LITERATURE CITED

(1) Baybarz, R.D., Weaver, B., Oak Ridge National Laboratory, Oak Ridge, Tenn., **ORNL-3185**, 1961.
(2) Baybarz, R.D., Weaver, B., Kinser, H.B., *Trans. Am. Nucl. Soc.* **5**, No. 1, 17 (1962).
(3) Culler, F.L., Bresse, J.E., *et al.*, Chem. Tech. Div. Ann. Prog. Rept. **ORNL-3452**, May 1963.
(4) Culler, F.L., Ferguson, D.E., *et al.*, *Ibid.*, **ORNL-3314**, June 1962.
(5) "Isotopes and Radiation Technology," **1**, No. 2, 206 (Winter 1963–1964), Oak Ridge National Laboratory, Oak Ridge, Tenn.
(6) Leuze, R.E., Baybarz, R.D., Weaver, B., *Nucl. Sci. Eng.* **17**, 252–8 (1963).
(7) Moore, F.L., *Anal. Chem.* **33**, 748 (1961).

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Phosphines and Phosphine Sulfides Containing Highly Condensed Aromatic Groups

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The preparation and properties of four new phosphines and six new phosphine sulfides are reported. Preparation of the phosphines is accomplished by condensation of a phosphorus trihalide, or substituted halide with the aryllithium compound in an inert atmosphere. The sulfides are prepared by refluxing the phosphine with sulfur in an appropriate solvent. The phosphines and sulfides are colorless solids.

SEVERAL compounds of the type PR_3, PR_2R', PRR_2', and the corresponding sulfides, where *R* is a highly condensed aromatic group and *R′* is a phenyl group, have been prepared as part of an over-all program concerned with studies of the donor properties of group V chalcogenides. These compounds may represent a unique type of coordinating agent, especially in the solid state, since they may be able to act as donors either through the aromatic ring systems, or by way of the free electron pair on the phosphorus atom in the phosphine, or on the sulfur atom in the phosphine sulfide.

Relatively few tertiary phosphines and phosphine sulfides containing highly condensed aromatic groups have been previously reported. Mikhailov and Kucherova (*5*) reported the preparation of tri-1-naphthyl-, tri-9-phenanthryl-, tri-9-anthryl-, tri-1,2-benzanthr-10-yl-, and tri-1,2-benzanthr-7-ylphosphine. Hart and Mann (*3*) reported the preparation of di-1-naphthylphenylphosphine, and Anschutz, Kraft, and Schmidt (*1*) prepared tri-1-naphthylphosphine and several of its derivatives. Worrall (*7*) reported the preparation of tri-4-biphenylphosphine and its sulfide.

PREPARATION

Phosphines. All phosphines were prepared by the reaction of the appropriate phosphorus halide with the aryllithium compound. The aryllithium compounds were prepared by the halogen-lithium interconversion method described by Jones and Gilman (*4*). The aryl bromide, in ethyl ether, was added dropwise with stirring to *n*-butyllithium under a dry nitrogen atmosphere. The phosphine was then prepared by the addition of 80% of the theoretical amount of the appropriate phosphorus halide dissolved ethyl ether. The mixture was refluxed for 1 to 1½ hours, hydrolyzed with 10% aqueous sodium hydroxide, and the organic layer was then separated and dried over anhydrous magnesium sulfate. Evaporation of the organic solvent under reduced pressure led directly to precipitation of the phosphine. The following reactions are involved:

$$ArBr + n\text{-}BuLi \rightarrow ArLi + n\text{-}BuBr$$

$$3ArLi + PCl_3 \rightarrow Ar_3P + 3LiCl$$

Phosphine Sulfides. All of the phosphine sulfides were prepared by refluxing the phosphine with an equivalent amount of sulfur in *n*-hexanol or *n*-butanol for 2 to 3 hours. The hot solution was filtered to remove the excess unreacted sulfur, and the crystalline product separated upon cooling. Purification was accomplished by several recrystallizations from an appropriate solvent. The list of compounds prepared, along with pertinent physical data, is given in Table I.

DISCUSSION

The triarylphosphines reported here were quite stable in air. Although condensations were carried out in an oxygen-free atmosphere, once the phosphine was isolated, all recrystallizations were carried out in the laboratory atmosphere and no evidence of oxide formation was noted. The melting points of several of the phosphines were redetermined after the compounds had been stored in screw-capped bottles for 1 or 2 months, and no changes were observed.

The reported yields are not necessarily the highest attainable since no organized study was made for this purpose.

Tri-1-naphthylphosphine has been prepared on at least three previous occasions. Mikhailov and Kucherova (*5*) reported its preparation in 1952 by the reaction of 1-naphthyllithium with phosphorus trichloride. They observed a melting point of 278 to 80° for the compound. Anschutz, Kraft, and Schmidt (*1*) reported in 1939 the preparation of tri-1-naphthylphosphine by the reaction of 1-naphthylmagnesium bromide with phosphorus trichloride. After recrystallization from dioxane, they observed a melting point of 282°. Plets (*6*) in 1938 reported a melting point of 189° to 90° for tri-1-naphthylphosphine (recrystallized from benzene–ethyl ether).

Table I. Physical Data for Phosphines and Phosphine Sulfides

Compound	Analytical Data[a]		M.P., ° C.	Previously Reported M.P., ° C.	Yield, %	Recrystn. Solvent	P-S Frequencies of Phosphine Sulfide	
	Calcd.	Found					λ(μ)	$\bar{\nu}$(cm.$^{-1}$)
Tri-1-naphthylphosphine	C-87.35 H- 5.13 P- 7.51	87.05 5.19 7.65	263–5	278–80(5) 282 (1) 189–90(6)	20	Benzene–ethyl ether	. . . . . .	. . . . . .
Tri-1-naphthylphosphine sulfide	C-81.05 H- 4.76 P- 6.97	80.85 4.96 6.85	255.5–6.5	. . .	21	Ethanol, *n*-butanol, *n*-hexanol	15.85[b] 16.10	631 621
Di-1-naphthylphenylphosphine	C-86.17 H- 5.28	85.97 5.41	210–12	207.5–8.5(3)	36	*n*-Butanol	. . .	. . .
Di-1-naphthylphenylphosphine sulfide	C-79.16 H- 4.85 P- 7.85	78.89 5.07 7.69	250.5–2.0	. . .	50	*n*-Butanol	15.90[b] 16.30	635 613
Diphenyl-1-naphthylphosphine	C-84.59 H- 5.49	84.42 5.55	118–19	. . .	45	*n*-Butanol, ethanol	. . .	. . .
Diphenyl-1-naphthylphosphine sulfide	C-76.72 H- 4.98 P- 9.00	76.80 5.06 8.84	170–2	. . .	67	Ethanol	15.95[b] 16.45	627 608
Tri-4-methylnaphthylphosphine	C-87.20 H- 5.99 P- 6.82	87.21 6.09 6.71	285.5	. . .	24	*n*-Butanol	. . .	. . .
Tri-4-methylnaphthylphosphine sulfide	C-81.45 H- 5.59 S- 6.59	81.20 5.83 6.27	361–4[c]	. . .	52	*n*-Hexanol	16.68[b]	600
Di-4-methylnaphthyl-phenylphosphine	C-86.12 H- 5.94 P- 7.94	85.89 5.99 7.90	176–7	. . .	47	Ethanol	. . .	. . .
Di-4-methylnaphthyl-phenylphosphine sulfide	C-79.59 H- 5.49 S- 7.59	79.43 5.30 7.57	233.5–4.0	. . .	82	*n*-Butanol	16.57	604
Diphenyl-4-methylnaphthyl-phosphine	C-84.64 H- 5.87 P- 9.49	84.35 5.85 9.46	112	. . .	58	Ethanol	. . .	. . .
Diphenyl-4-methylnaphthyl-phosphine sulfide	C-77.07 H- 5.34 S- 8.95	77.23 5.51 9.14	174–5	. . .	65	Ethanol	16.52	605

[a] All analyses were performed by Galbraith Laboratories, Knoxville, Tenn. [b] In these molecules, the fundamental P-S frequency cannot be unequivocally established. The splitting may be due to the fundamental vibration itself or it may be a combination band arising from the aryl C-P and P-S vibration. [c] Uncorrected.

By the reaction of 1-naphthyllithium with phosphorus trichloride, a compound was isolated for which the authors observed a melting point of 263° to 5° (following recrystallization from benzene–ethyl ether and then from 95% ethanol). Elemental analysis indicated that this compound was a trinaphthylphosphine.

The melting point of the authors' compound rose when a sample was held in the molten state for a considerable period of time. After heating for 1 hour at 280°, the melting point rose from 263° to 270°. This might indicate that volatile impurities were present which were boiled out of the solution at the high temperature, causing the observed melting point to rise. The latter observation may also be attributed to the formation of a new crystalline modification of the phosphine at a higher temperature.

The spectra of the phosphine sulfides and of the parent phosphines in the region of the fundamental P-S vibration (*8*) were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer, using CsBr optics. The KBr pellet technique was used. Measurements were made in the range of 600 to 635 cm.$^{-1}$ where the P-S frequency has been reported (*8*).

The C-P vibration in trimethylphosphine appears at 663 cm.$^{-1}$ (*2*). When the substituents on the P-atom are condensed aromatic groups, $\nu_{\text{P-C}}$ should be located at slightly lower frequencies because of the increased mass and could fall into the range of the P-S vibration. This can be seen in the spectra of tri-1-naphthyl-, di-1-naphthylphenyl-, and diphenyl-1-naphthylphosphine sulfides. In these molecules what appears to be a P-S doublet may be an overlapping of the C-P and P-S vibrations. On the other hand, the splitting may be due entirely to the P-S vibration itself, and in the latter case would probably arise from intermolecular association (*8*) although this fact has not been unequivocally established.

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LITERATURE CITED

(1) Anschutz, L., Kraft, H., Schmidt, K., *Ann.* **542**, 14 (1939).
(2) Daasch, L.W., Smith, D.C., *Anal. Chem.* **23**, 853 (1951).
(3) Hart, F.A., Mann, F.G., *J. Chem. Soc.*, **1955**, p. 4107.
(4) Jones, R.G., Gilman, H., "Organic Reactions," Vol. **VI**, Chap. VII, Wiley, New York, 1951.
(5) Mikhailov, B.M., Kucherova, N.F., *Zh. Obshch. Khim.* **22**, 792 (1952); *Dokl. Akad. Nauk. U.S.S.R.* **74**, 501 (1950).
(6) Plets, V.M., Dissertation, Kazan, 1938, in Kosolapoff, G.M., "Organophosphorus Compounds," p. 33, Wiley, New York, 1950.
(7) Worrall, D.E., *J. Am. Chem. Soc.* **52**, 2933 (1930).
(8) Zingaro, R.A., *Inorg. Chem.* **2**, 192 (1963).

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