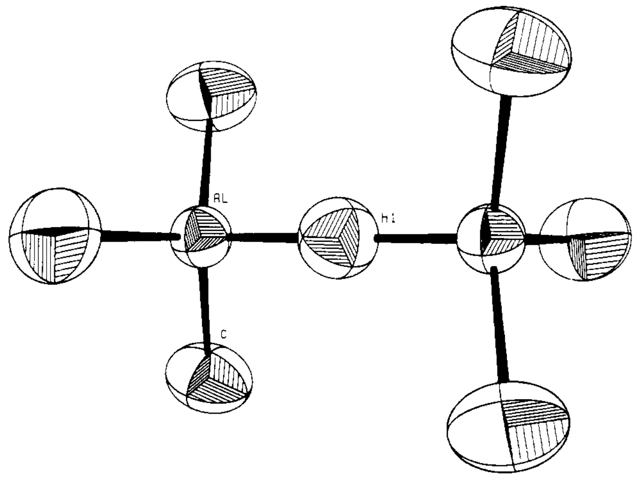


Figure 1. Structure of the $[(CH_3)_3Al-H-Al(CH_3)_3]^-$ anion with the atoms represented by their 50% probability ellipsoids for thermal motion.

A related point of interest concerns the effect of the solvent on the relative stability of the 1:1, $M[(CH_3)_3BH]$ (M = Li, Na), vs. the 2:1, $M[(CH_3)_3B-H-B(CH_3)_3]$, complexes. In an extensive study of the lithium salts, Brown and co-workers found that in poor solvating media (i.e., diethyl ether) only the 1:1 anions were formed.[12] In our system, aromatic solvents were used, but nevertheless the 2:1 complex resulted.

$Na[(CH_3)_3Al-H-Al(CH_3)_3]$ was prepared by the reaction of 0.005 mol of sodium hydride with 0.010 mol of trimethylaluminum in toluene with the addition of 0.001 mol of 15-crown-5. The reaction proceeded at once with the formation of the liquid-layering effect (liquid clathrate)[14] characteristic of the presence of a 2:1 anion. Crystals of the title compound began to deposit immediately. It appears that 0.001 mol of [Na·15-crown-5]-$[(CH_3)_3Al-H-Al(CH_3)_3]$ initially formed. This substance then faciliated the dissolution of NaH which in turn reacted with the available $Al(CH_3)_3$. Once formed, the crown-ether-free $Na[(CH_3)_3Al-H-Al(CH_3)_3]$ crystallized since it is of lower solubility than the crown-ether-containing analogue. The use of small amounts of macrocyclic ethers to effectively catalyze reactions of this sort is an important development and is under active investigation.

Crystals of the highly oxygen- and water-sensitive title compound belong to the cubic space group *Pa*3 with $a = 11.239$ (4) Å and $D_c = 0.79$ g cm^{-3} for four molecules in the unit cell. The final *R* value was 0.048 on the basis of 261 independent observed reflections. The structure of the anion, as determined from room temperature data, is shown in Figure 1. Although the position of the bridging hydrogen atom is required to occupy a $\bar{3}$ crystallographic site, the refinement of its isotropic thermal parameter[15] was unsatisfactory. We therefore recollected the data at low temperature (ca. 200 K). These results show that a refineable hydrogen atom does indeed exist at the aforementioned $\bar{3}$ site.[16] The Al-H bond length, 1.65 Å, is 0.14 Å longer than one would predict on the basis of covalent radii.[8] (Although several X-ray determinations of terminal Al-H bond lengths exist, none have been done with sufficient accuracy for comparisons to be made.) Agreement is found, however, between the linear, single-hydrogen bridge length and that given for the electron diffraction study of $[(CH_3)_2AlH]_2$.[8] It therefore appears that no weakening of the bridge bond results from the expansion of the angle from 103 to 180°. This in turn implies that metal···metal bonding may *not* be an important consideration in electron-deficient situations in general.

---

(14) Atwood, J. L. *Rec. Dev. Sep. Sci.* **1977**, *3*, 195.

(15) The positional parameters (*X*, *Y*, *Z*) are symmetry fixed at $^1/_2$, $^1/_2$, $^1/_2$ for the bridging hydrogen atom.

(16) The complete results of the low-temperature study are to be published. It should be noted, however, that no substantive differences between the low-temperature and the room temperature parameters are observed (i.e., Al-H = 1.665 (1) Å from the refinement of the low-temperature data).

Acknowledgment. We are grateful to the National Science Foundation (J.L.A) and the University of Alabama School of Mines and Energy Development (J.L.A.) for support of the research program.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

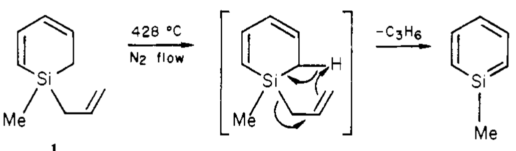
A Rearrangement-Elimination Sequence to 1-Silatoluene

Thomas J. Barton* and Michael Vuper

Department of Chemistry
Iowa State University, Ames, Iowa 50011

Received July 20, 1981

In 1978 we reported the first unambiguous generation and trapping of a silabenzene.[1] At that time we employed a thermally induced retro-ene elimination of propene from allylsilacyclohexadiene **1** to produce silatoluene (**2**) which was trapped by a variety of reagents. Since then this route has been used to obtain the UV and IR spectra of **2** isolated in a frozen argon matrix,[2] to obtain the PES spectrum of **2** in the gas phase,[3] and to produce derivatives of **2**.[4]



1

2

We report here an alternate route to silatoluene which provides an example of the synthetic use of a 1,3-sigmatropic rearrangement of an allylsilane,[5] an example of silene generation through thermally induced β elimination of a silyl ether from a β-(alkoxysilyl)silane, and additional evidence that **2** is actually formed as a discrete species in the gas phase.

The synthesis of our desired alternate precursor of silatoluene began with the conversion of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene (**3**)[6] to 1-methoxysilacyclohexadiene **4** by treatment with methanol/Et_3N [**4**: NMR (CCl_4) δ 0.18 (s, 3 H), 1.48 (m, 2 H), 3.30 (s, 3 H), 5.83 (m, 3 H), 6.8 (d of m, 1 H); *m/e* (relative intensity) 140 (24, M+), 125 (53, M − OMe), 108 (26, M − MeOH), 95 (29), 75 (57), 59 (100); >90% yield]. Diene **4** was metalated with lithium diisopropylamide (LDA)[8] in THF at −78 °C, and the resulting pentadienyl anion **5** was quenched with chlorotrimethylsilane to afford silacyclohexadiene **6** as a colorless oil after vacuum distillation [**6**: NMR (CCl_4) δ 0.0 (s, 9 H), 0.13 (s, 3 H), 2.91 (m, 1 H), 3.31 (s, 3 H), 5.61 (d of d, 2 H, $J_{HC=CH}$ = 14.5 Hz), 6.81 (d of d, 2 H, *J* = 14.5 and 4.5 Hz); M_r calcd for $C_{10}H_{20}Si_2O$ 212.1053, measured 212.1048; *m/e* (relative intensity) 212 (17), 197 (1.6)8 124 (15), 108 (54), 73 (100), 59 (48)].

---

(1) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246.

(2) Kreil, C. L.; Chapman, O. L.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 841.

(3) Bock, H.; Bowling, R. A.; Solouki, B.; Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1980**, *102*, 429.

(4) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem.* **1980**, *92*, 58.

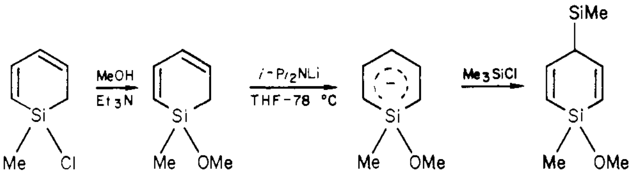
(5) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.

(6) Diene 3 is prepared by copyrolysis (600 °C, N_2 flow) of 1,1,2,2-tetrachloro-1,2-dimethyldisilane and cyclopentadiene and is contaminated by a very small amount of the nonconjugated isomer.[7]

(7) Barton, T. J.; Banasiak, D. S. *J. Am. Chem. Soc.* **1977**, *99*. 5199

(8) Metalation of silacyclohexadienes with alkyllithium reagents has been reported: Chernyshev, E. A., et al *Zh. Obsch. Khim.* **1974**, *44*, 226. Barton, T. J.; Banasiak, D. S. *J. Organomet. Chem.* **1978** *157*, 255.

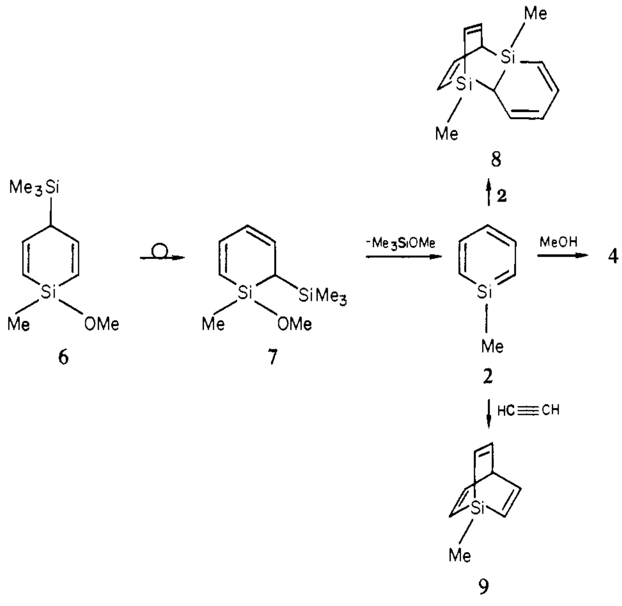
0002-7863/81/1503-6788$01.25/0



3 4 5 6

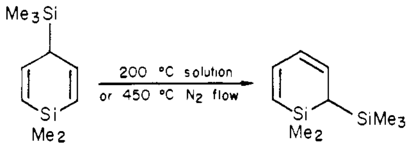
Silacyclohexadiene **6** was the desired precursor of silatoluene **2** as it was hoped that this system would undergo thermally induced 1,3-migration of the trimethylsilyl group to afford conjugated diene **7** followed by β elimination of trimethylmethoxysilane. Precedent for 1,3-sigmatropic migration of silicon on an all-carbon framework is found in the work of Kwart.[5] Precedent for silene generation via thermal β elimination of Me$_3$SiOMe from a Me$_3$Si–CHR–SiR$_2$OMe unit was recently provided in the synthesis of 6-silafulvene.[9] Flash vacuum pyrolysis of **6** (660 °C, 2×10^{-4} torr, horizontal 1-ft quartz-packed tube) afforded a light yellow liquid pyrolysate representing a 46% mass recovery. Gas chromatographic separation allowed isolation of silatoluene dimer **8** in 14% yield.[10] The NMR and mass spectra of **8** were superimposable with those of the authentic material[2] prepared from **1**. Further trapping of silatoluene was accomplished by flow copyrolysis of **6** and a tenfold molar excess of methanol in a vertical quartz tube packed with quartz chips heated to 450 °C in a 1-ft tube furnace with a continuous 30-mL/m flow of nitrogen carrier gas. GC and GC/MS analysis revealed a 50.4% yield of **4** (mass balance 61%; yield based on reacted **6**). Although it is conceivable that the conversion of **6** to **4** is simply a desilylative methanolysis of **6** followed by isomerization, this same conversion has been employed in the trapping of **2** from **1**, and the use of MeOD produces the expected ring-deuterated product.[2] In the case of precursor **6** the use of MeOD would obviously do nothing to remove any mechanistic ambiguities. However, further confirmation of the intermediacy of **2** was obtained through the use of acetylene as a trapping agent. Acetylene (30 mL/m) was used both as reactant and as carrier gas in the pyrolysis (450 °C) of **6** to afford a product mixture containing some unreacted **6** and adduct **9**, 1-methyl-1-silabicyclo[2.2.2]octatriene, in 28.5% yield. The NMR and mass spectra of **9** were identical with those of authentic 1-methylsilabarralene derived from the copyrolysis of **1** and acetylene.[1]

There are two points with regard to this route to a silabenzene which beg discussion. It would be expected that the β elimination of Me$_3$SiOMe would be dependent on the stereochemistry of **7**, since a cis relationship of Me$_3$Si and OMe groups would presumably be required for concerted elimination.[11] Thus the stereochemistry of **6** could control the ultimate formation of silatoluene. As **6** is synthesized by kinetic quenching of anion **5** where the ring silicon is two carbons removed from the site of attack, little stereochemical preference was expected. However, the NMR spectrum of **6** (vide supra) clearly reveals it to be a single diastereomer. We presume that **6** is formed only as the isomer with Me$_3$Si and OMe groups in a syn relationship. Thus it would appear that the methoxyl group must interact with the incoming silicon and direct it to the same side of the ring.



8 6 7 2 9

Although we have depicted the conversion of **6** to silatoluene as proceeding through the intermediacy of **7**, there have in fact been no reported examples of this rearrangement on a silacyclohexadiene ring. In order to establish the feasibility of this rearrangement in this sequence, 1,1-dimethyl-4-(trimethylsilyl)-1-silacyclohexa-2,4-diene (**10**)[8] was heated in benzene-d_6 solution (degassed; sealed NMR tube) and the reaction monitored by NMR spectroscopy. After 6 h at 200 °C all signals due to **10** had virtually disappeared. The methine proton of **10** resonating at δ 2.68 (overlapped t of t, J = 5 and 1.5 Hz) was replaced by a doublet at δ 1.4 (J = 4.5 Hz), reflecting the change of environment from diallylic to α-silylallylic for this hydrogen. The clean olefinic absorption of symmetrical **10** at δ 5.83 (d of d, 2 H, J = 15 and 1.5 Hz) and δ 6.75 (d of d, 2 H, J = 15 and 5 Hz) was replaced by complex multiplets centered at δ 5.9 and 6.9 Thus it would appear that **10** is cleanly rearranged to the conjugated isomer **11** [m/e (relative intensity) 196 (6%, M+), 181 (2%), 108 (74%), 73 (100%)]. A vertical flow pyrolysis of **10** (450 °C: N$_2$, 30 mL/m) also cleanly afforded **11**. Likewise when a degassed solution of **6** in diphenyl ether was heated at 150 °C, after 10 h essentially all **6** was rearranged to **7** which was isolated by preparative GC [**7**: NMR (CCl$_4$) δ 0.0 (s, 9 H), 0.18 (s, 3 H), 1.4 (d, 1 H, J = 5 Hz), 3.2 (s, 3 H), 5.9 (m, 3 H), 6.82 (m, 1 H); mass spectral fragmentation as for **6**].



10 11

Currently we are attempting to utilize this sequence of rearrangement—elimination—in the synthesis of other novel, unsaturated silacycles.

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by the National Science Foundation (Grant CHE-8024678) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

---

[9] Barton, T. J.; Burns, G. T.; Arnold, E. V.; Clardy, J. *Tetrahedron Lett.* **1981**, 7.

[10] Although no effort was made to isolate Me$_3$SiOMe, its considerable presence in this reaction mixture was confirmed by GC/MS.

[11] No existing data rule out a stepwise radical process at this time.