Lab., Shionogi & Co., Japan, for his suggestions and help in identifying the *cis*- and *trans*-2,4,4-trimethylcyclopentanols.

Registry No.—2,5-Dimethylcyclopentyl tosylhydrazone, 65378-86-1; 2,2,5-trimethylcyclopentyl tosylhydrazone, 65378-87-2; lithium aluminum hydride, 16853-85-3; methyllithium, 917-54-4.

References and Notes

(1) Address correspondence to the National Science Council.

(2) (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and C. A. Morrison, "Conformational Analysis", Interscience, New York, N.Y., 1965; (b) M. Hanack, "Conformation Theory", Academic Press, New York, N.Y., 1965, p 75 ff; (c) see A. V. Kamernitzky and A. A. Akhrem, *Tetrahedron*, **18**, 705 (1962), for an excellent review of the stereochemistry of nucleophilic addition to cyclic ketones; (d) E. L. Eliel and Y. Senda, *ibid.*, **26**, 2411 (1970); (e) E. C. Ashby and J. T. Laemmle, *Chem. Rev.*, **75**, 521 (1975).

(3) J. A. Berson in "Molecular Rearrangements", P. de Mayo, Ed., Interscience, New York, N.Y., 1963, Chapter 3.

(4) (a) C. G. Le Fivre and R. J. W. Le Fivre, *J. Chem. Soc.*, 3549 (1956); (b) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959); (c) R. J. Abraham and K. A. McLauchlau, *Mol. Phys.*, **5**, 513 (1962); (d) C. Altona, H. R. Buys, H. J. Hageman, and E. Havinga, *Tetrahedron*, **23**, 2265 (1967).

(5) W. Hückel and E. Mogle, *Justus Liebigs Ann. Chem.*, **649**, 13 (1961).

(6) A. P. Krapcho and D. E. Horn, *Tetrahedron Lett.*, 6107 (1966).

(7) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1247 (1964).

(8) G. F. Hennion and F. X. O'Shea, *J. Am. Chem. Soc.*, **80**, 614 (1958).

(9) H. C. Brown and H. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).

(10) B. Fuchs and R. G. Haber, *Tetrahedron Lett.*, 1323 (1966).

(11) M.-H. Rei, unpublished results.

(12) In general, a Varian 1200 equipped with a flame ionization detector was used. Quadral (5%) or DEGS (5%) on a Chromosorb W (80–100 mesh) packed column (12 ft × 1/8 in.) was programmed 10°/min from room temperature to 120 °C.

(13) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 4106 (1959).

(14) S. P. Acharya and H. C. Brown, *J. Am. Chem. Soc.*, **89**, 1925 (1967).

(15) R. H. Shapiro and M. J. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967).

(16) M.-H. Rei, Ph.D. Thesis, Purdue University, West Lafayette, Ind. More reactions including the uses of three Grignard reagents and other methyl-substituted cyclopentanones were reported herein.

(17) E. L. Eliel, S. H. Shroeter, T. J. Brett, F. J. Biros, and J. C. Richer, *J. Am. Chem. Soc.*, **88**, 3327 (1966).

(18) H. C. Brown and V. J. Varma, *J. Am. Chem. Soc.*, **88**, 2871 (1966).

(19) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(20) H. Booth, *Prog. Nucl. Magn. Reson. Spectrosc.*, **5**, 144, 214 (1970).

(21) W. J. Hammer, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1967.

(22) (a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965). (b) S. R. Landor, P. W. O'Connor, A. R. Tatchell, and I. Blair, *J. Chem. Soc., Perkin Trans. 1*, 473 (1973).

(23) A. F. Cockerill and D. M. Rackham, *Tetrahedron Lett.*, 5149 (1970).

(24) N. Mueller and W. C. Tosch, *J. Chem. Phys.*, **37**, 1167 (1962).

(25) H. Haubenstook and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2363 (1962).

(26) J. B. Lambert, *Acc. Chem. Res.*, **4**, 87 (1971).

(27) (a) J. B. Lambert, J. J. Papay, S. A. Khan, K. A. Kappauf, and E. S. Magyar, *J. Am. Chem. Soc.*, **96**, 6112 (1974); (b) R. Steyn and H. Z. Sable, *Tetrahedron*, **25**, 3579 (1969); (c) H. J. Jakobsen, *Tetrahedron Lett.*, 1991 (1967).

(28) (a) R. L. Lipnick, *J. Am. Chem. Soc.*, **96**, 2941 (1974); (b) *J. Mol. Struct.*, **21**, 411, 423 (1974).

(29) The nomenclature of the stereochemistry of these alcohols follows the 1974 IUPAC Commission. The hydroxyl group of the alcohol is used as the reference and is indicated by *r* before its locant. The steric relationship of the methyl substituent to the hydroxyl group is affixed by a cis or trans, followed by the locant of the methyl group. For the ketone, the carbornyl group is used as the starting point of the numering system, and the plane of the ring is the reference of the stereochemistry. Affixes cis or trans are used to indicate the stereochemistry of the methyl substituent in the ring.

New Mass Spectrometric Rearrangements Involving Silicon. A Study of Trimethylsilylated Di- and Polyamines and Their Isotopically Labeled Analogues

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The electron-impact spectra of six trimethylsilylated di- and polyamines and 12 deuterium labeled analogues have been examined. Structures of several ions in the spectra of the unlabeled compounds, unexplained by simple fragmentations, have been assigned consistent with the observed changes in *m/e* values of the corresponding labeled ions. The composition of these ions suggests molecular decomposition processes not previously reported for trimethylsilylated compounds. These include a McLafferty rearrangement involving hydrogen migration to an even-electron siliconium center and a 1,5-alkyl migration of a methyl group initially bonded to silicon. The primary impetus for these rearrangements is the high reactivity of the silicon center; however, in addition, the proximities of the various amine centers affect the fragmentation processes.

Trimethylsilyl (TMS) groups are widely utilized for protection of polar functions during synthetic and chromatographic (including coupled gas chromatography–mass spectrometry) procedures, and the mass spectra of a large number of trimethylsilylated compounds have been recorded. In many instances, primarily involving *O*-trimethylsilyl compounds, electron-impact induced rearrangements have been described which involve interaction between a TMS group and a second functional group.[1] Such interactions between functional groups are also observed in mass spectra of alkanes possessing multiple polar substituents,[2] e.g., the di- and polyamines[3] and their N-substituted derivatives.[4]

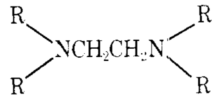
In view of our interest in the analysis of physiological polyamines using GC–MS techniques[5] and the impressive detection sensitivity reported for trimethylsilyldiamines,[6] we have investigated extensively the electron-impact mass spectrometry of TMS derivatives of selected di- and polyamines. Mass spectrometric data for the compounds studied (**1**–**18**, Chart I), which include a variety of specifically deuterated analogues, are recorded in Tables I–VI.

The novel rearrangements described in this study are excellent examples of the versatility of silicon-containing compounds upon activation by electron impact and provide some interesting insights into the *N*-trimethylsilyl group.[7] The migration of a TMS methyl group to a γ-methylene carbon represents one of a limited number of authenticated 1,5-alkyl rearrangements.[9-11] Another decomposition process is a McLafferty rearrangement, different in that a hydrogen migrates to a dimethylsiliconium center.

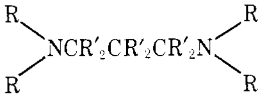
Results and Discussion

Isotopic Analyses. The per cent deuterium incorporation into the di- (**7** and **10**) and polyamines (**13**, **16**, and **17**) was determined from the intensities of ions in the $[M - CF_3\cdot]^+$ ion

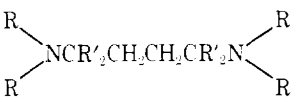
Chart I



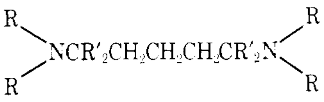
1, R = TMS
2, R = TMS-d_9



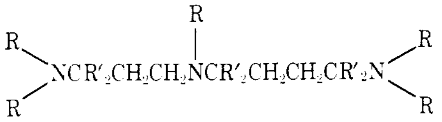
3, R = TMS; R′ = H
4, R = TMS; R′ = ^{2}H
5, R = TMS-d_9; R′ = H



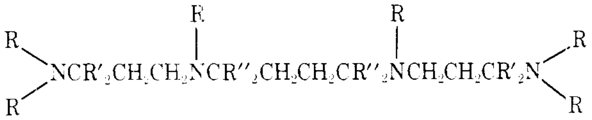
6, R = TMS; R′ = H
7, R = TMS; R′ = ^{2}H
8, R = TMS-d_9; R′ = H



9, R = TMS; R′ = H
10, R = TMS; R′ = ^{2}H
11, R = TMS-d_9; R′ = H

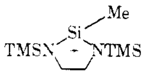


12, R = TMS; R′ = H
13, R = TMS; R′ = ^{2}H
14, R = TMS-d_9; R′ = H



15, R = TMS; R′ = R″ = H
16, R = TMS; R′ = ^{2}H; R″ = H
17, R = TMS; R′ = R″ = ^{2}H
18, R = TMS-d_9; R′ = R″ = H

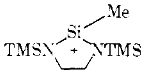
Table I. Principal Ions Observed in Mass Spectra of Tetra(trimethylsilyl)-1,2-diaminoethanes 1 and 2

Ion, m/e		Relative intensity,[a] %	Structure assignment
1	**2** (d_{36})		
348	384	0.1	$M^{+\cdot}$
333	377	2	$[M-Me]^+$
259	283	4	$(TMS)_2NCH_2CH_2{=}N\text{-}Si^+Me_2$
245	266	6	
174	192	100[b]	$CH_2{=}N(TMS)_2$
100	109	6	$HC{\equiv}N^+TMS$
86	92	13	$CH_2{=}NSi^+Me_2$

[a] Relative intensities are for ions in the spectrum of the nondeuterated analogue 1. [b] Σ_{80} = 53%.

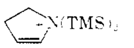
isotope cluster in spectra of the respective trifluoroacetylated derivatives.[5] This particular ion cluster appeared, in all instances, to be observable free from interference by ions resulting from other competing processes. The calculated per cent deuterium content (following a correction for natural abundance ^{13}C) at the designated sites was 96–97% for each of the di- and polyamines. This high level of isotopic enrichment greatly facilitated analysis of the mass spectra since essentially all of the ion intensity was expressed in the $^2H_{max}$ and $^2H_{max-1}$ ions. For example, for compound **17** (97% $^2H_8$) the intensities of ions in $^2H_{max}$ ion clusters are $^2H_8$, 77%, and $^2H_7$, 20%; for compounds **7, 10, 13,** and **16,** which possess equally high isotopic enrichments and fewer enriched sites, $^2H_{max}$ ions account for more than 80% of the total intensities of ion isotope clusters. As a result, the isotopic contents of ions in the various mass spectra can be determined qualitatively by inspection. The fact that the calculated isotopic enrichment levels of certain ions produced by simple fragmentation processes appear to be slightly lower than those calculated using the $^2H_{max}$ ions noted suggests that hydrogen scrambling may be occurring to a limited extent; it does not interfere with the analyses presented.

Table II. Principal Ions Observed in Mass Spectra of Tetra(trimethylsilyl)-1,3-diaminopropanes 3–5

Ion, m/e			Relative intensity,[a] %	Structure assignment
3	**4** (d_6)	**5** (d_{36})		
362	368	398	0.8	$M^{+\cdot}$
347	353	380	0.6	$[M-Me]^+$
273	278	297	0.2	$(TMS)_2NCH_2CH_2\text{-}CH{=}NSi^+Me_2$
259	265	297	1	
201	206	219	65	$\cdot CH_2CH_2CH{=}N(TMS)_2$
174	176	192	100[b]	$CH_2{=}N^+(TMS)_2$
172	175	187	26	$CH_2{=}CHN(TMS)\text{-}Si^+Me_2$
160	163	175	48	$CH_2{=}N^+(TMS)Si\text{-}Me_2H$
130	130	142	5	$[(Me_2Si)_2N]^+$
100	101	109	6	$HC{\equiv}N^+TMS$
86	88	92	14	$CH_2{=}NSi^+Me_2$

[a] Relative intensities are for ions in the spectrum of the nondeuterated analogue **3.** [b] Σ_{80} = 27%.

Table III. Principal Ions Observed in Mass Spectra of Tetra(trimethylsilyl)-1,4-diaminobutanes 6–8

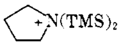
Ions, m/e			Relative intensity,[a] %	Structure assignment
6	**7** (d_4)	**8** (d_{36})		
376	380	412	2	$M^{+\cdot}$
361	365	394	5	$[M-Me]^+$
214	217	232	14	
200	204	215	8	$CH_2{=}CHCH_2CH_2N\text{-}(TMS)Si^+Me_2$
187	188	205	2.3	$CH_2{=}CH\dot{N}^+(TMS)_2$
174	176	192	100[b]	$CH_2{=}N^+(TMS)_2$
130	130	142	4.7	$[(Me_2Si)_2N]^+$
100	101		4.5	$HC{\equiv}N^+TMS$
86	88	92	9	$CH_2{=}NSi^+Me_2$

[a] Relative intensities are for ions in the spectrum of the nondeuterated analogue **6.** [b] Σ_{80} = 39%.

Rearrangements. A variety of electron-impact induced rearrangements are known which involve trimethylsilyl groups. These rearrangements often involve migration of groups containing a heteroatom to the charged silicon center generated by the loss of a TMS methyl radical.[1] Phenyl groups have also been shown to migrate to the silicon center under electron impact.[1a,12] Groups have been shown to migrate from both near and remote positions, relative to the TMS group, showing little sensitivity to ring size for the transition state.

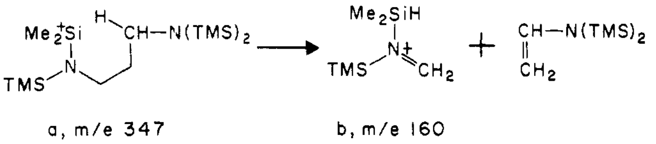
McLafferty-Type Rearrangements. McLafferty rearrangements have been extensively reviewed;[13] the reported participation of TMS groups in McLafferty rearrangements has been limited to that of a migration species. Migrations of a TMS group to carbonyl oxygen and sp^2 carbon have been reported.[14] The mass spectrum of trimethylsilylated 1,3-diaminopropane **3** exhibits a relatively intense ion (b, 48% of the base ion) at m/e 160, which is due to a quite different McLafferty-type rearrangement of an even-electron ion (a, m/e 347) involving hydrogen migration to silicon (Scheme I).

Table IV. Principal Ions Observed in Mass Spectra of Tetra(trimethylsilyl)-1,5-diaminopentanes 9–11

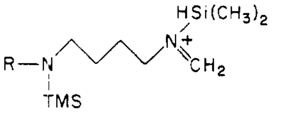
Ion, *m/e*			Relative intensity,[a] %	Structure assignment
9	10 (d_4)	11 (d_{36})		
390	394	426	1.2	$M^{+\cdot}$
375	399	408	16	$[M-Me]^+$
229	232	247	1.1	$\cdot CH_2CH_2CH_2CH_2-CH{=}N^+(TMS)_2$
216	218	234		
200	201	218	2	$CH_2{=}CH{-}CH{=}N^+(TMS)_2$
174	176	192	100[b]	$CH_2{=}N^+(TMS)_2$
130	130	142	4	$[(Me_2Si)_2N]^+$
100	101	109	4	$HC{\equiv}N^+TMS$
86	88	92	5	$CH_2{=}NSi^+Me_2$

[a] Relative intensities are for ions in the spectrum of the nondeuterated analogue **9**. [b] Σ_{80} = 45%.

Scheme I



Ions derived from similar rearrangements are observed in spectra of the 1,8-diamino-4-azaoctane (spermidine) and 1,12-diamino-4,9-diazadodecane (spermine)[15] derivatives (**12–14** and **15–18**, respectively) which possess trimethylsilylated 1,3-diaminopropane moieties. Because these derivatives (**12–18**) are unsymmetrical about the 1,3-diaminopropane molecular segment, the rearrangement in each case gives rise to two ions. In addition to ion b (*m/e* 160), ions c (*m/e* 303) and d (*m/e* 432) are observed in the spectra of TMS derivatives of 1,8-diamino-4-azaoctane (spermidine, **12**) and 1,12-diamino-4,9-diazadodecane (spermine, **15**), respectively. That the rearrangement involves, at least primarily,[16] migration of a hydrogen α to the adjacent uncharged amine center is demonstrated by changes in *m/e* values for the corresponding ions observed in the spectra of analogues **13, 16,** and **17** (Tables V and VI) in which specific α hydrogens have been replaced by deuterium.

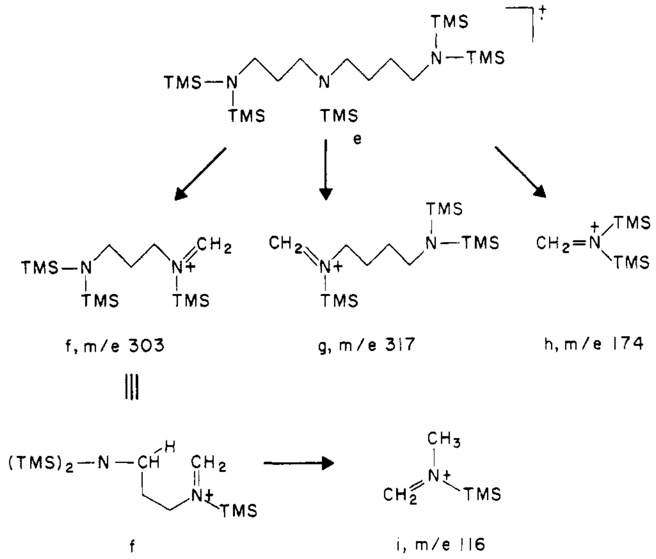


c, R = TMS; m/e 303
d, R = $(CH_2)_3N(TMS)_2$; m/e 432

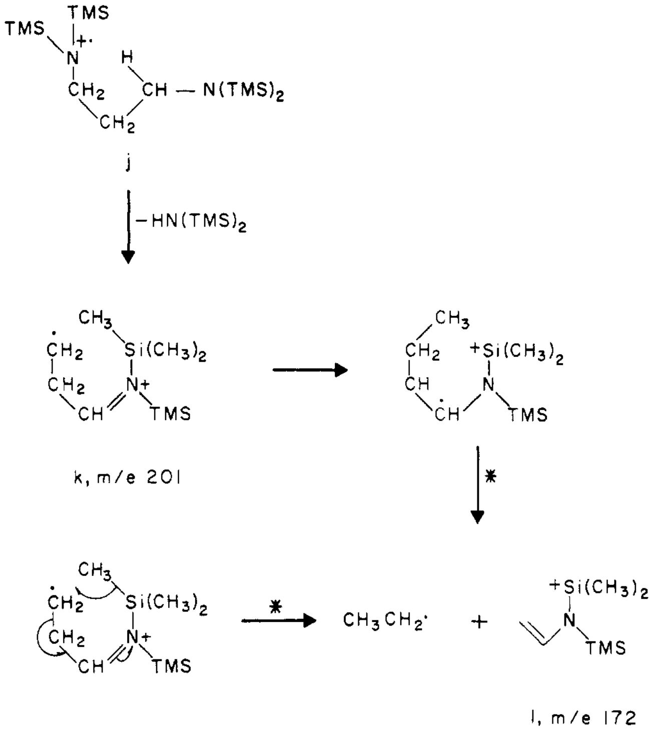
Rearrangements of hydrogen to silicon previously have been reported in the elimination of an olefin from a siliconium ion.[17] The migrating hydrogen in these rearrangements has been shown to originate from the β-carbon.[18]

Ion i (*m/e* 116), observed in the spectra of penta(trimethylsilyl)-1,8-diamino-4-azaoctane **12** and hexa(trimethylsilyl)-1,12-diamino-4,9-diazadodecane **15**, results from McLafferty-like rearrangement of another even-electron ion (f, *m/e* 303). This rearrangement, shown in Scheme II, involves 1,5 migration of a γ hydrogen as shown by deuterium labeling (Tables V and VI).[16] Previous reports have described McLafferty rearrangements involving even-electron immonium ions which were not specific for the β hydrogen;[19] the selectivity of hydrogen transfer in the present case[16] is presumably due to stabilization of the resulting carbon radical by the adjacent amine center.

Scheme II

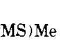


Scheme III



1,5-Methyl Migration. Ion k (65% of the base ion intensity) at *m/e* 201 in the spectrum of the 1,3-diaminopropane TMS derivative **3** appears to be derived from the molecular ion by abstraction of a hydrogen α to one nitrogen by the other nitrogen followed by loss of disilazane (Scheme III). Ion k further decomposes to an ion l at *m/e* 172 (26% of the base ion) as established by the appearance of a metastable ion centered at *m/e* 147. This process can be explained by a 1,5-methyl rearrangement followed by the loss of an ethyl radical to yield the resonance-stabilized ion l. As shown in Scheme III, the formation of ion l may be either a synchronous process or a two-step sequence. Ions k (*m/e* 201) and l (m/e 172) are also present in the spectra of the polyamine TMS derivatives **12** and **15**, which also possess the trimethylsilylated 1,3-diaminopropane moiety. The change in *m/e* value for ion k in the spectra of the isotopically labeled analogues of these polyamine derivatives (Tables V and VI). again indicates the primary origin of the hydrogen abstracted.[16] The polyamine derivatives **12** and **15**, which are unsymmetrical about the

Table V. Principal Ions Observed in Mass Spectra of Penta(trimethylsilyl)-1,8-diamino-4-azaoctanes (Spermidines) 12–14

Ions, *m/e*			Relative intensity,[a] %	Structure assignment
12	13 (d_6)	14 (d_{45})		
505	511	550	0.5	$M^{+\cdot}$
490	496	532	6	$[M-Me]^+$
344	350	371	6	$\cdot CH_2CH_2CH{=}N^+(TMS)(CH_2)_4N(TMS)_2$
317	321	344	6	$CH_2{=}N^+(TMS)(CH_2)_4N(TMS)_2$
303-A	308	327	3.5[b]	$CH_2{=}N^+(SiMe_2H)(CH_2)_4N(TMS)_2$
303-B	307	330	3.5[b]	$CH_2{=}N^+(TMS)(CH_2)_3N(TMS)_2$
214	217	232	12	 $^+N(TMS)_2$
201	202	219	22	$\cdot CH_2CH_2CH{=}N^+(TMS)_2$
174	176	192	97	$CH_2{=}N^+(TMS)_2$
172	173	187	29	$CH_2{=}CHN(TMS)Si^+Me_2$
160	162	175	36	$CH_2{=}N^+(TMS)SiMe_2H$
156	160	165	39	$CH_2{=}CHCH_2CH_2N^+(TMS){=}CH_2$
144	149	153	100[c]	 $^+$NHTMS, $CH_2{=}N^+(TMS)C_3H_7$,  $N^+(TMS)Me$
116	119	125	63	$CH_2{=}N^+(TMS)Me$
86	88	92	36	$CH_2{=}NSi^+Me_2$

[a] Relative intensities are for ions in the spectrum of the nondeuterated analogue 12. [b] This intensity represents the sum of the *m/e* 303-A and *m/e* 303-B ions, which are present in a 2:1 ratio as determined from the spectra of 13 and 14. [c] Σ_{80} = 12%.

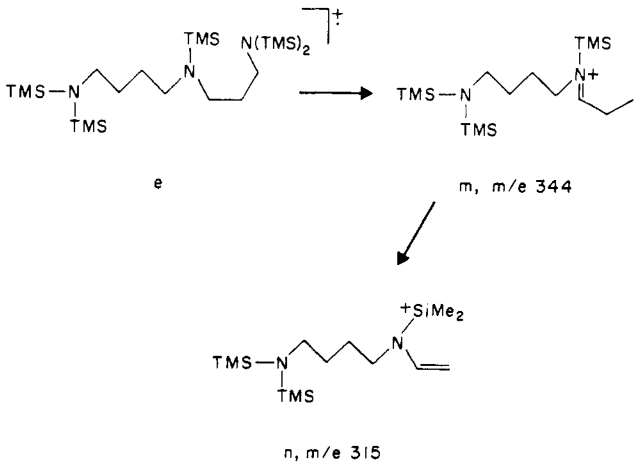
Table VI. Principal Ions Observed in Mass Spectra of Hexa(trimethylsilyl)-1,12-diamino-4,9-diazadodecanes (Spermines) 15–18

Ions, *m/e*				Relative intensity,[a] %	Structure assignment
15	16 (d_4)	17 (d_8)	18 (d_{54})		
634	638	642	688	0.2	$M^{+\cdot}$
619	623	617	670	2.0	$[M-Me]^+$
446	448	452	482	1.5	$CH_2{=}N^+(TMS)(CH_2)_4N(TMS)(CH_2)_3N(TMS)_2$
432	435	439	465	0.6	$CH_2{=}N^+(SiMe_2H)(CH_2)_4N(TMS)(CH_2)_3N(TMS)_2$
329	331	332	356	14	$CH_2{=}CHCH{=}N^+(TMS)(CH_2)_3N(TMS)_2$
303	305	307	330	3	$CH_2{=}N^+(TMS)(CH_2)_3N(TMS)_2$
201	202	202	219	44	$\cdot CH_2CH_2CH{=}N^+(TMS)_2$
174	176	176	192	94	$CH_2{=}N^+(TMS)_2$
172	173	173	187	32	$CH_2{=}CHN(TMS)Si^+Me_2$
160	162	162	175	73	$CH_2{=}N^+(TMS)SiMe_2H$
156	156	160	165	38	$CH_2{=}N^+(TMS)(CH_2)_2CH{=}CH_2$
144	146	149	153	100[b]	 NHTMS, $CH_2{=}N^+(TMS)C_3H_7$,  $N^+(TMS)Me$
116	117	119	125	89	$CH_2{=}N^+(TMS)Me$
86	88	88	92	44	$CH_2{=}N(TMS)Si^+Me_2$

[a] Relative intensities are for ions in the spectrum of the nondeuterated analogue 15. [b] Σ_{80} = 8.7%.

1,3-diaminopropane unit, show the same process at the carbon-substituted ends, giving rise to ions at higher *m/e* values (see, e.g., Scheme IV). These higher mass ions, however, are of much lower abundance, and no corresponding metastable ions are observed.

Scheme IV



These processes appear to be among the few authenticated cases of a 1,5-alkyl rearrangement occurring in a mass spectrometer. Goldsmith et al. have reported a 1,5-methyl migration in a McLafferty-type rearrangement in the spectrum of dipropyl ketoxime.[9] A possible 1,5-methyl rearrangement ion in the mass spectrum of acetophenone azine can also be accounted for by a 1,3 migration,[10] a process encountered more frequently in mass spectrometry. Also, a 1,5-phenyl rearrangement has been reported in the mass spectral decomposition of 3-(β-hydroxy-β-phenylethyl)-2-iminothiazolidine.[17]

Polyamine Base Ion. In the mass spectra of both penta(trimethylsilyl)-1,8-diamino-4-azaoctane 12 and hexa(trimethylsilyl)-1,12-diamino-4,9-diazadodecane 15 the base ion appears at *m/e* 144. In the spectra of the deuterated analogues 13 and 17 the mass of this ion is shifted to *m/e* 149, while that of the deuterated analogue 16 shifts to *m/e* 146.[16] Derivatization with deuterated TMS reagents shifts the base ion to *m/e* 153 (14 and 18), indicating the presence of three TMS derived methyl groups.[16] Keeping the number of bonds to be broken and formed to a minimum, these data suggest the

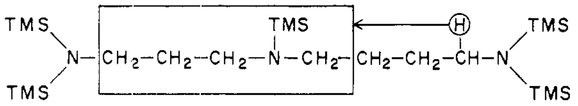
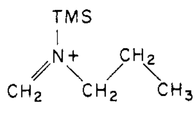


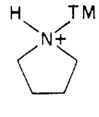
Figure 1. Composition of ion at *m/e* 144 for derivative **12**.

composition of the ion at *m/e* 144 to be that shown in Figure 1.

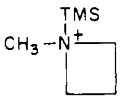
The data require that a α hydrogen at one end of the butylene group be abstracted by another atom at or near the other end of this alkyl chain as shown in Figure 1. Structure o for this ion at *m/e* 144 can be formed from four bond breaking and formation steps; two other possible structures for this ion (p and q) each require five steps.



o



p



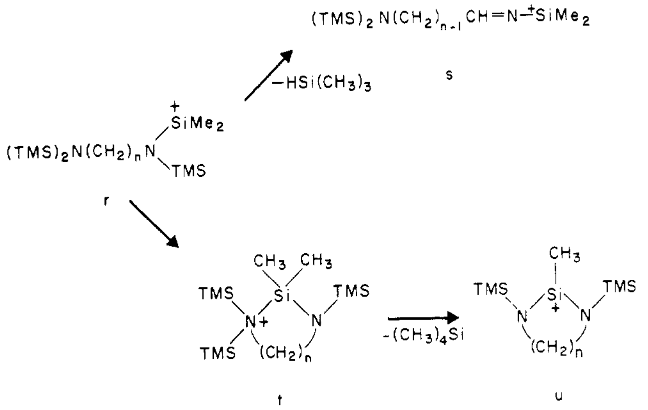
q

Sterically Induced Rearrangements. The longer chain trimethylsilylated diamine homologues exhibit the simplest mass spectra. The base ion h (*m/e* 174) in the mass spectra of all of the diamine derivatives arises by cleavage between the α and β-carbons, giving the stabilized immonium structure. In the mass spectrum of the TMS derivative of 1,5-diaminopentane (Table IV), this ion constitutes 45% of the total ionization (Σ_{80}). In the shorter chain homologues, the proximity of the amine centers gives rise to a wider variety of ions.

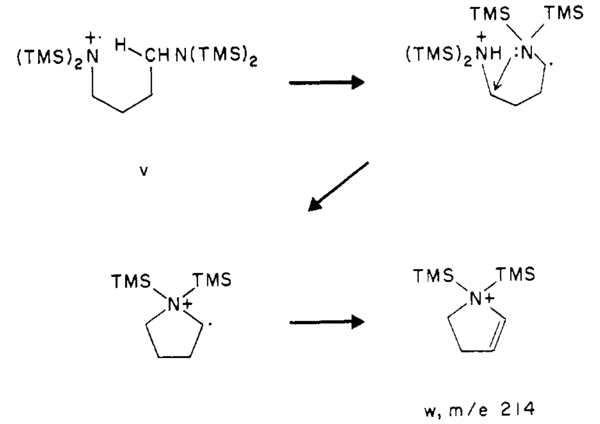
The spectra of the shorter chain diamine TMS derivatives exhibit ions at M − 89 and M − 103, i.e., *m/e* 259 and 245 for **1**, *m/e* 273 and 259 for **3**, and *m/e* 287 and 273 for **6**. The intensities of these two ions are 4 and 6%, respectively, for the diaminoethane derivative **1** and decrease with increasing chain length to 0.04 and 0.1% for the diaminobutane derivative **6**. Neither process is observed in the spectra of higher homologues. The proposed pathways (Scheme V) leading to these ions, assigned structures s and u, respectively, are consistent with the mass changes exhibited by the various deuterium labeled analogues.[16] The trend for these ions to become more intense with shorter methylene chain length suggests that these processes occur to relieve the steric strain between the four TMS groups. The process producing ion s has, however, been shown to occur as a decomposition pathway of *N*-ethyldisilazane, in which case the hydrogen migration is specifically from the α-carbon.[8a] Ion u arises from cyclization of ion r followed by expulsion of tetramethylsilane. Bond formation between a positively charged silicon atom and an atom bearing either nonbonding or π electrons is a process frequently invoked to explain rearrangements of trimethylsilyl compounds in which a neutral fragment is lost.[1] Although this process should be favored by the formation of five- and six-membered rings, similar intramolecular ring formation has been observed in longer chain aliphatic systems.[1d,e]

An ion of significant abundance (14% of the base ion) in the spectrum of the 1,4-diaminobutane TMS derivative **6** appears at *m/e* 214. The probable structure of this ion (w) and a plausible mode for its formation are shown in Scheme VI. This process parallels that outlined by Mayerl and Hesse[3c] for a similar decomposition of underivatized 1,4-diaminobutane (putrescine).

Scheme V



Scheme VI



Experimental Section

Instrumental. Mass spectra were obtained using a DuPont 21-491B mass spectrometer interfaced with a Varian 2700 gas chromatograph and were recorded on oscillographic recording paper. The ionizing voltage was 70 eV, and the source temperature was 270 °C. The gas chromatograph was equipped with a 1.2 m × 2 mm glass column packed with 1.5% OV-101 coated 100–120 mesh Gas Chrom Q.

Materials. The nondeuterated amines 1,3-diaminopropane, 1,2-diaminoethane, 1,4-diaminobutane dihydrochloride, 1,5-diaminopentane dihydrochloride, 1,8-diamino-4-azaoctane trihydrochloride, and 1,12-diamino-4,9-diazadodecane tetrahydrochloride were obtained commercially. Standard 1.0 mM solutions of each amine were prepared in 1.0 N aqueous hydrochloric acid.

1,3-Diaminopropane-*1,1,2,2,3,3-*d_6 Dihydrochloride. Malononitrile (100 mg, 1.52 mmol) was dissolved in 10 mL of *O*-deuterioethanol (95% in deuterium oxide, 99% *d*), 1.0 mL of deuterium chloride (37% in deuterium oxide) and 100 mg of platinum oxide were added, and the mixture was shaken under 30 psi of deuterium gas (99.5% *d*) until gas uptake ceased. The mixture was filtered to remove the platinum, and the solvents were removed under reduced pressure to give an off-white solid. Recrystallization of the product from 100% ethanol yielded 104 mg of 1,3-diaminopropane-*1,1,2,2,3,3*-d_6 dihydrochloride, mp 248–250 °C (lit. mp 243 °C[20] for unlabeled 1,3-diaminopropane dihydrochloride).

1,4-Diaminobutane-*1,1,4,4*-d_4 Dihydrochloride. Preparation of this diamine, similar to that described for deuterated 1,3-diaminopropane, utilized 0.80 g (10 mmol) of succinonitrile, 20 mL of *O*-deuterioethanol, 3 mL of deuterium chloride solution, and 100 mg of platinum oxide. Recrystallization of the isolated product from 100% ethanol gave 0.66 g of 1,4-diaminobutane-*1,1,4,4*-d_4 dihydrochloride, mp >310 °C (lit. mp 290[21] and 315 °C[22] for unlabeled 1,4-diaminobutane dihydrochloride).

1,5-Diaminopentane-*1,1,5,5*-d_4 Dihydrochloride. Preparation of this diamine, similar to that described for deuterated 1,3-diaminopropane, utilized 0.94 g (10 mmol) of glutaronitrile in 20 mL of *O*-deuterioethanol and 3 mL of deuterium chloride solution and 100 mg of platinum oxide. Recrystallization of the isolated product from 100% ethanol gave 0.96 g of 1,5-diaminopentane-*1,1,5,5*-d_4 dihydrochloride, mp 258–260 °C (lit. mp 255[23] and 275 °C[22] for unlabeled 1,5-diaminopentane dihydrochloride).

1,12-Diamino-4,9-diazadodecane-*1,1,12,12*-d_4 Tetrahydrochloride. This compound was prepared by the addition of 2 equiv of acrylonitrile to 1,4-diaminobutane (as described by Tabor et al.[24]) followed by catalytic deuteration of the nitrile groups as described above for deuterated 1,3-diaminopropane. The product, 1.8 g, was recrystallized by dissolving it in 13 mL of 12% aqueous HCl and adding this solution to 130 mL of hot 100% ethanol.[25] Upon cooling, 1.1 g was obtained of crystalline 1,12-diamino-4,9-diazadodecane-*1,1,12,12-*d_4 tetrahydrochloride, mp 299–308 °C (lit. mp 310–311 °C[25] for the unlabeled tetrahydrochloride salt).

1,8-Diamino-4-azaoctane-*1,1,5,5,8,8-*d_6 Trihydrochloride and 1,12-Diamino-4,9-diazadodecane-*1,1,5,5,8,8,12,12-*d_8 Tetrahydrochloride. To a suspension of 0.16 g (1.0 mmol) of 1,4-diaminobutane-*1,1,4,4-*d_4 dihydrochloride in 20 mL of ethanol was added 0.2 mL of 3.8 N aqueous NaOH, and the mixture was stirred for 10 min. Acrylonitrile (60 μL, 0.9 mmol) was added slowly, and the mixture was stirred for 24 h. The reaction was quenched with 2.0 mL of 6 N HCl, and the solvents were completely removed under reduced pressure. The residue was dissolved in 15 mL of deuterium oxide followed by the addition of 1.0 mL of 37% deuterium chloride and 50 mg of platinum oxide. This mixture was shaken under 30 psi of deuterium for 36 h. The platinum was removed by filtration, and the solvent was removed to dryness. The solid residue was dissolved and diluted to 50 mL using 1.0 N HCl. The concentrations of the various components of this solution were determined by selected ion monitoring analysis of an equal volume mixture of this solution and a solution 1.0 mM in each of the nondeuterated di- and polyamines. The concentrations were 5.2, 7.3, and 2.5 mM for 1,4-diaminobutane-*1,1,4,4-*d_4, 1,8-diamino-4-azaoctane-*1,1,5,5,8,8-*d_6, and 1,12-diamino-4,9-diazadodecane-*1,1,5,5,8,8,12,12-*d_8, respectively.

Per Cent Deuterium Incorporation. The di- (**7** and **10**) and polyamines (**13**, **16**, and **17**) were trifluoroacetylated[5] and their mass spectra determined. The intensities of ions in the $[M - CF_3\cdot]^+$ ion isotope cluster were measured, and, following a correction for natural abundance ^{13}C, the per cent deuterium was calculated; in each compound the enrichment was 96–97% of the indicated level.

Trimethylsilylation. Aliquots taken from aqueous solutions of the various di- and polyamine hydrochlorides were evaporated to dryness under a stream of nitrogen. The residue was treated with a 2:2:1 mixture of pyridine, *N,O*-bis(trimethylsilyl)acetamide, and trimethylchlorosilane and placed either in a sonic bath or a steam bath for 15 min. Upon cooling, the samples were examined by GC–MS, and the derivatizations were shown to be essentially complete to replace every N hydrogen with a trimethylsilyl group. Perdeuteriotrimethylsilylation was achieved in the same manner using a 2:2:1 mixture of pyridine, *N,O*-bis(tri(methyl-d_3)silyl)acetamide, and tri(methyl-d_3)chlorosilane.

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Registry No.—**1**, 5577-69-5; **2**, 65898-72-8; **3**, 39772-64-0; **4**, 65898-73-9; **5**, 65898-74-0; **6**, 39772-63-9; **7**, 65372-71-6; **8**, 65898-75-1; **9**, 65898-76-2; **10**, 65898-77-3; **11**, 65898-78-4; **12**, 65898-79-5; **13**, 65898-80-8; **14**, 65898-81-9; **15**, 65898-82-0; **16**, 65898-83-1; **17**, 65898-84-2; **18**, 65898-85-3; malononitrile, 109-77-3; 1,3-diaminopropano-*1,1,2,2,3,3-*d_6 2HCl, 65898-86-4; succinonitrile, 110-61-2; 1,4-diaminobutane-*1,1,4,4-*d_4 2HCl, 65372-65-8; glutaronitrile, 544-13-8; 1,5-diaminopentane-*1,1,5,5-*d_4 2HCl, 65372-66-9; acrylonitrile, 107-13-1; 1,4-diaminobutane, 110-60-1; 1,12-diamino-4,9-diazadodecane-*1,1,12,12-*d_4 4HCl, 65898-87-5; 1,8-diamino-4-azaoctane-*1,1,5,5,8,8-*d_6 3HCl, 65372-67-0; 1,12-diamino-4,9-diazadodecane-*1,1,5,5,8,8,12,12-*d_8 4HCl, 65372-68-1; 1,4-diaminobutane 2HCl, 333-93-7; 1,5-diaminopentane 2HCl, 1476-39-7; 1,8-diamino-4-azaoctane 3HCL= 334–5]–9: [=[2–DIAMINO–4=9–DIAZA-DODECANE 4HCl, 306-67-2.

References and Notes

(1) See, for example, (a) J. Dieckman, J. B. Thompson, and C. Djerassi, *J. Org. Chem.*, **32,** 3904 (1967), and references cited therein; (b) W. J. Richter and A. L. Burlingame, *Chem. Commun.*, 1158 (1968); (c) G. Eglinton, C. H. Hunneman, and A. McCormick, *Org. Mass Spectrom.*, **1,** 593 (1968); (d) G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *ibid.*, **1,** 669 (1968); (e) E. White, V, and J. A. McCloskey, *J. Org. Chem.*, **35,** 4241 (1970); (f) W. P. Weber and H. G. Boettger, *Intra Sci. Chem. Rep.*, **7,** 109 (1973), and references cited therein; (g) W. P. Weber, R. A. Felix, and A. K. Willard, *J. Am. Chem. Soc.*, **91,** 6544 (1969); (h) T. Ito and W. P. Weber, *J. Org. Chem.*, **39,** 1691 (1974); (i) *ibid.*, **39,** 1694 (1974).

(2) See, for example, H. Bosshardt and M. Hesse, *Angew. Chem., Int. Ed. Engl.*, **13,** 252 (1974), and references cited therein.

(3) See, for example, (a) P.-A. Blanc, G. A. Singy, and A. Buchs, *Org. Mass Spectrom.*, **11,** 995 (1976); (b) G. Eckhardt, K. J. Goebel, G. Tondorf, and S. Goenechea, *ibid.*, **9,** 1073 (1974); (c) F. Mayerl and M. Hesse, *Helv. Chim. Acta*, **59,** 127 (1976); (d) F. Roessler and M. Hesse, *ibid.*, **60,** 380 (1977).

(4) See, for example, (a) H. J. Veith, A. Guggisberg, and M. Hesse, *Helv. Chim. Acta*, **54,** 653 (1971); (b) E. Lerch and M. Hesse, *ibid.*, **55,** 1883 (1972); (c) E. Schopp and M. Hesse, *ibid.*, **56,** 124 (1973); (d) A. Guggisberg, R. W. Gray, and M. Hesse, *ibid.*, **60,** 112 (1977).

(5) (a) R. G. Smith and G. D. Daves, Jr., *Biomed. Mass Spectrom.*, **4,** 146 (1977); (b) F. Bartos, D. Bartos, D. P. Grettie, R. A. Campbell, L. J. Marton, R. G. Smith, and G. D. Daves, Jr., *Biochem. Biophys. Res. Commun.*, **75,** 915 (1977); (c) R. G. Smith, G. D. Daves, Jr., and D. P. Grettie, "Advances in Polyamine Research", Vol. 2, R. A. Campbell, D. R. Morris, D. Bartos, G. D. Daves, Jr., and F. Bartos, Ed., Raven Press, New York, N.Y., 1978, pp 23–35.

(6) F. P. Abramson, M. W. McCaman, and R. E. McCaman, *Anal. Biochem.*, **57,** 482 (1974).

(7) Only a few studies have examined the mass spectral behavior of disilazanes.[8]

(8) See, for example, (a) J. Tamas and P. Miklos, *Org. Mass Spectrom.*, **10,** 859 (1975); (b) K. Bargstrom, J. Gurtler, and R. Blomstrand, *Anal. Biochem.*, **34,** 74 (1970); (c) O. Glemser and H. Kluver, *Chem. Ber.*, **103,** 366 (1970).

(9) D. Goldsmith, D. Becher, S. Sample, and C. Djerassi, *Tetrahedron Suppl.*, **7,** 145 (1966).

(10) S. E. Scheppele, R. D. Grigsby, E. D. Mitchell, D. W. Miller, and G. R. Waller, *J. Am. Chem. Soc.*, **90,** 3521 (1968).

(11) B. R. Webster, *Chem. Commun.*, 124 (1966).

(12) W. P. Weber, R. A. Felix, and A. K. Willard, *Tetrahedron Lett.*, 907 (1970).

(13) D. G. I. Kingston, J. T. Bursey, and M. M. Bursey, *Chem. Rev.*, **74,** 215 (1974).

(14) (a) W. P. Weber, R. A. Felix, and A. K. Willard, *J. Am. Chem. Soc.*, **92,** 1420 (1970); (b) W. P. Weber, A. K. Willard, and H. G. Boettger, *J. Org. Chem.*, **36,** 1620 (1971); (c) W. P. Weber, R. A. Felix, A. K. Willard, and H. G. Boettger, *ibid.*, **36,** 4060 (1971).

(15) The terminology used in this paper for the two polyamines is based upon the modified aza nomenclature (IUPAC Rule 814.6) for ease in naming specifically labeled deuterium analogues. The Chemical Abstracts nomenclature for spermidine and spermine are *N*-(3-aminopropyl)-1,4-butanediamine and *N,N'*-bis(3-aminopropyl)-1,4-butanediamine, respectively.

(16) The conclusions based on interpretation of spectra of deuterated analogues are qualitative in that accurate isotopic distributions of fragment and rearrangement ions were not determined. However, in every instance the ion noted is the most intense of the ion isotope cluster.

(17) (a) D. B. Chambers, F. Glackling, and J. R. C. Light, *Q. Rev., Chem. Soc.*, **22,** 317 (1968); (b) B. Y. K. Ho, L. Spialter, and L. D. Smithson, *Org. Mass Spectrom.*, **10,** 361 (1975).

(18) T. H. Kinstle, P. J. Ihrig, and E. J. Goettert, *J. Am. Chem. Soc.*, **92,** 1780 (1970).

(19) C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, **87,** 5752 (1965).

(20) T. Haga and R. Majima, *Chem. Ber.*, **36,** 334 (1903).

(21) C. Naegeli and P. Lendorff, *Helv. Chim. Acta*, **15,** 49 (1932).

(22) G. Klein and D. Boser, *Arch. Pharm. Ber. Dtsch. Pharm. Ges.*, **270,** 374 (1932).

(23) S. T. Kanewskaja, *Zh. Russ. Fiz. Khim. Ova., Chast Khim.*, **59,** 649 (1927).

(24) C. W. Tabor, H. Tabor, and U. Bachrach, *J. Biol. Chem.*, **239,** 2194 (1964).

(25) H. P. Schultz, *J. Am. Chem. Soc.*, **70,** 2666 (1948).