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Heterocondensed 1,4-Diphosphinines

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ABSTRACT: *A reaction of phosphorus tribromide with a compound containing two 2,5-dimethyl-1-arylpyrrolyl-3 residues bound through a phosphorus atom gave rise to a new phosphorus-containing heterocyclic system, 1,4-diphosphinine. The new products thus obtained have been characterized and described.* © 2002 John Wiley & Sons, Inc. Heteroatom Chem 13:46–52, 2002; DOI 10.1002/hc.1105

INTRODUCTION

The synthetic access to C-phosphorylated five-membered heterocycles via the electrophilic phosphorylation with P(III) halides in basic media enables both one and two phosphorus-containing substituents to be introduced in a heterocyclic molecule [1–4]. Of particular preparative interest are heterocycles for which the P-containing substituents can be introduced at the neighboring carbon atoms. We believe heterocyclic systems of this kind will be promising in the synthesis of heterocondensed 1,4-diphosphinines. Here, this synthetic line is exemplified by the use of 2,5-dimethyl-*N*-arylpyrroles as starting systems (previously we reported their mono and bisphosphorylation [3]). Our synthetic strategy on the pathway to 1,4-diphosphorines included binding two pyrrole residues by a phosphorus atom and cyclizing the molecule by treating it with phosphorus tribromide.

RESULTS AND DISCUSSION

The dipyrrolylthioamide (**1**) was found to react with phosphorus tribromide in pyridine to yield 1,4-diphosphinine (**2**), which has been identified by its ^{31}P NMR spectrum ($\delta P = 35.0$; 136.0 ppm) and characterized by converting it into thioamide (**3**), thioesters (**4**) and (**5**), and phosphinic acid (**6**).

The structures of compounds **3–6** were determinant by ^{31}P and ^{1}H NMR spectroscopy (see Tables 1 and 2) and the composition was supported by elemental analyses (see Table 1).

The molecular structure of compound **3c** was determined by x-ray diffraction. The perspective view of molecule **3c** is shown in Fig. 1 [5], and the selected geometrical parameters are given in Table 3. The P(1)P(1′)N(2)N(2′)C(5–8)C(5′–8′) central tricyclic system is planar: deviations from the least-squares plane do not exceed 0.019 Å, the dihedral angle between six- and five-membered cycles being only 1.5°. The C(11–16) benzene ring is turned out from this plane by 79.0°. Bond lengths and angles in **3c** are unexceptional [6,7].

There is an another scheme for the synthesis of 1,4-diphosphinine with the same substituents at the phosphorus atom. At first, 2,5-dimethyl-*N*-(*p*-tolyl)pyrrole (**7**) was reacted with phosphorus tribromide in pyridine in a 2:1 ratio to form

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TABLE 1 Yields, Data of Elemental Analysis, and ^{31}P NMR Spectroscopic Characteristics for Compounds **3–25**

					Found (%) Calcd. (%)	
No.	*Yield (%)*	*mp (°C)*	*δP (CHCl$_3$)*	*Formula*	*P*	*N*
3	67	335	34.6	$C_{34}H_{42}N_4O_2P_2S_2$	9.21 (9.32)	8.51 (8.43)
4	76	180	34.0; 56.0	$C_{31}H_{37}N_3O_2P_2S_2$	10.01 (10.16)	7.12 (6.89)
5	62	147	34.8; 56.5	$C_{36}H_{39}N_3O_2P_2S_2$	9.25 (9.22)	6.18 (6.25)
6	55	170	34.8; 23.0d $J_{HP} = 280$ Hz	$C_{30}H_{35}N_3O_2P_2S_2$	10.54 (10.99)	7.14 (7.46)
9	74	321	39.1	$C_{26}H_{26}Br_2N_2P_2$	10.18 (10.53)	4.45 (4.76)
10	67	250	55.7	$C_{28}H_{32}N_2O_2P_2S_2$	10.91 (11.17)	4.92 (5.05)
11	68	234	54.8	$C_{38}H_{36}N_2O_2P_2S_2$	8.87 (9.13)	3.81 (4.13)
12	73	160	55.1	$C_{38}H_{34}F_2N_2O_2P_2S_2$	8.74 (8.67)	4.08 (3.92)
13	43	295	20.1	$C_{40}H_{42}N_4P_2S_2$	8.88 (8.79)	8.14 (7.95)
14	64	198	20.3	$C_{40}H_{36}F_6N_4P_2S_2$	7.34 (7.62)	6.55 (6.89)
15	47	165	21.0	$C_{38}H_{36}Br_2N_4P_2S_2$	7.13 (7.42)	6.93 (6.71)
16	64	234	−3.4	$C_{36}H_{38}N_4P_2S_2$	10.01 (9.49)	8.82 (8.58)
17	58	221	−6.3	$C_{44}H_{42}N_4P_2S_2$	8.51 (8.23)	7.35 (7.44)
18	53	279	47.0d $J_{HP} = 150$ Hz	$C_{26}H_{28}N_2O_2P_2$	13.64 (13.40)	5.75 (6.06)
20	62	254	−2.9	$C_{26}H_{28}N_2O_2P_2S_2$	11.42 (11.76)	4.98 (5.32)
22	65	168	60.2;83.5	$C_{29}H_{36}N_2O_3P_2S_2$	10.84 (10.56)	5.11 (4.77)
23	53	320	8.1	$C_{26}H_{28}N_2O_4P_2$	12.37 (12.53)	5.78 (5.67)
24	63	215	16.6	$C_{34}H_{42}N_4O_4P_2$	9.71 (9.79)	9.07 (8.86)
25	67	246	18.4	$C_{46}H_{52}N_6O_2P_2$	8.17 (7.91)	10.84 (10.73)

Values within parentheses represent the percentage.

bromophosphine (**8**), which, when treated with phosphorus tribromide (1 equivalent), led to 1,4-diphosphinine (**9**), isolated in an analytically pure state and in high yield. It is a crystalline compound, stable in the absence of atmospheric moisture, with the structure confirmed by the ^{31}P and ^{1}H NMR spectra (see Tables 1 and 2) and the composition supported by the elemental analyses (see Table 1).

Because of the accessibility of bisbromophosphine **9**, it became possible to obtain thiophosphonates **10–12**, thioamides **3, 13–15**, phosphine thioxides **16, 17**, and bisphosphinous acid **18**.

TABLE 2 ^{1}H NMR Data for Compounds **3–25** in CDCl$_3$: δ, Multiplicity, *J* (Hz)

	Tol					
No	*m-Tol*	*o-Tol*	*JHH*	*Me-Tol*	*Me-Het*	*Other Signals*
3	7.10	7.34	7.8	2.46	2.38	3.2m (8H, CH$_2$—N); 3.6m (8H, CH$_2$—O)
4	7.11	7.35	8.1	2.40	2.40	3.2m (4H, CH$_2$—N); 3.47d $J_{HP} =$ 11.0 (3H, Me—O); 3.6m (4H, CH$_2$—O)
5				2.40	2.40	3.2m (4H, CH$_2$—N); 3.6m (4H, CH$_2$—O); 7.3m (13H, Ar)
6	7.11	7.35	8.1	2.40	2.40	3.2m (4H, CH$_2$—N); 3.6m (4H, CH$_2$—O); 7.58d $J_{HP} =$ 280 (1H, H—P)
9	7.05	7.30	8.0	2.57	2.20	
10	7.12	7.34	8.0	2.46	2.41	3.50d $J_{HP} = 16.0$ (6H, Me—O)
11	6.95	7.04	8.0	2.43	2.21	7.2m (10H, Ph)
12	6.93	7.06	8.2	2.43	2.25	7.4m (8H, Ar)
13				2.50	2.34	7.3m (18H, Ar$^+$ NH)
14				2.50	2.34	7.4m (18H, Ar$^+$ NH)
15				2.45	2.35	7.4m (18H, Ar$^+$ NH)
16	6.95	7.10	8.1	2.60	2.20	3.95s (6H, Me-Het); 6.13dd $J_{HH} = 3.0$ $J_{HP} =$ 7.1 (1H; H^3); 6.6m (1H; H^4); 6.9m (1H; H^5)
17				2.58	2.20	3.27s (6H, Me-Het); 7.5m (18H, Ar$^+$ Het)
18	7.11	7.35	8.1	2.46	2.26	7.37d $J_{HP} =$ 150 (1H, H—P)
20	7.31	7.55	8.5	2.40	2.33	9.5s[a] (2H, OH)
22	6.98	7.59	8.2	2.35 2.44	1.98 2.12	3.22d $J_{HP} =$ 38 (3H, OMe); 3.58d $J_{HP} =$ 18 (6H, OMe); 6.33d $J_{HP} =$ 5.6 (1H, H-Het)
23	7.11	7.36	8.1	2.46	2.34	8.5s[a] (2H, OH)
24	7.09	7.35	8.1	2.46	2.33	3.2m (8H, CH$_2$—N); 3.6m (8H, CH$_2$—O)
25		7.35	7.8	2.44	2.33	3.10m (16H, CH$_2$—N); 6.50dd $J_{HH} =$ 8.1, $J_{HH} = 1.7$ (2H, *p*-Ph); 6.75dd $J_{HH} =$ 8.1, $J_{HH} = 1.7$ (4H, *o*-Ph); 7.1m (8H, *m*-Tol + *m*-Ph)

[a] Broadened.

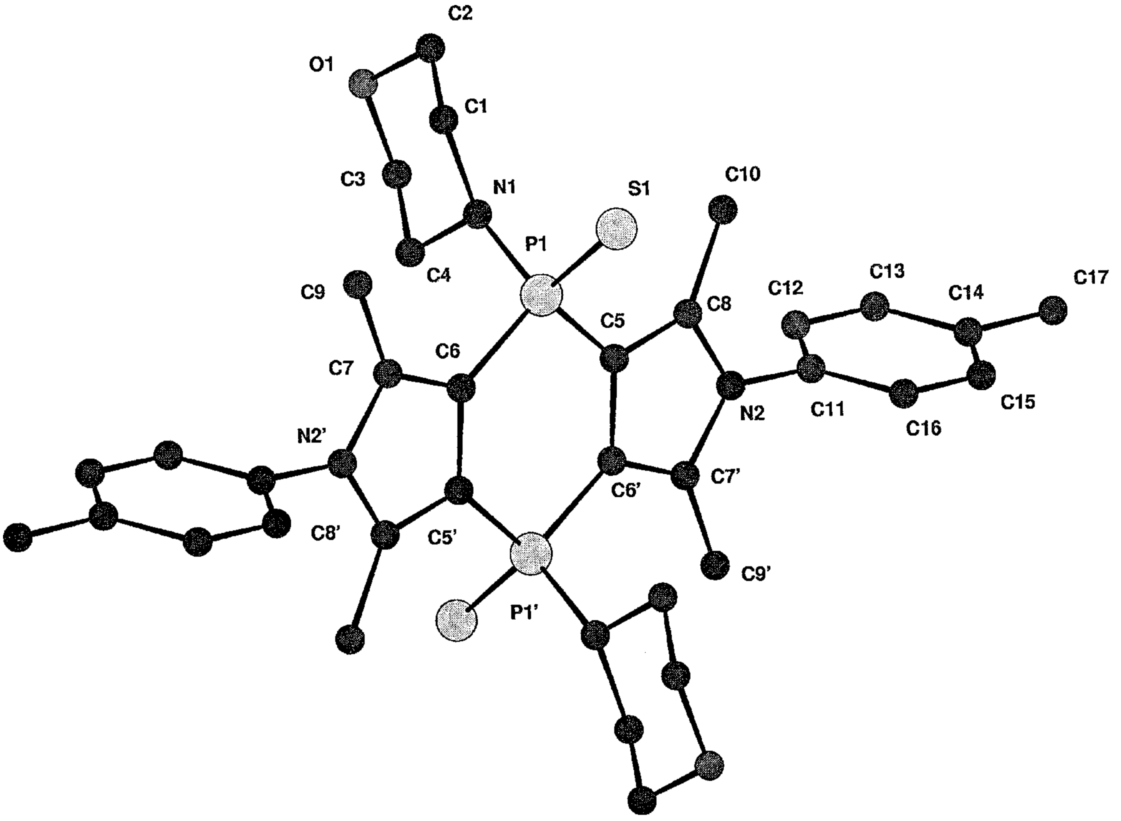
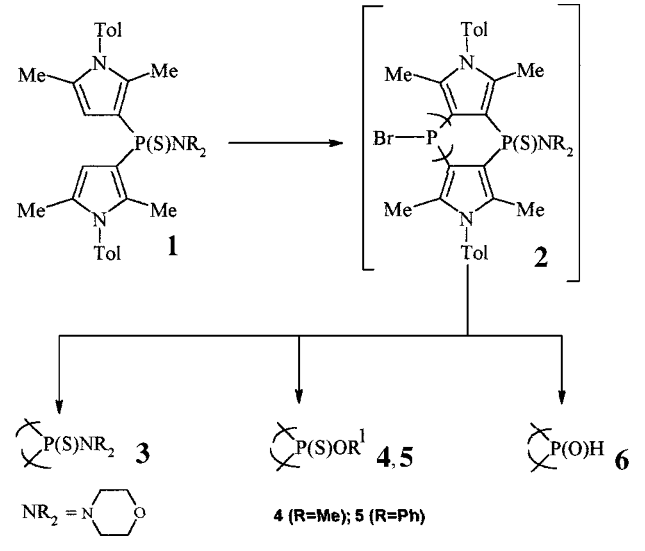
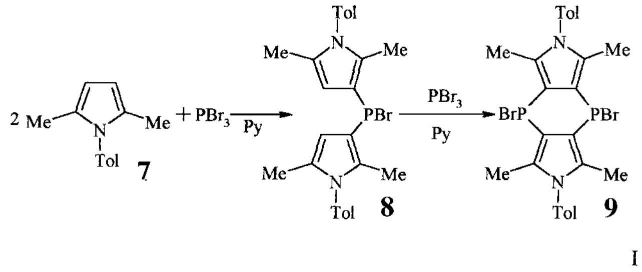


FIGURE 1 Perspective view and labeling scheme for molecule **3c** (hydrogen atoms are omitted for clarity). The primed atoms are generated from the asymmetric unit using the inversion center.

The phosphorus atom in 1,4-diphosphinine (**9**) was quite readily oxidized with elemental sulfur to give the corresponding thiodibromophosphine (**19**); if treated with water, the latter was converted into bisthiophosphinic acid (**20**).



SCHEME 1



SCHEME 2

As an interesting finding, one C—P bond is cleaved under the action of excess methanol to form phosphonate **21**, which has been isolated, on oxidizing it with sulfur, in the form of thiophosphonate **22** (as evidenced by nonequivalent methyl groups, the presence of an ^{3}H proton).

By the Todd–Atherton reaction, bisphosphinous acid **18** was used to obtain, with good yields, bisphosphinic acid **23** and bisaminophosphinates **24** and **25**.

TABLE 3 Selected Bond Lengths (Å) and Angles (deg) in **3c**

Bond lengths	
S(1)—P(1)	1.9474(9)
P(1)—N(1)	1.665(2)
P(1)—C(5)	1.779(2)
P(1)—C(6)	1.780(2)
N(2)—C(7′)	1.377(3)
N(2)—C(8)	1.377(3)
N(2)—C(11)	1.439(3)
C(5)—C(6′)	1.431(3)
C(5)—C(8)	1.375(3)
C(6)—C(7)	1.379(3)
Bond angles	
S(1)—P(1)—N(1)	111.14(8)
S(1)—P(1)—C(5)	114.29(9)
N(1)—P(1)—C(5)	104.22(11)
S(1)—P(1)—C(6)	114.04(8)
N(1)—P(1)—C(6)	108.87(11)
C(5)—P(1)—C(6)	103.56(11)
C(7′)—N(2)—C(8)	110.3(2)
P(1)—C(5)—C(6′)	128.74(18)
C(6′)—C(5)—C(8)	108.1(2)
P(1)—C(6)—C(5′)	127.67(18)
P(1)—C(6)—C(7)	125.41(19)
N(2′)—C(7)—C(6)	107.6(2)
N(2)—C(8)—C(5)	107.0(2)

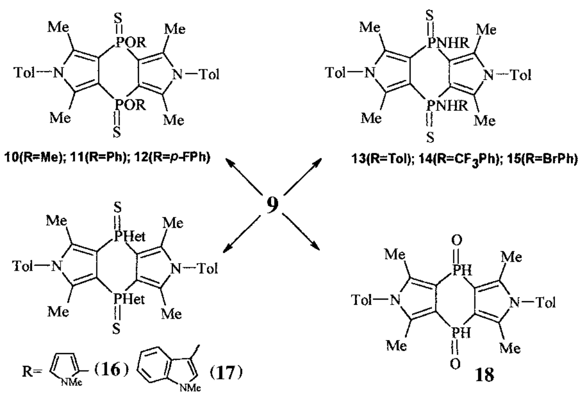
The primed atoms are generated from the asymmetric unit using the inversion center.

EXPERIMENTAL

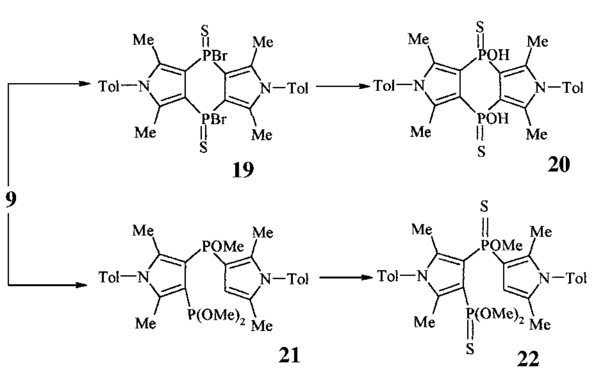
^{1}H and ^{31}P NMR spectra were run on a Varian-VXR 300 spectrometer with TMS being used as an internal standard for ^{1}H signals, and 85% H_3PO_4 as an external standard for ^{31}P signals. All manipulations were carried out in anhydrous solvents.

X-ray Structure Determination of **3c**

Crystal data: $C_{34}H_{42}N_4O_2P_2S_2 \cdot 3C_6H_6$, $M = 899.14$ monoclinic, $a = 13.787(2)$, $b = 16.011(2)$, $c = 12.307(2)$ Å, $\beta = 114.25(1)°$, $V = 2476.9$ Å^3, $Z = 2$, $d = 1.21$ g · cm^{-1}, space group P2$_1$/c, $\mu = 18.95$ cm^{-1}, crystal size ca. 0.31 × 0.41 × 0.47 mm. All crystallographic measurements were performed at 18°C on a CAD-4-Enraf-Nonius diffractometer operating in the ω–2θ scan mode (the ratio of the scanning rates $\omega/2\theta = 1.2$). Intensity data were collected within the range $2 < \theta < 65°$ ($0 < h < 17$, $0 < k < 19$, $-15 < l < 15$) using graphite monochromated Cu K$_\alpha$ radiation ($\lambda = 1.54178$ Å). Intensities of 4585 reflections (4217 unique reflection, $R = 0.023$) were measured. Data were corrected for Lorentz and polarization effects and an empirical absorption correction based on azimuthal scan data [8] was applied. The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation using the CRYSTALS program package [9]. In the refinement 3212 reflections with $I > 3\sigma(I)$ were used. Most (ca. 80%) of the hydrogen atoms were located in the different Fourier maps; the remaining H atoms were placed in calculated positions. All H atoms were included in the final refinement with fixed positional and thermal parameters. Convergence was obtained at $R = 0.049$ and $R_w = 0.053$, GOF = 1.101 (280 refined parameters;



SCHEME 3



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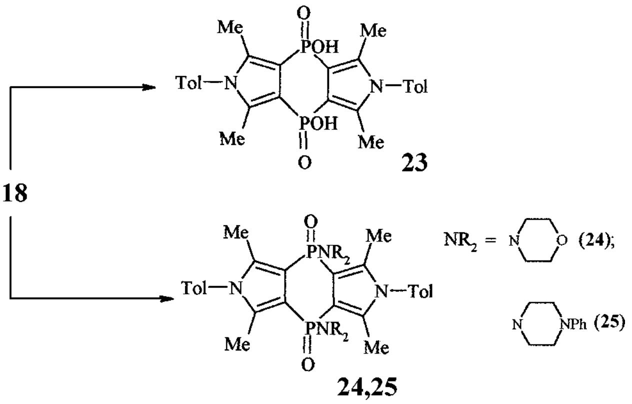

SCHEME 5

TABLE 4 Coordinates of Atoms and Equivalent Isotropic Thermal Parameters B_{eq} (Å) in **3c**

Atom	*x*	*y*	*z*	B_{eq}
S(1)	0.50629 (6)	0.17690 (5)	0.65882 (6)	0.0524
P (1)	0.54755 (5)	0.10322 (4)	0.55918 (5)	0.0327
O (1)	0.79268 (19)	0.21839 (17)	0.4543 (2)	0.0797
N (1)	0.63752 (16)	0.14847 (13)	0.52056 (18)	0.0386
N (2)	0.30433 (16)	0.09208 (13)	0.24727 (18)	0.0382
C (1)	0.7112 (3)	0.2121 (2)	0.5934 (3)	0.0602
C (2)	0.7445 (3)	0.2658 (2)	0.5152 (4)	0.0751
C (3)	0.7204 (3)	0.1579 (2)	0.3818 (3)	0.0740
C (4)	0.6843 (2)	0.0994 (2)	0.4537 (3)	0.0556
C (5)	0.44181 (18)	0.07647 (15)	0.4209 (2)	0.0342
C (6)	0.59738 (19)	0.00460 (15)	0.6253 (2)	0.0345
C (7)	0.68290 (19)	−0.00732 (16)	0.7331 (2)	0.0383
C (8)	0.38018 (19)	0.13501 (16)	0.3405 (2)	0.0378
C (9)	0.7526 (2)	0.05349 (19)	0.8236 (2)	0.0551
C (10)	0.3849 (2)	0.22774 (17)	0.3438 (2)	0.0489
C (11)	0.22318 (19)	0.13106 (16)	0.1449 (2)	0.0396
C (12)	0.2476 (2)	0.1621 (3)	0.0556 (3)	0.0692
C (13)	0.1695 (3)	0.2016 (3)	−0.0405 (3)	0.0770
C (14)	0.0675 (2)	0.2093 (2)	−0.0499 (2)	0.0523
C (15)	0.0453 (2)	0.1778 (3)	0.0398 (3)	0.0720
C (16)	0.1224 (2)	0.1392 (2)	0.1372 (3)	0.0660
C (17)	0.0159 (3)	0.2530 (3)	−0.1554 (3)	0.0776
C (18)	1.2220 (4)	0.0599 (3)	0.7278 (6)	0.1146
C (19)	1.2032 (5)	0.0100 (4)	0.8066 (5)	0.1209
C (20)	1.1030 (5)	−0.0036 (4)	0.7947 (5)	0.1293
C (21)	1.0211 (5)	0.0309 (5)	0.7042 (7)	0.1403
C (22)	1.0379 (5)	0.0796 (5)	0.6246 (7)	0.1556
C (23)	1.1397 (6)	0.0945 (4)	0.6367 (6)	0.1423
C (24)	0.5075 (3)	−0.0190 (3)	0.8957 (3)	0.0735
C (25)	0.4906 (3)	−0.0812 (2)	0.9620 (4)	0.0763
C (26)	0.5169 (3)	0.0619 (3)	0.9332 (3)	0.0726

The C(18)–C(24) atoms belong to the solvate benzene molecules.

obs./variabl. 11.5; the largest and minimal peaks in the final difference map, 0.30 and −0.37 $e/Å^3$). The Chebushev weighting scheme [10] with parameters 1.46, −0.29, 0.72, −0.40, and 0.10 was used. The final atomic coordinates are listed in Table 4.

Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 158332.

*Pyrrolo[3′,4′:5,6][1,4]diphosphorino[2,3-c]pyrrole-2,4,6,8-tetrahydro-1,3,5,7-tetramethyl-2,6-bis(4-methylphenyl)-4,8-di(4-morpholinyl)-4,8-disulfide (***3***).* To a stirred solution of dipyrrolylthioamide **1** [3] (0.01 mol) in pyridine (30 ml), a solution of phosphorus tribromide (0.01 mol) was added dropwise over 5 min; 24 h later (δP = 35.0; 136.0 ppm), a solution of morpholine (0.02 mol) and triethylamine (0.03 mol) in benzene (100 ml) was added dropwise to the stirred reaction mixture over 20 min. After 5 h, sulfur (0.01 mol) was poured into the mixture and then it was kept at 60°C for 4 h. The solvent was evaporated under vacuum, and the resulting residue was boiled with water (100 ml), filtered off, and crystallized from ethanol.

*Pyrrolo[3′,4′:5,6][1,4]diphosphorino[2,3-c]pyrrole-2,4,6,8-tetrahydro-4-methoxy-1,3,5,7-tetramethyl-2,6-bis(4-methylphenyl)-8-(4-morpholinyl)-4,8-disulfide (***4***).* To a stirred solution of dipyrrolylthioamide **1** (0.01 mol) in pyridine (30 ml), a solution of phosphorus tribromide (0.01 mol) was added dropwise over 5 min; 24 h later (δP = 35.0; 136.0 ppm), a solution of methanol (0.02 mol) and triethylamine (0.03 mol) in benzene (50 ml) was added dropwise to the stirred reaction mixture over 20 min and sulfur (0.01 mol) was then poured into it. After having been allowed to stand at 60°C for 4 h, the mixture was evaporated under vacuum. The resulting residue was boiled with water (100 ml), filtered off, and crystallized from the mixture ethanol:water (1:1).

*Pyrrolo[3′,4′:5,6][1,4]diphosphorino[2,3-c]pyrrole-2, 4, 6, 8-tetrahydro-1, 3, 5, 7-tetramethyl-2, 6-bis (4-methylphenyl)-4-(4-morpholinyl)-8-phenoxy-4,8-disulfide (***5***).* To a stirred solution of dipyrrolylthioamide **1** (0.01 mol) in pyridine (30 ml), a solution of phosphorus tribromide (0.01 mol) was added dropwise over 5 min; 24 h later ($\delta P = 35.0$; 136.0 ppm), a solution of phenol (0.01 mol) and triethylamine (0.03 mol) in benzene (50 ml) was added dropwise to the stirred reaction mixture over 20 min and sulfur (0.01 mol) was then poured into it. After having been allowed to stand at 80°C for 6 h, the mixture was evaporated under vacuum. The resulting residue was boiled with water (100 ml), filtered off, and crystallized from the mixture ethanol:water (1:2).

*Pyrrolo[3′,4′:5,6][1,4]diphosphorino[2,3-c]pyrrole-2, 4, 6, 8, 8, 8-hexahydro-1, 3, 5, 7-tetramethyl-2, 6-bis (4-methylphenyl)-4-(4-morpholinyl)-8-oxo-, 4-sulfide (***6***).* To a stirred solution of dipyrrolylthioamide **1** (0.01 mol) in pyridine (30 ml), a solution of phosphorus tribromide (0.01 mol) was added dropwise over 5 min; 24 h later ($\delta P = 35.0$; 136.0 ppm), the reaction mixture was evaporated under vacuum and the residue was dissolved in methylene chloride (100 ml). On filtration of the mixture, water (20 ml) was poured into the filtrate. After 24 h, the organic layer was separated, washed with water (20 ml), dried with sodium sulfate, and evaporated under vacuum. The product was purified by precipitating it from ethanol by addition of water.

*Pyrrolo[3′,4′:5, 6][1,4]diphosphorino[2, 3-c]pyrrole, 14,8-dibromo-2,4,6,8-tetrahydro-1,3,5,7-tetramethyl-2,6-bis(4-methylphenyl) (***9***).* To a stirred solution of pyrrole (0.01 mol) in pyridine (50 ml), a solution of phosphorus tribromide (0.005 mol) in pyridine (10 ml) was added dropwise over 5 min; 2 h later, the same portion of a pyridinec solution of phosphorus tribromide was added to the reaction mixture in the same manner. After 72 h ($\delta P = 136.0$ ppm), the mixture was filtered and the filtrate was evaporated under vacuum. The residue was dissolved in benzene (100 ml), filtered off, and the filtrate was evaporated under vacuum. The product was crystallized from the mixture benzene: heptane (1:1).

General Procedure for Preparation of Thiophosphonites **10–12**

To a solution of bisbromophosphine **9** (0.01 mol) in pyridine (50 ml), sulfur (0.02 mol) was added, and then a solution of the corresponding alcohol ROH (0.02 mol) and triethylamine (0.02 mol) in pyridine (20 ml) was added dropwise to the stirred reaction mixture. After the mixture had been held at 60°C for 5 h, it was evaporated under vacuum. The resulting residue was boiled with water (100 ml), and the precipitate was filtered off. The product was crystallized from ethanol.

General Procedure for Preparation of Thioamidophosphonites **13–15**

To a solution of bisbromophosphine **9** (0.01 mol) in pyridine (50 ml), sulfur (0.02 mol) was added and then a solution of aniline (0.02 mol) and triethylamine (0.02 mol) in pyridine (20 ml) was added dropwise to the stirred reaction mixture. After the mixture had been held at 60°C for 5 h, it was evaporated under vacuum. The resulting residue was boiled with water (100 ml), and ethanol (50 ml) and the precipitate was filtered off.

General Procedure for Preparation of Thioxides **16, 17**

To a stirred solution of bisbromophosphine **9** (0.01 mol) in pyridine (50 ml), a solution of heterocycle (0.2 mol) and triethylamine (0.02 mol) in pyridine (20 ml) was added dropwise; 72 h later, sulfur (0.02 mol) was added to the reaction mixture and it was allowed to stand at 60°C for 5 h. After filtration, the filtrate was evaporated under vacuum. The resulting residue was boiled with water (100 ml), and the precipitate was filtered off. The product was crystallized from ethanol.

*Pyrrolo[3′,4′:5, 6][1,4]diphosphorino[2,3-c]pyrrole-2, 4, 4, 4, 6, 8, 8, 8-octahydro-1,3,5, 7-tetramethyl-2, 6-bis(4-methylphenyl)-4,8-dioxide (***18***).* To a solution of bisbromophosphine **9** (0.01 mol) in methylene chloride (100 ml), water (20 ml) was added. After 24 h, the organic layer was separated, washed with water (20 ml), dried with sodium sulfate, and evaporated under vacuum to afford the residue which was boiled with ether (20 ml).

*Pyrrolo[3′,4′:5,6][1,4]diphosphorino[2,3-c]pyrrole, 2,4,6,8-tetrahydro-4,8-dihydroxy-1,3,5,7-tetramethyl-2,6-bis(4-methylphenyl)-,4,8-disulfide (***20***).* To a solution of bisbromophosphine **9** (0.01 mol) in benzene (100 ml), sulfur (0.02 mol) was added and the mixture was boiled for 10 h. On evaporation under vacuum, the resulting residue was boiled first with water (100 ml) and then with ether (50 ml).

Phosphonothioic acid [4-[[2,5-dimethyl-1-(4-methylphenyl)-1H-pyrrol-3-yl]methoxyphosphinothioyl]-2,5-dimethyl-1-(4-methylphenyl)-1H-pyrrol-3-yl]

*O,O-dimethyl ester (***22***).* To a solution of bisbromophosphine **9** (0.01 mol) in pyridine (50 ml), methanol (0.1 mol) was added and the reaction mixture was kept at 50°C for 10 h. After filtration, the filtrate was evaporated under vacuum and the resulting residue was boiled with water (100 ml). The product was purified by precipitation from ethanol by addition of water.

*Pyrrolo[3′,4′:5,6][1,4]diphosphorino[2,3-c]pyrrole-2, 4, 6, 8-tetrahydro-4, 8-dihydroxy-1,3,5,7-tetramethyl-2,6-bis(4-methylphenyl)-4,8-dioxide (***23***).* To a solution of bisbromophosphine **18** (0.01 mol) in benzene (100 ml), triethylamine (0.02 mol) and carbon tetrachloride (0.02 mol) were added, and the reaction mixture was boiled for 5 h. After addition of water (5 ml), it was boiled for another 3 h. The solvent was evaporated under vacuum to provide the residue which was boiled successively with water (20 ml) and ether (30 ml).

General Procedure for Preparation of Amidophosphonites **24, 25**

To a solution of bisbromophosphine **18** (0.01 mol) in benzene (100 ml), triethylamine (0.04 mol), carbon tetrachloride (0.02 mol), and the corresponding amine (0.02 mol) were added, followed by boiling of the reaction mixture for 15 h. After evaporation of the solvent under vacuum, the resulting residue was boiled successively with water (50 ml) and ether (50 ml).

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