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The Reaction of Methylchlorodisilanes with *t*-Butyl Hydroperoxide

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The authors wished to get two new organosilyl peroxides with a silicon-silicon linkage, *t*-butylperoxypentamethyldisilane $[(CH_3)_3SiSi(CH_3)_2(OOC(CH_3)_3)]$ and 1, 2-di-*t*-butylperoxytetramethyldisilane $[((CH_3)_3COO)(CH_3)_2SiSi(CH_3)_2(OOC(CH_3)_3)]$, by the reaction of the corresponding chlorodisilanes with *t*-butyl hydroperoxide. The reaction, however, did not give the desired product; rather, it led to the formation of *t*-butoxypentamethyldisiloxane $[(CH_3)_3SiOSi(CH_3)_2(OC(CH_3)_3)]$ and 1-*t*-butoxy-3-*t*-butylperoxytetramethyldisiloxane $[((CH_3)_3CO)(CH_3)_2SiOSi(CH_3)_2(OOC(CH_3)_3)]$ respectively, substances which are believed to have resulted from the intramolecular rearrangement of the desired peroxydisilanes.

Chlorosilanes react readily with alkyl hydroperoxides to form fairly stable alkylperoxysilanes with the Si–O–O–C group. The literature on organosilicon compounds contains no example of a disilane with peroxy substituents. The present investigation was undertaken to prepare two derivatives of this class of compounds, *t*-butylperoxypentamethyldisilane (I) and 1, 2-di-*t*-butylperoxytetramethyldisilane (II), by treating the corresponding chlorodisilanes[1] with *t*-butyl hydroperoxide in the presence of pyridine:

$$Me_3SiSiMe_2Cl + HOOCMe_3 \xrightarrow{C_5H_5N} Me_3SiSiMe_2(OOCMe_3)$$
(I)

$$ClMe_2SiSiMe_2Cl + 2\,HOOCMe_3 \xrightarrow{C_5H_5N} (Me_3COO)Me_2SiSiMe_2(OOCMe_3)$$
(II)

However, these products were not obtained. The reaction between *t*-butyl hydroperoxide and pentamethylchlorodisilane gave a non-peroxidic compound, *t*-butoxypentamethyldisiloxane (III), the formation of which may well be ascribed to the intramolecular rearrangement of the unstable peroxide intermediate. Proof for the structure of

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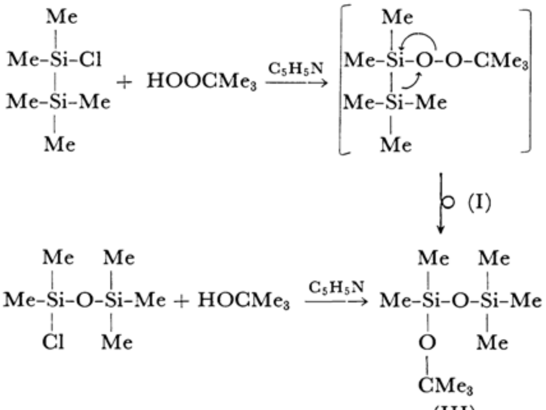
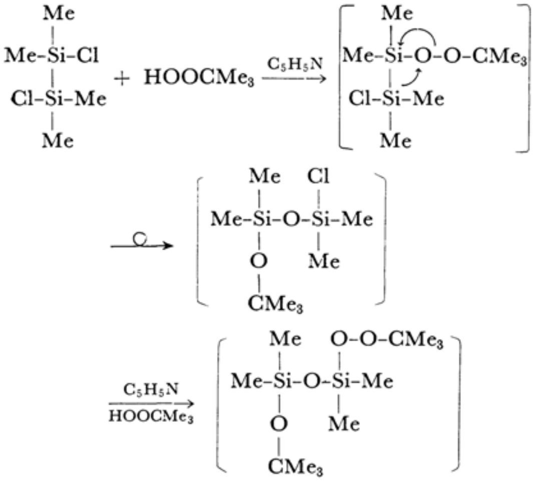
[1] M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina, *J. Org. Chem.*, **21**, 1264 (1956).

III was afforded by its unambiguous synthesis from pentamethylchlorodisiloxane and *t*-butyl alcohol:



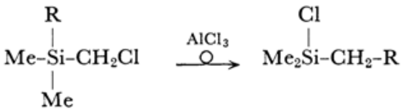
(III)

Similarly, from the reaction between 1, 2-dichlorotetramethyldisilane and *t*-butyl hydroperoxide, 1-*t*-butoxy-3-*t*-butylperoxytetramethyldisiloxane (IV) was obtained instead of the corresponding peroxidic compound (II). Apparently, the reaction proceeded as follows:



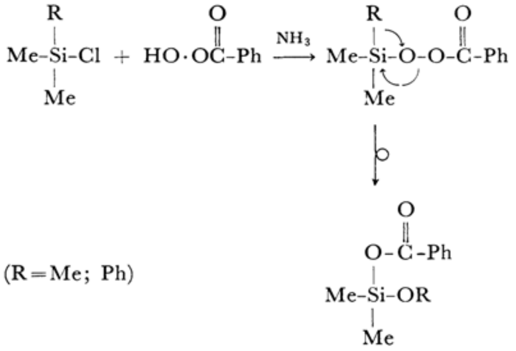
(IV)

These results indicate that both silyl groups, Me_3Si and $ClMe_2Si$, have much greater migratory aptitudes than the methyl group, as was observed previously by Kumada and his collaborators[2] in the case of the intramolecular rearrangement of chloromethyldisilanes with anhydrous aluminum chloride:



($R=-SiMe_3$, $-SiMe_2Cl$)

Intramolecular rearrangements of organosilyl peroxides have been reported by Buncel and Davies.[3] They observed the rearrangement only when they attempted to prepare acylperoxysilanes from the reaction between peroxybenzoic acid and trimethylchlorosilane or dimethylphenylchlorosilane:



($R=Me$; Ph)

Similar nucleophilic 1, 2-rearrangements have been reported with other organometallic and organometalloidal compounds.[4,5]

Experimental

Starting Materials.—*Pentamethylchlorodisilane and 1, 2-Dichlorotetramethyldisilane.*—These were obtained by the method reported in detail by Kumada and his collaborators.[1]

t-Butyl Hydroperoxide.—The authors used *t*-butyl hydroperoxide-90, produced by Wallace & Tiernan, Inc., the purity of which is 90%.

Pentamethylchlorodisiloxane.—This was prepared from 1, 3-dichlorotetramethyldisiloxane ($ClMe_2SiOSiMe_2Cl$)[6,7] by methylation with the Grignard reagent.

The Reaction between Pentamethylchlorodisilane and *t*-Butyl Hydroperoxide.—A 500-ml. four-necked flask was fitted with an air-tight stirrer, a thermometer, a dropping-funnel and a reflux condenser with a calcium chloride tube. In the flask these were then placed 27 g. (0.27 mol.) of *t*-butyl hydroperoxide, 20 g. (0.253 mol.) of pyridine, and 200 ml. of petroleum ether. Into this mixture, a mixture of 41.7 g. (0.25 mol.) of pentamethylchlorodisilane and 50 ml. of petroleum ether was stirred over a 75-minute period. At once pyridine hydrochloride was precipitated. During the addition, the mixture was cooled with an ice-bath below 10°C. After the addition, the mixture was stirred over 5 hr. at room temperature. When the mixture was filtered, the organic layer was obtained. The ether was removed, and the residual oil was then distilled under reduced pressure to give 39 g. of a liquid boiling over the range from

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[2] M. Kumada, J. Nakajima, M. Ishikawa and Y. Yamamoto, *J. Org. Chem.*, **23**, 292 (1958).

[3] E. Buncel and A. G. Davies, *Chem. & Ind.*, **1957**, 492.

[4] A. G. Davies and J. E. Packer, *J. Chem. Soc.*, **1959**, 3164.

[5] H. Hock and F. Ernst, *Chem. Ber.*, **92**, 2716 (1959).

[6] W. I. Patnode and O. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).

[7] G. Greber and L. Metzinger, *Makromol. Chem.*, **39**, 167 (1960).

62°C/71 mmHg to 95°C/40 mmHg. The distillate was fractionally distilled through a 1.5×40 cm. Fenske column to give 22.1 g. of a colorless liquid (A), b. p. 55°C/18.5 mmHg. The yield was estimated to be 70—80% by gas chromatography. The physical properties and analytical data for this product A are listed in Table I.

TABLE I. PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR A AND B

	Found A	Found B	Calcd. for I	Calcd. for III
b. p.	55°C/18.5 mmHg	155°C		
n_D^{20}	1.3910	1.3916		
d_4^{20}	0.8255	0.8233		
M. R.	63.5	63.7	68.0	63.6
M. W.	213.0	221.1	220.5	220.5
Active oxygen (%)	0.3		7.25	0
Analyses C	48.82	48.78	49.02	49.02
H	10.74	10.81	10.97	10.97
Si	25.5	25.0	25.47	25.47

***t*-Butoxypentamethyldisiloxane (III).**—In a three-necked flask equipped with a stirrer, a dropping funnel and an efficient reflux condenser with a calcium chloride tube, 14.8 g. (0.2 mol.) of *t*-butyl alcohol was added to a mixture of 30 g. (0.164 mol.) of pentamethylchlorodisiloxane (Found: Cl, 19.3. Calcd. for $C_5H_{15}OSi_2 \cdot Cl$: 19.0%), 15.6 g. (0.197 mol.) of pyridine, and 200 ml. of dry ether. During the reaction, the mixture was cooled with an ice-bath below 10°C. After the addition of the *t*-butyl alchol, the reaction mixture was refluxed over a period of one hour with stirring. The pyridine hydrochloride was then removed by filtration. The evaporation of ether from the filtrate, followed by fractional distillation, gave 13.9 g. of a liquid, b. p. 47—49°C/14.5 mmHg. Redistillation under ordinary pressure gave a colorless liquid (B), b. p. 155°C. The physical properties and analytical data for this product B also are shown in Table I.

The Reaction between 1, 2-Dichlorotetramethyldisilane and *t*-Butyl Hydroperoxide.—This reaction was carried out in essentially the manner described above, except that 28.1 g. (0.15 mol.) of 1, 2-dichlorotetramethyldisilane was added to a mixture of 32.4 g. (0.324 mol.) of *t*-butyl hydroperoxide, 24 g. (0.3 mol.) of pyridine in 300 ml. of dry petroleum ether. We thus obtained 11.9 g. of a colorless liquid (C), b. p. 89—89.5°C/13 mmHg; its physical properties and analytical data are listed in Table II.

TABLE II. PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR C

	Found C	Calcd. for II	Calcd. for IV
b. p.	89—89.5°C/13 mmHg		
n_D^{20}	1.4016		
d_4^{20}	0.8889		
M. R.	80.6	84.9	80.5
M. W.	302.8	294.6	294.6
Active oxygen (%)	5.44	10.86	5.43
Analyses C	48.73	48.91	48.91
H	10.00	10.26	10.26
Si	18.9	19.07	19.07

Results and Discussion

From the two reactions of *t*-butyl hydroperoxide with pentamethylchlorodisilane and with 1, 2-dichlorotetramethyldisilane, two new compounds, III and IV, were isolated, but no organosilyl peroxide that contains both silicon-silicon and one or two peroxy groups was obtained.

Evidence for this conclusion was afforded by determinations of the active oxygen contents, the molecular refractions, and the retention times by means of gas chromatography and a study of the infrared spectra. The infrared spectrum of A agreed with that of B in all ranges. The retention time of A in the gas chromatogram agreed with that of B. The other physical properties (cf. Tables I and II) also supported these results.

Summary

Pentamethylchlorodisilane and 1, 2-dichlorotetramethyldisilane easily react with *t*-butyl hydroperoxide; they give not the corresponding peroxides with the silicon-silicon linkage, but *t*-butoxypentamethyldisiloxane and 1-*t*-butoxy-3-*t*-butylperoxytetramethyldisiloxane respectively. The formation of these two products through the intramolecular rearrangement of the unstable peroxy intermediates has been discussed.

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