0.55 g was obtained (29% yield): ir (neat) 2950, 2920, 2900, 2850, 1460, 1250, 980, 850, 800, 780, 760, 680 cm^{-1}; NMR (benzene) δ 0.34 (s, $SiMe_2$, 6 H), 0.44 (s, $SiMe_3$, 18 H), 1.27 (s, Si-*t*-Bu, 9 H).

Anal. Calcd for $C_{12}H_{33}NSi_3O$: C, 49.41; H, 11.43; N, 4.80; Si, 28.88. Found: C, 49.34; H, 11.43; N, 4.55; Si, 28.40.

References and Notes

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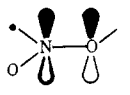
(14) The HOMO in tris(organosilyl)hydroxylamines has been calculated through ab Initio Gaussian lobe SCF computations to be i, which has the proper



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Irreversible Thermal Rearrangement of Tris(organosilyl)hydroxylamines[1]

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Abstract: Tris(organosilyl)hydroxylamines undergo a general, intramolecular rearrangement at temperatures of 180 °C and above to give silylaminosiloxanes with high product selectivity. An organosilyl group bound to nitrogen appears to insert into the N–O bond (see eq 1 in text). The reactions follow first-order kinetics over at least 4 half-lives with $t_{1/2}$ at 205 °C as follows: $(Me_3Si)_2NOSiMe_3$ (**1**), 5800; $(Me_3Si)_2NOSiMe_2$-*t*-Bu (**11**), 3600; $(Me_3Si)_2NOSiMe_2H$ (**5**), 2200; and $Me_3Si(PhMe_2Si)NOSiMe_3$ (**9**), 1800 s. Kinetic evidence and the high product selectivity rule out a simple one- or two-step mechanism. A three-step mechanism which is consistent with kinetic and product data is suggested, involving the formation of a tight radical pair followed by formation of a dipolar intermediate leading to product.

Introduction

In 1971, Boudjouk and West reported preliminary results on the thermal rearrangement of tris(organosilyl)hydroxylamines into isomeric silylaminosiloxane[2,3] (eq 1). This type

$$(R_3Si)_2NOSiR_3 \xrightarrow[\Delta]{O} R_3SiN(R)SiR_2OSiR_3 \qquad (1)$$

of hydroxylamine rearrangement is unique in both silicon and carbon chemistry.[4,5] It provides the first example of the insertion of an organosilicon moiety into the nitrogen–oxygen bond[6] and is the first clear case in which a substituent is transferred from silicon to nitrogen.[7] The present study was undertaken to study effects of change of organosilyl substituents on the reaction and to try to determine the mechanism of rearrangement.

It was found during this study that tris(organosilyl)hydroxylamines, when heated, undergo a reversible intramolecular 1,2 exchange of organosilyl groups between oxygen and nitrogen. The kinetics and mechanism of this reversible rearrangement are discussed in a companion paper.[8]

Synthesis

The preparations of the tris(organosilyl)hydroxylamines are reported in the accompanying paper.[8] *N*- and *O*-methylbis(trimethylsilyl)hydroxylamines, **25** and **26,** were prepared by the method of Wannagat and Smrekar.[9] Three of the thermolysis products, compounds **10, 13,** and **22,** were synthesized by an alternate route for structure verification. This involved synthesis of an organosilyl-substituted alkyl or aryl amine,[10] which was deprotonated with *n*-butyllithium and treated with pentamethylchlorodisiloxane to give a silylaminosiloxane of known structure (eq 2). All compounds gave ir and ^1H NMR spectra consistent with proposed structures.

$$R_3SiCl + R'NH_2 \longrightarrow R_3SiN(R')H$$

$$R_3SiN(R')H \xrightarrow[2.\ Me_2SiOSiMe_2Cl]{1.\ n\text{-BuLi}} R_3SiN(R')SiMe_2OSiMe_3 \qquad (2)$$

10, $R_3 = Me_3$; $R' = Ph$
13, $R_3 = t$-$BuMe_2$; $R' = Me$
22, $R_3 = Et_3$; $R' = Me$

Results

The simplest compounds investigated are **1** and **3,** in which only one type of organosilyl group is present in the molecule. Both compounds react cleanly and quantitatively to give the

corresponding silylaminosiloxanes **2** and **4,** respectively (eq 3 and 4).

$$(Me_3Si)_2NOSiMe_3 \xrightarrow[190\ ^\circ C]{} Me_3SiN(Me)SiMe_2OSiMe_3 \quad (3)$$
1 **2**

$$(Et_3Si)_2NOSiEt_3 \xrightarrow[190\ ^\circ C]{} Et_3SiN(Et)SiEt_2OSiEt_3 \quad (4)$$
3 **4**

For tris(organosilyl)hydroxylamines with different organosilicon groups in the same molecule, several silylaminosiloxane isomers might be formed by thermal rearrangement. It is rather surprising that in many cases only one isomer is produced to the exclusion of all others. For example, the thermal rearrangement of **5** or **6** yields only the N–H product, **7,** in quantitative yield (eq 5). In this system the reversible

$$(Me_3Si)_2NOSiMe_2H \rightleftharpoons \begin{matrix} Me_3Si \\ HMe_2Si \end{matrix}\!\!>\!NOSiMe_3 \longrightarrow Me_3SiN(H)SiMe_2OSiMe_3 \quad (5)$$
5 **6** **7**

rearrangement, **5** ⇌ **6,** is known to occur at a much lower temperature (140–160 °C) than the rearrangement to **7.**[8] At 190 °C, either pure hydroxylamine isomer will form an equilibrium mixture of both isomers within a few minutes (K_{eq} [**5**]/[**6**] = 0.24). We believe that **7** is formed only from compound **6** (see Discussion). Similarly, thermolysis of **8** or **9** yields only the *N*-phenylsilylaminosiloxane **10** in greater than 95% yield[11] (eq 6). Compounds **8** and **9** also undergo the positional

$$(Me_3Si)_2NOSiMe_2Ph \rightleftharpoons \begin{matrix} PhMe_2Si \\ Me_3Si \end{matrix}\!\!>\!NOSiMe_3 \longrightarrow Me_3SiN(Ph)SiMe_2OSiMe_3 \quad (6)$$
8 **9** **10**

exchange isomerism, **8** ⇌ **9** (K_{eq} [**8**]/[**9**] = 0.49),[8] with **10** apparently coming from compound **9** (see Discussion).

Thermolysis of **11** also gives a single product, **12,** in nearly quantitative yield (eq 7). Spectral means did not allow us to

$$(Me_3Si)_2NOSiMe_2t\text{-}Bu \xrightarrow[190\ ^\circ C]{} Me_3SiN(Me)SiMe_2OSiMe_2t\text{-}Bu \quad (7)$$
11 **12**

distinguish between **12** and its isomer **13.** Compound **13** was

$$t\text{-}BuMe_2SiN(Me)SiMe_2OSiMe_3$$
13

synthesized by alternate synthesis (eq 2) and shown to have a different ^1H NMR spectrum than the thermolysis product of **11** (see Figure 1), establishing the above structure for **12.** Compound **14** (the positional isomer of **11**) yields an inseparable mixture of products under thermolysis conditions (eq 8). The ^1H NMR of the mixture indicates that **13** is present as the major product along with one other compound, probably having the structure **15,** since it has an *N*-methyl resonance. None of compound **12** was detected by ^1H NMR. This is in agreement with previous findings that there is no exchange isomerism in *tert*-butyldimethylsilylhydroxylamines.[8]

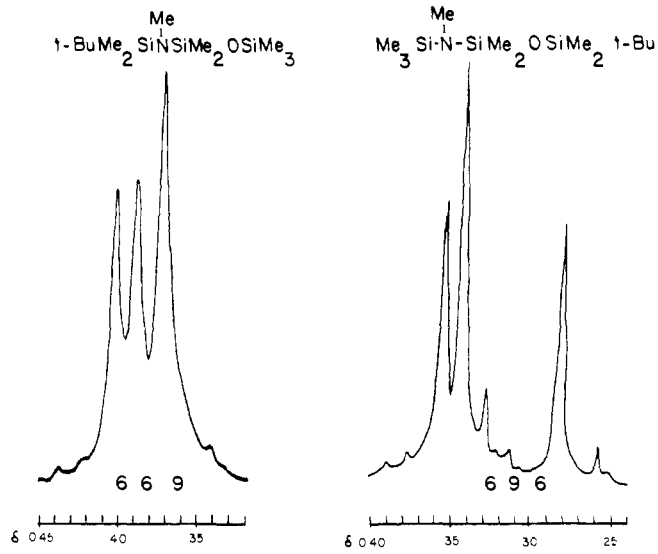


Figure 1. Proton NMR spectra in the silylmethyl region for compound **13** (left) and compound **12** (right).

$$\begin{matrix} Me_3Si \\ t\text{-}BuMe_2Si \end{matrix}\!\!>\!NOSiMe_3$$
14

$$\xrightarrow[190\ ^\circ C]{} t\text{-}BuMe_2SiN(Me)SiMe_2OSiMe_3 + Me_3SiN(Me)SiMe(t\text{-}Bu)OSiMe_3 \quad (8)$$
13 **15**

Compound **16** rearranges with insertion of a *tert*-butyldimethylsilyl group into the nitrogen bond and transfer of a methyl group to nitrogen (eq 9). Alternate synthetic attempts

$$(t\text{-}BuMe_2Si)_2NOSiMe_3 \xrightarrow[190\ ^\circ C]{} t\text{-}BuMe_2SiN(Me)SiMe(t\text{-}Bu)OSiMe_3 \quad (9)$$
16 **17**

to produce **17** failed, but the structure was established by hydrolysis to the known *tert*-butyldimethylsilanol (**18**) and the disiloxane **19.**

$$17 \xrightarrow[\Delta]{H^+,\ H_2O} t\text{-}BuMe_2SiOH + [Me_3SiOSiMe(t\text{-}Bu)]_2O \quad (10)$$
18 **19**

The structure of **19** was verified by spectral methods (see Experimental Section).

Compound **20,** heated to 190 °C for 20 h, yielded all three possible silylaminosiloxane products, **21, 22,** and **23,** accounting for quantitative conversion of starting material (eq 11).[12] Similarly, **24,** under the same conditions, rearranges

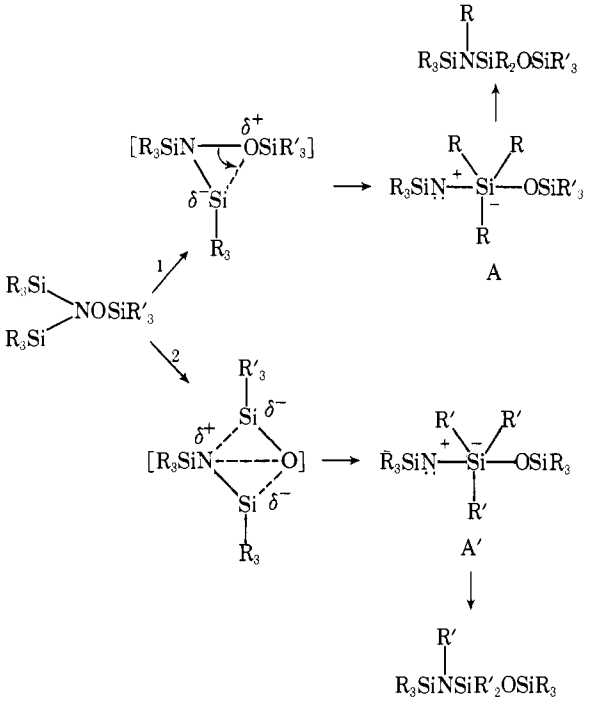
$$(Me_3Si)_2NOSiEt_3 \xrightarrow[190\ ^\circ C]{} Me_3SiN(Et)SiEt_2OSiMe_3$$
20 **21** 29%

$$+ Et_3SiN(Me)SiMe_2OSiMe_3 + Me_3SiN(Me)SiMe_2OSiEt_3 \quad (11)$$
22 29% **23** 42%

quantitatively into **21, 22,** and **23,** but the product ratios were significantly different (eq 12).

$$\begin{matrix} Et_3Si \\ Me_3Si \end{matrix}\!\!>\!NOSiMe_3 \xrightarrow[190\ ^\circ C]{} \mathbf{21} + \mathbf{22} + \mathbf{23} \quad (12)$$
24 40% 40% 20%

Scheme I



Thermolyses of a few alkyl-substituted hydroxylamines were attempted to determine if the reaction was general for any silyl-substituted hydroxylamine.[13a,b] Surprisingly, *O*-methyl-*N*,*N*-bis(trimethylsilyl)hydroxylamine (**25**) is unaltered even after 24 h at 200 °C. Only a slight yellowing occurs and the ^{1}H NMR is unchanged. When *N*-methyl-*N*,*O*-bis(trimethylsilyl)hydroxylamine (**26**) is heated to 190 °C, it decomposes rapidly to give hexamethyldisiloxane (**27**), a white polymer, and tar.[14] Zon and his co-workers have recently reported similar results for this compound.[15] *N*,*N*-Diethyl-*O*-trimethylsilylhydroxylamine (**28**) decomposes at 190 °C to yield **27**, tar, and a volatile product, possibly ethylamine. The thermal rearrangement does not appear to apply to alkyl-substituted silylhydroxylamines, but the difference in stability between **25** and **26** at high temperatures may indicate that the presence of an organosilyl group on oxygen is necessary for thermal reaction to proceed easily.[16]

Discussion

Boudjouk and West have suggested two possible mechanistic pathways for the rearrangement reaction[2] (Scheme I). Pathway 1 involves insertion of the silicon bonded to nitrogen into the nitrogen-oxygen bond, whereas in pathway 2 the silicon bonded to oxygen becomes inserted. The first point which must be settled in connection with the mechanism is which of these possibilities is correct.[17]

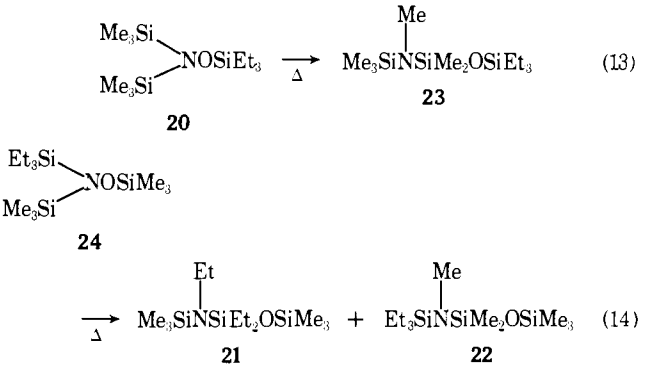
There are two compounds for which the evidence is unequivocal. Compound **11** rearranges to give only **12** and compound **16** yields only **17**; both of the products are ones resulting from insertion of the nitrogen-bound silicon into the N-O bond. Neither **11** nor **16** undergoes dyotropic exchange of organosilicon substituents to give isomeric trisorganosilylhydroxylamines,[8] so that we are dealing with a single reactant in each case.

Results of the thermolysis of **20** and **24** also indicate that the silicon atom initially attached to nitrogen becomes inserted. Rearrangement of **20** and **24** yields the same three products, but in different amounts (eq 11 and 12). A gas chromatographic study of the products as a function of time (Table I) shows that the products from N-Si insertion are formed in the greatest amount early in the reaction (eq 13 and 14). It is only after approximately 5 h at 190 °C that the ratios of **21**, **22**, and **23** approach final reaction-product distributions. These shifts in product proportions during the thermolysis can be accounted for by simultaneous partial interconversion of **20** and **24**.[8] The silylaminosiloxane products are stable at 200 °C; if pure **22** obtained by alternate synthesis is subjected to thermolysis conditions, no trace of **21** or **23** is detected by VPC. The difference in final product distributions from **20** and **24** also eliminates the possibility of a common reaction intermediate for isomeric trisorganosilylhydroxylamines, such as tris(organosilyl)amine oxide, $(R_3Si)_3N \rightarrow O$.[18]

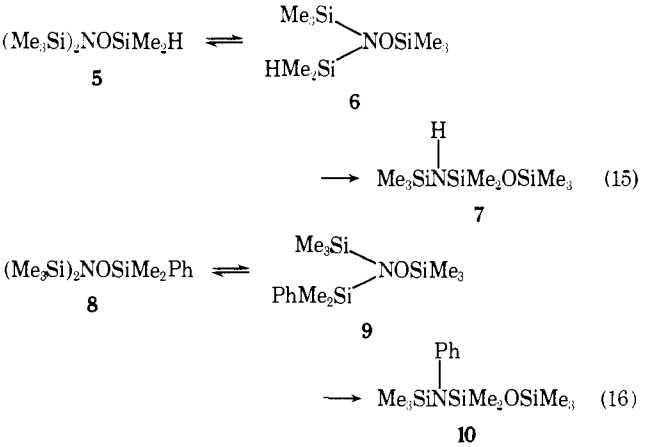
Table I. Relative Ratios of Products from Thermolysis of Bis(trimethylsilyl)triethylhydroxylamines[a]

	Time at 190 °C	% conversion	Ratio of products 23	22	21
20	90 min	9	86	7	7
	270 min	62	50	25	25
	320 min	74	48	26	26
	20 h	100	42	29	29
24	180 min	35	10	45	45
	300 min	66	18	41	41
	20 h	100	20	40	40

[a] Percentages determined by integration of peak areas from VPC analysis.



From the above results, it is clear that different tris(organosilyl)hydroxylamine isomers produce different products and that an organosilyl group bound to nitrogen inserts into the nitrogen-oxygen bond. Therefore, compound **7** is most probably formed only from **6** (eq 15) and compound **10** only from **9** (eq 16).



Kinetics and Mechanism

Results of kinetic studies of the rate of rearrangement of compounds **1**, **5**, **9**, and **11** are shown in Figure 2 and Table II. The rates are all first order in reactant over at least 4 half-lives. The velocity of thermal rearrangement is only slightly affected

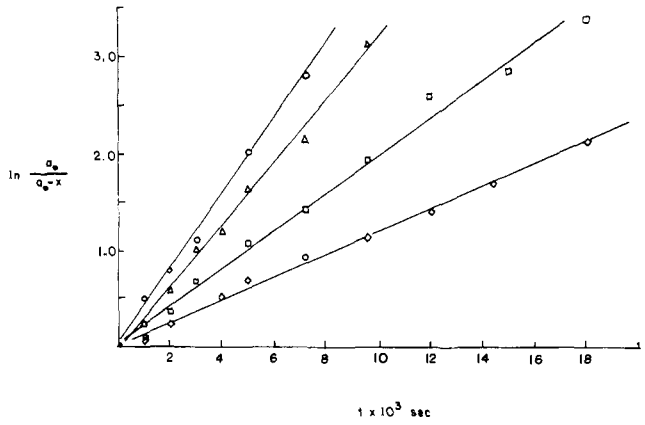


Figure 2. A plot of the logarithm of the appearance of silylaminosiloxane products vs. time for **1** (◇), **5** (△), **9** (○), and **11** (□) at 205 °C.

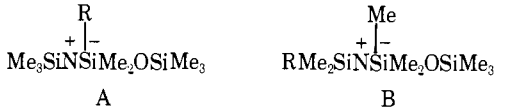
Table II. Rates of Thermal Rearrangement of Some Tris(organosilyl)hydroxylamines at 205 °C

Compd	$k \times 10^4$, s^{-1}
1 (neat)	1.16
1 (20% in PhCN)	1.05
1 (20% in decalin)	1.33
11 (neat)	1.92
5 (neat)	3.21
9 (neat)	3.85

by the nature of the substituents on silicon, the fastest rate being only 3.3 times as rapid as the slowest. The rate of rearrangement of **1** was studied in decalin and benzonitrile as well as neat and showed very little solvent dependence.[19]

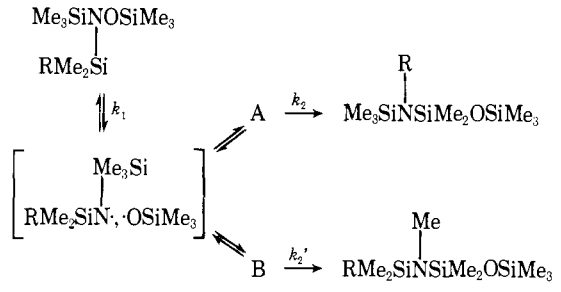
Although the substituents on silicon have little effect on the overall rate of rearrangement, they strongly affect the nature of the products. In the thermolysis of **5** (or **6**) only the N-H compound, **7**, was observed. Isomers with *N*-methyl groups could have been no more than 2% of the total. Likewise in the rearrangement of **8** or **9** the *N*-phenyl compound **10** is formed with a product specificity of at least 50:1. A major problem in interpreting the results is to reconcile this high product selectivity with the low rate selectivity.

It is apparent that the reaction must proceed in at least two steps, such that the product-determining step is different from the rate-determining step. Let us suppose that pathway 1 of Scheme I represents the mechanism which involves a rate-determining N-O bond insertion to give the dipolar intermediate A, followed by a product-determining migration of a substituent (H, methyl, or phenyl) to nitrogen. The last step is compatible with the observed products in that H or phenyl is expected to migrate to a positive center more rapidly than methyl, but the high product specificity is nevertheless hard to explain.[20,21] The rearrangement of **5** or **8** can give rise to two different dipolar intermediates, A and B. The rates of formation of A and B should not be very different, since the overall rates are similar. Once intermediate B is formed, it would be expected to migrate a methyl group to give the *N*-methyl product, which is not observed.[22]

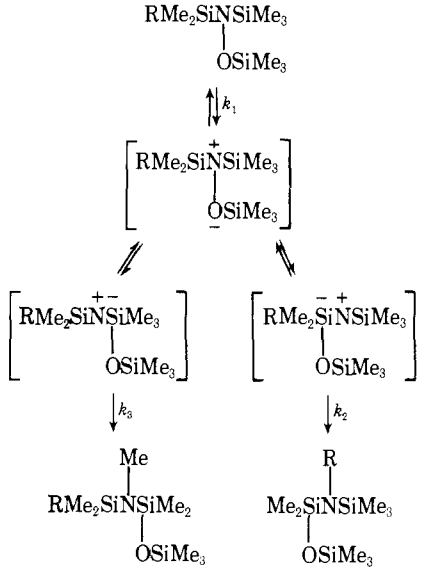


To avoid this problem it might be postulated that the formation of A and B from the reactant is reversible, and that the barrier to methyl migration is high enough so that B nearly always reverts to reactant. But this is incompatible with the observed kinetics, which show that the all-methyl compound **1** rearranges nearly as fast as **5** and **8**. If the intermediates A and B are formed in a pre-equilibrium step, the overall rate must reflect the rate of the final step, the migration of a substituent to nitrogen. The latter must be more rapid for hydrogen and phenyl than for methyl by at least a factor of 100.[23]

Scheme II



Scheme III



A possible three-step mechanism compatible with the observed results is shown in Scheme II. The first step is rate-determining homolytic cleavage of the N-O bond into a tight radical pair. This is followed by rapid, reversible attack of the siloxy radical on either silicon to give the dipolar intermediate A or B, which can either revert to radical pairs or undergo migration to product. Now if the barrier for methyl migration product is reasonably high, B will revert to radicals almost exclusively, so that the product will be almost entirely derived from A, and if the barrier for H or phenyl migration in A is low, the product specificity can be accounted for.[23]

This mechanism fits the kinetic data in that no great difference in the rate of homolytic bond cleavage is expected for different organosilicon substituents. The small rate differences which do occur could result from minor effects of the silicon substituents on the N-O bond strength. Rate dependence on solvent polarity would be expected to be small, as observed, because, there is no charge development in the rate-determining step. Addition of cumene as a radical trap or AIBN as a radical initiator did not change the course of the reaction, but this would not be expected for a caged radical pair.

An alternate mechanistic pathway perhaps consistent with our evidence is one proceeding through reversible formation of a tight ion pair instead of a tight radical pair (Scheme III). This mechanism is a modification of one recently proposed by Bassindale et al. for the thermal rearrangement of α-substituted silanes and has the advantage that it is homogeneous with

respect to charge types throughout. The slight decrease in reaction rate with increasing solvent polarity (Table II) is evidence against an ion-pair mechanism, but is probably not decisive, and it may be impossible at present to distinguish between these two mechanistic possibilities.

Attempts to Detect Other Possible Intermediates. A thermolysis of **1** was run in the presence of an excess of diphenylacetylene in order to trap any possible silylene intermediate as a 1,4-disilacyclohexa-2,5-diene.[25] After 20 h at 190 °C, **2** was isolated as the only silicon containing product in quantitative yield. The presence of amine products which might result from nitrene insertion into C–H bonds in reactants, solvents, or products was never detected by VPC.[15,26]

Experimental Section

Analytical and preparative gas chromatography was carried out using a Varian Aerograph Model 90-P chromatograph. The analytical columns used were a ¼ in. × 15 ft 20% SE-30 on 60/80 Chromosorb W (A) and a ¼ in. × 15 ft 20% QF-1 on 60/80 Chromosorb W (B). The preparative columns used were a ⅜ in. × 15 ft 20% SE-30 45/60 mesh Chromosorb W (C) and a ⅜ in. × 20 ft 20% Carbowax 20M on 60/80 Chromosorb W (D). All columns used were aluminum. The analytical work was done using a helium flow of 60 ml/min and preparative work employed 200 ml/min. Both analytical and preparative separations were done isothermally. Proton NMR spectra were determined on a Varian A60A spectrometer equipped with a variable-temperature probe, a Varian T-60 spectrometer, or a JEOL-MH-100 spectrometer. Chemical shifts were obtained by internal referencing with benzene in 5–10% v/v solutions, except where noted otherwise. Ir spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer and were consistent with proposed structures in every case. All boiling points and melting points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Labs or Galbraith Laboratories, Inc. The ozonolysis experiment was done with a Welsbach T-23 ozonator as ozone source.

Materials. All chemicals used were reagent grade materials. Solvents such as THF, ether, hexane, benzene, decalin, triglyme, benzonitrile, cumeme, or cyclooctane were refluxed over lithium aluminum hydride or sodium and distilled before use. Carbon tetrachloride was refluxed over P_2O_5 and distilled before use.

Trimethylchlorosilane was obtained from Dow Corning Corp. and was distilled before use. Triethylchlorosilane, phenyldimethylchlorosilane, and dimethylchlorosilane were obtained from PCR, Inc. and were used without further purification. Hydroxylamine hydrochloride (Mallinckrodt), *O*-methylhydroxylamine hydrochloride, and *N*-methylhydroxylamine hydrochloride (Aldrich) were placed over Drierite in an evacuated desiccator for 24 h before using. *N,N*-Diethylhydroxylamine (Aldrich) was distilled before use. *O*-Trimethylsilylhydroxylamine was prepared by the method of Wannagat.[9] Hydroxylamine was prepared by the method of Hurd.[27] Triethylamine was distilled from barium oxide immediately before use. *tert*-Butyldimethylchlorosilane was prepared by treating dimethyldichlorosilane with 1 equiv of *tert*-butyllithium.[28] Purity of chlorosilanes was checked by analytical gas chromatography prior to use. *n*-Butyllithium was obtained as a 1.6 M solution in hexane from Foote Mineral Co.

All preparations were carried out in Pyrex glassware dried in a 130 °C oven for at least 3 h and then purged with dry nitrogen before use. A nitrogen atmosphere was maintained in all preparations. Filtration was carried out by vacuum filtration through a glass frit under a nitrogen atmosphere and filtrate was collected in dry nitrogen-filled flasks. Distillations were conducted under nitrogen or at reduced pressure.

All hydroxylamine thermolyses were carried out in sealed Pyrex tubes (o.d. 5 mm) or in sealed ^{1}H NMR tubes (o.d. 5 mm). The tubes were dried for at least 3 h in a 130 °C oven and purged with dry nitrogen before use. A nitrogen atmosphere was used in all thermolyses. The heating bath for thermolyses was a beaker of Dow Corning 700 fluid maintained at 190 °C with a heater–stirrer hot plate.

Kinetic data on compounds **1**, **5**, **9**, and **11** were obtained by sealing several Pyrex tubes (o.d. 4 mm) containing 100 μl of compound and placing them in a beaker in a thermostatically controlled muffle furnace at 205 °C for various lengths of time (usually multiples of 1000 s). The tubes were removed at set intervals, cooled, opened, and analyzed by gas chromatography (column A) or ^{1}H NMR.

Compounds **1** and **20** were prepared according to the procedure of Wannagat and Smrekar.[9] The synthesis of **5**, **6**, **8**, **9**, **11** and **24** is reported elsewhere.[8] Compound **16** was prepared by the method of West and Boudjouk.[29]

Tris(triethylsilyl)hydroxylamine (3). Hydroxylamine, triethylamine, and triethylchlorosilane were combined according to Wannagat's procedure[30] to give a 60% yield of *N,O*-bis(triethylsilyl)hydroxylamine: bp 103–108 °C (3 Torr); ir (neat) 3300, 2950, 2900, 1460, 1415, 1250, 1020, 790, 730 cm^{-1}; ^{1}H NMR δ 0.9 (m, $SiEt_3$, 30 H), 5.20 (s, N–H, 1 H). Anal. Calcd for $C_{12}H_{31}NSi_2O$: C, 55.11; H, 11.95; N, 5.36; Si, 21.48. Found: C, 54.99; H, 11.98; N, 5.34; Si, 21.54.

A solution of 8 mmol of the lithium salt of the anion of bis(triethylsilyl)hydroxylamine was prepared and reacted with 1.3 g (8 mmol) of triethylchlorosilane. A reflux period of 15 min was needed to initiate LiCl precipitation. Distillation of filtrate gave 2.5 g (91%) of **8**: bp 52–62 °C (0.3 Torr); ir (neat) 2950, 2900, 2880, 1460, 1415, 1245, 980, 840, 750 cm^{-1}; ^{1}H NMR δ 0.9 (m, $SiEt_3$, 45 H). Anal. Calcd for $C_{18}H_{45}NSi_3O$: C, 57.51; H, 12.07; N, 3.73; Si, 22.42. Found: C, 57.80; H, 12.20; N, 3.48; Si, 22.20.[30]

***N,N*-Bis(*tert*-butyldimethylsilyl)-*O*-trimethylsilylhydroxylamine (16).** *N,O*-Bis(*tert*-butyldimethylsilyl)hydroxylamine was prepared from *tert*-butyldimethylchlorosilane, hydroxylamine, and triethylamine by Wannagat's procedure,[30] isolated[3] by distillation [bp 72 °C (2 Torr)], and used without further purification. A solution of the lithium salt of the bissilylhydroxylamine was prepared by treating 4.2 g (16 mmol) of the compound with 10 ml (16 mmol) of a 1.6 M solution of *n*-butyllithium. The salt was reacted with 1.8 g (16 mmol) of trimethylchlorosilane. The filtrate was distilled, giving 4.2 g (88% yield) of **1**; bp 102 °C (4 Torr); ir (neat) 2960, 2930, 2900, 2860, 1470, 1250, 970, 950, 830, 790, 700, 670 cm^{-1}; ^{1}H NMR δ 0.24 (s, $SiMe_2$, 12 H), 0.31 (s, $SiMe_3$, 9 H), 1.11 (s, Si-*t*-Bu, 18 H). Anal. Calcd for $C_{12}H_{39}NSi_3O$: C, 53.98; H, 11.79; N, 4.90; Si, 25.25. Found: C, 54.11; H, 11.65; N, 4.21; Si, 25.51.[2]

Alkylorganosilylhydroxylamines. *N,N*-Bis(trimethylsilyl)-*O*-methylhydroxylamine (**25**) and *N,O*-bis(trimethylsilyl)-*N*-methylhydroxylamine (**26**) were prepared according to Wannagat's procedure.[9]

***N,N*-Diethyl-*O*-trimethylsilylhydroxylamine (28).** To a well stirred solution of 8.9 g (100 mmol) of *N,N*-diethylhydroxylamine and 10.2 g (100 mmol) of triethylamine in 250 ml of a 4:1 mixture of hexane and THF at 0 °C was added a solution of 10.9 g (100 mmol) of trimethylchlorosilane in 20 ml of THF. Immediate formation of a white precipitate occurred. The reaction was stirred for 12 h and filtered under N_2. The filtrate was distilled to give 15.1 g (94%) of **28**: bp 58–60 °C (42 Torr); ir (neat) 2960, 2900, 2880, 2840, 1450, 1380, 1250, 1060, 950, 890, 850, 770, 700 cm^{-1}; ^{1}H NMR δ 0.42 (s, $SiMe_3$, 9 H), 1.19 (t, NCH_2CH_3, 6 H, J = 7 Hz), 2.92 (q, NCH_2CH_3, 4 H, J = 7 Hz). Anal. Calcd for $C_7H_{19}NSiO$: C, 52.11; H, 11.87; N, 8.69; Si, 17.41. Found: C, 51.98; H, 11.70; N, 8.72; Si, 17.27.

Thermolysis of Tris(organosilyl)hydroxylamines. General Procedure. Pure tris(organosilyl)hydroxylamines (0.5 g) were syringed through a septum into a clean, dry nitrogen-filled Pyrex tube (o.d. 5 mm). The contents were frozen down in liquid nitrogen and the tube sealed with a gas-oxygen torch. The tubes were placed in an oil bath maintained at constant temperature at 190 °C, with a heater stirrer. The tubes were immersed so that the level of the liquid in the tube was below the level of the oil. The tubes were heated for 20 h, then cooled, opened, and fitted with a septum. The opened tubes were stored in a desiccator when not in use. All conversions appeared quantitative in conversion of the starting material, although in a few cases more than one product was formed. All products were isolated by preparative gas chromatography and characterized.

Thermolysis of Tris(trimethylsilyl)hydroxylamine (1). **1** (0.5 g, 2 mmol) was thermolyzed to give [trimethylsilyl(methyl)amino]pentamethyldisiloxane (**2**) in quantitative yield. Analytical gas chromatography showed no impurity (column A, 135 °C, 12 min); ir (neat) 2950, 2900, 1440, 1250, 1060, 915, 840, 780 cm^{-1}; ^{1}H NMR δ 0.23 (s, $SiMe_3$, 9 H), 0.24 (s, $SiMe_2$, 6 H), 0.25 (s, $SiMe_3$, 9 H), 2.50 (s, NMe, 3 H). Anal. Calcd for $C_9H_{27}NSi_3O$: C, 43.31; H, 10.90; N, 5.61; Si, 33.76. Found: C, 43.59; H, 10.77; N, 5.61; Si, 33.89.

Thermolysis of Tris(triethylsilyl)hydroxylamine (3). **3** (0.5 g, 1.5 mmol) was thermolyzed to give [triethylsilyl(ethyl)amine]pentaethyldisiloxane (**4**) in quantitative yield: ir (neat) 2950, 2900, 2880, 1450, 1415, 1245, 1165, 1060, 1010, 920, 750 cm^{-1}; ^{1}H NMR δ 0.9 (m, SiEt and NCH_2CH_3, 43 H), 2.93 (q, NCH_2CH_3, 2 H, J = 7 Hz).

Anal. Calcd for $C_{18}H_{45}NSi_3O$: C, 57.93; H, 12.07; N, 3.73; Si, 22.42. Found: C, 57.58; H, 12.05; N, 3.74; Si, 22.50.[30]

Thermolysis of *N,N*-Bis(trimethylsilyl)-*O*-dimethylsilylhydroxylamine (5). **5** (0.5 g, 2.1 mmol) was thermolyzed to give [trimethylsilylamino]pentamethyldisiloxane (**7**) in quantitative yield. Analytical gas chromatography showed no impurities (Column A, 140 °C, 9 min): ir (neat) 3370, 2950, 2900, 1410, 1250, 1180, 1060, 940, 880, 850, 810, 760, 690 cm^{-1}; ^1H NMR (CCl_4, benzene standard) δ 0.16 (s, $SiMe_2$, 6 H), 0.22 (s, $SiMe_3$, 9 H), 0.25 (s, $SiMe_3$, 9 H), N–H not observed. Anal. Calcd for $C_8H_{25}NSi_3O$: C, 40.79; H, 10.70; N, 5.95. Found: C, 40.74; H, 10.87; N, 5.66.

Thermolysis of *N,O*-Bis(trimethylsilyl)-*N*-dimethylsilylhydroxylamine (6). **6** (0.5 g, 2.1 mmol) was thermolyzed to give a single product in quantitative yield. The product was identical with **7** produced from **5.**

Thermolysis of *N,N*-Bis(trimethylsilyl)-*O*-phenyldimethylsilylhydroxylamine (8). **8** (0.5 g, 1.7 mmol) was thermolyzed to give [trimethylsilyl(phenyl)amino]pentamethyldisiloxane (**10**) in 90% yield. There were two components in the preparative gas chromatography trace (column C, 165 °C) in the ratio of 9:1 with retention times of 14 and 28 min, respectively. The major peak was **10** and the minor peak from ir and ^1H NMR appeared to be *N,N*-bis(pentamethyldisiloxy)aniline: ir (neat) 3060, 3040, 2960, 2900, 1430, 1260, 1120, 1080, 1060, 970, 920, 850, 810, 790, 710 cm^{-1}; ^1H NMR (CCl_4 with benzene standard) δ 0.15 (2 very close s, SiMe, 30 H), 7.25 (m, SiPh, 5 H).

10: ir (neat) 3080, 3040, 2960, 2900, 1590, 1480, 1410, 1250, 1220, 1050, 980, 970, 910, 840, 750, 690, 520 cm^{-1}; ^1H NMR (CCl_4 with benzene standard added later) δ 0.13 (s, $SiMe_2$, 6 H), 0.20 (s, $SiMe_3$, 9 H), 0.23 (s, $SiMe_3$, 9 H), 7.16 (m, NPh, 5 H). Anal. Calcd for $C_{14}H_{29}NSi_3O$: C, 53.95; H, 9.40; N, 4.49; Si, 27.03. Found: C, 53.51; H, 9.35; N, 4.45; Si, 26.78.

Thermolysis of *N,O*-Bis(trimethylsilyl)-*N*-phenyldimethylsilylhydroxylamine (9). **9** (0.5 g, 2.1 mmol) was thermolyzed to give the same mixture of products as **8** yielded. The main product was identical with **10** produced from **8.** Thermolysis in a tube wrapped with foil reduced the amount of the minor component to less than 5%.

Alternate Synthesis of 10. Trimethylsilylaniline was prepared by published procedures.[10] To a solution of 1.4 g (10 mmol) of trimethylsilylaniline in 100 ml of 4:1 hexane and THF at −78 °C was added via syringe 6.3 ml (10 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. After 0.5 h, 1.83 g (10 mmol) of pentamethylchlorodisiloxane in 5 ml of hexane was added and the −78 °C bath was removed after addition. As the solution warmed to room temperature, salt precipitation occurred. The mixture was allowed to stir for 1 h, then was filtered, and solvent was removed by evaporation. Preparative gas chromatography was used to isolate the main component (75% by peak integration), which proved to be identical with **10** from thermolysis of **8** or **9.**

Thermolysis of *N,N*-Bis(trimethylsilyl)-*O*-*tert*-butyldimethylsilylhydroxylamine (11). **11** (0.5 g, 1.8 mmol) was thermolyzed to give a single compound, 1-trimethylsilyl(methyl)amino-1,1,3,3-tetramethyl-3-*tert*-butyldisiloxane (**12**), in >95% yield. Analytical gas chromatography (column A, 165 °C) showed only one main peak with a retention time of 24 min, but ^1H NMR showed a trace of impurity (<5%). The structure was determined by alternate synthesis of the other possible isomer, [*tert*-butyldimethylsilyl(methyl)amino]pentamethyldisiloxane (**13**) (see below).

12: ir (neat) 2960, 2900, 2880, 2820, 1470, 1260, 1060, 930, 890, 860, 830, 810, 770, 620 cm^{-1}; ^1H NMR δ 0.28 (s, $SiMe_3$, 6 H), 0.34 (s, $SiMe_3$, 9 H), 0.35 (s, $SiMe_2$, 6 H), 1.12 (s, Si-*t*-Bu, 9 H), 2.64 (s, NMe, 3 H). Anal. Calcd for $C_{12}H_{33}NSi_3O$: C, 49.41; H, 11.43; N, 4.80; Si, 18.88. Found: C, 49.51; H, 11.39; N, 4.63; Si, 18.46.

Synthesis of 13. *tert*-Butyldimethylsilyl(methyl)amine was synthesized according to published procedures.[10] The lithium salt was prepared by reaction of 2.9 g (20 mmol) of amine with 12.5 ml (20 mmol) of a 1.6 M solution of *n*-butyllithium in hexane at −78 °C. This mixture was allowed to stir for 0.5 h and then warmed to room temperature. Pentamethylchlorodisiloxane (3.65 g, 20 mmol) in 25 ml of THF was added. The resulting solution was refluxed gently for 15 min before salt precipitation occurred. The solution was filtered and solvent was removed. **13** was isolated by preparative gas chromatography on column C (165 °C, 24 min). The ^1H NMR showed it was not the product of thermolysis of 11: ir (neat) 2960, 2930, 2900, 2860, 2820, 1440, 1250, 1150, 1050, 960, 870, 840, 790, 670 cm^{-1}; ^1H NMR δ 0.35 (s, $SiMe_3$, 9 H), 0.36 (s, $SiMe_2$, 6 H), 0.37 (s, $SiMe_2$, 6 H), 1.29 (s, Si-*t*-Bu, 9 H), 2.67 (s, NMe, 3 H). Anal. Calcd for $C_{12}H_{33}NSi_3O$: C, 49.41; H, 11.43; N, 4.80; Si, 28.88. Found: C, 49.35; H, 11.34; N, 4.71; Si, 28.51.

Thermolysis of *N,O*-Bis(trimethylsilyl)-*N*-*tert*-butyldimethylsilylhydroxylamine (14). **14** (0.5 g, 1.8 mmol) was thermolyzed to give a mixture of compounds which were inseparable by gas chromatography or distillation. ^1H NMR of the mixture gave peaks which matched those for **13** as well as peaks due to another product. The other compound is presumably an isomer of **13** arising from insertion of the *tert*-butyldimethylsilyl group, followed by methyl transfer to nitrogen, i.e., **15.** The NMR spectrum of **12** showed no peaks coincident with those of the mixture, establishing that **12** was not formed in the rearrangement of **14.**

Thermolysis of *N,N*-Bis(*tert*-butyldimethylsilyl)-*O*-trimethylsilylhydroxylamine (16). **16** (2.0 g, 6 mmol) was thermolyzed to give 1-*tert*-butyldimethylsilyl(methyl)amino-1-*tert*-butyl-1,3,3,3-tetramethyldisiloxane (**17**) in 95% yield. The structure of **17** was confirmed by analysis of hydrolysis products (see below). Pure **17** was obtained by preparative gas chromatography on column C (135 °C, 24 min): ir (neat) 2950, 2900, 2850, 1470, 1250, 1060, 1040, 910, 840, 780 cm^{-1}; ^1H NMR (dioxane) δ 0.14 (s, $SiMe_2$, 6 H), 0.15 (s, $SiMe_3$, 9 H), 0.16 (s, SiMe, 3 H), 1.18 (s, Si-*t*-Bu, 9 H), 1.19 (s, Si-*t*-Bu, 9 H), 1.72 (s, NMe, 3 H). Anal. Calcd for $C_{15}H_{33}NSi_3O$: C, 53.98; H, 11.79; N, 4.70; Si, 25.25. Found: C, 54.77; H, 11.59; N, 4.42; Si, 25.31.

Hydrolysis of 17 and Identification of Products. **17** (1.0 g, 3 mmol) was placed in a clean 10-ml flask and 1 ml of water was added. A condenser was placed on the flask and the mixture was stirred for 5 days. After this period, a sample of **17** was withdrawn and VPC analysis showed no change. The flask was then heated to reflux for 2 weeks, cooled, and a sample withdrawn. Gas chromatographic analysis (column A, 135 °C) showed the presence of two products along with **17.** The first product, **18,** with a retention time of 6 min, proved identical with *tert*-butyldimethylsilanol. The second product, with a retention time of 17 min, was shown to be 1,1,1,3,5,7,7,7-octamethyl-3,5-di-*tert*-butyl-2,4,6-trisiloxane (**19**): ir (neat) 2970, 2940, 2860, 1470, 1260, 1100, 1060, 1020, 880, 850, 800, 780, 700 cm^{-1}; ^1H NMR (CCl_4 with benzene standard) δ 0.09 (s, SiMe, 6 H), 0.24 (s, $SiMe_3$, 18 H), 0.96 (s, Si-*t*-Bu, 18 H). Mass calcd for $C_{16}H_{42}Si_4O_3$ was 394.22110. Obsd 394.22114 (0.1 ppm error).

Thermolysis of *N,N*-Bis(trimethylsilyl)-*O*-triethylsilylhydroxylamine (20). **20** (2.0 g, 7.3 mmol) was thermolyzed to give a mixture of three isomeric products: 1-trimethylsilyl(ethyl)amino-1,1-diethyl-3,3,3-trimethyldisiloxane (**21**), [triethylsilyl(methyl)amino]-pentamethyldisiloxane (**22**), and 1-trimethylsilyl(methyl)amino-1,1-dimethyl-3,3,3-triethylsiloxane (**23**) in yields of 29, 29, and 42%, respectively, accounting for quantitative reaction of **23.** The isomers were purified using preparative gas chromatography. Column D (140 °C) with retention time of 44, 52, and 58 min, respectively.

21: ir (neat) 2950, 2900, 2860, 1450, 1250, 1160, 1060, 930, 840, 785, 760 cm^{-1}; ^1H NMR δ 0.18 (s, $SiMe_3$, 9 H), 0.22 (s, $SiMe_3$, 9 H), 0.9 (m, SiEt and NCH_2CH_3, 13 H), 2.88 (q, NCH_2CH_3, 2 H, J = 7.5 Hz).

22: ir (neat) 2950, 2900, 2880, 1440, 1250, 1060, 910, 840 cm^{-1}; ^1H NMR δ 0.24 (s, $SiMe_3$, 9 H), 0.26 (s, $SiMe_2$, 6 H), 0.9 (m, $SiEt_3$, 15 H), 2.48 (s, NMe, 3 H).

23: ir (neat) 2950, 2900, 2880, 1450, 1250, 1060, 910, 840 cm^{-1}; ^1H NMR δ 0.24 (s, $SiMe_3$, 9 H), 0.26 (s, $SiMe_2$, 6 H), 0.9 (m, $SiEt_3$, 15 H), 2.54 (s, NMe, 3 H).

Anal. Calcd for $C_{12}H_{33}NSi_3O$: C, 49.42; H, 11.41; N, 4.80; Si, 28.89. Found for **21:** C, 49.26; H, 11.42; N, 4.71; Si, 28.62. Found for **22:** C, 49.15; H, 11.54; N, 4.90; Si, 29.06. Found for **23:** C, 49.17; H, 11.61; N, 4.66; Si, 29.16.

Alternate Synthesis of 22. Triethylsilyl(methyl)amine was prepared by the method of Osthoff and Kantor.[10] Pentamethylchlorodisiloxane was prepared by the reaction of 28 g (250 mmol) of sodium trimethylsilanolate with 32.5 g (250 mmol) of dimethyldichlorosilane in 250 ml of ether at −78 °C. The chlorosilane was added dropwise to a solution of the silanolate and immediate formation of NaCl occurred. The mixture was filtered and distilled to give 21.6 g (53% yield) of pentamethylchlorodisiloxane, bp 120 °C (760 Torr). To 1.78 g (10 mmol) of triethylsilyl(methyl)amine in 250 ml of 4:1 hexane and THF at −78 °C was added 7.5 ml (12 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. After 2 h, 2.2 g (12 mmol) of pentamethylchlorodisiloxane in 5 ml of hexane was added. Salt precipitation occurred almost immediately. The solution was filtered and solvent re-

moved by rotovap. The main product (>70% by peak area) was purified by preparative gas chromatography on column D (140 °C, 52 min) and was identical in every way with **22** from the thermolysis of **20.**

Thermolysis of *N,O*-Bis(trimethylsilyl)-*N*-triethylsilylhydroxylamine (24). **24** (2.0 g, 7.3 mmol) was thermolyzed to give a mixture of **21**, **22**, and **23** in yields of 40, 40, and 20%, respectively. The isomers were purified by preparative gas chromatography on column D (140 °C) with retention times of 43, 52, and 58 min and proved identical with **21**, **22**, and **23** isolated from the thermolysis of **20.**

Thermolyses of Alkylorganosilylhydroxylamines. Thermolysis of *N,N*-Bis(trimethylsilyl)-*O*-methylhydroxylamine (25). **25** (0.5 g, 2.9 mmol) was heated to 180 °C for 24 h. The liquid in the tube was identical with unheated **25.**

Thermolysis of *N,O*-Bis(trimethylsilyl)-*N*-methylhydroxylamine (26). **26** (0.5 g, 2.9 mmol) was heated to 180 °C for 20 h. The clear colorless liquid turned to clear brown and a white polymer separated from solution. Gas chromatographic analysis (column A, 140 °C) showed hexamethyldisiloxane (3 min) and unreacted **26** (4.5 min) as the main volatile products. A possible thermolysis product, *N,N*-dimethylaminopentamethyldisiloxane, was independently synthesized from lithium diethylamide and pentamethylchlorodisiloxane, but did not appear to be one of the components of the mixture.

Thermolysis of *N,N*-Diethyl-*O*-trimethylsilylhydroxylamine. A neat sample of 0.5 g (3.1 mmol) of this compound was heated at 180 °C for 20 h. The resulting brown solution was cooled in liquid nitrogen and the tube opened. As the solution thawed it bubbled violently. The gas chromatograph (column A, 100 °C) showed hexamethyldisiloxane (5 min) as the product. The tarry residue would not go through the column.

Attempted Thermal Reactions of Silylaminosiloxanes. The pure silylaminosiloxanes, obtained from thermolysis or alternate synthesis and preparative gas chromatography, were syringed through a septum into clean, dry, nitrogen-filled NMR tubes. The reactions were run either neat or as 20% v/v solutions in high-boiling solvents (benzonitrile or decalin). The tubes were frozen in liquid nitrogen and sealed with a torch. They were then placed in an oil bath maintained at constant temperature (190 °C) with a heater stirrer. After 20 h the tubes were removed and the ^{1}H NMR spectra were taken to determine if any change had occurred. In all cases tried (compounds **7**, **10**, **12**, **13**, and **22**) no change was observed. Compound **10** was run in a tube wrapped with aluminum foil to avoid photolytic decomposition. The mixtures of compounds **21**, **22**, and **23** obtained from thermolysis of **20** and **24** were heated in separate tubes under identical conditions in the oil bath for 20 h. Gas chromatographic analysis of the contents showed no change in the isomer distributions.

Kinetic Investigations of the Thermal Rearrangement. All experiments were done in clean, dry nitrogen-filled Pyrex tubes (o.d. 4 mm). The compound (100 μl of **1**, **5**, **9**, or **11**) was syringed into the tube through a rubber septum. The tubes were then frozen in liquid nitrogen and sealed with a gas-oxygen torch. The tubes were placed in beakers in a thermostatically controlled muffle furnace at 205 °C. Tubes were withdrawn at predetermined intervals (usually multiples of 1000 s), cooled immediately to room temperature in a water bath, dried, and opened. Analyses of the contents were done by gas chromatography (column A) or by dissolving the contents in 400 μl of dry benzene and running a ^{1}H NMR spectrum and integrating the peak areas of product vs. starting material.

Investigations of rates in different solvents were done in a similar manner. Solutions of **1** (20% v/v) in benzonitrile and decalin were made. These solutions (100 μl) were placed in tubes, sealed, heated in the oven for specific intervals, and removed for analysis.

Thermolysis of 1 in the Presence of Diphenylacetylene.[30] To a clean, dry nitrogen-filled Pyrex tube were added 0.5 g (2 mmol) of **1** and 5 g (28 mmol) of diphenylacetylene. The tube was sealed and placed in a 180 °C oil bath for 20 h. During this time, the white diphenylacetylene crystals melted and changed from pale yellow to pale green. The tube was removed, cooled, and opened. Upon cooling, the diphenylacetylene solidified. The solid mass in the tube was dissolved in dry benzene, forming a pale green solution. The ^{1}H NMR showed only **2** and diphenylacetylene present. No 1,4-disilacyclohexane product was isolated.

AIBN Experiment. To a clean, dry nitrogen-filled NMR tube were added 0.5 g (2.0 mmol) of **1** and 28 mg (0.33 mmol) of azobisisobutyronitrile (AIBN). The contents were frozen in liquid nitrogen and the tube was sealed with a torch. The ^{1}H NMR spectrum was taken after thawing. The tube was then heated to 100 °C in an oil bath for 1 h (sufficient time to decompose AIBN completely). The spectrum remained unchanged; no *N*-methyl peak was seen. The ir of the solution showed no ν_{SiOSi} of silylaminosiloxane.

Ozonolysis of Tris(trimethylsilyl)amine. Tris(trimethylsilyl)amine (1.17 g, 5 mmol) was dissolved in 50 ml of dry methylene chloride and syringed into a clean, dry, 100-ml three-neck flask fitted with a condenser, drying tube, and ozone inlet. Ozone was bubbled in for a period of 1–6 h at temperatures from −78 to +25 °C. ^{1}H NMR and infrared of recovered material showed no change when compared to pure $N(SiMe_3)_3$.

References and Notes

(1) Research sponsored by U.S. Air Force Office of Scientific Research (NC)-AFSC, Grant Nos. AF-AFOSR 70-1904 and 74-2644.
(2) P. Boudjouk and R. West, *J. Am. Chem. Soc.*, **93**, 5901 (1971).
(3) R. West, P. Boudjouk, and P. Nowakowski, 3rd International Symposium of Organosilicon Chemistry, Madison, Wisc., Aug 1972.
(4) No analogous thermal rearrangements of hydroxylamines are known in carbon chemistry, although oxaziridines undergo thermal rearrangement into amides [M. Lamchen in *Mech. Mol. Migr.*, **1**, 1 (1968)]. These exhibit nitrogen–oxygen bond cleavage and alkyl transfer from carbon to nitrogen, but not insertion into the nitrogen–oxygen bond. There is also a thermal rearrangement of an organic hydroxylamine anion, discovered by Carey and Hayes [F. Carey and L. Hayes, *J. Am. Chem. Soc.*, **92**, 7613 (1970)], in which there is transfer of a hydrogen from carbon to oxygen and a transfer of an organic group from oxygen to nitrogen.
(5) Recently groups in the U.S. [R. Dannley and A. K. Shubber, *J. Org. Chem.*, **36**, 3784 (1971)] and the Soviet Union [V. Yablokov, A. Sunin, L. Isaeva, and N. Kostina, *J. Gen. Chem. USSR*, **43**, 1296 (1973)] have reported a similar rearrangement of bis(organosilyl)peroxides $R_3SiOOSiR_3 \rightarrow R_3SiOSiR_2OR$.
(6) The formation of an extra Si-O bond (106 kcal) [E. A. V. Ebsworth in "The Bond to Carbon", A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968, Chapter 1] at the expense of the weak N–O bond (51 kcal) [R. T. Sanderson, "Chemical Bonds and Bond Energies", Academic Press, New York, N.Y., 1971] provides the driving force for the reaction. Other bonds broken in the reactants are balanced closely by those formed in the products.
(7) Thermal decomposition of triphenylsilylazide at 680 °C gave up to 60% yield of hexaphenylcyclodisilazane. This reaction could have involved an Si=N species and would have involved phenyl transfer from silicon to nitrogen. See W. T. Reichle, *Inorg. Chem.*, **3**, 402 (1964).
(8) P. Nowakowski and R. West, *J. Am. Chem. Soc.*, preceding paper in this issue.
(9) U. Wannagat and O. Smrekar, *Monatsh. Chem.*, **100**, 760 (1969).
(10) R. Osthoff and S. Kantor, *Inorg. Synth.*, **5**, 55 (1957).
(11) The remaining 5% appears to be a photodecomposition product of **10.** Ir and ^{1}H NMR indicate the structure $PhN(SiMe_2OSiMe_3)_2$. Neither **8** nor **9** is photosensitive and have been stored in clear glass vials for months without change. Compound **10** will turn yellow in a few days under the same conditions.
(12) The structure of **21** was assigned from ^{1}H NMR data. The structures of **22** and **23** were established by alternate synthesis of **22** (eq 2). Product ratios were determined by VPC.
(13) It is known that some organosilylalkylperoxides rearrange thermally to give products analogous to those obtained from bis(organosilyl)peroxides:

$$ArR_2SiOOCR'_3 \xrightarrow[120\ °C]{} ArOSiR_2OCR'_3 + \text{radical decomposition products}$$

R = alkyl or aryl, R′ = aryl

(a) K. Kawazumi and B. Murai, *Bull. Chem. Soc. Jpn.*, **39**, 1951 (1966); (b) V. Yablokov, A. Tabarina, N. Yablokovna, and A. Zezina, *J. Gen. Chem. USSR*, **42**, 2472 (1972).
(14) To insure that the probable product of rearrangement, $Me_2NSiMe_2OSiMe_3$, was not decomposing at this temperature, it was synthesized independently and pyrolyzed at 200 °C. It yielded a volatile product, probably Me_2NH, some $(Me_3Si)_2O$, and octamethylcyclotetrasiloxane $(SiMe_2O)_4$ along with some tar. Therefore, it is not a product of the thermal decomposition of **26** (see Experimental Section).
(15) G. Zon, F. Tsui, and T. Vogel, *J. Am. Chem. Soc.*, **96**, 7144 (1974).
(16) It seems reasonable that at first both the irreversible rearrangement of tris(organosilyl)hydroxylamines and the decomposition of **26** go by a similar path to the "bridged" state in Scheme I (see Discussion). Compound **26** cannot proceed to the next step (insertion into the N–O bond) and decomposes into hexamethyldisiloxane and tar, as observed. A similar pathway is not available to **25.** This may be because the organosilicon group on oxygen assists in the rearrangement by stabilizing an intermediate state.
(17) Trindle and Shillady have recently argued that a mechanism involving insertion of an organosilicon group from nitrogen (path 1) or oxygen (path 2) into the N–O bond is consistent with phase conservation in high-lying MO's during the rearrangement proposed by Scheme I. The silicon 3d orbitals stabilize the "ring" arrangements leading to A or A′. It must be noted that path 1 is a least motion pathway for the rearrangement, which does not involve the extra transfer of an organosilicon group from nitrogen to oxygen as path 2 requires: see C. Trindle and D. Shillady, *J. Am. Chem. Soc.*, **95**, 703 (1973).
(18) A tris(organosilyl)amine oxide had been suggested as a possible reaction intermediate, forming by a "reverse Meisenheimer" type of rearrangement.

This is unlikely, since we get a different product distribution from the $(R_3Si)_2NOSiR_3 \rightarrow (R_3Si)_3N^+ \rightarrow O^- \rightarrow R_3SiN(R)SiR_2OSiR_3$ isomeric hydroxylamines **20** and **24**, which would form the same amine oxide intermediate by such a mechanism. An attempt was made to synthesize such a compound from $(Me_3Si)_3N$ and ozone (see Experimental Section).
(19) Raw rate data available upon request from the authors.
(20) (a) R. A. Abramovitch in "Organic Reactive Intermediates", S. P. McManus, Ed., Academic Press, New York, N.Y., 1973, Chapter 3; (b) S. P. McManus and C. V. Pittman, Jr. in *ibid.*, Chapter 4; (c) P. T. Lansbury in "Nitrenes", W. Lwowski, Ed., Interscience, New York, N.Y., 1970, Chapter 11.
(21) Y. Pocker in "Molecular Rearrangements", P. deMayo, Ed., Wiley, New York, N.Y., 1964, Chapter 1.
(22) The preference for methyl migration instead of *tert*-butyl migration to nitrogen in compounds **14** and **16** may be for steric reasons.
(23) It must be noted that in the compounds **5**, **6**, **8**, and **9** the methyl groups greatly outnumber the hydrogen or phenyl substituents and should be favored statistically by Scheme I by at least a factor of two and possibly more.
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(25) (a) P. P. Gaspar and B. J. Herold in "Carbene Chemistry", 2d ed, W. Kirmse, Ed., Academic Press, N.Y., 1971, Chapter 13; (b) R. West and R. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963); (c) T. J. Barton and J. Kilgour, *ibid.*, **96**, 7150 (1974).
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Correlation of Rates of Solvolysis of Secondary Tosylates with Tertiary Benzylic Derivatives[1]

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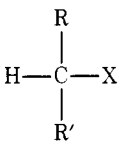
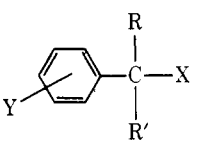
Abstract: A linear free-energy relationship, $\log (k/k_0) = \rho\gamma^+$, with group constants, γ^+, was defined. The group constants are characteristic of the ability of a group to stabilize an adjacent cationic center. These groups can be aromatic or nonaromatic. The γ^+ for hydrogen was determined to be 2.53. This group constant allows for the first time the direct correlation of acetolysis of secondary tosylates with their analogous tertiary benzylic derivatives. Such correlations were found to be general, and excellent $\rho\gamma^+$ plots were obtained. This relationship was applied in the elucidation of anchimeric assistance and shown to be valuable in evaluating neighboring group effects.

From the pioneering work of Winstein and co-workers, rates of solvolysis for secondary substrates have been usually compared in terms of acetolysis of *p*-toluenesulfonates (**1**) (tosylates, X = OTs).[2] Brown, Gassman, Tanida, and other workers have investigated the rates of solvolysis of various tertiary benzylic systems, **2**.[3]



1



2

In the solvolysis of benzyl derivatives, it is possible to increase the electron demand of the cationic center by varying the substituent on the aryl group. Thus, a linear free-energy relationship can be obtained by treatment of the kinetic data with the Hammett–Brown relationship:[4]

$$\log (k/k_0) = \rho\sigma^+ \qquad (1)$$

Equation 1 is based on the fact that as the substituent, Y, is varied the logarithms of the rate constants for aromatic side chain reactions are linearly related to one another.

The substituent constant, σ^+, is characteristic only of the substituent on the aryl group in **2** and represents the ability of the substituent, Y, to attract and repel electrons by a combination of inductive and resonance effects.

Until now a unifying theory correlating rates of reaction of **1** with **2** was lacking. However, reported here is the application of a linear free-energy relationship for correlating rates of solvolysis of secondary substrates (**1**) with the corresponding tertiary benzylic analogues (**2**).

Results and Discussion

In the past solvolysis of tertiary benzylic derivatives have been used extensively in the evaluation of phenomena occurring in secondary substrates. However, such an approach has been questioned.[5] Indeed, one worker has suggested that this practice "can be treacherous".[5a] Other workers have cautioned against extraneous steric effects.[5b,c] Although these suggestions are intuitive, they appear somewhat questionable.[6]

In order to correlate nonaromatic with aromatic derivatives, a linear free-energy relationship was defined with group constants, γ^+, and is represented by:

$$\log (k/k_0) = \rho\gamma^+ \qquad (2)$$

The group constant is characteristic of the ability of an entire group (for example, aryl or hydrogen) to stabilize an adjacent cationic center. The γ^+ values for aryl groups will be the same as the σ^+ values for the substituent on that aryl group.

Since the difference between **1** and **2** is a hydrogen group vs. an aryl group, a group constant for a hydrogen group is needed to correlate the solvolysis of secondary substrates with their analogous tertiary benzylic derivatives via eq 2.

This γ^+ value has to include a correction for the difference in leaving group and solvent.[7]

Group constants (nee substituent constants) are usually determined from the solvolysis of *tert*-cumyl chlorides; however, in certain cases indirect methods have been employed.[8] The 7-norbornyl system offers an alternative route to determine the γ^+ value for a hydrogen group.[9] Because of the importance of 7-phenyl-7-norbornyl *p*-nitrobenzoate, the rate constant was redetermined to be 2.00×10^{-11} s^{-1} at 25 °C in 70% dioxane. This value gave a better correlation and a ρ of −5.25.