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Dipyrrolophosphinanes

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ABSTRACT: *The reaction of trivalent phosphorus halides with dipyrrolylmethane derivatives provides an entry to a new phosphorus-containing heterocyclic system. Properties of the newly obtained phosphorus-containing heterocycles have been studied.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:107–114, 2000

INTRODUCTION

By now, a plethora of studies have been devoted to syntheses of condensed phosphorus-containing heterocyclic systems. At the same time, heterocyclic entities in which the phosphorus-containing cycle is condensed to two other heterocycles remain sparsely investigated [1–9]. In the past decade, we have been exploring the phosphorylation of electron-rich heterocyclic compounds with phosphorus (III) halides in basic media [10,11]. The method developed by us affords heterocycles with a phosphorus atom in an aromatic ring [12] including those condensed with another heterocyclic moiety [13]. We first reported the applicability of this method for constructing tricyclic phosphorus-containing molecules in a preliminary communication on the synthesis of a heterocyclic system with the central azaphosphepine cycle [14]. The molecules to be phosphorylated should consist of two bound electron-rich heterocycles. Pyrroles being the most reactive heterocycles in reactions with trivalent phosphorus halides, one might expect their derivatives to be reactive enough to form condensed polycyclic systems. Here we focus on the application of the method developed to the synthesis of phosphorus-containing condensed heterocycles with the aim to offer a route to a new type tricyclic system in which the central phosphorus-containing nucleus is condensed to two pyrrole rings. Synthetic methods to and properties of 1-aryl-2,5-dimethylpyrrole geminal derivatives were described by us previously [15].

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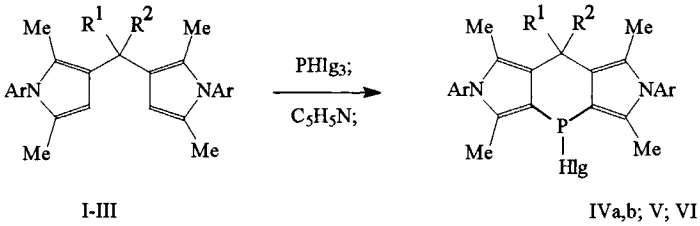
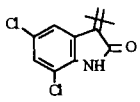
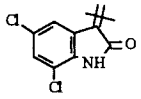
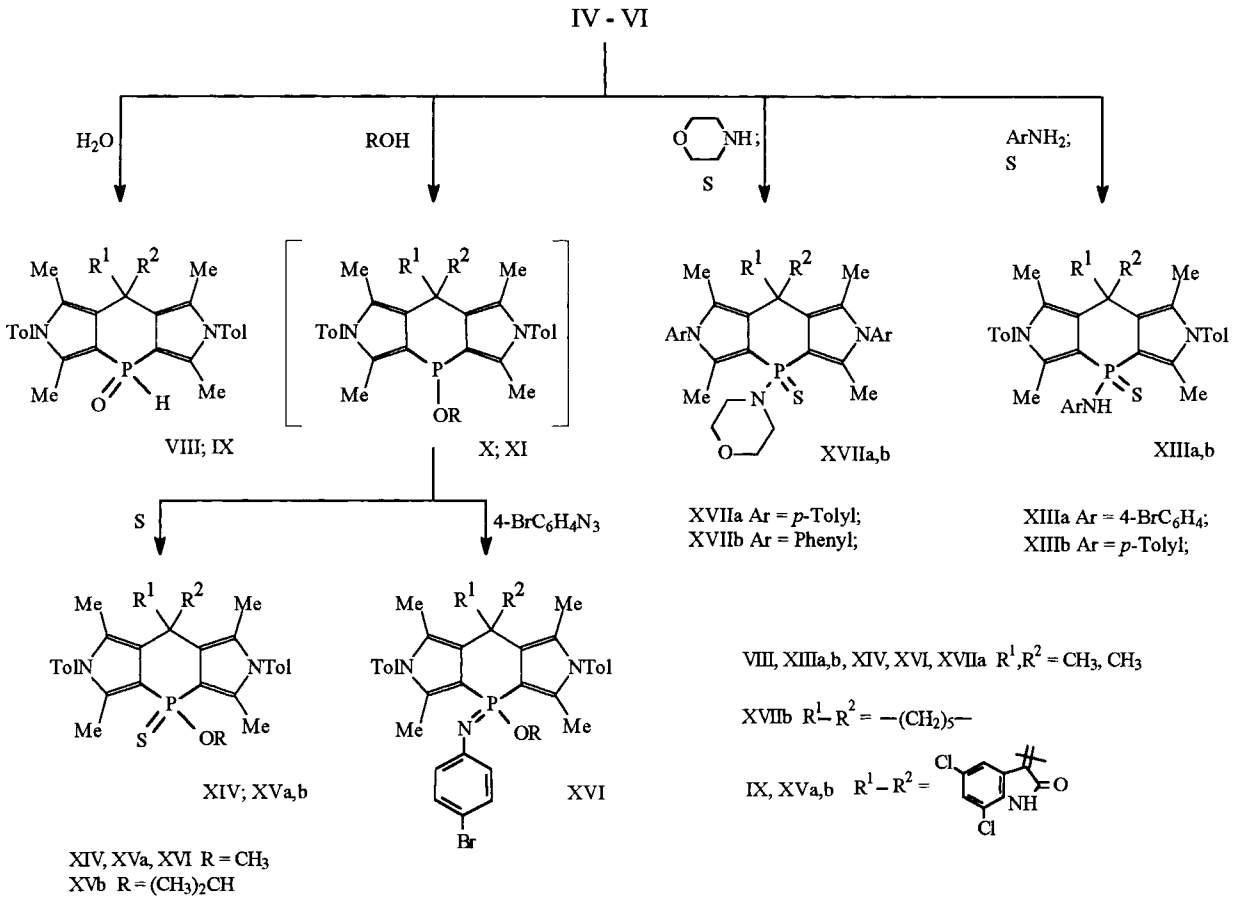
RESULTS AND DISCUSSION

Phosphorylation of *gem*-dipyrrolylalkanes I–III with phosphorus(III) halides afforded new linear tricyclic halogenophosphinanes IV–VI. The formation of cyclic phosphorus halides IV–VI is confirmed by ^{1}H and ^{31}P NMR as well as mass spectroscopy. The absence of a signal at δ = 5.5–6.0 attributed to the 4-H of pyrrole is the most convincing evidence. On mixing equimolar amounts of *bis*-pyrrole derivatives I–III with phosphorus tribomide or trichloride, the reaction proceeds at room temperature in pyridine. The completion of the process is marked by a phosphorous signal emerging in the region of δ = 40–50. The cyclization requires 4 hours with phosphorus tribromide and 8 hours with phosphorus trichloride. It is of interest to compare these reaction times with the evidence we gained formerly for the reaction of phosphorus trichloride with 1-aryl-2,5-dimethylpyrroles [11]. If carried out with equimolar amounts of PCl_3 and arylpyrrole, the reaction does not come to completion at all; only with a three-fold excess of phosphorus trichloride is it complete in 12 hours to give the corresponding dichlorophosphines. A plausible reason for a faster formation of cyclic systems IV and V, in spite of steric hindrance in the starting compounds I and II, is a smaller rate of a reverse

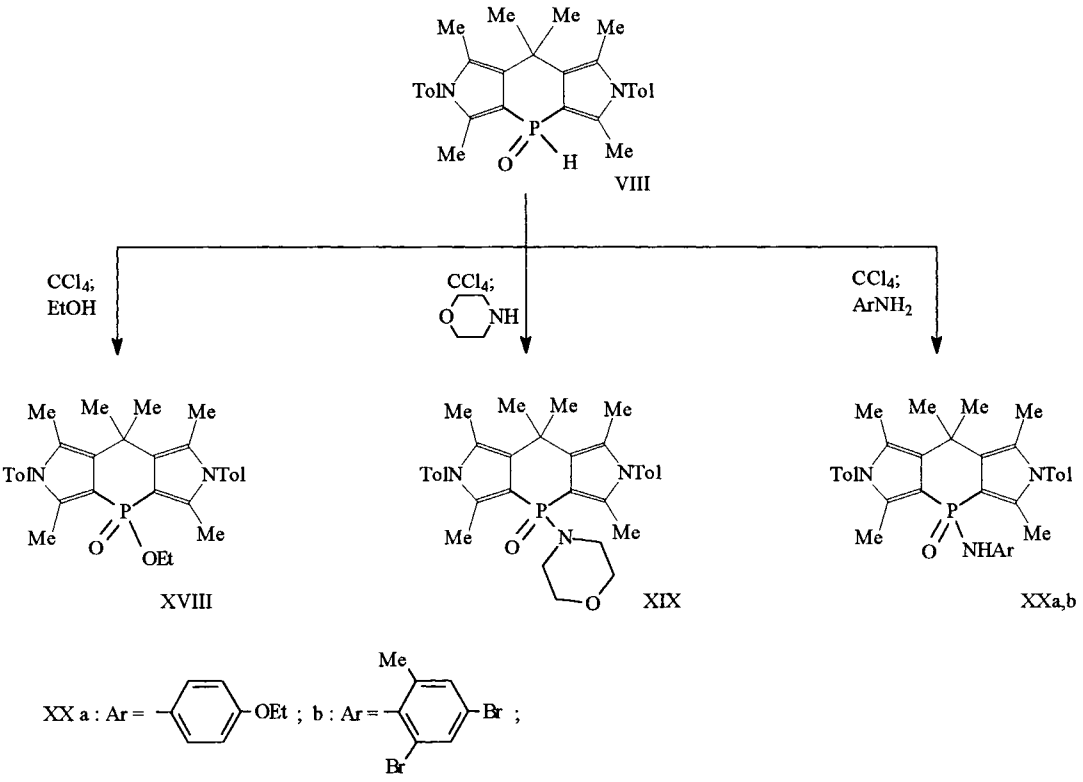


	I	II	III	IVa	IVb	V	VI
Ar	*p*-$CH_3C_6H_4$-	C_6H_5-	*p*-$CH_3C_6H_4$-	*p*-$CH_3C_6H_4$-	*p*-$CH_3C_6H_4$-	C_6H_5-	*p*-$CH_3C_6H_4$-
R^1, R^2	CH_3, CH_3	-$(CH_2)_5$-		CH_3, CH_3	CH_3, CH_3	-$(CH_2)_5$-	
Hlg	-	-	-	Br	Cl	Br	Br

SCHEME 1



SCHEME 2



SCHEME 3

dephosphorylation process normally occurring in reactions of phosphorus (III) halides with electron-rich compounds [16]. It is also noteworthy that the attempted preparation of 4,4′-diphospha-analogs of compounds I and II by adding 1 equivalent of dipyrrolylalkane I or II to 2 equivalents of phosphorus tribromide resulted in a 1:1 mixture of the cyclic product and phosphorus tribromide. The evidence presented suggests the stability of the novel heterocyclic system.

The ease of preparation and high stability of the dipyrrolophosphinane heterocycle can account for the formation of spiro compound VI, though an alternative cyclization at the oxygen atom could be rationalized based on the great affinity of phosphorus for oxygen [17]. Compound VI is stable in inert solvents, polymerization being ruled out presumably by the low nucleophilicity of the nitrogen atom in the indolinone ring as well as by steric hindrance caused by the presence of the methyl groups. The structure of compound VI is supported by the signal at $\delta = 9$ assigned to the NH-proton and by the conversion of VI into XV.

When treated with active nucleophilic reagents like water, alcohols, or amines, cyclic halogenoderivatives of phosphinous acid IV–VI undergo a halogen substitution to afford phosphinous acid VIII and its derivatives X–XII that can be oxidized into compounds XIII–XVII stable in the air.

The phosphorus atom in compound VIII manifests the properties typical of hydrophosphoryl compounds. Thus, starting from VIII, phosphinous acid derivatives XVIII–XX were obtained by the Todd-Atherton reaction.

Compounds IVb, VI, VIII, IX, and XIII–XX are solids. ^{31}P and ^{1}H NMR spectral parameters for the substances synthesized are listed in Tables 1 and 2.

EXPERIMENTAL

The ^{31}P and ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer using tetramethylsilane (TMS) as an internal standard for ^{1}H signals and 85% H_3PO_4 as an external standard for ^{31}P signals. High-resolution mass spectra were obtained on a KRATOS MS 890 mass spectrometer operating at 70 eV with a source temperature of 250°C.

4-Chloro-1,3,5,7,8,8-hexamethyl-2,6-di(4-tolyl)-2,4,6,8-tetrahydropyrrolo[3′,4′:5,6]-phosphinino[2,3-c]pyrrole (**IVb**)

To a stirred solution of 2,2-di(2,5-dimethyl-1-(*p*-tolyl)pyrrolyl-3)propane (10 mmol) in pyridine (20

TABLE 1 Yields, Analytical Data, and ^{31}P NMR Spectra of the Compounds IV, VI, VII, IX, XIII–XX

Compound	*M.p.* (°*C*)	*Yield* (%)	*Formula*	^{31}P *NMR* (*ppm*) (*solvent*)	*Found* (*Calculated*) %	
					N	*P*
IVb	280	60	$C_{29}H_{32}ClN_2P$	45.2 $CHCl_3$	5.6 (5.9)	6.8 (6.52)
VI	256–260 decom.	55	$C_{34}H_{29}BrCl_2N_3OP$ *0,5$C_4H_8O_2$	40.25 $CHCl_3$	5.4 (5.82)	4.03 (4.29)
VIII	210	53	$C_{29}H_{33}N_2OP$	−15 CH_2Cl_2	6.03 (6.14)	6.82 (6.78)
IX	310–315	7.8	$C_{34}H_{30}Cl_2N_3O_2P$	−17.5 $CHCl_3$	6.7 (6.84)	5.4 (5.05)
XIIIa	275	53	$C_{35}H_{37}BrN_3PS$	36.2 $CHCl_3$	6.4 (6.54)	5.1 (4.82)
XIIIb	260	46	$C_{36}H_{40}N_3PS$	37.1 $CHCl_3$	7.3 (7.27)	5.6 (5.36)
XIV	275	62	$C_{30}H_{35}N_2OPS$	52.6 DMSO	5.8 (5.57)	6.2 (6.16)
XVa	305	33	$C_{35}H_{32}Cl_2N_3O_2PS$	55 $CHCl_3$	6.47 (6.36)	4.54 (4.69)
XVb	315	46	$C_{37}H_{36}Cl_2N_3O_2PS$	49 $CHCl_3$	6.05 (6.1)	3.98 (4.5)
XVI	250	72	$C_{36}H_{39}BrN_3OP$	25.2 $CDCl_3$	6.87 (6.56)	5.06 (4.84)
XVIIa	248	73	$C_{33}H_{40}N_3OPS$	34.1 $CHCl_3$	7.3 (7.53)	5.7 (5.55)
XVIIb	216–217	69	$C_{34}H_{40}N_3OPS$	41 $CHCl_3$	7.03 (7.38)	5.4 (5.44)
XVIII	159–160	64	$C_{31}H_{37}N_2O_2P$	26.4 CH_2Cl_2	5.67 (5.6)	5.9 (6.19)
XIX	180	54	$C_{33}H_{40}N_3O_2P$	15.3 $CHCl_3$	7.8 (7.76)	5.7 (5.72)
XXa	290	51	$C_{37}H_{42}N_3O_2P$	9.9 $CHCl_3$	7.21 (7.1)	5.3 (5.23)
XXb	320	67	$C_{36}H_{38}Br_2N_3OP$	27 $CHCl_3$	6.15 (5.84)	4.07 (4.3)

mL), phosphorus trichloride (30 mmol) was added. After 8 hours, pyridine was evaporated in vacuo. The residue was boiled with pentane, and the liquid was decanted. After benzene had been poured over the precipitate and filtered off, the filtrate was evaporated in vacuo. The residue was washed with pentane.

4-Bromo-1,3,5,7-tetramethyl-2,6-di(4-tolyl)-2,4,6,8-tetrahydropyrrolo[3′,4′:5,6] phosphinino[2,3-c]pyrrole-8-spiro-3′-(5′,7′-dichloro-2′-indolinone) 1/2 dioxane (**VI**)

To a stirred solution of III (5 g, 8.8 mmol) in pyridine (30 mL), phosphorus tribromide (0.84 mL, 8.8 mmol) was added at 10°C, and the mixture was allowed to stand for 24 hours ($\delta^{31}P = 48$). After evaporation of the pyridine in vacuo, the residue was dissolved in dioxane (30 mL), and the undissolved part was filtered off (the fraction of C_5H_5N*HBr in the precipitate amounts to 2.9 g). On addition of heptane (about 2 mL) to the filtrate, it was maintained at room temperature for 24 hours, and the resulting precipitate was filtered off. Heptane (10 mL) was added to the mother liquor and after the mixture had been maintained at room temperature for 24 hours, the product that precipitated was filtered off and dried.

1,3,5,7,8,8-Hexamethyl-4-oxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydropyrrolo[3′,4′:5,6]-phosphinino[2,3-c]pyrrole (**VIII**)

To a stirred solution of phosphorus tribromide (10 mmol) in pyridine (20 mL), 2,2-di(2,5-dimethyl-1-(*p*-tolyl)pyrrolyl-3)propane (10 mmol) was added. After 5 hours, the reaction mixture was evaporated in vacuo. The residue was washed with hexane (3 × 20 mL) and dissolved in methylene chloride (100 mL), and water (100 mL) was poured into the solution

TABLE 2 ^{1}H NMR Spectral Data for Compounds IV, VI, VIII, IX, XIII–XX

Compound	*^{1}H NMR Spectral Characteristic (ppm)*
IVb[a]	$(CH_3)_2C$ 1.71(s) 6H, 1,7-CH_3 2.16(s) 6H, 3,5-CH_3 2.23(s) 6H, 4Ar-CH_3 2.44(s) 6H, 2,6Ar-H 7.06(d J_{HH} = 8.0Hz) 4H, 3,5Ar-H 7.33(d J_{HH} = 8.0Hz) 4H
VI[a]	1,7-CH_3 1.642(s) 6H, 3,5-CH_3 2.256(s) 6H, 4Ar-CH_3 2.409(s) 6H, dioxane 3.71(s) 4H, 2,6Ar-H 6.99(m) 4H, 3,5Ar-H&6′ Ar′ 7.176–7.274(m) 5H, 4′ Ar′ 7.631(s) 1H, NH 8.989(s) 1H
VIII[a]	$(CH_3)_2C$ 1.72(s) 6H, 1,7-CH_3 2.13(s) 6H, 3,5-CH_3 2.3(s) 6H, 4Ar-CH_3 2.44(s) 6H, 2,3,5,6Ar-H 7.11(m) 8H, P-H 8.26(d J_{PH} = 480Hz) 1H
IX[a]	1,7-CH_3 1.46(s) 6H, 3,5-CH_3 2.33(s) 6H, 4Ar-CH_3 2.404(s) 6H, 2,3,5,6Ar-H&4′, 6′ Ar′ 7.0–7.3(m) 10H, P-H 8.5(d J_{PH} = 494Hz) 1H, NH 9.11(s) 1H
XIIIa[b]	$(CH_3)_2C$ 1.66(s) 3H 1.77(s) 3H, 1,7-CH_3 2.11(s) 6H, 3,5-CH_3 2.3(s) 6H, 4Ar-CH_3 2.48(s) 6H, Ar-H 6.6–7.6(m) 12H
XIIIb[b]	$(CH_3)_2C$ 1.62(s) 3H 1.78(s) 3H, 1,7-CH_3 2.1(s) 6H, 4′ Ar′-CH_3 2.13(s) 3H, 3,5-CH_3 2.38(s) 6H, 4Ar-CH_3 2.48(s) 6H, Ar-H 6.6–7.4(m) 12H
XIV[b]	$(CH_3)_2C$ 1.69(s) 6H, 1,7-CH_3 2.1(s) 6H, 3,5-CH_3 2.28(s) 6H, 4Ar-CH_3 2.41(s) 6H, OCH_3 3.39(d J_{POCH} = 15Hz) 3H, 2,6Ar-H 7.18(d J_{HH} = 8.0Hz) 4H, 3,5Ar-H 7.38(d J_{HH} = 8.0Hz) 4H
XVa[a]	1,7-CH_3 1.57(s) 6H, 4Ar-CH_3 2.409(s) 6H, 3,5-CH_3 2.47(s) 6H, OCH_3 3.74(d J_{POCH} = 14, 7Hz) 3H, 2,3,5,6Ar-H&4′, 6′ Ar′ 7.0–7.3(m) 10H, NH 8.771(s) 1H
XVb[a,c]	$(CH_3)_2C$ 1.13 6H, 1,7-CH_3 1.427 6H, 3,5-CH_3&4Ar-CH_3 2.42 12H, OCH 4.57 1H, 2,6Ar-H 7.04 4H, 3,5Ar-H&4′,6′ Ar′ 7.24 6H, NH 8.143 1H
XVI[a]	$(CH_3)_2C$ 1.7(s) 3H 1.75(s) 3H, 1,7-CH_3 2.11(s) 6H, 3,5-CH_3 2.29(s) 6H, 4Ar-CH_3 2.43(s) 6H, OCH_3 3.56(d J_{POCH} = 12Hz) 3H, 2,3,5,6Ar-H& 2′,3′,5′,6′ Ar′-H 7.0–7.5(m) 12H
XVIIa[a]	$(CH_3)_2C$ 1.68(s) 6H, 1,7-CH_3 2.11(s) 6H, 3,5-CH_3 2.22(s) 6H, 4Ar-CH_3 2.25(s) 6H, NCH_2 2.9–3.1(m) 4H, OCH_2 3.4–3.6(m) 4H, 2,6Ar-H 7.17(d J_{HH} = 8.1Hz) 4H, 3,5Ar-H 7.38(d J_{HH} = 8.1Hz) 4H
XVIIb[a]	CH_2 1.525(m) 4H, CH_2 1.686(m) 2H, 1,7-CH_3 2.13(s) 6H, 3,5-CH_3 2.3(s) 6H, CH_2 2.35(t) 2H, CH_2 2.52(t) 2H, NCH_2 3.13(m) 4H, OCH_2 3.65(m) 4H, 2,6Ar-H 7.12(d J_{HH} = 7.8Hz) 2H 7.22(d J_{HH} = 7.8Hz) 2H, 3,4,5Ar-H 7.48(m) 5H
XVIII[a]	CH_3C 1.23(t J_{HH} = 7.0Hz) 3H, $(CH_3)_2C$ 1.7(s) 3H 1.73(s) 3H, 1,7-CH_3 2.11(s) 6H, 3,5-CH_3 2.29(s) 6H, 4Ar-CH_3 2.44(s) 6H, OCH_2 3.82(m) 2H, 2,6Ar-H 7.1(d J_{HH} = 8.0Hz) 4H, 3,5Ar-H 7.32(d J_{HH} = 8.0Hz) 4H
XIX[a]	$(CH_3)_2C$ 1.67(s) 3H 1.7(s) 3H, 1,7-CH_3 2.11(s) 6H, 3,5-CH_3 2.26(s) 6H, 4Ar-CH_3 2.44(s) 6H, NCH_2 3.0–3.1(m) 4H, OCH_2 3.6–3.7(m) 4H, 2,6Ar-H 7.1(d J_{HH} = 6.8Hz) 4H, 3,5Ar-H 7.29(d J_{HH} = 6.8Hz) 4H
XXa[a]	CH_3C 1.34(t J_{HH} = 6.9Hz) 3H, $(CH_3)_2C$ 1.73(s) 3H 1.76(s) 3H, 1,7-CH_3 2.11(s) 6H, 3,5-CH_3 2.17(s) 6H, 4Ar-CH_3 2.41(s) 6H, OCH_2 3.91(q J_{HH} = 6.9Hz) 2H, NH 5.5(s) 1H, 2,6Ar-H 6.65(d J_{HH} = 10.5Hz) 4H, Ar′-H 6.95(d J_{HH} = 7.8Hz) 2H, Ar′-H 7.09(d J_{HH} = 7.8Hz) 2H, 3,5Ar-H 7.22(d J_{HH} = 10.5Hz) 4H
XXb[a]	$(CH_3)_2C$ 1.71(s) 3H 1.73(s) 3H, 1,7-CH_3&2′ Ar′-CH_3 2.12(s) 9H, 3,5-CH_3 2.37(s) 6H, 4Ar-CH_3 2.45(s) 6H, 2,6Ar-H 7.07(d J_{HH} = 7.5Hz) 4H, 3,5Ar-H 7.18(d J_{HH} = 7.5Hz) 4H, 3′,5′ Ar′-H&NH 7.25–7.35(m) 3H

[a]$CDCl_3$.
[b]DMSO-D_6.
[c]All signals are broadened.

TABLE 3 Fragment Ions in the Mass Spectra of the Compounds XVa and XVIIa

Compound	*Fragment Ions and Their Intensities[a], $[M\text{-}E]^+$ (Intensity, %)*
XVa	M^+ 664(2.22) 663(4.87) 662(8.4) 661(27.88) 660(16.87) 659(42.59), M^+-(S) 630(14.5) 629(9.9) 628(18.45), M^+-(S)-(CH_3) 616(100) 614(91.59) 612(89.19), M^+-(S)-(CH_3)-(PO) 569(21.09) 568(16.32) 567(31.29), M^+-(S)-(CH_3)-(PO)-(O) 551(18.42) 549(14.89), M^+-(S)-(CH_3)-(PO)-(O)-(CN) 526(20.89) 524(34.53), $C_{13}H_{14}N$ 185(30.04) 184(33.78), $C_9H_{10}N$ 132(31.58), C_7H_8N 107(8.76) 106(12.65), C_7H_7 91(54.61), CH_3SH 48(54.41), CH_3S 47(73.11)
XVIIa	M^+ 558(2.83) 557(7.33), M^+-(CH_3) 542(13.05), M^+-(C_4H_8NO) 472(42.02) 471(100), M^+-(C_4H_8NO)-(S) 440(31.6) 439(90.85), M^+-(C_4H_8NO)-(S)-(CH_4) 424(27.84) 423(40.02), $C_{15}H_{18}N$ 213(8.11) 212(26.79), $C_9H_{10}N$ 132(10.54), C_7H_8N 107(8.12) 106(10.5), C_7H_7 91(18.06), C_4H_8NO 87(16.55) 86(9.35), C_2H_3NO 57(24.71)

[a]Values of the Major Ions.

obtained. After the mixture had been stirred for 3 hours, the organic layer was separated, dried over Na_2SO_4, and evaporated in vacuo. The dry residue appearing as a white powder and was washed with ether (2 × 50 mL).

1,3,5,7-Tetramethyl-4-oxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydropyrrolo[3′,4′:5,6]-phosphinino[2,3-c]pyrrole-8-spiro-3′-(5′,7′-dichloro-2′-indolinone) (**IX**)

A stirred solution of VI (6 g) in pyridine was exposed to air for 4 hours, followed by evaporation of the pyridine in vacuo and crystallization of the residue from ethanol twice.

4-(4-Bromanilino)-1,3,5,7,8,8-hexamethyl-4-thioxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo[3′,4′:5,6]phosphinino[2,3-c]pyrrole (**XIIIa**)

To a stirred solution of 2,2-di(2,5-dimethyl-1-(*p*-tolyl)pyrrolyl-3)propane (10 mmol) in pyridine (20 mL), phosphorus tribromide (10 mmol) was added dropwise. Four hours later, *p*-bromoaniline (10 mmol), triethylamine (30 mmol), and sulfur (10 mmol) were added to the reaction mixture. After having been refluxed for 2 hours and the mixture having been filtered, the filtrate was evaporated to dryness. The residue was boiled first with water (100 mL) and then with ethanol (20 mL).

1,3,5,7,8,8-Hexamethyl-4-thioxo-4-(4-toluidino)-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo-[3′,4′:5,6]phosphinino[2,3-c]pyrrole (**XIIIb**)

To a stirred solution of 2,2-di(2,5-dimethyl-1-(*p*-tolyl)pyrrolyl-3)propane (10 mmol) in pyridine (20 mL), phosphorus tribromide (10 mmol) was added dropwise. Four hours later, *p*-toluidine (10 mmol), triethylamine (30 mmol), and sulfur (10 mmol) were added to the reaction mixture. After having been refluxed for 2 hours and the mixture having been filtered, the filtrate was evaporated to dryness. The residue was boiled first with water (100 mL) and then with ethanol (20 mL).

4-Methoxy-1,3,5,7,8,8-hexamethyl-4-thioxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo-[3′,4′:5,6]phosphinino[2,3-c]pyrrole (**XIV**)

To a stirred solution of 2,2-di(2,5-dimethyl-1-(*p*-tolyl)pyrrolyl-3)propane (10 mmol) in pyridine (20 mL), phosphorus tribromide (10 mmol) was added dropwise. Four hours later, sulfur (10 mmol) was added, and methanol (10 mmol) and triethylamine (30 mmol) were then added to the reaction mixture dropwise. After standing at 50°C for 2 hours the mixture was evaporated to dryness. The oily remainder, when boiled with water (100 mL) and then cooled, solidified to a powder. The latter was filtered off and boiled with ether (20 mL).

4-Methoxy-1,3,5,7-tetramethyl-4-thioxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo[3′,4′:5,6]phosphinino [2,3-c]pyrrole-8-spiro-3′-(5′,7′-dichloro-2′-indolinone) (**XVa**)

To a solution of VI (1.985 g, 2.75 mmol) and triethylamine (1.1 ml, 8.25 mmol) in dioxane (10 mL), methanol (0.11 mL, 2.75 mmol) and then 10 minutes later sulfur (0.09 g, 2.75 mmol) were added. The mixture was stirred until the sulfur had dissolved. The resulting precipitate of triethylammonium bromide was filtered off and the mother liquor was evaporated in vacuo. The residue was crystallized from isopropyl alcohol.

4-Isopropoxy-1,3,5,7-tetramethyl-4-thioxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo[3′,4′:5,6]phosphinino[2,3-c]pyrrole-8-spiro-3′-(5′,7′-dichloro-2′-indolinone) (**XVb**)

To a stirred solution of III (0.5 g, 0.88 mmol) in pyridine (10 mL), phosphorus tribromide (0.08 mL, 0.88 mmol) was added and the reaction mixture was allowed to stand for 24 hours. Then 2-propanol (0.07 mL, 0.88 mmol) and sulfur (0.03 g, 0.88 mmol) were added, and the mixture was stirred until the sulfur had dissolved. After evaporation of the pyridine in vacuo, the residue was triturated with water, filtered off, dried, and crystallized from benzene.

4-(4-Bromophenylimino)-4-methoxy-1,3,5,7-tetramethyl-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo[3′,4′:5,6]phosphinino[2,3-c]pyrrole (**XVI**)

To a stirred solution of 2,2-di(2,5-dimethyl-1-(*p*-tolyl)pyrrolyl-3)propane (10 mmol) in pyridine (20 mL), phosphorus tribromide (10 mmol) was added dropwise. Four hours later, into the stirred reaction mixture, methanol (10 mmol) and triethylamine (30 mmol) were added dropwise, and *p*-bromophenyl azide (10 mmol) was added after 5 minutes. The mixture was maintained at 50°C until the nitrogen evolution had stopped (for about 7 hours), and then pyridine was evaporated in vacuo. The oily residue was boiled with water (100 mL). The resulting solid precipitate was filtered off, dried, and washed with hot octane (2 × 20 mL).

4-Morpholino-1,3,5,7,8,8-hexamethyl-4-thioxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo-[3′,4′:5,6]phosphinino[2,3-c]pyrrole (**XVIIa**)

To a stirred solution of 2,2-di(2,5-dimethyl-1-(*p*-tolyl)pyrrolyl-3)propane (10 mmol) in pyridine (20 mL), phosphorus tribromide (10 mmol) was added dropwise. Four hours later, sulfur (10 mmol) was added, and morpholine (10 mmol) and triethylamine (30 mmol) were then added to the reaction mixture dropwise. After having been maintained at 50°C for 3 hours, the mixture was evaporated to dryness in vacuo and the residue was boiled with water (100 mL). The powder obtained was filtered off and boiled with ethanol (20 mL).

4-Morpholino-1,3,5,7-tetramethyl-4-thioxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo[3′,4′:5,6]phosphinino[2,3-c]pyrrole-8-spiro-1′-cyclohexane (**XVIIb**)

To a stirred solution of II (0.5 g, 1.2 mmol) in pyridine (10 mL), phosphorus tribromide (0.12 mL, 1.2 mmol) was added. Within 2 hours, a signal at $\delta = 57$ was observed in the ^{31}P NMR spectrum. Morpholine (0.2 mL, 2.4 mmol) and sulfur (0.04 g, 1.2 mmol) were added to the stirred mixture and it was kept stirred until the sulfur had dissolved. After evaporation of the pyridine to dryness, hot benzene was poured over the residue. After having been cooled, the mixture was filtered. The mother liquor was evaporated in vacuo and the residue was crystallized from 2-propanol.

4-Ethoxy-1,3,5,7,8,8-hexamethyl-4-oxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo[3′,4′:5,6]-phosphinino[2,3-c]pyrrole (**XVIII**)

A mixture of phosphinite VIII (1 mmol), carbon tetrachloride (1 mL), and triethylamine (0.5 mL) in ethanol (20 mL) was refluxed for 4 hours and then evaporated in vacuo. The residue was boiled with water, and the precipitate was filtered off. The product appeared as a white powder and was washed on the filter with ethanol (5 mL) and then with ether (5 mL).

4-Morpholino-1,3,5,7,8,8-hexamethyl-4-oxo-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo[3′,4′:5,6]-phosphinino[2,3-c]pyrrole (**XIX**)

A mixture of phosphinite VIII (10 mmol), carbon tetrachloride (20 mL), and morpholine (15 mL) was refluxed for 4 hours and then evaporated in vacuo. The residue was boiled with water (20 mL) and the precipitate obtained was filtered off. The product appeared as a light-yellow powder that was washed on the filter with ethanol (5 mL) and then with ether (5 mL).

4-(4-Ethoxyphenylamino)-4-oxo-1,3,5,7-tetramethyl-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo[3′,4′:5,6]phosphinino[2,3-c]pyrrole (**XXa**)

A suspension of phosphinite VIII (1 mmol), phenetidine (1 mmol), triethylamine (5 mL), and carbon tetrachloride (10 mL) was refluxed for 4 hours and then evaporated in vacuo. The residue was boiled with water (20 mL), and the precipitate was filtered off. The product was washed on the filter, first with ethanol (5 mL) and then with ether (5 mL).

4-(2,4-Dibromo-6-methylphenylamino)-4-oxo-1,3,5,7-tetramethyl-2,6-di(4-tolyl)-2,4,6,8-tetrahydro-4λ⁵-pyrrolo[3′,4′:5,6]phosphinino-[2,3-c]pyrrole (**XXb**)

A suspension of phosphinite VIII (1 mmol), 2,4-dibromo-6-methylaniline (1 mmol), and triethylamine (5 mL) in carbon tetrachloride (10 mL) was refluxed for 4 hours and then evaporated in vacuo. The residue was boiled with water (20 mL), and the precipitate obtained was filtered off. The product appeared as a light-yellow powder and was washed on the filter with ethanol (5 mL) and then with ether (5 mL).

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