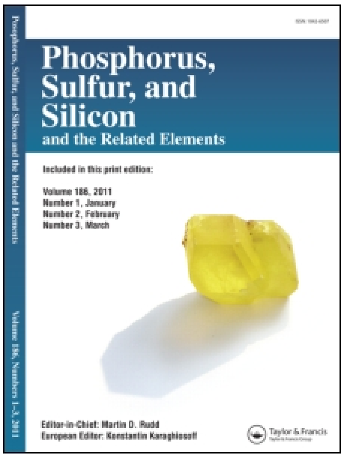

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PREPARATION AND REACTIONS OF METHYLTHIOMETHYL-SUBSTITUTED PHOSPHORUS HALIDES[1]

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PREPARATION AND REACTIONS OF METHYLTHIOMETHYL-SUBSTITUTED PHOSPHORUS HALIDES[1]

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Methylthiomethylphosphonous dichloride, $MeSCH_2PCl_2$ (**1**), is synthezised by the reaction of $MeSCH_2SnBu^n_3$ with phosphorus trichloride. Substitution reactions to give $MeSCH_2PX_2$ ($X = NEt_2, OPr^i, F, Ph$) are described. The phosphorus(III) compounds are readily converted to the corresponding phosphonyl and thiophosphonyl derivatives, $MeSCH_2P(Z)X_2$ ($Z = O, S$), and the phosphorane, $MeSCH_2PF_4$, respectively. Chlorination of the methylene group to give compounds of the type $MeSCHClP(O)X_2$ and $MeSCCl_2P(O)X_2$ is reported.

Key words: Methylthiomethylphosphorus compounds; phosphorus halides; carbon–tin cleavage

INTRODUCTION

In the course of our work on methylene-bridged diphosphorus[1,2] and phosphorus-sulfur[3] compounds we became interested in the preparation of compounds of the type SCH_2P with tricoordinate phosphorus. Dialkyl[(alkylthio)methyl]phosphonates and dialkyl[(arylthio)methyl]phosphonates with phosphorus(V) have been known for some time. Since interest has mainly focussed on the use of the phosphonates in Horner–Wittig reactions, several methods now exist for the synthesis of these reagents.[4,5] The preparation of methylthiomethyl-substituted phosphorus halides and the derivatization at phosphorus(III), however, has been neglected.

On the other hand, there have been a few reports on the synthesis of phosphines, such as $MeSCH_2PR_2$ ($R = Me, Ph$), and their use as ligands in transition metal chemistry.[6–10] We now wish to report on the preparation of methylthiomethyl-substituted phosphorus halides which may serve as precursors for a variety of other phosphorus compounds.

RESULTS AND DISCUSSION

Since it is known that the tin–carbon bond can be cleaved by phosphorus halides,[11–14] we have used this approach to prepare methylthiomethylphosphon/ous acid dichloride **1** (Scheme I). Methylthiomethyl derivatives of tin,

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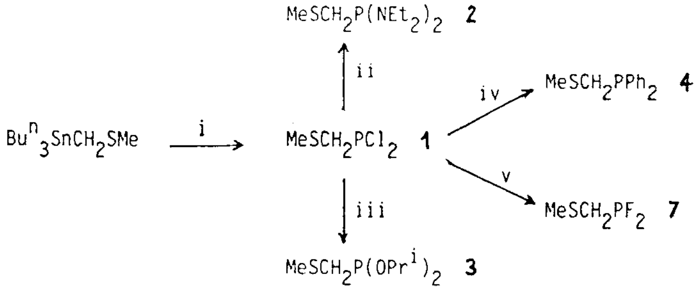

i) PCl_3. ii) Et_2NH. iii) Pr^iOH/Et_3N). iv) PhMgCl. v) SbF_3

SCHEME I

$MeSCH_2SnR_3$, as starting materials may be obtained from triorganotin chlorides and $MeSCH_2Li$[6]. Thus, phosphorus trichloride reacted with $MeSCH_2SnBu^n_3$ to give **1** in 61% yield; the tin chloride was recovered and used again. With $MeSCH_2SnMe_3$ a similar reaction took place but the products, **1** and Me_3SnCl, were difficult to separate from each other.

Substitution reactions at phosphorus in **1** led to the phosphonous acid derivatives **2** and **3**, and to the phosphine **4** as indicated in Scheme I. Compounds **2** and **3** were also obtained by the direct action of $MeSCH_2Li$ on $ClPX_2$ (1), a reaction which has been used for the preparation of **4**[6a,8]

$$MeSCH_2Li + ClPX_2 \rightarrow MeSCH_2PX_2 \qquad (1)$$
$$\mathbf{2}\ (X = NEt_2);\ \mathbf{3}\ (X = OPr^i)$$

from $ClPPh_2$. Reaction conditions had to be adjusted carefully because metallation of **2** with $MeSCH_2Li$ was observed which left some $ClP(NEt_2)_2$ unreacted. During distillation ligand exchange took place with the formation of $MeSCH_2P(NEt_2)Cl$ **5** and $(Et_2N)_3P$. Therefore, scrambling reactions were conducted for mixtures of **1** and **2**, and of **2** and PCl_3, respectively. As shown by NMR spectroscopy the formation of **5** could be confirmed; isolation of compound **5** by fractional distillation, however, was not achieved.

Complication also arose from the decomposition of $MeSCH_2Li$ to $MeSLi$[6,15] which, in the case of $ClP(OPr^i)_2$ (Equation 1), was responsible for the formation of the thioester, $MeSP(OPr^i)_2$, as by-product. Compound **3** was also prepared from **1** and the silylether, Me_3SiOPr^i, although it always was contaminated with $MeSCH_2P(OPr^i)Cl$ **6**, even when an excess of the silylether was used.

For the preparation of the fluoride **7** the reaction of **1** with antimony trifluoride was employed. The fluorination was conducted in the presence of *N,N*-dimethylaniline to avoid any redox-reaction,[16] known to convert phosphorus(III)-chlorides (and fluorides) to phosphoranes.[17] An alternative route to **7**, the cleavage of the tin–carbon bond in $MeSCH_2SnBu^n_3$, with phosphorus trifluoride, was not successful. Compound **7** is thermally not very stable and decomposes at elevated temperature to the phosphorane $MeSCH_2PF_4$ (**8**) and a polyphosphine $(MeSCH_2P)_n$.

In the presence of chlorine, compound **1** reacted with antimony trifluoride to give **8** in reasonable yields. The phosphorane was further characterized by the reaction (2) with the silylamine Me_2NSiMe_3 yielding the trifluorophosphorane **9**, a typical substitution reaction for phosphoranes.[17] The cleavage of the tin–carbon bond in $MeSCH_2SnBu^n_3$ with phosphorus pentafluoride was also investigated. Although useful for the synthesis of tetrafluorophosphoranes from other stannanes[14] led, in our case, to a mixture of **8** and Bu^nPF_4[18] in approximately equal amounts. Attempts to separate both phosphoranes by high-vacuum distillation were unsuccessful.

$$\mathbf{1} \xrightarrow{Cl_2/SbF_3} MeSCH_2PF_4\ \mathbf{8} \xrightarrow{Me_2NSiMe_3} MeSCH_2PF_3NMe_2\ \mathbf{9} \qquad (2)$$

Oxidation of **1** to the phosphonyl chloride **10** in high yields was conducted using dimethylsulfoxide. Compound **10** (and alkylthiomethylphosphonyl chlorides in general) has been obtained before by the reaction of $MeSCH_2Cl$

$$\underset{}{\mathbf{1}} \rightarrow \underset{\mathbf{10}\,(Z=0);\ \mathbf{11}\,(Z=S)}{MeSCH_2P(Z)Cl_2} \rightarrow \underset{\mathbf{12}(Z=0);\ \mathbf{13}\,(Z=S)}{MeSCH_2P(Z)F_2} \qquad (3)$$

with phosphorus trichloride in the presence of catalytic amounts of Lewis acids.[19] The conversion of **1** to **11** (Equation 3) was achieved with $PSCl_3$. Oxidation with elemental sulfur was a very slow reaction and conversion was low, even in the presence of $AlCl_3$. Whereas the reaction of **10** with P_4S_{10}[20] gave only impure **11**, the sulfur–oxygen exchange in **10** with $PSCl_3$ in the presence of $AlCl_3$ furnished **11** in excellent yields. Both chlorides, **10** and **11**, were converted to the corresponding fluorides **12** and **13** employing sodium fluoride in acetonitrile (3). Two other substitution reactions were performed with **10**; in the reaction with Me_2NSiMe_3 the amide $MeSCH_2P(O)(NMe_2)_2$ **14** was obtained, with isopropanol the ester $MeSCH_2P(O)(OPr^i)_2$ was formed. Thiophosphonyl derivatives, $MeSCH_2P(S)(NEt_2)_2$ **16** and $MeSCH_2P(S)(OPr^i)_2$ **17**, were easily obtained from the phosphorus(III) compounds **2** and **3**, respectively, by addition of sulfur.

The synthesis of α-chloro sulfides of the type $MeSCHClP(O)(OR)_2$ and $MeSCCl_2P(O)(OR)_2$ by chlorination of the methylene group was reported.[21,22] A recent investigation[23] showed that α-chloromethanephosphonates were obtainable by using *N*-chlorosuccinimide in slight excess without dichloro-substituted phosphonates to be present. In the case of the compounds **10**, **12**, and **15** the derivatives $MeSCHClP(O)X_2$ **18** ($X = Cl$), **19** ($X = F$) and **20** ($X = OPr^i$) were obtained when *N*-chlorosuccinimide (NCS) was applied in a 1 : 1 molar ratio. In the presence of toluenesulfonic acid and slight excess NCS the compounds $MeSCCl_2P(O)X_2$ **21** ($X = Cl$), **22** ($X = F$) and **23** ($X = OPr^i$) were formed.

EXPERIMENTAL

All experiments were carried out under exclusion of moisture in an oxygen-free atmosphere of nitrogen. Boiling and melting points are uncorrected. NMR spectra were recorded with a Jeol C 60 HL (^1H, ^{19}F, ^{31}P), Varian XL-100 (^{31}P) or Bruker WM 250 (^1H, ^{13}C) spectrometer. Standards were tetramethylsilane (^1H, ^{13}C), $CFCl_3$ (^{19}F) and 85% H_3PO_4 (^{31}P). Mass spectra were measured on a Varian MAT CH-7A spectrometer. Microanalyses were performed by the Microanalytical Laboratory Beller, Göttingen (FRG).

Methylthiomethylphosphonous dichloride **1**

a) To 24.0 g (175 mmol) phosphorus trichloride was added dropwise $MeSCH_2SnBu^n_3$[6] (61.45 g; 175 mmol). An exothermic reaction took place. For completion, the mixture was stirred 4 h at 60°C. Distillation under vacuum gave $MeSCH_2PCl_2$ with a yield of 61%; b.p. 65°C/10 mmHg. NMR: ^1H; $\delta = 2.31$ (3H, $^4J_{HH} = 0.9$ Hz); 3.29 (2 H, $^2J_{HP} = 16.3$ Hz). ^{13}C; $\delta = 17.7$ (CH_3, $^3J_{CP} = 2.9$ Hz); 44.9 (CH_2, $^1J_{CP} = 52.6$ Hz). ^{31}P; $\delta = 159.8$. (Found: C, 15.28; H, 3.08. Calcd. for $C_2H_5Cl_2PS$: C, 14.74; H, 3.09%).

b) The amide **2** (11.8 g; 50 mmol) was placed into a heavy-wall glass tube and ca. 50 ml diethylether added. The contents of the tube were cooled and HCl (7.3 g; 200 mmol) was condensed in. After sealing the tube the mixture was allowed to warm up, followed by shaking for 3 h at room temperature. Solid and solvent were removed and the remaining liquid distilled to give **1** in 77% yield.

Methylthiomethylphosphonous bis(diethylamide) **2**

a) To a solution of 16.3 g(100 mmol) **1** in 250 ml diethylether at −30°C was added diethylamine (30.0 g; 410 mmol) diluted with 50 ml diethylether. The reaction mixture was warmed up under stirring and the hydrochloride separated by filtration. Fractional distillation gave $MeSCH_2P(NEt_2)_2$ (80%) with a b.p. of 77°C/0.2 mmHg. NMR: ^1H; $\delta = 1.04$ (12 H, $^3J_{HH} = 7$ Hz); 2.20 (3 H); 2.75 (2 H, $^2J_{HP} = 13.2$ Hz); 3.0 (8 H). ^{13}C: $\delta = 17.3$ (CH_3S, $^3J_{CP} = 10.6$ Hz); 32.0 (SCH_2P, $^1J_{CP} = 13.0$ Hz); 42.7 (CH_2N, $^2J_{CP} = 15.8$ Hz); 14.9 (CH_3, $^3J_{CP} = 3.4$ Hz) ^{31}P: $\delta = 79.4$. (Found: C, 51.22; H, 10.52. Calcd. for $C_{10}H_{25}N_2PS$: C, 50.82; H, 10.66%).

b) At −50°C a suspension of $MeSCH_2Li$[6] (550 mmol) in hexane was added dropwise under stirring to $ClP(NEt_2)_2$ (115.9 g; 550 mmol). After the exothermic reaction had subsided stirring was continued for 6 h at room temperature. Lithium chloride was centrifuged and, after evaporating the solvent, compound **2** was obtained in 80% yield by distillation.

Scrambling reactions of **2** *with* PCl_3, $ClP(NEt_2)_2$ *and* $MeSCH_2PCl_2$ **1**

a) Compound **2** (13.5 g; 57 mmol) was added slowly to PCl_3 (15.6 g; 114 mmol). The exothermic reaction was completed by heating at 80°C for 2 h. Distillation gave a liquid boiling at 60–70°C/9 mmHg. The ^{31}P NMR spectrum showed absorptions for **1** and Cl_2PNEt_2 (intensity ratio 1 : 2).

b) Equimolar amounts of **2** and $ClP(NEt)_2$ were mixed at −20°C and then warmed up to room temperature. NMR spectra revealed that ligand exchange had taken place (ca. 45%) and that the mixture contained **2**, $MeSCH_2P(NEt_2)Cl$ **5** ($\delta_P = 126.0$), $ClP(NEt_2)_2$ and $P(NEt_2)_3$. Prolonged heating at 60°C gave rise to decomposition with the formation of solid material.

c) Equimolar amounts of **2** and **1** were mixed at −20°C, slowly warmed up to room temperature and then distilled. The fraction at 55–60°C/0.2 mmHg contained $MeSCH_2P(NEt)Cl$ **5** ($\delta_P = 128.0$) but was not analytical pure.

Methylthiomethylphosphonous diisopropylester **3**

a) A solution of 5.25 g (79.4 mmol) *i*-propanol and 8.1 g (80.1 mmol) triethylamine in 100 ml petroleum ether was prepared. The chloride **1** (6.47 g; 39.7 mmol), diluted with 20 ml solvent, was added at −45°C. The mixture was allowed to warm up, kept at room temperature for 2 h and worked up. Distillation furnished $MeSCH_2P(OPr^i)_2$ in 60% yield; b.p. 90°C/9 mmHg. NMR: ^1H; $\delta = 1.11$ (12 H, $^3J_{HH} = 6.3$ Hz); 2.19 (3 H); 2.48 (2 H, $^2J_{HP} = 7.1$ Hz); 4.1 (2 H). ^{13}C; $\delta = 17.3$ (CH_3S, $^3J_{CP} = 5.5$ Hz); 37.5 (CH_2P, $^1J_{CP} = 25.2$ Hz); 71.3 (CHO, $^2J_{CP} = 16.1$); 24.7 and 25.6 (diastereotopic CH_3, $^3J_{CP} = 2.2$ and 0.7 Hz). ^{31}P; $\delta = 162.3$ (Found: C, 45.92; H, 9.09. Calcd. for $C_8H_{19}O_2PS$: C, 45.70; H, 9.11%).

b) At −70°C a suspension of $MeSCH_2Li$ (ca. 160 mmol) in 150 ml hexane was added to $ClP(OPr^i)_2$ (30.3 g; 164.2 mmol). Under stirring the temperature was slowly raised to room temperature, then the solid was removed and the remaining liquid fractionated. After a fore-run of $MeSP(OPr^i)_2$ pure **3** was obtained (59% yield).

c) Trimethylsilylisopropylether (5.90 g; 44.6 mmol) and **1** (3.64 g; 22.3 mmol) were allowed to react under reflux for 4 h. The NMR spectra showed two compounds being present, **3** and presumable $MeSCH_2P(OPr^i)Cl$ **6** ($\delta_P = 171.5$); separation was not successful.

Methylthiomethyl(diphenyl)phosphine **4**

Phenylmagnesium chloride (13.7 g; 100 mmol) in 200 ml tetrahydrofurane (THF) reacted with **1** (7.5 g; 46 mmol) in 100 ml THF at −30°C. After hydrolysis with a saturated NH_4Cl-solution the organic phase was separated, dried over Na_2SO_4 and fractionally distilled to give 75% of $MeSCH_2PPh_2$; b.p. 143–144°C/0.01 mmHg. NMR; ^{31}P; $\delta = -20.9$ (Lit. 6; $\delta = -21.0$).

Methylthiomethylphosphonous difluoride **7**

Antimony trifluoride (10.8 g; 60 mmol) was suspended in 40 ml *N*,*N*-dimethylaniline. To the stirred mixture was added dropwise **1** (7.24 g; 44.4 mmol). The exothermic reaction was controlled by cooling so that the temperature did not exceed 50°C. After 6 h the volatile products were removed at 10 mmHg and trapped at −196°C. High vacuum trap-to-trap distillation furnished $MeSCH_2PF_2$ trapped at −83°C with 48% yield. Redistillation gave a b.p. of 28°C/10 mmHg. NMR: ^1H; $\delta = 2.20$ (3 H, $^4J_{HH} = 0.8$ Hz, $^4J_{HP} = 0.8$ Hz); 2.58 (2 H, $^2J_{HP} = 14.5$ Hz, $^3J_{HF} = 10.2$ Hz). ^{13}C; $\delta = 17.0$ (CH_3, $^3J_{CP} = = 2.9$ Hz); 38.6 (CH_2, $^1J_{CP} = 46.9$ Hz, $^2J_{CF} = 8.5$ Hz). ^{19}F; $\delta = -92.9$ ($^1J_{FP} = 1165$ Hz). ^{31}P; $\delta = 207.3$ Mol. wt. (mass spectr.): 130. Calcd. for $C_2H_5F_2PS$: 130.1.

Methylthiomethyltetrafluorophosphorane **8**

a) Antimony trifluoride (3.17 g; 17.7 mmol) was placed into a heavy-wall glass tube; chlorine (0.54 g; 15.2 mmol) and **8** (1.97 g; 15.0 mmol) were condensed in. The tube was sealed and then allowed to warm up to room temperature. After shaking for 0.5 h the volatile products were fractionated under high vacuum. $MeSCH_2PF_4$ (46%) retained at −78°C. NMR: ^1H; $\delta = 2.28$ (3 H); 3.07 (2 H, $^2J_{HP} = 9.5$ Hz, $^3J_{HF} = 7.4$ Hz). ^{13}C; $\delta = 17.3$ ($^3J_{CP}$ and $^4J_{CF}$ not observed); 32.7 ($^1J_{CP} = 208.0$ Hz, $^2J_{CF} = 20.7$ Hz). ^{19}F; $\delta = -48.4$ ($^1J_{FP} = 990$ Hz). ^{31}P; $\delta = -37.0$.

b) The same procedure as described in a) was employed for the reaction of $MeSCH_2SnBu^n_3$ (26.3 g; 74.8 mmol) with PF_5 (9.40 g; 74.8 mmol). A 1:1 mixture of **8** and Bu^nPF_4 was obtained at −78°C as shown by ^{19}F NMR.

Methylthiomethyl(dimethylamino)trifluorophosphorane **9**

In a glass tube were placed Me_2NSiMe_3 (1.39 g; 11.8 mmol) and **8** (1.95 g; 11.6 mmol). The mixture was kept at room temperature for 2 h. A small amount of solid precipitated from which the volatile products were removed. Distillation gave $MeSCH_2(Me_2N)PF_3$; b.p. 65°C. NMR: ^{19}F; $\delta = -34.0$ (F_{ax}, $^1J_{FP} = 841$ Hz, $^2J_{FF} = 59$ Hz); −69.9 (F_{eq}, $^1J_{FP} = 972$ Hz). ^{31}P; $\delta = -41.6$. Mol. wt. (mass spectr.): 193. Calcd. for $C_4H_{11}F_3NPS$: 193.17.

Methylthiomethylphosphonic dichloride **10**

In 20 ml methylene chloride at −78°C **1** (1.7 g; 10.4 mmol) was treated with dimethylsulfoxide (0.82 g; 10.4 mmol). After raising the temperature the mixture was kept at 20°C for 2 h. Fractional distillation gave $MeSCH_2P(O)Cl_2$ (89% yield); b.p. 68°C/0.4 mmHg. NMR: ^1H, $\delta = 2.42$ (3 H, $^4J_{HH} = 2.9$ Hz); 3.47 (2 H, $^2J_{HP} = 4.9$ Hz). ^{13}C; $\delta = 17.7$ (CH_3, $^3J_{CP} = 0.4$ Hz); 44.4 (CH_2, $^1J_{CP} = 103.0$ Hz). ^{31}P; $\delta = 41.6$. (Found: C, 13.21; H, 2.80. Calcd. for $C_2H_5Cl_2OPS$: C, 13.42; H, 2.82%).

Methylthiomethylthiophosphonic dichloride **11**

a) A mixture of **1** (7.84 g; 48.1 mmol) and $PSCl_3$ (8.15 g; 48.1 mmol) was heated for 4 h at 100°C. At this temperature phosphorus trichloride distilled off continuously. Pure $MeSCH_2P(S)Cl_2$ was obtained with 70% yield; b.p. 77°C/1.5 mmHg. NMR: ^1H; $\delta = 2.48$ (3 H); 3.72 (2 H, $^2J_{HP} = 2.5$ Hz). ^{13}C; $\delta = 18.4$ (CH_3, coupling not observed); 52.0 (CH_2, $^2J_{CP} = 74.4$ Hz). ^{31}P; $\delta = 80.9$. (Found: C, 12.76; H, 2.81; P, 15.61. Calcd. for $C_2H_5Cl_2PS_2$: C, 12.31; H, 2.58; P, 15.88%).

b) the dichloride **10** (8.96 g; 50 mmol) and $PSCl_3$ (16.9 g; 100 mmol) together with a small amount of $AlCl_3$ were heated in a sealed glass tube for 20 h at 165°C and for 14 h at 185°C. Distillation furnished **11** (83% yield).

Methylthiomethylphosphonic difluoride **12**

The chloride **10** (30.0 g; 165 mmol) was added to a suspension of NaF (28.2 g; 670 mmol) in 250 ml acetonitrile and stirred at 50°C for 2 h. The solid was removed by filtration and the liquid fractionated. $MeSCH_2P(O)F_2$ was obtained at 60°C/10 mmHg, (72% yield). NMR: ^1H; $\delta = 2.36$ (3 H); 3.02 (2 H, $^2J_{HP} = 12.7$ Hz, $^3J_{HF} = 4.0$ Hz). ^{13}C; $\delta = 17.2$ (CH_3, $^3J_{CP} = 1.3$ Hz, $^4J_{CF} = 0.6$ Hz); 24.2 (CH_2, $^1J_{CP} = 153.4$ Hz, $^2J_{CF} = 22.1$ Hz). ^{19}F; $\delta = -68.7$ ($^1J_{FP} = 1134$ Hz). ^{31}P; $\delta = 18.4$. (Found: C, 16.33; H, 2.80. Calcd. for $C_2H_5F_2OPS$: C, 16.44; H, 2.82%).

Methylthiomethylthiophosphonic difluoride **13**

Following the same procedure as for **12**, $MeSCH_2P(S)F_2$ was obtained boiling at 85–87°C/10 mmHg (70% yield). NMR: ^1H; $\delta = 2.35$ (3 H); 3.21 (2 H, $^2J_{HP} = 8.5$ Hz, $^3J_{HF} = 4.4$ Hz). ^{13}C; $\delta = 17.5$ (CH_3, $^3J_{CP} = 1.2$ Hz, $^4J_{CF} = 1.2$ Hz); 34.6 (CH_2, $^1J_{CP} = 110.0$ Hz, $^2J_{CF} = 21.7$ Hz). ^{19}F; $\delta = -47.0$ ($^1J_{FP} = 1162$ Hz). ^{31}P; $\delta = 97.6$. Elemental analysis not conducted.

Methylthiomethylphosphonic bis(diethylamide) **14**

To a solution of **10** (3.60 g; 20 mmol) in 20 ml methylene chloride was added Me_2NSiMe_3 (5.20 g; 44 mmol). After the exothermic reaction had subsided the mixture was stirred under reflux for 1 h. Subsequent removal of volatile products and crystallisation of the residue (CH_2Cl_2/petroleum ether) furnished 90% of $MeSCH_2P(O)(NMe_2)_2$, m.p. 28°C. NMR: ^1H; $\delta = 2.32$ (3 H, $^4J_{HP} = 2.0$ Hz); 2.50

(12 H, $^3J_{HP} = 9.8$ Hz); 2.69 (2 H, $^2J_{HP} = 10.8$ Hz). ^{31}P; $\delta = 31.7$. (Found: C, 36.81; H, 8.60. Calcd. for $C_6H_{17}N_2OPS$: C, 36.72; H, 8.73%).

Methylthiomethylphosphonic acid diisopropylester **15**

Compound **10** (20.0 g; 120 mmol) in 200 ml diethylether was treated with a mixture of isopropanol (20.1 g; 240 mmol) and triethylamine (22.6 g; 240 mmol) at 0°C. After heating under reflux for 1 h the usual work-up procedure gave 74% of $MeSCH_2P(O)(OPr^i)_2$; b.p. 56°C/0.05 mmHg. NMR: ^{1}H; $\delta = 1.21$ (12 H, $^3J_{HH} = 6.3$ Hz); 2.16 (3 H, $^4J_{HP} = 1.5$ Hz); 2.54 (2 H, $^2J_{HP} = 13.2$ Hz); 4.6 (2 H, multiplett). ^{31}P; $\delta = 21.6$. (Found: C, 42.49; H, 8.30. Calcd. for $C_8H_{19}O_3PS$: C, 42.46; H, 8.46%).

Methylthiomethylthiophosphonic bis(diethylamide) **16**
Methylthiomethylthiophosphonic acid diisopropylester **17**

The amide **2** (4.92 g; 21 mmol) was treated with sulfur (0.93 g; 29 mmol) in 20 ml toluene at room temperature (1 h) and at 90°C (1 h), respectively. Excess sulfur was removed and the product obtained by distillation. Similarly, the ester **3** was converted.

$MeSCH_2P(S)(NEt_2)_2$; b.p. 130°C/0.01 mmHg (75% yield). NMR: ^{1}H; $\delta = 1.13$ (12 H, $^3J_{HH} =$ 7.2 Hz); 2.32 (3 H, $^4J_{HP} = 2$ HZ); 3.06 (2 H, $^2J_{HP} = 9.5$ Hz); 3.1 (8 H). ^{31}P; $\delta = 76.1$. (Found: C, 44.53; H, 9.21. Calcd. for $C_{10}H_{25}N_2PS_2$: C, 44.75; H, 9.39%).

$MeSCH_2P(S)(OPr^i)_2$; b.p. 55°C/0.01 mmHg (72% yield). NMR: ^{1}H; $\delta = 1.15$ (12 H, $^3J_{HH} =$ 6.3 Hz); 2.18 (3 H, $^4J_{HP} = 1.5$ Hz); 2.78 (2 H, $^2J_{HP} = 11.0$ Hz); 4.7 (2 H, m). ^{31}P; $\delta = 86.0$. (Found: C, 39.78; H, 8.01. Calcd. for $C_8H_{19}O_2PS_2$: C, 39.65; H, 7.90%).

Halogenation with N-chlorosuccinimide

General procedure. For the preparation of the chloro(methylthio)methylphosphonic acid derivatives **18**, **19**, **20** an equimolar amount of *N*-chlorosuccinimide was added in portions to a stirred solution of the phosphorus compound (**10**, **12**, **15**) in 50 ml carbon tetrachloride. After heating the mixture for 30 min at 60°C the solid and the solvent were removed and the residue distilled. For the synthesis of the dichloro(methylthio)methylphosphonic acid derivatives **21**, **22**, **23** the phosphorus compounds were added to two equivalents of *N*-chlorosuccinimide in the presence of a catalytic amount of p-toluenesulfonic acid. $MeSCHlP(O)Cl_2$ (**18**); 53°C/0·01 mmHg (89%). NMR. ^{1}H; $\delta = 2.49$ (3 H, $^4J_{HP} = 2.3$ Hz); 5.33 (1 H, $^2J_{HP} = 3.5$ Hz). ^{13}C; $\delta = 13.9$ (CH_3, $^3J_{CP} = 3.0$ Hz); 66.3 (CHCl, $^1J_{CP} = 126.8$ Hz). ^{31}P; $\delta = 33.8$. (Found: C, 11.97; H, 1.92. Calcd. for $C_2H_4Cl_3OPS$: C, 11.25; H, 1.89%).

$MeSCHClP(O)F_2$ (**19**); b.p. 58°C/9 mmHg (89%). NMR: ^{1}H; $\delta = 2.47$; 5.28 ($^2J_{HP} = 13.8$ Hz). ^{13}C; $\delta = 13.3$ (CH_3, $^3J_{CP} = 4.1$); 51.3 (CH, $^1J_{CP} = 183.9$ Hz; $^2J_{CF} = 26.2$ Hz). ^{19}F; $\delta = -72.0$ (diastereotopic F-atoms, $^1J_{FP} = 1159$ Hz); -74.7 ($^1J_{FP} = 1140$ Hz). ^{31}P; $\delta = 3.6$. (Found: C, 13.84; H, 2.23. Calcd. for $C_2H_4ClF_2OPS$ C, 13.31; H, 2.11%).

$MeSCHClP(O)(OPr^i)_2$ (**20**); b.p. 83°C/0.2 mmHg (95%). NMR: ^{1}H; $\delta = 2.24$; 5.23 ($^2J_{HP} =$ 12.0 Hz). ^{31}P; $\delta = 12.2$. (Found: C, 36.74; H, 6.71. Calcd. for $C_8H_{18}ClOPS$: C, 36.86; H, 6.96%).

$MeSCCl_2P(O)Cl_2$ (**21**); m.p. 57°C (85%). NMR: ^{1}H; $\delta = 2.63$ ($^4J_{HP} = 2.1$ Hz). ^{13}C; $\delta = 18.7$ (CH_3, coupling not observed); 90.6 (CCl_2, $^1J_{CP} = 148.3$ Hz). ^{31}P; $\delta = 32.5$. (Found: C, 9.94; H, 1.28. Calcd. for $C_2H_3Cl_4OPS$: C, 9.69; H, 1.22%).

$MeSCCl_2P(O)F_2$ (**22**); b.p. 44°C/9 mmHg (76%). NMR: ^{1}H; $\delta = 2.62$. ^{13}C; $\delta = 17.9$ (CH_3, coupling not observed); 78.2 (CCl_2, $^1J_{CP} = 214.2$ Hz, $^2J_{CF} = 28.8$ Hz). ^{19}F; $= -83.4$ ($^1J_{FP} = 1166$ Hz). ^{31}P; $= -7.0$. (Found: C, 11.64; H, 1.60. Calcd. for $C_2H_3Cl_2F_2OPS$: C, 11.17; H, 1.41%).

$MeSCCl_2P(O)(OPr^i)_2$ (**23**); b.p. 77°C/0.05 mmHg (83%). NMR: ^{1}H; $\delta = 2.44$ (CH_3S, $^4J_{HP} =$ 6.5 Hz). ^{31}P; $\delta = 6.2$. (Found: C, 32.83; H, 5.80. Calcd. for $C_8H_{17}Cl_2O_3PS$: C, 32.55; H, 5.81%).

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