Synthesis and thermal stability of silicon-containing esters of phosphorus acids

5.* The relative migration ability of substituents at the silicon atom in the thermal rearrangement of trialkylsilylmethyl diphenyl phosphates

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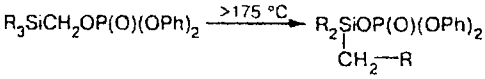
A number of trialkylsilylmethyl diphenyl phosphates $MeRR'SiCH_2OP(O)(OPh)_2$ (**1a—e**: R = Et (**a**), Pr (**b**), $CF_3CH_2CH_2$ (**c**, **e**), Me_3SiCH_2 (**d**); R′ = Me (**a—d**), Et (**e**)) were synthesized and their thermal rearrangement, of the 1,2-shift type, was studied. The rearrangement consists of the migration of an alkyl group from Si atom to the methylene carbon atom and gives the corresponding silyl esters. The rate of the rearrangement was found to increase in the order **1d** < **1b** < **1a** < **1** (R = R′ = Me) < **1c** corresponding to the enhancement of the total inductive effect (−*I*) of the substituents at the Si atom. The relative migration ability of the substituents at the Si atom, determined by GC/MS analysis of the disiloxane fraction resulting from hydrolysis of pyrolyzed phosphates **1a—e**, increases in the order R = Pr < Et < $CF_3CH_2CH_2$ < Me ≪ Me_3SiCH_2, which differs substantially from the order in which the rate of the rearrangement of phosphates **1a—d** changes. The electronegativity of the migrating group affects noticeably the relative ability to migrate.

Key words: trialkylsilylmethyl diphenyl phosphates, thermal rearrangement, relative migration ability of substituents.

The ability of various alkyl substituents at the Si atom to migrate in rearrangements of the 1,2-shift type has been studied mainly in relation to rearrangements of trialkyl(chloromethyl)silanes either catalyzed by Lewis acids (mostly $AlCl_3$)[2] or caused by fluoride ions.[3,4] By now, thermally induced rearrangements of the 1,2-shift type have been discovered and studied fairly comprehensively for a large number of silylmethyl esters of oxygen-containing acids of pentavalent phosphorus.[1,5—10] However, the relative migration ability (RMA) of substituents at the Si atom has not been studied systematically. It is known that a hydride ion migrates more preferably than a methyl group,[10] and during the thermal rearrangement of dimethylphenylsilylmethyl diphenyl phosphate, only the phenyl group migrates.[9]

The present study is devoted to the determination of relative migration abilities of alkyl groups in the thermal rearrangement of trialkylsilylmethyl phosphates.

Previously we have shown[9] that on heating above 175 °C, trialkylsilylmethyl diphenyl phosphates undergo rearrangement accompanied by the migration of an alkyl radical R from the Si atom to the methylene C atom to give the corresponding silyl esters.



$$R_3SiCH_2OP(O)(OPh)_2 \xrightarrow{>175\ ^\circ C} R_2\underset{\begin{array}{c}|\\ CH_2-R\end{array}}{Si}OP(O)(OPh)_2$$

It was found that the rearrangement rate increases in the following sequence of substituents: R = Pr < Et < Me < $CF_3CH_2CH_2$.

To study the RMA of substituents at the Si atom, we chose a series of dimethylalkylsilylmethyl diphenyl phosphates (**1a—d**) and compared the rates of migration of the groups R with that of the methyl group. In order to find out whether or not the RMA depends on the nature of the neighboring substituents attached to the Si atom, we also studied the thermolysis of ethyl(methyl)(3,3,3-trifluoropropyl)silylmethyl diphenyl phosphate (**1e**).

Phosphates **1a—e** were synthesized by the previously described[9] procedure (Scheme 1).

The rearrangement of phosphates **1a—d** can give two types of silyl esters (**5a—d** and **6a—d**) resulting from the migration of radical R or one of the methyl groups attached to the Si atom, respectively (Scheme 2).

The rearrangement of phosphate **1e** can, in principle, give three silyl esters (**7—9**), the products of migration of the methyl, ethyl, or trifluoropropyl group from the Si atom, respectively (Scheme 3).

In fact, the ^1H NMR spectra of the four pyrolyzates obtained by heating phosphates **1a—d** for 5 h at 200 °C,

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* For Part 4, see Ref. 1.

[†] Deceased.

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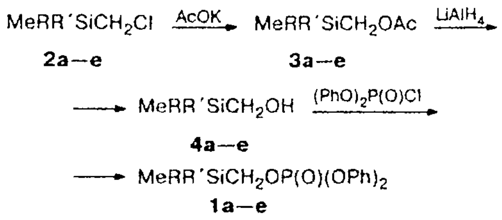
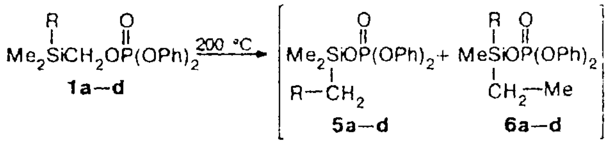
Scheme 1



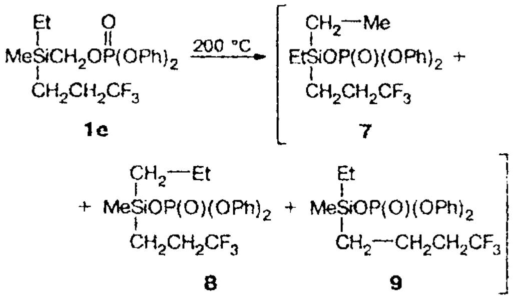
R = Et (**a**), Pr (**b**), $CF_3CH_2CH_2$ (**c**, **e**), Me_3SiCH_2 (**d**);
R' = Me (**a**—**d**), Et (**e**)

Scheme 2



in addition to the signals of the initial compounds, contained two singlets in the region typical of silylmethyl protons in the rearranged silyl esters (δ 0.17—0.25). This indicates the formation of two rearranged products. The ^{1}H NMR spectrum of the pyrolyzate formed from phosphate **1e**, together with the signal for the silylmethyl groups of the initial compound, contained two singlets belonging to the methyl groups in silyl esters **8** and **9** (silyl phosphate **7** does not contain Me groups attached to the Si atom).

Scheme 3



When phosphates **1a**—**e** were kept at 200 °C for 5 h, one unresolved broad signal with δ −20 to −21 from the thermolysis products appeared in the ^{31}P NMR spectra in all cases. The degree of rearrangement was determined from the ratio of the signal areas of the initial phosphate and the resulting silyl esters. The rate of rearrangement of phosphates **1a**—**e**, as in the case of the thermal rearrangement of the trialkylsilylmethyl diphenyl phosphates studied previously,[9] increased with an increase in the total inductive effect −*I* ($\Sigma\sigma_I$) of the substituents R and R' at the Si atom (Table 1). Thus for compounds **1a**—**d**, the rearrangement rate increases in the order R = Me_3SiCH_2 < Pr < Et < Me < $CF_3CH_2CH_2$.

Table 1. Degree of rearrangement (η) of phosphates **1a**—**e**

Starting compound	R	R'	$\Sigma\sigma_I$	η (%)
1a	Et	Me	−0.080	39
1b	Pr	Me	−0.080	37
1c	$CF_3CH_2CH_2$	Me	0.007	65
1d	Me_3SiCH_2	Me	−0.120	30
1e	$CF_3CH_2CH_2$	Et	−0.013	63
$Me_3SiCH_2OP(O)(OPh)_2$		Me	−0.060	58[7]

Note. The $\Sigma\sigma_I$ values were calculated using the σ_I values reported in the literature.[11]

The relative migration ability of substituent R at the Si atom (θ_R) in compounds **1a**—**d** was calculated based on the ratio of the yield of silyl phosphate **5a**—**d** (Q_{5a-d}) to the yield of the corresponding silyl phosphate **6a**—**d** (Q_{6a-d}) using Eq. (1) with allowance for the probability coefficient. The RMAs of the trifluoropropyl and ethyl groups in relation to the methyl group during thermal rearrangement of phosphate **1e** were calculated from Eqs. (2) and (3), respectively.

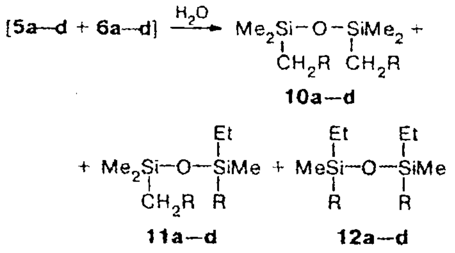
$$\theta_R = 2Q_{5a-d}/Q_{6a-d} \qquad (1)$$

$$\theta_{CF_3CH_2CH_2} = Q_9/Q_7 \qquad (2)$$

$$\theta_{Et} = Q_8/Q_7 \qquad (3)$$

To determine the yields of the silyl esters resulting from thermolysis of phosphates **1a**—**e**, the pyrolysis products were hydrolyzed. Hydrolysis of the mixture of silyl esters **5a**—**d** and **6a**—**d** gave a ternary mixture of the corresponding isomeric disiloxanes **10**—**12** (Scheme 4).

Scheme 4



Hydrolysis of the products of thermolysis of phosphate **1e**, silyl esters **7**—**9**, gave a six-component mixture consisting of isomeric disiloxanes **13**—**18** (Scheme 5).

The qualitative and quantitative compositions of the disiloxane fractions of the hydrolysis products were determined by GC/MS analysis. The GC/MS data are presented in Table 2.

Table 2. Data of GC/MS analysis of the products of hydrolysis of pyrolyzed phosphates **1a—e**

Starting compound	Products of the pyrolyzate hydrolysis[a]	MS,[b] m/z (I_{rel} (%))	S (%)[c]
1a	**10a**	202 $[M-Me-1]^+$ (11), 174 $[M-Pr-1]^+$ (7), 133 $[M-2Pr+1]^+$ (100)	4.6
	11a	202 $[M-Me-1]^+$ (7.5), 188 $[M-Et-1]^+$ (24), 174 $[M-Pr-1]^+$ (18), 147 $[M-Et-Pr+1]^+$ (100)	60.8
	12a	202 $[M-Me-1]^+$ (13), 188 $[M-Et-1]^+$ (78), 161 $[M-2Et+1]^+$ (100)	34.6
1b	**10b**	230 $[M-Me-1]^+$ (34), 188 $[M-Bu-1]^+$ (21), 133 $[M-2Bu+1]^+$ (100)	5.5
	11b	230 $[M-Me-1]^+$ (100), 216 $[M-Et-1]^+$ (27), 202 $[M-Pr-1]^+$ (19), 188 $[M-Bu-1]^+$ (53), 147 $[M-Pr-Bu+1]^+$ (100)	65.0
	12b	230 $[M-Me-1]^+$ (59), 216 $[M-Et-1]^+$ (42), 202 $[M-Pr-1]^+$ (27), 188 $[M-2Et+1]^+$ (62), 161 $[M-2Pr+1]^+$ (61)	29.5
1c	**10c**	151 $[M-2R_FCH_2+F]^+$ (100),[d] 77 $[Me_2SiF]^+$ (36)	6.5
	11c	165 $[M-R_FCH_2-R_F+F]^+$ (33), 147 $[M-R_FCH_2-R_F+1]^+$ (100), 91 $[MeEtSiF]^+$ (38)	54.3
	12c	179 $[M-2R_F+F]^+$ (10), 91 $[MeEtSiF]^+$ (16)	39.2
1d	**10d**	319 $[M-Me]^+$ (100), 133 $[M-2Me_3SiCH_2CH_2+1]^+$ (33), 73 $[Me_3Si]^+$ (58)	69.7
	11d	319 $[M-Me]^+$ (100), 305 $[M-Et]^+$ (42), 233 $[M-Me_3SiCH_2CH_2]^+$ (20), 189 $[M-Me_3SiCH_2CH_2-Et-Me]^+$ (22), 131 $[M-Me_3SiCH_2CH_2-Me_3SiCH_2-Me]^+$ (36), 73 $[Me_3Si]^+$ (61)	17.1
	12d	319 $[M-Me]^+$ (75), 305 $[M-Et]^+$ (27), 233 $[M-Me_3SiCH_2-Me+1]^+$ (43), 73 $[Me_3Si]^+$ (100)	13.2
1e	**13**	207 $[M-2R_F+F]^+$ (7), 183 $[M-2R_F-Pr+2F]^+$ (9), 165 $[M-2R_F-Pr+F+1]^+$ (32), 161 $[C_6H_{17}OSi_2]^+$ (100), 141 $[M-2R_F-2Pr+2F+1]^+$ (15)	6.1
	14	193 $[M-R_F-R_FCH_2+F]^+$ (44), 183 $[M-R_F-R_FCH_2-Et+2F]^+$ (15), 165 $[M-R_F-R_FCH_2-Et+F+1]^+$ (23), 161 $[C_6H_{17}OSi_2]^+$ (100), 151 $[M-R_F-R_FCH_2-Pr+F+1]^+$ (78), 141 $[M-R_F-R_FCH_2-Et-Pr+2F+1]^+$ (52)	14.2
	15	207 $[M-2R_F+F]^+$ (17), 183 $[M-2R_F-Pr+2F]^+$ (6), 165 $[M-2R_F-Pr+F+1]^+$ (42), 161 $[C_6H_{17}OSi_2]^+$ (100), 155 $[M-2R_F-Pr-Et+2F]^+$ (25), 151 $[M-2R_F-2Et+F+2]^+$ (36)	25.4
	16	179 $[M-2R_FCH_2+F]^+$ (27), 169 $[M-2R_FCH_2-Et+2F]^+$ (22), 161 $[C_6H_{17}OSi_2]^+$ (100), 151 $[M-2R_FCH_2-Et+F+1]^+$ (40), 141 $[M-2R_FCH_2-2Et+2F+1]^+$ (11)	8.0
	17	193 $[M-R_F-R_FCH_2+F]^+$ (79), 183 $[M-R_F-R_FCH_2-Et+2F]^+$ (44), 165 $[M-R_F-R_FCH_2-Et+F+1]^+$ (67), 161 $[C_6H_{17}OSi_2]^+$ (100), 155 $[M-R_F-R_FCH_2-2Et+2F+1]^+$ (71)	28.5
	18	207 $[M-2R_F+F]^+$ (27), 197 $[M-2R_F-Et+2F]^+$ (13), 179 $[M-2R_F-Et+F+1]^+$ (22), 169 $[M-2R_F-2Et+2F+1]^+$ (29), 161 $[C_6H_{17}OSi_2]^+$ (76), 151 $[M-2R_F-2Et+F+2]^+$ (78)	17.8

[a] Disiloxane fraction.

[b] The most characteristic ions.

[c] The relative area of the chromatographic peak.

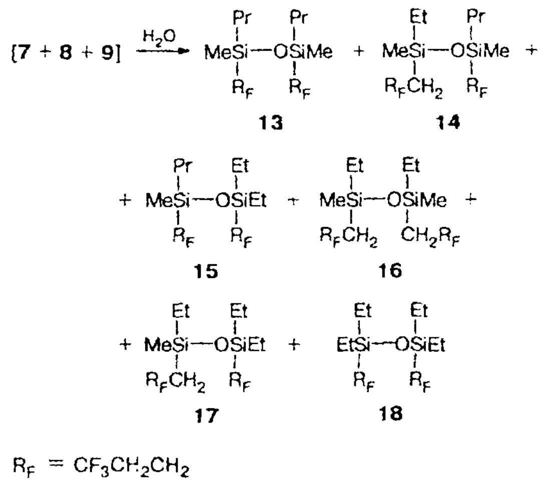
[d] $R_F = CF_3CH_2CH_2$.

The mass spectra of disiloxanes **10a,b,d** contain a peak for the $[M-2RCH_2+1]^+$ fragment ion. The fragmentation of asymmetrical disiloxanes **11a,b** yields the $[M-RCH_2-1]^+$ ions, and in the case of disiloxane **11d**, the $[M-RCH_2]^+$ ions are produced. The most characteristic peak in the mass spectra of compounds **12a,b** corresponds to the $[M-2R+1]^+$ ion.

The mass spectra of the disiloxane fraction of the products of hydrolysis of the pyrolyzed phosphates **1c,e** mainly exhibit peaks of rearranged ions, formed evidently upon migration of the F atom to the positively charged center on the Si atom. Thus the mass spectrum of disiloxane **10c** contains peaks of the $[Me_2SiF]^+$ and $[M-2R_FCH_2+F]^+$ ions formed upon skeletal rearrangements. The mass spectrum of asymmetrical disiloxane **11c** contains a peak for the $[M-R_FCH_2-R_F+1]^+$ ion, in addition to the peaks for the $[MeEtSiF]^+$ and $[M-R_FCH_2-R_F+F]^+$ ions. Fragmentation of disiloxane **12c** yields a rearranged ion, $[M-2R_F+F]^+$.

The mass spectra of disiloxanes **13—18**, in addition to the peaks of ions resulting from skeletal rearrangement involving the abstraction of two heaviest groups

Scheme 5



from the Si atom under the action of electron impact and migration of the F atom to Si, contain as well characteristic intense peaks of rearranged ions resulting from more extensive decay that involves abstraction of three substituents from the disiloxane molecule. The observed fragmentation permits in each case unambiguous assignment of the compounds. For ternary mixtures of isomeric disiloxanes **10**—**12**, the retention time of disiloxanes increases in the sequences **10a**—**c** < **11a**—**c** < **12a**—**c** and **12d** < **11d** < **10d**. The retention times of the disiloxanes obtained by hydrolysis of the pyrolyzed phosphate **1e** increase in the order **13** < **14** < **15** < **16** < **17** < **18**.

From the data on the percentages of components in the disiloxane mixtures obtained by hydrolysis of pyrolyzed phosphates **1a**—**e**, we calculated the yields of compounds **5a**—**d**, **6a**—**d**, and **7**—**9** using Eqs. (4)—(8), respectively.

$$Q_{5a-d} = 2S_{10a-d} + S_{11a-d}, \qquad (4)$$

$$Q_{6a-d} = S_{11a-d} + 2S_{12a-d}, \qquad (5)$$

$$Q_7 = S_{15} + S_{17} + 2S_{18}, \qquad (6)$$

$$Q_8 = 2S_{13} + S_{14} + S_{15}, \qquad (7)$$

$$Q_9 = S_{14} + 2S_{16} + S_{17}. \qquad (8)$$

where S is the relative area of the corresponding chromatographic peak.

The calculated RMA values for substituents at the Si atom in the thermal rearrangement of phosphates **1a**—**e** are listed below.

R	Me	Et	Pr	$CF_3CH_2CH_2$	Me_3SiCH_2
θ	1.00	0.56 (**1a**) 0.58 (**1e**)	0.51	0.71 (**1c**) 0.66 (**1e**)	7.20

The results obtained indicate that the RMAs of substituents at the Si atom increase in the following sequence of R: Pr < Et < $CF_3CH_2CH_2$ < Me ≪ Me_3SiCH_2. This sequence differs appreciably from the order of variation of the degree of rearrangement of phosphates **1a**—**d**; it virtually does not depend on the environment of the Si atom (*cf.* the RMA of the Et and $CF_3CH_2CH_2$ groups in molecules **1a** and **1e** and in molecules **1c** and **1e**, respectively) and agrees with the known Kharasch electronegativity series[12] Me_3SiCH_2 > Me > Pr > *s*-Alk.[13] Thus, the aptitude of an alkyl group for migration is largely determined by its ability to hold the electron pair during the migration from the Si atom to the methylene C atom.

Meanwhile, the overall rate of rearrangement markedly depends on the total inductive effect ($-I$) of the substituents attached to the Si atom, which facilitates or hampers the nucleophilic attack on this atom; this shows the important role of nucleophilic assistance to the thermally induced rearrangement of siliconeopentyl esters of phosphorus acids, due to the attack by the P=O group on the Si atom.

The results obtained are consistent with the rearrangement mechanism proposed in our previous study,[9] which includes nucleophilic attack by the O atom of the phosphoryl group on the Si atom and migration of a group with the electron pair from Si to the methylene C atom.

Experimental

NMR spectra were recorded on a Bruker WP-200SY spectrometer in $CDCl_3$ using $CHCl_3$ (^1H NMR), CF_3COOH (^{19}F NMR), and H_3PO_4 (^{31}P NMR) as external standards. The GC/MS analysis was performed using a Varian-3400 chromatograph with a DB-1 capillary column (30 m × 0.32 mm; 0.25 mm thick layer) with temperature programming from 60 to 250 °C at a rate of 6 °C/min. A Finnigan-MAT 800 AT ion trap was used as the detector; the electron impact energy was 70 eV.

The boiling points and the n_D^{20} values for compounds **2a**,[14] **2b**,[2] **2d**,[15] **3a**,[14] **3b**,[15] **4a**,[14] **4b**,[16] and **4d** [16] correspond to the published data.

Methyldialkylsilylmethyl diphenyl phosphates (1a—e) (general procedure). Diphenyl chlorophosphate (0.020 mol) in 5 mL of CH_2Cl_2 was added dropwise with stirring and cooling (water) to a mixture of compound **4a**—**e** (0.020 mol) and Et_3N (0.022 mol) in 5 mL of CH_2Cl_2. The reaction mixture was stirred for 2 h and left overnight. The precipitated $Et_3N \cdot HCl$ was filtered off and washed with ether, the filtrate was evaporated, and the residue was passed through an Al_2O_3 layer (using pentane as the eluent). Evaporation of the solvent gave phosphates **1a**—**e**. The yields, the n_D^{20} and d_4^{20} values, and the elemental analysis and $^{31}P-\{^1H\}$ NMR spectroscopy data for phosphates **1a**—**e** are listed in Table 3.

The ^1H NMR spectra of compounds **1**—**4(a**—**d)** are presented in Table 4.

Ethyl(methyl)(3,3,3-trifluoropropyl)silylmethyl diphenyl phosphate (1e). ^1H NMR ($CDCl_3$), δ: 0.05 (s, 3 H, MeSi); 0.56—0.62 (m, 3 H, $CH_2C\underline{H}_3$); 0.77—0.81 (m, 2 H, $C\underline{H}_2CH_3$); 0.90—0.96 (m, 2 H, $CH_2C\underline{H}_2Si$); 1.94—2.01 (m, 2 H, CF_3CH_2); 4.01 (d, 2 H, CH_2O, J = 5.7 Hz); 7.08—7.36 (m, 10 H, C_6H_5).

Table 3. Yields, main parameters, data of elemental analysis, and the ^{31}P NMR spectra of phosphates **1a—e**

Compound	Yield (%)	n_D^{20}	d_4^{20}	$\frac{\text{Found}}{\text{Calculated}}$ (%)				Molecular formula	^{31}P-{^{1}H} NMR (CDCl$_3$), δ
				C	H	P	Si		
1a	64	1.5153	1.1181	58.07 58.27	6.88 6.62	8.77 8.84	7.70 8.02	$C_{17}H_{23}O_4PSi$	−9.88
1b	78	1.5123	1.0959	59.18 59.32	6.92 6.91	8.43 8.50	7.53 7.71	$C_{18}H_{25}O_4PSi$	−9.78
1c	75	1.4879	1.2120	51.65 51.67	5.26 5.30	7.32 7.40	6.56 6.71	$C_{18}H_{22}F_3O_4PSi$	−9.55
1d	88	1.5054	1.2059	55.77 55.82	7.23 7.15	7.08 7.58	13.39 13.75	$C_{19}H_{29}O_4PSi_2$	−9.38
1e	86	1.4812	1.5507	52.51 52.76	5.81 5.60	7.17 6.79	6.51 6.47	$C_{19}H_{24}F_3O_4PSi$	−9.70

Chloromethyl(ethyl)dimethylsilane (2a). Chloro(chloromethyl)dimethylsilane (**19**) (21.45 g, 0.15 mol) in 30 mL of THF was added dropwise to a solution of the Grignard reagent prepared from EtBr (16.35 g, 0.15 mol) and Mg (3.60 g, 0.15 mol) in 70 mL of anhydrous ether. The solution was refluxed for 2 h and allowed to stand overnight. The reaction mixture was quenched by a solution of H_2SO_4 (30 mL) in 90 mL of water, the organic layer was separated, and the aqueous layer was extracted three times with ether. The combined ethereal extracts were washed with water and a saturated solution of $NaHCO_3$, and dried with $MgSO_4$. Evaporation of the solvent followed by vacuum distillation gave 12.1 g (59%) of chloromethylsilane **2a**, b.p. 60 °C (60 Torr), n_D^{20} 1.4292.

Chloromethyl(dimethyl)propylsilane (2b) was synthesized similarly to compound **2a** by the reaction of the Grignard reagent, prepared from Pr^{n}Cl (12.56 g, 0.16 mol) and Mg (3.84 g, 0.16 mol) in 75 mL of anhydrous ether, with compound **19** (21.45 g, 0.15 mol) in 70 mL of THF. The reaction gave 12.8 g (57%) of chloromethylsilane **2b**, b.p. 72 °C (60 Torr), n_D^{20} 1.4319.

Chloromethyl(dimethyl)(3,3,3-trifluoropropyl)silane (2c) was synthesized similarly to compound **2a** by the reaction of the Grignard reagent, prepared from $CF_3CH_2CH_2Cl$ (26.5 g, 0.20 mol) and Mg (4.8 g, 0.20 mol) in 80 mL of anhydrous ether, with compound **19** (22.9 g, 0.16 mol) in 80 mL of THF. The reaction gave 17.0 g (52%) of chloromethylsilane **2c**, b.p. 74 °C (44 Torr), n_D^{20} 1.4319 (*cf.* Ref. 17). Found (%): C, 35.99; H, 6.04; Cl, 17.33; F, 27.16; Si, 13.64. $C_6H_{12}ClF_3Si$. Calculated (%): C, 35.20; H, 5.91; Cl, 17.32; F, 27.84; Si, 13.72.

Chloromethyl(dimethyl)(trimethylsilylmethyl)silane (2d) was synthesized similarly to compound **2a** by the reaction of the Grignard reagent, prepared from Me_3SiCH_2Cl (29.55 g, 0.24 mol) and Mg (5.78 g, 0.24 mol) in 100 mL of anhydrous ether, with compound **19** (34.32 g, 0.24 mol) in 80 mL of THF. The reaction gave 29.6 g (73%) of chloromethylsilane **2d**, b.p. 85 °C (20 Torr), n_D^{20} 1.4470.

Chloromethyl(ethyl)(methyl)(3,3,3-trifluoropropyl)silane (2e). The Grignard reagent, prepared from $CF_3CH_2CH_2Cl$ (79.5 g, 0.6 mol) and Mg (14.4 g, 0.6 mol) in 400 mL of

Table 4. Parameters of the ^{1}H NMR spectra (δ, *J*/Hz) of compounds $Me_2(R)SiCH_2X$ (X = OP(O)(OPh)$_2$ (**1a—d**), Cl (**2a—d**), OAc (**3a—d**), OH (**4a—d**)) in CDCl$_3$

Compound	Me_2Si, δ (s)	Signals of R: $SiCH_2C$, δ	C—CH$_2$—C: δ	C—CH$_2$—C: J_{H-H}	CH$_3$, δ (m)	C$\underline{H}_2$X: δ	C$\underline{H}_2$X: J_{H-P}	X, δ
1a	0.01	0.47—0.60 (m)	—	—	0.86—0.93	3.67 (d)	5.7	7.09—7.34 (m)
1b	0.02	0.51—0.60 (m)	0.91 (t)	7.2	1.21—1.39	3.36 (d)	5.6	7.11—7.35 (m)
1c	0.12	0.80—0.89 (m)	1.96—2.10 (m)	—	—	4.05 (d)	5.7	7.18—7.42 (m)
1d*	0.06	−0.36 (s)	—	—	0.04	3.99 (d)	6.0	6.90—7.42 (m)
2a	0.07	0.59—0.66 (m)	—	—	0.91—0.98	2.75 (s)	—	—
2b	0.09	0.58—0.66 (m)	0.96 (t)	7.2	1.27—1.46	2.76 (s)	—	—
2c	0.15	0.83—0.92 (m)	1.96—2.20 (m)	—	—	2.80 (s)	—	—
2d*	0.13	−0.27 (s)	—	—	0.07	2.61 (s)	—	—
3a	0.04	0.43—0.55 (m)	—	—	0.83—0.91	3.70 (s)	—	1.95 (s)
3b	0.03	0.47—0.56 (m)	0.89 (t)	7.2	1.20—1.96	3.70 (s)	—	1.97 (s)
3c	0.05	0.73—0.82 (m)	1.90—2.14 (m)	—	—	3.74 (s)	—	1.99 (s)
3d*	0.12	−0.29 (s)	—	—	0.09	3.86 (s)	—	1.82 (s)
4a	0.07	0.44—0.52 (m)	—	—	0.82—0.91	3.62 (s)	—	2.70 (s)
4b	0	0.51—0.59 (m)	0.93 (t)	7.2	1.24—1.40	3.35 (s)	—	1.51 (s)
4c	0.05	0.75—0.84 (m)	1.93—2.18 (m)	—	—	3.38 (s)	—	1.99 (s)
4d*	0.19	−0.22 (s)	—	—	0.15	3.29 (s)	—	

* In C_6D_6.

anhydrous THF, was added dropwise to a solution of dichloro(chloromethyl)methylsilane (81.8 g, 0.5 mol) in 150 mL of anhydrous THF. The reaction mixture was refluxed for 2 h, and then EtMgBr, prepared from EtBr (54.5 g, 0.5 mol) and Mg (12.0 g, 0.5 mol) in 400 mL of anhydrous THF was added. The mixture was refluxed for an additional 2 h, diluted with 200 mL of THF, refluxed for 1 h, and allowed to stand overnight. The subsequent workup, similar to that described above for compound **2a**, and vacuum distillation gave 30.6 g (28%) of chloromethylsilane **2e**, b.p. 68—70 °C (14 Torr), n_D^{20} 1.4066, d_4^{20} 1.1074. Found (%): C, 38.41; H, 6.37; Cl, 16.04; F, 26.02; Si, 13.03. $C_7H_{14}ClF_3Si$. Calculated (%): C, 38.52; H, 6.47; Cl, 16.04; F, 26.14; Si, 12.83. ^1H NMR ($CDCl_3$), δ: 0.11 (s, 3 H, MeSi); 0.63—0.70 (m, 3 H, $CH_2C\underline{H}_3$); 0.86—0.90 (m, 2 H, $C\underline{H}_2CH_3$); 0.95—0.99 (m, 2 H, $CH_2C\underline{H}_2Si$); 2.02—2.14 (m, 2 H, CF_3CH_2); 2.80 (s, 2 H, CH_2Cl).

[Ethyl(dimethyl)silyl]methyl acetate (3a). A mixture of compound **2a** (11.8 g, 0.09 mol), AcOK (8.8 g, 0.09 mol), and 40 mL of DMF was stirred for 2 h at 145°. Then the reaction mixture was cooled, 30 mL of water was added, the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were washed with water and dried with $MgSO_4$. Evaporation of the solvent followed by vacuum distillation of the residue gave 8.8 g (64%) of acetate **3a**, b.p. 57 °C (18 Torr), n_D^{20} 1.4181.

[Dimethyl(propyl)silyl]methyl acetate (3b) was synthesized similarly to **3a** by the reaction of compound **2b** (8.3 g, 0.05 mol) and AcOK (5.9 g, 0.06 mol) in 25 mL of DMF. This gave 6.8 g (71%) of acetate **3b**, b.p. 70 °C (18 Torr), n_D^{20} 1.4212.

[Dimethyl(3,3,3-trifluoropropyl)silyl]methyl acetate (3c) was synthesized similarly to **3a** by the reaction of compound **2c** (12.0 g, 0.06 mol) with AcOK (5.9 g, 0.06 mol) in 25 mL of DMF. This gave 11.5 g (85%) of acetate **3c**, b.p. 83 °C (18 Torr), n_D^{20} 1.3910, d_4^{20} 1.0828. Found (%): C, 41.94; H, 6.57; F, 25.31; Si, 12.14. $C_8H_{15}F_3O_2Si$. Calculated (%): C, 42.09; H, 6.62; F, 24.95; Si, 12.30.

[Dimethyl(trimethylsilylmethyl)silyl]methyl acetate (3d) was synthesized similarly to **3a** by the reaction of compound **2d** (13.6 g, 0.07 mol) with AcOK (7.5 g, 0.08 mol) in 100 mL of DMF. This gave 11.5 g (75%) of acetate **3d**, b.p. 100 °C (17 Torr), n_D^{20} 1.4358, d_4^{20} 0.8890. Found (%): C, 49.42; H, 10.11; Si, 25.55. $C_9H_{22}O_2Si_2$. Calculated (%): C, 49.48; H, 10.15; Si, 25.72.

[Ethyl(methyl)(3,3,3-trifluoropropyl)silyl]methyl acetate (3e) was synthesized similarly to **3a** by the reaction of compound **2e** (12.0 g, 0.06 mol) with AcOK (5.9 g, 0.06 mol) in 30 mL of DMF. This gave 10.3 g (77%) of acetate **3e**, b.p. 90—92 °C (14 Torr), n_D^{20} 1.4003, d_4^{20} 1.0750. Found (%): C, 44.46; H, 7.08; F, 23.56; Si, 11.42. $C_9H_{17}F_3O_2Si$. Calculated (%): C, 44.61; H, 7.08; F, 23.54; Si, 11.56. ^1H NMR ($CDCl_3$), δ: 0.03 (s, 3 H, MeSi); 0.50—0.54 (m, 2 H, $C\underline{H}_2CH_3$); 0.75—0.84 (m, 2 H, $SiC\underline{H}_2CH_3$); 0.90—0.98 (m, 3 H, $CH_2C\underline{H}_3$); 1.99 (s, 3 H, $COCH_3$); 1.89—2.16 (m, 2 H, CF_3CH_2); 3.78 (s, 2 H, CH_2O).

[Ethyl(dimethyl)silyl]methanol (4a). Acetate **3a** (8.8 g, 0.06 mol) in 20 mL of ether was added dropwise with stirring to a suspension of $LiAlH_4$ (1.6 g, 0.04 mol) in 10 mL of anhydrous ether. The mixture was stirred for 2 h and quenched with aqueous H_2SO_4. The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic extracts were washed with water, and dried with $MgSO_4$. Evaporation of the solvent and vacuum distillation of the residue gave 4.2 g (65%) of silylmethanol **4a**, b.p. 57 °C (18 Torr), n_D^{20} 1.4308.

[Dimethyl(propyl)silyl]methanol (4b) was synthesized similarly to compound **4a** by the reaction of acetate **3b** (6.8 g, 0.04 mol) with $LiAlH_4$ (1.1 g, 0.03 mol). This gave 3.7 g (71%) of silylmethanol **4b**, b.p. 67 °C (14 Torr), n_D^{20} 1.4340.

[Dimethyl(3,3,3-trifluoropropyl)silyl]methanol (4c) was synthesized similarly to compound **4a** by the reaction of acetate **3c** (10.6 g, 0.05 mol) with $LiAlH_4$ (1.3 g, 0.04 mol). This gave 6.8 g (79%) of silylmethanol **4c**, b.p. 73 °C (18 Torr), n_D^{20} 1.3921, d_4^{20} 1.0984. Found (%): C, 38.47; H, 6.80; F, 30.75; Si, 15.02. $C_6H_{13}F_3OSi$. Calculated (%): C, 38.69; H, 7.04; F, 30.60; Si, 15.08.

[Dimethyl(trimethylsilylmethyl)silyl]methanol (4d) was synthesized similarly to compound **4a** by the reaction of acetate **3d** (7.0 g, 0.03 mol) with $LiAlH_4$ (1.1 g, 0.03 mol). This gave 4.4 g (64%) of silylmethanol **4d**, b.p. 96—98 °C (21 Torr), n_D^{20} 1.4488.

[Ethyl(methyl)(3,3,3-trifluoropropyl)silyl]methanol (4e) was synthesized similarly to compound **4a** by the reaction of acetate **3e** (7.5 g, 0.05 mol) with $LiAlH_4$ (0.9 g, 0.02 mol). This gave 5.0 g (81%) of silylmethanol **4e**, b.p. 86 °C (114 Torr), n_D^{20} 1.4041. Found (%): C, 41.74; H, 7.55; F, 28.34; Si, 13.84. $C_7H_{15}F_3OSi$. Calculated (%): C, 41.98; H, 7.56; F, 28.49; Si, 13.97. ^1H NMR ($CDCl_3$), δ: 0.03 (s, 3 H, MeSi); 0.59 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.9 Hz); 0.76—0.86 (m, 2 H, $SiC\underline{H}_2CH_3$); 0.95 (t, 3 H, $CH_2C\underline{H}_3$, J = 7.9 Hz); 1.75 (s, 1 H, OH); 1.89—2.20 (m, 2 H, CF_3CH_2); 3.42 (s, 2 H, CH_2O).

Thermolysis of dialkylmethylsilylmethyl diphenyl phosphates 1a—e. Phosphate **1a—e** (0.7—1.0 g) was heated in a sealed tube at 200 °C for 5 h.

Hydrolysis of the pyrolyzates obtained from phosphates 1a—d. The pyrolyzates obtained from phosphates **1a—d** were hydrolyzed by treatment with 5 mL of water, the products were extracted with ether, and the combined organic extracts were dried with $MgSO_4$ and filtered through an Al_2O_3 layer. The filtrate was subjected to GC/MS analysis.

Hydrolysis of the pyrolyzate obtained from phosphate 1e. A mixture of the pyrolyzate from phosphate **1e** (0.1 g), C_6H_6 (0.5 mL), and aqueous H_2SO_4 (3 : 1) (0.5 mL) was refluxed for 1 h in a tube and cooled. The products were extracted with ether, and the combined organic extracts were dried with $MgSO_4$ and filtered through an Al_2O_3 layer. The filtrate was subjected to GC/MS analysis.

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