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PRELIMINARY NOTE

Organometallic radicals

II. 1,1-Dimethyl-2,5-diphenyl- and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene radical anions and dianions*

Recent interest in silacyclopentadiene chemistry[1] has led to a study of the reaction of certain substituted silacyclopentadienes with alkali metals. The course of this reaction has been followed by electron spin resonance and visible spectrophotometry. Evidence for the preparation of the anion radicals and dianions is presented in this paper.

1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene[1a] is a bright yellow-green solid. In dimethoxyethane (DME) this compound has an absorption maximum at 374 $m\mu$ (A in Fig. 1). With sodium or potassium, reduction to the radical anion occurs easily as detected by electron spin resonance (ESR). A new peak appears at 622 $m\mu$ simultaneously with the ESR signal. Upon further reduction the intensity of the 374 $m\mu$ peak decreases while the intensities of the 622 $m\mu$ peak and the ESR signal increase (B, C, and D in Fig. 1). However, extended reaction with potassium leads to a *decrease* in the ESR signal, a decrease in the 622 $m\mu$ peak and the formation of a new absorption maximum at 530 $m\mu$. Eventually no ESR signal is detected (G and H in Fig. 1).

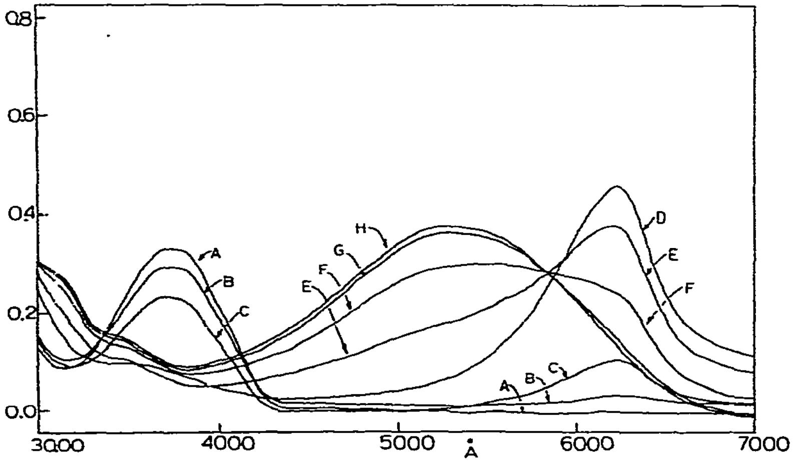

Fig. 1. Potassium reduction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene in 1,2-dimethoxyethane. Curves A through H were obtained by progressively exposing the solution to a potassium mirror in a glass cell attached to a 0.2 mm pyrex optical cell. Solutions were prepared under high vacuum conditions and run in a Cary 14 Spectrophotometer. The reduction steps are very rapid. All the traces shown are obtained within a few minutes of reaction time.

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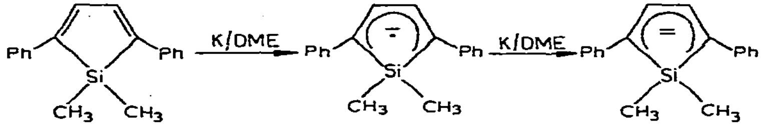
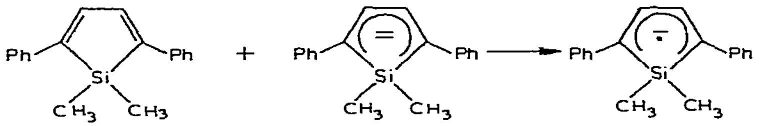
The sequence of observations are in accord with the formation of the diphenylsilacyclopentadiene radical anion which is further reduced to the dianion:



(1)

The 622 mμ absorption is attributed to the radical anion and the 530 mμ absorption to the dianion. Good resolution of the ESR spectrum (over 100 peaks) is only obtained after extensive reduction has taken place. Rapid electron transfer with the parent organosilane probably occurs initially but at later stages of the reaction, electron transfer with the dianion is slower and line broadening less significant.

Solutions of the dianion mixed with the parent organosilane produce the radical anion:



(2)

Whether this radical anion disproportionates (reverse of reaction (2)) is not known at this time but inspection of the absorption spectra in Fig. 1 suggests that this reaction is not significant.

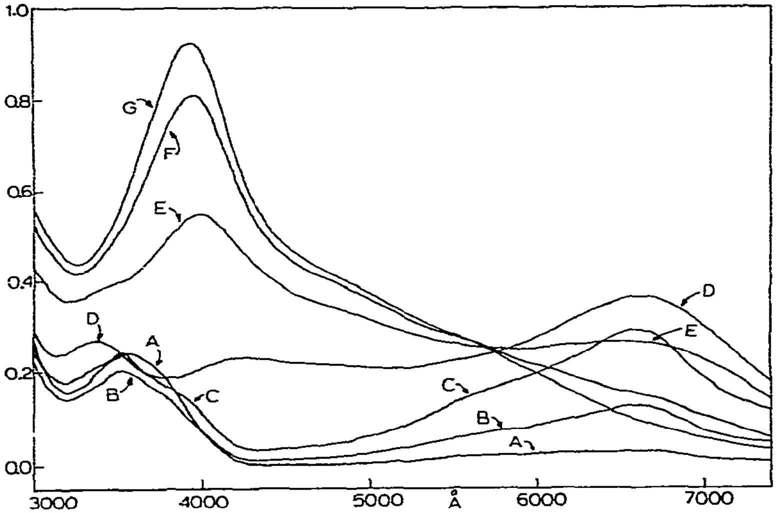


Fig. 2. Potassium reduction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene in 1,2-dimethoxyethane. B and C contain appreciable amounts of free radicals.

Similar observations were made with 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene^{1a}. Potassium reduction provides absorption maxima at 570 and 660 mμ (Fig. 2) and a well-resolved ESR spectrum (approximately 60 lines). However, on further reduction these peaks remain strong while the ESR signal vanishes entirely (Curve D in Fig. 2). Clearly the radical anion and dianion have closely overlapping absorption bonds. Further exposure to potassium for prolonged periods of time generates a very strong new absorption at 393 mμ which appears to result from conver-

tion of the dianion to a new species. Only a trace of radical is detected at this time. A possible cleavage product might be a 1,2,3,4-tetraphenylbutadiene dianion derivative but the parent dianion has an absorption maximum at 435 mμ in tetrahydrofuran (lithium gegenion)^2.

The silacyclopentadiene radicals described here are the smallest organosilane ring systems studied to date*. Efforts are in progress to solve the very complex ESR spectra and fit the coupling constants to MO calculations. This will provide good heteroatom parameters for the construction of a molecular orbital picture for silacyclopentadienes and the anions. The dianions are particularly interesting since they contain 6 π-electrons in a five-membered ring. Preliminary calculations using coulomb and overlap integrals suitable for carbon–silicon bonds in other cyclic organosilane radical anions give resonance stabilization energies of 1.8 and 3.0 β for the radical anion and dianion.**

Further studies are in progress.

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1 (a) W. H. ATWELL, D. R. WEYENBERG AND H. GILMAN, *J. Org. Chem.*, 32 (1967) 885; (b) K. RÜHLMANN, *Z. Chem.*, 5 (1965) 354.
2 R. WAACK AND M. A. DORAN, *J. Organometal. Chem.*, 3 (1965) 92.
3 M. D. CURTIS AND A. L. ALLRED, *J. Am. Chem. Soc.*, 87 (1965) 2554.

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* Certain dibenzasilole and 5,10-disilanthrene radical anion derivatives have also been investigated. These results will be described elsewhere.

** $n = -1.2$ and $k = 0.4$, see ref. 3.

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