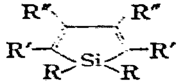
The preparation of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene

To date only three silacyclopentadiene derivatives have been prepared and characterized. 1,1,2,3,4,5-Hexaphenyl-1-silacyclopentadiene[1] (I) and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene[2] (II) have been prepared by reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene with the appropriate dichlorosilane. 1,1-Dimethyl-1-silacyclopentadiene[3] (III) was obtained by the high temperature catalytic dehydrogenation of 1,1-dimethyl-1-silacyclopentane.



(I), $R = R' = R'' = Ph$
(II), $R = Me$, $R' = R'' = Ph$
(III), $R = Me$, $R' = R'' = H$
(IV), $R = Me$, $R' = Ph$, $R'' = H$

We have previously reported that Diels-Alder reactions of (I)[4] and (II)[2] (with acetylenic dienophiles) provide access to the unusual and highly reactive 7-silanorbornadiene compounds. These latter bicyclic compounds are especially important in view of their use as possible precursors to "divalent silicon" (silene) species[2,4,5]. A study of the preparation and properties of various silacyclopentadienes was important for an extension of the above[2,4] studies concerned with polymers.

We are now reporting the preparation of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (IV). The reaction of styrene, dichlorodimethylsilane, and lithium has been reported[6] to proceed readily in tetrahydrofuran to give 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (V). In our hands this reaction also gave (V) as the major product (45 %), b.p. 139.5–140°/0.2 mm (Todd column), n_D^{20} 1.5781 (lit.[6b] 136–137°/0.2 mm, n_D^{20} 1.5768)[*]. G. p. c. analysis (Dow Corning silicone gum rubber column SE 30 at 290°) gave a single peak. However, the NMR spectrum of (V) (CCl_4, relative to cyclohexane standard) shows the presence of three different types of silicon-methyl groups with bands centered at 9.79, 10.13, and 10.64 τ in a 1:3:1 ratio, respectively. This spectrum is compatible with a *cis–trans* mixture of (V), and from peak intensities we estimate a *trans/cis* ratio of 1.5.

Treatment of the *cis–trans* mixture of (V) with two equivalents of *N*-bromosuccinimide gave a mixture of apparently isomeric 2,5-dibromo-1,1-dimethyl-2,5-diphenyl-1-silacyclopentanes (VI), m.p. 90–100° decomp. (88 %)[**]. Refluxing the mixture (VI) in the presence of potassium acetate using acetonitrile as solvent gave the silacyclopentadiene (IV) (65 %) (Found: Si, 10.82, 10.75. $C_{18}H_{18}Si$ calcd.: Si, 10.70 %.)

Compound (IV) is a bright yellow-green solid, m.p. 132–133°. This compound exhibits a brilliant blue fluorescence in ultraviolet light in the solid state and shows the following ultraviolet absorption maxima (cyclohexane) in mμ (log ε): 370 (4.315), 230 (4.179)[***].

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[*] The workers in ref. 6b did not determine the position of the phenyl substituents in (V). For a reported dehydrogenation of this 1,1-dimethyl-*x*,*x'*-diphenyl-1-silacyclopentane see ref. 3b.

[**] This material was not isolated in an analytically pure state, but was utilized immediately in subsequent reactions.

[***] These properties are to be compared with those reported[2] for 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (II): 357 (3.999), 247 (4.413).

The NMR spectrum of (IV) (CCl_4) shows, in addition to the aromatic multiplet, a sharp silicon-methyl singlet at 9.52 τ. The aromatic (olefinic proton included under this area)/aliphatic proton ratio was 2.01 (calcd. 2.00). The NMR spectrum (CCl_4) of the previously reported 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (II) also contains a silicon-methyl singlet at 9.52 τ. In this latter case the aromatic/aliphatic proton ratio was 3.20 (calcd. 3.33).

Complete details of this work, including the preparation and properties of other silacyclopentadienes will be reported later.

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