mechanism with 1-bromoadamantane through the corresponding unsaturated compound with a double bond at the bridgehead (in violation of Bredt's rule) have been unsuccessful. The only reaction so far observed has been halogen–metal exchange.

CONTRIBUTION NO. 2605 LAWRENCE K. MONTGOMERY
GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA JOHN D. ROBERTS

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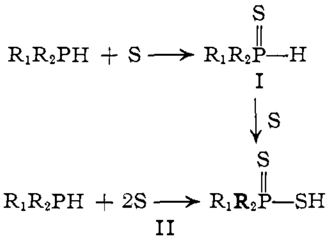
SECONDARY PHOSPHINE SULFIDES

Sir:

We wish to report the preparation of a new class of compounds, secondary phosphine sulfides $R_1R_2P(S)H$ (I), by the oxidation of secondary phosphines with elemental sulfur. Oxidation of secondary phosphines to the corresponding dithiophosphinic acids (II) has long been known,[1] but the addition of only one atom of sulfur to secondary phosphines has not been accomplished previously.



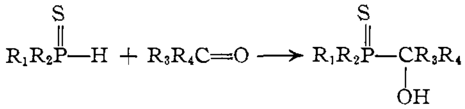
$$R_1R_2PH + S \longrightarrow R_1R_2\overset{\overset{\displaystyle S}{\|}}{P}-H \quad \text{I} \quad \Big\downarrow S$$

$$R_1R_2PH + 2S \longrightarrow R_1R_2\overset{\overset{\displaystyle S}{\|}}{P}-SH \quad \text{II}$$

Successful control of the process is effected by the addition under nitrogen of one equivalent of sulfur to a solution of a secondary phosphine in an inert solvent, such as benzene or carbon tetrachloride. Disappearance of the sulfur signals completion of the reaction, whereupon the product is obtained in a fair state of purity by removing the solvent under reduced pressure. Further purification of liquid products by distillation is accompanied by decomposition which reduces the yield of purified material considerably. By this method there were obtained: di-*n*-butylphosphine sulfide (100% crude yield, 36% distilled, b.p. 122–125° (1.5 mm.); *anal.* Calcd. for $C_8H_{19}PS$: P, 17.38; S, 17.99. Found: P, 17.69; S, 18.00), di-isobutylphosphine sulfide (65% yield, m.p. 61–62° from ligroin; *anal.* Calcd. for $C_8H_{19}PS$: C, 53.89; H, 10.74; S, 17.99. Found: C, 53.89; H, 11.06; S, 18.29), cyclohexyl-2-cyanoethylphosphine sulfide (liquid, 56% yield; *anal.* Calcd. for $C_9H_{16}NPS$: P, 15.39; S, 15.93. Found: P, 15.42; S, 16.01), bis-(2-carbethoxyethyl)-phosphine sulfide (liquid, 82% yield; *anal.* Calcd. for $C_{10}H_{19}PO_4S$: C, 45.10; H, 7.19; P, 11.63. Found: C, 45.26; H, 7.19; P, 11.88), 2,4,6-triisopropyl-3,5-dioxa-1-phosphacyclohexane-1-sulfide (57% distilled yield, b.p. 107–112° (1.5 mm.), m.p. 37°; *anal.* Calcd. for $C_{12}H_{25}PO_2S$: C, 54.52; H, 9.53; P, 11.72; S, 12.13. Found C, 54.03; H, 9.48; P, 11.44; S, 11.78), and diphenylphosphine sulfide (100% yield, m.p. 95–97° from acetonitrile; *anal.* Calcd. for $C_{12}H_{11}PS$: C, 66.03; H, 5.08; P, 14.19; S, 14.69. Found: C, 65.93; H, 5.23; P, 14.47; S, 14.78).

Spectral analyses[2] indicate that secondary phosphine sulfides exist in the thiono, rather than the thiolo, form. A characteristic P–H absorption band of weak to medium intensity is exhibited in the infrared at 2320 ± 10 cm.$^{-1}$ (half intensity band width of 35 wave numbers) together with a P=S (CsBr disc) at 600 cm.$^{-1}$ (alkyl) or 640 cm.$^{-1}$ (aryl). Nuclear magnetic resonance spectra in the phosphorus region show a doublet centered near −22 p.p.m. (relative to 85% H_3PO_4) with an average splitting of 28 p.p.m. which is consistent with the proposed structure.

Secondary phosphine sulfides have been further characterized by base-catalyzed addition of aldehydes and ketones to form α-hydroxy-substituted tertiary phosphine sulfides (III). Typical examples



$$R_1R_2\overset{\overset{\displaystyle S}{\|}}{P}-H + R_3R_4C{=}O \longrightarrow R_1R_2\overset{\overset{\displaystyle S}{\|}}{P}-\underset{\underset{\displaystyle OH}{|}}{C}R_3R_4$$

III

are di-*n*-butyl-α-hydroxybenzylphosphine sulfide (75% yield; m.p. 54–55° from heptane; *anal.* Calcd. for $C_{15}H_{25}POS$: C, 63.35; H, 8.86; S, 11.27. Found: C, 63.56; H, 8.98; S, 11.49), bis-(2-cyanoethyl)-1-hydroxy-1-methylethylphosphine sulfide (70% yield; m.p. 113–115° from benzene; *anal.* Calcd. for $C_9H_{15}N_2OPS$: C, 46.94; H, 6.57; S, 13.93. Found: C, 46.92; H, 6.51; S, 13.88), and diphenyl-1-hydroxy-1-methylethylphosphine sulfide (75% yield, m.p. 118–120° from benzene; *anal.* Calcd. for $C_{15}H_{17}OPS$: C, 65.19; H, 6.20; S, 11.60. Found: C, 65.11; H, 6.99; S, 11.25).

In addition, secondary phosphine sulfides can be oxidized by elemental sulfur to the corresponding dithiophosphinic acids (II). Details of this reaction and the carbonyl addition will be presented in a broader study of the chemistry of the secondary phosphine sulfides.

[1] A. W. Hofmann and F. Mahla, *Ber.*, **25**, 2436 (1892); L. Malatesta and R. Pizzotti, *Gazz. Chim. Ital.*, **76**, 167 (1946).

[2] We are indebted to N. B. Colthup for the infrared spectral data, and to J. E. Lancaster for the n.m.r. results.

CHEMICAL RESEARCH DEPARTMENT
CENTRAL RESEARCH DIVISION GRACE PETERS
AMERICAN CYANAMID COMPANY
STAMFORD, CONNECTICUT

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ARYLSULFUR TRIFLUORIDES AND PENTAFLUORIDES

Sir:

We wish to report the first synthesis of arylsulfur pentafluorides and the first general syntheses of arylsulfur trifluorides.

Perfluoroalkylsulfur trifluorides and pentafluorides are known derivatives of sulfur tetrafluoride and hexafluoride, respectively, prepared in general, by oxidative fluorination reactions.[1] Although other sulfur hexafluoride derivatives such as S_2F_{10},[1b]

[1] (a) Lovelace, Rausch and Postelnek, "Aliphatic Fluorine Compounds," Chapter 13, Reinhold Publishing Corp., New York, N. Y., 1958; (b) Special Publication No. 12, "Chemical Society Symposia, Bristol, 1958," The Chemical Society, Burlington House, W. I., London, 1958, p. 317–327.