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Substitution of 2-Phosphaindolizines by Bromine and by Chlorophosphines

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ABSTRACT

Bromine does not add to phosphorus in a 2-phosphaindolizine **1** *but substitutes its 1-position. The 1-bromo derivatives* **2** *are best prepared with* Br_2/NEt_3 *or N-bromosuccinimide. Their hydrolysis is remarkable; it involves a debromination of C-1, an oxidation of P and a selective opening of the P/C-3 bond.*

PCl_3 *also causes a substitution of the 1-position. The resulting 1-dichlorophosphino derivatives* **5** *easily undergo a substituent exchange at the exocyclic phosphorus. More 1-phosphino derivatives are formed in the reaction of* **1** *with phenyl and diazaphospholyl dichlorophosphine.*

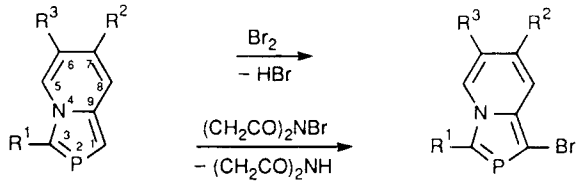
INTRODUCTION

2-Phosphaindolizines have recently become available by the condensation of 1,2-dialkylpyridinium salts with phosphorus trichloride [1]. Starting from 2-methylpyridines, 1-unsubstituted 2-phosphaindolizines (**1**) are obtained, together with their 1-dichlorophosphino derivatives. The latter are formed in a secondary reaction of the unsubstituted phosphaindolizine with excess PCl_3. More details of this substitution reaction are given in the present paper.

A similar substitution at the carbon adjacent to the two-coordinate phosphorus by PCl_3 is known for the 1,2,3-diazaphospholes [2–4]. For a further comparison of the two systems the bromination of 2-phosphaindolizines has been investigated.

Bromination of 2-Phosphaindolizines

Two-coordinate tervalent phosphorus should be expected to add bromine to give the corresponding pentavalent compound. This has indeed been found also for cyclic compounds such as phosphinines [6] and 1,2,4,3-triazaphospholes [7]. From the reaction of equimolar amounts of the phosphaindolizine **1c** with bromine, the substitution product **2c** is formed in low yield instead of the dibromophosphorane. Good yield of the 1-bromo-2-phosphaindolizines **2** are obtained when triethylamine is used to bind the hydrogen bromide or when *N*-bromosuccinimide is used for bromination (Method B and C, see Table 4).



1 **2**

	R^1	R^2	R^3
a	COPh	H	H
b	COPh	Me	H
c	COPh	H	*n*-Bu
e	CO_2Et	Me	H
f	CO_2Et	H	*n*-Bu
g	CN	Me	H

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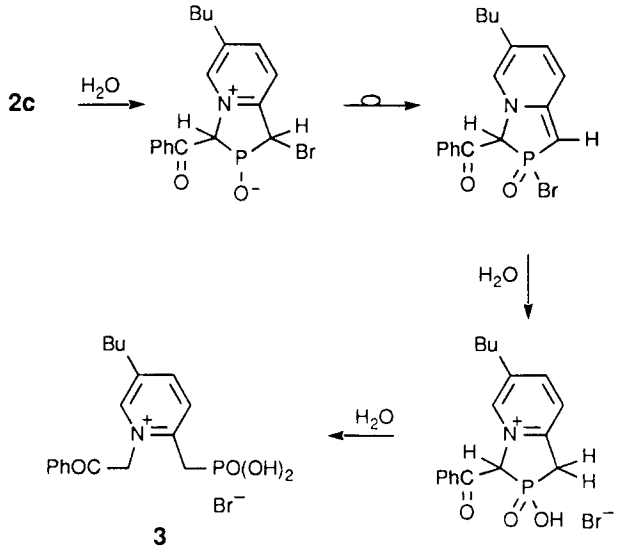
The reaction can readily be interpreted as an electrophilic substitution. It should be noted that this reaction is more straightforward than the bromination of indolizines which, moreover, seems not to be well investigated [8]. In an early paper unstable multiple brominated products are said to result from the reaction [9].

The only other heterophospholes, for which a bromination of the carbon adjacent to phosphorus is found instead of the oxidative addition of bromine to phosphorus, are the 1,2,3-diazaphospholes. Here the reaction has been shown to proceed via a 1,2-addition of Br_2 and a 1,2-elimination of HBr [10].

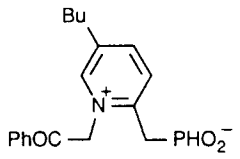
The identity of compounds **2** follows from their NMR spectra (Tables 1 and 2). As compared to **1** their ^{31}P NMR signals are shifted just slightly to higher field. As in **1** $\delta^{31}P$ strongly depends on R^1 and is larger for COPh than for CO_2Et and CN. The H/Br exchange at C-1 is accompanied by a high field shift of the NMR signal of this carbon atom by $\Delta\delta \sim 9$ and by an increase of ^1J(P, C-1) by approximately 13 Hz. As in other 3-benzoyl-substituted phosphaindolizines [1] the four bond P,C-coupling to the *ortho*-carbon atom of the benzoyl substituent in **2a** (7.1 Hz) and **2c** (7.6 Hz) is remarkably large.



3

In the reactions of 4-bromo-1,2,3-diazaphospholes with protic reagents we have observed analogous redox interactions between the adjacent P and C members of the ring [12].

Compound **3** is clearly identified by its ^{31}P-, ^1H- and ^{13}C-NMR spectra (see *Experimental*). They correspond largely to the respective spectra of the (1-phenacylpyridinio)methylphosphonite **4**, obtained from the hydrolysis of **1c** [1]. As compared to **4** compound **3** has a hydroxyl group bonded to phosphorus in place of a hydrogen atom which implies an oxidation of the phosphorus. The pentavalent state of phosphorus in **3** is reflected by the large value of $^1J_{PC}$ = 126.7 Hz as compared to 66.4 Hz in **4** [1] and by the observed long range coupling constants $^{4,5,7}J_{PC}$ to C-4, and C-5 and to the β-carbon atom of the *n*-butyl group [13].



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Hydrolysis of 1-Bromo-2-phosphaindolizines

The 1-bromo-2-phosphaindolizines **2** are mostly crystalline, but in some cases are oily products. They are somewhat more sensitive to water than **1**. The hydrolysis has been investigated using **2c** as an example. With an equimolar amount of water, it stayed in part unreacted while the rest gave a number of not identified products, seemingly different stages of a multistep hydrolysis. With more water, the (1-phenacylpyridinio)methylphosphonic acid **3** resulted as the final product. This product is surprising as it means that phosphorus and the adjacent carbon change their oxidation states during the hydrolysis: The phosphorus becomes oxidized while the carbon is debrominated. The reaction can tentatively be explained by the mechanism shown below: Addition of a first water molecule may result in a zwitterionic pyridiniophosphinate which very likely undergoes a 1,2-halogenotropic rearrangement. Such rearrangements are known for bromoalkylphosphines with electron-withdrawing substituents at carbon [11] and can consequently also be expected in the case of the suggested intermediate. Two more water molecules cleave the PBr bond and the PC bond to the benzoyl-substituted carbon.

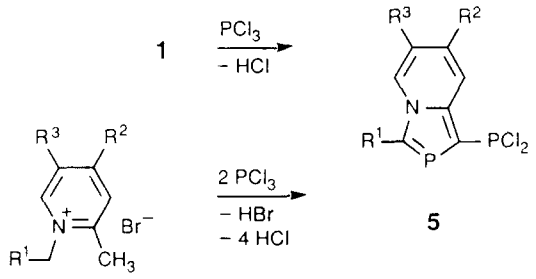
Substitution of 2-Phosphaindolizines by PCl_3

2-Phosphaindolizines, as has been realized during their synthesis [1] and as has been mentioned already in the introduction, readily react with phosphorus trichloride to give 1-dichlorophosphino derivatives **5**. This reaction is performed in the presence of triethylamine, but it may work also without the help of an amine. Most economically, compounds **5** can be prepared directly from 1-alkyl-2-methylpyridinium bromides and two equivalents of PCl_3 in the presence of triethylamine.

TABLE 1 ^{31}P- and ^{1}H-NMR data of the 1-bromo-2-phosphaindolizines **2** (in $CDCl_3$).

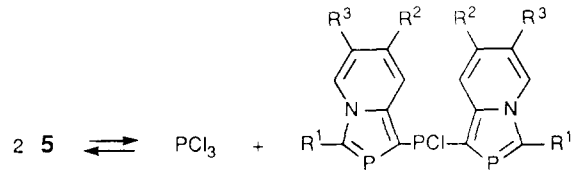
δ / J [Hz]	**2a**	**2b**	**2c**	**2e**	**2f**	**2g**
P	176.8	177.9	175.0	161.0	157.1	160.5
5-H	10.18[a]	10.17	10.13	9.61	9.74	8.40
^3J(5-H, 6-H)	7.3	7.3		7.3		7.0
6-H	6.95[b]	6.88		6.63		6.83
^5J(P, 6-H)	1.0			1.5		
7-H	7.30		7.26		7.10	
^5J(P, 7-H)	0.6		1.5			
^3J(7-H, 8-H)	9.0		9.2		8.0	
8-H	7.66[c]	7.50	7.65	7.29	7.59	7.46
Ph: o-H	7.76	7.84	7.84			
m-H	7.37	7.44	7.45			
p-H	7.46	7.53	7.54			
OEt: CH_2				4.25	4.33	
CH_3				1.28	[d]	
^3J(H, H)				7.2	7.0	
6-Bu: α-CH_2			2.69		2.59	
β-CH_2			1.67		[d]	
γ-CH_2			1.40		[d]	
CH_3			0.94		0.80	
7-CH_3		2.48		2.31		2.41

[a] ^4J(5-H, 7-H) = 1.0 Hz, ^5J(5-H, 8-H) = 0.8 Hz, ^4J(P, 5-H) = 0.6 Hz.
[b] ^3J(6-H, 7-H) = 6.7 Hz, ^4J(6-H, 8-H) = 1.6 Hz.
[c] ^4J(P, 8-H) = 0.8 Hz.
[d] Not evaluated due to overlapping.



	R^1	R^2	R^3
a	COPh	H	H
b	COPh	Me	H
c	COPh	H	*n*-Bu
d	CO_2Et	H	H
e	CO_2Et	Me	H
h	$C_6H_4NO_2$-4	H	H

The ^{31}P-NMR spectrum of the reaction mixture in some cases shows, besides the AB-signals of **5** (Table 3), A_2B-signals of a second product **6** (Table 3) in which two chlorine atoms of PCl_3 are substituted by 2-phosphaindolizinyl moities. If a pure sample of **5** is dissolved, the ^{31}P-NMR spectrum of the solution likewise reveals the presence of **5** and an equivalent amount of PCl_3 with the relative intensity of their signals increasing when the solution is allowed to stand and to warm. This indicates a disproportionation equilibrium:



This easily occurring substituent exchange seems most remarkable, as, in the case of phenylchlorophosphines, it takes temperatures of 200°C and more [14]. An exchange at room temperature has also been found for 1,4,2-diazaphospholylchlorophosphines [5].

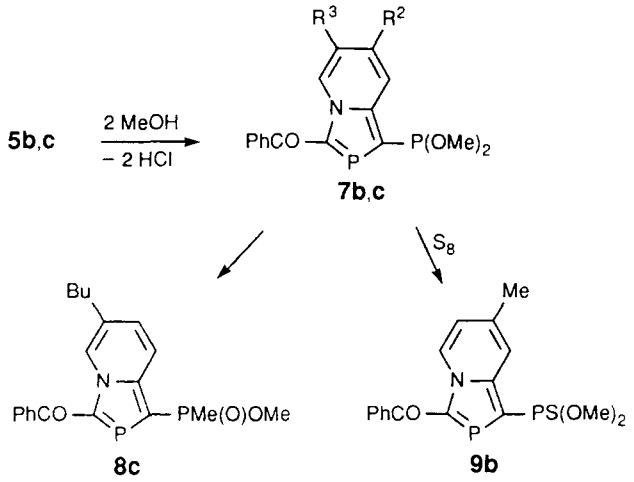
Compounds **5** at room temperature do not react with elemental sulfur. They are rather sensitive to water. It should be noted that hydrolysis breaks the PC-bond which was formed in the 2-phosphaindolizine substitution. When a compound of type **5** is dissolved in acetonitrile which is not absolutely dry, the ^{31}P-NMR spectrum shows, besides the signals of **5**, the signal of **1**, and its relative intensity indicates the amount of water present. With two equivalents of water the cleavage is complete. A basic medium gives no other result.

$$5 + 2H_2O \rightarrow 1 + 2HCl + [HPO_2]$$

The easy hydrolytic cleavage of the PC-bond in **5** is in contrast to the respective stability in other

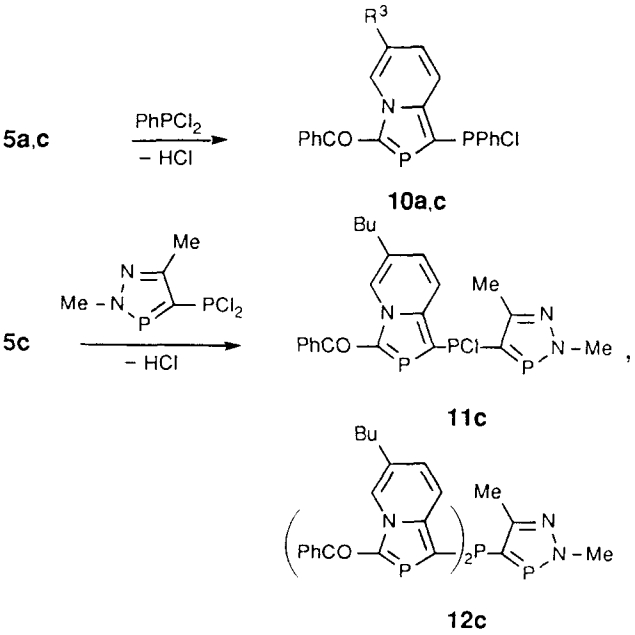
aryldichlorophosphines. It is known, however, for dichlorophosphines such as Ph_3CPCl_2 and Cl_3CPCl_2 [14].

With methanol in the presence of triethylamine, just the minor part of **5** suffers cleavage of the PC-bond; the major part is converted to the phosphonite ester **7**, which easily rearranges to the phosphinate ester **8** or can be oxidized to the thiophosphonate ester **9**.

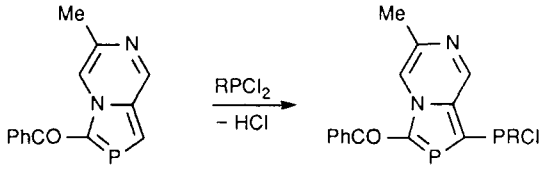


Substitution of 2-Phosphaindolizines by Aryldichlorophosphines

Phenyldichlorophosphine also gives a 1-substitution product of **1**. The reactions are slower, however, and the products were identified only by their ^{31}P-NMR spectra (Table 3). With 4-dichlorophosphino-2,4-dimethyl-1,2,3-diazaphosphole, the 1-substitution of one molecule and of two molecules of **1c** yielding **11c** and **12c**, respectively, is observed.



The reactions of the 7-aza-2-phosphaindolizine **13** with PCl_3 and $PhPCl_2$ ae analogous to those of the 2-phosphaindolizines **1** but significantly slower.



13 **14**, R = Cl; **15**, R = Ph

In contrast to the ready substitution of **1** encountered with chlorophosphines, and despite the known fact that indolizines can be acylated in a non-catalyzed reaction with benzoyl chloride [15], no acylation of **1a, b** is observed by acetyl or benzoyl chloride in the presence of triethylamine, even at 120°C.

NMR-Spectra of 1-Phosphino-2-phosphaindolizines

The ^{31}P-NMR spectra of the 1-phosphino- and 1-phosphoryl-2-phosphaindolizines show AB- or more complex spin systems (Table 3) with the resonance of the ring phosphorus (P_A) in the same region but at a somewhat lower field than for the unsubstituted starting compound **1**. As mentioned before [1], δP_A depends only weakly on the 1-substituents; including the present results, δP_A increases, ceteris paribus, with the 1-substituents in the order Br < Ph < H < Me < PCl_2, $P(OMe)_2$ < PPhCl < $PS(OMe)_2$. As for other 2-phosphaindolizines (see [1] and above), δP_A here again increases rather strongly with the 3-substituents in the order 4-$NO_2C_6H_4$ < CO_2Et < COPh.

Characteristic of the 1-dichlorophosphino-2-phosphaindolizines **5** is the large two-bond coupling constant ^2J(P, P), which also increases with the 3-substituents in the order 4-$NO_2C_5H_4$ < CO_2Et < COPh. When one or both chlorine atoms of the phosphino substituent are replaced, the coupling constant drops.

The four-bond coupling between the two types of two-coordinate phosphorus in **11** and **12**, ^4J(P, P) = 32.8 and 15.2 Hz, respectively, are unusually high; the former seems the highest ^4J(P, P) value so far reported.

The structure of **5a** is further supported by its ^{13}C-NMR spectrum (Table 2). The signals of the azaphosphole ring, of C-8 and of the carbonyl group show coupling with both phosphorus nuclei.

EXPERIMENTAL

All operations are carried out in dry equipment under nitrogen or argon. ^{31}P NMR: Jeol FX-90-Q and GSX-270 at 36.2 and 109.7 MHz. ^{1}H NMR: Jeol FX-90-Q and EX-400 at 90 and 400 MHz. ^{13}C NMR:

TABLE 2 ^{13}C-NMR data of the 2-phosphaindolizines **2b**, **c**, **e**, **5a** and **11c** (in $CDCl_3$ except **5a** in CD_2Cl_2)

δ / J [Hz]	**2b**	**2c**	**2e**[a]	**5a**	**11c**[b]
C-1	116.5	117.9	114.3	135.0	136.4[c]
^1J(P, C)	55.9	55.9	55.1	56.8[d], 69.0[e]	60.7[d], 39.3[e]
C-3	143.9	143.9	136.3	148.8	147.9
^1J(P, C)	59.7	60.7	55.8	59.8	62.1[f]
^3J(P, C)				15.0	5.6
C-5	129.9	128.5	128.3	131.8	130.6
^3J(P, C)	3.8	4.3	3.8	2.8	2.8
C-6	117.6	130.1	116.7	116.6	128.5
^4J(P, C)	3.8	4.3	3.8	2.1	4.3
C-7	138.4	129.0	135.4	128.7	129.1
^4J(P, C)	2.9	2.8	2.6	1.5[d, e]	3.8
C-8	116.5	117.4	116.6	119.3	117.6
^3J(P, C)	5.7	6.2	5.8	4.4[d], 9.6[e]	4.7[d], 14.7[e]
C-9	144.8	143.5	143.7	147.3	147.0
^2J(P, C)	10.4	10.4	10.3	5.8[d], 19.1[e]	7.6[d], 34.1[e]
C-0	187.3	187.5	163.3	187.9[g]	187.8
^2J(P, C)	25.6	25.6	19.3	25.0	24.6
Ph: C-*i*	141.4	141.4		141.2	140.8
C-*o*	129.6	129.6		129.8	129.6
^4J(P, C)	7.1	7.6		7.0	7.6
C-*m*	128.0	127.9		128.3	127.9
C-*p*	131.3	131.4		132.1	131.4
6-Bu: α-CH_2		32.5			32.5
β-CH_2		32.8			32.7
γ-CH_2		22.2			22.1
CH_3		13.9			13.8
7-CH_3	21.3		20.9		

[a] Et: δ = 60.4 (CH_2), 14.4 (CH_3).
[b] Diazaphosphole ring: δ = 149.1 (ddd, ^1J(P, C) = 55.0 Hz, 36.0 Hz, ^3J(P, C) = 7.6 Hz, C-4'), 156.6 (dd, ^2J(P, C) = 26.2 Hz, 5.4 Hz, C-5'), 41.4 (d, ^2J(P, C) = 18.0 Hz, NCH_3), 15.1 (d, ^3J(P, C) = 8.1 Hz, (CH_3).
[c] ^3J(P, C) = 7.1 Hz.
[d] Coupling to the ring phosphorus atom.
[e] Coupling to the exocyclic phosphorus atom.
[f] ^5J(P, C) = 1.6 Hz.
[g] ^4J(P, C) = 1.5 Hz.

Jeol EX-400 at 100.5 MHz. The chemical shifts refer to 85% H_3PO_4 (external) or TMS (internal).

1-Bromo-2-phosphaindolizines **2** (*Table* 4)

Method A: 1.48 g (5 mmol) of **1c** are dissolved in 20 ml CCl_4 and the solution is cooled to 0°C. To this is added a solution of 0.80 g (5 mmol) bromine in 10 ml CCl_4 slowly with continuous stirring, the temperature being maintained below 5°C. A pale yellow precipitate falls out soon. The reaction mixture is allowed to come to room temperature slowly and stirring is continued for another 1 hour. The solid is filtered off and washed with 5 ml CCl_4. The solvent from the combined filtrate is removed under reduced pressure and the syrupy mass is dissolved in 10 ml of acetonitrile and left in the refrigerator, whereupon fine needle shaped crystals of **2c** are obtained.

Method B: To 1 mmol **1b** in 20 ml CCl_4, 1 mmol triethylamine is added and the resulting solution is cooled to 0°C. A solution of 1 mmol bromine in 5 ml CCl_4 is added dropwise with stirring. After the addition, the reaction mixture is allowed to come to r.t. The solvent is now evaporated *in vacuo*, the residue extracted with diethyl ether and the ether solution left in the refrigerator whereupon yellow crystals of **2b** deposit.

Method C: To a solution of 1 mmol 2-phosphaindolizine **1** in 20 ml CH_2Cl_2 a solution of 1 mmol N-bromosuccinimide in 5 ml CH_2Cl_2 is added slowly with stirring at r.t. After 1 hour, the solvent is removed under reduced pressure and the residue extracted two times with 50 ml hexane. The combined extracts are concentrated and left in the refrigerator, whereupon cream to yellow crystals of **2a, d, f** separate which are filtered off, washed with cold hexane and dried. In the case of **2e**, no crystals separate and complete evaporation of the solvent affords a yellow sticky mass.

Hydrolysis of **2c**

When an equimolar amount of water (1.8 μl) was added to 37.4 mg (0.1 mmol) of **2c** in 1 ml CD_3CN,

TABLE 3 ^{31}P-NMR data of the phosphaindolizines **5** (AB), **6** (A_2B), **7-10**(AB), **11** (ABC)[a], **12** (A_2BC)[b] and **14, 15** (AB) (P_A: phosphaindolizine-P, P_B: exocyclic-P)

	$\delta^{31}P_A$	$\delta^{31}P_B$	$^2J(P,P)$ [Hz]	Solvent
5a	197.2	158.8	169.2	C_6D_6
	197.1	159.5	165.0	$CDCl_3$
5b	200.7	155.0	180.4	$CDCl_3$
5c	195.6	159.1	173.9	$CDCl_3$
5d	180.4	161.2	159.8	$CDCl_3$
5e	180.3	162.1	158.7	MeCN
5h	142.4	164.3	130.0	MeCN
14	197.8	152.0	152.0	$CDCl_3$
7b	200.7	158.2	34.2	$CDCl_3$
7c	197.5	159.2	33.5	$CDCl_3$
8c	203.9	24.0	79.3	$CDCl_3$
9b	206.4	85.3	87.9	MeCN
6a	199.2	68.0	47.3	C_6D_6
	198.3	69.4	46.1	MeCN
6c	197.9	69.2	51.3	MeCN
6d	181.8	69.7	42.3	MeCN
10a	199.7	74.6	57.0	MeCN
10c	198.8	74.8	60.9	MeCN
15	200.0	67.3	56.8	MeCN
11c	201.5	59.6	50.3	$CDCl_3$
12c	202.3	−61.4	10.4	$CDCl_3$

[a] $\delta^{31}P_C$ = 246.4, $^2J_{BC}$ = 24.4 Hz, $^4J_{AC}$ = 32.8 Hz, diazaphosphole-P.
[b] $\delta^{31}P_C$ = 247.2, $^2J_{BC}$ = 8.2Hz, $^4J_{AC}$ = 15.2 Hz, diazaphosphole-P.

a dark brown solution resulted and its ^{31}P NMR spectrum showed a number of signals in the range of $\delta = 0$ to 30. Then approximately two more equivalents of water were added, and the solution was left for 2 days when it became colorless and NMR studies indicated the almost exclusive formation of **3**.

^{31}P-NMR (CD_3CN): δ = 17.2 (t), $^2J_{PH}$ = 22.4 Hz.-^{1}H-NMR (CD_3CN): δ = 3.77 (d, 2H, $^2J_{PH}$ = 22.7 Hz, P-CH_2), 6.53 (s, 2H, N-CH_2), 8.09 (m, 2H, o-H), 7.54 (m, 2H, p-H), 7.69 (m, 1H p-H), 8.09 (d, 1H, $^3J_{HH}$ = 8.2 Hz, 3-H), 8.31 (d, 2H, $^3J_{HH}$ = 8.2 Hz, 4-H), 8.62 (s, 1H, 6-H), 2.73 (t, 2H, $^3J_{HH}$ = 7.7 Hz, α-CH_2), 1.61 (m, 2H, β-CH_2), 1.32 (m, 2H, γ-CH_2), 0.89 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_3).-^{13}C-NMR (CD_3CN): δ = 34.0 (d, $^1J_{PC}$ = 126.7 Hz, P-CH_2), 65.3 (s, N-CH_2), 150.2 (d, $^2J_{PC}$ = 8.5 H, C-2), 131.5 (d, $^3J_{PC}$ = 4.9 Hz, C-3), 147.4 (d, $^4J_{PC}$ = 2.4 Hz, C-4), 142.6 (d, $^5J_{PC}$ = 2.8 Hz, C-5), 147.6 (s, C-6), 190.9 (s, C=O), 134.6 (s, C-i), 129.8 (s, C-o), 130.0 (s, C-m), 135.8 (s, C-p), 32.4 (s, α-CH_2), 32.7 (d, $^7J_{PC}$ = 0.6 Hz, β-CH_2), 22.7 (s γ-CH_2), 14.0 (s, CH_3). The assignment of the ^{13}C-NMR signals is based on a ^{1}H, ^{13}C, shift-correlated 2D-NMR spectrum.

3-*Benzoyl-1-dichlorophosphino-2-phosphaindolizine* (**4a**)

Method A: To 240 mg (1 mmol) **5a** in 10 ml acetonitrile 0.14 ml (1 mmol) triethylamine are added and the resulting solution is cooled to 0°C. A solution of 1 mmol PCl_3 in 5 ml acetonitrile is added within 0.5 hour with stirring. The reaction mixture is allowed to come to room temperature and the solvent is evaporated *in vacuo*. The dry residue is extracted two times with 30 ml diethyl ether. On concentrating and cooling the extract, yellow crystals of **5a** separate which are filtered off and dried. Yield 66 mg (39%), the compound decomposes at 115°C. Anal. Calcd. for $C_{14}H_9Cl_2NOP_2$ (340.1): C, 49.44; H, 2.67; N, 4.12. Found: C, 49.38; H, 3.88; N, 4.23.

^{1}H-NMR ($CDCl_3$): δ = 10.05 (d, 1H, $^3J_{HH}$ = 7.1 Hz, 5-H), 6.15 (dd, 1H, $^3J_{HH}$ = 6.8 Hz, 7.1 Hz, 6-H), 6.51 (dd, 1H, $^3J_{HH}$ = 6.8 Hz, 9.0 Hz, 7-H), 7.84 (m, 1H, p-H), 7.0–7.2 (m, 5H, o, m-H, 8-H). For ^{13}C- and ^{31}P-NMR data see Table 2 and 3 respectively.

In the same way **5b**, mp 119 – 121°C, was obtained in 55% yield. **5d** was prepared this way only for spectroscopic identification (Table 3).

Method B: To a suspension of 5.26 g (18 mmol) 2-methyl-1-phenacylpyridinium bromide in 50 ml

TABLE 4 Yields Physical and Analytical Data of the 1-Bromo-2-phosphaindolizines **2**

	Prep. Method	Yield %	Color mp [°C]	Formula M	Calcd. Found	C	H	N
2a	C	59	yellow	$C_{14}H_9BrNOP$		52.86	2.85	4.40
			137–140[a]	318.1		52.26	2.98	4.43
2b	B	75	yellow	$C_{15}H_{11}BrNOP$		54.24	3.34	4.22
			152–154	332.1		53.24	3.91	4.17
2c	A	20	yellow	$C_{18}H_{17}BrNOP$		57.77	4.58	3.74
			79–81	374.2		59.12	5.09	3.50
2d	C	70	yellow	$C_{11}H_{11}BrNO_2P$		44.03	3.69	4.67
			76–77	300.1		43.52	3.90	4.68
2e	C	56	yellow	$C_{14}H_{17}BrNO_2P$		49.14	5.01	4.09
			syrupy	342.2				
2f	C	56	cream	$C_9H_6BrN_2P$		42.72	2.39	11.07
			137–138	253.0		43.15	3.10	10.66

[a] Decomposition.

actonitrile cooled to 0°C were added 12.6 ml (90 mmol) triethylamine followed by addition of a solution of 3.2 ml (36 mmol) phosphorus trichloride in 5 ml acetonitrile with stirring over a period of 0.5 hour. The reaction mixture was allowed to come to room temperature slowly and stirring was continued for 2 hours. The solvent was thereafter removed under reduced pressure and the residue was extracted two times with 80 ml diethyl ether. The ether solution was concentrated to one fourth of its volume and left in the refrigerator, whereupon yellow crystals were obtained which were filtered off and dried. Yield 3.73 g (61%). Anal. Found C, 50.13; H, 2.96; N, 3.71.

The analogous formation of **5e** and **5h** is indicated by the ^{31}P NMR spectra of the reaction mixtures (see Table 3).

3-Benzoyl-6-n-butyl-1-dichlorophosphino-2-phosphaindolizine (**5c**)

To 1.48 g (5.0 mmol) **1c** in 25 ml acetonitrile 0.44 ml (5.0 mmol) phosphorus trichloride are added with stirring. A yellow crystalline precipitate forms which after 15 hours is filtered off and dried. Yield 1.70 g (86%). Anal. Calcd. for $C_{18}H_{17}Cl_2NOP_2$ (396.2): C, 54.57; H, 4.32; N, 3.54. Found: C, 54.27; H, 4.49; N, 3.62.

The analogous reaction of **13** gave compound **14** but was only half complete after 4 weeks as shown by the ^{31}P NMR spectra of the reaction mixture (Table 3).

Hydrolysis of **5c**

To 99 mg (0.25 mmol) **5c** in (a) 5 ml acetonitrile and (b) in 10 ml toluene and 70 μl (0.5 mmol) triethylamine 9 μl (0.5 mmol) water are added. In both cases the ^{31}P-NMR spectrum shows exclusively the signal at δ = 180.3 for **1c**. No product resulting from the exocyclic phosphorus can be identified.

Methanolysis of **5b, c**

To 198 mg (0.5 mmol) **5c** in 10 ml toluene are added with stirring 140 μl (1 mmol) triethylamine and 41 μl (1 mmol) methanol. The ^{31}P-NMR spectrum shows the AB-signals of **7c** (Table 3) together with the signal of **1c**. The solvent is evaporated and the residue extracted with diethyl ether. Evaporating the ether leaves a pale yellow solid. Its ^{31}P-NMR spectrum shows in addition to the foregoing signals the AB-signal of **8c** (Table 3). Adding a drop of methyl iodide results in a complete conversion of **7c** to **8c**.

In the same way **7b** (Table 3) is obtained from **5b** as a yellow syrupy mass. Warming its solution in acetonitrile with the equivalent amount of sulfur to 50°C for 2 hours completely transforms it to **9b** (Table 3).

4-(2-phosphaindolizinyl-1-phosphino)-1,2,3-diazaphospholes **11c** *and* **12c**

A solution of 1.4 g (4.8 mmol) **5c** and 0.5 g (4.8 mmol) triethylamine in 20 ml acetonitrile is added during 15 minutes to a stirred solution of 1.0 g (4.8 mmol) 4-dichlorophosphino-2,5-dimethyl-1,2,3-diazaphosphole in 20 ml acetonitrile at −40°C. When the solution is allowed to come to room temperature it turns brown and triethylammonium chloride precipitates. After 72 hours and filtration the solvent is evaporated *in vacuo* and the brown residue extracted with 20 ml diethyl ether. Evaporation of the extract leaves a yellow oil which according to the ^{31}P-NMR spectrum contains **11c** and **12c** together with some unreacted starting compounds. By extraction with two times 10 ml hexane the oil is separated into two fractions which contain **11c** and **12c** in a ratio of 15:1 (extract) and 4:1 (residue).

11c: For ^{13}C- and ^{31}P-NMR data see Table 2 and 3 respectively. ^{1}H-NMR ($CDCl_3$): δ = 0.96 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_3 of n-Bu), 1.41 (tq, 2H, $^3J_{HH}$ = 7.6 Hz, 7.3 Hz, γ-CH_2), 1.69 (quintet, 2H, $^3J_{HH}$ = 7.6 Hz, β-CH_2), 2.44 (t, 3H, $^4J_{PH}$ = 1.5 Hz, 5-CH_3 of diazaphosphole ring), 2.71 (t, $^3J_{HH}$ = 7.6 Hz, α-CH_2), 3.98 (d, 3H, $^3J_{PH}$ = 7.8 Hz, 2-CH_3 of diazaphosphole ring), 7.36 (dd, 1H, $^3J_{HH}$ = 9.1 Hz, $^5J_{PH}$ = 1.7 Hz, 7-H), 7.46 (m, 2H, m-H), 7.55 (m, 1H, p-H), 7.89 (m, 2H, o-H), 8.03 (d, 1H, $^3J_{HH}$ = 9.1 Hz, 8-H), 10.12 (s, 1H, 5-H).-**12c:** For ^{31}P-NMR data see Table 3.

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