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Sulfur and Selenium Derivatives of 2-Phosphaindolizines

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ABSTRACT: *The 2-phosphaindolizines* **1** *react with hydrogen sulfide and elemental sulfur to give the new zwitterionic heterocyclic systems* **2** *of the N-pyridiniomethyl dithiophosphinate type. In contrast, no reaction is observed with sulfur alone. MeI methylates* **2e,f** *at sulfur. The analogous pyridiniodiselenophosphinate* **5** *results from the reaction of* **1a** *with 1,3,2,4-diselenadiphosphetane-2,4-diselenide,* **4a**, *in the absence of an additional base. As a further product, the perselenophosphinic anhydride* **6** *is identified. In the presence of triethylamine,* **1a** *reacts with each of the diselenides* **4a–c** *to give the new triethylammonium diselenophosphinates* **7a–c**, *respectively. This reaction can be extended to 1-aza-2-phosphaindolizine,* **8**, *which yields with each of* **4a,b** *and* NEt_3 *the diselenophosphinates* **9a,b**, *respectively. The anhydride* **6** *and the diselenophosphinates* **7** *and* **9** *result from an electrophilic substitution at the phosphaindolizine ring.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:445–452, 1998

INTRODUCTION

In azaphospholes, the center of reactivity is represented by the dicoordinate phosphorus atom. A large number of 1,1-addition reactions to the phosphorus atom and 1,2-addition reactions of various reagents to the P = C or P = N double bond have been reported [1–4]. The 1,2-additions may or may not be accompanied by an oxidation of the phosphorus atom. In some cases, the 1,2-addition may be followed by a 1,2-elimination, resulting in an overall substitution at the position adjacent to the phosphorus atom in the azaphosphole ring. As many azaphospholes are readily available, this reactivity offers a considerable synthetic potential, which has been used only little so far.

2-Phosphaindolizines have become recently accessible through the [4 + 1]cyclocondensation of 1,2-dialkylpyridinium bromides with phosphorus trichloride in the presence of triethylamine [5–7]. Investigating the reactivity of these heterocycles, we reported their bromination and dichlorophosphinylation at the 1-position [8]. Hydrolysis caused an opening of the azaphosphole ring with formation of zwitterionic phosphinates [5]. Here, we report on the reaction of 2-phosphaindolizines with hydrogen sulfide and elemental sulfur, as well as with 1,3,2,4-di-

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Dedicated to Prof. Dr. Dr. mult. h.c. Heinrich Nöth on the occasion of his seventieth birthday.

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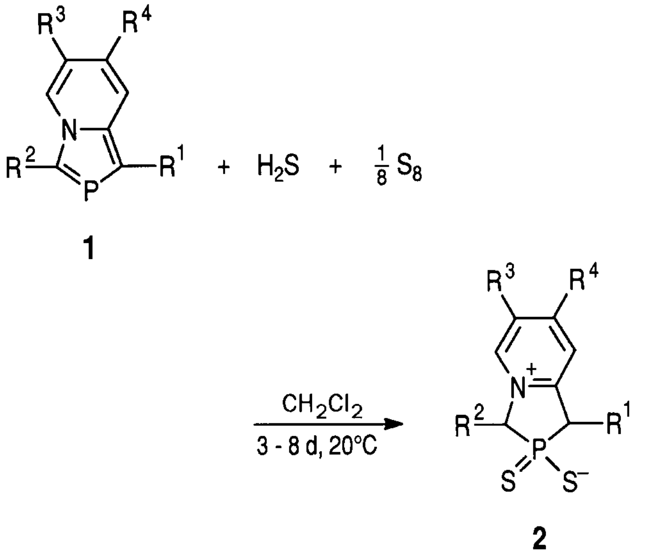
selenadiphosphetane-2,4-diselenides, which provide routes to new dithio- and diselenophosphinates, respectively.

Reaction of 2-Phosphaindolizines with H_2S and Sulfur

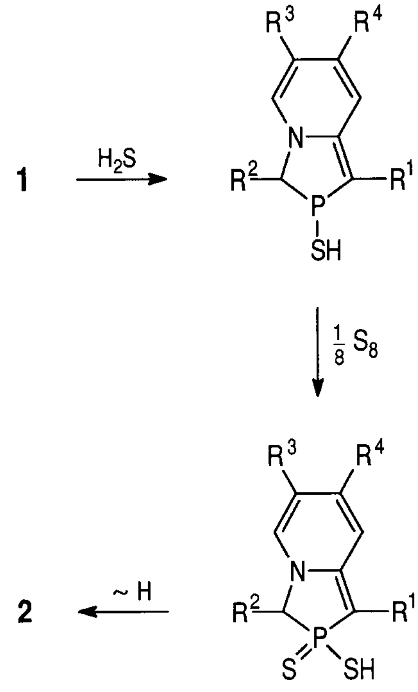
The 2-phosphaindolizines **1a–g** react with hydrogen sulfide and an equimolar amount of elemental sulfur in dichloromethane at ambient temperature to give the new pyridiniodithiophosphinates **2a–g**.



	R^1	R^2	R^3	R^4
a	H	COPh	*n*Bu	H
b	Me	COPh	H	H
c	H	COPh	H	Me
d	Me	CO_2Me	H	H
e	H	COPh	Et	H
f	H	CO*t*Bu	Et	H
g	Me	$4\text{-}NO_2C_6H_4$	H	H

In the case of **1d**, the reaction has to be initiated by addition of a drop of glacial acetic acid. The dithiophosphinates **2** are high melting, sparingly soluble, colorless to pale yellow crystalline solids.

When **1b** is reacted with H_2S alone, the compound **2b** is obtained only in very low yield together with an insoluble pale yellow solid as the main product. No reaction of **1d** with sulfur alone occurs even on refluxing in methylene chloride for several days. These results indicate that the oxidation of the phosphorus atom by sulfur is most probably preceded by the 1,2-addition of hydrogen sulfide to the P=C bond. A 1,3-prototropic shift leads to the zwitteronic heterocycle **2**.



An analogous reaction is reported for thiazolo[2,3-*e*][1,2,4,3]triazaphospholes, which undergo 1,2-addition with hydrogen sulfide, followed by opening of the triazaphosphole ring in each case to give the respective zwitteronic product [9]. The behavior of 2-phosphaindolizines toward H_2S and sulfur resembles that of thiazolo[2,3-*e*][1,2,4,3]triazaphospholes only in part - 1,2-addition and concomitant oxidation of phosphorus occur to form zwitterionic products **2**, but, in contrast, ring opening does not take place.

The identity of each of the heterocycles **2** results from its ^{31}P- and ^{1}H-NMR data (Table 1) and is further supported by the ^{13}C-NMR data of **2a** (Table 2). The increase in coordination number of phosphorus in going from the 2-phosphaindolizines **1** to the dithiophosphinates **2** is accompanied by a high field shift of its NMR signal; $\delta^{31}P$ of **2** falls, with values of 78–95, into the range typical for tetracoordinate phosphorus [10]. In each of the cases **2b, 2d,** and **2g,** formation of two diastereomers is expected due to the presence of a second chiral center at C-1 in addition to that at C-3. In fact, according to the ^{31}P-NMR spectrum, **2d** and **2g** are found to be mixtures of two diastereomers each [**2d:** $\delta^{31}P$ = 92.6 (83%), −84.2 (17%); **2g:** $\delta^{31}P$ = 107.8 (72%), 96.1 (28%)]. Separate ^{1}H-NMR signals of the minor isomer could not be resolved for these compounds except for

TABLE 1 ^{31}P- and ^{1}H-NMR Data[a,b] for the Pyridiniodithiophosphinates **2,** Their Methylation Products **3,** and for the Pyridiniodiselenophosphinate **5** (coupling constants *J* in Hz)

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**3e**	**3f**	**5**
δ^{31}P	78.1	95.0	80.6	92.6, 84.2[e]	80.5	78.8	107.8, 96.1[e]	74.1, 68.0[e]	69.2	23.7
δ^{1}H 1-CH$_2$/1H	4.09, 4.02	3.94	3.86	3.92	3.96	4.13, 3.79	3.84	[c]	4.12	4.48, 4.24
^{2}J(P, H)	10.9, 10.5	15.0	10.2	14.0	10.7	11.2, 11.0	14.0		11.7	11.0, 8.6
^{2}J(H, H)	17.3					14.0				17.1
^{3}J(H, H)		7.5		7.0			7.0			
3-H	6.79	7.04	7.03	5.94	7.02	6.51	7.27	8.41	8.42	7.03
^{2}J(P, H)	9.0	9.0	9.3	9.3	9.0	9.0	6.8	10.0	9.3	7.6
5-H	8.19	8.91	8.68	9.04	8.80	8.29	9.05	9.05, 8.77[e]	9.37	
^{3}J(5-H, 6-H)		7.0	6.3	6.1			6.3			
6-H		7.84	8.03	7.86			8.03			
^{3}J(6-H, 7-H)		7.0		7.0			7.4			
7-H	8.24	8.44		8.49	8.26	8.10	8.57	8.41[d]	8.23	8.09
^{3}J(7-H, 8-H)	8.3	8.0		7.0	8.4	8.3	8.3		8.3	8.3
8-H	7.90	8.12	7.84	7.90	7.92	7.78	8.19	8.02	8.01	
phenyl										
o-H	8.14	8.12	8.03		8.08		8.31	8.15		8.05
m-,*p*-H	7.59, 7.71	7.4–7.6	7.6–7.7		7.5–7.6		7.76	7.6–7.8		7.43, 7.55

[a] In CDCl$_3$/d^6-DMSO except for **2a,5** (CD$_2$Cl$_2$), **2c** (CD$_3$CN/d^6-DMSO), **3c** (CD$_3$CN), and **3f** (CDCl$_3$).

[b] **2a:** $\delta = 2.80$, α-CH$_2$, 1.67, β-CH$_2$, 1.40, γ-CH$_2$, 0.95, Me (*n*-Bu); ^{4}J(5-H, 7-H) = 2.0 Hz. **2b:** $\delta = 1.71$, ^{3}J(P,H) = 18.5 Hz, 1-Me. **2c:** $\delta = 2.56$, 7-Me. **2d:** $\delta = 3.80$, 3.84, CO$_2$Me; 1.66, ^{3}J(P,H) = 18.5 Hz, 1-Me. **2e:** $\delta = 2.78$, CH$_2$, 1.26, Me, ^{3}J(H,H) = 7.6 Hz (Et). **2f:** $\delta = 1.34$ (CO*t*Bu), 2.79, CH$_2$, 1.27, Me, ^{3}J(H,H) = 7.8 Hz (Et). **2g:** $\delta = 1.75$, ^{3}J(P,H) = 17.8 Hz, 1-Me. **3e** $\delta = 2.85$, CH$_2$, 1.27, Me, ^{3}J(H,H) = 8.0 Hz (Et); 2.52, 2.16, ^{3}J(P,H) = 16.7, 16.1 Hz, SMe. **3f:** $\delta = 1.44$, CO*t*Bu; 2.87, CH$_2$ 1.33, Me, ^{3}J(H,H) = 7.6 Hz (Et); 2.65, ^{3}J(P,H) = 17.1 Hz, SMe. **5:** $\delta = 2.68$, α-CH$_2$, 1.55, β = CH$_2$, 1.28, γ-CH$_2$, 0.83, Me, δ^{77}Se = 87.6, ^{1}J(Se,P) = 741.9 Hz, 95.1, ^{1}J(Se,P) = 691.0 Hz.

[c] $\delta = 3.9$–4.7, poorly resolved multipletts.

[d] Overlaps with the signal of 3-H.

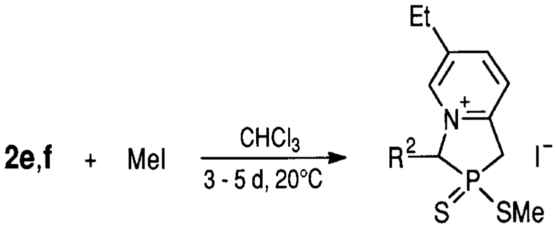
[e] Signal due to the minor diastereomer.

OCH$_3$ in **2d.** In the case of **2b,** however, only one isomer is observed in the reaction mixture as well as in the product after recrystallization.

Characteristic for **2** are the NMR signals of the protons in the 1- and 3-position. The signals of the protons in the 1-position appear at $\delta = 3.8$–4.1. In the 1-unsubstituted derivatives, the two methylene protons are diastereotopic. However, only in the case of **2a** and **2f** are the shift differences large enough for the ^{1}H-NMR spectrum to show the AB-part of a typical ABX spectrum. The signal of 3-H is found at lower field ($\delta = 5.0$–7.3) with a characteristic coupling ^{2}J(P,H) = 9.0–9.5 Hz. Remarkable in the ^{13}C NMR data of **2a** are the unusually low values for $^{1}J_{PC}$ for C-1 and C-3 of 44.6 and 19.4 Hz, respectively.

Methylation of 2e *and* 2f

Both **2e** and **2f** react with an equimolar amount of methyl iodide in chloroform at ambient temperature to give the *S*-methylated heterocycles **3e** and **3f,** respectively.

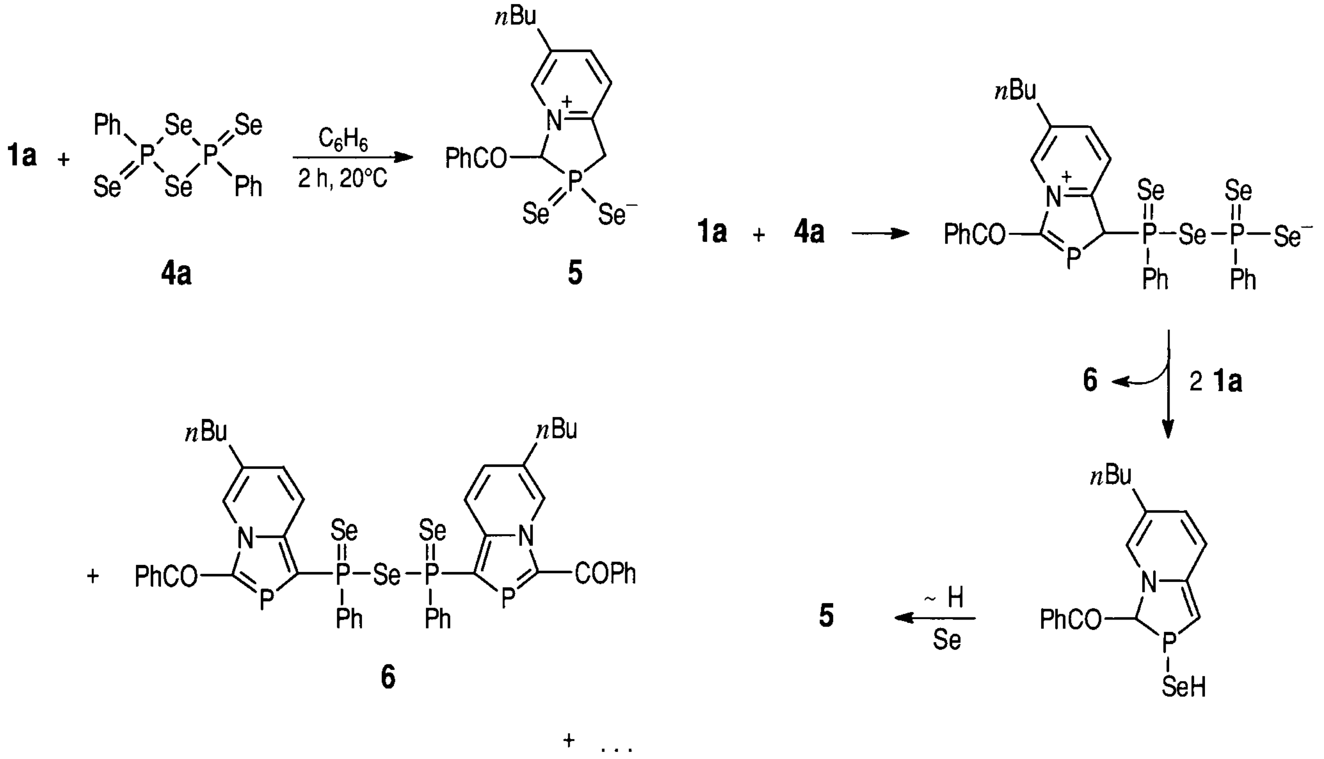


3e,f

The compounds **3** are isolated as yellow crystalline solids, which are soluble in acetonitrile and chloroform. The methylation generates a new chiral center at phosphorus in addition to that at C-3, and hence, two diastereomers of **3** in each case are possible. For **3e,** two ^{31}P-NMR signals are found at $\delta = 74.1$ (80%) and 68.0 (20%), corresponding to the two diastereomers. In the ^{1}H-NMR spectrum, distinct signals due to the second isomer could be observed only for 5-H and SMe (Table 1). In the case of **3f,** however, the ^{31}P-NMR signal at $\delta = 69.2$ indicates the formation of one diastereomer only, which might be due to the presence of the bulky pivaloyl group at the adjacent carbon atom.

Reaction with 1,3,2,4-Diselenadiphosphetane-2,4-diselenides

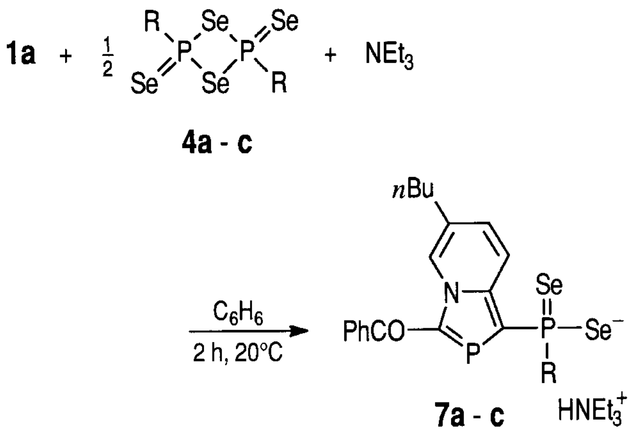
The synthesis of pyridiniodiselenophosphinates analogous to **2** according to the route described earlier would require the use of hydrogen selenide, which is difficult to handle. Preparatively more convenient is the reaction of **1** with the 1,3,2,4-diselenadiphosphetane-2,4-diselenides **4** [11, 12]. They represent the homologues of Lawesson's Reagent and, like this, can be used for the synthesis of selenocarbonyl compounds [13]. However, no O/Se exchange is observed, when **1a** is reacted with an equimolar amount of **4a** in benzene at ambient temperature. Instead, the pale yellow crystalline air- and moisture-sensitive pyridiniodiselenophosphinate **5** is isolated.

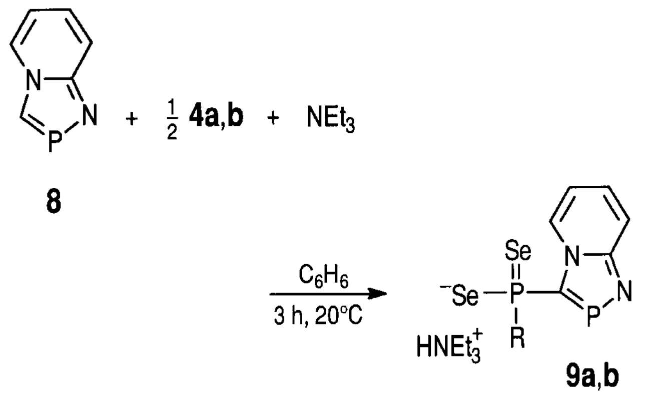


The structure of **5** results from its ^{31}P-, ^{77}Se-, ^{1}H-, and ^{13}C-NMR data (Tables 1 and 2). As in **2a**, the methylene protons exhibit the AB part of an ABX spectrum. The two selenium atoms show the expected diastereotopy as well. The ^{77}Se chemical shifts (δ = 87.6, 95.1) are found at lower field compared to δ^{77}Se in phosphine selenides. The Se,P-coupling constants (^{1}J = 741.9, 691.0 Hz) are typical for one-coordinated selenium, bonded to a four-coordinated phosphorus atom [14].

The ^{31}P-NMR spectrum of the reaction solution shows the presence of several phosphorus compounds, from which the perselenophosphinic anhydride **6** can be identified from its ^{31}P-NMR data (see Experimental). It forms a nearly 1:1 mixture of two diastereomers and results from an electrophilic substitution at position 1 of the phosphaindolizine ring. We therefore assume that the reaction is initiated by the nucleophilic attack of the phosphaindolizine at the phosphorus of the diselenide **4a.** It causes the opening of the P_2Se_2 ring with formation of a zwitterionic intermediate. Analogous zwitterionic species have been observed in the reaction of diselenides **4** with secondary amines [15]. Reaction with a second phosphaindolizine molecule yields the anhydride **6** and generates formally H_2Se, which adds to a third phosphaindolizine molecule. Selenation of the primary addition product, probably by the diselenide **4a,** yields the diselenophosphinate **5.**

Thus, the formation of **5** in this reaction is due to the action of the phosphaindolizine as a base in an electrophilic substitution with the diselenide **4a.** The suggested mechanism is further supported by the observation that **5** is not formed when an additional base is present. With NEt_3 and use of the right stoichiometry, the diselenophosphinate **7a** is obtained as the only reaction product. This reaction can be extended to other 1,3,2,4-diselenadiphosphetane-2,4-diselenides **4** as well. In place of the phosphaindolizine **1a,** the 1-aza-2-phosphaindolizine **8** [16] can be used to give the corresponding diselenophosphinates **9a,b.**





	R
a	H
b	4-MeOC$_6$H$_4$
c	4-Me$_2$NC$_6$H$_4$

As expected, the reaction is influenced by the nucleophilicity of the phosphaindolizine as well as by the electrophilicity of the phosphorus atoms in the diselenides **4**. Thus, while **1a** reacts readily with **4c** to give **7c**, no reaction is observed between the less nucleophilic compound **8** and the *p*-dimethylaminophenyl-substituted diselenide **4c**, the phosphorus atoms of which are expected to show the lowest electrophilicity.

Only a few diselenophosphinates have been reported in the literature so far [17–20]. The compounds **7** and **9** are new diselenophosphinates having a heterocyclic ring attached to the phosphorus. They are isolated as colorless to yellow air- and moisture-sensitive crystalline solids, which are readily soluble in dichloromethane and acetonitrile. Their constitution results from the ^{31}P-, ^{77}Se-, ^{1}H-, and ^{13}C-NMR data (Tables 3 and 4).

TABLE 2 ^{13}C-NMR Data[a] for the Pyridiniodithiophosphinate **2a** and Its Selenium Homologue **5** (in CD$_2$Cl$_2$, coupling constants J in Hz)

	2a	5
C-1	49.8	51.8
^1J(P, C)	44.6	29.4
C-3	86.0	85.6
^1J(P, C)	19.4	4.7
C-5	141.8	141.7
^3J(P, C)	3.8	3.3
C-6	141.9	142.1
^4J(P, C)	0.9	1.0
C-7	145.8	146.0
C-8	127.0	127.0
^3J(P, C)	9.0	8.1
C-9	156.4	156.6
^2J(P, C)	2.8	3.8
COPh		
C=O	189.0	188.9
C-*i*	135.2	135.4
C-*o*	130.2	130.4
C-*m*	128.9	129.0
C-*p*	134.6	134.8
n-Bu		
α-CH$_2$	32.4	32.4
β-CH$_2$	32.2	32.3
γ-CH$_2$	22.1	22.3
CH$_3$	13.5	13.6

[a] The assignment of the ^{13}C-NMR signals is based on ^{1}H,^{13}C-HETCOR experiments for both compounds.

On substitution, the ^{31}P-NMR signal of the phosphaindolizine is shifted to lower field (δ = 200–229) as compared to that of the unsubstituted **1a** (δ = 180.0 [5]) and **8** (δ = 195.0 [16]. The signal of the four-coordinated phosphorus is found at δ = 0 to -10 and is accompanied by one pair of ^{77}Se satellites, arising from the isotopomer with one ^{77}Se nucleus. The ^{77}Se chemical shift appears at low field (δ = 88–148), and ^1J(Se,P) values (598–616 Hz) are slightly lower than in phosphine selenides R$_3$P=Se [14]. Remarkable are the large values of ^3J(Se,P) of the dicoordinated phosphorus of 24–39 Hz.

The ^{13}C chemical shifts of the phosphaindolizine ring in the diselenophosphinates **7** and **9** (Table 4) parallel those of the unsubstituted phosphaindolizines **1a** and **8**, except for C-1 and C-3, respectively, which are shifted to lower field. The P,C coupling constant of the dicoordinated phosphorus in **7** to C-*o* in COPh over four bonds is remarkably large (^4J = 11–14 Hz) but typical for this type of phosphaindolizine [5].

EXPERIMENTAL

All reactions were performed under dry nitrogen using the Schlenk technique. The solvents were dried according to standard procedures. The 2-phosphaindolizines **1** and the 1-aza-2-phosphaindolizine **8** were prepared as reported in the literature [5, 16]. The 1,3,2,4-diselenadiphosphetane 2,4-diselenides **4** were obtained from the corresponding cyclopentaphosphines and elemental selenium [11, 21]. All other reagents were commercially available.

The NMR spectra were recorded on a Jeol FX-90-Q spectrometer at 36.23 MHz (^{31}P) and 89.55 MHz (^{1}H), on a Jeol GSX-270 spectrometer at 109.7 MHz (^{31}P), and on a Jeol EX-400 spectrometer at 100.5 MHz (^{13}C) and 399.8 MHz (^{1}H). The chemical shifts are referred to 85% H_3PO_4 (for ^{31}P) as external standard and to TMS (for ^{1}H and ^{13}C) as internal standard. Melting points were determined with a Linström apparatus and are uncorrected.

Pyridiniodithiophosphinates 2

To a solution of the 2-phosphaindolizine **1** (2 mmol) in 20 mL dichloromethane, an equimolar amount of elemental sulfur was added, and after the mixture had been stirred for 10–15 minutes at ambient temperature, dry H_2S was slowly passed into the mixture over a period of 1 hour. During this time, the color of the reaction mixture changed from yellow to brown and a colorless to pale yellow crystalline solid precipitated. In the case of **2d,** the reaction was initiated by the addition of 1–2 drops of glacial acetic acid. Stirring was continued at ambient temperature until the reaction was completed (3–8 days, as monitored by ^{31}P-NMR spectroscopy). The crystalline solid was separated by filtration, washed with 3 × 5 mL dichloromethane, and recrystallized from acetonitrile. Yields and physical data are given in Table 5, and the analytical data, in Table 6. ^{31}P- and ^{1}H-NMR data are comprised in Table 1, and the ^{13}C-NMR data of **2a** are given in Table 2.

S-Methylpyridiniodithiophosphinic Ester Iodides 3

To a suspension of the pyridiniodithiophosphinate **2** (1 mmol) in 10 mL of dry chlroform, an equimolar amount of methyl iodide was added, and the reaction mixture was stirred at ambient temperature until the reaction was completed (3–5 days, as monitored by ^{31}P-NMR spectroscopy). In the case of **3e,** concentration of the reaction mixture yielded a crystalline solid, which was separated by filtration, washed with 3 × 5 mL of diethyl ether, and recrystallized from dichloromethane. In the case of **2f,** the solvent was completely removed *in vacuo,* the oily residue macerated with 30 mL of diethyl ether, and the resulting solid was separated by filtration and dried in vacuo. For yields and physical data, see Table 5, and for analytical data, Table 6. The ^{31}P- and ^{1}H-NMR data are provided in Table 1.

TABLE 3 ^{31}P-, ^{77}Se-, and ^{1}H-NMR Data[a] of the Diselenophosphinates **7** (in CD_2Cl_2) and **9** (in CD_3CN, coupling constants *J* in Hz)

	7a	**7b**	**7e**	**9a**	**9b**
δ^{31}P σ^2-P	201.9	201.0	200.6	228.9	225.1
σ^4-P	−0.4	−1.4	−1.2	−9.3	−10.6
^2J(P,P)	82.4	82.4	80.9	35.0	32.0
δ^{77}Se	88.5	88.9	88.4	148.2	147.7
^1J(Se,P)	603.5	599.6	598.2	609.2	615.7
^3J(Se,P)	27.1	27.4	24.4	38.6	36.9
δ^1H 5-H	10.04	9.95	9.97	9.02	9.06
6-H				6.88	6.91
7-H	7.17	7.24	7.22	7.35	7.36
8-H	8.05	8.14	8.25	7.51	7.52
^3J(5-H, 6-H)				7.1	7.1
^3J(6-H, 7-H)				6.8	6.6
^3J(7-H, 8-H)	9.0	9.0	9.5	9.0	9.3
^4J(5-H, 7-H)				1.2	1.2
^4J(6-H, 8-H)				1.2	1.2
^4J(P, 5-H)				1.2	1.2
^4J(P, 8-H)	1.7	1.9	2.2	1.4	1.5
COPh					
o-H	7.88	7.92	7.81		
m-H	7.50	7.50	7.48		
p-H	7.58	7.58	7.56		
n-Bu	2.66	2.72	2.63		
α-CH_2					
β-CH_2	1.63	1.63	1.60		
γ-CH_2	1.39	1.38	1.35		
CH_3	0.94	1.03	0.91		
P-Ph					
o-H	8.10	8.12	7.89	8.14	8.10
^3J(P, H)		13.9	13.7		13.9
m,*p*-H	7.2–7.3	6.83	6.62	7.3–7.4	6.91
$HNEt_3^+$					
NH	9.7	9.7	8.9	8.5	9.2
CH_2	3.25	3.19	3.11	3.08	3.10
CH_3	1.31	1.23	1.20	1.20	1.19
^3J(H, H)	7.3	7.3	7.3	7.3	7.3

[a] The assignment of the ^{1}H-NMR signals is based on ^{1}H, ^{1}H-COSY45-NMR spectra for **7a** and **9a.**

Pyridiniodiselenophosphinate 5

A 1.3 g (4.5 mmol) amount of the phosphaindolizine **1a** and 2.4 g (4.5 mmol) of the diselenadiphosphetane diselenide **4a** in 15 mL of dry benzene was stirred at ambient temperature for 2 hours. During this time, the red diselenide **4a** dissolved completely, the color of the solution changing to dark yellow, and a crystalline yellow solid was formed. The solid was separated by filtration and dissolved in 10 mL dichloromethane. The insoluble residue (mainly gray selenium) was filtered off, and the clear pale yellow filtrate evaporated to dryness *in vacuo* to give pale

TABLE 4 ^{13}C-NMR Data[a] of the Diselenophosphinates **7** (in CD_2Cl_2) and **9** (in CD_3CN, coupling constants *J* in Hz)

	7a	**7b**	**7c**	**9a**	**9b**
C-1	144.6	144.0	144.2		
^3J(P,C)	51.1	68.6	65.3		
	45.2	61.5	58.5		
C-3	145.2	144.4	144.9	167.4	167.9
^1J(P,C)	49.8	61.2	59.2	80.1	80.6
				46.9	46.0
C-5	128.7	128.7	128.8	130.7	130.3
^3J(P,C)	3.4	3.4	3.3	3.3	4.3
C-6	130.0	129.9	129.9	112.6	112.3
^4J(P,C)	2.7	3.4	2.5	<2.0	1.9
C-7	128.1	128.0	128.4	128.0	128.3
C-8	120.6	119.9	120.0	119.6	119.5
^3J(P,C)	4.6	4.7	4.1	8.5	8.1
	3.4	4.0	3.3		
C-9	143.5	143.1	143.2	156.9	156.8
^2J(P,C)	12.2	13.1	12.6	10.5	10.9
	7.6	8.4	7.9		
^3J(P,C)				9.8	10.9
P-phenyl					
C-*i*	145.0	133.5	132.7	140.8	131.4
^1J(P,C)	75.4	69.9	60.9	64.5	71.6
C-*o*	131.5	132.5	133.0	132.0[b]	134.0[b]
^2J(P,C)	11.9	13.5	12.3	12.3	13.7
C-*m*	127.5	112.8	110.6	128.5	113.8
^3J(P,C)	12.3	13.4	13.3	12.3	13.7
C-*p*[c]	129.5	160.8	152.2	129.2	162.2
COPh					
C=O	188.0	187.9	187.9		
^2J(P,C)	24.1	26.2	26.1		
^4J(P,C)	1.8	3.4	2		
C-*i*	142.4	142.4	143.4		
C-*o*	130.3	129.6	129.7		
^4J(P,C)	7.9	7.4	7.1		
C-*m*	127.9	127.9	127.9		
C-*p*	130.9	131.0	131.0		
n-Bu					
α-CH_2	32.5	32.6	32.7		
β-CH_2	32.7	33.0	33.0		
γ-CH_2	22.4	22.3	22.4		
CH_2	14.0	13.7	13.5		
R		55.4	40.1		56.0
$HNEt_3$					
CH_2	45.6	46.2	46.1	47.3	47.2
CH_3	8.3	8.5	8.5	9.2	9.1

[a] The assignment of the ^{13}C-NMR signals is based on ^{1}H-,^{13}C-HETCOR experiments for **7a** and **9a.**
[b] ^4J(P,C) = 1,4 Hz.
[c] ^4J (P,C) = 2.7 Hz (**7b**), 2.8 Hz (**9b**).

TABLE 5 Yields and Physical Data of the Pyridiniodithiophosphinates **2,** Pyridiniodithiophosphinic Acid Ester Iodides **3,** Pyridiniodiselenophosphinate **5,** and Triethylammonium Diselenophosphinates **7,9**

	Color	*Yield (%)*	*mp (°C)*
2a	colorless	45	193–195
2b	pale yellow	42	162–163
2c	colorless	26	215–217
2d	colorless	40	193–195
2e	colorless	38	175–178
2f	colorless	32	218–220
2g	pale yellow	40	200–202
3e	yellow	51	123–125
3f	yellow	54	115–118
5	pale yellow	27	118–120
7a	yellow	87	88–90
7b	yellow	60	93–96
7c	yellow	86	123–126
9a	pale yellow	42	130–133
9b	pale yellow	46	118–120

TABLE 6 Analytical Data of the Pyridiniodithiophosphinates **2,** Pyridiniodithiophosphinic Acid Ester Iodides **3,** Pyridiniodiselenophosphinate **5,** and the Triethylammonium Diselenophosphinates **7,9**

Formula M	*Calcd. Found*	*C*	*H*	*N*
2a	$C_{18}H_{20}NOPS_2$	59.81	5.58	3.87
	361.47	59.75	5.74	3.93
2d	$C_{10}H_{12}NO_2PS_2$	43.95	4.43	5.12
	273.32	43.79	4.23	5.33
2g	$C_{14}H_{13}N_2O_2PS_2$	49.99	3.90	8.33
	336.38	48.70	3.28	8.66
3c	$C_{17}H_{19}NOPS_2I$	42.97	4.03	2.95
	475.20	42.74	4.02	2.89
5	$C_{18}H_{20}NOPSe_2$	47.49	4.43	3.08
	455.26	47.18	4.33	3.05
7a	$C_{30}H_{38}N_2OP_2Se_2$	54.39	5.78	4.23
	662.51	54.03	5.72	4.31
7b	$C_{31}H_{40}N_2O_2P_2Se_2$	53.76	5.82	4.05
	692.54	53.55	5.65	4.01
7c	$C_{32}H_{43}N_3OP_2Se_2$	54.47	6.14	5.96
	705.58	54.14	5.97	5.84
9a	$C_{18}H_{25}N_3P_2Se_2$	42.96	5.01	8.35
	503.28	42.78	5.16	8.28
9b	$C_{19}H_{27}N_3OP_2Se_2$	42.79	5.10	7.88
	533.31	42.64	5.09	7.76

yellow crystalline **4a.** For yield and physical data, see Table 5, and for the analytical data, Table 6. The ^{31}P-, ^{77}Se-, and ^{1}H-NMR data are provided in Table 1, and the ^{13}C-NMR data, in Table 2. The ^{31}P-NMR spectrum of the reaction solution shows the presence of the anhydride **6** as a 1:1 mixture of two diastereomers. Diastereomer I: AA′XX′ spectrum, $\delta_A = 208.0$, σ^2-P, $\delta_x = 66.6$, σ^4-P, $J_{AB} = {}^2J(P,P) = 86.0$ Hz, $J_{BB'} = {}^2J(P,P) = 52.8$ Hz, $J_{AB'} = {}^4J(P,P) = 0.3$ Hz, $^4J_{AA'} = {}^6J(P,P) = 5.1$ Hz, $^1J(Se,P) = 622.7$ Hz, 379.9 Hz; diastereomer II: AA′XX′ spectrum, $\delta_A = 201.8$, σ^2-P, $\delta_x = 68.0$, σ^4-P, $J_{AB} = {}^2J(P,P) = 75.2$ Hz,

$J_{BB'} = {}^2J(P,P) = 39.0$ Hz, $J_{AB'} = {}^4J(P,P) = -0.5$ Hz, $J_{AA'} = {}^6J(P,P) = 6.2$ Hz. The signs of the coupling constants result from the iterative spectral fitting [22] on the assumption of a positive sign for ${}^2J(P,P)$ [23].

Triethylammonium Diselenophosphinates 7

To 1.1 g (3.6 mmol) of the phosphaindolizine **1a** and 1.8 mmol of the diselenide **4a–c** in 10 mL of dry benzene was added 0.4 g (3.7 mmol) of triethylamine, and the resulting reaction mixture was stirred at ambient temperature for 2 hours. After 15 minutes, the color of the reaction mixture changed to yellow, and the diselenide **4** began to dissolve. The reaction was completed when no more solid **4** remained. The solvent was removed *in vacuo* and the solid residue washed with 3 × 40 mL diethyl ether to give yellow crystalline **7**, which was dried *in vacuo*. For yields and physical data, see Table 5, and for analytical data, Table 6. The ^{31}P-, ^{77}Se-, and ^{1}H-NMR data are provided in Table 3, and the ^{13}C-nMR data, in Table 4.

Triethylammonium Diselenophosphinates 9

To 1.0 g (7.6 mmol) of 1-aza-2-phosphaindolizine **8** and 3.0 mmol of each of the diselenide **4a,b** in 15 mL of dry benzene was added 0.9 g (7.7 mmol) of triethylamine, and the resulting reaction mixture was stirred at ambient temperature for 3 hours. In the course of the reaction, the color of the reaction mixture changed to yellow, the red diselenide dissolving completely, while a crystalline pale yellow solid was formed. It was separated by filtration, washed with 2 × 3 mL benzene and dried *in vacuo*. For yields and physical data, see Table 5, and for analytical data, Table 6. The ^{31}P-, ^{77}Se-, and ^{1}H-NMR data are given in Table 3, and the ^{13}C-NMR data, in Table 4.

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