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3-Phosphorylated N-Alkylindoles*

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ABSTRACT

The reactions of N-alkylindoles with phosphorus(III) halides have been studied. Synthetic methods for 3-phosphorylated N-alkylindoles, including dihalogenphosphines, have been developed, and the chemical properties of the 3-phosphorylated indoles have been investigated. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Derivatives of indoles, including C-phosphorylated indoles, have attracted much attention of researchers in connection with their high physiological activity. 2- and 3-Phosphorylated indoles have been obtained, both by reaction of indolylmagnesium halides with phosphorus halides [1,2] and by classical cyclizations commonly used for syntheses of indoles [3–5]. In spite of extensive research, the compounds having a bond between a phosphorus atom and the 3-carbon atom of the ring have continued to be only difficultly available, and the indolyl-substituted halogen- and dihalogenphosphines could not be obtained at all.

Recently, we have shown that the electron-rich heteroaromatic compounds, such as indolizine [6], pyrrole, furan, and thiophene [6–10], as well as some aromatic compounds [11,12] and enamines [13,14], can undergo C-phosphorylation with phosphorus(III) halides under basic conditions. It was of interest to use these reactions for phosphorylation of N-alkylindoles. The most recent report about phosphorylation of 1,2-dimethylindole was published by us [15].

RESULTS AND DISCUSSION

We have found that, in the presence of bases, the phosphorus(III) halides react with N-alkylindoles (**1a,b**) or with the more reactive N-alkyl-2-methylindoles (**1c,d**) to form 3-indolyl-substituted halogenphosphines (**2–4**) and the phosphines **10–12**.

The reaction was successfully carried out both with phosphorus tribromide and phosphorylating reagents that are considerably less reactive, in particular, diphenylchlorophosphine. Thus, the phosphorylation of 1-ethyl-2-methylindole (**1d**) with diphenylchlorophosphine in pyridine solution at 20°C was completed after 2 days, and, in the case of 1-ethylindole **1b**, the reaction was completed only to the extent of 20%. More than 1 month was needed to complete the reaction (Scheme 1).

Among dihalogenphosphines (**2a,b** and **3a,b**), dibromophosphine **3b** (δ_p = 135.17) possesses the least stability; it undergoes decomposition during several hours at 25°C. Although most of the dichlorophosphines were not isolable in an analytically pure state, they were successfully used for preparation of different derivatives. The phosphines **12** are stable, crystalline compounds in air, but phosphines **10** and **11** are oxidized rapidly by oxygen of the air. They were identified on the basis of ^{31}P NMR spectral data

Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

*C-Phosphorylated electron-rich heterocycles III.

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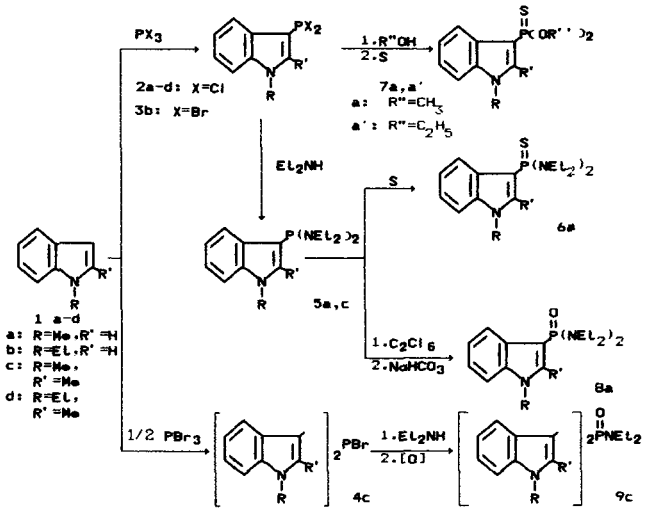


SCHEME 1

and characterized as oxides, thiooxides, and imino derivatives (Scheme 2).

A wide variety of phosphorylated indoles with either a trivalent (**5a,c**) or a pentavalent phosphorus atom (**6–9,13–18**) were synthesized from compounds **2–4** and **10–12**.

Earlier we had shown [16,17] that β-phosphorylated enamines with a trivalent phosphorus atom display an especial lability of the C–P bond. In these compounds, there is a similarity to the reactivity of the P–N bond of amides of trivalent phosphorus acids. Since indoles contain an enamine moiety in their structure, the 3-phosphorylated indoles can be considered to be β-phosphorylated enamines; therefore a similar lability of the bond could be expected for these compounds. Indeed, the introduction of dry HCl gas into a benzene solution of the dichlorophosphine **2** or phosphine **12** led to the formation of phosphorus trichloride or diphenylchlorophosphine, respectively. However, this type of reaction takes place more slowly than in the case of β-phosphorylated enamines.

$$2 \xrightarrow{HCl} PCl_3 + \text{1-HCl}$$

$$12 \xrightarrow{HCl} Ph_2PCl + \text{1-HCl}$$

Some lability of the C–P bond is also apparent in the case of the amides **5**. If these compounds are not removed from the reaction mixture and are allowed to stand for 1 day in the presence of the dimethylammonium hydrochloride, the ^{31}P NMR spectrum of the mixture shows the signals of hexaethyltriamidophosphite (δ = 122.4) and diethylamidophosphonite in approximately 25% yield. If the amides were purified from the mixtures of hydrochlorides, the process of symmetrization did not occur. Although, under the action of dry HCl, the C–P bond in C-phosphorylated indoles with a trivalent phosphorus atom is cleaved; this bond is quite stable under the action of water or alcohols, in contrast to the β-phosphorylated enamines. For example, **12d** could be recrystallized from a mixture of alcohol with water. However, on the whole, it can be confirmed that the phosphines **10–12** are considerably more stable to oxygen of the air than similar derivatives of phosphorylated enamines [13,14].

It is known that, if the first and third positions at the indole molecule carry substituents, the reaction of electrophilic substitution often occurs at the second position. However, for 1,2,3-trimethylindole, the reactions with electrophiles proceed at the methyl group located at the second position. In particular, acylation with the anhydride of trifluoroacetic acid occurs in this manner [18]. Phosphorylation with phosphorus(III) halides has been proved to take place at the same position. For instance, phosphorylation of the N,N-dimethylhydrazone of 1-methyl-3-formylindole (**21**) with diphenyliodophosphine in pyridine solution gives the phosphine **22**, which is tolerant to oxygen of air (Scheme 3).

However, phosphorylation of 1,2,3-trimethylindole **23** with diphenyliodophosphine for two months, followed by oxidation, presumably leads to the formation of the phosphine oxide **24**. This substitution reaction is likely to occur at the stage of the formation of the indoleninic salt [16] (Scheme 4).

The compositions of the compounds obtained were confirmed by elemental analysis data and their structure by data of ^{1}H and ^{31}P NMR spectroscopy. For the dichlorophosphines **2** and the phosphinoxide **24**, the ^{13}C NMR spectra were obtained. In the ^{13}C NMR spectrum, the signals of the second and ninth carbon atoms appeared, respectively, at δ 134.32 and 111.32, with constants $J_{c\text{-}p}$ = 71.24 Hz and $J_{c\text{-}p}$ = 50.58 Hz being the most characteristic ones. The presence of the $-CH_2-P(O)Ph_2$ moiety in compound **24** is confirmed by the observed doublet with $J_{c\text{-}p}$ = 68.0 Hz at δ 29.05 of the ^{13}C NMR spectrum.

EXPERIMENTAL

A Varian Gemini-200 instrument was used to record the ^{31}P and ^{13}C NMR spectra. The ^{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.

3-(1-Ethylindolyl)dichlorophosphine (**2b**). A solution that was prepared by addition of a solution of

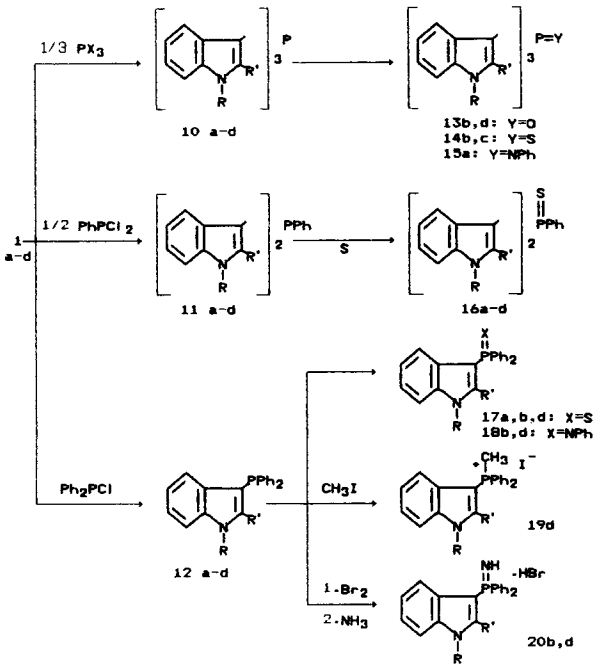
TABLE 1 Yield, Analytical Data, and ^{31}P NMR Spectra of the Compounds **2–24**

Compound No.	Mp (°C)	Yield (%)	Formula	^{31}P (solvent) δ	Found (%) (calculated)		
					N	S or Cl	P
1	2	3	4	5	6	7	8
				154.32		29.01	12.21
2b	122–123	90	$C_{10}H_{10}Cl_2NP$	(CH_2Cl_2)		(28.86)	(12.60)
				84.60	13.08		9.65
5a	oil	95	$C_{17}H_{28}N_3P$	(CH_2Cl_2)	(13.17)		(10.16)
				93.26	13.25		10.04
5c	oil	85	$C_{18}H_{30}N_3P$	(C_6H_6)	(13.16)		(9.71)
				69.04	12.02		8.89
6a	oil	90	$C_{17}H_{28}N_3PS$	(CH_2Cl_2)	(12.46)		(9.19)
				86.97	6.01		13.42
7a	oil	70	$C_{11}H_{14}NO_2PS$	($CHCl_3$)	(6.22)		(13.77)
				24.828	12.76		9.92
8a	99–100	52	$C_{17}H_{28}N_3OP$	(CH_2Cl_2)	(13.08)		(9.65)
				25.9	10.27		7.72
9c	83–84	70	$C_{24}H_{30}N_3OP$	(C_6H_6)	(10.31)		(7.60)
				−29.5	4.21		9.23
12c	146–147	80	$C_{22}H_{20}NP$	(C_6H_6)	(4.25)		(9.40)
				4.58	8.12		6.21
13b	210–215	68	$C_{30}H_{30}N_3$ OP	(C_6H_6)	(8.76)		(6.47)
				8.81	7.96		6.03
13d	158–160	60	$C_{33}H_{39}N_3OP$	(CH_3CN)	(8.01)		(5.91)
				2.69	8.62		6.43
14b	248–250	82	$C_{30}H_{30}N_3PS$	($CHCl_3$)	(8.48)		(6.26)
				6.87	8.53		6.31
14c	230–232	80	$C_{30}H_{30}N_3PS$	($CHCl_3$)	(8.48)		(6.26)
				2.23	12.04		5.72
15a	130–135	65	$C_{33}H_{29}N_4P$	(C_6H_6)	(12.50)		(6.05)
				17.26	7.21		8.03
16a	246–247	72	$C_{24}H_{21}N_2PS$	($(CH_3)_2SO$)	(7.17)		(7.94)
				17.03	6.68		7.35
16b	243–244	78	$C_{26}H_{25}N_2PS$	($CHCl_3$)	(6.54)		(7.24)
				31.53	6.42		7.17
16c	225–226	62	$C_{26}H_{25}N_2PS$	($CHCl_3$)	(6.54)		(7.24)
				31.64	6.21		6.92
16d	222–223	58	$C_{28}H_{29}N_2PS$	($CHCl_3$)	(6.14)		(6.79)
				28.93		9.02	9.02
17a	151–152	57	$C_{21}H_{18}NPS$	($CHCl_3$)		(9.22)	(8.93)
				31.14		8.93	8.61
17b	172–173	58	$C_{22}H_{20}NPS$	($CHCl_3$)		(8.86)	(8.58)
				31.83		8.62	8.32
17d	159–160	55	$C_{23}H_{22}NPS$	($CHCl_3$)		(8.53)	(8.26)
				−1.30	6.23		7.17
18b	142–143	61	$C_{28}H_{25}N_2P$	($CHCl_3$)	(6.67)		(7.38)
				−1.70	6.57		7.28
18d	146–147	53	$C_{29}H_{27}N_2P$	($CHCl_3$)	(6.45)		(7.14)
				11.85	3.02		6.53
19d	204–205	62	$C_{24}H_{25}JNP$	($CHCl_3$)	(2.87)		(6.39)
				22.93	6.43		7.08
20b	168–170	63	$C_{22}H_{22}BrN_2P$	($CHCl_3$)	(6.58)		(7.29)
				26.63	6.29		7.11
20d	246–247	60	$C_{23}H_{24}BrN_2P$	($CHCl_3$)	(6.37)		(7.06)
				−31.79	10.13		7.61
22a	147–149	61	$C_{24}H_{24}N_3P$	(piridin)	(10.90)		(8.05)
				15.97	3.74		8.75
24a	226–227	75	$C_{23}H_{22}NPO$	(C_6H_6)	(3.90)		(8.62)

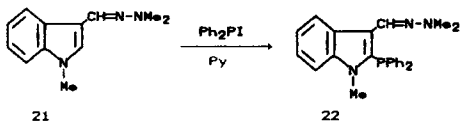
TABLE 2 3-Substituted Indoles: ^{1}H NMR δ[a] Multiplicity[b]

No.	H_2	H_4	H_5	H_6	H_7	$C\text{–}CH_3$	$N\text{–}CH_3$	$N\text{–}C_2H_5$ CH_2	$N\text{–}C_2H_5$ CH_3	OAr	Others
1	2	3	4	5	6	7	8	9	10	11	12
	7.42d										7.27m
2b[c]	3.2	8.18m						3.92q	1.31t		($H_{5,6,7}$)
											3.14q, 1.09t
											(P–NEt_2)
5a[e]	7.36d	7.65m			7.03m		3.77s				7.17m ($H_{5,6}$)
											3.26q, 1.03t
											(P–NEt_2)
5c[c]		8.05m			6.98m	2.45s					7.26m ($H_{5,6}$)
											3.17q, 0.99t
	7.73d										(P–NEt_2)
6a[d]	4.8	7.82m					3.74s				7.15m ($H_{5,6,7}$)
											3.65d (OCH_3)
	7.49d										7.25m
7a[f]	5.00	7.81m					3.91s				($H_{5,6,7}$)
											1.06t (CH_3)
	7.63d										3.17q (CH_2)
8a[d]	4.9	7.90m					4.19m				7.27m ($H_{5,6,7}$)
											3.25m, 1.17t
											(P–NEt_2)
9c[c]		8.23m			6.94m	2.64s	2.69s				7.16m ($H_{5,6}$)
											7.24m
12c[e]					7.01m	2.57s	3.65s				($H_{1,5,6,7}$,Ph)
	7.75d										
13b[d]	5.0	8.25m	7.30m	7.52m	7.02m			4.15q	1.43t		
13d[f]		7.46m		7.04m		2.50s		4.31q	1.36t		6.65m ($H_{5,7}$)
	7.74d										
14b[d]	5.1	8.25m	7.30m	7.51m	7.02m			4.14q	1.42t		
		7.25d									
14c[d]		7.5		7.08m		2.58s	3.71s				6.69m ($H_{5,7}$)
	7.48d										
15a[d]	5.0	7.67m	7.04m	7.36m	6.95m		3.75s				7.25m (Ph)
											7.54m
16a[d]					7.30m		3.95s			8.02m	($H_{2,5,6}$,Ph)
	7.46d										
16b[d]	5.0	7.56m	7.23m	7.35m	7.04m					7.94m	7.40m (Ph)
										8.00dd	
16c[d]		7.27m	6.78m	7.10m	6.56d	2.54s	3.70s			7.0;10.5	7.44m (Ph)
16d[d]			6.76m	7.10m	6.43m	2.55s		4.17q	1.35t	7.99	7.46m (Ph)
										7.81dd	7.35m
17a[d]					7.06m		3.80s			7.0;10.5	($H_{2,4,5,6}$,Ph)
										7.82dd	7.45m
17b[d]					7.05m			4.19q	1.49t	7.0;10.5	($H_{2,4,5,6}$,Ph)
										7.87dd	
17d[d]		7.29m	7.00m	7.12m	6.58m	2.38s		4.17q	1.35t	7.0;10.5	7.46m (Ph)
	7.61d									7.92dd	
18b[d]	4.70	7.45m	6.87m	7.00m	6.65m			4.19q	1.47t	7.0;10.5	7.49m (Ph)
										7.85dd	
18d[d]		7.16m	6.85m	6.98m	6.59m	2.44s		4.17q	1.36t	7.0;10.5	7.41m (Ph)
											3.05d (CH_3NP)
19d[d]		7.45m	7.01m	7.31m	6.58m	2.31s		4.32q	1.46t		7.76m (Ph)
	8.38d									7.90m	6.11s NH
20b[d]	5.00				7.06m			4.30q	1.58t	7.0;10.5	7.5m (Ph)
										7.93dd	6.29m (H_7,NH)
20d[d]		7.14m	6.86m	6.98m		2.51s		4.22q	1.41t	7.0;10.5	7.54m (Ph)
											7.33m
											($H_{4,5,6,7}$,Ph)
22a[d]							3.60s				8.53m (CH=N)

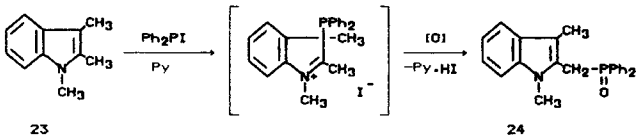
[a]All spectra were taken using a Bruker WP-200 with respect to internal standard TMS.
[b]s, Singlet; d, doublet; t, triplet; q, quartet; m, multiplet.
[c]Spectrum was taken in C_6D_6.
[d]Spectrum was taken in $CDCl_3$.
[e]Spectrum was taken in CD_3CN.
[f]Spectrum was taken in $(CD_3)_2CO$.



SCHEME 2



SCHEME 3



SCHEME 4

PCl_3 (0.048 mol) in pyridine (5 mL) to an ice-cooled and stirred solution of 1-ethylindole (0.048 mol) in pyridine (10 mL) was allowed to stand at 20°C for 2 hours. Benzene (30 mL) was added, and the precipitated material was filtered off. The filtrate was evaporated to dryness and allowed to stand in a vacuum during 1 hour.

3-(1-Methylindolyl)tetraethyldiamidophosphonite (**5a**). Et_2NH (0.18 mol) was added dropwise during 10 minutes to an ice-cooled and stirred suspension of 3-(1-methylindolyl)dichlorophosphine (**2a**) (0.03 mol) prepared in the same manner as **2b** (^{31}P NMR spectrum of **2a** (CH_2Cl_2): δ = 155.50) in benzene. After addition of petroleum ether (20 mL) to the reaction mixture, a precipitate that formed was filtered off. The filtrate was evaporated to dryness, and the residue was reprecipitated by addition of hexane to a CH_2Cl_2 solution of the compound.

3-(1,2-Dimethylindolyl)tetraethyldiamidophosphonite (**5c**). Compound **5c** was obtained similarly as **5a** from the corresponding intermediate 3-(1,2-dimethylindolyl)dichlorophosphine (**2c**) (^{31}P NMR spectrum: δ = 155.50).

3-(1-Methylindolyl)tetraethyldiamidothiophosphonate (**6a**). Powdered sulfur (0.03 mol) was added to a solution of 3-(1-methylindolyl)tetraethyldiamidophosphonite (**5a**) (0.03 mol) in benzene (30 mL). The reaction mixture was boiled for 1 hour, cooled, and evaporated to dryness. The oil so obtained was dissolved in ether (100 mL). The product that was precipitated on refrigeration was collected by filtration and triturated with petroleum ether.

3-(1-Methylindolyl)dimethoxythiophosphonate (**7a**). A solution of anhydrous CH_3OH (0.06 mol) in benzene (10 mL) was added at room temperature to a stirred suspension of 3-(1-methylindolyl)dichlorophosphine (**2a**) (0.03 mol) and Et_3N (0.06 mol) in benzene. There was observed a signal at δ = 162.20 in the ^{31}P spectrum of the phosphonite formed. After 2 hours, powdered sulfur was added to the reaction mixture, which was then boiled for 1 hour and cooled. The precipitate that had formed was filtered off, and the filtrate was evaporated to dryness. The product was crystallized from CH_3CN.

3-(1-Methylindolyl)diethoxythiophosphonate (**7a'**). Compound **7a'** was obtained similarly to **7a**.

3-(1-Methylindolyl)tetraethyldiamidophosphonate (**8a**). Hexachloroethane (0.04 mol) was added at room temperature to a stirred solution of 3-(1-methylindolyl)tetraethyldiamidophosphonite (**5a**) (0.04 mol) in petroleum ether (50 mL). The precipitate of the phosphonium salt that was formed (δ_P = 55.90) was filtered off, dissolved in CH_2Cl_2 (30 mL), and stirred with a water solution of Na_2CO_3 (10%). The separated organic layer was dried over Na_2SO_4 and evaporated to dryness. The product was crystallized from petroleum ether.

Bis(3-(1,2-dimethylindolyl))diethylamidophosphinate (**9c**). A solution prepared by addition of a solution of PBr_3 (0.024 mol) in benzene (10 mL) to a stirred solution of 1,2-dimethylindole (0.048 mol) and triethylamine (0.05 mol) in benzene (50 mL) was allowed to stand at 20°C for 1 hour and then stirred

at the boiling point for 0.5 hour. The bromophosphine (**4c**, δ_p = 61.5) was transformed into the amide in the same manner as for (**5a**) and then into the amidophosphonate similarly to (**8a**). The oil so obtained was dissolved in ether (100 mL). The product that precipitated on refrigeration was collected by filtration and triturated with petroleum ether.

3-(1,2-Dimethylindolyl)diphenylphosphine (**12c**). A mixture of 1,2-dimethylindole (0.005 mol), pyridine (45 mL) and diphenylchlorophosphine (0.05 mol) was allowed to stand at 20°C for 48 hours, and then the mixture was filtered. The filtrate was evaporated to dryness to give the product.

Tris(3-(1-ethylindolyl))phosphine Oxide (**13b**). A solution prepared by addition of a solution of PBr_3 (0.02 mol) in pyridine (20 mL) to a stirred solution of 1-ethylindole (0.06 mol) and triethylamine (0.07 mol) in pyridine (50 mL) was boiled for 3 hours. The phosphine (**10b**, δ_p = −78.38) was oxidized by the standard method (with the use of hexachloroethane). The precipitate that formed was collected and washed with hot benzene (50 mL).

Tris(3-(1-ethyl-2-methylindolyl))phosphine Oxide (**13d**). Compound **13d** was obtained similarly to **13b** from the corresponding intermediate tris(3-(1-ethyl-2-methylindolyl))phosphine (**10d**) (^{31}p NMR spectrum: δ = −77.56).

Tris(3-(1-ethylindolyl))phosphine Thiooxide (**14b**). A solution prepared by addition of PBr_3 (0.02 mol) in pyridine (20 mL) to a stirred solution of 1-ethylindole (0.06 mol) and triethylamine (0.07 mol) in pyridine (50 mL) was boiled for 3 hours (δ_p = −78.20). After addition of powdered sulfur (0.06 mol), the mixture was boiled for 1 hour and evaporated to dryness. The residue was crystallized from a mixture $CH_3CN/CHCl_3$ (2:1).

Tris(3-(1,2-dimethylindolyl))phosphine Thiooxide (**14c**). This compound was obtained similarly to **14b** from the corresponding intermediate tris(3-(1,2-dimethylindolyl))phosphine (**10c**) (^{31}p NMR spectrum: δ = −77.69).

Tris(3-(1-methylindolyl))phenyliminophosphine (**15a**). Tris(3-(1-methylindolyl))phosphine (**10a**, δ_p = 78.23) was obtained in the same manner as (**13b**). Phenyl azide (0.06 mol) was added, and the reaction mixture was agitated at room temperature for 2 hours. An insignificant precipitate was filtered off. The filtrate was evaporated to dryness. The residue was reprecipitated from benzene by addition of petroleum ether.

Bis(3-(1-methylindolyl))phenylphosphine Thiooxide (**16a**). A stirred mixture of 1-methylindole (0.06 mol), pyridine (45 mL), triethylamine (0.06 mol), and phenyldichlorophosphine (0.03 mol) was heated to 80°C for 5 hours (**11a**, δ_p = −54.34). The thiooxide was isolated by the standard method.

Bis(3-(1-ethylindolyl))phenylphosphine Thiooxide (**16b**), Bis(3-(1,2-dimethylindolyl))phenylphosphine Thiooxide (**16c**), Bis(3-(1-ethyl-2-methylindolyl))phenylphosphine Thiooxide (**16d**). These compounds were obtained similarly to (**16a**) from the corresponding intermediates: bis(3-(1-ethylindolyl))phenylphosphine (**11b**, δ_p = −54.51), bis(3-(1,2-dimethylindolyl))phenylphosphine (**11c**, δ_p = −53.92), and bis(3-(1-ethyl-2-methylindolyl))phenylphosphine (**11d**, δ_p = −53.87), respectively.

3-(1-Methylindolyl)diphenylphosphine Thiooxide (**17a**). A mixture of 1-methylindole (0.05 mol), pyridine (45 mL), triethylamine (0.05 mol), and diphenylchlorophosphine (0.05 mol) was kept at 20°C for 1 month (or heated at 80°C for 4 hours). 3-(1-Methylindolyl)diphenylphosphine (**12a**, δ_p = 27.52) prepared in this manner was transformed into the thiooxide by the standard method.

3-(1-Ethylindolyl)diphenylphosphine Thiooxide (**17b**), *and 3-(1-Ethyl-2-methylindolyl)diphenylphosphine Thiooxide* (**17d**). These compounds were obtained similarly to **17a** from the corresponding intermediates: 3-(1-ethylindolyl)diphenylphosphine (**12b**, δ_p = −27.63) and 3-(1-ethyl-2-methylindolyl)diphenylphosphine (**12d**, δ_p = −28.51).

3-(1-Ethylindolyl)diphenylphenyliminophosphine (**18b**). 3-(1-Ethylindolyl)diphenylphosphine has been obtained in the same manner as **17b**. Phenyl azide (0.05 mol) was added, and the reaction mixture was stirred at room temperature for 2 hours. The precipitate that had formed was filtered off, and the filtrate was evaporated to dryness. The product was crystallized from acetone.

3-(1-Ethyl-2-methylindolyl)diphenylphenyliminophosphine (**18d**). Compound **18d** was obtained similarly to (**18b**) from the corresponding intermediate: 3-(1-ethyl-2-methylindolyl)diphenylphosphine (**12d**, δ_p = −28.51).

Methyldiphenyl-3-(1-ethyl-2-methylindolyl)-phosphonium Iodide (**19d**). 3-(1-ethyl-2-methylindolyl)diphenylphosphine (**12d**) (0.05 mol) was obtained as described for **17d**. The precipitate having been filtered off, the filtrate was evaporated to dry-

ness. After dissolution of the residual phosphine in benzene (30 mL), CH_3I (0.06 mol) was added. The reaction mixture was agitated at 60°C for 1 hour. Benzene was decanted after cooling. The resulting oil was triturated with ether. The precipitate obtained was collected by filtration.

3-(1-Ethylindolyl)diphenylphosphazohydride hydrobromide (**20b**). After addition of Br_2 (0.06 mol) to a solution of the phosphine (**12b**) (0.05 mol), obtained in the same manner as (**17b**), in benzene (30 mL), the mixture was allowed to stand for 30 minutes. The precipitate that had formed was filtered off, dissolved in CH_2Cl_2 (30 mL), and then subjected to the action of a stream of anhydrous ammonia gas for 30 minutes. The precipitate that had formed was filtered off, and the filtrate was evaporated to dryness. The residual product was crystallized from acetone.

3-(1-Ethyl-2-methylindolyl)diphenylphosphazohydride Hydrobromide (**20d**). This compound was obtained similarly to (**20b**) from the corresponding intermediate (**12d**), obtained in the same manner as in the preparation of (**17d**).

Dimethylhydrazone of 2-(1-methyl-2-formylindolyl)diphenylphosphine (**22**). A solution of 3-(N,N-dimethyl-1-methylindolyl)methylhydrazone (0.0027 mol) in pyridine was added to a solution of diphenyliodophosphine (0.0027 mol) in pyridine. The mixture was heated at 100°C for 6 hours, treated with benzene and water, then agitated. The benzene solution was dried over Na_2SO_4 and filtered. The filtrate was mixed with octane. An undissolved oil and crystals were removed, and the octane solution was evaporated to dryness. The residual product was crystallized from acetone.

2-(1,3-Dimethylindolyl)methylenphosphine Oxide (**24**). A solution of diphenyliodophosphine (0.02 mol) in pyridine (5 mL) was added to a solution of 1,2,3-trimethylindole (0.02 mol) in pyridine (10 mL) and allowed to stand for 2 months. A stopper was opened, and the solution was allowed to stand for 2 days. Pyridine was evaporated in vacuum. The residue was treated with methanol. The precipitate was filtered off.

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