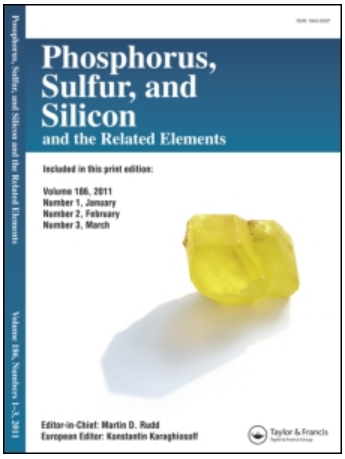

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF DIETHYL N-(PERFLUOROALKANESULFONYL) PHOSPHORAMIDATES AND N-(PERF'LUOROALKANESULFONYL) PHOSPHORAMIDIC ACIDS

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To cite this Article Zhu, Shizheng , Xu, Guoling , Qin, Chaoyue , Xu, Yong and Chu, Qianli(1998) 'SYNTHESIS OF DIETHYL N-(PERFLUOROALKANESULFONYL) PHOSPHORAMIDATES AND N-(PERF'LUOROALKANESULFONYL) PHOSPHORAMIDIC ACIDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 140: 1, 53 — 61
To link to this Article: DOI: 10.1080/10426509808035731
URL: http://dx.doi.org/10.1080/10426509808035731

Phosphorus, Sulfur and Silicon, 1998, Vol. 140, pp. 53-61
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SYNTHESIS OF DIETHYL N-(PERFLUOROALKANESULFONYL) PHOSPHORAMIDATES AND N-(PERFLUOROALKANESULFONYL) PHOSPHORAMIDIC ACIDS

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(Received 18 February, 1998)

N-(perfluoroalkylsulfonyl)phosphoramidates are prepared by the reaction of diethylchloro phosphate $ClP(O)(OEt)_2$ with sodium perfluoroalkylsulfonylamides R_fSO_2NHNa or sodium N-trimethylsilylperfluoroalkylsulfonylamides $R_fSO_2N(Na)SiMe_3$ respectively. Hydrolysis of diethyl N-(perfluoroalkylsulfonyl) phosphoramidates under acidic condition did not give the expected $R_fSO_2NHP(O)(OH)_2$ but led to a brake of the N-P bond forming the corresponding perfluoroalkylsulfonylamides. Silylation of $R_fSO_2NEP(O)(OR)_2$ with Me_3SiBr give high yields of $R_fSO_2NHP(O)(OSiMe_3)_2$ which were then treated with water at room temperature to afford the title phosphoramidic acids.

Keywords: N-(perfluoroalkanesulfonyl) phosphoramidates; phosphoramidic acids

INTRODUCTION

Synthesis and the chemical translation of the aminophosphonates and their derivatives have aroused great interest[1–4]. It is well known that the incorporation of a fluorine atom or fluorine-containing group into the molecule can increase the biochemical activity of the compound. Therefore it is valuable to develop a synthetic method for the preparation of the fluorine-containing aminophosphonates. To the best of our knowledge, dialkyl

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N-(perfluoroalkylsulfonyl) phosphoramidates and phosphoramidicacids $R_fSO_2NHP(O)(OR)_2$ (R: Me, Et, H) are unknown compounds till present.

In this paper we wish to report a general method for the preparation of these compounds from readily available starting materials.

RESULTS AND DISCUSSION

During the studies of bis(perfluoroalkylsulfonyl)imines, it was noticed that the sodium salt of perfluoroalkylsulfonylamides R_fSO_2NHNa **1** was not reactive enough to react with perfluoroalkylsulfonyl fluoride to introduce another R_fSO_2- group[5–6]. However, **1** reacted readily with diethyl chlorophosphate at room temperature forming a P-N bond:

$$\underset{\mathbf{1}}{R_fSO_2NHNa} + \underset{\mathbf{2}}{ClP(O)(OEt)_2} \xrightarrow[R.T.,\ 12h]{CH_3CN} \underset{\mathbf{3}}{R_fSO_2NH_2} + \underset{\mathbf{4\ (a-d)}}{R_fSO_2NHP(O)(OEt)_2}$$

$$+\ \underset{\mathbf{5\ (a-d)}}{R_fSO_2N(Na)P(O)(OEt)_2}$$

R_f: CF_3 **(1a)**; C_4F_9 **(1b)**; $ICF_2CF_2OCF_2CF_2$ **(1c)**; $ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2$ **(1d)**.

It was noteworthy that, in adddition to the expected product **4**, perfluoroalkylsulfonylamide **3** (~40%) and 5 was also formed due to the further reaction of **1** with the product **4** which has a more acidic proton >NH (the ^1H NMR chemical shift of $CF_3SO_2NHP(O)(OEt)_2$ is 10.3 ppm, in CD_3CN).

To avoid this by-reaction, the silylated sulfonamide $R_fSO_2N(Na)SiMe_3$ **6** was used to react with **2**. Recently Harger has reported that phosphonic chloride $R_2P(O)Cl$ reacted with a N-silane compound forming a P-N bond by eliminating trimethylsilyl chloride[7]. Also in our previous works, the reaction of **6** with perfluoroalkylsulfonyl fluoride[5–6] gave $(R_fSO_2)_2NNa$ by eliminating trimethylsilyl fluoride. In the reaction of **6** with diethyl chlorophosphate, however, two products formed by elimination of Me_3SiCl or NaCl respectively, thus:

$$\underset{\mathbf{6}}{R_fSO_2N(Na)SiMe_3} + 2 \xrightarrow[R.T.]{CH_3CN} \begin{cases} \xrightarrow{-\ SiMe_3Cl} \underset{\mathbf{5}}{R_fSO_2N(Na)P(O)(OEt)_2} \\ \xrightarrow{-\ NaCl} \underset{\mathbf{7}}{R_fSO_2N(SiMe_3)P(O)(OEt)_2} \end{cases}$$

Rf: CF_3 **(6a)**; C_4F_9 **(6b)**.

7 are fully characterized by ^{19}F NMR, ^1H NMR, IR and MS. They are very moisture sensitive. When exposure to air, they are transform to **4** completly.

Dechlorination of $ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2SO_2N(Na)P(O)(OEt)_2$ **5c** by heating it with zinc power in Ac_2O gave a high yield of the fluoronated vinyl ether containing two functional groups i.e. sulfonimide and phosphonate:

$$\mathbf{5d} \xrightarrow[100\ ^\circ C,\ 12h]{Zn\ /\ Ac_2O} CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2N(Na)P(O)(OEt)_2 \qquad \underline{\mathbf{8}}$$

Being an attractive monomer for the preparation of the functional membrane[8], the copolymerization of **8** with tetrafluoroethylene is under inverstigation.

Attempts to prepare N-[(perfluoroalkylsufonyl)amino]phosphonic acids $R_fSO_2NHP(O)(OH)_2$ **10** by hydrolysis of **4** have failed. We have successfully prepared $R_fSO_2NHSO_2CF_2CF_2OCF_2CF_2P(O)(OH)_2$ by hydrolysis of the phosphonates $R_fSO_2NHSO_2CF_2CF_2OCF_2CF_2P(O)(OEt)_2$ with concertrated hydrochloric acid[9]. Under the same reaction condition, however, **4** gave only the N-P bond broken product:

$$\mathbf{4} \xrightarrow[100\ ^\circ C,\ 12h]{HCl} R_fSO_2NH_2 + P(O)(OH)_2$$

Under basic condition, for example, **4** was heated with 2N KOH at 60 °C for 12 h, no hydrolysis occured.

Silylation of the phosphonate with trimethylsilylbromide gave a nearly quantinative yield of the silyl product, which was then treated with water at room temperature for 7 days forming the corresponding phosphoric acid, thus:

$$\underset{\mathbf{4(a\text{-}c)}}{R_fSO_2NHP(O)(OR)_2} \xrightarrow[70\ ^\circ C,\ 48h]{Me_3SiBr} \underset{\mathbf{9\ (a\text{-}c)}}{R_fSO_2NHP(O)(OSiMe_3)_2}$$

$$\underset{\mathbf{9\ (a\text{-}c)}}{R_fSO_2NHP(O)(OSiMe_3)_2} \xrightarrow[R.T.,\ 7\ days]{H_2O} \underset{\mathbf{10\ (a\text{-}c)}}{R_fSO_2NHP(O)(OH)_2}$$

More polar products **10** did not disolved in $CHCl_3$ and CH_3CN, their NMR spectura were recorded in aceton-d_6, the chemical shift of ^1H NMR are 8.10 and 6.80 ppm for OH and NH respectively. Literature has reported a fluoro-containing phosphonic acid, its chemical shift of OH is 8.3 in DMSO-d_6 [10].

In summary, the title N-(perfluoroalkanesulfonyl)phosphoramidic acids are synthesized by silylation followed by hydrolysis of the corresponding phosphoramidates which are obtained by the reaction of $ClP(O)(OR)_2$ with R_fSO_2NHNa or $R_fSO_2N(SiMe_3)Na$.

The prepared N-(perfluoroalkanesulfonyl)phosphoramidates **4** and corresponding phosphoramidic acids **10** are summerized in Table I.

TABLE I Products 4 and 10 prepared

Compounds 4 and 10	*M.p. or b.p. (°c)*	*Yield (%)*	*Elemental analysis (Found/Calcd.)*
4a	115–8/0.03 torr	52	C: 20.98/21.05, H: 4.00/3.86, N: 5.10/4.91
4b	119–123/0.03torr	54	C: 22.01/22.07, H: 2.64/2.53, N: 3.32/3.22
4c	180–2/0.01 torr	67	C :17.34/17.17, H: 2.04/1.97, N: 2.72/2.50
4d	138–142/0.03 torr	48	C: 20.04/20.33, H: 1.72/1.69, N: 2.21/2.16
10a	121–4	78	C: 5.05/5.24, H: 1.51/1.31, N: 6.01/6.11
10b	93–5	76	C: 12.33/12.66, H: 0.92/0.79, N: 3.41/3.69
10c	oil	69	C: 9.30/9.54, H: 0.98/0.60, N: 2.57/2.78

EXPERIMENTAL

The melting points were taken on a Mel-temp apparatus are uncorrected. IR spectra were recorded using a Perking-Elmer 1430 ratio recording instrument. ^{19}F NMR, ^{1}H NMR and ^{31}P NMR were obtained on IBM NR200AF spectrometer using $CFCl_3$, TMS and H_3PO_4 as internal or external standants (CD_3CN, $CDCl_3$ and $(CD_3)_2CO$ as solvent). ^{19}F NMR chemical shifts are positive when found at a lower field than that of $CFCl_3$. MS spectra were obtained from a HP Hewlett packed GC-MS 5890 instrument. Elemental analysis are performed in Shanghai Institute of Organic Chemistry.

Preparation of $CF_3SO_2NHP(O)(OEt)_2$ 4a

$ClP(O)(OEt)_2$ (1.72g, 10 mmol) was injected into a 25 ml flask containing a solution of CF_3SO_2NHNa (1.71g, 10 mmol) and CH_3CN (15 ml). This reaction mixture was stirred for 9h at room temperature. After removal of the solvent, the residue was distilled under vacuum giving $CF_3SO_2NH_2$ (0.6g, 40%) and **4a** (0.7g, 25%). The remaining solid was acidified by HCl

(3N, 5 ml), extracted with Et_2O (10 ml × 2), dried with Na_2SO_4. After removal of Et_2O, vacuum distillation gave **4a** (0. 77g, 27%). The overal yield of **4a** is 52%.

IR (KCl, ν_{max} cm^{-1}) : 3357 (m, NH), 3000(m), 2952 (m, CH_3CH_2), 1394 (s, SO_2), 1238 (m, P=O), 1038 (s, P-O-C).

^1H NMR (δ)($CDCl_3$): 10.3 (s, NH), 4.23 (m, CH_2), 1.35 (t, CH_3).

^{19}F NMR (δ): −79.4 (s, CF_3).

MS (m/e, %) (EI): 286 (M^+H, 15.1), 284 (M^+-H, 2.6), 244(M^+H-C_3H_6, 100.0), 230(M^+H-C_4H_8, 11.2), 216(M^+-CF_3, 32.1), 160(M^+-CF_3-C_4H_8, 96.3), 142(M^+-CF_3-C_2H_5-OC_2H_5, 18.3), 69(CF_3^+, 11.3).

Similarly compounds 4b, 4c and 4d were prepared

$C_4F_9SO_2NHP(O)(OEt)_2$ **4b**

IR (KCl, ν_{max} cm^{-1}) : 3378 (m, NH), 3293(m, NH), 2996(m, C_2H_5), 1397(s, SO_2), 1237 (s, P=O), 1037(s, P-O-C).

^1H NMR (δ)($CDCl_3$): 9.94(s,NH), 4.18(m,CH_2), 1.36(t,CH_3).

^{19}F NMR (δ) : −80.4(s, CF_3), −113.2(t, CF_2S), −120.6(t, CF_2), −125.3(t, CF_2).

MS(m/e, %): 436(M^+H, 3.9), 420(M^+-CH_3, 1.0), 418(M^+-H-O, 7.1), 362 ($C_4F_9SO_2NHP^+(O)(OH)_2$ 6.2), 282($C_4F_9SONH^+$, 1.3), 216(M^+-C_4F_9, 62.9), 188(M^+-C_4F_9-C_2H_4, 100.0), 160(M^+-C_4F_9-C4H_8, 43.2), 152(M^+-$C_4F_9SO_2$, 12.6), 137($(EtO)_2PO^+$, 14.7), 69(CF_3^+, 30.0).

$ICF_2CF_2OCF_2CF_2$ $SO_2NHP(O)(OEt)_2$ **4c**

IR (KCl, ν_{max} cm^{-1}) : 3375 (s, NH), 2995(s), 2948(m) (CH_2CH_3), 1380(s, SO_2), 1238(s, P=O), 1220 – 1110 (vs, CF).

^1H NMR (δ)(CD_3CN): 9.38(s, NH), 4.23(m,CH_2), 1.33(m,CH_3).

^{19}F NMR (δ): −69.0(s, ICF_2), −82.5(m, CF_2), −86.0(m, CF_2O), −116.3(s, CF_2S).

MS(m/e, %): 560 (M^+H, 2.3), 542 (M^+-H-O, 6.1), 503 ($R_fSO_2NHP^+(O)(OH)_2$, 7.3), 423(M^+H-$P(O)(OEt)_2$, 27.6), 227(ICF_2CF_2,6.8), 216(M^+-R_f, 100.00), 177(ICF_2, 8.1).

a b c d e f g

$ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2SO_2NHP(O)(OEt)_2$ **4d**: b.p. 138–142°C / 3×10^{-3}mmHg.

IR (KCl, $\nu_{max}cm^{-1}$) : 3293(m), 3195(m, NH), 2996(s), 2947(m) (CH_2CH_3), 1395(s, SO_2), 1240(s, P=O), 1036(s, P-O-C).

^1H NMR (δ)(CD_3CN): 9.87(s, NH), 4.33(m,CH_2), 1.41(t,CH_3).

^{19}F NMR (6): −70.6(s, δ_a), −76.5(m, δ_b), −77.9(m, δ_c), −144.8(t, δ_d), −79.0(s, δ_e), 83.2, −84.8(m, δ_f), −116.4(s, δ_g).

Preparation of $CF_3SO_2N(SiMe_3)P(O)(OEt)_2$ 7a

Into a 25 ml flask containing a solution of anhydrous CH_3CN (15 ml) and $CF_3SO_2N(Na)SiMe_3$ (2.4g, 10 mmol), which was prepared according to the literature[11], diethyl chlorophosphate (1.72g, 10mmol) was injected. This reaction mixture was stirred for 12h at room temperature. After removal of the solvent, vacuum distillation gave **7a** (1.5, 43%). The residue was acidified using hydrochloric acid, extracted with Et_2O and then distillated giving **4a** (0.7g, 25%). b.p. 108–112 °C / 3×10^{-3} mmHg.

IR (KCl, ν_{max} cm^{-1}) : 2994(s), 2947(s), 2847(m), 2762(m)(CH_3,CH_2), 1397(s, SO_2), 1261(vs, P=O), 1037(s, P-O-C).

^1H NMR (δ)($CDCl_3$): 0.30(s,$SiMe_3$), 1.34(t,C$\underline{H}_3CH_2$), 4.23(m,C$\underline{H}_2CH_3$),.

^{19}F NMR (δ): −80.0(s, CF_3).

MS(m/e, %): 337(M^+-H-F, 0.9), 329(M^+H-C_2H_5, 1.1), 271(M^+-CF_3-H-O, 2.9), 283(M^+-H-$SiMe_3$), 267(M^+-2EtO, 10.0),201(M^+-$SiMe_3$-F-SO_2, 35.7), 185(M^+-$SiMe_3$-F-SO_2-O, 9.8), 151 ($Me_3SiNP(O^+(OH)_2$, 51.6), 135($Me_3SiNP(O)^+H$, 52.3), 131(CF_3SON^+, 29.0), 101(CF_3S^+, 48.4), 87(Me_3SiN^+, 33.4), 85(CF_3O^+, 100.0), 73(Me_3Si^+, 1.1), 69(CF_3^+, 20.3).

Similarly $C_4F_9SO_2N(SiMe_3)P(O)(OEt)_2$ 7b was prepared (yield: 32%)

b.p. 121–125 °C / 3×10^{-3} mmHg.

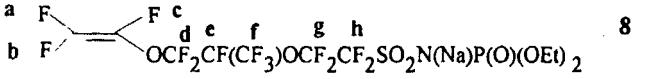
IR (KCl, ν_{max} cm^{-1}) : 2990(s), 2948(s), 2853(s), 2758(m)(CH_3,CH_2), 1389(s, SO_2), 1256(s, P=O), 1037(s, P-O-C).

^1H NMR (δ)($CDCl_3$): 0.31(s, $SiMe_3$), 1.35(t, C$\underline{H}_3CH_2$), 4.29(m, C$\underline{H}_2CH_3$),.

^{19}F NMR (δ): −81.3(t, CF_3),-113.6(t, CF_2S), −121.7(m, CF_2), −126.6(m, CF_2).

MS(m/e, %): 463(M^+H-3 × CH_3, 3.7), 435(M^+H-$SiMe_3$), 407(M^+H-$SiMe_3$-C_2H_5, 2.8), 362($C_4F_9SO_2NP^+(OH)_2$, 6.9), 244(M+H-3 × CH_3-C_4F_9, 100.0), 216(M^+H-$SiMe_3$-C_4F_9-C_2H_4, 38.7), 160(M^+-$SiMe_3$-C_4F_9-C_2H_5-C_2H_4, 67.2), 73(Me_3Si^+, 2.5), 69(CF_3^+, 13.0).

Preparation of



8

A mixture of Ac_2O (10 ml), zinc power (1.5g, 11 mmol) and $ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2SO_2N(Na)P(O)(OEt)_2$ **4d** (3.4g, 5 mmol) prepared by neutralization of **4c** with sodium carbonate in a 50 ml flask was heated at 100 °C for 9h. The excess zinc power and the formed $ZnCl_2$ was filtered the filtrate was heated under reduced pressure to remove Ac_2O, the residue was evaporated to dryness under vacuum at 80 °C for 24h to give the crude product **8** (2.7g, 90%), pure compound was obtained by acidifying this product then neutrarized with Na_2CO_3. m.p. 108–110 °C.

IR (KCl, ν_{max} cm^{-1}) : 2989 (m), 2938 (m) (CH_2CH_3), 1839 (m, CF_2=CF-), 1336 (s, SO_2), 1233(s, P=O), 1036(s, P-O-C).

^1H NMR (δ)(CD_3CN): 4.20(m,CH_2), 1.32(t,CH_3).

^{19}F NMR (δ): – 112.2 (d-d, δ_a), –120.9 (d-d, δ_b), –135.5 (d-d, δ_c), –78.0 (m, δ_d), –144.3(t, δ_e),-79.0(s, δ_f), –83.8(m, δ_g), –116.3(s, δ_h).

Hydrolysis of 4a

A mixture of **4a** (1.43g, 5 mmol), HCl 11N, 1 ml) and water (5 ml) was stirred at 100 °C for 12h. Et_2O (2 × 10 ml) was added ant the extrate was dried with Na_2SO_4, and distilled under vacuum giving only $CF_3SO_2NH_2$ (0.6g, 81%).

Silylation of compounds 4

Compound **4a** (2.9g, 10 mmol) was placed in a 25 ml dry flask and Me_3SiBr (7.6g, 50 mmol) was added dropwise at room temperature. The reaction mixture was stirred at 60 – 70 °C for 48h. The excess Me_3SiBr and C_2H_5Br were removed under vacuum, ant the silylester was left as a viscous oil (3.6g, 95%). Spectral data of **9a** obtained are as follows:

IR (KCl, ν_{max} cm^{-1}) : 3350 (s, NH), 2985(s), 2887(s) (CH_3), 1240(s, P=O), 1020 (m, P-O-C).

^1H NMR (δ)(CD_3Cl): 7.53(s, NH), .0.23(s, CH_3).

^{19}F NMR (δ) : −79.0(s, CF_3).

MS(m/e, %): 284(M^+-$OSiMe_3$, 1.12), 73($^+SiMe_3$, 100.00).

Hydrolysis of $CF_3SO_2NHP(O)(OSiMe_3)_2$ 9a

A mixture of **9a** (3.6g, 10 mmol) and H_2O (0.4g, 22 mmol) was stirred at room temperature for 7 days. Sublimation at room temperature under vacuum (5×10^{-3} mmHg) to remove the excess water gave a small amount of $CF_3SO_2NH_2$ (0.5g), the residure was continously sublimated at 60 – 70 °C (5×10^{-3} mmHg) to give the white solid $CF_3SO_2NHP(O)(OH)_2$ **10a**(1.8g, 78%). m.p. 121–4 °C.

IR (AgCl, solid, ν_{max} cm^{-1}) : 3388, 3341, 3279 (s, NH, OH), 1355 (s, SO_2), 1235 (s, P=O), 1189 – 1156 (s, CF).

^1H NMR (δ): 6.80 (s, NH), 8.10 (s, OH).

^{19}F NMR (δ): −79.5 (s, CF3).

^{31}P NMR(H_3PO_4, 85%) (δ): 2.08.

Elemental analysis Calcd. for $CH_3F_3NO_5PS$:

Cald: C, 5.24; H, 1.31; N, 6.11%.

Found: C, 5.05; H, 1.51; N, 6.01%.

Similarly treatment of 4b and 4c gave 10b and 10c respectively

$C_4F_9SO_2NHP(O)(OH)_2$ **10b** (white solid)

IR (AgCl, solid, ν_{max} cm^{-1}) : 3393 – 3340, 3282 (s, NH, OH), 1350 (s, SO_2), 1243 (s, P=O), 1200 – 1120 (s, CF).

^1H NMR (δ): 4.76 (s, NH, 8.13 (s, OH).

^{19}F NMR (δ): −81.3 (s, CF_3), −113.9 (s, CF_2S), −120.8 (m, CF_2), −126.6 (m, CF_2),

$ICF_2CF_2OCF_2CF_2SO_2NHP(O)(OH)_2$ **10c** (a high boiling point oil).

IR (AgCl, ν_{max} cm^{-1}) : 3390, 3345, 3282 (s, NH, OH), 1352 (s, SO_2), 1240 (s, P=O), 1200 – 1110 (s, CF).

^1H NMR (δ): 7.08 (s, NH), 8.10 (s, OH).

^{19}F NMR (δ): −69.3(s, ICF_2), −81.6(m, OCF_2), −85.6(m, CF_2O), −116.3(s, CF_2S).

^{31}P NMR (δ) : 0.31 (s).

Acknowledgements

The authors thank the National Natural Science Foundation of China (NNSFC)(No. 29632003 and No. 29672041) for financial support.

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