# Chemistry of phosphorus pentaselenide. II. Its reaction with amines

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The reaction of phosphorus pentaselenide with amines may yield, as products, selenophosphoric triamides,  $(RNH)_3PSe$ ; alkylammonium diselenophosphoric diamides,  $(RNH)_2P(Se)Se^-RNH_3^+$ ; or alkylammonium monoacidbis(diselenophosphoric diamides),  $\{[(RNH)_2P(Se)Se]_2H\}^-RNH_3^+$ , where R is an alkyl group. The preparation of potassium diselenophosphoric diamides,  $(RNH)_2P(Se)Se^-K^+$ , is also described.

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This paper describes the reaction of phosphorus pentaselenide with primary amines. The reactions of phosphorus pentaselenide which were previously reported have been reviewed in the first paper of this series (1). In this part, selenophosphoric triamides,  $(RNH)_3PSe$  (1); alkylammonium diselenophosphoric diamides,  $(RNH)_2P(Se)Se^-RNH_3^+$  (2); potassium diselenophosphoric diamides,  $(RNH)_2P(Se)Se^-K^+$  (3); and alkylammonium monoacidbis(diselenophosphoric diamides),  $\{[(RNH)_2P(Se)Se]_2H\}^-$ RNH<sub>3</sub><sup>+</sup> (4), where R is an alkyl group, have been prepared by the reactions of P<sub>2</sub>Se<sub>5</sub> with primary amines.

The nature of the reaction of phosphorus pentasulfide with primary amines has been known for several years (2) and the subject has been reviewed by Cowley (3). The reaction of  $P_2Se_5$ with primary amines has not been the subject of previous investigations.

### Experimental

#### Reagents

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All amines were purchased from the Baker Chemical Company and were stored over sodium hydroxide. They were distilled just prior to use. Red phosphorus powder was purchased from Mallinckrodt Chemical Company. It was washed several times with anhydrous ethyl ether and dried *in vacuo* over phosphorus pentoxide before use. Selenium powder was supplied by the Canadian Copper Refiners Ltd. Heptane (96-100°) and ligroin (66-75°) was purchased from Eastman Organic Chemicals Company. Ethanol (absolute) was purchased from the U.S. Industrial Chemical Company.

#### Phosphorus Pentaselenide

Phosphorus pentaselenide was prepared according to the procedure described by Kudchadker *et al.* (1). Stoichiometric amounts of dry red phosphorus powder were intimately mixed with selenium powder. The mixture was sealed in a glass container under an atmosphere of nitrogen and was then heated to  $450^{\circ}$  for 12 h. After cooling to room temperature, the glass container was broken and the glassy, grayish black  $P_2Se_5$  was removed and ground into a fine powder in a ball-mill before use.

#### N,N',N''-Tris(cyclohexyl)selenophosphoric Triamide

This compound was prepared by the dropwise addition of a stoichiometric amount (0.9 mole) of cyclohexylamine to a suspension of powdered  $P_2Se_5$  (0.1 mole) in 200 ml of heptane at 50°, with stirring, under an atmosphere of nitrogen, over a period of 2 h. After the reaction mixture was stirred for an additional 3 h, the solid cyclohexylammonium hydrogen selenide which precipitated was separated, along with other solids, from the reaction mixture. The filtrate, which contained a suspension of colloidal selenium, was allowed to remain in a stoppered flask until the red selenium converted to the stable gray form which settled rapidly. Finally, the filtrate was refiltered and the product (C<sub>6</sub>H<sub>11</sub>NH)<sub>3</sub>PSe was recovered from the second filtrate by evaporation of the heptane solvent in a film-type evaporator at reduced pressure. Purification was accomplished by first washing the solid product with ligroin. It was redissolved in the minimum volume of a cool heptane-ethanol mixture. The solvents were slowly removed by evaporation at reduced pressure until the crystalline product separated. The latter was removed, dried in vacuo, and stored in evacuated, sealed glass tubes.

### Alkylammonium Diselenophosphoric Diamides

Compounds of the type  $(RNH)_2P(Se)Se^-RNH_3^+$  were prepared by the addition of a stoichiometric amount of the amine (0.7 mole) to a suspension of powdered  $P_2Se_5$ (0.1 mole) in heptane. The reaction conditions and methods of recovery and purification were the same as those just described for the preparation of  $N_NN'_N''_$ tris(cyclohexyl)selenophosphoric triamide. It must be emphasized that the solution containing the compound should not be evaporated to dryness. Continued pumping on the solvent-free crystals will cause the loss of a mole of amine and conversion to the acid salt.

# Potassium N,N'-Bis(butyl)diamidodiselenophosphate

Potassium N,N'-bis(butyl)diamidodiselenophosphate,  $(C_4H_9NH)_2P(Se)Se^-K^+$ , was prepared by the reaction of butylammonium N,N'-bis(butyl)diamidodiselenophosphate (0.01 mole) with a stoichiometric amount of alcoholic potassium hydroxide (0.01 mole) in ethanol under an atmosphere of nitrogen. After refluxing the reaction mixture for 2 h, the solution was filtered and evaporated to dryness at reduced pressure (0.1 mm).

Compound		Calcd. (%)	Found (%)	Melting point (°C)	Yield (%)	$\nu(P=Se)$ (cm <sup>-1</sup> )
N,N',N''-Tris(cyclohexyl)selenophos- phoric triamide	C H P Se	53.46 8.97 7.66 19.52	53.35 8.91 7.62 19.28	168–169	10	599
Hexylanımonium N,N'-bis(hexyl)diami- dodiselenophosphate	C H P Se	43.99 9.02 6.30 32.13	43.87 9.12 6.42 32.05	88-89 (decomp.)	4	543
Butylammonium N,N'-bis(butyl) diami- dodiselenophosphate	C H P Se	35.38 7.93 10.31 7.60 38.77	35.61 8.02 10.42 7.80 39.01	117-120 (decomp.)	6	540
Isobutylammonium N,N'-bis(isobutyl)- diamidodiselenophosphate	C H P Se	35.38 7.93 7.60 38.77	35.15 8.06 7.33 38.50	164-166 (decomp.)	7	552
sec-Butylammonium N,N'-bis(sec-butyl)- diamidodiselenophosphate	C H P Se	35.38 7.93 7.60 38.77	35.49 8.00 7.57 38.52	132–134 (decomp.)	11	547
Isobutylammonium monoacidbis[N,N'- bis(isobutyl)diamidodiselenophosphate]	C H P Se	32.39 7.20 9.45 8.35 42.60	32.30 7.34 9.26 8.54 43.04	86	11	580
<pre>sec-Butylammonium monoacidbis[N,N'- bis(sec-butyl)diamidodiselenophosphate]</pre>	C H P Se	32.39 7.20 8.35 42.60	32.08 7.25 8.18 42.10	95–96	8	566
Potassium N,N'-bis(butyl)diamidodiseleno- phosphate	C H Se	25.82 5.37 42.44	25.64 5.50 42.25	Above 300°	Quanti- tative based on onium salt	545

	TABLE I	
Data for	selenophosphoric	amides*

\*Analyses were performed by the Galbraith Laboratories, Knoxville, Tennessee, and by the Schwarzkopf Laboratories, Woodside, New York.

The resulting solid was purified by dissolution in the minimum volume of a heptane-ethanol mixture at room temperature followed by filtration and evaporation under reduced pressure until crystals of the solid separated.

### Isobutylammonium Monoacidbis[N,N'-bis(isobutyl)diamidodiselenophosphate]

 $\{[(C_4H_9NH)_2P(Se)Se]_2H\}^-C_4H_9NH_3^+$  was prepared by the evaporation, at reduced pressure (0.1 mm), of a heptane-ethanol solution (1:1 by volume) of isobutylammonium N,N'-bis(isobutyl)diamidodiselenophosphate. Following the complete removal of the solvent, pumping was continued on the crystals until they acquired a constant weight. Free amine was collected in the cold trap of the vacuum pump. Purification of the resulting solid product was accomplished in the manner described for the compounds prepared in the preceding sections. The same procedure was used for the preparation of secbutylammonium monoacidbis[N,N'-bis(sec-butyl)diamidodiselenophosphate].

Spectra

The infrared spectra of all of the compounds were recorded on a Beckman IR 12 double beam spectrophotometer. The KBr pellet technique was used. Samples were scanned between 200 and 4000 cm<sup>-1</sup>. Nuclear magnetic reasonance (n.m.r.) spectra were run on a Varian A-60 n.m.r. spectrometer.

# **Results and Discussion**

The eight selenophosphoric amides which were prepared in this study are listed in Table I along with other pertinent physical data. All of the selenophosphoric amides were found to be

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unstable in air. This was especially true of the alkylammonium salts of the diselenophosphoric diamides (2). For, this reason, all reactions and recovery and recrystallization of the products were carried out in a dry, nitrogen atmosphere. The reported yields are not the highest attainable. No systematic study was made for the purpose of maximizing the yields.

In contrast with the analogous reactions of  $P_2S_5$  with primary amines in which large amounts of  $H_2S$  are evolved, viz.

$$12RNH_2 + P_4S_{10} \rightarrow 4(RNH)_3PS + 6H_2S$$

 $8RNH_2 + P_4S_{10} \rightarrow 4(RNH)_2P(S)SH + 2H_2S$ ,

 $H_2Se$  and  $(RNH)_2P(Se)SeH$  were never isolated as the free acids, but only as the alkylammonium salts,  $RNH_3^+HSe^-$  and  $(RNH)_2P(Se)$ - $Se^-RNH_3^+$ . Both  $H_2Se$  and the selenophosphoric acids are expected to be stronger acids than the corresponding thio-derivatives. Thus, they readily form salts with the excess amine present in the reaction mixture. The formation of the products that were isolated is described by the following reactions.

 $9RNH_{2} + P_{2}Se_{5} \rightarrow 2(RNH)_{3}PSe + 3RNH_{3}^{+}HSe^{-}$  $7RNH_{2} + P_{2}Se_{5} \rightarrow 2(RNH)_{2}P(Se)Se^{-}RNH_{3}^{+}$ 

 $+ RNH_3^+HSe^-$ 

 $(RNH)_{2}P(Se)Se^{-}RNH_{3}^{+} + KOH \xrightarrow{EtOH} (RNH)_{2}P(Se)Se^{-}K^{+} + RNH_{2} + H_{2}O$ 

 $2(RNH)_2P(Se)Se^-RNH_3^+ \xrightarrow{vacuum}$ 

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 $\{[(RNH)_2P(Se)Se]_2H\}^-RNH_3^+ + RNH_2$ 

In comparison with the reaction of  $P_2Se_5$  with alcohols in which compounds containing bridged  $Se_2$  and  $Se_3$  bonds were formed (1), the reactions of  $P_2Se_5$  with primary amines proceeded in the manner expected. This was probably due to the fact that the free acids that were formed were rapidly converted to the stable alkylammonium salts. This precluded any secondary reactions involving the unstable, free acids.

Except for the reaction of cyclohexylamine, triamides were not isolated at atmospheric pressure. Since Buck and co-workers (2) reported that dithiophosphoric diamides were intermediates in the formation of thiophosphoric triamides, the conversion of selenophosphoric diamides to the triamides may be possible if the reactions are carried out under pressure. It is probable that the failure to isolate ethyl or n-propyl derivatives was due to the loss of these volatile amines under the conditions under which these reactions were carried out. These derivatives could probably be prepared under reaction conditions which would involve the use of high pressures.

### Infrared and N.M.R. Spectra

The assignment of the P—Se vibration was based on previous work which established the location of the fundamental P—Se vibration (4-6) and was corroborated in the case of the selenophosphoric triamide by a comparison of the series of molecules  $(C_6H_{11}NH)_3P$ —O (7),  $C_6H_{11}NH)_3P$ —S, and  $(C_6H_{11}NH)_3P$ —Se. The fundamental P—Se vibrational band of all selenophosphoric amides occurs as a singlet in the predicted region. The frequencies observed for v(P—Se) are listed in Table I.

Nuclear magnetic resonance spectra did not distinguish between the protons on the corresponding ammonium, (RNH)<sub>2</sub>P(Se)Se<sup>-</sup>RNH<sub>3</sub><sup>+</sup>, and ammonium monoacid salts,  $\{[(RNH)_2P(Se) Se_{2}H^{-}RNH_{3}^{+}$ . The protons on the ammonium cation and any acid proton, if present, appeared as a rather broad peak at 5.99  $\tau$  with respect to tetramethylsilane. When treated with D<sub>2</sub>O, this peak disappeared very rapidly showing that any acid proton was in rapid exchange with the protons attached to the N-onium atom. No resonance peaks were observed at 8.75  $\tau$  which Lalezari and Sharghi (8) have recently reported as the region for the Se-H proton in selenols. The infrared spectra of the alkylammonium and alkylammonium monoacid salts were essentially identical.

A hydrogen bond between two selenium atoms, Se—H…Se may possibly exist in anions of the type (4) prepared in this study. This is very unlikely, however, because of the relatively large size and low electronegativity of selenium. It is more likely that the proton is associated, probably through hydrogen bonding, to the smaller, electronegative nitrogen atoms attached to the phosphorus.

# X-ray Data

Preliminary X-ray crystallographic data on a single crystal of isobutylammonium monoacidbis[N,N'-bis(isobutyl)diamidodiselenophosphate] indicates a triclinic space group and a molecular weight of  $(730 \pm 10)/p$ , where p is an integer (the actual molecular weight is 741.45).

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It was found that a = 11.24 Å, b = 19.96 Å, c = 15.88 Å,  $\gamma = 93.0^{\circ}$ ,  $\alpha = 93.5^{\circ}$ , and  $\beta =$ 93.5°.1 Inasmuch as the assumed molecular weight is that of the acid salt and because the molecular weight of any other reasonable species is totally inconsistent with these data, the assumption of a structure involving an acid anion seems very reasonable. The final results of this X-ray study should prove to be most interesting.

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