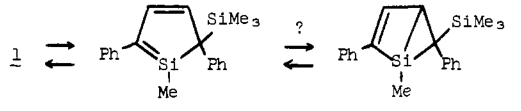
(indeed, only one isomer each of **2, 5, 6,** and **7** are formed), but this seems a bit unlikely. In addition the ratio of **8**:**9** moves to 2:1 when a huge excess of MeOH is employed in the reaction. If MeOH were only reacting with **3** to produce **8** and **9,** the product ratio should be independent of the methanol concentration. Thus, it would appear that we have at least one intermediate other than **3.** While further study is obviously called for, we must consider the possibility that **3** is in equilibrium with silabicyclo[2.1.0]pentene (**10**).[7] It is therefore possible that adducts **2, 5, 6** and **7** arise from addition to **10.** This would be in keeping with the well-established stereospecific additions of multiple bonds to bicyclo[2.1.0]pentanes,[10] if the bulk of the trimethylsilyl group forces **3** to fold in only one direction in closing to **10.** This and other possibilities are being experimentally checked at this time.



3

10

Acknowledgment. The partial support of this work by a grant from Dow Corning Corporation is much appreciated. The diffractometer used in this work was purchased with a grant from the National Science Foundation.

Supplementary Material Available: Tables of fractional coordinates, bond distances, bond angles, and observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Larrabee, R. B. *J. Organomet. Chem.* **1974,** *74,* 313, and references therein.

(2) Crystals of **5** belong to the orthorhombic crystal class with $a = 9.509$ (2), $b = 17.394$ (3), and $c = 17.545$ (3) Å. Systematic extinctions indicated the chiral space group $P2_12_12_1$ and density measurements indicated one molecule of $C_{34}H_{34}Si_2$ per asymmetric unit. All unique diffraction maxima within a Mo Kα sphere of 0.93 Å were collected and 2074 (96%) were judged observed ($F_o \geq 3\sigma(F_o)$). Solution and refinement were uneventful and the current crystallographic residual is 0.036 for the observed data. All crystallographic calculations were done on a Prime 400 computer operated by the Materials Science Center and the Department of Chemistry, Cornell University. The principal programs used were REDUCE and UNIQUE, data reduction programs, M. E. Leonowicz, Cornell University, 1978; BLS, block-diagonal least-squares refinement, K. Hirotsu, Cornell University, 1978; ORFLS (modified), full matrix least squares, W. R. Busing, K. O. Martin, and H. S. Levy, Oak Ridge, ORNL-TM-305; ORTEP, crystallographic illustration program, C. Johnson, Oak Ridge, ORNL-3794; BOND, structural parameters and errors, K. Hirotsu, Cornell University, 1978; MULTAN-76, direct methods and fast fourier transform, G. Germain, P. Main and M. Woolfson, University of York.

(3) The parent 1-methyl-1-silanorbornadiene has been prepared from an unexpected C–H insertion by the carbene produced upon photolysis of 4-diazo-1,1-dimethyl-1-silacyclohexa-2,5-diene: Barton T. J.; Banasiak, D. S., unpublished results.

(4) While adduct **6** formally represents a 1,4 addition of the carbonyl group across **3,** we have no way of knowing whether or not the initial cycloaddition was "[2 + 2]" followed by rearrangement to **6.**[5]

(5) A similar mechanistic dilemma exists in the work of Weber: Valkovich P. B.; Weber, W. P. *Tetrahedron Lett.* **1975,** 2153; *J. Org. Chem.* **1975,** *40,* 229.

(6) Gusel'nikov L. E.; Flowers, M. C. *Chem. Commun.* **1967,** 864 (1967).

(7) Closure of 1-sila-1,3-butadienes to silacyclobutenes has been reported by Block[8] and by Sakurai.[9] The intermediate dienes in these reports did not possess C-5 hydrogens.

(8) Block C.; Revelle, L. K. *J. Am. Chem. Soc.* **1978,** *100,* 1630.

(9) Nakadaira, Y.; Kanouchi, S.; Sakurai, H. *J. Am. Chem. Soc.* **1974,** *96,* 5621.

(10) Gassman, P. G. *Acc. Chem. Res.* **1971, 4,** 128.

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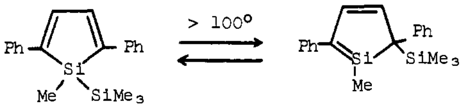
Serendipitous Synthesis of a Sila-α-pyran—Convenient, Penultimate Precursor to Dimethylsilanone

Sir:

Recently we established that 1-disilanyl-1,3-butadienes undergo thermal rearrangement via 1,5-silyl migration to produce 1-sila-1,3-butadienes.[1] For example, 2,5-diphenyl-1-trimethylsilylsilole (**1**) undergoes reversible rearrangement to **2** at temperatures above 100 °C.



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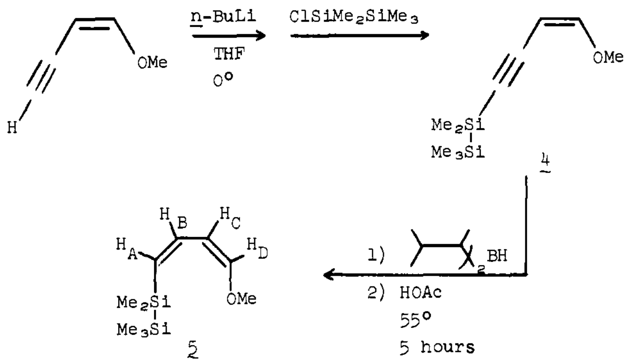
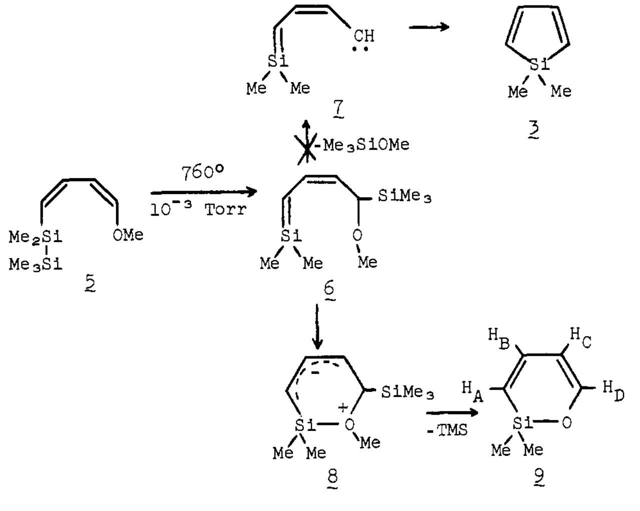
We thought to put this rearrangement to use in a synthesis of silole **3** which would be the first example of a silole with all the ring-carbons unsubstituted. To this end we prepared (*Z*)-1-pentamethyldisilanyl-4-methoxybut-1-yn-3-ene (**4**) from *n*-butyllithium-induced coupling of pentamethylchlorodisilane and (*Z*)-4-methyoxybut-1-yn-3-ene in 76% yield.[2] Attempted cis reduction of the triple bond with hydrogen and Lindlar's catalyst afforded only mixtures of randomly reduced **4.** However, hydroboration with disiamylborane followed by acidic cleavage of the vinyl borane in acetic acid[3] provided (*Z,Z*)-1-pentamethyldisilanyl-4-methoxy-1,3-butadiene (**5**) in 37% yield.[4]



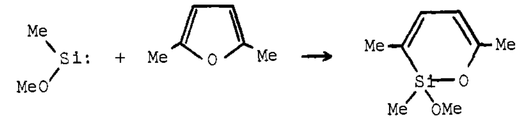
Our hope was that thermal rearrangement of **5** to silene **6** would be followed by α elimination of trimethylmethoxysilane to produce carbene **7** which would cyclize to the desired silole **3.** However, flow pyrolysis of **5** (760 °C at 10^{-3} Torr) afforded in 52% yield a product which resulted from the loss of the elements of tetramethylsilane[5] from **5.** This product was identified as 2,2-dimethyl-1-oxo-2-silacyclohexa-3,5-diene (**9,** oxasilin) on the basis of its spectra: NMR (CCl_4) δ 0.29 (6 H, s), 5.07 (H_C, t of d, $J_{CD} = J_{CB} = 6, J_{AC} = 1.0$ Hz), 5.54 (H_A,



d of t, $J_{AB} = 14$, $J_{AD} \sim J_{AC}$), 6.54 (H_D, overlapped with H_B), 6.71 (H_B, d of d of d, $J_{BD} \sim 1$ Hz); mass spectrum *m/e* (rel intensity) 126 (19.5), 111 (M − CH_3, 100), 85 (M − CH_3 + C_2H_2, 14), calcd for $C_6H_{10}OSi$ 126.0501, obsd 126.0498.

The formation of **9** is easily rationalized when it is recognized that the methoxyl oxygen of **6** is in close proximity to an undoubtedly polar silicon–carbon double bond. Silicon–oxygen bond formation to produce zwitterion **8** would render the methoxyl methyl labile with regard to involvement in the elimination of tetramethylsilane.[6]

Oxasilin **9** is the second example of this ring system to be reported. Weber obtained 2-methoxy-2,3,6-trimethyl-1-oxo-2-silacyclohexa-3,5-diene (**10**) in yields of "... never better than a few percent ..." from the reaction of methoxymethylsilylene and 2,5-dimethylfuran.[7] Unfortunately, an insufficient amount of **10** was accumulated to attempt any chemical investigations.



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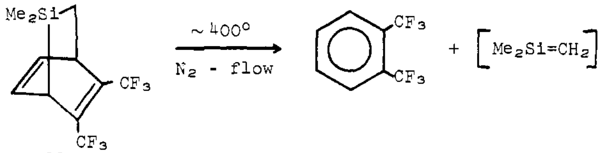
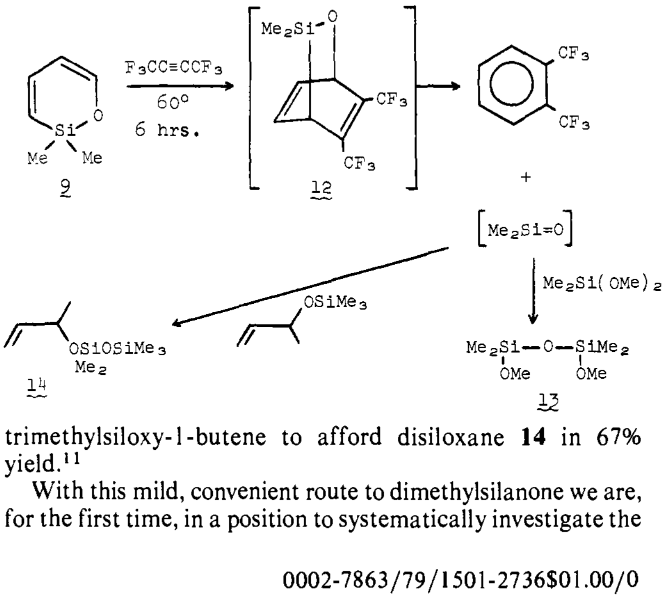
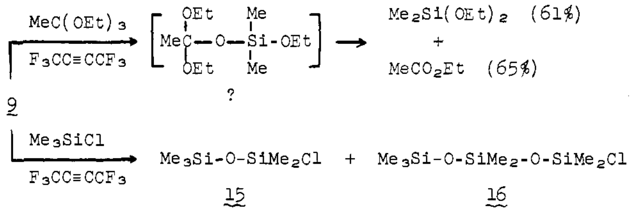
The 1,2-oxasilin ring system is one which we have long coveted, as we viewed it as a potential penultimate precursor to silanones—compounds containing a silicon–oxygen (p–p)π double bond. It has been established that 7-silabicyclo[2.2.2]-octadiene ring system **11** extrudes the silene bridge at high temperatures (~400 °C) in the gas phase.[8] Thus, we thought to react **9** with an acetylene in a Diels–Alder fashion to produce the corresponding bicyclic silanone precursor. To our surprise, while perfluoro-2-butyne reacts completely with **9** in ~1 day at room temperature (6 h at 60 °C), *o*-bis(trifluoromethyl)-benzene is formed at the same rate (as observed by NMR). We have never observed the intermediate adduct **12**.[9] Thus, it appears that the initial adduct **12** quickly decomposes even at room temperature through extrusion of the silanone bridge. This assumption was dramatically verified by conducting the cycloaddition in the presence of excess dimethoxydimethylsilane and obtaining the dimethylsilanone insertion product **13**[10] in 76% yield. Likewise, dimethylsilanone was trapped by 3-trimethylsiloxy-1-butene to afford disiloxane **14** in 67% yield.[11]



11



With this mild, convenient route to dimethylsilanone we are, for the first time, in a position to systematically investigate the chemistry of this intriguing system. Indeed, at this time we can report the first example of silanone insertion into a silicon–chlorine bond. When **9** is reacted with perfluoro-2-butyne and excess trimethylchlorosilane (65 °C, 8 h), siloxanes **15** (37%) and **16** (17%) are obtained.[12] This represents the first report of silanone trapping by the Si–Cl bond. When **9** is reacted with perfluoro-2-butyne in the presence of excess triethyl orthoacetate, a 61% yield of dimethyldiethoxysilane[10] is obtained.



Presumable this arises from silanone insertion into a C–O bond, followed by disproportionation of the resulting ortho ester.

Acknowledgment. We thank the Dow Corning Corporation for partial support of this work.

References and Notes

(1) Barton, T. J.; Wulff, W. D.; Arnold, E. V.; Clardy, J. C. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) NMR (CCl_4) δ 0.13 (9 H, s), 0.21 (6 H, s), 3.85 (3 H, s), 4.50 (1 H, d, $J = 7$ Hz), 5.62 (1 H, d, $J = 7$ Hz); mass spectrum *m/e* (rel intensity) 2.2 (0.9), 211 (0.3), 197 (74), 171 (70), 73 (100), calcd for $C_{10}H_{19}OSi_2$ 211.0975, obsd 211.0977.

(3) The procedure followed was from Zweifel, G.; Polston, N. L. *J. Am. Chem. Soc.* **1970**, *92*, 4068.

(4) NMR (CCl_4) δ 0.03 (9 H, s), 0.15 (6 H, s), 3.63 (3 H, s), 5.05 (H_C, d of d of d, $J_{BC} = 12$, $J_{CD} = 6.5$, $J_{AC} = 1.0$ Hz), 5.32 (H_A, d of t, $J_{AB} = 14$, $J_{AD} = 1.0$ Hz), 5.84 (H_D, d of t, $J_{BD} = 0.5$ Hz), 7.01 (H_B, d of d of d); mass spectrum *m/*e (rel intensity) 199 (M − CH_3, 10.5), 111 (54), 89 (21), 73 (100), calcd for $C_9H_{19}OSi_2$ 199.0975, obsd 199.0971.

(5) Tetramethylsilane was identified as a product of this pyrolysis by gas chromatographic–mass spectral comparison with an authentic sample.

(6) We cannot exclude the possibility of a mechanistic route to **9** involving homolytic cleavage of the Si–Si bond followed by S_H2 displacement on oxygen by silyl radical. However, the 1,5-silyl migration is precedented while S_H2 displacement from ether oxygen is very rare.

(7) Childs, M. E.; Weber, W. P. *J. Org. Chem.* **1976**, *41*, 1799.

(8) Barton, T. J.; Kline, E. *J. Organomet. Chem.* **1972,** *42*, C21.

(9) Reaction of **9** with maleic anhydride does produce the expected, stable Diels–Alder adduct. Other dienophiles are currently being investigated.

(10) Identified by NMR and mass spectral comparison with an authentic sample.

(11) NMR (CCl_4) δ 0.04 (6 H, s), 0.10 (9 H, s), 1.26 (3 H, d, $J = 3$ Hz), 4.46 (1 H, m), 5.19 (2 H, m), 5.98 (1 H, m); *m/e* (rel intensity) 218 (10), 203 (24), 149 (100), 147 (41), 73 (10), 55 (44), calcd for $C_9H_{22}O_2Si_2$ 218.1158, obsd 218.1158.

(12) **15:** NMR (CCl_4) δ 0.15 (9 H, s), 0.42 (6 H, s); *m/*e (rel intensity) 169 (43), 167 (100, M − CH_3), 147 (10, M − Cl), 76 (13), 73 (14). **16:** δ 0.10 (15 H, s), 0.42 (6 H, s); *m/e* (rel intensity) 243 (29), 241 (68, M − CH_3), 221 (4), 133 (11), 113 (11), 73 (100). Yields are based on *o*-bis(trifluoromethyl)-benzene.

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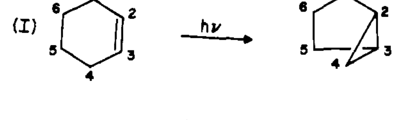
Spin-Inversion and Orbital Symmetry Conspiracy in Type A Lumiketone Rearrangements

Sir:

Type A lumiketone rearrangement is known to originate from a triplet state[1,2] with evidence suggesting a $^3\pi\pi^*$ reactive state.[2b-d] The reaction (I) can be viewed as a formal $[2_\pi + 2_\sigma]$



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