and **1b**, which were then eliminated by passing the mixture through an Al_2O_3 (Activity II–III) column using diethyl ether (each fraction 5 mL): fractions 3–5 (**3b**, trace), fraction 6 (**2b**, 122 mg, 47%), and fractions 7–14 (**1b** + **2b**). The structure of **2b** was characterized by the spectral data: mass spectrum *m/e* (rel intensity) 118 (M^+) (100), 91 (69), 78 (76), 67 (10), 66 (18), 65 (23), 64 (58), 63 (29), 53 (13), 52 (45), 51 (55), and 50 (34); IR ν_{max} (liquid film) 3350, 2180, 1270, and 1630 cm^{-1}; UV λ_{max} (MeOH) 274 nm (ϵ 10 400); NMR (δ in CCl_4) 6.45 (m, 1 H, H_5, $J_{4,5} \sim J_{5,6} \sim$ 2–3 Hz), 6.40 (m, 1 H, H_6, $J_{1,6} \sim$ 2 Hz), 4.72 (q, 1 H, H_1, $J_{1,4} \sim$ 3 Hz), 3.86 (m, 1 H, H_4), 3.86 (s, 1 H, H_7), and 2.52 (bs, 1 H, NH).

Photolysis of Ethyl 2-(2-Pyridyl)propionate (1c) in Alkaline Media. A 25-mM aqueous NaOH solution (600 mL) of ethyl 2-(2-pyridyl)propionate (**1c**) (0.4 g) was irradiated at 253.7 nm for 5 h. The reaction mixture was extracted into diethyl ether and was condensed, after being dried on Na_2SO_4, to yield an oil, which was passed through a basic Al_2O_3 (Activity II–III, Merck) column using diethyl ether as an eluant (each fraction 5 mL). Fractions 6–7 mainly involve **2c** (R = Et) (50 mg, 12.5%). Further purification was done with a column (Al_2O_3) in order to eliminate a small amount of **1c** from the contaminated **2c**: UV λ_{max} (MeOH) 292 nm; NMR (CCl_4) δ 6.53 (m, 1 H, H_5), 6.33 (m, 1 H, H_6), 4.64 (m, 1 H, H_1), 4.26 (m, 1 H, H_4), 4.00 (q, 2 H, CH_2), 1.64 (s, 3 H, Me), 1.20 (t, 3 H, Me), 2.2 (bs, 1 H, NH).

Hydration of Photoproducts (2). Addition of CO_2-free H_2O to **2** (ca. 10^{-4} M) at 15 °C causes the change from λ_{max} of **2** (284 nm for **2a**, 274 nm for **2b**, and 292 nm for **2c**) to λ_{max} of their hydration products (380, 383, and 384 nm, respectively). Their first-order rate constants of decomposition were measured by spectrophotometry to 1.7×10^{-2} min^{-1} for **2a** (R = Me), 0.98×10^{-2} min^{-1} for **2b**, and 0.73×10^{-2} min^{-1} for **2c**.

Thermolysis of Photoproducts (2). When a 8.1×10^{-5} M *t*-BuOH solution of **2a** was heated at 100 °C in an oil bath under air, the spectrum of **2a** was gradually restored to **1a**. On refluxing for 46 h, the starting **2a** disappeared and formation of **1a** was observed on the basis of UV and TLC (R_f 0.1 with benzene). But in the case of **2b**, restoration of **1b** was less quantitative, though its decomposition was almost complete within 16 h. The main product from **2b** was not identified.

Photolysis of Photoproducts (2). The photolysis of a 10^{-4} M diethyl ether solution of **2a** (R = Me) by a high-pressure Hg lamp (HIP 300-W) afforded methyl anthranilate (**3a**) quantitatively. Stoichiometric spectral change was observed from 284 nm to 248 and 337 nm with isosbestic points at 258 and 304 nm. Irradiation of **2b** in diethyl ether results in the formation of **3b** in view of spectrophotometry. The formation of **3** was further confirmed by TLC with benzene as an eluant (R_f 0.4 for **3a** and 0.45 for **3b**).

Preparative photolysis of **2a** (12.2 mg) in diethyl ether (100 mL) afforded only a single product (**3a**) (>90%).

Registry No.—**1a** (R = Me), 1658-42-0; **1a** (R = Et), 2739-98-2; **1b**, 2739-97-1; **1c**, 5552-85-2; **2a** (R = Et), 64741-21-5; **2a** (R = Et), 64741-24-8; **2b**, 64741-25-9; **2c**, 64741-26-0; **3a** (R = Et), 87-25-2; **3b**, 1885-29-6.

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(2) Photolysis of the acetate (**1a**) also results in the formation of a single photoproduct (**2a**) in the presence of a reducing agent, $NaBH_4$, where pyridine was transformed to 2-azabicyclo[2.2.0]hex-5-ene through hydrogenation of Dewar pyridine,[3] but there was no formation of the 1,2-dihydro analogue of **4**.
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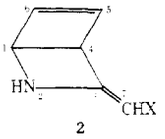
(4) The numbering system and coupling constants for the photoproduct (**2**) are as follows:



2

$J_{4,5} \sim J_{5,6} \sim J_{1,4} \sim J_{1,6} \sim$ 2–3 Hz

(5) The most significant feature in the IR spectra of the β-cyanovinylamine is the lowering of the C≡N band to 2200 cm^{-1} compared to the band with simple α,β-unsaturated nitrile (2230 cm^{-1}). This displacement is associated with a reduction in the triple bond character of the C≡N group and may be attributed to the contribution of the ionic resonance structure.[6] NCH=CHC≡N ⟷ $^+$N=CHCH=C=N$^-$.
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Chemistry of Heterocyclic Compounds. 27. An Improved Preparation of Pyridyldiphenylphosphines

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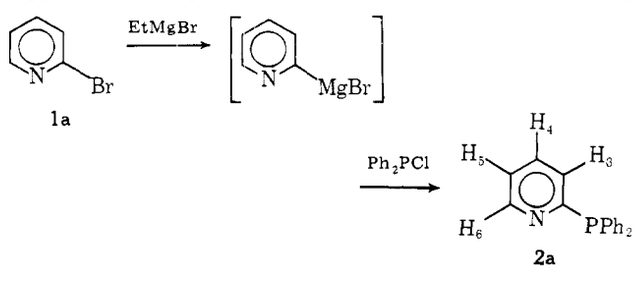
Received July 18, 1977

Presently, the preparation of pyridyldiphenylphosphine ligands is via the treatment of lithiopyridines with an appropriate halophosphine. In order to circumvent the major drawbacks of that procedure, i.e., low yields and the formation of unwanted pyridine side products, lithium diphenylphosphide has herein been shown to react smoothly with halopyridines to generate pyridyldiphenylphosphines. The general procedures for the synthesis of both the pyridylphosphines and the corresponding P→O have been described.

In 1948, Mann and Watson[1] reported a series of tertiary 2-pyridylamines, phosphines, and arsines synthesized during a chemotherapeutic investigation conducted toward the later half of World War II. In that classic work, the reaction of 2-pyridylmagnesium bromide[2,3a] on chlorodiphenylphosphine was used to prepare (20.4%) 2-pyridyldiphenylphosphine (**2a**). Similarly, other 2-pyridylphosphines (and arsines) were prepared via action of the same organometallic reagent on an appropriate chloride.[1] This basic procedure has been utilized by numerous researchers desirous of pyridylphosphines.[3]



1a **2a**

In 1955, it was reported that both 2-chloro- and 2-bromopyridine failed to react when subjected to either the Arbuzov or Michaelis–Becker reaction conditions.[4] Even though 2-halopyridines are relatively unreactive[5] toward nucleophilic

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Table I. Pyridylphosphines Prepared by Reaction of $LiPPh_2$ with Halopyridines[a]

Reactant	Registry no.	Phosphine	Registry no.	Reaction temp, °C	Yield,[b] %	Mp, °C (solv)[c]	Phosphine oxide	Registry no.	Yield,[b] %	Mp, °C (solv)
1a	109-04-6	**2a**	37943-90-1	65	55	83–84[d] (petroleum ether)	**3a**	64741-30-6	85	109–110 (C_6H_{12})
1b	109-09-1	**2a**		65	50	83–84 (petroleum ether)				
1d	626-61-9	**2b**	54750-98-0	25	*e*	64–66[f] (hexane)	**3b**	54750-99-1	42[g]	149–150[h] (EtOAc)
1e	626-05-1	**2c**	64741-27-1	25	*e*	124–125[i] (hexane)	**3c**	64741-31-7	32[g]	229–230 (acetone)
1f	17228-64-7	**6**	64741-28-2	65	36	192–193 (EtOAc)	**7**	64741-32-8	80	206–207 (EtOAc)
1g	49669-22-9	**8**	64741-29-3	65	21	198–199 ($CHCl_3$)	**9**	64741-33-9	89	>300 ($CHCl_3$)

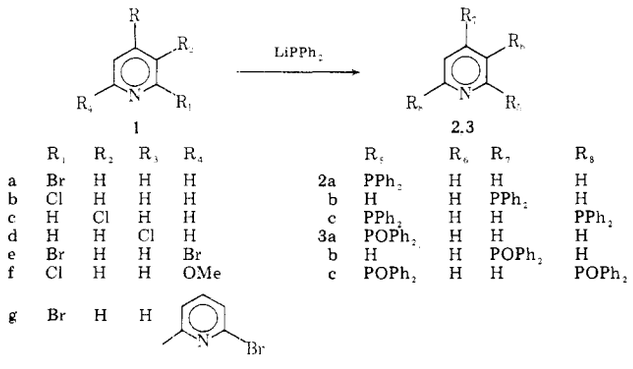
[a] Satisfactory analytical data (±0.4% for C, H, and N) were obtained for all compounds listed. [b] Yields are of isolated products. [c] Recrystallization solvent. [d] Lit.[1] mp 84–85 °C (aqueous methanol). [e] Phosphine undergoes facile air oxidation; isolation can be accomplished with difficulty under anaerobic conditions. (Also see ref 11.) [f] Lit.[11] mp 66–69 °C (hexane under a nitrogen atmosphere). [g] Isolated yield without isolating the intermediary phosphine. [h] Lit.[11] mp 153–155 °C. [i] Prepared (92%) from **3c** by reduction according to the procedure of Cremer and Chorrat;[15] see Experimental Section.

substitution, the recent statement[6] that pyridyl halides do not react with phosphorus nucleophiles seemed to overstate the results which were based on limited available data.[4a] Interestingly, however, 2-chloroquinoline did react with sodium dibutylphosphite at 140 °C in xylene to afford the desired ester, which was smoothly hydrolyzed to 2-quinolylphosphonic acid in 28.5% yield.[4a] In view of our reported synthesis of macrocycles possessing a pyridine subunit[7] via direct nucleophilic substitution under similar reaction conditions to that of Burger et al.,[4a] we herein report the facile synthesis of pyridyldiphenylphosphines via direct nucleophilic substitution of a pyridyl halide by lithium diphenylphosphide.

Results and Discussion

Lithium diphenylphosphide was conveniently prepared from chlorodiphenylphosphine and lithium metal in ethereal solvent.[8e] However, alternate procedures are available from either diphenylphosphine,[8a] prepared from chlorodiphenylphosphine upon treatment with lithium aluminum hydride,[9] with phenyllithium or triphenylphosphine,[8b,c] or diphenylphosphine[8d] with lithium in THF. The general ease of preparation, along with its enhanced nucleophilicity in substitution reactions, even of arylhalides,[8c] makes lithium diphenylphosphide an ideal reagent to attempt displacement of a pyridyl halide.

Table I summarizes the pyridylphosphines prepared by reaction of lithium diphenylphosphide with various halopyridines. No efforts were made to maximize the product yields. The reaction of lithium diphenylphosphide with 2-bromopyridine is presented in the Experimental Section as a typical procedure.[10] Although most pyridylphosphines can be isolated as the free phosphines, upon either prolonged exposure to air or mild oxidizing agents they were smoothly converted to the corresponding P oxides. Heteroaryl phosphines are normally

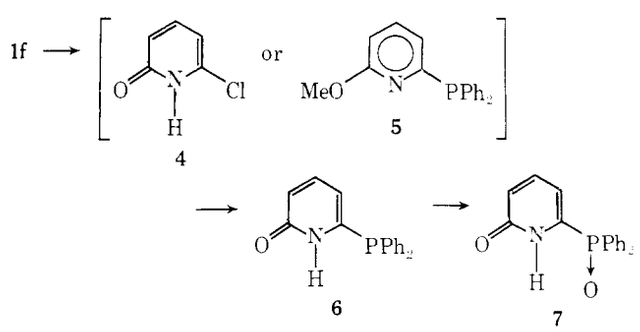


	R_1	R_2	R_3	R_4		R_5	R_6	R_7	R_8
a	Br	H	H	H	2a	PPh_2	H	H	H
b	Cl	H	H	H	b	H	H	PPh_2	H
c	H	Cl	H	H	c	PPh_2	H	H	PPh_2
d	H	H	Cl	H	3a	$POPh_2$	H	H	H
e	Br	H	H	Br	b	H	H	$POPh_2$	H
f	Cl	H	H	OMe	c	$POPh_2$	H	H	$POPh_2$
g	Br	H	H						

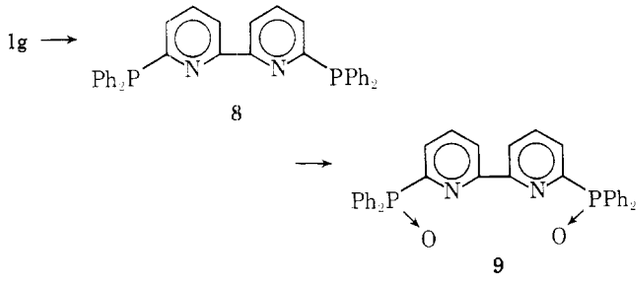
difficult to isolate without minor oxide contaminants; e.g., phosphine **2b** can be isolated with difficulty under anaerobic conditions.[11] Phosphine oxides were easily prepared from the free phosphine via treatment with ethanolic hydrogen peroxide.[12] The degree of P oxide formation can be ascertained from the ^1H NMR spectral data in that the P→O causes a dramatic deshielding of the pyridyl hydrogens. The greatest effect of P→O formation is experienced by the 3-pyridyl hydrogen with a 0.8 to 0.9 ppm downfield shift, whereas, the other pyridyl hydrogens also show a measurable, but diminished, downfield shift. These observations are similar to those reported for tri-2-pyridylphosphine,[3c,e] its oxide,[3c,e] and selenide.[3e]

Reaction of 3-chloropyridine (**1c**) with lithium diphenylphosphide was attempted; however, only unreacted starting material was isolated. Although 3-halopyridine is generally resistant to nucleophilic substitution,[13] this result was unusual in light of the reactivity of this reagent toward simple aryl halides.[8c] Stronger phosphorus nucleophiles, e.g., $LiPEt_2$, or more rigorous conditions may be necessary to effect the displacement.

Treatment of **1f** with lithium diphenylphosphide afforded pyridone **6.** Two possible routes to **6** are possible: (1) displacement of the halide to afford **5** followed by demethylation or (2) demethylation to give **4,** which undergoes nucleophilic substitution. Similarly with nonheterocyclic ethers, Mann and Pragnell have reported the facile dealkylation of certain alkyl aryl ethers by diphenylphosphide ion.[14] Pyridone **6** was converted into the corresponding P oxide (**7**) by standard conditions.



6,6′-Dibromo-2,2′-bipyridyl (**1g**) was smoothly transformed into the bis(phosphine) **8,** subsequent oxidation with hydrogen peroxide generated the bis(phosphine oxide) **9** in 89% yield.



Conclusions

2- and 4-halopyridines react smoothly with lithium diphenylphosphide under mild conditions to generate the corresponding phosphines in greatly improved yields. The lithium phosphide reagent is much easier to prepare and handle than pyridyllithiums and is less subject to side reactions. Thus, this procedure offers a convenient route to novel, previously difficult to prepare, pyridylphosphine ligands.

Experimental Section

All melting points were taken in capillary tubes with a Thomas-Hoover Uni-Melt and are uncorrected. Infrared spectra (IR) were recorded on a Beckmann IR-7 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained using a Varian A-60-A spectrometer and are recorded in parts per million downfield from the internal standard of tetramethylsilane. All compounds were confirmed by mass spectral analysis obtained on a Hitachi Perkin-Elmer RMS-4 spectrometer by Mr. J. Murphy. Elemental analyses were performed by Mr. R. Seab in these laboratories.

Lithium Diphenylphosphide (50-mmol Solution). To a stirred mixture of lithium (700 mg, 100 mmol) in anhydrous tetrahydrofuran (50 mL) under nitrogen, a solution of freshly distilled chlorodiphenylphosphine (9 mL, 50 mmol) in dry THF (30 mL) was added dropwise over 1 h. After the addition was completed and appearance of a dark red coloration, the solution was refluxed for an additional 2 h prior to use.

General Reaction Procedure. 2-Pyridyldiphenylphosphine (2a). A stirred THF solution of lithium diphenylphosphide (50 mmol) was brought to reflux under nitrogen, then a solution of 2-bromopyridine (7.2 g, 45 mmol) in dry THF (25 mL) was added over a 30-min period, followed by an additional hour of reflux. After cooling to room temperature, the solution was concentrated in vacuo and aqueous hydrochloric acid (3 N, 50 mL) was added and then extracted with chloroform. The aqueous layer was neutralized with a dilute sodium carbonate solution. The resultant precipitate was dried and recrystallized from petroleum ether (bp 30–60 °C) to afford 2-pyridyldiphenylphosphine as colorless crystals: 6.5 g (55%); mp 83–84 °C (lit.[1] mp 84–85 °C); NMR ($CDCl_3$) δ 7.12 (m, 5-Pyr-H, 1 H), 7.32 (s, PPh_2), 7.25–7.6 (m, 3,4-Pyr-H), 8.71 (ddd, 6-Pyr-H, J = 6, 2, 1.5 Hz, 1 H); IR ($CHCl_3$) 2990, 1560, 1550, 1465, 1440, 1420, 1410, 1170, 1080, 980 cm^{-1}; mol wt (mass spectrum) m/e 263 (M^+).

2c: NMR ($CDCl_3$) δ 7.2–8.0 (m, all Pyr- and Ph-H); IR ($CHCl_3$) 2960, 1560, 1455, 1410, 1140, 1070, and 905 cm^{-1}.

6: NMR ($CDCl_3$) δ 6.09 (ddd, 5-PyrH, J = 7, 7, 1 Hz, 1 H), 6.45 (dd, 3-PyrH, J = 9, 1 Hz, 1 H), 7.1–7.8 (m, 4-PyrH and Ph-H, 12 H); IR ($CHCl_3$) 3380 (N–H), 2950, 1670 (amide), 1610, 1475, 1450, 1170, 1140, 1000, 975, 800 cm^{-1}; mol wt (mass spectra m/e 279 (M^+).

8: NMR ($CDCl_3$) δ 7.05–7.83 (m, 4,4′,5,5′-Pyr-H and Ph-H, 24 H), 8.25 (d, 3,3′-Pyr-H, J = 8 Hz, 2 H); IR ($CHCl_3$) 2995, 1550, 1530, 1465, 1405, 1170, 1140, 1080, 1065, 975 cm^{-1}; mol wt (mass spectra) m/e 524 (M^+).

General Procedure for the Preparation of Phosphine Oxides. 2-Pyridyldiphenylphosphine Oxide (3a). A mixture of **2a** (500 mg, 1.9 mmol), hydrogen peroxide (0.5 mL, 30%), and absolute ethanol (40 ml) was refluxed for 30 min. The solution was poured into water (ca. 100 mL) and extracted with chloroform. The organic extract was dried over magnesium sulfate, filtered, and concentrated to afford a white solid which was recrystallized from cyclohexane to give **3a:** 450 mg (85%); mp 109–110 °C; NMR ($CDCl_3$) δ 7.25–7.5 (m, 3,4,5-Ph-H, 5-Pyr-H, 7 H), 7.65–8.0 (m, 2,6-Ph-H, 4-Pyr-H, 5 H), 8.28 (ddd, 3-Pyr-H, J = 6,2,1.5 Hz, 1 H), 8.7 (ddd, 6-Pyr-H, J = 6,2,1.5 Hz, 1 H); IR ($CHCl_3$) 2970, 1585, 1560, 1480, 1420, 1300, 1160 (s, P→O), 1130, 1110, 985 cm^{-1}; mol wt (mass spectra) m/e 279 (M^+).

3b: NMR ($CDCl_3$) δ 7.28–7.93 (m, 3,5-Pyr-H and Ph-H, 12 H), 8.80 (ddd, 2,6-Pyr-H, J = 4.5, 4.5, 1.3 Hz, 2 H); IR ($CHCl_3$) 2995, 1575, 1480, 1435, 1400, 1315, 1220, 1175 (s, P→O), 1120, 975 cm^{-1}; mol wt (mass spectra) m/e 279 (M^+).

3c: NMR ($CDCl_3$) δ 7.00–8.45 (m, Pyr- and Ph-H); IR (KBr) 3000, 1575, 1495, 1445, 1200, 1160 (s, P→O), 1125, 1100, 1080, 990 cm^{-1}; mol wt (mass spectra) m/e 479 (M^+).

7: NMR ($CDCl_3$) δ 6.42 (dd, 5-Pyr-H, J = 7, 7 Hz, 1 H), 6.65 (d, 3-Pyr-H, J = 9 Hz, 1 H), 7.2–7.9 (m, 4-Pyr-H and Ph-H, 12 H), 8.2 (bs, NH, 1 H); IR ($CHCl_3$) 3350 (N–H), 2980, 2920, 1650 (amide), 1590, 1420, 1160 (s, P→O), 1120, 995, 890 cm^{-1}; mol wt (mass spectra) m/e 295 (M^+).

9: NMR ($CDCl_3$) δ 7.33–7.68 (m, 3,4,5-Ph-H, 12 H), 7.70–8.17 (m, 4,4′-Pyr-H and 2,6-Ph-H, 10 H), 8.20–8.48 (m, 3,3′,5,5′-Pyr-H, 4 H); IR ($CHCl_3$) 2970, 1570, 1550, 1420, 1370, 1170 (s, P→O), 1150, 1090, 1070, 990 cm^{-1}; mol wt (mass spectra) m/e 556 (M^+).

2,6-Bis(diphenylphosphino)pyridine (2c) was prepared (92%), according to the procedure of Cremer and Chorrat[15] by the reduction of **3c** with trichlorosilane in the presence of triethylamine: mp 124–125 °C (hexane); NMR ($CDCl_3$) δ 7.00 (m, 3,5-Pyr-H, 2 H), 7.08–7.48 (m, 4-Pyr-H, Ph-H, 21 H); IR ($CHCl_3$) 3000, 1565, 1490, 1430, 1375, 1180, 1100, 990 cm^{-1}. Anal. Calcd for $C_{29}H_{23}NP_2$: C, 77.84; H, 5.18; N, 3.13. Found: C, 77.77; H, 5.20; N, 3.00.

Acknowledgments. The authors gratefully acknowledge partial support of this work by a Public Health Service grant from the National Institutes of Health. We also wish to thank Professor Hansen (Lamar University) for his helpful comments to D.C.H.

Registry No.—$LiPPh_2$, 4551-02-0.

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