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C-Phosphorylation of 2,5-Dimethyl-N-arylpyrroles

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ABSTRACT: *C-Phosphorylation of 2,5-dimethylpyrroles with phosphorus (III) halides has been studied. Synthetic methods have been elaborated that provide an access to 3-phosphorylated 2,5-dimethylpyrroles, including pyrrole-substituted halogeno and dihalogeno phosphines; on this basis, a variety of trivalent and pentavalent phosphorus derivatives has been obtained. Ortho-diphosphorylated 2,5-dimethyl-N-arylpyrrole derivatives have been synthesized for the first time.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:223–230, 1999

INTRODUCTION

As shown by us previously, N-methylpyrrole is readily phosphorylated with phosphorus (III) halides at the position **2** of the heterocycle. For N-arylpyrroles, the reaction is not regioselective but instead affords a mixture of 2- and 3-phosphorylated pyrroles [1].

Up to now, there has been no evidence of 3-phosphorylated N-arylpyrroles available in the literature. It was of interest to us to study the phosphorylation of accessible 2,5-dimethyl-N-arylpyrroles with phosphorus (III) halides in the presence of a base, with the goal of synthesizing 3-phosphorylated and 3,4-diphosphorylated derivatives. Outcomes of investigation previously performed were reported briefly in our recent article [2].

RESULTS AND DISCUSSION

Phosphorus tribromide and even the much less reactive phosphorus trichloride react with 2,5-dimethyl-N-arylpyrroles **1a,b** in the presence of a base to afford dihalogenophosphines **2a,b**. For a preparative synthesis of dichlorophosphines **2a,b**, use of a twofold excess of PCl_3 is advantageous. Reaction with phenyldibromophosphine as well as with phosphorus tribromide enables us to prepare compounds having two heterocyclic residues bound to the same phosphorus atom (compounds **3a** and **4a**). 2,5-Dimethyl-N-arylpyrroles **1a,b** react with diphenylbromophosphine to give phosphines of the type of **5a**. An attempt to prepare compounds in which three pyrrole residues are bound to the same phosphorus atom has failed, which is evidently attributable to steric hindrance at the phosphorus atom.

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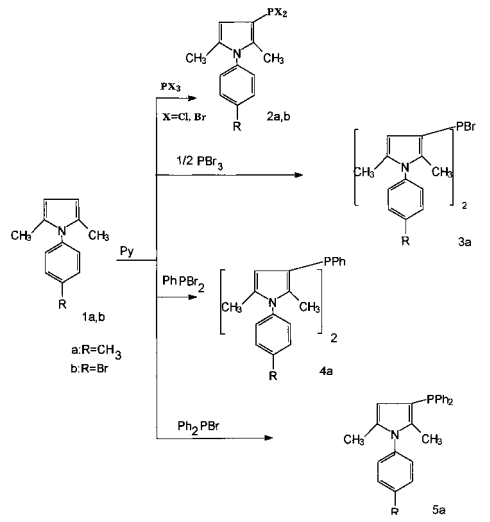
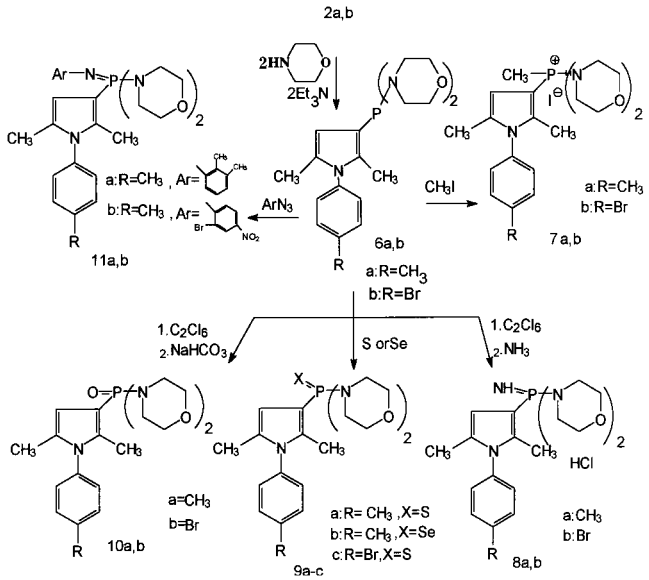
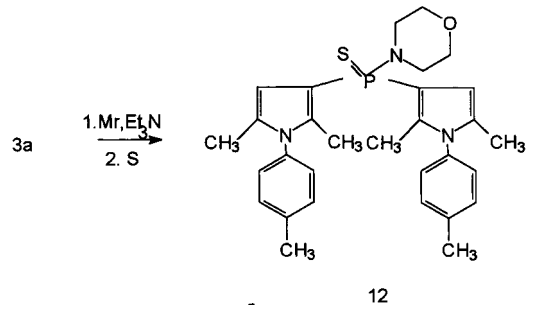


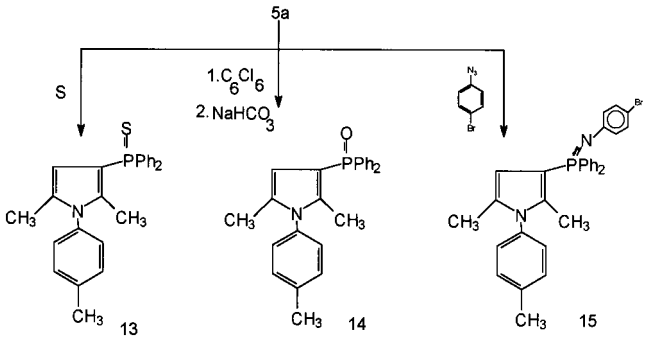
Dihalogenophosphines **2a,b** were converted into amidophosphonites **6a,b** that gave rise to a variety of derivatives, including oxides, sulfides, selenoxides, and imino derivatives. Amidophosphonites **6a,b** are quite stable crystalline compounds that persist for a long time in the absence of atmospheric moisture.

The C–P bond strength in C-phosphorylated heterocyclic compounds is known to depend on formation of a suitable protonated position in the heterocycle [3]. Indeed, in 3-phosphorylated N-arylpyrroles containing a trivalent phosphorus atom, in contrast to 3-phosphorylated indoles [4], the C–P bond is quite stable, and therefore, the former do not undergo disproportionation in either solution or on standing. This stability may be ascribed to the ability of pyrroles to undergo protonation at the position **2** [5], as distinct from the behavior of indoles.

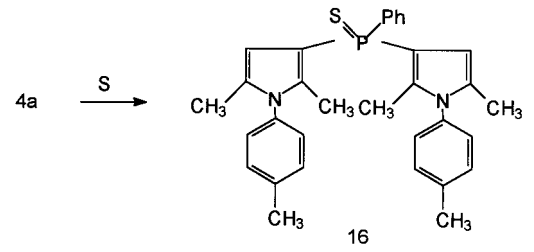




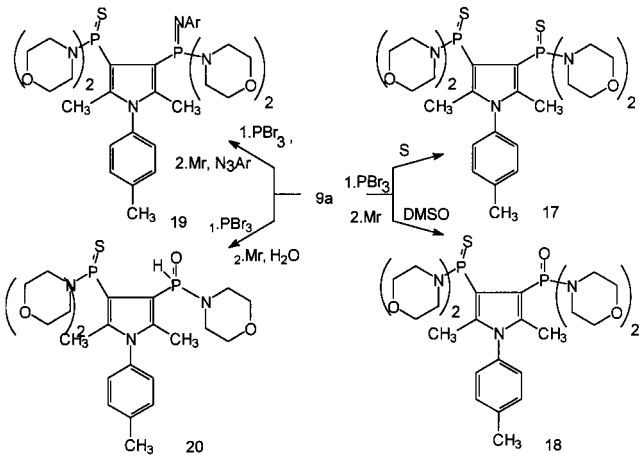
Unlike 1-methylpyrrolyl-2-diphenylphosphine [1], 2,5-dimethyl-N-arylpyrrolyl-3-diphenylphosphine **5a** is a rather stable crystalline substance, stable over a long period in the absence of atmospheric moisture. Starting from it, pentavalent phosphorus derivatives **13–15** have now been synthesized.



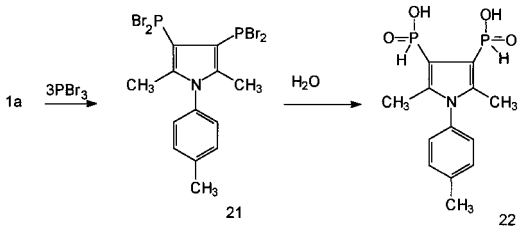
Based on examination of ^{31}P NMR spectra, a large number of by-products were formed together with phosphine **4a,** and therefore, **4a** was converted into the sulfide **16** for characterization.



3-Phosphorylated 2,5-dimethyl-N-arylpyrroles can undergo a second phosphorylation although, as expected, being much less reactive than the initial pyrroles **1a,b**. For instance, on refluxing compound **9a** with a 10-fold excess of PCl_3, the starting substance was isolated unchanged and formation of a dichlorophosphine was not observed even by ^{31}P NMR spectroscopy. However, sulfide **9a** reacts with phosphorus tribromide in pyridine to provide phosphonous acid bromo derivatives that were identified after they had been converted to the corresponding compounds **17–20**.



Two phosphorus atoms can be introduced into the molecule of 2,5-dimethyl-N-tolylpyrrole **1a** not only stepwise but by a single-step reaction as well. On reacting pyrrole **1a** with excess phosphorus tribromide, diphosphonous acid bromo derivative **21** was isolated.



A triplet at δ 117.5 in the ^{13}C NMR spectrum and the absence of ^{1}H NMR resonances in the region of 6.6 to 6.8 both unambiguously portray the structure of the product obtained. Unfortunately, we have failed to prepare the simplest derivatives of compound **21,** as, for instance, **17**. Only the product of hydrolysis, diphosphite **22,** has been isolated. A study of the chemical properties of **21** will be the subject of further study.

The presently reported orthodiphosphorylated pyrroles **17–22** are the first examples of orthodiphosphorylated heterocyclic compounds. The compositions of the substances synthesized were corroborated by elemental analysis, and their structures were supported by ^{31}P and ^{1}H NMR spectra (Tables 1 and 2).

EXPERIMENTAL

A Varian Gemini–200 instrument was used to record the ^{31}P, ^{1}H, and ^{13}C NMR spectra. The ^{1}H and ^{13}C signals were registered with respect to the internal standard tetramethylsilane, and the ^{31}P signals, to the external standard, 85% H_3PO_4 (unless otherwise stated).

2,5-Dimethyl-1-(p-tolyl)-3-pyrrolyldichlorophosphine **(2a).** To a stirred solution of 13.75 g of phosphorus trichloride (0.1 mol) in pyridine (30 mL), a solution of 9.25 g of 2,5-dimethyl-1-(*p*-tolyl)pyrrole (0.05 mol) in pyridine (20 mL) was added dropwise over 30 minutes. After maintenance of the reaction mixture at room temperature for 24 hours and addition of hexane (100 mL), the mixture was filtered. The filtrate was evaporated to dryness. The product was extracted from the residue with hexane (3 × 50 mL).

2,5-Dimethyl-1-(p-tolyl)-3-pyrrolyldiphenylphosphine **(5a).** To a solution of 2.65 g of diphenylbromophosphine (0.01 mol) in pyridine (10 mL), a solution of 1.85 g of 2,5-dimethyl-1-(*p*-tolyl)pyrrole (0.01 mol) and 1.01 g of triethylamine (0.01 mol) in pyridine (10 mL) was added; 48 hours later, the resulting precipitate was filtered off, and the filtrate was evaporated. The remainder was crystallized from anhydrous acetonitrile.

2,5-Dimethyl-1-(p-tolyl)pyrrolyl-3-phosphonous Dimorpholide **(6a).** To a stirred and ice-cooled solution of 28.60 g of compound **2a** (0.1 mol) in benzene (30 mL), a solution of 20.20 g of triethylamine (0.2 mol) and 17.40 g of morpholine (0.2 mol) in benzene (40 mL) was added dropwise. After 3 hours, the reaction mixture was filtered and the filtrate was evaporated in vacuo. The product was crystallized from heptane.

2,5-Dimethyl-1-(p-bromophenyl)pyrrolyl-3-phosphonous Dimorpholide **(6b).** To a stirred solution of 13.75 g of phosphorus trichloride (0.1 mol) in pyridine (30 mL), a solution of 12.50 g of 2,5-dimethyl-1-(*p*-bromophenyl)pyrrole (0.05 mol) in pyridine (20 mL) was added dropwise over 30 minutes. After the reaction mixture had been maintained at room temperature for 24 hours and after addition of hexane (100 mL), it was filtered. To the stirred and ice-cooled filtrate, a solution of 20.20 g of triethylamine (0.2 mol) and 17.40 g of morpholine (0.2 mol) in benzene (40 mL) was added. After 3 hours, the reaction mixture was filtered, and the filtrate was evaporated in vacuo. The product was crystallized from heptane.

Dimorpholinomethyl[2,5-dimethyl-1-(p-tolyl)-3-pyrrolyl]-phosphonium iodide **(7a)** *and Dimorpholinomethyl[2,5-dimethyl-1-(p-bromophenyl)-3-pyrrolyl]-phosphonium Iodide* **(7b).** To a solution of 3.87 g of amide **6a** or 4.57 g of **6b** (0.01 mol) in benzene (20 mL), 2.84 g of methyl iodide (0.02 mol) was added. The reaction mixture was heated at 50°C for 1 hour. The precipitate that had formed was filtered off.

TABLE 1 Yield, Analytical Data, and ^{31}P Spectra of Compounds **2–22**

N	M.p. (°C)	*Yield* (%)	*Formula*	*NNR*^{31}P δ, *m. d.* (*solvent*)	*Found* (%) (*calculated*)	
					N	*P*
2a	39–40	85	$C_{13}H_{14}Cl_2NP$	155.96 (C_6H_6)	5.02 (4.89)	10.75 (10.84)
5a	124–125	90	$C_{25}H_{24}NP$	−29.03 (pyridin)	4.08 (3.79)	8.81 (8.40)
6a	125–128	85	$C_{21}H_{30}N_3PO_2$	91.20 (C_6H_6)	10.88 (10.85)	8.04 (7.99)
6b	170–172	90	$C_{20}H_{27}BrN_3PO_2$	89.20 (C_6H_6)	9.43 (9.29)	6.89 (6.86)
7a	60–65	80	$C_{22}H_{33}IN_3PO_2$	−9.63 ($CHCl_3$)	7.82 (7.94)	(5.86) 5.98
7b	125–130	83	$C_{21}H_{30}BrIN_3PO_2$	−10.02 ($CHCl_3$)	7.21 (7.07)	(5.21) (5.38)
8a	260–262	52	$C_{21}H_{32}ClN_4PO_2$	39.66 ($CHCl_3$)	12.91 (12.78)	(7.06) 6.92
8b	290–293	58	$C_{20}H_{29}BrClN_4PO_2$	39.10 ($CHCl_3$)	11.21 (11.12)	(6.15) 6.10
9a	165–166	95	$C_{21}H_{30}N_3PO_2S$	71.30 ($CHCl_3$)	9.91 (10.02)	(7.38) 7.32
9b	178–180	90	$C_{21}H_{30}N_3PO_2Se$	69.19 ($CHCl_3$)	9.13 (9.01)	(6.65) 6.72
9c	149–150	95	$C_{20}H_{27}BrN_3PO_2S$	71.30 ($CHCl_3$)	8.77 (8.68)	(6.40) 6.52
10a	82–83	70	$C_{21}H_{30}N_3PO_3$	24.60 ($CHCl_3$)	10.58 (10.42)	7.74 (7.79)
10b	146–148	80	$C_{20}H_{27}BrN_3PO_3$	24.80 ($CHCl_3$)	8.81 (8.97)	(6.62) 6.49
11a	200–205	60	$C_{29}H_{39}N_4PO_2P$	17.10 ($CHCl_3$)	11.21 (11.07)	(6.13) 6.08
11b	220–225	65	$C_{27}H_{33}BrN_5O_4P$	18.75 ($CHCl_3$)	11.51 (11.62)	(5.15) 5.28
12	120–122	69	$C_{30}H_{36}N_3PS$	52.90 ($CHCl_3$)	8.45 (8.38)	(6.19) 6.22
13	170–172	90	$C_{25}H_{24}NPS$	33.09 ($CHCl_3$)	3.51 (3.39)	(7.73) 7.69
14	144–145	75	$C_{25}H_{24}NPO$	24.57 ($CHCl_3$)	3.61 (3.64)	(8.05) 8.09
15	38–40	51	$C_{31}H_{28}BrN_2P$	−1.56 ($CHCl_3$)	5.28 (5.19)	(5.75) 5.83
16	120–122	48	$C_{32}H_{33}N_2PS$	21.90 ($CHCl_3$)	5.65 (5.51)	(6.10) 6.17
17	238–240	73	$C_{29}H_{45}N_5O_4P_2S_2$	72.4 ($CHCl_3$)	11.77 (11.88)	(10.50) 10.34
18	135–136	54	$C_{29}H_{45}N_5O_5P_2S$	22.30; 72.50 ($CHCl_3$)	11.07 (10.99)	(9.74) 10.01
19	112–113	67	$C_{35}H_{49}BrN_6O_4P_2S$	15.10; 72.40 ($CHCl_3$)	10.75 (10.62)	(7.84) 7.71
20	133–134	76	$C_{25}H_{38}N_4O_4P_2S$	71.70; 17.10(d) J_{PH} = 550 Hz (C_6H_6)	10.54 (10.98)	(12.16) 12.20
21	194–195	42	$C_{13}H_{13}Br_4NP_2$	132.20 (pyridin)	—	11.02 (10.97)
22	185–186	74	$C_{11}H_{11}NO_4P_2$	10.38 ($CHCl_3$)	—	17.32 (17.46)

TABLE 2 3-Phosphorylated Pyrroles: ^{1}H NMR δ^a Multiplicity^b

N	*H-Het*	*C_2-CH_3*	*C_5-CH_3*	*N_{Mr}-CH_2*	*O_{Mr}-CH_2*	*Ar*	*Others*
2a	6.42 d J_{HP} = 3,0 Hz	2.19 s	2.00 s			2.43 s(CH_3, Tol) 7.05 d, J_{HH} = 8.1 Hz (m-H, Tol) 7.30 d J_{HH} = 8.1 Hz (o-H, Tol)	
5a	5.65 s	2.14 s	1.95 s			2.41 s (CH_3, m-H, Tol)	7.00–7.55 m (o, m-H, Tol; o, m, p-H, Ph)
6a	6.21 s	2.04 s	2.02 s	3.00–3.30 m	3.59 t J_{HH} = 4.4 Hz	2.16 s (CH_3, Tol) 6.77 d, J_{HH} = 8.1 Hz (m-H, Tol) 6.86 d J_{HH} = 8.1 Hz (o-H, Tol)	
6b	6.28 s	2.09 s	2.05 s	3.00–3.30 m	3.61 t J_{HH} = 4.5 Hz	6.86 d, J_{HH} = 8.5 Hz (o-H, Ar) 7.03 d J_{HH} = 8.5 Hz (m-H, Ar)	
7a	6.36 d J_{HP} = 3.0 Hz	2.11 s	1.97 s	3.00–3.30 m	3.40–3.90 m	2.41 s(CH_3, Tol) 7.09 d, J_{HH} = 8.1 Hz (m-H, Tol) 6.47 d J_{HH} = 8.1 Hz (o-H, Tol)	2.24 s (CH_3-P)
7b	6.47 d J_{HP} = 3.0 Hz	2.331 s	2.11 s	3.00–3.30 m	3.40–3.90 m	7.11 d, J_{HH} = 8.5 Hz (o-H, Ar) 7.70 d J_{HH} = 8.5 Hz (m-H, Ar)	2.24 s (CH_3-P)
8a	6.13 d J_{HP} = 3.0 Hz	2.01 s	1.95 s	3.08 t J_{HH} = 4.5 Hz	3.54 t J_{HH} = 4.4 Hz	2.50 s (CH_3, Tol) 7.69 d, J_{HH} = 8.1 Hz (m-H, tol) 6.81 d J_{HH} = 8.1 Hz (o-H, Tol)	2.21 s (NH = P)
8b	6.37 d J_{HP} = 3.0 Hz	2.13 s	1.97 s	3.00–3.30 m	3.67 t J_{HH} = 4.5 Hz	7.37 d, J_{HH} = 8.5 Hz (o-H, Ar) 7.80 d J_{HH} = 8.5 Hz (m-H, Ar)	2.23 s (NH = P)
9a	6.09 dd J_{HH} = 3.7 Hz J_{HH} = 0.7 Hz	2.29 d J_{HH} = 1.5 Hz	1.95 s	3.00–3.30 m	3.68 t J_{HH} = 4.4 Hz	2.43 s (CH_3, Tol) 7.03 d, J_{HH} = 8.1 Hz (m-H, Tol) 7.28 d J_{HH} = 8.1 Hz (o-H, Tol)	
9b	6.10 d J_{HP} = 3.7 Hz	2.30 s	1.95 s	3.00–3.30 m	3.67 t J_{HH} = 4.4 Hz	2.43 s (CH_3, Tol) 7.03 d, J_{HH} = 8.1 Hz (m-H, Tol) 7.30 d J_{HH} = 8.1 Hz (o-H, Tol)	
9c	6.09 s	2.30 s	1.96 s	3.00–3.30 m	3.70 t J_{HH} = 4.5 Hz	7.03 d, J_{HH} = 8.5 Hz (o-H, Ar) 7.64 d J_{HH} = 8.5 Hz (m-H, Ar)	
10a	5.91 d J_{HP} = 3.0 Hz	2.24 s	1.96 s	3.00–3.20 m	3.67 t J_{HH} = 4.4 Hz	2.43 s (CH_3, Tol) 7.05 d, J_{HH} = 8.4 Hz (m-H, Tol) 7.28 d J_{HH} = 8.4 Hz (o-H, Tol)	
10b	6.07 d J_{HP} = 3.0 Hz	2.30 s	2.07 s	3.00–3.20 m	3.70 t J_{HH} = 4.5 Hz	7.13 d, J_{HH} = 8.5 Hz (o-H, Ar) 7.74 d J_{HH} = 8.5 Hz (m-H, Ar)	
11a	6.34 d J_{HP} = 3.0 Hz	2.24 s	1.97 s	3.00–3.30 m	3.35–3.80 m	2.40 s (CH_3, Tol)	2.12 s (o, m-CH_3); 7.00–7.70 m (o, m-H Ar, o, m, p-H Ar-N)

TABLE 2 (*Continued*) 3-Phosphorylated Pyrroles: ^{1}H NMR δ^a Multiplicity^b

N	*H-Het*	*C_2-CH_3*	*C_5-CH_3*	*N_{Mr}-CH_2*	*O_{Mr}-CH_2*	*Ar*	*Others*
11b	6.12 d J_{HP} = 3.0 Hz	2.13 s	2.00 s	3.00–3.40 m	3.45–3.90 m	2.44 s (CH_3, Tol) 7.05 d, J_{HH} = 8.1 Hz (m-H, Tol) 7.43 d J_{HH} = 8.1 Hz (o-H, Tol)	6.98–7.52 m (o,m-H Ar-N)
12	5.90–6.00 m, 6.17 d J_{HP} = 4.4 Hz	2.13 s 2.29 s	1.96 s	3.00–3.20 m	6.75 t J_{HH} = 4.0 Hz	2.42 s (CH_3, Tol), 7.00–7.10 m (m-H, Tol) 7.20–7.30 m (o-H, Tol)	
13	5.56 d J_{HP} = 5.0 Hz	2.03 s	1.92 s			2.42 s (CH_3, Tol) 7.07 d, J_{HH} = 8.4 Hz (m-H, Tol) 7.22 d J_{HH} = 8.4 Hz (o-H, Tol)	7.40–8.04 m (o, m, p-H Ph)
14	5.63 d J_{HP} = 4.0 Hz	2.06 s	1.92 s			2.41 s (CH_3, Tol) 7.05 d, J_{HH} = 8.4 Hz (m-H, Tol) 7.24 d J_{HH} = 8.4 Hz (o-H, Tol)	7.40–7.95 m (o, m, p-H Ph)
15	5.96 d J_{HP} = 3.0 Hz	1.94 s	1.78 s			2.36 s (CH_3, Tol) 6.62 d, J_{HH} = 8.5 Hz (m-H, Tol) 7.10 d J_{HH} = 8.5 Hz (o-H, Tol)	7.16 d, J_{HH} = 8.5 Hz (o-H Ar-N) 7.33 d, J_{HH} = 8.5 Hz (m-H ArN) 7.50–7.65 m (p-H Ph) 7.72–7.85 m (o, m-H Ph)
16	5.75 s	2.10 s	1.93 s			2.41 s (CH_3, Tol) 7.05 d, J_{HH} = 8.4 Hz (m-H, Tol) 7.23 d J_{HH} = 8.4 Hz (o-H, Tol)	7.40–7.55 m (p-H Ph) 7.70–8.10 m (o, m-H Ph)
17	—	2.27 s	2.27 s	3.00–3.30 m	3.77 t J_{HH} = 4.4 Hz	2.47 s (CH_3, Tol) 7.03 d, J_{HH} = 8.0 Hz (m-H, Tol) 7.35 d J_{HH} = 8.0 Hz (o-H, Tol)	
18	—	2.26 s	2.10 s	3.00–3.30 m	3.60–3.90 m	2.46 s (CH_3, Tol) 7.00 d, J_{HH} = 8.1 Hz (m-H, Tol) 7.33 d J_{HH} = 8.1 Hz o-H, Tol)	
19	—	2.44 s	2.19 s	3.00–3.20 m	3.50–3.70 m	2.58 s (CH_3, Tol)	7.30–7.50 m (o, m-H Tol, o, m-H Ar-N)
20	—	2.25 s	2.18 s	3.00–3.20 m	3.70–3.80 m	2.45 s (CH_3, Tol) 7.01 d, J_{HH} = 7.5 Hz (m-H, tol) 7.28 d, J_{HH} = 7.5 Hz (o-H, Tol)	8.70 d J_{HP} = 550 Hz (H-P)
21	—	2.26 s	2.26 s			2.46 s (CH_3, Tol) 7.11 d, J_{HH} = 8.1 Hz (m-H, Tol) 7.35 d, J_{HH} = 8.1 Hz (o-H, Tol)	
22	—	2.30 s	2.30 s			2.46 s (CH_3, Tol) 7.11 d, J_{HH} = 8.1 Hz (m-H, Tol) 7.35 d, J_{HH} = 8.1 Hz (o-H, Tol)	7.40 d J_{HP} = 150 Hz (H-P) 9.70 s (OH)

[a]Spectra were taken in CDCl.
[b]s, singlet; d, doublet; t, triplet; m, multiplet.

2,5-Dimethyl-1-(p-tolyl)pyrrolyl-3-dimorpholinophosphimine Hydrochloride **(8a)** *and 2,5-Dimethyl-1-(p-bromophenyl)pyrrolyl-3-dimorpholinophosphimine Hydrochloride* **(8b).** To a solution of 3.87 g of amide **6a** or 4.57 g of **6b** (0.01 mol) in benzene (10 mL), 2.37 g of hexachloroethane (0.01 mol) was added; 3 hours later, the benzene solution was decanted, and the remaining oil was dissolved in methylene chloride. Ammonia was bubbled into the solution for 1 hour. After the precipitate of salts had been filtered off and the filtrate evaporated to dryness, the product was crystallized from acetone.

2,5-Dimethyl-1-(p-tolyl)pyrrolyl-3-thiophosphonic Dimorpholide **(9a)** *and 2,5-Dimethyl-1-(p-bromophenyl)pyrrolyl-3-thiophosphonic Dimorpholide* **(9c).** To a solution of 3.87 g of amide **6a** or 4.57 g of **6b** (0.01 mol) in benzene (5 mL), 0.32 g of sulfur (0.01 mol) was added. The reaction mixture was refluxed for 5 minutes and then allowed to stand at room temperature for 12 hours. The precipitate that had formed was filtered off.

2,5-Dimethyl-1-(p-tolyl)pyrrolyl-3-selenophosphonic Dimorpholide **(9b).** To a solution of 3.87 g of amide **6a** (0.01 mol) in benzene (5 mL), 0.79 g of selenium (0.01 mol) was added. The reaction mixture was refluxed with stirring for 2 hours and then was followed by evaporation of the solvent. The product was crystallized from acetone.

2,5-Dimethyl-1-(p-tolyl)pyrrolyl-3-phosphonic Dimorpholide **(10a)** *and 2,5-Dimethyl-1-(p-bromophenyl)pyrrolyl-3-phosphonic Dimorpholide* **(10b).** To a solution of 3.87 g of amide **6a** or 4.57 g of **6b** (0.01 mol) in benzene (10 mL), 2.37 g of hexachloroethane (0.01 mol) was added; 3 hours later, the benzene solution was decanted, the remaining oil being dissolved in methylene chloride and washed with 10% aqueous $NaHCO_3$. After evaporating it to dryness, the product was extracted from the remainder with hexane.

2,5-Dimethyl-1-(p-tolyl)-3-pyrrolyl-2,3-dimethylphenylimino-phosphonic Dimorpholide **(11a)** *and 2,5-Dimethyl-1-(p-tolyl)-3-pyrrolyl-2-bromo-4-nitrophenylimino-phosphonic Dimorpholide* **(11b).** To a solution of 3.87 of amide **6a** (0.01 mol) in toluene (10 mL), 1.47 g and 2.43 g of the corresponding azide (0.01 mol) were added. After refluxing the reaction mixture with stirring for 3 hours, the resulting precipitate was filtered off. The product was crystallized from ethanol.

Di[2,5-dimethyl-1-(p-tolyl)pyrrolyl-3]thiophosphonic Morpholide **(12).** To a stirred solution of 3.70 g of 2,5-dimethyl-1-(*p*-tolyl)pyrrole (0.02 mol) in pyridine (20 mL), a solution of 2.71 g of phosphorus tribromide (0.01 mol) in pyridine (10 mL) was added dropwise; 5 hours later, a solution of 1.74 g of morpholine (0.02 mol) and 3.03 g of triethylamine (0.03 mol) in benzene (30 mL) was added to the reaction mixture. Addition of 0.32 g of sulfur (0.01 mol) after 3 hours and hexane (30 mL) after an additional 24 hours was followed by filtration. The filtrate was evaporated in vacuo. The product was crystallized from the mixture $C_2H_5OH : H_2O$ (2:1).

2,5-Dimethyl-1-(p-tolyl)pyrrolyl-3-diphenylphosphine Sulfide **(13).** To a solution of 3.69 g of phosphine **5a** (0.01 mol) in toluene (30 mL), 0.32 g of sulfur (0.01 mol) was added. The reaction mixture was refluxed for 0.5 hours and then evaporated. The product was crystallized from ethanol.

2,5-Dimethyl-1-(p-tolyl)pyrrolyl-3-diphenylphosphine Oxide **(14).** To a solution of 3.69 g of phosphine **5a** (0.01 mol) in beneze (40 mL), 2.37 g of hexachloroethane (0.01 mol) was added; 0.5 hour later, the benzene solution was decanted, and the remaining oil was dissolved in methylene chloride and washed with 5% aqueous $NaHCO_3$. After separation of the organic layer, it was dried over anhydrous Na_2SO_4 and evaporated to dryness. The product was crystallized from ethanol.

2,5-Dimethyl-1-(p-tolyl)-3-pyrrolyldiphenylphosphonic p-Bromo-phenylimide **(15).** To a solution of 3.69 g of phosphine **5a** (0.01 mol) in benzene (20 mL), 1.98 g of *p*-bromophenyl azide (0.01 mol) was added, and the reaction mixture was refluxed for 2 hours with stirring. After evaporation of the solvent, the product was crystallized from ethanol.

Di(2,5-dimethyl-1-(p-tolyl)-3-pyrrolyl)phenylphosphine Sulfide **(16).** To a solution of 1.85 g of 2,5-dimethyl-1-(*p*-tolyl)pyrrole (0.01 mol) in pyridine (20 mL), 1.34 g of phenyldibromophosphine (0.005 mol) was added. On refluxing of the reaction mixture for 48 hours, a ^{31}P NMR resonance at $\delta = -21$ was detected. After addition of 0.32 g of sulfur (0.01 mol), the mixture was refluxed for another 0.5 hour. The precipitate that had formed was filtered off, and the filtrate was evaporated. The product was crystallized from acetonitrile.

3,4-Bis(dimorpholinothiophosphonyl)-2,5-dimethyl-1-(p-tolyl)pyrrole **(17).** To a stirred solution of 4.19 g of thiophosphonic dimorpholide **9a** (0.01 mol) in pyridine (5 mL), a solution of 2.71 g of phos-

phorus tribromide (0.01 mol) in pyridine (5 mL) was added. Within 48 hours after this, signals at δ = 109.77 and 77.90 were observed in the ^{31}P NMR spectrum. To the cooled and stirred reaction mixture, a solution of 1.74 g of morpholine (0.02 mol) and 3.03 g of triethylamine (0.03 mol) in benzene (20 mL) was added dropwise; 3 hours later, the precipitate that had formed was filtered off. To the stirred filtrate, 0.32 g of sulfur (0.01 mol) was added, and, after 4 hours, the reaction mixture was evaporated. The product was crystallized from ethanol.

2,5-Dimethyl-4-dimorpholinophosphonyl-3-dimorpholinothio-phosphonyl-1-(p-tolyl)pyrrole **(18).** A solution of 4.19 g of thiophosphonic dimorpholide **9a** (0.01 mol) and 2.71 g of phosphorus tribromide (0.01 mol) in pyridine (15 mL) was maintained at 20°C for 48 hours. To the reaction mixture, a solution of 1.74 g of morpholine (0.02 mol) and 3.03 g of triethylamine (0.03 mol) in benzene (10 mL) was added; 1 hour later, DMSO (1 mL) was added, and the mixture was heated at 70°C for 5 hours. After filtering off the precipitate that had formed, the filtrate was evaporated. The product was crystallized from octane.

2,5-Dimethyl-4-dimorpholino(p-bromophenylimino)phosphonyl-3-dimorpholinothiophosphonyl-1-(p-tolyl)pyrrole **(19).** A solution of 4.19 g of thiophosphonic dimorpholide **9a** (0.01 mol) and 2.71 g of phosphorus tribromide (0.01 mol) in pyridine (15 mL) was maintained at 20°C for 48 hours. To the reaction mixture, a solution of 1.74 g of morpholine (0.02 mol) and 3.03 g of triethylamine (0.03 mol) in benzene (10 mL) was added; 4 hours later, the precipitate that had formed was filtered off, and a solution of 1.98 g of *p*-bromophenyl azide (0.01 mol) in benzene (10 mL) was added to the filtrate. After refluxing of the mixture for 2 hours, benzene was evaporated in vacuo. The precipitate formed was thoroughly triturated in water and filtered off.

2,5-Dimethyl-3-dimorpholinothiophosphonyl-4-morpholinophenylthiophosphinyl-1-(p-tolyl)pyrrole **(20).** A solution of 4.19 g of thiophosphonic dimorpholide **9a** (0.01 mol) and 2.71 g of phosphorus tribromide (0.01 mol) in pyridine (15 mL) was maintained at 20°C for 48 hours. To the reaction mixture were added first a solution of 1.74 g of morpholine (0.02 mol) and 3.03 g of triethylamine (0.03 mol) in pyridine (10 mL) and 4 hours later 0.18 g of water (0.01 mol). After another 4 hours, filtration of the reaction mixture and evaporation of the filtrate to dryness were carried out.

2,5-Dimethyl-3,4-tetrabromodiphosphino-1-(p-tolyl)pyrrole **(21).** To a stirred solution of 8.13 g of phosphorus tribromide (0.03 mol) in pyridine (20 mL), a solution of 1.85 g of 2,5-dimethyl-1-(*p*-tolyl)pyrrole (0.01 mol) in pyridine (20 mL) was added dropwise; 12 hours later, hexane (50 mL) was added to the reaction mixture. The precipitate that had formed was filtered off, and the filtrate was evaporated in vacuo. The product was crystallized from octane. The following resonances were registered in the ^{13}C NMR spectrum (with chemical shifts δ measured in ppm relative to C_5D_5N): 12.59 s (Het-CH_3); 20.93 s (Ar-CH_3); 117.75 t, J_{CP} = 27.20 Hz [Het C(3), C(4)]; 127.82 s [Ar C(3), C(5)]; 130.76 s [Ar C(2), C(6)]; 133.06 s [Ar C(4)]; 140.11 s [Ar C(1)]; 141.95 t, J_{CP} = 16.40 Hz [Het C(2), C(5)].

3,4-Diphosphinit-2,5-dimethyl-1-(p-tolyl)pyrrole **(22).** To a solution of 5.65 g of compound **21** (0.01 mol) in methylene chloride (100 mL), H_2O (20 mL) was added. After 24 hours, the organic layer was separated, dried over Na_2SO_4, and evaporated. The residue was refluxed with diethyl ether (20 mL).

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