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Fluorinated phosphorus compounds Part 11. The reactions of some fluorinated amines with dialkyl and bis(fluoroalkyl) phosphorochloridates

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Abstract

Dimethyl phosphorochloridate reacted with $R_FCH_2NH_2$ in ether in the presence of Et_3N to afford $(MeO)_2P(O)NHCH_2R_F$, where $R_F = CF_3$ and C_2F_5, in 39 and 47% yield, respectively. Similar reactions with di-*n*-propyl and diisopropyl phosphorochloridates could be effected only with $H_2NCH_2CF_3$ when 4-dimethylaminopyridine catalyst was added and $(n\text{-PrO})_2P(O)NHCH_2CF_3$ and $(i\text{-PrO})_2P(O)NHCH_2CF_3$ were isolated in 49 and 25% yield, respectively. Treatment of $POCl_3$ with one molar equivalent each of $H_2NCH_2CF_3$ and Et_3N permitted the synthesis of $Cl_2P(O)NHCH_2CF_3$ in 43% yield. Bis(fluoroalkyl) phosphorochloridates $(R_FO)_2P(O)Cl$, where $R_F = C_2F_5CH_2$, $C_3F_7CH_2$ and $(CF_3)_2CH$, reacted with 2,2,2-trifluoroethylamine and 2,2,3,3,3-pentafluoropropylamine to furnish phosphoramidates $(R_FO)_2P(O)NHCH_2R$, where $R = CF_3$ or C_2F_5, in yields of 32–67%.
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Keywords: Bis(fluoroalkyl) *N*-(fluoroalkyl)phosphoramidate; Dialkyl *N*-(fluoroalkyl)phosphoramidate; Fluorinated amine; Fluoroamine; 2,2,3,3,3-Pentafluoropropylamine; 2,2,2-Trifluoroethylamine

1. Introduction

Recent papers from this laboratory detail methods for the preparation of phosphorus compounds containing fluoroalkyl groups. This paper outlines our investigations into the phosphorylation of fluorinated aliphatic amines to produce dialkyl *N*-fluoroalkylphosphoramidates. Related compounds **A**–**D** reported in the literature [1–6] are shown in Fig. 1. We have previously described a simple method for producing dialkyl *N*-(fluoroalkyl)phosphoramidates which involved reaction between dialkyl phosphorochloridates and fluoroamines [7] and products with trifluoroethyl or pentafluoropropyl amino substituents were isolated (Scheme 1). In this study, we explore further the scope of such chemistry. The work is novel from the point of view of the fluoroamines, whose chemistry has scarcely been explored.[1]

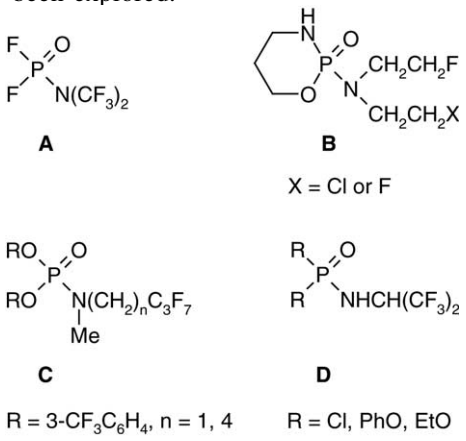

Fig. 1. Literature phosphorus compounds with *N*-fluoroalkylamino groups.

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[1] Known derivatives made in one step from 2,2,2-trifluoroethylamine include its hydrochloride salt [8], diazoethane CF_3CHN_2 [9] and isocyanate CF_3CH_2NCO [10].

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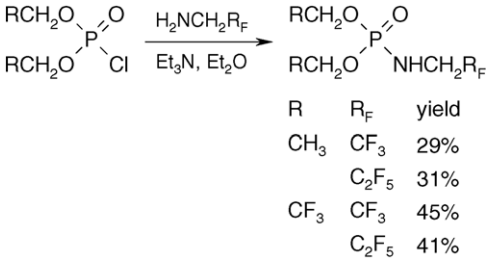


Scheme 1.

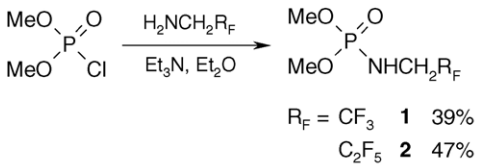
2. Results and discussion

2.1. Dialkyl N-fluoroalkylphosphoramidates

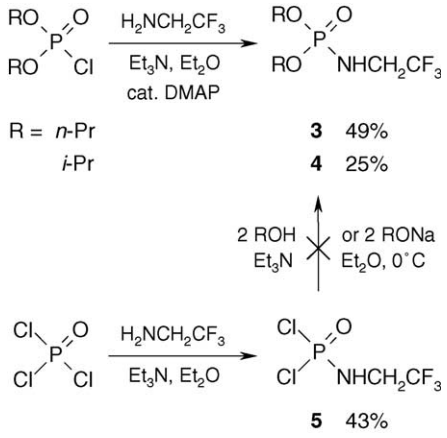
The low basicity of fluoroalkylamines ($CF_3CH_2NH_2$, pK_b 8.3) compared with their non-fluorinated counterparts ($CH_3CH_2NH_2$, pK_b 3.3) [8] should lower their reactivity towards electrophiles. Despite this, dimethyl phosphorochloridate reacted with an equimolar mixture of 2,2,2-trifluoroethylamine and triethylamine to give dimethyl *N*-trifluoroethylphosphoramidates **1** and **2** in moderate yield (Scheme 2). Comparable reactions with diethyl phosphorochloridate gave analogous products [7].

The longer the ester groups of dialkyl phosphorochloridates, the greater the electron density on the phosphorus atom, making it less prone to nucleophilic attack. Branching of the ester groups sterically hinders the phosphorus atom. For these reasons, no reaction between di-*n*-propyl or diisopropyl phosphorochloridate and 2,2,2-trifluoroethylamine was observed at room temperature. Addition of the catalyst 4-dimethylaminopyridine (DMAP) was required to effect conversion to phosphoramidates **3** and **4** (Scheme 3). The greater yield of *n*-propyl versus isopropyl product reflects the difference in reactivity of the chloridates, di-*n*-propyl phosphorochloridate reacting better than diisopropyl phosphorochloridate, due to its less hindered nature.

An alternative route to phosphoramidates **3** and **4** was also explored. Treatment of phosphorus oxychloride with a molar equivalent of 2,2,2-trifluoroethylamine and triethylamine gave *N*-(2,2,2-trifluoroethyl)phosphoramidic dichloride **5** as a liquid. However, this compound failed to react cleanly with *n*-propanol or isopropanol in the presence of triethylamine, or with sodium *n*-propanolate or isopropanolate in ether at 0 °C, which prevented access to the desired phosphoramidates by a second route. Analytical data for the new compounds appear in Table 1.



Scheme 2.



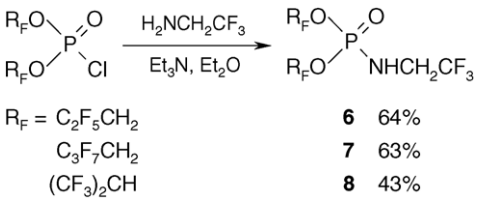
Scheme 3.

2.2. Bis(fluoroalkyl) N-fluoroalkylphosphoramidates

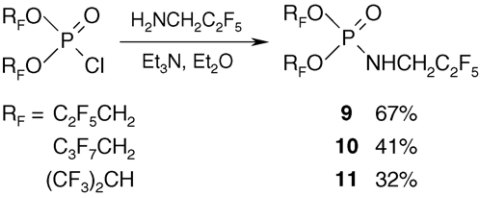
Bis(fluoroalkyl) phosphorochloridates are more susceptible to nucleophilic attack than dialkyl phosphorochloridates because the electronegative fluoroester groups render their phosphorus atom more electron deficient [11,12]. The greater ease of combination of 2,2,2-trifluoroethylamine with $(CF_3CH_2O)_2P(O)Cl$ compared to $(CH_3CH_2O)_2P(O)Cl$ was noted earlier [7]. Here, we show that a range of other bis(fluoroalkyl) phosphorochloridates reacted with 2,2,2-trifluoroethylamine to give the desired products **6**–**8** in yields greater than those with the corresponding dialkyl phosphorochloridates (Scheme 4). Compounds **6** and **7** were liquids, whereas compound **8** was a low melting white solid.

The same phosphorochloridates reacted with 2,2,3,3,3-pentafluoropropylamine to furnish homologues **9**–**11** in reasonable yield (Scheme 5). All three were low melting white solids.

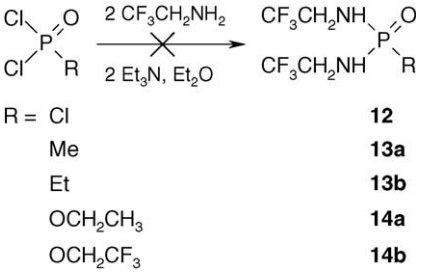
An interesting property of the fluorinated phosphoramidates is that their boiling points are higher than those of their perprotio analogues (physical data for the latter appear in



Scheme 4.



Scheme 5.



Scheme 6.

ref. [13]). Most of the fluorinated phosphoramidates are solids at room temperature, whereas their unfluorinated counterparts are liquids. The difference is presumably due to strong intermolecular NH. . .F bonding in the fluorinated series.

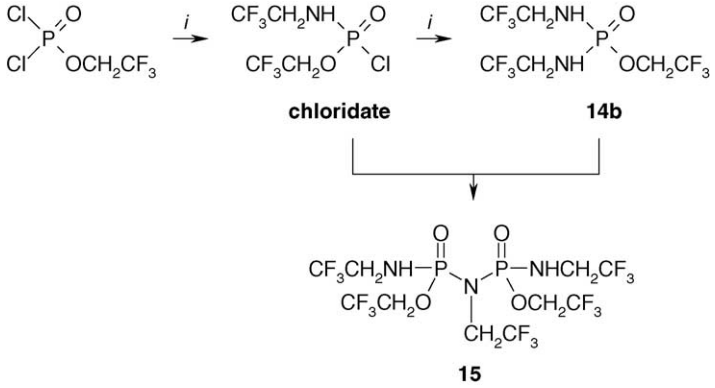
2.3. Bis(2,2,2-trifluoroethylamino) derivatives

Attempts to prepare phosphorodiamidic chloride **12**, phosphonodiamidates **13a–b** and phosphorodiamidates **14a–b** by treatment of various phosphorus dichlorides with two molar equivalents of 2,2,2-trifluoroethylamine and triethylamine gave mixtures of products (Scheme 6). Although phosphorus oxychloride, and methyl and ethylphosphonic dichloride, did furnish some of the desired products **12** and **13a** and **b**, respectively, as identified by GC–MS analyses, they decomposed on attempted purification (see Sections 3.5 and 3.6). A similar situation was observed with the product derived from ethyl phosphorodichloridate, compound **14a**. Trifluoroethyl phosphorodichloridate produced a 1:2 mixture of phosphorodiamidate **14b** and a similar-boiling product of molecular mass 585, probably structure **15**, formed by condensation of the chloridate intermediate with **14b** (Scheme 7). Again, apparent instability of the products prevented their purification (see Section 3.7).

Non-fluorinated relatives of **15** have been made by condensing chloridates with phosphoramidates; a stronger base than triethylamine is usually employed to deprotonate the NH bond and accelerate coupling [14]. In our case, the enhanced acidity of the NH proton, due to the inductive effect of the CF_3CH_2 group, probably permitted deprotonation by triethylamine.

3. Experimental

Dipropyl phosphite $(n\text{-PrO})_2P(O)H$ was obtained from phosphorus trichloride and three molar equivalents of propanol in the absence of base: our sample had bp 54 °C/0.02 mmHg [15]. Diisopropyl phosphite $(i\text{-PrO})_2P(O)H$ was purchased from Aldrich Ltd. (Gillingham, UK). Passage of an excess of chlorine gas through the phosphites in ether at 0–5 °C, removal of solvent, and distillation gave chloridates $(n\text{-PrO})_2P(O)Cl$ and $(i\text{-PrO})_2P(O)Cl$ with bp 48 °C/0.015 mmHg and 58 °C/0.7 mmHg, respectively, in accordance with literature values [16]. 2,2,2-Trifluoroethyl phosphorodichloridate [11] and bis(fluoroalkyl) phosphorochloridates [17] were obtained in >98% purity using known chemistry. Fluoroamines were purchased from Apollo Scientific Ltd. (Stockport, UK) and other reagents, including anhydrous solvents, from Aldrich Ltd (Gillingham, UK). NMR spectra were obtained on a JEOL Lambda 500 instrument (operating at 500 MHz for ^1H, 125 MHz for ^{13}C, 470 MHz for ^{19}F and 202 MHz for ^{31}P spectra) or a JEOL Lambda 300 instrument (operating at 300 MHz for ^1H, 75 MHz for ^{13}C, 282 MHz for ^{19}F and 121.5 MHz for ^{31}P spectra) as solutions in $CDCl_3$, with internal reference $SiMe_4$ for ^1H and ^{13}C, external $CFCl_3$ for ^{19}F and external $(MeO)_3P$ (δ 140 ppm) for ^{31}P spectra. IR spectra were recorded as liquid films on a Nicolet SP210 instrument. Reaction mixtures were monitored by gas chromatography–mass spectrometry (GC–MS) using a Finnigan MAT GCQ instrument with chemical ionisation (CI) using methane as reagent gas. High-resolution mass spectrometry (HRMS) data were obtained using instrumentation and conditions described elsewhere [18].



Reagents and conditions: i. $H_2NCH_2CF_3$, Et_3N, Et_2O, 0-5°C

Scheme 7.

3.1. Dimethyl N-(fluoroalkyl)phosphoramidates (**1** and **2**)

A solution of fluorinated amine (40 mmol) and triethylamine (5.6 ml, 40 mmol) in ether (10 ml) was added dropwise by cannula to a stirred solution of dimethyl phosphorochloridate (5.8 g, 40 mmol) in ether (40 ml) at 0–5 °C. After addition, the mixture was allowed to warm to room temperature and was left for 14 h. The precipitate of triethylamine hydrochloride was filtered off and the filtrate concentrated to reveal a liquid. Bulb-to-bulb distillation under reduced pressure using a Kugelrohr apparatus, gave the title compounds as white crystalline solids.

3.1.1. Dimethyl N-(2,2,2-trifluoroethyl)-phosphoramidate **1**

Bp 72 °C/0.03 mmHg. Mp 54 °C. ^{1}H NMR δ = 3.76 (6H, d, J = 11 Hz, OCH_3), 3.51 (2 H, br m, NCH_2), 3.32 (1 H, br m, NH). ^{13}C NMR δ = 124.5 (q, J = 278 Hz, CF_3), 53.5 (d, J = 6 Hz, OCH_3), 43.5 (q, J = 35 Hz, NCH_2). ^{19}F NMR δ = −73.2 (t, J = 9 Hz, CF_3). ^{31}P NMR δ = 8.6. IR ν_{max} = 3176 (NH), 1479, 1405, 1298, 1271, 1232 (P=O), 1146, 1057, 962, 881, 839, 768, 654, 474 cm^{-1}. HRMS: calculated for $C_4H_9F_3NO_3P$ 207.088 ([M − F]$^+$ = 188.090), found 188.088 (error 1.1 ppm).

3.1.2. Dimethyl N-(2,2,3,3,3-pentafluoropropyl)-phosphoramidate **2**

Bp 69 °C/0.02 mmHg. Mp 42 °C. ^{1}H NMR δ = 3.68 (6H, d, J = 11 Hz, OCH_3), 3.48 (3 H, br m, $NHCH_2$). ^{13}C NMR δ = 116.9 (tq, J = 286 and 35 Hz, CF_3), 110.1 (tq, J = 254 and 5 Hz, CF_2), 53.3 (d, J = 6 Hz, OCH_3), 41.5 (t, J = 24 Hz, NCH_2). ^{19}F NMR δ = −123.3 (2F, m, CF_2), −83.6 (3F, m, CF_3). ^{31}P NMR δ = 8.8. IR ν_{max} = 3178 (NH), 1462, 1348, 1292, 1238 (P=O), 1190, 1157, 1136, 1045, 955, 839, 795, 721, 594, 534 cm^{-1}. HRMS: calculated for $C_5H_9F_5NO_3P$ 257.095 ([M − F]$^+$ = 238.097), found 238.094 (error 3.2 ppm).

3.2. Dipropyl and diisopropyl N-(fluoroalkyl)-phosphoramidates (**3** and **4**)

The same method as described above was used but a catalytic amount of DMAP (5% mol) was added. Kugelrohr distillation under reduced pressure gave compound **3** as a colourless liquid and compound **4** as a white solid.

3.2.1. Di-n-propyl N-(2,2,2-trifluoroethyl)-phosphoramidate **3**

Bp 72 °C/0.02 mmHg. ^{1}H NMR δ = 3.98 (2 H, complex m, CH_2CF_3), 3.59 (1 H, br m, NH), 3.50 (4 H, br m, OCH_2), 1.71 (4 H, sextet, J = 7 Hz, CH_2), 0.96 (6 H, t, J = 7 Hz, CH_3). ^{13}C NMR δ = 124.5 (tq, J = 278 and 35 Hz, CF_3), 68.3 (d, J = 6 Hz, OCH_2), 43.5 (q, J = 35 Hz, NCH_2), 23.5 (d, J = 7 Hz, CH_2), 10.0 (s, CH_3). ^{19}F NMR δ = −73.1 (t, J = 11 Hz, CF_3). ^{31}P NMR δ = 6.3. IR ν_{max} = 3199 (NH), 1649, 1606, 1468, 1394, 1300, 1281, 1238 (P=O), 1151, 1005, 887, 829, 750, 661, 542 cm^{-1}. HRMS: calculated for $C_8H_{17}F_3NO_3P$ 263.196 ([M − F]$^+$ = 244.198), found 244.195 (error 2.9 ppm).

3.2.2. Diisopropyl N-(2,2,2-trifluoroethyl)-phosphoramidate **4**

Bp 58 °C/0.02 mmHg. Mp 34 °C. ^{1}H NMR δ = 4.62 (2 H, br m, OCH), 3.51 (3 H, br m, $NHCH_2$), 1.32 (12 H, dd, each 9 Hz, CH_3). ^{13}C NMR δ = 124.4 (tq, J = 278 and 35 Hz, CF_3), 71.3 (d, J = 6 Hz, CH), 43.4 (q, J = 34 Hz, NCH_2), 23.4 (4C, br s, CH_3). ^{19}F NMR δ = −72.8 (t, J = 9 Hz, CF_3). ^{31}P NMR δ = 4.3. IR ν_{max} = 3201 (NH), 2981, 2939, 1469, 1389, 1281, 1236 (P=O), 1151, 1109, 993, 897, 852, 829, 777, 663, 548 cm^{-1}. HRMS: calculated for $C_8H_{17}F_3NO_3P$ 263.196 ([M − F]$^+$ = 244.198), found 244.193 (error 1.8 ppm).

3.3. N-(2,2,2-Trifluoroethyl)phosphoramidic dichloride (**5**)

A solution of 2,2,2-trifluoroethylamine (5.9 g, 60 mmol) and triethylamine (8.4 ml, 60 mmol) in ether (50 ml) was added dropwise to a stirred solution of phosphorus oxychloride (9.1 g, 60 mmol) in ether (50 ml) at 0–5 °C. After addition, the mixture was allowed to warm to room temperature and was left for 14 h. The precipitate of triethylamine hydrochloride was filtered off and the filtrate concentrated to reveal a liquid. Bulb-to-bulb distillation under reduced pressure gave the title compound as a colourless liquid (5.6 g, 43%). Bp 62 °C/0.02 mmHg. ^{1}H NMR δ = 5.73 (1 H, br m, NH), 3.71 (2H, 'septet', J = 9 Hz, NCH_2). ^{13}C NMR δ = 123.3 (dq, J = 8 and 278 Hz, CF_3), 43.4 (q, J = 36 Hz, NCH_2). ^{19}F NMR δ = −71.9 (t, J = 9 Hz, CF_3). ^{31}P NMR δ = 15.5. IR (film) ν = 3180 (NH), 2903, 1460, 1439, 1395, 1299, 1280, 1264, 1158 (P=O), 1089, 995, 963, 865, 832, 662, 570, 544 cm^{-1}. HRMS: calculated for $C_2H_3Cl_2F_3NOP$ 215.926 ([M − Cl]$^+$ = 180.473), found 180.472 (error 4.2).

3.4. Bis(fluoroalkyl) N-(fluoroalkyl)phosphoramidates (**6–11**)

A solution of fluorinated amine (40 mmol) and triethylamine (5.6 ml, 40 mmol) in ether (10 ml) was added dropwise by cannula to a stirred solution of the bis(fluoroalkyl) phosphorochloridate (40 mmol) in ether (40 ml) at 0–5 °C. After addition, the mixture was allowed to warm to room temperature and was left for 14 h. The precipitate of triethylamine hydrochloride was filtered off and the filtrate concentrated to reveal a viscous liquid or white solid depending on the fluorinated amine and phosphorochloridate used. The liquids were distilled under reduced pressure using a Kugelrohr apparatus; in most cases, a white crystalline solid sublimed in the receiver bulb. Physical constants for the title compounds appear in Table 1.

Table 1
Analytical data for bis(fluoroalkyl) *N*-(fluoroalkyl)phosphoramidates $(R_FO)_2P(O)NHR$ **6–11** (NMR data measured in $CDCl_3$)

Compound	R_F	R	Bp (°C/mm Hg)	^1H NMR δ, J (Hz)	$^{13}C\{^1H\}$ NMR δ, J (Hz)	^{19}F NMR δ, J (Hz)	$^{31}P\{^1H\}$ NMR δ	IR ν (cm^{-1})	HRMS analysis
6	C_2F_5	CF_3	59/0.015	4.46 (4 H, m, 8, OCH_2), 4.31 (1 H, br m, NH), 3.52 (2 H, br m, NCH_2)	125–111 (br m, CF_2 and CF_3), 62.3 (dt, J = 4, 29, OCH_2), 43.2 (q, J = 35, NCH_2)	−124.5 (4F, t, J = 11, CF_2), −83.4 (6F, m, CF_3), −74.1 (3F, t, J = 8, NCH_2CF_3)	6.0	3203 (NH), 1460, 1356, 1302, 1205 (P═O), 1159, 1128, 1070, 1030, 968, 937, 881	Calc. for $C_8H_7F_{13}NO_3P$ 443.096, found 443.094 (error 2 ppm)
7	C_3F_7	CF_3	69/0.04	4.46 (4 H, m, 13, OCH_2), 4.3 (1 H, br m, NH), 3.52 (2 H, br m, NCH_2)	127–106 (br m, CF_2 and CF_3), 62.6 (dt, J = 4, 29, OCH_2), 43.4 (q, J = 36, NCH_2)	−126.8 (4F, m, CF_2), −120.9 (4F, m, CF_2), −80.1 (6F, m, CF_3), −73.5 (3F, t, J = 8, NCH_2CF_3)	6.3	3207 (NH), 1460, 1356, 1302, 1232 (P═O), 1182, 1132, 1080, 1016, 968, 930	Calc. for $C_{10}H_7F_{17}NO_3P$ 543.11, found 543.061 (error 10 ppm)
8	$(CF_3)_2CH$	CF_3	50/0.015, Mp 44 °C	5.05 (2 H, m, OCH), 4.11 (1 H, br m, NH), 3.57 (2 H, m, 18, NCH_2)	124–116 (br m, CF_3), 71.5 (dsept, J = 4, 36, OCH), 43.2 (q, J = 36, NCH_2)	−73.2 and −73.4 (15F, m, CF_3),	6.9	3212 (NH), 1470, 1403, 1383, 1370, 1296, 1210 (P═O), 1200, 1182, 1160, 1094, 970, 907	Calc. for $C_8H_5F_{15}NO_3P$ 479.076, found 479.078 (error 5 ppm)
9	C_2F_5	C_2F_5	Mp 76 °C	4.53–4.35 (4 H, m, OCH_2), 4.25 (1 H, m, NH), 3.54 (2 H, m, NCH_2)	124–108 (br m, CF_2 and CF_3), 62.1 (dt, J = 4, 29, OCH_2), 41.2 (t, J = 24, NCH_2)	−124.6 (4F, t, J = 14, CF_2), −123.5 (2F, t, J = 14, CF_2), −84.4 (6F, m, CF_3), −74.6 (3F, t, J = 8, NCH_2CF_3)	6.3	3172 (NH), 1460, 1406, 1375, 1350, 1200 (P═O), 1149, 1109, 1090, 1028, 958, 935, 885	Calc. for $C_9H_7F_{15}NO_3P$ 493.103, found 493.098 (error 12 ppm)
10	C_3F_7	C_2F_5	73/0.1, Mp 49 °C	4.46 (4 H, m, OCH_2), 4.28 (1 H, br m, NH), 3.57 (2 H, m, NCH_2)	123–106 (br m, CF_2 and CF_3), 62.5 (t, J = 28, OCH_2), 41.6 (t, J = 24, NCH_2)	−126.7 (4F, m, OCH_2CF_2), −122.7 (2F, m, NCH_2CF_2), −120.8 (4F, m, $OCH_2CF_2CF_2$), −83.1 (3F, m, CF_3), −78.9 (6F, m, CF_3)	6.3	3184 (NH), 1458, 1406, 1348, 1230, 1201 (P═O), 1132, 1088, 1032, 1016, 964, 928, 885	Calc. for $C_{11}H_7F_{19}NO_3P$ 593.117, found 593.111 (error 20 ppm)
11	$(CF_3)_2CH$	C_2F_5	83/0.03, Mp 58 °C	5.06 (2 H, m, OCH), 3.81 (1 H, br s, NH), 3.62 (2 H, m, NCH_2)	124–116 (br m, CF_3), 71.7 (dsept, J = 4, 35, OCH), 41.7 (t, J = 23, NCH_2)	−122.5 (2F, d, J = 14, CF_2), −83.2 (3F, m, CF_3), −73.2 (12F, m, CF_3),	7.0	1371, 1292, 1236, 1209 (P═O), 1147, 1113, 1090, 1034, 908, 735, 652	Calc. for $C_9H_5F_{17}NO_3P$ 529.083, found 529.051 (error 4 ppm)

3.5. Reaction of 2,2,2-trifluoroethylamine with phosphorus oxychloride

A solution of 2,2,2-trifluoroethylamine (2 g, 20.2 mmol) and triethylamine (2.8 ml, 20.2 mmol) in ether (25 ml) was added dropwise to a stirred solution of phosphorus oxychloride (1.54 g, 10.1 mmol) in ether (35 ml) at 0–5 °C. Reaction was instantaneous and a white precipitate formed. After 12 h, the precipitate was filtered off and the filtrate concentrated to reveal an oily solid, which was shown by GC–MS analysis to contain a variety of obscure products, but a small amount of the desired product **12**. The solid decomposed on attempted bulb-to-bulb vacuum distillation (5 mmHg) and on chromatography on silica gel eluting with hexane–acetone mixtures.

3.6. Reaction of 2,2,2-trifluoroethylamine with methyl or ethylphosphonic dichloride

A solution of 2,2,2-trifluoroethylamine (1 g, 10.1 mmol) and triethylamine (1.4 ml, 10.1 mmol) in ether (8 ml) was added dropwise to a stirred solution of methyl or ethylphosphonic dichloride (5 mmol) in ether (15 ml) at 0–5 °C. Reaction was instantaneous and a white precipitate formed. After 12 h, the precipitate was filtered off and the filtrate concentrated to reveal an oily solid, which was shown by GC–MS analysis to contain about 25% of the desired product (**13a** and **b**) and two other unidentified products. The solid decomposed during heating on attempted Kugelrohr distillation under reduced pressure (5 mmHg). Analysis of the liquid distillate by GC–MS revealed a small amount of the desired product plus three uncharacterised products. The solid also decomposed on attempted chromatography over silica gel eluting with hexane–acetone mixtures.

3.7. Reaction of 2,2,2-trifluoroethylamine with 2,2,2-trifluoroethyl phosphorodichloridate

A solution of 2,2,2-trifluoroethylamine (1.38 g, 13.9 mmol) and triethylamine (1.93 ml, 13.9 mmol) in ether (20 ml) was added dropwise to a stirred solution of 2,2,2-trifluoroethyl phosphorodichloridate (5 mmol) in ether (30 ml) at 0–5 °C. Reaction was instantaneous and a white precipitate formed. After 12 h, the precipitate was filtered off and the filtrate concentrated to reveal a liquid, which was shown by GC–MS analysis to contain about a 1:2 mixture of the desired product **14b** and a by-product, probably structure **15**. This mixture decomposed on attempted Kugelrohr distillation under reduced pressure (5 mmHg) and on passage through a chromatography column of silica gel eluting with hexane–acetone mixtures.

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