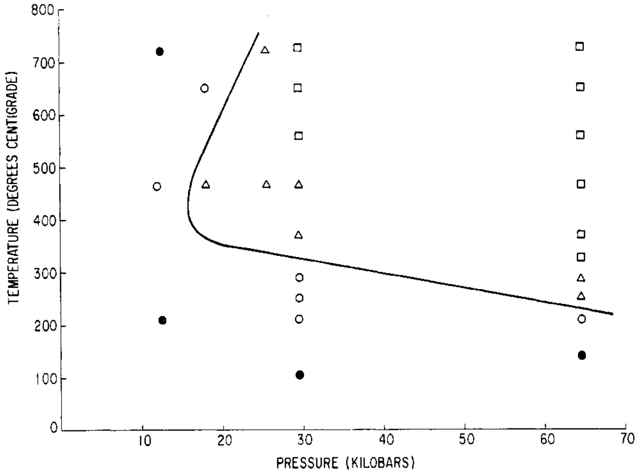

Figure 1.—Pressure–temperature diagram for the reaction of sulfur with covellite to form cubic copper disulfide. Two-minute runs produce the pyrite structure only, □; mostly pyrite structure, △; mostly covellite, ○; and no reaction, ●.

TABLE I

SPACING AND INDEXING OF THE REFLECTIONS OF CUBIC COPPER DISULFIDE[a]

d, A	hkl	Intens	d, A	hkl	Intens
3.32	111	m	1.054	521	m
2.89	200	vs	1.022	440	m
2.57	210	ms	1.005	522	w
2.35	211	ms	0.990	530	vw
2.04	220	s	0.978	531	m
1.92	300	w	0.963	600	m
1.86	310	vw	0.950	610	vw
1.73	311	s	0.939	611	m
1.66	222	m	0.913	620	m
1.59	320	m	0.903	621	m
1.54	321	m	0.895	541	w
1.40	410	mw	0.883	533	m
1.36	411	w	0.873	622	m
1.325	331	m	0.864	630	vw
1.291	420	m	0.854	631	m
1.260	421	m	0.828	700	m
1.231	332	w	0.819	710	m
1.180	422	mw	0.811	711	mw
1.158	500	w	0.804	640	ms
1.132	510	w	0.796	720	mw
1.112	511	ms	0.788	721	mw
1.073	520	m			

[a] Copper $K\alpha_1$ nickel-filtered radiation employed with a Norelco camera of diameter 114.59 mm.

temperature and pressure. This synthesis was carried out in the "belt" superpressure apparatus[3] using a cell constructed of sodium chloride with a graphite heater. The cell was calibrated at room temperature with the bismuth 25.5- and 27-kbar and the barium 58-kbar transformations. Temperatures were determined from the readings of a Pt—Pt-10% Rh thermocouple present during some of the runs. When a sample consisting of a mixture of CuS (covellite) and sulfur in a 1:1.2 mole ratio was subjected to the appropriate temperature and pressure conditions (Figure 1) and then washed with boiling CS_2 to extract the excess sulfur, a dark purplish red material was obtained. Chemical analysis indicated the formula $CuS_{1.9}$ and the X-ray reflections (Table I) showed that it had the cubic (NiS_2) pyrite structure, $a = 5.796$ A. The calculated density is 4.44 g cm^{-3}. The low pycnometric density, 4.24 ± 0.10 g cm^{-3}, may be ascribed to sulfur vacancies in the lattice. Between 200 and 300° in an inert atmosphere, CuS_2 decomposes to yield covellite, some digenite, and somewhat more than 1 mole of sulfur per mole of CuS_2. Further decomposition, which occurs between 400 and 475°, produces Cu_2S (chalcocite) and nearly 0.5 mole of sulfur.

Acknowledgment.—The author wishes to acknowledge the able assistance of D. R. Ochar in making the X-ray diffraction patterns and analyses and also helpful discussions with Dr. John S. Kasper. Dr. Lester Bronk performed the thermogravimetric measurement.

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A Novel Synthesis of Arylphosphine Selenides. Reaction of Arylphosphines with Potassium Selenocyanate[1]

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Tertiary phosphine selenides have been prepared either by direct fusion of the tertiary phosphine with elemental selenium[3] or by refluxing the phosphine with selenium in an inert solvent.[4] We wish to report a novel synthesis of several arylphosphine selenides. Compared with the usual preparative routes for tertiary phosphine selenides, the reaction of a tertiary phosphine with potassium selenocyanate in acetonitrile is extremely simple (eq 1).

$$R_3P + KSeCN \xrightarrow{CH_3CN} R_3PSe + KCN \tag{1}$$

Experimental Section

Reagent grade triphenylphosphine (Metal and Thermit) and potassium selenocyanate (Alfa) were not purified further. Acetonitrile was purified according to the procedure of Muney and Coetzee.[5]

Preparation of Triphenylphosphine Selenide.—The following preparation of $(C_6H_5)_3PSe$ illustrates a specific example of the synthetic procedure used to obtain tertiary phosphine selenides. To potassium selenocyanate (7.2 g, 0.05 mole) in 60 ml of acetonitrile was added rapidly, with stirring, triphenylphosphine (13.1 g, 0.05 mole) dissolved in 60 ml of warm acetonitrile. A white crystalline material began precipitating immediately. The reaction was stirred for 1 hr and then the solvent was evaporated. The solid residue was transferred to a sintered glass funnel and

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[1] The authors gratefully acknowledge the financial support of Grant DA-ARO-(D)-31-124-G500 from the U. S. Army Research Office (Durham).

[2] Public Health Service Predoctoral Fellow, 1965–1966.

[3] R. A. Zingaro and R. E. McGlothlin, *J. Chem. Eng. Data*, **8**, 226 (1963).

[4] G. M. Kosolapoff, "Organophosphorous Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 98.

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TABLE I

CHARACTERIZATION DATA OF THE PHOSPHINE SELENIDES

Compound	Yield, %	Mp, °C[a]	P=Se infrared band, cm^{-1}[9]	% C		% H		% Se	
				Calcd	Found[b]	Calcd	Found[b]	Calcd	Found[b]
$(p\text{-}CH_3C_6H_4)_3PSe$[c]	95	198–198.5[d]	544	65.80	65.56	5.52	5.45	20.60	20.81
$(m\text{-}CH_3C_6H_4)_3PSe$[c]	94	139–140	574	65.80	65.57	5.52	5.50	20.60	20.36
$(CH_3)_2NCH_2CH_2CH_2P(Se)(C_6H_5)_2$[c]	87	90–91	532	58.29	58.52	6.33	6.50	22.54	22.30
$(C_6H_5)_2P(Se)CH_2CH_2P(Se)(C_6H_5)_2$[e]	84	194–195	539	56.13	56.37	4.35	4.42	28.39	28.09
$(C_6H_5)_2P(Se)CH_2CH{=}CH_2$[c]	89	78–79	[f]	59.03	58.99	4.95	5.13	25.87	25.62

[a] Uncorrected melting point (generally the crude melting point) was only 1–3° lower than that of the pure compound. [b] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. [c] Recrystallized from absolute ethanol. [d] Lit. 193° [A. Michaelis, *Ann.*, **315,** 43 (1901)]. [e] Recrystallized from 1-butanol. [f] Indeterminate due to other strong absorptions.

was washed with 300 ml of distilled water to remove the potassium cyanide, then with 10 ml of cold absolute ethanol, and finally with anhydrous ethyl ether. The crude product, after drying for 12 hr over P_4O_{10} *in vacuo,* melted at 183–186° and weighed 16.4 g (yield 96%). Small white crystals of analytical purity were obtained after one recrystallization from absolute ethanol, mp 187–188° (lit. 184–186°,[6] 187–188°[7]). The P=Se stretching frequency was assigned at 562 cm^{-1} (Nujol mull) (lit.[8] 560 cm^{-1}).[9]

Anal. Calcd for $C_{18}H_{15}PSe$: C, 63.35; H, 4.43; Se, 23.11. Found: C, 63.36; H, 4.45; Se, 23.00.

Preparation of Other Arylphosphine Selenides.—Table I lists the characterization data of the phosphine selenides which were prepared by the above procedure.

Discussion

The reaction of arylphosphines and alkyl–arylphosphines with potassium selenocyanate rapidly provides solid phosphine selenides of high purity. For example, triphenylphosphine and *o*- and *m*-tolylphosphines give 94–96% yields of products which melt within 1–3° of the pure compound. The ease with which the reaction is accomplished and the product isolated, and the high purity of the resulting material, make this reaction particularly advantageous for preparations of selenide derivatives of solid phosphines.[10]

An important advantage of this synthesis is that the investigator handles solid, relatively nonodorous selenium compounds throughout. Three arylphosphine selenides and three aryl–alkylphosphine selenides were prepared readily by this reaction. No trialkylphosphines were employed because of the odor and handling problems associated with the low molecular weight liquid alkylphosphine selenides.

The reaction of potassium selenocyanate with triphenylarsine failed to produce triphenylarsine selenide; triphenylarsine was recovered nearly quantitatively. Although triphenylarsine selenide has been reported,[11] it was not characterized. Recently, Zingaro and Merijanian[12] failed to prepare $(C_6H_5)_3AsSe$ by the reported procedure, owing probably to the inherent instability of the compound.

One very interesting aspect of the reaction between tertiary phosphines and KSeCN is that the analogous reaction with KSCN[13] or KOCN does not yield tertiary phosphine sulfides or phosphine oxides, respectively. This difference in reactivity and the mechanism of the KSeCN reaction will be investigated further.

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(7) C. Screttas and A. F. Isbell, *J. Org. Chem.*, **27,** 2573 (1962).

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(9) The strong to very strong P=Se stretching frequencies were determined in Nujol mulls with a Beckman IR-9 high-resolution infrared spectrometer by comparing the spectrum of each compound with that of the parent phosphine.

(10) Phosphines which are oxidized by air must be protected with a nitrogen atmosphere during the initial phase of the synthesis.

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(12) R. A. Zingaro and A. Merijanian, *Inorg. Chem.*, **3,** 580 (1964).

(13) P. D. Bartlett and R. E. Davis, *J. Am. Chem. Soc.*, **80,** 2513 (1958).

Correspondence

Energy States of the Tetrachloroplatinate(II) Ion[1]

Sir:

The polarized spectra of single K_2PtCl_4 crystals at 15°K in the visible and ultraviolet regions were recently reported from this laboratory.[2] In this work the locations of the band maxima were compared with energy states calculated by means of strong-field matrix elements for the d^8 configuration with square-planar geometry published earlier.[3] Perumareddi[4] recently called our attention to some errors among these matrix elements. Consequently, elements in the two tables of both the strong-field and weak-field matrices[3] have been redetermined and tested by the transformation matrices of the weak-field to strong-field basis functions. Corrections, which were found for the earlier paper, are included in the Appendix.

The energy levels for the square-planar d^8 system have now been recalculated with the revised set of matrix elements and the parameters of the previous

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1858.

(2) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **4,** 1682 (1965).

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