Binary Phosphorus Selenides. Tetraphosphorus Heptaselenide

CHARLES D. MICKEY and RALPH A. ZINGARO*

The compounds $P_4Se_7 \cdot 2C_5H_5N$, $P_4Se_7 \cdot 2CH_3C_5H_4N$, $P_4Se_7 \cdot 3C_2H_5C_5H_4N$, $P_4Se_8 \cdot 6C_2H_5C_5H_4N$, and $[C_9H_7NH^+]_3[HP_2Se_7{}^{3-}]$ have been characterized by elemental analysis and infrared and mass spectroscopy. The infrared study shows absorptions characteristic of the P=Se, P—Se—P, and P—N stretching vibrations. The presence of the ions $P_2Se_5{}^+$, $P_2Se_3{}^+$, $P_2Se_2{}^+$, and PSe^+ in the mass spectra of the different phosphorus selenide–amine derivatives reflects the stability of these ions and supports the proposal that these phosphorus selenides are structurally similar to each other. The experimental data are similar to those reported for the phosphorus sulfides. This suggests that the tetraphosphorus heptaselenides possess a cage-type structure like that of the corresponding sulfides. The coordination of the heteroaromatic amine molecules to the bonded phosphorus atoms is indicated. Powder X-ray scattering patterns of the phosphorus selenide–amine compounds show that they are highly crystalline.

Introduction

The phosphorus sulfides, *viz.*, tetraphosphorus trisulfide, P_4S_3, tetraphosphorus pentasulfide, P_4S_5, tetraphosphorus heptasulfide, P_4S_7, and tetraphosphorus decasulfide, P_4S_{10}, are commercially available and well characterized.[1] Considerably less is known about the corresponding selenium compounds. Since Berzelius[2] first reported that phosphorus and selenium react in various proportions, the synthesis and characterization of three phosphorus selenides has been well established. In the case of phosphorus triselenide, P_4Se_3, soluble[3] and insoluble forms have been reported. However, Meyer[4] may have been dealing with P_2Se_5 since all subsequent investigations have yielded a soluble compound. Tetraphosphorus pentaselenide, P_4Se_5,[5] and diphosphorus pentaselenide, P_2Se_5,[6] are also well recognized.

Tetraphosphorus triselenide[7,8] and tetraphosphorus pentaselenide[5] have structures which are isomorphous with those of their sulfide analogs. Their structures have been determined by single-crystal X-ray techniques and are supported by ^{31}P nuclear magnetic resonance[3] and Raman spectroscopy.[3,8] The structure of diphosphorus pentaselenide, made by fusing red phosphorus and gray selenium in a sealed tube,[6] has not been determined. It is completely amorphous and has been reported to be polymeric.[9]

Tetraphosphorus heptaselenide has not been reported. Hence, the number of binary phosphorus selenides is incomplete with respect to the known number of binary phosphorus sulfides. Mai[10] has reported that a red compound, $P_4Se_3I_2$, is formed when powdered iodine is allowed to react with tetraphosphorus triselenide in dry carbon disulfide. Penney and Sheldrick[5] have quite recently isolated tetraphosphorus pentaselenide, in trace quantities, from the reaction of bromine with tetraphosphorus triselenide in carbon disulfide.

It has been found in the work reported here that when P_2Se_5 is heated in pyridine, large quantities of an orange solid are formed. Elemental analysis revealed that the orange deposit was a binary phosphorus selenide–heteroaromatic

amine adduct which has been identified as $P_4Se_7 \cdot 2py$.

This paper describes the first preparation and characterization of a tetraphosphorus heptaselenide derivative as well as the preparation and characterization of other novel but related binary phosphorus selenide–heteroaromatic amine compounds.

Results and Discussion

Diphosphorus pentaselenide, P_2Se_5, was converted into tetraphosphorus heptaselenide–bis(pyridine). The conversion was accomplished by refluxing P_2Se_5 in anhydrous pyridine. Similar treatment of P_2Se_5 using 4-methylpyridine gave tetraphosphorus heptaselenide–bis(4-methylpyridine), $P_4Se_7 \cdot 2CH_3C_5H_4N$. The extreme oxidative and hydrolytic instability of the heptaselenides presents certain special problems. Inherent among these are the difficulties in performing the indicated elemental analyses without bringing about changes in the composition of the compounds. Purification of these compounds, by recrystallization, could not be effected due to their lack of solubility in all solvents tested and their extreme sensitivity to traces of oxygen and water.

The pyridine, 4-methylpyridine, and 4-ethylpyridine derivatives of tetraphosphorus heptaselenide were obtained in good yield with excellent stoichiometric reproducibility. The other derivatives, however, were more difficult to prepare reproducibly.

The composition of the phosphorus selenide–amine adduct formed by allowing P_2Se_5 to react with 4-ethylpyridine varied with the time of the reaction. When the reaction was allowed to proceed for about 2 hr, a compound having a stoichiometry approaching that of tetraphosphorus octaselenide–hexakis(4-ethylpyridine), $P_4Se_8 \cdot 6C_2H_5C_5H_4N$, was isolated. When the reaction time was extended to 12 hr, tetraphosphorus heptaselenide–tris(4-ethylpyridine), $P_4Se_7 \cdot 3C_2H_5C_5H_4N$, was formed.

When P_2Se_5 was allowed to react with isoquinoline, a compound corresponding to triisoquinolinium pyroselenophosphate, $[C_9H_7NH^+]_3[HP_2Se_7{}^{3-}]$, was formed. The appearance of a mass peak corresponding to the $PSe_4{}^+$ fragment found only in the mass spectrum of this compound is taken as evidence of the pyroselenophosphate structure.

Diphosphorus pentaselenide was also allowed to react with 2-methylpyridine, 3-ethylpyridine, quinoline, triethylamine, and thiophene. Except in the case of thiophene, a reaction occurs in all cases. Attempts to isolate any products from these reactions using the established procedures were unsuccessful.

The pertinent analytical data for the binary phosphorus

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Table I. Analytical Data for the Compounds Isolated from the Reaction of P_2Se_5 with Aromatic Amines[a]

	C		H		N		P		Se[b,c]		
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Yield, %
$P_4Se_7 \cdot 2C_5H_5N$	14.37	14.43	1.20	1.87	3.35	3.32			66.23	66.47	76
$P_4Se_7 \cdot 2CH_3C_5H_4N$									64.08	63.64	85
$P_4Se_7 \cdot 3C_2H_5C_5H_4N$									55.41	54.98	81
$P_4Se_8 \cdot 6C_2H_5C_5H_4N$					6.01	5.52	8.87	8.01	45.21	44.02	45
$[C_9H_7NH^+]_3[HP_2Se_7{}^{3-}]$	32.21	33.29	2.48	2.47			6.16	5.88	54.97	53.58	91

[a] Elemental analyses were performed by the Galbraith Laboratories, Knoxville, Tenn. [b] Selenium was determined according to the method of E. S. Gould, *Anal. Chem.*, 23, 1502 (1951). [c] Average values from several determinations.

selenide-heteroaromatic amine compounds prepared are summarized in Table I.

In working with this series of compounds speculation regarding their structures was inevitable because the phosphorus sulfides, P_4S_3, P_4S_5, P_4S_7, and P_4S_{10}, and the phosphorus selenides, P_4Se_3 and P_4Se_5, are well-defined crystalline solids.

Powder X-ray scattering patterns of the phosphorus selenide-amine compounds show that they are definitely crystalline. Ideally, their structures should be determined crystallographically and these structures should be in accord with the data compiled by other physical methods. However, these phosphorus selenide-amine adducts have been found to be insoluble or subject to rapid decomposition in a large variety of solvents. Therefore, the preparation of solutions for the purpose of making physical measurements or the growing of crystals suitable for crystallographic studies have been thus far unsuccessful. Such studies are being continued at the present time.

The molecular structure of diphosphorus pentaselenide, because it is a noncrystalline, amorphous solid, is not well known. However, it has been suggested[11] that each phosphorus atom in P_2Se_5 has a tetrahedral environment on the basis of ^{31}P nuclear magnetic resonance studies. If their assignment is correct, P_4Se_{10} probably has a structure like that of the well-known P_4S_{10} cage.

The observation from this laboratory that the ratio of phosphorus to selenium in the amine adducts increases with increasing reaction time points to the formation of the crystalline tetraphosphorus heptaselenide–amine adduct from a P_4Se_{10} cage by a degradative process. This observation combined with the proposal of Baidakov and Shcherbakov[11] lends support to the idea that the P_4Se_7 moiety is isomorphous with the well-known P_4S_7 cage (I).
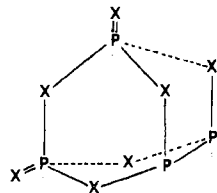
I, X = S, Se

The spectral data indicate that the characteristic absorptions of the amine molecules are considerably modified on coordination. This perturbation has been previously described[12-14] as a typical result of the coordination of the base. The assignment of frequencies in the spectrum of pyridine have been given by Wilmshurst and Bernstein[14] and their ideas are utilized in this discussion.

The four principal bands between 1600 and 1430 cm^{-1}, due to the C=C and C=N stretching vibrations, are shifted to higher frequencies in the complexes. Absorption in the 1230-1430-cm^{-1} region is considerably enhanced at 1388, 1328, and 1245 cm^{-1}. The appearance of two or three bands in this region has also been reported[15] in the spectra of a number of other coordination compounds formed by these bases.

The strong band at 705 cm^{-1}, the out-of-plane C-H deformation, and the band at 748 cm^{-1}, the out-of-plane ring deformation, which are observed in the spectrum of pyridine are shifted to 678 and 741 cm^{-1}, respectively, in the spectrum of the compounds. Also, the ring vibrations in pyridine at 405 and 605 cm^{-1} are shifted to 420 and 615 cm^{-1}. These shifts are characteristic of the coordination of pyridine through the nitrogen atom.[16,17]

The exocyclic P=Se stretching frequency[18,19] appears to be unperturbed in the spectra of the compounds which indicates that the P=Se bond is probably not directly involved in the complex formation. The skeletal P-Se-P stretching vibrations should be observable at lower frequencies. A pair of well-defined bands, the one at the higher frequency of greater intensity, is observed in the case of the pyridine derivative at 420 and 405 cm^{-1} and in the case of the 4-methylpyridine derivative at 418 and 398 cm^{-1}. Pyridine absorbs at 400 cm^{-1}, but 4-methylpyridine is transparent in this region. These may well represent the asymmetric and symmetric P-Se-P skeletal stretching vibrations.

The P_4Se_7 amine derivatives are characterized by strong but very broad absorptions in the 880-980-cm^{-1} region. Singh and Burg[20] reported the frequency of the P-N stretching vibration at 973 cm^{-1} while Bellamy[21] suggested a range, 950-980 cm^{-1}, as the region for this vibration. Erleth, Freeman, and Wagner[22] reported to have observed the same vibration at 950-980 cm^{-1}. The observation of this absorption in the compounds which are the subject of this study suggests that the aromatic amines are coordinated to the P_4Se_7 cage *via* phosphorus atoms. The appearance of P_2 fragments in the mass spectral patterns (to be discussed) suggests the presence of a P-P bond in the molecules. Although neither of these lines of evidence is conclusive, they indicate that P_4Se_7 is isomorphous with P_4S_7 and that the

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amine molecules are coordinated to the bonded phosphorus atoms.

In the mass spectra of both tetraphosphorus heptaselenide-bis(pyridine) and triisoquinolinium pyroselenophosphate, P-Se$^+$ forms the base peak. This confirms the stability of the P-Se$^+$ ion which is isoelectronic with the stable, neutral carbon monoxide molecule. In the spectra of tetraphosphorus heptaselenide-bis(4-methylpyridine) and tetraphosphorus octaselenide-hexakis(4-ethylpyridine), the ion Se$^+$ represents the base peak, whereas the P-Se$^+$ fragments have relative abundances of 44.8 and 68.6, respectively.

Inorganic cage molecules which have been studied by mass spectroscopy are the boron hydrides,[23] boron halides,[24] polynuclear metal carbonyls,[25] and phosphorus sulfides.[26] The principal factor dominating the fragmentation pathway of the halides or carbonyls is the elimination of stable neutral species, *e.g.*, Cl, BCl$_3$, and CO. In contrast, the phosphorus sulfides and phosphorus selenides are characterized by the tendency to form even-electron ions. Apparently the stability of the ionic rather than the neutral species dictates the fragmentation pathway to be followed by these unique inorganic cage molecules. The spectra for the binary phosphorus selenide-heteroaromatic amines recorded in this work are quite similar and are summarized in Table II.

Conspicuous by their absence are the molecular ions and fragments which contain portions of both amine and phosphorus selenide moieties. This suggests that thermal decomposition precedes vaporization. Excluding the respective amine and its characteristic fragments, all of the spectra are essentially identical. The most notable differences are found in the relatively small variations in the relative abundances for the respective ions and the unique appearance of the PSe$_4^+$ fragment in the spectrum of triisoquinolinium pyroselenophosphate which furnishes evidence in support of the P$_2$Se$_7^{4-}$ structure. The absence of any binary phosphorus selenide molecular ions, for any of these heavier species, is consistent with the trends of instability suggested by the data of Penney and Sheldrick.[26]

The phosphorus selenide-amine adducts appear to fragment by the elimination of the respective amine followed by the dissociation of the phosphorus selenide moiety into P$_2$Se$_5$ and P$_2$Se$_2$ or P$_2$Se$_3$. The dissociation of P$_4$S$_{10}$ into two P$_2$S$_5$ molecules, in the vapor, was previously reported in thermodynamic studies conducted by Stock and von Bezold[27] and Forthmann and Schneider[28] and more recently in the mass spectroscopic studies of Penney and Sheldrick.[26] Alternately, the phosphorus selenide moiety may decompose by the rapid, stepwise loss of P-Se to give P$_2$Se$_5^+$ as the first stable ion species to be recorded in any of the spectra.

The formation of the ions P$_2$Se$_5^+$, P$_2$Se$_3^+$, P$_2$Se$_2^+$, and P-Se$^+$ from the different phosphorus selenide-amine adducts reflects their stabilities and further supports the proposal that these phosphorus selenides are structurally similar to each other and to the corresponding binary phosphorus sulfides. Most of the ions observed in the spectra of these compounds find their counterparts in the mass spectra of the corresponding binary phosphorus sulfides.[26]

Table II. Phosphorus Selenide Ion Abundances in the Mass Spectra of the Phosphorus Selenide-Amine Adducts

m/e	Ion	P$_4$Se$_7$· 2C$_5$H$_5$N	P$_4$Se$_7$· 2C$_6$H$_7$N	P$_4$Se$_8$· 6C$_7$H$_9$N	P$_2$Se$_7$· 3C$_9$H$_7$N
31	P$^+$ [a]	10.29			
62	P$_2^+$ [a]	3.43	4.5	13.0	11.2
80	Se$^+$ [a]	41.2	100.0	100.0	71.0
111	PSe$^+$ [a]	100.0	44.8	68.6	100.0
142	P$_2$Se$^+$ [a]	21.27	7.6	9.4	14.4
160	Se$_2^+$ [a]	65.2	32.5	66.2	82.5
173	P$_3$Se$^+$ [a]	3.43	3.4	5.2	4.0
191	PSe$_2^+$ [a]	13.72	2.8	3.1	5.6
222	P$_2$Se$_2^+$ [a]	6.9	3.6	10.4	9.6
240	Se$_3^+$ [a]	12.0	0.6	1.0	1.3
271	PSe$_3^+$ [a]	7.55	0.6	1.0	2.1
302	P$_2$Se$_3^+$ [a]	65.2	5.9	6.8	18.6
320	Se$_4^+$	6.86			
351	PSe$_4^+$				0.2
365	NPSe$_4^+$				0.5
382	P$_2$Se$_4^+$ [a]		0.6	0.7	2.0
400	Se$_5^+$				0.8
462	P$_2$Se$_5^+$ [a]	34.3	0.6	2.1	6.4

[a] Isostructural ions appear in the mass spectrum of P$_4$S$_7$.[26]

The fragmentation pathways, of major importance, for the phosphorus selenides are shown in Scheme I. Initially, the ion P$_2$Se$_5^+$ (I) loses Se$_2$. This may result from the rapid, stepwise loss of the two exocyclic selenium atoms from I or by elimination of the Se-Se unit from the ring, to form P$_2$Se$_3^+$ (II). The appearance of the Se$_2^+$ mass peak in the spectra is, in part, suggestive of the latter transition. The formation of P$_2$Se$_3^+$ (II) is followed by the loss of Se, giving rise to P$_2$Se$_2^+$ (III), which may have a structure analogous to the tetrahedral P$_4$ molecule with selenium atoms occupying two of the sites normally occupied by phosphorus. Elimination of P-Se leaves P-Se$^+$ (IV) which may be followed by the loss of P or Se to form Se$^+$ (V) or P$^+$ (VI), respectively.

A second fragmentation pathway is suggested by path B. The initial elimination of Se$_2$ from I to form P$_2$Se$_3^+$ (II) is followed by the elimination of P-Se to form the planar PSe$_2^+$ species VII. The loss of P-Se from PSe$_2^+$ (VII) may terminate the pathway with the formation of Se$^+$ (V). However, the loss of Se by PSe$_2^+$ (VII) allows the pathway to be extended for an additional step *via* the formation of P-Se$^+$ (IV). This pathway is ultimately terminated with the formation of P$^+$ (VI) or Se$^+$ (V).

A third fragmentation pattern is indicated by path C. This pathway shows the stepwise elimination of Se$_2$ from P$_2$Se$_5^+$ (I) and P$_2$Se$_3^+$ (II), to form P$_2$Se$^+$ (VIII). The transition leading to the formation of P$_2$Se$^+$ (VIII) is followed by the loss of P or P$_2$ which gives rise to P-Se$^+$ (IV) or Se$^+$ (IX), respectively. Subsequently, the pathway may be terminated by the loss of P or Se from P-Se$^+$ (IV) to form Se$^+$ (IX) or P$^+$ (VI).

There were no mass peaks observed in any of these spectra which could be associated with metastable transitions.

Experimental Section

General Methods. Evaporations were performed under diminished pressure on a rotary evaporator. Compounds which were sensitive to moisture were handled in a drybox desiccated with phosphorus pentoxide.

Infrared spectra were measured with a Beckman IR-12 infrared spectrophotometer. Samples were in the form of KBr pellets.

The mass spectra were recorded with CEC-21-104 or CEC-21-110 mass spectrometers operated at an ionizing potential of 70 eV and an ion current of 100 μA. The accelerating potential was 8 kV. The source temperatures used ranged from 180 to 350°.

Microanalyses for carbon, hydrogen, nitrogen, and phosphorus were performed by the Galbraith Analytical Laboratories, Inc., Knoxville, Tenn. Selenium was determined in this laboratory, according to the method of Gould.[29]

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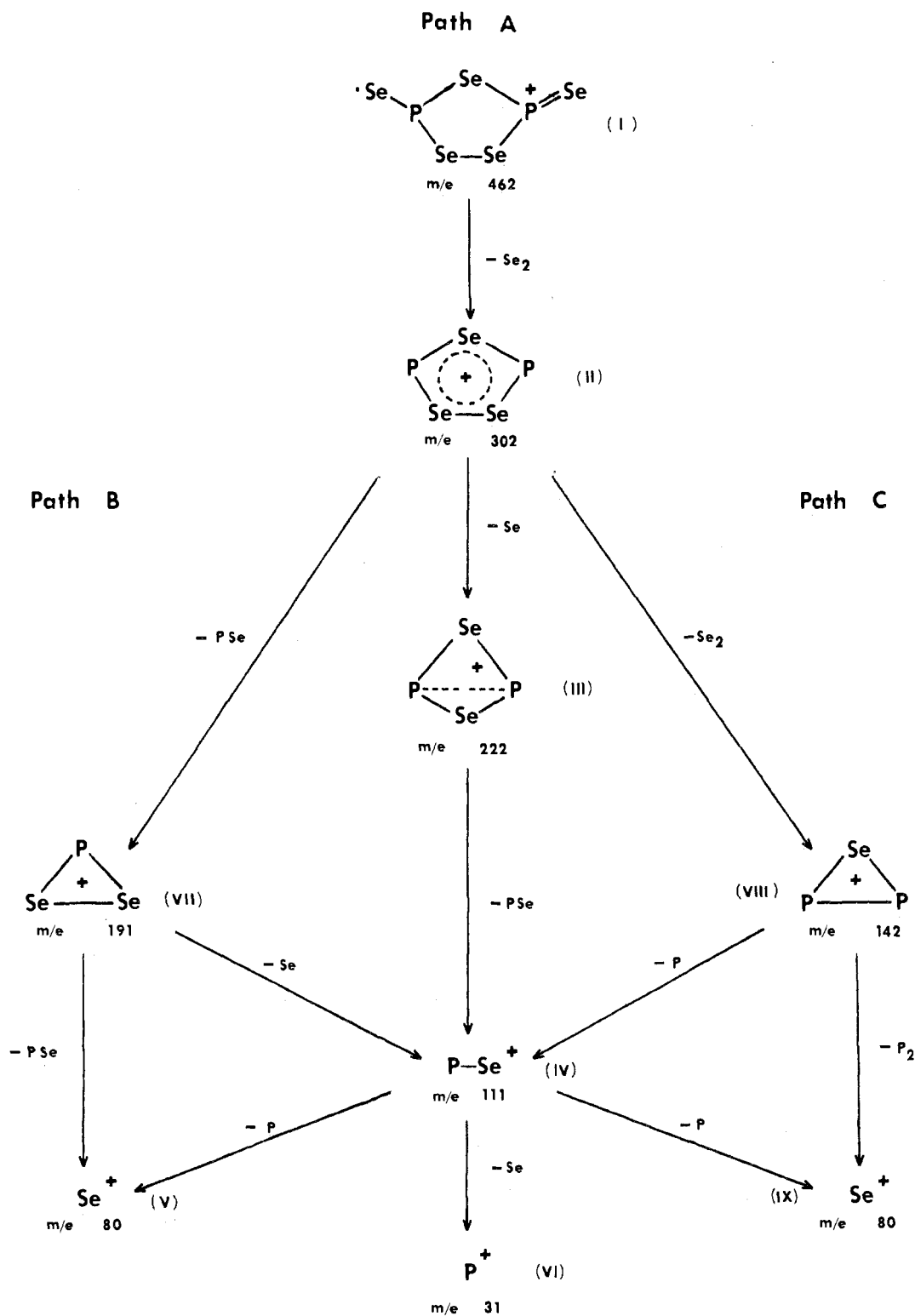(24) A. G. Massey and D. S. Urch, *Chem. Ind. (London)*, 607 (1965).

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Scheme I

Diphosphorus Pentaselenide. Diphosphorus pentaselenide was prepared by the method of Kudchadker, *et al.*[6] Stoichiometric amounts of dry red phosphorus and selenium powder were intimately mixed by rolling in a ball mill for 12 hr. The mixture was transferred to a heavy-walled glass bomb which was evacuated and sealed *in vacuo*. The bomb was heated to 450° for 12 hr. After cooling to room temperature the bomb was broken and the glassy black P_2Se_5 was placed in a desiccator over calcium chloride. Just prior to use the P_2Se_5 was ground into a very fine powder.

Tetraphosphorus Heptaselenide–Bis(pyridine). A 250-ml three-necked round-bottom flask was equipped with a mechanical stirrer, reflux condenser, and a nitrogen inlet which was used to maintain a positive nitrogen pressure during the reaction. The reaction temperature was controlled by an oil bath. The reaction flask was charged with 100 ml of dry pyridine, distilled from potassium hydroxide, and stirring was initiated, followed by the addition of 4.57 g (0.01 mol) of finely ground P_2Se_5. The reaction mixture was allowed to reflux for 48 hr and cooled to room temperature. The excess pyridine was decanted leaving the insoluble orange tetraphosphorus heptaselenide-bis(pyridine) in the reaction flask. The precipitate was suspended in, and throughly washed with, 50 ml of dry benzene. It was collected

by filtration, under a stream of dry nitrogen, and subsequently washed with three 25-ml portions of dry benzene. The product, which formed in 76% yield, based on the amount of P_2Se_5 used, was dried *in vacuo* over phosphorus pentoxide.

Tetraphosphorus Heptaselenide–Bis(4-methylpyridine). This adduct was prepared in the manner described for tetraphosphorus heptaselenide–bis(pyridine) except that 25 ml of 4-methylpyridine was allowed to react with 1.5 g (3.3 × 10⁻³ mol) of finely ground P_2Se_5 at 100° for 3.5 hr. The insoluble orange product, which formed in 85% yield, was isolated and dried *in vacuo* over phosphorus pentoxide.

Tetraphosphorus Octaselenide–Hexakis(4-ethylpyridine). By allowing 25 ml of 4-ethylpyridine to react with 1.5 g (3.3 × 10⁻³ mol) of finely ground P_2Se_5 in the manner described for the preparation of the bis(pyridine) adduct, at 100° for a period not greater than 2 hr, tetraphosphorus octaselenide–hexakis(4-ethylpyridine) was isolated from the reaction mixture as an insoluble orange powder, in 45% yield.

Tetraphosphorus Heptaselenide–Tris(4-ethylpyridine). By allowing the reaction time to be extended to 12 hr and otherwise employing the same set of conditions as described for the preparation of the octaselenide, tetraphosphorus heptaselenide–tris(4-ethylpyridine) was isolated, as an insoluble orange powder, in 81% yield.

Triisoquinolinium Pyroselenophosphate. A reaction flask equipped with a mechanical stirrer, reflux condenser, and a nitrogen inlet was charged with 50 ml of isoquinoline, and stirring was initiated, followed by the addition of 1.5 g (3.3 × 10⁻³ mol) of finely ground P_2Se_5. The reaction was allowed to continue, at a temperature maintained between 27 and 35° for 12 hr. The insoluble orange powder, triisoquinolinium pyroselenophosphate, was collected by filtration under a stream of dry nitrogen, washed with three 25-ml portions of dry toluene, and dried *in vacuo* over phosphorus pentoxide. The yield, based on the weight of P_2Se_5 used, was 91%.

Contribution from the Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322

Reactions of Dimethylaminodifluoroarsine. Coordination with Boron Acids and Cleavage by Hydrogen Chloride[1]

JOSEPH G. MORSE* and KAREN W. MORSE

Reactions of dimethylaminodifluoroarsine with boron trifluoride, diborane, and borane–carbonyl were studied. Evidence for coordination of boron trifluoride at the nitrogen atom and of borane at the arsenic atom is presented. The reaction of dimethylaminodifluoroarsine with hydrogen chloride resulted in cleavage of the arsenic–nitrogen bond. Evidence for the formation of chlorodifluoroarsine is presented.

The compound dimethylaminodifluorophosphine has proved to be a most interesting compound both as a synthetic intermediate and as a Lewis base. Its reactions include cleavage by hydrogen halides to give mixed halophosphines[2,3] and coordination to various Lewis acids through either the phosphorus or nitrogen donor site.[4-7] It was the object of this study to determine to what extent these roles might differ in the arsenic analog, $(CH_3)_2NAsF_2$.[8]

I. Reactions of Dimethylaminodifluoroarsine with Boron Acids

1. Reaction of $F_2AsN(CH_3)_2$ with Trifluoroborane. $(CH_3)_2NAsF_2$ undergoes reaction with excess trifluoroborane to give a 1:1 adduct. The product is a white solid with dissociation pressure at room temperature (25°) of 1 mm. Coordinated trifluoroborane can be removed slowly with pump-

ing. On standing at room temperature for an extended period of time, decomposition other than by dissociation apparently occurs as indicated by the formation of a solid residue, slightly yellowed, which does not move under extended pumping in the vacuum line.

The infrared spectrum of $F_3B \cdot (CH_3)_2NAsF_2$ was obtained by preparing the compound on the KBr windows of a low-temperature cell. The resulting spectrum was very similar to that observed for $F_3B \cdot (CH_3)_2NPF_2$. In the arsine adduct, the peak observed in pure, solid $(CH_3)_2NAsF_2$ at 2800 cm⁻¹ had disappeared and a very weak peak at 2880 cm⁻¹ was observed. The entire spectrum in the C–H region was dramatically reduced in intensity from that of the uncoordinated compound. This is apparently a result of constraint on vibrational motion in the solid phase and was also observed in the phosphine case.[9] The spectra of the free arsine ligand and of the BF_3 adduct were also obtained in CCl_4 solution at room temperature. Some decomposition of the adduct is expected under the latter conditions but there was nonetheless clear evidence of a dramatic reduction of intensity of the 2800-cm⁻¹ peak in the coordinated species. This peak at about 2800 cm⁻¹ appears to be a reliable indicator of whether the nitrogen in a CH_3N group is coordinated.[5,7,10] Its

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(8) $(CH_3)_2NAsF_2$ was reported by G. Olah and A. Oswald, *Can. J. Chem.*, **38**, 1428 (1960). We were unsuccessful in our attempts to reproduce this work, presumably at the separation stage. Small quantities are conveniently prepared by the method described here.

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(10) J. T. Braunholtz, E. A. V. Ebsworth, J. G. Mann, and N. Sheppard, *J. Chem. Soc.*, 2780 (1958).