

The Synthesis of the First Spiropentasilane, Octamethylspiropentasilane

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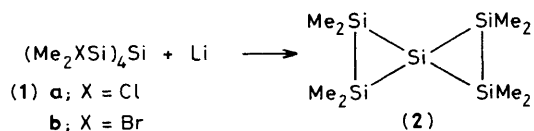
The action of lithium metal on tetrakis(dimethylbromosilyl)silane or tetrakis(dimethylchlorosilyl)silane in tetrahydrofuran produces the first spiropentasilane, a highly strained polysilane that undergoes efficient cleavage reactions with lithium aluminium hydride, methylmagnesium bromide, and phosphorus pentachloride.

Small ring systems containing one or more silicon atoms have attracted considerable attention in the past decade because these highly strained molecules have unusual reaction patterns,¹ possess interesting bonding features,² and are the sources of novel reactive intermediates containing silicon.^{1,3} In this paper we describe the synthesis and some properties of the first spiropentasilane, (2), the most highly strained polysilane yet reported.

In a typical synthesis that is a modification of the route to spiropentane,⁴ 1.6 mmol of (1b)[†] in 10 ml of tetrahydrofuran

(THF) was added to a slurry of 6.5 mmol of lithium powder in 10 ml of THF at -78°C . The reaction mixture was then allowed to warm slowly to room temperature during which time nearly all of the lithium was consumed to give a pale yellow solution.

The reaction can be monitored by ^1H n.m.r. spectroscopy. Upon conversion of (1b) into (2) the proton singlet at δ 0.93 of (1b) was replaced by a new singlet at δ 0.70 which we assign to

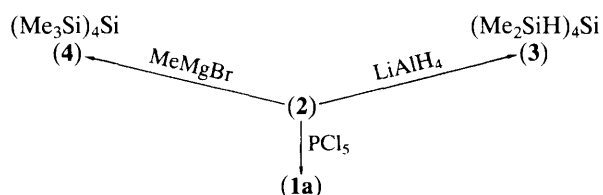


[†] Compound (1b), prepared by bromination of (3)⁶ using $\text{Br}_2\text{-CCl}_4$, is new and has been characterized by elemental analysis, and by mass and n.m.r. spectroscopy.

(2). The ^1H n.m.r. spectrum of the product mixture indicated nearly complete conversion into (2): the signal for (1b) disappeared and the dominant peak became the one at δ 0.70. The reaction was very clean as evidenced by the appearance of only a few low intensity absorptions in the region above δ 0.70. Surprisingly, analysis by ^{13}C n.m.r. spectroscopy was not very helpful in adding to the characterization of (2) since (1a), (1b), and (2) each gave only one peak with essentially the same chemical shift, δ 6.51 in $[\text{}^2\text{H}_8]\text{THF}$.

Solutions of (2) are stable for several days at room temperature if rigorous precautions are taken to exclude oxygen and moisture. However, attempts to isolate (2) from these solutions by preparative gas chromatography, distillation, or low temperature crystallization have so far been unsuccessful.

When the reaction mixture was treated with lithium aluminium hydride a surprisingly clean reaction gave the tetrahydride (3) in 60% yield based on the quantity of (1b) used.⁵ Similarly, treatment with MeMgBr gave tetrakis-(trimethylsilyl)silane (4).⁶



Electrophilic halogenation was most efficient with phosphorus pentachloride. Thus, a solution of (2) prepared from the bromide (1b) gave a 69% yield of the tetrachloride (1a)⁷ when treated with PCl_5 in boiling CCl_4 for 1 h. When refluxed in carbon tetrachloride for 1 h, (2) produced (1a) in only 20% yield.

The stability of (2) is surprising in view of the small groups on silicon. We are now trying to prepare more highly substituted spiropentasilanes in an effort to obtain isolable derivatives that will permit structural studies and more thorough chemical investigations.

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References

- 1 D. Seyferth, D. C. Annarelli, M. L. Shannon, J. Escudie, and D. P. Duncan, *J. Organomet. Chem.*, 1982, **225**, 177.
- 2 M. S. Gordon, *J. Am. Chem. Soc.*, 1980, **102**, 7419; M. S. Gordon, P. Boudjouk, and F. Anwari, *ibid.*, 1983, **105**, 4972.
- 3 C. W. Carlson and R. West, *Organometallics*, 1982, **2**, 1792.
- 4 D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Org. Chem.*, 1958, **23**, 1715.
- 5 H. Gilman, J. M. Holmes, and C. L. Smith, *Chem. Ind. (London)*, 1965, 848.
- 6 H. Gilman and C. L. Smith, *J. Organomet. Chem.*, 1967, **8**, 245.
- 7 H. Sakurai, T. Watanabe, and M. Kumada, *J. Organomet. Chem.*, 1967, **9**, 11.