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Phosphorus-containing disiloxanes: synthesis and thermal rearrangement of the 1,2-shift type

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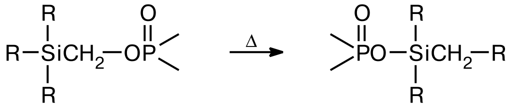
Methods for the synthesis of tetramethylbis(ω-phosphoryloxyalkyl)disiloxanes were developed. Thermal rearrangement of the 1,2-shift type of tetramethylbis(phosphoryloxymethyl)disiloxanes was studied. The 1,2-shift rearrangement of dimethyl(diphenoxyphosphoryloxymethyl)silyl hydrogen sulfate was found.

Key words: phosphorus-containing disiloxanes, synthesis, thermal 1,2-shift rearrangement.

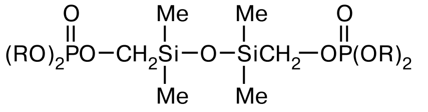
Thermally initiated rearrangements of the 1,2-shift type have been discovered and rather widely studied[1—8] to date for many silylmethyl esters of oxygen-containing acids of pentavalent phosphorus. The rearrangement is the migration of radical R from the silicon atom to the methylenic carbon atom to form the corresponding silyl esters of phosphorus acids (Scheme 1).

Scheme 1



In all cases studied, the R substituent is a hydrogen atom or a hydrocarbon radical (alkyl or aryl). The migration of heteroatomic substituents from the silicon atom in the 1,2-shift rearrangements is poorly studied and described only for several chloromethylsilanes (the migrating group is PhMeN, PhO,[9] or Me_3Si[10]).

We studied the 1,2-shift rearrangement in the series of disiloxanes, *viz*., diphosphorylated derivatives of 2,2,4,4-tetramethyl-2,4-disila-3-oxapentane-1,5-diol (**1a,b**).



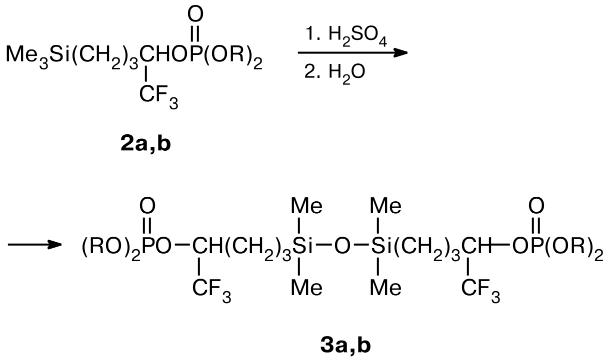
$$(RO)_2P(O)-CH_2Si(Me)_2-O-Si(Me)_2CH_2-OP(O)(OR)_2$$

1a,b

R = Ph (**a**), CH_2CF_3 (**b**)

The classical method for the synthesis of functionalized disiloxanes is the reaction of the corresponding trimethylsilyl compounds with concentrated sulfuric acid followed by hydrolysis.[11] In this case, the functional group should be stable toward hydrolysis under the reaction conditions. We have shown that for phosphates **2a,b**, which are potentionally stable to the 1,2-shift rearrangement due to the remote position of the silicon atom from the functional group, this method produces disiloxanes **3a,b** (Scheme 2).

Scheme 2



The reaction accompanied by methane evolution begins already on heating to 45 °C, and after hydrolysis with water the target disiloxanes **3a,b** are formed in ~100% yield.

Thus, both diphenoxyl- and bis(trifluoroethoxy)phosphoryl groups are stable on heating with concentrated sulfuric acid, whereas the resulting disiloxanes **3a,b** are thermally stable (at least on heating at 200 °C for 5 h).

When $Me_3SiCH_2OP(O)(OR)_2$ (**4a,b**) is treated with concentrated sulfuric acid, the reaction begins only on

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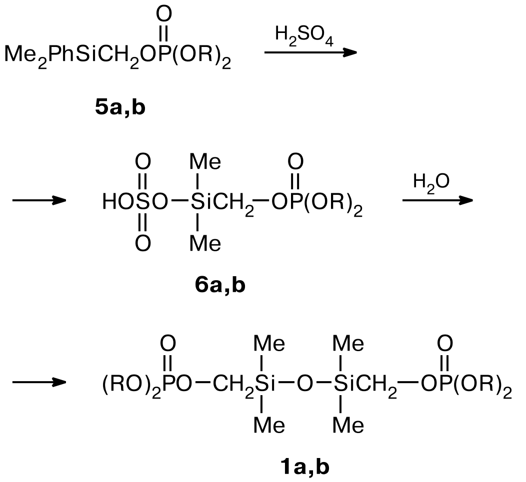
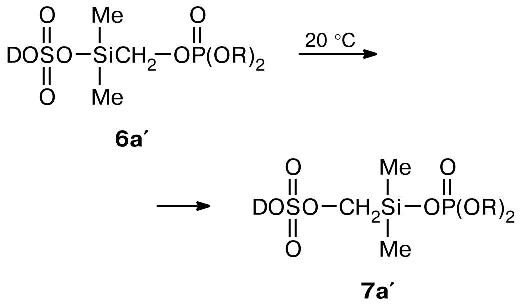
heating to 70 °C and is accompanied by the complete decomposition of the starting substrate. Since sulfuric acid eliminates the phenyl group from the silicon atom under milder conditions than the methyl group does,[12] the target disiloxanes **1a,b** were synthesized by the reaction between dimethyl(phenyl)silylmethyl phosphates $Me_2PhSiCH_2OP(O)(OR)_2$ (**5a,b**) and sulfuric acid followed by the hydrolysis of the intermediate reaction product, namely, silyl hydrogen sulfate (**6a,b**) (Scheme 3).

Scheme 3



According to the data of the ^{31}P NMR spectra, after 5 min the reaction mixture contains no starting phosphate **5a,b**. However, the yield of disiloxanes **1a,b** decreases substantially with an increase in the duration of the first reaction step. If the hydrolysis is carried out several hours after sulfuric acid addition, the disiloxane cannot be isolated. To study this fact, we carried out the reaction of phosphate **5a** with deuterated sulfuric acid and monitored the reaction course by NMR. At 20 °C, already after 20 min, the ^{1}H NMR spectrum of the reaction mixture contains a singlet signal at δ 5.79 (~10%) along with the doublet of the CH_2 protons of silyl hydrogen sulfate **6a´** at δ 5.59. The intensity of the singlet signal in the ^{1}H NMR spectrum increases gradually during the reaction. After 9 h, the doublet signal disappears completely, and the only signal is observed in the region of CH_2 protons: the singlet at δ 5.18. Similarly, after 20 min, the ^{31}P NMR spectrum of the reaction mixture contains the signal of silyl hydrogen sulfate **6a´** at δ −11.33 and an additional signal at δ −18.16. After 9 h, the single signal appears in the ^{31}P NMR spectrum at δ −14.64, which corresponds, most likely, to free diphenylphosphoric acid. These data suggest that phosphate **6a´** undergoes the rearrangement at room temperature: the hydrogen sulfate group migrates from the silicon atom to the methylenic carbon atom to form silyl phosphate **7a´** (Scheme 4).

Scheme 4



Probably, this rearrangement is a reason for the decrease in the yield of disiloxanes on prolonged storage of the reaction mixture. Therefore, the reactions of phosphates **5a,b** with concentrated sulfuric acid were further carried out in methylene chloride with cooling to 0 °C, and the reaction mixture was hydrolyzed 5 min after the reactants were mixed. This procedure enabled us to obtain disiloxanes **1a** and **1b** in 77 and 73% yields, respectively.

Phosphorylated disiloxanes **1a,b** were heated at 150 °C. According to the data of the ^{1}H and ^{31}P NMR spectra (Table 1), at this temperature the disiloxanes undergo the 1,2-shift rearrangement.* The siloxy group migrates dur-

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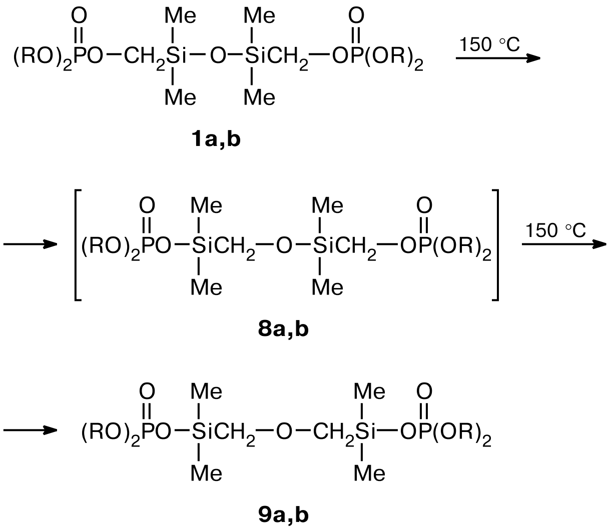
* According to the NMR spectral data, the rearrangement of disiloxanes **1a,b** begins already on heating to 125 °C.

Table 1. Some parameters of the ^{1}H and ^{31}P NMR spectra of compounds **1**, **8**, and **9** in the reaction mixtures after heating of phosphorus-containing disiloxanes **1a,b** at 150 °C for 5 h

Starting compound	NMR, δ, *J*/Hz							
	^{1}H (region of $SiCH_2$ protons)				^{31}P			
	1	**8**		**9**	**1**	**8**		**9**
	$SiCH_2OP$ (d)	$SiCH_2OP$ (d, $J_{H,P}$ = 6.2)	$SiCH_2OSi$ (s)	$SiCH_2OCH_2$ (s)	$SiCH_2OP$ (s)	$SiCH_2OP$ (s)	CH_2SiOP	CH_2SiOP
1a	3.70 ($J_{H,P}$ = 6.2)	3.87	2.81	2.96	−9.87	−10.01	−20.50 (br.s)	
1b	3.71 ($J_{H,P}$ = 5.8)	3.92	3.00	3.19	−0.07	−0.24	−10.43 (br.s)	

ing the rearrangement from the silicon atom to the methylenic carbon atom to form intermediate silylmethyl ester **8a,b**, and then the silylmethoxy group of the latter migrates to produce ether **9a,b** (Scheme 5).

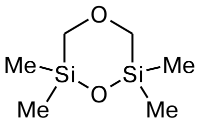
Scheme 5



After compound **1a** was heated for 5 h, two signals of approximately equal intensities appeared along with the doublet signal of the starting compound (δ 3.70) in the ^{1}H NMR spectrum in the region of signals of the CH_2 protons: a doublet signal at δ 3.87 and a singlet at δ 2.81. They are attributed, most likely, to the $SiCH_2OP$ protons and $SiCH_2OSi$ protons of phosphate **8a** (13% in the mixture). This spectrum also contains a low-intensity signal at δ 2.96 (the CH_2OCH_2 protons of the products of complete rearrangement of **9a**, 2%). The further heating results in a decrease in the intensity of the signal of the methylene protons of the starting compound and an increase followed by a decrease in the intensity of the doublet downfield signal and the singlet signal at δ 2.81. The intensity of the singlet signal at δ 2.96 increases gradually. After 90 h, this signal remains the only one in the region where methylene protons appear. A similar transformation of the signal of the methylenic protons is detected in the ^{1}H NMR spectrum when disiloxane **1b** is heated (see Table 1).

The ^{31}P NMR spectra of phosphorus-containing disiloxanes **1a,b** after their heating at 150 °C for 5 h exhibit, along with the signal of the starting phosphate, the appearance of an additional closely lying singlet, which corresponds, most likely, to the phosphorus atom of the non-rearranged fragment of disiloxane **8**, and a broad signal in the region where silyl phosphates appear. This signal is assigned to non-separated signals of the phosphorus atom of the CH_2SiOP group of phosphates **8** and **9**. After 90 h, the signal of silyl ether **9** remains the only signal in the ^{31}P NMR spectrum.

The product of complete rearrangement, *viz.*, phosphorus-containing ether **9a,b**, was hydrolyzed with water and extracted with ether; phenol and $(PhO)_2P(O)OH$ were removed by washing out with a saturated solution of Na_2CO_3. After the solvent was distilled off, the disiloxane fraction was partially polymerized. According to the data of GC-MS and ^{1}H NMR spectroscopy, the structure of cyclic disiloxane **10** can be ascribed to the main monomeric component of the resulting disiloxane fraction (see Experimental). This structure indirectly confirms the structure of silyl ether **9**.



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Thus, we developed the methods for the synthesis of phosphorus-containing disiloxanes and showed that phosphates based on dimethylsilylmethanol containing the oxy substituent at the silicon atom undergo the 1,2-shift thermal rearrangement that consists in the migration of the oxy substituent (OSO_3H, $OSiMe_2CH_2$—, OCH_2SiMe_2—) from the Si atom to the methylenic carbon atom. The presence of the oxy group at the silicon atom decreases substantially the thermal stability of silylmethyl phosphates compared to that of silylmethyl phosphates containing three carbon substituents at the silicon atom. In addition, the thermal stability of silylmethyl phosphates decreases with an enhancement of the electron-withdrawing ability of the oxy substituent. For example, phosphates **6a,b** containing the most withdrawing sulfate group are rearranged even at room temperature, whereas trialkylsilylmethyl phosphates are stable[3] on heating to 175 °C. The rearrangement of compounds **1**, **6**, and **8** involved no migration of the methyl group, which is well consistent with the previously[8] obtained data that the most electronegative substituent migrates predominantly from the silicon atom during the 1,2-shift.

Experimental

NMR spectra were recorded on a Bruker WP-200SY instrument in $CDCl_3$. The signals of residual protons of the deuterated solvent were used as the internal standard for ^{1}H NMR spectra, and the external standard for ^{31}P NMR spectra was H_3PO_4. GC-MS analysis was carried out on a Varian-3400 chromatograph with the DB-1 capillary column (30 m×0.32 mm; layer thickness 0.25 μm) in the temperature-programmed regime from 60 to 250 °C. The rate of the programmed temperature increase was 6 °C min^{-1}, a Finnigan-MAT 800 AT ion trap was used as the detector, and electron impact energy was 70 eV.

The yields, physicochemical constants, and results of elemental analyses of phosphates **1—3** are presented in Table 2. The data of ^{1}H, ^{19}F {^{1}H}, and ^{31}P{H} NMR spectra are given in Table 3. The data of ^{1}H and ^{31}P{^{1}H} NMR spectroscopy for compounds **9a,b** are presented in Table 4.

Table 2. Yields, physicochemical constants, and elemental analysis data for phosphates **1—3**

Compound	Yield (%)	n_D^{20}	Found/Calculated (%) C	H	P	Si	Molecular formula
1a	77	1.5282	55.14 54.70	5.63 5.51	8.99 9.40	8.64 8.53	$C_{30}H_{36}O_9P_2Si_2$
1b	73	1.3775	24.99 24.64	3.56 3.54	8.66 9.08	8.34 8.23	$C_{14}H_{24}F_{12}O_9P_2Si_2$
2a	50	1.4810	53.41 53.80	5.58 5.87	9.96 6.94	6.30 6.29	$C_{20}H_{26}F_3O_4PSi$
2b	69	1.3720	31.75 31.45	4.47 4.40	6.39 6.76	6.22 6.13	$C_{12}H_{20}F_9O_4PSi$
3a	94	1.4851	52.20 51.93	5.45 5.28	7.05 7.05	6.21 6.39	$C_{38}H_{46}F_6O_9P_2Si_2$
3b	97	1.3745	29.27 29.28	3.91 3.80	6.77 6.68	6.13 6.22	$C_{22}H_{34}F_{18}O_9P_2Si_2$

Table 3. ^1H, ^{19}F, and ^{31}P NMR spectral data for phosphates **1—3a,b**

Compound	Solvent	NMR, δ, *J*/Hz: ^1H MeSi (s)	$SiCH_2$	$CH_2C\underline{H}_2CH_2$ (m)	$C\underline{H}_2CH$ (m)	CH (m)	R (m)	$^{19}F\{^1H\}$ CF_3CH (s)	CF_3CH_2 (s)	$^{31}P\{^1H\}$ (s)
1a	$CDCl_3$	0.15	3.93 (d, $J_{H,P}$ = 6.2)	—	—	—	7.21—7.39	—	—	−9.89
1b	$CDCl_3$	0.31	3.93 (d, $J_{H,P}$ = 5.8)	—	—	—	4.50—4.96	—		0.17
2a	C_6D_6	−0.39	0.24—0.55 (m)	1.18—1.52	1.58—1.82	5.73—5.91	7.05—7.32		—	−11.87
2b	C_6D_6	−1.23	0.34—0.57 (m)	1.19—1.56	1.58—1.87	4.52—4.72	4.16—4.39	0.05	2.42, 2.29*	−2.48
3a	C_6D_6	0.12	0.31—0.67 (m)	1.31—1.99		5.05—5.26	6.85—7.00 (*p*-H); 7.03—7.10 (*m*-H); 7.34—7.38 (*o*-H)	0.83	—	−12.01
3b	C_6D_6	0.19	0.37—0.79 (m)	1.32—1.93		4.74—5.00	3.94—4.24	−0.08	2.10, 2.28*	−2.65

* Signals of magnetically nonequivalent CF_3CH_2 groups.

Table 4. ^1H and ^{31}P NMR spectral data for ethers **9a,b**

Compound	NMR, δ: ^1H MeSi (s)	$SiCH_2$ (s)	R (m)	$^{31}P\{^1H\}$ (s)
9a	0.26	3.20	6.86—7.46	−20.29
9b	0.56	3.53	3.99—4.03	−10.88

Synthesis of disiloxanes 1a,b (general procedure). Phosphate **5a,b** [5] (0.01 mol) in anhydrous CH_2Cl_2 (15 mL) was added with stirring and ice-cooling (~0 °C) for 1—2 min to a mixture of concentrated H_2SO_4 (5 mL) and anhydrous CH_2Cl_2 (15 mL). The reaction mixture was stirred for 5 min, poured onto ice, and extracted with ether (3×30 mL). The organic extracts were washed with a saturated solution of $NaHCO_3$ (20 mL), dried with $MgSO_4$, and chromatographed on Al_2O_3 (eluent ether). The solvent was distilled off *in vacuo*.

Rearrangement of disiloxanes 1a,b. Disiloxane **1a** or **1b** was heated in a sealed NMR tube for 90 h at 125 °C. The course of rearrangement was monitored by ^1H and ^{31}P NMR spectroscopy.

(1,1,1-Trifluoro-5-trimethylsilylpent-2-yl)diphenyl phosphate (2a). A mixture of 1,1,1-trifluoro-5-trimethylsilylpentan-2-ol[13]

(2.35 g, 0.011 mol), diphenyl chlorophosphate (2.67 g, 0.010 mol), and Mg (0.012 g, 0.0005 mol) was heated at 160 °C for 12 h until HCl evolution ceased. The reaction mixture was cooled, kept for 0.5 h in a vacuum of a water-jet pump, and chromatographed on Al_2O_3 (ether as eluent). The solvent was distilled off, and the residue was distilled *in vacuo*. Phosphate **2a** (2.23 g) was obtained, b.p. 178—179 °C (1 Torr).

(1,1,1-Trifluoro-5-trimethylsilylpent-2-yl)bis(2,2,2-trifluoroethyl) phosphate (2b). Similarly to the synthesis of **2a**, phosphate **2b** (2.51 g, b.p. 78—79 °C (1 Torr)) was obtained from 1,1,1-trifluoro-5-trimethylsilylpentan-2-ol (1.87 g, 0.009 mol), bis(2,2,2-trifluoroethyl) chlorophosphate (2.22 g, 0.008 mol), and Mg (0.0095 g, 0.0004 mol) by the 5-h reaction at 160 °C.

Synthesis of disiloxanes 3a,b (general procedure). A mixture of phosphate **2a,b** (0.01 mol) and concentrated H_2SO_4 (5 mL) was heated at 45 °C until methane evolution ceased. The reaction mixture was poured onto ice and extracted with ether (3×30 mL). The organic extracts were washed with a saturated solution of $NaHCO_3$ (20 mL), dried with $MgSO_4$, and chromatographed on Al_2O_3 (ether as eluent). The solvent was distilled off *in vacuo*.

1,4-Dioxa-2,6-disila-2,2,6,6-tetramethylhexane (10). Phosphate **1a** (6.6 g, 0.01 mol) was heated for 4 h at 200 °C. The reaction mixture was hydrolyzed with water (10 mL) and extracted with ether (30 mL). The organic layer was washed with a saturated solution of Na_2CO_3 (3×10 mL) and dried with $MgSO_4$. The solvent was distilled off. A siloxane fraction (1.7 g, 96%) was obtained. Cyclic disiloxane **10** (purity 80%, 0.3 g, 17%) was obtained from this fraction on heating to 200 °C in a vacuum of a water-jet pump (10 Torr). Mass spectrum, m/z (I_{rel} (%)): 177 $[M + 1]^+$ (12), 161 $[M - Me]^+$ (71), 133 $[Me_2SiOSiMe_2 + 1]^+$ (100), 103 $[M - SiMe_2 + 1]^+$ (48), 73 $[Me_2SiCH_2 + 1]^+$ (87), 59 $[Me_2Si + 1]^+$ (70). ^1H NMR (C_6D_6), δ: 0.21 (s, 12 H, MeSi); 3.30 (s, 4 H, CH_2).

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