

A Novel Organosilicon Cyclophane and its Radical Anion

By FRED WUDL,* ROBERT D. ALLENDOERFER, J. DEMIRGIAN, and J. M. ROBBINS

(Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214)

Summary Dodecamethyldioxa[1,1]-di-*p*-disilincyclophane was prepared and reduced to its radical anion which was shown to be fully delocalized (*via* transannular interactions); delocalization involved the Si-O-Si moiety only to a very small extent.

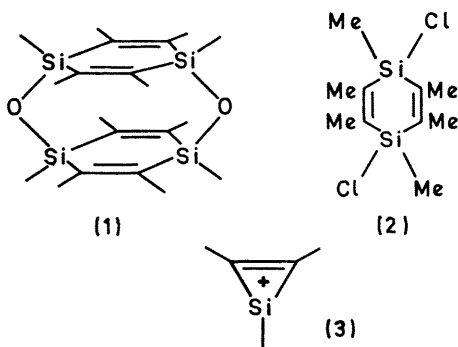
We report the isolation, and evidence corroborating the structure determination, of a [1,1]paracyclophane analogue (1).

of the crystalline compound, produced in 1–5% yield, agree well with structure (1). Although this was an accidental synthesis, we succeeded in the preparation of (1) by an independent route thus obtaining additional proof of structure. Reaction of equimolar amounts of 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene² and 1,4-dihydroxyhexamethyl-1,4-disilacyclohexa-2,5-diene² in the presence of triethylamine in very dilute, dry tetrahydrofuran solution, afforded (1) plus polymer.

Compound (1) crystallizes from a dilute ether solution in perfect hexagonal prisms, is thermally stable, and sublimates near 268°. Its thermal stability allows purification *via* g.l.c. (60 × 0.6 cm column SE-30 on silanized Chromosorb W 30–60 mesh; injection 300°; column, 200°; detector, 300°).

The presence of a prominent parent peak in the mass spectrum of (1) (*m/e* 420, 100% relative intensity) establishes the molecular weight of the substance and is indicative of its stability towards electron bombardment. The most efficient fragmentation process is loss of a methyl group (75% rel. intensity) presumably from silicon, which is not an unexpected result.⁴ An exact mass measurement of the parent peak and consideration of the silicon and carbon isotope peaks established the empirical formula (C₂₀H₃₆O₂-Si₄) to within 2 p.p.m. Exact mass measurement of an *m/e* 97 peak (14% rel. intensity) revealed that it was due to [C₈H₉Si]⁺. This corresponds to a silirene structure (3).

The n.m.r. spectrum of (1) (CS₂ solvent, Me₄Si int. standard) shows only two single lines in a ratio of 2:1 at δ1.7 and 0.15 p.p.m., respectively. The i.r. spectrum



In connection with other work we had the occasion to prepare a 1,4-dichlorohexamethyl-1,4-disilacyclohexa-2,5-diene (2) *via* standard procedures.^{1,2} Treatment of (2) with anhydrous hydrazine³ afforded polymers plus a crystalline solid. The n.m.r., i.r., mass, and e.s.r. spectra (*vide infra*)

revealed the expected absorptions at 2950 (C-H), 1250 (Si-CH₃), 1012 (Si-O),⁵ and 850 (Si-CH₃) cm⁻¹. The u.v. spectrum showed λ_{\max} (end-absorption) at 200 nm and a shoulder at 220 nm.

Additional confirmation for the structure of (1) was obtained from the e.s.r. spectrum of its radical anion. A green radical anion was obtained by reduction of (1) with potassium in 1,2-dimethoxyethane at -80°. The radical anion was stable for several hours at -80° but decayed rapidly when warmed to room temperature. The experimental e.s.r. spectrum is practically superimposable upon that computed with the simulation program SESRS⁶ (Line width 4.6 gauss; $a_{\text{CMe}}^{\text{H}} = 2.5$, $a_{\text{SiMe}}^{\text{H}} = 1.25$ gauss; g value = 2.00169.) The spectrum is well reproduced by

assuming the ratio $a_{\text{CMe}}^{\text{H}}/a_{\text{SiMe}}^{\text{H}}$ is 2.0 except for the slight alternation in peak heights. This might arise from small deviations of the coupling constant ratio from 2 or from an alternating line-width effect⁷ caused by time dependent motions of the cation.

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