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 $C_{12}H_{22}PS$: 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.]

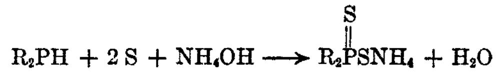
Anomalous Reaction of Bis(2-cyanoethyl)phosphine with Sulfur

M. M. RAUHUT, HELEN A. CURRIER, GRACE A. PETERS,
F. C. SCHAEFER, AND V. P. WYSTRACH

Received May 4, 1961

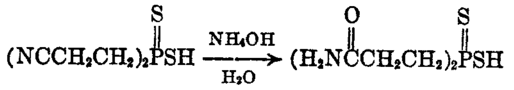
Bis(2-cyanoethyl)phosphine reacts with sulfur in dilute ammonium hydroxide solution to give the ammonium salt of bis(2-thiocarbamoylethyl)phosphinic acid instead of the expected bis(2-cyanoethyl)dithiophosphinic acid. Analogous reactions occur with cyclohexyl-2-cyanoethylphosphine and with bis(2-cyanoethyl)phosphine 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]

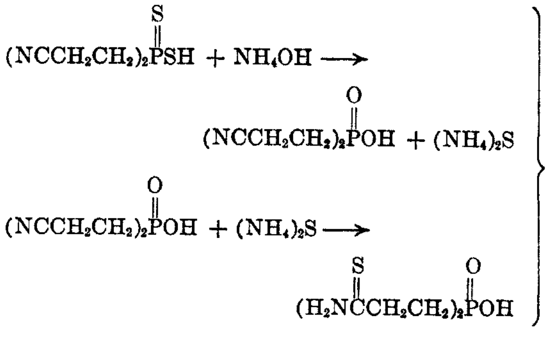


$$R_2PH + 2\,S + NH_4OH \longrightarrow R_2\overset{\overset{S}{\|}}{P}SNH_4 + H_2O$$

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).



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



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

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

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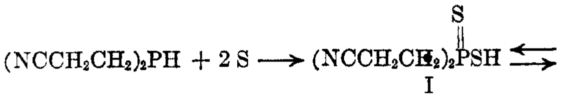
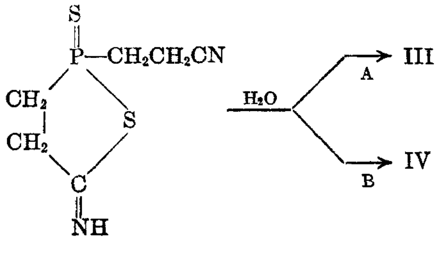
[1] M. M. Rauhut, H. A. Currier, and V. P. Wystrach, *J. Org. Chem.*, 26, 5133 (1961.)

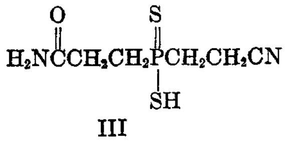


$$(NCCH_2CH_2)_2PH + 2\,S \longrightarrow (NCCH_2CH_2)_2\overset{S}{\overset{\|}{P}}SH \rightleftarrows$$

I

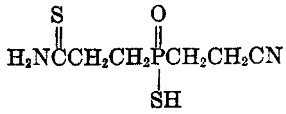


II



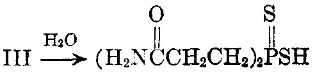
$$H_2N\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{S}{\overset{\|}{\underset{\underset{SH}{|}}{P}}}CH_2CH_2CN$$

III



$$H_2N\overset{S}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{\underset{\underset{SH}{|}}{P}}}CH_2CH_2CN$$

IV



$$III \xrightarrow{H_2O} (H_2N\overset{O}{\overset{\|}{C}}CH_2CH_2)_2\overset{S}{\overset{\|}{P}}SH$$

VI

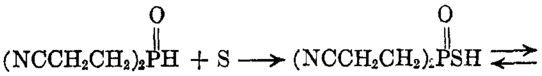
$$IV \xrightarrow{H_2O} (H_2N\overset{S}{\overset{\|}{C}}CH_2CH_2)_2\overset{O}{\overset{\|}{P}}OH$$

VII

In view of the rapid reaction of secondary phosphines with sulfur,[1] it seemed reasonable that the expected dithiophosphinic acid I (in equilibrium with its ammonium salt) was indeed formed initially but rapidly equilibrated with the cyclic intermediate II through intramolecular addition of sulfhydryl to the cyano group.

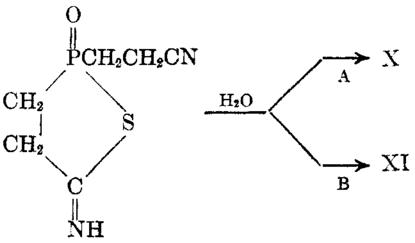
Intermediate II, which is a cyclic anhydride, might then be attacked by hydroxide either at the imide carbon atom yielding III or at the phosphorus atom yielding IV. Both III and IV contain the 2-cyanoethylthiophosphinic acid structure present in I, and a repetition of the cyclization-hydrolysis sequence would yield either the dicarbamoyldithiophosphinic acid VI or the dithiocarbamoylphosphinic acid VII.

In order to test this mechanism and, at the same time, determine, if possible, which of the alternative hydrolysis paths was followed, the reaction of bis(2-cyanoethyl)phosphine oxide with sulfur was investigated. The alternative paths for this reaction according to the cyclization-hydrolysis mechanism are shown below:

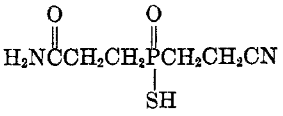


$$(NCCH_2CH_2)_2\overset{O}{\overset{\|}{P}}H + S \longrightarrow (NCCH_2CH_2)_2\overset{O}{\overset{\|}{P}}SH \rightleftarrows$$

VIII

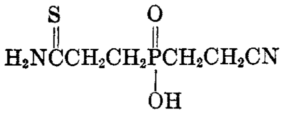


IX



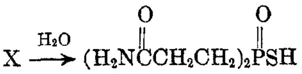
$$H_2N\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{\underset{\underset{SH}{|}}{P}}}CH_2CH_2CN$$

X



$$H_2N\overset{S}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{\underset{\underset{OH}{|}}{P}}}CH_2CH_2CN$$

XI



$$X \xrightarrow{H_2O} (H_2N\overset{O}{\overset{\|}{C}}CH_2CH_2)_2\overset{O}{\overset{\|}{P}}SH$$

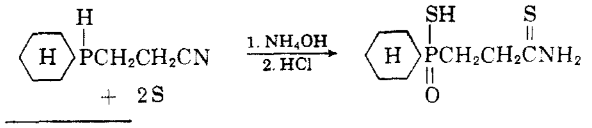
XII

Cyclization of VIII, which contains the 2-cyanoethylthiophosphinic acid structure present in IV, would give the anhydride IX. Reaction with water would then give the thiophosphinic acid X or the phosphinic acid XI. Intermediate X, however, would be expected to repeat the cyclization-hydrolysis sequence to form the diamide XII, while XI, since it does not contain the active sulfhydryl group, should not undergo further reaction.

The product from the reaction was a white, crystalline acid. Its analysis and infrared spectrum were in complete accord with 2-cyanoethyl-2-thiocarbamoylethylphosphinic acid, XI, but not with bis(2-carbamoylethyl)thiophosphinic acid, XII. This result clearly indicated that reaction was taking place by mechanism B, and that the product obtained from the reaction of bis(2-cyanoethyl)phosphine with sulfur was bis(2-thiocarbamoylethyl)phosphinic acid, VII. The phosphinic acid VII was, therefore, prepared unambiguously by the reaction of bis(2-cyanoethyl)phosphinic acid and hydrogen sulfide in the presence of triethylamine and pyridine.[2]

The infrared spectrum of the authentic phosphinic acid, VII, was identical to the spectrum of the product obtained from bis(2-cyanoethyl)phosphine and sulfur, and a mixed melting point was not depressed.

Intramolecular attack leading to thioamide seems to be general for compounds containing a 2-cyanoethyl group and a sulfhydryl group bonded to phosphorus. Cyclohexyl-2-cyanoethylphosphine reacted with sulfur to give cyclohexyl-2-thiocarbamoylethylthiophosphinic acid in 75% yield.



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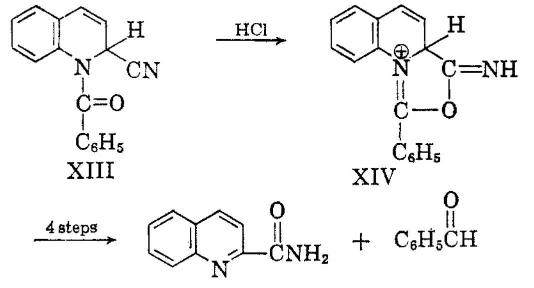
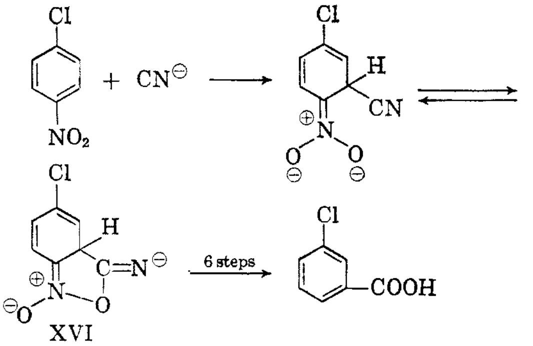
(2) *Cf.* A. E. Fairfield, J. L. Lowe, and D. A. Peak, *J. Chem. Soc.*, 742 (1952).

In this case, only one cyclization-hydrolysis sequence is possible, and the product still contains one sulfur atom bonded to phosphorus.

Mechanisms involving cyclic intermediates have been used in the past to account for unusually facile reactions of cyano groups. Cobb and McEwen[3] have proposed the occurrence of intermediate XIV in the conversion of the Reissert compound XIII to quinoldamide and benzaldehyde to account for experimental evidence that quinaldonitrile is not an intermediate, and Bunnett and Rauhut[4] proposed intermediate XVI to account for the conversion of *p*-chloronitrobenzene to *m*-chlorobenzoic acid in the von Richter reaction, where they showed that *m*-chlorobenzonitrile is not an intermediate.

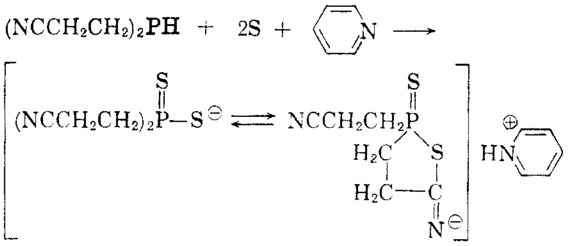




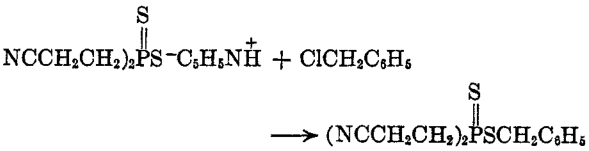
In the present example, cyclic intermediate II seems necessary to explain the formation of a thiocarbamoyl group in a reaction where sulfur attacks initially at phosphorus, as well as to account for the unexpected ease with which the cyano group reacts.

An effort was made to prepare bis(2-cyanoethyl)-dithiophosphinic acid under anhydrous conditions. Bis(2-cyanoethyl)phosphine reacted with sulfur in anhydrous pyridine to give pyridinium bis(2-cyanoethyl)dithiophosphinate in 95% yield.

However, attempts to convert the pyridinium salt to the free acid under anhydrous conditions gave oils which were instantly hydrolyzed to bis(2-thiocarbamoylethyl)phosphinic acid on exposure to the atmosphere. The pyridinium salt, itself, was rapidly hydrolyzed by moist air.

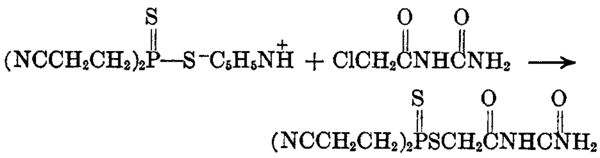


Reaction of pyridinium bis(2-cyanoethyl)dithiophosphinate with benzyl chloride proceeded without rearrangement to give benzyl bis(2-cyanoethyl)-dithiophosphinate in 100% yield.



$$(NCCH_2CH_2)_2\overset{S}{\overset{\|}{P}}S^{-}C_5H_5\overset{+}{N}H + ClCH_2C_6H_5 \longrightarrow (NCCH_2CH_2)_2\overset{S}{\overset{\|}{P}}SCH_2C_6H_5$$

Similarly, reaction with chloroacetylurea gave ureidocarbonylmethyl bis(2-cyanoethyl)dithiophosphinate in 79% yield.



$$(NCCH_2CH_2)_2\overset{S}{\overset{\|}{P}}{-}S^{-}C_5H_5\overset{+}{N}H + ClCH_2\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}NH_2 \longrightarrow (NCCH_2CH_2)_2\overset{S}{\overset{\|}{P}}SCH_2\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}NH_2$$

EXPERIMENTAL[5]

Materials. Bis(2-cyanoethyl)phosphine was prepared by the base-catalyzed reaction of phosphine with acrylonitrile.[6] Bis(2-cyanoethyl)phosphine oxide was prepared by the air oxidation of bis(2-cyanoethyl)phosphine.[7] Cyclohexyl-2-cyanoethylphosphine was prepared by the reaction of 2-cyanoethylphosphine with cyclohexene in the presence of α,α-azobisisobutyronitrile.[8]

Bis(2-cyanoethyl)phosphinic acid. A solution of 35 g. (0.35 mole) of 34% aqueous hydrogen peroxide in 40 ml. of glacial acetic acid was added dropwise with stirring during 30 min. to a solution of 24.9 g. (0.18 mole) of bis(2-cyanoethyl)-phosphine in 100 ml. of glacial acetic acid. The reaction was exothermic, and the temperature was held at 85–90° by cooling. The reaction mixture was concentrated under reduced pressure, and the crystalline residue was recrystallized from 200 ml. of 2-B ethanol to obtain 14.7 g. (48%) of the phosphinic acid, m.p. 124–125°.

Anal. Calcd. for $C_6H_9N_2O_2P$: N, 16.28; P, 18.00. Found: N, 16.50; P, 18.17.

Bis(2-thiocarbamoylethyl)phosphinic acid from bis(2-cyanoethyl)phosphine and sulfur. A mixture of 5.0 g. (0.036 mole) of bis(2-cyanoethyl)phosphine, 2.5 g. (0.078 g.-atom) of sulfur, 10 ml. of concd. ammonium hydroxide solution and 10 ml. of water was warmed on the steam bath under a nitrogen atmosphere for 1 hr. The reaction mixture was cooled to room temperature, freed from excess sulfur by filtration, and acidified. The solution after standing for 3 hr. at 0° deposited 6.3 g. (73%) of the phosphinic acid

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(3) R. L. Cobb and W. E. McEwen, *J. Am. Chem. Soc.*, **77**, 5042 (1955).

(4) J. F. Bunnett and M. M. Rauhut, *J. Org. Chem.*, **21**, 944 (1956).

(5) Melting points are uncorrected.

(6) M. M. Rauhut, I. Hechenbleikner, Helen A. Currier, F. C. Schaefer, and V. P. Wystrach, *J. Am. Chem. Soc.*, **81**, 1103 (1959).

(7) M. M. Rauhut and Helen A. Currier, *J. Org. Chem.*, **26**, 4626 (1961).

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

m.p. 178–179° dec. The acid was insoluble in hot benzene, methanol, acetone, ethyl acetate, and dimethylformamide, but could be recrystallized from hot water or glacial acetic acid to give white plates melting at 179° dec. It was soluble in dilute alkali and appreciably soluble in 10% hydrochloric acid.

Anal. Calcd. for $C_6H_{13}N_2O_2PS_2$: C, 29.99; H, 5.45; N, 11.66; P, 12.89. Found: C, 30.03; H, 5.57; N, 11.40; P, 12.76.

Bis(2-thiocarbamoylethyl)phosphinic acid from bis(2-cyanoethyl)phosphinic acid and hydrogen sulfide. A solution of 5.16 g. (0.03 mole) of bis(2-cyanoethyl)phosphinic acid in 9.1 g. (0.09 mole) of triethylamine and 15 ml. of pyridine[2] was shaken for a short time in a conventional Parr low-pressure hydrogenation system charged to 2.2 atm. with dry hydrogen sulfide and then allowed to stand for about 60 hr. The dark green reaction mixture was poured into 50 ml. of water, and the solution was treated with 20 ml. of 10% sodium hydroxide solution. The solution was extracted five times with 25-ml. portions of chloroform. The extracts were discarded, and the pale green aqueous solution was filtered and acidified. After standing for several hours, the solution deposited 5.2 g. (72%) of white plates, m.p. 178–179° dec. A mixed melting point with the product obtained from bis(2-cyanoethyl)phosphine and sulfur was not depressed, and the infrared spectra of the two products were identical.

2-Cyanoethyl-2-thiocarbamoylethylphosphinic acid. A mixture of 10.0 g. (0.064 mole) of bis(2-cyanoethyl)phosphine oxide, 2.0 g. (0.063 g.-atom) of sulfur, and 30 ml. of moist isopropyl alcohol was refluxed under a nitrogen atmosphere for 1.5 hr. White crystals (6.0 g., 50%) separated on cooling. Recrystallization from a mixture of acetone and isopropyl alcohol gave an analytically pure sample, m.p. 142°.

Anal. Calcd. for $C_6H_{11}N_2O_2PS$: C, 34.94; H, 5.38; N, 13.58; P, 15.02. Found: C, 35.09; H, 5.52; N, 13.93; P, 15.31.

Cyclohexyl-2-thiocarbamoylethylthiophosphinic acid. Cyclohexyl-2-cyanoethylphosphine (5.1 g., 0.03 mole) was added gradually to a stirred mixture of 2.5 g. (0.078 g.-atom) of sulfur, 30 ml. of concd. aqueous ammonium hydroxide, and 50 ml. of water, under nitrogen. The mixture became warm and most of the sulfur dissolved. The reaction mixture was stirred for two additional hours at room temperature. The excess sulfur was filtered, and the filtrate was acidified with dilute hydrochloric acid. After cooling at −10° overnight, the white crystalline thiophosphinic acid separated. Two recrystallizations from a benzene-methanol mixture provided 5.7 g. (75%) of an analytically pure sample, m.p. 115–116° dec.

Anal. Calcd. for $C_9H_{18}NOPS_2$: C, 43.01; H, 7.22; P, 12.32. Found: C, 43.22; H, 7.12; P, 12.23.

Pyridinium bis(2-cyanoethyl)dithiophosphinate. A slurry of 10.8 g. (0.336 g.-atom) of sulfur in 75 ml. of pyridine was treated with 23.6 g. (0.168 mole) of bis(2-cyanoethyl)-phosphine added dropwise so as to maintain a temperature below 60°. A clear yellow solution was obtained which deposited 45 g. (95%) of product on cooling.

Recrystallization from benzene containing a little pyridine provided an analytically pure sample, m.p. 95–96°.

Anal. Calcd. for $C_{11}H_{14}N_3PS_2$: N, 14.83; P, 10.93; S, 22.63. Found: N, 14.54; P, 10.90; S, 22.33.

Benzyl bis(2-cyanoethyl)dithiophosphinate. A mixture of 5.7 g. (0.02 mole) of pyridinium bis(2-cyanoethyl)dithiophosphinate, 2.6 g. (0.02 mole) of benzyl chloride, and 25 ml. of acetone was refluxed under nitrogen for 3 hr. The reaction mixture was cooled and poured into 75 ml. of cold water. An oil separated which crystallized on standing. The solid was collected to obtain 5.9 g. (100%) of the benzyl ester, m.p. 75–79°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 30–60°) provided an analytical sample, m.p. 80–82°.

Anal. Calcd. for $C_{13}H_{15}N_2PS_2$: P, 10.52; N, 9.51; S, 21.78. Found: P, 10.62; N, 9.76; S, 22.27.

The properties and infrared spectrum of the product were in complete accord with the assigned structure.

Ureidocarbonylmethyl bis(2-cyanoethyl)dithiophosphinate. A mixture of 2.72 g. (0.02 mole) of chloroacetylurea, 5.66 g. (0.02 mole) of pyridinium bis(2-cyanoethyl)dithiophosphinate, and 25 ml. of acetone was refluxed under nitrogen for 3 hr. The reaction mixture was poured into 75 ml. of water to obtain 4.8 g. (79%) of the ester, m.p. 131–133°. Recrystallization from water gave needles, m.p. 132–134°.

Anal. Calcd. for $C_9H_{13}N_4O_2PS_2$: N, 18.41; P, 10.18; S, 21.07. Found: N, 17.92; P, 10.23; S, 20.88.

Acknowledgment. The authors are indebted to Mrs. E. C. Grim and Dr. J. A. Kuck for microanalyses and to N. B. Colthup for assistance in interpreting infrared spectra.

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[CONTRIBUTION FROM THE STAMFORD LABORATORIES, CHEMICAL RESEARCH DEPARTMENT, AMERICAN CYANAMID CO.]

The Free Radical Addition of Phosphines to Unsaturated Compounds

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

Received May 4, 1961

The free radical–initiated addition of phosphine and several primary and secondary phosphines to carbon-carbon double bonds was investigated with the aim of improving reaction conditions and expanding the reaction scope. The reaction was found to be an excellent synthetic method for the preparation of primary and tertiary organophosphines and certain secondary phosphines. The addition of phosphines to acetylenic compounds was studied briefly.

Phosphine adds to olefinic double bonds under the influence of strong, nonoxidizing acids,[1] strong bases,[2] or free radical initiation[3] to give organophosphines. Of these three methods, the latter approach appeared most promising as a general synthetic method. Stiles, Rust, and Vaughan,[3] using ultraviolet light or di-*t*-butyl peroxide, found that with six olefinic compounds, primary, second-

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(1) M. C. Hoff and P. Hill, *J. Org. Chem.*, 24, 356 (1959); H. C. Brown, U. S. Patent 2,584,112 (Feb. 5, 1952).

(2) M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer, and V. P. Wystrach, *J. Am. Chem. Soc.*, 81, 1103 (1959).

(3) A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **74**, 3282 (1952); U. S. Patent **2,803,597** (Aug. 20, 1959).