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PHOTOCHEMISTRY OF ORGANOSILICON COMPOUNDS I. PHOTODIMERIZATION OF 1, 1-DIMETHYL-2, 5-DIPHENYL-1-SILACYCLOPENTADIENE

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It has been reported that irradiation of cyclopentadiene in ethanol resulted in an intramolecular [2 + 2] cycloaddition to give [2, 1, 0] bicyclopentene (1), and that on sensitized irradiation three dimers, i. e. two [4 + 2] and one [2 + 2] dimers, are obtained in approximately equal amounts (2). Photochemical behaviors of cyclopentadiene analogues, five membered heterocyclic compounds, are reported by several investigators and it has been disclosed that the course of the reaction depends on properties of elements and substituents involved in the ring (3).

In connection with our current interest in the chemistry of silylene (4), photolyses of several silicon-containing heterocyclic compounds were examined. Although, one of the silicon analogue, 1, 1-dimethyl-2, 3, 4, 5-tetraphenyl-1-silacyclopentadiene, is reported to be photochemically inactive (5), a similar compound, 1, 1-dimethyl-2, 5-diphenyl-1-silacyclopentadiene (I), is now found to give a dimer (IIa) readily on irradiation with a high-pressure mercury arc lamp in tetrahydrofuran. On the other hand, irradiation in ethanol or in benzene yielded other two dimers (IIb and IIc), as minor products along with IIa. The structure determination and chemical and physical properties of these dimers are reported in this communication (6, 7).

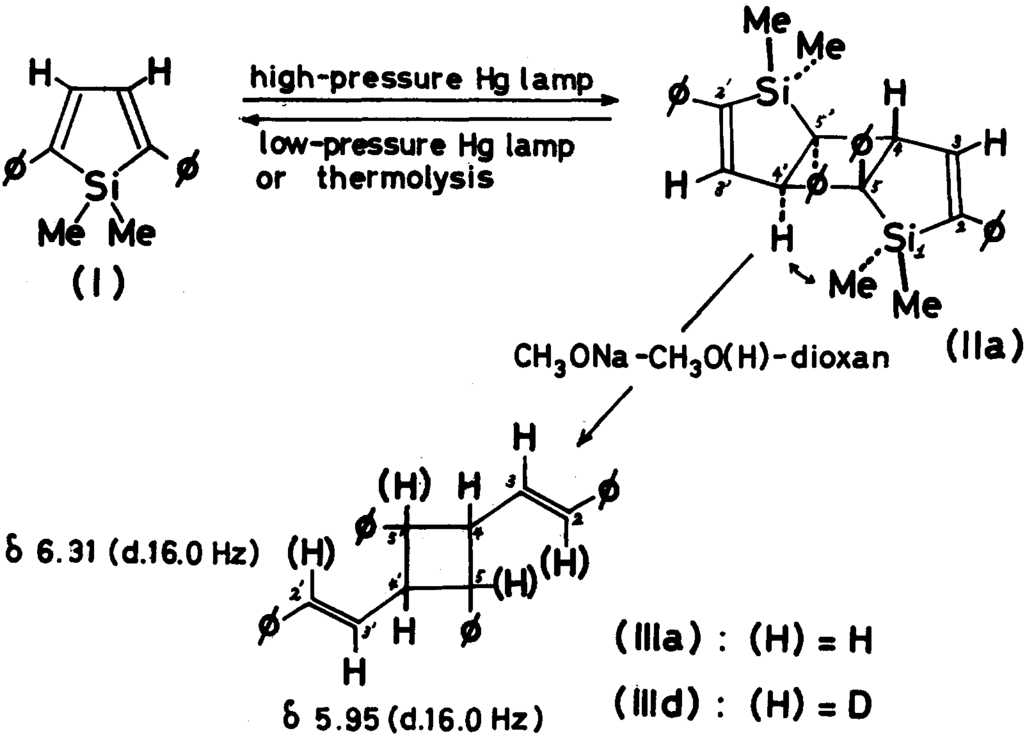
Irradiation of I in THF (0. 01 M) with a 450w high-pressure mercury arc lamp, under nitrogen atomosphere using a Pyrex filter for ca. 2 hrs. afforded a dimer (IIa) almost quantitatively; IIa, mp. 183-4°, $C_{36}H_{36}Si_2$ [MW. 524, obs. 535 (vapor pressure osmometer)], $\lambda_{max}^{n\text{-}hexane}$ 273. 5 nm (ε 21, 300), 262 nm (ε 17, 700).

Treatment of IIa with sodium methoxide in methanol-dioxane (5 : 2) under reflux for 36 hrs. gave a desilylation product (IIIa) in ca. 70% , which was separated by tlc; mp. 85-7°, $C_{32}H_{28}$ m/e 412, nmr (δ, $CDCl_3$), 5. 95 (d. J= 16. 0 Hz, H-3), 6. 31 (d. J= 16. 0 Hz, H-2), 3. 85 (m. H-4, H-5), 7. 20 - 6. 90 (m. Ar-H). Inspection of the nmr spectra shows clearly that the stereochemistry of the double bond was retained in this reaction. Furthermore, the protons at 2 and 5 positions (see Scheme) were deuterated by desilylation in methanol-O-d.

This suggests that a vinyl and a benzyl carbanion may be involved in the desilylation process with retention of the configuration. The thermolysis of IIa at 310° gave quantitatively I, which was identified by comparisons of nmr spectra and behaviors on tlc with those of the authentic sample. The calorimetric measurement of IIa showed a sharp endothermic transition at 197°C showing that the thermal conversion occured at this temperature.

Irradiation of IIa in tetrahydrofuran (0.004M) with a 160w low-pressure mercury arc lamp under nitrogen atomosphere for 2 hrs. gave I nearly quantitatively (8).

Scheme



The nmr signals of IIa (see Table) and IIIa require their structures to be symmetric and the presence of a vinyl and an allyl proton signals in IIa, *i. e.*, H-3 and H-4, allows only the [2 + 2] structure for the photodimer (IIa), which is compatible with the results on its thermolysis. In the mass spectrum of IIIa, no noticeable fragment due to diphenylacetylene or due to one come from the removal of diphenylacetylene from the molecular ion was observed. This fact indicates the *anti*-structure for IIa, since in the case of the *syn*-structure, these fragments must be significant.

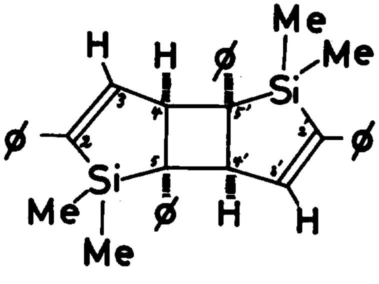
The structure of IIa is further substantiated by the NOE measurements. While irradiation of the methyl signal at -0.28 ppm did not affect the signal due to H-4, irradiation of the other methyl signal at 0.38 ppm caused an increase (ca. 6%) in the integrated intensity of the H-4 signal. This shows C_5-Si bond and H-4 and/or H-4' to be cis (9). The nmr spectrum of IIa requires ring junctions to be either both cis or both trans, and the later can be eliminated from considerations of a molecular model. This leads to the conclusion that IIa is the anti-trans dimer.

When I was illuminated with a high-pressure mercury arc lamp in ethanol or in benzene, two other dimers (IIb, mp. $137-141^{\circ}$ and IIc, mp. $162-165^{\circ}$), were isolated from reaction mixtures by tlc together with IIa. The nmr signals of these two dimers are quite similar to those of IIa as summerized in the Table.

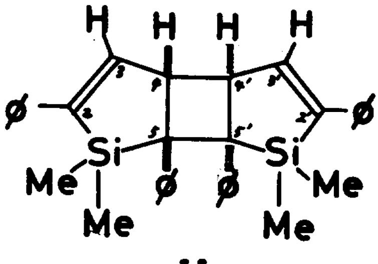
Table. Nmr Spectra of Photodimers (δ)

	Me_1	$Me_{1'}$	H - 3	H - 4
IIa	-0.28	0.38	7.12 (d. 3.6 Hz)	4.34 (d. 3.6 Hz)
IIb	-0.39	0.46	7.40 (d. 3.6 Hz)	4.26 (d. 3.6 Hz)
IIc	-0.27	0.63	6.89 (m.)	4.37 (m.)

Spectra were taken at 100 MHz in $CDCl_3$ solution containing a trace of acetone for field-frequency lock. The δ values of H-3 were obtained by spin decoupling of H-4 signals.



IIb



IIc

However, in contrast to the case of IIa, irradiation of the methyl signal of IIb at 0.46 ppm, not at -0.39 ppm, caused an increase in the integrated intensity of the H-3 signal. This requires IIb to be an anti-cis structure. Comparisons of patterns of the signals due to H-4 and aromatic protons in these dimers indicate a syn-structure for IIc and consideration of the stereochemistry favors a syn-anti structure for IIc.

The facile photodimerization of I is quite unique among cyclopentadiene anologues. Further work is in progress on the photochemistry of silicon-containing compounds and will be reported at a later date.

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6. When we had finished the most part of the work, we became aware of brief report presented to the meeting of the American Chemical Society (7), in which photochemical behavior of I was examined. Irradiation of I in ether with a high-pressure mercury arc lamp was described to give one dimer, to which an anti-structure was assigned from X-ray analysis, and it was also noted that the dimer was photolysed back to I by irradiation with high energy light.
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