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Reduction of Polysilacycloallenes by Sodium: Structure of the Donor-Free Sodium Salt of an Allyl Anion

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Summary: The reduction of the tetrasilacyclohepta-1,2-diene ***1*** *afforded the stable allyl anion* ***2****. The structure of* ***2*** *(Na salt) was determined by a single-crystal X-ray diffraction analysis. The reaction of allyl anion* ***2*** *with methyl iodide gave the methyl adducts* ***3a,b****.*

Interest in the reactivity, structure, and bonding of allylic metal compounds,[1,2] especially allylic lithium and sodium compounds, has increased remarkably in recent years. Acyclic allenes are reduced by sodium to form the respective allyl anion, an example being the intermolecular "dibenzene sodium sandwich" double cones.[1a,3] Cyclic allenes have been the subject of considerable current interest as strained unsaturated cyclic compounds. However, to date no studies have been reported concerning the reduction of cyclic allenes. We had occasion to investigate the action of sodium on a polysilacycloallene.[4] Stabilization of carbanionic species bonded to silicon is well-known.[5,6] Herein we report the crystal structure of a donor-free sodium salt of an allyl anion which was obtained by the reduction of 1,3-diphenyl-4,5,6,7-tetrasilacyclohepta-1,2-diene (**1**).

The tetrasilacyclohepta-1,2-diene **1** readily reacted with a sodium mirror in diethyl ether under Ar to give a dark red solution.[7] Air- and moisture-sensitive red crystals suitable for X-ray diffraction were obtained by recrystallization from hexane and diethyl ether (Scheme 1). The structure of allyl anion **2** was established by an X-ray crystallographic analysis.[8] It is remarkable that **2** crystallizes without coordinated solvent from diethyl ether solution. As shown in Figure 1, allyl anion **2** has a bicyclic structure, resulting from the migration of a silyl group. The sodium ion is five-coordinate with Na−C distances of 2.89−2.65 Å (Figure 1); the Na−Si4 bond length is 3.409 Å. The allyl unit exhibits a C−C−C bond angle of 123.9(4)° and an average C−C−C

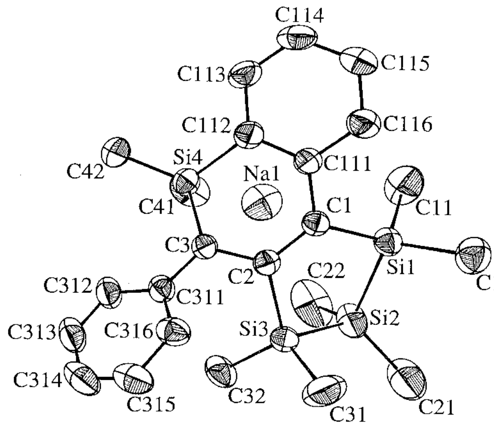
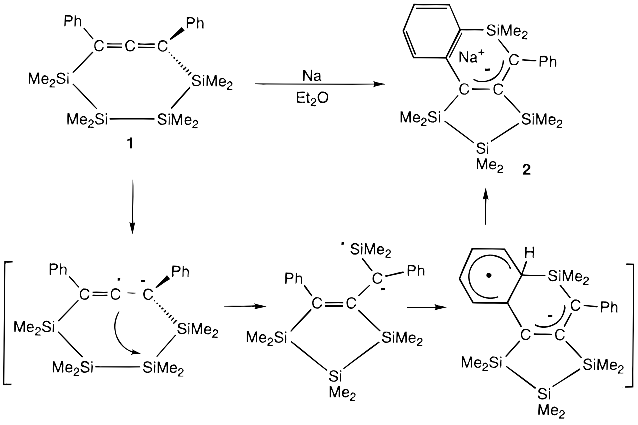


Figure 1. X-ray structure of **2** showing 50% probability ellipsoids. Selected bond distances (Å) and angles (deg) and torsion angles (deg): C1−C2 = 1.417(7), C2−C3 = 1.433(7), C3−Si4 = 1.828(5), C2−Si3 = 1.917(5), C1−Si1 = 1.875(5), C1−C111 = 1.479(7), C111−C112 = 1.421(7), C3−C311 = 1.460(7), Na−C3 = 2.656(5), Na−C2 = 2.763(5), Na−C1 = 2.882(5), Na−C111 = 2.669(6), Na−C112 = 2.878(6); C1−C2−C3 = 124.4(4); C3−C1−C2−Si3 = 10.8(0.4), Si1−C1−C2−C3 = 20.64(0.4); C111−C1−C2−C3 = 11.99(0.7); C1−C2−C3−Si4 = 30.68(0.6), C1−C2−C3−C311 = 15.57(0.5).

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

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(7) To a 100 mg sodium mirror (4.35 mmol), produced by vacuum distillation, was added 10 mL of diethyl ether, which had been dried over a potassium mirror, and 500 mg of tetrasilacyclohepta-1,2-diene **1** (1.18 mmol) at room temperature under Ar. After the mixture was stirred for 5 h, air- and moisture- sensitive red crystals suitable for X-ray diffraction were obtained by recrystallization from hexane, which had been dried over a potassium mirror.

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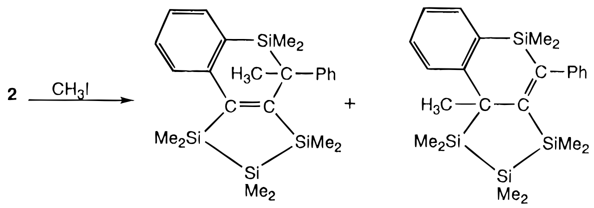
Scheme 2

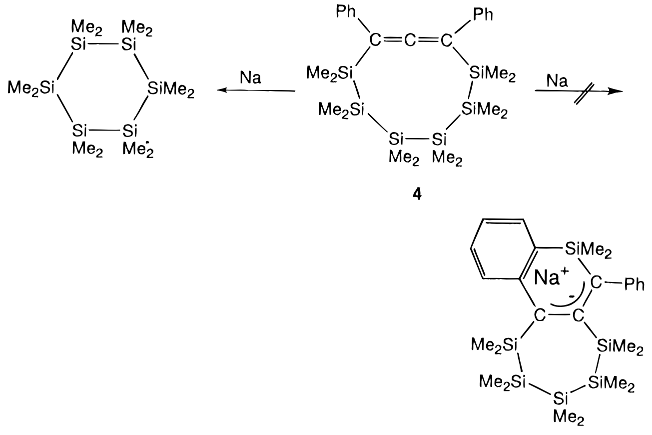


3a and **3b**

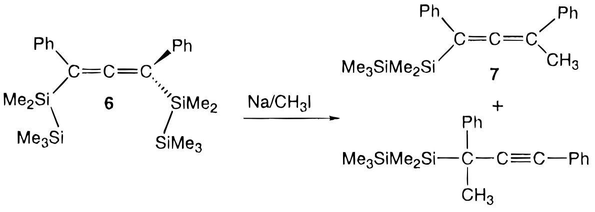
bond length of 1.425(7) Å. The torsional angles of C3−C1−C2−Si3, Si1−C1−C2−C3, C111−C1−C2−C3, C1−C2−C3−Si4, and C1−C2−C3−C311 are 10.8(0.4), 20.64(0.4), 12.11(0.7), 30.53(0.6), and 15.34(0.5)°, respectively. Of the atoms directly attached to the allyl unit, C111 and C311 are bent toward the Na atom and Si1, Si4 and Si3 are bent in the opposite direction. The ^{29}Si NMR spectrum of **2** exhibits four resonances at −48.9, −27.0, −16.7, and −13.4 ppm. The tetrasilacyclohepta-1,2-diene **1** was reduced only to the radical anion by sodium. Subsequently, the silicon atom β to the allene unit was attacked by the central allene carbon to give a silyl radical. Intramolecular homolytic substitution of the resulting silyl radical gave allyl anion **2**. Allyl anion **2** was reacted with methyl iodide to give the corresponding adducts **3a**,**b** in 43% and 42% yields, respectively (Scheme 2).[9]

The reaction of the hexasilacyclonona-1,2-diene **4** with a sodium mirror was carried out under conditions similar to those used in the reaction of **1** with a sodium mirror. However, no allyl anion **5** could be detected; only dodecamethylcyclohexasilane[10] (30% yield) and a complex mixture were obtained (Scheme 3).

Scheme 3



Scheme 4



Since the distance from the central allene carbon to the Si atom β to the allene unit is small and the conformation of **1** rigid, tetrasilacyclohepta-1,2-diene **1**, upon Na reduction, gave allyl anion **2** via a silyl migration. However, since the distance from the central allene carbon to the Si atom β to the allene unit is long in **4** and the conformation flexible, the Na reduction of **4** does not lead to the formation of **5**.

Acyclic allene **6** was reduced similarly by sodium, and methyl iodide was added as a quencher (Scheme 4). Adducts **7** and **8** were formed in 32% and 33% yields, respectively.[11] The formation of allene **7** and acetylene **8** can be explained by the reaction of CH_3I with an allenyl anion that had been generated by scission of a silicon−carbon bond in the radical anion. In this reaction methyl adducts of the allyl anion were not obtained.

In contrast to the case for silacycloallenes, reaction of 4,5,9,10-tetrasilacyclodeca-1,2,6,7-tetraene (*dl*) **9** with a sodium mirror in ether afforded a dark red solution. After removal of sodium, addition of an excess of CH_3I to this solution afforded **10** in 34% yield.[12] The formation of **10** clearly shows that bis(allene) **9** was readily reduced with sodium to afford the tetramethyleneethane dianion **12** as an interesting intermediate (Scheme 5). As expected, the transannular sp carbon distance in **9**

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(8) Crystal data for **2**: $C_{23}H_{33}Si_4Na$, $M_r = 444.84$, triclinic space group $P2_1/c$, $a = 11.491(1)$ Å, $b = 18.486(1)$ Å, $c = 12.723(2)$ Å, $\alpha = 90.00(1)°$, $\beta = 100.47(1)°$, $\gamma = 90.00(1)°$, $V = 2657.7$ Å^3, $Z = 4$, $D_c = 1.11$ g cm^{-3}, $F(000) = 952$, Mo Kα radiation, $\lambda = 0.709\ 30$ Å, $\mu = 2.4$ cm^{-1}, $T = 296$ K. The structure was solved from 5859 collected independent reflections ($2\theta \le 50°$, $|F_o^2| > 3\sigma|F_o^2|$) measured on an Enraf-Nonius CAD4 diffractometer using an $\omega-\theta$ scan. The structure was solved by direct methods, and hydrogen atoms were located and their positions and isotropic thermal parameters refined to $R = 0.050$ ($R_w = 0.063$).

(9) After the reaction of 300 mg of tetrasilacyclohepta-1,2-diene (0.709 mmol) with 500 mg of sodium mirror (21.75 mmol) as in ref 7, 142 mg of methyl iodide (1.00 mmol) was added at room temperature. The precipitate was removed by filtration, and the solvent was removed. The crude product was purified by medium-pressure silica gel column chromatography to give 133 mg of **3a** (43% yield) and 127 mg of **3b** (42% yield). Since the spectral data of **3a** and **3b** are similar, the structure could not be determined on the basis of the spectral data alone. Compound **3a**: colorless oil. Anal. Calcd for $C_{24}H_{36}Si_4$: C, 65.98; H, 8.31. Found: C, 65.85; H, 8.27. LRMS (EI, 70 eV): *m/e* 436 (M$^+$), 362, 347, 319, 304 (100%), 289, 245, 73. ^{1}H NMR (C_6D_6, 90 MHz): δ −0.06 (s, 3H), 0.09 (s, 3H), 0.14 (s, 3H), 0.23 (s, 3H), 0.30 (s, 3H), 0.38 (s, 3H), 0.43 (s, 3H), 0.51 (s, 3H), 1.60 (s, 3H), 6.8−7.7 (m, 9H). ^{13}C NMR (C_6D_6, 22.5 MHz): δ −8.5 (q), −8.3 (q), −5.4 (q), −4.1 (q), 0.5 (q), 0.6 (q), 1.2 (q), 3.6 (q), 21.9 (q), 38.4 (s), 125.2 (d), 127.1 (d), 127.8 (d), 128.4 (d), 128.6 (s), 130.1 (d), 133.7 (d), 145.5 (d), 146.8 (s), 156.5 (s), 158.4 (s), 166.6 (s). ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −57.6, −13.1, −11.2, −6.9. IR (neat): 1599, 1253, 1067, 1000, 832, 806, 779 cm^{-1}. Compound **3b**: colorless oil. Anal. Calcd for $C_{24}H_{36}Si_4$: C, 65.98; H, 8.31. Found: C, 65.92; H, 8.26. LRMS (EI, 70 eV): *m/e* 436 (M$^+$), 362, 347, 319, 304 (100%), 289, 245, 73. ^{1}H NMR (C_6D_6, 90 MHz): δ −0.66 (s, 3H), −0.28 (s, 3H), −0.08 (s, 3H), 0.02 (s, 3H), 0.09 (s, 3H), 0.25 (s, 3H), 0.38 (s, 6H), 1.60 (s, 3H), 7.0−7.6 (m, 9H). ^{13}C NMR (C_6D_6, 22.5 MHz): δ −6.6 (q), −5.7 (q), −4.8 (q), −3.3 (q), 0.0 (q), 1.2 (q), 1.3 (q), 3.0 (q), 27.4 (q), 47.0 (s), 124.9 (d), 126.6 (d), 128.2 (d), 128.3 (d), 128.8 (s), 129.1 (d), 129.9 (d), 134.1 (d), 146.7 (s), 151.6 (s), 152.6 (s), 167.1 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ −50.9, −27.7, −18.9, −2.6. IR (neat): 1251, 988, 837, 804 cm^{-1}.

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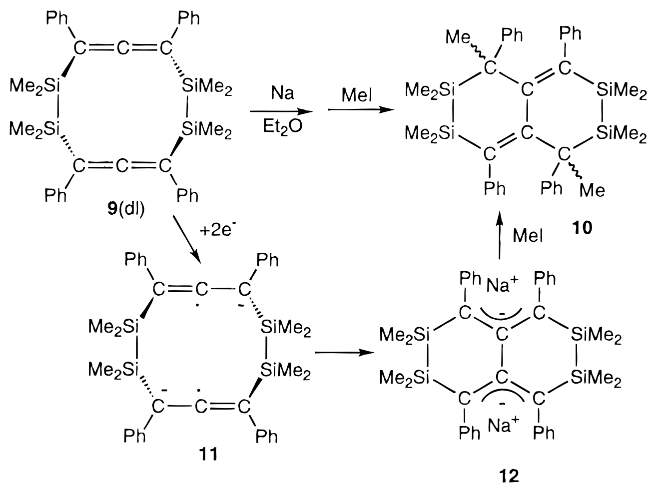
(11) Compound **7**: colorless oil. Anal. Calcd for $C_{21}H_{28}Si_2$: C, 74.93; H, 8.38. Found: C, 74.02; H, 8.53. LRMS (EI, 70 eV): *m/e* 336 (M$^+$), 263, 248, 186, 159, 131 (100%), 73. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.20 (s, 9H), 0.43 (s, 3H), 0.44 (s, 3H), 2.14 (s, 3H), 7.1−7.7 (m, 10H). ^{13}C NMR (C_6D_6, 22.5 MHz): δ −2.3 (q), −2.1 (q), −1.3 (q), 16.3 (q), 97.9 (s), 102.8 (s), 126.0 (d), 126.9 (d), 128.7 (d), 128.8 (d), 129.1 (d), 129.2 (d), 137.9 (s), 138.5 (s), 210.2 (s). ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −20.5, −18.5. IR (neat): 1912 (C=C=C), 1599, 1493, 1247, 833, 797, 760, 692 cm^{-1}. UV (cyclohexane): λ_{max} (ϵ) 278 (11 000). Compound **8**: colorless oil. Anal. Calcd for $C_{21}H_{28}Si_2$: C, 74.93; H, 8.38. Found: C, 74.87; H, 8.45. LRMS (EI, 70 eV): *m/e* 336 (M$^+$), 263, 248, 186, 159, 131 (100%), 73. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.17 (s, 9H), 0.26 (s, 3H), 0.27 (s, 3H), 1.83 (s, 3H), 7.0−7.8 (m, 10H). ^{13}C NMR (C_6D_6, 22.5 MHz): δ −4.64 (q), −4.55 (q), −0.7 (q), 23.8 (q), 30.7 (s), 85.7 (s), 96.3 (s), 125.3 (s), 125.9 (d), 127.1 (d), 128.0 (d), 128.7 (s), 129.0 (d), 132.2 (d), 144.5 (s). ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −18.3, −4.2. IR (neat): 2224 (C≡C), 1599, 1491, 1247, 833, 797, 754, 690 cm^{-1}. UV (cyclohexane): λ_{max} (ϵ) 273 (10 000).

Scheme 5



is 3.42 Å, which is similar to the van der Waals radius of carbon.[13] The tetramethyleneethane dianion can be formed by combination of the two radical anions **11**.

In conclusion, we have shown that reduction of a cycloallene by sodium produces a radical anion which interacts with the transannular silicon or sp carbon to form a stable allyl anion.

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Supporting Information Available: Figures giving additional views and a crystal packing diagram, text giving X-ray experimental details, and tables of crystal data, positional and thermal parameters, bond distances and angles, and torsion angles for **2** (25 pages). Ordering information is given on any current masthead page.

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(12) Compound **10**: mp >300 °C. Anal. Calcd for $C_{40}H_{50}Si_4$: C, 74.77; H, 7.79. Found: C, 74.87; H, 8.12. LRMS (EI, 70 eV): *m*/*e* 642 (M^+), 73 (100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −0.48 (s, 6H), 0.20 (s, 6H), 0.28 (s, 6H), 0.63 (s, 6H), 1.98 (s, 6H), 6.6−7.8 (m, 10H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −3.4 (q), −3.0 (q), −2.6 (q), 1.0 (q), 32.2 (q), 43.1 (s), 122.9 (d), 125.2 (d), 127.5 (d), 128.2 (d), 128.9 (s), 130.1 (d), 141.3 (s), 142.7 (s), 150.5 (s), 158.2 (s). ^{29}Si NMR ($CDCl_3$, 60 MHz): δ −7.0, 6.1. IR (neat): 2972, 1597, 1493, 1439, 1247 cm^{-1}. UV (cyclohexane): λ_{max} (ϵ) 225 (sh, 34 200), 285 (sh, 5060) nm.

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