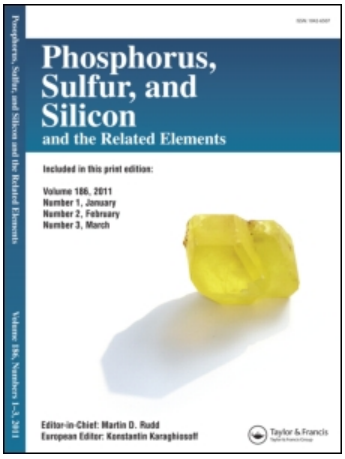

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CHEMISTRY OF S-TRIFLUOROMETHYL ORGANOPHOSPHOROTHIOATES AND THEIR STRUCTURAL ANALOGS A CONVENIENT SYNTHESIS OF ORGANOPHOSPHORUS FLUORIDATES

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CHEMISTRY OF S-TRIFLUOROMETHYL ORGANOPHOSPHOROTHIOATES AND THEIR STRUCTURAL ANALOGS A CONVENIENT SYNTHESIS OF ORGANOPHOSPHORUS FLUORIDATES

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New organophosphorus compounds containing one or two different S-trifluoromethyl functionalities are synthesized in the reaction between the tri-coordinate phosphorus esters and bis-(trifluoromethane) disulfide. The catalytic effect exerted by the nucleophilic species such as the fluoride anion or tertiary amine on the decomposition of S-trifluoromethyl organophosphorus derivatives is documented. This observation is utilized for the preparation of different types of organophosphorus fluoridates.

Key words: Bis-(trifluoromethane) disulfide; alkyl(aryl)-S-trifluoromethyl phosphinothioate; alkyl(0-alkyl)-S-trifluoromethyl phosphonothioate; 0-(S-trifluoromethyl)alkyl-S-trifluoromethyl N,N-dialkyl-amidophosphorothioate; alkyl(aryl)phosphinofluoridate; 0-(alkyl-S-trifluoromethyl)alkyl N,N-dialkyl-amidophosphorofluoridate.

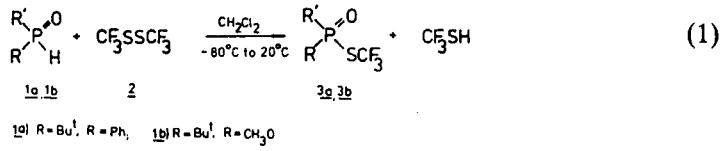
Dialkyl S-trifluoromethyl phosphorothioates $R'RP(O)SCF_3$ **3** (R = R′ = alkoxy) have recently become of interest as insecticides[1,2] as well as anticholinesterase active compounds.[3] Their synthesis based, mostly, on the reaction of trifluoromethanesulfenyl chloride, with trialkyl- and dialkyl-phosphites.[1–5] However, such an approach to the synthesis of **3**, suffers from two main drawbacks: i) the ester produced is contaminated by the dialkylphosphorochloridate; ii) only moderate yields are obtained and purification of **3** is troublesome, due to the low stability of these compounds under the reaction conditions. Recently, an alternative route to the esters, **3** (R = R′ = alkoxy), i.e. alcoholysis of trifluoromethyl thiophosphorochloridate, has been proposed by Haas.[6] According to this method, several esters of type **3** including their thiophosphoryl analogs, were obtained.

We have recently developed still another synthetic route to **3**, utilizing the reaction between tri- or dialkyl-phosphites and bis-(trifluoromethane)disulfide **2**.[7,8] In this method, the formation of undesirable reaction byproducts which have a negative influence on the stability of **3** has been avoided. It has also been found that, in the case of cyclic phosphites, the reaction leads to the acyclic products, thus providing the first route to novel organophosphorus compounds, **9** and **11**, containing two different F_3CS-functionalites. In this paper, we also present an extension of this method to the preparation of different organophosphorus fluoridates, RR′P(O)F from the esters **3**, **7**, **9** and **11** in high yield and purity.

RESULTS AND DISCUSSION

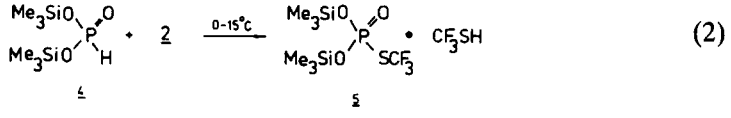
Reaction between esters of tri-coordinate phosphorus and the disulfide 2.

As can be seen from the experimental part, the reaction described in Equation 1 is general in scope and different tri-coordinate organophosphorus compounds **1**, **4**, **6** and **8** including secondary phosphine oxides, phosphonates and silylated phosphites, react with the disulfide, **2** to give the compounds of type **3** of high



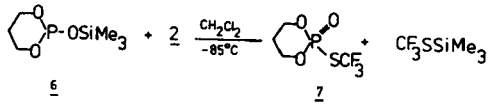
(1)

stability and in high yield. The reaction is carried out either in dichloromethane solution or without solvent at temperatures from −80°C to 20°C, and the products are usually isolated from the reaction mixture by distillation without decomposition. For example, 0,0-bis-trimethylsilylphosphite, **4** reacts smoothly with excess **2**, used as the solvent, at 0–15°C to give 0,0-bis-trimethylsilyl S-trifluoromethyl phosphorothioate **5** in good yield. Compound **5** is a colorless, mobile liquid



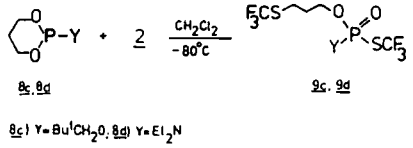
(2)

showing no indication of limited stability contrary to a literature report,[3] and is distillable in vacuo without decomposition. We have also observed a vigorous reaction between 2-trimethylsilyloxy-1,3,2-dioxaphosphorinane, **6** and **2**, leading



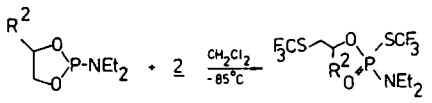
(3)

to 2-fluoromethylthio-2-oxo-1,3,2-dioxaphosphorinane, **7**. Both cyclic esters of tri-coordinate phosphorus, **8c** and **8d**, react smoothly at low temperatures with the disulfide **2** in dichloromethane solution with the opening of the 1,3,2-dioxaphosphorinanyl ring, and formation of compounds **9c** and **9d** containing two chemically different —SCF_3 groups. Similar results were obtained when deriva-



(4)

tives of the 1,3,2-dioxaphospholane ring system **10** were employed. The esters **10e–10g** react vigorously with **2** at −85°C to form **11e–11g** in high yield and purity.



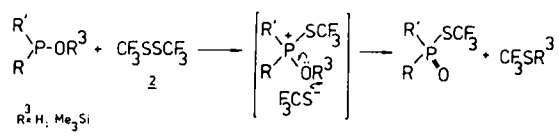
(5)

10e-10g 11e-11g

10e) R^2=H; 10f) R^2=CH_3; 10g) R^2=$ClCH_2$

Esters of type **9** and **11** represent a new class of organophosphorus compounds. They are stable and do not decompose during their separation from the reaction mixture by distillation in vacuo. Their ^{31}P NMR spectra show a characteristic quartet at δ 17–20 and $^3J(^{31}P-^{19}F)$ ranging between 6–9 Hz. Accordingly, in the ^{19}F NMR spectra signals of two different SCF_3 groups are observed, the doublet centered at 31–34 ppm characteristic of the $F_3CS-\overset{|}{\underset{|}{P}}(O)$ arrangement, and another single resonance line at 40–42 ppm ($CFCl_3$) for the fluorine atom of the CF_3S group bonded to the carbon atom in the alkoxy substituent at phosphorus. It was established by means of ^1H, ^{31}P and ^{19}F NMR that the reaction of cyclic amidophosphites **10f** and **10g** with **2**, results in the formation of esters **11f** and **11g** which are 1 : 1 mixtures of diastereoisomers.

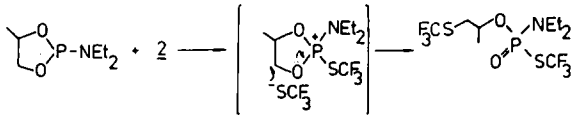
The reaction of the tri-coordinated phosphorus esters **1**, **4** and **6** with disulfide **2** can be regarded as a process involving the formation of the phosphonium intermediate **12**.[9–13] For the reaction of the cyclic esters **8** and **10** with the



(6)

R³ = H; Me_3Si 2 12

disulfide **2**, the formation of a similar intermediate **13** can be postulated. Intermediate **13** is cleaved selectively in the next step at the primary ring carbon



(7)

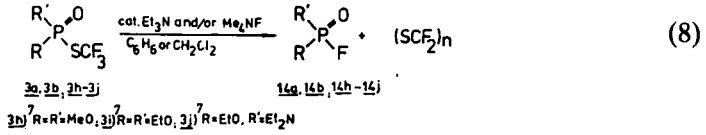
13

atom. Most probably, the lifetime of intermediates such as **12** and **13** is very short and the F_3CS^- anion is almost instantaneously consumed, so it can no longer serve as the source of fluoride anion, as was observed in the other cases.[14–15] The reaction is indeed very efficient and practically the formation of otherwise expected phosphorofluoridates is avoided.[5–6] Formation of other side products is also suppressed; thus the reaction presented compares favourably with earlier analogous procedures.[16–17]

*The conversion of esters **3**, **9** and **11** into the fluoridates **14–16**.*

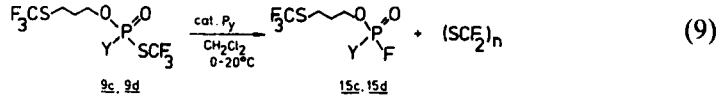
The organophosphorus S-trifluoromethylthioates $R'RP(O)SCF_3$ obtained by our method are stable compounds and can be stored for prolonged time in a neutral

environment. However, we have observed that their stability decreases dramatically when they are synthesized in the presence of any kind of nucleophilic impurities, or when a catalytic amount of fluoride anion or amine is introduced to the solution of pure sample of **3**. In the latter case, vigorous reaction occurs and the corresponding fluoridates **14** are formed. They are separated from the reaction mixture by distillation in good yield. Identical behaviour of **9** and **11**



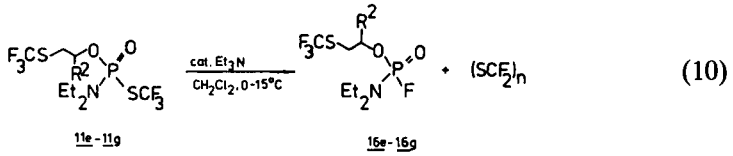
(8)

towards tertiary amine was observed. The esters **9** and **11** under these conditions, undergo transformation into the fluoridates **15** and **16**. **9c**) $Y = Bu^tCH_2O$; **9d**) $Y = Et_2N$.



(9)

Taking into account the ease of preparation and high yield, the procedures presented here may become the method of choice for the preparation of organophosphorus fluoridates,[18] especially the ones involving diversified functionalities in the alkyl chain of the substitutent at phosphorus.



(10)

EXPERIMENTAL

The solvents and reagents were purified before use by standard methods. All b.ps. are uncorrected. ^{1}H NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded on a Bruker MSL-300 spectrometer, using Me_4Si, H_3PO_4 and $CFCl_3$ as the external standards, respectively. Negative ^{19}F chemical shift values are assigned to signals upfield of the reference.

Warning. Because of the high toxicity of organophosphorus fluoridates their preparation and handling must be carried out with proper precautions.

The reaction of tri-coordinated phosphorus esters **1**, **6**, **8** *and* **10** *with the disulfide* **2**. *General procedure.* The disulfide **3**, 2.42–10.71 g (0.012–0.053 mole) was added to the dichloromethane solution (15–30 ml) of the appropriate ester **1**, **6**, **8** and **10** (0.01–0.05 mole). During the addition the temperature of the reaction mixture was maintained at −85°C to −80°C. Stirring was continued for 20–30 min. at this temperature and the cooling bath was removed. The reaction mixture was then stirred for 5 hrs at 15–20°C. The solvent and the volatile products were removed at 10–15 mmHg pressure, at a bath temperature of 10–15°C. The crude products were separated by distillation in a high vacuum. Exactly by this procedure the following compounds were synthesized.

t-Butyl(phenyl) S-Trifluoromethyl Phosphinothioate, **3a**. Colorless crystals; m.p. 40–45°C; yield 85%; b.p. 98–101°C/0.05 mmHg; ^{31}P NMR (CH_2Cl_2) δ 66.73; ^{19}F NMR (C_6D_6) δ-30.9 (d, $^3J_{P-F}$ 0.77 Hz). Found: C, 46.89; H, 5.30; P, 10.61; Calcd. for $C_{11}H_{14}F_3OPS$: C, 46.81; H, 4.99; P, 10.97.

t-Butyl(0-Methyl) S-Trifluoromethyl Phosphonothioate, **3b**. Colorless liquid; yield 77%; b.p. 30–32°C/0.01 mmHg; ^{31}P NMR (CH_2Cl_2) δ 59.46 (q, $^3J_{P-F}$ 1.25 Hz); ^{19}F NMR (CD_2Cl_2) δ-31.10 (d, $^3J_{P-F}$ 1.18 Hz); Found: C, 30.48; H, 4.85; P, 14.11; Calcd. for $C_6H_{12}F_3O_2PS$: C, 30.51; H, 5.12; P, 13.11.

2-*S-Trifluoromethyl-2-oxo-1,3,2-dioxaphosphorinane*, **7**. Oily liquid; solidified after standing; yield 78%; b.p. 72–73°C/0.05 mmHg; ^{31}P NMR (CD_2Cl_2) δ 2.7 (q, $^3J_{P-F}$ 7.32 Hz); ^{19}F NMR (CD_2Cl_2) δ-31.8 (d, $^3J_{P-F}$ 7.40 Hz): Found: C, 21.80; H, 2.70; P, 14.02; Calcd. for $C_4H_6F_3O_3PS$: C, 21.63; H, 2.71; P, 13.94.

0-(3-*S-trifluoromethyl*)*Propyl* 0-(2,2-*dimethyl*)*Propyl S-Trifluoromethyl Phosphorothioate*, **9c**. Colorless liquid; yield 78%; b.p. 80–81°C/0.08 mmHg (bath temperature 115°C); ^{31}P NMR (CD_2Cl_2) δ 11.8 (q, $^3J_{P-F}$ 9.9 Hz); ^{19}F NMR (CD_2Cl_2) δ-30.9 (d, $^3J_{P-F}$ 9.9 Hz, $F_3CS-\overset{|}{\underset{|}{P}}=O$); δ-39.8 (s, F_3CS-C); Found: C, 30.38; H, 4.40; P, 8.21; S, 15.80; Calcd. for $C_{10}H_{17}F_6O_3PS_2$: C, 30.46; H, 4.34; P, 7.85; S, 16.26.

0-(3-*S-trifluoromethyl*)*Propyl S-Trifluoromethyl N,N-Diethylamidophosphorothioate*, **9d**. Oily liquid; yield 85%; b.p. 65–66°C/0.01 mmHg; ^{31}P NMR (CH_2Cl_2) δ 19.3 (q, $^3J_{P-F}$ 6.6 Hz); ^{19}F NMR (CD_2Cl_2) δ-34.31 (d, $^3J_{P-F}$ 6.71, $F_3CS-\overset{|}{\underset{|}{P}}=O$); δ-41.65 (s, F_3CS-C); Found: C, 29.00; H, 4.55; N, 3.99; P, 8.63; S, 16.54; Calcd. for $C_8H_{16}F_6NO_2PS_2$: C, 28.50; H, 4.25; N, 3.69; P, 8.16; S, 16.90.

0-(2-*S-trifluoromethyl*)*Ethyl S-Trifluoromethyl N,N-Diethylamidophosphorothioate*, **11e**. Liquid; yield 81%; b.p. 60–63°C/0.01 mmHg (bath temperature 88–92°C); ^{31}P NMR (CH_2Cl_2) δ 20.29 (q, $^3J_{P-F}$ 6.70 Hz); ^{19}F NMR (CD_2Cl_2) δ-34.22 (d, $^3J_{P-F}$ 6.69 Hz, $F_3CS-\overset{|}{\underset{|}{P}}=O$); δ-42.40 (s, F_3CS-C); Found: 26.02; H, 4.05; N, 3.75; P, 8.43; S, 17.48; Calcd. for $C_8H_{14}F_6NO_2PS_2$: C, 26.3; H, 3.83; P, 8.47; S, 17.55.

0-(1-*methyl*, 2-*S-trifluoromethyl*)*Ethyl S-Trifluoromethyl N,N-Diethylamidophosphorothioate*, **10f**. Liquid; yield 83%; b.p. 72–73°C/0.01 mmHg (bath temperature 115–120°C); (1:1) mixture of two diastereoisomers; ^{31}P NMR (CH_2Cl_2) δ 19.87 (q, $^3J_{P-F}$ 6.63 Hz), δ 20.21 (q, $^3J_{P-F}$ 6.63 Hz); ^{19}F NMR (CD_2Cl_2) δ-34.05 (d, $^3J_{P-F}$ 6.90 Hz), δ-34.20 (d, $^3J_{P-F}$ 6.90 Hz); δ-41.28 (s, F_3CS-C), δ-41.23 (s, F_3CS-C); ^{1}H NMR ($CDCl_3$) δ 1.11 (6H, t, $^3J_{H-H}$ 6.6 Hz, $\underline{CH_3}$-CH_2); δ 1.43 (3H, d, $^3J_{H-H}$ 8.6 Hz, $\underline{CH_3}$-CH); δ 1.48 (3H, d, $^3J_{H-H}$ 8.6 Hz, $\underline{CH_3}$-CH); δ 3.10 (6H, M, —CH_2—), δ 4.84 (1H, m, CH_3-$\underline{CH}$); Found: C, 29.05; H, 4.58; N, 3.69; P, 8.17; S, 16.90; Calcd. for $C_9H_{16}F_6NO_2PS_2$: C, 28.05; H, 4.25; N, 3.69; P, 8.17; S, 16.90.

0-(1-*chloromethyl*, 2-*S-trifluoromethyl*)*Ethyl S-Trifluoromethyl N,N-Diethylamidophosphorothioate*, **10g**. Pale yellow liquid; yield 79%; b.p. 78–80°C/0.01 mmHg (bath temperature 117–120°C); (1:1) mixture of two diastereoisomers; ^{31}P NMR (CH_2Cl_2) δ 20.88 (q, $^3J_{P-F}$ 6.63 Hz), δ 21.07 (q, $^3J_{P-F}$ 6.63 Hz); ^{19}F NMR (CD_2Cl_2) δ-34.05 (d, $^3J_{P-F}$ 6.7 Hz), δ-34.20 (d, $^3J_{P-F}$ 6.7 Hz); δ-41.51 (s, F_3CS-C), δ-41.40 (s, F_3CS-C); ^{1}H NMR ($CDCl_3$) δ 1.11 (6H, t, $^3J_{H-H}$ 4.5 Hz, CH_3); δ 3.46 (6H, m, —CH_2—); δ 4.6 (1H, m, Cl-CH_2-$\underline{CH}$); Found: C, 26.48; H, 3.93; P, 7.70; N, 3.38; S, 15.70; Calcd. for $C_9H_{15}ClF_6NO_2PS_2$: C, 26.13; H, 3.65; N, 3.39; P. 7.49.

0,0-*Bistrimethylsilyl S-Trifluoromethyl Phosphorothioate*, **5**. For the preparation of this compounds a somewhat modified procedure was used. To a 10 g of the disulfide, **2**, was added with stirring 5.0 g (0.022 mole) of 0,0-bistrimethylsilylphosphite **4** at −85°C. The cooling bath was removed and the temperature of the reaction mixture was raised to 15°C during 50 min. Stirring was continued for the next 5 hrs at these conditions. The volatile product (CF_3SH) and excess of disulfide **2** was removed in vacuo (10 mmHg; bath temperature 10–12°C) and the crude ester **5** was recovered by distillation. Colorless mobile liquid; yield 5.16 g (75%); b.p. 28–30°C/0.009 mmHg (bath temperature 40–45°C); ^{31}P NMR (neat) δ 8.98 (q, $^3J_{P-F}$ 8.79 Hz); ^{19}F NMR (CD_2Cl_2) δ-33.28 (d, $^3J_{P-F}$ 8.80 Hz); Found C, 26.00; H, 5.65; P, 9.5; Calcd. for $C_7H_{18}F_3O_3PSSi_2$: C, 25.75; H, 5.55; P, 9.48; (lit.[3]: viscous pale yellow oil, δ ^{31}P 5.23; $^3J_{P-F}$ 9.9 Hz).

The conversion of the esters **3**, **9** *and* **11** *into fluoridates* **14–16**. *General procedure*. To a stirred

solution of 0.01–0.05 mole of the corresponding esters **3**, **9** or **11**, in 10–20 ml of dry dichloromethane (or benzene) 1–3 drops of triethylamine (or pyridine) or a few crystals of tetramethylammonium fluoride (or cesium fluoride) were added. During addition of the catalysts the reaction vessel was cooled by an ice bath to control the exothermic reaction. The reaction mixture was stirred for 10–20 min., at 0–5°C and the cooling bath was removed. The solution was stirred for 2–4 hrs at 10–20°C. Then the solvent was removed under vacuum and the pure fluoridates **14–16** were separated by fractional distillation from the residual oily liquid in 70–90% yield. The following organophosphorofluoridates were obtained.

t-Butyl(phenyl)phosphinofluoridate, **14a**. Colorless liquid; solidified after standing at room temperature; yield 90%; b.p. 68–70°C/0.2 mmHg; ^{31}P NMR (CH_2Cl_2) δ 57.71 (d, J_{P-F} 1046 Hz); ^{19}F NMR (CD_2Cl_2) δ-68.71 (d, J_{P-F} 1047 Hz); ^{1}H NMR (CCl_3) δ 1.3 (9H, d, $^3J_{P-F}$ 16 Hz, Bu^t); δ 7.83 (5H, m, C_6H_5); Found: C, 59.89; H, 7.01; P, 15.60; Calcd. for $C_{10}H_{14}FOP$: C, 60.00; H, 7.04; P, 15.47 (lit.[19] δ ^{31}P 58.63; J_{P-F} 1048 Hz).

t-Butyl O-Methylphosphonofluoridate, **14b**. Mobile liquid; yield 83%; b.p. 18–23°C/0.01 mmHg; ^{31}P NMR (CD_2Cl_2) δ 36.73 (d, J_{P-F} 1103 Hz); Found: C, 38.78; H, 7.85; P, 19.7; Calcd. for $C_5H_{12}FO_2P$: C, 38.97; H, 7.84; P, 20.09.

O,O-Dimethylphosphorofluoridate, **14h**. Liquid; yield 73%; b.p. 40–41°C/8 mmHg; ^{31}P NMR (CH_2Cl_2) δ-9.57 (d, J_{P-F} 979 Hz); ^{19}F NMR (CD_2Cl_2) δ-80.16 (d, J_{P-F} 980 Hz); Found: C, 65.01; H, 4.70; P, 24.71; Calcd. for $C_2H_6FO_3P$: C, 65.03; H, 4.71; P, 24.19.

O,O-Diethylphosphorofluoridate, **14i**. Liquid; yield 85% b.p. 20–21°C/0.1 mmHg; ^{31}P NMR (neat) δ-8.01 (d, J_{P-F} 970.1 Hz); ^{19}F NMR (CD_2Cl_2) δ-78.5 (lit.[20] δ ^{19}F-77.5; ^{31}P δ-11.0, J_{P-F} 977 Hz).

O-Methyl N,N-Diethylamidophosphorofluoridate, **14j**. Liquid; yield 78%; b.p. 30–31°C/0.12 mmHg; ^{31}P NMR (CH_2Cl_2) δ 7.24 (d, J_{P-F} 969 Hz); ^{19}F NMR (CD_2Cl_2) δ-85.9 (d, J_{P-F} 970 Hz); Found: C, 35.61; H, 7.51; P, 18.31; Calcd. for $C_5H_{13}FNO_2P$: C, 35.51; H, 7.74; P, 18.65.

O-(3-S-trifluoromethyl)Propyl O-(2.2-dimethyl)Propyl Phosphorofluoridate, **15c**. Oily liquid; yield 85%; b.p. 60–61°C/0.05 mmHg; ^{31}P NMR (CH_2Cl_2) δ 13.40 (d, J_{P-F} 978.3 Hz); ^{19}F NMR (CD_2Cl_2) δ-76.8 (d, J_{P-F} 979.2 Hz); δ-40.1 (s, F_3CS–C); Found: C, 35.11; H, 5.35; P, 10.03; S, 11.2; Calcd. for $C_9H_{17}F_4O_3PS$: C, 34.62; H, 5.48; P. 9.91; S, 10.26.

O-(3-S-trifluoromethyl)Propyl N,N-Diethylamidophosphorofluoridate, **15d**. Liquid; yield 83%; b.p. 75–76°C/0.3 mmHg; ^{31}P NMR (neat) δ 19.88 (d, J_{P-F} 964.3 Hz); ^{19}F NMR (CD_2Cl_2) δ-86.07 (d, J_{P-F} 965.1 Hz) δ-40.8 (s, F_3CS–C); Found: C, 32.82; H, 5.75; N, 4.98; P. 10.95; S, 10.11; Calcd. for $C_8H_{16}F_4NO_2PS$: C, 32.32; H, 5.42; N, 4.71; P, 10.42; S, 10.78.

O(2-S-trifluoromethyl)Ethyl N,N-Diethylamidophosphorofluoridate, **16e**. Mobile liquid; yield 73%; b.p. 48–49°C/0.5 mmHg (bath temperature 68–70°C); ^{31}P NMR (CH_2Cl_2) δ 15.49 (d, J_{P-F} 972.1 Hz); ^{19}F NMR (CD_2Cl_2) δ-85.1 (d, J_{P-F} 973.0 Hz); δ-42.3 (s, F_3CS–C); Found: C, 29.31; H, 4.87; N, 5.01; P, 11.12; S, 12.02; Calcd. for $C_7H_{14}F_4NO_2PS$: C, 29.68; H, 4.98; N, 4.94; P, 10.93; S, 11.32.

O-(1-methyl,2-S-trifluoromethyl)Ethyl N,N-Diethylamidophosphorofluoridate, **16f**. Pale yellow liquid; yield 86%; b.p. 48–50°C/0.01 mmHg (bath temperature 75–82°C); (1:1) mixture of the diastereoisomers; ^{31}P NMR (CH_2Cl_2) δ 13.28 (d, J_{P-F} 989.7), δ 13.32 (d, J_{P-F} 989 Hz); ^{19}F NMR (CD_2Cl_2) δ-72.79 (d, J_{P-F} 990.30 Hz), δ-73.48 (d, J_{P-F} 990.30 Hz); δ-41.53 (s, F_3CS–C), δ-41.57 (s, F_3CS–C); ^{1}H NMR ($CDCl_3$) δ 1.13 (6H, t, $^3J_{H-H}$ 7.17 Hz, $\underline{CH_3}$–CH_2), δ 1.43, δ 1.47 (3H, d, $^3J_{H-H}$ 6.27 Hz, $\underline{CH_3}$–CH), δ 3.12 (6H, m, $\underline{CH_2}CH_3$), δ 4.87 (1H, m, $\underline{CH_3}$–$\underline{CH}$–CH_2–); Found: C, 31.55; H, 5.40; N, 4.60; P, 10.02; S, 10.62; Calcd. for $C_8H_{16}F_4NO_2PS$: C, 32.32; H, 5.42; N, 4.71; P, 10.41; S, 10.78.

O-(1-chloromethyl,2-S-trifluoromethyl)Ethyl N,N-Diethylamidophosphorofluoridate, **16g**. Liquid; yield 80%; b.p. 69–70°C/0.01 mmHg (bath temperature 100°C); (1:1) mixture of diastereoisomers, ^{31}P NMR (CH_2Cl_2) δ 13.36 (d, J_{P-F} 974.3 Hz), δ 13.42 (d, J_{P-F} 974.3 Hz); ^{19}F NMR (CD_2Cl_2) δ-73.56 (D, J_{P-F} 972.5 Hz), δ-74.00 (d, J_{P-F} 972.5 Hz); δ-41.83 (s, F_3CS–C), δ-41.87 (s, F_3CS–C); ^{1}H NMR ($CDCl_3$) δ 1.38 (6H, t, $^3J_{H-H}$ 4.3 Hz, CH_3–); δ 3.21; δ 3.97 (6H, m, $-CH_2$–); δ 4.9 (1H, m, $ClCh_2\underline{CH}$); Found: C, 28.97; H, 4.61; N, 4.33; P, 9.61; S, 10.8; Calcd. for $C_8H_{15}F_4ClNO_2PS$: C, 28.96; H, 4.55; N, 4.22; P, 9.33; S, 9.66.

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