

References and Notes

- (1) Work performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy.
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- (7) Manuscript in preparation.
- (8) It is important to note that no CIDNP can originate in the radical pair $\text{O}_2\text{CCH}_2\text{-CH}_2\text{CO}_2^-$. Thus, the $\text{-CH}_2\text{CO}_2^-$ radical has undergone polarization prior to dimerization. The CIDNP observed in acetate suggests that the dominant polarization pathways for $\text{-CH}_2\text{CO}_2^-$ involve encounter with e_{aq}^- or D. However, such $\text{-CH}_2\text{CO}_2^-$ polarization pathways fail to explain the high-field enhanced absorption seen in succinate. Related CIDNP studies of chloroacetate radiolysis suggest that an Overhauser mechanism may also contribute (but to a lesser extent) to $\text{-CH}_2\text{CO}_2^-$ radical polarization. This less important Overhauser CIDNP gives enhanced absorption in succinate. (Manuscript in preparation.)
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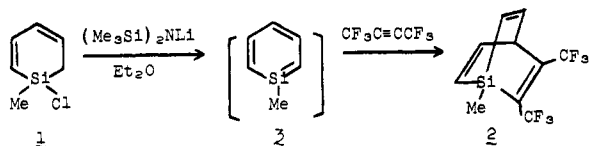
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Unambiguous Generation and Trapping of a Silabenzene

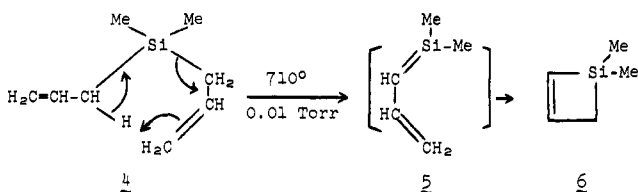
Sir:

Recently we reported the results of a reaction which appeared to involve generation and trapping of a long-awaited silabenzene.¹ Thus, when 1-chloro-1-methyl-1-silacyclohexadiene (**1**) was reacted with *N*-lithiohexamethyldisilazane in the presence of excess perfluoro-2-butyne, silabarralene **2** was obtained in 28% yield. While all of the results of that study



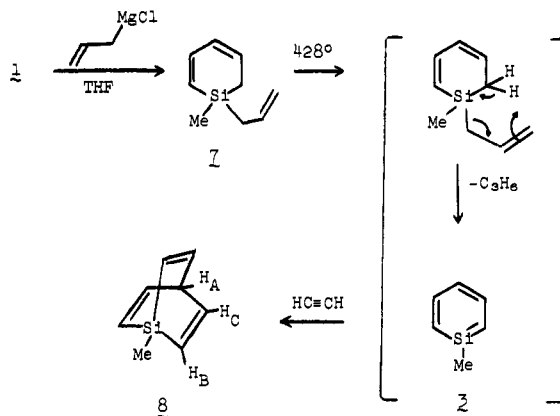
were totally consistent with the intermediacy of 1-methyl-1-silacyclohexa-1,3,5-triene (**3**), we could not totally rule out a mechanism involving carbanionic attack by an initially formed pentadienyl anion followed by intramolecular displacement of chloride. Thus, we have sought a less ambiguous route to silabenzenes and will report here such a route.

The elegant synthesis of silacyclobutenes recently reported by Block² suggested a simple route to silabenzene **3**. Block found that vacuum flow pyrolysis of, for example, diallylsilane **4** produced silete **6** in 41% yield. The reasonable mechanism suggested was a retro-ene reaction of **4** to generate silabuta-



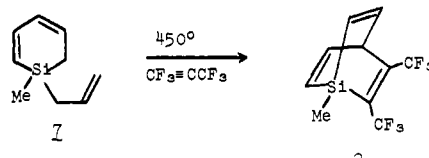
diene **5**, which in turn closes to the silacyclobutene.

Recognizing that an allylsilacyclohexadiene might possibly behave in the same fashion, we prepared 1-methyl-1-allyl-1-silacyclohexa-2,4-diene (**7**) from the reaction of chlorosilane **1**³ and allylmagnesium chloride in THF. Pyrolysis of **7** was conducted in a vertical quartz tube packed with quartz chips heated to 428 °C in a tube furnace. Acetylene (20 mL/min) was used both as reactant and carrier gas to produce a product mixture containing unreacted **7** (48%) and adduct **8**, 1-methyl-1-silabicyclo[2.2.2]octatriene, in 33.6% yield based on reacted **7**.⁴



Adduct **8** was identified from its 100-MHz ¹H NMR spectrum ((DCCl₃) δ 0.81 (s, 3 H, SiMe), 5.15 (q of q, 1 H_A, J_{AB} = 1.6 Hz, J_{AC} = 7 Hz, *hν* at 6.57 collapses to q), 6.57 (d of d, 3 H_B, J_{BC} = 11 Hz, *hν* at 5.15 collapses to d), 7.41 (d of d, 3 H_C, *hν* at 5.15 collapses to d)) and its high resolution mass spectrum which showed a molecular ion peak at *m/e* 134.0547 (15% calcd for C₈H₁₀Si 134.0552) with prominent ions at 119 (100%, M⁺ - CH₃) and 93 (35%, M⁺ - CH₃ - HC=CH).

In a like manner copyrolysis of **7** and perfluoro-2-butyne (20 mL/min) at 450 °C afforded adduct **2** (~20%), which was



identical in all respects with **2** synthesized via dehydrochlorination of **1**.¹

This latter observation not only further demonstrates the utility of this method of silabenzene synthesis, but also strengthens our earlier claim that formation of **2** from the base-induced dehydrochlorination of **1** in the presence of perfluoro-2-butyne is evidence for the production of silabenzene **3** in that reaction.⁵

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References and Notes

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- (2) E. Block and L. K. Revelle, *J. Am. Chem. Soc.*, **100**, 1630 (1978).
- (3) Compound **1** is conveniently prepared from the reaction of methylchlorosilylene and cyclopentadiene.¹ Triene **7** must be purified by GC and the yield, 61.4%, thus represents a minimum.
- (4) This is a calibrated GC yield of **8** which was prepared at 150 °C on a 27-ft, 15% SE-30 on Chromosorb W column. Propene was identified in the product mixture by GC-MS.
- (5) Previous attempts to prepare silabenzene derivatives are reviewed by P. Jutzl, *Angew. Chem., Int. Ed. Engl.*, **14**, 232 (1975).

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