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Intramolecular O → Si Donor–Acceptor Interaction in $R_2P(=O)CH_2CH_2SiF_3$ Molecules: Synthesis of Dialkyl [2-(Trifluorosilyl)ethyl]phosphonate and Bis[(chloromethyl)dimethylsilyl] Styrylphosphonate

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Abstract—The reaction of diethyl [2-(triethoxysilyl)ethyl]phosphonate with boron trifluoride etherate was used to synthesize diethyl [2-(trifluorosilyl)ethyl]phosphonate. The reaction of bis(trimethylsilyl) styrylphosphonate with chloro(chloromethyl)dimethylsilane gave bis[(chloromethyl)dimethylsilyl] styrylphosphonate. Multinuclear ^1H, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR spectroscopy established the absence of a P=O → Si coordination bond in these compounds and the four-coordinate state of the silicon atom. Evidence for this finding was obtained by B3LYP/6-31G(d) quantum-chemical calculations. However, the same calculations for $R_2P(=O)\cdot CH_2CH_2SiF_3$ (R = Me, Me_2N) showed the presence in such molecules of an O → Si coordination bond both in the gas phase and in $CHCl_3$ solution. The distance between the O and Si atoms in this series molecules decreases with R in the order: MeO > Me > Me_2N. The axial Si–F bond length increases in the same order and parallels the order of the Hammet σ_m^0 constants of these substituents, relating to their interaction with π-electron systems.

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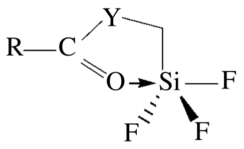
Earlier we discovered a new class of intramolecular complex compounds of five-coordinate silicon atom of general formula **I**,

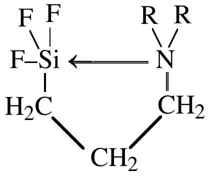


I

R = alkyl, aryl, alkoxyl; Y = O, S, NR', CH_2; R' = H, Alk.

More recently we devoted to such compounds a great number of publications which were mostly cited in [2, 3]. This class of compounds can also be considered to include (N → Si) (3-aminopropyl)trifluorosilane and its methyl derivatives [4, 5].

Furthermore, we established that *N*-trimethylsilyl derivatives of acylamides, lactams, cyclic amides, carbamide and acylhydrazines with chloro(chloromethyl)dimethylsilane afford (O → Si) chelate *N*-chlorodimethylsilylmethyl five-coordinate silicon derivatives with coordination heterocycle **V** [6–10]. Such compounds are formed in three consecutive steps: (1) persilylation reaction, (2) kinetically controlled intramolecular O-silylmetylation of intermediate **III**, and (3) thermodynamically controlled unusual Chapmen rearrangement of the resulting zwitter-ionic “isoamide” derivative **IV** into chelate reaction product **V** [6–10].



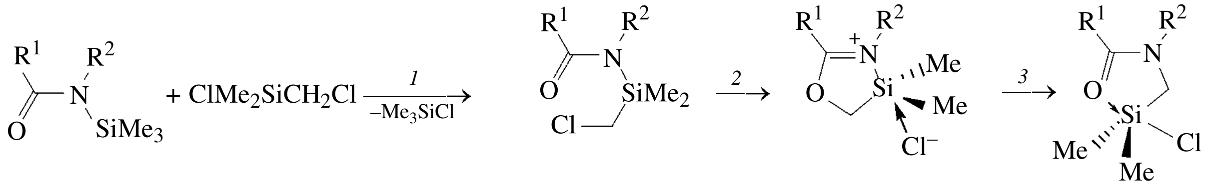
II

R = H, Me.

[†] Deceased.

Table 1. Parameters of the ^{1}H NMR spectra of compounds **XVI** and **Xb**

Comp. no.	$SiCH_2$	EtOSi		EtOP		CH_2P
		Me	CH_2O	Me	CH_2O	
XVI	0.85 m	1.21 t	3.81 q	1.31 t	4.09 d.q	1.75 m
Xb	1.32 m	–	–	1.35 t	4.32 m	2.17 m

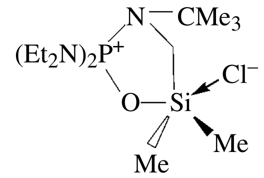


III **IV** **V**

R^1, R^2 = Alk, $-(CH_2)_n-$, n = 3–5; R = $NAlk_2$, R^2 = H, Alk.

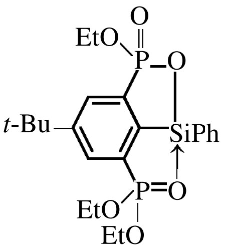
Proceeding with these studies we set ourselves the aim to synthesize chelate derivatives with a five-coordinate silicon in which the latter is bonded with phosphoryl group by a donor–acceptor bond.

Our first attempt to prepare such a complex containing an endocyclic P=O→Si bond gave un unexpected result [11]: The reaction of *N,N,N',N'*-tetraethyl-*N''*-*tert*-butylphosphoric triamide with BuLi and then with (chloromethyl)dimethylsilane yielded a cyclic five-coordinate silicon derivative containing an endocyclic POSi group with the silicon atom coordinated with Cl^- anion.

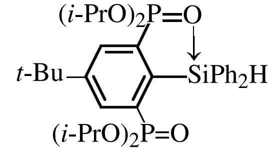


VI

First five-coordinate silicon compounds with a P=O→Si coordination bond (**VII**, **VIII**) were prepared quite recently [12, 13].

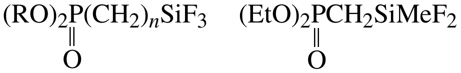


VII



VIII

We studied the possibility of existence of an intramolecular P=O→Si coordination bond.

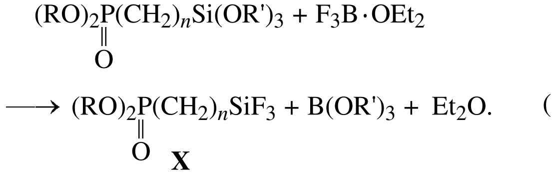


$$(RO)_2\underset{\displaystyle O}{\overset{}{\underset{\|}{P}}}(CH_2)_nSiF_3 \qquad (EtO)_2\underset{\displaystyle O}{\underset{\|}{P}}CH_2SiMeF_2$$

XI

R = Me, Et, n = 1 (**IX**); n = 2 (**X**), n = 2, R = Me (**Xa**), R = Et (**Xb**), R = Me, Et (**Xc**).

Such compounds were synthesized by the following scheme.



$$(RO)_2\underset{\displaystyle O}{\underset{\|}{P}}(CH_2)_nSi(OR')_3 + F_3B\cdot OEt_2$$
$$\longrightarrow (RO)_2\underset{\displaystyle O}{\underset{\|}{P}}(CH_2)_nSiF_3 + B(OR')_3 + Et_2O. \quad (1)$$

X

Compounds **IX** and **XI** (obtained by the same procedure) proved to be unstable and could not be isolated individual, because they decomposed on distillation to form $MeP(O)(OEt)_2$ (**XII**). Nevertheless, they were identified in the reaction mixture by ^{1}H, ^{12}C, ^{29}Si, and ^{31}P NMR and mass spectrometry. As the decomposition products of difluoride **XI** we also identified by the latter method $(F_2MeSi)_2O$ and $EtP(O)(OEt)_2$.

Phosphonate **Xb** was isolated individual as a colorless liquid, bp 163–165°C (12 mm Hg). Its composition and structure are confirmed completely by elemental analysis and multinuclear NMR (Tables 1 and 2).

Table 2. Parameters of the ^{13}C, ^{19}F, ^{29}Si and ^{31}P NMR spectra of compounds **XVI**^{a} and **Xb**^{b}

Comp. no.	CH_2Si	EtOP		EtOSi		CH_2P	δ_{Si}	δ_F	δ_P
		Me	CH_2O	Me	CH_2O				
XVI	2.24 d	16.14 d	61.17 d	17.93	58.22	18.50 d	–47.33 d	–	33.89
Xb	–0.98 d.q	15.65 d	66.91	–	–	16.00 d	–61.2 q.d	–137.61	33.21

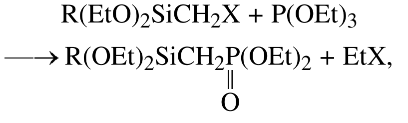
[a] Coupling constants for **XVI**: $^{2}J_{C–C–P}$ 8.1, $^{3}J_{C–C–O–P}$ 5.9, $^{2}J_{C–O–P}$ 6.63, $^{1}J_{C–P}$ 141.9, $^{3}J_{Si–C–C–P}$ 36.45 Hz. [b] Couplinf constants for **Xb**: $^{2}J_{C–Si–F}$ 22.0, $^{3}J_{C–C–O–P}$ 5.5, $^{1}J_{C–P}$ 146, $^{1}J_{Si–F}$ 277.5, $^{3}J_{Si–C–C–P}$ 37.4 Hz.

The ^{29}Si, ^{31}P, and ^{19}F chemical shifts and ^{29}Si–^{19}F and ^{29}Si–^{31}P coupling constants, as well as the invariability of the ^{29}Si chemical shift in the temperature range from –20 to +50°C ($CDCl_3$) or from 25 to 70°C ($CD_3C_6D_5$) attest the absence of intramolecular P=O → Si interaction in **Xb**, or this interaction is very weak.

Compounds **Xc** and **IX** have the same structure, as follows from their NMR chemical shifts: $F_3SiCH_2 \cdot CH_2P(O)(OMe)OEt$ (**Xc**): δ_{Si} –60 ppm, δ_F –134 ppm, $J_{Si–F}$ 270.7 Hz; $F_3SiCH_2P(O)(OEt)_2$ (**IX**): δ_{Si} –72.2 ppm, δ_F –146 ppm. These values are almost coincident with the chemical shifts of the model four-coordinate compound $ClCH_2SiF_3$ [14]: δ_{Si} –71.3 ppm, δ_F –144 ppm, $J_{Si–F}$ 267 Hz, thus providing further evidence for the absence of the P=O → Si coordination bond.

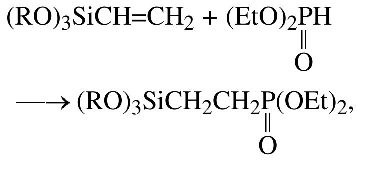
We failed to confirm the absence of the P=O → Si coordination bond in **IX**–**XI** by IR spectroscopy, since absorption bans of the SiF_3 groups in the range 700–1000 cm^{-1} overlapped with the following absorption bands: ν(P–C) 765, ν_s(P–O) 796, ν_{as}(P–O) 1160, and ν(P–O–C) 900–1100 cm^{-1} [15].

Precursors of compounds **IX** and **XI** were prepared by the Arbuzov reaction [16].



$$R(EtO)_2SiCH_2X + P(OEt)_3 \longrightarrow R(OEt)_2SiCH_2\underset{\underset{O}{\|}}{P}(OEt)_2 + EtX, \quad (2)$$

Precursors of compounds **Xa**–**Xc** were prepared by the addition of diethyl hydrogen phosphite to the corresponding vinyltrialkoxysilane in the presence of AIBN.

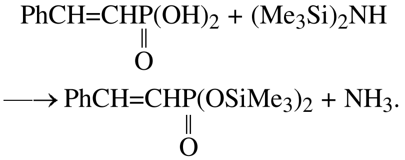


$$(RO)_3SiCH{=}CH_2 + (EtO)_2\underset{\underset{O}{\|}}{P}H \longrightarrow (RO)_3SiCH_2CH_2\underset{\underset{O}{\|}}{P}(OEt)_2, \quad (3)$$

R = Me (**XVb**), R = Et (**XVI**).

It is noteworthy that compound **XVb** is not the major reaction product. Simultaneously, $(MeO)_3Si \cdot CH_2CH_2P(O)(OMe)OEt$ (**XVc**) and $(MeO)_3SiCH_2 \cdot CH_2P(O)(OMe)_2$ (**XVa**) are formed by alkoxyl exchange between phosphorus and silicon. According to NMR and mass spectral data, the **XVa** : **XVb** : **XVc** molar ratio is 1 : 1 : 2.

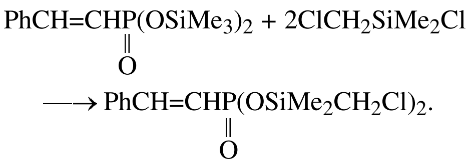
We also studied the possibility of formation of five-coordinate silicon compounds containing a P=O → Si bond in the reaction of $ClCH_2SiMe_2Cl$ with earlier unknown bis(trimethylsilyl) styrylphosphonate (**XVII**). The latter compound was prepared by the reaction of styrylphosphonic acid with hexamethyldisilazane in the presence of a catalytic amount of chlorotrimethylsilane.



$$PhCH{=}CH\underset{\underset{O}{\|}}{P}(OH)_2 + (Me_3Si)_2NH \longrightarrow PhCH{=}CH\underset{\underset{O}{\|}}{P}(OSiMe_3)_2 + NH_3. \quad (4)$$

XVII

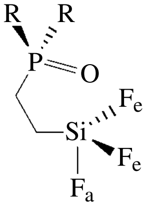
Further persilylation of phosphonate **XVII** with chloro(chloromethyl)dimethylsilane gave bis[(chloromethyl)dimethylsilyl] styrylphosphonate (**XVIII**). This compound contains no P=O → Si bond, and its silicon atom is four-coordinate, as evidenced by ^{29}Si NMR data (δ_{Si} 14.20 ppm).



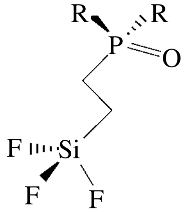
$$PhCH{=}CH\underset{\underset{O}{\|}}{P}(OSiMe_3)_2 + 2ClCH_2SiMe_2Cl \longrightarrow PhCH{=}CH\underset{\underset{O}{\|}}{P}(OSiMe_2CH_2Cl)_2. \quad (5)$$

XVIII

Compound **XVIII** undergoes no changes on prolonged heating in boiling toluene or in nitrobenzene at 80°C, as well as under microwave irradiation. To reveal the possibility of formation of a P=O → Si coordination bond in compounds **Xa** and **Xb** and related compounds **XIX** and **XX** (structures **A** or **B**), we applied quantum-chemical calculations by the B3LYP/6-31G(d) method.



A



B

R = OEt (**Xb**), OMe (**Xa**), NMe_2 (**XIX**), Me (**XX**).

The positive sign and the value of the experimentally measured ^{29}Si coordination shift in **Xb**, $\Delta\delta_{Si} = \delta_{Si}(\mathbf{Xb}) - \delta_{Si}(ClCH_2SiF_3) = 10.1$ ppm, provide indirect evidence for the absence of Si←O coordination bonding in this molecule in $CDCl_3$ solution. This conclusion is confirmed by quantum-chemical calculations which show that in structure **A** of **Xa**, where the oxygen lone pair is directed to the silicon atom, the distance between O and Si is 2.917 Å in the gas phase and 3.176 Å in $CHCl_3$ solution. These distances are only slightly shorter then the sum of the van der Waals radii of the oxygen and silicon atoms (3.62 Å) and much longer than the O–Si bond length in alkoxysilanes (1.63 Å) [17]. The axial Si–F bond length in form **A** of **Xa** is close to the equatorial bond lengths and to the Si–F distance in noncoodinated form **B** (Table 3). The calculated ^{29}Si chemical shifts δ_{Si} in **Xa** and coordination shifts $\Delta\delta_{Si}$ for structures **A** and **B** differ insignificantly and are close to experimental values for **Xb**. The small upfield shift (~4 ppm) of the silicon signal in structure **A** with respect to that in **B** can point to a very weak electrostatic interaction between the O and Si atoms in the coordinated form of **Xa**. Structures **Xa** and **Xb** are practically equal in energy. Inclusion of entropy factors results in further stabilization of the noncoodinated form (by 1.6–1.9 kcal mol^{-1}).

Replacement of two methoxy groups on phosphorus in **Xa** by the more electron-donor Me_2N groups significantly shortens the distance between Si and O (to 2.177 Å). Therewith, the axial Si–F bond is elongated by 0.28 Å and the deviation of the silicon atom from the plane of three equatorial fluorine atoms (δ_{Si}) is diminished by 0.238 Å. The coordination shift $\Delta\delta_{Si}$ in chelate form **A** of **XIX** in the gas phase is –17.3 ppm. In whole, the structural and spectral parameters of molecule **XIX** in coordinated form **A** show the existence of a P=O→Si coordination bond. These data point to equilibrium between the coordinated and noncoordinated forms of **XIX** in the gas phase. At the same time, in $CHCl_3$ solution the coordinated form of **XIX** is preferred over noncoordinated by more than 2 kcal mol^{-1}. The P=O→Si bond in solution is found to be 0.192 Å shorter than in the gas phase, the axial Si–F bond is 0.024 Å longer, and silicon shielding enhances by 9 ppm.

Table 3. Selected structural and spectral characteristics and relative energetics of coordinated (**A**) and noncoordinated (**B**) forms of **Xa** molecule in gas phase and in $CHCl_3$ solution

Form	A		B	
	vacuum	$CHCl_3$	vacuum	$CHCl_3$
Si–O, Å			5.108	5.117
Si–F_a, Å	2.917	3.176	1.596	1.599
Si–F_e(1), Å	1.605	1.604	1.597	1.599
Si–F_e(2), Å	1.603	1.596	1.595	1.598
C–Si–F_e(1), deg	1.591	1.599	111.1	111.6
C–Si–F_e(2), deg	117.0	114.0	111.5	111.9
O–Si–F_a, deg	179.2	172.8	–	–
Δ_{Si}, Å[a]	0.453	0.470	0.584	0.595
O–P–C–C, deg	20.3	57.8	–56.2	–57.8
P–C–C–Si, deg	–63.0	–57.7	179.3	179.0
ΔE, kcal mol^{-1} [b]	0.1	0.6	0.0	0.0
ΔH, kcal mol^{-1} [b]	–0.2	0.5	0.0	0.0
ΔG, kcal mol^{-1} [b]	–1.9	–1.6	0.0	0.0
δ_{Si}, ppm[c]	–63.0	–60.4	–59.0	–59.1
$\Delta\delta_{Si}$, ppm[d]	9.6	12.2	13.6	13.5

[a] Deviation of the silicon atom from the plane defined by three equatorial fluorine atoms. [b] The energy in form **B** is taken equal to be zero. [c] The δ_{Si} of **Xa** was measured against internal TMS. [d] Coordination shift defined as a difference of the δ_{Si} vales of **Xa** and the model compound $ClCH_2SiF_3$.

The calculated O→Si and axial Si–F bond lengths in dimethyl[1-(trifluorosilyl)ethyl]phosphine oxide in the gas phase are 2.268 and 1.626 Å, respectively. In $CHCl_3$ solution, the Si–O bond is shortened to 1.994 Å and Si–F is elongated to 1.657 A. In isolated **XX** molecules, the chelate (**A**) and noncoordinated (**B**) forms are in equilibrium. In $CHCl_3$ solution, this equilibrium is shifted to form **A**. Inclusion of entropy factors in chloroform makes form **A** preferred over form **B** by 1.1 kcal mol^{-1}.

The calculated distances between the oxygen and silicon atoms in **Xa**, **XIX**, and **XX** are 2.917, 2.177, and 2.268 Å, respectively. In the $R_2P(O)CH_2CH_2SiF_3$ series, this distance decreases with R in the order (parenthesized are the σ_m^0 values of the substituents): MeO (0.06) > Me (–0.07) > Me_2N (–0.12). The axial Si–F bond length in **Xa**, **XX**, and **XIX** increases in the same order (1.605, 1.626, and 1.885 Å, respectively) and parallels the order of the Hammet σ_m^0 constants of these substituents, relating to their interaction with π-electron systems (in our case, the ⩾P=O group).

EXPERIMENTAL

The mass spectra were registered on a Shimadzu QP5050A GC–MS instrument (SPB-5MS column, length 60 m, internal diameter 250 nm, film thickness 0.25 nm; injector temperature 220°C, carrier gas helium, flow rate 0.7 ml $\min^{-1}$, programmed temperature at a rate of 10 deg $\min^{-1}$; electron energy 70 eV; ion source temperature 200°C; detected mass range 34-650 D; total ion monitoring).

The IR spectra were registered on a Specord IR-75 spectrophotometer for thin films and KBr pellets.

The NMR spectra were registered on a Bruker DPX-400 instrument for 5–10% $CDCl_3$ solutions against internal HMDS.

All calculations were performed with full geometry optimization on a B3LYP/6-31G(d) level of theory using Gaussian-03 [18]. Correspondence of the resulting structures to potential energy minima was confirmed by positive values of the corresponding Hessians. Medium effects were included in the framework of the Tomasi polarized continuum model [19].

The total energies of the structures (*E*) are corrected for zero-point vibration energy (*ZPE*). The enthalpies (*H*) and Gibbs energies (*G*) were calculated for standard conditions (298.15 K, 1 atm). The *ZPE*, *H*, and *G* values were not scaled.

The magnetic properties were calculated by the B3LYP/6-311++G(2d,p) procedure for the B3LYP/6-31G(d) geometry using the GIAO approach [20].

The starting compounds for the synthesis of diethyl (trifluorosilyl)methylphosphonate (**IX**) and diethyl [difluoro(methyl)silyl]methylphosphonate (**XI**) were diethyl (triethoxysilyl)methylphosphonate (**XIII**) and diethyl [diethoxy)methylsilyl]methylphosphonate (**XIV**), respectively.

Diethyl (triethoxysilyl)methylphosphonate (XIII). A mixture of 10.7 g (0.06 mol) triethyl phosphite and 27.0 g (0.13 mol) of (chloromethyl)triethoxysilane was heated for 1 h at 157–196°C. Vacuum distillation gave 6 g (32%) of compound **XIII**, bp 120–122°C (4 mm Hg), n_D^{25} 1.4200. Published data [16]: bp 96.5–97°C (2 mm Hg), n_D^{20} 1.4234. ^1H NMR spectrum, δ, ppm: 1.31 d (PCH_2Si, $^2J_{H-P}$ 24 Hz), 1.23 t (9H, CH_3CH_2OSi, ^3J 6.8 Hz), 3.87 q (6H, $CH_3CH_2\cdot OSi$), 1.31 t (6H, $C\mathit{H}_3CH_2OP$), 4.08 · (4H, $CH_3C\mathit{H}_2\cdot OP$). ^{13}C NMR spectrum, δ_C, ppm: 10.1 d (PCH_2Si, J_{C-P} 131.5 Hz), 17.88 ($\mathit{C}H_3CH_2OSi$), 58.64 ($CH_3CH_2\cdot OSi$), 16.7 ($\mathit{C}H_3CH_2OP$), 61.22 d ($CH_3\mathit{C}H_2OP$, J_{PC} 6.13 Hz). ^{29}Si NMR spectrum: δ_{Si} –54.9 ppm. ^{31}P NMR spectrum: δ_P 30.45 ppm.

Diethyl [(diethoxy)methylsilyl]methylphosphonate (XIV) was prepared similarly, yield 36%, bp 150–151°C (18 mm Hg), n_D^{20} 1.4277. Published data [16]: bp 99–99.5°C (1 mm Hg), n_D^{20} 1.4277. ^1H NMR spectrum, δ, ppm: 1.30 d (2H, PCH_2Si, $^2J_{PC}H$ 22.38 Hz), 0.30 s (3H, MeSi), 1.21 t (6H, $C\mathit{H}_3CH_2\cdot OSi$, ^3J 7.02 Hz), 3.79 q (4H, $CH_3C\mathit{H}_2OSi$), 1.31 t (6H, $C\mathit{H}_3CH_2OP$, ^3J 7.17 Hz), 4.08 d.q (4H, $CH_3C\cdot \mathit{H}_2OP$, $^3J_{P-H}$ 4.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.54 d (PCH_2Si, $^1J_{C-P}$ 129.97 Hz), –3.80 (MeSi), 17.96 ($\mathit{C}H_3CH_2OSi$), 58.20 ($CH_3\mathit{C}H_2OSi$), 16.13 d ($\mathit{C}H_3CH_2OP$, $^3J_{C-P}$ 6.52 Hz), 61.03 ($CH_3\mathit{C}H_2OP$, $^2J_{C-P}$ 6.13 Hz). ^{29}Si NMR spectrum: δ_{Si} –13.6 ppm.

Diethyl [2-(triethoxysilyl)ethyl]phosphonate (XVI). Triethoxy(vinyl)silane, 5.4 g (0.03 mol) and 0.12 g of AIBN were added with stirring to 8.3 g (0.06 mol) of diethyl hydrogen phosphite at 120°C. The reaction mixture was heated at the same temperature for an additional 1 h. Yield 3.73 g (38%), bp 186–188°C (6 mm Hg), n_D^{25} 1.4216. Published data [21]: bp 141°C (2 mm Hg), n_D^{25} 1.4216. The NMR spectral data are listed in Tables 1 and 2. Mass spectrum, *m/e* (I_{rel}, %): 328 ($[M]^{+\cdot}$, 7), 300 (53), 283 (33), 282 (23), 255 (56), 254 (10), 238 (15), 227 (100), 226 (12), 210 (18), 199 (66), 182 (11), 171 (26), 163 (25), 153 (25), 143 (13), 125 (50), 119 (25), 109 (10), 91 (13), 81 (10), 79 (42), 63 (22), 62 (13), 45 (28).

Reaction of trimethoxy(vinyl)silane with diethyl hydrogen phosphite (XVa–XVc). A mixture of 20.7 g (0.14 mol) of $(MeO)_3SiCH{=}CH_2$ and 0.26 g (0.0016 mol) of AIBN was added dropwise to 20.1 g (0.14 mol) of $(EtO)_2P(O)H$ at 120°C. The reaction mixture was heated at the same temperature for an additional 4 h. Vacuum distillation gave 4.0 g of a fraction boiling at 174–176°C (6 mm Hg). According to NMR and mass spectral data, it contains $(MeO)_3\cdot SiCH_2CH_2P(O)(OMe)OEt$ (**XVc**), $(MeO)_3SiCH_2CH_2\cdot P(O)(OMe)_2$ (**XVa**), and $(MeO)_3SiCH_2CH_2P(O)(OEt)_2$ (**XVb**) in a 2 : 1 : 1 molar ratio. Correspondingly, its elemental composition obeys to empirical formula $C_8H_{21}O_6PSi$. Found, %: H 8.29; Si 10.05; P 10.82. $C_8H_{21}O_6PSi$. Calculated, %: H 7.77; Si 10.31; P 11.38. ^1H NMR spectrum, δ, ppm: 3.73 (MeOSi), 0.86 (CH_2Si), 1.74 (PCH_2), 1.30 ($C\mathit{H}_3CH_2OP$), 4.08 ($CH_3C\mathit{H}_2OP$), 3.79 (POMe). ^{13}C NMR spectrum, δ_C, ppm: 50.6 (MeOSi), 1.39 d (CH_2Si), 18 t (PCH_2, $^2J_{C-P}$ 7.67 Hz), 16 d ($\mathit{C}H_3CH_2OP$, $^3J_{C-P}$ 5.75 Hz), 61.04

($CH_3C\textit{H}_2OP$, $J_{P–C}$ 6.13 Hz). ^{29}Si NMR spectrum: δ_{Si} –45 ppm. ^{31}P NMR spectrum: δ_P: 33.5 ppm.

Compound XVa, mass spectrum, *m/e* (I_{rel}, %): 258 ($[M]^{+\cdot}$, 59), 241 (15), 231 (32), 227 (40), 214 (18), 213 (55), 210 (25), 203 (18), 201 (13), 200 (15), 199 (100), 198 (24), 185 (61), 184 (13), 182 (24), 172 (13), 171 (31), 170 (29), 154 (26), 153 (69), 140 (23), 139 (36), 135 (21), 123 (17), 121 (34), 109 (19), 107 (27), 95 (11), 93 (13), 91 (60), 90 (15), 83 (15), 82 (16), 81 (13), 79 (13), 77 (42), 65 (14), 63 (12), 61 (24), 60 (12), 59 (27), 57 (11), 55 (13), 47 (24), 45 (27), 44 (16), 43 (19), 41 (18).

Compound XVb, mass spectrum, *m/e* (I_{rel}, %): 272 ($[M]^{+\cdot}$, 53), 255 (22), 241 (17), 227 (52), 213 (39), 199 (100), 185 (45), 171 (27), 153 (34), 139 (35), 135 (31), 125 (11), 109 (19), 107 (24), 93 (16), 91 (28), 82 (12), 81 (14), 77 (52), 59 (20), 47 (11), 45 (21), 44 (12), 43 (16), 41 (14).

Compound XVc, mass spectrum, *m/e* (I_{rel}, %): 286 ($[M]^{+\cdot}$, 61), 270 (12), 269 (34), 268 (20), 259 (12), 258 (12), 255 (11), 242 (19), 241 (70), 231 (12), 227 (24), 224 (15), 214 (11), 213 (100), 210 (25), 203 (11), 199 (30), 196 (13), 185 (97), 184 (13), 173 (12), 171 (11), 168 (11), 167 (33), 157 (29), 153 (13), 149 (28), 139 (53), 125 (25), 121 (17), 111 (15), 109 (28), 105 (25), 93 (33), 91 (12), 83 (13), 82 (12), 81 (17), 79 (18), 77 (31), 76 (12), 65 (14), 63 (41), 59 (18), 57 (11), 55 (17), 47 (14), 45 (38), 44 (24), 43 (19), 41 (16).

Diethyl (trifluorosilyl)methylphosphonate (IX). A mixture of 2.3 g (0.007 mol) of compound **XIII** and 1.5 g (0.01 mol) of $BF_3 \cdot OEt_2$ was heated under reflux for 3.5 h. Volatile components were removed by distillation to leave 1 g of a viscous liquid which, according to elemental analysis and multinuclear NMR spectroscopy, is compound **IX**. Found, %: C 25.35; P 12.89. $C_5H_{12}F_3O_3PSi$. Calculated, %: C 25.42; P 10.60. ^1H NMR spectrum, δ, ppm: 1.39 ($C\textit{H}_3CH_2OP$), 4.32 ($CH_3C\textit{H}_2OP$), 2.13 ($SiCH_2P$). ^{13}C NMR spectrum, δ_C, ppm: 13 ($SiCH_2P$), 15.74 ($\textit{C}H_3CH_2OP$), 67.36 ($CH_3\textit{C}H_2OP$). ^{29}Si NMR spectrum: δ_{Si} –72.2 ppm. ^{31}P NMR spectrum: δ_P 36.4 ppm. ^{19}F NMR spectrum: δ_F –146 ppm [$J_{Si–F}$ 254.4 Hz].

Vacuum distillation of this residue yielded as little as 0.2 g of diethyl methylphosphonate (**XII**), bp 86°C (3 mm Hg). Found, %: C 39.30; H 8.53; P 19.87. $C_5H_{13}O_3P$. Calculated, %: C 39.46, H 8.60; P 20.37. ^1H NMR spectrum, δ, ppm: 1.33 (CH_3), 1.31 ($C\textit{H}_3 \cdot CH_2O$, $J_{P–H}$ 17.46 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.16 (CH_3), 59.75 (OCH_2), 11.73, 10.30 (PCH_2, $^3J_{C–P}$ 6.13 Hz). ^{31}P NMR spectrum: δ_P 30.85 ppm. IR spectrum, ν, cm^{-1}: 765 (P–C), 796 ν_s(P–O), 1160 ν_{as}(P–O), P=O (1230), 900–1100 (P–O–C).

Diethyl [2-(trifluorosilyl)ethyl]phosphonate (Xb). Compound **XVI**, 3 g (0.009 mol), and 2.9 g (0.02 mol) of $F_3B \cdot OEt_2$ was heated with distilling off low-boiling compounds. The residue was distilled in a vacuum to isolate 1 g (44.4%) of compound **Xb**, bp 163–165°C (12 mm Hg). Found, %: H 5.24; P 12.82; Si 11.59. $C_6H_{14}O_3PF_3Si$. Calculated, %: H 5.64; P 12.39; Si 11.22. The NMR spectral data are listed in Tables 1 and 2.

Reaction of compounds XVa–XVc with boron trifluoride etherate. A 1 : 1 : 2 mixture of compounds **XVa**–**XVc**, 1.34 g (0.005 mol), and 0.71 g (0.005 mol) of boron trifluoride etherate was heated under reflux for 1.5 h. Low-boiling compounds were removed by distillation to isolate 0.8 g of a mixture of compounds **Xa**–**Xc** with the empirical formula $C_5H_{12}F_3O_3PSi$. Found, %: H 5.61; F 24.10; P 12.98. $C_5H_{12}F_3O_3PSi$. Calculated, %: H 5.12; F 24.10; P 13.12.

The NMR spectrum of the product obviously relates to compound **Xc**. ^1H NMR spectrum, δ, ppm: 1.13 (CH_2Si), 1.80 (PCH_2), 1.28 ($C\textit{H}_3CH_2OP$), 4.08 ($CH_3C\textit{H}_2OP$), 3.76 (P–OMe). ^{13}C NMR spectrum, δ_C, ppm: 0 86 (CH_2Si), 18 (PCH_2), 16 ($\textit{C}H_3CH_2OP$), 61.5 ($CH_3\textit{C}H_2OP$). ^{29}Si NMR spectrum: δ_{Si} –60 ppm. ^{19}F NMR spectrum: δ_F –134 ppm. ^{31}P NMR specrum: δ_P 31.5 ppm ($J_{Si–F}$ 270.7 Hz).

Diethyl [difluoro(methyl)silyl]methylphosphonate (XI). A solution of 0.7 g (0.002 mol) of compound **XIV** and 0.5 g (0.003 mol) of $BF_3 \cdot OEt_2$ in 1.5 ml of benzene was heated under reflux for 1.5 h. Volatile components were removed by distillation to isolate 0.2 g of compound **XI**. Found, %: P 10.45. $C_6H_{15}F_2O_3PSi$. Calculated, %: P 10.19. ^1H NMR spectrum, δ, ppm: 1.29 ($C\textit{H}_3CH_2OP$), 4.23 ($CH_3 \cdot C\textit{H}_2OP$). ^{13}C NMR spectrum, δ_C, ppm: 12.20 (PCH_2Si). ^{31}P NMR spectrum, δ_P, ppm: 36.32. We failed to accumulate the ^{29}Si signal.

When injected to the chromatograph, compound **XI** decomposed. The chromatogram contained peaks of three compounds with the relative contents 91, 6, and 2%. By mass spectral library search the main component (τ = 9.7 min) was identified as diethyl methylphosphonate (SI : 97) and the second (τ = 11.6 min), as diethyl ethylphosphonate (SI : 93). The third component (τ = 13.5 min) obviously is 1,3-dimethyltetrafluorodisiloxane; its main characteristic peak in the mass spectrum is at *m/e* 159 $[M - F]^+$.

Bis(trimethylsilyl) styrylphosphonate (XVII). A mixture of 1.3 g (0.007 mol) of styrylphosphonic acid, 2.3 g (0.014 mol) of hexamethyldisilazane, and a catalytic amount of chlorotrimethylsilane was heated for 3 h under reflux. Unreacted starting materials were removed by distillation to isolate 1.7 g (74%) of a liquid compound **XVII**, n_D^{20} 1.4950. Found, %: C 50.89; H 7.94; P 8.94. $C_{14}H_{25}O_3PSi_2$. Calculated, %: C 51.18; H 7.67; P 9.44. ^1H NMR spectrum, δ, ppm: 0.29 s ($SiMe_3$), 6.29 t (CHP, $J \sim {}^2J_{P-H}$ 17.67 Hz), 7.35 d.d (PhC*H*=, $^3J_{P-H}$ 6.0 Hz), 7.45 m (H_o), 7.35 m ($H_{m,p}$). ^{13}C NMR spectrum, δ_C, ppm: 0.73 (MeSi), 117.95 d (PCH=, $^1J_{C-P}$ 199.14 Hz), 127.17, 128.52 ($C_{o,m}$), 129.50 (C_p), 134.97 d (C_i, $^3J_{C-P}$ 24 Hz), 145.34 d (PhCH=, $^2J_{C-P}$ 6.47 Hz). ^{29}Si NMR spectrum: δ_{Si} 20.84 ppm ($^2J_{sip}$ 6.32 Hz). ^{31}P NMR spectrum: δ_P 0.96 ppm. IR spectrum, ν, cm^{-1}: 850 ($SiMe_3$), 990 (SiOP), 1220, 1250 (P=O).

Bis[(chloromethyl)dimethylsilyl)] styrylphosphonate (XVIII). A mixture of 2.5 g (0.008 mol) of phosphonate **XVIII**, 2.9 g (0.02 mol) of chloro(chloromethyl)dimethylsilane and 5 ml of toluene was heated under reflux for 20 h. Toluene was distilled off to isolate a liquid compound **XVIII**, n_D^{20} 1.4640. Found, %: Cl 17.87; Si 13.64; P 7.53. $C_{14}H_{23}Cl_2O_3 \cdot PSi_2$. Calculated, %: Cl 17.84; Si 14.14; P 7.80. ^1H NMR spectrum, δ, ppm: 0.42 s (MeSi), 2.92 s (CH_2Cl), 6.31 t (PCH=, $^2J_{P-H} \sim {}^3J_{P-H}$ 18 Hz), 7.45–7.35 m (PhCH=). ^{13}C NMR spectrum, δ_C, ppm: –2.55 (MeSi), 28.84 (CH_2), 116.30 (PCH=, $^1J_{C-P}$ 200 Hz), 128.49, 127.24 ($C_{o,m}$), 129.75 (C_p), 130.50 (C_i, $^3J_{C-P}$ 24.14 Hz), 146.51 (PhCH=, $^2J_{C-P}$ 6.0 Hz). ^{29}Si NMR spectrum: δ_{Si} 14.20 ppm ($^2J_{sip}$ 5.83 Hz). ^{31}P NMR spectrum: δ_P 2.36 ppm.

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