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OXIDATION OF SILICON—SILICON AND SILICON—HYDROGEN BONDS WITH MOLECULAR OXYGEN AND BIS(TRIMETHYLSILYL) PEROXIDE*

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Summary

The silicon—silicon bond which is either strained or substituted with more than two fluorine atoms is easily oxidized with molecular oxygen and bis(trimethylsilyl) peroxide (BSPO) at or below room temperature to form mainly the corresponding disiloxane. The former aerobic oxidation is inhibited by 2,4,6-tri(t-butyl)phenol, while the latter is not. Oxidation of the Si—H bond with BSPO and the preparation of three new (fluoro)methyldisilanes are also described.

Introduction

Although there have been many reports concerning oxidative cleavage of the silicon—silicon bond [1], relatively few reactions involving the insertion of oxygen into the Si—Si bond have been studied. To our knowledge, such reactions are limited to those involving perbenzoic acid [2], ozone [3], nitrogen oxides [4] and tertiary amine oxide [5], and the recently discovered interesting reaction of perchloropolysilanes which serve as excellent deoxygenating agents for phosphine oxides, sulfoxides and amine oxides [6]. The Si—Si bonds in organopolysilanes have been considered for many years to be stable to air oxidation [7], although the strained Si—Si bond involved in small rings has been found to be an unusual case [1,8]. We have previously reported [9,10] that 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane is readily oxidized below room temperature by molecular oxygen and bis(trimethylsilyl) peroxide (BSPO), while the permethylated and the phenyl-substituted analogs are not. These findings suggest that fluorine substituents exert an oxidation-facilitating effect and that BSPO acts as an oxygen-transfer agent to the Si—Si bond. Recently, much interest has been shown in the behavior of silyl peroxides [11], and during the preparation of this paper, a review concerning various types of reactions of BSPO has

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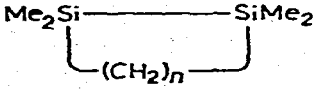
appeared [12]. A photosensitized oxygenation of certain Si—Si bonds has also been reported [13].

We have now investigated the action of molecular oxygen and/or BSPO on fluoropentamethyl- (I) [14], 1,2-difluorotetramethyl- (II) [14], 1,1-difluorotetramethyl- (III), 1,1,2-trifluorotrimethyl- (IV) and 1,2-dimethyltetrafluorodisilane (V), and 1,1,2,2-tetramethyl-1,2-disilacycloalkanes (VIa-d) [15], as well as oxidation of some hydrosilanes, with BSPO.



(VI) a, $n = 3$
b, $n = 4$
c, $n = 5$
d, $n = 6$

Results and discussion

Preparation of new fluoromethyldisilanes III - V

Compounds III-V were prepared from the corresponding (ethoxy)methyldisilanes [14] by dissolving them in cold concentrated sulfuric acid and subsequently treating with ammonium hydrogen fluoride. Attempts to prepare 1,1,1-trifluorotrimethyldisilane in a similar manner, from the 1,1,1-triethoxy derivative, resulted in the formation of highly volatile products, suggesting almost complete cleavage of the Si—Si bond. Some physical constants and analytical data are listed in Table 1, and ^{1}H NMR data in Table 2. Compound V exhibited a triplet with unresolved fine splitting.

Oxidation with molecular oxygen

Oxygen was bubbled through the neat liquids at room temperature. Compound VIa, which contains the angle-strained Si—Si bond [15], absorbed about 0.8 equivalent of oxygen exothermally. GLC analysis revealed that the starting substance was no longer present. 2,2,6,6-Tetramethyl-1-oxa-2,6-disilacyclo-

TABLE 1

YIELDS FROM THE CORRESPONDING ETHOXY DERIVATIVES, SOME PHYSICAL CONSTANTS AND FLUORINE CONTENT OF NEW FLUORINE SUBSTITUTED METHYLDISILANES

Compound	Yield (%)	B.p. (°C)	n_D^{20}	d_4^{20}	Fluorine content found (calcd.) (%)
III	84.5	85-86	1.3797	0.9108	25.14 (24.93)
IV	85	75-77	1.3586	1.0428	35.45 (36.01)
V	69	56-58	1.3288	1.1850	46.33 (46.84)

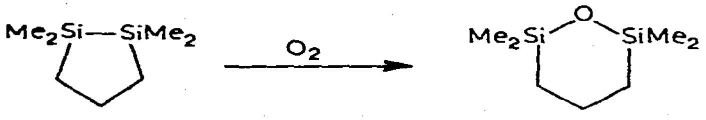
TABLE 2

^{1}H NMR DATA FOR FLUORINE SUBSTITUTED METHYLDISILANES AND DISILOXANES[a]

Compound	Chemical shift[b] (δ, ppm)		$J(^{19}F—H)$ (Hz)	
	$CH_3{}^1$	$CH_3{}^2$	$CH_3{}^1$	$CH_3{}^2$
$Me_3{}^1SiSiMe_2{}^2F$	0.10(s)	0.27(d)		9
$Me_3{}^1SiSiMe^2F_2$	0.22(s)	0.34(t)		7
$FMe_2SiSiMe_2F$	0.39(d)[c]		7	
$FMe_2{}^1SiSiMe^2F_2$	0.45(d)	0.42(t)[c]	8	7.5
$F_2MeSiSiMeF_2$	0.51(m)		d	
$Me_3{}^1SiOSiMe_2{}^2F$	0.12(s)	0.15(d)		ca. 4.5
$Me_3{}^1SiOSiMe^2F_2$	0.18(s)	0.28(t)		4.5
$FMe_2SiOSiMe_2F$	0.23(d)		6	
$FMe_2{}^1SiOSiMe^2F_2$	0.28(d)	0.36(t)	7	4.5

[a] Carbon tetrachloride solution with cyclohexane as an internal standard; s = singlet, d = doublet, t = triplet, m = multiplet. [b] The chemical shifts are given in ppm down field from TMS. [c] Somewhat complex signals due to the small long-range coupling. [d] Complex triplet with unresolved fine splitting.

hexane was obtained in 72% yield by distillation, leaving nonvolatile viscous polysiloxanes:



(VIa)

Compound II also reacted exothermally with oxygen. As it absorbed up to ca. 0.8 equivalent of oxygen paraformaldehyde precipitated and at this point the rate of absorption suddenly decreased. Deposition of a small amount of water also occurred. From several products, difluorotetramethyldisiloxane was isolated in 35% yield:

$$\text{II} \xrightarrow{O_2} FMe_2SiOSiMe_2F + (CH_2O)_n + H_2O + \text{polysiloxanes}$$

The oxidation of IV and V proceeded in a more complicated fashion. After a 10 min induction period, they began to absorb oxygen rapidly and exothermally, and considerable amounts of paraformaldehyde deposited with the formation of a complicated mixture of products. The corresponding trifluoromethyldisiloxane was the sole characterizable product from IV, while tetrafluorodimethyldisiloxane could not be obtained from V.

The oxidation of the 1,1-difluoro derivative III proceeded quite slowly relative to II, 1,1-difluorotetramethyldisiloxane being the main product. Fluoropentamethyldisilane (I), 1,2-dichlorotetramethyldisilane and hexamethyldisilane

[3] did not react with oxygen under similar conditions or even after a prolonged reaction time (80°C, 10 h). Control experiments indicated that n-propylmethyldifluorosilane did not absorb oxygen at all even after 20 h at room temperature.

The oxidation of II was completely inhibited by the addition of a small amount of 2,4,6-tri(t-butyl)phenol.

Consequently, from the previous and present observations, it is seen that the oxidation of the Si—Si bond with oxygen has the following features: (1) the Si—Si bond which is either angle-strained or substituted with more than two fluorine atoms is easily oxidized; (2) a radical mechanism is operative; (3) the "insertion" of oxygen into the Si—Si bond proceeds stereospecifically [9].

Although the aerobic oxidation is not simple and requires further study, the mechanism proposed for the oxidation of the Sn—Sn and Pb—Pb compounds [7] suggests a mechanism involving the intermediate formation of a disilyl peroxide via the attack of molecular oxygen on the Si—Si bond (process 1). Processes 3 [16] and 5 [17] have been discussed previously and process 6 is well-known. Process 2 has been independently confirmed in the previous [9,10] and present papers (*vide infra*). Although initial attack of oxygen on the methyl groups can not be ruled out, the pyrophoric properties of polydifluorosilylene, $(SiF_2)_n$ [18], seem consonant with process 1. It is of interest to compare the present autoxidation of polyfluorodisilanes with the facile autoxidation of tetrafluoroethylene [19] to form mainly polymeric tetrafluoroethylene peroxide, $(CF_2CF_2OO)_n$.

$$R_3SiSiR_3 + O_2 \rightarrow R_3Si \xrightarrow{O_2} SiR_3 \rightarrow R_3SiOOSiR_3 \qquad (1)$$

$$R_3SiOOSiR_3 + R_3SiSiR_3 \rightarrow 2R_3SiOSiR_3 \qquad (2)$$

$$R_3SiOOSiR_3 \rightarrow 2R_3SiO\cdot \qquad (3)$$

$$\equiv SiCH_3 + R_3SiO\cdot \rightarrow \equiv SiCH_2\cdot + R_3SiOH \qquad (4)$$

$$\equiv SiCH_2\cdot + O_2 \rightarrow \equiv SiCH_2OO\cdot \rightarrow \equiv SiO\cdot + CH_2O \qquad (5)$$

$$2R_3SiOH \rightarrow R_3SiOSiR_3 + H_2O \qquad (6)$$

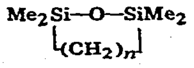
Oxidation of disilanes by BSPO

Compounds I-VI were allowed to react with BSPO and the results are summarized in Table 3. The reactivity order is similar to that observed in the oxidation by oxygen. Thus, compounds II-V and VIa reacted with BSPO exothermally at or below room temperature, while I reacted slowly at room temperature, and VIb, VIc and hexamethyldisilane required more drastic reaction conditions. The eight membered ring VId did not react with BSPO.

Compounds I, III, VIa and VIb gave the corresponding disiloxanes in quantitative yields, and BSPO was converted into hexamethyldisiloxane; II formed traces of fluoropentamethyldisiloxane, in addition to difluorotetramethyldisiloxane. The reactions of IV and V with BSPO were not so simple and afforded a mixture of products, including trimethylfluorosilane. As in the aerobic oxidation, tetrafluorodimethyldisiloxane could not be isolated from V. The disiloxanes formed were isolated by preparative GLC and characterized by ^1H NMR

TABLE 3

OXIDATION OF DISILANES WITH BIS(TRIMETHYLSILYL) PEROXIDE

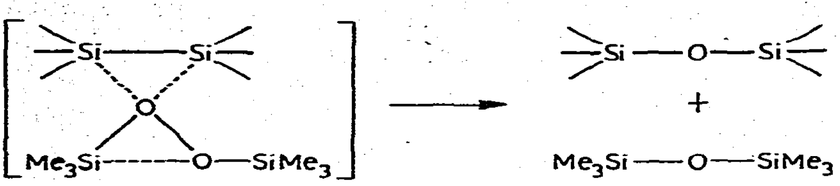
Compound, mmol		BSPO (mmol)	Conditions		Products^{a}, (yield, %)
			Temp. (°C)	Time (h)	
Me_6Si_2,	0.27	0.48	80	42	$Me_3SiOSiMe_3$^{b}
I,	1.42	1.73	r.t.	45	$Me_3SiOSiMe_2F$, (~100)
II,	0.91	1.03	r.t.	3.5	$FMe_2SiOSiMe_2F$, (92) $Me_3SiOSiMe_2F$, (trace)
III,	1.62	1.91	r.t.	4	$Me_3SiOSiMeF_2$, (~100)
IV,	0.70	0.78	0	1.5	Me_3SiF $FMe_2SiOSiMeF_2$ $Me_3SiOSiMeF_2$ ^{c} $Me_3SiOSiMe_2F$ (trace) and others
V,	4.08	4.71	—10	1	Me_3SiF, $Me_3SiOSiMeF_2$^{d} and others
VIa,	0.62	1.23	r.t.	1.5	 $Me_2Si—O—SiMe_2$ $(CH_2)_n$ $n = 3$, (95)
VIb,	0.19	0.56	80	16	$n = 4$, (98.5)
VIc,	1.47	2.49	80	45	$n = 5$, (64)^{e}
VId,	0.94	1.65	80	45	No reaction

[a] Hexamethyldisiloxane is not indicated. [b] About 40% of hexamethyldisilane was converted to hexamethyldisiloxane. [c] $Me_3SiF/FMe_2SiOSiMeF_2/Me_3SiOSiMeF_2 \simeq 0.48/1/0.16$. [d] $Me_3SiF/Me_3SiOSiMeF_2 \simeq 2/1$. [e] Conversion is indicated.

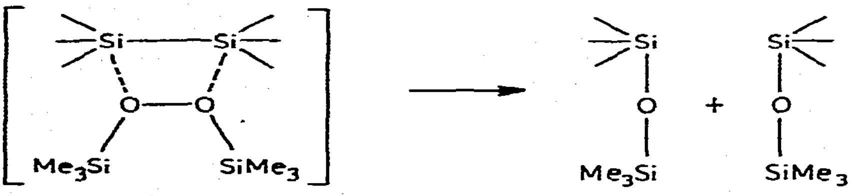
(Table 2), IR (Table 4) spectra and elemental analysis (Table 4). Interestingly, methyl proton resonances on silicon atom(s) bearing fluorine atom(s) in disiloxanes occur at higher fields compared with those in the parent disilanes.

It was confirmed that the reaction of II with BSPO was *not* inhibited by 2,4,6-tri(t-butyl)phenol. Compound VIa did not react (80°C, 60 h) with di-t-butyl peroxide, which is the carbon analog of BSPO, suggesting an important role of vacant *d*-orbitals of the silicon atom, not available to the hydrocarbon peroxide. Furthermore, the previous report [9] described that the BSPO oxidation of the Si—Si bond proceeds stereospecifically.

A molecular mechanism involving the intermediate formation of A via the nucleophilic attack of the peroxide oxygen atom on the Si—Si bond seems consistent with the results mentioned above. Another molecular intermediate B may also be formed in a minor reaction path. However, in cases of IV and V, an other mechanism should be involved.



(A)



(B)

One of the other likely mechanisms may involve the formation of trimethylsilylperoxy radicals from BSPO by S_H2 reaction at silicon [11c], induced by certain radical species which would be formed. A recent report [13] has dealt with the oxidation of the Si—Si bond by alkylperoxy radicals.

Oxidation of hydrosilanes with BSPO

The reactions of triethylsilane, phenyldimethylsilane and pentamethyldisilane with BSPO were examined. The results are summarized in Table 5. In

TABLE 4

INFRARED ν(Si—O) FREQUENCIES AND ANALYTICAL DATA FOR DISILOXANES

Compound	ν(Si—O) (cm^{-1})	Analysis found (calcd.) (%)		
		C	H	F
$Me_3SiOSiMe_2F$	1070^a			11.53 (11.42)
$FMe_2SiOSiMe_2F$	1090^a			21.97 (22.31)
$Me_3SiOSiMeF_2$	1100^a			22.11 (22.31)
$FMe_2SiOSiMeF_2$	1110^a			32.01 (32.65)
$Me_2Si{-}O{-}SiMe_2$ $\llcorner(CH_2)_n\lrcorner$				
$n = 3$	987^b	48.07 (48.21)	10.52 (10.40)	
$n = 4^c$	1020^b	50.77 (50.99)	10.55 (10.70)	
$n = 5$	1040^b	53.62 (53.39)	11.01 (10.92)	

^{a}A carbon tetrachloride solution. ^{b}Neat. $^c n_D^{20}$ 1.4350, d_4^{20} 0.8859 (lit. [23]: n_D^{20} 1.4340, d_4^{20} 0.8794.

TABLE 5

REACTION OF HYDROSILANES WITH BIS(TRIMETHYLSILYL) PEROXIDE

Compound,	mmole	BSPO mmol	Conditions^a		Conversion^b (%)	Products^c, (yield, %)^b
			Temp. (°C)	Time (h)		
Et_3SiH,	0.188	0.318	80	25	100	Et_3SiOH, (32.4) $Et_3SiOSiMe_3$, (40.6)
Et_3SiH,	0.396	0.460	20	40	12	Et_3SiOH, (trace) $Et_3SiOSiMe_3$, (6.6)
$PhMe_2SiH$,	0.291	0.607	80	27	89	$PhMe_2SiOSiMe_3$, (66.3) $(PhMe_2Si)_2O$, (14.4)
$Me_3SiSiMe_2H$,	0.276	0.617	80	23	100	$Me(Me_2SiO)_2SiMe_3$, (31.9) $Me(Me_2Si)_2OSiMe_3$, (19.7) $(Me_5Si_2)_2O$, (trace) $Me(Me_2SiO)_3SiMe_3$, (trace)
$Me_3SiSiMe_2H$,	0.340	0.133	80	23	47.6	$Me(Me_2SiO)_2SiMe_3$, (4.0)^d $Me(Me_2Si)_2OSiMe_3$, (57.8)^d

[a] In a sealed tube. [b] Determined by GLC using an internal standard. [c] In all cases, $Me_3SiOSiMe_3$ and water were formed. [d] Based on unrecovered hydrodisilane.

all cases, two kinds of products, R_3SiOH and $R_3SiOSiMe_3$, were formed as primary products. The symmetrical $R_3SiOSiR_3$ may be regarded as the secondary condensation product of the former. The $R_3SiOH/R_3SiOSiMe_3$ ratio tends to decrease in the order $Et_3SiH > PhMe_2SiH > Me_5Si_2H$.

Experimental

^1H NMR spectra were taken on a Jeol Model C-60H spectrometer in carbon tetrachloride solution and IR spectra were measured on a Hitachi EPI-G3 grating spectrophotometer in carbon tetrachloride solution for volatile compounds. A Varian Aerograph Model 90P was used for isolation of products.

Preparation of fluoromethyldisilanes

The starting (ethoxy)methyldisilanes were prepared from the corresponding (chloro)methyldisilanes [20,21] according to the method reported previously [14]. Fluorine contents were determined by the back titration method: a small thin wall glass ball containing a weighed sample was broken in a stopped flask which contained a sufficient amount of sodium hydroxide standard solution and ethanol. After standing for several hours the excess alkali was titrated with hydrochloric acid standard solution.

1,1-Diethoxytetramethyldisilane. Yield 78%; b.p. 87°C/54 Torr, n_D^{20} 1.4208, d_4^{20} 0.8451. (Found: C, 46.73; H, 10.92. $C_8H_{22}O_2Si_2$ calcd.: C, 46.54; H, 10.74%.)

1,1,1-Triethoxytrimethyldisilane. Yield 69%; b.p. 74-76°C/18 Torr, n_D^{20}

1.4160, d_4^{20} 0.8812. (Found: C, 45.98; H, 10.03. $C_9H_{24}O_3Si_2$ calcd.: C, 45.71; H, 10.23%.)

The following procedure is typical for the preparation of (fluoro)methyldisilanes.

1,1-Difluorotetramethyldisilane (III). To ice-cooled concentrated sulfuric acid (200 g) was added dropwise 38 g (0.184 mol) of 1,1-diethoxytetramethyldisilane and the mixture was vigorously stirred for 1 h at 0°C. With cooling, 26 g (0.46 mol) of ammonium hydrogen fluoride was added in several portions. The resulting organic layer was separated and distilled in a slow stream of dry nitrogen to give 24 g (84.5% yield) of III as a colorless liquid.

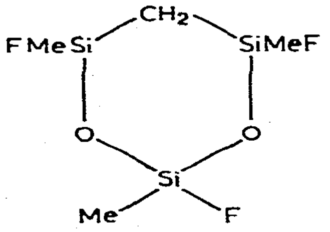
Attempted preparation of 1,1,1-trifluorotrimethyldisilane. 1,1,1-Triethoxytrimethyldisilane (20 g) was treated similarly with sulfuric acid to form a yellow insoluble material; a vigorous effervescence occurred. Addition of ammonium hydrogen fluoride caused the solid to dissolve. The organic layer which separated in a small amount was distilled under nitrogen to give a liquid (4 g) boiling over the range of 40-80°C, leaving 2 g of residue. The IR spectrum of the distillate showed the presence of the siloxane bonds.

n-Propylmethyldifluorosilane. Prepared in a similar manner in 67 % yield, b.p. 54-57°C, n_D^{20} 1.3370, d_4^{20} 0.9184. (Found: F, 30.15. $C_4H_{10}F_2Si$ calcd.: F, 30.60%.)

Reaction of oxygen

A closed system was used. The reaction was carried out in a glass tube (15 mm × ca. 20 cm) and oxygen was bubbled through the neat liquid sample via a constant gas-circulation pump. The volume of absorbed oxygen was measured by means of a gas buret connected with the reaction system. Two typical reactions are described in detail.

With 1,2-difluorotetramethyldisilane (II). This compound (15.4 g, 0.10 mol) was allowed to react with oxygen at room temperature. An exothermic reaction occurred. After 1.3 l absorption of oxygen (ca. 8 h), a white insoluble solid began to deposit and the rate of absorption immediately decreased. It took more than 30 h to complete the reaction and at that time about 1.37 l (0.061 mol) of oxygen had been absorbed. The reaction mixtures from three similar runs were combined and filtered to remove the white solid, which was washed with hexane and dried (0.7 g). The IR spectrum of the solid was essentially the same as that of commercially available paraformaldehyde. [Found: C, 39.31; H, 6.61. $(CH_2O)_n$ calcd.: C, 40.01; H, 6.71%.] The filtrate weighed 42.0 g and involved about 0.3 g of an insoluble liquid (possibly water). The organic layer of the filtrate was distilled under reduced pressure to give 39.5 g of a liquid boiling up to 95°C/10 Torr, which was collected in a Dry-Ice/acetone trap, leaving 2 g of residue. The above distillate was fractionally distilled through a short column packed with glass helicies under atmospheric pressure to give 18.0 g (35% yield) of *sym*-difluorotetramethyldisiloxane, b.p. 82°C, n_D^{20} 1.3390 (lit. [22] b.p. 71-72°C/751 Torr, n_D^{20} 1.3360, d_4^{20} 0.9605), and a second fraction (b.p. 91-150°C, 9.5 g) consisting of two major products and a few minor ones, leaving 7 g of residue. The two major products were isolated in a satisfactorily pure state by preparative GLC (Silicone DC 550, 70°C) and identified tentatively as VII (mol. wt. found: 232. $C_4H_{11}F_3O_2Si_3$ calcd.: 232.38), ^1H NMR (δ): 0.25 (d, 9H, J(F—H) 6Hz), 0.26 (d, 2H, J(F—H) 5Hz), and as VIII (mol. wt. found: 228. $C_6H_{18}F_2OSi_3$ calcd.: 228.46)), ^{1}H NMR (δ); 0.15 (d, 6H, J(F—H) 6Hz), 0.27 (d, 6H, J(F—H) 2Hz), 0.34 (d, 6H, J(F—H) 6 Hz). Compound VIII reacted with bromine, consistent with the presence of the silicon—silicon bond, while VII did not. The product ratio $(FMe_2Si)_2$-O/VII/VIII was estimated as 1.0/0.12/0.04.



(VII)

$FMe_2SiSiMe_2OSiMe_2F$

(VIII)

Inhibition by 2,4,6-tri(t-butyl)phenol. When oxygen was bubbled through 7.7 g of II containing 20 mg of 2,4,6-tri(t-butyl)phenol, little absorption of the gas was observed even after 26 h.

With 1,1,2,2-tetramethyl-1,2-disilacyclopentane (VIa). Oxygen was bubbled through 3.2 g (20 mmol) of VIa at room temperature. Exothermic absorption was immediately observed. After 328 ml of absorption (8.5 h), GLC analysis of the reaction mixture showed that the starting material was no longer present. The mixture remained clear, but had a pungent odor and contained a small amount of an insoluble liquid, possibly water. Distillation gave 2.5 g (72% yield) of 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane, b.p. 38-39°C/16 Torr, along with 0.5 g of residue.

Reaction with bis(trimethylsilyl) peroxide (BSPO)

The reaction was carried out in a small glass sealed tube, with the exception of compounds IV and V whose reactions were carried out in a tube with cooling in an ice or ice/salt bath. Reaction conditions, products and yields are summarized in Table 3 for disilanes and Table 5 for hydrosilanes. The products were characterized by IR (Table 4), ^{1}H NMR (Table 2) spectra and elemental analysis (Table 4). The products from hydrosilanes were also characterized by comparison with authentic samples and had satisfactory spectral and analytical data.

BSPO was prepared by a modified Hahn-Metzinger's method [16]. In a 500 ml three-necked flask, fitted with a stirrer, a condenser and a pressure-equalizing dropping funnel, were placed 20 ml of ether and 3.2 ml of 90% hydrogen peroxide under cooling in an ice bath. To the cooled solution was then added dropwise, with stirring, a solution of 21.8 g (0.20 mol) of trimethylchlorosilane in 20 ml of ether over a 30 min period. After stirring for another 30 min the mixture was diluted with 300 ml of ether and dry ammonia gas was introduced in order to remove the hydrogen chloride formed. Filtration, evaporation of solvent and subsequent distillation under reduced pressure through a short Vigreux column gave 6.5 g (36.5% yield) of BSPO boiling at 35-36°C/25 Torr.

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