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Diphenylselenoarsinous and Diphenyldiselenoarsinic Acid Piperidinium Salts: Selective Synthesis, Isolation, Characterization, Structure, and Reaction

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Diphenylselenoarsinous and diphenyldiselenoarsinic acid piperidinium salts were synthesized and characterized spectroscopically and crystallographically.

Introduction

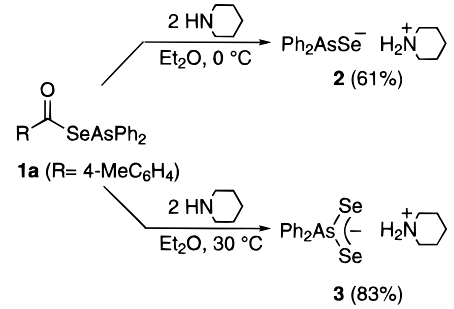
Molecules with bonds between heavy main group elements are of interest due to their synthetic and structural implications. However, little is known about organoarsenic chalcogenolate anion species, such as R_2AsE^- (E = S, Se, Te), which are some of the simplest reagents for introducing the arsenic−chalcogen framework into molecules.[1,2] The reactions of alkali metal diorganoarsanides with elemental chalcogens are a possible route for the preparation of diorganoarsenic chalcogenolate anion species. In our experiments, the preparation of $R_2AsE^-M^+$ (E = S, Se, Te; M = alkali metals) by reacting elemental chalcogens with $R_2As^-M^+$ appeared to be impractical. In the course of studies concerning chalcogenocarboxylic acid derivatives, we observed that the bonds between the carbonyl carbon and chalcogen atoms are readily cleaved by nucleophiles such as alkali metal alkoxides and amines.[3−5] This stimulated us to prepare diorganoarsenic chalcogenolate anion species. We describe here the selective syntheses of diphenylselenoarsinous (**2**) and diphenyldiselenoarsinic acid piperidinium salts (**3**) along with their isolation, characterization, structure, and reactions.

Results and Discussion

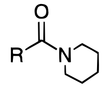
Table 1. Reaction of *Se*−Diphenylarsanyl Selenoester 1a with Piperidine

	conditions		yield, %				
entry	solv.	temp, °C	**2**	**3**	**4**	**5**	**6**
1	Et_2O	0	61	0	62	0	0
2		30	0	83	62	34	0
3		20	∼5	72	60	∼10	0
4		0	*a*	*a*	*a*	0	30
5		30	*a*	*a*	*a*	0	21

[a] Not determined.



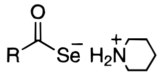
(1)



4

$Ph_2AsAsPh_2$

5



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Selective Synthesis of Diphenylselenoarsinous (2) and Diphenyldiselenoarsinic Acid Piperidinium Salts (3). Selective synthesis of the salts **2** and **3** was effected from the reaction of *Se*−diphenylarsanyl selenoester **1a**[5b] with piperidine by control of the reaction temperature (0 or 30 ° C) (eq 1, Table 1).[6] Thus, at 0 °C the reaction gave the diphenylselenoarsinous acid piperidinium salt (**2**, 61%) as pale yellow needles. The corresponding piperidide **4** (62%) was also obtained from the resulting filtrate. The same reaction performed at 30 °C (entry 2) gave the diphenyldiselenoarsinic acid piperidinium salt (**3**, pale yellow prisms, 82%) along with piperidide **4** (62%) and diarsane **5** (34%). The salt of **2** could not be detected in the crude products spectroscopically. The reaction, when carried out at 20 °C (entry 3), led to results similar to those in entry 2. Other amines, $PhCH_2NH_2$, $PhNH_2$, Et_2NH, and *i*-Pr_2NH, also reacted with **1a** in this manner, but isolation of the desired ammonium salts (**2** or **3**) failed due to

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(1) (a) Agos, L.; Burford, N.; Cameron, T. S.; Curtis, J. M.; Richardson, J. F.; Robertson, K. N.; Yhard, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 3225. (b) *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: New York, 1994. (c) du Mont, W.-W.; Hensel, R.; Kubiniok, S.; Lange, L. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 2, Chapter 15, pp 591−656. (d) Barton, D. H. R.; Dadoun, H.; Gourdon, A. *Nouv. J. Chim.* **1982**, *6*, 53. (e) Coucouvanis, D. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley & Sons: New York, 1979; Vol. 26, pp 301−469; 1970; Vol. 11, pp 233−371. (f) Manoussakis, G. E.; Tsipis, C. A.; Hadjikostas, C. C. *Can. J. Chem.* **1975**, *53*, 1530.

(2) See the preparation and some of the reactions of $R_2As^-M^+$: Doak, G. O.; Freedman, L. D. *Synthesis* **1974**, 328.

(3) Unpublished results. See: (a) Kageyama, H.; Kido, K.; Kato, S.; Murai, T. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1083 and references therein.

(4) Ishihara, H.; Yoshimi, M.; Hara, N.; Ando, H.; Kato, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 835.

(5) (a) Kanda, T.; Koike, T.; Kagohashi, S.; Mizoguchi, K.; Murai, T.; Kato, S. *Organometallics* **1995**, *14*, 4975. (b) Kanda, T.; Mizoguchi, K.; Koike, T.; Murai, T.; Kato, S. *Synthesis* **1994**, 282. (c) Kanda, T.; Mizoguchi, K.; Koike, T.; Murai, T.; Kato, S. *J. Chem. Soc., Chem. Commun.* **1993**, 1631.

(6) Similarly, the reaction using other esters **1** ($RCOSePh_2$, R = 4-$MeOC_6H_4$, 3-Cl-2,6-$(MeO)C_6H_2$, 4-ClC_6H_4) successfully proceeded, whereas the desired salts **2** and **3** could not be isolated.

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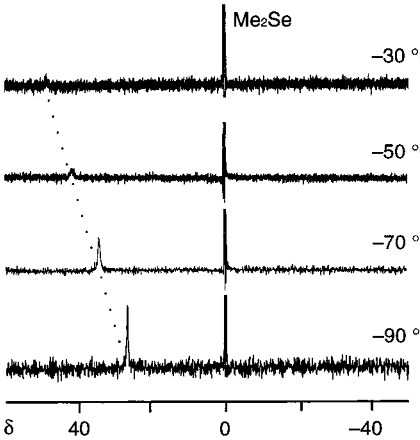

Figure 1. Variable low-temperature ^{77}Se NMR (^{1}H-coupled) spectra for **2** taken in THF-d_8.

difficulties in purification of the products. The reaction was also dependent upon the concentration of piperidine in the reaction solution (entries 4 and 5). When an ether solution of piperidine was added very rapidly at 0 or 30 °C to the solution of **1a**, the corresponding selenoic acid piperidinium salt **6** was obtained and the desired salts **2** and **3** were produced only in a very small amount.

Assignments of **2** and **3** were established by IR and ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy. The salt of **3** was characterized in a similar manner. No examples of the isolation of selenoarsinous and diselenoarsinic acid salts have been reported thus far.[1,7]

The salts of **2** and **3** were pale yellow needles and prisms, respectively, thermally labile and unstable toward oxygen. For example, upon exposure to air at 20 °C, they completely decomposed within a few hours into a complex mixture containing amorphous selenium. However, these salts could be stored at −20 °C under an argon atmosphere without decomposition for a few months.

In the ^{77}Se NMR (^{1}H-coupled) spectra, the broad signal due to the selenium atom of **2** at −90 °C broadened with an increase in temperature and disappeared completely at temperatures higher than −50 °C (Figure 1). Moreover, in the ^{1}H NMR spectra, a broad ammonium proton signal was observed in aprotic polar solvents (δ 6.80−8.00 ($CDCl_3$) and 8.50−9.00 (THF)).[8] Similar temperature and solvent effects were observed in the ^{77}Se (^{1}H-coupled) and ^{1}H NMR spectra of **3** (see Experimental Section), respectively. These results suggest an interaction between selenium and the piperidinium proton atoms in the solutions of salts **2** and **3**.

X-ray Crystal Structure. The structures of salts **2** and **3** were determined by X-ray crystallography.[9,10]

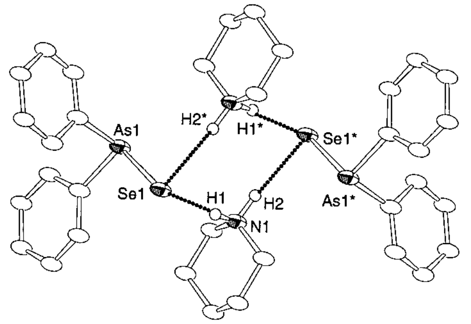

Figure 2. ORTEP drawing for **2** showing all non-hydrogen atoms at the 50% probability level (hydrogen bonding ···).

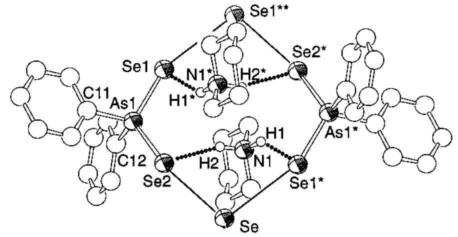

Figure 3. ORTEP drawing for **3** showing all non-hydrogen atoms at the 50% probability level (hydrogen bonding ···; intermolecular interaction —).

ORTEP drawings of **2** and **3** are shown in Figures 2 and 3, respectively. Selected bond lengths and angles are listed in Table 2. The structure determined for **2** shows that it exists as a dimer in the solid state, where the nonbonding contacts between Se1 and N1 or N1* are shorter than the sum of the van der Waals radii of these two atoms (ca. 3.5 Å).[11] This clearly indicates the presence of N−H···Se hydrogen bonding between the molecules.[12,13] Since these hydrogen bonds are almost linear (∠N1−H1···Se1= 174.33°, ∠N1*−H2*···Se1= 163.86°), a Coulombic interaction would play an important role in the bonding.[14] The salt of **3** exists as a dimer, in which each selenium is bridged by N−H···Se

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(7) Only one short description has appeared, ref 1c, which refers to the preparation of $Me_2As(Se)SeNa$ from the corresponding sodium cacodylate and H_2Se in EtOH. However, no details concerning the preparation and spectrum of the salt has been described. See the sulfur analogues: Kuchen, W.; Förster, M.; Hertel, H.; Höhn, B. *Chem. Ber.* **1972**, *105*, 3310.

(8) In the ^{1}H NMR spectra, the signals due to the ammonium protons of **2** and **3** were not observed in CD_3OD and $(CD_3)_2CO$, respectively.

(9) Selected crystallographic data for **2**: $C_{17}H_{22}AsNSe$; $M_n = 394.25$, $P2_1/c$ (No. 14), $a = 6.521(3)$ Å, $b = 16.908(6)$ Å, $c = 15.484(5)$ Å, $\beta = 92.61(3)°$, $V = 1705.3(10)$ Å^3, $Z = 4$, $F(000) = 792.00$, $\rho_{calc} = 1.535$ g cm^{-3}, μ(Mo Kα) 41.20 cm^{-1}; R (R_w) = 0.075 (0.086), GOF = 2.49. A total of 4412 reflections ($2\theta_{max} = 55.0°$) were collected at 193 K.

(10) Selected crystallographic data for **3**: $C_{17}H_{22}AsNSe_2$; $M_n = 473.21$, $P2_1/n$ (No. 14), $a = 6.850(1)$ Å, $b = 17.545(2)$ Å, $c = 15.786(2)$ Å, $\beta = 97.22(1)°$, $V = 1882.1(4)$ Å^3, $Z = 4$, $F(000) = 928.00$, $\rho_{calc} = 1.670$ g cm^{-3}, μ(Cu Kα) 67.98 cm^{-1}; R (R_w) = 0.041 (0.062), GOF = 2.33. A total of 3189 reflections ($2\theta_{max} = 120.1°$) were collected at 296 K.

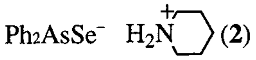
(11) (a) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr.* **1985**, *B41*, 274. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(12) Few examples of N−H···Se hydrogen bonding are known. They almost all contain a polarized selenocarbonyl selenium atom (selenourea, dimethylselenourea, 1-benzoyl-3-phenyl-2-selenourea, 3-carbamoyl-4-phenyl-1,3-oxazolidine-2-selone, diselenouracil, and *N*-phenyl-*N′*-benzoylselenourea): (a) Wu, R.; Hernández, G.; Odom, J. D.; Dunlap, R. B.; Silks, L. A. *J. Chem. Soc., Chem. Commun.* **1996**, 1125. (b) Pathiana, H. M. K. K.; Weiss, T. J.; Reibenspies, J. H.; Zingaro, R. A.; Meyers, E. A. *Z. Kristallogr.* **1994**, *209*, 697. (b) Rauchfuss, T. B. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Chapter 6, pp 339−347. (c) Rutherford, J. S.; Calvo, C. *Z. Kristallogr.* **1969**, *128*, 229 and references cited threin. (d) Hope, H. *Acta Crystallogr.* **1965**, *18*, 259. Very recently, linear N−H···Se hydrogen bonding in $[Mn(en)_3]_2[Mn_4(en)_9Sb_4Se_{16}]$ has been reported, see: (e) Bensch, W.; Näther, C.; Schur, M. *J. Chem. Soc., Chem. Commun.* **1997**, 1773.

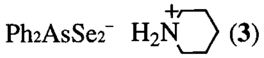
(13) C−H···Se hydrogen bonding: (a) Iwaoka, M.; Komatsu, H.; Tomoda, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1825. (b) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *114*, 4463. O−H···Se hydrogen bonding: (c) Green, D. C.; Eichhorn, B. W. *J. Solid State Chem.* **1995**, *120*, 12. (d) Chekhlov, A. N.; Zavorin, S. I.; Lermontov, S. A.; Zefirov, A. N. S. *Dokl. Akad. Nauk SSSR* **1991**, *319*, 671; *Chem. Abstr.* **1991**, *115*, 291696a. (e) Derkosch, J.; Mikenda, W.; Baumgartner, O.; Mereiter, K.; Preisinger, A. *J. Raman Spectrosc.* **1986**, *17*, 75. (f) Lutskii, A. E.; Mitichkin, A. I.; Marchenko, T. N.; Sheremet′eva, G. I. *Zh. Obshch. Khim.* **1976**, *46*, 1103.

(14) Taylor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320 and references therein.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Salts 2 and 3

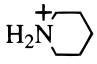
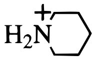

$Ph_2AsSe^-\ H_2N^+$ (2)

Selected Bonds			
Se(1)–As(1)	2.341(2)	Se(1)•••N(1)	3.34(1)
Se(1)•••N(1*)	3.39(1)	Se(1)•••H(1)	2.402
Se(1)•••H(2*)	2.424		
Selected Angles			
Se(1)–As(1)–C(11)	103.4(4)	Se(1)–As(1)–C(21)	99.6(4)
C(11)–As(1)–C(21)	98.6(6)	As(1)–Se(1)•••H(1)	95.38
As(1)–Se(1)•••H(2*)	91.05	N(1)–H(1)•••Se(1)	174.33
N(1)–H(2*)•••Se(1)	163.86		


$Ph_2AsSe_2^-\ H_2N^+$ (3)

Selected Bonds			
Se(1)–As(1)	2.2498(7)	Se(2)–As(1)	2.2637(8)
Se(1)•••N(1*)	3.608(6)	Se(2)•••N(1)	3.463(6)
Se(1)•••H(1*)	2.805	Se(2)•••H(2)	2.582
Se(1*)•••Se(1**)	3.396(1)	Se(1**)•••Se(2*)	3.5402(9)
Selected Angles			
Se(1)–As(1)–Se(2)	114.49(3)	Se(1)–As(1)–C(11)	110.6(1)
Se(2)–As(1)–C(11)	109.4(1)	Se(1)–As(1)–C(21)	110.8(1)
Se(1)–As(1)–C(21)	110.3(1)	As(1)–Se(2)•••H(2)	86.2
N(1*)–H(1*)•••Se(1)	142.9	N(1)–H(2)•••Se(2)	155.0
As(1)–Se(1)•••Se(1**)	157.55(3)	Se(1)•••Se(1**)•••Se(2*)	93.30(2)

Table 3. Reactions of 2 and 3 with RC(O)Cl and Ph_2AsCl

	salt		chloride (E-Cl)	product	
run[a]		no.	E	no.	yield, %
1	Ph_2AsSe^- 	2	2-$MeC_6H_4C(O)$	**1b**	84
2			4-$ClC_6H_4C(O)$	**1c**	43
3			4-$BrC_6H_4C(O)$	**1d**	88
4			Ph_2As	**7**	quant
5	$Ph_2AsSe_2^-$ 	3	2-$MeC_6H_4C(O)$	**1b**	42
6			4-$ClC_6H_4C(O)$	**1c**	52
7			4-$BrC_6H_4C(O)$	**1d**	26
8			Ph_2As	**7**	quant

[a] In the reaction of **3** (entries 5–8), the yield of deposited amorphous selenium was not determined.

hydrogen bonding, similar to that of **2**.[11] Salt **3** also has an eight-membered ring structure achieved by means of an intermolecular Se•••Se interaction (nonbonding interaction)[11,15] along with the hydrogen bonding. No examples of N–H•••Se hydrogen bonding involving a selenium anion have appeared in the literature.[12] In addition, such an eight-membered ring structure involving triselenide linkages (Se–Se–Se) has not been described.[16]

The arsenic centers of **2** and **3** are in a tetrahedral environment with As–Se bond distances of 2.341(2) and 2.257 Å (average), respectively. Considering the As–Se bond lengths of the latter salt, the lengths of **3** are almost equal and shorter than that of an ordinary As–Se single bond, suggesting the possibility that the negative charge is located equally on the two selenium atoms of **3**.[17]

Reaction of 2 and 3 with RC(O)Cl and Ph_2AsCl. Reactions of piperidinium salts **2** and **3** with RC(O)Cl (R = 2-MeC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4) and Ph_2AsCl were examined (eqs 2 and 3, Table 3). The salt of **2** reacts

$$\mathbf{2} \xrightarrow[\text{Et}_2\text{O, 0 °C, 3.5 h}]{\text{E-Cl}} \underset{\mathbf{1}\text{ or }\mathbf{7}}{Ph_2AsSe\text{-}E} \qquad (2)$$

$$\mathbf{3} \xrightarrow[\text{Et}_2\text{O, 0 °C, 3.5 h}]{\text{E-Cl}} \underset{\mathbf{1}\text{ or }\mathbf{7}}{Ph_2AsSe\text{-}E} \qquad (3)$$

E: 2-$MeC_6H_4C(O)$, 4-$ClC_6H_4C(O)$, 4-$BrC_6H_4C(O)$, Ph_2As

with the chlorides at 0 °C in ether to give the corresponding selenoarsinous acid derivatives **1b–d** (entries 1–3) or **7** (entry 4). No deposition of amorphous selenium was observed during the reaction. In contrast to the reaction of **2**, salt **3** gave **1b–d** (entries 5–7) or **7** (entry 8) and amorphous selenium was deposited in every case.

Mechanism. The reaction in eq 1 is dependent upon both the concentration of piperidine in the reaction medium and on the reaction temperature. Presumably, an equilibrium process would be obtained in the initial reaction stage. In the kinetically determined process, piperidine attacks the arsenic atom of **1** to generate transient selenoic acid **8**,[18] which is deprotonated by the excess of piperidine used to give the corresponding salt **6**, in the case of entry 8 in Table 1. Alternatively, piperidine attacks the carbonyl atom of **1** in the thermodynamically determined process to give the salt of **2** and piperidide **4**. When the reaction was carried out at 30 °C, diarsane **5** was obtained, suggesting the possibility of disproportionation of **2** to **3**. To clarify this, **2** in ether was heated at 30 °C for 24 h with stirring (eq 4). *Se*–Arsanyl ester **1a** (60%), **4** (100%), and **5** (37%) were obtained after addition of 4-$MeC_6H_4C(O)Cl$, indicating that the disproportionation of **2** to **3** takes

$$\mathbf{2} \xrightarrow[\text{Et}_2\text{O, 30 °C, 24 h}]{} \xrightarrow[\text{0 °C, 3.5 h}]{\text{4-MeC}_6\text{H}_4\text{C(O)Cl}} \mathbf{1a}\ (60\%) + \mathbf{4}\ (100\%) + \mathbf{5}\ (37\%) + \text{Se} \qquad (4)$$

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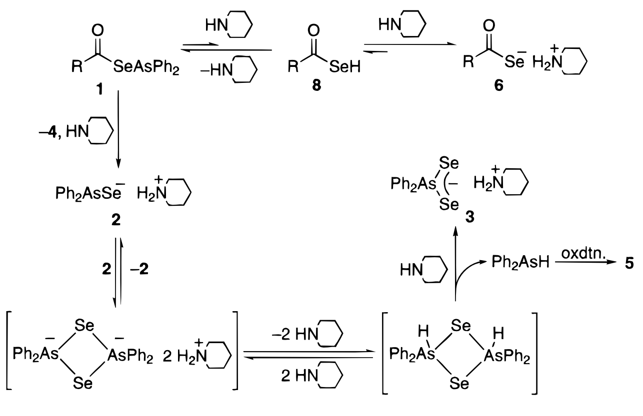
[15] Intermolecular nonbonded contact of Se•••Se is shorter than the sum of the van der Waals radii of selenium (3.80 Å).[11]

[16] Eight-membered ring structures involving As–Se–As linkages have been reported, see: (a) Smith, D. M.; Park, C.-W.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 6682. (b) Ansari, M. A.; Ibers, J. A.; O'Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Polyhedron* **1992**, *11*, 1877. (c) Mercier, H. P.; Angilella, V. E.; Belin, C. H. *Nouv. J. Chim.* **1990**, *14*, 121. (d) Angilella, V. E.; Mercier, H. P.; Belin, C. H. *J. Chem. Soc., Chem. Commun.* **1989**, 1654.

[17] The ordinary length of an As–Se single bond is ca. 2.3–2.4 Å, see: (a) Meyers, E. A.; Applegate, C. A.; Zingaro, R. A. *Phosphorus, Sulfur, and Silicon* **1987**, *29*, 317. (b) Sheldrick, W. S.; Kaub, J. *Z. Naturforsch.* **1985**, *40B*, 1020. (c) Thiele, G.; Rotter, H. W. *Ibid.* **1984**, *39B*, 1344. Zavodnick et al. performed an X-ray investigation of Et_3AsSe and *i*-$Pr_2PhAsSe$ for which the bond lengths of Se–As were 2.234 and 2.227 Å, respectively, see (d) Zavodnik, V. E.; Abalonin, B. E.; Bel'skii, V. K. *Metaloorg. Khim.* **1992**, *5*, 439; *Chem. Abstr.* **1992**, *117*, 191960e.

[18] The isolation and characterization of RC(O)SeH has already been reported, see: Kageyama, H.; Murai, T.; Kanda, T.; Kato, S. *J. Am. Chem. Soc.* **1994**, *116*, 2195.

Scheme 1



place when the reaction temperature is raised.[19] These observations lead us to the plausible reaction mechanism shown in Scheme 1. The mechanism is compatible with the fact that piperidide **4** is produced in the reaction of eq 4.

Experimental Section[20]

Materials. The materials are commercially available except 4-methylbenzoic diphenylarsinous anhydroselenide (**1a**).[5b] Piperidine, diethyl-, isopropyl-, and benzylamine, and aniline were purified by the published literature.[21] AcOEt was distilled from P_2O_5. Et_2O and hexane were refluxed with sodium metal and distilled before use.

X-ray Structural Analysis. The structures for **2** and **3** were solved and refined using the teXsan crystallographic software package on an IRIS Indigo work station (SGI). X-ray quality crystals of **2** and **3** were obtained by slow diffusion of hexane into ethyl acetate solutions of each of the samples. The crystals used were cut off from the grown crystals. Because samples **2** and **3** were unstable in the air, the crystals mounted on a glass fiber were coated with an epoxy resin. The cell dimensions were determined by a least-squares refinement of the diffractometer angles for 25 automatically centered reflections. An empirical absorption correction (DIFABS)[22] was applied. The structure was solved by direct methods (SHELX86)[23] and expanded using DIRDIF.[24] Scattering factors for neutral atoms were from Cromer and Waber,[25] and anomalous dispersion[26] was used. A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least-squares cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times that of the connecting atom.

Synthesis of Diphenylselenoarsinous Acid Piperidinium Salt (2) (Entry 1 in Table 1). Into a dried 200-mL three-necked flask containing a stir bar (henceforth "standard apparatus") was added **1a** (R = 4-MeC_6H_4, 0.654 g, 1.5 mmol) and Et_2O (40 mL) at 0 °C. To this solution, an ether solution (5 mL) of piperidine (0.261 g, 3.1 mmol) was added dropwise using a dropping funnel, with stirring over 5 min. The solvent was removed under reduced pressure followed by stirring at the same temperature for 1.5 h. On recrystallization from a mixed solvent (AcOEt/hexane = 2/1, 18 mL), pure **2** (0.333 g, 61%) was obtained as pale yellow needles. Piperidide **4** (0.189 g, 62%) was obtained from the resulting filtrate.

Synthesis of Diphenyldiselenoarsinic Acid Piperidinium Salt (3) (Entry 2 in Table 1). The standard apparatus was charged with **1a** (R = 4-MeC_6H_4, 1.772 g, 4.1 mmol) and Et_2O (100 mL) at 0 °C. To this solution, an ether solution (15 mL) of piperidine (0.706 g, 8.3 mmol) was added dropwise, with stirring over 5 min. The solvent was removed under reduced pressure followed by stirring at the same temperature for 1.5 h. Recrystallization from a mixed solvent (AcOEt/hexane = 2/1, 45 mL) gave pure **3** (0.809 g, 83%) as pale yellow prisms. Piperidide **4** (0.809 g, 62%) and tetraphenyldiarsane (**5**, 0.160 g, 34%) were obtained from the filtrate.

General Procedure for Trapping of 2 with Carboxylic Acid Chlorides (Table 3, Entries 1−3). The standard apparatus was charged with **2** (0.5 mmol) and Et_2O (5 mL) at 0 °C. To this solution, an ether solution (1 mL) of the acid chloride (0.5 mmol) was added at 0 °C. After the mixture was stirred at 0 °C for 3.5 h, the precipitate (piperidinium chloride) was filtered with a sintered glass filter. The filtrate was evaporated under reduced pressure (20 °C/2 Torr). Recrystallization of the resulting solid from a mixed solvent (Et_2O/AcOEt = 1/1) gave diphenylselenoarsinous anhydroselenides **1** in 40−90% yields.

Trapping of 2 with Ph_2AsCl (Table 3, Entry 4). In a 20-mL two-necked flask, **2** (0.243 g, 0.6 mmol), Et_2O (5 mL), and a stir bar were placed at 0 °C. To this solution, an ether solution (2 mL) of Ph_2AsCl (0.137 g, 0.6 mmol) was added at 0 °C. After the mixture was stirred at 0 °C for 3.5 h, the resulting precipitate (piperidinium chloride) was filtered. The filtrate was evaporated under reduced pressure (20 °C/2 Torr) to give **7** in quantitative yield (^1H and ^{13}C NMR analysis).

General Procedure for Trapping of 3 with Carboxylic Acid Chlorides (Table 3, Entries 5−7). In a 20-mL two-necked flask, **3** (0.5 mmol), Et_2O (5 mL), and a stir bar were placed at 0 °C. To this solution, an ether solution (1 mL) of carboxylic acid chloride (0.5 mmol) was added at 0 °C. After the mixture was stirred at 0 °C for 3.5 h, amorphous selenium was gradually deposited. The resulting precipitates (piperidinium chloride and amorphous selenium) were filtered. The filtrate was evaporated under reduced pressure (20 °C/2 Torr). Recrystallization of the solid with a mixed solvent (Et_2O/AcOEt = 1/1) gave carboxylic diphenylselenoarsinous anhydroselenides **1** in 20−50% yields.

Trapping of 3 with Ph_2AsCl (Table 3, Entry 8). In a 20-mL two-necked flask, **3** (0.223 g, 0.47 mmol), Et_2O (5 mL), and a stir bar were placed at 0 °C. To this solution, an ether solution (2 mL) of Ph_2AsCl (0.126 g, 0.47 mmol) was added at 0 °C. After the mixture was stirred at 0 °C for 3.5 h, amorphous selenium was gradually deposited. The resulting precipitate (piperidinium chloride and amorphous selenium) was filtered. The filtrate was evaporated under reduced pressure (20 °C/2 Torr) to give **7** in quantitative yield (^1H and ^{13}C NMR analysis).

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(19) In eq 4, several attempts to isolate the salt of **3** failed.

(20) Melting points were determined using a Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured on a Perkin-Elmer FT-IR 1640 spectrophotometer. The ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL α-400 spectrometer with Me_4Si as an internal standard. ^{77}Se NMR (76 MHz) spectra were measured on the same spectrometer with Me_2Se as an external reference. The mass spectra were recorded on a Shimadzu GCMS QP1000 (EI mode) mass spectrometer. The high-resolution mass spectroscopy (HRMS) was performed on a Shimadzu GCMS 9020 high-resolution mass spectrometer. Elemental analyses were performed by the Analytical Center of Kyoto University. X-ray structural analyses of **2** and **3** were performed on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα (λ = 0.710 69 Å) and Cu Kα (λ = 1.541 78 Å) radiation at −80 and 23 °C, respectively. All manipulations were carried out under an argon atmosphere.

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Disproportionation of 2 to 3 (Eq 4). In a 30 mL two-necked flask, **2** (0.116 g, 0.3 mmol), ether (12 mL), and a stir bar were placed at 0 °C. This suspension was heated at 30 °C for 24 h with stirring. After the mixture was cooled to 0 °C, 4-methylbenzoyl chloride (0.045 g, 0.3 mmol) was added to the above solution and stirred at 0 °C for 3.5 h (amorphous selenium was gradually deposited). Removal of the solvent under reduced pressure (20 °C/2 Torr) followed by filtration of the resulting precipitate gave a mixture containing **1a** (60%), **4** (100%), and **5** (37%), whose yields were determined by ^{1}H NMR analysis.

4-Methylbenzoic Diphenylarsinous Anhydroselenide (1a).[5b] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.36 (s, 3 H, CH_3), 7.20 (d, $J = 8.1$ Hz, 2 H, Ar), 7.22−7.34 (m, 6 H, Ar), 7.54−7.61 (m, 4 H, Ar), 7.85 (d, $J = 8.1$ Hz, 2 H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.7, 128.4, 128.8, 129.1, 129.4, 133.7, 136.6, 138.1, 144.8, 192.8.

2-Methylbenzoic Diphenylarsinous Anhydroselenide (1b).[5b] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.40 (s, 3 H, CH_3), 7.05−7.90 (m, 14 H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.8, 125.7, 128.9, 129.0, 129.3, 129.6, 132.0, 133.3, 133.5, 137.8, 139.1, 192.6.

4-Chlorobenzoic Diphenylarsinous Anhydroselenide (1c).[5b] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32−7.38 (m, 6 H, Ar), 7.41 (d, $J = 8.8$ Hz, 2 H, Ar), 7.56−7.63 (m, 4 H, Ar), 7.90 (d, $J = 8.8$ Hz, 2 H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.9, 129.0, 129.3, 129.6, 133.3, 133.7, 137.6, 140.2, 190.8.

4-Bromobenzoic Diphenylarsinous Anhydroselenide (1d). Mp: 118−120 °C (dec). IR (KBr): 1637 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31−7.39 (m, 6 H, Ar), 7.56 (d, $J = 8.5$ Hz, 2 H, Ar), 7.57−7.63 (m, 4 H, Ar), 7.81 (d, $J = 8.5$ Hz, 2 H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.9, 129.0, 129.3, 129.6, 132.0, 133.7, 137.8, 137.9, 192.6. Anal. Calcd for $C_{19}H_{14}AsBrOSe$: C, 46.37; H, 2.87. Found: C, 46.61; H, 2.99.

Diphenyldiselenoarsinous Acid Piperidinium (2). Pale yellow needles: mp 111.5−145.0 °C (dec). IR (KBr): 2926, 2672, 2473, 2379, 1560, 1466, 1430, 1383, 1302, 1165, 1073, 1022, 744, 734, 694, 483, 455 cm^{-1}. ^{1}H NMR (THF-d_8, 400 MHz): δ 1.71−1.79 (m, 2 H, piperidine), 1.86−1.96 (m, 4 H, piperidine), 3.05−3.17 (m, 4 H, piperidine), 7.38−7.56 (m, 6 H, Ar), 7.95−8.23 (m, 4 H, Ar), 8.50−9.00 (brs, 2 H, NH_2). ^{13}C NMR (THF-d_8, 100 MHz): δ 23.6, 23.9, 44.7, 128.2, 128.6, 133.6, 133.7. ^{77}Se NMR (THF-d_8, 76 MHz): δ 27.1 (−90 °C), 32.5 (−70 °C), 41.8 (−50 °C), (−30 °C). Anal. Calcd for $C_{17}H_{22}AsNSe$: C, 51.79; H, 5.62. Found: C, 51.41; H, 5.36.

Diphenyldiselenoarsinic Acid Piperidinium (3). Pale yellow prisms: mp 140.0−167.5 °C (dec). IR (KBr): 2939, 2670, 2479, 2370, 1560, 1434, 1274, 1073, 1022, 734, 694, 483 cm^{-1}. ^{1}H NMR (THF-d_8, 400 MHz): δ 1.85−1.90 (m, 2 H, piperidine), 2.00−2.08 (m, 4 H, piperidine), 3.55−3.58 (m, 4 H, piperidine), 5.90−6.75 (brs, 2 H, NH_2), 7.51−7.60 (m, 6 H, Ar), 8.37−8.39 (m, 4 H, Ar). ^{13}C NMR (THF-d_8, 100 MHz): δ 22.3, 22.6, 44.3, 128.2, 129.9, 130.0, 141.3. ^{77}Se NMR (THF-d_8, 76 MHz): δ 26.4 (−90 °C), 33.7 (−70 °C), 41.9 (−50 °C), (−30 °C). Anal. Calcd for $C_{17}H_{22}AsNSe_2$: C, 43.15; H, 4.69. Found: C, 43.34; H, 4.61. In the ^{1}H NMR spectra, a broad ammonium proton signal was observed in aprotic polar solvents (δ 6.95−7.95 ($CDCl_3$) and δ 5.90−6.75 (THF)).[8]

***N*-4-Methylbenzoylpiperidine (4).** Assignment of this compound was established by the comparison of the ^{1}H and ^{13}C NMR spectra with those of the sample prepared from the corresponding carboxylic acid chloride and piperidine: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40−1.70 (br, 6 H, piperidine), 2.37 (s, 3 H, CH_3), 3.20−3.85 (br, 4 H, piperidine), 7.19 (d, $J = 7.9$ Hz, 2 H, Ar), 7.29 (d, $J = 7.9$ Hz, 2 H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 21.3, 24.6, 43.2, 48.4, 126.9, 133.6, 139.4, 170.5.

Tetraphenyldiarsane (5).[27] Mp: 130−131 °C (lit. 129−130 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43−7.49 (m, 12 H, Ar), 7.51−7.57 (m, 8 H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 129.2, 130.7, 133.6, 139.4; MS (rel intensity) m/z 458 (M^+, 3), 229 (27), 152 (100).

4-Methylbenzenecarboselenoic Acid Piperidinium Salt (6). Pale yellow crystals; mp 76−83 ° C (dec). IR (KBr): 3130, 2993, 1608, 1588, 1517, 1398, 1206, 1173, 1120, 910, 835 $^{-1}$. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.48−1.63 (m, 2 H, piperidine), 1.68−1.96 (m, 4 H, piperidine), 2.35 (s, 3 H, CH_3), 3.10−3.29 (m, 4 H, piperidine), 7.15 (d, $J = 7.8$ Hz, 2 H, Ar), 8.13 (d, $J = 7.8$ Hz, 2 H, Ar), 8.37−9.27 (br, 2 H, NH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 22.2, 22.4, 44.6, 128.2, 128.8, 141.8, 142.9, 215.6.

Bis(diphenylselenoarsinous) Anhydroselenide (7). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.11−7.16 (m, 12 H, Ar), 7.38−7.45 (m, 8 H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.6, 128.8, 133.2, 140.3. ^{77}Se NMR ($CDCl_3$, 76 MHz): δ 161.8. HRMS calcd for $C_{24}H_{20}As_2{}^{80}Se$ 537.9162, found 537.9155.

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Supporting Information Available: Tables of crystallographic data (positional and thermal parameters and bond distances and angles) for **2** and **3** (25 pages). Ordering information is given on any current masthead page.

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