TABLE I

VARIATION OF TOTAL POLARIZATION ($P_{2\infty}$) AND DIPOLE MOMENT (μ) WITH TEMPERATURE[a]

T, °K.	$P_{2\infty}$	μ (D)
291.16	60.8	1.26
298.16	61.4	1.28
311.14	61.7	1.32
323.76	59.7	1.31
468.2	52.8	1.39[b]
490.3	53.6	1.44[b]

[a] The experimental error is about 1 cc. in $P_{2\infty}$, or 0.02 D. Atomic polarization is neglected throughout. [b] These measurements were made by Rogers and Cannon (ref. 3).

The infrared spectra of the solid and molten dione were determined from 2–15 μ. No bands appeared from the liquid which were not shown by the solid, although the relative areas of certain bands changed slightly upon melting.

The Raman spectrum of the solid compound consisted of seven bands between 726 and 1500 cm.$^{-1}$. There were 24 infrared bands (Nujol mull) in this region, and there was a coincidence for each Raman band. Such a high degree of coincidence is inconsistent with I.

The conclusion drawn is that 1,4-cyclohexanedione exists predominantly in the flexible form near room temperature under all conditions studied in the present work (solid, liquid and solution in inert solvents), and also in the gas phase at higher temperatures. This is the first reported example of a molecule which exists preferentially in the boat form, not because of steric constraints imposed by substituents,[9] but because of the nature of the ring itself.

Acknowledgments.—The authors are indebted to Professor R. C. Taylor, University of Michigan, for determining the Raman spectrum, and for helpful conversation regarding it, and also wish to thank Professor M. T. Rogers, Michigan State University, for a copy of his manuscript prior to publication.

[9] R. D. Stolow and C. B. Boyce, *J. Am. Chem. Soc.*, **83**, 3722 (1961); and references therein.

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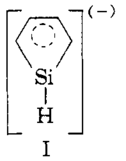
RECEIVED SEPTEMBER 29, 1961

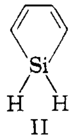
THE FIRST EXAMPLE OF AN AROMATIC SILICON SYSTEM

Sir:

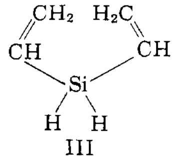
We wish to report the synthesis and characterization of the anion of silacyclopentadiene (I). This constitutes the first example of an aromatic system containing the silicon atom.



I



II



III

Reduction of 1,1-dichlorosilacyclopentadiene[1] with lithium aluminum hydride in dimethylcarbitol, resulted in a 60% yield of silacyclopentadiene (II); b.p. 60–62°; n^{25}_{D} 1.4265; $\lambda^{\text{ether}}_{\max}$ 232 mμ; log $\epsilon_{\max}$ 3.8.

Anal. Calcd. for C_4H_6Si: C, 58.4; H, 7.35. Found: C, 58.27; H, 7.61.

Compound II formed an adduct with hexachlorocyclopentadiene which melted at 35–36°.

Anal. Calcd. for $C_9H_6Cl_6Si$: C, 30.45; H, 1.70; Cl, 60.00. Found: C, 30.22; H, 1.84; Cl, 60.31.

Conversion of II to the anion I was accomplished with potassium sand in tetrahydrofuran, a solvent in which the product is soluble and colored. The structure of I is indicated by the n.m.r. spectral data: (1) 1,1-dichlorosilacyclopentadiene with a doublet C-H peak (relative areas 1:1) at 2.48τ; (2) silacyclopentadiene (II) with doublet C-H peaks at 2.96τ and Si–H peak at 4.12τ (relative areas 1:1:1); (3) anion I in tetrahydrofuran with C–H peaks at 2.70 and 2.90τ and an Si–H peak at 3.95τ (relative areas 1:1:0.5). There was a noteworthy absence of extraneous peaks.

Treatment of I with excess bromobenzene (after removal of any remaining potassium metal by amalgamation[2]) yielded a mixture of 1-phenylsilacyclopentadiene and 1,1-diphenylsilacyclopentadiene.[1] Identification of these two products was achieved unequivocally by hydrogenating them catalytically to 1-phenylsilacyclopentane and 1,1-diphenylsilacyclopentane, respectively. The latter two compounds were identical in every respect (*e.g.*, infrared and retention time by vapor phase chromatography) to authentic samples prepared by standard routes.

The reaction of II with potassium proceeded smoothly in non-polar solvents such as benzene or octane, in which I was essentially insoluble and much less reactive toward bromobenzene.

It is striking that under identical conditions divinylsilane (III), which is the open-chain analog of II, is essentially unaffected by potassium sand in benzene or tetrahydrofuran. This would indicate that substantial resonance stabilization of the anion is a prerequisite for metalation on the silicon atom.

It is of interest that the absorption spectrum of I and that of potassium cyclopentadienide in tetrahydrofuran are very similar, implying similar orbital energies. Indeed an LCAO-MO calculation, including silicon d-orbital participation, suggests considerable resonance stabilization.

The foregoing work clearly implies that the silicon atom might be incorporated successfully into an aromatic six-membered ring (*e.g.*, silabenzene) and/or a seven-membered system (*e.g.*, silatropylium cation). Experiments designed to test these possibilities are presently under way in our laboratory.

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[1] R. A. Benkeser, R. F. Grossman and G. M. Stanton, *J. Am. Chem. Soc.*, **83**, 3716 (1961).

[2] H. Gilman and co-workers, *ibid.*, **74**, 561 (1952).