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# SYNTHESIS AND OXIDATION OF 1,1,2,2-TETRAMETHYL-3,4,5,6-TETRAPHENYL-1,2-DISILA-3,4-CYCLOHEXADIENE

YASUHIRO NAKADAIRA and HIDEKI SAKURAI
*Department of Chemistry, Faculty of Science, Tohoku University, Sendai (Japan)*

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## SUMMARY

The synthesis of 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disila-3,4-cyclohexadiene, (I), from 1,4-dilithiotetraphenylbutadiene and 1,2-dichlorotetramethyldisilane is described. (I) is reluctant to react with singlet oxygen, in contrast to its carbon analogue, but the Si–Si bond of (I) is readily oxidized to give 2,2,7,7-tetramethyl-3,4,5,6-tetraphenyl-1-oxo-2,7-disila-3,5-cycloheptadiene. The mechanism of the formation of this siloxane is discussed, and a peroxy radical shown to act as an important intermediate in the oxidation.

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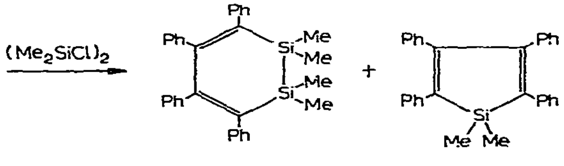
## INTRODUCTION

Although several silacyclopentadiene derivatives have been described in recent years[1-5], no 1,2-disilacyclohexadiene derivative has previously been reported. We describe below the synthesis and oxidation of novel 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-disila-3,4-cyclohexadiene (I).

## RESULTS AND DISCUSSION

Reaction of 1,4-dilithiotetraphenylbutadiene, made from diphenylacetylene and lithium, with 1,2-dichlorotetramethyldisilane gave the cyclic disilane (I), in 55% yield, along with 1,1-dimethyl-2,3,4,5-tetraphenyl-1-sila-2,4-cyclopentadiene (II) as a by-product in 10/1 ratio; the latter was identified by comparing its NMR spectrum with that of an authentic sample. The structural assignment of (I) is based on its physical properties. The UV absorption maximum was located at considerably shorter wave-

$$2\,\mathrm{PhC{\equiv}CPh} \xrightarrow{\mathrm{Li/THF}} \mathrm{PhCLi{=}CPh{-}CPh{=}CLiPh}$$

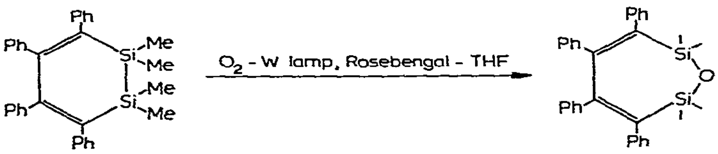


(I) (II)

length for (I) than for (II). This hypsochromic shift can be rationalized by noting, from a molecular model, the non-planar geometry of the diene chromophore caused by the longer Si–Si bond in (I).

In connection with these spectral properties, it became of interest to gain some information on the chemical behavior of the strained diene and the Si–Si bond. The cyclic disilane (I) was thus subjected to photosensitized oxygenations, and it was of particular interest to compare its reactions with that of the carbon analogue, 1,2,3,4,5-phenyl-1,3-cyclopentadiene, which is reported to yield an *endo*-peroxide under these conditions[6].

The oxygenation of (I) did not proceed in acetone, but gave the cyclic disiloxane, (III), smoothly in THF under the usual conditions, as depicted in the following equation:



(I) (III)

No detectable oxidation of (I) occurred in the dark. The structure of (III) was determined on the basis of its spectral properties (see Experimental). A sample of (III) was obtained in practically quantitative yield by treatment of (I) with *m*-chloroperbenzoic acid in dichloromethane:

$$(\mathrm{I}) \xrightarrow{m\text{-}\mathrm{Cl}-\mathrm{C_6H_4CO_3H}} (\mathrm{III})$$

Since the diene moiety remains intact in these oxidation processes, and an olefin function is generally oxidized more readily than an Si–Si bond by a peracid[7], the Si–Si bond in (I), must thus be activated by ring strain toward oxidations. This is further indicated by the fact that oxidation of 1,2-diphenyltetramethyldisilane, (IV), did not occur with singlet oxygen even in THF and only extremely slowly with *m*-chloroperbenzoic acid, although the Si–Si bond in (IV) must be under the influence of similar electronic effects of substituents as that in (I), but without ring strain. Oxidations of cyclic disilanes with various oxidizing agents have been reported to give the corresponding disiloxanes, and ring strain has been observed to increase the reactivity of a disilane[8,9].

The fact that a hydroperoxide was generated from THF under the photosensitized oxygenation conditions[10] implies that a peroxy radical is involved in the photo-oxidation of (I) in THF to give (III). This is substantiated by oxidations of (I) under the various conditions shown in Table 1. Thus, the result of run 1 may be rationalized in terms of an intermediate cumylperoxy radical, which is formed initially by autoxidation of the solvent cumene and then reacts with (I) to yield (III). In runs 2 and 3, (I) reacted with tert-butyl hydroperoxide rather readily to give (III) in quite good yields. Under such conditions, homolysis of the hydroperoxide may be responsible for the initiation of the reaction. It is significant that the oxygenation could be induced at low temperatures, at which spontaneous decomposition of the hydroper-

TABLE 1

OXIDATION OF (I)

| *Run* | *Concn.* ($10^2$ *M*) | *Solvent* | *Oxidizing agent* | *Temp.* (°C) | *Time* (*h*) | *Yield* (%)[a] (*III*) | (*I*)[b] |
|---|---|---|---|---|---|---|---|
| 1 | 1.1 | Cumene | t-BuOO-t-Bu (0.07 *M*)/$O_2$ | 100 | 3 | 89 | |
| 2 | 2.0 | PhCl | t-BuOOH (0.19 *M*)/$N_2$ | 97 | 7 | 78 | |
| 3 | 1.1 | PhCl | t-BuOOH (0.1 *M*)/Argon | 55–59 | 21 | 77 | 4 |
| 4 | 1.1 | PhCl | t-BuOOH (0.1 *M*)/Argon/ DBH[c] (0.0036 *M*) | 38–44 | 20 | 83 | 13 |

[a] Isolated yield by preparative TLC on silica gel. [b] Recovered. [c] Di-tert-butyl hyponitrite.

oxide is almost negligible, by addition of a small amount of di-tert-butyl hyponitrite[11] (run 4). It is well established that decomposition of tert-butyl hydroperoxide at low temperature is induced by the action of an initiator, such as di-tert-butylperoxyoxalate, to yield the tert-butylperoxy radical as an intermediate[12]. These facts indicate that peroxy radicals must play an important role in the disiloxane formation.

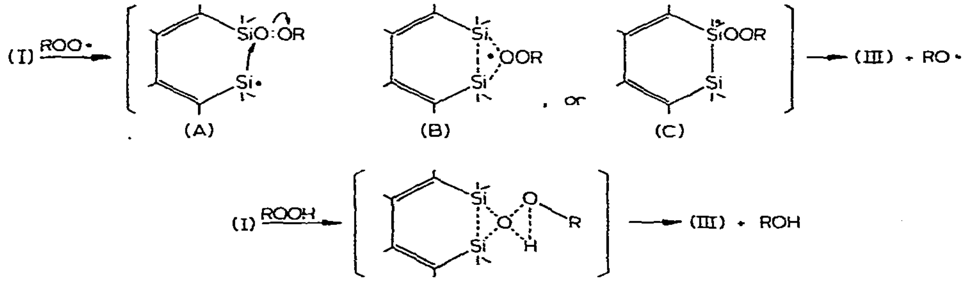
$$\text{t-BuON=NO-t-Bu} \rightarrow 2\ \text{t-BuO}^{\cdot} + N_2$$

$$\text{t-BuO}^{\cdot} + \text{t-BuOOH} \rightarrow \text{t-BuOH} + \text{t-BuOO}^{\cdot}$$

$$\text{t-BuOO}^{\cdot} + (\text{I}) \rightarrow \text{t-BuO}^{\cdot} + (\text{III})$$

The main features of these oxygenations can thus be accounted for in terms of the intermediacy of peroxy radicals as follows, although the molecular mechanism shown in Scheme 1 still cannot be completely excluded simply on the basis of the observations described above.

SCHEME 1



The oxygenation proceeds by attack of a peroxy radical on (I), to form a transition state or an intermediate such as (A), (B) or (C), which then decomposes to give the disiloxane (III) and an alkoxy radical.

(*A*). A peroxy-radical cleaves the Si–Si bond in an $S_H2$ reaction to produce a silyl radical, which ejects an alkoxy radical from the peroxidic function; an $S_H2$ type cleavage of an Si–Si bond by a bromine radical has been reported recently[13,14].

(*B*). A peroxy radical and the disilane form a three membered transition state, as depicted in Scheme 1.

(*C*). A peroxy radical attacks one of the silicon atoms of the Si–Si bond to give a pentacovalent silicon intermediate.

## EXPERIMENTAL

Melting points are uncorrected. UV spectra were measured with a Hitachi EPS-3 spectrophotometer. NMR spectra were obtained at 100 MHz using a Varian HA-100 spectrometer.

### 1,1,2,2-*Tetramethyl*-3,4,5,6-*tetraphenyl*-1,2-*disila*-3,4-*cyclohexadiene* (*I*)

A mixture of 10 g (0.055 mol) of diphenylacetylene and 0.39 g (0.055 g-atom) of cut lithium wire in 60 ml of anhydrous ether was stirred magnetically under nitrogen for 36 h. To this mixture 225 ml of THF was added with mechanical stirring, and the stirring was continued while 13.7 g (0.073 mol) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane in 30 ml of THF was added dropwise. After work-up, 8 g of a solid material was obtained. Recrystallization of the solid from acetone containing a small amount of ethanol gave yellow crystals contaminated with a strongly fluorescent material which was identified as 1,1-dimethyl-2,3,4,5-tetramethyl-1-sila-2,4-cyclopentadiene (II). Further recrystallization from acetone yielded pure (I), m.p. 174–175° ; $M^+$ at *m/e* 472; $\lambda_{max}$(n-hexane): 243 nm ($\varepsilon$ 28800), 340 nm ($\varepsilon$ 3900); $\delta(CDCl_3)$: 0.10 (12 H, Si–Me), 6.6–7.2 ppm (20 H, arom.) (Found: C, 81.17; H, 6.93. $C_{32}H_{22}Si_2$ calcd.: C, 81.29; H, 6.82%.)

### 2,2,7,7-*Tetramethyl*-3,4,5,6-*tetraphenyl*-1-*oxo*-2,7-*disila*-3,5-*cycloheptadiene* (*III*)

To a solution of 250 mg (0.53 mmol) of (I) in 20 ml of methylene chloride was added a solution of 185 mg (1,1 mmol) of *m*-chloroperbenzoic acid. The mixture was stirred at room temperature for 2 h, during which time the yellow color of (I) disappeared. Recrystallization of the crude product from ethanol gave (III) as colorless crystals, 255 mg (in 97% yield): m.p. 137-138° ; $M^+$ at *m/e* 488; $\lambda_{max}$(EtOH), 253 nm ($\varepsilon$ 19500), 278 nm ($\varepsilon$ 14700); $\delta(CDCl_3)$: 0.36 (12 H, Si–Me), 6.7–7.3 ppm (20 H, arom); $\nu$(KBr): 1000 cm$^{-1}$ (Si–O–Si). (Found: C, 78.54; H, 6.79. $C_{32}H_{32}Si_2O$ calcd.: C, 78.63; H, 6.60%.)

### *Photooxygenation of* (*I*) *in acetone*

A solution of 20 mg of (I) in 0.7 ml of acetone, containing a trace of Rosebengal, in an NMR tube was irradiated with a 250 W tungsten lamp under oxygen. The reaction mixture was examined after 1 h, and only starting material was detected by silica gel TLC, developed with n-hexane/benzene (4/1). After irradiation under oxygen for another 2 h, a faint spot corresponding to (III) was detected on TLC, along with a strong spot due to the starting material.

### *Photooxygenation of* (*I*) *in THF*

A solution of 20 mg of (I) in 10 ml THF was irradiated similarly. After 1.5 h, only (III) was detected and no starting disilane (I) was found on silica gel TLC. Recrystallization of the product from ethanol gave pure (III) as crystals, m.p. 137–138°.

### *Autoxidation of* (*I*) *in cumene*

A solution of 50 mg of (I) in 10 ml of cumene containing 100 mg di-tert-butylperoxide was stirred magnetically for 3 h at 100° under oxygen. After cooling, 50 ml of ether was added to the reaction mixture. After the treatment with aqueous sodium thiosulfate, the ethereal solution was dried over sodium sulfate, and evaporated under reduced pressure to leave an oil. Preparative TLC of the oil on silica gel gave (III), 46 mg (89% yield).

*Reaction of* (*I*) *with tert-butyl hydroperoxide*

(*i*). A solution of 50 mg of (I) in 5.5 ml of chlorobenzene containing 95 mg of tert-butyl hydroperoxide was stirred magnetically for 7 h at 97° under nitrogen. Preparative TLC of the oily product on silica gel gave (III), 41 mg (78% yield).

(*ii*). A solution of 100 mg of (I) in 20 ml of chlorobenzene containing 180 mg of tert-butyl hydroperoxide was degassed by two freeze-thaw cycles. The reaction mixture was then stirred magnetically at 55–59° for 21 h under argon. The usual work-up gave 80 mg (77% yield) of (III).

(*iii*). A solution of 102 mg of (I) in 20 ml of chlorobenzene containing 182 mg of tert-butyl hydroperoxide was degassed and kept at 38–40° for 7 h. Only a faint spot corresponding to (III) could be detected on TLC after this time. A solution of 15 mg of di-tert-butyl hyponitrite in 0.5 ml of chlorobenzene was then added to the reaction mixture, which was stirred magnetically at 43°. After 3 h, a fairly intense spot of (III) was observed on TLC. After 17 h stirring at 38–44°, 88 mg (83% yield) of (III) and the starting disilane (13 mg, 13% yield) were obtained.

*Oxidation of* 1,2-*diphenyltetramethyldisiloxane with m-chloroperbenzoic acid*

A solution of 270 mg of 1,2-diphenyltetramethyldisiloxane and 350 mg of *m*-chloroperbenzoic acid in 50 ml of methylene chloride was stirred at room temperature. Only a trace of the disiloxane was detected on VPC after 2 h. After 21 h, the disiloxane formed was shown by VPC analysis to be less than 6%.

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## REFERENCES

1 E. H. Braye, W. Hübel and I. Caplier, *J. Amer. Chem. Soc.*, 83 (1961) 4406.
2 H. Gilman, S. G. Cottis and W. H. Atwell, *J. Amer. Chem. Soc.*, 86 (1964) 1596.
3 W. H. Atwell, D. R. Weyenberg and H. Gilman, *J. Org. Chem.*, 32 (1967) 885.
4 J. C. Brunet, B. Resibois and J. Bertrand, *Bull. Soc. Chim. Fr.*, (1967) 3424.
5 M. D. Curties, *J. Amer. Chem. Soc.*, 91 (1969) 6011.
6 G. R. Evanega, W. Bergman and J. English, Jr., *J. Org. Chem.*, 27 (1962) 13.
7 (a) H. Sakurai, T. Imoto, N. Hayashi and M. Kumada, *J. Amer. Chem. Soc.*, 87 (1965) 4001;
(b) H. Sakurai, N. Hayashi and M. Kumada, *J. Organometal. Chem.*, 18 (1969) 351.
8 K. Tamao, M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, 31 (1971) 17.
9 K. Tamao and M. Kumada, *J. Organometal. Chem.*, 31 (1971) 35.
10 G. O. Schenck, H. D. Becker, K. H. Schulte-Elte and C. H. Krauch, *Chem. Ber.*, 96 (1963) 509.
11 H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, (1966) 6163.
12 R. Hiatt, J. Clipsham and T. Visser, *Can. J. Chem.*, 42 (1964) 2754.
13 A. Hosomi and H. Sakurai, *J. Amer. Chem. Soc.*, 94 (1972) 1384.
14 A. Hosomi and H. Sakurai, *Chem. Lett.*, (1972) 193.