* 119 from the $[M-H]^+$ ion (Fig. 2(B)) for **III** are similar except for the expected poorer resolving power seen in Fig. 2(B). Because the spectra are nearly identical, the metastably produced ion of *m*/*z* 119 that is generated from the ion of *m*/*z* 281 must have the formula C_8H_7O.

We are now in a position to propose a mechanism for the formation of the ion of *m*/*z* 119 from **I** (see Scheme 1). Similar mechanisms for the decompositions of **II** and **III** are expected. The Si—O bond is stretched in the $[M-H]^+$ ion, **1**, and the ion–dipole interaction between the TMS cation and the π electrons of the aromatic ring, **2**, allows for the formation of an ion–neutral complex. Similar complexes were proposed by Grützmacher and co-workers[36,37] to account for migration of H^+ and other positively charged groups across aromatic rings. The migration across the benzene ring of the TMS cation, which is stabilized by hyperconjugation, can also take place easily through this complex. The ion of *m*/*z* 119, **5**, which is formed by the loss of $(CH_3)_3SiOSi(CH_3)_3$, is most favored in the metastable-ion dissociations. Upon collisional activation, however, the $[M-H]^+$ ions of all the aromatic TMS ethers give the ion of *m*/*z* 73 as the major fragment. This process is kinetically simple and hence is favored when the ion internal energy is high. The d_4 analog of **III** undergoes the expected fragmentation to yield ions of *m*/*z* 122. This indicates that three deuterium atoms remain in the ion of *m*/*z* 122, consistent with the proposed mechanism of a TMS cation rearrangement through an ion–neutral complex.

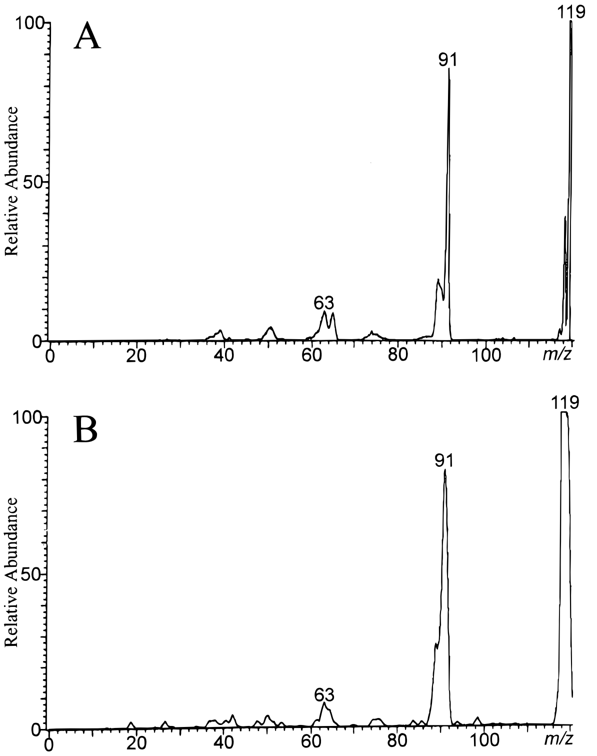
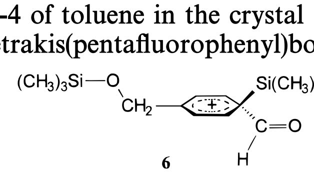


Figure 2. CAD spectra of (A) $C_8H_7O^+$ and (B) metastably produced ion of *m*/*z* 119 from 1,2-*bis*(trimethylsilyloxymethyl)-benzene.

We proposed that the intermediate in the migration of $Si(CH_3)_3^+$ is an ion–neutral or π complex. An alternative intermediate is a set of σ complexes produced by migration of the $Si(CH_3)_3^+$ and bonding to the aromatic ring (see structure **6**). The question of σ vs π complexes of $Si(CH_3)_3^+$ and aromatic rings has a long and colorful history. In early work by Wojtyniak and Stone,[41] the silylation adduct that forms as a result of the attack of a TMS cation on the aromatic substrates in the gas phase was proposed to have a π-bonded structure rather than an σ-bonded structure because they were unable to deprotonate it. A radiolytic study, however, suggested that the classical σ-bonded complex is stable, but its deprotonation was prevented by a more competitive desilylation by the nucleophilic oxygenated acceptors.[38–40] When stronger bases than those used by Wojtyniak and Stone[41] were used, deprotonation could be achieved in accord with an σ complex.

Lambert *et al.*[42] reported the bond distance between Si and the C-4 of toluene in the crystal structure of triethylsilyl tetrakis(pentafluorophenyl)borate prepared



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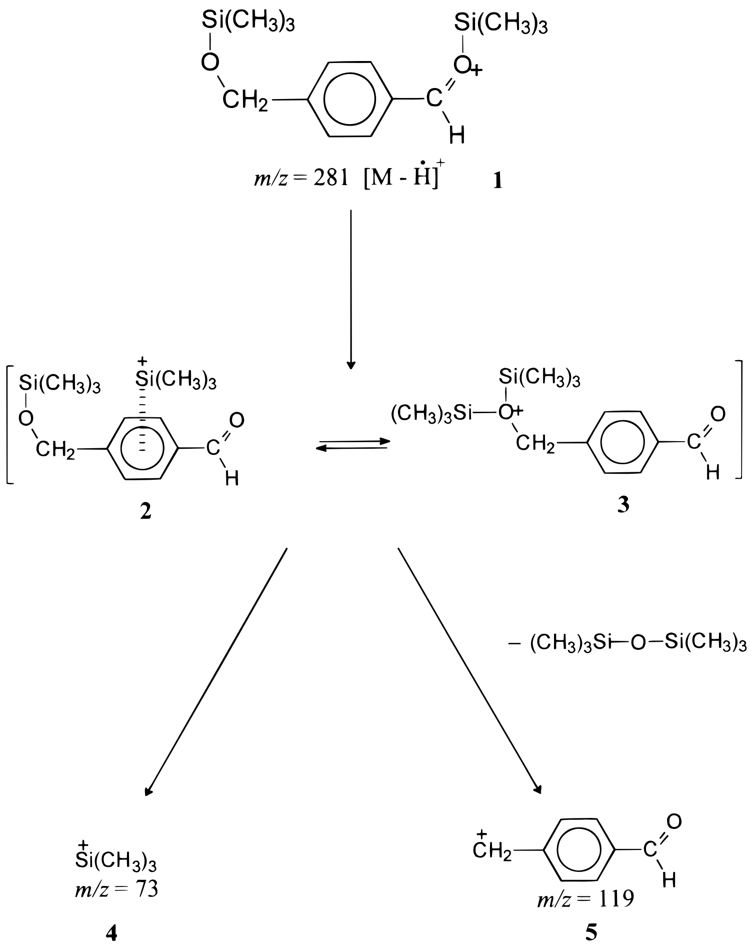


Scheme 1.

from toluene solution is too long for σ bonding. The x-ray results agree well with the calculated bond lengths and bond angles, which were obtained by the use of a Gaussian-92 series of programs.[43] Reed *et al.*[44] also calculated the charge density on Si in the gas-phase complex of $(CH_3)_3Si^+$ and toluene. The amount of charge in toluene was also experimentally determined from the ^{13}C NMR shift.[32] All these results, in our opinion, favor a π complex in which the toluene ring is nearly planar and the charge is predominantly on the silicon atom.

$[M - CH_3]^+$ ion from aromatic TMS ethers

The decompositions of metastable $[M - CH_3]^+$ ions from the three aromatic TMS ethers, **I–III**, yield three principal fragment ions of *m/z* 237, 147 and 119 (Fig. 3). The ion of *m/z* 237 is produced by the loss of a neutral formaldehyde, involving the cleavage of the C—C and Si—O bonds and the formation of a C—Si and a C—O bond (see Scheme 2). Production of the *m/z* 237 ion is the major metastable dissociation process for the para isomer whereas formation of the *m/z* 119 ion is the major metastable decomposition process for ortho and meta isomers.

The decompositions of metastable [Fig. 4(A)] and collisionally activated [Fig. 4(B)] *m/z* 237 ions for **I** were investigated to establish the relationship of precursor and product ions. This ion may be a silicon analog

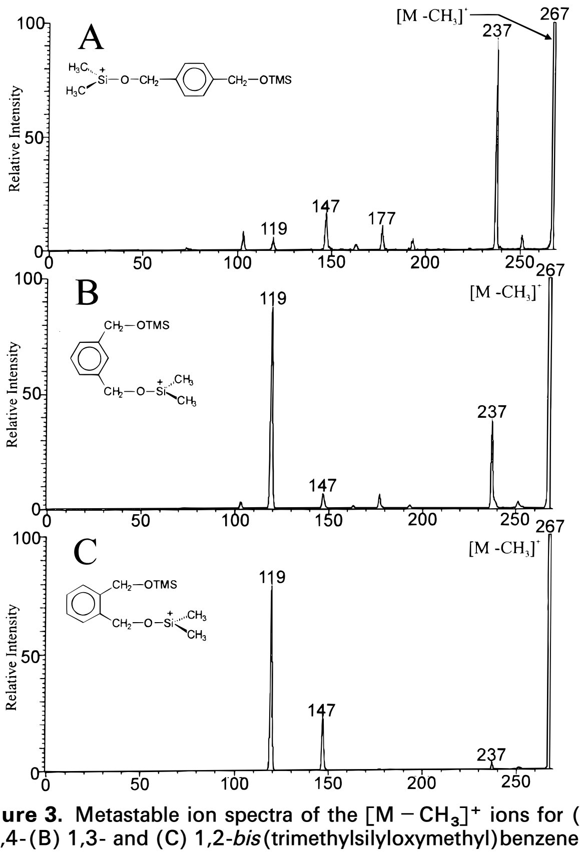
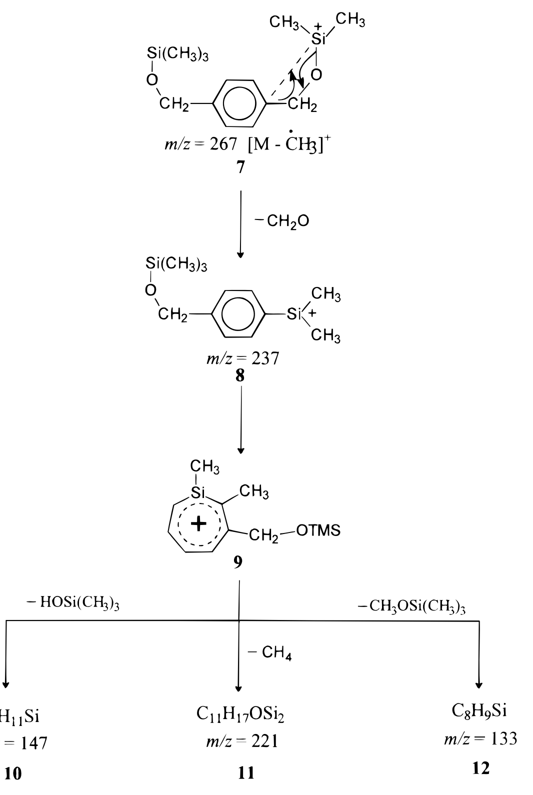


Figure 3. Metastable ion spectra of the $[M - CH_3]^+$ ions for (A) 1,4-(B) 1,3- and (C) 1,2-*bis*(trimethylsilyloxymethyl)benzene.



Scheme 2.

of a tropylium ion, **9**, which decomposes to ions of *m*/*z* 221, 147 and 133. The ion of *m*/*z* 147, **10**, which is a different species that is produced directly from the ion of *m*/*z* 267, contains only one silicon atom (see Scheme 2).

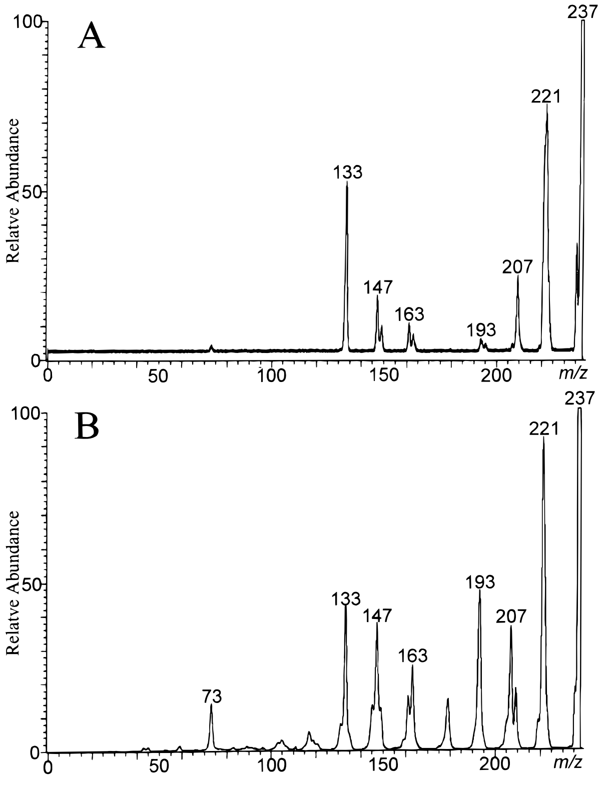
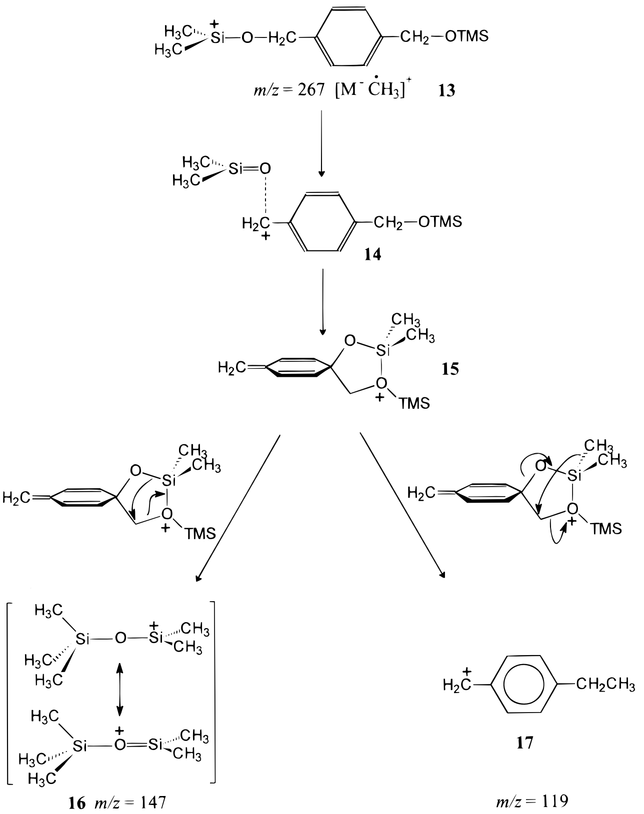


Figure 4. Metastable-ion (A) and CAD (B) mass spectra of the ion of *m*/*z* 237 for 1,4-*bis*(trimethylsilyloxymethyl)benzene.



Scheme 3.

A fragmentation mechanism for the formation of the ion of *m*/*z* 147, **16**, from the $[M - CH_3]^+$ ion (*m*/*z* 267) of the para isomer (see Scheme 3) begins with stretching the bond between neutral $(CH_3)_2Si{=}O$ and the incipient cation. Resonance charge delocalization in the cation allows the $(CH_3)_2Si{=}O$ species to interact at various positions of the aromatic ring, opening a reaction channel for the migration of $(CH_3)_2Si{=}O$ and formation of the *m*/*z* 147 ion. The rearrangement of $(CH_3)_2Si{=}O$ across the rigid group may occur via an ion–neutral complex and ultimately a five-membered ring intermediate is formed. For the case of the meta isomer, a six-membered ring intermediate would be formed to accommodate the different charge delocalization of the benzene ring.

The principal fragment ions generated from the $[M - CH_3]^+$ ions from the three isomers and their relative abundances in the metastable-ion spectra are summarized in Table 1. The formation of the ion of *m*/*z* 119 from the $[M - CH_3]^+$ ion is the most favorable metastable decomposition process for **II** and **III**, whereas the formation of this ion is less favored for **I**. This *m*/*z* 119 ion has a different elemental composition from an isobaric fragment that is produced from the $[M - H]^+$ ion. The formation of the ion of *m*/*z* 147 is less favorable than formation of the *m*/*z* 237 of **I** (Fig. 3(A)) or of the ion of *m*/*z* 119 of **II** and **III** isomers (Fig. 3(B) and (C)). The relative abundances of fragment ions of *m*/*z* 119 and 147 indicate that the ion of *m*/*z* 147 from **I** is more favored than the ion of *m*/*z* 119, whereas the ion of *m*/*z* 147 from **II** or **III** is less favored. The proposed mechanism for decomposition of **I** (Scheme 3) shows that C—O and Si—O bond cleavages followed by C—O and Si—O bond formations are required to generate the *m*/*z* 147 ion. The production of the ion of *m*/*z* 119 also requires C—O and Si—C bond cleavages, C—C and Si—O bond formations, as well as Si—O bond breaking.

The CAD mass spectrum for the ortho isomer was examined to determine whether the two trimethylsilyloxy groups interact with each other to produce the ions of *m*/*z* 119 and 147. The metastable-ion [Fig. 3(C)] and the CAD (Fig. 5) mass spectra show that the reactions to form these two ions are competitive. The generation of ion of *m*/*z* 147 by an Si—O bond cleavage in the five-membered ring intermediate, **19** in Scheme 4, is a kinetically favored simple cleavage process. Direct interaction of the two trimethylsilyloxy groups, which is not possible for the meta and para isomers, allows transfer of a trimethylsilyloxy group to an oxygen of the neighboring TMS group. An alternative explanation is that this isomer also fragments via an ion–neutral complex; this explanation is consistent with the similar fragmentation chemistry that occurs for the three isomers.

The metastable-ion mass spectra of $[M - CH_3]^+$ ion from isomeric TMS ethers shows that the *m*/*z* 119 ion is commonly formed. This ion is the most abundant metastable fragment ion for the ortho TMS isomer. On the basis of the proposed mechanism (Scheme 4), the formula of the ion is C_9H_{11}. An MS/MS/MS experiment was carried out to confirm the formula of this ion and to determine whether the fragment is different than that of the $[M - H]^+$ ion. The CAD mass spectrum [Fig. 6(A)] of the source-produced $C_9H_{11}^+$ ion (selected at a resolving power of 10 000) and that of the metastably produced ion of *m*/*z* 119 from the $[M - CH_3]^+$ ion (Fig. 6(B)) from the ortho isomer are similar. This is good evidence that the latter ion has the formula C_9H_{11} and is probably produced by the loss of the neutral, $O{=}Si(CH_3)OSi(CH_3)_3$, which is formed directly or via an ion–neutral complex.

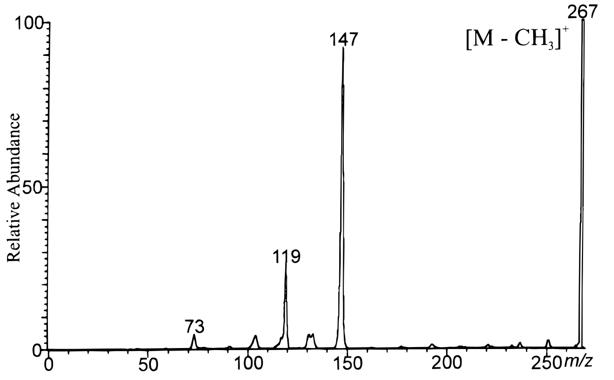
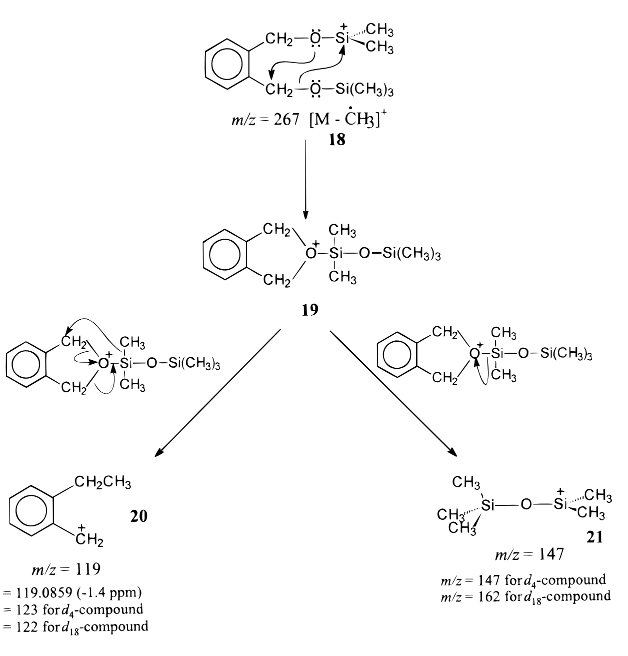


Figure 5. CAD mass spectrum of the $[M - CH_3]^+$ ions for 1,2-*bis*(trimethylsilyloxymethyl)benzene.



Scheme 4.

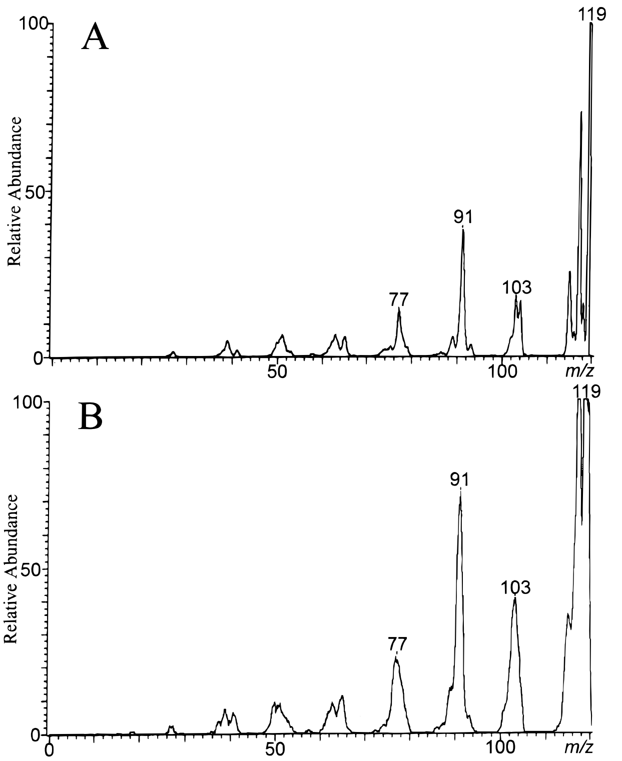


Figure 6. CAD spectra of (A) the $C_9H_{11}^+$ produced in the ion source and (B) the $C_9H_{11}^+$ produced in a metastable-ion decomposition of 1,2-*bis*(trimethylsilyloxymethyl)benzene.

Aliphatic ethers

The collisionally activated decompositions of the fragment ions produced by the losses of R (R = H, CH_3 and C_2H_5) from the carbon atom or of a methyl radical linked to the silicon atom for di-TMS ethers that were synthesized from but-2-yne-1,4-diol, 2,5-dimethylhex-3-yne-2,5-diol and 3,6-dimethyloct-4-yne-3,6-diol (**IV**–**VI**) were examined to investigate the generality of the fragmentation mechanisms. It was not possible to investigate the molecular radical cation of these aliphatic ethers because they are not detected. Important common fragment ions and their relative abundances are summarized in Table 2.

As observed for aromatic TMS ethers, the formation of the ion of *m*/*z* 147 is an important metastable

Table 2. Fragment ions and their relative abundances produced from $[M-R]^+$, where R is the group bonded to the carbon skeleton, and $[M-CH_3]^+$ ions from the aliphatic TMS ethers

Precursor ion	Fragment ion	Compound IV	V	V-d_{18}	VI
$[M-R]^+$	$[M-R-(CH_3)_3SiOH]^+$ R = H	ND[a]			
	$[M-R-(CD_3)_3SiOH]^+$ R = CH_3			100	
	$[M-R-(CH_3)_3SiOH]^+$ R = C_2H_5				100
	m/z 147 ion	100		47[b]	15
$[M-CH_3]^+$	$[M-CH_3-(CD_3)_3SiOH]^+$			20	
	$[M-CH_3-(CH_3)_3SiOH]^+$	ND			
	m/z 147 ion	100		100[b]	
$[M-R]^{+c}$ and $[M-CH_3]^+$	$[M-CH_3-(CH_3)_3SiOH]^+$		100		100
	m/z 147 ion		70		28

[a] Not detected.
[b] *m/z* 162 in V-d_{18}.
[c] Loss of R and CH_3 from $M^{+\cdot}$ cannot be distinguished.

process, indicating that this predominant ion is formed by a low-energy reaction. The *m/z* 147 ion is also produced readily in the ion source. Exact mass measurement for the source-produced *m/z* 147 ion showed that its formula is $C_5H_{15}Si_2O$. The relative abundances of A, A + 1 and A + 2 at *m/z* 147, 148 149, respectively, are also consistent with the formula. The structure of the *m/z* 147 ion was confirmed by its CAD spectrum, which is nearly identical with that of the $[M-CH_3]^+$ fragment of hexamethyldisiloxane (see Fig. 7). Upon collisional activation, the two ions of *m/z* 147, which have two different sources, produce abundant common fragments at *m/z* 131, 117, and 73.

The abundances of $[M-R]^+$ ions that are formed in the ion source from aliphatic TMS ethers are greater for losses of the large alkyl than the small alkyl radicals. The $[M-H]^+$ ion from 1,4-*bis*(trimethylsilyloxy)-but-2-yne is of low abundance and decomposes to produce the ions of *m/z* 201, 147 and 73. The metastable-ion decompositions of the ions formed by the losses of either methyl from the molecular ion of **V** or ethyl from the molecular ion of **VI** produce the *m/z* 147 ion and the $[M-R-90]^+$ ion. The neutral of mass 90 is $(CH_3)_3Si{-}OH$, which may be expelled from the $[M-R]^+$ ion by means of a charge-remote process. The formation of this ion is a dominant metastable-ion decomposition of the $[M-R]^+$.

The $[M-CH_3]^+$ ion from 2,5-dimethyl-2,5-*bis*(trimethylsilyloxy)-hex-3-yne dissociates by a metastable-ion process to produce major fragment ions of *m/z* 197 and 181 in addition to that of 147 [see Fig. 8(A)]. The ion of *m/z* 197 is produced by the migration across the triple bond of the trimethylsilyl ion, which then abstracts a hydride from a methyl group linked to the carbon. The ion of *m/z* 181 from the two different $[M-CH_3]^+$ precursors is formed by the loss of $(CH_3)_3Si{-}OH$, possibly by means of a charge-remote fragmentation.

There are two possible sites in the hexyne compound (**V**) for the elimination of the methyl radical. To understand the fragmentation pathways of the different $[M-CH_3]^+$ ions, the metastable-ion mass spectra of the d_{18}-labeled analog was examined [Fig. 8(B) and (C)]. The fragments from the $[M-CH_3]^+$ ion generated by the loss of methyl radical bound to the carbon atom between the triple bond and oxygen are of *m/z* 190 and 162 [see Fig. 8(B)]. The ion of *m/z* 190, $[M-CH_3-(CD_3)_3SiOH]$, is formed by the major metastable decomposition. The ion of *m/z* 147 now shifts to *m/z* 162.

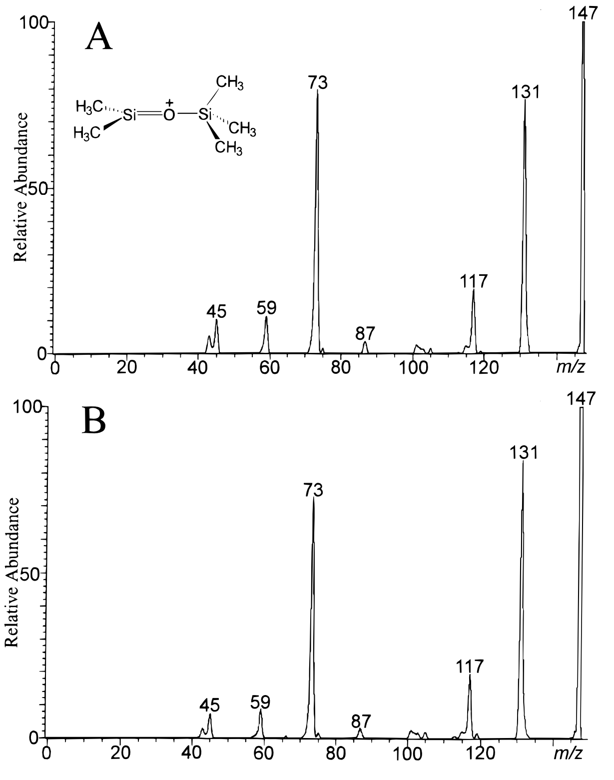


Figure 7. CAD spectra of (A) *m/z* 147 ion produced from hexamethyldisiloxane and (B) *m/z* 147 ion generated in the source from 2,5-dimethyl-2,5-*bis*(trimethylsilyloxy)hex-3-yne.

On the other hand, the product ion from loss of the deuterated methyl radical from the silicon atom is of *m*/*z* 286 for **V**-d_{18}. The fragments from the [M − CD$_3$]$^+$ ion are of *m*/*z* 187, 162 and 107 [see Fig. 8(C)]. The ion of *m*/*z* 187, [M − CD$_3$ − (CD$_3$)$_3$SiOH], is produced by a metastable-ion loss of (CD$_3$)$_3$SiOH, possibly through a charge-remote fragmentation. The shift of the *m*/*z* 147 ion to *m*/*z* 162 for the TMS-d_{18} ether of hexynediol establishes that the ion contains five methyl groups, two silicons and one oxygen. The ion of *m*/*z* 107, having only carbons and hydrogens, is produced by the loss of $C_5HD_{15}Si_2O_2$. The CAD mass spectrum for the (M − CD$_3$)$^+$ ion indicates that the formation of the ion of *m*/*z* 162 is kinetically favored.

The formation of the ion of *m*/*z* 109 from the [M − CH$_3$]$^+$ ion from the d_{18}-labeled analog is also expected to be a metastable dissociation. This ion may be produced by the loss of neutral hexamethylsiloxane-d_{18}. The reaction is likely to be a one-step process involving interaction of the two trimethylsilyloxy groups. The ions of *m*/*z* 119 from [M − H]$^+$ ions of aromatic TMS ethers are produced by a similar dissociation process except that the production of the *m*/*z* 109 ion in **VI** is less favored than that of *m*/*z* 119 in aromatic TMS ethers. Because a triple bond has lower charge delocalization capability than does a benzene ring, the production of the [M − CH$_3$ − (CD$_3$)$_3$Si—O—Si(CD$_3$)$_3$]$^+$ ion for the hexyne compound is less favorable than the ion formed from the same loss from the analogs containing an aromatic ring.

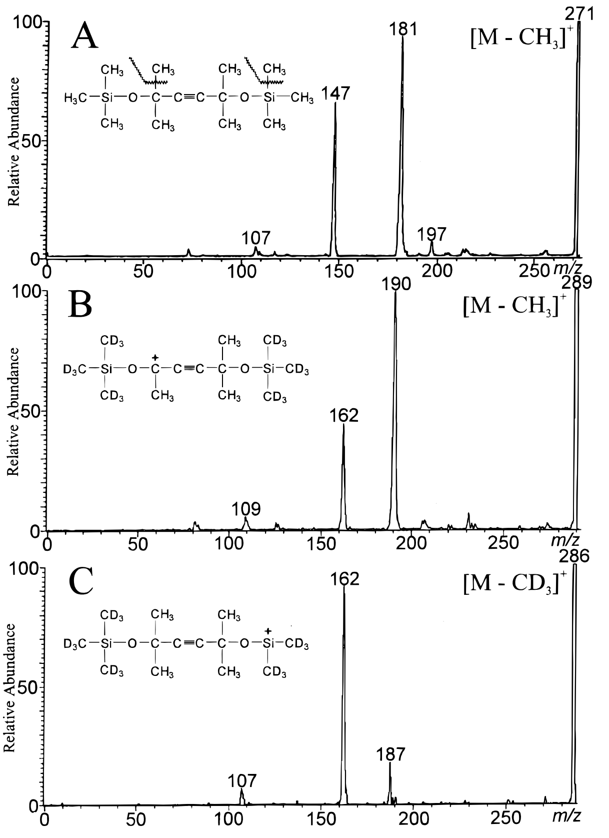
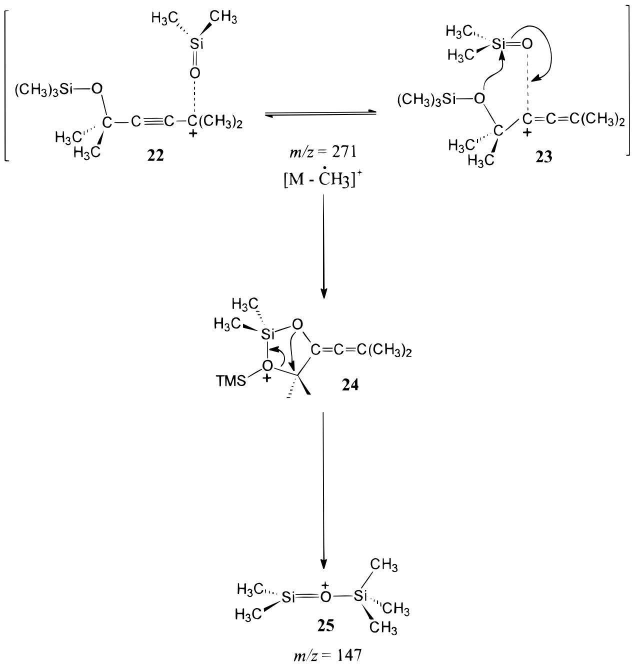


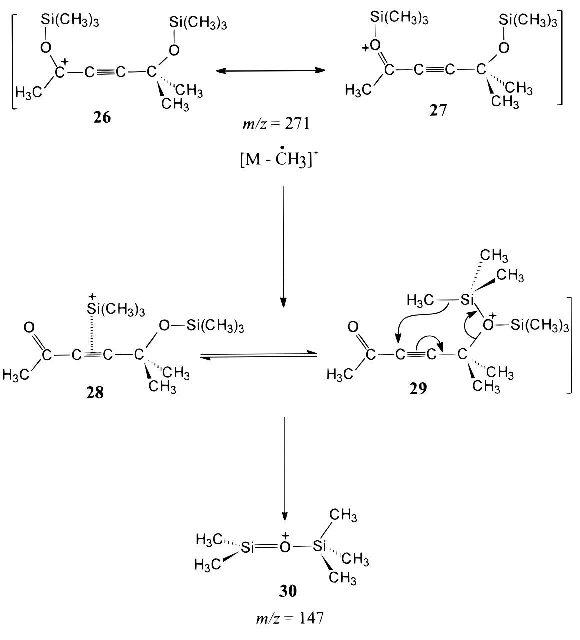
Figure 8. Metastable-ion spectra of (A) the [M − CH$_3$]$^+$ ion for 2,5-dimethyl-2,5-*bis*(trimethylsilyloxy)hex-3-yne, (B) [M − CH$_3$]$^+$ and (C) the [M − CD$_3$]$^+$ ion for 2,5-dimethyl-2,5-*bis*-(trimethylsilyloxy)hex-3-yne-d$_{18}$.



Scheme 5.

A mechanism for the formation of the ion of *m*/*z* 147 that is generated from the fragment produced by the loss of methyl radical bound to the silicon atom is proposed in Scheme 5 to involve the migration of (CH$_3$)$_2$Si=O to give a five-membered ring intermediate, **24**. The electropositive silicon atom in (CH$_3$)$_2$Si=O bonds strongly with the electronegative oxygen atom of a remote trimethysilyloxy group. On the basis of the proposed mechanism, the Si—O and C—O bonds are formed and broken to produce the ion of *m*/*z* 147. As in the case of aromatic TMS ethers, the *m*/*z* 147 ion from the aliphatic compounds may form by means of an intermediate ion–neutral complex, **23**.

If the methyl radical is lost from the carbon atom of the molecular ion, an Si—O bond can be broken (**28**)



Scheme 6.

and the $Si(CH_3)_3^+$ ion migrates to the trimethylsilyloxy group through either an ion–neutral or σ complex (Scheme 6). If the latter were involved, positive charge moves on to the carbon skeleton to give a vinyl carbocation, a σ complex that is less favored than that in an aromatic system. In the π complex, however, the positive charge remains principally on silicon, which should be even more favored for these systems than those with aromatic systems. The final product is then favored by transfer of a methyl group to one of the carbons of the triple bond, **29**. This transfer should be facile because the silicon–methyl carbon bond is unusually long and weak.

CONCLUSION

The rearrangement of the trimethylsilyl (TMS) cation during the EI-induced metastable-ion decomposition of trimethylsilyl ethers leads to an interaction of the trimethylsilyloxy groups in the TMS ethers of aromatic and aliphatic compounds. This long-distance interaction occurs via intermediate ion–neutral complexes.

For the aromatic compounds, the metastable-ion spectra of the $[M-H]^+$ ion strongly support a TMS cation migration by means of an intermediate ion–neutral complex. Futhermore, spectra of metastable $[M-CH_3]^+$ ions show that the $(CH_3)_2Si{=}O$ group migrates, possibly through an ion–neutral complex, en route to fragment ions of *m*/*z* 119 and 147.

For aliphatic TMS ethers, the ions generated by the loss of hydrogen, methyl and ethyl radicals from the carbon backbones of various butyne, hexyne and octyne TMS diethers, respectively, also undergo the TMS cation rearrangement whereas the $[M-CH_3]^+$ ion that is produced by the loss of a methyl group linked to the silicon atom undergoes $(CH_3)_2Si{=}O$ migration. These migration/rearrangements are likely to occur via ion–neutral complexes.

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REFERENCES

1. A. G. Sharkey, R. A. Friedel, Jr, and S. H. Langer, *Anal. Chem.* **29**, 770 (1957).
2. H. Budzikiewicz,. C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, pp. 471–476. Holden-Day, San Francisco (1967).
3. J. A. McCloskey, R. N Stillwell and A. M. Lawson, *Anal. Chem.* **40**, 233 (1968).
4. J. Diekman, J. B. Thomson and C. J. Djerassi, *J. Org. Chem.* **33**, 2271 (1968).
5. M. Annan, P. W. LeQuesne and P. Vouros, *J. Am. Soc. Mass Spectrom.* **4**, 327 (1993).
6. G. Peterson, *Org. Mass Spectrom.* **6**. 565 (1972).
7. W. P. Weber, R. A. Felix and A. K. Willard, *J. Am. Chem. Soc.* **92 : 5**, 1420 (1970).
8. S. Sloan, D. J. Harvey and P. Vouros, *Org. Mass Spectrom.* **5**, 789 (1971).
9. C. J. W. Brooks, D. J. Harvey, B. S. Middledich and P. Vouros, *Org. Mass Spectrom.* **7**, 925 (1973).
10. I. Björkhen, J. Gustafsson and L. Sjövall, *Org. Mass Spectrom.* **7**, 277 (1973).
11. C. J. W. Brooks, D. J. Harvey and B. S. Middleditch, *J. Org. Chem.* **37**, 3365 (1972).
12. T. J. Odiorne, D. J. Harvey and P. Vouros, *J. Phys. Chem.* **76**, 3217 (1972).
13. M. R. Ellenburger, M. L. Henderwerk, D. A. Well, W. E. Forneth and D. A. Dixon, *Anal. Chem.* **54**, 1309 (1982).
14. R. N. Still, D. I. Carroll, J. G. Nowlin and E. C. Horning, *Anal. Chem.* **55**, 1313 (1983).
15. I. A. Blair and J. H. Bowie, *Aust. J. Chem.* **32**, 1389 (1979).
16. D. Clemens and B. Munson, *Org. Mass Spectrom.* **20**, 368 (1985).
17. R. Orlando, F. Strobel, D. P. Ridge and B. Munson, *Org. Mass Spectrom.* **22**, 597 (1987).
18. R. Orlando, D. P. Ridge and B. Munson, *Org. Mass Spectrom.* **23**, 527 (1988).
19. C. G. Pitt, M. M. Bursey, D. A. Chatfield and R. S. Greenberg, *J. Organomet. Chem.* **9**, 269 (1975).
20. S. Gaskell, A. G. Smith and C. J. W. Brooks, *Biomed. Environ. Mass Spectrom.* **2**, 148 (1975).
21. W. J. Richter and J. A. McCloskey, *Chem. Commun.* 1158 (1968).
22. R. D. Bowen and D. H. Williams, *J. Am. Chem. Soc.* **100**, 7454 (1978).
23. R. D. Bowen, B. J. Stapleton and D. H. Williams, *J. Chem. Soc., Chem. Commun.* 25 (1978).
24. T. H. Morton, Tetrahedron **38**, 3195 (1982).
25. D. J. McAdoo, *Mass Spectrom. Rev.* **7**, 363 (1988).
26. P. Longevialle, *Mass Spectrom. Rev.* **11**, 157 (1992).
27. G. H. Draffan, R. N. Stillwell and J. A. McCloskey, *Org. Mass Spectrom.* **1**, 669 (1968).
28. G. Petersson, *Org. Mass Spectrom.* **6**, 577 (1972).
29. P. Longevialle, *Spectrosc. Int. J.* **5**, 43 (1987).
30. L. Pauling, *Science* **263**, 983 (1994).
31. G. A. Olah, G. Rasul, X. Li, H. A. Buchholz and G. K. S. Prakash, *Science* **263**, 983 (1994).
32. J. B. Lambert and S, Zhang, *Science* **263**, 984 (1994).
33. C. A. Reed and Z. Xie, Science **263**, 985 (1994).
34. M. L. Gross, E. K. Chess, P. A. Lyon, F. W. Crow and H. Tudge *Int. J. Mass Spectrom. Ion Phys.* **42**, 243 (1982).
35. D. J. Burinsky, R. C. Cooks, E. K. Chess and M. L. Gross, *Anal. Chem.* **54**, 295 (1982).
36. U. Filges and H.-F. Grützmacher, *Org. Mass Spectrom.* **21**, 673 (1986).
37. H.-F Grützmacher and U. Zalfen, *Org. Mass Spectrom.* **25**, 323 (1990).
38. S. Fornarini, *J. Org. Chem.* **53**, 1314 (1988).
39. F. Cacace, E. Crestoni, S. Fornarini and R. Garbrielli, *Int. J. Mass Spectrom. Ion Processes* **84**, 17 (1988).
40. X. Li and J. A. Stone, *Int. J. Mass Spectrom. Ion Processes* **87**, 17 (1990).
41. A. C. M. Wojtyniak and J. A. Stone, *Int. J. Mass Spectrom. Ion Processes* **74**, 59 (1986).
42. J. B. Lambert, S. Zhang, C. L. Stern and J. C. Huffman, *Science* **260**, 1917 (1993).
43. P. v. R. Schleyer, P. Buzek, T. Muller, Y. Apeloig and H. U. Siehl, *Angew. Chem.* **105**, 1558 (1993).
44. C. A. Reed, Z. Xie, R. Bau and R. Benesi, *Science* **262**, 402 (1993).