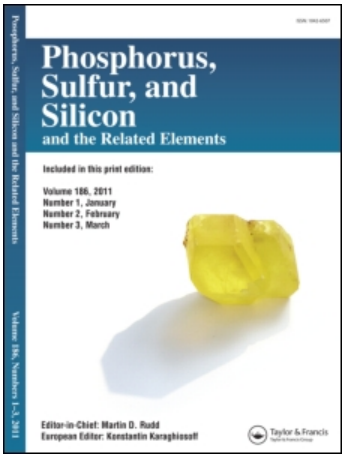

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METHOXY AND METHYLTHIO DERIVATIVES OF TETRAKIS(TRIFLUOROMETHYL)-SPIRO [1,3,2λ⁵-DIOXAPHOSPHOLANE-2,2'[1,3,2λ⁵] DIOXAPHOSPHOLANE]

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METHOXY AND METHYLTHIO DERIVATIVES OF TETRAKIS(TRIFLUOROMETHYL)-SPIRO [1,3,2λ^5-DIOXAPHOSPHOLANE-2,2′[1,3,2λ^5] DIOXAPHOSPHOLANE]

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2-Chloro-1,3,2-dioxaphospholane **1** reacted with ammonium perfluoropinacolate **2** to give the stable tetraoxa(hydro)spirophosphorane **3**, which upon u.v. irradiation in the presence of dimethyldisulfide yielded the methylthio derivative **8**. Compound **8** was available also from 2-methylthio-1,3,2-dioxaphospholane **7** and hexafluoroacetone whereas 2-methoxy-1,3,2-dioxaphospholane **4** furnished a 1 : 1 mixture of the 1,3,2λ^5 and 1,3,4λ^5-dioxaphospholane, **5** and **6**. Bis(trimethylsilyl)ethyleneglycolether **11** and 2,2-difluor-2-methylthio-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2λ^5-dioxaphospholane **9** did not form **8**. The ^{1}H NMR spectrum of **3** was analyzed as an AA′BB′X spin system. A ^{19}F—^{19}F homocorrelated 2 D spectrum indicated a 2-CF_3 ··· 5-F_3C coupling interaction, probably via a non-bond mechanism.

INTRODUCTION

1,1,1,4,4,4-Hexafluoro-2,3-bis(trifluoromethyl)-butane-2,3-diol(perfluoropinacol), $HOC(CF_3)_2C(CF_3)_2OH$, or its ammonium salt react with 2-dimethylamino-4,4,5,5,-tetramethyl-,[1] 2-chloro-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholane[2] or 2-chloro-1,3,2-dioxaphosphorinane[3] to form hydrospirophosphoranes which do not show tautomeric equilibria in solution between a tri- and penta-coordinated species. 2-Chloro-1,3,2-dioxaphospholane[4] **1** should furnish a hydrophosphorane, too. The properties of the methoxy and corresponding methylthio derivative will give more information about the expected spiro ring system.

RESULTS AND DISCUSSION

Using a modified literature method,[1] 2-chloro-1,3,2-dioxaphospholane **1** and ammonium perfluoropinacolate[3] **2** reacted to form the title compound **3**, a colourless,

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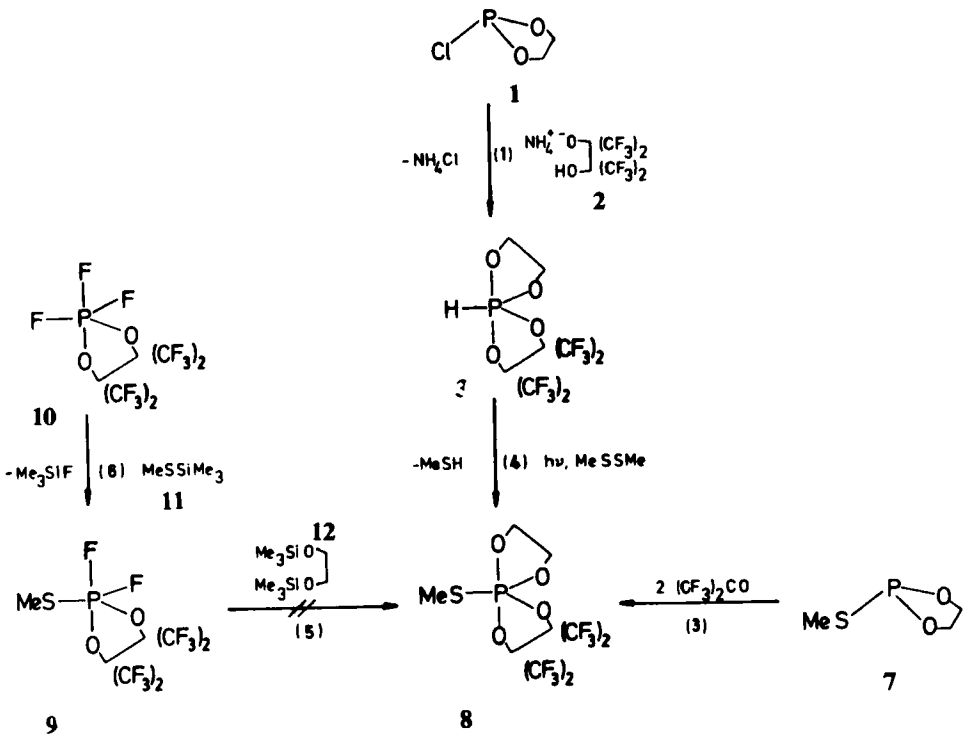
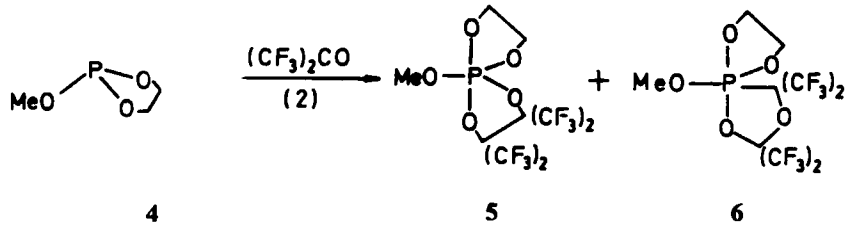


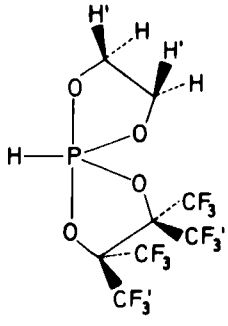
SCHEME 1

moisture-sensitive liquid (b.p. 72–73°C/5 Torr) (eq. 1). The methoxy derivative **5** was obtained together with its 1,3,4λ^5-isomer **6** in a 1 : 1 ratio when 2-methoxy-1,3,2-dioxaphospholane[5] **4** was treated with hexafluoroacetone at room temperature (eq. 2). (In the case of the phenoxy analogue the same mixture of isomers was isolated.)[1] Compound **6** could not be separated from **5** by distillation nor be converted thermally into isomer **5**. The composition of the mixture was not altered after heating for two days at 80°C.

2-Methylthio-1,3,2-dioxaphospholane[6] **7** and hexafluoroacetone yielded only one isomer, **8**, which was obtained also from irradiation[7] of a solution of **3** and dimethyldisulfide in benzene (eq. 3, 4). A third pathway, starting from the difluoromethylthiophosphorane **9** and the bis(trimethylsilyl)ethyleneglycolether[8] **11**



was not effective. The thiophosphorane **9** was prepared using the trifluorophosphorane[9] **10** and (trimethylsilyl)methylthioether[10] **12** (eq. 6). The 30 eV *mass spectra* of **3**, **8** and **9** exhibited the molecular ion M^+ only for **3**. Typical fragments were M^+—H (**3**), M^+—F (**3**, **8**, **9**).



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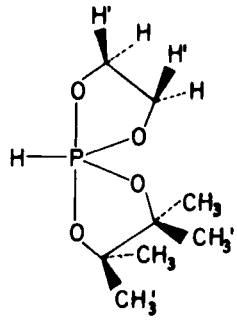

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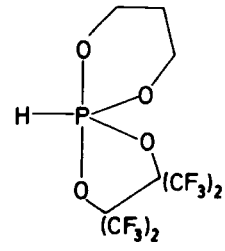

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The ^1H NMR pattern of the OCH_2CH_2O grouping in **3** was analyzed as an AA'BB'X spin system similar to the related compound[11] **13**. The corresponding parameters (Table I) were obtained by iterative simulation (Program PANIC from the Bruker Software). Two magnetically non-equivalent pairs of protons (δ_H = 3.988, 4.054) and CF_3 groups (δ_F = −67.71, −70.13) led to the conclusion that the "high energy" process[1,11] of a two step intramolecular substituent exchange in a trigonal bipyramid was slow on the NMR time scale. The multiplet splitting is consistent with a $^4J_{FF'}$ coupling (8.7 Hz) of the geminal CF_3 groups and additional through-bond ($^5J_{FF}$) and/or non-bond interaction[12] of *cis* 4-CF_3 and 5-CF_3 groups ($J_{F\cdots F}$, $J_{F'\cdots F'}$) (vide infra). The position of the sets of protons H or H' and CF_3 or CF_3' relative to the hydrogen bonded to phophorus could not be determined.

TABLE I

^1H, ^{19}F and ^{31}P NMR data of **3** (J in Hz)

δ_H[a] OCH_2CH_2O	δ_F[a]	δ_P[a]
3.988(4-H', 5-H')	−67.71(4'-CF_3, 5'-CF_3)	−23.37
$^2J_{HH'}$ = −9.2	$^4J_{FF'}$ = 8.7	
$^3J_{PH'}$ = 15.9[b]	J_{FF} = 8.7[c]	
$^3J_{4\text{-}H,5\text{-}H'}$ = 6.3	−70.13(4'-CF_3', 5'-CF_3')	
$^3J_{4\text{-}H',5\text{-}H'}$ = 6.5	$^4J_{PF'}$ = 5.6	
4.054(4-H, 5-H)	$J_{F'F'}$ = 8.7[c]	
$^3J_{PH}$ = 12.6		
$^4J_{HH}$ = −0.2		

[a] Signals upfield to TMS, CCl_3F and 85% H_3PO_4 are measured as negative.

[b] δ_H(PH) = 7.317 ($^1J_{PH}$ = 893.6).

[c] $^5J_{FF}$ and/or "through-space" coupling.

The larger group electronegativity of CF_3 caused an increase in s-character[13] of the P—H bond in **3** ($^1J_{PH}$ = 894 Hz) compared with **13** ($^1J_{PH}$ = 812 Hz). In comparison, the hydrophosphorane **14** containing a 1,3,2λ^5-dioxaphosphorinane ring exhibits only one signal[3] for all four CF_3 groups indicating rapid pseudorotation, because of the lower activation energy barrier for the equatorial-equatorial arrangement of the six-membered ring[14,15] at phosphorus in the trigonal bipyramidal structure. The phosphorus nucleus in **3** (δ_P = −23.57) is more deshielded relative to **14** (δ_P = −35.75) which can be explained in terms of a greater distortion in **3** towards a rectangular pyramid along the "Berry coordinate".[16,17] A similar observation was made in compound **5** (δ_P = −27.71) (Table II) and the 1,3,2-dioxaphosphorinane analogue (δ_P = −47.95[3]).

In the 1,3,4λ^5 − dioxaphospholane **6**, isomer of **5** substituent exchange processes were slow on the NMR time scale producing a chiral centre with five different ligands at phosphorus. All four CF_3 groups, two doublets of septets at lower field (A, B; $PC(CF_3)_2O$, $^3J_{PF}$ = 3.75 Hz) and two septets in the upfield region (C, D; $OC(CF_3)_2$)[18,19] (Table II, Figure 1) were magnetically non-equivalent (also observed for the phenoxy derivative[14]). The septet splitting can only be explained by assuming

TABLE II

^1H, ^{19}F and ^{31}P NMR data of **5**, **6**, **8**, and **9** (*J* in Hz)

	δ_H[a] CH_3 ($^3J_{PH}$)	δ_F[a] CF_3 ($^4J_{FF}$)	δ_P[a]
5[b]	3.77 (14.23)	−69.20	−27.71
6[c]	3.76 (14.23)	−68.46[d,e] −68.51[d,e] (9.50) −80.18[e,f] −81.31[e,f] (9.50)	−16.33
8[g]	2.24 (21.02)	−68.79[h,i] (8.22) −70.19[i,j] (8.22)	−2.45[k]
9[l]	2.43 (24.56)	−68.91	−14.62

[a] Signals upfield to TMS, CCl_3F and 85% H_3PO_4 are measured as negative.
[b] $\delta_H(OCH_2CH_2O)$ = 4.01 ($^3J_{PH}$ = 15.37).
[c] $\delta_H(OCH_2CH_2O)$ = 3.92–4.22 (m).
[d] $PC(CF_3)_2O$, $^3J_{PF}$ = 3.75.
[e] $^6J_{FF}$ and/or "through-space" coupling 9.50.
[f] $OC(CF_3)_2O$.
[g] $\delta_H(OCH_2CH_2O)$ = 4.08 ($^3J_{PH}$ = 14.52).
[h] CF_3.
[i] $^5J_{FF}$ and/or "through-space" coupling 8.22.
[j] CF_3'.
[k] Quartet of quintets.
[l] $\delta_F(PF)$ = −37.76 ($^1J_{PF}$ = 1032.2).

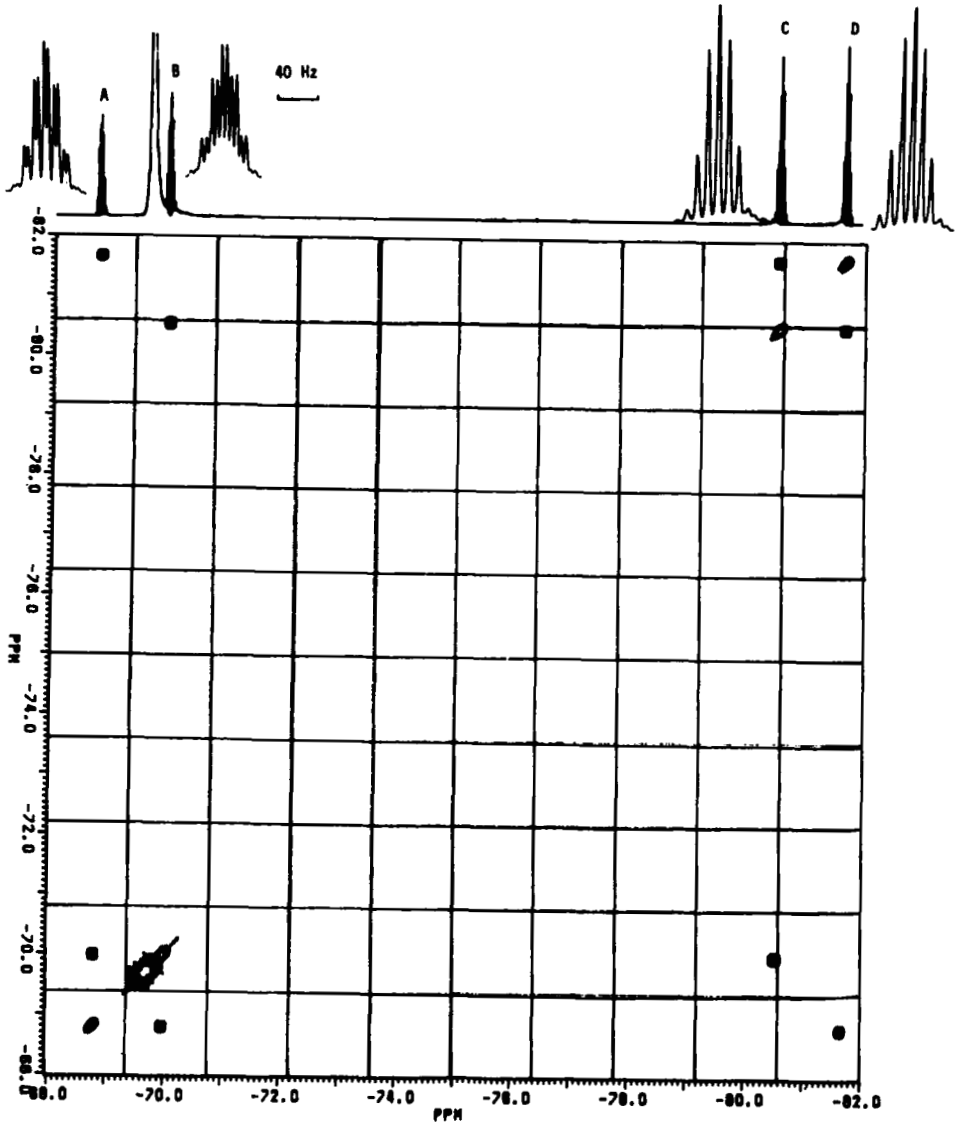
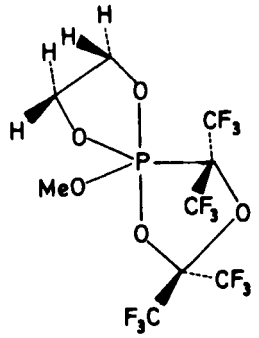


FIGURE 1 $^{19}F—^{19}F$ homocorrelated 2 D spectrum of **6**.

a $^4J_{FF}$ coupling (9.5 Hz) of the geminal 2-CF_3 or 5-CF_3 groups *and* a non-bond interaction[12] of each CF_3 group with a CF_3 group in *cis* position; a coupling constant of 9.5 Hz via six bonds without a π-system seems not very likely[12]. A $^{19}F—^{19}F$ homocorrelated 2 D spectrum (Figure 1, Experimental Part) proved the existence of a scalar 2-CF_3 ··· 5-CF_3 interaction (CF_3(A) ··· F_3C(D), CF_3(B) ··· F_3C(C)). The orientation relative to the MeO group could not be determined. The resonance between signal A and B is due to the four equivalent CF_3 groups of **5**.



6

The ^1H spectrum of **8** showed a A_4X pattern ($^3J_{PH}$ = 14.52 Hz) whereas two multiplets for two non-equivalent CF_3 pairs in the ^{19}F spectrum characterized a "frozen" high energy process[1,11] (Table II). (The exchange rate of both nuclei is depending on the shift differences of the resonances in question.) The multiplicity of signals can be derived from geminal $^4J_{FF}$ (8.22 Hz) coupling and through-bond ($^5J_{FF}$) and/or non-bond interaction of *cis* CF_3 groups by the same coupling constant ($J_{F\ldots F}$ = 8.22 Hz).

The methylthio substituent in **9** is responsible for the deshielding effect in comparison to the MeO analogue;[20] δ_H = 2.43 (3.87), δ_F(PF) = −37.76 (−64.0), and δ_p = −14.62 (−52.8). The coupling constants $^3J_{PH}$ and $^1J_{PF}$ are considerably larger in the case of **9**, $^3J_{PH}$ = 24.56 (15.1), $^1J_{PF}$ = 1032.2 (903). One signal in the CF_3 region indicated pseudorotation rapid on the NMR time scale, equilibrating all four CF_3 groups.

EXPERIMENTAL

The appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work

Solvents were dried by standard procedures. Mass spectra were taken on a Varian MAT CH-7 instrument at 30 eV. The IR spectrum of **3** was recorded on a Perkin Elmer 577 spectrometer. NMR spectra were obtained on a Bruker WH 360 spectrometer at 360.08 MHz (^1H, internal Standard TMS), 338.68 MHz (^{19}F, external CCl_3F), and 145.72 MHz (^{31}P, external H_3PO_4). Solutions ca. 10% (V/V) in $CDCl_3$ were measured. The ^{19}F—^{19}F homocorrelated 2 D spectrum was obtained under proton decoupling conditions.[21] The second pulse angle was 45°. The data size was 2 K points in t_2 direction (16 single scans) and 512 experiments in t_1 direction, which were zero filled to 1 K for processing. Both dimensions were multiplied by a sine bell function prior to transformation. After transformation, the full spectrum was symmetrized.

The irradiation experiment was carried out with a 450 W Hanovia medium-pressure mercury lamp in a pyrex glass system. The following compounds were prepared according to literature procedures: **1**[4], **2**[3], **4**[5], **7**[6], **10**[9], **11**[8], **12**[10].

4,4,5,5-Tetrakis(trifluoromethyl)-spiro[1,3,2λ⁵-dioxaphospholane-2,2'[1,3,2λ⁵]-dioxaphospholane](**3**). Compound **2**, 10.47 (30 mmole) were added to 3.79 g (30 mmole) **1** and hold at 60°C for 12 hours. The reaction mixture was washed with 100 ml petrolether. After removing the solvent the residue was distilled two times. Yield of **3** 8.87 g (70%, b.p. 72–73/5 Torr).

MS (30 eV, 30°C): *m/e*: 424 (M^+, 2%), 423 (M^+—H, 17), 405 (M^+—F, 8), 394 (M^+—CH_2O, 34), 381 (M^+—C_2H_4F, 9), 355 (M^+—CF_3, 100), 197 ($C_4F_7O^+$, 52), 91 ($PO_2C_2H_4^+$, 48), 69 (CF_3^+, 24) and other

fragments. IR: 2970 s, 2895 s (ν_{CH}); 2455 m (ν_{PH}); 1300–1150 vs (ν_{CF}) [cm^{-1}]. $C_8H_5F_{12}O_4P$ (424.08): Calcd.: C, 22.66; H, 1.19; F, 53.70; P, 7.30. Found: C, 22.81; H, 1.24; F, 53.60; P, 7.39.

2-Methoxy-4,4,5,5-tetrakis(trifluoromethyl)-spiro-[1,3,2λ⁵-dioxaphospholane-2,2'[1,3,2λ⁵]-dioxaphospholane] (**5**) *and 2-Methoxy-3,3,5,5-tetrakis(trifluoromethyl)-spiro[1,3,4λ⁵-dioxaphospholane-2,2'-[1,3,2λ⁵]-dioxaphospholane]* (**6**). Compound **4**, 3.30 g (27 mmole) and 9.00 g (54 mmole) hexafluoroacetone reacted for 24 hours at room temperature. Excess hexafluoroacetone was removed. The residue was recrystallized from pentane. The yield of **5** and **6** was 96% (m.p. 30°C). The ^{31}P NMR indicated a 1 : 1 mixture. Heating for two days at 80°C did not change the composition of the mixture.

$C_9H_7F_{12}O_5P$ (454.10): Calcd.: C, 23.80, H, 1.55; F, 50.20, Found: C, 24.16; H, 1.66; F, 49.50.

2-Methylthio-4,4,5,5-tetrakis(trifluoromethyl)-spiro-[1,3,2λ⁵-dioxaphospholane-2,2'[1,3,2λ⁵]-dioxaphospholane] (**8**). Compound **7**, 3.45 g (25 mmole) and 8.30 g (50 mmole) hexafluoroacetone react for 24 hours at room temperature to give 11.75 g 100%) **8** (b.p. 115°C/15 Torr).

MS: (30 eV, 30°C): *m/e*: 470 (M^+, −), 425 (M^+—F, 2%), 424 (M^+—SCH_2, 112), 423 (M^+—SCH_3, 100), 401 (M^+—CF_3, 12), 397 (M^+—SC_3H_5, 6), 69 (CF_3, 51) and other fragments. $C_9H_7F_{11}O_4PS$ (470.17): Calcd.: C, 22.99; H, 1.50; F, 48.49. Found: C, 23.05; H, 1.50; F, 48.30.

A solution of 0.85 g (2 mmole) **3** and 0.18 g (2 mmole) dimethyldisulfide was irradiated through Pyrex at 20°C with a medium-pressure 450-W Hanovia mercury lamp. After 2 hours the ^{31}P NMR spectrum of the solution showed the presence of 80% **8**. The ^1H NMR spectrum indicated the presence of methyl mercaptan.

2,2-Difluoro-2-methylthio-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2λ⁵-dioxaphospholane (**9**). Compound **10**, 6.30 g (15 mmole) and 1.81 g (15 mmole) methyl(trimethylsilyl)thioether[10] **12** were hold for one week at room temperature. The reaction mixture was distilled at 25 Torr. 6.00 g **9** (b.p. 65/25 Torr) were obtained.

MS (30 eV, 30°C): *m/e*: 448 (M^+—SCH_3, 82), 379 (M^+—CF_3, 30), 159 ($C_3F_4OP^+$, 41), 97 ($C_2F_3O^+$, 20), 69 (CF_3^+, 100). $C_7H_3F_{13}O_2PS$ (448.12): Calcd.: C, 18.76; H, 0.67; F, 59.35; S, 7.16. Found: C, 18.88; H, 0.70; F, 58.8; S, 7.29.

Reaction of **9** *with bis(trimethylsilyl)ethyleneglycolether* (**11**). Compound **9**, 4.50 g (10 mmole) and 2.10 g (10 mmole) **11** were heated for two days at 80°C. The starting materials could be recovered unchanged.

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