

# Lithiation and silylation reactions of 1,4-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl) benzene

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## Abstract

1,4-Bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)benzene forms tri- and tetralithio derivatives which react readily with  $(\text{CH}_3)_3\text{SiCl}$  or  $(\text{CH}_3)_2\text{SiCl}_2$  to form the expected derivatives. Silicon is shown to be weakly coordinated to oxygen in 2,5-bis(trimethylsilyl)-1,4-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)benzene.

**Keywords:** Silicon; Lithium

## 1. Introduction

In 1979, Perozzi and Martin reported that 1,1,1,3,3,3-hexafluoro-2-hydroxy-2-phenylpropane, obtained from Friedel–Crafts condensation of hexafluoroacetone (HFA) with benzene [1] readily lithiates in the ortho position to give lithium 1,1,1,3,3,3-hexafluoro-2-(*o*-lithiophenyl)-2-propoxide [2]. This important result has led to the synthesis of a variety of Group 14–16 derivatives of the ligand, many of which are hypervalent [2,3]. The lithiation of further condensation products of HFA with benzene such as 1,4-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-2-propyl)benzene, **1**, has not been previously reported although it should yield suitable starting materials for the synthesis of additional monomeric and polymeric examples of Groups 14–16 element hypervalent derivatives. To this end we have investigated the lithiation of **1** and the reaction of its tri- and tetralithio derivatives with chlorotrimethylsilane and dichlorodimethylsilane, and we report our results at this time.

## 2. Results and discussion

As shown in Scheme 1, compound **1** reacts with *n*-butyllithium in the presence of TMEDA to give a

mixture of tri- and tetralithiated products which react with chlorotrimethylsilane to yield silylated derivatives, **2** and **3**. Compounds **2** and **3** hydrolyze to form a mixture of 2-trimethylsilyl- and 2,5-bis(trimethylsilyl)-substituted **1** (**4** and **5** respectively). As reported in the earlier literature [2], the TMEDA concentration (70 to 90 mol% TMEDA to butyllithium) does not appear to affect the yield in this reaction; it does, however, affect

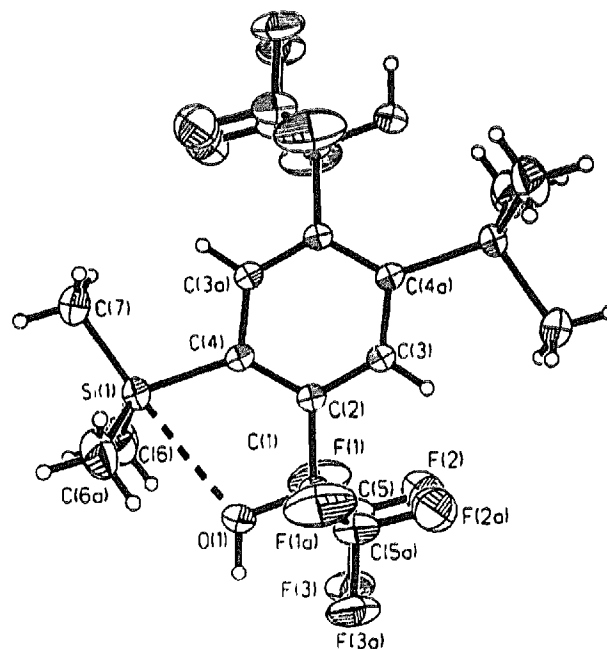
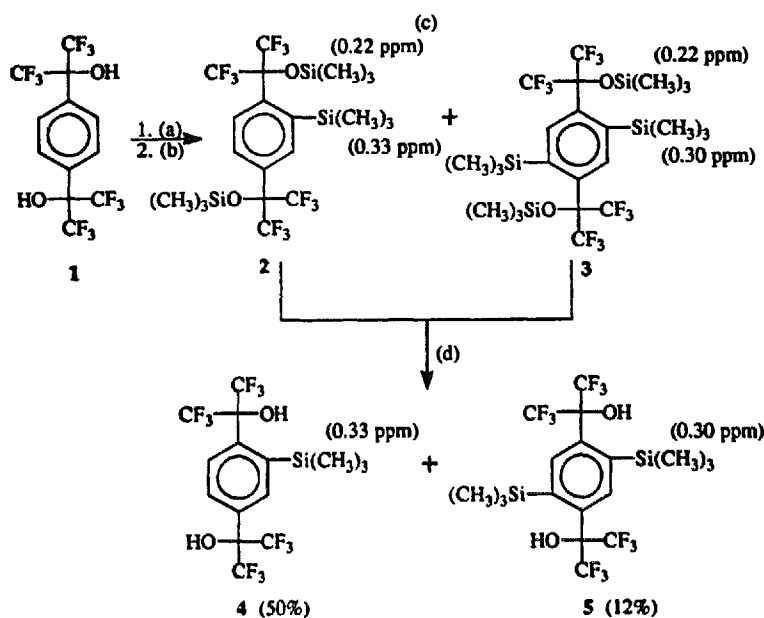


Fig. 1. ORTEP view of compound **5**.

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Scheme 1. (a)  $n\text{-C}_4\text{H}_9\text{Li}$ , TMEDA, THF–hexane (0 °C to 25 °C; 4 h); (b)  $(\text{CH}_3)_3\text{SiCl}$ ; (c)  $^1\text{H NMR}$ ,  $\text{CDCl}_3$ ;  $\delta(\text{ppm})$ ; (d) 55% aq. ethanol, 24 h.

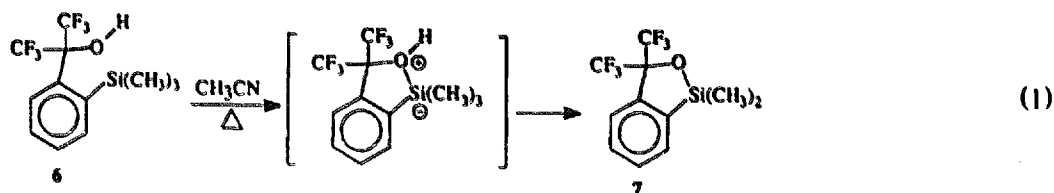
the rate. The hydrolyzed reaction mixture is initially obtained as a viscous, brown oil from which pure **4** and **5** can be isolated chromatographically [4]. Compounds **2** and **3** can also be isolated as a mixture if the reaction is worked up without hydrolysis.

Proton NMR spectroscopy allows ready detection of **2**–**5**, even when present in complex mixtures (Scheme 1). The conversion of **2** and **3** to **4** and **5** is conveniently followed by monitoring the disappearance of the Si–CH<sub>3</sub> resonance at 0.22 ppm as the arylhexafluoro-2-propoxy-silyl bonds are hydrolyzed. The presence of the *o*-trimethylsilyl group slows this reaction noticeably; the 1-(1,1,1,3,3,3-hexafluoro-2-trimethylsilyloxy-2-propyl) group in **2** requires 24 h for complete hydrolysis, whereas the analogous group in the 4-position in compound **2** is hydrolyzed within 1 or 2 h.

The crystal structure of **5** (Fig. 1) [5] shows a silicon-to-oxygen distance, [Si(1)–O(1)], of 2.765 Å, which is

where the intermolecular Si–O distance is 2.721 Å and indicates that the oxygen is weakly coordinated to the silicon atom [7]. There is also distortion toward trigonal bipyramidal geometry in the trimethylsilyl groups (Fig. 1). The C(4)–Si(1)–C(6)/C(6A) bond angles are 113.1(2)° and the C(6)–Si(1)–C(6A) angle is 113.9(3)°; whereas, the C(4)–Si(1)–C(7) bond angle is 106.3(3)° and the C(6)–Si(1)–C(7) angle is 104.8(3)°. These distortions toward trigonal bipyramidal geometry at silicon confirm an interaction between silicon and oxygen in **5**.

The interaction between the hydroxyl group and the silicon atom in **6** was first suggested in the mechanism proposed by Yamamoto et al. for the facile conversion of **6** to **7** in polar aprotic solvents (Eq. (1)) [8]. Their proposed pentacoordinate intermediate (or transition state) in Eq. (1) is consistent with the crystal structure of **5**.

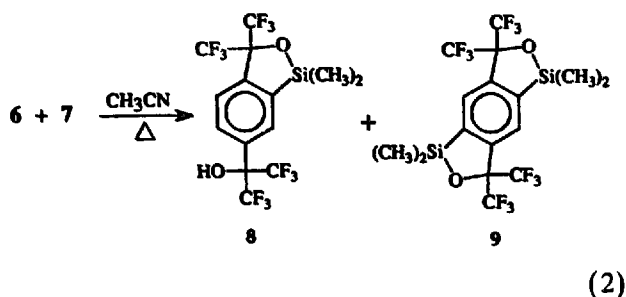


(1)

considerably shorter than the sum of the silicon and oxygen van der Waals radii (3.60 Å) [6]. It is, however, typical of associated compounds such as silyl acetate

We also observe quantitative cyclization of **4** and **5** when heated for 2 or 3 h in the presence of anhydrous acetonitrile (Eq. (2)). Bicyclic **8**, being much less solu-

ble than monocyclic **8**, precipitates from the reaction mixture upon cooling, providing a convenient separation of the two compounds.



Compounds **2** and **3** (see Scheme 1) can also be pyrolyzed at 180 °C (0.2 Torr) to give cyclized products **8** (30%) and **9** (10%) in low yield. Tetramethylsilane is the expected by-product of this ring closure, but it has not yet been isolated.

It is also possible to obtain **8** and **9** by lithiating **1** and treating the mixture of tri- and tetralithio derivatives with dimethyldichlorosilane [9]. The ratio of **8** to **9** is affected by lithiation conditions. If the reaction is started at 0 °C and allowed to warm to room temperature as it stirs, **8** is isolated in 50% yield while **9** is obtained in 11% yield. When the reaction is conducted without external cooling **8** is obtained in 40% yield and **9** in 20% yield. Conditions were not found which would give **8** or **9** exclusively, and the compounds are most efficiently separated by flash chromatography on an alumina column using benzene as the eluant.

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- [4] A solution of **1** (5.00 g, 12.2 mmol) in THF (10 ml) was added dropwise (0 °C, argon atmosphere) to a vigorously stirred mixture of *n*-butyllithium (29.3 ml of 2.5 M hexane solution, 73.2 mmol) and TMEDA (7.65 g, 65.9 mmol). The mixture was allowed to warm to room temperature and stirred for 4 h. Chlorotrimethylsilane (7.95 g, 73.2 mmol) was added; the reaction was stirred for 2 h and then hydrolyzed in aqueous ethanol. The crude product was isolated by ether extraction to give a dark brown oil from which **4** (m.p. 68.3–68.9 °C; yield, 50%); and **5** (m.p. 194.6–194.8 °C; yield, 12%) were isolated by chromatography using benzene over silica. **4**. Anal. Found: C, 37.24; H, 2.93. C<sub>15</sub>H<sub>14</sub>F<sub>12</sub>O<sub>2</sub>Si. Calc.: C, 37.34; H, 2.90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.33 (s, 9H), 3.38 (s, 1H), 3.72 (m, 1H), 7.73 (s, 2H), 8.17 (s, 1H). **5**. Anal. Found: C, 38.65; H, 4.01. C<sub>8</sub>H<sub>22</sub>F<sub>12</sub>O<sub>2</sub>Si<sub>2</sub>. Calc.: C, 38.98; H, 3.97%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.312 (s, 18H), 3.62 (s, 2H), 8.05 (s, 2H). Caution: hexafluoroacetone and some of its derivatives are toxic.
- [5] Crystal data compound **5**: empirical formula C<sub>22</sub>H<sub>28</sub>F<sub>12</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>2</sub> (includes two molecules of CH<sub>3</sub>CN); colorless; monoclinic; size 0.4 × 0.6 × 0.7 mm<sup>3</sup>; *a* = 15.520(5), *b* = 12.1340(10), *c* = 10.1920(10) Å; β = 127.640(0)°; *V* = 1519.8 Å<sup>3</sup>; *Z* = 2; space group, *C*2/*m*; absorption coefficient, 2.12 cm<sup>-1</sup>; diffractometer used, Siemens R3mm/V; radiation Mo Kα (λ = 0.71073 Å); 2θ (3.5 to 43.5°); reflections collected 1187; observed reflections 814 (*F* > 4.0σ(*F*)); system used, Siemens SHELXPL PLUS (PC version); structure solution by direct method; refinement by full-matrix least squares; *R* = 0.0506; *wR* = 0.0787. Bond lengths (Å, see Fig. 1 for atom numbering): Si(1)–C(4), 1.907(5); Si(1)–C(7), 1.859(10); C(1)–C(2), 1.538(6); C(1)–O(1), 1.376(7); C(2)–C(3), 1.370(7); C(3)–C(4A), 1.411(5); C(5)–F(1), 1.319(6); C(5)–F(3), 1.315(4); Si(1)–C(6), 1.848(5); Si(1)–C(6A), 1.848(5); C(1)–C(5), 1.531(7); C(1)–C(5A), 1.531(7); C(2)–C(4), 1.421(9); C(4)–C(3A), 1.411(5); C(5)–F(2), 1.325(7). Bond angles (degrees, see Fig. 1 for atom numbering): C(4)–Si(1)–C(6), 113.1(2); C(6)–Si(1)–C(7), 104.8(3); C(2)–C(1)–C(5), 110.8(2); C(5)–C(1)–O(1), 107.7(3); C(1)–C(2)–C(3), 118.5(6); C(3)–C(2)–C(4), 120.7(4); Si(1)–C(4)–C(2), 131.7(3); C(2)–C(4)–C(3A), 113.1(4); C(1)–C(5)–F(2), 114.3(4); C(1)–C(5)–F(3), 112.6(3); F(2)–C(5)–F(3), 106.5(5); C(4)–Si(1)–C(7), 106.3(3); C(6)–Si(1)–C(6A), 113.9(3); C(2)–C(1)–O(1), 109.2(5); C(5)–C(1)–C(5A), 110.5(6); C(1)–C(2)–C(4), 120.8(4); C(2)–C(3)–C(4A), 126.2(6); Si(1)–C(4)–C(3A), 115.2(5); C(1)–C(5)–F(1), 109.5(5); F(1)–C(5)–F(2), 107.0(4); F(1)–C(5)–F(3), 106.5(3).
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- [9] Compounds **8** (m.p. 131–136 °C; yield 50% at 0 °C, 40% at room temperature) and **9** (sublimes; yield 11% at 0 °C, 20% at room temperature) were prepared exactly as for **4** and **5** from **1** (5.00 g, 12.2 mmol) in THF (10 ml) and dimethyldichlorosilane (4.77 g, 37 mmol) using a TMEDA: *n*-butyllithium mol ratio of 0.7 to 1.0. **8**. Anal. Found: C, 36.08; H, 1.97. C<sub>14</sub>H<sub>10</sub>F<sub>12</sub>O<sub>2</sub>Si. Calc.: C, 36.05; H, 2.15%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.52 (s, 6H), 3.45 (s, 1H), 7.78–8.00 (m, 3H). **9**. Anal. Found: C, 36.87; H, 2.56. C<sub>16</sub>H<sub>14</sub>F<sub>12</sub>O<sub>2</sub>Si<sub>2</sub>. Calc.: C, 36.78; H, 2.68%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.53 (s, 12H), 7.86(s, 2H).