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Phosphorylated Indolizines

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ABSTRACT

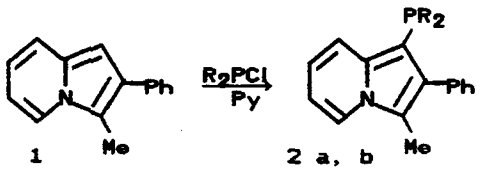
Preparative methods of synthesis of 1- and 3-phosphino-indolizines by interaction between 2-substituted indolizines with phosphorus(III) halogenides in the presence of bases have been developed. It was found that originally this reaction results in the formation of 1-phosphino-indolizines which then undergo izomerization into 3-phosphino isomers. One, two, or three indolizine substituents can be consecutively attached to the phosphorus atom. New methods of syntheses of 1,3-diphosphino-indolizines have been developed.

INTRODUCTION

Recently, we have used direct substitution of electron-rich aromatic and unsaturated compounds with phosphorus(III) halides to synthesize phosphorylated enamines [1,2], cyclic ketones [3,4], naphthalenes [5], hydrazones [6], indoles [7], pyrroles [8], furans, and thiophenes [9,10]. Reactions of indolizines with phosphorus halides have not been studied yet, although data on phosphorylation of 2-phosphaindolizines have been reported by Karaghiosoff et al. [11]. Acylation of indolizines with acyl halides and acid anhydrides is also well known [12,13]. It usually proceeds at position 3, and 1-substituted indolizines are often formed as additional products.

RESULTS AND DISCUSSION

We have found that 2-phenyl-3-methylindolizine **1** reacts readily with PCl_3 or diphenylchlorophosphine in pyridine solution, leading to the formation of 1-phosphorylated indolizines **2** [14].



R = Cl (a), Ph (b).

Reaction of 2-phenyl- and 2-methylindolizine with PCl_3 or diphenylchlorophosphine under similar conditions led to the formation of mixtures of 1- and 3-phosphinoindolizines as judged from ^{31}P NMR spectroscopy. If carried out in benzene in the presence of triethylamine at a temperature of no more than 15°C, the same reactions will give 3-phosphinoindolizines. Compounds **4** and **6** can be isolated individually in high yields. They can be stored for a few days without isomerization in the solid state or in pyridine, benzene, or CCl_4 solutions. Many hours of boiling of compounds **4** and **6** in benzene solution results in complete isomerization of these compounds into compounds **5** and **7**, respectively, also isolated in high yields.

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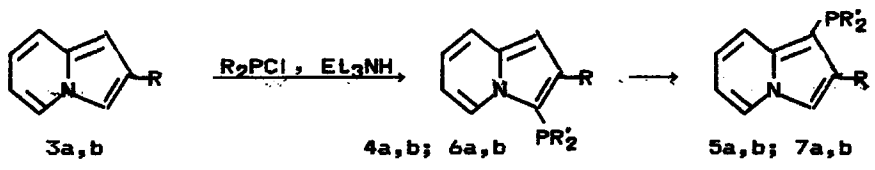


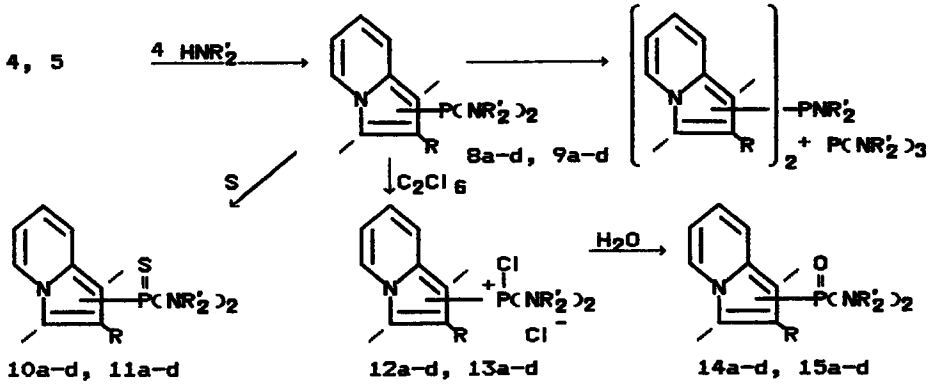
Since in ^{31}P NMR spectra of isomerizing mixture signals of 1,3-diphosphorylated indolizines, described below, also appear, isomerization is probably an intermolecular process. This isomerization goes on much faster in such solvents as chloroform, acetonitrile, and methylene chloride. In the ^{31}P NMR spectra of the dichlorophosphine **4a**, dissolved in these solvents, a single signal corresponding to the 1-phosphinoindolizine **5a** can be observed. The similar 2-phenyl substituted dichlorophosphine **4b** isomerizes in methylene chloride somewhat slower, during 2–3 hours. Isomerization of phosphines **6a,b** proceeds even more slowly. For quantitative isomerization, the solution of phosphine **6a** in methylene chloride must be maintained for 3 days and the solution of phosphine **6b** for 5 days. In all cases, addition of pyridine slows down the process of isomerization, probably because of binding of acidic impurities. It should be noted that, in the literature, there is information about a similar migration of the trifluoroacetyl group from position 3 of indolizine to position 1, but this reaction was complicated by side processes and proceeded in low yield [15].

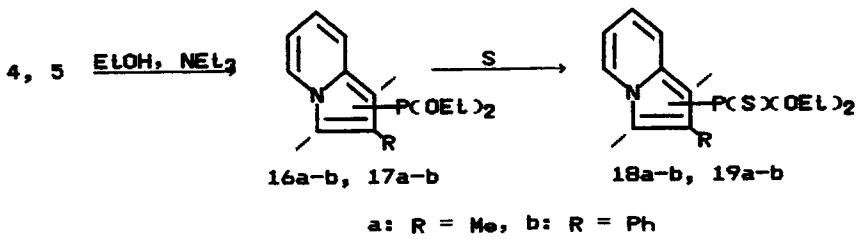
Phosphinoindolizines are vinylogues of aminophosphines and that possibly explains the facility of C–P bond breaking. We have observed the same ease of this bond breaking previously in the case of β-phosphinoamines [1–4], including heterocyclic ones.

Indolizines with the dichlorophosphine group in position 1 or 3 react in the normal fashion with secondary amines, leading to the formation of two series of amides **8** and **9**. Attempts to accomplish 3 → 1 isomerization in the case of these compounds were not successful. Boiling of compounds **8** results in the formation of hexaalkyltriamidophosphites and dialkylamidophosphinites. In this case, when the starting amides are heated, the formation of a mixture of phosphinites in which phosphorus is linked to both the 1 and 3 positions in all possible combinations is observed.

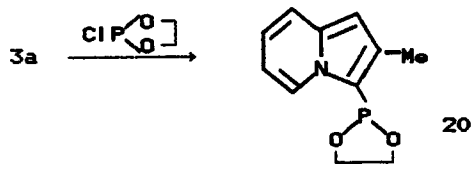
Both 1- and 3-diamidophosphonites were transformed into thiophosphonates, **10** and **11**, by reaction with sulfur and into chlorophosphonium chlorides, **12** and **13**, by reaction with hexachloroethane. Subsequent hydrolysis of **12** and **13** led to phosphonates **14** and **15**. Two series of ethers were obtained by use of the reaction of dichlorophosphines **4** and **5** with ethanol in the presence of triethylamine.

Phosphonites **16** with the diethoxyphosphonyl



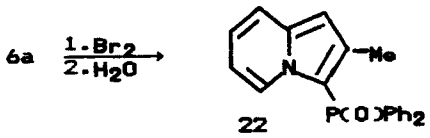


group in the 3-position, like other compounds of such type, are tolerant to oxygen and moisture of the air. In contrast, compound **17a**, in which the heterocycle is probably mere electron-donating toward phosphorus, can be isolated in analytically pure state only in the absence of oxygen and moisture. Prolonged boiling of phosphonites **16a,b** in acetonitrile does not cause isomerization, and only triethyl phosphite arises as an impurity. The readily formed thiophosphonates, **18** and **19**, are stable compounds, also not susceptible to migration of the thiophosphonate group on boiling. Attempts to obtain phosphonates **16a,b** by the reaction of diethoxychlorophosphines with indolizine were not successful. However, when the more electrophilic ethylene chlorophosphite is treated with 2-methylindolizine, the phosphonite **20** is formed in high yield.



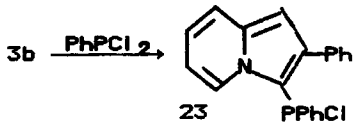
It is interesting that, in the case of less reactive 2-phenylindolizine, the analogous reaction results in a mixture of 1- and 3-phosphorylated indolizines in approximately equal amounts.

Like diamides **8**, phosphine **6a** was converted into the phosphine oxide **22** by use of the reaction with bromine with subsequent hydrolysis. However, we were unable to carry out the reaction of sulfur addition that usually proceeds very readily. Probably sulfur reacts, not only with the phosphorus atom, but also with indolizine's carbon atom [16]. Probably for the same reason, it is impossible to carry out a direct alkylation conventional for phosphines.

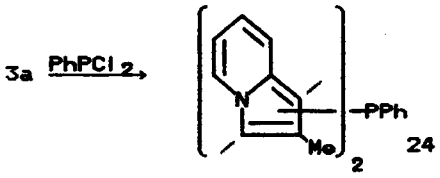


Oxide **22** is quite stable, and boiling it in various solvents, including those in the presence of trialkylammonium chloride, does not lead to isomerization.

Two or three indolizine fragments can be introduced at a single phosphorus atom. It is interesting that reaction of phenyldichlorophosphine with phenylindolizine ceases at the stage of chlorophosphine **23** formation.

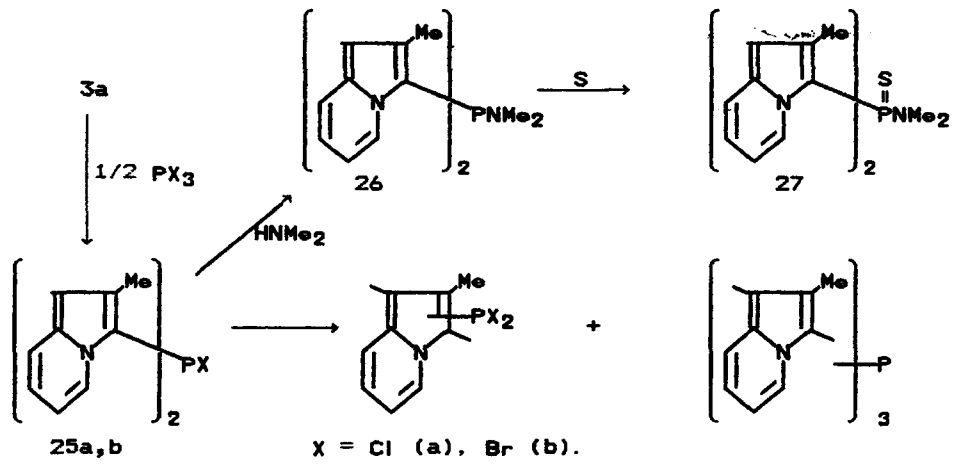


In the case of the more reactive 2-methylindolizine, replacement of two chlorine atoms takes place, leading to the formation of a mixture of phosphines **24**.



Reaction of 2 equivalents of the indolizine **3a** with PCl_3 or PBr_3 leads to the formation of halogenophosphines **25**. Both of these compounds, in attempts to isolate them from the solution, begin to symmetrize with the formation of a mixture of dihalogenophosphines **4,5** and phosphines with 1- and 3-indolizinyl groups. However, halogenophosphines **25** can be smoothly transformed into amidophosphinite **26** and amidothiophosphinate **27**.

In order to bind three indolizine residues with one phosphorus atom, it is more convenient to use PBr_3. On mixing one mole of PBr_3 with 3 moles of indolizine in pyridine, the reaction mixture ac-



cording to ^{31}P NMR data, δ_P = −72.9, −75.9, −80.9, −84.4, contains four phosphines. However, if the reaction mixture is allowed to stand for 2 months, it becomes possible to isolate tris-(3-indolizinyl)phosphine **28** in high yield (see Table 1). The mixture isomerizes into a single phosphine, **28**. Here we can see the first example of 1 → 3 isomerization. It should be noted that phosphines having a 3-indolizinyl group can be oxidized much easier than 1-indolizinylphosphines.

TABLE 1 Yields, Data on analysis, and ^{31}P NMR Spectra

No.	Yield (%)	Mp (°C)	Formula	$\delta^{31}P\{^1H\}$ (Solvent)	Found % (Calculated %)		
					N	P	S or Cl
2a	75	152–153	$C_{15}H_{12}Cl_2NP$	155.2 (benzene)		9.89 (10.06)	22.91 (23.01)
2b	80	94–96	$C_{27}H_{22}NP$	−30.1 (benzene)	3.59 (3.58)	7.64 (7.92)	
4a	72	95–96	$C_9H_8Cl_2NP$	120.4 (benzene)	5.89 (6.04)	13.20 (13.35)	30.21 (30.56)
4b	86	123–126	$C_{14}H_{10}Cl_2NP$	123.1 (benzene)	4.61 (4.76)	10.28 (10.54)	23.98 (24.11)
5a	97	96–97	$C_9H_8Cl_2NP$	152.1 (CH_2Cl_2)	5.81 (6.04)	13.21 (13.35)	30.36 (30.56)
5b	95	121–123	$C_{14}H_{10}Cl_2NP$	152.8 (CH_2Cl_2)	4.59 (4.76)	10.41 (10.54)	24.02 (24.11)
6a	72	89–91	$C_{21}H_{18}NP$	−38.0 (CH_2Cl_2)	4.34 (4.44)	9.71 (9.82)	
6b	79	132–133	$C_{26}H_{20}NP$	−24.2 (benzene)	3.65 (3.71)	8.09 (8.21)	
7a	87	93–95	$C_{21}H_{18}NP$	−33.0 (CH_2Cl_2)	4.23 (4.44)	9.76 (9.82)	
7b	87	121–123	$C_{26}H_{20}NP$	−21.4 (benzene)	3.59 (3.71)	8.13 (8.21)	
8a	93	oil	$C_{13}H_{20}N_3P$	95.2 (petrol)	16.67 (16.86)	12.29 (12.42)	
8b	88	oil	$C_{18}H_{22}N_3P$	86.4 (benzene)	13.39 (13.50)	9.90 (9.95)	
8c	64	oil	$C_{17}H_{28}N_3P$	86.4 (benzene)	14.01 (13.76)	10.19 (10.14)	
8d	89	oil	$C_{22}H_{30}N_3P$	85.0 (petrol)	11.60 (11.44)	8.75 (8.43)	

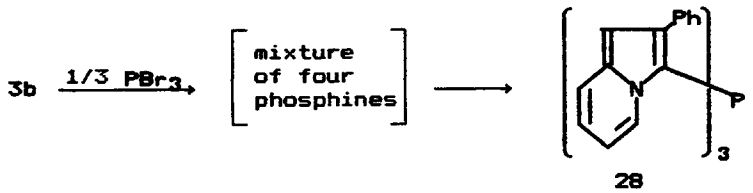
TABLE 1 Continued

No.	Yield (%)	Mp (°C)	Formula	$\delta^{31}P\{^1H\}$ (Solvent)	Found % (Calculated %) N	P	S or Cl
9a	67	oil	$C_{13}H_{20}N_3P$	96.1 (CH_3CN)	16.73 (16.86)	12.38 (12.42)	
9b	74	oil	$C_{18}H_{22}N_3P$	92.2 (benzene)	13.42 (13.50)	9.87 (9.95)	
9c	77	oil	$C_{17}H_{28}N_3P$	92.2 (benzene)	13.53 (13.76)	9.89 (10.14)	
9d	71	oil	$C_{22}H_{30}N_3P$	91.5 (CH_3CN)	11.53 (11.44)	8.56 (8.43)	
10a	83	136–138	$C_{13}H_{20}N_3PS$	67.3 (petrol)	14.90 (14.94)	10.89 (11.01)	11.25 (11.39)
10b	95	141–142	$C_{18}H_{22}N_3PS$	64.8 (benzene)	12.19 (12.24)	8.91 (9.02)	9.16 (9.34)
10c	76	oil	$C_{17}H_{28}N_3PS$	66.2 (benzene)	12.27 (12.45)	9.01 (9.18)	9.34 (9.50)
10d	80	111–113	$C_{22}H_{30}N_3PS$	63.2 (benzene)	10.34 (10.52)	7.56 (7.75)	7.87 (8.02)
11a	63	142–144	$C_{13}H_{20}N_3PS$	75.2 (petrol)	14.78 (14.94)	10.88 (11.01)	12.09 (11.39)
11b	72	147–149	$C_{18}H_{22}N_3PS$	72.4 (benzene)	12.34 (12.24)	8.91 (9.02)	9.18 (9.34)
11c	87	oil	$C_{18}H_{22}N_3PS$	72.5 (benzene)	12.23 (12.45)	9.28 (9.18)	9.61 (9.50)
11d	66	117–119	$C_{17}H_{28}N_3PS$	75.6 (benzene)	10.45 (10.52)	7.89 (7.75)	8.11 (8.02)
12a	75	181–183	$C_{13}H_{20}Cl_2N_3P$	47.9 ($CDCl_3$)	13.03 (13.12)	9.45 (9.67)	22.02 (22.15)
12b	91	199–201	$C_{18}H_{22}Cl_2N_3P$	51.3 ($CHCl_3$)	11.20 (10.99)	7.94 (8.10)	18.67 (18.55)
12c	69	159–160	$C_{17}H_{28}Cl_2N_3P$	46.5 ($CHCl_3$)	11.23 (11.17)	8.09 (8.23)	18.92 (18.84)
12d	86	161–164	$C_{22}H_{30}Cl_2N_3P$	53.8 ($CHCl_3$)	9.72 (9.59)	6.86 (7.06)	16.05 (16.18)
13a	74	186–188	$C_{13}H_{20}Cl_2N_3P$	59.8 ($CHCl_3$)	13.06 (13.12)	9.38 (9.67)	22.10 (22.15)
13b	79	207–209	$C_{18}H_{22}Cl_2N_3P$	63.8 ($CHCl_3$)	11.14 (10.99)	7.87 (8.10)	18.35 (18.55)
13c	56	163–165	$C_{17}H_{28}Cl_2N_3P$	61.3 ($CHCl_3$)	11.09 (11.17)	8.13 (8.23)	18.76 (18.84)
13d	81	192–194	$C_{22}H_{30}Cl_2N_3P$	67.5 ($CHCl_3$)	9.39 (9.59)	6.91 (7.06)	16.01 (16.18)
14a	87	91–93	$C_{13}H_{20}N_3OP$	22.3 ($CHCl_3$)	14.98 (15.24)	11.51 (11.67)	
14b	69	105–107	$C_{18}H_{22}N_3OP$	20.2 ($CHCl_3$)	12.91 (12.84)	9.26 (9.46)	
14c	79	oil	$C_{17}H_{28}N_3OP$	11.4 ($CHCl_3$)	13.21 (13.08)	9.58 (9.64)	
14d	73	85–87	$C_{22}H_{30}N_3OP$	12.8 ($CHCl_3$)	11.03 (10.97)	7.94 (8.09)	
15a	82	103–105	$C_{13}H_{20}N_3OP$	28.9 (ether)	15.80 (15.84)	11.63 (11.67)	
15b	68	113–115	$C_{18}H_{22}N_3OP$	25.9 ($CHCl_3$)	12.92 (12.84)	9.53 (9.46)	
15c	91	oil	$C_{17}H_{28}N_3OP$	20.5 ($CHCl_3$)	13.04 (13.08)	9.76 (9.66)	
15d	78	97–99	$C_{22}H_{30}N_3OP$	18.4 ($CHCl_3$)	11.03 (10.97)	8.16 (8.09)	
16a	83	oil	$C_{13}H_{18}NO_2P$	156.0 (CH_3CN)	5.59 (5.57)	12.29 (12.33)	

TABLE 1 Continued

No.	Yield (%)	Mp (°C)	Formula	$\delta^{31}P\{^1H\}$ (Solvent)	Found % (Calculated %) N	P	S or Cl
16b	76	oil	$C_{18}H_{20}NO_2P$	157.1 (CH_3CN)	4.55 (4.47)	9.82 (9.88)	
17a	85	oil	$C_{13}H_{18}NO_2P$	164.9 (benzene)	5.60 (5.57)	12.28 (12.33)	
17b	92	oil	$C_{18}H_{20}NO_2P$	163.3 (CH_3CN)	4.52 (4.47)	9.97 (9.88)	
18a	71	oil	$C_{13}H_{18}NO_2PS$	72.2 (benzene)	5.03 (4.94)	10.88 (10.93)	11.37 (11.32)
18b	79	79–81	$C_{18}H_{20}NO_2PS$	69.9 (benzene)	3.98 (4.06)	9.03 (8.97)	9.16 (9.28)
19a	76	oil	$C_{13}H_{18}NO_2PS$	80.5 (benzene)	4.91 (4.94)	11.01 (10.93)	11.26 (11.32)
19b	64	87–89	$C_{18}H_{20}NO_2PS$	79.8 (CH_3CN)	5.99 (4.06)	9.10 (8.97)	9.32 (9.28)
20	88	oil	$C_{11}H_{12}NO_2P$	171.8 (benzene)	6.16 (6.33)	14.12 (14.00)	
22	83	134–136	$C_{21}H_{18}NOP$	21.8 ($CHCl_3$)	4.31 (4.23)	9.32 (9.35)	
27	71	87–89	$C_{22}H_{26}N_3PS$	34.1 (benzene)	10.58 (10.63)	7.79 (7.83)	8.17 (8.11)
28	79	184–185 (decomp)	$C_{42}H_{30}N_3P$	−76.1 (benzene)	6.83 (6.92)	5.16 (5.10)	
30a	71	183–185 (decomp)	$C_{33}H_{27}NP_2S_2$	1–28.7; 3–31.5 (benzene)	2.53 (2.49)	10.92 (10.99)	11.47 (11.38)
30b	67	257–258 (decomp)	$C_{38}H_{29}NP_2S_2$	1–28.1; 3–28.9 (benzene)	2.15 (2.23)	9.81 (9.90)	10.19 (10.25)
31a	86	151–153	$C_9H_7Cl_4NP_2$	1–146.9; 3–118.9 (benzene)	4.28 (4.21)	18.52 (18.60)	42.71 (42.60)
31b	71	182–185	$C_{14}H_9Cl_4NP_2$	1–146.0; 3–119.5 (benzene)	3.47 (3.55)	15.78 (15.69)	35.91 (35.90)
32a	84	91–93	$C_{17}H_{31}N_5P_2$	1–96.1; 3–88.2 (benzene)	19.11 (19.06)	16.79 (16.86)	
32b	87	129–131	$C_{22}H_{33}N_5P_2$	1–92.2; 3–86.4 (benzene)	16.38 (16.31)	14.37 (14.42)	
33a	69	197–200	$C_{17}H_{31}N_5P_2S_2$	1–74.5; 3–64.3 (benzene)	16.35 (16.23)	14.26 (14.35)	14.73 (14.86)
33b	82	223–224	$C_{22}H_{33}N_5P_2S_2$	1–72.5; 3–64.8 (benzene)	14.13 (14.19)	12.63 (12.55)	13.07 (12.99)

[a]All spectra were taken using a Bruker WP-200 operating at 81.026 MHz, with 85% H_3PO_4 as external reference.



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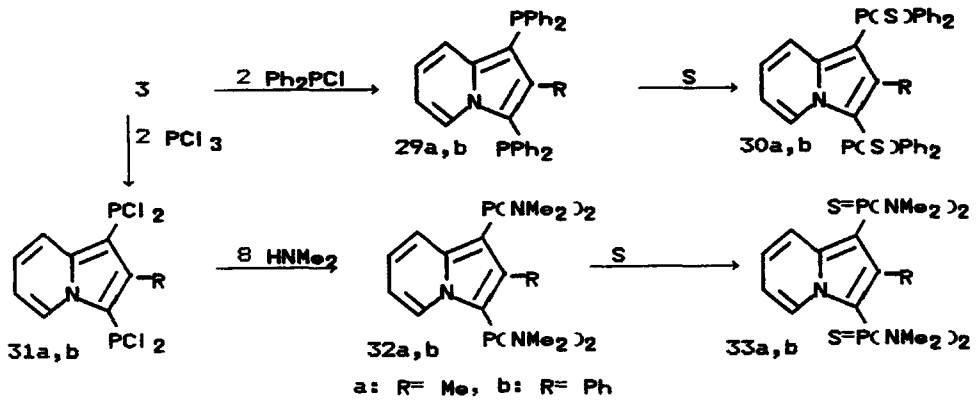
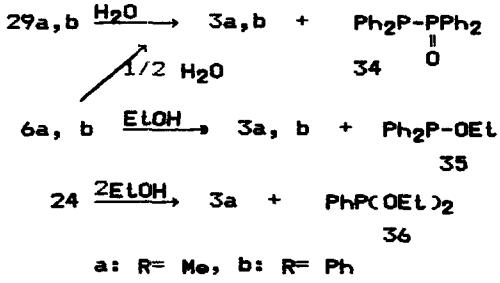
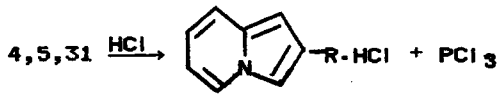
It is known that bisacylation of indolizines with acyl halides and acid anhydrides is possible only under very drastic conditions [13]. However, bisphosphorylation of indolizines can be achieved using PCl_3 at room temperature [16]. For preparative purposes, it is more convenient to use an excess of PCl_3. Bisdichlorophosphines **31** can be transformed into compounds **32** and **33** by conventional methods. Formation of bisdiphenylphosphine **29** takes place much slower. Since both activated positions in compound **29** are occupied, sulfur addition proceeds in the ordinary way, in contrast to the case of phosphine **24**.

The unusual lability of the C–P bond in phos-

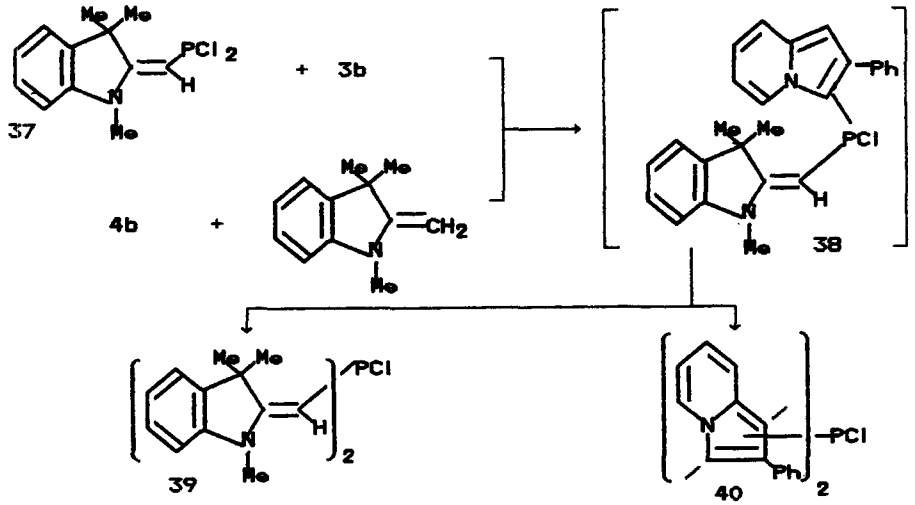


phinoindolizines is displayed, not only in reactions of isomerization, but also in a number of other transformations as well.





Attempts to obtain the chlorophosphine **38** by reaction of 1,3,3-trimethyl-2-methyleneindolene with dichlorophosphine **4b** or by reaction of the dichlorophosphine **37** with indolisine **3b** offer additional interesting illustrations of the case of C–P bond cleavage. In both cases, mixtures of chlorophosphines **39** and **40**, which are certainly products of the symmetrization of the unstable compound **38**, are formed.



Reactions of phosphines **6** and **29** with trace amounts of water lead to the formation of indolizine and the P–P compound **34**. The rupture of the C–P bond in phosphines **6** and **24** takes place when dissolving these compounds in chloroform containing less than 1% of alcohol with the formation of phosphinite **34** and phosphonite **36**. The C–P bond breaks instantly in chloro- and dichlorophosphines **4**, **5** and **31** under the action of dry HCl.

The compositions of the compounds obtained were confirmed by the elemental analysis data (see Table 1) and their structures by spectral data (see Tables 1–7) and by chemical transformations that were carried out. Unambiguous conclusions about the positions of phosphorus-containing groups could be made on the basis of ^{1}H NMR spectra and also on the basis of ^{13}C or ^{31}P NMR spectra.

Signals of protons and of ^{13}C, ^{31}P nuclei are

TABLE 2 3-Substituted Indolizines: ^{1}H NMR δ,[a] (Multiplicity),[b] J(Hz)

N	H^1	H^5	H^6	H^7	H^8	*2-Me*	*2-Ph*	*Others*	
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	
4a[c]	5.88(d)	8.92(dd)	6.12(m)	6.44(m)	6.86(d)	2.14(d)			
	6.8	7.2, 1.0			8.8	1.0			
4b[c]	6.25(s)	9.02(d)	6.19(m)	6.48(m)	6.93(d)		7.42(m)		
		7.0			9.0		7.15(m)		
6a[c]	6.45(d)	7.85(dd)	6.22(m)	6.70(m)	7.27(m)	2.34(s)		7.27(m)	Ph
	3.2	7.0, 1.0							
6b[c]	6.11(d)	7.67(dd)	6.31(m)	6.64(m)	6.83(d)			7.11–7.44(vbs)	all Ph
	3.4	7.0, 1.0			8.4				
8a[c]	6.43(d)	8.41(d)	6.24(m)	6.50(m)	7.21(d)	2.76(s)		2.53(d)	NMe_2

TABLE 3 1-Substituted Indolizines: ^{1}H NMR δ,[a] (Multiplicity),[b] J (Hz)

N	*H*^{3}	*H*^{5}	*H*^{6}	*H*^{7}	*H*^{8}	*2-Me*	*2-Ph*	*Others*	
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	
2a[d]		7.85(d) 7.0	6.84(m)	7.08(m)	8.26(d) 9.0		7.34(m)	2.29(s)	Me
2b[d]		7.76(d) 7.2	6.5(m)		6.85(d) 8.4		7.10–7.30(m) all Ph:	2.40(s)	Me
5a[d]	7.13(s)	7.90(d) 7.0	6.50(m)	6.99(m)	7.86(d) 9.2	2.54(s)			
5b[d]	7.28(d) 5.2	8.04(d) 7.0,	6.80(m)	7.12(m)	8.31(d) 9.2		7.37–7.50(m) all Ph		
7a[d]	7.10(s)	7.87(d) 6.4	6.39(m)	6.55(m)	7.77(d) 8.4	2.44(d) 0.8		7.20–7.40(m)	Ph
7b[d]	7.13(s)	7.92(d) 6.5	6.41(m)	6.59(m)	7.83(d) 8.3	2.51(s)	7.20–7.40(m) all Ph		
9a[d]	7.28(s)	7.96(dq) 7.0, 1.2	6.46(m)	6.68(m)	7.46(d) 9.2	2.19(d) 0.8		2.74(m)	NMe_2
9b[d]	7.32(s)	8.01(d) 7.2	6.52(m)	6.71(m)	7.49(d) 9.3		7.23–7.67(m)	2.78(m)	NMe_2
9c[d]	7.31(s)	7.89(d) 7.0	6.48(m)	6.72(m)	7.52(d) 9.0	2.25(s)		2.97(m) 0.93(t), 8.2	NCH_2 Me
9d[d]	7.22(s)	7.98(d) 7.0	6.47(m)	6.69(m)	7.80(d) 9.4		7.18–7.50(m)	2.90(m) 0.86(t), 7.0	NCH_2 Me
11a[d]	7.15(d) 3.8	7.09(dq) 5.8, 1.2	6.55(m)	6.85(m)	8.11(d) 9.2	2.49(d) 0.8		2.64(d) 12.6	NMe_2
11b[d]	7.16(s)	7.21(d) 6.0	6.63(m)	6.91(m)	8.15(d) 9.0		7.21–7.37(m)	2.52(d) 11.8	NMe_2
11c[d]	7.13(d) 3.4	7.03(d) 5.9	6.51(m)	6.86(m)	8.07(d) 9.3	2.51(d) 0.7		2.81(m) 0.83(t), 7.1	NCH_2 Me
11d[c]	7.22(s)	7.16(dq) 5.7, 1.1	6.58(m)	6.87(m)	8.14(d) 9.2		7.19–7.41(m)	3.13(m) 1.04(t), 7.0	NCH_2 Me
13a[d]	7.07(s)	7.78(d) 5.6	7.45(m)	7.66(m)	8.59(d) 8.6	2.38(s)		2.92(d), 12.8	NMe_2
13b[d]	7.12(s)	7.81(d) 5.7	7.49(m)	7.67(m)	8.63(d) 8.7		7.28–7.39(m)	2.97(d), 12.7	NMe_2
13c[d]	7.09(s)	7.76(d) 5.5	7.45(m)	7.71(m)	8.55(d) 8.5	2.33(s)		3.18(m) 1.07(m)	NCH_2 Me
13d[d]	7.10(s)	7.83(d) 5.7	7.47(m)	7.69(m)	8.61(d) 8.6		7.28–7.39(m)	3.14(m) 1.12(m)	NCH_2 Me
15a[d]	7.14(d) 3.4	7.89(m)	6.54(m)	6.82(m)	7.89(m)	2.41(s)		2.65(d), 10.0	NMe_2
15b[d]	7.19(d) 3.5	7.93(m)	6.58(m)	6.87(m)	7.93(m)		7.14–7.56(m)	2.77(d), 10.7	NMe_2
15c[d]	7.12(d) 3.2	7.87(m)	6.52(m)	6.79(m)	7.87(m)	2.45(s)		3.45(m) 1.23(m)	NCH_2 Me
15d[d]	7.17(d) 3.5	7.91(m)	6.59(m)	6.81(m)	7.91(m)		7.21–7.58(m)	3.47(m) 1.21(m)	NCH_2 Me
17a[d]	7.05(s)	7.77(d) 6.8	6.43(m)	6.71(m)	7.87(d) 9.0	2.42(s)		3.87(m) 1.36(m), 8.2	OCH_2 Me
17b[d]	6.48(d) 3.0	7.65(d) 6.8	6.68(m)	7.05(m)	7.87(d) 8.4		7.23–7.39(m)	3.05(m) 1.36(t), 7.0	OCH_2 Me
19a[d]	7.07(d) 4.0	7.83(dt) 7.0, 1.2	6.54(m)	6.87(m)	8.28(d) 9.8	2.44(s)		4.11(m) 1.31(t), 7.0	OCH_2 Me
19b[d]	6.24(d) 4.0	7.91(d) 5.8	6.61(m)	6.94(m)	8.31(d) 9.2		7.35(m) 7.59(m)	3.95(m) 1.05(t), 7.0	OCH_2 Me

[a–d]As for Table 2.

TABLE 4 Bisphosphorylated Indolizines ^{1}H NMR δ,[a] (Multiplicity),[b] J (Hz)

No. 1	H^5 2	H^6 3	H^7 4	H^8 5	2-Me 6	2-Ph 7	Others 8
30a[d]	8.53(d)	6.47(m)	6.59(m)	6.77(m)	2.54(s)		7.24(m) Ph
	6.8						7.61(m) o-Ph
30b[d]	8.65(d)	6.55(m)	6.55(m)	6.91(m)		6.36(m)	7.20(m) Ph
	6.8					6.77(m)	7.65(m) o-Ph
31a[d]	9.03(d)	7.05(m)	7.42(m)	8.23(d)	2.76(d)		
	7.0			8.8	0.8		
31b[d]	9.18(dd)	7.18(m)	7.40(m)	8.50(d)		7.49(m)	
	6.8, 0.8			9.2			
32a[c]	8.74(d)	6.35(m)	6.78(m)	8.05(d)	2.76(s)		2.31(d), 9.1 NMe_2
	7.6			9.4			2.47(d), 9.1 NMe_2
32b[c]	8.66(d)	6.36(m)	6.70(m)	8.84(d)		7.14(m)	2.28(d), 9.2 NMe_2
	7.2			9.0		7.56(d), 7.6	2.45(d), 9.2 NMe_2
33a[d]	9.33(d)	6.71(m)	7.05(m)	8.23(d)	2.76(s)		2.34(d), 10.5 NMe_2
	7.0			9.2			2.41(d), 11.6 NMe_2
33b[d]	8.49(d)	6.86(m)	7.17(m)	8.15(d)		7.35(m)	2.36(d), 10.8 NMe_2
	7.0			9.0			2.44(d), 11.4 NMe_2

[a–d]As for Table 2.

characteristic in positions 1 and 3 of the indolizine ring. Usually in PMR spectra of 3-phosphinoindolizines (Table 2), the signal of H-1 is found in the strongest field. Also, as a rule, this signal is a doublet or a wide singlet when in position 2 a methyl or phenyl group, respectively, present.

In PMR spectra of 1-phosphinoindolizines, the signal of H-3 is also readily identified, but its spin-spin coupling constant with the phosphorus atom is frequently significantly less than with that of H-1. Signals of H-5 and H-8 and their coupling constants are also characteristic. Not depending on substituents in the indolizines, values of coupling constants Jhh H-5 and H-8 are 5.5–7.2 and 8.1–9.8 Hz, respectively. Chemical shifts of the H-5 and H-8 protons can be used as supplementary evidence of the site of phosphorylation: in 1-phosphinoindolizines, the signal of H-8 is shifted toward low field, and, in 3-phosphinoindolizines, the same happens with the signals of H-5.

Signals of the phosphorus atom in ^{31}P NMR spectra of 1-phosphinoindolizines are always located in lower field in comparison with those in the spectra of 3-phosphinoindolizines, and this allows one, not only to identify the structure, but also to follow the processes of isomerization (Table 1). It is also possible to identify structures on the basis of ^{13}C NMR spectra (Tables 5–7). Spectral assignments of ^{13}C chemical shifts were made on the basis of the data reported for derivatives of indolizine [17]. Chemical shifts C-1 and C-5 are the most lowfield and upfield ones, respectively among CH signals of the indolizine nucleus. The signals of 1-phosphinoindolizines for C-1 appear as a doublet with characteristic CP coupling. The signals of 3-phosphinoindolizines as compared to unsubstituted indolizines for C-5 are shifted significantly upfield and sometimes appear as a doublet with CP coupling.

EXPERIMENTAL SECTION

1-(2-Phenyl-3-methylindolizinyl)dichlorophosphine **2a**

A mixture of compound **1** (0.01 mol), PCl_3 (0.01 mol), pyridine (1 mL), and benzene (25 mL) was left to stand for 5 hours at 20°C, then the pyridine salt was separated by filtration, and the filtrate was evaporated almost completely. The product was precipitated by addition of 60 mL of petroleum ether and washed with petroleum ether.

1-(2-Phenyl-3-methylindolizinyl)diphenylphosphine **2b**

A mixture of compound **1** (0.01 mol), chlorodiphenylphosphine (0.01 mol) and pyridine (25 mL) was heated for 2 hours at 70°C. The pyridine salt was separated by filtration, and the filtrate was evaporated almost completely. The product was precipitated by addition of petroleum ether and crystallized from the same solvent.

3-(Indolizinyl)dicholorophosphines **4a,b**

A mixture of compound **3** (0.01 mol), dry benzene (70 mL), Et_3N (0.011 mL), and PCl_3 (0.01 mol) was

TABLE 5 3-Substituted Indolizines ^{13}C {^1H} NMR δ,[a] (Multiplicity),[b] J (P–C, Hz)

N *1*	*C¹* *2*	*C²* *3*	*C³* *4*	*C⁵* *5*	*C⁶* *6*	*C⁷* *7*	*C⁸* *8*	*C⁹* *9*	*Others* *10*		
4a[c]	103.3(d) 7.2	139.1(d) 46.1	117.6(d) 88.3	128.5(d) 2.9	111.9(s)	123.6(s)	118.8(s)	141.1(d) 2.1	12.5(d),	19.7	2-Me
4b[c]	102.6(d) 6.5	134.7(d) 3.9	144.1(d) 41.5	127.0(d) 5.0	112.4(s)	123.7(s)	119.5(s)	140.8(s)	131.0(d), 128.6(s) 129.0(s)	7.4	o-Ph m-Ph p-Ph
6a[c]	103.0(d) 7.0	135.4(d) 7.7	111.9(d) 15.2	126.0(d) 8.3	109.8(s)	119.2(s)	118.5(s)	137.5(s)	14.0(d), 137.8(d), 132.5(d), 128.9(d), 128.0(s)	11.4 20.7 17.8 5.9	2-Me i-Ph o-Ph m-Ph p-Ph
6b[c]	103.5(d) 7.0	135.7(d) 7.2	114.6(d) 14.6	126.2(d) 6.8	110.5(s)	121.4(s)	119.3(s)	138.7(s)	131.5(d), 127.4(s) 138.6(d), 132.5(d), 128.4(d), 128.5(s)	3.0 10.5 18.5 6.2	C-Ph-o C-Ph-p P-Ph-i P-Ph-o P-Ph-m P-Ph-p
8a[c]	103.8(d) 2.2	132.1(d) 13.4	109.7(d) 39.7	125.4(d) 4.6	109.7(s)	118.2(s)	117.3(s)	136.1(d) 2.7	13.6(d), 40.9(d),	2.6 17.2	2-Me N-Me
8b[c]	102.3(d) 1.6	131.0(d) 7.4	129.6(d) 21.1	124.7(d) 3.5	110.4(s)	119.0(s)	118.2(s)	137.5(s)	132.3(d), 129.0(s) 44.5(d),	9.8 16.0	C-Ph-o C-Ph-p N-Me
8c[c]	104.0(d) 7.0	133.4(d) 18.1	114.8(d) 20.1	126.1(d) 4.3	110.6(s)	117.0(s)	119.9(s)	139.1(s)	13.1(d), 44.8(d), 15.4(d),	3.1 11.9 3.6	2-Me N-CH_2 CH_2-*Me*
8d[c]	104.9(s)	139.1(d) 11.8	119.0(d) 17.2	128.4(d) 6.5	110.8(s)	118.9(s)	120.0(s)	140.2(s)	137.1(s) 132.2(s) 128.7(s) 127.5(s)		C-Ph-i C-Ph-o C-Ph-m C-Ph-p
10a[d]	103.4(d) 11.3	134.1(d) 13.8	109.2(d) 120.0	127.4(s)	110.5(s)	120.2(s)	117.8(s)	137.2(d) 8.9	15.6(d), 13.9(s) 37.0(d),	4.0 4.3	CH_2-*Me* 2-Me N-Me
10b[d]	104.2(d) 7.8	132.0(d) 7.6	111.4(d) 118.5	126.9(s)	110.3(s)	120.0(s)	119.1(s)	137.8(s)	132.9(d), 129.1(s) 39.0(d),	7.8 6.2	C-Ph-o C-Ph-p N-Me
10c[d]	104.0(d) 10.1	135.0(d) 14.5	111.7(d) 124.5	126.6(s)	111.0(s)	119.0(s)	118.3(s)	138.1(s)	13.6(d), 40.0(d), 14.9(d),	2.9 10.7 3.2	2-Me N-CH_2 CH_2-*Me*
10d[d]	104.6(d) 7.0	133.5(d) 7.6	108.9(d) 119.8	128.0(s)	111.0(s)	120.1(s)	120.0(s)	138.9(s)	137.0(s) 132.1(s) 128.7(s) 127.6(s) 40.7(d), 14.1(d),	14.5 2.5	C-Ph-i C-Ph-o C-Ph-m C-Ph-p N-CH_2 CH_2-*Me*
12a[d]	107.2(d) 14.5	141.5(d) 19.2	111.1(d) 19.7	127.7(s)	115.5(s)	119.1(s)	118.0(s)	142.0(d) 1.4	13.6(s) 37.9(d),	10.0	2-Me N-Me
12b[d]	106.5(d) 7.2	139.8(d) 7.4	119.6(d) 13.5	128.4(s)	116.1(s)	120.0(s)	119.2(s)	140.7(s)	133.1(d), 129.0(s) 38.0(d),	7.6 6.4	C-Ph-o C-Ph-p N-Me
12c[d]	106.7(d) 11.6	140.5(d) 10.5	112.3(d) 17.5	127.6(s)	116.0(s)	120.0(s)	119.3(s)	140.9(s)	13.8(d), 40.3(d), 15.0(d),	3.9 11.5 4.6	2-Me N-CH_2 CH_2-*Me*
12d[d]	107.0(d) 7.4	138.9(d) 7.6	113.6(d) 19.8	128.1(s)	116.0(s)	119.1(s)	117.8(s)	142.0(s)	137.0(s) 131.9(s) 128.5(s) 127.6(s) 42.7(d), 15.1(d),	13.2 4.5	C-Ph-i C-Ph-o C-Ph-m C-Ph-p N-CH_2 CH_2-*Me*
14a[d]	102.2(d) 9.9	134.0(d) 15.0	108.7(d) 195.1	127.4(s)	110.1(s)	119.7(s)	117.3(s)	136.7(d) 9.3	13.2(s) 35.6(d),	4.5	2-Me N-Me

TABLE 5 Continued

N	C^1	C^2	C^3	C^5	C^6	C^7	C^8	C^9	Others		
1	2	3	4	5	6	7	8	9	10		
14b[d]	103.2(d)	132.9(d)	110.2(d)	126.9(d)	110.3(s)	120.0(s)	118.1(s)	137.0(s)	133.4(d),	7.6	C-Ph-o
	8.9	13.2	185.8	3.4					128.6(s)		C-Ph-m
									130.1(s)		C-Ph-p
									36.0(d),	11.8	N-Me
14c[d]	103.0(d)	134.0(d)	109.1(d)	127.6(s)	110.2(s)	119.6(s)	118.0(s)	136.9(s)	14.5(d),	4.9	2-Me
	7.8	9.6	180.2						39.0(d),	12.6	$N\text{-}CH_2$
									15.0(d),	2.9	CH_2-*Me*
14d[d]	104.0(d)	133.5(d)	107.5(d)	127.1(s)	110.1(s)	119.3(s)	118.1(s)	136.9(s)	137.0(s)		C-Ph-i
	7.6	7.8	196.6						130.2(s)		C-Ph-o
									128.6(s)		C-Ph-m
									127.5(s)		C-Ph-p
									45.7(d),	12.6	$N\text{-}CH_2$
									15.6(d),	6.2	CH_2-*Me*
16a[d]	101.4(d)	134.5(d)	124.6(d)	127.1(d)	109.7(s)	119.2(s)	117.8(s)	136.0(d)	12.7(d),	14.3	2-Me
	4.5	30.3	7.9	4.6				1.6	17.0(d),	6.2	CH_2-*Me*
									63.2(d),	16.3	$O\text{-}CH_2$
16b[d]	100.6(d)	135.9(d)	140.0(d)	128.3(s)	110.4(s)	119.9(s)	118.6(s)	136.2(s)	130.3(d),	6.0	C-Ph-i
	5.9	2.1	32.1						129.8(d),	5.4	C-Ph-o
									127.9(s)		C-Ph-m
									126.9(s)		C-Ph-p
									17.1(d),	6.2	CH_2-*Me*
									63.8(d),	18.4	$O\text{-}CH_2$
18a[d]	103.7(d)	136.3(d)		127.1(s)	111.1(s)	121.0(s)	118.2(s)	137.0(d)	15.0(s),		2-Me
	13.1	18.1						9.8	16.2(d),	7.8	CH_2-*Me*
									62.3(d),	5.4	$O\text{-}CH_2$
18b[d]	102.4(d)	133.6(d)	115.3(d)	128.0(s)	112.5(s)	110.0(s)	117.3(s)	136.8(d)	129.7(d),	5.6	C-Ph-i
	8.9	7.8	178.1					8.0	128.3(d),	5.2	C-Ph-o
									127.6(s)		C-Ph-m
									126.0(s)		C-Ph-p
									16.1(d),	6.2	CH_2-*Me*
									61.8(d),	8.5	$O\text{-}CH_2$
20[d]	102.4(s)	132.2(d)		124.3(d)	110.4(s)	119.1(s)	118.2(s)	135.8(d)	12.7(d),	3.7	2-Me
		10.2		9.7				1.4	64.8(d),	8.9	$O\text{-}CH_2$
22[d]	103.6(d)	134.7(d)	108.6(d)	127.6(s)	110.9(s)	120.9(s)	117.8(s)	137.5(d)	13.9(s)		2-Me
	10.2	15.1	130.7					7.4	134.9(d),	65.6	P-Ph-i
									132.0(d),	10.6	P-Ph-o
									128.8(d),	12.6	P-Ph-m
									132.1(s)		P-Ph-p
27[d]	103.7(d)	133.7(d)		127.4(d)	110.5(s)	120.6(s)	117.8(s)	137.6(s)	12.4(s)		2-Me
	10.6	14.1		2.1					36.7(d),	6.5	N-Me
29[d]	96.9(s)	112.6(s)	109.5(d)	125.4(s)	110.4(s)	119.4(s)	117.6(s)	135.7(s)	126.5(s)		C-Ph-o
			2.0						129.1(s)		C-Ph-m
									126.9(s)		C-Ph-p

[a]All spectra were taken using a Gemini-200 operating at 50.0 MHz, with TMS as internal reference.
[b]s = singlet, d = doublet, and t = triplet.
[c]Spectrum was taken in benzene.
[d]Spectrum was taken in chloroform.

left to stand under argon for 12 hours at 20°C. Triethylamine salt was separated by filtration, and the filtrate was evaporated almost completely. The residue was treated with 15 mL of dry heptane, and crystals that precipitated were washed with dry heptane.

3-(Indolizinyl)diphenylphosphines **6a,b**

To a mixture of compound **3** (0.01 mol), dry benzene (30 mL), and Et_3N (0.012 mol), chlorodiphenylphosphine (0.01 mol) was added with cooling, and the mixture was left to stand at 20°C under argon

TABLE 6 1-Substituted Indolizines ^{13}C {^1H} NMR δ,[a] (Multiplicity),[b] J (P-C, Hz)

N	*C*^{1}	*C*^{2}	*C*^{3}	*C*^{5}	*C*^{6}	*C*^{7}	*C*^{8}	*C*^{9}	*Others*		
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*		
2a[c]	119.1(d)	118.7(d)	123.8(s)	123.7(s)	113.8(s)	121.7(s)	120.4(d)	133.7(d)	9.8(s)		3-Me
	18.7	1.4					3.3	3.9	131.4(d),	4.6	C-Ph-o
									127.9(s)		C-Ph-m
									128.5(s)		C-Ph-p
2b[c]	100.4(d)	118.7(d)	119.5(d)	126.8(s)	111.4(s)	122.8(s)	117.9(s)	135.7(d)	10.0(s)		3-Me
	5.5	6.6	2.9					10.1	131.4(d),	3.0	C-Ph-o
									127.6(s)		C-Ph-m
									127.8(s)		C-Ph-p
									138.8(d),	9.8	P-Ph-i
									132.6(d),	18.5	P-Ph-o
									128.3(d),	6.0	P-Ph-m
									128.4(s)		P-Ph-p
5a[d]	106.4(d)	130.3(d)	115.0(d)	126.1(s)	112.6(s)	122.8(s)	118.3(d)	138.5(d)	11.8(d),	9.7	2-Me
	55.2	22.6	5.1				9.9	36.4			
5b[d]	102.7(d)	135.5(d)	112.0(d)	127.9(s)	113.7(s)	122.3(s)	120.4(d)	137.5(d)	133.3(d),	2.0	C-Ph-i
	80.1	40.6	6.4				2.9	15.1	130.1(d),	7.1	C-Ph-o
									128.5(s)		C-Ph-m
									128.8(s)		C-Ph-p
7a[e]	102.6(d)	138.5(d)	113.9(d)	125.8(s)	110.9(s)	118.9(s)	118.4(s)	135.8(d)	12.6(d),	7.7	2-Me
	6.2	8.5	4.7					7.3	135.4(d),	7.0	P-Ph-i
									132.4(d),	13.2	P-Ph-o
									128.5(d),	6.0	P-Ph-m
									127.9(s)		P-Ph-p
7b[d]	103.9(d)	134.8(d)	114.2(d)	124.8(s)	111.0(s)	119.2(s)	117.4(s)	134.5(d)	132.4(d),	4.5	C-Ph-o
	6.8	7.9	4.5					6.9	128.3(s)		C-Ph-m
									129.0(s)		C-Ph-p
									139.2(d),	7.8	P-Ph-i
									133.2(d),	16.7	P-Ph-o
									129.4(d),	7.2	P-Ph-m
									129.3(s)		P-Ph-p
9a[f]	105.8(d)	127.5(d)	113.8(d)	125.2(s)	109.7(s)	118.9(s)	117.4(s)	133.3(d)	11.2(d),	2.4	2-Me
	11.6	15.6	4.5					14.1	40.6(d),	15.9	N-Me
9b[f]	104.9(d)	127.0(d)	113.6(d)	125.0(s)	110.3(s)	119.3(s)	117.8(s)	134.4(d)	40.6(d),	15.9	N-Me
	10.8	15.2	5.0					12.8	131.7(d),	4.8	C-Ph-o
									128.6(s)		C-Ph-m
									129.0(s)		C-Ph-p
9c[f]	105.6(d)	127.2(d)	113.4(d)	125.4(s)	110.0(s)	119.1(s)	117.6(s)	134.1(d)	12.1(d),	3.0	2-Me
	11.4	14.8	4.8					13.2	43.6(d),	17.2	N-CH_2
									14.2(d),	4.2	CH_2-*Me*
9d[f]			113.0(s)	126.7(s)	111.3(s)	120.9(s)	119.7(s)		130.2(d),	4.5	C-Ph-o
									128.0(s)		C-Ph-m
									129.9(s)		C-Ph-p
									43.8(d),	16.8	N-CH_2
									14.3(d),	4.6	CH_2-*Me*
11a[d]	97.7(d)	129.0(d)	114.1(d)	124.9(s)	110.9(s)	120.0(s)	119.0(s)	136.3(d)	13.1(s)		2-Me
	156.4	12.6	13.5					22.2	36.1(d),	3.1	N-Me
11b[d]	99.0(d)	129.5(d)	113.9(d)	125.0(s)	111.3(s)	120.2(s)	118.6(s)	135.7(d)	41.5(d),	14.8	N-Me
	155.8	13.2	12.2					18.8	131.5(d),	4.6	C-Ph-o
									128.5(s)		C-Ph-m
									128.8(s)		C-Ph-p
11c[d]	100.2(d)	128.4(d)	114.4(d)	124.9(s)	110.5(s)	119.7(s)	118.0(s)	135.0(d)	12.2(d),	4.2	2-Me
	160.4	13.8	10.8					15.4	44.2(d),	18.1	N-CH_2
									14.1(d),	4.6	CH_2-*Me*
11d[d]	99.6(d)	127.6(d)	113.1(s)	125.1(s)	110.9(s)	119.8(s)	118.2(s)	135.5(d)	131.0(d),	4.8	C-Ph-o
	158.0	12.4						16.8	128.3(s)		C-Ph-m
									128.8(s)		C-Ph-p
									44.2(d),	15.4	N-CH_2
									15.1(d),	5.0	CH_2-*Me*
13a[f]	118.3(d)	129.6(d)	112.4(s)	126.7(s)	114.4(s)	123.1(s)	117.6(s)	140.3(d)	11.7(d),	7.1	2-Me
	17.0	5.3						17.6	37.0(d),	4.7	N-Me

TABLE 6 Continued

N	C^1	C^2	C^3	C^5	C^6	C^7	C^8	C^9	*Others*		
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*		
13b[f]	117.9(d)	128.4(d)	113.5(d)	125.4(s)	112.4(s)	123.2(s)	118.1(s)	140.1(d)	39.4(d),	8.2	N-Me
	16.7	4.9						18.0	130.1(d),	3.8	C-Ph-o
									128.6(s)		C-Ph-m
									128.8(s)		C-Ph-p
13c[f]	118.2(d)	128.8(d)	113.0(s)	125.7(s)	111.5(s)	122.8(s)	118.4(s)	139.1(d)	120.8(d),	5.0	2-Me
	17.1	5.1						16.9	40.4(d),	12.1	$N\text{-}CH_2$
									13.7(d),	3.2	CH_2-*Me*
13d[f]	118.6(d)	129.0(d)	113.2(s)	126.3(s)	113.3(s)	122.0(s)	117.5(s)	138.7(d)	130.5(d),	4.0	C-Ph-o
	16.8	5.8						16.7	128.3(s)		C-Ph-m
									128.8(s)		C-Ph-p
									40.1(d),	13.0	$N\text{-}CH_2$
									13.8(d),	3.2	CH_2-*Me*
15a[d]	96.7(d)	128.9(d)	113.5(d)	124.7(s)	110.7(s)	119.5(s)	119.1(s)	137.4(d)	12.3(s)		2-Me
	165.4	11.1	13.5					15.0	35.9(d),	3.7	N-Me
15b[d]	97.1(d)	129.0(d)	113.7(d)	124.4(s)	111.2(s)	119.3(s)	119.2(s)	137.6(d)	40.5(d),	4.8	N-Me
	162.2	12.3	12.8					15.8	131.3(d),	4.5	C-Ph-o
									128.7(s)		C-Ph-m
									128.9(s)		C-Ph-p
15c[d]	98.5(d)	128.2(d)	114.0(d)	125.0(s)	111.0(s)	120.0(s)	119.0(s)	137.3(d)	12.3(s)		2-Me
	164.8	11.9	13.2					15.9	39.7(d),	12.8	$N\text{-}CH_2$
									14.2(d),	4.4	CH_2-*Me*
15d[d]	97.8(d)	128.0(d)	113.9(d)	125.1(s)	110.5(s)	119.8(s)	118.6(s)	137.2(d)	130.8(d),	5.0	C-Ph-o
	166.0	12.0	13.8					16.2	128.2(s)		C-Ph-m
									128.8(s)		C-Ph-p
									40.1 (d),	13.0	$N\text{-}CH_2$
									14.7 (d),	4.8	CH_2-*Me*
17a[d]	107.9(d)	128.7(d)	112.7(d)	124.7(s)	110.3(s)	118.5(s)	119.0(d)	135.5(d)	11.8(d),	8.5	2-Me
	15.4	22.0	4.5				3.3	13.6	62.1(d),	11.4	$O\text{-}CH_2$
									17.0(d),	5.5	CH_2-*Me*
17b[d]	106.3(d)	128.3(d)	113.2(d)	124.8(s)	110.4(s)	118.9(s)	119.6(s)	136.0(d)	131.1(d),	5.1	C-Ph-o
	16.2	20.8	4.3					14.0	128.4(s)		C-Ph-m
									128.8(s)		C-Ph-p
									61.5(d),	12.2	$O\text{-}CH_2$
									16.6(d),	5.2	CH_2-*Me*
19a[d]	99.8(d)	128.6(d)	114.0(d)	125.5(s)	111.8(s)	118.9(s)	121.2(s)	137.8(d)	12.8(s)		2-Me
	182.1	12.1	14.8					29.7	61.8(d),	5.6	$O\text{-}CH_2$
									16.3(d),	7.9	CH_2-*Me*
19b[d]	99.7(d)	133.2(d)	113.7(d)	125.6(s)	112.3(s)	121.3(s)	119.5(s)	137.5(d)	134.9(s)		C-Ph-i
	183.2	10.0	13.2					29.0	130.0(s)		C-Ph-o
									127.6(s)		C-Ph-m
									127.1(s)		C-Ph-p
									61.9(d),	6.0	$O\text{-}CH_2$
									15.6(d),	8.5	CH_2-*Me*

[a–d]As for Table 5.
[e]Spectrum was taken in CH_2Cl_2.
[f]Spectrum was taken in acetonitrile.

for 1 day in the case of compound **6a** and for 3 days in the case of compound **6b**. Triethylamine salt was separated by filtration, and the solvent was evaporated in vacuum from the filtrate.

1-(Indolizinyl)dicholorophosphines **5a,b** *and 1-(Indolizinyl)diphenylphosphines* **7a,b** *Isomerization of 3-Phosphinoindolizines* **4,6**

Compounds **4** or **6** were dissolved in dry methylene chloride and were left to stand at 20°C under argon: **4a**—for 3 hours, **4b**—for 10 hours, **6a**—for 3 days, and **6b**—for 5 days.

*3- and 1-(Indolizinyl)*tetramethyldiamidophosphonites **8a–d, 9a–d**

To a solution of dichlorophosphine **4**, **5** (0.06 mol) in 25 mL of dry benzene, a solution of dialkylamine (0.3 mol) in 10 mL of benzene was added dropwise with cooling to 5–10°C and stirring. The mixture was stirred for 30 minutes, the precipi-

TABLE 7 Bisphosphorylated Indolizines ^{13}C {^1H} NMR δ,[a] (Multiplicity),[b] J (P-C, Hz)

N	C^1	C^2	C^3	C^5	C^6	C^7	C^8	C^9	Others		
1	2	3	4	5	6	7	8	9	10		
30a[d]				131.5(s)	107.4(s)	124.7(s)	117.3(s)		13.5(dd),	13.9,	21.7 2-Me
30b[d]				127.3(s)	112.8(s)	123.7(s)	120.2(s)				
31a[d]				129.1(d) 2.2	114.1(s)	126.8(s)	119.6(d) 6.5		12.0(dd),	15.0,	23.6 2-Me
31b[d]				129.7(d) 2.2	115.2(s)	127.3(s)	121.2(d) 2.2		131.7(t), 128.6(s) 129.6(s)	5.1	C-Ph-o C-Ph-m C-Ph-p
32a[c]		137.4(dd) 11.4 2.8		127.1(d) 5.2	110.9(s)	120.8(s)	118.9(s)	140.3(d) 13.0	40.8(d), 41.6(d), 12.0(dd),	18.2 18.2 11.8,	N-Me N-Me 24.0 2-Me
32b[c]		136.9(dd) 10.8 2.4		126.6(d) 4.5	110.6(s)	120.6(s)	118.6(s)	139.8(d) 12.8	40.6(d), 41.5(d), 138.5(s) 131.4(d), 126.1(s) 125.4(s)	17.5 17.5 2.5	N-Me N-Me C-Ph-i C-Ph-o C-Ph-m C-Ph-p
33a[c]	103.8(dd) 159.9 10.1	141.0(dd) 10.8 13.6	115.0(dd) 194.0 13.6	128.2(s)	113.0(s)	123.5(s)	120.0(s)	140.3(dd) 22.8 9.0	37.0(d), 37.6(d), 134.9(s) 130.9(s) 126.5(s) 127.0(s)	5.2 4.0	N-Me N-Me C-Ph-i C-Ph-o C-Ph-m C-Ph-p
33b[c]	103.7(dd) 161.9 9.7	140.2(dd) 11.1 13.3	114.7(dd) 193.8 13.3	128.0(s)	112.8(s)	123.4(s)	119.9(s)	139.7(dd) 22.6 8.6	134.7(s) 130.8(s) 126.4(s) 127.0(s) 36.9(d), 37.5(d),	5.0 3.9	C-Ph-i C-Ph-o C-Ph-m C-Ph-p N-Me N-Me

[a–d]As for Table 5.

tated solid was filtered off, and the solvent was evaporated. The residue was dissolved in 50 mL of petroleum ether, filtered, and then the solvent was evaporated from the filtrate.

3- and 1-(Indolizinyl)tetramethyldiamidothiophosphonates **10a–d, 11a–d**

To a solution of amide **8**, **9** (0.01 mol) in 20 mL of benzene, finely ground sulfur was added, and the mixture was stirred until the sulfur had dissolved. The solution was filtered, and the solvent was evaporated from the filtrate.

3- and 1-(Indolizinyl)tetramethyldiamidochlorophosphonium Chlorides **12a–d, 13a–d**

To a solution of amide **8**, **9** (0.02 mol) in 40 mL of a mixture of benzene and petroleum ether (1:1), a solution of hexachloroethane (0.02 mol) in 30 mL of petroleum ether was added. A solid that precipitated was collected by filtration, washed with petroleum ether, and dried in a vacuum.

3- and 1-(Indolizinyl)tetramethyldiamidophosphonates **14a–d, 15a–d**

To a solution of compound **12**, **13** (0.015 mol) in 20 mL of chloroform, 50 mL of a 10%-solution of Na_2CO_3 was added. The mixture was shaken several times in a separatory funnel, the organic layer was separated, dried over anhydrous Na_2SO_4, and then evaporated in vacuo.

Diethyl 3- and 1-(Indolizinyl)phosphonites **16a,b** *and* **17a,b**

To a mixture of dichlorophosphine **4**, **5** (0.02 mol), benzene (50 mL), and Et_3N (0.44 mol), a solution of ethanol (0.44 mol) in 10 mL of benzene was added with stirring and cooling to 5–10°C. The mixture was left to stand for 30 minutes at 20°C. A solid that had precipitated was filtered off, and the sol-

vent was evaporated from the filtrate in vacuo. In the isolation of ethers **17**, dry and oxygen-free solvents were needed.

Diethyl 3- and 1-(Indolizinyl)thiophosphonates **18a,b** *and* **19a,b**

To a solution of the ether **16**, **17** (0.01 mol) in 20 mL of benzene, finely ground sulfur (0.01 mol) was added, and the mixture was stirred until the sulfur had dissolved. The solution was filtered, and the solvent was evaporated from the filtrate.

Ethylene 3-(2-Methylindolizinyl)phosphonite **20**

To a mixture of **3a** (2 mol), benzene (20 mL), and Et_3N (0.022 mol), ethylenechlorophosphite (0.02 mol) was added. The reaction mixture was left to stand for 24 hours at 20°C. The solid that had formed was separated by filtration, and the solvent was evaporated from the filtrate in vacuo.

Attempt to obtain ethylene 3-(2-phenylindolizinyl)phosphonite

The reaction was carried out under the conditions similar to the previous example. The reaction mixture was left to stand for 3 days at 20°C. According to the ^{31}P NMR spectra, a mixture of 1- and 3-phosphorylated derivatives was formed: δ = 158.78 and 170.73. We were unable to separate the isomers.

Attempted Sulfur Addition to Diphenylphosphine **6a**

To a solution of diphenylphosphine **6a** (4.8 mmol) in benzene (20 mL), finely ground sulfur (4.8 mmol) was added. The sulfur dissolved in 5 minutes, but in the ^{31}P NMR spectrum of the crude product, there were two signals with equal intensity, δ = −38.42 and 27.12. After 4 hours of boiling, the reaction mixture turned dark and became partially tarry. In the ^{31}P NMR spectra, a number of signals of different intensities in the range from δ = −38.5 to 83.4 appeared.

3-(2-Methylindolizinyl)diphenylphosphine oxide **22**

To a solution of diphenylphosphine **6a** (3.2 mmol), a solution of bromine (3.2 mmol) in benzene (15 mL) was added. The precipitated solid was filtered off, washed with benzene, dried, and dissolved in chloroform. Then a 10% solution of Na_2CO_3 (30 mL) was added, and this mixture was shaken several times in a separatory funnel. The organic layer was separated, dried with anhydrous Na_2SO_4, and evaporated in vacuo.

Reaction of **3b** *with Dichlorophenylphosphine*

To a solution of **3b** (0.012 mol) in pyridine (30 mL), dichlorophenylphosphine (0.012 mol) was added, and the mixture was heated for 3 hours at 70°C. The reaction mixture turned dark; ^{31}P NMR spectrum (C_5H_5N): δ = 54.1 − **23**.

Reaction of **3a** *with Dichlorophenylphosphine*

To a solution of **3a** (0.011 mol) in pyridine (20 mL), dichlorophenylphosphine (0.012 mol) was added, and the mixture was heated for 3 hours at 70°C. The reaction mixture turned dark; ^{31}P NMR spectrum (C_5H_5N): δ = −61.0, −58.1 (of approximately equal intensity).

Reaction of P(III) Halogenides with Two Moles of **3a**

To a solution of **3a** (0.0359 mol) in 40 mL of a mixture of benzene and pyridine (1:1), PCl_3 or PBr_3 (0.01795 mol) was added under argon, and the mixture was left to stand for 4 days at 20°C; ^{31}P NMR spectrum, δ = 38.27 − **25a**; 29.87 − **25b**. After the solvent had been evaporated in vacuo with heating up to 60°C and subsequent dissolution of the residue in benzene, the ^{31}P NMR spectrum exhibited a number of signals corresponding to the compounds of types **4**, **5**, and **29**, with the P atom both in positions 1 and 3.

Bis-3-(2-methylindolizinyl)dimethylamidophosphinite **26**

To a reaction mixture from the previous experiment, a solution of dimethylamine (0.075 mol) in 10 mL of benzene was added with cooling to 5°C. After 1 hour, the precipitate was filtered off, and the solvent was evaporated; ^{31}P NMR spectrum (C_6H_6): δ = 23.20.

Bis-3-(2-methylindolizinyl)dimethylamidothiophosphonate **27**

To a solution of **26** (0.01 mol) in benzene (15 mL), sulfur was added (0.01 mol); after 30 minutes, the solvent was evaporated. An oil solidified on treatment with heptane and was reprecipitated with heptane from benzene.

Tris-3-(2-phenylindolizinyl)phosphine **28**

To a mixture of indolizine **3a** (0.01 mol), pyridine (15 mL), and Et_3N (0.03 mol), a solution of PBr_3 (0.033 mol) in pyridine (5 mL) was added; the mixture was left to stand at room temperature. After 24 hours, the ^{31}P NMR spectrum (C_5H_5N) showed δ = −84.4, −80.9, −75.9, −72.9. Two months later the reaction mixture was poured into 250 mL of

water, and the precipitate was separated by filtration, washed with water, and dried in vacuum; ^{31}P NMR spectrum (C_6H_6): δ = −76.08.

1,3-(Indolizinediyl)bis(diphenylphosphine-sulfides) **30a,b**

A mixture of **3** (0.01 mol), chlorodiphenylphosphine (0.02 mol), and pyridine (50 mL) was left to stand for 3 days at 20°C. The formation of biphosphines **29a,b** was confirmed by examination of the ^{31}P NMR spectrum: δ_1 = −31.98, d, δ_3 = −36.34, d, J_{PP} 7.4 Hz − **29a**; δ_1 = −31.89, d, δ_3 = −35.96, d, J_{PP} 7.0 Hz − **29b**. To the mixture, sulfur (0.02 mol) was added, and after it had dissolved, the reaction mixture was mixed with 200 mL of water. The precipitate that formed was separated by filtration and dried.

1,3-(Indolizinediyl)bis(dichlorophosphines) **31a,b**

A mixture of indolizine **3** (0.01 mol), PCl_3 (0.08 mol), and pyridine (50 mL) was left to stand for 48 hours at 20°C, then evaporated in vacuo to the volume of 15 mL. Benzene (50 mL) was added, pyridine salt was separated by filtration, and the filtrate was evaporated to the volume of 15 mL, the product was precipitated by addition of 100 mL of heptane.

1,3-(Indolizinediyl)bis(tetramethyldiamido-phosphonites) **32a,b**

To a solution of compound **31a** or **31b** (0.01 mol) in benzene (40 mL), a solution of dimethylamine (0.09 mol) in benzene (10 mL) was added dropwise with cooling. After 2 hours, the precipitated salt was filtered off, and the filtrate was evaporated to half its volume. The product was then precipitated by addition of 100 mL of heptane.

1,3-(Indolizinediyl)bis(tetramethyldiamidothio-phosphonates) **33a,b**

To a solution of compound **32a** or **32b** (3 mmol) in benzene (15 mL), sulfur (6 mmol) was added with stirring. After its dissolution, the newly precipitated **33a** or **33b** was collected by filtration, washed with heptane, and dried in vacuum.

Reactions of Phosphines **29,6** *with water*

To a solution of phosphine **29** or **6** (1 mmol) in pyridine (10 mL), 0.02 mL of water was added, and the mixture was heated for 3 hours at 60°C. The ^{31}P NMR spectrum of the reaction mixture corresponds to the presence of the compound **34** (δ = −22.09 d, 34.95 d, J_{PP} 218.5 Hz) that can be collected by filtration after evaporation of pyridine and consequent dissolving of the residue in chloroform.

Reactions of Phosphines **6,24** *with Ethanol*

When phosphines **6** were dissolved in chloroform containing about 1% of ethanol, the ^{31}P NMR spectrum corresponded to the presence of compound **35** ($CHCl_3$): δ = 111.6. When the phosphine **24** was dissolved, the new ^{31}P NMR spectrum corresponded to the presence of compound **36**: δ = 156.1.

Reaction of Compounds **4,5,31** *with Dry Hydrogen Chloride*

Through a solution of dichlorophosphine **4**, **5**, **31** (0.01 mol) in dry benzene (15 mL), dry hydrogen chloride was passed; in 30 minutes, indolizine hydrochloride began to precipitate. HCl was passed through 30 minutes more, and then the reaction mixture was left to stand for 2 hours. In the ^{31}P NMR spectrum of the solution, only one signal corresponding to PCl_3 was observed.

Attempt to Obtain Chlorophosphine **38**

When equimolar quantities of **37** and **3b** or 1,3,3-trimethyl-2-methyleneindoline and **4b** were mixed, only the signals corresponding to the products of symmetrization were observed in the ^{31}P NMR spectrum taken in pyridine: δ = 85.9 − **39**; 69.5 and 56.2 − **40**.

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REFERENCES

[1] A. A. Tolmachev, A. N. Kostyuk, E. S. Kozlov, *Zh. Obshch. Khim., 61*, 1991, 1333–1341.
[2] A. A. Tolmachev, A. N. Kostyuk, E. S. Kozlov, *Zh. Obshch. Khim., 60*, 1990, 1752–1761.
[3] A. A. Tolmachev, A. N. Kostyuk, E. S. Kozlov, A. N. Chernega, A. M. Pinchuk, *Heteroatom Chem.*, 1992, Vol. 3, No. 2, 163–176.
[4] A. A. Tolmachev, A. N. Kostyuk, E. S. Kozlov, L. N. Morozova, R. D. Lampeka, A. M. Pinchuk, *Zh. Obshch. Khim., 61*, 1991, 1607–1617.
[5] A. A. Tolmachev, S. P. Ivonin, A. V. Charchenko, E. S. Kozlov, *Zh. Obshch. Khim., 60*, 1990, 2674–2679.
[6] A. A. Tolmachev, L. M. Potikha, A. A. Yurchenko, E. S. Kozlov, A. M. Pinchuk, *Zh. Obshch. Khim., 61*, 1991, 2358–2360.
[7] A. A. Tolmachev, S. P. Ivonin, A. V. Charchenko, E. S. Kozlov, *Zh. Obshch. Khim., 60*, 1990, 1668–1669.

[8] A. A. Tolmachev, S. P. Ivonin, A. V. Charchenko, E. S. Kozlov, *Zh. Obshch. Khim., 62*, 1992, 1060–1064.
[9] A. A. Tolmachev, S. P. Ivonin, A. V. Charchenko, E. S. Kozlov, *Zh. Obshch. Khim., 61*, 1991, 859–863.
[10] A. A. Tolmachev, S. P. Ivonin, A. V. Charchenko, E. S. Kozlov, *Zh. Obshch. Khim., 61*, 1991, 2780–2781.
[11] K. Karaghiosoff, C. Cleve, A. Schmidpeter, *Phosphorus Sulfur, 28*, 1986, 289.
[12] S. I. Bobrovskiy, E. D. Lushnikov, Y. G. Bundel, *Khim. Geterotsikl. Soedin., 12*, 1989, 1634–1638.
[13] N. S. Prostakov, O. B. Baktibaev, *Uspekhi. Khim., 44*, 1975, 1649–1687.
[14] A. A. Tolmachev, A. A. Yurchenko, E. S. Kozlov, *Zh. Obshch. Khim., 61*, 1991, 1480–1481.
[15] S. I. Bobrovskiy, E. D. Lushnikov, Y. G. Bundel, *Zh. Organ. Khim. 25*, 1989, 2251–2252.
[16] A. A. Tolmachev, A. A. Yurchenko, E. S. Kozlov, *Zh. Obshch. Khim., 62*, 1992, 1190–1192.
[17] K. Matsumoto, T. Uchida, Y. Ikemi, T. Tanaka, M. Asahi, T. Kato, H. Konishi, *Bull. Chem. Soc. Jpn., 60*, 1987, 3645–3653.