

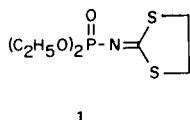
Dithietanes. Synthesis of *N*-Substituted 2-Imino-1,3-dithietanes and 2-Imino-1,3-dithietane Hydrochloride (1)

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The reaction of diethylphosphoryl isothiocyanate with potassium hydrosulfide gave potassium diethoxyphosphinyldithiocarbamate (**3a**). This salt, with methylene bromide, afforded 2-diethoxyphosphinylimino-1,3-dithietane (**5a**) in high yield. In concentrated hydrochloric acid, **5a** was hydrolyzed to 2-imino-1,3-dithietane which was isolated as a stable hydrochloride (**7**). The synthesis of some other *N*-substituted 2-imino-1,3-dithietanes is also described.

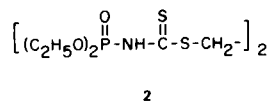
Previous work in these laboratories led to a new series of insecticidal heterocyclic dialkoxyphosphinylimides exemplified by 2-diethoxyphosphinylimino-1,3-dithiolane (**1**) (**2**). Compound **1** and its analogs were prepared in high yields by phosphorylation of 2-imino-1,3-dithiolanes and dithianes. Good syntheses of the required 2-imino-1,3-dithiolane and dithiane salts were developed from the reaction of 1,2- and 1,3-dithiols and cyanogen chloride (**3**) and, more recently, from the acid-promoted ring-closure of the ammonium salts of hydroxyalkyldithiocarbamic acids (**4**).



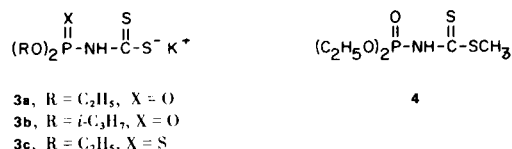
This paper describes results of some related work directed toward synthesis of new compounds having P–N bonds by starting with the addition of thiols to phosphoryl isothiocyanates.

RESULTS

A few addition reactions of thiols and alcohols to the NCS group attached to phosphorus have been reported (**5**). Our own observation was that the sodium salt of ethanedithiol added very rapidly to diethylphosphoryl isothiocyanate even in a heterogeneous benzene mixture to give, on acidification, the bis-dithiocarbamate, **2** (**6**).

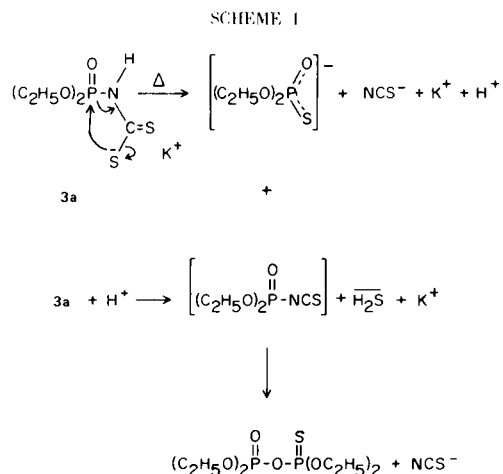


Thus stimulated, further experiments showed that potassium hydrosulfide would also add rapidly to diethylphosphoryl isothiocyanate to give, as an isolable salt in high yield, potassium diethoxyphosphinyldithiocarbamate (**3a**). Salt **3a** and some of its analogs (**3b** and **3c**) represented, for our purposes, intermediates of considerable potential.

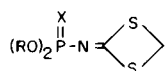


Salt **3a** was readily converted to the iminodithiolanyl phosphate **1** by reaction with ethylene bromide. This fact, together with the elemental analyses, the presence of a maxima at 3040 cm^{-1} in the infrared assignable to an N–H, and the identification of hydrogen sulfide, potassium thiocyanate, and of tetraethyl thiopyrophosphate formed by decomposition of the salt as suggested by Scheme 1, served to establish the structure of **3a** (**7**). Alkylation with methyl iodide afforded the simple methyl ester **4** in good yield.

It was anticipated that the reaction of **3a** with methylene bromide would give methylene bis-diethoxyphosphinyldithiocarbamate. However, when the crude product from the initial reaction gave a strong band at *ca.* 1600 cm^{-1} in the infrared, it appeared that ring-closure to give 2-diethoxyphosphinylimino-1,3-dithietane (**5a**) had occurred instead. The experiment was repeated using a 10 molar excess of methylene bromide and an equivalent of sodium bicarbonate in methanol and this afforded, on simple work-up, an 89% yield of **5a**. That dithietane formation had indeed occurred was confirmed by the elemental analyses, molecular weight, and the nmr spectrum. As shown by the effect of varying the ratio of salt



3a and methylene bromide (Table I), a yield of 75% of **5a** could be realized even where only a small excess of methylene bromide was used. Whereas the reaction went slowly in methanol, in dimethylformamide it proceeded exothermically to give **5a** in high yield and purity (Table I).



- 5a**, R = C₂H₅, X = O
5b, R = *i*-C₃H₇, X = O
5c, R = C₂H₅, X = S
5d, R = CH₃, X = S
5e, R = CH₃, X = O

Replacement of salt **3a** by potassium diisopropoxyphosphinyldithiocarbamate (**3b**) and by potassium diethoxyphosphinothioylidithiocarbamate (**3c**) in the methylene

bromide reaction afforded the respective diisopropoxyphosphinyl and diethoxyphosphinothioyliminodithietanes **5b** and **5c**. Product **5c** was also prepared in a sequential reaction by addition of diethylthiophosphoryl isothiocyanate to sodium hydrosulfide in methanol followed by addition of methylene bromide and sodium bicarbonate (58% of recrystallized **5c**). This latter procedure was also used to make 2-dimethoxyphosphinothioylimino-1,3-dithietane (**5d**) starting with dimethylthiophosphoryl isothiocyanate. A major by-product in this case was *O,O,S*-trimethyl phosphorodithioate, presumably derived from methylation by **5d** of the dimethylphosphorodithioate anion formed through partial decomposition of the intermediate sodium dimethoxyphosphinothioylidithiocarbamate (as in Scheme 1).

Attempts to extend the reactions of dithiocarbamate salt **3a** to form 4-substituted-2-imino-1,3-dithietanes by reaction with such *gem*-dihalides as benzal bromide, 1,1-dibromoethane, or ethyl dibromoacetate failed. These reactions generally led to reversion of **3a** to diethylphosphoryl isothiocyanate.

The excellence of the ring-closure reaction with methylene bromide and the phosphinyldithiocarbamate salts indicated that dithietane formation should also be expected, at least to some extent, with alkylidithiocarbamate salts. No examples were found in the literature.

In the better of two experiments, using isopropylammonium isopropylidithiocarbamate in a 1:3 ratio with methylene bromide in dimethylformamide, a 46% yield of 2-isopropylimino-1,3-dithietane was obtained. The structure was consistent with analyses and ir and nmr spectra. Its hydrochloride gave the theoretical neutralization equivalent and $pK_a = 4.3$. At a 1.5 to 1 methylene bro-

TABLE I

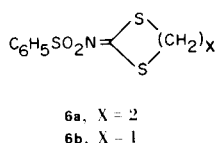
Yields of 2-Diethoxyphosphinylimino-1,3-dithietane (**5a**)
from Potassium Diethoxyphosphinyldithiocarbamate (**3a**)

Expt.	Solvent	Mole CH ₂ Br ₂ per Mole 3a	Temperature	Reaction Time	n_D^{25}	Yield %
1	CH ₃ OH	10	Room	3 days	1.5348	89 (a)
2	CH ₃ OH	1.1	Room	2 days (b)		60
3	CH ₃ OH	1.3	Room	2 days	1.5346	73
4	CH ₃ OH	1.5	Room	28 hours		77
5	CH ₃ OH	1.5	Reflux	1 hour	1.5136 (c)	68
6	DMF	1.5	30-35° (exothermic)	1 hour	1.5339 (d)	75

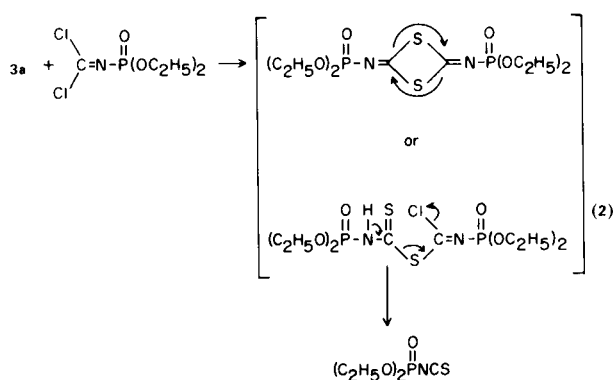
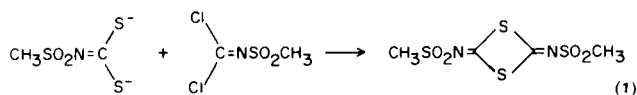
(a) High purity by analysis, tlc, and nmr. (b) Reaction close to completion after *ca.* 6 hours (by ir). (c) Product also qualitatively less pure than expt. 1 by ir, tlc, and nmr. (d) Product same as expt. 1 by ir and tlc; nmr showed minor contamination.

mide to dithiocarbamate salt ratio and a lower dilution, the yield was only 13%. The major product appeared to be, from infrared data, methylene bis-isopropylidithiocarbamate.

The reaction of ethylene bromide with the disodium salt of benzenesulfonyldithiocarbamic acid generated in dimethylformamide from benzenesulfonamide, carbon disulfide, and sodium hydroxide has been reported to give 2-benzenesulfonylimino-1,3-dithiolane (**6a**) in high yield (8). However, with methylene bromide we obtained only a 2% yield of 2-benzenesulfonylimino-1,3-dithietane (**6b**). The major product, even when a large excess of methylene bromide was used, was methylene bis-benzenesulfonyldithiocarbamate.



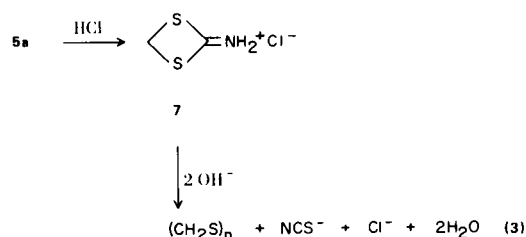
A most interesting case is reported of dithietane formation from the dipotassium salt of methanesulfonyldithiocarbamic acid and methanesulfonylisocyanide dichloride (eq. 1) (9). The product reverted to methanesulfonyl isothiocyanate at the "melting point" (9). When we tried the analogous reaction with **3a** and diethoxyphosphinylisocyanide dichloride at 0°, the major product was diethylphosphoryl isothiocyanate as shown in equation 2.



2-Imino-1,3-dithietane Hydrochloride (**7**).

In 12 *N* hydrochloric acid, 2-dialkoxyphosphinylimino-1,3-dithietanes **5a** and **5b** reacted exothermically to give,

on dilution with acetone, a crystalline salt. The salt analyzed correctly for 2-imino-1,3-dithietane hydrochloride (**7**); ir, nmr, and uv spectra were consistent with this structure. In water, the salt titrated as a strong acid ($\text{p}K_a$ ca. 3.7) taking up exactly *twice* the calculated amount of standard alkali to give a titration curve with a single break. A precipitate began to form as soon as titration was begun and this organic-insoluble solid, inferred to be a thioformaldehyde polymer from the infrared spectrum and by elemental analysis, was isolated in 97% yield. The other base-induced degradation product was identified as thiocyanic acid by isolation of cuprous thiocyanate in 96% yield. The overall reaction with alkali is, therefore, as shown by equation 3.



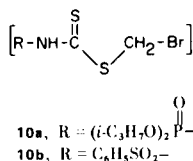
In a benzene-aqueous bicarbonate mixture suitable for the isolation of 2-imino-1,3-dithiolane from its hydrochloride, (3), salt **7** gave only polymer. That the presumed free imine has a finite existence, however, was demonstrated by its generation from **7** in acetic anhydride with sodium acetate to give 2-acetylimino-1,3-dithietane in 91% yield. By addition of sodium acetate to mixtures of **7** in *O,O*-dimethyl phosphorochloridothioate and dimethyl phosphorochloridate (no solvent), 2-dimethoxyphosphinoylimino-1,3-dithietane (**5d**) and 2-dimethoxyphosphinylimino-1,3-dithietane (**5c**) were isolated in 51% and 42% yields, respectively. Generation of the imine in the presence of methyl isocyanate gave 2-methylcarbamoylimino-1,3-dithietane.

DISCUSSION

In addition to the case already referred to (9), several instances of the formation of 1,3-dithietanes from the reaction of dithioacid salts with methylene halides have been reported. Dittmer and co-workers prepared the dicyanomethylene derivative **8** in 65% yield by the reaction of the dipotassium salt of 2,2-dicyanodithioacetic acid with methylene iodide (10). In work more closely analogous to ours, Timmons and Wittenbrook obtained 2-cyanoimino-1,3-dithietane (**9**) in 29% yield from dipotassium cyanodithioimidocarbonate and methylene iodide (11).



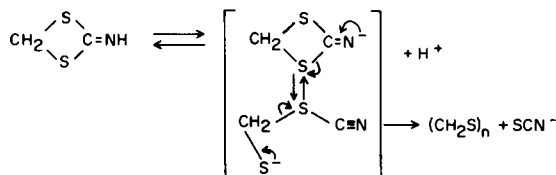
The generally good yields of dithietanes which resulted from the reaction of the phosphinyldithiocarbamate salts with methylene bromide means that ring-closure at the intermediate stage **10a** competed favorably with intermolecular attack by a second dithiocarbamate anion. The thiono sulfur atom of **10a** remains strongly nucleophilic.



As mentioned earlier, benzenesulfonyldithiocarbamate salts react with ethylene bromide to give 2-benzenesulfonylimino-1,3-dithiolane in high yield (**8**). Our work with methylene bromide in either dimethylformamide or methanol resulted in almost exclusive formation of methylene bis-benzenesulfonyldithiocarbamate, *i.e.* four-membered ring formation was non-competitive. Base titration of this ester in aqueous alcohol gave an approximate pK_a of 3.4 whereas the *O,O*-diisopropyl analog of ester **4** gave a pK_a of about 6.1. A similarly large difference would be expected between the bromomethyl esters **10a** and **10b** and, as a reflection of reduced electron density at the thiono sulfur atom, may account for a reduced rate of ring-closure for **10b**.

As indicated, attempts to isolate free 2-imino-1,3-dithietane at 25° were not successful. The aqueous titration experiment which showed polymer formation as soon as the first drop of base was added attests to the instability, at least in water, of the free imine. This fact, together with the quantitative isolation of a thioformaldehyde polymer and thiocyanate ion allows Scheme 2 to be written for the breakdown. This is formally analogous to the decomposition of 2-imino-1,3-oxathiolane to give

SCHEME 2



ethylene sulfide and cyanate ion (**12**). The increased instability of 2-imino-1,3-dithietane *vs.* 2-imino-1,3-dithiolane undoubtedly results from increased ring strain. This manifests itself in (1) a decreased basicity (pK_a *ca.* 3.70 *vs.* pK_a 5.85 for the respective hydrochloride salts) and consequent increased ease of loss of the remaining proton from nitrogen and (2) a probable lack of reversibility of the ring-opening reaction. The approximately 140-times greater acidity of **7** over 2-imino-1,3-dithiolane hydrochloride parallels the 100-fold difference reported between the conjugate acids of cyclobutanone and cyclopentanone (**13**).

Timmons and Wittenbrook reported on the expected higher stretching frequency of the C=N group in the cyanoimino-dithietane **9** (1555 cm^{-1}) *vs.* that of 2-cyanoimino-1,3-dithiolane (1504 cm^{-1}) (**11**). In this work, values of 1605 (chloroform) and 1666 (neat) cm^{-1} were obtained for **5a** and 2-isopropylimino-1,3-dithietane, respectively. The respective values for the dithiolanyl analogs are 1565 (chloroform) and 1600 (neat) cm^{-1} (**14**).

EXPERIMENTAL (15)

The dialkoxyphosphoryl and dialkoxythiophosphoryl isothiocyanates were prepared by reported procedure (**16**).

Potassium Diethoxyphosphinyldithiocarbamate (**3a**).

To a mixture of 57.6 g. (0.51 mole) of potassium *t*-butoxide in 650 ml. of *t*-butyl alcohol saturated with hydrogen sulfide was added 100.0 g. (0.51 mole) of diethylphosphoryl isothiocyanate in 50 ml. of *t*-butyl alcohol over *ca.* 1 hour. The mildly exothermic reaction was maintained at about 25-30° with a water bath, and, after an additional hour, the solids were collected and washed with *t*-butyl alcohol-benzene (10:1), benzene, and ether. After vacuum drying overnight, the yellow salt weighed 122.7 g. (89%), m.p. 97.99° dec., at 3°/min; ν max (mineral oil) 1010 (C₂H₅OP), 1265 (P=O), and 3040 (NH) cm^{-1} ; nmr (deuterium oxide), τ 5.8 (m, 4H, -POCH₂-), 8.67 (t, 6H, CH₃, J=7Hz), 5.5 (exchangeable proton).

Anal. Calcd. for C₅H₁₁NO₃PS₂K: C, 22.46; H, 4.15; N, 5.24; P, 11.59; S, 23.99. Found: C, 21.77, 21.67; H, 4.29; N, 4.95, 4.81; P, 11.28; S, 24.46, 24.65.

The salt can be kept if refrigerated. Samples in a capillary at *ca.* 25° showed decomposition after 24 hours (m.p. *ca.* 84-87°) and partial liquifaction after 48 hours. On the steam bath, the salt rapidly became colorless with partial liquifaction, generated hydrogen sulfide, and formed a white solid (potassium thiocyanate by comparison of the infrared spectrum with authentic material; deep red color with ferric chloride solution).

After two days in DMF, 1.00 g. of the salt afforded, on work-up, 0.32 g. of an oil, largely ethyl thiopyrophosphate,

(C₂H₅O)₂P(=O)-O-P(=S)(OC₂H₅)₂, by comparison of ir and nmr spectra with authentic material (**17**).

Methyl Diethoxyphosphinyldithiocarbamate (**4**).

A mixture of 6.4 g. of **3a** and 1.6 ml. of methyl iodide in

85 ml. of ether was stirred overnight. The (mostly decolorized) mixture was filtered, and the yellow solid recovered from the ether was recrystallized from hexane to give 4.3 g. (76%) of pale yellow plates, m.p. 69.8-72.0°; recrystallized from ether, m.p. 71.0-72.0°;

ν max (mineral oil), 3100 and 1480 ($-\text{NH}-\overset{\text{S}}{\parallel}{\text{C}}-$) cm^{-1} ; nmr (deuteriochloroform), τ 3.0 (d, 1H, $-\text{NH}$, $J=7\text{Hz}$), 5.7 (m, 4H, $-\text{CH}_2\text{O}-$), 7.38 (s, 3H, $-\text{SCH}_3$), 8.62 (t, 6H, $-\text{C}-\text{CH}_3$).

Potassium Diisopropoxyphosphinyldithiocarbamate (**3b**).

The procedure was the same as for **3a** except that the product was soluble in *t*-butyl alcohol. The mixture was concentrated *in vacuo* adding several portions of benzene to improve *t*-butyl alcohol removal. The remaining yellow solids (m.p. 105-107° dec.) showed the presence of some thiocyanate salt (2040 cm^{-1}). After several hours, this band was stronger in the infrared, and hydrogen sulfide generation was apparent.

A sample was converted to methyl diisopropoxyphosphinyldithiocarbamate in 69% yield using methyl iodide in methanol, (m.p. 83.0-84.4° from hexane); a 0.3080 g. sample in 45 ml. of 15% aqueous methanol required 11.20 ml. of 0.1 *N* sodium hydroxide (theory, 11.36 ml.). The pH at the half-neutralization point was 6.1.

Anal. Calcd. for $\text{C}_8\text{H}_{18}\text{NO}_3\text{PS}_2$: C, 35.41; H, 6.69; N, 5.16; P, 11.42; S, 23.63. Found: C, 35.66; H, 6.65; N, 5.27; P, 11.34; S, 23.58.

Potassium Diethoxyphosphinothioylidithiocarbamate (**3c**).

The *t*-butyl alcohol soluble salt was obtained in the same way as was **3b** and dried in a vacuum desiccator at 0° over potassium hydroxide. It decomposed over the range of 79-90°. The strong N-H band was present at 3050 cm^{-1} ; there was weak thiocyanate absorption at 2050 cm^{-1} . Salt **3c** was kept several weeks at -15° but became gummy after several hours at ca. 25°.

2-Diethoxyphosphinylimino-1,3-dithietane (**5a**).

A mixture (yellow) of 5.0 g. (0.019 mole) of **3a**, 13 ml. (10 *M* excess) of methylene bromide, and 1.6 g. (0.019 mole) of sodium bicarbonate in 50 ml. of methanol was stirred over a weekend (colorless; some hydrogen sulfide evolved). After addition of benzene, the salts were filtered off and the filtrate concentrated and remixed with ether-benzene. Three washes with 1:1 water-saturated salt solution freed the mixture of thiocyanate ion and drying and concentrating *in vacuo* afforded 4.0 g. (89%) of **5a** as a pale yellow oil; $n_{\text{D}}^{25} = 1.5348$; ν max 1240 (P=O) and 1600 (C=N) cm^{-1} ; λ max (methanol), 233 μ ($\epsilon = 15,000$); nmr (deuteriochloroform), τ 5.9 (m, P-O-CH₂-) and 6.07 (s, -S-CH₂-S-) integrating together as 6H and 8.6 (t, 6H, -CH₃, $J=8\text{Hz}$).

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{NO}_3\text{PS}_2$: C, 29.87; H, 5.01; N, 5.81; P, 12.84; S, 26.50; M.W. 241. Found: C, 29.97; H, 5.12; N, 5.97; P, 12.52; S, 26.27; M.W. (acetone) 250.

Molecular distillation (100-110°/1.5 u) gave colorless **3a**, $n_{\text{D}}^{25} = 1.5342$, the same by tlc and nmr as the undistilled product. Solubility in water is 4 to 8% at ca. 25°. For results for other runs, see Table I.

With DMF as solvent, a ratio of 5 ml. per 0.01 mole of **3a** was used. After pouring into 10 ml. of water, the mixture was extracted twice with 25 ml. of benzene. Three water washes (10 ml.) freed the benzene mixture of DMF.

2-Isopropoxyphosphinylimino-1,3-dithietane (**5b**).

The reaction, carried out as for **5a**, afforded from 54.4 g. (0.18

mole) of **3b** and 26 ml. (0.37 mole) of methylene bromide, 36.2 g. (76%) of **5b**: $n_{\text{D}}^{25} = 1.5163$; ν max 1240 (P=O) and 1610 (C=N) cm^{-1} ; nmr (deuteriochloroform), τ 5.1-5.7 (m, $>\text{CH}-\text{O}-$, 2H), 6.12 (s, S-CH₂-S, 2H), and 8.65 (d, -CH₃, 12H, $J=6\text{Hz}$).

Anal. Calcd. for $\text{C}_8\text{H}_{16}\text{NO}_3\text{PS}_2$: C, 35.67; H, 5.99; N, 5.20; P, 11.50; S, 23.81. Found: C, 35.90; H, 6.16; N, 5.45; P, 11.50; S, 23.66.

2-Diethoxyphosphinothioylimino-1,3-dithietane (**5c**).

To an ice-cooled mixture of 1.90 g. (0.047 mole) of sodium hydroxide in 50 ml. of methanol which had been saturated with hydrogen sulfide was added 10.0 g. (0.047 mole) of diethylthiophosphoryl isothiocyanate. After 20 minutes, 4.40 g. (0.052 mole) of sodium bicarbonate was added followed by 10 ml. (0.14 mole) of methylene bromide. After standing over the weekend, the mixture was worked-up as was **5a**, with the inclusion of an alkali wash, and afforded 10.6 g. of yellow oil which crystallized on standing. Recrystallization from ca. 50 ml. of 1:1 ether-petroleum ether (30-60°) gave 5.8 g. of colorless crystals, m.p. 41.8-42.8°, and a second crop, m.p. 38-42° (total 7.2 g., 58%); ν max 1600 (C=N) cm^{-1} ; nmr (deuteriochloroform), τ 5.7 (m, P-O-CH₂) and 5.83 (s, -S-CH₂-S-) integrating together as 6H and 8.6 (t, 6H, -CH₃), $J=7\text{Hz}$).

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{NO}_2\text{PS}_3$: C, 28.00; H, 4.70; N, 5.44; P, 12.04; S, 37.38. Found: C, 27.98; H, 4.80; N, 5.72; P, 12.03; S, 37.10.

2-Dimethoxyphosphinothioylimino-1,3-dithietane (**5d**).

(a) From 2-Imino-1,3-dithietane Hydrochloride (**7**).

To a well-stirred mixture of 8.0 g. (0.056 mole) of **7** in 20 ml. of *O,O*-dimethyl phosphorochloridothioate was added 10.2 g. (0.13 mole) of finely ground sodium acetate. After ca. 1.5 hours, the mixture was diluted with ether-benzene and washed (including alkali). After removal of solvent, excess *O,O*-dimethyl phosphorochloridothioate was stripped off a film evaporator at 100°/0.25 mm. The 8.5 g. of oily residue, showing extraneous absorption at 1230 cm^{-1} (probably P=O), was freed on this contaminant by rapid passage through 40 g. of silica gel (Merck 0.2-0.5 mm.) using 400 ml. of benzene and 200 ml. of 9:1 benzene-methanol and collecting five fractions. Fractions 1 and 2 (6.7 g.) showed only slight contamination by tlc (silica gel HF, ether-hexane 1:1; uv light and iodine vapor visualization; R_f ca. 0.3). Activated charcoal treatment in methanol gave slight color improvement; pale orange oil (6.6 g., 51%); $n_{\text{D}}^{25} = 1.6374$; ν max 1600 (C=N) cm^{-1} nmr (deuteriochloroform), τ 5.94 (s, 2H, -S-CH₂-S) and 6.24 (d, 6H, -CH₃, $J=14\text{Hz}$).

Anal. Calcd. for $\text{C}_4\text{H}_8\text{NO}_2\text{PS}_3$: C, 20.96; H, 3.52; N, 6.11; P, 13.51; S, 41.96. Found: C, 21.25, 21.01; H, 3.92, 3.70; N, 6.33; P, 13.48, 13.22; S, 42.13.

(b) From Dimethylthiophosphoryl Isothiocyanate.

The reaction was carried out as for **5c** (24 hours reaction time). The crude oil showed two major components by tlc (silica gel, 1:1 ether-hexane; palladium chloride detection). A major contaminant was shown, by nmr, to be *O,O*-dimethyl-S-methyldithiophosphate, which was removed on a film evaporator at 100°/0.3 mm. to give 41% of **5d** identical by ir and nmr spectra to the analyzed material.

2-Dimethoxyphosphinylimino-1,3-dithietane (**5e**).

The crude oil from salt **7** and dimethylphosphorochloridate, after washing with aqueous acid-salt and base-salt mixtures, was obtained in 47% yield; $n_{\text{D}}^{25} = 1.5756$; ν max 1240 (P=O) and 1590

(C=N) cm^{-1} ; nmr (deuteriochloroform), τ 6.08 (s, 2H, $-\text{S}-\text{CH}_2\text{S}-$) and 6.20 (d, 6H, CH_3 , $J=12\text{Hz}$).

Anal. Calcd. for $\text{C}_4\text{H}_8\text{NO}_3\text{PS}_2$: C, 22.53; H, 3.78; N, 6.57; P, 14.53; S, 30.08. Found: C, 22.68; H, 3.90; N, 6.72; P, 14.47; S, 30.14.

The product later crystallized, m.p. 57.4-58.8° (ether-petroleum ether).

2-Imino-1,3-dithietane Hydrochloride (7).

To 10.6 g. (0.04 mole) of **5a** was added over 15 minutes with stirring 25 ml. of concentrated hydrochloric acid (0.3 mole of hydrochloric acid) (exothermic). After another 90 minutes, the mixture was ice-cooled and 75 ml. of acetone added. The crystalline product, collected on a glass filter and washed with acetone and ether, amounted to 4.7 g. (75%). A sample totally sublimed at 110°/0.2 mm., but the infrared spectrum and melting point behavior were unchanged; λ max (methanol), 230 μ ($\epsilon = 11,440$); ν max (mineral oil), 1525, 1635, 1716, and 2855 (all associated

with $-\text{S}-\text{C}=\text{NH}_2^+$) cm^{-1} ; nmr (deuterium oxide), τ 5.62 (s, $-\text{S}-\text{CH}_2-\text{S}$).

Anal. Calcd. for $\text{C}_2\text{H}_4\text{ClNS}_2$: C, 16.96; H, 2.85; Cl, 25.03; N, 9.89; S, 45.27. Found: C, 16.72; H, 2.82; Cl, 25.14; N, 9.92; S, 45.11.

The salt gave a negative test for ammonium ion (Nessler's Reagent; also no absorption at 1400 cm^{-1}). In a capillary, at 1°/minute, discoloration began at 150° (orange) and there was strong gas evolution at 166-167°. The gas was hydrogen chloride (precipitated with silver nitrate solution: negative for thiocyanic acid or hydrogen sulfide by ferric chloride and lead acetate solution). Duplicate titrations required *two* equivalents of 0.1 *N* sodium hydroxide, e.g., 21.60 ml. for 0.1499 g. of **7** in 25 ml. of water, pH at the half-neutralization point was 3.70. The titration mixture was reacidified, and solids, which began appearing as soon as titration had begun, were collected, washed, and dried *in vacuo*: 0.0471 g. (light brown) or 97% as $(\text{CH}_2\text{S})\text{n}$; m.p. ca. 220-235°; ν max (mineral oil), 708, 732, 886, 1175, 1365 cm^{-1} (some shifts in position but not greatly different from *s*-trithiane).

Anal. Calcd. for CH_2S : C, 26.05; H, 4.38; S, 69.57. Found: C, 26.10; H, 4.31; S, 69.32.

A 0.2464 g. sample of **7** in 10 ml. of water, after adding 35 ml. of 0.1 *N* sodium hydroxide and reacidifying to pH 6.2, was filtered free of polymer. The solution afforded 0.2043 g. (96%) of cuprous thiocyanate (18); ν max (mineral oil), 2080 (SCN^-) cm^{-1} .

2-Acetylimino-1,3-dithietane.

To an ice-cooled mixture of 2.0 g. (0.001 mole) of **7** in 20 ml. of acetic anhydride was added 4.0 g. (0.02 mole) of sodium acetate. After stirring overnight, the mixture was stirred with ice and then saturated with potassium bicarbonate added in small portions. Extraction of the mixture with benzene-ether gave 1.9 g. (91%) of crystalline product, m.p. 54.0-55.6°; after sublimation (40°/0.2 mm.) m.p. 55.0-55.8°; ν max (carbon tetrachloride), 1520 (C=N) and 1676 (C=O) cm^{-1} .

Anal. Calcd. for $\text{C}_4\text{H}_5\text{NOS}_2$: C, 32.63; H, 3.42; N, 9.52; S, 43.56. Found: C, 32.75; H, 3.34; N, 9.53; S, 43.77.

2-Methylcarbamoylimino-1,3-dithietane.

To an ice-cooled mixture of 2.00 g. (0.01 mole) of **7** and 5.0 ml. (0.08 mole) of methyl isocyanate in 15 ml. of benzene was added 1.2 g. (0.03 mole) of sodium acetate in portions. After stirring overnight, the solids were collected and extracted with boiling acetone. The solids (2.1 g.) recovered from the acetone

were combined with 0.2 g. from evaporation of the benzene. Recrystallization from benzene afforded 1.72 g., m.p. 155.6-156.6° dec., and 0.2 g., m.p. 154.2-155.0° dec., (1.98 g. total; 86%) of colorless needles; ν max (mineral oil) 1540 (C=N), 1650 (split, C=O), and 3250 (N-H) cm^{-1} .

Anal. Calcd. for $\text{C}_4\text{H}_6\text{N}_2\text{OS}_2$: C, 29.61; H, 3.73; N, 17.27; S, 39.53. Found: C, 29.61; H, 3.70; N, 17.29; S, 39.42.

2-Benzenesulfonylimino-1,3-dithietane (6b).

The procedure was that described for the dithiolane analog, **6a**, but methylene bromide replaced ethylene bromide (7). The reaction mixture from a 0.1 mole (benzenesulfonamide and methylene bromide) run gave 1.2 g. of crude crystalline product on pouring into water. Recrystallization from benzene-hexane gave 0.60 g. (2%) of **6b** as tan crystals, m.p. 119.8-121.2°; ν max (mineral oil), 1155 and 1320 ($-\text{SO}_2-$), 1510 and 1535 (C=N) cm^{-1} ; nmr (acetone-*d*) τ 5.62 (s, 2H, $-\text{CH}_2-$) and ca. 2.1 (m, 5H aromatic). Compound **6b** is water insoluble.

Anal. Calcd. for $\text{C}_8\text{H}_7\text{NO}_2\text{S}_3$: C, 39.16; H, 2.88; N, 5.71; S, 39.21. Found: C, 39.30; H, 2.76; N, 5.59; S, 39.17.

From other experiments using dipotassium benzenesulfonyldithiocarbamate in methanol (19), acidification of the reaction residue afforded methylene bis-benzenesulfonyldithiocarbamate (recrystallized from chloroform), m.p. 144.0-144.8° (with hydrogen sulfide evolution); ν max (mineral oil), 1150, 1160, 1170, 1355, and 3200 cm^{-1} ; nmr (acetone-*d*) τ 5.02 (s, 2H, $-\text{CH}_2-$) and 1.8-2.3 (m, 10H, aromatic). A 0.0943 g. sample in 35 ml. 5:2 methanol-water required 3.90 (± 0.02) ml. of 0.0995 *N* sodium hydroxide (theory for a dibasic acid is 3.96 ml.). The pH at the half-neutralization point was 3.4.

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4\text{S}_6$: C, 37.63; H, 2.95; N, 5.85; S, 40.19. Found: C, 37.66; H, 2.96; N, 5.82; S, 40.05.

2-Isopropylimino-1,3-dithietane.

Isopropylammonium isopropylidithiocarbamate (19.4 g., 0.10 mole) in 65 ml. of DMF was added over 90 minutes with cooling (reaction at 30-33°) to a mixture of 14.0 ml. (0.10 mole) of triethylamine and 21 ml. (0.30 mole) of methylene bromide in 100 ml. of DMF. After another hour, the mixture was poured into 300 ml. ice-water and the precipitated oil was partitioned into ether-benzene. After water washing, the organic phase was extracted with hydrochloric acid (10 ml. of concentrated hydrochloric acid/100 ml. water; 0.12 mole). The cooled aqueous extract was stirred with ether and made alkaline with sodium hydroxide (5.2 g., 0.13 mole/100 ml. water). The dried ether-phase was concentrated (Vigreux column) and distillation afforded 6.7 g. (46%) of 2-isopropylimino-1,3-dithietane collected in three fractions at 74-77°/2.5 mm. GLC (2 ft column, 2% GE XE-60 on Gas Chrom Z at 85°) showed three components. The product, of intermediate (70 sec) retention, represented ca. 95% of the total: $n_D^{25} = 1.5664$; ν max 1666 (C=N) cm^{-1} ; nmr (carbon tetrachloride) τ 6.12 (s, 2H, $-\text{S}-\text{CH}_2-\text{S}$), 6.8 (m, 1H, $-\overset{|}{\text{C}}-\text{H}$) and 8.88 (d, 6H, $-\text{CH}_3$, $J=6\text{Hz}$).

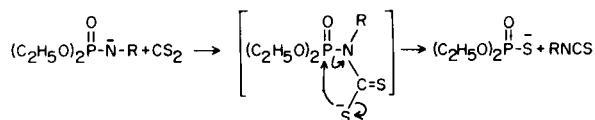
Anal. Calcd. for $\text{C}_5\text{H}_9\text{NS}_2$: C, 40.78; H, 6.16; N, 9.51; S, 43.55. Found: C, 41.03; H, 6.17; N, 9.60; S, 43.51.

A 0.7215 g. sample in ether was converted to 0.844 g. (94%) of the hydrochloride salt, m.p. 115.8-116.4°; ν max (mineral oil) 1610 (C=N) and 2300-2700 ($=\text{NHR}^+$) cm^{-1} . A 0.0993 g. sample of the salt in water (0.10 *M*) required 5.42 ml. of 0.1 *N* sodium hydroxide; neut. equiv.: calcd. 183.7; found 183.2. The pK_a

calculated from the 10%, 50%, and 90% neutralization points was 4.21, 4.25, and 4.25, respectively.

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- (6) In *Chemical Abstracts*, diethylphosphoryl isothiocyanate is ethyl phosphor(isothiocyanatidate) $[(C_2H_5O)_2(SCN)PO]$ and dimethylthiophosphoryl isothiocyanate is methyl phosphor(isothiocyanatido)thioate $[(CH_3O)_2(SCN)PS]$. By *Chemical Abstract* nomenclature, **5a** becomes cyclic methylene diethoxyphosphinylimidodithiocarbonate, and **7** becomes cyclic methylene dithioimidocarbonate hydrochloride.
- (7) The initial stage of degradation of **3** (Scheme 1) is analogous to that proposed for the reaction of phosphoramides and carbon disulfide under basic conditions, *i.e.*



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