of 1 N NaOH, and an additional 3.00 g (1.6 mmol) of 4 was added to the reaction mixture. After 7 h, the pH had dropped to 5.9. The pH was raised to 8.5 and an additional 2.50 g (1.3 mmol) of 4 was added. After 11 h, the pH had dropped to 6.1, the pH was raised to 8.5, and another 2.50 g (1.3 mmol) of 4 was added. After 5 h the pH had dropped to 6.7, the pH was raised to 8.5, and another 2.5 g (1.3 mmol) of 4 was added. After 8 h, the pH had dropped to 6.4, the pH was raised to 8.5, and another 2.0 g (1.1 mmol) of 4 was added. After 60 h, the pH had dropped to 6.2. The pH was raised to 7.8 and the solution was extracted with three 30-mL portions of ether to remove unhydrolyzed diester. The organic layers were discarded. The aqueous phase was acidified with 4 N HCl to pH 2.2, saturated with NaCl, and extracted with four 50-mL portions of ether. The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to give 11.2 g (81%) of a slightly yellow oil.

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Registry No. 4, 56652-39-2; (*S*)-**5**, 56652-40-5; (±)-**6a**, 87173-15-7; (*S*)-**6a**, 60665-97-6; (±)-**6b**, 87137-46-0; (*S*)-**6b**, 87173-16-8; (±)-**6c**, 87137-47-1; (*S*)-**6c**, 87173-17-9; (*R*)-**6c**, 87173-23-7; (±)-**6d**, 87137-48-2; (*S*)-**6d**, 87173-18-0; (±)-**6e**, 87137-49-3; (*S*)-**6e**, 87173-19-1; (±)-**6f**, 87137-50-6; (*S*)-**6f**, 87173-20-4; (±)-**6g**, 87137-51-7; (±)-**6h**, 87137-52-8; (±)-**6i**, 87137-53-9; (*S*)-**6i**, 87173-21-5; (±)-**6j**, 87137-54-0; (*S*)-**6j**, 87173-22-6; (*R*)-**7a**, 36567-73-4; (*R*)-**7b**, 87137-55-1; (*R*)-**7c**, 87137-56-2; (*R*)-**7e**, 87137-57-3; (*R*)-**7i**, 87137-58-4; PLE, 9013-79-0; *tert*-butyl 3-hydroxy-3-methyl-5-hexenoate, 87137-59-5; (*S*)-mevalonolactone, 19022-60-7.

(*N*-Alkylthiocarbamoyl)thionophosphonic Acid Esters[1]

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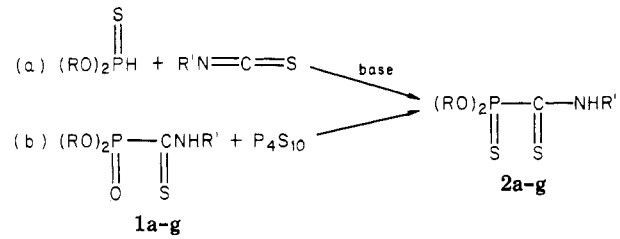
The title compounds **2** were prepared by the reaction of dialkyl thiophosphites and alkyl isothiocyanates. The diphenyl derivative **2f** was also prepared by heating the phosphoryl analogue **1f** with P_4S_{10}. The spectral differences between the present series **2** and the known phosphoryl series **1** are discussed. Both thiono functions of **2a**, **2c**, and **2e** react with methyl iodide, producing the phosphoryl-containing, synthetically useful zwitterion **7**.

Our interest in the chemistry of thiocarbamoyl phosphonic acid esters **1**[1,2] as possible precursors for different α-substituted phosphonates led us to investigate the analogous series of thiophosphoryl compounds **2**, which to our knowledge have not yet been described.

Two synthetic methods (Scheme I) were tried for the synthesis of **2**: (a) base-catalyzed reaction of dialkyl or diaryl thiophosphite with alkyl isothiocyanate and (b) "Thionation" of the phosphoryl analogues **1** with phosphorus pentasulfide. Since the thiophosphites are somewhat inconvenient to prepare[3,4] and to handle, we tried to develop method b which circumvents the usage of thiophosphites, but only in the case of conversion of **1f** to **2f** did the thionation reaction prove satisfactory. In all other cases only small amounts of the desired products could be identified (usually only by their TLC spots), whereas most of the starting materials were degraded to tars.

Five bases were used for catalyzing reaction a: sodium ethoxide and sodium methoxide as their appropriate alcoholic solutions, sodium hydride, potassium *tert*-butoxide, and triethylamine. It seems that even though all were applicable, sodium hydride or preferably sodium alkoxides were of advantage in the synthesis of the aliphatic esters

Scheme I[a]



[a] a, R = CH_3, R' = CH_3; *b*, R = CH_3, R' = benzyl; **c**, R = C_2H_5, R' = CH_3; d, R = C_2H_5, R' = benzyl; e, R = *n*-C_4H_9, R' = CH_3; f, R = phenyl, R' = CH_3; g, R = phenyl, R' = benzyl.

2a–e, while triethylamine proved to be the best for the synthesis of the aromatic esters **2f,g**. The same pattern was also found in the preparation of compounds **1**,[2] except that the thiophosphites are less selective in their choice of bases. This lower selectivity can be explained if it is assumed that the thiophosphites are more acidic than the phosphites, so they are ionized more readily by bases.

Following the addition of some of the base an exothermic reaction took place, instantly producing a yellow color. TLC, taken as soon as the reaction subsided, revealed a considerable amount of **2** accompanied by the remaining thiophosphite. The reaction mixture was then heated to 75 °C for 10–20 min. Higher temperatures and long heating periods resulted in a brown coloration and lower yields. The products could be not be distilled and were isolated by chromatography as yellow viscous oils, except for **2f** which crystallized. The yields were in the range of

(1) Part 3 of (*N*-Alkylthiocarbamoyl)phosphonic Acid Esters. Part 2: Z. Tashma, *Tetrahedron*, in press.
(2) Z. Tashma, *J. Org. Chem.*, **47**, 3012 (1982).
(3) T. Yamasaki, *Sci. Rep. Tohoku Univ.*, 11, 73 (1959); *Chem. Abstr.*, 24 24339*i* (1960). The procedures are quoted in: "Methoden der Organischen Chemie (Houben–Weyl)", Phosphor-Verbindungen II, 4th ed., Georg Thieme Verlag, Stuttgart, 1964, p 84.
(4) J. Michalski and C. Krawiecki, *Chem. Ind. (London)* 1323 (1957). C. Krawiecki and J. Michalski, *J. Chem. Soc.*, 881 (1960).

0022-3263/83/1948-3966$01.50/0

Table I. Yields and NMR Data for Compounds 2a-g

compd	% yield	solvent	chemical shift, ppm: $P(OR)_2$ protons	chemical shift, ppm: NR protons[a]
2a	45	$CDCl_3$	3.83 (d, 6 H, CH_3O, J_{POCH} = 17 Hz)	3.27 (dd, 3 H, CH_3N, J_{PCNCH} = 1.8 Hz; J_{HNCH} = 5 Hz)
2a		C_6D_6	3.43 (d, 6 H, CH_3O, J_{POCH} = 14 Hz)	2.44 (dd, 3 H, CH_3N, J_{PCNCH} = 1.8 Hz, J_{HNCH} = 5 Hz)
2b	40	$CDCl_3$	3.83 (d, 6 H, CH_3O, J_{POCH} = 13.5 Hz)	7.35 (br s, 5 H, aromatic), 4.83 (dd, 2 H, benzylic, J_{PCNCH} = 1.8 Hz, J_{HNCH} = 5.5 Hz)
2b		C_6D_6	3.44 (d, 6 H, CH_3O, J_{POCH} = 14 Hz)	6.98 (m, 5 H, aromatic), 4.49 (dd, 2 H, benzylic, J_{PCNCH} = 1.7 Hz, J_{HNCH} = 5.5 Hz)
2c	60	$CDCl_3$	4.10 (m, 4 H, CH_2O), 1.35 (t, 6 H, CH_3C, J_{HCCH} = 7 Hz)	3.26 (dd, 3 H, CH_3N, J_{PCNCH} = 1.7 Hz, J_{HNCH} = 5.2 Hz)
2c		C_6D_6	4.06 (m, 4 H, CH_2O), 1.03 (t, 6 H, CH_3C, J_{HCCH} = 7 Hz)	2.48 (dd, 3 H, CH_3N, J_{PCNCH} = 1.8 Hz, J_{HNCH} = 4.9 Hz)
2d	60	$CDCl_3$	4.10 (m, 4 H, CH_2O), 1.36 (t, 6 H, CH_3C, J_{HCCH} = 6.5 Hz)	7.35 (br s, 5 H, aromatic), 4.84 (dd, 2 H benzylic, J_{PCNCH} = 2.2 Hz, J_{HNCH} = 5.5 Hz)
2d		C_6D_6	4.10 (m, 4 H, CH_2O), 1.00 (t, 3 H, CH_3C, J_{HCCH} = 7 Hz)	6.98 (m, 5 H, aromatic), 4.51 (dd, 5 H, benzylic, J_{PCNCH} = 1.6 Hz, J_{HNCH} = 6 Hz)
2e	65	$CDCl_3$	4.10 (m, 4 H, CH_2O), 1.8-0.8 (m, CH_2 CH_2CH_2), 0.92 (t, CH_3, J_{HCCH} = 6.2 Hz)	3.25 (dd, 3 H, CH_3N, J_{PCNCH} = 1.6 Hz, J_{HNCH} = 5 Hz)
2e		C_6D_6	4.10 (m, 4 H, CH_2O), 1.4-0.6 (m, CH CH_2CH_2), 0.77 (t, CH_3, J_{HCCH} = 6 Hz)	2.52 (dd, 3 H, CH_3N, J_{PCNCH} = 1.8 Hz, J_{HNCH} = 5.2 Hz)
2f	70,[b] 30[c]	$CDCl_3$	7.20-7.39 (m, 10 H, aromatic)	3.27 (dd, 3 H, CH_3N, J_{PCNCH} = 1.7 Hz, J_{HNCH} = 5 Hz)
2f		C_6D_6	7.36 (d, 4 H, aromatic, ortho), 6.96 (m, 4 H, aromatic, meta), 6.82 (t, 2 H, aromatic, para)	2.31 (dd, 3 H, CH_3N, J_{PCNCH} = 2 Hz, J_{HNCH} = 5 Hz)
2g	50	$CDCl_3$	7.35-7.2 (m, 15 H, aromatic), 4.90 (d,[d] 2 H, CH_2N, J_{HNCH} = 5.5 Hz)	
2g		C_6D_6	7.35-6.8 (m, 15 H, aromatic), 4.40 (d,[d] 2 H, CH_2N, J_{HNCH} = 5 Hz)	

[a] NH protons appear at ca. 9-10 ppm. [b] Starting from diphenyl thiophosphite. [c] Starting from 1f. [d] Unresolved doublet of doublets.

40–70%, and isolating the products was not too difficult.

Spectral Properties of (N-Alkylthiocarbamoyl)thionophosphonates 2

The spectral properties of **2** significantly resemble those of the related series **1**.[2] The differences will be pointed out in the following discussion.

The UV–visible spectra of compounds **2**, measured in ethanol, contained the two peaks that generally exist in the spectra of thioamides, namely, a $\pi \rightarrow \pi^*$ transition at 285 nm (log $\epsilon \sim 4$) and a low intensity $n \rightarrow \pi^*$ transition at 386 nm for **2a,c,e** and at 391 nm for **2f** (log $\epsilon \sim 1.50$ and 1.60, respectively). In hexane, the $n \rightarrow \pi^*$ band shifted to higher wavelengths: λ_{max} = 408 nm for **2a,c,e**, and λ_{max} = 412 nm for **2f**. Regarding both the location of the peaks and the magnitude of the shift caused by hexane, compounds **2** resemble **1**, even though the values found for **2** are somewhat closer than those of **1** to the values found for simple thioamides.[5]

In the IR spectra of **2** there is the obvious replacement of the P=O stretch at ca. 1250 cm^{-1} by a P=S stretch at 770 cm^{-1}. All the peaks usually attributed to secondary thioamides[6] are present, and the general patterns of the spectra are rather similar to the spectra of compounds **1**.

Proton NMR data for compounds **2** are compiled in Table I. By comparing the figures with those of **1**,[2] it becomes obvious that in chloroform solutions the two series do not differ very much. However, the upfield shift of the N–CH protons caused by replacing $CDCl_3$ with C_6D_6 as a solvent[7] is larger for **2** than for **1**. Thus, the shift of about 1 ppm found for **2f** is unusually high[7] and exceeds even the value found for **1f** (0.77 ppm). The shifts recorded for the alkyl esters **2a,c,e** are also very high (0.83, 0.78, and 0.73 ppm, respectively) especially when compared to the moderate value of 0.28 ppm found for **1c**. The *N*-benzyl derivatives reveal smaller shifts than the *N*-methyl compounds, a phenomenon that occurred also in the spectra of phosphoryl series **1**, but here too the shift values of 0.33–0.50 ppm are considerably higher than what was found in **1** (0–0.35 ppm).

The shift is believed to be caused by alignment of benzene molecules of the solvent parallel to the thioamide plane;[7] therefore it can be assumed that molecules of type **2** can accommodate the benzene ring nearer or in a better geometry than their phosphoryl analogues **1**.[8]

The electron-impact mass spectrometry of **2** reveals the molecular peaks, the typical olefinic and alkoxy cleavages of the phosphonate ester groups[9] (in one case, **1f**, a significant RSH splitting was also observed), and framgents correponding to the thiophosphite and isothiocyanate to which the molecule was cleaved probably due to the thermal reversibility of reaction a. Fragmentation of the thioamide moiety occurs less readily than in **1**. The N–R cleavage is small and the nitrilium fragment $(RO)_2(P{=}S){-}C{\equiv}N^+R$, which is abundant in the spectra of **1**,[2] is sometimes totally absent. Thus, breaking bonds in the

(5) H. Hosoya, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **33**, 850 (1960); M. J. Janssen, *Recl. Trav. Chim. Pays-Bas*, **79**, 464 (1960); W. Walater and J. Voss in "The Chemistry of Amides", E. Jabicki, Ed., Interscience, New York, 1970, p 400.

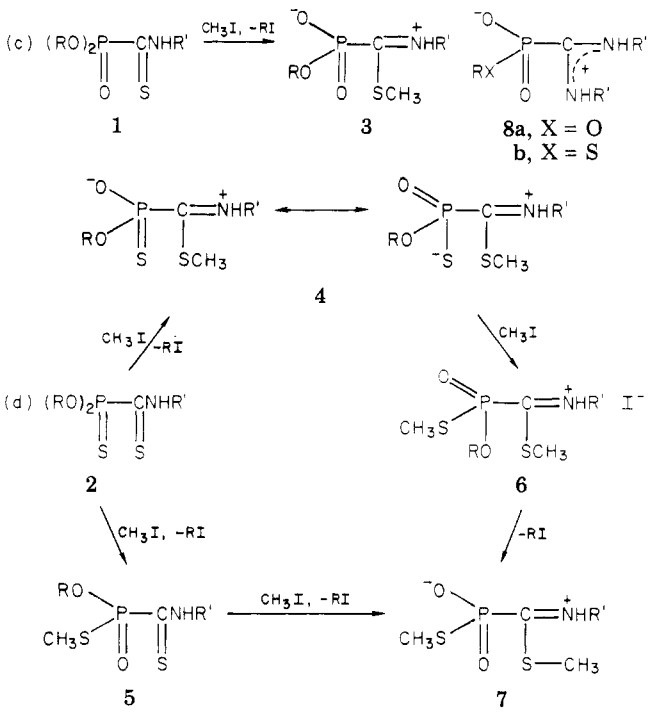
(6) K. A. Jansen and P. H. Nielsen, *Acta Chem. Scand.*, **20**, 597 (1966).

(7) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960); **5**, 139 (1962); R. C. Neuman, Jr., and L. Brewster Young, *J. Phys. Chem.*, **69**, 1977 (1965).

(8) An X-ray examination of **1f** indicated that in the crystalline state intermolecular P=O···H—N hydrogen bonds hold the phosphoryl molecules of this type in pairs.

(9) T. Nishiwaki, *Tetrahedron*, **22**, 1383 (1966); Z. Tashma, J. Katzhendler and J. Deutch, *Org. Mass Spectrom.*, **7**, 955 (1973).

Scheme II



thiophosphonate moiety of **2** should be much easier than breaking bonds in the thioamidic side of the molecule, unlike the situation in series **1**.

Chemical Properties of (Thiocarbamoyl)thionophosphonates 2

Compounds **2** (except for **2f**) are considerably less stable than their analogues of series **1**, and upon standing at room temperature for a few weeks they deteriorate appreciably.

It was reported[1] than when the phosphoryl compounds **1** were refluxed in methyl iodide, the aliphatic esters were converted to zwitterions of type **3** (reaction c, Scheme II) by a combination of thioamide methylation and phosphonate ester dealkylation. It is also known[10] that the ROP=S function reacts readily with methyl iodide to give the $CH_3SP{=}O$ group. It was thus of considerable interest for us to see whether compounds **2**, which contain both types of reactive moieties, will react with methyl iodide to give thiono zwitterions **4**, phosphoryl thioamides **5**, or phosphoryl zwitterions **7** which result from two successive attacks by the alkyl halide (reaction d).

When compounds **2a,c,e** were refluxed with methyl iodide in hexane for 48 h, a crystalline precipitate appeared which was totally colorless after recrystallization, revealing the absence of a thioamide function, while the replacement of the P=S by a P=O group was evident from the IR spectrum. Further spectroscopical and chemical studies of the product fully identified it as (**7**, R' = CH_3).

In order to get a better insight into the mechanism of reaction d, 10-mg quantities of **2a** and **2c** were mixed with 0.05 mL of methyl iodide and 0.5 mL of deuterated chloroform in an NMR tube, kept at 50 °C, and periodically checked in a 60-MHz NMR instrument.

Under these conditions there usually was a lag period of up to 24 h when only little reaction took place, followed by 4–5 days in which the reaction proceeded practically to completion. During this period the amount of methyl iodide considerably declined due to evaporation, and in the case of **2c** also due to its consumption, so that a further quantity of 0.015–0.025 mL of the reagent was added on the fourth day.

Rather unexpectedly, there was no clear evidence for the existence of significant amounts of intermediates. Both S–CH_3 signals seem to develop at about the same rate and at their final positions, as did the other expected peaks of **7**. (Some minor signals appeared during the experiment, did not belong to **2**, **7**, or ethyl iodide, could not originate from the intermediates **4**, **5**, or **6** as they persisted all through the experiment, and possibly belonged to unidentified byproducts.) Thus, it is likely that the first of the two consecutive reactions is slow and rate limiting, while the second is relatively quick so that only little of the intermediates accumulated.

Since the thioamide function in intermediate **5** is not expected to react much faster with methyl iodide than **2**, it is reasonable that the main routh from **2** to **7** is through intermediates **4** and **6**. Indeed, anions containing the structure (P=O)(—OR)—S^-, are known to be S-alkylated easily,[11] while the methylation product **6** should be rapidly dealkylated by halides[1,12] to give the end product **7**.

The conversion of **2** to the zwitterion **7** occurred only with the aliphatic compounds **2a,c,e**. The other compounds of series **2** which carried either aromatic ester groups or an *N*-benzyl group, though reacting with methyl iodide, yielded unidentified sticky products.[13] This is unlike what was found in the phosphoryl series **1** where phenyl esters were totally unreactive whereas alkyl esters of *N*-benzyl compounds reacted normally to give **3** (R = alkyl, R' = benzyl). The different outcome of the reaction when the analogous thiophosphoryl compounds were employed might be due to the reactivity of the thiophosphoryl bond.

Compound **7** (R = CH_3) is the common product of the different *N*-methyl dialkyl esters **2** studied. Because of both yield and convenience it was usually prepared starting from dibutyl thiophosphite. Compound **7** (R = CH_3) closely resembles the zwitterions **3**, except for having a *thio*ester function instead of the ester function of **3**. This structural difference can have a significant meaning for further manipulation, as the thiomethyl group is far more easily hydrolyzed than the alkoxy analogue.

Thus, while compounds **3** can react with primary amines to give monoalkyl esters of amidinophosphonic acid (**8a**),[14] these products are difficult to dealkylate further to the dianions. Compound **7**, on the other hand, can also be converted to amidinophosphonates **8b**, which seem (by NMR spectroscopy[15]) prone to hydrolysis to give the free amidinophosphonic acid. The $(RO)_2P{=}S$ group might therefore prove useful as a masked $(HO)_2P{=}O$ moiety in

(10) F. W. Hoffmann and T. R. Moore, *J. Am. Chem. Soc.*, **80**, 1150 (1958); M. I. Kabachnik and T. Y. Medved, *Izv. Akad. Nauk SSSR*, 604 (1961); *Chem. Abstr.*, **55**, 23319*g* (1961).

(11) M. I. Kabachnik and T. A. Mastryuka, *Zh. Obshch. Khim.*, **25**, 1924 (1955); *Chem. Abstr.*, **50**, 8499*c* (1956); M. I. Kabachnik, T. A. Mastryuka, N. I. Kurochkin, N. P. Rodionova and E. M. Popov, *Zh. Obshch. Khim.*, **26**, 2228 (1956); *Chem. Abstr.*, **51**, 1823*f* (1957).

(12) A similar rapid dealkylation by Cl^- is described by G. H. Birum and J. D. Wilson, *J. Org. Chem.*, **37**, 2730 (1972), for the amidinophosphonate $(EtO)_2(P{=}O)C(NMe_2)(=NMe_2^+)$.

(13) By adding ethanolic benzylamine and subsequent crystallization, about 10% yield of $MeS(PO_2^-)C(NH—benzyl)(=NH^+—benzyl)$ could be recovered, showing that some (**7**, R' = benzyl) was found.

(14) G. J. Durant, C. R. Young, and Z. Tashma, European Pat. Appl. 7326; *Chem. Abstr.* **93**, 168317 (1980).

(15) In a preliminary experiment, we tried to effect an alkaline hydrolysis of the thiol ester by dissolving 6 mg of **8b** in 0.5 mL of alkaline D_2O (initial pD ca. 11). NMR spectra revealed a gradual replacement of the CH_3SP doublet by a singlet at 1.85 ppm (probably CH_3S^-) which was completed within 30 min. The CH_3N singlet, on the other hand, changed much more slowly, yielding eventually two multiplets at 2.30 (probably $CH_3N(C{=}O)P$) and at 2.80 ppm (unidentified). Catalyzed hydrolysis of the thioester moiety of **8b** by oxidants or by heavy metal ions is also planned.

Table II. Microanalytical Data for Compounds 2a-g and 8b

	calcd					found				
compd	C	H	N	P	S	C	H	N	P	S
2a	24.12	5.00	7.04	15.58	32.16	24.70	5.51	6.72	15.27	32.76
2b	43.64	5.09	5.09	11.27	23.27	43.76	5.40	5.76	10.75	24.38
2c	31.72	6.17	6.17	13.66	28.19	30.99	6.36	6.59	13.66	28.69
2d	47.52	5.94	4.62	10.23	21.12	48.02	5.81	5.14	10.10	21.65
2e	42.40	7.77	4.95	10.95	22.61	42.51	8.03	4.84	11.23	23.12
2f	52.01	4.33	4.33	9.60	19.81	52.25	4.28	4.64	9.93	20.27
2g	60.15	5.31	3.51	7.77	16.04	60.58	5.72	3.89	8.01	16.50
8b	26.37	6.04	15.38	17.03	17.58	26.08	6.34	15.67	16.82	17.89

this system. This subject is under investigation.

Experimental Section

UV spectra were recorded on a Varian Technotron 635 UV–vis spectrophotometer and infrared spectra on a Perkin-Elmer 457 spectrophotometer. NMR spectra were measured on Bruker WP and on Bruker WH-300 instruments with Me_4Si as an internal standard. Low-resolution mass spectra were obtained on a Varian CH5DF instrument. Elemental analyses for compounds **2a-g** and **8** are given in Table II.

Materials. The phosphites and isothiocyanates were purchased from Aldrich Chemical Co. and were redistilled prior to use. Sodium hydride was used in the form of an 80% dispersion in oil without prior removal of the oil.

In the preparation of dimethyl thiophosphite by the reaction of dimethyl phosphite and P_4S_{10},[4] it should be noted that on certain occasions the exothermic reaction that occurs above ca. 95 °C goes out of control, and the gaseous products spontaneously ignite. This seems to be dependent on some contamination in the P_4S_{10}, as certain bottles caused the violent reaction while others did not. It is thus recommended to keep the reaction mixture at 80 °C for 3 h, avoiding higher temperatures. The yield is not much affected by the change.

Of the thiophosphites used only the diphenyl derivative seems not to be adequately described in the literature.[16] Its preparation is as follows.

Diphenyl Thiophosphite. To 11.7 g (0.05 mol) of diphenyl phosphite was added 4.4 g (0.01 mol) P_4S_{10}, and the mixture was stirred and heated to 90 °C under nitrogen for 2 h. After the mixture cooled, 100 mL of water was added, and the aqueous solution was extracted (3 × 50 mL) with chloroform which was dried over $MgSO_4$ and evaporated. Chromatography through silica gel (eluent dichloromethane) gave about a 50% yield of the thiophosphite as a viscous colorless liquid which solidified (reversibly) in a freezer. The compound had satisfactory analysis for C, H, P, and S, a P=S stretch in the IR at 760 cm^{-1}, and a P—H stretch at 2420 cm^{-1}. Mass spectra showed the molecular peak and major fragments at m/e values of 157, 110 (probably thiophenol), 94, and 77.

Dibutyl (*N*-Methylthiocarbamoyl)thionophosphonate (2e). To a magnetically stirred mixture of 10.5 g (0.05 mol) of redistilled dibutyl thiophosphite and 4 g (0.055 mol) of methyl isothiocyanate kept under nitrogen, about 1 mL of concentrated solution of sodium methoxide in methanol was added dropwise quickly. The mixture became deep yellow, and the temperature rose to about 45 °C. After the mixture was heated at 75 °C for 20 min, 50 mL of salt water was added, and the product was extracted (3 × 50 mL) with chloroform which was then dried over magnesium sulfate and evaporated. The yellow oily residue was purified by silica gel column chromatography (dichloromethane eluent); yield 65%.

Diphenyl (*N*-Methylthiocarbamoyl)thionophosphonate (2f). To a magnetically stirred mixture of 12.5 g (0.05 mol) of diphenyl thiophosphite and 4 g (0.056 mol) of methyl isothiocyanate was added about 1 mL of triethylamine dropwise. The reaction mixture turned yellow, and heat was evolved. The mixture was kept at 75 °C for another 20 min. The product, purified by silica gel chromatography, crystallized: mp 95 °C; yield 70%.

Diphenyl (*N*-Methylthiocarbamoyl)thionophosphonate (2f). A mixture of 3.07 g (0.01 mol) of **1f**, 4.44 g (0.01 mol) of P_4S_{10}, and 15 mL of toluene was stirred under nitrogen and gradually heated to reflux. After 90 min TLC revealed that only a little of **1f** was left. The mixture was cooled, 30 mL of water was added, and the aqueous phase was extracted with chloroform (3 × 25 mL). The extract was then dried over sodium sulfate and concentrated by evaporation. The product, which was purified by silica gel column chromatography (eluent dichloromethane; yield 30%) was identical in every respect with that prepared by the previous method. By continuation of the chromatography, some of the starting material could also be recovered (eluent acetone and dichloromethane, 1:20).

***N*,*S*,*S*-Trimethylthioimidoylthiolophosphonic Acid Monoester, Inner Salt (7, R′ = CH_3).** Recently prepared and purified **2e** (2.83 g, 0.01 mol) (or an equivalent amount of **2a** or **2c**) was dissolved in a mixture of 15 mL of hexane and 15 mL of methyl iodide and refluxed for 48 h. The product crystallized out, giving a crude yield of about 70%. After recrystallization from acetonitrile and ether the yield was ca. 50%; mp 145 °C dec. As **7** (R = CH_3) is a very hygroscopic and reactive compound, it was difficult to obtain accurate microanalysis. The iR spectrum showed clearly the replacement of the P=S stretch by a P=O signal at 1240 cm^{-1}: NMR ($CDCl_3$) 3.30 (d, 3 H, CH_3N, J_{PCNCH} = 1.5 Hz), 3.17 (s, 3 H, CH_3SC), 2.15 ppm (d, 3 H, CH_3SP, J_{PSCH} = 13 Hz).

***N*,*N*′,*S*-Trimethylamidinophosphonothiolic Acid Monoester, Inner Salt (8, R = R′ = CH_3; X = S).** Ethanolic methylamine 33%, 2 mL, 0.022 mol) was added to 2.0 g (0.015 mol) of **7** (R′ = CH_3) in 15 mL of chloroform. The precipitated colorless crystals were collected by filtration, washed with ether, and recrystallized from acetonitrile and ether: yield 60%; mp 235 ° dec; M_r = 182 (MS); IR (KBr) 1630, 1400, 1255 and 1095 cm^{-1}; NMR (D_2O) 3.24 and 2.89 (2 s, 6 H, geometrical isomers of CH_3N groups), 2.15 ppm (d, 3 H, CH_3S, J_{HCSP} = 15 Hz); in an alkaline solution the NCH_3 signals collapsed to one singlet at 2.92 ppm.

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Registry No. **1f**, 81940-07-0; **2a**, 86835-78-1; **2b**, 86835-79-2; **2c**, 86835-80-5; **2d**, 86835-81-6; **2e**, 86835-82-7; **2f**, 86835-83-8; **2g**, 86835-84-9; **7** (R′ = CH_3), 86835-86-1; **8b**, 86835-85-0; methyl isothiocyanate, 556-61-6; benzyl isothiocyanate, 622-78-6; diphenyl phosphite, 4712-55-4; dimethyl thiophosphite, 5930-72-3; diethyl thiophosphite, 999-01-9; dibutyl thiophosphite, 17529-47-4; diphenyl thiophosphite, 58045-33-3.

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