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Phosphorylation of 1-Alkylimidazoles and 1-Alkylbenzimidazoles with Phosphorus(III) Halides in the Presence of Bases

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ABSTRACT: *Phosphorylation of 1-alkyl substituted imidazoles and benzimidazoles with P(III) halides in pyridine was shown to proceed at the 3-N atom of the heteroaryl ring and was followed by triethylamine-induced migration of the phosphorus group to the 2-C atom. Preparative methods were developed for the synthesis of a range of 2-phosphorylated derivatives of the indicated imidazoles. The latter were found to undergo alkylation either at P(III) or 3-N centers, depending on the alkylating agent.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 585–597, 1999

INTRODUCTION

Phosphorylated imidazoles have attracted the attention of chemists and biochemists in the last decade because they are promising as synthons, pesticides, and drugs [1]. Lithiated and trimethylsilylated imidazoles and benzimidazoles are currently employed for synthesis of the 2-phosphorylated derivatives. This method was used to prepare a range of tertiary phosphines [2]. Recently, the direct C-2-phosphorylation of 1-alkyl substituted imidazoles and benzimidazoles was performed with phosphorus(V) chlorides in the presence of bases [3]. However, a much more promising route to the compounds that we extensively studied in recent years proved to be the phosphorylation with phosphorus(III) halides in pyridine-triethylamine medium [4,5]. The extension of the procedure to 1-alkylimidazoles and 1-alkylbenzimidazoles introduces a new way to synthesize the corresponding key halogeno-and dihalogenophosphines, the valuable precursors to various three-and four-coordinated phosphorus compounds.

RESULTS AND DISCUSSION

When halogenodiphenylphosphine Ph_2PHlg (Hlg = Cl, Br, I) is added in equimolar quantity to a solution of 1-alkylimidazole **1a,b** in pyridine, a signal tentatively ascribed to adduct **2** appears at δ_P ~30 ppm in the ^{31}P NMR spectrum of the reaction mixture. The adduct is decomposed by diethylamine into diethylaminodiphenylphosphine and the starting imidazole. Similar intermediates were observed in the reaction of 1-alkylimidazoles with acyl chlorides [6a,b].

In time, a new signal due to phosphines **3** arises at δ_P ca. −30 ppm and progressively increases in intensity. Triethylamine considerably accelerates the rearrangement of the adduct **2** into **3** (Scheme 1).

Phosphorus trichloride reacts with alkylimida-

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Dedicated to Alfred Schmidpetger on the occasion of his seventieth birthday. Prof. Dr. Schmidpeter has maintained tight scientific contacts with Kiev's chemists for many years, and he was a good friend of Professors Kirsanov and Markovsky.

Phosphorylated Azoles, II.

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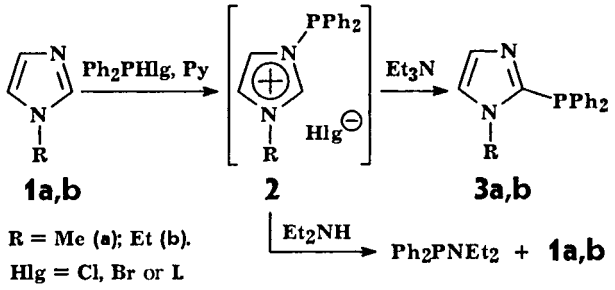


SCHEME 1

zoles in a similar way (Scheme 2, Hlg = Cl, A = H + H). Although the intermediate adducts **4** and the end dichlorophosphines **5** were not characterized in this case by ^{31}P NMR spectra because of low solubility in pyridine and other solvents, the formation of the compounds was confirmed by the reaction with dialkylamines, which produced tris(dialkylamino)phosphines **6** and the starting imidazoles from **4** or diaminophosphines **7** from **5**. The low solubility of dichlorophosphines **5** is likely to be due to intermolecular association into dimers or polymers **5′** [7].

Because of the solubility factor, the major product **7** was contaminated by triaminophosphines **6** (5–10%) and aminophosphines **8** (5–15%). In most instances, the compounds can be separated by vacuum distillation. Only in the case of dimorpholinophosphine **7c** were we forced to treat the reaction mixture with elemental selenium, crystallize the resulting selenide, and reduce it with hexapropylphosphorous triamide to isolate pure **7c** [8].

Phosphorus tribromide proved to be the most appropriate phosphorylating agent for 1-alkylbenzimidazoles **1c,d,** because it provided the highest yield of product **7** and minimum formation of **6** and **8** (Scheme 2, Hlg = Br, A = $(-CH=CH-)_2$). The corresponding dibromophosphines **5,** like dichloro(imidazolyl)phosphines, are difficulty soluble compounds most probably existing as associates **5′**. Because of this, they could not be characterized by ^{31}P NMR spectra.

It is a good preparative practice to perform the phosphorylation in one step, using pyridine-triethylamine as a solvent. The reactions of $PhPCl_2$, PCl_3, and PBr_3 with two or three equivalents of 1-alkylimidazoles or 1-alkylbenzimidazoles in this medium give tertiary phosphines **9** and **10** in high yield (Scheme 3).

A wide range of phosphorus(V) derivatives **11–16** were obtained from phosphines **3, 7–10** (Scheme 4).

Compounds **3** and **7** (Scheme 5), which are similar to phosphorylated imidazo[1,2-*a*]pyridines [5], can undergo alkylation either at the nitrogen atom in the heterocycle or at the exocyclic phosphorus center, depending on the alkylating agent. The first route is realized with hard alkylating agents such as Meerwein's salts or dimethyl sulfate and leads to products **17**. The alkylation with methyl iodide gives, in most cases, phosphonium salts **18**. With the exception of phosphine **9a** (Scheme 6), which is methylated at the nitrogen atom, obviously due to steric crowding around phosphorus created by heteroaryl residues [9].

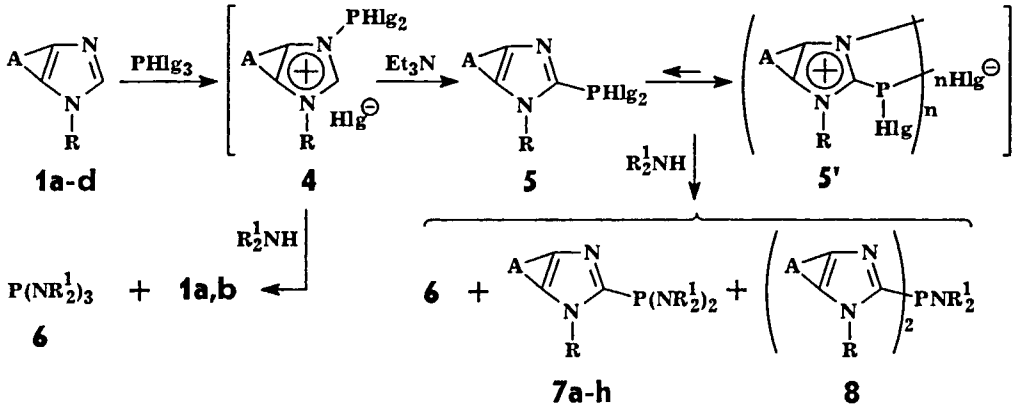
Electron-withdrawing phosphoryl substituents in **11, 14**, and **16** do not hamper the alkylation at the endocyclic nitrogen to yield imidazolium salts **20** (Scheme 7).

N-Alkylated phosphines **17a,b** dissolve in water or ethanol and are stable in these media. In contrast, phosphines **19** are easily hydrolyzed even in moist air and degrade in alcohols with elimination of one imidazole residue. Phosphorylated imidazoles carrying phosphorus(V) substituents are, as a rule, hydrolytically stable. The sole exception is provided by aryliminophosphoranes. We have found that the imines, when heated under reflux in wet solvents, decompose into starting imidazoles and amides of type **21** (Scheme 8).

The position of phosphorus-containing substituents in the products was unequivocally established by ^{1}H, ^{13}C, and ^{31}P NMR spectra (see Tables 1–4). Thus, the ^{1}H NMR signal of 2-H in the starting imidazoles (δ_H 7–8 ppm) disappears after phosphorylation. In ^{13}C NMR spectra, the low-field signal of 2-C is displaced to δ_C 140–150 ppm and split into a doublet with $J_{C\text{-}P}$ = 3–10 Hz. The position of alkylation is easily determined by the ^{31}P and ^{1}H NMR data. Thus, in compounds **17** and **19** alkylated at the nitrogen atom, the incoming methyl group gives a singlet signal, and the phosphorus chemical shift changes only little compared with the starting compounds. The *P*-methylated products **18** exhibit a doublet proton signal of CH_3-P and the shift of the phosphorus resonance to the region characteristic of phosphonium salts. It should be noted that the values of $J_{C\text{-}P}$ for *N*-alkylated products are almost by an order of magnitude greater than for the starting substrates; this is apparently due to a considerable contribution from the resonance structures with C=P bonds in the former.

EXPERIMENTAL

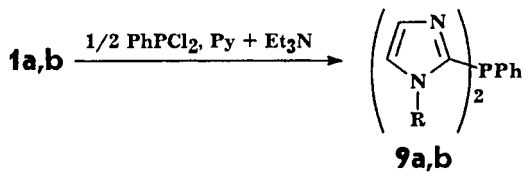
All the manipulations with air-sensitive compounds were performed under dry argon. Solvents were purified by conventional procedures. Melting points



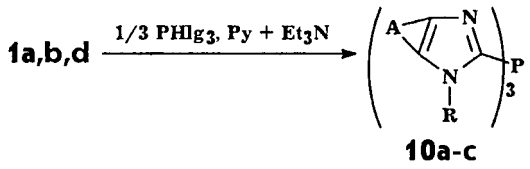
Hlg = Cl, Br.

Comp.	A	R	R^1 (R^1+R^1)	Comp.	A	R	R^1 (R^1+R^1)
1c	(-CH=CH-)$_2$	Me	—	7e	H+H	Et	Et
1d	(-CH=CH-)$_2$	Et	—	7f	(-CH=CH-)$_2$	Me	Me
7a	H+H	Me	Me	7g	(-CH=CH-)$_2$	Me	Et
7b	H+H	Me	Et	7h	(-CH=CH-)$_2$	Et	Et
7c	H+H	Me	O(CH$_2$CH$_2$)$_2$	8	H+H	Me	Et
7d	H+H	Et	Me				

SCHEME 2



R = Me (a), Et (b).



Hlg = Cl, Br.

Comp.	A	R
10a	H+H	Me
10b	H+H	Et
10c	(-CH=CH-)$_2$	Et

SCHEME 3

were determined with an electrothermal capillary melting point apparatus and were not corrected.

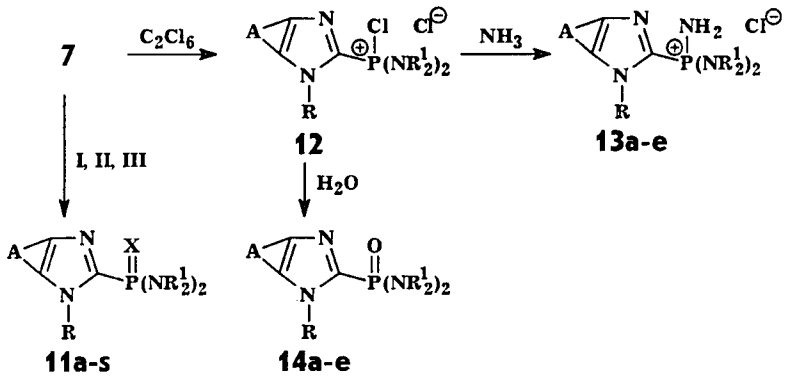
The ^{31}P, ^{1}H, ^{13}C NMR spectra were measured on a spectrometer Varian VXR-300 (121, 300, and 75 MHz, respectively). Chemical shifts are reported relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P).

General Procedure for Synthesis of Phosphines 3

Halogenodiphenylphosphine (20 mmol) dissolved in pyridine (5 mL) was added dropwise, at 5–10°C, to a stirred solution of 1-alkylimidazole **1a,b** (20 mmol) in the same solvent (10 mL) and was followed, after 30 minutes, by triethylamine (20 mmol). With diethylamine added in place of triethylamine, the reaction mixture shows only the ^{31}P NMR signal at δ_P 60.8 ppm, relating to diethylaminodiphenylphosphine. If there is no need in tracing adduct **2,** triethylamine can be added before the phosphorylating agent. After 24 hours, the mixture was diluted with benzene (10 mL), and the precipitate was filtered off and washed with benzene. The filtrate was evaporated in vacuo to leave the residue, which slowly crystallized when triturated with hexane.

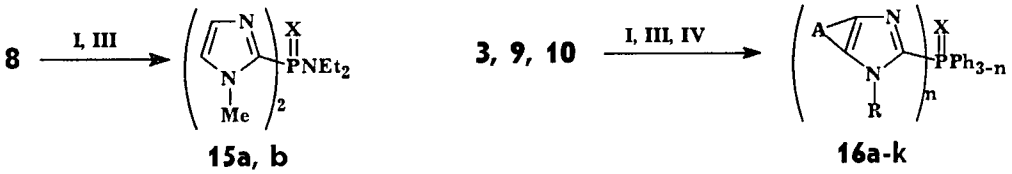
General Procedure for Synthesis of Aminophosphines 7a,b,d–h *and* 8

To a stirred mixture of 1-alkylimidazole **1a,b** or 1-alkylbenzimidazole **1c,d** (0.1 mol), triethylamine (0.15 mol), and pyridine (200 mL) preliminarily cooled to −5 to 0°C, phosphorus trichloride (phosphorus tribromide in the case of **1c,d**) (0.1 mol) in pyridine (25 mL) was added dropwise. The reaction mixture was allowed to stand overnight at room temperature and then treated at −5 to −10°C with the



Comp.	A	R	R^1 (R^1+R^1)	X	Comp.	A	R	R^1	X
11a	H+H	Me	Me	NTol-*p*	**11k**	(-CH=CH-)$_2$	Me	Et	S
11b	H+H	Me	Et	S	**11l**	(-CH=CH-)$_2$	Me	Et	NPh
11c	H+H	Me	Et	NPh	**11m**	(-CH=CH-)$_2$	Me	Et	NTol-*p*
11d	H+H	Me	Et	NTol-*p*	**11n**	(-CH=CH-)$_2$	Me	Et	NC_6H_4Ac-*p*
11e	H+H	Me	$O(CH_2CH_2)_2$	S	**11o**	(-CH=CH-)$_2$	Et	Et	S
11f	H+H	Me	$O(CH_2CH_2)_2$	Se	**11p**	(-CH=CH-)$_2$	Et	Et	Se
11g	H+H	Et	Me	S	**11q**	(-CH=CH-)$_2$	Et	Et	NPh
11h	H+H	Et	Me	NTol-*p*	**11r**	(-CH=CH-)$_2$	Et	Et	NTol-*p*
11i	H+H	Et	Et	Se	**11s**	(-CH=CH-)$_2$	Et	Et	NC_6H_4Ac-*p*
11j	(-CH=CH-)$_2$	Me	Me	S					

Comp.	A	R	R^1	Comp.	A	R	R^1 (R^1+R^1)
13a	H+H	Me	Me	**14a**	H+H	Me	Et
13b	H+H	Me	Et	**14b**	H+H	Me	$O(CH_2CH_2)_2$
13c	H+H	Et	Et	**14c**	(-CH=CH-)$_2$	Me	Me
13d	(-CH=CH-)$_2$	Me	Et	**14d**	(-CH=CH-)$_2$	Me	Et
13e	(-CH=CH-)$_2$	Et	Et	**14e**	(-CH=CH-)$_2$	Et	Et

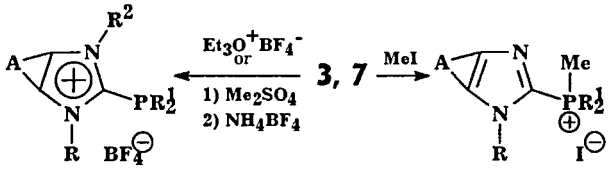


X = S (a), NPh (b).

Comp.	n	A	R	X	Comp.	n	A	R	X
16a	1	H+H	Me	O	**16g**	2	H+H	Me	NC_6H_4Br-*p*
16b	1	H+H	Me	S	**16h**	2	H+H	Et	S
16c	1	H+H	Me	NC_6H_4Br-*p*	**16i**	3	H+H	Me	S
16d	1	H+H	Et	O	**16j**	3	H+H	Et	S
16e	2	H+H	Me	O	**16k**	3	(-CH=CH-)$_2$	Et	S
16f	2	H+H	Me	S					

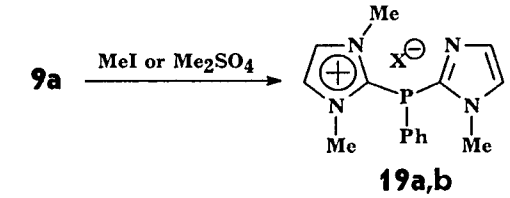
I : S; II : Se; III : ArN_3; IV : H_2O_2.

SCHEME 4



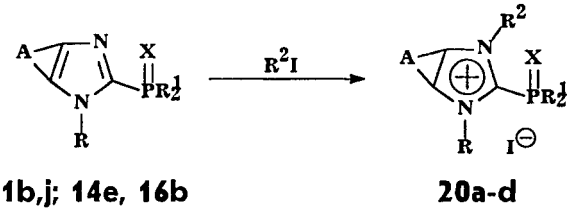
Comp.	A	R	R^1	R^2
17a	H+H	Me	Ph	Me
17b	H+H	Me	Ph	Et
17c	H+H	Me	NEt_2	Et
17d	H+H	Et	Ph	Et
17e	H+H	Et	NEt_2	Et
17f	(-CH=CH-)$_2$	Me	NEt_2	Et
18a	H+H	Me	Ph	—
18b	H+H	Et	NEt_2	—
18c	(-CH=CH-)$_2$	Me	NEt_2	—

SCHEME 5



X = I (a), $MeSO_4$ (b).

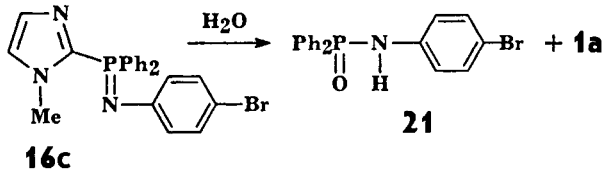
SCHEME 6



Comp.	A	R	R^1	R^2	X
20a	H+H	Me	Ph	Me	S
20b	H+H	Me	NEt_2	Me	S
20c	(-CH=CH-)$_2$	Et	NEt_2	Et	O
20d	(-CH=CH-)$_2$	Me	NMe_2	Me	S

SCHEME 7

appropriate secondary amine (0.5 mol), which was added at such a rate that the temperature did not exceed 0°C. After vigorous stirring for 2 hours at ambient temperature, the precipitate was filtered off and washed with benzene. The filtrate was diluted



SCHEME 8

with hexane (300 mL) and allowed to stand overnight; then it was filtered and evaporated. The residue was distilled in an oil-pump vacuum to give **6** (5–10%) in the first cut, **7** (the major product) in the second cut, and **8** (5–15%) in the third cut. On standing or after trituration with hexane, product **8** solidified. The solid was filtered off, washed with hexane, and recrystallized. In the case of 1-alkylbenzimidazoles, the products **6** and **8** are formed in a much lesser yield, and the latter cannot be isolated by vacuum distillation because of a high boiling point.

1-Methyl-2-imidazolyldimorpholinophosphine **7c** *and 1-Methyl-2-imidazolyldimorpholinophosphine Selenide* **11f**

Phosphorus trichloride (0.1 mol) in pyridine (5 mL) was added to a stirred mixture of 1-methylimidazole **1a** (0.1 mol), triethylamine (0.15 mol), and pyridine (20 mL) at −5 to 0°C and allowed to stand overnight at ambient temperature. The reaction mixture was then treated with morpholine (0.5 mol) at a temperature of no more than 0°C. After stirring for 2 hours, the solvent was evaporated in vacuo to dryness, and the residue was mixed with benzene (50 mL), stirred for 30 minutes, and filtered, then washing the solids with benzene (15 mL). Selenium (0.11 gram-atom) was added to the filtrate, and the mixture was heated under reflux for 30 minutes, filtered while hot, and concentrated to 30 mL. Compound **11f** precipitated on cooling. In order to reduce **11f** to **7c**, the selenide was dissolved in benzene and treated with a 1- to 5-fold excess of hexapropylphosphorous triamide. After 2 hours, benzene was evaporated, and the residue was mixed with hexane and kept overnight at −20°C. Precipitated phosphine **7c** was filtered off, washed with hexane, and dried.

General Procedure for Synthesis of Bis(1-alkyl-2-imidazolyl)phenylphosphines **9**

Dichlorophenylphosphine (10 mmol) was added to a stirred mixture of 1-alkylimidazole **1a,b** (20 mmol), triethylamine (20 mmol), and pyridine (15 mL), pre-

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

Compound	*Yield (%)*	M.p. B.b.(°*C*)	*Formula*	$\delta^{31}P$ (^{1}H) (*Solvent*)	*Found (%) (Calculated, %)*	
					N	*P*
3a	79	80–82 (MeOH)	$C_{16}H_{15}N_2P$	−32.2 (benzene)	10.45 (10.52)	11.54 (11.63)
3b	81	68–70 (MeOH)	$C_{17}H_{17}N_2P$	−33.4 (pyridine)	9.81 (9.99)	11.01 (11.05)
7a	69	69–72/ 0.04 mm	$C_8H_{17}N_4P$	79.0 (benzene)	27.78 (27.98)	15.49 (15.47)
7b	67	95–97/ 0.04 mm	$C_{12}H_{25}N_4P$	69.9 (benzene)	21.75 (21.86)	11.89 (12.08)
7c	68	82.0–83.5 (hexane)	$C_{12}H_{21}N_4P$	75.7 (benzene)	19.65 (19.71)	10.56 (10.89)
7d	81	74–76/ 0.04 mm	$C_9H_{19}N_4P$	76.8 (benzene)	26.06 (26.15)	14.64 (14.46)
7e	74	105–108/ 0.04 mm	$C_{13}H_{27}N_4P$	66.8 (CD_3CN)	20.56 (20.72)	11.23 (11.46)
7f	75	120–123/ 0.04 mm	$C_{12}H_{19}N_4P$	79.8 (benzene)	22.19 (22.39)	12.12 (12.38)
7g	82	133–135/ 0.04 mm	$C_{16}H_{27}N_4P$	71.0 (benzene)	18.09 (18.29)	9.89 (10.11)
7h	78	123–125/ 0.04 mm	$C_{17}H_{29}N_4P$	67.9 (benzene)	17.21 (17.49)	9.49 (9.67)
8	11	127–130/ 0.04 mm	$C_{12}H_{20}N_5P$	22.6 (CD_3CN)	26.17 (26.40)	11.46 (11.68)
9a	73	125–128 (*i*-PrOH)	$C_{14}H_{15}N_4P$	−47.2 (benzene)	20.45 (20.73)	11.21 (11.29)
9b	62	113–116 (EtOH)	$C_{16}H_{19}N_4P$	−46.6 (benzene)	18.59 (18.78)	10.09 (10.38)
10a	84	201–202 (benzene)	$C_{12}H_{15}N_6P$	−58.7 (pyridine)	30.41 (30.64)	11.01 (11.29)
10b	71	209–210 (benzene)	$C_{15}H_{21}N_6P$	−61.1 (benzene)	26.31 (26.57)	9.56 (9.79)
10c	62	220 (benzene)	$C_{27}H_{27}N_6P$	−52.0 (benzene)	18.09 (18.01)	6.72 (6.64)
11a	79	36 (hexane)	$C_{15}H_{24}N_5P$	3.8 (benzene)	23.03 (22.93)	10.39 (10.14)
11b	88	Oil	$C_{12}H_{25}N_4PS$	57.5 (benzene)	19.13 (19.43)	10.56 (10.74)
11c	75	Oil	$C_{18}H_{30}N_5P$	3.6 (benzene)	19.93 (20.16)	8.78 (8.91)
11d	79	Oil	$C_{19}H_{32}N_5P$	2.9 (hexane)	19.12 (19.37)	8.39 (8.57)
11e	89	151–152 (MeOH)	$C_{12}H_{21}N_4O_2PS$	56.7 (MeCN)	17.92 (17.71)	9.91 (9.79)
11f	92	151–152 (benzene)	$C_{12}H_{21}N_4O_2PSe$	54.0 (benzene)	15.29 (15.43)	8.59 (8.53)
11g	91	57–59 (decane)	$C_9H_{19}N_4PS$	60.3 (benzene)	22.51 (22.75)	12.34 (12.58)
11h	71	51–53 (octane)	$C_{16}H_{26}N_5P$	5.1 (benzene)	22.09 (21.93)	9.91 (9.70)
11i	88	124–127 (*i*-PrOH)	$C_{13}H_{27}N_4PSe$	51.3 (benzene)	15.78 (16.04)	8.56 (8.87)
11j	94	103–105 (EtOH)	$C_{12}H_{19}N_4PS$	59.7 (benzene)	19.45 (19.84)	11.10 (10.97)
11k	76	Oil	$C_{16}H_{27}N_4PS$	58.3 (benzene)	16.32 (16.55)	8.89 (9.15)
11l	77	77–79 (PE)	$C_{22}H_{32}N_5P$	4.1 (benzene)	17.34 (17.62)	7.45 (7.79)
11m	62	91–93 (*i*-PrOH)	$C_{23}H_{34}N_5P$	6.2 (benzene)	16.78 (17.02)	7.34 (7.53)

TABLE 1 (Continued) Yields, Analytical Data, and ^{31}P NMR Spectra

Compound	*Yield (%)*	M.p. B.b.(°*C*)	*Formula*	$\delta^{31}P$ (^{1}H) (*Solvent*)	*Found (%) (Calculated, %)*	
					N	*P*
11n	59	131–133 (*i*-PrOH)	$C_{24}H_{34}N_5OP$	8.0 (benzene)	16.09 (15.93)	6.87 (7.05)
11o	84	45–47 (octane)	$C_{17}H_{29}N_4PS$	56.0 ($CDCl_3$)	15.56 (15.90)	8.61 (8.79)
11p	88	88–90 (EtOAc)	$C_{17}H_{29}N_4PSe$	53.4 (benzene)	13.69 (14.03)	7.48 (7.76)
11q	69	81–84 (heptane)	$C_{23}H_{34}N_5P$	6.1 (toluene)	16.78 (17.02)	7.32 (7.53)
11r	58	89–90 (PE)	$C_{24}H_{36}N_5P$	4.8 (toluene)	16.21 (16.46)	6.99 (7.28)
11s	54	142–144 (*i*-PrOH)	$C_{25}H_{36}N_5OP$	8.9 (toluene)	15.28 (15.44)	6.64 (6.83)
13a	71	156–158 (EtOAc)	$C_8H_{19}ClN_5P$	31.0 (MeCN)	27.65 (27.82)	12.11 (12.31)
13b	69	142–144 (EtOAc)	$C_{12}H_{27}ClN_5P$	29.3 (MeCN)	22.49 (22.75)	9.87 (10.06)
13c	66	131–133 (EtOAc)	$C_{13}H_{29}ClN_5P$	28.7 (MeCN)	2139 (21.76)	9.34 (9.62)
13d	84	152–154 (EtOH)	$C_{16}H_{29}ClN_5P$	28.7 (MeCN)	19.21 (19.57)	8.29 (8.66)
13e	71	123–125 (EtOAc)	$C_{17}H_{31}ClN_5P$	30.5 (MeCN)	18.59 (18.83)	8.09 8.33
14a	58	Oil	$C_{12}H_{25}N_4OP$	15.5 (benzene)	20.24 (20.57)	11.12 (11.37)
14b	61	140–141 (heptane)	$C_{12}H_{21}N_4O_3P$	12.9 (benzene)	18.32 (18.66)	10.11 (10.31)
14c	62	Oil	$C_{12}H_{19}N_4OP$	18.4 (CH_2Cl_2)	20.89 (21.04)	11.41 (11.63)
14d	71	70–72 (benzene-hexane)	$C_{16}H_{27}N_4OP$	18.6 (benzene)	17.09 (17.38)	9.29 (9.61)
14e	60	Oil	$C_{17}H_{29}N_4OP$	16.6 (benzene)	16.89 (16.65)	9.47 (9.21)
15a	82	119–120 (MeOH)	$C_{12}H_{20}N_5PS$	37.5 (benzene)	23.76 (23.55)	10.73 (10.42)
15b	71	78–81 (octane)	$C_{18}H_{25}N_6P$	9.9 (benzene)	23.89 (23.58)	8.82 (8.69)
16a	69	103–104 (cyclohexane)	$C_{16}H_{15}N_2OP$	19.0 (CH_2Cl_2)	10.28 (9.92)	11.27 (10.97)
16b	85	128–130 (CCl_4)	$C_{16}H_{15}N_2PS$	30.0 (benzene)	9.62 (9.39)	10.59 (10.38)
16c	72	163–165 (toluene)	$C_{22}H_{19}BrN_3P$	−11.5 (toluene)	9.92 (9.63)	7.41 (7.10)
16d	64	98–101 (*i*-PrOH)	$C_{17}H_{17}N_2OP$	20.2 ($CHCl_3$)	9.15 (9.45)	10.85 (10.45)
16e	68	155–157	$C_{14}H_{15}N_4OP$	9.2 (CH_2Cl_2)	19.89 (19.57)	11.14 (10.82)
16f	79	189–191 (*i*-PrOH)	$C_{14}H_{15}N_4PS$	19.16 ($CDCl_3$)	18.27 (18.53)	10.61 (10.24)
16g	72	113–115 (EtOAc)	$C_{20}H_{19}BrN_5P$	−15.3 (benzene)	15.71 (15.91)	7.34 (7.04)
16h	81	147–149 (EtOAc)	$C_{16}H_{19}N_4PS$	18.0 (benzene)	17.29 (16.96)	9.61 (9.38)
16i	72	225–227 (benzene)	$C_{12}H_{15}N_6PS$	10.2 ($CHCl_3$)	27.72 (27.44)	10.39 (10.11)
16j	79	229–231 (benzene)	$C_{15}H_{21}N_6PS$	9.5 (benzene)	23.91 (24.12)	9.17 (8.89)
16k	69	235–237 (toluene)	$C_{27}H_{27}N_6PS$	17.9 (benzene)	17.09 (16.86)	6.54 (6.21)

TABLE 1 (Continued) Yields, Analytical Data, and ^{31}P NMR Spectra

Compound	*Yield (%)*	M.p. B.b.(°*C*)	*Formula*	$\delta^{31}P$ (^{1}H) (*Solvent*)	*Found (%) (Calculated, %)* *N*	*P*
17a	81	134–135 (*i*-PrOH)	$C_{17}H_{18}BF_4N_2P$	−26.2 ($CDCl_3$)	7.89 (7.61)	8.67 (8.41)
17b	85	126–128 (EtOH)	$C_{18}H_{20}BF_4N_2P$	−28.1 ($CDCl_3$)	7.09 (7.33)	7.89 (8.11)
17c	91	Oil	$C_{14}H_{30}BF_4N_4P$	84.6 (CH_2Cl_2)	15.35 (15.05)	8.59 (8.32)
17d	87	151–153 (EtOAc)	$C_{19}H_{22}BF_4N_2P$	−29.0 (CH_2Cl_2)	7.31 (7.07)	8.14 (7.82)
17e	89	Oil	$C_{15}H_{32}BF_4N_4P$	86.6 (CH_2Cl_2)	14.79 (14.51)	8.31 (8.02)
17f	82	Oil	$C_{18}H_{32}BF_4N_4P$	87.0 (CH_2Cl_2)	13.59 (13.27)	7.61 (7.34)
18a	82	168–170 (*i*-PrOH)	$C_{17}H_{18}IN_2P$	12.4 (CD_3CN)	67.13 (6.86)	7.81 (7.59)
18b	69	Oil	$C_{14}H_{30}IN_4P$	43.2 (CH_2Cl_2)	13.81 (13.59)	7.84 (7.51)
18c	81	146 (EtOAc)	$C_{17}H_{30}IN_4P$	44.0 (MeCN)	12.79 (12.50)	7.23 (6.91)
19a	74	110–112	$C_{15}H_{18}IN_4P$	−50.3 (MeOH)	13.78 (13.59)	7.79 (7.51)
19b	71	100–102	$C_{16}H_{21}N_4O_4PS$	−53.2 (MeCN)	14.42 (14.13)	8.23 (7.81)
20a	90	169–172 (EtOAc)	$C_{17}H_{18}IN_2PS$	30.6 ($CDCl_3$)	6.06 (6.36)	6.87 (7.04)
20b	92	196–198 (*i*-PrOH)	$C_{13}H_{28}IN_4PS$	56.1 (MeCN)	12.84 (13.02)	6.97 (7.20)
20c	91	189–192 (*i*-PrOH)	$C_{19}H_{34}IN_4OP$	12.7 (CH_2Cl_2)	11.21 (11.38)	6.09 (6.29)
20d	89	212–215 (*i*-PrOH)	$C_{13}H_{22}IN_4PS$	59.3 (CH_2Cl_2)	13.05 (13.21)	6.93 (7.30)
20e	84	225–227 (*i*-PrOH)	$C_{18}H_{32}IN_4PSe$	53.8 (benzene)	10.31 (10.35)	6.11 (5.72)

liminarily cooled to 0 to 5°C, and allowed to stand at room temperature for 48 hours, after which time the reaction mixture was diluted with benzene (15 mL), filtered to remove solids, and evaporated in vacuo. The end product was extracted from the oily residue with hot heptane or octane, precipitated as colorless crystals on cooling the extract, and crystallized.

General Procedure for Synthesis of Tris(1-alkyl-2-imidazolyl)phosphines **10a,b**

Phosphorus trichloride (3.3 mmol) in pyridine (5 mL) was added dropwise to a stirred mixture of 1-alkylimidazole **1a,b** (10 mmol), triethylamine (10 mmol), and pyridine (20 mL) at 0 to 5°C. After 48 hours pyridine was removed in vacuo, and the solid residue was extracted with hot benzene (3 × 30 mL). The extract was concentrated to 5 mL, and the precipitated product was filtered off and crystallized.

Tris(1-ethyl-2-benzimidazolyl)phosphine **10c**

Phosphorus tribromide (10 mmol) in pyridine (30 mL) was slowly added to a stirred mixture of 1-ethylbenzimidazole **1d** (30 mmol), triethylamine (45 mmol), and pyridine (70 mL) at 0°C and allowed to stand for a week, after which time the reaction mixture was heated at 80°C for 5 hours and evaporated. The residue was dissolved in methylene dichloride (50 mL) and shaken with water (50 mL). The organic layer was separated and dried over anhydrous sodium sulfate. The solid product left after removal of the solvent was purified by reprecipitation with hexane from a benzene solution.

General Procedure for Synthesis of Phosphine Sulfides **11b,e,g,j,k,o, 15a, 16b,f,h-k**, *and Phosphine Selenides* **11f,i,p**

Finely crushed sulfur or selenium (0.01 gram-atom) was added to a solution of the appropriate phos-

TABLE 2 2-Phosphorylated 1-Alkylimidazoles: ^{1}H NMR δ (Multiplicity), J (Hz)

Compound	*Solvent*	*(1, 3)-N-R*	*4-H*	*5-H*	*Other Signals*
3a	$CDCl_3$	3.71(s)	7.31–7.51(m) + Ph	7.03(s)	7.31–7.81(m) Ph + 4-H
3b	$CDCl_3$	1.17(t), 7.2 4.57(q), 7.2	7.30–7.50(m) + Ph	7.06(s)	7.30–7.78(m) Ph + 4-H
7a	C_6H_6	3.16(s)	7.15(m)	6.63(m)	2.78(d), 9.2 $PNCH_3$
7b	CD_3CN	3.62(s)	7.02(d), 1.0	6.95(d), 1.0	1.02(t), 7.2 $PNCH_2\underline{CH_3}$, 3.18(q), 7.2 $PNCH_2$
7c	C_6D_6	3.15(s)	7.33(s)	6.50(s)	3.11(m), 3.31(m) $PNCH_2$, 3.58(m) OCH_2
7d	C_6D_6	1.28(t), 7.2 4.01(q), 7.2	7.06(m)	6.87(d), 1.0	2.82(d), 9.1 $PNCH_3$
7e	CD_3CN	1.31(t), 7.2 4.05(q), 7.2	7.04(m)	6.97(d), 1.0	1.04(t), 7.1 $PNCH_2\underline{CH_3}$, 3.18(m), 7.1 $PNCH_2$
8	CD_3CN	3.56(s)	7.12(dd), 1.2, 1.2	6.98(d), 1.2	0.90(t), 7.0 $PNCH_2\underline{CH_3}$ 3.22(m), 10.4, 7.0 $PNCH_2$
9a	$CDCl_3$	3.60(s)	7.17(d), 0.8	7.04(m)	7.31(m) 3,4,5-H-Ph 7.43(m), 2,6-H-Ph
9b	$CDCl_3$	1.18(t), 7.5 4.10(m), 7.5	7.28(s)	7.13(s)	7.30–7.60(m) Ph
10a	$CDCl_3$	3.63(s)	7.20(s)	7.00(s)	
10b	$CDCl_3$	1.04(t), 7.3 4.05(q), 7.3	7.15(s)	7.06(m)	
11a	$CDCl_3$	3.98(s)	7.18(s)	6.98(s)	2.24(s) C-CH_3 2.75(d), 10.5 $PNCH_3$ 6.69(d), 8.5 2,6-H-Ar 6.92(d), 8.5 3,5-H-Ar
11b	$CDCl_3$	3.99(s)	7.11(s)	6.99(s)	1.09(t), 7.0 $PNCH_2\underline{CH_3}$ 3.18(m), 7.0, 2.8 $PNCH_2$
11c	$CDCl_3$	4.03(s)	7.14(s)	6.96(s)	1.03(t), 7.3 $PNCH_2\underline{CH_3}$ 3.18(m) $PNCH_2$ 6.7(m), 7.1(m) Ph
11d	$CDCl_3$	4.04(s)	7.14(s)	6.92(s)	1.02(t), 7.0 $PNCH_2\underline{CH_3}$ 3.18(m) $PNCH_2$ 2.23(s) C-CH_3 6.64(d), 8.2, 2,6-H-Ph 6.90(d), 8.2 3,5-H-Ph
11e	$CDCl_3$	4.09(s)	7.18(s)	7.05(s)	3.23(m) $PNCH_2$ 3.68(m) OCH_2
11f	$CDCl_3$	4.08(s)	7.16(s)	7.04(m)	3.23(m) $PNCH_2$ 3.69(m) OCH_2
11g	$CDCl_3$	1.58(t), 7.3 4.95(q), 7.3	7.16(s)	7.08(m)	2.73(d), 11.3 $PNCH_3$
11h	$CDCl_3$	1.39(t), 7.2 4.57(q), 7.2	7.18(s)	7.05(s)	2.23(s) C-CH_3 2.69(d), 11.2 $PNCH_3$ 6.68(d), 8.1 3,5-H-Ar 7.05(d), 8.1 2,6-H-Ar
11i	$(CD_3)_2CO$	1.44(t), 7.2 4.5(q), 7.2	7.36(d), 2.0	7.05(d) 2.0	1.09(t), 7.1 $PNCH_2\underline{CH_3}$ 3.25(q), 7.1 $PNCH_2$
13a	$CDCl_3$	4.14(s)	7.25(m)	7.21(m)	2.28(d), 10.8 $PNCH_3$
13b	$CDCl_3$	4.18(s)	7.21(s)	7.10(s)	1.17(t), 7.1 $PNCH_2\underline{CH_3}$ 3.24(m), 7.1 $PNCH_2$ 7.00(d) 8.2 NH_2
13c	$CDCl_3$	1.58(t), 7.3 4.59(q), 7.3	7.26(s)	7.22(s)	1.19(t), 7.2 $PNCH_2\underline{CH_3}$ 3.24(m), 7.2 $PNCH_2$
14a	$CDCl_3$	4.03(s)	7.14(s)	6.96(s)	1.03(t), 7.3 $PNCH_2\underline{CH_3}$ 3.18(d), 7.3 $PNCH_2$
14b	$CDCl_3$	4.06(s)	7.20(s)	7.04(s)	3.19(m) $PNCH_2$ 3.65(m) OCH_2
15a	$(CD_3)_2CO$	3.94(s)	7.34(m)	7.02(m)	1.04(t), 7.2 $PNCH_2\underline{CH_3}$ 3.39(m), 13.4, 7.2 $PNCH_2$
15b	$(CD_3)_2CO$	3.87(s)	7.31(s)	7.04(s)	1.10(t), 7.2 $PNCH_2\underline{CH_3}$ 3.41(q), 7.2 $PNCH_2$ 6.7(m), 7.1(m) Ph

TABLE 2 (Continued) 2-Phosphorylated 1-Alkylimidazoles: ^{1}H NMR δ (Multiplicity), J (Hz)

Compound	*Solvent*	*(1, 3)-N-R*	*4-H*	*5-H*	*Other Signals*
16a	$CDCl_3$	3.97(s)	7.24(s)	7.08(s)	7.40–7.60(m) 3,4,5-H-Ph 7.81(m) 2,6-H-Ph
16b	$CDCl_3$	3.83(s)	7.20(d), 1.2		7.53(m) 3,4,5-H-Ph 7.81(m) 2,6-H-Ph
16c	$CDCl_3$	3.67(s)	7.30(s)	7.06(s)	6.64(d), 9.0 2,6-H-Ar 7.10(d), 9.0 3,5-H-Ar 7.47(m) 3,4,5-H-Ph 7.89 (m) 2,6-H-Ph
16d	$CDCl_3$	1.32(t), 7.1 4.45(q), 7.1	7.25(s)	7.13(s)	7.50(m) 3,4,5-H-Ph 7.78(m) 2,6-H-Ph
16e	$CDCl_3$	3.87(s)	7.21(s)	7.07(s)	7.50–7.60(m) 3,4,5-H-Ph 7.88(m) 2,6-H-Ph
16f	$CDCl_3$	3.91(s)	7.21(s)	7.15(s)	7.62(s) 3,4,5-H-Ph 7.98(m) 2,6-H-Ph
16g	$CDCl_3$	3.71(s)	7.28(s)	7.09(s)	6.71(d), 8.7 9.0 2,6-H-Ar 7.13(d), 8.7 9.0 3,5-H-Ar 7.49(m) 3,4,5-H-Ph 7.91(m) 2,6-H-Ph
16h	$CDCl_3$	1.30(t), 7.2 4.34(q), 7.2	7.18(s)		7.55(m), 3,4,5-H-Ph 7.88(d), 7.96(d), 8.2 2,6-H-Ph
16i	$CDCl_3$	3.92(s)	7.17(s)		
16j	$CDCl_3$	1.29(t), 7.2 4.28(q), 7.2	7.17(s)		
17a	CD_3OH	3.67(s)	7.73(s)		7.40–7.60(m) Ph
17b	$CDCl_3$	3.55(s) NCH_3 1.24(t), 7.4 $NCH_2\underline{CH_3}$ 4.36(q), 7.4 NCH_2	7.80(s)	7.73(s)	7.30–7.50(m) Ph
17c	CD_3CN	3.61(s) NCH_3 1.38(t), 7.2 $NCH_2\underline{CH_3}$ 4.34(q), 7.2 NCH_2	7.82(s)	7.75(s)	1.10(t), 7.1 $PNCH_2\underline{CH_3}$ 3.18(q), 7.1 $PNCH_2$
17d	$CDCl_3$	1.24(t), 7.4 4.34(q), 7.4	7.71(s)		7.35–7.55(m) Ph
17e	CD_3CN	1.46(t), 7.2 4.30(q), 7.2	7.56(s)		2.12(t), 7.1 $PNCH_2\underline{CH_3}$ 3.15(m), 7.1 $PNCH_2$
18a	CD_3CN	3.50(s)	7.44(s)	7.37(s)	2.91(d), 3.6 P^+-CH_3 7.70–7.90(m) Ph
18b	$CDCl_3$	1.61(t), 7.4 4.37(q), 7.4	7.54(m)	7.35(m)	1.24(t), 7.1 $PNCH_2\underline{CH_3}$ 2.64(d), 3.3 P^+-CH_3 3.26(m) $PNCH_2$
19a	CD_3OD	3.89(s) N^+-CH_3 3.93(s) N-CH_3	7.75(s) 7.3–7.6(m) + Ph	7.74(s)	7.3–7.6(m) Ph + 4-H, 5-H
19b	CD_3CN	3.87(s) N^+-CH_3 3.94(s) N-CH_3	7.63(s) 7.3–7.6(m) + Ph	7.62(s)	7.3–7.6(m) Ph + 4-H, 5-H
20a	$CDCl_3$	3.56(s)	7.94(s)		7.68(m) 3,4,5-H-Ph 8.26(d), 8.31(d) 6.2 2,6-H-Ph
20b	$CDCl_3$	4.23(s)	8.00(d), 2.0		1.2(t), 7.0 $PNCH_2\underline{CH_3}$ 3.28(m) $PNCH_2$

phine (10 mmol) in benzene (10–20 mL) and stirred until the sulfur or selenium completely dissolved. The reaction mixture was refluxed after dissolution of sulfur or selenium for 20 hours (**16i,j**) or 100 hours (**16k**). The solvent was evaporated, and the residue was crystallized.

General Procedure for Synthesis of Arylimino-phosphoranes **11a,c,d,h,l-n,q-s, 15b***, and* **16c,g**

A mixture of the appropriate phosphine **7, 3a**, or **9a** (1 mmol) and aryl azide (1 mmol) in benzene (50 mL) was heated at reflux until the evolution of nitro-

TABLE 3 2-Phosphorylated 1-Alkylbenzimidazoles: ^{1}H NMR δ (Multiplicity), *J* (Hz)

Compound	*Solvent*	(*1,3*)-*N*-*R*	*4-H*	*5-H*	*6-H*	*7-H*	*Other Signals*
7f	CD_3CN	3.86(s)	7.69(d), 6.8	7.29(m)		7.49(d), 7.4	2.80(d), 11.2 PNMe
7g	CD_3CN	3.84(s)	7.68(d), 6.6	7.27(m)		7.47(d), 7.6	1.14(t), 7.0 $PNCH_2C\underline{H}_3$, 3.27(m) $PNCH_2$
7h	CD_3CN	1.47(t), 7.1 4.48(q), 7.1	7.72(d), 6.8	7.33(m)		7.57(d), 6.4	1.29(t), 7.0 $PNCH_2C\underline{H}_3$ 3.37(m) $PNCH_2$
10c	$CDCl_3$	1.06(t), 7.2 4.43(q), 7.2	7.77(d), 7.2		7.10–7.50(m)		
11j	$(CD_3)_2CO$	4.07(s)	7.74(d), 7.6	7.33(m)		7.58(d), 7.2	2.81(d), 11.8 $PNCH_3$
11k	$(CD_3)_2CO$	4.05(s)	7.66(d), 7.4	7.24(m)		4.48(d), 7.4	1.06(t), 8.0 $PNCH_2C\underline{H}_3$ 3.23(m) $PNCH_2$
11l	$CDCl_3$	4.20(s)	7.83(d), 7.8	7.09(m)		7.35(m) + 2,6-H-Ph	1.06(t), 7.0 $PNCH_2C\underline{H}_3$ 3.25(m) $PNCH_2$ 6.70(m) 3,4,5-H-Ph 7.35(m) 2,6-H-Ph + 7-H
11m	$CDCl_3$	4.19(s)	7.83(d), 7.0		7.30–7.50(m)		1.06(t), 7.0 $PNCH_2C\underline{H}_3$ 2.22(s) C-CH_3 3.25(m) $PNCH_2$ 6.69(d) 8.6 Ar
11n	CD_3OD	4.13(s)	7.78(m) + 3,5-H-Ar	7.38(m)		7.57(d), 8.0	1.09(t), 7.1 $PNCH_2C\underline{H}_3$ 2.47(s) $C(O)CH_3$ 3.25(m) $PNCH_2$ 6.75(d), 8.2 2,6-H-Ar 7.78(m) 3,5-H-Ar + 4-H
11o	$CDCl_3$	1.52(t), 7.1 4.73(q), 7.1	7.85(d), 8.0	7.35(m)		7.45(d), 8.0	1.11(t), 7.0 $PNCH_2C\underline{H}_3$ 3.28(m) $PNCH_2$
11p	$CDCl_3$	1.55(t), 7.0 4.71(q), 7.0	7.82(d), 7.0		7.25–7.45(m)		1.14(t), 7.2 $PNCH_2C\underline{H}_3$ 3.32(m) $PNCH_2$
11q	$CDCl_3$	1.52(t), 7.0 4.98(q), 7.0	7.81(d), 7.2	7.37(m)		7.43(d), 7.4	1.03(t), 7.1 $PNCH_2C\underline{H}_3$ 3.23(m), $PNCH_2$ 6.64(t), 7.2 4-Ph 6.75(d), 7.1 2,6-Ph 7.11(t), 7.1 3,5-Ph
11r	$CDCl_3$	1.51(t), 7.1 4.98(q), 7.1	7.84(d), 7.6	7.31(m)		7.45(d), 7.6	1.02(t), 7.0 $PNCH_2C\underline{H}_3$ 2.25(s) C-CH_3 3.23(m) $PNCH_2$ 6.72(d), 8.0 2,6-Ar 6.94(d) 3,5-Ar
11s	$CDCl_3$	1.51(t), 7.0 4.89(q), 7.0	7.82(d), 7.8	7.33(m)		7.45(d), 7.8	1.05(t), 7.0 $PNCH_2C\underline{H}_3$ 2.51(s) $C(O)CH_3$ 3.24(s) $PNCH_2$ 6.78(d), 8.0 2,6-Ar 7.78(d), 8.0 3,5-Ar
13d	CD_3OD	4.10(s)	7.85(d), 8.0	7.41(t), 8.1	7.53(t), 8.1	7.69(d), 8.0	1.24(t), 7.0 $PNCH_2C\underline{H}_3$ 3.30(m) $PNCH_2$
13e	CD_3CN	1.53(t), 7.0 4.64(q), 7.0	7.78(d), 7.5	7.35(t), 6.8	7.46(t), 6.8	7.65(d), 7.7	1.15(t), 7.0 $PNCH_2C\underline{H}_3$ 3.25(m) $PNCH_2$ 7.05(br.s) NH_2
14c	$CDCl_3$	4.16(s)	7.86(d), 7.6		7.28–7.45(m)		2.75(d), 10.2 $PNCH_3$
14d	$CDCl_3$	4.19(s)	7.84(d), 7.8		7.28–7.46(m)		1.09(t), 7.0 $PNCH_2C\underline{H}_3$ 3.20(m) $PNCH_2$
14e	$CDCl_3$	1.48(t), 7.0 4.78(q), 7.0	7.84(d), 6.5	7.38(m)		7.44(d), 6.8	1.08(t), 7.0 $PNCH_2C\underline{H}_3$ 3.19(m) $PNCH_2$
16k	$CDCl_3$	1.41(t), 7.1 4.64(q), 7.1	7.79(d), 6.9	7.36(m)		7.53(d), 7.1	
17f	CD_3CN	4.16(s) NCH_3 1.38(t), 7.2 $NCH_2C\underline{H}_3$ 4.26(q), 7.2 NCH_2	7.76(d), 7.6	7.31(m)		7.42(d), 7.6	1.18(t), 7.0 $PNCH_2C\underline{H}_3$ 3.32(q), 7.0 $PNCH_2$

TABLE 3 (Continued) 2-Phosphorylated 1-Alkylbenzimidazoles: ^{1}H NMR δ (Multiplicity), *J* (Hz)

Compound	*Solvent*	*(1,3)-N-R*	*4-H*	*5-H*	*6-H*	*7-H*	*Other Signals*
18c	CD_3CN	4.00(s)	7.85(m)	7.40–7.60(m)			1.24(t), 7.0 $PNCH_2\underline{CH_3}$ 2.47(d), 13.4 $P^+\underline{CH_3}$ 3.29(m) $P^+\underline{NCH_2}$
20c	CD_3CN	1.44(t), 7.1 $NCH_2\underline{CH_3}$ 4.82(q), 7.1 $\underline{NCH_2}$	7.98(m) + 7-H	7.82(m)		7.98(m) + 4-H	1.09(t), 7.0 $PNCH_2\underline{CH_3}$ 3.21(m) $\underline{PNCH_2}$
20d	CD_3CN	4.29(s)	8.01(m) + 7-H	7.78(m)		8.01(m) + 4-H	2.92(d), 11.8 $PNCH_3$

TABLE 4 Some of the 2-Phosphorylated 1-Alkylimidazoles: ^{13}C NMR δ (Multiplicity), *J* (Hz)

Compound	*Solvent*	*^{13}C (^{1}H) NMR δ (Multplicity), J (P-C, Hz)*
3a	$CDCl_3$	145.82 (d), 2.7 C^2; 130.83 (d), 2.9 C^4; 123.65 (s), C^5; 134.80 (d), 4.1 (*ipso*-Ph); 133.80 (d), 20.4 o-Ph; 128.55 (d), 7.6 m-Ph; 129.12 (s) p-Ph; 34.0 (d), 14.0 N-Me.
7b	CD_3CN	150.09 (d), 10.9 C^2; 129.07 (d), 2.9 C^4; 123.61 (s) C^5; 34.17 (d), 10.9 N-Me; 44.30 (d), 17.0 $PNCH_2$; 15.32 (d), 3.6 C-Me.
9a	$CDCl_3$	142.71 (d), 3.8 C^2; 130.40 (d), 7.6 C^4; 124.67 (s) C^5; 132.19 (s) *ipso*-Ph; 132.76 (d), 19.6 o-Ph; 128.64 (d), 7.2 m-Ph; 129.17 (s) p-Ph; 34.29 (d), 9.1 N-Me.
17a	CD_3OD	144.68 (d), 52.0 C^2; 127.98 (s) $C^{4,5}$; 129.22 (d), 6.3 *ipso*-Ph; 134.18 (d), 20.5 o-Ph; 131.06 (d), 7.4 m-Ph; 132.07 (s) p-Ph; 38.08 (d), 9.2 N-Me.
17b	$CDCl_3$	142.21 (s) C^2; 128.02 (s) C^4; 125.03 (s) C^5; 127.48 (d), 6.3 *ipso*-Ph; 132.58 (d). 20.1 o-Ph; 129.85 (d), 7.4 m-Ph; 130.90 (s) p-Ph; 37.72 (s) N-Me; 45.68 (s) $N\text{-}CH_2$; 15.90 (s) C-Me.
17e	CD_3CN	146.70 (d), 73.1 C^2; 122.78 (s) $C^{4,5}$; 43.23 (d), 6.1 $N\text{-}CH_2$; 14.28 (s) $NCH_2\text{-}Me$; 44.19 (d), 19.0 $PN\text{-}CH_2$; 13.30 (d), 4.1 $PNCH_2\text{-}Me$.
19a	CD_3OD	138.67 (d), 12.0 C^2; 143.11 (d), 39.0 C^{2+}; 132.92 (d), 3.2 C^4; 127.96 (s) $C^{4+,5+}$; 127.88 (d), 1.8 C^5; 128.40 (s) *ipso*-Ph; 133.82 (d), 19.7 o-Ph; 130.94 (d), 7.1 m-Ph; 132.08 (s) p-Ph; 38.51 (d), 8.8 N^+-Me; 35.19 (d). 13.4 N-Me
19b	CD_3CN	137.09 (d), 14.3 C^2; 142.10 (d), 45.4 C^{2+}; 131.78 (d), 3.7 C^4; 126.53 (s) $C^{4+,5+}$; 126.43 (d), 2.0 C^5; 127.96 (s) ipso-Ph; 132.11 (d), 19.0 o-Ph; 129.47 (d), 6.9 m-Ph; 130.38 (s) p-Ph; 34.13 (d), 14.3 N-Me; 37.54 (d), 9.0 N^+-Me; 52.91 (s) $MeSO_4$.

gen ceased (1–2 hours). After removal of the solvent, the residue solidified when triturated with hexane and was recrystallized from the appropriate solvent (Table 1).

General Procedure for Synthesis of Aminophosphonium Chlorides **13**

Hexachloroethane (0.1 mol) that was dissolved in hexane (50 mL) was added to a solution of phosphine **7** (0.1 mol) in hexane (50 mL) or benzene (for **7g,h**). The intermediate chlorophosphonium chlorides **12** precipitated as fine crystals or slowly solidifying oils and were filtered off, washed with hexane, and dissolved in methylene dichloride (50 mL). Ammonia gas was bubbled through the resulting solution until the precipitation ceased (for ca. 20–30 minutes), the solids being removed by filtration, and the residue after evaporation of the filtrate was crystallized (Table 1).

General Procedure for Synthesis of Phosphine Oxides **14**

The appropriate chlorophosphonium chloride **12** (see previous section) was dissolved in methylene dichloride and shaken with a saturated solution of soda. The organic layer was separated, washed with water, dried over anhydrous sodium sulfate, and evaporated to leave an oily or solid residue. The oily residue was pumped in vacuo and the solid residue was recrystallized from the appropriate solvent (Table 1).

General Procedure for Synthesis of Phosphine Oxides **16a,d,e**

A solution of an appropriate phosphine **3** or **9** (10 mmol) in methylene dichloride (15 mL) was shaken with 5% hydrogen peroxide (6 mL) for 30 minutes in a separatory funnel. The organic layer was separated, washed with water, dried over anhydrous so-

dium sulfate, and evaporated. The residue was purified by crystallization (see Table 1).

General Procedure for Synthesis of Imidazolium and Benzimidazolium Salts **17b–f**

Triethyloxonium tetrafluoroborate (2 mmol) in methylene dichloride (10 mL) was added dropwise at −30°C to a stirred solution of phosphine **3** or **7** (2 mmol) in the same solvent (40 mL). The reaction mixture was stirred at room temperature for 3 hours, the solvent was evaporated, and the residue was triturated with diethyl ether to induce solidification.

Alternative Procedure for Synthesis of Imidazolium Salts **17a,b**

Dimethyl sulfate (1.5 mmol) in acetonitrile (5 mL) was slowly added to a cooled (0°C) and stirred solution of **3a,b** (1.5 mmol) in the same solvent (20 mL). After 24 hours the solvent was evaporated, and the oily residue was dissolved in a 5 M aqueous solution of ammonium tetrafluoroborate (10 mL). The settled oily product solidified after time.

General Procedure for Synthesis of Phosphonium Salts **18**

A mixture of phosphine **3** or **7** (1 mmol) and methyl iodide (1 mmol) in benzene (15 mL) was allowed to stand for 2 days at room temperature, after which time the precipitate was filtered off and washed with diethyl ether. If the product did not precipitate, the solvent was evaporated, and the residue was purified by reprecipitation with diethyl ether from an acetonitrile solution.

1,3-Dimethyl-2-[(1-methyl-2-imidazolyl)phenylphosphino]imidazolium Salts **19**

A mixture of phosphine **9a** (5 mmol) and methyl iodide or dimethyl sulfate (5 mmol) in benzene (20 mL) was allowed to stand for 2 days at room temperature. The settled oil was crystallized by trituration with diethyl ether.

General Procedure for Synthesis of Imidazolium Salts **20**

A mixture of the appropriate substrate **11b,j, 14e,** or **16b** (10 mmol) and alkyl iodide (13 mmol) was heated under reflux in benzene (25 mL) for 3–20 hours. The product precipitated after cooling of the reaction mixture and was separated by filtration and crystallized (see Table 1).

4-Bromoanilinodiphenylphosphine Oxide **21**

Iminophosphorane **16c** was heated for 5–10 minutes under reflux in 2-propanol (10 mL) containing 0.5% water. The hydrolysis product precipitated when the reaction mixture was cooled. Compound **21** proved to be identical with the authentic sample [10].

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