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AN UNUSUAL BICYCLIC TETRASILOXANE

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Summary

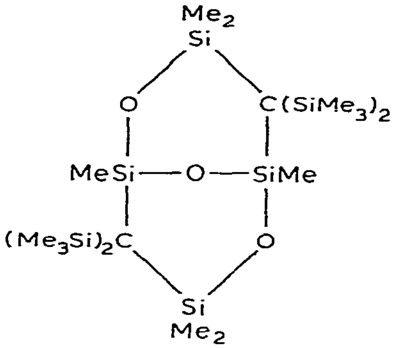
The compound $(Me_3Si)_3CSiPh_2I$ reacts with $AgClO_4$ in CH_3CN ("dried", but evidently containing some water) to give the tetrasiloxane 1,3,3′,5,7,7′-hexamethyl-4,4′,8,8′-tetra(trimethylsilyl)-2,6,9-trioxa-1,3,5,7-tetrasilabicyclo[3.3.1]nonane, the structure of which has been determined by an X-ray diffraction study. If more water is present, the same reaction gives $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$.

Introduction

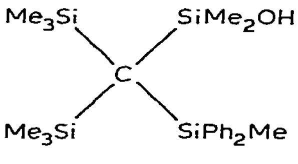
Studies of compounds of the type $(Me_3Si)_3CSiR_2X$, containing the tris(trimethylsilyl)methyl group (the "trisyl" group, denoted by Tsi) have revealed some highly novel chemistry [1—4]. We now describe the surprising formation of an unusual bicyclic tetrasiloxane derivative on treatment of $TsiSiPh_2I$ with $AgClO_4$ in CH_3CN (evidently containing some water) under conditions very similar to those which were observed previously to give the silanol $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$ [3].

Results and discussion

In an experiment in which $TsiSiPh_2I$ was treated under reflux with $AgClO_4$ (dried in vacuum) in CH_3CN which had been dried over a 4A molecular sieve, a solid was obtained (after work-up) which was shown by ^1H NMR spectroscopy to contain no aromatic groups. The mass spectrum indicated that the product had a molecular weight corresponding to the composition $[(Me_3Si)_2CSi_2Me_3O_{1.5}]_2$, i.e. a siloxane produced by dimerization of the triol formed by replacement of the iodine atom and both Ph groups of the $TsiSiPh_2I$ by hydroxyl groups; this product was isolated in 88% yield. A single crystal X-ray diffraction study showed that it was, in fact, the bicyclic tetrasiloxane 1,3,3′,5,7,7′-hexamethyl-4,4′,8,8′-tetra(trimethylsilyl)-2,6,9-trioxa-1,3,5,7-tetrasilabicyclo[3.3.1]nonane, I. (The compound is a tetrasiloxane because it contains the skeleton Si—O—Si—O—Si—O—Si.) Compound I reacted readily with CF_3CO_2H, to give a product with a ^1H NMR spectrum consistent with its being the expected tris(trifluoroacetate) $(Me_3Si)_2C(SiMe_2O_2CCF_3)[SiMe(O_2CCF_3)_2]$, formed by cleavage of all the Si—O bonds.



(I)



(II)

Structure determination

Crystal data: $C_{20}H_{54}O_3Si_8$, M = 567.3, monoclinic, a = 12.337(5), b = 17.499(3), c = 16.623(4) Å, β = 111.44(3)°, U = 3340.3 Å^3, Z = 4, D_c = 1.13 gcm^{-3}, $F(000)$ = 1240. Mo-K_α radiation, λ = 0.71069 Å, μ = 3.3 cm^{-1}. Space group $P2_1/n$ from systematic absences of $0k0$ for k odd, and $h0l$ for $h + l$ odd.

A crystal ca. 0.30 × 0.22 × 0.25 mm (obtained by crystallization from EtOH) was used for data collection on an Enraf-Nonius CAD4 diffractometer. Cell dimensions were derived from the setting angles for 25 reflections. Intensities for $hk \pm l$ data with $2 < \theta < 22$ were measured by a $\theta/2\theta$ scan with $\Delta\theta = (0.85 + 0.35 \tan\theta)°$ and monochromated Mo-K_α radiation. The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{-1} in θ with an initial acceptance limit ($I/\sigma I$) of 1. The final acceptance level was 20 with maximum recording time of 90 s. Three standard reflections monitored every 30 minutes showed no significant variation. After correction for Lorentz and polarisation effects but not for absorption, equivalent data were averaged and the 1505 reflections with $|F^2| > 3\sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were calculated as $[\sigma^2(I) + (0.05I)^2]^{1/2}/Lp$.

The non-hydrogen atoms were located by direct methods using the MULTAN program [7]. These atoms were refined by full matrix least squares with anisotropic temperature factors and converged at R = 0.080, R' = 0.103, with a maximum shift to error ratio of 0.02. The weighting scheme was $w = 1/\sigma^2(F)$. A final difference map had peaks of up to 0.4 eÅ^{-3}. No attempt was made to include hydrogen atoms.

The structure solution and refinement was done on a PDP11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms are taken from ref. 8. The structure and atom numbering scheme are shown in Fig. 1; the final atom coordinates are listed in Table 1, and bond lengths and angles in Table 2. Lists of temperature factors and final structure factors are available from the authors.

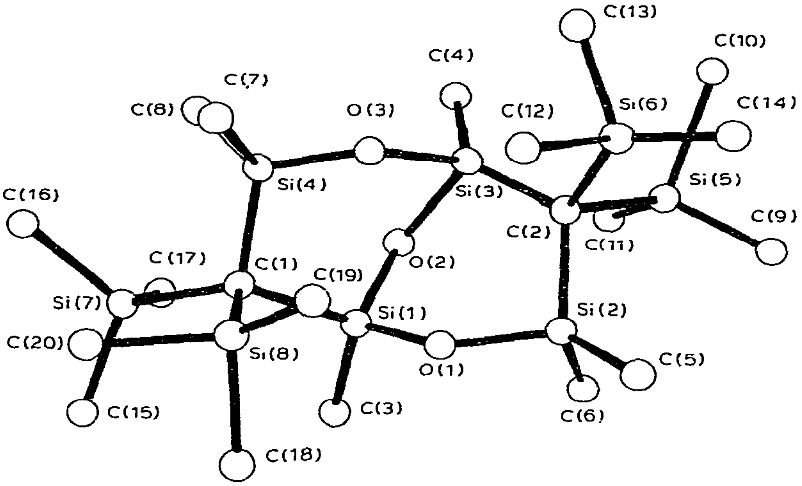


Fig. 1. Molecular structure of I, with numbering of atoms.

TABLE 1

FRACTIONAL ATOMIC COORDINATES (× 10^4) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	*y*	*z*
Si(1)	4139(4)	1231(3)	1515(3)
Si(2)	6567(4)	1712(3)	1902(3)
Si(3)	4561(4)	2803(3)	1403(3)
Si(4)	3145(4)	2355(3)	2419(3)
Si(5)	6665(5)	3159(4)	820(3)
Si(6)	6862(5)	3376(3)	2734(3)
Si(7)	1728(5)	873(3)	1674(4)
Si(8)	4061(5)	720(3)	3251(3)
O(1)	5507(9)	1263(6)	2111(6)
O(2)	3947(8)	2011(6)	910(5)
O(3)	4246(8)	2785(6)	2284(6)
C(1)	3225(13)	1278(9)	2225(9)
C(2)	6162(13)	2752(8)	1707(9)
C(3)	3836(17)	392(12)	778(12)
C(4)	3795(16)	3648(11)	694(11)
C(5)	7989(16)	1492(11)	2772(12)
C(6)	6630(17)	1171(12)	927(11)
C(7)	3207(17)	2603(11)	3546(11)
C(8)	1776(17)	2807(12)	1625(13)
C(9)	8194(14)	2866(11)	996(10)
C(10)	6628(17)	4236(11)	769(12)
C(11)	5667(18)	2799(14)	—309(11)
C(12)	6818(20)	2876(13)	3778(11)
C(13)	6064(18)	4298(11)	2659(13)
C(14)	8439(17)	3620(12)	2980(12)
C(15)	1679(16)	—231(11)	1643(14)
C(16)	695(15)	1167(12)	2218(12)
C(17)	992(20)	1161(16)	466(13)
C(18)	4636(20)	—209(11)	3010(16)
C(19)	5402(18)	1199(14)	4060(12)
C(20)	3035(16)	488(12)	3874(11)

TABLE 2

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

a) Bonds

Si(1)—O(1)	1.616(9)	Si(1)—O(2)	1.660(8)
Si(1)—C(1)	1.909(12)	Si(1)—C(3)	1.860(14)
Si(2)—O(1)	1.667(9)	Si(2)—C(2)	1.884(12)
Si(2)—C(5)	1.860(15)	Si(2)—C(6)	1.903(14)
Si(3)—O(2)	1.647(8)	Si(3)—O(3)	1.648(8)
Si(3)—C(2)	1.854(13)	Si(3)—C(4)	1.910(13)
Si(4)—O(3)	1.638(9)	Si(4)—C(1)	1.921(12)
Si(4)—C(7)	1.896(14)	Si(4)—C(8)	1.89(2)
Si(5)—C(2)	1.933(11)	Si(5)—C(9)	1.871(14)
Si(5)—C(10)	1.89(2)	Si(5)—C(11)	1.935(14)
Si(6)—C(2)	1.943(11)	Si(6)—C(12)	1.962(14)
Si(6)—C(13)	1.869(15)	Si(6)—C(14)	1.88(2)
Si(7)—C(1)	1.874(12)	Si(7)—C(15)	1.933(14)
Si(7)—C(16)	1.884(15)	Si(7)—C(17)	1.94(2)
Si(8)—C(1)	1.909(12)	Si(8)—C(18)	1.88(2)
Si(8)—C(19)	1.90(2)	Si(8)—C(20)	1.948(13)

b) Angles

O(1)—Si(1)—O(2)	103.2(4)	O(1)—Si(1)—C(1)	109.9(5)
O(1)—Si(1)—C(3)	110.1(7)	O(2)—Si(1)—C(1)	110.7(5)
O(2)—Si(1)—C(3)	107.5(6)	C(1)—Si(1)—C(3)	114.8(6)
O(1)—Si(2)—C(2)	108.2(5)	O(1)—Si(2)—C(5)	109.3(6)
O(1)—Si(2)—C(6)	102.8(6)	C(2)—Si(2)—C(5)	116.7(6)
C(2)—Si(2)—C(6)	115.1(6)	C(5)—Si(2)—C(6)	103.8(7)
O(2)—Si(3)—O(3)	102.2(4)	O(2)—Si(3)—C(2)	110.2(5)
O(2)—Si(3)—C(4)	108.1(5)	O(3)—Si(3)—C(2)	109.3(5)
O(3)—Si(3)—C(4)	109.8(6)	C(2)—Si(3)—C(4)	116.3(6)
O(3)—Si(4)—C(1)	109.4(5)	O(3)—Si(4)—C(7)	107.1(6)
O(3)—Si(4)—C(8)	106.6(6)	C(1)—Si(4)—C(7)	113.8(6)
C(1)—Si(4)—C(8)	112.3(6)	C(7)—Si(4)—C(8)	107.3(7)
C(2)—Si(5)—C(9)	111.4(6)	C(2)—Si(5)—C(10)	113.1(6)
C(2)—Si(5)—C(11)	110.7(6)	C(9)—Si(5)—C(10)	106.7(7)
C(9)—Si(5)—C(11)	108.1(7)	C(10)—Si(5)—C(11)	106.5(8)
C(2)—Si(6)—C(12)	112.3(6)	C(2)—Si(6)—C(13)	111.9(7)
C(2)—Si(6)—C(14)	114.2(6)	C(12)—Si(6)—C(13)	105.0(7)
C(12)—Si(6)—C(14)	105.6(7)	C(13)—Si(6)—C(14)	107.2(7)
C(1)—Si(7)—C(15)	114.0(6)	C(1)—Si(7)—C(16)	112.4(6)
C(1)—Si(7)—C(17)	114.3(6)	C(15)—Si(7)—C(16)	105.4(6)
C(15)—Si(7)—C(17)	103.5(8)	C(16)—Si(7)—C(17)	106.4(7)
C(1)—Si(8)—C(18)	112.1(7)	C(1)—Si(8)—C(19)	116.9(6)
C(1)—Si(8)—C(20)	109.7(6)	C(18)—Si(8)—C(19)	103.5(8)
C(18)—Si(8)—C(20)	107.6(7)	C(19)—Si(8)—C(20)	106.4(7)
Si(1)—O(1)—Si(2)	127.7(5)	Si(1)—O(2)—Si(3)	116.9(4)
Si(3)—O(3)—Si(4)	127.4(5)	Si(1)—C(1)—Si(4)	102.9(6)
Si(1)—C(1)—Si(7)	112.4(6)	Si(1)—C(1)—Si(8)	106.4(6)
Si(4)—C(1)—Si(7)	110.6(6)	Si(4)—C(1)—Si(8)	113.3(6)
Si(7)—C(1)—Si(8)	110.9(6)	Si(2)—C(2)—Si(3)	106.4(6)
Si(2)—C(2)—Si(5)	110.4(6)	Si(2)—C(2)—Si(6)	112.8(6)
Si(3)—C(2)—Si(5)	112.4(6)	Si(3)—C(2)—Si(6)	107.4(6)
Si(5)—C(2)—Si(6)	107.4(6)		

Structural features

The structure of the tetrasiloxane is not fully symmetrical, as might appear from the planar representation I. (The symmetry is C_2.) In Fig. 2 the bridging oxygen atom O(2) lies below the 8-membered ring, and thus is nearer to Si(5) and Si(7) than to Si(6) and Si(8); in keeping with this, the resonances for the Me_3Si groups in the ^1H NMR spectrum appear as a doublet (see Experimental section).

The Si—O bond lengths fall in the range observed for a series of cyclic organosiloxanes [9], but the mean Si—C bond length for all 26 such bonds, 1.90 Å, is probably significantly greater than the 1.87 Å usually regarded as normal for alkyl—silicon bonds [10]. The strain is mainly accommodated by minor adjustments of all the bond angles. The intracyclic Si—C—Si angles, Si(1)—C(1)—Si(4) and Si(2)—C(2)—Si(3) (mean 104.6) are probably significantly less than the tetrahedral angle, and there is apparently a closing up of Me—Si—Me angles, the mean being 105.5° (with r.m.s. deviation of 1.3°). The bridgehead O—Si—O angles O(1)—Si(1)—O(2) and O(2)—Si(3)—O(3), (mean 102.7°) are notably small. The Si(1)—O(2)—Si(3) angle at the bridging oxygen, 116.9°, is unusually low, and markedly smaller than the other Si—O—Si angles [Si(1)—O(1)—Si(2) and Si(3)—O(3)—Si(4)], which have a mean value, of 127.5°, at the bottom end of a wide range of Si—O—Si angles observed in cyclic organosiloxanes [9].

Formation of I

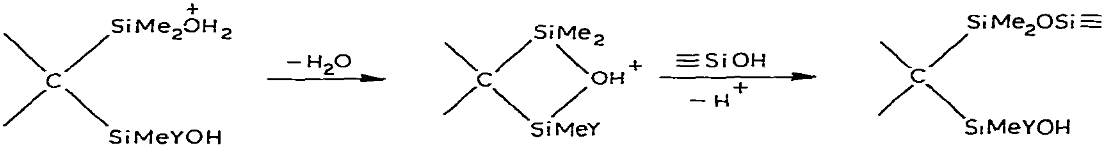
The isolation of the tetrasiloxane I in 88% yield from the reaction of $TsiSiPh_2I$ with "dried" $AgClO_4$ in "dried" CH_3CN contrasts with the isolation of the silanol $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$, II, in 50% yield from a similar reaction involving the use of $AgClO_4$ and CH_3CN without any drying [3]. In fact, using new batches of "dried" $AgClO_4$ and CH_3CN, we were never able to reproduce the 88% yield of I, but we were able to demonstrate that (contrary to what might be expected from stoichiometry) the formation of I is favoured by a low, and that of the simple silanol II by a high, water concentration, and the silanol is virtually the only product if the CH_3CN contains >1% of water. When we used a newly supplied batch of CH_3CN along with $AgClO_4$ from a newly opened bottle, the ^1H NMR spectrum of the isolated product mixture showed it to consist predominantly of the tetrasiloxane I; there were additional peaks present, including a relatively prominent singlet at δ 0.30 ppm, but none corresponding to the silanol. A similar result was obtained when the CH_3CN was dried by refluxing over and distillation from CaH_2 and the $AgClO_4$ was dried over P_2O_5 for 48 h at ca. 1 mmHg. With 1 vol % of water added to the CH_3CN the product was very predominantly the simple silanol II, and this was essentially the only product with 5 or 10 vol % of water present.

The first step in the formation of I from $TsiSiPh_2I$ in CH_3CN containing very small amounts of water can be confidently assumed to be the formation of the rearranged silanol II. This reaction will generate $HClO_4$, and with only a little water present to solvate it, this acid then presumably cleaves the Si—Ph bonds to give Si—OH bonds and benzene, whereas with more water present the acid is rendered less active and no cleavage occurs. In keeping with this, when a mixture of the silanol II and Me_3SiCl in CH_3CN was treated with $AgClO_4$ in order to generate $HClO_4$ (the CH_3CN and $AgClO_4$ being from the batches which gave predominantly I from $TsiSiPh_2I$), the ^1H NMR spectrum showed that benzene was formed, though a multiplet consistent with residual Si—Ph bonds was also apparent. The product mixture gave a complex ^{1}H NMR spectrum, which did not include peaks characteristic of I but did have a prominent peak at δ 0.30 ppm which also appeared in the spectrum of the mixture, consisting predominantly of I, obtained when $TsiSiPh_2I$ was treated with $AgClO_4$ containing only a little water (as noted above). It is likely that the mixture contained species in which only one of the original two Si—Ph bonds had been cleaved, possibly along with corresponding diol and siloxane species.

It is significant that when the related compounds $TsiSiMe_2Ph$ was treated with Me_3SiCl and $AgClO_4$ in CH_3CN, with the same reagents and solvents and under the same conditions as those used with II, no reaction occurred, and so some special factor must operate in II to facilitate the Si—Ph cleavage. There is evidence [5] that the OR group in structures such as $(Me_3Si)_2C(SiMe_2OR)$-$(SiMe_2X)$ can strongly assist the leaving of the group X, no doubt by a bridging similar in type, but much more powerful, than that by the Me group [2,4] *, and it seems likely that such bridging by the OH group assists the cleavage of the Si—Ph bonds in II. However, the oxygen of the siloxane $[(Me_3Si)_2C(SiPh_2$-$Me)(SiMe_2O_{0.5})]_2$ could probably provide the same type of assistance (possibly less effectively), and we cannot rule out the possibility that this is formed cleavage of a Si—Ph bond. When hydroxyl groups are present on two silicon atoms, bridging by one such group should facilitate disiloxane formation at the other silicon centre (see Scheme 1), and subsequently this disiloxane group would assist condensation of the remaining SiOH group. The question of whether the triol $(Me_3Si)_2C[SiMe(OH)_2](SiMe_2OH)$ is ever present during the formation of I or whether siloxane formation precedes cleavage of the second Si—Ph bond cannot be answered at present.

SCHEME 1

ILLUSTRATION OF ANCHIMERIC ASSISTANCE BY ONE SiOH TO SILOXANE FORMATION AT ANOTHER SiOH CENTRE



It is remarkable that the condensation of the initial silanol product(s) gives exclusively or very predominantly the cyclic dimeric species I when a range of cyclic and acyclic oligomers could, in principle, be formed.

Experimental

The CH_3CN was supplied by May and Baker, Ltd., as containing <0.3% of water; two different batches, A and B were used. The $AgClO_4$ was supplied by BDH Chemicals, Ltd.

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[*] We now believe that the anchimeric assistance by O_2CCH_3 and O_2CCF_3 groups involves bridging by the oxygen atom linked to silicon, not via the carbonyl oxygen as previously suggested [6].

The preparations of $TsiSiPh_2I$ [1] and $TsiSiMe_2Ph$ [11] have been described previously.

Reaction of $TsiSiPh_2I$ with $AgClO_4$ in CH_3CN

(a) For these experiments, CH_3CN from batch A was stored over an activated Molecular Sieve Type 4A for several days before use, and the $AgClO_4$ was dried at 0.2 mmHg for 6 h.

A mixture of $TsiSiPh_2I$ (0.50 g, 0.90 mmol), $AgClO_4$ (0.39 g, 1.4 mmol) and CH_3CN (15 cm^3) was refluxed for 2 h, then the solution was decanted from the AgI and evaporated under vacuum. The residual solid was recrystallized twice from EtOH to give I (0.45 g, 88%), m.p. 181°C; ^1H NMR (CCl_4): 0.23 (s, 18 H, $SiMe_3$), 0.27 (s, 18 H, Me_3Si), 0.38 (s, 18 H, $SiMe_2$ + SiMe) ppm (Found: C, 42.3; H, 9.5. Calcd. for $C_{20}H_{54}O_3Si_8$: C, 42.4; H, 9.5%). The mass spectrum showed a small molecular ion at m/e 566, and the expected large peak at 551 (M — Me); the main peaks (with relative intensities) were m/e 566(1), 551(100), 536(2), 463(9), 375(4), 265(6), 201(9), 73(35).

A similar experiment but with a different work-up, involving filtration of the product solution, addition of an excess of hexane, and repeated washing with water, followed by drying of the hexane extract, evaporation to dryness, and two recrystallizations of the residue from ethanol gave the same compound in slightly lower yield.

(b) In this experiment, CH_3CN of batch B and $AgClO_4$ were used as supplied.

A mixture of $TsiSiPh_2I$ (0.10 g, 0.18 mmol), $AgClO_4$ (0.060 g, 0.28 mmol) and CH_3CN (3 cm^3) was refluxed for 2 h. The solution was decanted from the AgI and added to hexane (10 cm^3), and the resulting solution was washed several times with water, then evaporated. The ^1H NMR spectrum of the residue showed it to consist predominantly of I, but there were other minor peaks, an additional prominent singlet in the Me_3Si region at δ 0.30 ppm, and a multiplet in the Ph region indicating that some Si—Ph bonds remained.

(c) The procedure described under (b) was repeated, but with CH_3CN of batch B 'dried' by refluxing over CaH_2 for 1 h and distillation from this hydride, and $AgClO_4$ dried over P_2O_5 at 1 mmHg for 48 h. The ^1H NMR of the product mixture was very similar to that described under (b).

(d) The procedure described under (b) was used but with CH_3CN to which 1 vol % of H_2O had been added. The ^1H NMR spectrum showed that the product consisted very predominantly of the silanol II. In similar experiments with CH_3CN containing 5 or 10 vol % of H_2O the product was virtually pure II.

Treatment of $(Me_3Si)_2C(SiPh_2Me)(SiMe_2OH)$, II, or $TsiSiMe_2Ph$ with Me_3SiCl and $AgClO_4$ in CH_3CN

In these experiments the $AgClO_4$ and CH_3CN used were as specified under (b) above.

(i) A mixture of silanol II (0.10 g, 0.23 mmol), Me_3SiCl (0.039 g, 0.36 mmol), $AgClO_4$ (0.068 g, 0.33 mmol), and CH_3CN (4 cm^3) was refluxed for 2 h. After this time the ^1H NMR spectrum of the cooled solution showed the presence of benzene. Work-up as in (b) gave a residue with a complex ^1H NMR spectrum; none of the peaks expected for siloxane I were present, but the singlet at δ 0.30 ppm noted under (b) was prominent, and there was a multiplet in the aromatic region indicating that Si—Ph bonds remained. GLC analysis showed the presence of 5 main and several minor components.

(ii) A mixture of $TsiSiMe_2Ph$ (0.10 g, 0.27 mmol), Me_3SiCl (0.043 g, 0.40 mmol), $AgClO_4$ (0.076 g, 0.37 mmol) and CH_3CN (5 cm^3) was refluxed for 2 h. After this time the ^1H NMR spectrum of the cooled solution showed that no benzene was present. Work-up as under (b) gave only unchanged $TsiSiMe_2Ph$.

Reaction of I with CF_3CO_2H

A solution of the siloxane I in CF_3CO_2H was made up in an NMR tube. The ^1H NMR spectrum (90 MHz) was consistent with the exclusive presence of $(Me_3Si)_2C[SiMe(O_2CCF_3)_2](SiMe_2O_2CCF_3)$; δ (ppm) 0.36 (s) and 0.39 (s) (of equal intensity, with combined integration of 18 H), 0.55 (s, 6 H), and 0.66 (s, 3 H).

Acknowledgments

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