Heteroatom Chemistry
Volume 6, Number 5, 1995

Phosphorylated Imidazo[1,2-a]pyridines*

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Received 22 June 1994; revised 19 October 1994

ABSTRACT

The reaction of phosphorus(III) halides with imidazo[1,2-a]pyridines in the presence of bases leads to the formation of 3-phosphorylated imidazo[1,2-a]pyridines. The reaction proceeds in high yield and requires no catalysts.

In the compounds obtained, in contrast to phosphorylated indolizines, the phosphorus–heterocycle bond is stable and not cleaved by dry hydrogen chloride, alcohols, or water.

Imidazo[1,2-a]pyridines with the phosphinic and phosphinous groups can be alkylated both at the phosphorus and at the nitrogen atom of the heterocycle, the alkylation direction being dependent on the strength of the alkylation reagent used. © *1995 John Wiley & Sons, Inc.*

INTRODUCTION

Previously, we showed that electron-rich aromatic heterocycles are readily phosphorylated with phosphorus(III) halides in the presence of bases [1–8]. The case of phosphorylation and the unusual chemical properties of the derivatives obtained, for example, the phosphorylated indolizines, deserve particular attention [9]. It was interesting to study the possibility of phosphorylation of aza analogues of indolizines, imidazo[1,2-a]pyridines, which are known to be less active than indolizines in electrophilic substitution reactions. Up to now, no acylation reactions with carboxylic acid halides and anhydrides in the absence of Lewis acids have been reported. However, there have been reports of formylation [10], acylation with isocyanates [11,12], Mannich reactions [13,14], and others.

Schmidpeter reported on phosphinylation of the corresponding 2-phosphaimidazo[1,2-a]pyridines [15].

The high nucleophilicity of the nitrogen atom in molecules of imidazo[1,2-a]pyridine enables one to expect unusual properties in their phosphorylated derivatives.

RESULTS AND DISCUSSION

Reactions of 2-substituted imidazo[1,2-a]pyridines **1** with phosphorus(III) halides in the presence of bases give 3-phosphorylated 2-methyl- and 2-phenylimidazo[1,2-a]pyridines in high yields. As in the case of other electrophilic substitution reactions, imidazo[1,2-a]pyridines with the electron-donor methyl group, **1a**, are much more reactive than those with the electron-accepting phenyl group, **1b**. Thus, for example, the reaction between compound **1a** and chlorodiphenylphosphine is complete within 3 hours, while that of **1b** with chlorodiphenylphosphine is not complete, even within several months, and phosphine **5b** can be obtained only via the reaction with the more reactive diphenylbromo- or diphenyliodophosphines. However, in the case of dichlorophenylphosphine and phosphorus trichloride, as well as with the less reactive 2-phenylimidazo[1,2-a]pyridine, the reaction proceeds rather rapidly, even at 20°C. The use of excess phosphorus trichloride or dichlorophenylphosphine, however, is a more convenient procedure from the experimental point of view.

Dichlorophosphines **3** were converted into amides **6–9** and ester **11**. Chlorophosphines **4** were

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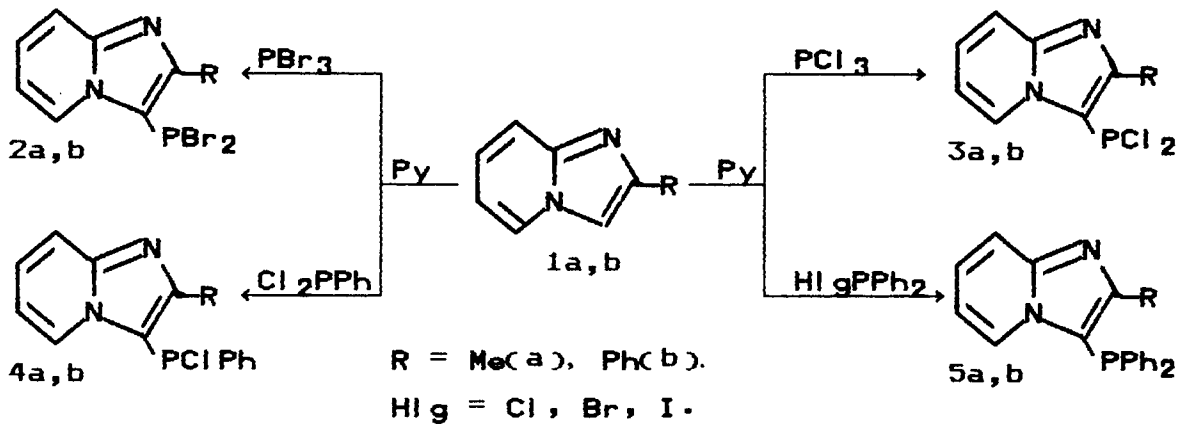
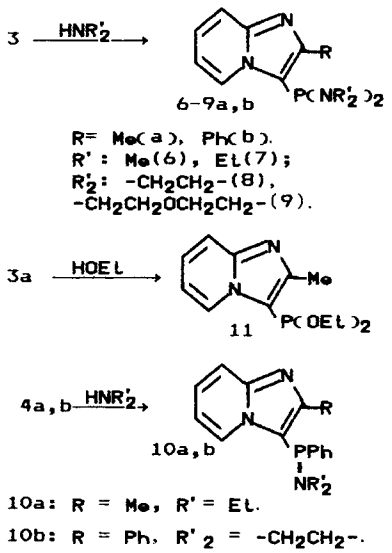
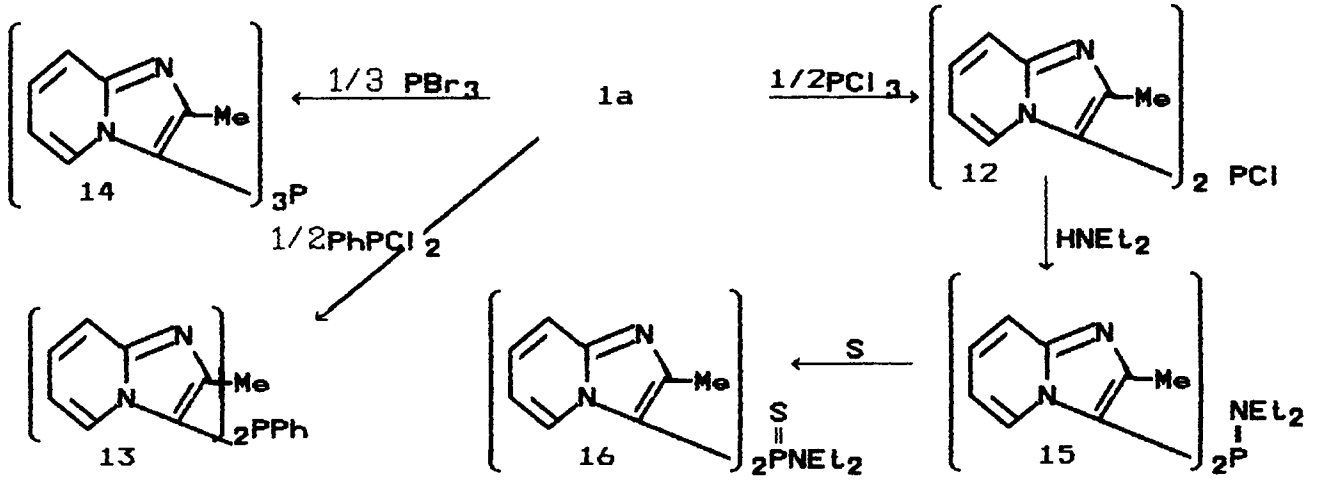


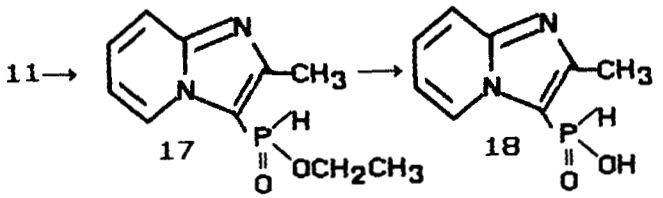
obtained in solution and were converted into amides **10**.



Due to the reactivity of 2-methylimidazo[1,2-a]pyridine in electrophilic substitution reactions, two and three heteroaromatic substituents can be successively introduced to one phosphorus atom. The chlorophosphine **12** was identified by ^{31}P NMR spectroscopy and isolated following its transformation into the amide **15**, which, in turn, was converted into the thiophosphinate **16** by reaction with sulfur. Phosphine **14** is stable to air and soluble in water without decomposition. The reaction of 2 equivalents of **1a** with 1 equivalent of dichlorophenylphosphine leads to phosphine **13**, which is not as stable to air and water as the phosphine **14**.

It should be noted that, although in phosphorylated indolizines the bond between the carbon and trivalent phosphorus atoms is labile and decomposes immediately under the action of water, alcohols, or dry hydrogen chloride [9], in phosphorylated imidazo[1,2-a]pyridines, structurally close to them, no cleavage of the C–P bond is observed. Phosphines **5** can be crystallized from alcohols and are water-stable. Phosphinite **11**, on standing in aqueous acetonitrile, is hydrolyzed with P–O (and not C–P) bond cleavage, and formation of the phosphonic acid **18** via the ethoxyphosphonite **17** occurs.

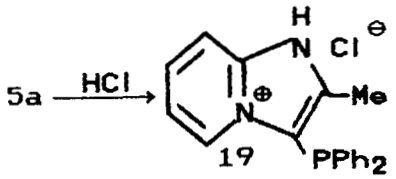




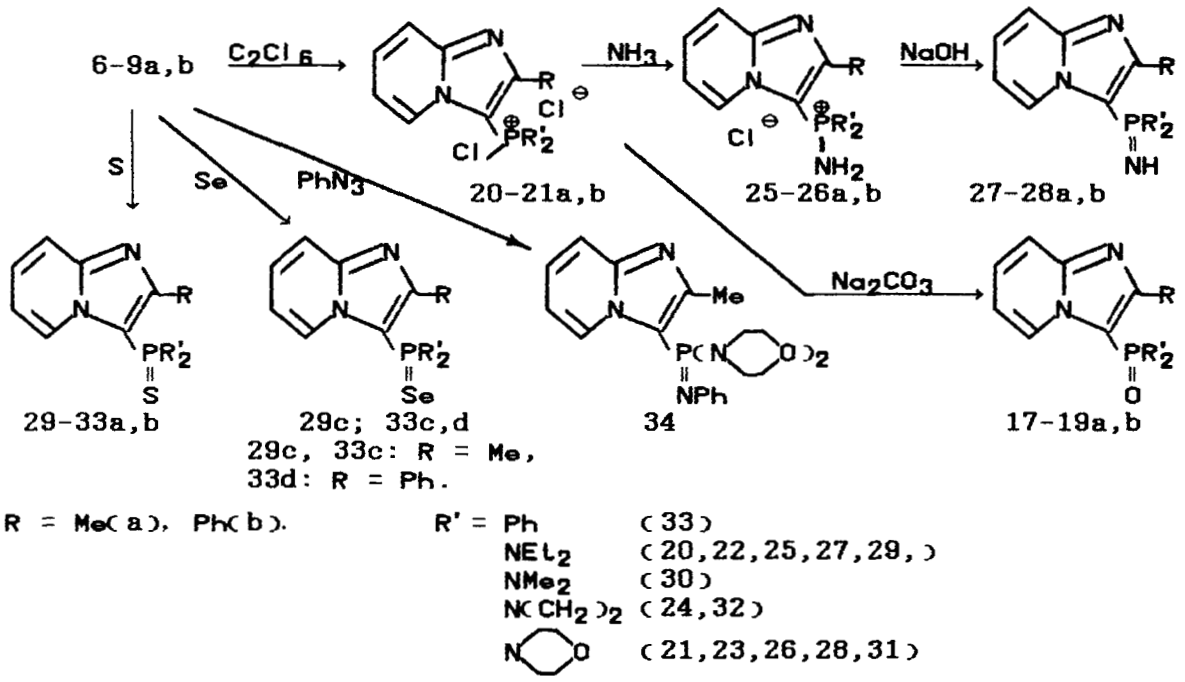
Also, no cleavage of the phosphorus-heterocycle bond occurs during reaction with dry hydrogen chloride; phosphine **5a** readily forms the salt **19**, the structure of which was uniquely confirmed by its ^{1}H and ^{31}P NMR spectra discussed subsequently.

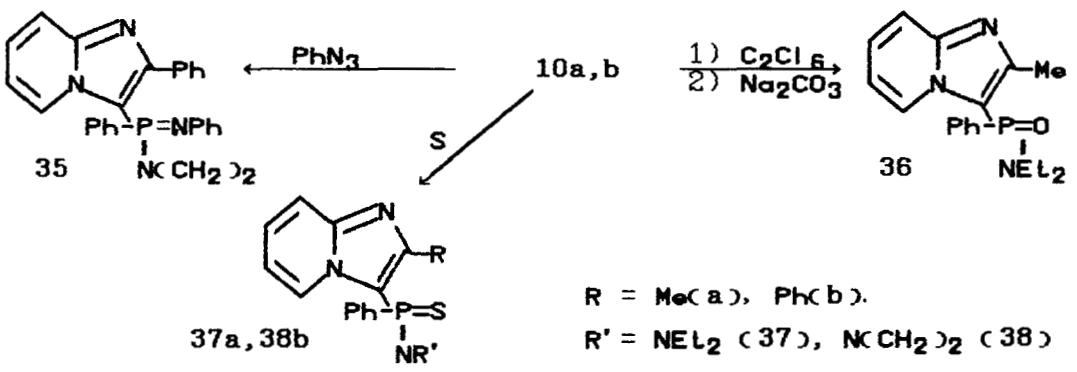
All the reactions with C–P bond cleavage in phosphorylated indolizines, like those proceeding with cleavage of the P–N bond in trivalent phosphorus acid amides, are acid-catalyzed. Therefore, one can assume that it is precisely the formation of salts of the type **19** that hinders reactions with C–P bond cleavage. However, the reaction of the amide **7a** with dry hydrogen chloride leads, not to the imidazo[1,2-a]pyridinium salt, similar to the behavior of compound **19**, but rather to P–N bond cleavage. On addition of an excess of hydrogen chloride, as in the case with common diamidophosphonites, the dichlorophosphine **3a** is formed.

$$7a \xrightarrow{HCl} 3a$$



In contrast to the behavior of indolizines, the addition reactions of sulfur and selenium with imidazopyridines, containing a trivalent phosphorus atom, proceed in the ordinary way. In order to study alkylation of phosphorylated imidazo[1,2-a]pyridines, we have synthesized a series of imi-



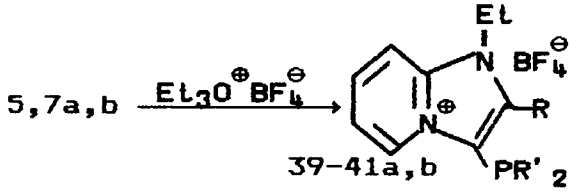


dazo[1,2-a]pyridine derivatives, containing a pentavalent phosphorus atom.

As mentioned in the Introduction, *N*-alkylation of the compounds, containing a trivalent phosphorus atom in the same molecule, has been reported only for bicyclic nitrogen-containing phosphines with a phosphorus atom in the main position of the molecule [16]. Some more simple phosphines with positively charged nitrogen atoms were obtained in a roundabout way. *N*-Alkylated phosphines have not so far been obtained.

We have found that alkylation reactions of trivalent phosphorus compounds that proceed readily with formation of phosphonium salts fail in the case of phosphorylated indolizines. This fact seems to be associated with high nucleophilicity at the carbon atoms in positions 1 and 3 of indolizine. The much higher nucleophilicity of the nitrogen atom in imidazo[1,2-a]pyridine suggested the possibility of an unusual direction of alkylation with phosphorylated imidazo[1,2-a]pyridines.

Studies of the reactions of compounds **5** and **7** with the Meerwein salt showed that the reaction not only of phosphine **5**, but also amide **7**, proceeds exclusively at the nitrogen atom to form the imidazopyridinium salts **39–41**. Thus, we have obtained the first amides of trivalent phosphorus, containing a positively charged nitrogen atom in the same molecule.

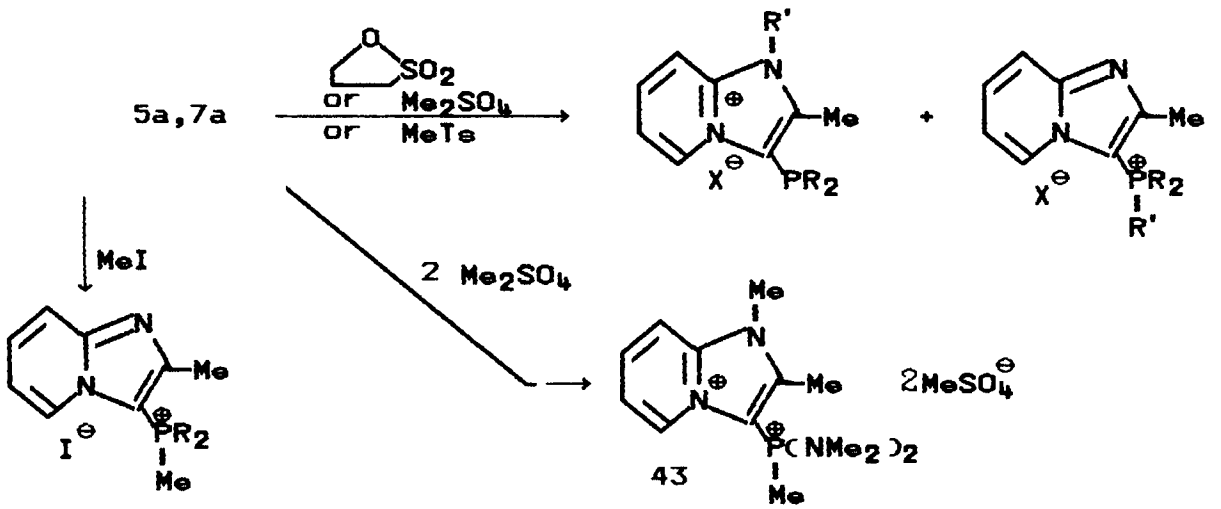


R = Me(a), Ph(b).
R'_2 = Ph (39), NEt_2 (40), NMe_2 (41).

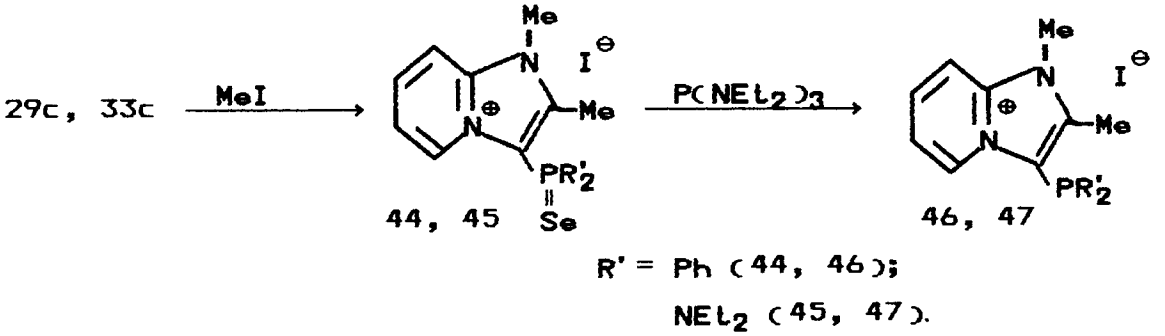
Reactions between phosphorylated imidazo[1,2-a]pyridines, containing a trivalent phosphorus atom, and sulfates, namely, dimethyl sulfate, methyl *p*-toluenesulfonate, and propane sultone are not regioselective. According to the data of ^{31}P NMR spectra, the ratio of *N*- and *P*-alkylated products in these cases is approximately 1:1.

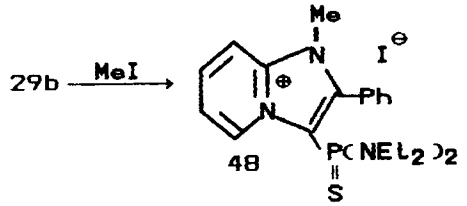
However, alkylation with weak alkylation reagents, such as methyl iodide, proceeds exclusively at the phosphorus atom. When an excess of dimethyl sulfate is used, *N*- and *P*-alkylation becomes possible.

Compound **39a**, like most tetrafluoroborates, is insoluble in water and almost insoluble in alcohols. Therefore, in order to obtain phosphines soluble in aqueous alcoholic media, it was of interest to synthesize *N*-alkylated compounds containing a trivalent phosphorus atom of the type shown in compounds **39–41**, with other anions. Due to the high nucleophilicity of the nitrogen atom in the imidazo[1,2-a]pyridine ring, the corresponding selenides **29c** and **33c,d** can be used for the protection of the trivalent phosphorus. Alkylation of these compounds with methyl iodide, like other imidazo[1,2-a]pyridine derivatives containing a pentavalent phosphorus atom **29–33**, proceeds exclusively at the nitrogen atom. The alkylated selenides **44**, **45** are rapidly reduced to the corresponding compounds containing trivalent phosphorus atom **46**, **47**, when mixed with hexaethyltriamidophosphite. Phosphine **46** is readily soluble in water and much more so in 50% ethanol; i.e., it can be assigned to the class of water-soluble phosphines.



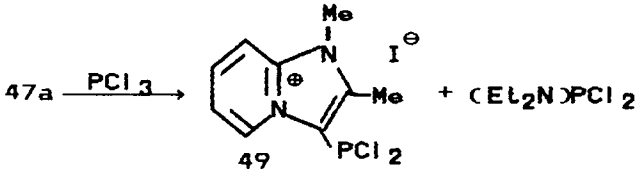
R = Ph (42a), R = NMe_2 (42b), R = NEt_2 (42c).





Since we have synthesized two series of isomeric salts, **42** and **46**, **47**, having the same anion, differing only in the position of the methyl group, we decided to investigate their possible interconversion. Migration of the alkyl group from an ammonium center to a trivalent phosphorus atom is known to proceed rather easily. In the present system, however, no such transformation was observed.

Up to the time of our investigations, only phosphines having a charged nitrogen atom have been reported. We have now obtained amides **40**, **41**, and **47** having a charged nitrogen atom 1-N. These can be the source of one more class of compounds, dichlorophosphines **49**, which have failed to be obtained by direct alkylation.



The phosphorylation positions were uniquely determined by the methods of ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy (see Tables 1–3). Thus, on phosphorylation of 2-substituted imidazo[1,2-a]pyridines, a signal for the proton 3-H (δ 7.30 in the starting compound) disappears from the PMR spectra and signals for other aromatic protons to undergo a low-field shift (especially detectable for 5-H: from δ 7.00 in the starting compound to δ 8.0–9.7). As in phosphorylated indolizines, signals for protons 5-H and 8-H can be distinguished by the $^{3}J_{HH}$ values (6.0–7.4 Hz for 5-H; 8.8–9.2 Hz for 8-H) (Table 2).

In the ^{13}C NMR spectra of phosphorylated imidazo[1,2-a]pyridines, signals for carbons 2-C, 3-C, 5-C, 9-C, and 2-Me appear as doublets, the greatest P, C coupling constant being naturally observed for C^3 (up to 160 Hz for pentavalent phosphorus compounds) (see Table 3). The large P, C coupling constants (10–40 Hz) for 9-C atoms are observed, and their chemical shifts (δ 141–155) allow us to identify them as 9-C (but not 3-C since their chemical shifts are δ 109–117).

It should be noted that the ^{31}P NMR spectra indicate a rather high-field signal for tris(imidazo[1,2-a]pyridyl)phosphine **14** (δ −93.0).

The alkylation position was also strictly confirmed by NMR spectroscopy. On alkylation at the nitrogen atom, 1-N, chemical shifts of the phosphorus atom in the ^{31}P NMR spectra are practically unchanged; whereas, on P-alkylation, a signal for the phosphorus atom is recorded in the range typical of phosphonium salts. In the PMR spectra, a signal for protons of the methyl group bound to the nitrogen atom, 1-N, appears as a singlet in the range of δ = 3.9–4.4, while that of the methyl group bound to the phosphorus atom appears as a doublet in the range of δ = 2.6–3.5 with the $^{2}J_{PH}$ = 10–12 Hz. Differences are also observed in the ^{13}C NMR spectra of phosphorylated imidazo[1,2-a]pyridines alkylated at the nitrogen or phosphorus atoms. Thus, a signal for carbon of the methyl group bound to the phosphorus atom appears as a doublet with a typical P, C coupling constant, while that of the methyl group at nitrogen is a singlet.

EXPERIMENTAL SECTION

A Bruker WP-200 spectrometer was used to take the ^{31}P NMR spectra and a Varian Gemini-200 to take the ^{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.

General Method for Synthesizing the Compounds **2–4**

To a solution of compound **1** (50 mmol) in dry pyridine (50 mL) containing triethylamine (50 mmol), a solution of the corresponding phosphorus(III) acid halide (50 mmol) was added dropwise with cooling to 0°C. After 24 hours, the solvent was half evaporated in vacuum, the residue dissolved in dry

TABLE 1 Yields, Data on Analysis, and 31p NMR Spectra

Compound	Yield (%)	Mp Bp (°C)	Formula	δ ^{31}p (^{1}H) (Solvent)	Found % (Calculated %)		
					N	P	S or Hlg
2a	82	100–102	$C_8H_7Br_2N_2P$	97.4 ($CHCl_3$)	8.83 (8.70)	9.43 (9.62)	49.76 (49.64)
2b	79	132–134	$C_{13}H_9Br_2N_2P$	100.6 ($CHCl_3$)	7.17 (7.29)	7.89 (8.06)	41.38 (41.62)
3a	86	86–89	$C_8H_7Cl_2N_2P$	122.5 ($CHCl_3$)	11.93 (12.02)	13.07 (13.29)	30.56 (30.43)
3b	82	112–114	$C_{13}H_9Cl_2N_2P$	124.1 ($CHCl_3$)	9.27 (9.49)	10.25 (10.49)	24.12 (24.03)
5a	86	118–120 (ELOH)	$C_{20}H_{17}N_2P$	−38.3 (benzene)	8.64 (8.86)	9.83 (9.79)	— —
5b	92	157–159 (*i*-PrOH)	$C_{25}H_{19}N_2P$	−35.3 ($CHCl_3$)	7.27 (7.40)	8.02 (8.18)	— —
6a	91	130–133 /0.03 mm	$C_{12}H_{19}N_4P$	88.1 (benzene)	22.21 (22.39)	12.41 (12.37)	— —
7a	88	150–152 /0.03 mm	$C_{16}H_{27}N_4P$	82.4 (petrol)	18.35 (18.29)	9.96 (10.11)	— —
7b	75	oil	$C_{21}H_{29}N_4P$	82.0 (benzene)	14.96 (15.21)	8.24 (8.41)	— —
8b	78	100–102 ($C_{10}H_{22}$)	$C_{17}H_{17}N_4P$	128.8 (benzene)	17.90 (18.17)	9.86 (10.04)	— —
9a	81	oil	$C_{16}H_{23}N_4O_2P$	84.8 (benzene)	16.59 (16.76)	9.01 (9.26)	— —
10a	76	98–101 (heptane)	$C_{18}H_{22}N_3P$	26.81 (benzene)	13.32 (13.50)	9.49 (9.95)	— —
10b	73	134–136 (octane)	$C_{21}H_{18}N_3P$	53.0 ($CHCl_3$)	11.98 (12.24)	8.87 (9.02)	— —
11	68	95–97 /0.03 mm	$C_{12}H_{17}N_2O_2P$	152.4 ($CHCl_3$)	10.95 (11.11)	12.11 (12.28)	— —
13	69	oil	$C_{22}H_{19}N_4P$	−64.8 (benzene)	15.01 (15.13)	7.98 8.36	— —
14	68	240–244 (benzene)	$C_{24}H_{21}N_6P$	−93.0 ($CHCl_3$)	19.67 (19.80)	7.14 (7.30)	— —
15	72	126–127 (heptane)	$C_{20}H_{24}N_5P$	10.7 (benzene)	19.58 (19.17)	8.18 (8.48)	— —
16	91	136–139 (ELOAc)	$C_{20}H_{24}N_5PS$	21.8 (benzene)	17.34 (17.62)	7.30 (7.79)	7.78 (8.07)
18	69	156 (dec)	$C_8H_9N_2O_2P$	4.1 (CH_3OH)	14.14 (14.28)	15.55 (15.79)	— —
19	82	138–140 (benzene)	$C_{20}H_{18}ClN_2P$	−37.8 (CH_2Cl_2)	7.75 (7.94)	8.56 (8.78)	9.73 (10.05)
20b	87	170–173	$C_{21}H_{29}Cl_2N_4P$	46.1 (CH_2Cl_2)	12.87 (12.75)	6.83 (7.05)	16.00 (16.14)
22a	78	oil	$C_{16}H_{27}N_4PO$	18.1 ($CHCl_3$)	17.23 (17.38)	9.72 (9.61)	— —
22b	75	oil	$C_{21}H_{29}N_4PO$	18.5 ($CHCl_3$)	14.39 (14.57)	7.82 (8.06)	— —
23a	79	140–141 (*i*-PrOH)	$C_{16}H_{23}N_4O_3P$	16.0 ($CHCl_3$)	16.09 (15.99)	8.68 (8.84)	— —
24b	82	136–138 (octane)	$C_{17}H_{17}N_4PO$	31.1 ($CHCl_3$)	17.11 (17.28)	9.34 (9.55)	— —
25a	83	185–187 (*i*-PrOH)	$C_{16}H_{29}ClN_5P$	31.4 (CH_2Cl_2)	19.39 (19.57)	8.52 (8.65)	9.83 (9.91)
26a	83	196–198 (*i*-PrOH)	$C_{16}H_{25}ClN_5O_2P$	29.2 (CH_3OH)	17.95 (18.15)	7.88 (8.03)	8.96 (9.19)
27a	79	145–147 /0.03 mm	$C_{16}H_{28}N_5P$	28.4 (benzene)	21.50 (21.79)	9.47 (9.64)	— —
27b	78	123–125	$C_{21}H_{30}N_5P$	28.6 ($CHCl_3$)	18.07 (18.26)	7.83 (8.08)	— —

TABLE 1 Continued Yields, Data on Analysis, and 31p NMR Spectra

Compound	Yield (%)	Mp Bp (°C)	Formula	δ ^{31}p (^{1}H) (Solvent)	Found % (Calculated %) N	P	S or Hlg
28a	80	165–167	$C_{16}H_{24}N_5O_2P$	28.9 (CH_3OH)	19.89 (20.05)	8.68 (8.86)	— —
29a	85	104–106 (ELOAc)	$C_{16}H_{27}N_4PS$	60.7 (benzene)	16.31 (16.55)	8.98 (9.15)	9.24 (9.47)
29b	87	80–83 (*i*-PrOH)	$C_{21}H_{29}N_4PS$	58.3 ($CHCl_3$)	13.82 (13.99)	7.65 (7.73)	8.11 (8.00)
29c	89	167–169 (BuOAc)	$C_{16}H_{27}N_4PSe$	54.7 ($CHCl_3$)	14.31 (14.54)	7.84 (8.04)	— —
30a	81	81–83	$C_{12}H_{19}N_4PS$	66.1 (benzene)	19.80 (19.84)	10.79 (10.97)	11.22 (11.35)
31a	89	oil	$C_{16}H_{23}N_4O_2PS$	61.4 ($CHCl_3$)	15.31 (15.29)	8.29 (8.45)	8.62 (8.75)
32b	86	159–162 (*i*-PrOH)	$C_{17}H_{17}N_4PS$	86.8 ($CHCl_3$)	16.30 (16.46)	8.87 (9.10)	9.28 (9.42)
33a	88	162–164 (hexane)	$C_{20}H_{17}N_2PS$	26.8 (benzene)	8.12 (8.04)	8.66 (8.89)	9.07 (9.20)
33b	86	160–162 (*i*-PrOH)	$C_{25}H_{19}N_2PS$	26.1 (benzene)	6.67 (6.82)	7.34 (7.54)	7.65 (7.81)
33c	92	162–164 (hexane)	$C_{20}H_{17}N_2PSe$	14.7 ($CHCl_3$)	6.98 (7.09)	7.65 (7.83)	— —
33d	90	146–148 (MeCN)	$C_{25}H_{19}N_2PSe$	15.8 ($CHCl_3$)	5.99 (6.12)	6.63 (6.77)	— —
34a	89	132–134 (*i*-PrOH)	$C_{22}H_{28}N_5O_2P$	5.9 ($CHCl_3$)	16.25 (16.46)	7.04 (7.28)	— —
35b	87	106–108	$C_{27}H_{23}N_4P$	10.0 ($CHCl_3$)	12.77 (12.90)	6.98 (7.13)	— —
36a	78	111–113 (ELOAc)	$C_{18}H_{22}N_3OP$	22.7 ($CHCl_3$)	12.75 (12.84)	9.28 (9.46)	— —
37a	89	131–132 (*i*-PrOH)	$C_{18}H_{22}N_3PS$	51.1 ($CHCl_3$)	12.07 (12.24)	8.86 (9.02)	9.19 9.34
38b	92	193 (dec) (ELOH)	$C_{21}H_{18}N_3PS$	63.5 (DMF)	11.01 (11.19)	8.09 (8.25)	8.43 (8.54)
39a	79	181–183	$C_{22}H_{22}BF_4N_2P$	−35.9 (CH_2Cl_2)	6.30 (6.48)	7.05 (7.17)	17.39 (17.58)
39b	78	157–159	$C_{27}H_{24}BF_4N_2P$	−33.8 (CH_2Cl_2)	5.49 (5.67)	6.17 (6.27)	15.22 (15.37)
40b	72	194–196	$C_{23}H_{34}BF_4N_4P$	74.4 (CH_2Cl_2)	11.44 (11.57)	6.21 (6.39)	15.50 (15.69)
41a	76	97–99	$C_{14}H_{24}BF_4N_4P$	82.9 (CH_2Cl_2)	15.17 (15.30)	8.39 (8.46)	20.58 (20.75)
42a	70	224–226	$C_{21}H_{20}IN_2P$	6.6 (CH_2Cl_2)	6.00 (6.11)	6.61 (6.76)	27.78 (27.69)
42b	81	272–274	$C_{13}H_{22}IN_4P$	45.8 (CH_2Cl_2)	14.09 (14.28)	7.78 (7.90)	32.24 (32.35)
42c	75	176–177	$C_{17}H_{30}IN_4P$	43.5 (CH_3CN)	12.57 (12.50)	7.02 (6.91)	28.23 (28.31)
43	77	216–218 (DMF)	$C_{16}H_{34}N_4O_8PS_2$	47.3 (DMF)	10.97 (11.15)	6.04 (6.16)	12.83 (12.76)
44	73	301–302 (ELOH)	$C_{21}H_{20}IN_2PSe$	16.7 ($CHCl_3$)	5.29 (5.21)	5.77 (5.76)	23.48 (23.62)
45	75	182–184 (ELOAc)	$C_{17}H_{30}IN_4PSe$	52.0 ($CHCl_3$)	10.56 (10.63)	5.94 (5.87)	23.88 (24.07)
46	89	220–222 (*i*-PrOH)	$C_{21}H_{20}IN_2P$	−35.4 ($CHCl_3$)	16.02 (6.11)	6.83 (6.76)	27.55 (27.69)
47	87	141–142	$C_{17}H_{30}IN_4P$	76.1 (CH_3OH)	12.36 (12.50)	6.99 (6.91)	28.25 (28.31)
48	77	264–266 (*i*-PrOH)	$C_{22}H_{32}IN_4PS$	53.3 (CH_2Cl_2)	10.21 (10.33)	5.64 (5.71)	23.23* (23.39)

*Analysis for I.

TABLE 2 3-Phosphorylated Imidazo[1,2-a]pyridines: ^{1}H NMR δ, (Multiplicity),[a] J (Hz)

Compound	*Solvent*	*5-H*	*6-H*	*7-H*	*8-H*	*2-Me*	*2-Ph*	*Others*
2a	$CDCl_3$	8.98 (d) 7.0	7.60 (t) 7.0	7.20 (t) 7.0	7.82 (d) 9.0	2.68 (s)		
2b	$CDCl_3$	9.21 (d) 7.0	7.52 (t) 7.0	7.91 (t) 7.0	8.37 (d) 8.8		7.80 (m) 0-Ph 7.58 (m) m, p-Ph	
3a	$CDCl_3$	8.91 (d) 7.0	7.10 (t) 6.8	7.53 (t) 6.8	7.76 (d) 9.0	2.67 (s)		
3b	$CDCl_3$	9.04 (d) 6.8	7.13 (t) 7.0	7.57 (t) 7.0	7.89 (d) 9.0		7.76 (s) O-Ph 7.56 (m) m, p-Ph	
5a	$CDCl_3$	7.86 (d) 6.0	6.45 (t) 7.0	7.08 (m) ^{1}Ph	7.56 (d) 8.4	2.46 (s)		7.08 (m) Ph
5b	$CDCl_3$	7.62 (d) 7.0	6.47 (t) 6.8	7.29–7.43 (m) ^{1}Ph	7.77 (d) 9.0		7.93 (dd) O-Ph 2.0, 7.8 7.29–7.43 (m) m, p-Ph + 7-H + PPh	7.29–7.43 (m) PPh + m, p-PH + 7-H
6a	CD_3CN	8.28 (d) 7.8	7.76 (t) 6.8	7.17 (t) 6.8	7.46 (d) 8.8	2.40 (s)		2.68 (d) $N(CH_3)_2$ 9.4
7a	C_6D_6	8.37 (d) 7.0	6.32 (t) 6.8	6.72 (t) 6.8	7.57 (d) 9.0	2.73 (d) 1.0		2.93 (m) NCH_2-, 0.92 (t) $NCH_2\underline{CH_3}$ 7.0
7b	C_5D_6	8.58 (dd) 1.2, 7.2	6.32 (td) 1.4, 7.0	6.72 (td) 1.2, 7.0	7.61 (dd) 1.2, 9.0		7.00 (d) 0-Ph 7.0 7.15–7.33 (m) m, p-Ph	2.74 (m) NCH_2-, 0.80 (t) $NCH_2\underline{CH_3}$ 7.1
8b	C_6D_6	9.83 (d) 6.8	6.31 (t) 6.8	6.69 (t) 6.8	7.59 (d) 8.8		8.52 (d) O-Ph 6.6 7.15–7.37 (m) m, p-Ph	1.52 (m) $NOCH_2O_2$
9a	CD_3CN	8.61 (d) 7.0	6.67 (t) 6.8	7.41 (t) 6.8	7.46 (d) 9.1	2.50 (s)		3.62 (t) O-CH_2, 3.05 (t) N-CH_2 5.1 5.1
10a	$CDCl_3$	8.71 (d) 7.2	6.74 (m)	7.22 (m)	7.43 (m)	2.56 (d) 1.2		1.21 (t) $NCH_2\underline{CH_3}$, 3.24 (m) NCH_2, 7.0 7.50–7.90 (m)
10b	$CDCl_3$	8.54 (d) 6.8	6.56 (t) 6.8	7.16–8.04 (m) + Ph	7.68 (d) 8.8		7.16–8.04 (m) Ph + PPh + 7-H	7.16–8.04 (m) Ph + PPh + 7-H
11	$CDCl_3$	8.75 (dd) 1.2, 7.0	6.77 (td) 1.2, 6.8	7.21 (td) 1.2, 6.8	7.55 (d) 9.0	2.62 (s)		3.92 (m) O-CH_2, 1.29 (t) $OCH_2\underline{CH_3}$ 7.0
13	$CDCl_3$	7.88 (d) 7.0	6.60 (t) 6.8	7.25 (t) 6.8	7.50 (d) 9.0	2.15 (s)		7.28–7.35 (m) PPh
14	$CDCl_3$	7.94 (d) 6.7	6.77 (td) 6.7, 1.2	7.27 (td) 6.7, 1.2	7.62 (d) 9.2	2.09 (s)		
15	CD_3CN	7.91 (d) 6.7	6.69 (t) 6.7	7.20 (t) 6.7	7.50 (d) 9.2	2.22 (s)		3.21 (m) NCH_2, 0.85 (t) $NCH_2\underline{CH_3}$ 6.7
16	$CDCl_3$	9.07 (d) 7.0	6.88 (t) 6.8	7.38 (t) 6.8	7.63 (d) 9.2	2.06 (s)		3.41 (m) NCH_2, 0.85 (t) $NCH_2\underline{CH_3}$ 6.7
18	CD_3OD	9.35 (d) 6.0	7.46 (td) 1.2, 7.0	7.92 (m)		2.73 (d) 1.2		7.76 (d) P-H 556.4
19	$CDCl_3$	8.23–8.32 (m) + 8-H	7.15 (t) 6.9	7.76 (t) 7.9	8.23–8.32 (m) + 5-H	2.50 (s)		7.26–7.43 (m) PPh
20b	$CDCl_3$	9.48 (d) 7.0	7.39 (t) 6.8	7.91 (t) 6.8	8.53 (d) 8.8		7.20–7.70 (m)	2.93 (q) NCH_2, 0.99 (t) $NCH_2\underline{CH_3}$ 7.2 7.2

benzene (50 mL), the precipitated triethylamine salt filtered off, and the filtrate evaporated in vacuum. To remove traces of salts, the residue was dissolved in dry benzene and filtered.

General Method for Synthesizing the Compounds **5a,b**

A mixture of compound **1** (10 mmol), diphenylhalogenophosphine (10 mmol), and pyridine (10 mL) was kept for 24 hours. Then the reaction mixture was diluted with benzene (30 mL). The precipitated pyridinium salt was separated and the filtrate was evaporated. The oily residue solidified under methanol.

General Method for Synthesizing the Compounds **6–9** *and* **10**

To a solution of dichlorophosphine **3** or chlorophosphine **4** (20 mmol) in benzene (30 mL), a solution of secondary amine (100 mmol) (50 mmol in

TABLE 2 Continued 3-Phosphorylated Imidazo[1,2-a]pyridines: ^{1}H NMR δ, (Multiplicity),[a] J (Hz)

Compound	*Solvent*	*5-H*	*6-H*	*7-H*	*8-H*	*2-Me*	*2-Ph*	*Others*
22a	$CDCl_3$	9.27 (d)	6.01 (t)	7.33 (t)	7.64 (d)	2.60 (d)		3.05–3.25 (m) NCH_2, 1.1 (t) NCH_2Cl
		7.0	6.8	6.8	9.0	1.2		7.1
22b	$CDCl_3$	9.17 (d)	6.95 (t)	7.30–7.55	7.68 (d)		7.30–7.55 (m)	2.89 (dq) NCH_2, 0.97 (t) $NCH_2\underline{CH_3}$
		7.0	6.6	(m) + Ph	9.0		Ph + 7-H	7.0, 17.6 7.2
23a	$CDCl_3$	9.28 (td)	6.88 (td)	7.34 (t)	7.59 (dd)	2.61 (d)		3.65 (t) OCH_2, 3.18 (m) NCH_2
		6.8, 1.0	6.8, 1.4	6.8	9.0, 1.3	1.4		4.6
24b	$CDCl_3$	9.32 (d)	6.97 (t)	7.27–7.99 (m)			7.27–7.99 (m)	2.19 (d) $NOCH_2O_2$
		7.0	7.0	'Ph			Ph + 7-H + 8-H	15.4
25a	CD_3OD	8.97 (d)	7.06 (t)	7.42 (t)	7.62 (d)	2.65 (d)		1.27 (t) $NCH_2\underline{CH_3}$, 3.27 (m) NCH_2
		7.0	7.0	7.0	9.0	1.2		7.0 7.21 (s) NH_2
26a	CD_3DD	8.73 (d)	7.33 (m)	7.71 (m)		2.66 (d)		3.70 (m) OCH_2, 3.29 (m) NCH_2
		7.0				1.2		7.2 (s) NH_2
27a	CD_3CN	9.66 (td)	6.83 (td)	7.26 (td)	7.46 (dd)	2.52 (d)		3.07 (m) NCH_2, 1.01 (m) $NCH_2\underline{CH_3}$
		7.2, 1.2	1.4, 6.8	1.4, 6.6	9.0, 1.2	1.4		
27b	$CDCl_3$	9.18 (d)	6.90 (t)	7.30–7.57	7.65 (d)		7.30–7.57 (m)	2.91 (dq) NCH_2, 0.97 (t) $NCH_2\underline{CH_3}$
		6.6	6.6	(m) + Ph	9.1		Ph + 7-H	7.0, 17.6 7.0
28a	CD_3OD	9.32 (d)	7.06 (td)	7.48 (t)	7.55 (d)	2.64 (d)		3.60 (m) OCH_2, 3.13 (m) NCH_2
		7.0	6.6, 1.4	6.6	9.0	1.4		
29a	$CDCl_3$	9.34 (d)	6.86 (t)	7.30 (t)	7.65 (d)	2.64 (d)		3.24 (m) NCH_2, 1.10 (t) $NCH_2\underline{CH_3}$
		7.0	7.0	7.0	8.8	1.4		7.0
29b	$CDCl_3$	9.02 (d)	6.93 (t)	7.32–7.59	7.67 (d)		7.32–7.59 (m)	2.93 (dq) NCH_2, 1.00 (t) $NCH\underline{CH_3}$
		7.0	7.0	(m) 'Ph	9.0		Ph + 7-H	7.0, 15.8 7.0
29c	$CDCl_3$	9.33 (d)	6.90 (t)	7.27–7.36 (m)		2.64 (d)		3.20–3.33 (m) NCH_2, 1.12 (t) NCH_2
		6.8	6.8			1.2		8.9
30a	$CDCl_3$	9.23 (d)	6.67 (t)	7.13 (t)	7.58 (d)	2.64 (s)		3.26 (d) NCH_3
		7.2	6.8	6.8	8.8			12.2
31a	$CDCl_3$	9.64 (d)	6.92 (td)	7.36 (t)	7.61 (dd)	2.72 (d)		3.7 (m) OCH_2, 3.2 (m) NCH_2
		7.0	7.1, 1.2	7.1	9.0, 1.3	1.2		
32b	$CDCl_3$	9.52 (d)	6.93 (td)	7.35–7.68	7.74 (d)		7.35–7.68 (m)	2.05 (d) $N(CH_2)_2$
		7.0	172, 7.0	(m) + Ph	9.0		Ph + 7-H	18.0
33a	$CDCl_3$	8.65 (d)	6.77 (td)	7.34 (m)	7.45–7.68	1.67 (s)		7.74–7.86 (m) O-Ph,
		7.0	1.2, 7.0		(m) + m, p-Ph			7.45–7.68 (m) m, p-Ph + 8-H
33b	$CDCl_3$	8.46 (d)	6.77 (t)	6.90–7.45 (m)			6.90–7.45 (m)	6.90–7.45 (m), 7.64–7.77 (m)
		7.2	6.2	'Ph + m, p-(PPh)			'Ph + m, p-PPh	'Ph + m, p-(PPh) 0-Ph
33c	$CDCl_3$	8.64 (d)	6.80 (td)	7.33 (m)	7.42–7.65	1.65 (s)		7.76–7.89 (m) O-Ph,
		6.8	1.2, 6.9		(m) + m, p-Ph			7.48–7.90 (m) m, p-Ph + 8-H
33d	$CDCl_3$	8.74 (d)	6.81 (t)	6.98 (m)	7.68–7.83		7.18–7.45 (m)	7.18–7.45 (m)
		7.0	7.0	'Ph	(m) + O-PPh		+ Ph + m, p-PPh	+ Ph + m, p-PPh
34a	$CDCl_3$	9.70 (s)	6.75 (m)	7.28 (m)	7.54 (d)	2.62 (d)		3.15 (m) OCH_2, 7.11 (m) O-Ph
					9.2	1.2		3.56 (m) NCH_2, 6.83 (m) m, p-Ph
35b	$CDCl_3$	6.89 (d)	6.95 (t)	6.67–8.00 (m)			6.67–8.00 (m)	6.67–8.00 (m) 1.65–2.05 (m)
		6.8	6.8	'Ph			'PPh + NPh' +7-H + B-H	Ph + PPh + NPh' $N(CH_2)_2$ +7-H + 8-H
36a	$CDCl_3$	9.28 (d)	6.83 (m)	7.28 (m)	7.57 (m)	2.55 (d)		1.16 (t) $NCH_2\underline{CH_3}$, 3.18 (m) NCH_2,
		7.4				1.2		7.1 7.52–7.85 (m) Ph
37a	$CDCl_3$	9.15 (d)	6.65 (t)	7.33 (t)	7.60 (d)	2.06 (d)		1.02 (t) $NCH_2\underline{CH_3}$, 3.31 (m) NCH_2,
		7.0	6.3	6.3	9.0	1.2		7.1 7.52–7.85 m) Ph

case of chlorophosphine 4) in benzene (10 mL) was added dropwise with stirring and cooling to 5°C. After 30 minutes, the precipitated solid was separated, the filtrate evaporated in vacuum, and the residue either allowed to stand or distilled in vacuum.

3-(2-Methylimidazo[1,2-a]pyridyl)diethylphosphonite **11**

To a solution of dichlorophosphine **3** (7 mmol) in benzene (20 mL), triethylamine (15 mmol) was added. The mixture was cooled to 5°C, and a so-

TABLE 2 Continued 3-Phosphorylated Imidazo[1,2-a]pyridines: ^{1}H NMR δ, (Multiplicity),[a] J (Hz)

Compound	*Solvent*	*5-H*	*6-H*	*7-H*	*8-H*	*2-Me*	*2-Ph*	*Others*
38b	$CDCl_3$	8.80 (d) 7.0	6.82 (t) 7.0	7.34–8.05 (m) +Ph	7.72 (d) 9.0		7.34–8.05 (m) Ph+ 7-H	1.59–2.08 (m) $N(CH_2)_2$
39a	$CDCl_3$	8.16–8.23 (m) + 8-H	7.28–7.40 (m) + Ph	7.96(t) 7.2	8.12–8.23 (m) + 5-H	2.55 (s)		7.28–7.40 (m) Ph + 6-H, 1.51 (t) NCH_2 4.56 (q) NCH_2 7.0 7.0
39b	$CDCl_3$	8.16 (td) 6.8, 1.0	7.21–7.53 (m) + Ph	8.04 (td) 7.0, 1.2	8.23 (td) 9.0, 1.0		7.21–7.53 (m) +6-H	3.21 (q) NCH_2, 1.37 (t) NCH_2CH_3 7.4 7.4
40b	CD_3CN	8.79 (d) 7.0		7.47–8.08 (m) + Ph			7.47–8.08 (m) + 6-H + 7-H + + 8-H	2.57–3.08 (m) NCH_2, 0.93 (t) NCH_2CH_3 7.2 4.11 (q) 1-NCH_2, 1.19 (t) 1-NCH_2CH_3 7.2 7.2
41a	CD_3CN	8.70 (d) 8.0	7.44 (m)	7.89–7.96 (m)		2.56 (d) 1.4		2.78 (d) NCH_3, 10.0 4.22 (q) NCH_2, 1.43 (t) NCH_2CH_3 7.3 7.3
42a	CD_3CN	8.17 (d) 6.4	7.09 (t) 6.8	7.53 (t) 6.8	7.71–7.92 (m) + Ph	1.95 (s)		3.42 (d) $PNCH_3$, 7.71–7.92 (m) Ph + 8 12.8
42b	CD_3CN	8.91 (d) 6.8	7.41 (t) 6.6	7.56 (t) 6.6	7.69 (d) 8.3	2.60 (d) 1.2		3.04 (d) NCH_3, 2.68 (d) $PNCH_3$ 10.8 13.4
42c	CD_3CN	8.20 (td) 7.0, 1.0	7.14 (td) 6.8, 1.4	7.52 (td) 6.8, 1.2	7.64 (td) 9.0, 1.4	2.47 (d) 1.2		1.15 (t) NCH_2CH_3, 2.25 (d) PCH_3 7.2 13.6 3.17 (m) NCH_2
43	CF_3CO_2D	8.76 (d) 6.4	7.82 (t) 7.2	8.31 (t) 7.2	8.18 (d) 9.0	2.87 (s)		2.61 (d) PCH_3, 3.11 (d) NCH_3 13.6 11.4 4.17 (s) 1-NCH_3, 3.95 (s) $MeSO_4$
44	$CDCl_3$	8.63 (d) 7.2	7.26 (t) 7.2	8.01 (t) 7.2	8.13–8.30 (m) + O-Ph	1.81 (d) 1.2		8.13–8.30 (m) O-Ph O H, 4, 10 7.63 (m) m, p-Ph
45	CD_3CN	9.50 (d) 7.0	7.64 (td) 6.8, 2.0	8.00 (m)		2.73 (d) 1.4		1.21 (t) NCH_2CH_3, 3.37 (m) NCH_2 7.0 3.96 (m) NCH_3
46	$CDCl_3$	8.20 (d) 6.9	7.26 (t) 7.2	8.01 (t) 7.2	8.56 (d) 9.3	2.60 (s)		7.41 (m) Ph, 4.30 (s) NCH_3
47	CD_3OD	8.74 (d) 7.0	7.49 (t) 6.6	8.05 (m)		2.63 (s)		1.14 (t) NCH_2CH_3, 3.21 (m) NCH_2 6.0 3.97 (s) NCH_3
48	$CDCl_3$	9.22 (d) 7.0		7.36–8.04 (m) +Ph			7.36–8.04 (m) + 6-H + 7-H + B-H	2.95 (dq) NCH_2, 1.08 (t) NCH_2CH_3 7.0, 12.6 7.0 3.84 (s) NCH_3

lution of anhydrous ethanol (14 mmol) in benzene (10 mL) was then added dropwise with stirring. After 30 minutes, the residue was separated, the solvent evaporated, and the oily residue distilled in vacuum.

Bis-3-(2-methylimidazo[1,2-a]pyridyl)phenylphosphine **13**

To a solution of compound **1a** (1 mmol) in pyridine (25 mL), containing triethylamine (1 mmol), dichlorophenylphosphine (0.5 mmol) was added. The reaction mixture was kept for 3 days at room temperature. After that, it was heated at 60°C for 5 hours and diluted with benzene (50 mL). Triethylamine hydrochloride was separated, the solvent evaporated in vacuum, and the residue reprecipitated with hexane from benzene.

Tris-3-(2-methylimidazo[1,2-a]pyridyl)phosphine ***14***

To a solution of compound **1a** (1 mmol) in pyridine (20 mL), triethylamine (1 mmol) was added. The mixture was cooled to 0°C, and phosphorus tribromide (0.33 mmol) was then added dropwise. The reaction mixture was kept for 3 days at room temperature. After that, it was heated at 60°C for 10 hours. The solvent was evaporated in vacuum to dryness, the residue extracted with hot benzene (3

TABLE 3 Phosphorylated Imidazo[1,2-a]pyridines ^{13}C {^{1}H} NMR δ,* J (P-C, Hz)

Compound	*Solvent*	*C²*	*C³*	*C⁵*	*C⁶*	*C⁷*	*C⁸*	*C⁹*	*Others*
1a	$CDCl_3$	143.2 (s)	109.5 (s)	125.2 (s)	111.6 (s)	116.6 (s)	123.8 (s)	145.0 (s)	14.4 (s) 2-C-$\underline{CH_3}$
2a	$CDCl_3$	149.9 (d) 4.3		130.3 (s)	114.2 (s)	117.1 (s)	128.9 (s)	152.1 (d) 41.9	15.2 (d) 2-C-$\underline{CH_3}$ 12.2
3a	$CDCl_3$	149.7 (d) 5.1		129.9 (s)	114.3 (s)	117.5 (s)	128.6 (s)	154.8 (d) 42.5	14.9 (s) 2-C-$\underline{CH_3}$
3b	$CDCl_3$	149.8 (d) 5.0		132.2 (s)	114.6 (s)	118.3 (s)			135.6 (s) *i*-Ph 130.2 (s) O-Ph 129.2 (s) *m*-Ph 130.5 (s) *p*-Ph
5a	$CDCl_3$	148.4 (d) 3.4		126.3 (d) 6.8	112.1 (s)	117.2 (s)	126.0 (s)	155.0 (d) 22.2	15.6 (d) 2-C-$\underline{CH_3}$ 7.3 133.9 (d) *i*-Ph 6.4 132.1 (d) O-Ph 18.1 129.7 (d) *m*-Ph 6.2 128.8 (s) *p*-Ph
7a	C_6D_6	147.3 (d) 5.2	111.7 (d) 21.9	126.8 (d) 5.9	110.6 (s)	117.1 (s)	123.5 (s)	149.2 (d) 9.2	14.5 (d) 2-C-$\underline{CH_3}$ 4.2 43.7 (d) NCH_2 17.7 16.2 (s) $CH_2\underline{CH_3}$
7b	C_6D_6	147.7 (d) 4.2	117.7 (d) 9.7	131.1 (d) 3.0	110.9 (s)	117.1 (s)	124.0 (s)	152.8 (d) 11.0	137.6 (d) *i*-Ph 2.3 128.5 (s) O-Ph 127.5 (s) *m*-Ph 128.0 (s) *p*-Ph 43.6 (d) NCH_2 18.2 14.3 (d) $CH_2\underline{CH_3}$
11a	$CDCl_3$	147.4 (d) 3.7		128.0 (s)	112.4 (s)	117.0 (s)	126.2 (s)	152.2 (d) 29.1	16.2 (s) 2-C-$\underline{CH_3}$ 64.2 (d) OCH_2 15.6 16.3 (s) $CH_2\underline{CH_3}$
29a	$CDCl_3$	147.7 (d) 11.7		128.3 (s)	111.8 (s)	116.4 (s)	126.6 (s)	150.1 (d) 12.1	13.9 (d) 2-C-$\underline{CH_3}$ 3.5 40.8 (d) NCH_2 4.9 16.1 (s) $CH_2\underline{CH_3}$
29b	$CDCl_3$	148.6 (d) 11.8	113.6 (d) 160.1	136.2 (s)	113.5 (s)	118.1 (s)	127.9 (d) 3.3	153.8 (d) 12.8	129.6 (d) *i*-Ph 8.1 131.3 (s) O-Ph 128.6 (s) *m*-Ph 129.3 (s) *p*-Ph 42.3 (d) NCH_2 5.1 16.8 (d) $CH_2\underline{CH_3}$ 32.2
39a	$CDCl_3$	141.0 (s)	117.3 (d) 36.0	127.6 (d) 8.6	111.9 (s)	117.8 (s)	129.9 (s)	143.9 (d) 22.6	14.5 (s) 2-C-$\underline{CH_3}$ 40.7 (s) NCH_2 10.4 (s) $CH_2\underline{CH_3}$ 129.6 (d) *m*-Ph 6.6 129.9 (s) *p*-Ph 123.1 (d) O-Ph 18.8 134.8 (s) *i*-Ph
41a	CD_3CN	194.0 (d) 10.7		130.1 (s)	110.2 (s)	117.5 (s)	128.6 (s)	141.7 (d) 11.4	13.3 (s) 2-C-$\underline{CH_3}$ 34.4 (d) $PNCH_3$ 22.2 40.3 (d) NCH_2 11.9 9.2 (s) $CH_2\underline{CH_3}$

TABLE 3 Continued Phosphorylated Imidazo[1,2-a]pyridines ^{13}C {^1H} NMR δ,* J (P-C, Hz)

Compound	*Solvent*	C^2	C^3	C^5	C^6	C^7	C^8	C^9	*Others*
42a	$CDCl_3$			129.6 (s)	116.3 (s)	117.8 (s)	127.5 (s)		16.4 (s) 2-C-$\underline{CH_3}$ 33.9 (d) PCH_3 23.7 135.8 (d) *i*-Ph 3.0 133.3 (d) O-Ph 11.4 129.9 (d) *m*-Ph 3.6 131.11 (d) *p*-Ph 9.5
42c	CD_3CN	141.0 (s)		129.6 (s)	115.6 (s)	127.7 (s)	128.8 (s)		14.1 (d) 2-C-$\underline{CH_3}$ 2.8 41.6 (d) NCH_2 4.4 16.2 (s) $CH_2\underline{CH_3}$ 11.7 (d) PCH_3 94.3
45	CD_3CN			135.6 (s)	111.9 (s)	118.0 (s)	130.8 (s)		14.4 (d) 2-C-$\underline{CH_3}$ 3.1 42.3 (d) NCH_2 9.9 11.3 (d) $CH_2\underline{CH_3}$ 12.5 32.3 (s) NCH_3
48	$CDCl_3$	141.4 (d) 8.6		134.7 (s)	112.6 (s)	117.3 (s)	124.9 (s)	141.6 (s)	131.5 (d) O-Ph 12.3 128.8 (s) *m*-Ph 129.8 (s) *p*-Ph 43.0 (d) NCH_2 3.2 15.7 (d) $CH_2\underline{CH_3}$ 1.7 33.3 (s) NCH_3

*Some ^{13}C NMR spectra are incomplete because some knot carbon signals do not appear despite long equisition.

× 30 mL), and the benzene extracts evaporated until the volume became 25 mL. The product precipitated on cooling.

Bis-3-(2-methylimidazo[1,2-a]pyridyl)diethylamidophosphinite **15**

To a solution of compound **1a** (2 mmol) in pyridine (20 mL), containing triethylamine (2 mmol), a solution of phosphorus trichloride (1 mmol) in pyridine (5 mL) was added with cooling to 0°C. The reaction mixture was heated at 70°C for 20 hours. The ^{31}P NMR spectrum recorded the formation of chlorophosphine **12** (δ_P = 28.79). After that, to the reaction mixture cooled to 0°C, diethylamine (4 mmol) was added. After 30 minutes, the precipitated solid was separated, the solvents evaporated in vacuum, and the residue recrystallized.

Bis-3-(2-methylimidazo[1,2-a]pyridyl)diethylamidothiophosphinate **16**

To a solution of compound **15** (0.5 mmol) in benzene (10 mL), finely dispersed sulfur (0.5 mmol) was added. The reaction mixture was agitated for 30 minutes with a magnetic mixer . When the sulfur had dissolved, the solvent was evaporated, and the residue was recrystallized.

3-(2-Methylimidazo[1,2-a]pyridyl)phosphonous Acid **18**

To a solution of phosphonite **11** (2 mmol) in dry acetonitrile (15 mL), water (2 mmol) was added. After 48 hours, the formation of ethoxyphosphonite **17** was recorded by the ^{31}P NMR spectrum. (^{31}P NMR spectrum (CH_3CN): δ_P = 8.1 (d), $^1J_{PH}$ 670 Hz). Then, one more portion of water (3 mmol) was added. After several days, the precipitated solid was filtered off and washed with acetonitrile and diethyl ether.

3-Diphenylphosphino-2-methyl-1H-imidazo[1,2-a]pyridinium Chloride **19**

To a solution of diphenylphosphine **5a** (1 mmol) in benzene (10 mL), a solution of hydrogen chloride (2 mmol) in diethyl ether was added. The precip-

itated solid was separated and washed with ether. On vacuum treatment and melting, the product evolved hydrogen chloride.

Reaction of 3-(2-methylimidazo[1,2-a]pyridyl)-tetraethyldiamidophosphonite **7a** *with Hydrogen Chloride*

To a solution of compound **7a** (1 mmol) in benzene (20 mL), dry hydrogen chloride (1 mmol) was added. Diethylamine hydrochloride precipitated immediately. The ^{31}P NMR spectrum of the reaction mixture showed a signal for dichlorophosphine **3a** (δ_P = 122.72) along with the signal for the starting diamidophosphonite **7a**. Then, hydrogen chloride was added, diethylamine hydrochloride was separated, and the residue was evaporated in vacuum. 3- (2-Methylimidazo[1, 2-a]pyridyl) dichlorophosphine remained, which is, judging by the ^{31}P NMR spectrum and the mixed melting sample in a sealed capillary, identical to that previously obtained.

General Method for Synthesizing the Compounds **20–21**

To a solution of the trivalent phosphorus compounds (10 mmol) in benzene (100 mL), a solution of hexachloroethane (11 mmol) in heptane or petroleum ether (50 mL) was added. After 30 minutes, the precipitated chlorophosphonium chloride was filtered off, washed with heptane and diethyl ether, and dried in vacuum.

General Method of Synthesizing the Compounds **22–24**

To a solution of chlorophosphonium chloride **20–21** (1 mmol) in methylene chloride (20 mL), a solution of sodium bicarbonate (10 g) in water (20 mL) was added and shaken in a graduated funnel. The organic layer was washed with water, separated, and dried over anhydrous sodium sulfate and evaporated. The residual phosphonate was crystallized from the corresponding solvent.

General Method of Synthesizing the Compounds **25, 26**

To a solution of chlorophosphonium chloride **20–21** (50 mmol) in methylene chloride (40 mL), excess dry ammonia was bubbled in until the precipitation of ammonium chloride was completed (about 30 minutes). The precipitated ammonium chloride was filtered off, the filtrate evaporated, and the residue recrystallized.

General Method for Synthesizing the Compounds **27, 28**

A solution of aminophosphonium chloride **25–26** (5 mmol) in methylene chloride (50 mL) was shaken in a graduated funnel with 10% NaOH (30 mL). The organic layer was separated and dried over anhydrous sodium sulfate. The residue was recrystallized or distilled over (in the case of compound **27a**).

General Method for Synthesizing the Compounds **29–33** *and* **37–38**

To a solution of the trivalent phosphorus compound (1 mmol) in benzene (15 mL), finely dispersed sulfur or selenium (1 mmol) was added. In the case of diphenylphosphines **5**, it requires 1 hour boiling to complete the reaction. Diamidophosphonites **6–9** under went reaction at room temperature. Sulfur or selenium being dissolved, the reaction mixture was filtered, the solvent evaporated in vacuum, and the compound obtained recrystallized from the corresponding solvent.

Phenylimido-3-(2-methylimidazo[1,2-a]pyridyl)dimorpholido-phosphonate **34a**, *Phenylimido-3-(2-phenylimidazo[1,2-a]pyridyl)-phenyldiethylamidophosphinate* **35b** (*General Method*)

To a solution of the trivalent phosphorus compound (1 mmol) in benzene (20 mL), phenyl azide (1 mmol) was added and the solution boiled until nitrogen evolution was completed (2–3 hours). The reaction mixture was then cooled and the solvent evaporated. The residue was recrystallized.

3-(2-Methylimidazo[1,2-a]pyridyl)phenyldiethylamidophosphinate **36a**

To a solution of compound **10a** (1 mmol) in benzene (20 mL), hexachloroethane (1 mmol) in petroleum ether (10 mL) was added. After 30 minutes, the precipitated solid was filtered off, dissolved in methylene chloride (30 mL), and shaken with 10% soda solution (30 mL). The organic layer was washed with water (20 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated. The residue was recrystallized.

General Method for Synthesizing the Compounds **39–41**

To a solution of compound **5** or **7** (1 mmol) in dry, freshly distilled methylene chloride (25 mL), a solution of triethyloxonium tetrafluoroborate (1 mmol) in methylene chloride (15 mL) was added dropwise with stirring and cooling to −30°C. The reaction mixture was stirred for 30–60 minutes at room temperature, the solvent evaporated, and the residue recrystallized (in the case of compound **39**) or kept under an oil pump vacuum (in the case of compounds **40** and **41**).

General Method for Synthesizing the Compounds **42a–d**

To a solution of compound **5–7** (1 mmol) in benzene (30 mL), the appropriate alkyl halide (1 mmol) was added. The reaction mixture was kept for several days or boiled for 3–5 hours. The precipitated solid was filtered off (most of salts **42** are highly hydroscopic) and recrystallized.

Methyl-3-(1,2-dimethylimidazo[1,2-a]pyridyl)tetraethyldiamidophosphonium Methylsulfate **43**

To a solution of compound **7a** (0.5 mmol) in petroleum ether (25 mL), dimethyl sulfate (1 mmol) was added, and the solution was boiled for 3 h. The reaction mixture was cooled and the precipitated solid was separated and recrystallized.

General Method for N-Alkylation of Sulfides and Selenides **29–33**

A mixture of compounds **29–33** (2 mmol), methyl iodide (2.5 mmol), and benzene (50 mL) was boiled for 10–50 hours until solid precipitation was completed. The precipitated salt was separated, washed with benzene, and recrystallized.

General Method for Synthesizing the Compounds **46** *and* **47** *from* **44** *and* **45**

To a mixture of salt **44** or **45** (3.35 mmol) and methylene chloride (20 mL), hexaethyltriamidophosphite (5 mmol) was added. In the process, the initial salt was completely dissolved. The reaction mixture was kept for 24 hours, the solvent evaporated, and the residue washed with benzene or ether and recrystallized.

Reaction of Compound **47** *with Phosphorus Trichloride*

To a solution of compound **47** (1 mmol) in methylene chloride (20 mL), phosphorus trichloride (5 mmol) was added. The reaction mixture was kept for 20 hours. The ^{31}P NMR spectrum of the reaction mixture showed a signal for dichlorophosphine **49** (δ_P = 120.34) along with the signal for the starting phosphorus trichloride and diethylamidochlorophosphite.

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