in 80% yield from ethyl chloroformate and sodium 3-hydroxypropyl mercaptide following a previously described general procedure.[3]

Anal. Calcd. for $C_6H_{12}O_3S$: C, 43.9; H, 7.3. Found: C, 43.6; H, 7.4.

Thiolcarbonate X (60.6 g., 0.37 mole), which was only slowly decomposed at 224° in the presence of 0.1 g. of sodium carbonate, was smoothly pyrolyzed at 192–204°/13 mm. in the presence of one pellet of sodium hydroxide. The resulting distillate (25 g.) had a boiling point of 72–75° upon redistillation. Seventeen grams of this mixture, when placed in 40 ml. of methyl iodide and allowed to stand overnight at room temperature, gave 24.2 g. of the sulfonium iodide (XII) as white needles, with a m.p. 97–98° (lit.[11] m.p. 97–98°).

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Preparation of Dithiophosphinates from Secondary Phosphines and Sulfur under Alkaline Conditions

M. M. RAUHUT, HELEN A. CURRIER, AND V. P. WYSTRACH

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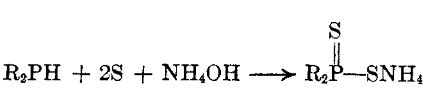
An improved synthesis for the preparation of dialkyldithiophosphinate salts is described. Dialkylphosphines react with sulfur in dilute aqueous ammonium hydroxide or sodium hydroxide to give dialkyldithiophosphinate salts in 25 to 91% yields. A number of new ammonium and nickel dithiophosphinates are reported. Dicyclohexylphosphine sulfide was isolated as an intermediate in the reaction of dicyclohexylphosphine with sulfur.

Although the reaction of sulfur with dialkylphosphines has been known for ninety years,[1] the processes involved are not well understood. The initial product obtained from diethylphosphine in ether solution has been reported to be a polysulfide, $R_2\overset{S}{\overset{\|}{P}}SS\overset{S}{\overset{\|}{P}}R_2$,[2] or a dithiophosphinic anhydride, $R_2\overset{S}{\overset{\|}{P}}—S—\overset{S}{\overset{\|}{P}}R_2$,[3] which on treatment with ammonium sulfide gives the ammonium dithiophosphinate, $R_2\overset{S}{\overset{\|}{P}}SNH_4$. The over-all yields reported for the dithiophosphinates have been low.[3,4]

We have found that the preparation of dithiophosphinate salts is simplified, and that the yields are considerably improved by treating a secondary phosphine with two equivalents of sulfur in dilute ammonium hydroxide solution.

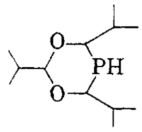


$$R_2PH + 2S + NH_4OH \longrightarrow R_2\overset{S}{\overset{\|}{P}}—SNH_4$$

The ammonium salts were obtained by evaporation of the reaction mixture or, less effectively, by extraction with ether. The results are shown in Table I. The ammonium salts of di-*n*-octyldithiophosphinic acid and di-*n*-dodecyldithiophosphinic acid were difficult to crystallize, and products from these reactions were characterized directly as the nickel salts.

TABLE I

$$R_2PH + 2\,S + NH_4OH \longrightarrow R_2\overset{S}{\overset{\|}{P}}SNH_4 + H_2O$$

R	Temp.	Time, Min.	Yield, %
n-C_4H_9	25–27	100	91[a]
n-C_8H_{17}	45–50	45	25[b]
n-$C_{12}H_{25}$	60	20	68[b]
C_6H_{11}	60	60	90[c]
$C_6H_5CH_2CH_2$	25–30	180	55[d]
	85	60	85[a]

[a] Ammonium salt. [b] Product isolated as the nickel salt. [c] Product isolated as the free acid. [d] A 26% yield of the ammonium salt was isolated directly. An additional 29% yield was obtained as the nickel salt.

Dicyclohexyldithiophosphinic acid and 2,4,6-triisopropyl-1,3-dioxa-5-phosphacyclohexane-5-dithioic acid were conveniently obtained as solids by acidifying solutions of the ammonium salts. The other dithiophosphinic acids, however, separated as oils which did not crystallize.

The sodium salt of 2,4,6-triisopropyl-1,3-dioxa-5-phosphacyclohexane-5-dithioic acid was prepared by the reaction of 2,4,6-triisopropyl-1,3-dioxa-5-phosphacyclohexane[5] with two equivalents of sulfur in dilute sodium hydroxide solution. The yield, however, was only 46% compared to the 85% yield of the ammonium salt obtained from the reaction in ammonium hydroxide solution.

In the reaction of dicyclohexylphosphine with sulfur, a dense white solid separated soon after the start of the reaction. This solid was evidently

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(1) A. W. Hofmann, *Ber.*, **4**, 430 (1871).

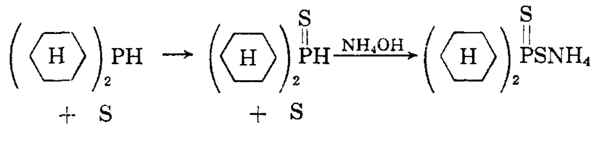
(2) A. W. Hofmann and F. Mahla, *Ber.*, **25**, 2436 (1892).

(3) L. Malatesta, *Gazz. Chim. Ital.*, **77**, 518 (1947).

(4) L. Malatesta, *Gazz. Chim. Ital.*, **77**, 509 (1947).

(5) S. A. Buckler and V. P. Wystrach, *J. Am. Chem. Soc.*, **80**, 6454 (1958).

an intermediate, as on further heating it dissolved, and the clear solution when acidified gave dicyclohexyldithiophosphinic acid in 90% yield. In a separate experiment, the intermediate solid was collected and was shown to be dicyclohexylphosphine sulfide[6] by analysis, molecular weight determination, and infrared and NMR (phosphorus) spectra.



EXPERIMENTAL[7]

Materials. The dialkyl phosphines were obtained from the reaction of phosphine with the corresponding olefins in the presence of α,α-azobisisobutyronitrile.[8]

2,4,6-Triisopropyl-1,3-dioxa-5-phosphacyclohexane was prepared by the reaction of phosphine with isobutyraldehyde in concentrated aqueous hydrochloric acid.[5]

Reactions of secondary phosphines with sulfur in dilute ammonium hydroxide solution. The reactions shown in Table I were carried out under nitrogen by adding the secondary phosphine dropwise during 10 min. to a stirred mixture of sulfur and 14% aqueous ammonium hydroxide solution as described below. The reaction mixtures were then stirred at the desired temperature as indicated in Table I. Reactions of dibutylphosphine and bis(2-phenylethyl)phosphine were exothermic and required initial cooling.

Ammonium and nickel di-n-butyldithiophosphinates. The filtered reaction mixture from 14.6 g. (0.1 mole) of di-*n*-butylphosphine, 7.0 g. (0.22 g.-atom) of sulfur, and 100 ml. of 14% aqueous ammonium hydroxide solution was divided into two equal portions.

The first portion was evaporated to dryness to obtain 10.3 g. (91%) of the ammonium dithiophosphinate, m.p. 82–88°. Two recrystallizations from benzene gave 8.4 g. of analytically pure product, m.p. 97–99°

Anal. Calcd. for $C_8H_{22}NPS_2$: P, 13.62; S, 28.20. Found: P, 13.50; S, 28.20.

The second portion was extracted with three 50-ml. portions of ether. Evaporation of the combined extracts gave a white crystalline solid. Recrystallization from benzene gave 5.1 g. (45%) of the ammonium salt, m.p. 94–97°. The aqueous residue from the extraction was combined with a solution of 6.0 g. of nickel chloride hexahydrate in 20 ml. of water and the resulting solution was extracted with three 50-ml. portions of ether. The dark blue extract was dried with anhydrous sodium sulfate and evaporated under vacuum to obtain 2.5 g. (21%) of the violet nickel salt, m.p. 83–86°. Recrystallization from methanol gave an analytical sample, m.p. 89–90°.

Anal. Calcd. for $C_8H_{18}PS_2Ni_{1/2}$: C, 40.26; H, 7.20. Found: C, 40.10; H, 7.33.

Nickel di-n-octyldithiophosphinate. The viscous reaction mixture from 10.0 g. (0.040 mole) of di-*n*-octylphosphine, 2.8 g. (0.088 g.-atom) of sulfur, and 100 ml. of 14% ammonium hydroxide was combined with a solution of 10.0 g. of nickel chloride hexahydrate in 550 ml. of water.

The resulting deep violet solution was extracted with three 100-ml. portions of ether. The extract was dried with anhydrous sodium sulfate, and the ether was removed under vacuum. The residual oil was dissolved in 85 ml. of warm butyl alcohol, and the solution was treated with 125 ml. of methanol. The nickel dithiophosphinate 6.9 g. (25%), m.p. 45–48° crystallized after standing overnight at 0°. Recrystallization from a benzene-methanol mixture gave an analytical sample, m.p. 49–51°.

Anal. Calcd. for $C_{16}H_{34}PS_2Ni_{1/2}$: P, 8.83; S, 18.28. Found: P, 8.79; S, 18.46.

Nickel di-n-dodecyldithiophosphinate. The filtered reaction mixture from 2.0 g. (0.005 mole) of di-*n*-dodecylphosphine, 0.39 g. (0.012 g.-atom) of sulfur, 20 ml. of 14% ammonium hydroxide, and 20 ml. of methanol was evaporated under reduced pressure to obtain a waxy solid. A solution of the solid in 20 ml. of water and 3 ml. of methanol, was combined with a solution of 1.0 g. of nickel chloride hexahydrate in 10 ml. of water. Extraction with three 35-ml. portions of ether and evaporation of the extract gave 1.7 g. (68%) of the nickel salt, m.p. 72–74°. Recrystallization from benzene-methanol gave 1.6 g., m.p. 72–73°.

Anal. Calcd. for $C_{24}H_{50}PS_2Ni_{1/2}$: C, 62.24; H, 10.88; P, 6.69. Found: C, 62.01; H, 10.53; P, 6.69.

Dicyclohexyldithiophosphinic acid. The filtered reaction mixture from 9.9 g. (0.05 mole) of dicyclohexylphosphine, 3.5 g. (0.11 g.-atom) of sulfur, 60 ml. of 14% ammonium hydroxide, and 20 ml. of 95% ethanol was acidified with concentrated hydrochloric acid, cooled to 5°, and filtered to obtain 11.9 g. (90%) of dicyclohexyldithiophosphinic acid, m.p. 97–100°. Recrystallization from petroleum ether (b.p. 30–60°) gave an analytical sample, m.p. 103–105°.

Anal. Calcd. for $C_{12}H_{23}PS_2$: P, 11.81; S, 24.44. Found: P, 11.87; S, 24.12.

Ammonium and nickel bis(2-phenylethyl)dithiophosphinates. The filtered reaction mixture from 9.5 g. (0.05 mole) of bis(2-phenylethyl)phosphine, 2.8 g. (0.088 g.-atom) of sulfur and 40 ml. of 14% ammonium hydroxide was evaporated to dryness under reduced pressure. The resulting gummy solid was recrystallized from a mixture of benzene and a little methanol to obtain 3.3 g. (26%) of the ammonium dithiophosphinate, m.p. 195–203°. Recrystallization from benzene-methanol followed by recrystallization from benzene–*n*-butyl alcohol gave a product melting at 201–203°

Anal. Calcd. for $C_{16}H_{22}NPS_2$: P, 9.58; S, 19.83. Found: P, 9.37; S, 19.98.

The filtrate from the first recrystallization was combined with a solution of 5.0 g. of nickel chloride hexahydrate in 25 ml. of water. Extraction with ether followed by evaporation of the extract gave 3.8 g. (29%) of the nickel dithiophosphinate, m.p. 141–145°. Recrystallization from a mixture of benzene and petroleum ether gave an analytical sample, m.p. 146–148°.

Anal. Calcd. for $C_{16}H_{18}PS_2Ni_{1/2}$: C, 57.40; H, 5.42; P, 9.25. Found: C, 57.82; H, 5.78; P, 9.10.

2,4,6-Triisopropyl-1,3-dioxa-5-phosphacyclohexane-5-dithioic acid. The warm reaction mixture from 235 g. (1.0 mole) of 2,4,6-triisopropyl-1,5-dioxa-5-phosphacyclohexane, 64 g. (2.0 g.-atom) of sulfur, and 700 ml. of 14% ammonium hydroxide was filtered and cooled to 0°. The ammonium dithiophosphinate, 265 g. (85%), crystallized on standing. Two recrystallizations from a benzene-acetone mixture gave an analytical sample, melting about 185° dec.

Anal. Calcd. for $C_{12}H_{28}NO_2PS_2$: C, 45.98; H, 9.00; P, 9.88. Found: C, 46.21; H, 8.99; P, 9.78.

A solution of 50.0 g. (0.16 mole) of the ammonium dithiophosphinate in 600 ml. of water was acidified with 10% hydrochloric acid solution. The solution was cooled and filtered to obtain 43.5 g. (92%) of the free dithiophosphinic acid, m.p. 49–52°.

Anal. Calcd. for $C_{12}H_{25}O_2PS_2$: P, 10.45; S, 21.63. Found: P, 10.56; S, 21.48.

Sodium salt of 2,4,6-triisopropyl-1,3-dioxa-5-phosphacyclohexane-5-dithioic acid. A stirred mixture of 23.5 g. (0.1 mole) of the phosphine, 6.4 g. (0.2 g.-atom) of sulfur, 4.0 g. (0.1 mole) of sodium hydroxide, and 70 ml. of water was heated at 75°, for 1 hr. The reaction mixture was filtered and

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(6) Isolation of other secondary phosphine sulfides has recently been reported. Grace A. Peters, *J. Am. Chem. Soc.*, 82, 4751 (1960).

(7) Melting points are uncorrected.

(8) M. Rauhut, Helen A. Currier, A. M. Semsel, and V. P. Wystrach, *J. Org. Chem.*, 26, 5138 (1961).

evaporated to dryness. The crystalline residue was extracted with acetone, and the extract was evaporated to dryness. Recrystallization of the residue from a mixture of benzene and acetone gave 14.9 g. (46%) of the sodium salt, m.p. 283–285° dec. A second recrystallization provided an analytical sample, m.p. 286–287° dec.

Anal. Calcd. for $C_{12}H_{24}O_2PS_2Na$: P, 9.72; S, 20.14. Found: P, 9.65; S, 19.97.

Dicyclohexylphosphine sulfide. A mixture of 9.9 g. (0.05 mole) of dicyclohexylphosphine, 3.5 g. (0.11 g.-atom) of sulfur, and 60 ml. of 14% ammonium hydroxide was heated at 50–55° with stirring for 1 hr. A dense white solid separated and was collected. The solid was dissolved in 50 ml. of acetone and the solution was filtered from unchanged sulfur. The filtrate was poured into 400 ml. of water to obtain 7.0 g. (61%) of crude dicyclohexylphosphine sulfide, m.p. 84–100°. Two recrystallizations from 2B ethanol gave an analytical sample, m.p. 107–108°.

Anal. Calcd. for $C_{12}H_{23}PS$: C, 62.83; H, 9.67; P, 13.50; S, 13.98; mol. wt., 229.5. Found: C, 62.79; H, 9.69; P, 13.77; S, 13.92; mol. wt., 215 (Boiling point rise in acetone).

The NMR phosphorus spectrum of the sulfide showed a 1–1 doublet (−61 p.p.m. and −33 p.p.m. referred to 85% phosphoric acid), and the infrared spectrum showed a weak P—H absorption band at 2300 cm.$^{-1}$

The filtrate from the reaction mixture was acidified to obtain 4.9 g. (37%) of dicyclohexyldithiophosphinic acid, m.p. 99–101°.

Acknowledgment. The authors are indebted to Mrs. E. C. Grim and Dr. J. A. Kuck for microanalyses, and to Dr. J. E. Lancaster for the NMR results.

STAMFORD, CONN.

[CONTRIBUTION FROM THE STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Anomalous Reaction of Bis(2-cyanoethyl)phosphine with Sulfur

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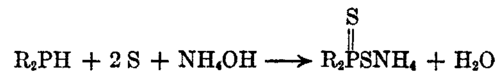
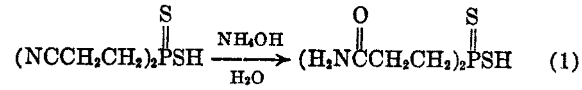
Bis(2-cyanoethyl)phosphine reacts with sulfur in dilute ammonium hydroxide solution to give the ammonium salt of bis(2-thiocarbamoylethyl)phosphinic acid instead of the expected bis(2-cyanoethyl)dithiophosphinic acid. Analogous reactions occur with cyclohexyl-2-cyanoethylphosphine and with bis(2-cyanoethyl)phosphine oxide. A mechanism involving a cyclic intermediate is proposed.

The reaction of dialkylphosphines with sulfur in dilute ammonium hydroxide has been found to be a good general method for the preparation of ammonium dialkyldithiophosphinates.[1]

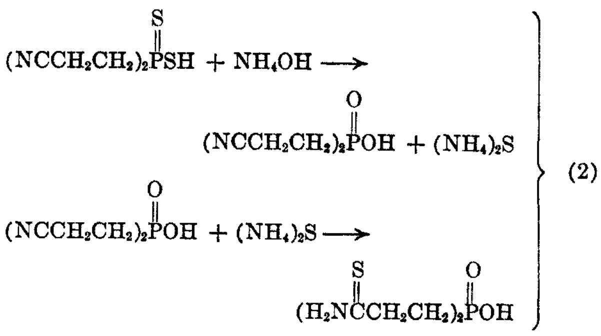


$$R_2PH + 2\,S + NH_4OH \longrightarrow R_2\overset{\overset{\displaystyle S}{\|}}{P}SNH_4 + H_2O$$

Application of this method to the reaction of bis(2-cyanoethyl)phosphine with sulfur, followed by acidification, would be expected to give bis(2-cyanoethyl)dithiophosphinic acid. When the reaction was carried out, however, an unexpected result was obtained. Although the product was, indeed, a white, water-insoluble, crystalline acid, elemental analysis indicated that the elements of two molecules of water had been incorporated into the expected structure. Moreover, the infrared spectrum of the compound lacked the characteristic nitrile group absorption band at 2260 cm.$^{-1}$ and contained bands at 1630, 3140, and 3310 cm.$^{-1}$, which were suggestive but not definitively characteristic of a carboxylic amide. While hydration of the nitrile groups was indicated, hydration would not normally be expected to occur under the mild conditions employed. Moreover, neither bis(2-cyanoethyl)phosphine nor bis(2-cyanoethyl)phosphinic acid were found to be attacked by dilute ammonium hydroxide, or by dilute ammonium sulfide under the conditions used. The latter results demonstrated that reaction did not take place according to either of the straightforward paths indicated by equations (1) or (2).



$$(NCCH_2CH_2)_2\overset{\overset{\displaystyle S}{\|}}{P}SH \xrightarrow[H_2O]{NH_4OH} (H_2N\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2)_2\overset{\overset{\displaystyle S}{\|}}{P}SH \qquad (1)$$



$$\left.\begin{aligned}&(NCCH_2CH_2)_2\overset{\overset{\displaystyle S}{\|}}{P}SH + NH_4OH \longrightarrow \\ &\qquad (NCCH_2CH_2)_2\overset{\overset{\displaystyle O}{\|}}{P}OH + (NH_4)_2S \\ &(NCCH_2CH_2)_2\overset{\overset{\displaystyle O}{\|}}{P}OH + (NH_4)_2S \longrightarrow \\ &\qquad (H_2N\overset{\overset{\displaystyle S}{\|}}{C}CH_2CH_2)_2\overset{\overset{\displaystyle O}{\|}}{P}OH\end{aligned}\right\} \quad (2)$$

With these possibilities eliminated, two alternative mechanisms involving a cyclic intermediate appeared to be likely possibilities.

---

[1] M. M. Rauhut, H. A. Currier, and V. P. Wystrach, *J. Org. Chem.*, 26, 5133 (1961.)