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PHOTOCHEMISTRY OF ORGANOMETALLIC COMPOUNDS. II
PHOTOOXYGENATION REACTION OF SILOLE DERIVATIVES.

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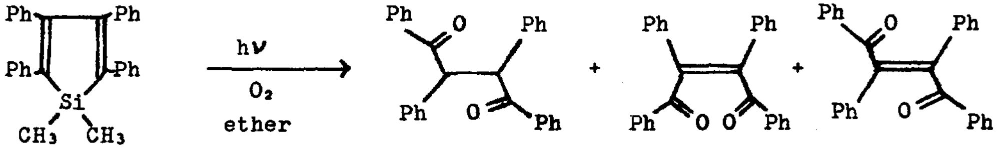
During the course of investigations on the photochemical behaviour of organometallic compounds,(1) we came across to a finding that an unusual photochemical oxygenation-reduction occurred with the silole derivatives.

Under the irradiation of ultraviolet light, 1,1-dimethyl-2,3,4,5-tetraphenylsilole (I) does not suffer any change in the nitrogen stream, but it gives oxygenation products in the oxygen stream.

The major component of this oxygenation products was unexpectedly isodidesyl (II, m.p. 159.0-160.0°, 31 %) together with the minor amounts of cis-dibenzoylstilbene (III, m.p. 212.0-213.0°, 6 %) and trans-dibenzoylstilbene (IV, m.p. 227.0-228.0°, 2 %).



I II III IV

The formation of cis- and trans-dibenzoylstilbene are well known for photooxygenation of tetraphenylcyclopentadienone,(2) tetraphenyl-furan and -thiophene (3) but the formation of isodidesyl, in which the double bond of III and IV is photochemically reduced, has not been reported before.

This is thus considered to be the first examples that the double bond is reduced in the condition of photooxygenation.(4)

Since the double bond in III or IV has been reduced during the reaction, there must be hydrogen abstraction steps in this photochemical conversion.

There can be two possible origins for the hydrogens of the isodidesyl : i.e. the α hydrogen of the solvent ether and methyl hydrogen of I.

From two reasons described below, we conclude that two hydrogens in isodidesyl come from methyl groups on silicon. First, isodidesyl was produced in the same yield when I was irradiated in CS_2 which has no hydrogen to be abstracted. Secondly, no isodidesyl was detected when hexaphenylsilole which had no methyl group on the silicon was irradiated under the same conditions.

Table I. Product Distributions in Photooxygenation of Siloles

Compound	Solvent	II %	III %	IV %
I	Ether	31	6	2
	CS_2	31	9	6
Hexaphenylsilole	Ether	...	14	14

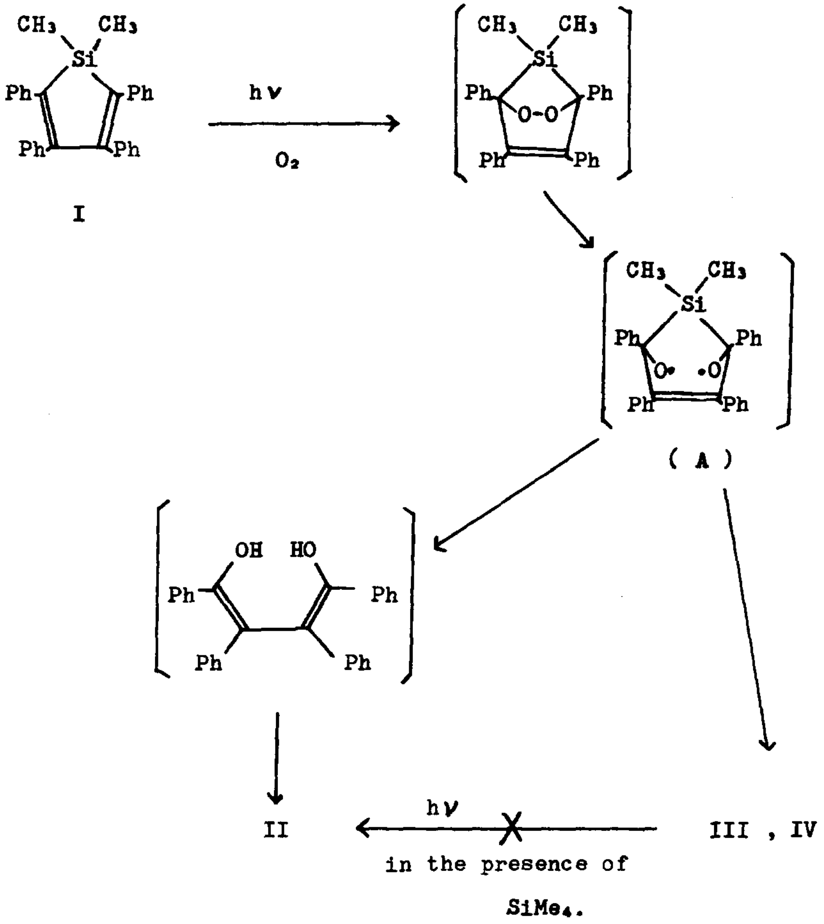
Concerning the addition of hydrogen atoms to an α,β-unsaturated carbonyl system, Griffin and co-workers reported that photolysis of 1,2-dibenzoylethylene in the presence of benzophenone and isopropyl alcohol lead to the reduction of the double bond to give 1,2-dibenzoylethane as the major product.(5)

However, this is not the case for the present case. Because isodidesyl was not formed at all when III or IV was irradiated in the presence of tetramethylsilane.

An additional observation is that the same isodidesyl is produced when I is oxidized by singlet oxygen.(6)

In methanol, the treatment of I with sodium hypochlorite-hydrogen peroxide produced II in 15 % yield.

After these experiments, we propose the following mechanism for the present photochemical transformation.



As cyclopentadiene analogues are known to react with oxygen to form 1,4-endoperoxide,(4) I may form a similar endoperoxide at the first step.

Then, this peroxide decomposes rapidly into a diradical **A** which gives the product II , III and IV.

Splittings of two C-Si bonds in A will produce cis- and trans-dibenzoylstilbene while the facile intramolecular hydrogen abstraction followed by cleavages of C-Si bonds will give a dienol which will ketonize to produce isodidesyl.

The preferred formation of isodidesyl over dibenzoylstilbene indicates that the intramolecular hydrogen abstraction at the intermediate diradical is extremely facile reaction although it forms 5-membered cyclic transition state.

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