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Silylene Reactions with *N*-Methylpyrrole: Cycloadditions and Rearrangements[1,2]

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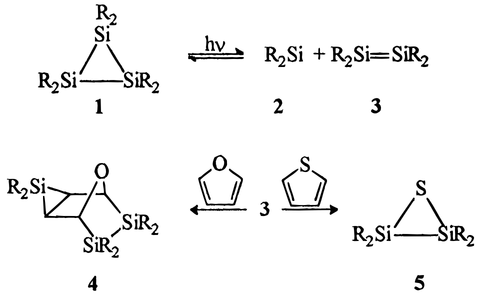
*Summary: Di-tert-butylsilylene (**2**), generated by photolysis of hexa-tert-butylcyclotrisilane, reacts with N-methylpyrrole possibly via an intermediate [2 + 1] cycloadduct to furnish 3,3-di-tert-butyl-2-methyl-2-aza-3-silabicyclo[2.2.0]hex-5-ene (**7**). On heating, **7** rearranges by an electrocyclic reaction to provide the correspondingly substituted 1-aza-2-silacyclohexa-3,5-diene **8**. Further treatment of **7** with **2** gives, presumably through a tricyclic compound, the final product 2,2,5,5-tetra-tert-butyl-1-methyl-1-aza-2,5-disilacyclohepta-3,6-diene (**10**), which was characterized by an X-ray structure analysis.*

Introduction

The Diels−Alder reaction, which in its simplest form comprises the cycloaddition of an olefin to a diene, is one of the most versatile synthetic procedures in organic chemistry. Although disilenes, compounds containing an Si═Si double bond, are often more reactive than alkenes, no [2 + 4] cycloadditions of the stable tetraaryldisilenes with 1,3-dienes have as yet been described.[3] However, the recently reported reaction of tetramesityldisilene with 3,4,5-trimethoxybenzoyl chloride, in which the Si═Si double bond forms a [2 + 4] cycloadduct with the oxygen atom and a ring carbon atom, provides first indications of reactions of the abovementioned type.[4]

Tetra-*tert*-butyldisilene (**3**) has proved to be somewhat more reactive than the tetraaryldisilenes. Compound **3** is prepared together with di-*tert*-butylsilylene (**2**) most simply by photolysis of the cyclotrisilane **1** (Scheme 1).[5] Thus, the reaction of **3** with 2,3-dimethylbutadiene gives rise to the Diels−Alder product, albeit in very low yield and together with other compounds.[6]

Scheme 1[a]



[a] R = CMe_3.

We have recently isolated a [2 + 4] cycloadduct from the reaction mixture after photolysis of **1** in the presence of cyclopentadiene and elucidated its structure by X-ray crystallography.[7] The reaction of **3** with furan (Scheme 1) also commences with a [2 + 4] cycloaddition but proceeds by addition of the silylene concomitantly formed in the photolysis to the remaining double bond of the cycloadduct to furnish the tricyclic system **4**. Thiophene behaves differently; the isolated disilathiirane **5** is presumably the result of a subsequent extrusion from the [4 + 2] cycloadduct.[7] Since a simple change of the heteroatom in this type of five-membered ring system had such a pronounced effect on the product formation, we have extended our investigations to include pyrroles and now report on the photolysis reactions of **1** in the presence of *N*-methylpyrrole. This reaction does indeed follow a different course than the previously mentioned reactions.

Results and Discussion

In order to avoid a possible silylene insertion[8] into the N−H bond, we subjected *N*-methylpyrrole, and not

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

[1] Silicon Compounds with Strong Intramolecular Steric Interactions. 62. Part 61: Weidenbruch, M.; Will, P.; Peters, K. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1811.

[2] Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

[3] Reviews: (a) West, R. *Angew. Chem.* **1987**, *99*, 1231; *Angew. Chem. Int Ed. Engl.* **1987**, *26*, 1202. (b) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds Part 2*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K. 1989; p 1015. (c) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem.* **1991**, *103*, 916; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (d) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275. (e) Okazaki, R.,;West, R. In *Multiply Bonded Main Group Metals and Metalloids*; West, R., Stone, F. G. A., Eds.; Academic Press: San Diego, CA, 1996; p 232.

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[5] Review: Weidenbruch, M. *Chem. Rev.* **1995**, *95*, 1479.

[6] Masamune, S.; Murakami, S.; Tobita, H. *Organometallics* **1983**, *2*, 1464.

[7] Kroke, E.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Organometallics* **1995**, *14*, 5695.

[8] Reviews: Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1978; Vol. 1, p 229. *Ibid.* 1981; Vol. 2, p 335. *Ibid.* 1985; Vol. 3, p 333.

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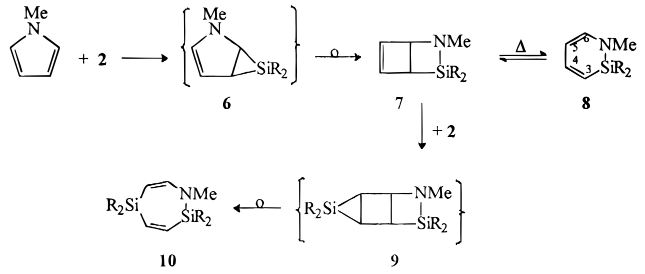
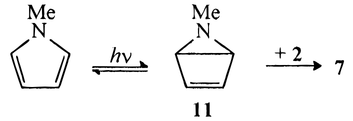
Scheme 2[a]



[a] R = CMe$_3$.

Scheme 3



the parent compound, to photolysis with **1**. Irradiation of these two components at −20 °C initiates a smooth reaction that is complete after 5 h. From the reaction mixture, we isolated a colorless liquid in high yield. On the basis of the elemental analysis, molecular mass determination, and mass spectroscopy, this is a 1:1 adduct of the pyrrole and **2**. However, the obvious assumption, in analogy to previous reactions with, for example, cyclopentadiene,[7] that this was the [2 + 1] cycloadduct **6** was not confirmed by the NMR data (Scheme 2). For example, the ^{29}Si NMR spectrum shows a signal with a chemical shift of about 24 ppm, which differs drastically from the values of other siliranes (usually −40 to −60 ppm).[9]

The lack of sensitivity of the product toward air and moisture, as well as its failure to undergo typical silirane reactions with the heavier chalcogens[10] or aryl isocyanides,[11] clearly demonstrate that the putative primary cycloadduct **6** has experienced a rearrangement. Indeed, the NMR data, including 2-D spectra, and subsequent reactions can best be explained by assuming the bicyclic constitution **7** for the product. A photochemically induced valence isomerization of the pyrrole to the bicyclic system **11** could also be responsible for the unexpected formation of **7**.[12] Insertion of the silylene **2** into the strained C−N bond of the three-membered ring would then provide a plausible explanation for the isolation of product **7** (Scheme 3). However, experimental evidence for this process as well as for the alternatively proposed [2 + 1] cycloaddition is still lacking.

The most important result of this reaction is that the silylene **2**, but not the disilene **3**, reacts exclusively with the cycloheterodiene. The *trans*-1,1,2,3,3,4-hexa-*tert*-butylcyclotetrasilane[7,13] and other products that always occur when **2** but not **3** undergo reaction with a suitable partner[5] were obtained as the subsequent products of the disilene **3**.

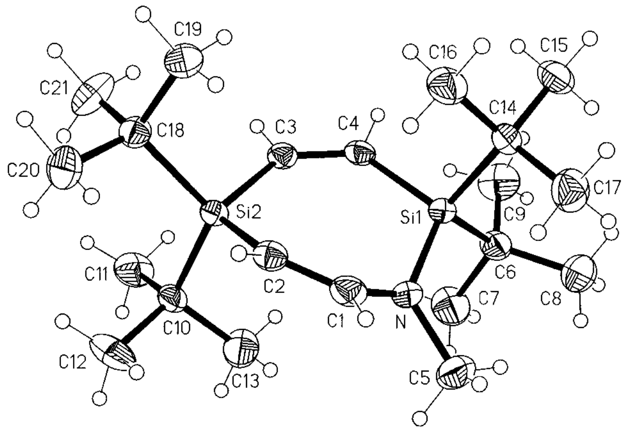


Figure 1. Thermal ellipsoid representation and labeling scheme for **10**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (pm) and bond angles (deg): Si(1)−N 175.4(2), N−C(1) 140.3(3), C(1)−C(2) 133.0(3), C(2)−Si(2) 185.1(3), Si(2)−C(3) 186.8(2), C(3)−C(4) 133.2(3), C(4)−Si(1) 186.4(3); C(4)−Si(1)−N 111.86(11), Si(1)−N−C(1) 124.0(2), N−C(1)−C(2) 128.9(2), C(1)−C(2)−Si(2) 131.0(2), C(2)−Si(2)−C(3) 111.49(11), Si(2)−C(3)−C(4) 129.2(2), C(3)−C(4)−Si(1) 133.2(2).

When **7** is heated in a sealed tube at 100 °C, a rearrangement occurs and furnishes the six-membered ring product **8** in quantitative yield after 14 days. The structure elucidation of **8** was again based on a complete NMR analysis, including H,H- and C,H-COSY spectra, which, among other features, clearly shows that four neighboring olefinic hydrogen atoms must be present. The mechanism of formation of the dark yellow liquid **8** is not surprising since cyclobutene derivatives can be smoothly converted under thermal conditions via an electrocyclic rearrangement to 1,3-dienes, which in turn absorb light on account of their color and recreate the cyclobutene structure.[14]

Renewed cophotolysis of **7** or **8** with **1** finally gives the seven-membered ring product **10** as a low-melting, colorless, crystalline substance, which again was characterized by extensive NMR analysis and low-temperature X-ray crystallography (Figure 1).

The most important feature in the structure of **10** is the determination of the direct adjacency of the nitrogen atom and a silicon atom, which also provides further indirect confirmation for the ring-constitutional assignments of compounds **7** and **8**. Otherwise the endo- and exocyclic bond lengths and angles are all within the expected ranges. The seven-membered ring adopts a "twist" conformation in which Si1, Si2, C1, C3, and C4 are coplanar to within 6 pm, with N 61 pm and C2 38 pm from opposite sides of the plane. The formation of compound **10** can be explained most simply by another [2 + 1] cycloaddition of the silylene **2** to the strained double bond of **7** to furnish the intermediate **9**. The strained tricyclic system of **9** then undergoes rearrangement to the isolated ring system **10** by cleavage of two σ-bonds and formation of two π-bonds.

The reactions described above again demonstrate that a change of the heteroatom can lead to a completely

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(9) Williams, E. A. In *The Chemistry of Organic Silicon Compounds Part 1*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; p 511.

(10) For example: (a) Seyferth, D.; Duncan, D. P.; Haas, C. K. *J. Organomet. Chem.* **1979**, *164*, 305. (b) Boudjouk, P.; Black, E.; Kumarathasan, R.; Samaraweera, U.; Castellino, S.; Oliver, J. P.; Kampf, J. W. *Organometallics* **1994**, *13*, 3715.

(11) Kroke, E.; Willms, S.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Tetrahedron Lett.* **1996**, *37*, 3675.

(12) Reviews: (a) Padwa, A. In *Rearrangements in the Ground and Exited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 501. (b) van Tamelen, E. E. *Acc. Chem. Res.* **1972**, *5*, 186.

(13) Boudjouk, P.; Samaraweera, K.; Sooriyakumaran, R.; Chrisciel, K.; Anderson, K. R. *Angew. Chem.* **1988**, *100*, 1406; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355.

(14) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992; p 1110.

different reaction course in the photolyses of **1** with cyclopentadienes.

Experimental Section

General Procedures. All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. Photolyses were carried out by using a high-pressure mercury immersion lamp (Heraeus TQ 150).

The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM 300 spectrometer using C_6D_6 as solvent. The ^{29}Si and two-dimensional NMR spectra were recorded on a Bruker AMX 300 spectrometer. IR spectra were taken on a Bio-Rad FTS-7 spectrometer. Mass spectra were recorded on a Varian-MAT 212 instrument. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

The cyclotrisilane **1** was prepared according to the literature procedure.[15]

3,3-Di-*tert*-butyl-2-methyl-2-aza-3-silabicyclo[2.2.0]hex-5-ene (7). A solution of **1** (0.58 g, 1.35 mmol) and *N*-methylpyrrole (0.91 g, 11.2 mmol) in *n*-hexane (80 mL) was irradiated at −20 °C for 5 h. After this time, the reaction was shown to be complete by the disappearance of **1** (TLC-monitoring). The solvent was removed by vacuum distillation, and the residue was transferred to a molecular still. Distillation at 60 °C/1.5 mbar yielded 0.28 g (93%) of colorless **7**; mp −20 °C; ^{1}H NMR δ 0.70 (dd, 1H, $^{3}J = 4.9$ Hz, $^{n}J = 1.2$ Hz), 1.02 (s, 9H), 1.23 (s, 9H), 1.86 (dd, 1H, $^{3}J = 4.9$ Hz, $^{n}J = 1.2$ Hz), 2.10 (s, 3H), 5.82 (m, 1H, $^{3}J = 8.1$ Hz, $^{n}J = 1.2$ Hz), 6.87 (m, 1H, $^{3}J = 8.1$ Hz, $^{n}J = 1.2$ Hz); ^{13}C NMR $\delta = 19.17$ (C_q, *t*Bu), 19.80 (C_q, *t*Bu), 28.29 (C_p, *t*Bu), 30.37 (C_p, *t*Bu), 31.35 (CH), 48.44 (CH_3), 48.46 (CH), 130.87 (CH), 150.36 (CH). C_p and C_q refer to primary and quaternary carbon atoms. ^{29}Si NMR δ 23.68; IR (KBr) ν 1547 (vw), 1472 (m) (C=C) cm^{-1}; MS (CI, isobutane) *m*/*z* 224 (MH^{+}, 100). Molecular mass determination (cryoscopically in benzene) calcd, 223; found, 224. Anal. Calcd for $C_{13}H_{25}NSi$: C, 69.88; H, 11.28; N, 6.27. Found: C, 69.69; H, 11.04; N, 6.02.

The distillation residue was dissolved in a minimum amount of *n*-hexane/ethyl acetate (1:1). Cooling at −30 °C afforded colorless crystals. Recrystallization from *n*-hexane provided 100 mg (32%) of pure 1,1,2,3,3,4-hexa-*tert*-butylcyclotetrasilane, which was identified by mp, ^{1}H and ^{13}C NMR spectra, a mass spectrum and comparison with an authentic sample of this compound.[7] On prolonged cooling at −30 °C for 4 days, 40 mg (12%) of hepta-*tert*-butylcyclotetrasilane was obtained. This compound was also identified by comparison with an authentic sample.[17]

Attempted Reactions of 6 or 7. (a) With Sulfur. A mixture of **7** (300 mg, 1.34 mmol), lithium chloride (120 mg, 2.82 mmol), and sulfur (60 mg, 0.23 mmol) in THF (6 mL) was heated at 60 °C for 1 h. The solvent was removed, the residue dissolved in *n*-hexane (5 mL), and all insoluble compounds were filtered off. After removal of *n*-hexane, **7** was recovered almost quantitatively.

(b) With Aryl Isocycanides. The attempted insertion reactions into one of the Si−C bonds of the presumed compound **6** with phenyl isocyanide, *p*-nitrophenyl isocyanide, or 2,6-diisopropylphenyl isocyanide, with or without palladium(II) acetate as a catalyst, did not take place. In each case, the starting material was recovered in high yield.

2,2-Di-*tert*-butyl-1-methyl-1-aza-2-silacyclohexa-3,5-diene (8). Compound **7** (200 mg) was dissolved in C_6D_6 (0.5 mL) and heated at 100 °C in a sealed NMR tube for 14 days. After this time, the rearrangement **7** → **8** was shown to be complete by NMR analysis. **8**: dark yellow oil; ^{1}H NMR δ 1.00 (s, 18H, *t*Bu), 2.68 (s, 3H, CH_3), 4.88 (m, 1H, H5, $^{3}J_{H5,H6} = 7.2$ Hz, $^{3}J_{H5,H4} = 6.1$ Hz, $^{4}J_{H5,H3} = 1.0$ Hz), 5.40 (m, 1H, H3, $^{3}J_{H3,H4} = 14.1$ Hz), 6.03 (m, 1H, H6, $^{4}J_{H6,H4} = 1.05$ Hz), 7.01 (m, 1H, H4). The assignment was confirmed by two-dimensional H,H- and H,C-COSY NMR spectra. ^{13}C NMR δ 23.07 (C_p, *t*Bu), 29.57 (C_q, *t*Bu), 99.47 (C5), 109.09 (C3), 143.49 (C6), 153.75 (C4); ^{29}Si NMR δ 1.39; mass spectrum (CI, isobutane) *m*/*z* 223 (M^{+}, 95), 166 (M^{+} − *t*Bu, 100). Anal. Calcd for $C_{13}H_{25}NSi$: C, 69.88; H, 11.28; N, 6.27. Found: C, 68.92; H, 11.40; N, 5.82.

2,2,5,5-Tetra-*tert*-butyl-1-methyl-1-aza-2,5-disilacyclohepta-3,6-diene (10). A solution of **7** (200 mg, 0.90 mmol) and **1** (0.53 g, 1.2 mmol) in *n*-hexane (80 mL) was irradiated at room temperature for 3.5 h. After this time, the reaction was shown to be complete by the disappearance of **1** (TLC monitoring). The solvent was distilled off, and the remaining yellow oil was transferred to a molecular still. Distillation at 80 °C/0.01 mbar furnished 170 mg of a colorless liquid. Crystallization from ethyl acetate yielded 120 mg (32%) of colorless crystals, mp 52 °C. ^{1}H NMR δ 1.20 (s, 18H, *t*Bu), 1.25 (s, 18H, *t*Bu), 2.69 (s, 3H, CH_3), 4.16 (dd, 1H, $^{3}J = 12$ Hz, $^{n}J = 1.6$ Hz), 6.50 (d, 1H, $^{3}J = 12$ Hz), 6.96 (d, 1H, $^{3}J = 19$ Hz), 7.10 (dd, 1H, $^{3}J = 19$ Hz, $^{n}J = 1.6$ Hz); ^{13}C NMR δ 19.77 (C_q), 22.85 (C_q), 29.08 (C_p), 29.90 (C_p), 41.40 (C_p, $N{-}CH_3$), 93.65, 146.94, 148.50, 157.43; ^{29}Si NMR $\delta = -5.10$, 0.26; IR (KBr) ν 1597 (s), 1468 (s) (C=C) cm^{-1}; MS (CI, isobutane) *m*/*z* 366 (M^{+}, 100). Anal. Calcd for $C_{21}H_{43}NSi_2$: C, 68.96; H, 11.85; N, 3.83. Found: C, 68.84; H, 11.98; N, 3.73.

X-ray Structure Analysis of Compound 10. Single crystals were grown from a saturated solution in ethyl acetate at −50 °C Crystal data: $C_{21}H_{43}NSi_2$, fw 365.74, triclinic, space group $P\bar{1}$, $a = 891.6(3)$ pm, $b = 1161.6(3)$ pm, $c = 1333.6(4)$ pm; $\alpha = 114.94(2)°$, $\beta = 90.16(2)°$, $\gamma = 108.38(2)°$, $V = 1.1737(6)$ nm^{3}, $Z = 2$, $D_x = 1.035$ Mg m^{-3}, λ (Mo Kα) = 0.710 73 Å, $\mu = 0.15$ mm^{-1}, $T = -130$ °C. Data collection and reduction: A colorless tablet with dimensions of 0.65 × 0.4 × 0.2 mm was mounted in inert oil. Data were collected to $2\theta_{max}$ 50° on a Stoe STADI-4 diffractometer (scan type ω/θ). Of the 4947 measured data, 4130 were unique (R_{int} 0.022). Structure solution and refinement: The structure was solved by direct methods and refined anisotopically on F^2 using all reflections.[16] Hydrogen atoms were included using the riding model or rigid methyl groups. The final $wR(F^2)$ was 0.114 for 230 parameters and all reflections, conventional $R(F)$ 0.049 for $F > 4\sigma(F)$. $S = 1.02$; max Δ/σ 0.001; max $\Delta\rho$ + 340, −178 e pm^{-3}.

Acknowledgment. Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Tables of crystal data, atomic coordinates for H atoms, bond lengths, bond angles, and anisotropic displacement coefficients for **10** (5 pages). Ordering information is given on any current masthead page.

OM970043X

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[16] Sheldrick, G. M. *SHELXL 93. Program for crystal structure refinement*; Universität Göttingen: Göttingen, Germany, 1993.

[17] Weidenbruch, M.; Kroke, E.; Pohl, S.; Saak, W.; Marsmann, H. *J. Organomet. Chem.* **1995**, *499*, 229.