as the 2,4-DNP of 3,3-dimethylbicyclo[3.2.1]octan-2-one (lit.[12] mp 103-105 °C): IR (KBr) 3320 (m, NH), 3118, 3080 (w, ArCH), 2980-2880 (s, CH), 1620 (s, C=N) (s, NH), 1510-1500 (s, NO_2), 1460, 1420 1375 (m, CH), 1340 (s, NO_2); NMR ($CDCl_3$, Me_4Si) 11.2 (br s, 1 H, NH), 9.2 (s, 1 H, aromatic), 8.34 and 8.02 (d, 2 H, aromatic), 2.52 and 2.47 (overlapped s, 2 H, bridgehead), complex pattern with peaks at 2.22, 2.05, 1.69, 1.56 (8 H, CH_2), 1.3 and 1.24 (d, 6 H, $(CH_3)_2CC{=}N$). Further elution produced additional colored bands, but there was no clear separation. Identification of the other 2,4-DNP components by TLC also failed as all three of the major products had the same R_f value upon elution with petroleum ether and benzene mixtures.

Acknowledgment. We thank the National Science Foundation for grants (MPS-75-09309, CHE-78-04805) to R.A.A. in support of the research carried out in Tuscaloosa and at Clemson. The donors of the Petroleum Research Fund, administered by the American Chemical Society, are acknowledged for partial support of the research carried out in Huntsville.

Registry No. 1 (n = 4), 1120-56-5; 1 (n = 5), 1528-30-9; 1 (n = 6), 1192-37-6; 2 (n = 5), 2146-37-4; 2 (n = 6), 1003-64-1; 2 (n = 7), 10494-87-8; 2 (n = 8), 19780-51-9; 3 (n = 5), 765-83-3; 3 (n = 6), 5749-72-4; 3 (n = 7), 7087-36-7; 3 (n = 8), 30718-63-9; 4 (R = R′ = Me; n = 5), 75600-20-3; 4 (R = R′ = Me; n = 6), 75600-21-4; 4 (R = R′ = Me; n = 7), 75600-22-5; 4 (R =R′ = Me; n =8), 75600-23-6; 5 (n = 5), 75600-24-7; 5 (n = 6), 75600-25-8; 5 (n = 7), 75600-26-9; 5 (n = 8), 75626-84-5; 6 (n = 4), 120-92-3; 6 (n = 4) 2,4-DNP derivative, 2057-87-6; 6 (n = 5), 108-94-1; 6 (n = 5) 2,4-DNP derivative, 1589-62-4; 6 (n = 6), 502-42-1; 6 (n = 6) 2,4-DNP derivative, 3349-73-3; 7 (n = 5), 583-60-8; 7 (n = 5) 2,4-DNP derivative, 5138-30-7; 7 (n = 6), 932-56-9; 7 (n = 6) 2,4-DNP derivative, 970-95-6; 7 (n = 7), 10363-27-6; 7 (n = 7) 2,4-DNP derivative, 73674-39-2; 7 (n = 8), 73674-37-0; 7 (n = 8) 2,4-DNP derivative, 73674-40-5; 8 (n = 5), 1193-47-1; 8 (n = 5) 2,4-DNP derivative, 5212-74-8; 8 (n = 6), 7228-52-6; 8 (n = 6) 2,4-DNP derivative, 22612-83-5; 8 (n = 7), 42393-51-1; 8 (n = 7) 2,4-DNP derivative, 42393-52-2; 8 (n = 8), 75600-27-0; 8 (n = 8) 2,4-DNP derivative, 75600-28-1; 9 (n = 5), 13388-93-7; 9 (n = 5) 2,4-DNP derivative, 75600-29-2; 9 (n = 6), 2890-62-2; 9 (n = 6) 2,4-DNP derivative, 2890-63-3; 9 (n = 7), 75600-30-5; 9 (n = 7) 2,4-DNP derivative, 75600-31-6; 9 (n = 8), 75600-32-7; 9 (n = 8) 2,4-DNP derivative, 75600-33-8; 12, 75658-54-7; 12 2,4-DNP derivative, 75600-34-9; 13, 75658-55-8; 13 2,4-DNP derivative, 75600-35-0; 14, 55682-09-2; 15, 42393-53-3; 15 2,4-DNP derivative, 42393-54-4; PNBSA, 4547-62-0; IPBH, 4696-14-4; 26, 75600-36-1; isopropyl bromide, 75-26-3; norcamphor, 497-38-1.

Investigation of Thermally Induced α-Deoxysilylation of Organosilylated Hydroxylamine Derivatives as a General Method for Nitrene Production

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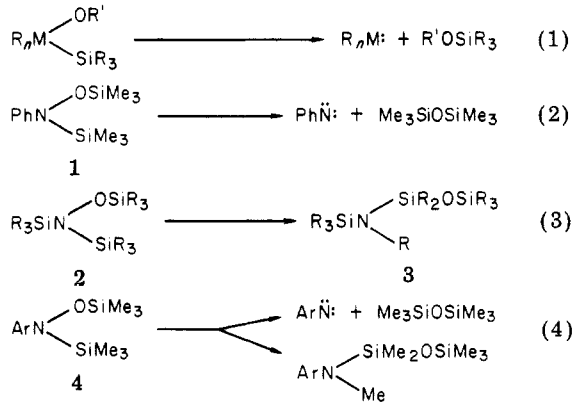
Received August 5, 1980

A variety of organosilylated hydroxylamine derivatives have been synthesized and studied as possible nitrene generators by thermally induced α-deoxysilylaton: $GN(OR')SiR_3 \rightarrow G\ddot{N}: + R'OSiR_3$, where G = EtO_2C, ArCO, $ArSO_2$, Me, H, and Ph_2PO. The methods used to assess nitrene formation include trapping product characterization, substitutent variation, kinetic activation parameter measurements, Hammett studies, and solvent effects. While the latter two types of precursors were only briefly investigated because of their marked resistance to fragmentation, the combined data for the remaining compounds are consistent with the intermediacy of a nitrene. The existence of alternative deoxysilylation pathways is discussed in some cases, and for comparison with the nitrogen systems reported herein, kinetic activation parameters for α-deoxysilylation about carbon and silicon have been determined.

We have previously reported[3,4] that the thermally induced α-deoxysilylation reaction (eq 1) known for carbon[5] (M = C) and silicon[6] (M = Si) systems also obtains for the nitrogen case where M = N and G = Ph. Thus, as shown in eq 2, heating *N*-phenyl-*N*,*O*-bis(trimethylsilyl)-hydroxylamine (1) leads to formation of hexamethyldisiloxane and phenylnitrene, which may be intercepted by various trapping agents.[3,4] This fragmentation contrasted markedly with the rearrangement (eq 3) of structurally related tris(organosilyl)hydroxylamines (2) to (silylamino)disiloxanes (3) discovered by West and coworkers;[7] however, our subsequent studies with phenyl-



substituted derivatives of 1 (4) have shown that partitioning between the fragmentation and rearrangement pathways is controlled by the aryl group electronic interactions with nitrogen (eq 4).[8] The effect is illustrated by

(1) Dow Corning Corporation Research Fellow, 1977-1979.
(2) Recipient of a Dow Corning Corp. Research Award, 1977-1979.
(3) F. P. Tsui, T. M. Vogel, and G. Zon, *J. Am. Chem. Soc.*, **96**, 7144 (1974).
(4) F. P. Tsui, Y. H. Chang, T. M. Vogel, and G. Zon, *J. Org. Chem.*, **41**, 3381 (1976).
(5) (a) W. H. Atwell, D. R. Weyenberg, and J. G. Uhlmann, *J. Am. Chem. Soc.*, **91**, 2025 (1969); (b) A. G. Brook and P. J. Dillon, *Can. J. Chem.*, **47**, 4347 (1969).
(6) (a) W. H. Atwell and D. R. Weyenberg, *J. Am. Chem. Soc.*, **90**, 3438 (1968); (b) W. H. Atwell and D. R. Weyenberg, *J. Organomet. Chem.*, **5**, 594 (1966); (c) T. J. Barton and M. Juvet, *Tetrahedron Lett.*, 3893 (1975).
(7) (a) P. Boudjouk and R. West, *J. Am. Chem. Soc.*, **93**, 5901 (1971); (b) R. West, P. Boudjouk, and P. Nowakowski, 3rd International Symposium of Organosilicon Chemistry, Madison, WI, Aug 1972; (c) R. West, P. Nowakowski, and P. Boudjouk, *J. Am. Chem. Soc.*, **98**, 5620 (1976).

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the divergent behavior of *m*- and *p*-anisyl isomers of **4** which undergo essentially complete fragmentation and rearrangement, respectively.[8]

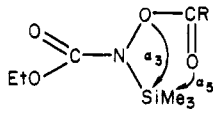
In view of these developments, it was of interest to further explore the thermal chemistry of variously structured organosilylated hydroxylamines [$GN(OR')SiR_3$] in order to evaluate the scope and utility of nitrene formation by α-deoxysilylation. At the same time, complementary information concerning the possible rearrangement of such compounds would be obtained. We now report the results of extensive trapping product and kinetic studies which collectively demonstrate that nitrene generation prevails in model reaction systems with G = EtO_2C, ArCO, $ArSO_2$, and Me. A wide range of kinetic activation parameters for these thermolyses has been found, and the values have been compared with those measured for α-deoxysilylation about carbon and silicon. Mechanistic details have also been probed by Hammett studies, solvent variation, and structural modification at the reacting silicon and oxygen centers shown in eq 1. The work is described in major sections dealing with individual compound classes, with each section further divided into synthesis, thermolysis product studies, and kinetic measurements.

Results and Discussion

I. *N,O*-Bis(trimethylsilyl)-*N*-carbethoxyhydroxylamine and Related Compounds. A. Synthesis. Conversion of *N*-carbethoxyhydroxylamine (**5**) into its bis(trimethylsilyl) derivative (**6**) was achieved in good yield (ca. 90%) by reaction with a 6-fold molar excess of Me_3SiCl and Et_3N in ether for 24 h (eq 5). The chemical composition of VPC-purified **6** was readily established from integrated intensities of the ^1H NMR ethyl and methyl signals.

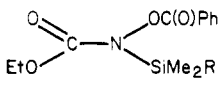
$$\underset{\mathbf{5}}{EtO_2CNHOH} \xrightarrow[-2Et_3N\cdot HCl]{Me_3SiCl/Et_3N} \underset{\mathbf{6}}{EtO_2CNO(SiMe_3)_2} \quad (5)$$

Decreasing the steric "bulk" of the oxygen-bound substituent in **1** by replacement of Me_3Si with Me has been shown[4] to have little effect upon the rate of α-deoxysilylation. Consequently, it was of interest to incorporate a carbonyl moiety at this position which allows for nitrene generation by alternative α_3- and α_5-elimination pathways (eq 6), with the α_5 mode possibly having a lower free-energy



$$\rightarrow EtO_2C\ddot{N}: + Me_3SiO_2CR \quad (6)$$

of activation due to steric factors and/or the greater nucleophilicity of C=O vs. C—O oxygen. Compound **7** was

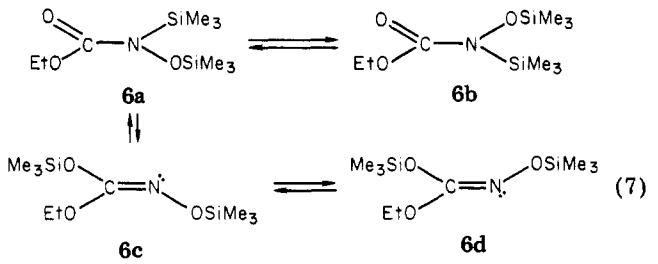


7, R = Me
8, R = *t*-Bu

therefore prepared (85%) by analogy to eq 5 by starting with *O*-benzoyl-*N*-carbethoxyhydroxylamine and was ultimately purified by VPC. The *tert*-butyldimethylsilyl derivative (**8**) was similarly synthesized to test whether this structural modification would lead to stabilization of the N–Si bond toward hydrolysis without significantly effecting the rate of α-deoxysilylation.

Numerous attempts were made to cyclize EtO_2CNHOH with $ClMe_2SiOSiMe_2Cl$; however, polymer formation was extensive, and there was no evidence (gas chromatography/mass spectroscopy) of product formation. The desired heterocycle, $EtO_2CNSiMe_2OSiMe_2O$, was particularly intriguing in that α-deoxysilylation could generate $SiMe_2OSiMe_2O$, which is of interest in organosilicon chemistry.

Structural Dynamics. ^{13}C NMR was used to obtain information regarding the isomerization of **6** (eq 7) that



(7)

might arise from relatively slow rotation about the amide linkage (**6a** ⇄ **6b**), 1,3-migration of Me_3Si between N and O (**6a** ⇄ **6c**), and/or linear inversion at N (**6c** ⇄ **6d**).[9] The 25-MHz ^{13}C NMR spectrum of a $CDCl_3$ solution of **6** at 20 °C features two absorptions at 157.8 and 157.6 ppm in a ca. 1:2 ratio, respectively, which are very close to the 157–159-ppm range of chemical shifts reported[10] for a series of analogous ethyl organosilylurethanes. On the basis of variable-temperature ^{13}C and ^{29}Si NMR data, it has been concluded[10] that the latter compounds exist exclusively in the amide form and that there is hindered rotation ($\Delta G^{\ddagger} \simeq 12$ kcal/mol) about the C(O)–N bond. We therefore assume that **6a** ⇄ **6b** is representative of the dynamical structure for **6** in solution.

As in the case of **6**, intramolecular isomerization of **7** and **8** must be considered, and the molecular dynamics were investigated by variable-temperature ^1H NMR spectroscopy at 220 MHz. At 20 °C in $CDCl_3$ solution both compounds appear to be two-component mixtures: $SiMe_2R$ resonance doubling with $\Delta\nu_{AB} = 15$ Hz. Increasing the probe temperature led to gradual signal coalescence followed by line narrowing, while cooling reversed these spectral changes. Measurement of relative signal intensities at various slow-exchange temperatures in the range of 20–30 °C indicated that there were no significant population changes for either **7** (36:64) or **8** (38:62), and free energies of activation at the coalescence temperature (T_c) were calculated from the unequal doublet equation.[11] For both **7** (T_c = 36 °C) and **8** (T_c = 40.5 °C) a value of $\Delta G^{\ddagger}$ = 16.5 kcal/mol was obtained for passage from the lower to higher energy ground states. By analogy to **6**, we assume the existence of amide forms for **7** and **8**, which indicates a somewhat higher C(O)–N rotational barrier than the ca. 12-kcal/mol value previously cited.[10]

B. Trapping Product Studies. After **6** was heated (100 °C, 25 h) in a 50-fold molar excess of cyclohexane, VPC analysis indicated the absence of starting material and near-quantitative formation of $Me_3SiOSiMe_3$, the expected α-deoxysilylation byproduct. Of the seven additional VPC components, the two most abundant were collected and identified by ^1H NMR as ethyl *N*-cyclo-

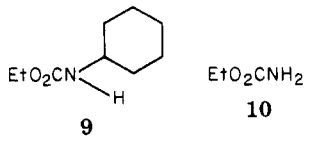
(8) F. P. Tsui and G. Zon, unpublished work.

(9) For the sake of simplicity, organosilylated compounds such as **6**, which are capable of silyl group migration, are named as hydroxylamine derivatives.

(10) H. Jancke, G. Englehardt, S. Wagner, W. Dirnens, G. Herzog, E. Thieme, and K. Rühlmann, *J. Organomet. Chem.*, **134**, 21 (1977). See also: A. R. Bassindale and T. B. Posner, *ibid.*, **175**, 273 (1979); S. A. Matlin, P. G. Sammes, and R. M. Upton, *J. Chem. Soc., Perkin Trans. 1*, 2478 (1979).

(11) W. Egan, Ph.D. Thesis, Princeton University, 1971.

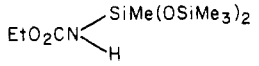
hexylurethane (9, 80%) and ethylurethane (10, 8%).



9 10

Product 9 is the formal product of singlet carbethoxynitrene ($EtO_2C\ddot{N}$:) insertion into a cyclohexane C–H bond; however, the presence of H-abstraction product 10 suggests that a portion of 9 may arise from cyclohexyl and ethylurethanyl radical combination. Photochemical decomposition of 6 in cyclohexane (λ_{max} 220 nm) was briefly investigated for comparative purposes, and after 58 h of irradiation at 254 nm, VPC indicated the presence of 9 (45%), 10 (55%), and $Me_3SiOSiMe_3$ (75%). The observation that the 9/10 product ratio changed from 10 to 0.8 clearly indicates a fundamental difference between thermal and photoinduced α-deoxysilylation.

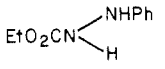
Thermal decomposition of 6 (100 °C, 20 h) in the presence of a 5-fold molar excess of bis(trimethylsiloxy)-methylsilane, $(Me_3SiO)_2MeSiH$, led to a 90% yield (VPC) of ethyl *N*-[[bis(trimethylsiloxy)methyl]silyl]urethane (11),



11

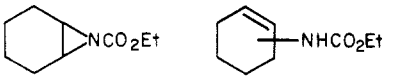
which was isolated by VPC and identified by ^1H NMR. Thermolysis of phenyl azide in silanes also affords products of overall insertion into Si–H bonds; however, a radical chain mechanism has been suggested for these azide reactions.[12] By way of contrast, the kinetics for production of 11 from 6 are first order.

The thermal reaction of 6 in aniline gave a 58% yield of ethyl phenylhydrazoformate (12), which was also isolated by VPC and was identified from ^1H NMR and melting point data. Hafner et al.[13] have obtained 12 by the analogous thermolysis of ethyl azidoformate, EtO_2CN_3.



12

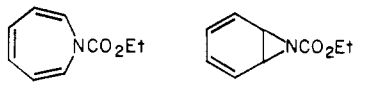
Heating 6 in cyclohexene gave a product distribution likewise indicative of $EtO_2C\ddot{N}$: generation. After 72 h at 90 °C in a 15-fold molar excess of the olefin, 13 was ob-



13 14

tained (VPC) in 42% yield together with a mixture of three isomers represented by structure 14 (10%) and a relatively small amount of 10 (ca. 2%). A control experiment demonstrated the thermal stability of 13 under the above reaction conditions and thus ruled out the possibility that 14 arises from secondary decomposition. Products 13 and 14 have been previously obtained from thermolysis of ethyl azidoformate.[14]

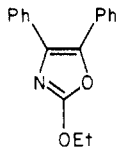
In benzene as solvent, thermolysis of 6 gave *N*-carbethoxyazepine (15, 57%) and a trace of 10. Compound 15 was isolated by TLC and identified by comparison of its ^1H NMR spectrum with that reported for a sample of 15



15 16

which was derived from photolysis of ethyl azidoformate in benzene.[15] The formation of 15 from reaction of the azide precursor is believed[16] to result from electrophilic attack of the aromatic ring by $Et_2OC\ddot{N}$: to give 7-carbethoxy-7-azabicyclo[4.1.0]heptadiene (16) which then undergoes ring opening.

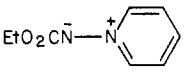
The major product from thermal reaction of 6 with diphenylacetylene is the same as that obtained by ethyl azidoformate thermolysis.[17] Heating 6 (90 °C, 72 h) in a 10-fold molar excess of the acetylene in hexafluorobenzene (C_6F_6) solvent led to isolation of 2-ethoxy-4,5-diphenyloxazole (17, 20%). The oxazole could arise from



17

1,3-dipolar addition of $EtO_2C\ddot{N}$: ↔ $EtOC(O^-)=N:^+$ to the triple bond or from rearrangement of an initially formed unstable azirine.

α-Deoxysilylation of 6 (100 °C, 25 h) in a 15-fold molar excess of pyridine gave the same pyridinium ylide (18, 40%) as that obtained from similar nucleophilic trapping during thermolysis of tetramethylene bis(azidoformate).[18] An alternative pathway to 18 involves a two-step process initiated by nitrene addition to C=N in pyridine.



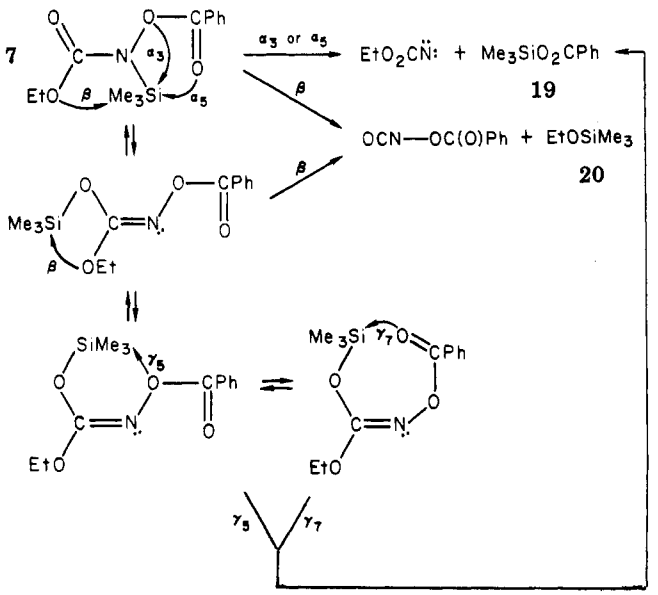
18

The apparent efficiency of bis(trimethylsiloxy)methylsilane as a nitrene trapping agent during thermolysis of 6 led to our selection of this material for analogous studies with nitrene precursors 7 and 8. The *O*-benzoyl compounds were each heated (100 °C, 30 h) with a 20-fold molar excess of the silane trap, and VPC of the reaction mixtures led to the isolation of the expected product, 11 (40%). In the case of 7, the anticipated byproduct, Me_3SiO_2CPh (19, 35%), was accompanied by $EtOSiMe_3$ (20, 20%). Formation of 11, 19, and 20 from 7 suggests that the thermolysis proceeds by competing fragmentation pathways. Scheme I illustrates the various thermolysis mechanisms for the amide and imidate forms of 7, which are presumed to be in rapid equilibrium at 100 °C, given the relatively low energy barrier ($\Delta G^{\ddagger}$ = 15–20 kcal/mol) for 1,3-migration of Me_3Si in cognate systems.[10] Differentiation of, for example, the α_3 and α_5 pathways could utilize ^{18}O labeling; however, the possibility of label scrambling by degenerate rearrangement of 19 (1,3-Me_3Si shifts between oxygens) prompted our use of kinetic measurements to address this question (vide infra).

C. Kinetic Studies. The rate constant (k) for disappearance of 6 in C_6F_6 was obtained by ^1H NMR monitoring of the Me_3Si region, which allowed for calculation of the

(12) F. A. Carey and C. W. Hsu, *Tetrahedron Lett.*, 3885 (1970).
(13) K. Hafner, D. Zinser, and K. L. Mortiz, *Tetrahedron Lett.*, 1733 (1964).
(14) W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, 87, 1947 (1965).
(15) K. Hafner and C. König, *Angew. Chem.*, 75, 89 (1963).
(16) W. Lwowksi and T. J. Maricich, *J. Am. Chem. Soc.*, 87, 3630 (1965).
(17) R. Huisgen and H. Blaschke, *Chem. Ber.*, 98, 2985 (1965).
(18) T. J. Prosser, A. F. Marcantonio, and D. S. Breslow, *Tetrahedron Lett.*, 2479 (1964).

Scheme I

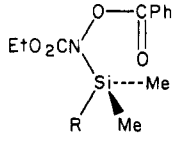


relative concentration of starting material and $Me_3SiOSiMe_3$ as a function of time. The k values for **6** at 100 °C which are listed in Table I indicate that the rate of reaction was independent of initial concentration. Measurements with **6** at 90–120 °C afforded a good linear least-squares fit of log (k/T) vs. T^{-1} that gave $\Delta H^{\ddagger} = 23.4$ kcal/mol and $\Delta S^{\ddagger} = -17.6$ eu, which reveals a substantially more negative entropy term than the −3.8-eu value for α-deoxysilylation of analogue **1** in toluene.[4]

The overall rate for disappearance of **7** in C_6F_6 was measured by ^1H NMR using Me_3Si signal intensities of starting material, **19**, and **20** at probe temperatures of 130, 140, and 150 °C. First-order plots of ln $(7_0/7_t)$ vs. time (t) gave $k_{overall} = 3.26 \times 10^{-5}$, 5.98×10^{-5}, and 10.1×10^{-5} s^{-1}, respectively. A duplicate set of measurements with analogue **8** indicated that $k_{overall} = 1.86 \times 10^{-5}$, 3.64×10^{-5}, and 6.96×10^{-5} s^{-1}, respectively, and thus demonstrated that t-Bu for Me substitution has little influence upon the overall thermolysis rate.

For comparison with **6**, it was of interest to extract from $k_{overall}$ the rate constant associated with nitrene formation, and subsequent analysis[19] of the aforementioned ^1H NMR kinetic data gave the following activation parameters: **7**, $\Delta H^{\ddagger} = 16.4$ kcal/mol, $\Delta S^{\ddagger} = -39.9$ eu, $\Delta G^{\ddagger}$ (100 °C) = 31.3 kcal/mol; **8**, $\Delta H^{\ddagger} = 20.4$ kcal/mol, $\Delta S^{\ddagger} = -31.3$ eu, $\Delta G^{\ddagger}$ (100 °C) = 32.1 kcal/mol. The somewhat lower free energy of activation for **6** [$\Delta G^{\ddagger}$ (100 °C) = 30.0 kcal/mol], relative to **7** and **8**, together with the more negative $\Delta S^{\ddagger}$ terms for **7** and **8** can be rationalized in terms of the α_3 fragmentation mode for **6**–**8** (eq 7); however, further experiments are needed to test this suggestion.

Our final kinetic studies with **7** and **8** concerned their relative rates of N–Si bond hydrolysis. As illustrated in structure **21** there is an exposed tetrahedral face about Si

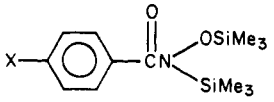


21

for intramolecular attack by O in both cases, regardless of which oxygen is actually involved; however, backside intermolecular attack at Si by H_2O leading to hydrolysis is relatively hindered with R = t-Bu. Compound **8** thus served as a model for strategically modifying a nitrene precursor such that a "normal" rate of deoxysilylation would be achieved in concert with increased hydrolytic stability.

The rates of N–Si bond cleavage in **7** and **8** were obtained by ^1H NMR at 220 MHz in 40% v/v $CD_3OD/CDCl_3$ rather than D_2O due to solubility. Pseudo-first-order solvolysis rate constants (k') at 20 °C were derived from the Me_3Si spectral region: for **7**, $k' = 5.18 \times 10^{-3}$ s^{-1}, $\tau_{1/2} = 2.3$ min; for **8**, $k' = 1.80 \times 10^{-6}$ s^{-1}, $\tau_{1/2} = 106$ h. These results demonstrate that the t-$BuMe_2Si$ compound is ca. 3000 times more stable than **7** under the solvolysis conditions, and, in view of their comparable thermolysis rates, it thus appears that the above rationale for **21** may be of value for additional structure–reactivity manipulations.

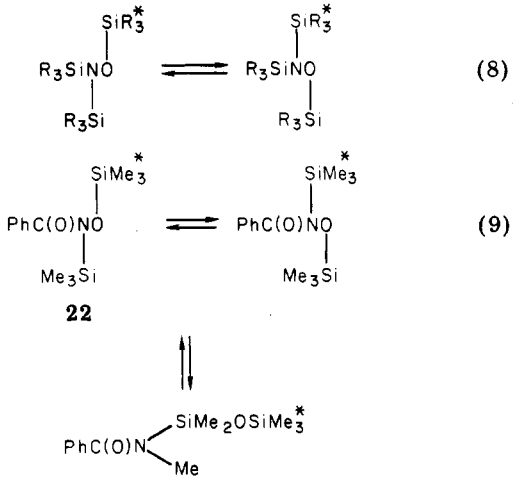
II. *N*-Aroyl-*N*,*O*-bis(trimethylsilyl)hydroxylamines. A. Synthesis. Members of a series of para-substituted *N*-aroyl-*N*,*O*-bis(trimethylsilyl)hydroxylamines (**22**–**26**) were prepared in ca. 90% yield by overnight re-



22, X = H
23, X = OMe
24, X = Me
25, X = F
26, X = Cl

action of the corresponding hydroxylamines with a 4-fold molar excess of Me_3SiCl/Et_3N in ether at room temperature. In each case, the ^1H NMR spectrum was consistent with the presence of one major isomer. Alternative routes to **22** which involve coupling of PhCOCl with either HN-$(SiMe_3)OSiMe_3$ or $(Me_3Si)_2NOSiMe_3$ have been subsequently reported by King et al.[20]

Several years ago, West and co-workers[7b,21] reported that tris(organosilyl)hydroxylamines (**2**) undergo reversible dyotropic rearrangement (eq 8) prior to irreversible (silylamino)disiloxane formation (eq 2). Compound **22** was studied with regard to the possibility of its similar behavior (eq 9); however, ^1H NMR spectra recorded up to a temperature of 148 °C failed to provide evidence of the expected signal coalescence. Instead, one observed the



(8)

(9)

22

(19) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism, A Study of Homogeneous Chemical Reactions", Wiley, New York, 1961.

(20) F. D. King, S. Pike, and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 351 (1978).

(21) P. Nowakowski and R. West, *J. Am. Chem. Soc.*, **98**, 5616 (1976).

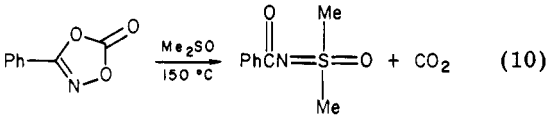
Table I. Kinetic Parameters for Thermolysis of Organosilylated Hydroxylamine Derivatives

compd	[compd], M	temp, °C	k,[a] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ (100 °C), kcal/mol
6	0.50	90	7.82×10^{-6}	23.4	−17.6	30.0
	0.50	100	2.02×10^{-5}			
	0.38	100	2.08×10^{-5}			
	0.25	100	2.32×10^{-5}			
	0.12	100	2.12×10^{-5}			
	0.50	110	4.50×10^{-5}			
	0.50	120	1.03×10^{-4}			
7[b]	1.00	130	1.90×10^{-5}	16.4	−39.9	31.3
	0.75	130	1.95×10^{-5}			
	0.50	130	1.93×10^{-5}			
	0.50	140	3.24×10^{-5}			
	0.50	150	5.32×10^{-5}			
8[b]	1.00	130	1.06×10^{-5}	20.4	−31.3	32.1
	0.75	130	1.11×10^{-5}			
	0.50	130	1.07×10^{-5}			
	0.50	140	2.02×10^{-5}			
	0.50	150	3.73×10^{-5}			
22[c]	0.75	80	1.91×10^{-6}	25.8	−11.8	30.2
	0.50	80	1.98×10^{-6}			
	0.25	80	2.01×10^{-6}			
	0.12	80	1.94×10^{-6}			
	0.75	90	5.41×10^{-6}			
	0.75	100	1.45×10^{-5}			
	0.75	110	3.71×10^{-5}			
23	0.75	100	2.04×10^{-5}	26.2	−10.0	29.9
	0.75	110	5.28×10^{-5}			
	0.75	120	1.30×10^{-4}			
24	0.75	90	6.62×10^{-6}	26.2	−10.4	30.1
	0.75	100	1.80×10^{-5}			
	0.75	110	4.66×10^{-5}			
	0.75	120	1.15×10^{-4}			
25	0.75	100	1.34×10^{-5}	25.6	−12.4	30.2
	0.75	110	3.40×10^{-5}			
	0.75	120	8.24×10^{-5}			
26	0.75	100	1.06×10^{-5}	25.1	−14.4	30.5
	0.75	110	2.64×10^{-5}			
	0.75	120	6.27×10^{-5}			
29	0.50	100	7.10×10^{-7}	29.9	−6.8	32.4
	0.38	100	7.06×10^{-7}			
	0.25	100	7.48×10^{-7}			
	0.12	100	7.12×10^{-7}			
	0.50	110	1.63×10^{-6}			
	0.50	120	5.85×10^{-6}			
	0.50	140	3.94×10^{-5}			
30	0.50	100	9.14×10^{-7}	30.1	−5.8	32.3
	0.50	110	2.86×10^{-6}			
	0.50	120	8.03×10^{-6}			
31	0.50	100	1.06×10^{-6}	31.0	−3.0	32.1
	0.50	110	3.23×10^{-6}			
	0.50	120	9.38×10^{-5}			
	0.50	140	6.76×10^{-5}			
32	0.50	100	6.48×10^{-7}	29.9	−7.1	32.5
	0.50	110	1.91×10^{-6}			
	0.50	120	5.32×10^{-6}			
	0.50	140	3.57×10^{-5}			
33	0.50	100	5.08×10^{-7}	29.6	−8.2	32.7
	0.50	110	1.48×10^{-6}			
	0.50	120	4.09×10^{-6}			
	0.50	140	2.71×10^{-5}			
34	0.50	100	5.04×10^{-7}	29.5	−8.6	32.7
	0.50	110	1.47×10^{-6}			
	0.50	120	4.04×10^{-6}			
	0.50	140	2.65×10^{-5}			
42	1.12	140	4.14×10^{-6}	35.3	1.6	34.7
	1.12	150	1.13×10^{-5}			
	1.88	160	3.18×10^{-5}			
	1.12	160	3.17×10^{-5}			
	0.38	160	3.20×10^{-5}			

[a] First-order rate constant for disappearance of starting material in hexafluorobenzene, unless specified otherwise. All values were determined by ^{1}H NMR. [b] Kinetic values refer to formation of RMe_2SiO_2CPh as opposed to starting material disappearance (see text). [c] Values of $\Delta H^{\ddagger} = 33.0$ kcal/mol and $\Delta S^{\ddagger} = -2.2$ eu have been reported[20] for thermolysis of 22 in mesitylene solvent.

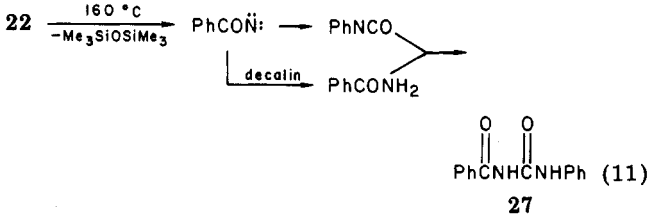
gradual disappearance of **22** ($\tau_{1/2}$ = 15 min) and concomitant formation of $Me_3SiOSiMe_3$. There was no evidence (NMe absorption) for the competing rearrangement shown in eq 9. Evidently, the relative rates of both dyotropic rearrangement and irreversible rearrangement to a (methylamino)disiloxane are slow relative to fragmentation, which *may* be the result of diminished electron density at N through carbonyl conjugation.

B. Trapping Product Studies. During the investigation of thermally induced α-deoxysilylation of **22–26** as a route to aroylnitrenes, it was expected that such nitrenes would readily undergo Lossen-type rearrangement to isocyanates; however, the possibility for their interception by a suitable trapping agent was suggested by the reported[22] reaction shown in eq 10.



(10)

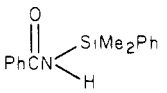
After 5 min of heating **22** in decalin at 160 °C, VPC analysis indicated the absence of starting material and formation of phenyl isocyanate (PhNCO, 86%) together with a small amount of 1-benzoyl-3-phenylurea (**27**, 6%); benzamide ($PhCONH_2$) was not detected. These findings may be rationalized according to eq 11 wherein PhCON:



(11)

partitions between rearrangement and, to a lesser extent, H-abstraction reactions with subsequent formation of the urea derivative. Support for this suggestion was obtained by demonstrating that PhNCO and $PhCONH_2$ react to give **27** (89%) under the thermolysis conditions applied to **22**. In this connection we note that King et al.[20] subsequently reported that the decomposition of **22** in cyclohexene as a potential trapping agent for PhCON: affords PhCNO (80%), $PhCONH_2$ (5–10%) and "unidentifiable polymer". The apparent inconsistency between our results and these findings is not fully understood but may be the result of differences between solvents and the starting concentration of **22**.

The presumed competition between bimolecular nitrene capture and intramolecular nitrene rearrangement prompted our investigation of a silane trapping agent; however, heating **22** (100 °C, 26 h) in a 10-fold molar excess of $PhMe_2SiH$ led to VPC isolation of only a small amount (5%) of *N*-(phenyldimethylsilyl)benzamide (**28**) in addition to PhNCO (82%).



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C. Kinteic Studies. The ^1H NMR method described above was again used to measure the disappearance rate constants (k) for **22–26** in C_6F_6 at 80–120 °C, and in all cases there was adherence to a first-order rate law (Table I). In view of the approximate constancy of $\Delta S^{\ddagger}$ for thermolysis of **22–26**,[23] a linear free-energy relationship was

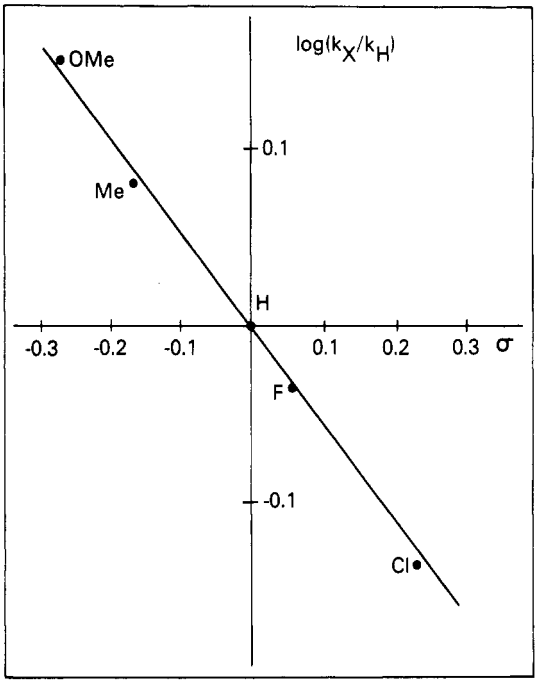
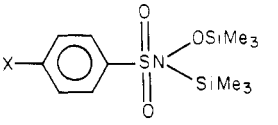


Figure 1. Hammett plot for thermolysis of para-substituted *N*-aroyl-*N*,*O*-bis(trimethylsilyl)hydroxylamines **22–26** (0.75 M) in hexafluorobenzene at 100 °C; ρ = −0.56. For values of k_X and k_H see Table I.

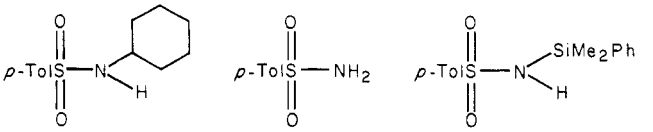
examined by using k values. A plot of log $(k_X/k_H)_{100°C}$ vs. the Hammett substituent constant σ indicated a good correlation and gave ρ = −0.56 (Figure 1). Thus, electron withdrawal by para substituents decelerates the fragmentation reaction, which is consistent with generation of an electron-deficient ArCON: species.

III. *N*-(Arylsulfonyl)-*N*,*O*-bis(trimethylsilyl)-hydroxylamines. A. Synthesis. The preparation of a series of *N*-(arylsulfonyl)-*N*,*O*-bis(trimethylsilyl)-hydroxylamines (**29–34**) from the respective group of hydroxylamines was analogous to that used for **22–26**; however, the yields (70–80%) were somewhat less. In each case ^1H NMR indicated the existence of a single isomer.



29, X = H
30, X = Me
31, X = OMe
32, X = F
33, X = Cl
34, X = Br

B. Trapping Product Studies. The *p*-tolyl derivative **30** was chosen as a representative compound for establishing the course of thermal reactions. After **30** was heated (120 °C, 48 h) in a 20-fold molar excess of cyclohexane, preparative TLC led to isolation of two components which were identified as **35** (90%) and **36** (1%), the



35 **36** **37**

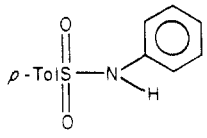
(22) J. Sauer and K. K. Mayer, *Tetrahedron Lett.*, 319 (1968).

(23) The isokinetic temperature[24] for **22–26** is −8 °C.

(24) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

expected products by analogy to thermolysis of *N,N*-dichloro-*p*-tolylsulfonamide with zinc in cyclohexane.[25] The high yield of **35** is consistent with the known[25] efficiency of sulfonylnitrene insertions into C–H bonds, and it was therefore not surprising to find that reaction of **30** in excess $PhMe_2SiH$ (130 °C, 30 h) similarly afforded product **37** in nearly quantitative yield.

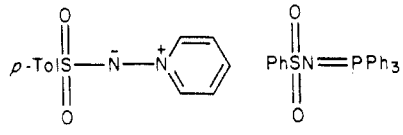
The result of heating **30** in benzene solvent was comparable to that obtained from azide and 1,2,4-triazolium ylide thermolyses.[26] After 8 h at 100 °C, **36** and *p*-tolylsulfanilide (**39**) were isolated (TLC) in 20% and 50%



39

yield, respectively. The formation of an anilide product from $MeSO_2N_3$ thermolysis has been rationalized[26,27] in terms of a singlet sulfonylnitrene which adds to benzene solvent to form an intermediate aziridine that then undergoes ring opening; however, direct C–H insertion is an alternative possibility.

Thermal α-deoxysilylations of **30** in pyridine (130 °C, 30 h) solvent or of **29** in benzene containing triphenylphosphine (120 °C, 48 h) gave samples of pyridinium ylide **40** (41%) and phosphinimine **41** (48%), respectively, which were expected on the basis of the results of earlier azide thermolyses.[28,29]



40 **41**

C. Kinetic Studies. Extension of the ^1H NMR kinetic measurements to **29–34** presented no difficulties, and all compounds obeyed a first-order rate law for disappearance in C_6F_6. First-order kinetics were also found for **30** in $PphMe_2SiH$. The k values and activation parameters determined in C_6F_6 at 100–140 °C are listed in Table I. A plot of log $(k_X/k_H)_{100°C}$ vs. σ gave a good linear correlation with $\rho = -0.64$ (Figure 2),[30] which indicates approximately the same sensitivity to electron withdrawal as in the aroyl systems ($\rho = -0.56$) and is likewise consistent with nitrene generation.

To evaluate the nature of solvent effects upon α-deoxysilylation of representative **30**, ^1H NMR monitoring of the reaction rate was carried out in five aromatic solvents, offering a reasonably wide spread of dielectric constants (ϵ). In each case, reaction at 100 °C was first order, and the values of k were found to vary over the range of $(8.91–12.1) \times 10^{-7}$ s^{-1}. A plot of ln k vs. $1/\epsilon$ is shown in Figure 3 and is roughly linear. The small rate enhancement with increasing solvent "polarity" (ϵ) is consistent with a concerted fragmentation process wherein some charge separation may be occurring. By way of comparison, the thermolysis rate ratio of 1.4 for **30** in $PhNO_2$ ($\epsilon = 34.8$) vs. Ph_2O ($\epsilon = 3.69$) is slightly greater than the rate

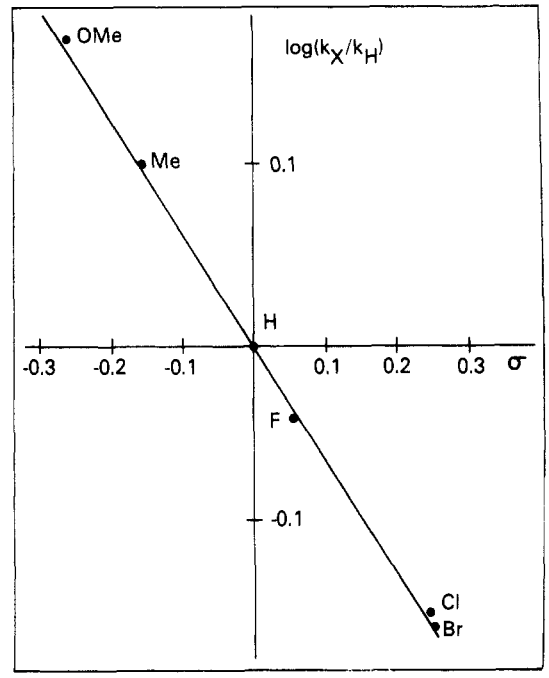


Figure 2. Hammett plot for thermolysis of para-substituted *N*-(arylsulfonyl)-*N,O*-bis(trimethylsilyl)hydroxylamines **29–34** (0.50 M) in hexafluorobenzene at 100 °C; $\rho = -0.64$. For values of k_X and k_H see Table I.

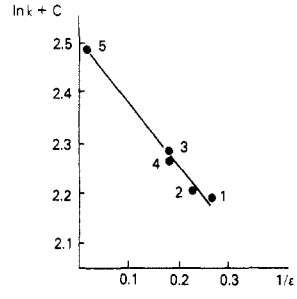
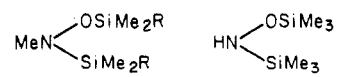


Figure 3. Plot of ln $k + C$ vs. $1/\epsilon$, where k is the ^1H NMR derived first-order themolysis rate constant for **30** (0.3 M) at 100 °C in the following solvents: 1, Ph_2O, $\epsilon = 3.69$, $k = 8.91 \times 10^{-7}$ s^{-1}; 2, PhOMe, $\epsilon = 4.33$, $k = 8.99 \times 10^{-7}$ s^{-1}; 3, PhCl, $\epsilon = 5.62$, $k = 9.75 \times 10^{-7}$ s^{-1}; 4, PhBr, $\epsilon = 5.40$, $k = 9.63 \times 10^{-7}$ s^{-1}; 5, $PhNO_2$, $\epsilon = 34.8$, $k = 12.1 \times 10^{-7}$ s^{-1}.

ratio of 1 reported for loss of nitrogen from either phenyl azide[31] or 2-azidobiphenyl[32] upon being heated in $PhNO_2$ vs. decalin ($\epsilon = 2.15$). Moreover, the influence of solvent on phenylnitrene formation from α-deoxysilylation of **1** has been found to be essentially identical with that for **30**.[33]

IV. *N*-Methyl-*N,O*-bis(trimethylsilyl)hydroxylamine and Related Compounds. A. Synthesis. *N*-Methyl compound **42**[7a] was obtained in ca. 90% yield from



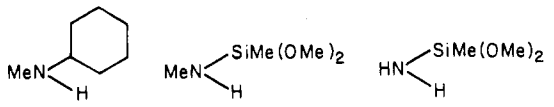
42, R = Me **44**
43, R = *t*-Bu

N-methylhydroxylamine (MeNHOH) by reaction with Me_3SiCl/Et_3N in ether. The preparation of anhydrous MeNHOH is somewhat tedious, and, consequently, an allernative albeit lower yielding (ca. 50%) route was developed and involved treatment of MeNHOH·HCl with $HN(SiMe_3)_2/Et_3N$ in pentane. The same general methods

(25) D. S. Breslow and M. F. Sloan, *Tetrahedron Lett.*, 5349 (1968).
(26) R. A. Abramovitch, T. D. Bailey, T. Takaya, and V. Uma, *J. Org. Chem.*, **39**, 340 (1974).
(27) R. A. Abramovitch, J. Roy, and V. Uma, *Can. J. Chem.*, **43**, 3407 (1965).
(28) (a) J. N. Ashley, G. L. Buchanan, and A. P. T. Easson, *J. Chem. Soc.*, **60** (1947); (b) T. Curtius and G. Kraemer, *J. Prakt. Chem.*, **125**, 323 (1930); (c) P. K. Datta, *J. Indian Chem. Soc.*, **24**, 109 (1947).
(29) J. E. Leffler and Y. Tsuno, *J. Org. Chem.* **28**, 902 (1963).
(30) The isokinetic temperature[24] for **29–34** is −8 °C.
(31) K. E. Russell, *J. Am. Chem. Soc.*, **77**, 3487 (1955).
(32) P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, **84**, 480 (1962).
(33) F. P. Tsui, Ph.D. Thesis, The Catholic University of America, (1978).

and results were found to extend to synthesis of analogue **43** as well as parent compound **44**.[34]

B. Trapping Product Studies. During the investigation of possible dyotropic rearrangement of **42**, Boudjouk and West[7a] observed formation of $Me_3SiOSiMe_3$ and therefore obtained the first evidence for α-deoxysilylation at a nigrogen center. Tsui et al.[3] subsequently examined thermolysis of **42** in cyclohexane as solvent and provided additional support for MeN̈: generation, viz., isolation of *N*-methyl cyclohexylamine (**45**, 5%), the formal C–H in-



45 **46** **47**

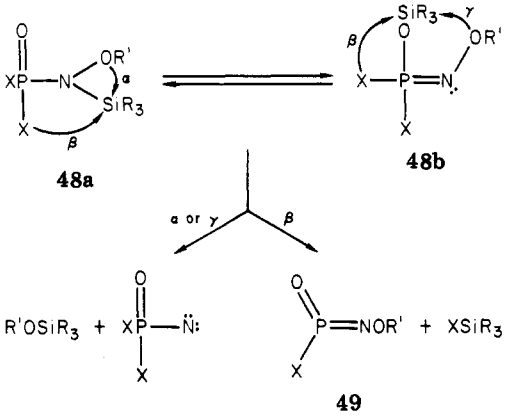
sertion product. To achieve increased efficiency of nitrene capture, we have used a silane trapping agent. Heating **42** in a 20-fold excess of $(MeO)_2MeSiH$ (150 °C, 37 h) led to a 40% yield (VPC) of insertion product **46**, which was readily characterized by ^1H NMR. The same silane trap with **44** at 250 °C for 24 h afforded **47** in 43% yield, which implies the generation of HN̈:; however, the severe conditions required for thermolysis of **44** militated against additional trapping studies.

Silylenes are known[6b] to undergo insertion into Si–O bonds (vide infra), and the possibility of a similar reaction for nitrenes was of interest as the reverse step in hydroxylamine α-deoxysilylations (cf. eq 1). This point was investigated by partially decomposing **43** in the presence of $Me_3SiOSiMe_3$; however, VPC analysis showed the absence of **42**, which is the expected "crossover" product from MeN̈: insertion into a Si–O bond of the disiloxane. Further attempts to address this mechanistic question by studying label exchange in $MeNSiMe_3(OSiMe_3\text{-}d_9)$ were foiled by our inability to synthesize the desired starting material with a high degree of $SiMe_3\text{-}d_9$ regioselectivity.

C. Kinetic Studies. From ^1H NMR monitoring of **42** in C_6F_6, it was found that starting material disappearance at 140–160 °C follows a first-order rate law and that the kinetic activation parameters are as listed in Table I. Similar analysis of **44** in 2-bromonaphthalene failed to provide reproducible data above 200 °C; however, it was found that <10% reaction occurs after 2 h at 170 °C, which indicates that first-order decomposition under these conditions is characterized by $k < 1.1 \times 10^{-5}$ s^{-1}.

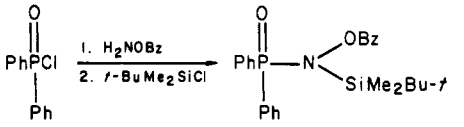
V. *N*-(Diphenylphosphoryl)-*N*-(*tert*-butyldimethylsilyl)-*O*-benzylhydroxylamine. Relatively little information[35] is currently available regarding phosphorylnitrenes, $X_2P(O)$N̈:, despite their formal similarity to sulfonylnitrenes. Our successful application of α-deoxysilylation to compound **30** prompted the consideration of the generalized case for phosphorus shown in Scheme II. The intramolecular 1,3-migration of R_3Si (**48a** ⇄ **48b**) in organosilylated phosphoramides has been previously studied, and conversion of the thermodynamically favored imide form (**48b**) into the amide is characterized by $\Delta G^{\ddagger}$ < ca. 25 kcal/mol in $(PhO)_2P(O)N(SiMe_3)Ph$,[36] which implies relatively rapid tautomerization at the anticipated thermolysis temperatures (>100 °C). For nucleophilic X groups such as halogen, alkoxy, and amino, two β-elimination pathways to a metaphosphorimidate (**49**) may compete with the α- and/or γ-elimination leading to $X_2P(O)$N̈:. Consequently, compound **50** was synthesized

Scheme II



48a **48b** **49**

(eq 12) as a candidate for exclusive formation of $Ph_2P(O)$N̈:.[37]

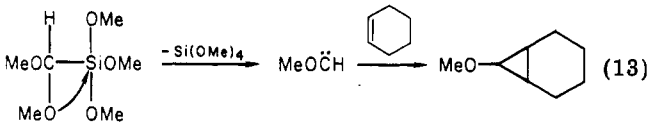


(12)

50

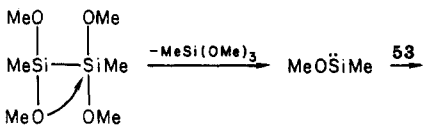
Recalling that α-deoxysilylation of sulfonylnitrene precursors requires heating at ca. 130 °C for 24 h, it was surprising to recover primarily unreacted **50** after 6 h at 195 °C in either cyclohexane or 2-bromonaphthalene; only a trace amount of $Ph_2P(O)NH_2$ (**51**) and some intractable material ("polymer") were found as products. Photochemical decomposition of **50** in cyclohexane at 254 nm for 24 h led to a 60% yield of **51** and "polymer"; however, there was again no evidence of the expected insertion product, $Ph_2P(O)NHC_6H_{11}$. While these data are rather limited, the obvious resistance of **50** to deoxysilylation suggests that these compounds are not promising candidates for $X_2P(O)$N̈: generators.

VI. Kinetics of α-Deoxysilylation at Carbon and Silion. The unavailability of kinetic information regarding α-deoxysilylation at carbon and silicon reaction centers for comparison with the nitrogen case led to studies of **52** and **53**, as the reactions shown in eq 13[6a] and 14[6b] have been previously reported.

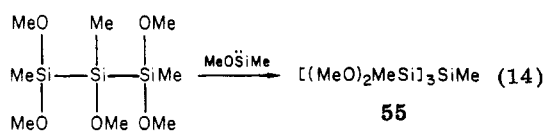


(13)

52



53



(14)

54 **55**

(34) O. Smrekar and U. Wannagat, *Monatsh. Chem.*, **100**, 760 (1969).
(35) W. Lwowski in "Nitrenes", W. Lwowski, Ed., Interscience, New York, 1970, p 424.
(36) P. K. G. Hodgson, R. Katz, and G. Zon, *J. Organomet. Chem.*, 117, C63 (1976).

(37) Reaction of $Ph_2P(O)Cl$ with H_2NOBz rather than H_2NOH was selected to preclude the possible formation of $Ph_2P(O)ONH_2$ with the latter reagent. It has been subsequently reported that this "unwanted" O-phosphorylation reaction does indeed take place [M. J. P. Harger, *J. Chem. Soc., Chem. Commun.*, 768 (1979)].

Table II. Kinetic Parameters for Thermolysis of Compounds 52 and 53

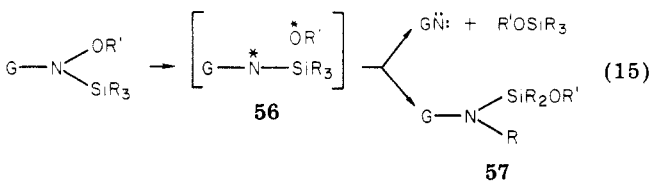
compd	temp, °C	k,[a] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ (100 °C), kcal/mol
52[b]	90	4.41×10^{-6}	12.0	−50.2	30.7
	100	7.74×10^{-6}			
	110	1.18×10^{-5}			
	120	1.72×10^{-5}			
53[c]	170	1.89×10^{-5}	17.9	−40.4	32.9
	180	3.59×10^{-5}			
	190	6.13×10^{-5}			

[a] First-order rate constant for disappearance of starting material determined by ^{1}H NMR. [b] Cyclohexene solvent. [c] Contained diphenylacetylene in hexafluorobenzene as solvent.

Cyclohexene was used as the solvent for **52** while a 4-fold molar excess of diphenylacetylene was utilized with **53** in order to minimize loss of this precursor via silylene interception.[6b] ^{1}H NMR monitoring of the organosilyl region and first-order kinetic plots derived from relative signal intensities gave the activation parameters listed in Table II. The striking feature of these data is that the rate-controlling free energy is strongly influenced by entropy factors rather than enthalpy. The very large negative values of $\Delta S^{\ddagger}$ imply significantly increased ordering of the transition vs. ground states, which is consistent with concerted bond reorganization for these comparative α-deoxysilylations.

Conclusions

Thermolysis of organosilylated hydroxylamines of general structure $GN(OR')SiR_3$ in the presence of nitrene trapping agents has given products consistent with α-deoxysilylation leading to GN̈:, where G = EtO_2C, ArCO, $ArSO_2$, and Me. For the EtO_2C systems with R′ = C(O)Ph (**7** and **8**), there is competing β elimination which is not seen with R′ = $SiMe_3$ and may result from decreased nucleophilicity of the OR′ oxygen via carbonyl conjugation. The kinetics for these α-deoxysilylation reactions are, as expected, concentration independent and first order. The entropy of activation varies substantially; however, it is almost always negative, as was also shown to be the case for α-deoxysilylation about carbon (**52**) and silicon (**53**). The increased transition- vs. ground-state ordering reflected in these $\Delta S^{\ddagger}$ values supports a mechanism involving concerted bond reorganization rather than complete ionization. Some degree of charge separation is, however, suggested by negative Hammett reaction constants for G = ArCO (ρ = −0.56) and G = $ArSO_2$ (ρ = −0.64) as well as a small rate acceleration with increasing solvent "polarity" (ϵ) in the latter system. An alternative mechanistic view of α-deoxysilylation involves rate-limiting N–O bond cleavage leading to **56** (eq 15), wherein the asterisks denote



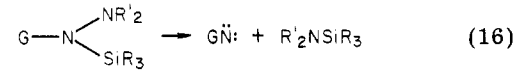
(15)

56 57

either a radical or ion pair. This reaction mode presumably obtains for G = R_3Si[7c] and should lead to competing rearrangement to form **57**; however, such products were never observed. The relatively large negative $\Delta S^{\ddagger}$ factors and slower reaction of **7** and **8** (R′O* = $PhCO_2$*) vs. **6** (R′O* = Me_3SiO*) also militate against eq 15; resonance stabilization of $PhCO_2$* should lead to faster reactions.

The unique thermal chemistry (rearrangement, eq 3) for systems with G = SiR_3 is not ascribable to additional (p → d)$_\pi$ bonding between N and Si since analogous (p → p)$_\pi$ delocalization exists when G = EtO_2C and ArCO, and these compounds undergo fragmentation. A better rationale may be the conjugative and/or inductive stabilization of **56** when G = SiR_3 or an electron-donating aryl group.[33]

With regard to further extensions of α-deoxysilylation, thermolysis of $ArP(OR')SiR_3$ may provide a new method for arylphosphene (ArP̈:) generation, while compounds of general structure **58** may afford nitrenes by analogous "α-deazasilylation" (eq 16). Consideration of eq 16 and



(16)

58

2 indicates, a priori, that the greater nucleophilicity of NR_2 vs. OR′ may lower the activation energy, while the energy difference between developing N–Si vs. O–Si bond strengths opposes this effect. Our preliminary studies[38] with $EtO_2CN(NMe_2)SiMe_3$ (**59**) have shown that first-order decomposition in C_6F_6 is characterized by $\Delta G^{\ddagger}$ (100 °C) = 34.1 kcal/mol and a *positive* entropy of activation, $\Delta S^{\ddagger}$ = 15.2 eu. In addition, thermolysis of **59** in cyclohexane does *not* afford **9**. Comparison with **6** thus suggests that eq 16 is not operative with prototype **59** and that its thermolysis proceeds by an as yet unidentified mechanism.

Experimental Section

Elemental analyses were performed by Chemalytics, Inc. Unless specified otherwise, ^{1}H NMR spectral data are referenced to internal Me_4Si and were obtained with either a Varian A-60 or EM-360A spectrometer. IR and UV measurements employed Perkin-Elmer 337 and Cary 15 instruments. VPC work was performed with Aerograph 90-P and Varian Aerograph 920 thermal conductivity instruments using 0.25-in. columns and 60/80-mesh Chromosorb G: column A, 3 ft, 5% SE-30; column B 6 ft, 15% SE-30; column G, 3 ft, 1% SE-30; column H, 5 ft, 5% SE-30; column I, 1.5 ft, 15% SE-30; column R, 6 ft, 5% SE-30. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. The preparation, storage, and handling of all organosilicon compounds were conducted with exclusion of atmospheric moisture by use of either high-purity dry nitrogen or argon. All solvents were purified and dried according to conventional methods.

***N,O*-Bis(trimethylsilyl)-*N*-carbethoxyhydroxylamine (6).** A magnetically stirred solution of *N*-carbethoxyhydroxylamine (**5**; 4.2 g, 0.04 mmol) in ether (20 mL) was cooled in an ice bath while 6-fold molar excesses of triethylamine and trimethylsilyl chloride were slowly added (5 min). The reaction mixture was then refluxed for 24 h, and Et_3N·HCl was removed by gravity filtration. Volatiles from the filtrate were removed in vacuo (1 mm) at room temperature, and the residual oil was Kugelrohr distilled [60–70 °C (0.1 mm)] to yield **6** (90%) as a colorless sweet-smelling oil which was made analytically pure by preparative VPC on column H (110 °C, 60 mL/min): NMR ($CDCl_3$) δ 3.8–4.2 (q, 2, CH_2CH_3), 1.1–1.5 (t, 3, CH_2CH_3), 0.17 (s, 9, $OSiMe_3$), 0.10 (s, 9, $NSiMe_3$); IR (neat) 2950, 2850, 1700, 1250, 1100, 850, 755 cm^{-1}; mass spectrum (70 eV), m/e 249 (parent), 162 (base peak). Anal. Calcd for $C_9H_{23}NO_3Si_2$: C, 43.33; H, 9.29. Found: C, 43.58; H, 9.19.

***O*-Benzoyl-*N*-carbethoxy-*N*-(trimethylsilyl)hydroxylamine (7).** To a magnetically stirred solution of *O*-benzoyl-*N*-carbethoxyhydroxylamine (4.2 g, 20 mmol) in ether (40 mL) were added 6-fold molar excesses of triethylamine and trimethylsilyl chloride. The reaction mixture was refluxed for 24 h, Et_3N·HCl was then removed by gravity filtration, and volatiles from the filtrate were removed in vacuo (1 mm) at room temperature. The

(38) Y. H. Chang and G. Zon, unpublished work.

Table III. Experimental Data for Compounds 22-26

compd	yield, %	NMR (hexafluorobenzene, Me_4Si),[c] δ aromatic	other	$OSiMe_3$	$NSiMe_3$	m/e for M[a]	t_{air},[b] s
22	94	7.3 (br s)		0.23 (s, 9)	0.21 (s, 9)	281	242
23	90	6.6, 6.7, 7.4, 7.6 (AA'BB')	3.8 (s, 3)	0.32 (s, 9)	0.29 (s, 9)	311	726
24	91	7.0, 7.1, 7.4, 7.5 (AA'BB')	2.3 (s, 3)	0.27 (s, 9)	0.24 (s, 9)	295	483
25	92	6.8-7.7 (m)		0.31 (s, 9)	0.28 (s, 9)	299	362
26	90	7.0, 7.2, 7.6, 7.7 (AA'BB')		0.33 (s, 9)	0.30 (s, 9)	315	603

[a] At 70 eV all compounds show a base peak at m/e 162. [b] VPC retention times refer to column G at 110 °C and a flow rate of 120 mL/min. [c] Multiplicity and the number of hydrogens given in parentheses.

residual sweet-smelling oil was Kugelrohr distilled [72–85 °C (0.1 mm)] to yield 85% of the crude product. Pure **7** was obtained by preparative VPC using column A (110 °C, 60 mL/min, t_{air} = 7.5 min): NMR (CCl_4) δ 0.12 (s, 9, $NSiMe_3$), 1.1 (t, 3, CH_2CH_3), 4.0 (q, 2, CH_2CH_3), 7.2–8.0 (m, 5, aromatic); mass spectrum (70 eV), m/e 282 (parent), 194 (base peak). Anal. Calcd for $C_{13}H_{19}NSiO_4$: C, 55.52; H, 6.76. Found: C, 55.74; H, 6.86.

***O*-Benzoyl-*N*-carbethoxy-*N*-(dimethyl-*tert*-butylsilyl)hydroxylamine (8).** To a magnetically stirred solution of *O*-benzoyl-*N*-carbethoxyhydroxylamine (4.2 g, 20 mmol) in ether (50 mL) was added a 6-fold molar excess of triethylamine and a 4-fold molar excess of dimethyl-*tert*-butylsilyl chloride. The reaction mixture was refluxed for 2 days, and Et_3N·HCl was then removed by filtration. Volatiles from the filtrate were removed in vacuo (1 mm) at room temperature, and the residue was Kugelrohr distilled [82–90 °C (0.1 mm)] to give an 85% yield of **8** as a white semisolid, which was further purified by repeated extraction into ether: NMR (CCl_4) δ 0.12 (s, 6, $SiMe_2$), 0.85 (s, 9, *t*-Bu), 1.4 (t, 3, CH_2CH_3), 3.85 (q, 2 CH_2CH_3), 7.6 (m, 5, aromatic). Anal. Calcd for $C_{16}H_{15}NSiO_4$: C, 61.34; H, 4.79. Found: C, 61.48; H, 4.88.

Ethyl *N*-[[Bis(trimethylsiloxy)methyl]silyl]carbamate (11). A magnetically stirred solution of ethyl carbamate (0.5 g, 5.6 mmol) in ether (40 mL) was treated with triethylamine (7.8 mL) and bis(trimethylsiloxy)methylchlorosilane (13 mL, 0.05 mol), and the reaction mixture was then refluxed for 24 h. Et_3N·HCl was removed by gravity filtration, volatiles from the filtrate were removed in vacuo (1 mm) at room temperature, and then residual oil was Kugelrohr distilled [80–90 °C (0.05 mm)] to yield (90%) a colorless oil which was identified as **11**: NMR (CCl_4) δ 0.10 (s, 3, SiMe), 0.17 (s, 18, $OSiMe_3$), 3.8–4.2 (q, 2, CH_2CH_3), 1.1–1.4 (t, 3, CH_2CH_3), 4.5 (br s, 1, NH). Compound **11** could be further purified by preparative VPC on column H (110 °C, 60 mL/min, t_{air} = 13 min).

***N*-Aroyl-*N*,*O*-bis(trimethylsilyl)hydroxylamines 22–26.** The *N*-aroylhydroxylamine starting materials were prepared according to the procedure of Shukla et al.[39] and were silylated by using the following method described for parent compound **22**. Pertinent experimental details for all products are given in Table III.

A magnetically stirred solution of *N*-benzoylhydroxylamine (274 mg, 2 mmol) in ether (10 mL) was maintained at room temperature during slow addition of 4.8 equiv of triethylamine (0.67 mL). Trimethylchlorosilane (0.56 mL, 4.4 mmol) in ether (5 mL) was added dropwise, and the reaction mixture was then refluxed for 24 h. Et_3N·HCl was removed by gravity filtration, and the volatiles were removed in vacuo (1 mm) at room temperature. Compound **22** was purified by VPC (see Table III).

***N*-(Phenyldimethylsilyl)benzamide (28).** A mixture of benzamide (1.21 g, 10 mmol), triethylamine (2.8 mL, 38 mmol), and phenyldimethylchlorosilane (1.9 mL, 11 mmol) in benzene (10 mL) was refluxed for 24 h and was then cooled prior to removal of Et_3N·HCl by filtration. Volatiles from the filtrate were removed in vacuo (1 mm) at room temperature, and the residue was analyzed by VPC using column A (110 °C, 120 mL/min). Compound **28** was isolated (t_{air} = 6 min 2 s) and identified by its NMR spectrum (CCl_4): δ 0.40 (s, 6, Me), 7.30 (m, 10, aromatic).

Table IV. Experimental Data for Compounds 29-34

compd	NMR (hexafluorobenzene, Me_4Si),[d] δ aromatic	other	$OSiMe_3$	$NSiMe_3$	m/e for M[a]
29[b]	7.1 (br s)		0.18 (s)	0.075 (s)	317
30[c]	7.2, 7.3, 7.5, 7.6 (AA'BB')	2.4 (s)	0.15 (s)	0.05 (s)	331
31	6.9, 7.1, 7.7, 7.9 (AA'BB')	3.9 (s)	0.20 (s)	0.15 (s)	347
32	7.7 (m)		0.21 (s)	0.10 (s)	335
33	7.8 (m)		0.28 (s)	0.17 (s)	352
34	8.9 (m)		0.29 (s)	0.20 (s)	396

[a] At 70 eV all compound show a base peak at m/e 162. [b] Anal. Calcd for $C_{12}H_{23}NO_3Si_2S$: C, 45.57; H, 7.28. Found: C, 45.72; H, 7.56. [c] Anal. Calcd for $C_{13}H_{25}NO_3Si_2S$: C, 47.13; H, 7.55. Found: C, 47.31; H, 7.18. [d] Multiplicity given in parentheses.

***N*-(Arylsulfonyl)-*N*,*O*-bis(trimethylsilyl)hydroxylamines 29–34.** The *N*-(arylsulfonyl)hydroxylamine starting materials were prepared according to the procedure of Fujimoto and Sakai[40] and were silylated by using the method described above for **22** except that a 10-fold molar excess each of trimethylchlorosilane and triethylamine was employed. After concentration of the filtrate, the residue was stirred with cold ether to extract the product, which was then reconcentrated in vacuo and again extracted into cold ether. Table IV gives pertinent experimental details for final samples of **29–34**, which were obtained in 70–80% yield.

***N*-(Phenyldimethylsilyl)-*p*-tolylsulfonamide (37).** A mixture of *p*-tolylsulfonamide (855 mg, 5 mmol), triethylamine (1.04 mL, 7.5 mmol), and phenyldimethylchlorosilane (1.07 mL, 7.5 mmol) in ether (40 mL) was refluxed for 24 h and cooled, and Et_3N·HCl was then removed by filtration. Volatiles from the filtrate were removed in vacuo (1 mm) at room temperature, and the residue was subjected to preparative TLC (alumina; benzene–ether, 1:1). The faster-eluting band (R_f 0.81) was identified as compound **37** from its NMR spectrum (CCl_4): δ 0.21 (s, 6, $SiMe_3$), 2.31 (s, 3, Me), 4.95 (br s, NH), 7.12 (m, 9, aromatic).

***N*-Methyl-*N*,*O*-bis(trimethylsilyl)hydroxylamine (42).** To a vigorously stirred suspension of *N*-methylhydroxylamine hydrochloride (200 mg, 2.4 mmol) in THF (2 mL) at room temperature was added triethylamine (0.33 mL, 2.4 mol), and the mixture was then allowed to stir for 12 h. Hexamethyldisilazane (9.6 mL, 4.8 mmol) was added, and, after 24 h, the mixture was filtered. Volatiles from the filtrate were removed in vacuo (1 mm) at room temperature, and compound **42** was then purified by VPC using column B (110 °C, 120 mL/min, t_{air} = 7 min 12 s; 86% yield): NMR (CCl_4) δ 0.15 (s, 9, $NSiMe_3$), 0.25 (s, 9, $OSiMe_3$), 2.88 (s, 3, NMe). Anal. Calcd for $C_7H_{21}NSi_2O$: C, 43.91; H, 11.05. Found: C, 43.98; H, 11.01.

***N*,*O*-Bis(dimethyl-*tert*-butylsilyl)-*N*-methylhydroxylamine (43).** Triethylamine (20.8 mL, 0.15 mol), dimethyl-*tert*-butylchlorosilane (11 g, 0.075 mol), and *N*-methylhydroxylamine (1.2 g, 0.025 mol) in ether (35 mL) were refluxed for 2 days, and Et_3N·HCl was then removed by filtration. Volatiles from the filtrate were removed in vacuo (1 mm) at room temperature, and the residue was subjected to preparative VPC using column A

(39) J. P. Shukla, Y. K. Agrawal, and K. P. Kuchya, *J. Indian Chem. Soc.*, 51, 437 (1974).

(40) M. Fujimoto and M. Sakai, *Chem. Pharm. Bull.*, 13, 248 (1965).

(100 °C, 120 mL/min). Compound **43** (t_{air} = 7 min, 80% yield) was identified by comparison of its NMR spectrum with that reported.[41]

***N,O*-Bis(trimethylsilyl)hydroxylamine (44).** To a well-stirred slurry of $HONH_2$·HCl (2 g, 28.8 mmol) in pentane (9 mL) and THF (3 mL) was added hexamethyldisilazane (12.7 mL, 60 mmol). After the mixture was refluxed for 24 h and the NH_4Cl filtered off, the volatiles were removed in vacuo (1 mm) at room temperature, and a second filtration was necessary. Compound **44** was purified by VPC using column I (100 °C, 60 mL/min, t_{air} = 2.5 min; 75% yield): NMR (1-bromonaphthalene/Me_4Si) δ 0.05 (s, 9, $NSiMe_3$), 0.15 (s, 9, $OSiMe_3$), 4.5 (br s, 1, NH).

***O*-Benzyl-*N*-(dimethyl-*tert*-butylsilyl)(diphenylphosphinyl)hydroxylamine (50).** A mixture of diphenylphosphinyl chloride (15 mmol), *O*-benzylhydroxylamine (15 mmol), and triethylamine (2.3 mL) in ether (100 mL) was stirred for 1 day and was then concentrated in vacuo. The crystalline residue was washed with water (3 × 70 mL) to remove Et_3N·HCl and was then recrystallized from hot benzene to give *O*-benzyl-(diphenylphosphinyl)hydroxylamine as white needles: mp 142.5–143.5 °C; 50% yield. Anal. Calcd for $C_{19}H_{18}NO_2P$: C, 70.58; H, 5.61; N, 4.33. Found: C, 70.74; H, 5.90; N, 4.10.

A mixture of the above intermediate (0.65 g, 2 mmol), dimethyl-*tert*-butylchlorosilane (0.6 g, 4 mmol), and triethylamine (0.65 mL, 4 mmol) in benzene (25 mL) was refluxed for 1 day, cooled, and filtered, and the filtrate was then dried with $MgSO_4$ and diluted with CCl_4 to afford **50** as white prisms: mp 74.5–75.5 °C; 65% yield; NMR ($CDCl_4$) δ 0.17 (s, 6, $SiMe_2$), 0.97 (s, 9, *t*-Bu), 4.05 (s, 2, OCH_2), 6.65–8.04 (m, 15, aromatic); IR (Nujol) 2980, 1485, 1383, 1262, 1200, 1130, 963, 842, 751, 691 cm^{-1}.

Thermolysis of 6 in the Presence of Various Trapping Agents. Cyclohexane. A solution of **6** (0.9 g, 3.6 mmol) in cyclohexane (19 mL) was heated at 100 °C for 25 h. After VPC determination[4] of $Me_3SiOSiMe_3$ (ca. 100%), the volatiles were removed in vacuo (1 mm) at room temperature, and a chloroform solution of the residue was subjected to preparative VPC using column H (110 °C, 120 mL/min). *O*-Ethyl-*N*-cyclohexylurethane (**9**, 80%) was found to be the major product (t_{air} = 6.8 min) on the basis of NMR (CCl_4) spectral comparison with published data:[14] δ 1.2 (t, 3, CH_2CH_3), 4.07 (q, 2, CH_2CH_3), 4.17 (br s, 1, NH), 2.6–1.4 (m, 10, ring CH_2), 3.42 (m, 1, ring CH). *O*-Ethylurethane (**10**, 8%, t_{air} = 2 min) was identified by comparison of its VPC retention time with that of authentic material.

Bis(trimethylsiloxy)methylsilane. A solution of **6** (100 mg, 0.4 mmol) in bis(trimethylsiloxy)methylsilane (0.5 g, 2 mmol) was heated at 100 °C for 26 h and was then analyzed by VPC using column H (110 °C, 60 mL/min). The major product (t_{air} = 13 min) was collected as a colorless oil and was assigned structure **11** (90%) on the basis of NMR spectral comparisons with authentic material (vide supra).

Aniline. A solution of **6** (200 mg, 0.8 mmol) in aniline (36.5 mL, 0.39 mol) was heated at 100 °C for 30 h, and the volatiles were then removed by Kugelrohr distillation at reduced pressure (1 mm, 40 °C). The residue was analyzed by VPC using column A (100 °C, 60 mL/min), and the major product (t_{air} = 5.3 min, 58%) was collected as an oil which crystallized upon cooling. Structure **12** was assigned to this material on the basis of its NMR spectrum (CCl_4): δ 1.2 (t, 3, CH_2CH_3), 4.08 (q, 2, CH_2CH_3), 2.83 (br s, 1, NH), 7.3–6.4 (m, s, aromatic); mp 81–84 °C (lit.[42] mp 82–83 °C).

Cyclohexene. A solution of **6** (0.5 g, 2 mmol) in cyclohexene (3 mL, 30 mmol) was heated at 90 °C for 72 h, and the volatiles were then removed in vacuo (1 mm) at room temperature. The residue was analyzed by VPC using column H (110 °C, 60 mL/min). 7-Carbethoxy-7-azabicyclo[4.1.0]heptane (**13**, 42%) was the major product collected (t_{air} = 9.3 min): NMR[14] (CCl_4) δ 1.2 (t, 3, CH_2CH_3), 4.05 (q, 2, CH_2CH_3), 1.4–1.1 (m, ring CH_2), 1.78 (m, ring CH_2), 2.53 (m, ring CH). *O*-Ethylurethane (**10**, 2% yield, t_{air} = 1.65 min) was identified by comparison of its VPC retention time with that of authentic material. The isomeric mixture of **14** was not resolved (t_{air} = ca. 10.1, 10.2, and 10.3 min, 10% yield) and was collected as one component for NMR analysis (CCl_4):[14] δ 1.22 (m, 3, CH_2CH_3), 4.05 (m, 2, CH_2CH_3), 4.72 (br s, NH), 1.72, 1.95 (m, ring CH_2), 4.05 (m, ring CH), 5.72 (m, ring CH).

A solution of **13** in cyclohexene was heated at 90 °C for 3 days, and VPC analysis with column A (100 °C, 60 mL/min) demonstrated that **14** was not present.

Benzene. A solution of **6** (180 mg, 0.7 mmol) in benzene (62 mL, 0.7 mol) was heated at 90 °C for 75 h, and the volatiles were then removed by Kugelrohr distillation at reduced pressure (1 mm, 40 °C. The residue was subjected to preparative TLC (alumina, benzene) and two bands were isolated: fast eluting, R_f 0.75; slow eluting, R_f 0.29. A 220 MHz ^1H NMR (CCl_4) analysis of the fast-eluting sample (57% yield) was consistent with structure **15**: δ 1.29 (t, 3, CH_2CH_3), 4.19 (q, 2, CH_2CH_3), 5.2–6.1 (m, 6, ring protons).[15] The second band was identified as **10** by comparison of its VPC retention time (column H, 110 °C, 60 mL/min, t_{air} = 1.65 min) with that of authentic material.

Diphenylacetylene. A solution of **6** (200 mg, 0.8 mmol) and diphenylacetylene (1.43 g, 8 mmol) in hexafluorobenzene (2 mL) was heated at 90 °C for 72 h. Volatiles including unreacted diphenylacetylene were removed by Kugelrohr distillation (80 °C, 0.5 mm), and the residue was subjected to preparative TLC (alumina, benzene). A small amount of diphenylacetylene was detected as a fast-eluting band (R_f 0.8–0.9). A slow-eluting band (R_f 0.41) was collected and recrystallized from low-boiling petroleum ether to afford material identified as **17** (20%) by comparison of its melting point (67–69 °C) with the reported[17] value (66–67 °C).

Pyridine. A solution of **6** (200 mg, 0.8 mmol) in pyridine (1.0 mL, 12 mmol) was heated at 100 °C for 25 h. Residual **6** and pyridine were removed by Kugelrohr distillation (60 °C, 1 mm), and the remaining material was subjected to preparative TLC (silica gel, benzene). The only product which eluted (R_f 0.38) was collected, recrystallized from low-boiling petroleum ether, and was identified as **18** (40%) by comparing its melting point (108–110 °C) with the reported value (lit.[13] mp 109 °C).

Thermolysis of 7 and 8 in Bis(trimethylsiloxy)methylsilane. A solution of **7** (520 mg, 1.85 mmol) in bis(trimethylsiloxy)methylsilane (8.3 mL, 37 mmol) was heated at 100 °C for 30 h. After concentration of the reaction mixture in vacuo, the residue was analyzed by VPC. Trimethylethoxysilane (**20**) was isolated by using column B (110 °C, 60 mL/min, t_{air} = 4 min; 20% yield) and was identified by comparison of its VPC retention time with that of authentic material and by NMR (CCl_4): δ 0.12 (s, 9, $SiMe_3$), 1.3 (t, 3, CH_2CH_3), 3.8 (q, 2, CH_2CH_3). Trimethylsilyl benzoate (**19**) was isolated by VPC using column B (110 °C, 60 mL/min, t_{air} = 6 min; 35% yield) and was identified by NMR (CCl_4): δ 0.21 (s, 9, $SiMe_3$), 7.1 (m, 5, aromatic). Product **11** was isolated by VPC using column H (110 °C, 60 mL/min, t_{air} = 13 min; 40% yield) and was identified by comparison of its NMR data with that of authentic **11** (vide supra).

A solution of **8** (610 mg, 1.9 mmol) in bis(trimethylsiloxy)-methylsilane (8.5 mL, 38 mmol) was heated at 100 °C for 30 h. After concentration of the reaction mixture in vacuo, the residue was analyzed by VPC using column H (110 °C, 60 mL/min), and product **11** (38%) was isolated and identified as described for **7**. Dimethyl-*tert*-butylsilyl benzoate was then isolated by VPC using column R (110 °C, 120 mL/min, t_{air} = 5 min; 35% yield) and was identified by NMR (CCl_4): δ 0.15 (s, 6, $SiMe_2$), 0.88 (s, 9, *t*-Bu), 1.4 (t, 3, CH_2CH_3), 3.88 (q, 2, CH_2CH_3). Dimethyl-*tert*-butylethoxysilane was isolated by VPC using column R (110 °C, 120 mL/min, t_{air} = 3 min; 20% yield) and was identified by NMR (CCl_4): δ 0.11 (s, 6, $SiMe_2$), 0.83 (s, 9, *t*-Bu), 1.2 (t, 3, CH_2CH_3), 3.78 (q, 2 CH_2CH_3).

Thermolysis of 22 in Decalin and Phenyldimethylsilane. Compound **22** (62 mg, 0.22 mmol) in decalin (0.5 mL) was heated at 160 °C for 5 min. The reaction mixture was analyzed by VPC using column H (120 °C, 120 mL/min). Phenyl isocyanate (86%, t_{air} = 1 min 12 s) was identified by comparison with an authentic sample. 1-Benzoyl-3-phenylurea (**27**; 5.7% yield, mp 203–206 °C) was identified by comparison with its reported melting point (lit.[43] mp 204–205 °C) after isolation by TLC (silica gel, ether–methylene chloride, 1:1; R_f 0.47). In a control experiment, a solution of

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benzamide (1.21 g) and phenyl isocyanate (1.08 mL) in *o*-dichlorobenzene was heated at 160 °C for 6 min, and compound **27** was isolated in 98% yield upon recrystallization from ethanol.

A solution of **22** (93 mg, 0.33 mmol) in phenyldimethylsilane (0.5 mL, 3.3 mmol) was heated at 100 °C for 26 h, and the reaction mixture was then analyzed by VPC using column A (110 °C, 120 mL/min). Product **28** (5%, t_{air} = 6 min) was identified by comparison of its NMR data and VPC retention time with those of authentic material (vide supra). Phenyl isocyanate (82%, t_{air} = 1 min) was isolated and identified by comparison of its VPC retention time with authentic material.

Thermolysis of 30 in the Presence of Various Trapping Agents. Cyclohexane. A solution of **30** (0.65 g, 2 mmol) in cyclohexane (3 mL) was heated at 120 °C for 2 days, and the volatiles were then removed by Kugelrohr distillation at reduced pressure [60 °C (0.05 mm)]. The residue was subjected to preparative TLC (silica gel, acetone–benzene, 80:20) which afforded fast-eluting (R_f 0.78) and slow-eluting (R_f 0.31) components. The former compound was identified as **35** (90%) from its NMR and melting point data: ^{1}H NMR (CCl_4) δ 2.3 (s, 3, Me), 2.8–1.6 (m, 10, cyclohexyl), 3.6 (m, 1, ring CH), 4.95 (br s, 1, NH), 7.1 (m, 4, aromatic); mp 85–87 °C (lit.[44] mp 86.0–87.5 °C). The slower band was identified as **36** (1%) by comparison of its melting point (136–138 °C) with that of authentic material (mp 137 °C).

Phenyldimethylsilane. A solution of **30** (1.08 g, 3.3 mmol) in phenyldimethylsilane (10 mL, 0.07 mol) was heated at 130 °C for 30 h, and the volatiles were then removed by Kugelrohr distillation at reduced pressure [70 °C (0.05 mm)]. The residue was subjected to preparative TLC (alumina, benzene–ether, 1:1), and two bands (R_f 0.81 and 0.41) were collected. The fast-eluting compound was identified as **37** (90%) by NMR comparison with authentic material (vide supra). The slow-eluting compound was identified as **36** by comparison of its melting point (135–137 °C) with that of authentic material (137 °C).

Benzene. A solution of **30** (2.3 g, 6.9 mmol) in benzene (13 mL, 0.14 mol) was heated at 100 °C for 8 days, and the volatiles were then removed by Kugelrohr distillation at reduced pressure [60 °C (0.05 mm)]. The residue which dissolved in benzene solvent was subjected to preparative TLC (silica gel, petroleum ether–benzene, 3:1). The major product (R_f 0.41) was identified as **39**: 50% yield; NMR (CCl_4) δ 2.27 (s, 3, Me), 5.68 (s, 1, NH), 7.5 (m, 9, aromatic); mp 101–104 °C (lit.[26] mp 103 °C). The minor product (R_f 0.28) was identified as **36** by comparison of its melting point (137–139 °C) with authentic material (137 °C).

Pyridine. A solution of **30** (1.8 g, 5.4 mmol) in pyridine (8.7 mL, 0.11 mol) was heated at 130 °C for 30 h and volatiles were then removed by Kugelrohr distillation at reduced pressure [70 °C (0.05 mm)] to give a dark brown solid. Decolorization with charcoal and recyrstallization from hot water–ethanol (1:1) gave crystals (mp 208–210 °C) which were identified as **40** (41%) by comparison with the reported[28b,c] melting point (210 °C).

Thermolysis of 29 in Triphenylphosphine. A solution of **29** (0.8 g, 2.5 mmol) and triphenylphosphine (6.6 g, 25 mmol) in benzene (20 mL) was heated at 120 °C for 50 h, and the volatiles were then removed by Kugelrohr distillation at reduced pressure [60 °C (0.05 mm)]. That portion of the residue which was soluble in benzene was subjected to preparative TLC (alumina, benzene) and the product (R_f 0.31) was identified as **41**: 48% yield; mp 156–160 °C (lit.[29] mp 154–157 °C).

Thermolysis of 42 in Methyldimethoxysilane. A solution of **42** (500 mg, 2.6 mmol) in methyldimethoxysilane (8 mL, 52 mmol) was heated at 150 °C for 37 h, and the volatiles were then removed by Kugelrohr distillation at reduced pressure [30 °C (10 mm)]. The benzene (5 mL)-soluble portion of the residue was analyzed by VPC using column B (110 °C, 60 mL/min, t_{air} = 3 min), and product **46** (40%) was isolated for identification by NMR (CCl_4): δ 0.02 (s, 3, SiMe), 2.71 (s, 3, NMe), 3.6 (s, 6, SiOMe); the NH resonance was not seen.

Thermolysis of 44 in Methyldimethoxysilane. A solution of **44** (500 mg, 2.8 mmol) in methyldimethoxysilane (13.6 mL, 84 mmol) was heated at 250 °C for 24 h. The reaction mixture was concentrated in vacuo (1 mm, 30 °C), and the residue was then sugjected to preparative VPC. Methyldimethoxysilylamine (**47**, 43%) was isolated by using column H (110 °C, 60 mL/min, t_{air} = 6 min) and identified by NMR (CCl_4): δ 0.02 (s, 3, SiMe), 3.6 (s, 6, SiOMe), 4.3 (br s, 2, NH_2).

Thermolysis of 43 in Hexamethyldisiloxane. A solution of **43** (277 mg, 1 mmol) and hexamethyldisiloxane (162 mg, 1 mmol) in hexafluorobenzene (0.1 mL) was heated at 120 °C for 2 days. The reaction mixture was analyzed by VPC using columns A and B; however, there was no evidence for either **42**, *N*-(trimethylsilyl)-*O*-(dimethyl-*tert*-butylsilyl)-*N*-methylhydroxylamine, or *N*-(dimethyl-*tert*-butylsilyl)-*O*-(trimethylsilyl)-*N*-methylhydroxylamine.

Photochemistry. A solution of **6** [0.80 mL; λ_{max} (C_6H_{12}) 220 nm] in cyclohexane (17 mL) was added to four quartz tubes (5 mL) and was then irradiated (Rayonet Model RPR-100) at 254 nm for 58 h; ambient temperature was ca. 45 °C. Quantitative VPC analysis using column B (150 °C, 120 mL/min) and comparison with authentic product samples indicated the formation of 45% **9**, 55% **10**, and 75% $Me_3SiOSiMe_3$ (35 °C column temperature).

A solution of **50** in cyclohexane (0.25 M) was irradiated for 1 day as described above. Removal of the volatiles under reduced pressure was followed by TLC (silica gel, $CHCl_3$–MeOH, 1:1), which afforded a 60% yield of **51** (R_f 0.48); by comparison with authentic material, there was no indication of $Ph_2P(O)NHC_6H_{11}$ (R_f 0.66).

Kinetic Studies. The NMR kinetic studies at various probe temperatures employed a Varian V-6040 temperature controller which has an estimated regulation range of ±1 °C. Ethylene glycol was used for temperature calibration and sample-temperature equilibration was assumed complete after ca. 15 min.

Compound 6. A VPC-purified sample of **6** (0.20 mmol) in hexafluorobenzene (0.4 mL) was degassed and sealed in vacuo (1 mm) in an NMR tube which was heated in an oil bath equilibrated at 100 ± 1 °C. Thermal decomposition was followed by periodically monitoring (over 85% reaction) the decreasing intensity (cut and weight method) of $NSiMe_3$ and $OSiMe_3$ singlets at 0 and 6 Hz (relative), which was accompanied by a comparable increase in the singlet absorption of the thermolysis product, $Me_3SiOSiMe_3$, at 1.5 Hz. A linear-least squares fit (±5% slope error) of a first-order plot of ln $([6]_0/[6]_t)$ vs. time (t) gave the value of k listed in Table I. Runs at other initial concentrations and temperatures were carried out in a similar fashion.

A 0.15 M solution of **6** in cyclohexane containing *o*-dichlorobenzene (0.02 M) as an internal VPC reference was heated at 100 ± 0.2 °C in a small Pyrex tube equipped with a stopcock. A rubber septum cap allowed for periodic removal of VPC samples and immediate analysis on column H (110 °C, 120 mL/min). A linear least-squares fit (±1% slope error) of ln $([6]_0/[6]_t)$ vs. t gave k = 1.92 × 10^{-5} s^{-1}. Repetition with 0.45 and 0.75 M solutions of **6** gave k = 2.01 × 10^{-5} and 1.99 × 10^{-5} s^{-1}, respectively.

Pyrex ampules containing aliquots (0.2 mL) of a 0.15 M solution of **6** in bis(trimethylsiloxy)methylsilane containing *o*-dichlorobenzene (0.02 M) as an internal VPC reference were sealed in vacuo (0.05 mm) and were then heated at 90 ± 0.2 °C. Tubes were removed periodically, stored at 0 °C, and analyzed under constant VPC conditions by using column H (110 °C, 120 mL/min). A linear least-squares fit (±3% slope error) as described above gave k = 7.5 × 10^{-6} s^{-1}, while repetition with 0.45 and 0.75 M solutions of **6** gave k = 7.8 × 10^{-6} and 7.4 × 10^{-6} s^{-1}, respectively.

A solution of **6** (37 mg, 0.15 mmol) in cyclohexene (0.4 mL) was sealed in vacuo (1 mm) in an NMR tube and was heated in an oil bath at 100 ± 0.2 °C. Kinetic data was obtained by NMR monitoring of $SiMe_3$ signal intensities (peak height) for the starting material and the fragmentation product ($Me_3SiOSiMe_3$). A linear least-squares fit (±2% slope error) as described above gave k = 1.88 × 10^{-5} s^{-1}, while repetition with 0.45 and 0.75 mmol of **6** gave k = 1.91 × 10^{-5} and 1.85 × 10^{-5} s^{-1}, respectively.

Compound 7. A solution of **7** (0.20 mmol) in hexafluorobenzene (0.4 mL) was sealed in vacuo (1 mm) in an NMR tube, and thermolysis was carried out at an NMR probe temperature of 130 ± 1 °C. The decrease in starting material concentration was accompanied by formation of **19** and **20**. A linear least-squares fit (±10% slope error) of ln $([7]_0/[7]_t)$ vs. t gave the overall first-order rate constant for thermolysis, as did comparable runs using 0.30 and 0.40 mmol of **7**: k_{av} = 3.26 ± 0.30 s^{-1}. To obtain rate data for the individual reaction paths, we expressed the

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formation of **19** as $[19] = (k_1[7]_0/k)(1 - e^{-kt})$, where k is the overall first-order rate constant for thermolysis, and k_1 is the specific rate constant for formation of **19** (Table I).

Compound 8. A solution of 8 (64.7 mg, 0.20 mmol) in hexafluorobenzene (0.4 mL) was sealed in vacuo (1 mm) in an NMR tube, and the thermolysis was monitored at probe temperatures of 130, 140, and 150 ± 1 °C. Runs were also carried out at 130 °C by using 0.30 and 0.40 mmol of 8; data analysis was similar to that described above for **7**.

Compounds 22–26. A solution of **22** (0.30 mmol) in hexafluorobenzene (0.4 mL) was sealed in vacuo (1 mm) in an NMR tube and was heated in an oil bath at 80 ± 0.2 °C. Relative $SiMe_3$ signal intensities for **22** and $Me_3SiOSiMe_3$ were utilized to periodically monitor thermolysis up to 30% reaction. At each of three higher temperatures (90, 100, and 110 ± 0.2 °C) an additional 15% reaction was monitored, and linear least-squares fits (±1% slope error) of $\ln([22]_0/[22]_t)$ vs. t gave the k values listed in Table I. The same procedure was employed with 0.05, 0.10, and 0.20 mmol of **22** at 80 ± 0.2 °C and with 0.30 mmol of **23–26** at (80–120) ± 0.2 °C (Table I).

Compounds 29–34. This series of compounds was studied by the same NMR method described above for analogues **22–26**. First-order kinetic plots had slope errors of ±3–5%; temperatures and rate data are summarized in Table I.

Compound 30 in Various Aromatic Solvents. Portions of **30** (0.12 mmol) in solvent (0.4 mL) were sealed in NMR tubes and heated simultaneously at 100 ± 0.2 °C for identical time periods. Kinetic analyses used the method described above, and the resultant data are presented in Figure 3.

Compound 30 in Phenyldimethylsilane. A solution of **30** (33.1 mg, 0.10 mmol) in phenyldimethylsilane (0.3 mL) and hexafluorobenzene (0.1 mL) was sealed in vacuo (1 mm) in an NMR tube which was then heated in an oil bath at 130 ± 0.2 °C. Thermal decomposition of **30** was followed by periodically monitoring (over 85% reaction) the decreasing intensity (cut and weight method) of the $NSiMe_3$ and $OSiMe_3$ signals at 0 and 6 Hz (relative) which was accompanied by an increase in the singlet absorption of $Me_3SiOSiMe_3$ at 1.5 Hz. A linear least-squares fit (±1% slope error) of $\ln[([30]_0/[30]_t)$ vs. t gave $k = 1.33 \times 10^{-5}$ s^{-1}, while runs using 0.05 and 0.15 mmol of **30** gave $k = 1.38 \times 10^{-5}$ and 1.35×10^{-5} s^{-1}, respectively.

Compound 42. Pyrex ampules containing **42** (0.45 mmol) in hexafluorobenzene (0.4 mL) containing *o*-dichlorobenzene (0.02 mmol) as an internal VPC reference were sealed in vacuo (1 mm) and were heated in an oil bath at 140, 150, and 160 ± 0.2 °C. Tubes were removed periodically, stored at 0 °C, and then analyzed under constant VPC conditions by using column B (110 °C, 120 mL/min); constant-volume injections confirmed the inertness of *o*-dichlorobenzene under the reaction conditions. Runs with 0.15 and 0.75 mmol of **42** were similarly carried out at 160 °C, and first-order kinetic plots (±4% slope error) afforded the data in Table I.

Compound 44. Pyrex ampules containing **44** (79.1 mg, 0.45 mmol) in VPC-purified α-bromonaphthalene (0.4 mL) containing *o*-dichlorobenzene (0.02 mmol) as an internal VPC reference were sealed in vacuo (0.05 mm) and were then heated at 170 ± 2 °C. Tubes were removed periodically, stored at 0 °C, and then analyzed under constant VPC conditions by using column B (110 °C, 60 mL/min). Runs at 170 °C with initial concentrations of 0.30 and 0.20 mmol of **44** failed to provide reasonable kinetic data.

Compound 52. A solution of VPC-purified **52** (0.20 mmol) and cyclohexene (0.8 mmol) in hexafluorobenzene (0.3 mL) was sealed in vacuo in an ampule and was then heated at 90 ± 0.2 °C. Thermal decomposition was followed over 30% reaction by monitoring the methoxysilyl NMR signals of **52** (δ 3.65) and $Si(OMe)_4$ (δ 3.55). At each higher reaction temperature (100, 110, and 120 ± 0.2 °C) an additional 15% reaction was monitored, and linear least-squares fits (±2% slope error) of first-order plots gave the values of k listed in Table II.

Compound 53. A solution of VPC-purified **53** (0.20 mmol) and diphenylacetylene (0.80 mmol) in hexafluorobenzene (0.3 mL) was sealed in vacuo (1 mm) in an NMR tube which was then heated in an oil bath at 170 ± 2 °C. Thermal decomposition was followed up to 30% reaction by monitoring the methylsilyl absorption of the starting material (δ 0.28) and the product signal for methylsilyl groups (δ 0.11). At each higher reaction temperature (180 and 190 ± 5 °C) an additional 15% reaction was monitored, and linear least-squares fits (±2% slope error) of first-order plots gave the values of k in Table II.

Solvolysis of 7 and 8. The 220-MHz ^1H NMR spectrum of **7** (0.04 mmol) in $CDCl_3$ (0.6 mL) was recorded at 20 ± 1 °C, and CD_3OD (0.4 mL) was then added. The solvolysis rate was determined by monitoring the decrease in intensity of the $SiMe_3$ resonance for **7**, while an identical run with **8** involved measurements of the decreasing $SiMe_2$ absorption of starting material. Pseudo-first-order plots of the kinetic data had slope errors of ±2%.

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