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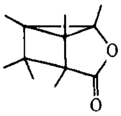
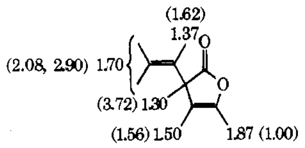
(7) H. Hart and P. Lavrik, *J. Org. Chem.*, **39**, 1793 (1974).
(8) The synthesis and acid-catalyzed rearrangement of **1** has been described: H. Hart, I. Huang, and P. Lavrik, *J. Org. Chem.*, **39**, 999 (1974).
(9) We are indebted to P. Lavrik for initial studies on this system.
(10) The chemical shift of this allylic methyl, which is at a remarkably high field, may be a consequence of shielding by the lactone carbonyl group.
(11) An alternative structure for **5** is



Although this structure seems highly unlikely from a mechanistic viewpoint (see Scheme III), it cannot be conclusively eliminated from the structural data available.
(12) In a future paper we will show that this is not always the only path followed by 2,4-cyclohexadienone 4,5-epoxides and that it depends in part on the substituents attached to the ring.
(13) C. S. Markos and W. H. Reusch, *J. Am. Chem. Soc.*, **89**, 3363 (1967).
(14) W. G. Dauben, G. Lodder, and J. Ipaktschi, *Fortschr. Chem. Forsch.*, **54**, 73 (1975); K. N. Houk, *Chem. Rev.*, **76**, 1 (1976); S. S. Hixson, P. S. Mariano and H. E. Zimmerman, *ibid.*, **73**, 531 (1973). **Note Added in Proof.** For recent pertinent stereochemical results, see B. Winter and K. Schaffner, *J. Am. Chem. Soc.*, **98**, 2022 (1976), and W. G. Dauben, G. Lodder, and J. D. Robbins, *ibid.*, **98**, 3030 (1976).
(15) D. A. Plank and J. C. Floyd, *Tetrahedron Lett.*, 4811 (1971).
(16) T. Matsuura and K. Ogura, *J. Am. Chem. Soc.*, **89**, 3850 (1967). For a recent review, see K. Schaffner, *Tetrahedron*, **32**, 641 (1976).
(17) For other examples of ketenes that are not trapped by methanol, see J. Griffiths and H. Hart, *J. Am. Chem. Soc.*, **90**, 3297 (1968), and H. Hart and G. M. Love, *ibid.*, **93**, 6266 (1971).
(18) G. F. Burkinshaw, B. R. David, and P. D. Woodgate, *J. Chem. Soc. C*, 1607 (1970).
(19) NMR spectra were measured in $CDCl_3$ or CCl_4 solutions using Me_4Si as an internal standard, on a Varian T-60 or HA-100 spectrometer. Ir spectra were recorded on a Perkin-Elmer 237 grating spectrophotometer and were calibrated against a polystyrene film. Uv spectra were obtained on a Unicam SP-800 spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 operated at 70 MeV; we are indebted to Mrs. Ralph Guile for this service. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.
(20) The NMR assignments for **4, 8, 9,** and **10,** are shown below in δ units, with relative downfield shifts in the presence of $Eu(fod)_3$ given in parentheses.



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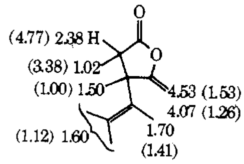

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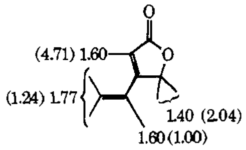

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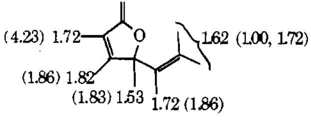

10

Thermal α-Deoxysilylation of *N*,*O*-Bis(Trimethylsilyl)-*N*-phenylhydroxylamine

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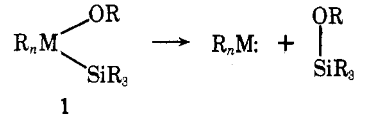
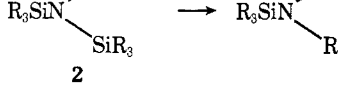
Heating *N*,*O*-bis(trimethylsilyl)-*N*-phenylhydroxylamine (**4**) at 100 °C in cyclohexene leads to expulsion of hexamethyldisiloxane and formation of mainly aniline (53%), together with a small amount (2%) of 7-phenyl-7-azabicyclo[4.1.0]heptane, and other minor products consistent with the intermediacy of phenylnitrene ($\mathrm{Ph\ddot{N}:}$). Attempts to trap $\mathrm{Ph\ddot{N}:}$ with stilbenes met with only very limited success; however, thermolysis of **4** in the presence of diethylamine, dibutylamine, and cyclohexylamine gave 85–95% yields of ring-expanded azepine trapping products. The yield of aniline varied (~20–80%) with solvent and was found to generally parallel the H-donating ability of a solvent. Kinetic experiments demonstrated that the thermal fragmentation of **4** is unimolecular and is characterized by $\Delta H^{\ddagger} = 27.7$ kcal/mol and $\Delta S^{\ddagger} = -3.8$ eu. The effect of inert solvent variation on the thermolysis rate of **4** is small; a maximal rate acceleration factor of ~6.5 obtains for benzonitrile vs. hexafluorobenzene. A limited amount of comparative thermolysis data was obtained for *O*-methyl-*N*-trimethylsilyl- (**9**) and *O*-methyl-*N*-triethylsilyl-*N*-phenylhydroxylamine (**10**). Various mechanistic aspects relating to the intermediacy of $\mathrm{Ph\ddot{N}:}$ are briefly discussed.

Thermally induced fragmentations of compounds represented by general structure 1 to afford an electron-deficient species and a silyl ether (eq 1) have been reported for cases wherein M = C[1] and Si,[2] thus providing a method for carbene ($R_2C:$) and silylene ($R_2Si:$) generation, respectively. While such α-deoxysilylation reactions do not apparently obtain for tris(organosilyl)hydroxylamines (2), which instead undergo rearrangement according to eq 2,[3] Boudjouk and West[3] were the first to note that hexamethyldisiloxane ($Me_3SiOSiMe_3$) was formed upon heating *N*,*O*-bis(trimethylsilyl)-*N*-methylhydroxylamine (3), and thereby obtained prima facie evidence for the operation of eq 1 in a system having reaction center M = N. We have subsequently reported[4] preliminary observations regarding the thermolytic behavior of analogous silylated hydroxylamine derivatives, and now present details of solvent trapping and kinetic experiments with *N*,*O*-bis(trimethylsilyl)-*N*-phenylhydroxylamine (4), together with ancillary studies of two of its *O*-methyl relatives. Our findings are consistent with unimolecular fragmentation of 4 to afford phenylnitrene ($\mathrm{Ph\ddot{N}:}$).



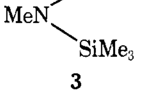
$$R_nM(OR)(SiR_3) \longrightarrow R_nM: + \begin{matrix} OR \\ | \\ SiR_3 \end{matrix} \qquad (1)$$

1



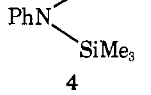
$$R_3SiN(OSiR_3)(SiR_3) \longrightarrow R_3SiN(SiR_2OSiR_3)(R) \qquad (2)$$

2



$MeN(OSiMe_3)(SiMe_3)$

3

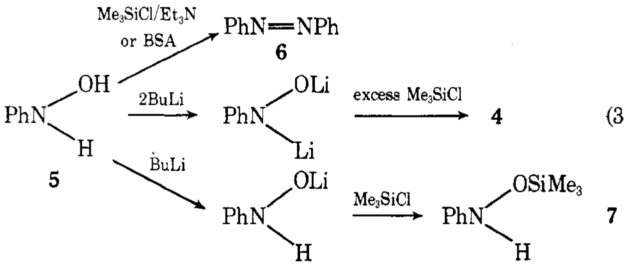


$PhN(OSiMe_3)(SiMe_3)$

4

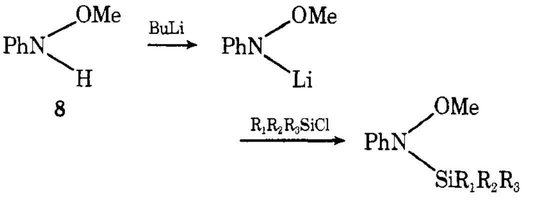
Results and Discussion

Synthesis. Selection of 4 for the investigation of N,O-bis(trimethylsilyl)hydroxylamine systems was based upon the existence of a large body of information[5] regarding PhN̈:, the expected nitrene fragment from α-deoxysilylation of **4**. As shown in eq 3, reaction of N-phenylhydroxylamine (**5**) according to the general procedure[6] for bis-silylation of N-alkylhydroxylamines with chlorotrimethylsilane (Me_3SiCl) and triethylamine unexpectedly afforded azobenzene (**6**), as did reaction of **5** with N,O-bis(trimethylsilyl)acetamide (BSA) under conditions used for hydroxyamines.[7] An optimized yield of **4** (~40%) was, however, eventually obtained by treatment of **5** with 2 equiv of butyllithium (BuLi) at −50 °C and subsequent reaction of the assumed bislithio intermediate with a twofold excess (4 equiv) of Me_3SiCl at temperatures between −50 and −20 °C. Monosilylation of **5** to give O-trimethylsilyl-N-phenylhydroxylamine (**7**) in ~50% yield was accomplished by means of a similar procedure.



(3)

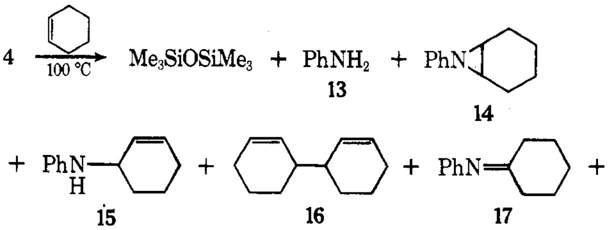
Extension of this approach to triorganosilylation of O-methyl-N-phenylhydroxylamine (**8**) was next studied as a means of providing analogues of **4** having graded steric bulk about the silicon bonded to nitrogen (eq 4). Compounds **9** and **10** were isolated in 4 and 7% yields, respectively; 1,2-anionic rearrangement[8a] of the N-lithio intermediate to give $PhN(CH_3)OLi$ and, hence, the corresponding O-silylated isomers of **9** and **10** was not in evidence.[8b] Attempts to prepare **11** and **12** were unsuccessful and led to formation of mainly **6**. These latter failures are attributed to facile coupling of the litho intermediate in eq 4 (see Experimental Section), relative to nucleophilic displacement of chloride ion in the sterically hindered chlorosilanes leading to **11** and **12**. In this connection, it was found that **8** cleanly undergoes decomposition to **6** and 2 equiv of methanol. Kinetic analyses, in which the decrease in [**8**] was followed (VPC) in toluene solution at 40 °C, gave concentration-dependent values for the disappearance rate constant: $2k = 1.46$ (0.20 M), 0.70 (0.10 M), and 0.26×10^{-6} $M^{-1}\ s^{-1}$ (0.05 M); reaction order $n = 2.04 \pm 0.06$. From a practical standpoint, long-term storage of **8** may be accommodated by use of cooled solutions: e.g., the half-life of 0.2 M **8** is ~6 months at 0 °C. Walter and Schaumann[9] have rationalized the production of **6** from the conjugate base of **8** in terms of PhN̈: intermediacy; however, we have been unable to detect even trace amounts of the expected[5] H-abstraction production, aniline (<1%, VPC), upon decomposition of **8** in toluene at 40 °C.



(4)

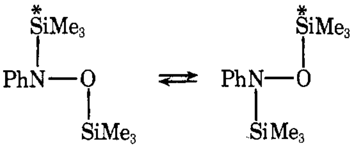
9, $R_1 = R_2 = R_3 = Me$
10, $R_1 = R_2 = R_3 = Et$
11, $R_1 = R_2 = R_3 = Pr$
12, $R_1 = R_2 = Me$; $R_3 = Ph$

Solvent Trapping Studies for Thermolysis of 4. Isolation of aziridines from reactions of potential arylnitrene generators in the presence of olefins has provided strong support for actual nitrene production;[10,11] consequently, investigation of the thermolysis of **4** in cyclohexene solution was of interest. After 16 h of heating **4** in a 100-fold molar excess of cyclohexene at 100 °C in Pyrex ampules, VPC analyses revealed essentially complete disappearance of **4** with near-quantitative formation of hexamethyldisiloxane ($Me_3SiOSiMe_3$), which is the expected organosilicon fragment from eq 1. Of the eight additional VPC components, four were isolated by preparative techniques and spectroscopically identified as aniline (**13**, 20%), 7-phenyl-7-azabicyclo[4.1.0]heptane (**14**, 2%), secondary amine **15** (4%), and bicyclohexyldiene **16** (22%) (eq 5). Lesser amounts (<1%) of N-phenylcyclohexylideneimine (**17**) and **6** were characterized by VPC retention time comparisons with authentic samples, and the two remaining trace components (<1%) are yet unidentified. Poor material balance (~25%) was attributed to formation of nonelutable (TLC) dark-colored material. A control experiment, which demonstrated that **14** is thermally stable (120 °C, 14 h) relative to the conditions used for its formation, ruled out the possibility of **15** and/or **17** being produced by decomposition of **14**. Thus, the inherently low yield of **14** parallels the ~5% isolated yield of its 7-ferrocenyl analogue obtained from thermolysis of ferrocenyl azide in cyclohexene.[10]



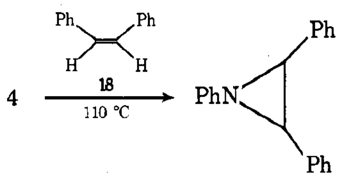
(5)

Inasmuch as the formation of products **13–17** may be rationalized[5] by the intermediacy of PhN̈:, which has been reported[12] to have a triplet ground state, CIDNP experiments were carried out. Pyrolysis of **4** in decalin led to formation of aniline (10%); however, rapid scanning of the aromatic ^1H NMR (60 MHz) region of decalin solutions of **4** (0.5 M) at 130 and 140 °C failed to reveal enhanced absorption or emission signals. While selection of these reaction conditions for **4** ($\tau_{1/2}$ ~ 10 and 3 min, respectively) was based upon a suggested[13] rate-range for exploratory CIDNP studies, our negative results do not rule out a radical (triplet) precursor for aniline. The trimethylsilyl ^1H region was similarly monitored during pyrolysis of **4** in decalin, and neither CIDNP effects nor transient signals associated with trimethylsilyl group-bearing intermediates were evident. We also noted that the N- and O-trimethylsilyl group singlet absorptions for **4** showed no exchange broadening due to possible degenerate dyotropic rearrangement[14] (eq 6) during the course of its decomposition in decalin at 140 °C. Similar dyotropic rearrangements have been found[15] for analogues of **4**; however, it is evident that further investigation of dyotropism in **4** will require an experimental probe other than ^1H NMR signal coalescence, such as deuterium labeling.[14b]



(6)

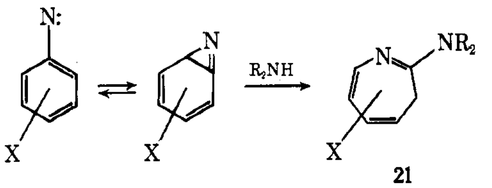
Utilization of cis- and trans-stilbene (**18** and **19**) as nitrene traps during thermolysis of **4** was patterned after studies by Abramovitch et al.,[11] which indicated that pentafluorophenylnitrene adds stereospecifically to these and other alkenes, presumably via a singlet species. Solutions of **4** in **18** as solvent (molar ratio **4**:**18** 1:25) were heated at 110 °C for 3 h,



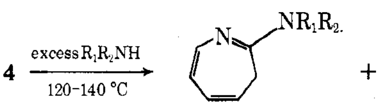
20

leading to ~90% reaction of **4.** Chromatography of the reaction mixture, which was complicated by the presence of a relatively large amount of soluble polymer, led to isolation of impure fractions containing trace amounts (<1%) of the expected 1,2,3-triphenylaziridine ring system (**20**); however, crystalline samples of **20** could not be obtained.[16] Azobenzene (**6**) was the major product. The yields of **20** from analogous experiments using **19** as the nitrene trap were too low to permit its detection, even with appropriate reaction scale-up and use of a 100-fold molar excess of **19.** Comparison of our reaction conditions (110 °C 3 h) with those reported by Huisgen and coworkers[17] for thermal ring opening of **20** (100 °C 60 h) indicates that the observed inefficiency of 1,2,3-triphenylaziridine production from **4** is real, rather than a consequence of thermally induced decomposition of **20** following its formation. It is interesting to note that while a dependence of aziridine yield on stilbene geometry was previously found[11] for pentafluorophenylnitrene, the relative efficiency order was opposit that presently reported, i.e., 0.6 and 32% yields of the aziridine from **18** and **19,** respectively. These differences are not understood at this time.

Production of 2-amino-3*H*-azepine derivatives (**21**) in reaction systems which generate arylnitrenes in the presence of amines is generally ascribed to intramolecular nitrene rearrangement to give 7-azabicyclo[4.1.0]heptatrienes followed by nucleophilic attack of amine (eq 7).[19] Extension of this trapping technique to thermolysis (100 °C) of **4** in a 125-fold molar excess of diethylamine solvent afforded $Me_3SiOSiMe_3$



(7)



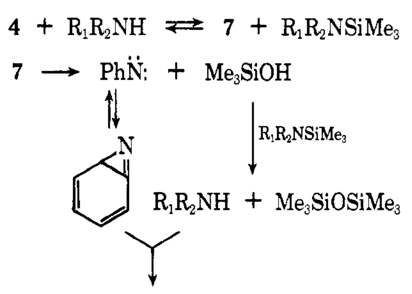
+ $Me_3SiOSiMe_3$ (8)

22, $R_1 = R_2 = Et$
23, $R_1 = R_2 = Bu$
24, $R_1 = H; = R_2 = c\text{-}C_6H_{11}$

and a 95% yield (VPC) of the well-characterized[20] 2-diethylamino-2*H*-azepine (**22**) product, without detectable amounts (<1%, VPC) of aniline (eq 8). A subsequent experiment revealed that the yield of azepine **22** was not appreciably altered upon lowering the relative proportion of diethylamine to only a tenfold molar excess. High yields (85–90%, VPC) of azepine products **23** and **24,** respectively, obtain for dibutylamine (Bu_2NH) and cyclohexylamine, even upon dilution of the reaction mixture with an inert solvent and further decrease of the molar excess of amine over **4** to a factor of 4–5. The virtual absence of aniline and the nonobservance of ^1H NMR CIDNP effects for **23** derived from rapid thermolyses of **4** ($\tau_{1/2}$ ~ 2 and 5 min) in Bu_2NH at 130 and 140 °C are consistent with (but do not demand) relatively facile intramolecular rearrangement of singlet $Ph\ddot{N}$:. This possibility has been previously discussed[19a] with respect to diethylamine interception of rearranged $Ar\ddot{N}$: obtained from phosphonite deoxygenation of nitroarenes.[21] Use of rigorously purified aniline, *p*-toluidine, or *N*-methylaniline as potential trapping agents failed to produce detectable amounts (<5%, NMR) of azepine.[22] Since Huisgen et al.[23] have previously reported isolation of a 2-anilinoazepine from pyrolysis of phenyl azide in aniline solvent, these contrasting results warrant further study.

In connection with the mechanistic details of eq 8, it was of importance to investigate the role, if any, played by the "trans-silylation" reaction shown in the first step of Scheme I. Production of **7** could conceivably be followed by its relatively rapid thermal (or amine-catalyzed) fragmentation to $Ph\ddot{N}$: and trimethylsilanol, with ultimate formation of the observed azepine derivatives and $Me_3SiOSiMe_3$. Evidence contrary to the operation of this sequence of transformations derives from a number of experimental tests. Firstly, no ^1H NMR signals characteristic of **7** or Bu_2NSiMe_3 were detectable during slow thermolysis of **4** in Bu_2NH at 55 °C. Secondly, an equilibrium constant favoring the left-hand side of the "trans-silylation" step in Scheme I was not evidenced by ^1H NMR upon reaction of **7** with Bu_2NSiMe_3 in Bu_2NH solvent, which afforded **6,** azoxybenzene [PhN(O)=NPh], and $Me_3SiOSiMe_3$ at 130 °C. Thirdly, heating **7** in Bu_2NH at 130 °C led to formation of these latter three products without detectable amounts of **23** being produced. Fourthly, the disappearance rate of **4** upon heating in *o*-dichlorobenzene was found to be independent of the amount of added Bu_2NH.

Scheme I



22-24

Next studied was the yield of aniline produced during thermolysis of **4** as a function of the H-donating ability of the solvent. Solutions of **4** (0.1 M) in cyclohexane, cyclohexene, and toluene were each heated at 110 °C for a period of time (16 h) needed to achieve complete reaction. Quantitative VPC analyses indicated respective aniline yields of 19, 53, and 30%, with ±2% being the average deviation for triplicate determinations.[25] The cyclohexane system also gave a small amount (5%) of *N*-cyclohexylaniline, which has been previously shown[12] to arise from triplet $Ph\ddot{N}$: during analogous thermal decomposition of phenyl azide. Normalization of these aniline yields to a basis of percent aniline per millimole of abstractable hydrogen from solvent gave relative values of 1.0:8.0:6.3, which qualitatively parallels the stability of radicals derived from these three solvents, respectively.[26] The high yield of dehydrogenated cyclohexene coupling product **16** (22%), relative to the amount of bibenzyl (1%) formed in toluene, may be reconciled by the possibility of 2-cyclohexenyl radical addition to cyclohexene. In any event, our data are consistent with a radical precursor to aniline. It is usually supposed[19a] that triplet arylnitrenes lead primarily to arylamine products; consequently, we explored the response of aniline yield from **4** to the presence of a heavy atom, which in some instances can promote intersystem crossing of singlet to triplet nitrenes.[28] For this study, the yield of aniline was determined (VPC, ±2%, average of duplicate runs) for completely reacted 0.1 M solutions of **4** in toluene containing increased molar proportions of *p*-bromotoluene. A plot of these results (Figure 1) reveals that a dramatic increase in aniline yield from 30 to 78% obtains, and that there is a roughly linear relationship between

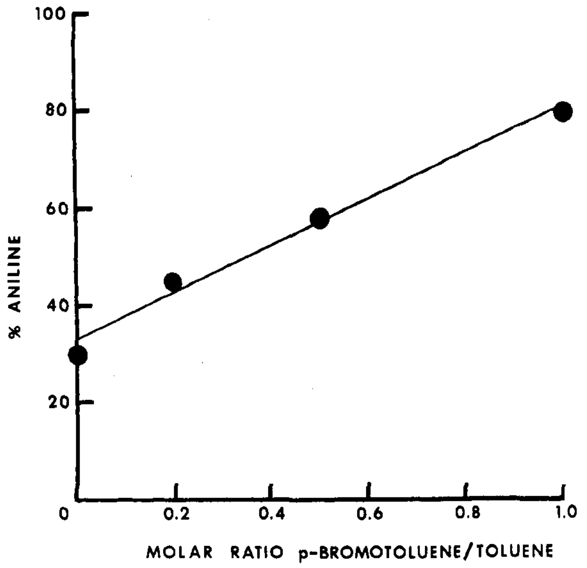


Figure 1. Plot of aniline yield (VPC, ±2%, average of duplicate runs) derived from complete thermolysis of 4 (0.1 M, 110 °C, 16 h) in toluene with increased amounts of *p*-bromotoluene.

Table I. Kinetic Parameters for Thermolysis of *O*-Silylated *N*-Phenylhydroxylamine Derivatives in Toluene

Compd	$[\text{Compd}]_0$, M	Temp, °C	$k \times 10^5$, sec^{-1} [a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
4 [b]	0.10	90	2.3	27.7	−3.8
	0.10	100	6.4		
	0.05	100	6.2		
	0.10	110	17.4		
9 [c]	0.20	70	0.032	27.6	−8.0
	0.10	70	0.036		
	0.05	70	0.031		
	0.20	80	0.11		
	0.20	90	0.32		
10	0.10	120	<0.03 [d]		

[a] First-order rate constant for disappearance of compound; obtained by standard VPC methods, except as indicated. [b] Approximately 80% reaction monitored. [c] Approximately 5–30% reaction monitored. [d] Limiting value based on <8% reaction after 80 h.

this increase and the *p*-bromotoluene content of the reaction medium.

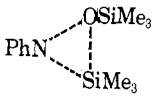
Solvent Trapping Studies for Thermolysis of 9. Comparative studies of **9** were hampered by the light sensitivity of this *O*-methyl analogue of **4**. For example, carefully prepared solutions of freshly purified (VPC) **9** in dry toluene changed from colorless to pale orange within hours at room temperature when not protected from light. The colored decomposition product was identified (TLC) as azobenzene (**6**). While handling and storage of **9** in the absence of light could virtually eliminate production of **6**, attempts to seal the Pyrex ampules used for pyrolysis resulted in variable amounts of sample degradation, with as much as a 50% decrease in the original concentration of **9**. Despite these difficulties, which attentuated our efforts, some reliable information regarding **9** was obtained. The thermal stability of **9** initially apparent from its survival during VPC isolation (100 °C residence time ~5 min) was confirmed in the course of kinetic studies (vide infra): 30% conversion of **9** took place after 34 h of heating at 90 °C in toluene to yield aniline (~15%) and **6** (~15%). While further heating results in the appearance and subsequently rapid formation of two unidentified products, it is worthwhile to note that an extrapolated aniline yield from **9** in toluene (~50% = ~15% × 100/30) is comparable to the amount of aniline (30%) derived from **4**. Low conversion studies with **9** also revealed substantial production (~50%, corrected) of methoxytrimethylsilane (MeOSiMe_3), as was anticipated by analogy to **4**. It thus appeared that while the initial mode of reaction for **9** parallels that of **4**, incursion of catalyzed side reactions becomes significant. A similarity in fragmentation characteristics between **9** and **4** in the gas phase was suggested by observing[29] that each of these compounds exhibits, upon electron impact (70 eV), a base peak at *m/e* 91 due to $\text{C}_6\text{H}_5\text{N}\cdot^{+}$.

Use of a ~100-fold molar excess of diethylamine as the pyrolysis solvent for **9** gave a minor product (~0.5%) having the same VPC retention time as **22**; however, positive identification of this material by TLC isolation could not be achieved. The yield of **6** was 15%. When a similar reaction was directly monitored by ^{1}H NMR, no azepine signals were detectable. The propensity of **8** toward formation of **6** (vide supra) suggested that this behavior of **9** in the presence of diethylamine, which markedly contrasts that of **4**, could be due to the intervention of a "trans-silylation" process (cf. Scheme I). Initial support for this possibility was obtained by ^{1}H NMR studies in CDCl_3, since treatment of **9** with 1 equiv of Bu_2NH led to relatively rapid formation of signals characteristic of **8** and $\text{Bu}_2\text{NSiMe}_3$. The production of $\text{Bu}_2\text{NSiMe}_3$ was confirmed by its VPC isolation and characterization by ir.

Kinetic Studies. As indicated in Table I, the disappearance rate constant (k) for **4** in toluene at 100 °C, which was obtained from a linear first-order decay plot, was independent of the initial concentration. Measurement of k for **4** at 90 and 110 °C thus afforded a linear least-squares fit of log (k/T) vs. T^{-1} giving $\Delta H^{\ddagger} = 27.7$ kcal/mol and $\Delta S^{\ddagger} = -3.8$ eu. Analogous behavior deduced for **9** (at low conversions), relative to **4**, was supported by finding first-order disappearance kinetics (5–30% reaction) for **9** with $\Delta H^{\ddagger} = 27.6$ kcal/mol and $\Delta S^{\ddagger} = -8.0$ eu. Determination of accurate rate data for **10** was foiled by nonreproducibility of data points and the small amounts of available **10**. However, a reliable value of $k < 3 \times 10^{-7}\ \text{s}^{-1}$ at 20 °C was obtained by finding in one case <8% reaction of **10** after 80 h of heating. Comparison of this limiting value with an extrapolated disappearance rate constant for **9** at 120 °C ($k = 650\ 10^{-7}\ \text{s}^{-1}$) indicated that **10** is at least 200 times less reactive than **9**.

The data presented in Table II demonstrate that the effect of solvent variation on k for **4** is small, with the rate being accelerated by a maximal factor of ~6.5 upon changing from hexafluorobenzene (ϵ 2.03) to benzonitrile (ϵ 25.20). By way of comparison, the relative disappearance rate ratio of ~4 exhibited by **4** in benzonitrile vs. decalin (ϵ 2.15) is somewhat greater than the relative rate ratio of ~1 reported for loss of nitrogen from either phenyl azide[30] or 2-azidobiphenyl[31] upon pyrolysis in nitrobenzene (ϵ 34.8) vs. decalin. The rates of methoxycarbene formation via thermal α-deoxysilylation have been found[1a] to be essentially identical in methanol vs. tetramethylethylene, which have widely different polarities.

Mechanism. A "concerted" elimination process for eq 1 has been previously suggested for α-deoxysilylation about C[1b] and Si.[2a] Evidence consistent with **4** undergoing similar one-step fragmentation via transition state **25** to $\text{Me}_3\text{SiOSiMe}_3$ and



25

$\text{Ph}\ddot{\text{N}}$: includes a number of observations: (a) the first-order fragmentation rate characterized by a negative $\Delta S^{\ddagger}$ [32] and small dependence on solvent polarity (ϵ), (b) the expected[5]

Table II. Effect of Solvent on the Thermolysis Rate of *N,O*-Bis(trimethylsilyl)-*N*-phenylhydroxylamine (4).

Solvent	$k \times 10^4$, s^{-1} [a]	Solvent	$k \times 10^4$, s^{-1} [a]
Hexafluorobenzene	1.17	Cyclohexylamine	5.71
Decalin	1.90	*o*-Dichlorobenzene	5.45
Toluene	3.83[b]	Benzonitrile	7.50
Dibutylamine	4.47		

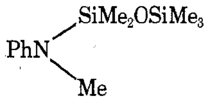
[a] First-order rate constant obtained by ^{1}H NMR techniques at 118 ± 3 °C over ~75% reaction, except as noted. [b] Calculated from activation parameters listed for **4** in Table I.

array of products obtained in the presence of cyclohexene, (c) isolation of **20** with *cis*-stilbene as the nitrene trap, (d) high azepine yields with alkylamine trapping agents, (e) the rational dependence of aniline yield on the nature of the four thermolysis solvents investigated, (f) isolation of *N*-cyclohexylaniline with cyclohexane as solvent, and (g) the absence of trimethylsilyl group-bearing intermediates via ^{1}H NMR monitoring experiments. Nucleophilic attack at silicon by oxygen implicit in **25** also provides a basis to understand the remarkable thermal stability of **7** (no reaction after 19 h at 100 °C), and **25** can be extended to its *O*-methyl analogues to account for the observed (Table I) disappearance rate inequities between **4**, **9**, and **10**: $k_4/k_9 = 7$ (90 °C) due to the electropositive[35a] nature of silicon vs. carbon, and $k_9/_{10} > 200$ (120 °C) due to increased steric hindrance of Et_3Si vs. Me_3Si.[35b]

A multistep fragmentation mode for **4** involving homolysis of the N–O bond to a tight radical pair followed by formation of intermediate **26** is an alternative possibility which is based


$$Ph\overset{+}{N}—\overset{-}{Si}Me_3OSiMe_3$$

26



27

on very recent mechanistic suggestions by West and Nowakowski[36] to account for thermal rearrangement of tris(organosilyl)hydroxylamines (eq 2). If such a sequence is operative with **4**, **26** would be expected[36,37] to yield **27**; however, we have been unable to obtain evidence for aminodisiloxane **27** in direct ^{1}H NMR monitoring experiments. Consequently, this homolytic pathway either bypasses the intermediacy of **26** and leads directly to $Ph\ddot{N}$: and $Me_3SiOSiMe_3$, or fragmentation of **26** to the nitrene and hexamethyldisiloxane is fast, relative to methyl migration giving **27**.[38] It should also be noted that rate-limiting N–Si bond homolysis in **4** to an anilino radical precursor to $Ph\ddot{N}$: cannot be excluded. Further experiments with more electron-deficient derivatives of **4** and electron-rich stereoisomeric olefin traps are under investigation.

Experimental Section

Elemental analyses were performed by Chemalytics, Inc. ^{1}H NMR spectra were recorded on a Varian A-60 instrument at ambient probe temperature, using ~10% v/v solutions in deuteriochloroform and tetramethylsilane as an internal reference, except as noted. Ir and uv measurements were respectively obtained with Perkin-Elmer Model 337 and Cary Model 15 spectrophotometers. Aerograph 90-P and Varian Aerograph 920 thermal conductivity instruments were used with 0.25-in. columns, and a Varian Aerograph 940 flame-ionization gas chromatograph utilized 0.125-in. columns. Unless specified otherwise, Chromosorb G (60/80 mesh) was used throughout: column A, 3 ft × 0.25 in., 5% SE-30; column B, 6 ft × 0.25 in., 15% SE-30; column C, 18 × 0.25 in., 5% SE-30; column D, 6 ft × 0.25 in., 15% polyphenyl ether 5-ring; column E, 6 ft × 0.125 in., 15% OV-101 on High Performance Chromosorb G, 100/120 mesh; column F, 6 ft × 0.25 in., 15% Apiezon L on Chromosorb W, 60/80 mesh; column G, 3 ft × 0.25 in., 1% SE-30; column H, 5 ft × 0.125 in., 5% SE-30; column I, 18 × 0.25 in., 15% SE-30; column J, 3 ft × 0.125 in., 1% SE-30; column K, 18 × 0.25 in., 1% SE-30. VPC yields refer to comparison of peak areas obtained either with standardized solutions (constant injection volume) or with internal reference compounds.

All reactions were run under an atmosphere of high-purity nitrogen. Ether refers to commercial anhydrous ether; all solvents and amines were purified by standard procedures.[39] Chlorotriethylsilane, chlorotripropylsilane, and chlorodimethylphenylsilane (PCR, Inc.) were distilled prior to use, while chlorotrimethylsilane (Aldrich Chemical Co.) and *N,O*-bis(trimethylsilyl)acetamide (BSA, Pierce Chemical Co.) were used as received. Phenylhydroxylamine[40] (**5**) was recrystallized from cold ether–pentane and stored at 0 °C. *Caution:* **5** is a severe skin irritant.

Thermolysis reactions were carried out in degassed and sealed Pyrex ampules, which were heated in a constant-temperature (±0.2 °C) oil bath, unless specified otherwise.

***O*-Trimethylsilyl-*N*-phenylhydroxylamine (7).** A magnetically stirred solution of **5** (1.5 g, 13.8 mmol) in ether (40 ml) was maintained at −50 °C while 1 equiv of butyllithium in hexane (1.67 M) was slowly added (30 min). Additional stirring (1–3 h) was followed by dropwise introduction (15 min) of chlorotrimethylsilane (3.5 ml, 27.6 mmol) in ether (10 ml) solution. The temperature of the reaction mixture was then allowed to gradually (1.5 h) rise to room temperature and after an additional period of time (2 h), LiCl was removed by gravity filtration under a blanket of N_2. Volatiles from the filtrate were removed in vacuo (1 mm) at room temperature and the residual oil was Kugelrohr distilled to yield (53%) a golden-colored liquid (bp 70–90 °C, 1 mm), which was identified as **7**: NMR δ 7.33–6.40 (m, 6, aromatic and NH) and 0.23 (s, 9, $SiMe_3$); ir (neat) 3050, 2970, 2900, 2390, 1601, 1500, 1260, and 720 cm^{-1}. Analytically pure **7** was obtained by preparative VPC on column G (95 °C, 120 ml/min).

Anal. Calcd for $C_9H_{15}NOSi$: C, 59.62; H, 8.34; N, 7.72. Found: C, 59.44; H, 8.47; N. 8.14.

***N,O*-Bis(trimethylsilyl)-*N*-phenylhydroxylamine (4).** A solution of **5** (1.5 g, 13.8 mmol) in ether (40 ml) was treated with 2 equiv of butyllithium in hexane (1.67 M), and then with excess chlorotrimethylsilane (7 ml, 55.7 mmol), in the same manner as described for the preparation of **7**. The reaction mixture was stirred at −50 °C (30 min) and the temperature was then allowed to rise to −20 °C: recooling to −50 °C followed by warming to −20 °C was repeated three more times. After final stirring at room temperature for 12 h, workup as with **7** and then Kugelrohr distillation gave **4** (40%) as a golden-colored oil (bp 40–85 °C, 1 mm); use of the theoretical amount of chlorotrimethylsilane (3.5 ml, 28 mmol) consistently gave **4** in ~20% yield, with increased amounts of by-product **6**. Ultimate purification of **4** was achieved by preparative VPC of the distillate on column G (95 °C, 120 ml/min): NMR δ 6.47–8.33 (m, 5, aromatic), 0.17 (s, 9, $OSiMe_3$), 0.10 (s, 9, $NSiMe_3$); ir (neat) 3080, 3050, 2975, 2915, 1600, 1490, 1260, 1175, 1083, 1032, 965, 850, 760, 700, and 625 cm^{-1}; λ_{max} (C_6H_{12}) nm (log ε 3.88).

Anal. Calcd for $C_{12}H_{23}NOSi_2$: C, 56.86; H, 9.15; N, 5.53. Found: C, 57.16; H, 9.32; N, 5.64.

Reaction of **5** according to general silylation procedures with either Et_3N/Me_3SiCl[6] or BSA in pyridine[7] led to isolation of mainly **6** upon workup and distillation of the crude product mixture.

***O*-Methyl-*N*-phenylhydroxylamine (8).** The following modified procedure of Walter and Schaumann resulted in a yield of **8** which was twice that reported by these authors. A solution of recrystallized *N,N'*-diphenyl-*N*-methoxyurea (31 g, 0.128 mol) in diethylamine (65 ml) was gently refluxed for 13 h with protection from light. After removal of diethylamine on a rotary evaporator at room temperature, the residue was subjected to rapid Kugelrohr distillation and yielded (35%) **8** as a pale yellow oil (bp 40–75 °C, 0.5 mm). ^{1}H NMR analyis was consistent with that reported for **8** (δ_{OCH_3} 3.75), and no methoxyl absorption (δ 3.35) from methanol contamination was evident. Decomposition of **8** into **6** and methanol may be effectively retarded by storage at low temperatures as a dilute solution in, e.g., ether. Kugelrohr distillation of a partially decomposed sample of **8** leads to separation of pure **8** from **6**, which remains as pot residue.

An ether solution of pure **8** (~0.1 M) was treated at −40 °C with 1 equiv of butyllithium in hexane (2 M) and was then allowed to warm to room temperature. The orange-colored solution was quenched with water and VPC analysis of the organic layer confirmed the presence of primarily **6**.

***O*-Methyl-*N*-phenyl-*N*-trimethylsilylhydroxylamine (9).** A solution of **8** (1.0 g, 8.1 mmol) in ether was sequentially reacted with 1 equiv of butyllithium in hexane (2 M) and 1 equiv of chlorotrimethylsilane as in the case of **4**. Precipitation of lithium chloride was first noted at ~0 °C. The usual workup followed by Kugelrohr distillation afforded **9** (43%) as a pale yellow oil (bp 60 °C, 0.5 mm): NMR δ 6.50–7.50 (m, 5, aromatic), 3.51 (s, 3, OMe), 0.23 (s, 9, $SiMe_3$); ir (neat) 3090, 3070, 3025, 2950, 2890, 2810, 1600, 1480, 1250, 1028, 938, 890, 840, 750, 695, and 620 cm^{-1}. VPC purification utilized column C (100 °C, 120 ml/min); significant amounts of other components having t_{air} values similar to **9** were not observed.

Toluene solutions (~0.1 M) of freshly collected pure **9** [λ_{max} (C_6H_{12}) 247 nm (log ϵ 3.93)] when allowed to stand at room temperature in the presence of light turned to a pale orange color after ~3 h; TLC analysis indicated the presence of **6**. Brief exposure of a frozen solution of pure **9** (0.1 M) in toluene to light emitted from molten Pyrex during ampule sealing was found (VPC) to result in variable amounts of decomposition, with as much as 50% decrease in the initial concentration of **9**.

Anal. Calcd for $C_{10}H_{17}NOSi$: C, 61.49; H, 8.77. Found: C, 61.67; H, 9.05.

***O*-Methyl-*N*-phenyl-*N*-triethylsilylhydroxylamine (10).** Seqential reaction of **8** (0.60 g, 4.8 mmol) with 1 equiv of buthyllithium and chlorotriethylsilane, as in the preparation of **9**, was followed by stirring at 0 °C for 7 days, during which time gradual precipitation of lithium chloride was noted. The usual workup and then Kugelrohr distillation led to collection of two fractions (bp 35–55 and 55–95 °C, 0.5 mm), which were both found by VPC analysis on column A (110 °C, 120 ml/min) to contain **6** (t_{air} = 6 min) and one additional major component (t_{air} = 4 min). Collection of the latter material led to its identification as **10** (7%): NMR δ 6.66–7.50 (m, 5, aromatic), 3.57 (s, 3, OMe), and 1.25–0.65 (m, 15, $SiEt_3$); ir (neat) 3050, 2960, 2910, 2880, 2805, 1600, 1490, 1245, 1026, 1004, 825, 740, and 695 cm^{-1}.

Anal. Calcd for $C_{13}H_{23}NOSi$: C, 65.77; H, 9.77; N, 5.90. Found: C, 65.77; H, 9.59; N, 6.12.

Attempted Synthesis of *O*-Methyl-*N*-phenyl-*N*-tripropylsilylhydroxylamine (11) and *N*-Dimethylphenylsilyl-*O*-methyl-*N*-phenylhydroxylamine (12). Reaction of **8** with butyllithium and then with either chlorotripropylsilane or chlorodimethylphenylsilane was carried out in the same manner as that described for **10**. In both cases, VPC analysis with column A (110 °C, 120 ml/min) of the Kugelrohr distillate (bp ~50–120 °C 0.5 mm) indicated the presence of mainly unreacted chlorosilane and **6**; additional minor components (<~5%) were not collected for identification.

***N*-Trimethylsilyldibutylamine.** A solution of butyllithium (31 mmol) in hexane (2 M) was added over a period of 0.5 h to a magnetically stirred solution of dibutylamine (6 ml, 35 mmol) in ether (50 ml) at −10 °C. After further stirring for 0.5 h, chlorotrimethylsilane (4 ml, 32 mmol) was added (0.5 h) to the cold solution and the mixture was then allowed to stir at ambient temperature (12 h). Lithium chloride was removed by gravity filtration under a blanket of N_2 and the filtrate was concentrated in vacuo (15 mm). VPC analysis using column A (90 °C, 120 ml/min) revealed the presence of essentially one product (t_{air} = 6.3 min), which was collected by preparative VPC and identified as *N*-trimethylsilyldibutylamine: NMR δ −0.04 (s, 9, $SiMe_3$), 0.65–1.70 (m, 14), 2.40–2.90 (m, 4, NCH_2); ir (neat) 1164 cm^{-1} (Si–N). The hydrolytic instability of this product was evident from the appearance and rapid increase in intensity of a Si–O bond at 830 cm^{-1} during ir analysis.

7-Phenyl-7-azabicyclo[4.1.0]heptane (14) and *N*-Phenylcyclohexylideneimine (17). Following the procedure of Clark,[41] phenyl azide (130 mg, 1.1 mmol) in cyclohexene (5 ml) was refluxed for 36 h (80% theoretical N_2 evolution). The reaction mixture was diluted with chloroform, filtered, concentrated on a rotary evaporator, and then Kugelrohr distilled to give a pale yellow oil (81 mg, bp 80–90 °C, 1 mm) that was found by VPC on column A (105 °C, 60 ml/min) to be a 60:40 mixture of two components having t_{air} values of 15 and 20 min, respectively. These two materials were isolated by preparative VPC and the faster eluting was identified as **14** by its ^1H NMR and ir spectra.[41] The slower eluting component was characterized as **17**: NMR δ 7.60–6.45 (m, 5, aromatic), 2.60–1.95 (m, 4, allylic), and 1.95–1.30 (m, 6); ir (neat) 1710 cm^{-1} (C=N). Positive identification of **17** was achieved by comparison with material that was prepared by condensation of aniline with cyclohexanone.

Thermolyses of 4. Cyclohexene Solvent. A solution of **4** (700 mg, 2.8 mmol) in cyclohexene (28 ml, 0.28 mol) was heated at 100 °C for 16 h. Volatiles were removed in vacuo (1 mm) at room temperature and a chloroform solution of the residue was subjected to preparative VPC using column A (100 °C, 120 ml/min). Aniline (t_{air} = 45 s) and **14** (t_{air} = 7.5 min) were isolated in 20 and 2% yields, respectively, and were identified by comparison (ir, ^1H NMR) with authentic material. Bicyclohexyldiene **16**[42] (100 mg, 22%; t_{air} = 3.4 min) was characterized by spectral and elemental analysis: δ 5.53 (broad s, 4, vinylic), 2.55–1.08 (m, 14); ir (neat) 3020, 2930, 2860, 2840, 1450, 1440, 1138, 899, 874, 867, 724, 647, and 600 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.08, 88.80; H, 11.42, 11.10.

Product **15** (4%, t_{air} = 10 min), which consumed 1 equiv of H_2 upon microhydrogenation over Pd/C in absolute ethanol, was identified spectroscopically: NMR δ 7.16–6.26 (m, 5, aromatic), 5.69 (s with additional splitting, 2, vinylic), 3.88 (m, 1, methine), 3.25 (broad s, 1, NH), 2.34–1.08 (m, 6, methylenes); ir (neat) 3410, 3050, 3025, 2930, 2855, 1601, 1500, 1430, 1320, 1260, 1248, 747, 725, and 691 cm^{-1}. Trace amounts of **17** (<1%) and **6** (<1%) were identified by coinjection with authentic samples on column E (120 °C, 15 ml/min), and two additional products (<1%) with t_{air} values similar to **17** remain uncharacterized. TLC (silica gel, ether) of the crude pyrolysis mixture confirmed the presence of **6** and indicated the formation of a relatively large amount of noneluting brown polymer. VPC analysis (column F, 60 °C, 60 ml/min) of the pyrolysis mixture before product isolation indicated that the yield of $Me_3SiOSiMe_3$ was ~100%, within experimental error (±10%), based on peak area comparisons with a solution of authentic $Me_3SiOSiMe_3$ of known concentration. Heating a solution of **14** in cyclohexene (0.1 M) for 14 h at 120 °C was shown, by VPC techniques, not to lead to production of detectable (<5%) amounts of either **15** or **17**.

Stilbene Solvents. A solution of **4** (200 mg, 0.8 mmol) in *cis*-stilbene (**18**, 4 ml, 20 mmol) was heated at 110 °C for 3 h. Unreacted **18** was removed by Kugelrohr distillation (80 °C, 0.5 mm) and the pot residue was subjected to preparative TLC (alumina, 30–60 °C petroleum ether). Residual **18** and a relatively large amount of **6** were detected as overlapping fast-eluting bands (R_f 0.8–0.9); two slow-eluting bands (R_f 0.7 and 0.4) were collected. ^1H NMR (220 MHz) analyses of each of these samples revealed a singlet absorption (δ 3.64) characteristic[17] of ring system **20**; however, the low integrated signal intensity ratio of this singlet to the aromatic protons indicated substantial contamination. The yield of **20** was roughly estimated to be <1%. Microcrystallization techniques failed to give a solid sample of **20**. Repetition of the above experiment using a mixture of **4** (3.5 g, 14 mmol) in *trans*-stilbene (**19**, mp 122–124 °C, 24.9 g, 0.14 mol) heated at 125 °C for 25 min did not give a detectable amount of **20**. Dissolution of a 1:10 molar mixture of **4**:**19** in a minimal amount of *o*-dichlorobenzene, followed by heating at 110 °C for 3 h, gave similar negative results for the formation of **20**.

Diethylamine Solvent. A solution of **4** (200 mg, 0.8 mmol) in diethylamine (10 ml, 0.1 mol) was heated at 100 °C for 62 h, concentrated on a rotary evaporator, and then analyzed by VPC using column G (100 °C 120 ml/min). A portion of the major product, which had the same retention time (3 min) as **4**, was collected and identified as **22** based on the reported[20] ^1H NMR spectrum of this azepine. Quantitative VPC measurements performed on the remaining crude material revealed a 95% yield of **22**; no aniline was detectable (<1%) by VPC, and only trace amounts (~1%) of **6** and azoxybenzene were seen. Similar results were obtained in a repeat experiment wherein **4** (200 mg, 0.8 mmol) was heated in diethylamine (0.8 ml, 8 mmol) at 100 °C for 16 h.

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.12; H, 9.82; N, 17.06. Found: C, 73.22; H, 9.86; N, 17.56.

Dibutylamine Solvent. A sample of **4** in a 100-fold molar excess of dibutylamine was reacted as above and volatiles (bp <~40°) were then removed by Kugelrohr distillation at reduced pressure (1 mm). The pot residue was subjected to preparative TLC (silica gel, 95:5 30–60 °C petroleum ether–ether) and the broad fluorescent band (R_f 0.3), which readily separated from a small amount of faster eluting by-product **6**, was further purified by preparative VPC on column A (130 °C, 120 ml/min) and identified as **23** from the close similarity of its ^1H NMR vinyl and allyl absorptions to that of **22**. Quantitative VPC measurements indicated that the yield of **23** was 85%.

Anal. Calcd for $C_{14}H_{24}N_2$: C, 76.31; H, 11.00; N, 12.70. Found: C, 76.13; H, 11.23; N, 12.47.

A similarly high azepine yield was obtained when **4** (100 mg, 0.4 mmol) and dibutylamine (0.30 ml, 1.76 mmol) were heated (55 °C) in an NMR tube for a period of 5 days; trimethylsilyl group signals characteristic of **7** (δ ~0.23) and Bu_2NSiMe_3 (δ ~0) were not observed during the course of this reaction. Reaction of a mixture of **7** (0.3 M) and Bu_2NSiMe_3 in dibutylamine at 130 °C was directly monitored by NMR over a period of 13 h. Characteristic signals for $Me_3SiOSiMe_3$, **6**, and azoxybenzene increased in intensity with time; however, neither **23** nor trimethylsilyl group signals indicative of **4** were detectable during the course of reaction. An NMR tube containing a solution of **7** (~1 M) in dibutylamine was monitored at 130 °C for 2 h. Azepine **23** was not detectable; however, signals for $Me_3SiOSiMe_3$, **6**, and azoxybenzene were evident. Production of the latter three products was confirmed by a combination of ir and VPC analysis.

Cyclohexylamine Solvent. A solution of **4** (70 mg, 0.28 mmol) in cyclohexylamine (0.33 ml, 28 mmol), which had been heated at 118 °C for 2 h, was analyzed by VPC using column C (140 °C, 120 ml/min) and the major product (t_{air} = 6.5 min) was collected as a pale yellow colored solid (mp 118–119 °C, 30–60 °C petroleum ether). Structure **24** was assigned to this material (88% yield, VPC) on the basis of ^1H NMR spectral similarities with **22**.

Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53. Found: C, 75.88; H, 9.76.

Attempted CIDNP Detection. A degassed ^1H NMR sample of **4** in decalin (0.5 M) was inserted into the preequilibrated and precalibrated (ethylene glycol) spectrometer probe at 130 ± 2 °C. After 30 s, repetitive scans (500-Hz sweep width, 100-s sweep time) of the aromatic proton region were obtained over ~30-s time intervals for 20 min; no evidence for CIDNP was apparent. In a duplicate experiment, the decreasing intensity of the $NSiMe_3$ and $OSiMe_3$ singlets at 0 and 6 Hz (relative) was accompanied by a comparable increase in the singlet absorption for $Me_3SiOSiMe_3$ at 1.5 Hz; the fragmentation half-life was ~10 min and neither CIDNP nor additional $SiMe_3$ signals were in evidence. Omission of the degassing in sample preparation had no effect on these results. Repetition of the experiments at 140 °C ($\tau_{1/2} \sim 3$ min) gave similar results and a 10% yield (VPC) of aniline. No significant decrease in the chemical shift difference between the $SiMe_3$ signals in **4**, or broadening of these signals ($W_{1/2}$), was evident at 140 °C, relative to spectra obtained at 35 °C. Pyrolyses of **4** in dibutylamine (0.5 and 1.3 M) at 130 °C were monitored (1000-Hz sweep width, 50-s sweep time) in the azepine ring proton region of **23** over ~30-s time intervals. CIDNP effects were not seen in these experiments, as well as in one at 140 °C (0.5 M), while near-exclusive production of **23** was evident from subsequent TLC analyses.

Determination of Aniline Yield from Thermolysis of 4 in Various Solvents. Three aliquots from each stock solution (0.1 M) prepared from **4** (20 mg, 0.08 mmol) and the various solvents 0.8 ml) were sealed in vacuo in small Pyrex ampules and heated simultaneously at 110 °C for 16 h. Complete reaction of **4** was evidenced by VPC on column G (90 °C, 120 ml/min) and the yield of aniline in each case was determined by VPC peak area comparisons (cut and weigh technique) with a standardized 0.1 M solution of aniline, using column F (105 °C, 120 ml/min): cyclohexane, 19%; cyclohexene, 53%; toluene, 28%; *p*-bromotoluene, 78%. The average deviation among all samples was ±2%. The homogeneity of the aniline peak derived from *p*-bromotoluene was established by comparison with pure aniline using combined VPC–mass spectrometry techniques. A 1 ± 0.05% yield of bibenzyl from the toluene system was determined by quantitative VPC analyses on columns E (150 °C) and J (105 °C). Repetition of the above experiment using duplicate 0.1 M solutions of **4** in pure toluene, and in 80:20 and 50:50 mol % toluene–*p*-bromotoluene mixtures gave 32, 45, and 58 ± 2% aniline, respectively.

Thermolysis of 9 in the Presence of Diethylamine. A frozen solution of compound **9** (195 mg, 1 mmol) in diethylamine (10 ml, 0.096 mol) was sealed quickly in a Pyrex ampule and was then heated at 110 °C for 36 h. After removal of solvent in vacuo, a small amount (15%) of unreacted **9** was detected by VPC using column C (100 °C, 120 ml/min) and was then collected for positive identification by ir. Azobenzene (15%) and a minor component (~0.5%) having the same retention time as the expected product **22** were also present; however, the latter material could not be isolated by TLC in sufficient quantities to confirm its tentative identification as **22**.

A frozen solution of pure **9** (0.4 M) in diethylamine was sealed in vacuo in an NMR tube; the ^1H spectrum indicated that no detectable photochemical decomposition of **9** had taken place (vide supra). Upon heating at 110 °C, gradual reaction to yield signals characteristic of **6** was evident; however, no absorptions for azepine **22** could be seen. In a control experiment, a $CDCl_3$ solution of **9** (0.5 M) and Bu_2NH (0.5 M) was sealed in an NMR tube and heated at 55 °C; only **8** and Bu_2NSiMe_3 were evident from their respective OCH_3 and $SiMe_3$ signals after 14 h. Preparative VPC of this NMR sample gave pure **8** (NMR) and Bu_2NSiMe_3 (ir 1165 cm^{-1}, Si–N).

Kinetic Studies. Compound 8. A 0.20 M solution of freshly distilled **8** in toluene containing *o*-dibromobenzene (0.02 M) as an internal VPC reference was heated at 40 ± 0.5 °C in a small Pyrex tube (5 × 50 mm; ~0.5 ml volume) equipped with a well-greased ground glass stopcock. A tight-fitting rubber septum cap allowed for periodic removal of VPC samples and immediate analysis on column I (90 °C, 100 ml/min). A standard[43] second-order kinetic plot of $([8]_0 - x)^{-1} - [8]_0^{-1}$ vs. time was linear over the monitored reaction period (48 h) and gave $2k = 1.46 \times 10^{-6}\ M^{-1}\ s^{-1}$, where $[8]_0$ is the initial concentration of **8** and x is the concentration of **6** at time t. Duplicate constant volume VPC injections demonstrated that the *o*-dibromobenzene did not undergo a detectable amount (<5%) of reaction. Repetition with 0.10 and 0.05 M solutions of **8** gave values of $2k = 7.00$ and $2.60 \times 10^{-7}\ M^{-1}\ s^{-1}$, respectively, indicating a reaction order $n = 2.04 \pm 0.06$.

Compound 4. Predried Pyrex ampules containing aliquots (~0.2 ml) of a 0.10 M solution of purified **4** in toluene containing *o*-dibromobenzene (0.02 M) as an internal VPC reference were sealed in vacuo and heated in a constant temperature oil bath at temperatures of 90, 100, and 110 ± 0.2 °C. Tubes were removed periodically, stored at 0 °C, and analyzed under constant VPC conditions using column A (100 °C, 120 ml/min). Duplicate constant volume injections confirmed the inertness of *o*-dibromobenzene under the reaction conditions. Linear least-squares fits (±5–10% slope error) of first-order plots of ln $([4]_0/[4]_t)$ vs. t gave the values of k listed in Table I. A comparative run at 100 °C and an initial concentration of **4** equal to 0.05 M demonstrated the unimolecular character of kinetics for **4**. A least-squares fit (±5% slope error) of log (k/T) vs. T^{-1} afforded the activation parameters given in Table I.

Measurement of k for **4** as a function of solvent was accomplished by ^1H NMR at a probe temperature of 118 ± 3 °C and using 0.50 M samples. Relative $SiMe_3$ signal intensities (cut and weigh method) for starting material and the $Me_3SiOSiMe_3$ fragmentation product were utilized to calculate $[4]_t$. Linear first-order plots (±5% slope error) were manually obtained over the monitored reaction period (~50%) and gave the values of k listed in Table II. The effect of added dibutylamine (0.17, 0.33, and 0.66 M) on the thermolysis rate of **4** (0.33 M) in *o*-dichlorobenzene was similarly studied and was found to be negligible.

Compound 9. VPC purified **9** was immediately diluted with toluene containing 0.02 M *o*-dichlorobenzene, as an internal VPC reference, to give 0.20, 0.10, and 0.05 M solutions, which were then heated (in the absence of light) at 70 ± 0.1 °C using the same type of reaction vessels as described above for **8**. VPC samples from each solution were removed at 20-h intervals for 6 days (5–30% reaction) and were analyzed on column H (90 °C, 15 ml/min). Linear least-squares fits (±5% slope error) of ln $([9]_0/[9]_t)$ vs. t gave first-order rate constants (Table I) having an average value of $k = 3.3 \pm 0.2 \times 10^{-7}\ s^{-1}$. In the 0.20 M run, after 28% reaction, the only two products detected by VPC were a 1:1 ratio of aniline and **6**. After ~30–40% reaction, the rate of disappearance of **9** noticeably accelerated, without further production of aniline or **6**. Instead, the decrease in **9** was accompanied by appearance of unidentified peaks having retention times comparable to and twice that of **6**.[44] A 50% (corrected) yield of methoxytrimethylsilane ($MeOSiMe_3$) at low conversion was determined by VPC using column F (75 °C, 60 ml/min) and a standardized solution of independently synthesized[45] $MeOSiMe_3$. Two unidentified VPC peaks with slightly shorter retention times than $MeOSiMe_3$ may be associated with the low yield of $MeOSiMe_3$ via possible thermal and/or catalyzed disproportionation reactions; however, $MeOSiMe_3$ in toluene was shown to be thermally stable under the reaction conditions. Addition of a catalytic amount of aniline had no observable effect on this stability.

Compound 10. A sample of **10** that had been purified twice by preparative VPC was dissolved in anhydrous toluene to give a 0.09 M stock solution; recrystallized biphenyl (0.02 M) was used as an internal VPC reference. In order to obtain reasonably reproducible VPC ratios of **10**:biphenyl (±4%), a newly prepared and conditioned column (K, 100 °C, 70 ml/min) was necessary. Sealed Pyrex ampules containing aliquots of the stock solutions were heated (120 ± 0.1 °C) in an oil bath for various time intervals and then analyzed under constant VPC conditions. A first-order disappearance plot for **10** was initially linear over a 24-h time period (~25% reaction) and then exhibited large deviations indicative of catalytic acceleration. In a duplicate run, no reaction was detectable (<8%; maximum error associated with VPC analysis) after 80 h of heating at 120 °C.

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24, 59859-55-1; chlorotrimethylsilane, 75-77-4; *N,N'*-diphenyl-*N*-methoxyurea, 59859-56-2; chlorotriethylsilane, 994-30-9; *N*-trimethylsilyldibutylamine, 3553-86-4; dibutylamine, 111-92-2; aniline, 62-53-3; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; diethylamine, 109-89-7; cyclohexylamine, 108-91-8.

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