between the diene and C-4 methoxy group which would arise in the endo transition state.

The next phase of our synthesis called for the introduction of the A and D target rings to the B and C rings, respectively, of **5**. Toward this end, **5** was converted to **10** by using an olefination and hydrolysis sequence[14] (91%). The hetero-Diels-Alder reaction of enone **10** with the ketene acetal of ethyl acetate in the presence of zinc iodide gave a single ortholactone which, in accord with the intended stereoinductive influence of its tricyclic subunit, underwent sterically and stereoelectronically controlled protonation at C-10 to provide a single keto ester **11** (72% for two steps). Benefiting similarly from the biases inherent in the tricyclic core of **11**, introduction of the D ring by using Seyferth's reagent[15] proceeded exclusively through addition to the less hindered, convex face of the C ring and gave *gem*-dibromocyclopropane **12** (92%). Finally, C-4, the fourth stereocenter, designed to arise under the guidance of the key tricycle, was indeed set through kinetically controlled addition of cyanide[16] to the sterically less encumbered face of ketone **12**, producing **13** (72%) with 92-95% isomeric selectivity. DIBAH reduction of both the nitrile and ester groups followed by Swern oxidation gave a dialdehyde from which **14**[8] was formed by base-catalyzed intramolecular aldol condensation[17] (31.5% for three steps). Completion of the tigliane carbon network and introduction of the desired C-3 oxygen as required for our pharmacophore model were achieved through a four-step conversion of **14** to **15**[20] (DIBAH reduction, higher order cuprate substitution of halide,[18] and allylic transposition,[19] 73% for four steps).

The final phase of our synthesis required cleavage of the ether bridge in **15** and introduction of the desired B-ring allylic alcohol. Accordingly, protection of the C-3 alcohol in **15** as its benzoyl ester and deprotection of the C-20 benzyl ether (ZnI_2 in TMSCN) produced the corresponding primary alcohol (64% for two steps) which was converted into iodide **16** by a two-step procedure. *tert*-Butyllithium treatment of the iodide resulted in cleavage of the ether at C-6 and cleanly gave tetracyclic compound **17** (51% for three steps). Protection of the C-3 alcohol and SeO_2 oxidation[21] of the B-ring exocyclic olefin produced a single isomeric allylic alcohol **18**. The remarkable regioselectivity of this allylic oxidation reflects in part the greater steric hindrance at C-5 relative to C-7. Transposition of the allylic functionality in **18** was accomplished by thionyl chloride in the presence of propylene oxide as an acid scavenger. Treatment of the resultant chloride **19** with silver acetate and potassium acetate-TMEDA complex in acetonitrile gave **20** (50% for four steps). Finally, hydrolysis of protecting groups provided phorboid **2** (>70%, oil).[8]

Phorboid **2** is the first compound possessing the complete tigliane skeleton and stereochemistry to be prepared through total synthesis. It incorporates seven of the eight stereocenters of PMA and the C-4, C-9, and C-20 functionalities putatively required for biological activity. However, unlike PMA but like the ingenane promoters, it is devoid of oxygenation at C-12 and C-13 and possesses A-ring functionalities required for conformational rigidity and for the attachment of lipophilic groups. The above strategy and the availability of phorboid **2** and its derivatives open new opportunities for the investigation of carcinogenesis at the molecular level. Pharmacological and further synthetic studies are in progress.

Acknowledgment. We gratefully acknowledge the National Cancer Institute for support of this work through Grant CA31841.

---

[14] Conia, J-M.; Limasset, J-C. *Bull. Soc. Chim. Fr.* **1967**, 1936. Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63.

[15] Seyferth, D.; Burlitch, J. M.; Minasz, R. J.; Mui, J. Y.-P.; Simmons, H. D., Jr.; Treiber, J. H.; Dowd, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 4259. Seyferth, D. *Acc. Chem. Res.* **1972**, *5*, 65.

[16] Evans, D. A.; Carroll, G. L.; Truesdale, L. K. *J. Org. Chem.* **1974**, *39*, 914.

[17] Corey, E. J.; Danheiser, R. L.; Chandrasekarau, S.; Siret, P.; Keck, G. E.; Gras, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 8031. Sodeoka, M.; Shibasaki, M. *Chem. Lett.* **1984**, 579.

[18] Harayama, T.; Fukushi, H.; Ogawa, K.; Yoneda, F. *Chem. Pharm. Bull.* **1985**, *33*, 3564.

[19] Clive, D. L. J.; Chittattu, G.; Curtis, N. J.; Menchen, S. M. *J. Chem. Soc., Chem. Commun.* **1978**, 770.

[20] The streochemistry of **15** was established by correlation with its 12-keto derivative whose identity was determined by X-ray crystallography: Keenan, R. M. Ph.D. Thesis, Stanford University, 1986.

[21] Sharpless, K. B.; Verhoeven, T. R. *Adrichimica Acta* **1979**, *12*, 63.

Matrix Isolation of the First Silanediimine, *N,N'*-Bis(trimethylsilyl)silanediimine

Steven S. Zigler, Kevin M. Welsh, and Robert West*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Josef Michl*

Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

Received November 13, 1986

Studies of multiple bonding between silicon and nitrogen[1-3] have recently culminated in the isolation of several kinetically stable silanimines.[1] However, the existence of the silanediimine structure (RN=Si=NR),[4] containing one more double bond than the related silanimine ($R_2Si{=}NR$), has yet to be unambiguously demonstrated. In this paper, we present data from UV spectroscopy and trapping experiments that provide compelling evidence for the formation of the first silanediimine, *N,N'*-bis(trimethylsilyl)silanediimine.

Photolysis (254 nm) of $(Me_3Si)_2Si(N_3)_2$[5] (**1**) in a mixture of Me_3SiOMe and methylcyclohexane at room temperature initially gives **2**, believed to result from addition of the alkoxysilane[6] to the silanimine formed from a 1,2-trimethylsilyl migration, eq 1. Further photolysis of this solution produces **3**, the formation of which is attributed to a second migration-addition step.[7,8]

$$\begin{aligned}&\underset{\mathbf{1}}{(Me_3Si)_2Si(N_3)_2} \xrightarrow{h\nu} [Me_3SiSi(N_3){=}NSiMe_3] \xrightarrow{Me_3SiOMe}\\&\underset{\mathbf{2}}{Me_3SiSi(OMe)(N_3)N(SiMe_3)_2} \xrightarrow{h\nu}\\&[(Me_3Si)_2NSi(OMe){=}NSiMe_3] \xrightarrow{Me_3SiOMe}\\&\qquad\underset{\mathbf{3}}{[(Me_3Si)_2N]_2Si(OMe)_2} \quad (1)\end{aligned}$$

---

[1] (a) Wiberg, N.; Schurz, K.; Fischer, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1053-1054. (b) Wiberg, N.; Schurz, K.; Reber, G; Müller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591-592. (c) Hesse, M.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 649-650.

[2] Sekiguchi, A.; Ando, W.; Honda, K. *Chem. Lett.* **1986**, 1029-1032. Zigler, S.; West, R.; Michl, J. *Chem. Lett.* **1986**, 1025-1028.

[3] Bock, H.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *24*, 111-112.

[4] Calculations on the parent silanediimine indicate that it should be a minimum on the H_2SiN_2 hypersurface. See: Thomson, C.; Glidewell, C. *J. Comput. Chem.* **1983**, *4*, 1-8.

[5] Diazide **1** was synthesized from $(Me_3Si)_2SiCl_2$ and NaN_3 in refluxing toluene and purified by vacuum distillation [55-57 °C (0.05 mm Hg)]. ^1H NMR ($CDCl_3$, 200 MHz) δ 0.28 (s); IR (neat) 3430, 2970, 2910, 2130, 2115, 1295, 1250, 835 cm^{-1}; HRMS (30 eV, EI) calcd for $C_6H_{18}Si_3N_6$ 258.0897, found 258.0901.

[6] Alkoxysilanes undergo addition across silicon-nitrogen double bonds. See: Elsheikh, M.; Pearson, N.; Sommer, L. *J. Am. Chem. Soc.* **1979**, *101*, 2491-2492. Wiberg, N.; Preiner, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 362-363.

[7] Compound **2** was isolated by preparative GC as a colorless liquid: ^1H NMR (C_6D_6, 270 MHz) δ 3.32 (s, 3 H), 0.25 (s, 18 H), 0.20 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 49.58, 4.85, -0.96; IR (neat) 3420, 2950, 2900, 2840, 2140, 1260, 1080, 955, 900, 850 cm^{-1}; HRMS (30 eV, EI) calcd for $C_9H_{27}Si_4N_4O$ ($M^+ - 15$) 319.1262, found 319.1265. Compound **3** was isolated in the same manner as a waxy solid (mp 139.0-142.5 °C): ^1H NMR (C_6D_6, 270 MHz) δ 3.30 (s, 6 H), 0.34 (s, 36 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 49.72, 5.23; IR (neat) 2950, 2900, 2840, 1270, 1255, 1120, 950, 910, 865, 850 cm^{-1}; HRMS (EI, 30 eV) calcd for $C_{13}H_{39}H_2O_2Si_5$ ($M^+ - 15$) 395.1858, found 395.1849. Anal. $(C_{14}H_{42}N_2O_2Si)_5$ C, H, N.

0002-7863/87/1509-4392$01.50/0

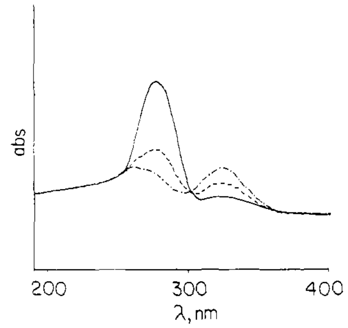
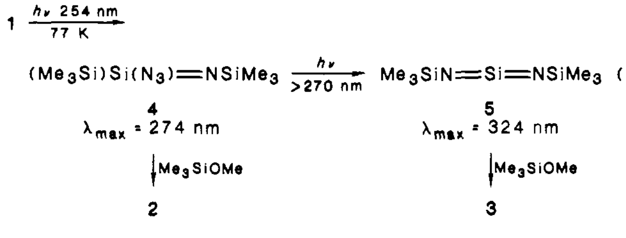


Figure 1. (—) Ultraviolet spectrum of $Me_3SiSi(N_3){=}NSiMe_3$ (**4**), generated by irradiation (254 nm) of **1** at 77 K. The 274-nm band is due to **4** while the band at 324 nm is due to a small amount of $Me_3SiN{=}Si{=}NSiMe_3$ (**5**) formed in the photolysis: (---) UV spectrum after photobleaching (>270 nm) for 30 min; (-··) UV spectrum after photobleaching for 60 min.

Irradiation (254 nm) of **1** in glassy 3-methylpentane (3-MP) at 77 K results in the appearance of two new bands in the UV at 274 and 324 nm (Figure 1). At first, the 274-nm band grows in more rapidly than the 324-nm band, showing that two different species are responsible for the UV spectrum. This is confirmed by bleaching experiments. Longer wavelength irradiation (>270 nm) reduces the 274-nm band with a concomitant increase in the 324-nm band (Figure 1).

The structures of the compounds responsible for the UV spectra were determined by trapping experiments. When the 254-nm irradiation is performed at 77 K in a 3-MP glass containing 0.2% Me_3SiOMe, compounds **2** and **3** are the only products observed after warming the sample to room temperature and analyzing the photolysate by GC.[10] The combined yields of **2** and **3** were 75–90% on the basis of consumed **1**. The molar ratio of **3**:**2** varies from 0.2 to 0.9, increasing with the duration of the 254-nm photolysis. If the glass is then irradiated at >270 nm (the same conditions that produce the changes in the UV spectrum shown in Figure 1) prior to warmup, the combined yields of **2** and **3** are unchanged, but the ratio of **3**:**2** increases to between 1.1 and 2.0.[11] 2.0.[11] These results, together with the information obtained from UV spectroscopy, indicate that (a) the azidosilanimine **4** is responsible for the 274-nm band, (b) **4** is a photochemical precursor of the silanediimine **5**, and (c) **5** has an absorption maximum at 324 nm (see eq 2).[12,13]



$$\begin{array}{ccc} \mathbf{1}\ \xrightarrow[77\ \text{K}]{h\nu\ 254\ \text{nm}} & & \\ (Me_3Si)Si(N_3){=}NSiMe_3 & \xrightarrow[>270\ \text{nm}]{h\nu} & Me_3SiN{=}Si{=}NSiMe_3 \quad (2) \\ \mathbf{4} & & \mathbf{5} \\ \lambda_{max} = 274\ \text{nm} & & \lambda_{max} = 324\ \text{nm} \\ \downarrow{\scriptstyle Me_3SiOMe} & & \downarrow{\scriptstyle Me_3SiOMe} \\ \mathbf{2} & & \mathbf{3} \end{array}$$

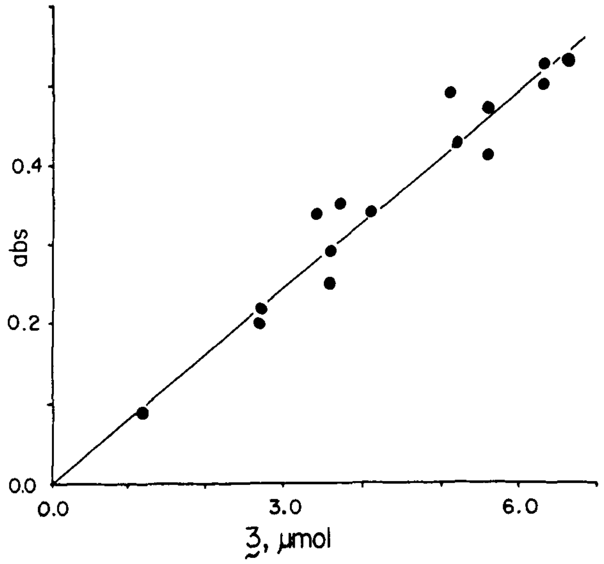


Figure 2. Plot of number of moles of **3** produced in the photolysis of **1** at 77 K versus the absorbance measured at 324 nm.

Further support for our assignment of the 324-nm band to **5** can be gained by plotting the number of moles of **3** produced vs. the absorbance measured at 324 nm. From the slope of the least-squares line of such a plot (Figure 2), the molar absorptivity (ϵ) of **5** is found to be 2130 ± 260 M^{-1} cm^{-1}. The linear nature of this plot provides convincing evidence that the absorption maximum at 324 nm is due to the precursor of **3**.[13]

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contracts F49620-86-C-0010 and 84-0065, and the National Science Foundation, Grant CHE-8318820-02. We thank Greg Gillette for obtaining ^{13}C NMR spectra.

Registry No. **1**, 106865-42-3; **2**, 106865-43-4; **3**, 106865-44-5; **4**, 106865-45-6; **5**, 106865-46-7; Me_3SiOMe, 1825-61-2; $EtMe_2SiOMe$, 52686-75-6; $(Me_3Si)_2SiCl_2$, 5181-42-0.

---

(8) Photolysis of $Ph_2Si(N_3)_2$ in the presence of *tert*-butyl alcohol has been reported[9] to give the product from migration of each phenyl group to a nitrogen and addition of 2 mol of alcohol (see below). The authors interpret

$$Ph_2Si(N_3)_2 \xrightarrow{h\nu} [PhN{=}Si{=}NPh] \xrightarrow{2(t\text{-}BuOH)} PhHNSi(O\text{-}t\text{-}Bu)_2NHPh$$

this as evidence for the intermediacy of *N,N'*-diphenylsilanediimine. Our results suggest that the silanediimine is not formed directly and that a mechanism involving two sequential migration–addition steps is operative.

(9) Ando, W.; Tsumaki, H.; Ikeno, M. *J. Chem. Soc., Chem. Commun.* **1981**, 597–598.

(10) UV spectra identical with those shown in Figure 1 are observed when 0.2% Me_3SiOMe is present in the glass.

(11) Control experiments demonstrated that **2** and **3** are not produced on irradiation (>270 nm) of **1** at 77 K for short periods of time (15 m). However, prolonged irradiation (4 h) does result in the formation of small amounts of both **2** and **3**.

(12) $EtMe_2SiOMe$ was also used as a trapping agent. Solution and glass experiments both produced the same products, identified as $Me_3SiSi(OMe)(N_3)N(SiMe_3)(SiMe_2Et)$ and $[(Me_3Si)(EtMe_2Si)N]_2Si(OMe)_2$.

(13) This analysis assumes that **5** is quantitatively trapped by Me_3SiOMe to give **3**. Our value of ϵ, therefore, represents an upper limit to the true value.

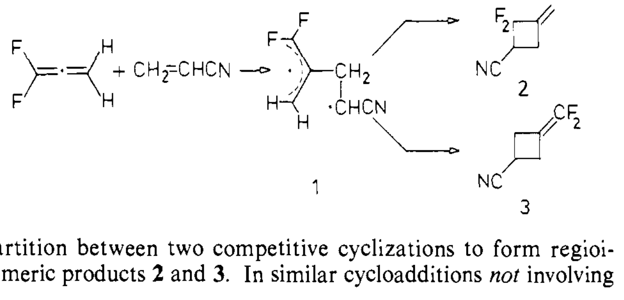
Pressure and Viscosity Effects on the [2 + 2] Cycloaddition of Styrene and Difluoroallene

William R. Dolbier, Jr.,* and Mark J. Seabury

Department of Chemistry, University of Florida
Gainesville, Florida 32611

Received January 26, 1987

The [2 + 2] cycloadditions of allenes provide special opportunities for probing the behavior of diradicals formed in nonconcerted cycloaddition processes. As exemplified for the reaction of difluoroallene with acrylonitrile,[1] all [2 + 2] cycloadditions involving allenic addends involve initial C–C bond formation at C_2 of the allene to form diradicals such as **1** which still must partition between two competitive cyclizations to form regioisomeric products **2** and **3**. In similar cycloadditions *not* involving



---

(1) Dolbier, W. R., Jr.; Burkholder, C. R. *J. Org. Chem.* **1984**, *49*, 2381.

0002-7863/87/1509-4393$01.50/0 © 1987 American Chemical Society