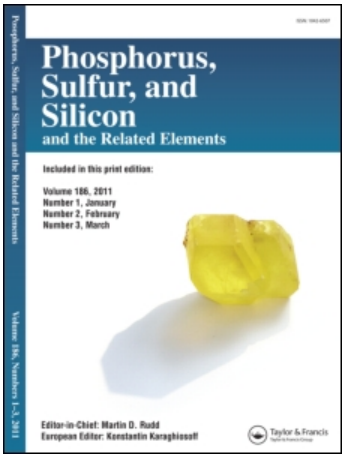

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Dialkyl *N*-Alkyl-*N*-Perfluoroalkanesulfonyl Phosphoramidates

Shi-Zheng Zhu[a]; Jie Zhang[a]; Bin Xu[a]; Aiwen Li[a]
[a] Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, China

To cite this Article Zhu, Shi-Zheng , Zhang, Jie , Xu, Bin and Li, Aiwen(1994) 'Synthesis of Dialkyl *N*-Alkyl-*N*-Perfluoroalkanesulfonyl Phosphoramidates', Phosphorus, Sulfur, and Silicon and the Related Elements, 89: 1, 77 — 82
To link to this Article: DOI: 10.1080/10426509408020435
URL: http://dx.doi.org/10.1080/10426509408020435

Phosphorus, Sulfur, and Silicon, 1994, Vol. 89, pp. 77–82
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF DIALKYL *N*-ALKYL-*N*-PERFLUOROALKANESULFONYL PHOSPHORAMIDATES

SHI-ZHENG ZHU,* JIE ZHANG, BIN XU and AIWEN LI
Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai 200032 China

(Received January 22, 1994; in final form March 28, 1994)

N-Halogenperfluoroalkanesulfonylamines $R_fSO_2N(R)X$ (X = Br, Cl) which are obtained by treatment of the sodium or potassium salt of *N*-alkylperfluoroalkanesulfonylamides $R_fSO_2N(R)M$ with bromine or chlorine react readily with triethyl phosphite $P(OEt)_3$ giving the title compounds $R_fSO_2N(R)P(O)(OEt)_2$. The reaction mechanism is discussed. Hydrolysis of these compounds gives the N—P bond broken products.

Key words: Phosphoramidate; synthesis; fluorine-containing; hydrolysis.

INTRODUCTION

Aminophosphonate and its derivatives have been drawing much attention due to their biological properties. Many of these compounds have been synthesized.[1–5] It is well known that introduction of a fluorine atom or fluorine-containing group into molecules can increase the chemical or biological activities of the compounds. Therefore it is valuable to develop some synthetic methods for the preparation of the fluorine-containing phosphonates.[6,7] During the investigation on the perfluoroalkanesulfonyl nitrene, it is found that treatment of perfluoroalkanesulfonylazides with triethylphosphite giving diethyl *N*-ethyl-*N*-perfluoroalkanesulfonylphosphoramidates.[8]

$$R_fSO_2N_3 \xrightarrow[Et_2O]{P(OEt)_3} R_fSO_2N{=}P(OEt)_3 \longrightarrow R_fSO_2N(Et)P(O)(OEt)_2$$

However, the yields are low (40–50%). In this paper, we wish to report a new method to prepare these compounds.

RESULTS AND DISCUSSION

N-Alkylperfluoroalkanesulfonylamides prepared by treatment of R_fSO_2F with amines[9] can be easily transformed to *N*-alkyl-*N*-haloperfluoroalkanesulfonylamide by one-pot procedure.

$$\underset{(1)}{R_fSO_2F} \xrightarrow{RNH_2} \underset{(2)}{R_fSO_2NHR} \xrightarrow[(ii)\ X_2]{(i)\ KOH\ or\ NaOH} \underset{(3)}{R_fSO_2N(X)R}$$

R_f: C_4F_9, $I(CF_2)_2O(CF_2)_2$, $Cl(CF_2)_2O(CF_2)_2$, $H(CF_2)_2O(CF_2)_2$; R: CH_3, C_2H_5; X: Br, Cl.

Similar to the *N,N*-dichloroperfluoroalkanesulfonylamine $R_fSO_2NCl_2$,[10] compounds (**3**) are unstable. When stored in a flask at room temperature, they decompose slowly to the corresponding R_fSO_2NHR (**2**). The purification of the chloride $R_fSO_2N(R)Cl$ can be accomplished by vacuum distillation. The bromide $R_fSO_2N(R)Br$, however, decomposes in large amount during the process of vacuum distillation. Reaction of (**3**) with triethyl phosphite proceeds smoothly at room temperature. After removing excess $P(OEt)_3$, the expected products $R_fSO_2(R)P(O)(OEt)_2$ (**4**) are obtained in high yield. The results are summarized in Tables I and II.

$$\underset{(3)}{R_fSO_2N(R)X} + P(OEt)_3 \xrightarrow[8\ h]{r.t.} \underset{(4)}{R_fSO_2N(R)P(O)(OEt)_2}$$

Compounds (**4**) are high boiling point yellowish oil. The pure products are obtained by column chromatography on silica gel with dichloromethane and ethyl acetate as eluent.

TABLE I

Preparation of (**2**)

R_fSO_2NHR (**2**)		b.p. (°c/Torr)	Yields(%)
R_f	R	or m.p.(°c)	
$HC_2F_4OC_2F_4$	Me (**2a**)	58/1	70
$HC_2F_4OC_2F_4$	Et (**2b**)	60/1	68
$IC_2F_4OC_2F_4$	Me (**2c**)	80/1	74
$IC_2F_4OC_2F_4$	Et (**2d**)	87/1	75
$ClC_2F_4OC_2F_4$	Me (**2e**)	70/1	72
C_4F_9	Et (**2f**)	68	67

TABLE II

Preparation of (**3**) and (**4**)

		$R_fSO_2N(R)X$ (**3**)			$R_fSO_2N(R)P(O)(OEt)_2$ (**4**)		
R_f	R X	b.p.(°c/Torr)	Yields(%)		b.p.(°c/Torr)	Yields(%)
$HC_2F_4OC_2F_4$	Me Cl(**3a**)	50/1	75	(**4a**)	180/1	81
$HC_2F_4OC_2F_4$	Et Cl(**3b**)	51/1	78	(**4b**)	190/1	78
$IC_2F_4OC_2F_4$	Me Br(**3c**)	50/(dec.)	73	(**4c**)	204/1	85
$IC_2F_4OC_2F_4$	Et Br(**3d**)	50/(dec.)	80	(**4d**)	210/1	68
$ClC_2F_4OC_2F_4$	Me Cl(**3e**)	32/1	70	/	/	/
C_4F_9	Et Br(**3f**)	50/(dec.)	65	(**4f**)	160/1	70

It is well known that the *N*-halogen bond can easily break homogeneously and trialkyl phosphites are a good radical capturer.[11,12] It is interesting to know whether this reaction undergoes a free radical process:

$$R_fSO_2N(R)X \xrightarrow{-X\cdot} R_fSO_2\dot{N}R \xrightarrow{P(OEt)_3} R_fSO_2N(R)\dot{P}(OEt)_3 \xrightarrow{-EtX} \textbf{(4)}$$

In order to verify the reaction mechanism, the reaction process was followed by ESR. However, no signal appeared. Dialkyl ether $(CH_2{=}CHCH_2)_2O$ was added, and after workup, no corresponding tetrahydrofuran derivative

$$R_fSO_2N(R)CH_2\overbrace{CHCH_2OCH_2CHCH_2}Br$$

was detected. These results indicate that no radical intermediate is involved in this reaction process. Similar to the reaction of $P(OEt)_3$ with alkyl-halides, this reaction is an ionic Arbouzov-type reaction:

$$R_fSO_2N(R)X \xrightarrow{P(OEt)_3} [R_fSO_2N(R)\overset{+}{P}(OEt)_3X^-] \xrightarrow{-EtX} \textbf{(4)}$$

Attempts to isolate the intermediate phosphonium salt failed.

In our previous work, we have successfully prepared perfluoroalkanesulfonylaminobenzylphosphonic acids $R_fSO_2NHCH(Ar)P(O)(OH)_2$,[13] which are synthesized from acidic hydrolysis of $R_fSO_2NHCH(Ar)P(O)(OEt)_2$ (**5**). Under the same reaction condition, hydrolysis of (**4**), however, gives only the N—P bond broken products.

$$\textbf{(4)} \xrightarrow[\text{reflux, 24 h}]{\text{HCl (36\%)}} R_fSO_2NHR + (EtO)_2P(O)(OH),$$

The structural difference between compounds (**4**) and (**5**) is that in compound (**5**) there is a carbon linkage between N atom and P atom and in compound (**4**) the N atom, which is attached by a strong electron-withdrawing group R_fSO_2—, bonds directly to the P atom. In an acidic medium the N atom is protonated and the N—P bond breaks easily. Basic hydrolysis, for example heating of (**4**) in aqueous Na_2CO_3, gives the same results. Literature has reported similar results.[14]

$$\textbf{(4)} \xrightarrow[\text{reflux, 10 h}]{Na_2CO_3\ (30\%,\ aq)} R_fSO_2NRNa + (EtO)_2P(O)ONa$$

In summary, *N*-alkyl-*N*-haloperfluoroalkanesulfonylamide react readily with $P(OEt)_3$ to give diethyl *N*-alkyl-*N*-perfluoroalkanesulfonylphosphoramidates in high yield. This reaction follows the Arbuzov-type reaction mechanism. Hydrolysis of this phosphoramidate leads to the N—P bond breaking.

EXPERIMENTAL

Melting points are measured on a Thiele apparatus and are reported uncorrected. ^1H NMR and ^{19}F NMR are recorded on a Varian 360 L instrument using TMS and CF_3COOH as internal or external standards, respectively. ^{31}P NMR are obtained on a Bruke AM-300, using 85% H_3PO_4 as external standards. IR spectra are obtained with an IR-440 Shimadzu spectrophotometer. Low-resolution mass spectra are obtained on a Finnigen GC-MS 4021 instrument.

Elemental analyses are performed by the Analysis Department of this Institute.

The starting material $C_4F_9SO_2F$ is commercially available. The other compounds (**1**) are prepared according to the literature.[15]

Preparation of N-alkylperfluoroalkanesulfonylamides **2a–f**. (A typical preparation): **1a** (30.0 g, 0.10 mol) is stirred in a three-necked flask in dry-ice bath, and excess CH_3NH_2 is bubbled through this liquid until it solidifys. After removing the excess amines, then H_2SO_4 (50 mL, 98%) is added. Heat to 80°C to drive off HF. The residue is distilled twice under vacuum to give pure **2a** (23.3 g, 75%). Yields and m.p. or b.p. are shown in Table I.

Compound **2a**: IR (film) (ν, cm^{-1}): 3320 (s), 2990 (w), 1430 (m), 1370 (s), 1330 (m), 1100–1220 (vs), 960 (m), 860 (m). ^1H NMR (δ): 5.86 (t, $^2J_{HF}$ = 54.0 Hz, HCF_2), 5.46 (s, NH), 2.76 (s, CH_3). ^{19}F NMR (δ): 4.3 (m, OCF_2), 11.0 (m, CF_2O), 38.8 (s, CF_2S), 61.7 (d, HCF_2).
MS (m/z, %): 312 (M^+ + 1, 1.33), 119 ($CF_3CF_2^+$, 16.9), 101 ($HC_2F_4^+$, 27.03), 95 ($CH_3NHSO_2^+$, 100.0), 78 (NSO_2^+, 34.0).
Anal.: Calcd. for $C_5H_5F_8NO_3S$ C 19.29, H 1.61, N 4.50, F 48.87.
Found: C 19.12, H 1.47, N 4.72, F. 48.53%.

Compound **2b**: IR (film) (ν, cm^{-1}): 3310 (s), 2990 (w), 1430 (m), 1370 (s), 1285 (s), 1100–1220 (vs), 1015 (w), 955 (m), 860 (w). ^1H NMR (δ): 5.85 (t, HCF_2), 5.66 (s, NH), 3.30 (q, CH_2), 1.26 (t, CH_3). ^{19}F NMR (δ): 4.4 (m, OCF_2), 11.4 (m, CF_2O), 39.3 (s, CF_2S), 61.8 (d, HCF_2).
MS (m/z, %): 326 (M^+ + 1, 2.13), 310 (M^+—CH_3, 8.1), 119 ($CF_3CF_2^+$, 28.6), 108 ($SO_2NHC_2H_5^+$, 100.0), 101 ($HCF_2CF_2^+$, 42.3), 51 (HCF_2^+, 18.7).
Anal.: Calcd. for $C_6H_7F_8NO_3S$ C 22.15, H 2.15, N 4.31, F 46.77.
Found: C 22.41, H 2.02, N 4.57, F 46.54%.

Compound **2c**: IR (film) (ν, cm^{-1}): 3310 (s), 1400 (s), 1340 (s), 1320 (s), 1280 (s), 1100–1200 (vs), 1065 (m), 970 (w), 900 (s), 820 (s), 740 (s), 700 (s), 580 (s). ^1H NMR (δ): 5.75 (broad, NH), 2.85 (s, CH_3). ^{19}F NMR (δ): −12.0 (s, ICF_2), 4.8 (m, OCF_2), 8.3 (m, CF_2O), 38.7 (s, CF_2S).
MS (m/z, %): 438 (M^+ + 1, 5.5), 310 (M^+—I, 30.0), 227 ($ICF_2CF_2^+$, 21.0), 177 (ICF_2^+, 12.5), 127 (I^+, 4.0), 94 ($SO_2NHCH_3^+$, 100.0), 78 (SO_2N^+, 41.0).
Anal.: Calcd. for $C_5H_4F_8INO_3S$ C 13.73, H 0.90, N 3.20, F 34.78.
Found: C 13.40, H 1.07, N 3.14, F 34.76%.

Compound **2d**: IR (film) (ν, cm^{-1}): 3300 (s), 2950 (w), 1420 (s), 1360 (s), 1325 (s), 1280 (s), 1100–1200 (vs), 990 (w), 940 (m), 900 (s), 750 (s), 710 (s), 600 (s). ^1H NMR (δ): 5.70 (t, NH), 3.28 (m, CH_2), 1.15 (t, CH_3). ^{19}F NMR (δ): −11.8 (s, ICF_2), 4.8 (m, OCF_2), 8.3 (m, CF_2O), 39.2 (s, CF_2S).
M/S (m/z, %): 452 (M^+ + 1, 4.6), 436 (M^+—CH_3, 5.5), 324 (M^+—I, 18.3), 227 ($ICF_2CF_2^+$, 27.5), 177 (ICF_2^+, 15.0), 108 ($^+SO_2NHEt$, 100.0), 92 ($SO_2NCH_2^+$, 25.8).
Anal.: Calcd. for $C_6H_6F_8INO_3S$ C 15.96, H 1.33, N 3.10, F 33.70.
Found: C 15.67, H 1.10, N 3.03, F 33.54%.

Compound **2e**: IR (film) (ν, cm^{-1}): 3310 (s), 2980 (w), 2930 (w), 1400 (s), 1320 (s), 1280 (s), 1100–1200 (vs), 1050 (m), 980 (w), 940 (m), 855 (m), 780 (m), 745 (m). ^1H NMR (δ): 5.68 (broad, NH), 2.80 (s, CH_3). ^{19}F NMR (δ): −3.5 (s, $ClCF_2$), 4.8 (m, OCF_2), 9.5 (m, CF_2O), 39.0 (s, CF_2S).
MS (m/z, %): 346/348 (M^+ + 1, 4.11/1.52), 135/137 ($ClC_2F_4^+$, 14.99/5.93), 119 ($CF_3C_2F^+$, 14.26), 100 ($C_2F_4^+$, 16.06), 95 ($SO_2NH_2Me^+$, 100.0), 85/87 ($ClCF_2^+$, 16.99/5.17), 80 ($SO_2NH_2^+$, 10.64), 78 (SO_2N^+, 45.33).
Anal.: Calcd. for $C_5H_4ClF_8NO_3S$ C 17.39, H 1.16, N 4.06, F 44.06.
Found: C 17.58, H 1.08, N 4.39, F. 44.19%.

Compound **2f**: IR (film) (ν, cm^{-1}): 3300 (s), 1350–1380 (w), 1180–1240 (w), 1130 (s). ^1H NMR (δ): 3.95 (broad, NH), 3.37 (m, CH_2), 1.25 (t, CH_3). ^{19}F NMR (δ): 5.2 (m, CF_3), 36.3 (s, CF_2), 44.7 (s, CF_2), 50.0 (s, CF_2S).
MS (m/z, %): 328 (M^+ + 1, 2.0), 312 (M^+—CH_3, 13.2), 248 ($C_3F_7SO_2NH^+$, 16.8), 219 ($C_4F_9^+$, 16.8), 178 ($CF_3SO_2NH_2Et^+$, 9.6), 149 ($CF_3SO_2NH_2^+$, 3.2), 131 (CF_3SON^+, 16.8), 119 ($CF_3CF_2^+$, 7.2), 108 (SO_2NHEt^+, 100.0), 80 ($SO_2NH_2^+$, 44.0), 69 (CF_3^+, 58.4).
Anal.: Calcd. for $C_6H_6F_9NO_2S$ C 22.02, H 1.83, N 4.28, F. 52.29.
Found: C 21.94, H 1.57, N 4.25, F. 52.31%.

Preparation of N-Alkyl-N-haloperfluoroalkanesulfonylamide **3a–f**: The typical procedure for preparing **3(a, b, e)** are as follows: **2e** (6.2 g, 0.018 mol), KOH (2.5 g) and H_2O (10 mL) are mixed in a 50 mL flask. Cl_2 gas is passed into the mixture for 10 hours at room temperature with stirring. The water layer is extracted by CH_2Cl_2 (3 × 10 mL). The organic phase is combined and dries over Na_2SO_4. After removing the CH_2Cl_2, the residue is distilled under vacuum to give **3e** (5.4 g, 79%, colorless liquid).

The compounds **3(c, d, f)** are prepared as follows: **2c** (4.4 g, 0.010 mol), NaOH (1.0 g) and H_2O (10 mL) are mixed in a 25 mL flask. The liquid bromine (4.0 g) is dropped into the flask. Continues stirring for 1 hour after dropping out. The water phase is exacted by CH_2Cl_2 (3 × 10 mL). The organic layer is combined and dries over Na_2SO_4. After removing the CH_2Cl_2, the residue is dried under high vacuum for 1 hour at room temperature to give **3c** (4.4 g, 85%, yellowish liquid).

Yields and m.p. or b.p. are shown in Table II.

Compound **3a**: IR (film) (ν, cm^{-1}): 2990 (w), 1430 (m), 1375 (s), 1330 (m), 1110–1220 (vs), 960 (m), 860 (m). ^1H NMR (δ): 5.85 (t, $^2J_{HF}$ = 54.0 Hz, HCF_2), 3.40 (s, CH_3). ^{19}F NMR (δ): 4.3 (m, OCF_2), 11.0 (m, CF_2O), 33.4 (s, CF_2S), 61.8 (d, HCF_2). MS (m/z, %): 312 (M^+ + 2—Cl, 1.67), 119 ($CF_3CF_2^+$, 17.24), 101 ($HCF_2CF_2^+$, 29.13), 100 ($CF_2CF_2^+$, 9.95), 95 ($SO_2NH_2CH_3^+$, 100.0), 78 (SO_2N^+, 33.47).
Anal.: Calcd. for $C_5H_4F_8NO_3S$ C 17.38, H 1.17, N 4.05, F 43.99.
Found: C 17.22, H 1.02, N 4.12, F. 43.72%.

Compound **3b**: Ir (film) (ν, cm^{-1}): 2990 (m), 1430 (m), 1370 (s), 1285 (s), 1100–1200 (vs), 1015 (w), 955 (m), 860 (w). ^1H NMR (δ): z5.86 (t, $^2J_{HF}$ = 54.0 Hz, HCF_2), 3.76 (q, 2H), 1.34 (t, 3H). ^{19}F NMR (δ): 4.3 (m, OCF_2), 11.0 (m, CF_2O), 34.5 (s, CF_2S), 60.4 (d, HCF_2). MS (m/z, %): 326 (M^+ + 2—Cl, 2.56), 310 (M^+ + 1—Cl—CH_3, 6.82), 119 ($CF_3CF_2^+$, 28.99), 108 (SO_2NHEt^+, 100.0), 101 ($HCF_2CF_2^+$, 43.98), 100 ($CF_2CF_2^+$, 11.59), 51 (HCF_2^+, 19.34).
Anal.: Calcd. for $C_6H_6F_8ClNO_3S$ C 20.06, H 1.67, N 3.90, F. 42.34.
Found: C 20.41, H 1.59, N 4.17, F 41.96%.

Compound **3c**: IR (film) (ν, cm^{-1}): 1400 (s), 1330 (s), 1290 (s), 1100–1200 (vs), 910 (s), 810 (s), 760 (s), 720 (s), 340–500 (vs). ^1H NMR (δ): 3.50 (s, CH_3). ^{19}F NMR (δ): −12.0 (s, ICF_2), 4.8 (m, OCF_2), 8.3 (m, CF_2O), 36.0 (s, CF_2S).
MS (m/z, %): 436 (M^+—Br, 1.6), 310 (M^+ + 1—I—Br, 16.8), 227 ($ICF_2CF_2^+$, 16.8), 177 (ICF_2^+, 14.0), 119 ($CF_3CF_2^+$, 17.7), 94 ($SO_2NHCH_3^+$, 100.0), 78 (SO_2N^+, 35.6).

Compound **3d**: IR (film) (ν, cm^{-1}): 1400 (s), 1330 (s), 1290 (s), 1100–1200 (vs), 940 (s), 910 (s), 760 (s), 600 (s), 300–400 (vs). ^1H NMR (δ): 3.60 (q, CH_2), 1.26 (t, CH_3). ^{19}F NMR (δ): −13.3 (s, ICF_2), 4.1 (m, OCF_2), 7.8 (m, CF_2O), 34.0 (s, CF_2S).
MS (m/z, %): 453 (M^+ + 2—Br, 1.6), 375 (M^+—I—Et, 5.6), 197 ($HOCF_2CF_2SO_2NH_2^+$, 6.4), 180 ($CF_2CF_2SO_2NH_2^+$, 5.0), 157 ($CF_2SO_2NEt^+$, 4.0), 45 ($EtNH_2^+$, 100.0).

Compound **3e**: IR (film) (ν, cm^{-1}): 2980 (w), 2930 (w), 1400 (s), 1320 (s), 1280 (s), 1100–1200 (vs), 1050 (m), 985 (w), 940 (m), 855 (m), 780 (m), 745 (m). ^1H NMR (δ): 3.43 (s, CH_3). ^{19}F NMR (δ): −3.6 (s, $ClCF_2$), 4.8 (m, OCF_2), 9.4 (m, CF_2O), 33.6 (s, CF_2S).
MS (m/z, %): 346/348 (M^+ + 2—Cl, 2.03/0.73), 135/137 ($ClCF_2CF_2^+$, 14.93/5.02), 119 ($CF_3CF_2^+$, 14.25), 100 ($CF_2CF_2^+$, 16.32), 95 ($SO_2NH_2Me^+$, 100.0), 85/87 ($ClCF_2^+$, 16.21/5.37), 78 (SO_2N^+, 37.23).
Anal.: Calcd. for $C_5H_3Cl_2F_8NO_3S$ C 15.83, H 0.79, N 3.69, F 40.11.
Found: C 15.59, H 1.01, N 3.88, F. 39.84%.

Compound **3f**: IR (film) (ν, cm^{-1}): 3300 (s), 1355–1390 (w), 1190–1250 (w), 1130 (s). ^1H NMR (δ): 3.8 (q, 2H), 1.45 (t, 3H). ^{19}F NMR (δ): 5.6 (m, 3F), 32.3 (s, 2F), 45.1 (s, 2F), 50.2 (s, 2F).
MS (m/z, %): 328 (M^+ + 2—Br, 6.0), 312 ($C_4F_9SO_2NCH_3^+$, 17.2), 248 ($C_3F_7SO_2NH^+$, 20.8), 219 ($C_4F_9^+$, 24.0), 178 ($CF_3SONH_2Et^+$, 12.0), 131 (CF_3SON^+, 20.0), 108 (SO_2NHEt^+, 100.0), 80 ($SO_2NH_2^+$, 38.2), 69 (CF_3^+, 45.6).

Preparation of **4**: A typical procedure for preparing **4** is as followed. $P(OEt)_3$ (1.0 mL, 5.7 mmol) is dropped into a 10 mL flask containing **3a** (1.55 g, 4.5 mmol) slowly. The reaction is vigorous and sets off white smoke. When dropping out, the flask is heated to 150°C for 1 hour. Under high vacuum and 80°C for one hour the excess $P(OEt)_3$ is moved away. The crude product is purified by column chromatography. Yields and b.p. are shown in Table II.

Compound **4a**: IR (film) (ν, cm^{-1}): 2990 (m), 2930 (m), 1440 (w), 1400 (s), 1320 (m), 1280 (s), 1120–1230 (vs), 1030 (s), 980 (m), 920 (m). ^1H NMR (δ): 5.85 (t, $^2J_{HF}$ = 54.0 Hz, HCF_2), 3.80 (m, 4H), 2.71 (d, $^3J_{HP}$ = 10.4 Hz, 3H), 0.94 (m, 6H). ^{31}P NMR: 2.97 (s). ^{19}F NMR (δ): 4.3 (m, OCF_2), 10.8 (m, CF_2O), 38.1 (s, CF_2S), 61.9 (d, HCF_2).
MS (m/z, %): 448 (M^+ + 1, 20.24), 420 (M^+ + 1—C_2H_4, 31.36), 392 (M^+ + 1—$2C_2H_4$, 15.87), 372 (M^+ − 1—Et—OEt, 6.14), 230 ($^+SO_2N(CH_3)P(O)(OEt)_2$, 50.97), 202 ($^+SO_2N(CH_2)P(O)(OEt)(OH)$, 55.21), 174 ($^+SO_2N(CH_3)P(O)(OH)_2$, 100.0), 166 ($^+N(CH_3)P(O)(OEt)_2$, 29.35), 138 ($^+N(CH_3)P(O)(OH)(OEt)$, 10.04), 122 ($HP(OEt)_2^+$, 42.63), 110 ($^+N(CH_3)P(O)(OH)_2$, 22.84), 101 ($HC_2F_4^+$, 35.86), 95 ($HP(OH)(OEt)^+$, 44.57).
Anal.: Calcd. for $C_9H_{14}F_8NO_6PS$ C 24.16, H 3.13, N 3.13.
Found: C 24.08, H 3.00, N. 3.45%.

Compound **4b**: IR (film) (ν, cm^{-1}): 3000 (m), 2920 (w), 1440 (w), 1400 (s), 1320 (m), 1280 (m), 1110–1230 (vs), 920 (m). ^1H NMR (δ): 5.85 (t, $^2J_{HF}$ = 54.0 Hz, HCF_2), 3.80 (m, 4H), 3.12 (m, 2H), 0.93 (m, 9H). ^{19}F NMR (δ): 4.3 (m, OCF_2), 10.7 (m, CF_2O), 38.6 (s, CF_2S), 61.8 (d, HCF_2). ^{31}P NMR: 2.98 (s).
MS (m/z, %): 461 (M^+, 1.85), 445 (M^+—CH_3—1, 7.57), 243 ($^+SO_2N(Et)P(O)(OEt)_2$ – 1, 47.5), 215 ($^+SO_2NHP(O)(OEt)_2$ – 1, 80.65), 188 ($^+SO_2N(Et)P(O)(OH)_2$, 100.0), 180 ($N(Et)P(O)(OEt)_2^+$, 64.06), 160 ($SO_2NHP(O)(OH)_2^+$, 83.29), 137 ($P(O)(OEt)_2^+$, 33.47), 119 ($CF_3CF_2^+$, 17.54), 51 (HCF_2^+, 14.23).
Anal.: Calcd. for $C_{10}H_{16}F_8NO_6PS$ C 26.03, H 3.47, N 3.03.
Found: C 25.80, H 3.61, N 3.27%.

Compound **4c**: IR (film) (ν, cm^{-1}): 3350 (m), 1400 (m), 1330 (m), 1290 (m), 1120–1200 (s), 1020 (s), 910 (m), 330–500 (vs). ^1H NMR (δ): 3.98 (m, 4H), 2.93 (d, $^3J_{HP}$ = 10.4 Hz, 3H), 1.04 (m, 6H). ^{31}P NMR: 2.97 (s). ^{19}F NMR (δ): –8.8 (s, ICF_2), 5.6 (m, OCF_2), 9.2 (m, CF_2O), 36.7 (s, CF_2S).
MS (m/z, %): 574 (M + 1, 1.0), 230 ($^+SO_2N(CH_3)P(O)(OEt)_2$, 36.0), 202 ($^+SO_2N(CH_3)P(O)(OEt)(OH)$, 47.3), 174 ($^+SO_2N(CH_3)P(O)(OH)_2$, 100.0), 166 ($^+N(CH_3)P(O)(OEt)_2$, 28.0) 138 ($^+N(CH_3)P(O)(OEt)(OH)$, 13.2), 109 ($^+N(CH_3)P(O)(OH)_2$, 29.1), 94 ($^+SO_2NHCH_3$, 29.7).
Anal.: Calcd. for $C_9H_{13}F_8O_6NPS$ C 16.75, H 2.27, N 2.44.
Found: C 16.95, H 2.45, N 2.39%.

Compound **4d**: IR (film) (ν, cm^{-1}): 3000 (m), 1440 (m), 1390 (s), 1280 (s), 1100–1200 (s), 1020 (s), 800 (s), 690 (s), 580 (m), 300–400 (s). ^1H NMR (δ): 4.08 (m, 4H), 3.37 (m, 2H), 1.24 (m, 9H). ^{31}P NMR: 2.97 (s). ^{19}F NMR (δ): –7.7 (s, ICF_2), 3.6 (m, OCF_2), 9.3 (m, CF_2O), 35.7 (s, CF_2S).
MS (m/z, %): 588 (M^+ + 1, 1.7), 572 (M^+—CH_3, 3.8), 532 (M^+ + 1—$2C_2H_4$, 1.8), 436 ($ICF_2CF_2OCF_2CF_2SO_2NCH_3^+$, 10.6), 324 (MH—I—$P(O)(OEt)_2^+$, 3.3), 263 ($FSO_2N(Et)P(O)(OEt)_2^+$, 65.1), 227 ($ICF_2CF_2^+$, 66.7), 216 ($SO_2N(Et)P(O)(OH)(OEt)^+$, 77.0), 188 ($SO_2N(Et)P(O)(OH)_2^+$, 84.8), 108 ($SO_2NH(Et)^+$, 100.0), 99 ($FSO_2NH_2^+$, 74.2).
Anal.: Calcd. for $C_{10}H_{15}F_8O_6NPS$ C 16.35, H 2.56, N 2.39.
Found: C 16.47, H 2.70, N 2.45%.

Compound **4f**: IR (film) (ν, cm^{-1}): 2980 (s), 1360 (w), 1180–1240 (w), 1135 (s). ^1H NMR δ: 3.74 (m, 4H), 3.25 (m, 2H), 0.87 (m, 9H). ^{31}P NMR: 2.97 (s). ^{19}F NMR δ: 4.7 (m, CF_3), 37.0 (s, CF_2), 44.8 (s, CF_2), 14.9 (s, CF_2).
MS (m/z, %): 464 (M^+ + 1, 0.4), 436 (M^+ + 2—Et, 0.8), 312 ($C_4F_9SO_2NCH_3^+$, 2.4), 263 ($FSO_2NP(OEt)_3^+$, 24.0), 235 ($FSO_2NP(OEt)_2(OH)^+$, 20.0), 207 ($FSO_2NP(OEt)(OH)_2^+$, 15.6), 179 ($FSO_2NP(OH)_3^+$, 15.6), 155 ($NH_2P(OEt)_2(OH)H^+$, 23.2), 127 $NH_2P(OEt)(OH)_2H^+$, 69.6), 99 ($NH_2P(OH)_3H^+$, 100.0), 81($P(O)(OH)_2^+$, 39.2).
Anal.: Calcd. for $C_{10}H_{15}F_9O_5NPS$ C 25.92, H 3.24, N 3.02.
Found: C 26.07, H 3.19, N 2.88%.

REFERENCES

1. S. Bauermeister and J. A. Modro, *Phosphorus Sulfur and Silicon*, **72,** 201 (1992).
2. L. Maier, *ibid*, **47,** 361 (1990).
3. A. Zwierzak and S. Pilichowska, *Synthesis*, 923 (1982).
4. I. V. Martynov, A. Y. Aksinonko, V. Sokolov, A. N. Chekhlov, A. W. Pushin and O. V. Korenchenko, *Phosphorus Sulfur and Silicon*, **45,** 223 (1990).
5. Y. C. Shen and W. Cen, *J. Fluorine Chem.*, **52,** 369 (1991).
6. D. Su, W. Cen, K. L. Kirchmeier and J. M. Shreeve, *J. Can. Chem.*, **67,** 1795 (1989).
7. D. J. Burton, A. S. Modak, R. Guneratne, D. Su, W. Cen, R. L. Kirchmeier and J. M. Shreeve, *J. Am. Chem. Soc.*, **111,** 1773 (1989).
8. S. Z. Zhu, to be published.
9. R. N. Haszeldine and T. Gramstad, *J. Chem. Soc.*, 173 (1956).
10. Shi-Zheng Zhu, AiWen Li and Bin Xu, *J. Fluorine Chem.*, **67,** 7 (1994).
11. W. G. Bentrude, *Acc. Chem. Res.*, **15,** 117 (1982).
12. W. G. Bentrude, J. T. L. Fu and P. E. Rogers, *J. Am. Chem. Soc.*, **95,** 3625 (1973).
13. Shi-Zheng Zhu and Xiang-Ling Jin, to be published.
14. D. J. Burton and A. Thenattan, *Tetrahedron Lett.*, 6113 (1989).
15. Perfluoro Sulfonic Acid Group, *Hua Xue Xue Bao*, **37,** 315 (1978), *CA*, 93:113886g.