

**Figure 1.** CIDEP spectra from 0.2 M sodium chloroacetate (pH  $\sim$ 13, 2- $\mu$ s delay,  $a_H = 21.2$  G, He): upper, "normal" S-T<sub>0</sub> CIDEP; lower, CIDEP with shift to emission observed when solution contains 0.5 M sodium hypophosphite. (Quartz transient deleted.)

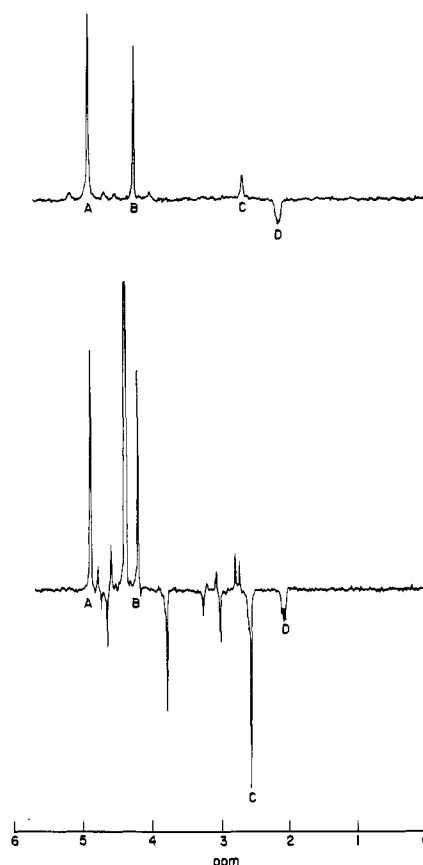
However, the field dependence of CIDNP in succinate, acetate, and other systems<sup>7</sup> implicates an S-T<sub>-1</sub> polarization mechanism in  $e_{aq}^-$  reaction with the phosphorus-centered radicals ( $a_p > 400$  G).

Irrespective of mechanism, for our purposes here it is important that by using such radicals we can prepare  $e_{aq}^-$  in an emissive electron spin state.

**CIDEP in the Acetate Radical.** Our submicrosecond time-resolved EPR studies have shown that, when the hydrated electron reacts with chloroacetate, it transfers its spin population to the resulting radical.<sup>4</sup> (This has also been observed by Verma and Fessenden.<sup>5</sup>) The time-resolved EPR spectrum of the acetate radical, obtained when  $e_{aq}^-$  is not polarized (Figure 1, upper), shows that  $e_{aq}^-$  simply transfers its equalized spin state population to the  $\cdot\text{CH}_2\text{CO}_2^-$  radical and the "normal" S-T<sub>0</sub> CIDEP is observed.<sup>4</sup> The low-field line is in emission, the center line is not polarized, and the high-field line is in enhanced absorption. When  $e_{aq}^-$  is prepared in emission (by generation in solutions containing phosphite, hypophosphite, carbonate, etc),  $\cdot\text{CH}_2\text{CO}_2^-$  CIDEP reflects this emission (Figure 1, lower). Now the CIDEP spectrum shows an overall shift to emission: the low-field emissive line is now more intense than the high-field enhanced absorption line, and the center line is now in emission as well. Clearly  $e_{aq}^-$  reacts with the substrate at least an order of magnitude faster than it relaxes ( $e_{aq}^- T_1 \approx 2-4 \mu\text{s}$ ).<sup>5</sup>

**CIDNP in Succinate.** We have described previously how NMR CIDNP experiments are carried out in radiation chemistry.<sup>6</sup> Briefly, we use a flow system that transfers solution from an irradiation cell in an external magnet (0-8 kG) to the spinning 5-mm tube in the NMR magnet (Bruker WP-80 FT NMR). Radical concentrations in our experiments are such that all chemistry is over in several microseconds and only the polarized products flow into the NMR probe. Our arrangement is well suited for routine variable field (0-8 kG) CIDNP study.

In a typical CIDNP study of acetate radiolysis, at high field we observe succinate in enhanced absorption (Figure 2, upper).<sup>8</sup> In contrast, when  $e_{aq}^-$  is emissively polarized (vide infra), we observe succinate in intense emission at a 3500-G field paralleling that of the X-band EPR field (Figure 2, lower). The transfer of the electron polarization to the nuclear polarization occurs by (dipolar) cross relaxation in the acetate



**Figure 2.** CIDNP spectra from 0.2 M sodium chloroacetate (pH  $\sim$ 13, 3500-G field, He): upper, CIDNP observed when solution contains 0.4 M sodium sulfite; lower, CIDNP observed when solution contains 0.4 M sodium carbonate. Assignments: A, HOD; B, chloroacetate; C, succinate; D, acetate.

radical. As long as the radical lifetime is not longer than the nuclear  $T_1$  in these radicals ( $T_1 \approx 10^{-5}$  s), this applies, and in our experiments the acetate radical half-life is typically in the range of 2-20  $\mu\text{s}$ .

In these experiments (with irradiation fields  $\sim$ 3500 G) nearly optimal conditions exist for polarization transfer from electron to nuclear spins, since electron-nuclear relaxation transition rates are comparable to the bimolecular reaction rate and the electron  $T_1$ .<sup>9</sup>

The Overhauser CIDNP effect has received much attention since it was the basis for the first explanation of the CIDNP phenomenon.<sup>10</sup> Over the years there has been much speculation as to whether Overhauser CIDNP contributes to CIDNP in some systems.<sup>11-13</sup> The studied systems to date involve transfer of "triplet" electron polarization in photolysis. Quinone systems have been studied in detail by Adrian and Wan.<sup>9</sup> Roth and coworkers have studied fluorine-substituted aryl alkyl ketones.<sup>14</sup>

In the pulse radiolysis experiments outlined above we believe to have a most clear-cut example of electron-nuclear polarization transfer. As we have found in all our CIDEP and CIDNP studies of radiation chemistry, the radical pair model is the dominant polarization mechanism. Overhauser CIDNP can be seen only in those products where the usual (RP) polarization routes are weak or nonexistent. Our ability to control both the magnetic field of reaction and the radical concentration makes this an ideal approach for the study of these phenomena. Furthermore, as the acetate system has been examined in the time domain 100 ns to  $\sim$ 50  $\mu\text{s}$  by EPR<sup>3,4</sup> and variable-field flow NMR,<sup>6</sup> no other chemical system has been so thoroughly examined by both CIDEP and CIDNP methods.

## References and Notes

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- (5) N. C. Verma and R. W. Fessenden, *J. Chem. Phys.*, **65**, 2139 (1976).
- (6) A. D. Trifunac and D. J. Nelson, *J. Am. Chem. Soc.*, **99**, 1745 (1977).
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- (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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A. D. Trifunac,\* D. J. Nelson

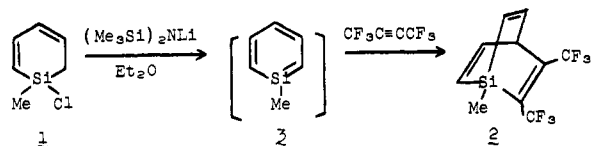
Chemistry Division, Argonne National Laboratory  
Argonne, Illinois 60439

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### Unambiguous Generation and Trapping of a Silabenzene

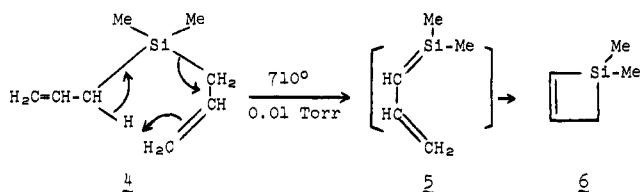
Sir:

Recently we reported the results of a reaction which appeared to involve generation and trapping of a long-awaited silabenzene.<sup>1</sup> 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



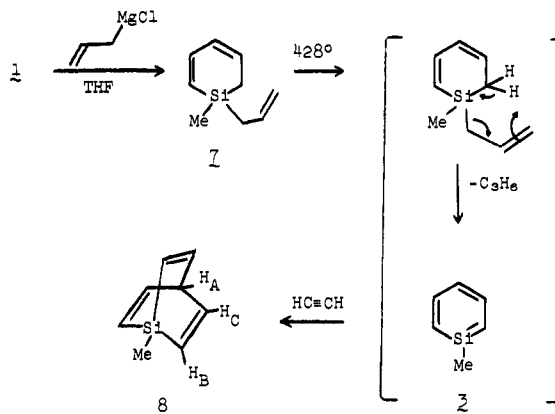
were totally consistent with the intermediacy of 1-methyl-1-silacyclohexa-1,3,5-triene (**3**), we could not totally rule out a mechanism involving carbanionic attack by an initially formed pentadienyl anion followed by intramolecular displacement of chloride. Thus, we have sought a less ambiguous route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

The elegant synthesis of silacyclobutenes recently reported by Block<sup>2</sup> 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-



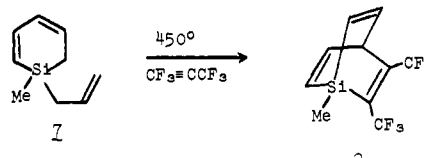
diene **5**, which in turn closes to the silacyclobutene.

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**<sup>3</sup> and allylmagnesium chloride in THF. Pyrolysis of **7** was conducted in a vertical quartz tube packed with quartz chips heated to  $428^\circ\text{C}$  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**.<sup>4</sup>



Adduct **8** was identified from its 100-MHz  $^1\text{H}$  NMR spectrum ( $(\text{DCCl}_3)$   $\delta$  0.81 (s, 3 H, SiMe), 5.15 (q of q, 1  $\text{H}_A$ ,  $J_{AB} = 1.6\text{ Hz}$ ,  $J_{AC} = 7\text{ Hz}$ ,  $h\nu$  at 6.57 collapses to q), 6.57 (d of d, 3  $\text{H}_B$ ,  $J_{BC} = 11\text{ Hz}$ ,  $h\nu$  at 5.15 collapses to d), 7.41 (d of d, 3  $\text{H}_C$ ,  $h\nu$  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  $\text{C}_8\text{H}_{10}\text{Si}$  134.0552) with prominent ions at 119 (100%,  $\text{M}^+ - \text{CH}_3$ ) and 93 (35%,  $\text{M}^+ - \text{CH}_3 - \text{HC}\equiv\text{CH}$ ).

In a like manner copyrolysis of **7** and perfluoro-2-butyne (20 mL/min) at  $450^\circ\text{C}$  afforded adduct **2** (~20%), which was



identical in all respects with **2** synthesized via dehydrochlorination of **1**.<sup>1</sup>

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.<sup>5</sup>

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### References and Notes

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- (3) Compound **1** is conveniently prepared from the reaction of methylchlorosilane and cyclopentadiene.<sup>1</sup> 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  $150^\circ\text{C}$  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. Eng.*, **14**, 232 (1975).

Thomas J. Barton,\* Gary T. Burns  
Gilman Hall, Department of Chemistry  
Iowa State University, Ames, Iowa 50011

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