CHEMISTRY LETTERS, pp. 771-772, 1982.

GENERATION, CHARACTERIZATION AND QUENCHING OF THE DIANION OF TETRAKIS(TRIMETHYLSILYL)ETHYLENE[1)]

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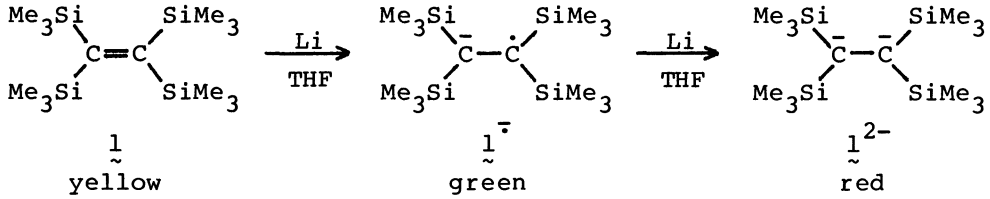
Reduction of tetrakis(trimethylsilyl)ethylene with excess lithium gave a stable dianion, the first dianion of nonconjugated olefin. NMR characteristics as well as quenching experiments are described.

Recently we have prepared a number of tetrasilylated ethylenes which show rather unusual physical and chemical properties.[2-4)] In this paper we report the formation of a dianion from tetrakis(trimethylsilyl)ethylene (1). To our knowledge, this is the first observation of a stable dianion of mono-olefin without π-conjugating group(s).

Reduction of 1 with excess lithium metal in THF at ambient temperature gives at first a dark green solution of the anion radical of 1.[2)] A strong ESR signal[2)] and a broad electronic absorption band with λ_{max} at 288.5 nm are characteristic to the anion radical. Further reduction with excess lithium, however, leads to the formation of a red solution of the dianion, 1^{2-}. Reduction of 1 to 1^{2-} is completed within a period of a few hours, which has been evidenced by the fact that the resulting solution shows sharp new NMR signals but no signal of 1. The electronic absorption spectrum of 1^{2-} has a very broad band with a peak at about 270 nm and its train extends beyond 500 nm.



The ^{13}C and ^{29}Si NMR spectra of 1^{2-} show upfield chemical shift changes at the electron rich atoms compared to the precursor (Table 1). This upfield shift change is expected since similar ^{13}C chemical shift changes ($\Delta\delta$) have been observed for dianions of conjugated hydrocarbons such as 1,4-diphenylbutadiene, stilbene and tetraphenylethylene.[5)] The average $\Delta\delta$[6)] for these dianions are in a range of -273 ± 3 ppm which is fairly constant but smaller than the predicted change in the magnitude of 320 ppm for the addition or removal of two electrons from the precursors.[5)]

O'Brien and Breeden have recently investigated dianions of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (2) and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-

Table 1 ^{13}C and ^{29}Si Chemical Shifts of Tetrakis(trimethylsilyl)ethylene and Its Dianion (1^{2-})

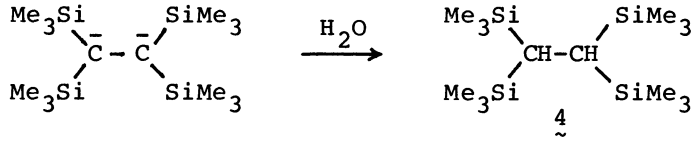
Compound	Solvent	^{13}C (δ ppm)		^{29}Si (δ ppm)
		SiMe	C(vinyl)	
1	$CDCl_3$	4.2	195.3	- 8.63
1^{2-}	THF	7.0	155.3	-17.27

silacyclopentadiene (3) which show somewhat a smaller upfield shift change than the average for hydrocarbon dianions: Δδ of 2^{2-} and 3^{2-} are -247.4 and -222.0 ppm, respectively.[5] They have qualitatively ascribed this decreased shielding to the silicon's ability to delocalize some of the negative charge, although no ^{29}Si NMR data has been reported.

The Δδ value of the dianion of 1 is -80 ppm. This is far smaller than Δδ value of 2^{2-} and 3^{2-} and must be partly due to the ability of four silicon atoms to delocalize the electron density. However, the ^{29}Si chemical shift change from 1 to 1^{2-} (-8.64×4 ppm) is not as great as expected for electron rich silicon.

The double bond of 1 is twisted by 29.6° (X-ray, at -70°C)[4] even in the ground state to escape steric overcrowding due to four bulky trimethylsilyl groups. The dianion 1^{2-} may take a larger torsion angle almost to 90°. Therefore, the situation of 1^{2-} is quite different from cases of hydrocarbon dianions, 2^{2-} and 3^{2-}, where a planar conjugated system is kept before and after reduction.

Aqueous quenching of a red solution of 1^{2-} afforded 1,1,2,2-tetrakis(trimethylsilyl)ethane (4)[7] in 21% yield together with 1% of recovered 1 and a small amount of unidentified colorless oily materials.



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Quenching of 1^{2-} with methanol also gave 4 in 12% yield, but no expected substitution product was obtained by quenching with trimethylchlorosilane, methyl iodide, palladium dichloride, and carbon dioxide. In all cases, a small amount of 4 was obtained. Apparently, steric overcrowding of 1^{2-} hindered further substitution by an electrophile other than proton.

References

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(Received April 2, 1982)