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Bis(dialkylamino)phosphines[1,2]

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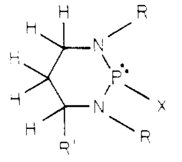
Reactions of $LiAlH_4$ with sufficiently sterically hindered $(R_2N)_2PCl$ derivatives (R = isopropyl and ethyl but not methyl) in diethyl ether give the corresponding $(R_2N)_2PH$ derivatives as air-sensitive, vacuum-distillable liquids. Analogous reactions of $LiAlH_4$ with sufficiently sterically hindered heterocycles $(CH_2)_n(NR)_2PCl$ (R = *tert*-butyl, $n = 2$ and 3; R $\neq$ methyl, $n \neq 2$) give the corresponding heterocyclic PH derivatives $(CH_2)_n(NR)_2PH$. The dialkylamino groups in $(R_2N)_2PH$ undergo successive alcoholysis with the alcohols R′OH (R′ = methyl, ethyl, isopropyl, and *tert*-butyl) to form $(R_2N)(R'O)PH$ and $(R'O)_2PH$ derivatives, which are identified by their phosphorus-31 NMR spectra. The derivatives $(R_2N)(R'O)PH$ (R = isopropyl; R′ = methyl, ethyl, isopropyl, and *tert*-butyl) can be isolated by vacuum distillation as air-sensitive liquids, but the derivatives $(R'O)_2PH$ generally decompose upon attempted vacuum distillation. The $(R_2N)_2PH$ derivatives undergo base-catalyzed addition to $(R_2N)_2PCH{=}CH_2$ to give the corresponding diphosphines $(R_2N)_2PCH_2CH_2P(NR_2)_2$, provided that the R_2N groups are not too bulky [i.e., for $(R_2N)_2 = (Et_2N)_2$ or $(CH_2)_3(NCMe_3)_2$ but not $(i\text{-}Pr_2N)_2$]. The mass spectra and NMR spectra of the new organophosphorus compounds are described.

Introduction

Bis(dialkylamino)phosphines, $(R_2N)_2PH$, are of interest since they can be regarded either as analogues of secondary phosphines, R_2PH, or as dialkyl amides of the $HP(OH)_2$ tautomer of hypophosphorous acid, $H_2P(O)OH$. They have the potential to exhibit diverse chemical reactivity owing to the presence of three reactive sites: the trivalent phosphorus atom, the phosphorus–hydrogen bond, and the phosphorus–nitrogen bonds. Thus bis(dialkylamino)phosphines are of interest for the preparation of transition-metal complexes through coordination of the trivalent phosphorus atom, for the preparation of polyphosphorus derivatives through addition reactions of the phosphorus–hydrogen bond to vinylphosphorus derivatives,[3-5] and for the preparation of other R_2NPXH and PX_2H derivatives through solvolysis reactions of the phosphorus–nitrogen bond(s).

Despite this potential importance of bis(dialkylamino)phosphines, very little was known about them when this research was initiated. An early attempt[6] to prepare $(Me_2N)_2PH$ by the reaction of $(Me_2N)_2PCl$ with $LiBH_4$ led instead to the borane adduct $(Me_2N)_2PH{\cdot}BH_3$. Much more recently, reactions of cyclic $R'C_3H_5(NR)_2PCl$ derivatives (I, X = Cl; R = *tert*-butyl; R′ = H and CH_3; or R = CH_3; R′ = CH_3) with $n\text{-}Bu_3SnH$ were reported[7] to give the corresponding $R'C_3H_5(NR)_2PH$ derivatives (I, X = H). Several [bis(trimethylsilyl)amino]phosphorus derivatives with phosphorus–hydrogen bonds are known, including $(Me_3Si)_2NPH_2$ (ref 8) $(Me_3Si)_2NP(R)H$ [R = *i*-Pr, *t*-Bu, CH_2SiMe_3, $N(SiMe_3)_2$, and Ph],[9] and $(Me_3Si)_2NP(H)N(H)SiMe_3$.[10] However, acyclic $(R_2N)_2PH$ derivatives containing silicon-free R groups were unknown at the start of this research.



I

Our entry into the study of $(R_2N)_2PH$ derivatives was facilitated by the discovery[1] that $LiAlH_4$ reduction of $(R_2N)_2PCl$ derivatives having sufficiently bulky R_2N groups leads directly to the desired $(R_2N)_2PH$ derivatives. This paper describes the details of these reactions, as well as some studies on the alcoholysis of $(R_2N)_2PH$ derivatives to give $(R_2N)(R'O)PH$ and $(R'O)_2PH$ derivatives and on the addition of $(R_2N)_2PH$ to $(R_2N)_2PCH{=}CH_2$ to give diphosphines of the type $(R_2N)_2PCH_2CH_2P(NR_2)_2$.

Experimental Section

Microanalyses and osmometric molecular weight determinations were performed by Atlantic Microanalytical Laboratory, Atlanta, GA, and Schwarzkopf Microanalytical Laboratory, Woodside, NY. All NMR spectra were taken on a JEOL FX-90Q spectrometer operating in the Fourier-transform mode. Chemical shifts (δ) are reported in parts per million *down*field from internal tetramethylsilane (for proton and carbon-13) and external 85% phosphoric acid (for phosphorus-31). Mass spectra were obtained on a Finnegan 4023 mass spectrometer operating in conjunction with a gas chromatograph. Relative intensities of ions in the mass spectra are given in parentheses following the ion formula.

All reactions were carried out in an efficient hood using aqueous calcium hypochlorite traps to decompose noxious materials in the effluent vapors before passing them into the hood exhaust. A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions; (b) handling air-sensitive organophosphorus compounds; and (c) filling evacuated vessels containing potentially air-sensitive materials. When necessary, Schlenk ware[11] or a polyethylene glove bag was used to provide the nitrogen atmosphere. All solvents were distilled under nitrogen over appropriate drying agents (Na/benzophenone or metal hydrides, except for chlorinated solvents) before use.

The secondary diamines $(CH_2)_n(NHCMe_3)_2$ [n = 2 (ref 12) or 3 (ref 13)] were prepared by the cited published procedures. All other starting materials were purchased from standard commerical suppliers, mainly Aldrich Chemical Co., Milwaukee, WI.

Preparation of $(i\text{-}Pr_2N)_2PCl$. The procedure described below appears to represent significant improvements in the reported

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[1] For a preliminary communication of some of this work, see King, R. B.; Sadanani, N. D.; Sundaram, P. M. *J. Chem. Soc., Chem. Commun.* **1983**, 477.

[2] Portions of this work were presented at the National Meetings of the American Chemical Society in Seattle, WA, Mar, 1983, and Washington, DC, Aug, 1983, and at the International Conference on Phosphorus Chemistry, Nice, France, Sept, 1983.

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procedure[14] for the preparation of $(i\text{-}Pr_2N)_2PCl$ in the relatively large quantities needed for this project.

A solution of 51 mL (80 g, 9.58 mol) of phosphorus trichloride in 100 mL of hexane was added dropwise to a solution of 325 mL (233 g, 2.30 mol) of diisopropylamine in 1 L of hexane with continuous stirring and cooling in an ice bath. The reaction mixture was allowed to warm to room temperature and then boiled under reflux for 30 h. After cooling to room temperature, the reaction mixture was filtered, and the precipitate was washed with hexane. Concentration of the hexane filtrate gave 85 g (55% yield) of $(i\text{-}Pr_2N)_2PCl$: mp 98–99 °C (lit.[15] mp 96–98 °C): mass spectrum, $(i\text{-}Pr_2N)_2PCl^+$ (18), $(i\text{-}Pr_2N)_2P^+$ (41), $i\text{-}Pr_2NPCl^+$ (100), $i\text{-}Pr_2NPH^+$ (76), $i\text{-}PrNP^+$ (82), $i\text{-}PrNPHCl^+$ (46); ^{31}P NMR (CH_2Cl_2) δ 140.8. This product was pure enough for the reactions described in this paper but could be purified further by vacuum sublimation at 95–100 °C (0.1 mm).

Preparation of $(i\text{-}Pr_2N)_2PH$. A solution of 20.0 g (75 mmol) of $(i\text{-}Pr_2N)_2PCl$, 4.0 g (105 mmol) of $LiAlH_4$, and 300 mL of diethyl ether was stirred for 72 h at room temperature. Solvent was then removed from the filtered reaction mixture at 25 °C (25 mm). The residue was extracted with pentane. Removal of solvent at 25 °C (25 mm) from the filtered pentane extract, followed by vacuum distillation, gave 10.0 g (57% yield) of $(i\text{-}Pr_2N)_2PH$: bp 80–85 °C (0.5–0.6 mm); mp 24–25 °C; mass spectrum, $(i\text{-}Pr_2N)_2PH^+$ (28), $i\text{-}Pr_2NPH^+$ (100), $i\text{-}PrNPH_2^+$ (55); ^{31}P NMR $(CDCl_3)$ δ 42.1 (J_{PH} = 254 Hz); ^1H NMR $(CDCl_3)$ δ 5.73 (d, J = 254 Hz, PH), 3.38 (m, 4 CH), 1.06 (dd, J_1 = 6 Hz, J_2 = 3 Hz, 8 CH_3); proton-decoupled ^{13}C NMR $(CDCl_3)$ δ 50.6 (d, J = 9 Hz, 4 CH), 24.1 (d, J = 4 Hz, 4 CH_3), 23.9 (d, J = 7 Hz, 4 CH_3); IR (liquid film) 2970 (s), 2930 (s), 2870 (m), 2295 (vw), 2225 (w), 1456 (m), 1386 (m), 1362 (s), 1310 (w), 1190 (s), 1156 (m), 1120 (m), 1050 (w), 1022 (m), 979 (w), 940 (s), 862 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{29}N_2P$: C, 62.1; H, 12.5; N, 12.1. Found: C, 60.9; H, 12.5; N, 11.4. Tissue paper impregnated with $(i\text{-}Pr_2N)_2PH$ ignited upon exposure to air.

Similar results were obtained by carrying out the reduction of $(i\text{-}Pr_2N)_2PCl$ with $LiAlH_4$ in tetrahydrofuran rather than diethyl ether. An analogous reduction of $(i\text{-}Pr_2N)_2PCl$ (2.66 g, 10 mmol) with $LiAlD_4$ (0.42 g, 10 mmol) in diethyl ether (45 mL) gave $(i\text{-}Pr_2N)_2PD$ (1.6 g, 69% yield): bp 55–63 °C (0.05–0.1 mm); IR ν (PD) 1622 cm^{-1}; ^{31}P NMR $(CDCl_3)$ δ 40.8 (J_{PD} = 39 Hz).

Preparation of $(Et_2N)_2PH$. The $(Et_2N)_2PCl$ required for this experiment [bp 85 °C (1.5 mm); ^{31}P NMR δ 159.2; mass spectrum, $(Et_2N)_2PCl^+$ (37), $(Et_2N)_2P^+$ (100), Et_2NPCl^+ (84), Et_2NPH^+ (73)] was prepared by reaction of phosphorus trichloride with diethylamine in hexane in a 1:4 mole ratio, followed by filtration and distillation of the filtrate.

A solution of 2.5 g (66 mmol) of $LiAlH_4$ in 200 mL of diethyl ether was treated dropwise at 0 °C with a solution of 8.5 mL (8.0 g, 38 mmol) of $(Et_2N)_2PCl$ in 50 mL of diethyl ether. After stirring for 64 h at room temperature, the reaction mixture was filtered. Solvent was removed from the filtrate at 25 °C (25 mm). The oily residue was extracted with 60 mL of pentane. Pentane was removed from the filtrate at 25 °C (25 mm). The liquid residue was distilled under vacuum with the addition of glass wool to prevent bumping to give 2.0 g (30% yield) of very air-sensitive malodorous $(Et_2N)_2PH$: bp 50–54 °C (1.1–1.2 mm); mass spectrum, $(Et_2N)_2PH^+$ (100), Et_2NPH^+ (83); ^{31}P NMR (C_6D_6) δ 77.0 (J_{PH} = 249 Hz); ^1H NMR (C_6D_6) δ 6.08 (d, J = 251 Hz, PH), 2.55 (q, J = 7 Hz, 4 CH_2), 1.02 (t, J = 7 Hz, 4 CH_3); proton-decoupled ^{13}C NMR $(CDCl_3)$ δ 46.5 (d, J = 12 Hz, 4 CH_2), 14.9 (d, J = 4 Hz, 4 CH_3); IR (liquid film) 2967 (s), 2930 (s), 2860 (s), 2272 (m), 1458 (m), 1373 (m), 1341 (w), 1290 (w), 1191 (s), 1097 (w), 1053 (w), 1031 (m), 1002 (m), 914 (m), 900 (m), 790 (m), 666 (m) cm^{-1}.

Reaction of $(Me_2N)_2PCl$ with $LiAlH_4$. A solution of 2.5 g (66 mmol) of $LiAlH_4$ in 100 mL of diethyl ether was treated dropwise at 0 °C with a solution of 10.0 g (65 mmol) of $(Me_2N)_2PCl$[15] in 20 mL of diethyl ether. The solution turned yellow immediately. The reaction mixture was stirred for 72 h at room temperature. The reaction mixture was then filtered. Removal of solvent from the filtrate gave 6.0 g of a liquid, shown by gas chromatography/mass spectrometry to be essentially pure $(Me_2N)_3P$: yield ~85% based on available Me_2N groups.

Preparation of $(CH_2)_3(NCMe_3)_2PCl$. A solution of 6.5 mL (10.2 g, 74 mmol) of phosphorus trichloride in 150 mL of hexane was treated dropwise at 0 °C with stirring with a solution of 26.0 g (140 mmol) of $(CH_2)_3(NHCMe_3)_2$ in 125 mL of hexane. The reaction mixture was boiled under reflux for 72 h. The reaction mixture was then filtered. Hexane was removed from the filtrate at ~25 °C (25 mm) to give 15.0 g (86% yield) of solid $(CH_2)_3(NCMe_3)_2PCl$: mp 220–225 °C; mass spectrum, $(CH_2)_3(NCMe_3)_2PCl^+$ (9), $(CH_2)_3(NCMe_3)(NCMe_2)PCl^+$ (20), $(CH_2)_3(NCMe_3)_2P^+$ (100), $(CH_2)_3(NCMe_3)PCl^+$ (10), $(CH_2)_3N_2(CMe_3)PH^+$ (32), $(CH_2)_3N_2(CMe_2)P^+$ (49), $(CH_2)_3N_2PH_2^+$ (80); ^{31}P NMR $(CDCl_3)$ δ 165.4; ^1H NMR $(CDCl_3)$ δ 3.13 (br, 2 CH_2), 1.9 (br, CH_2), 1.37 (s, 6 CH_3); proton-decoupled ^{13}C NMR $(CDCl_3)$ δ 57.6 (d, J = 20 Hz, 2 CH_2), 40.2 (d, J = 5 Hz, 2 C), 28.3 (d, J = 17 Hz, 6 CH_3), 26.1 (s, CH_2).

Preparation of $(CH_2)_3(NCMe_3)_2PH$. A solution of 9.0 g (36 mmol) of $(CH_2)_3(NCMe_3)_2PCl$ in 100 mL of diethyl ether was treated with 1.4 g (37 mmol) of $LiAlH_4$ at 0 °C. The reaction mixture was then stirred at room temperature for 72 h. Solvent was then removed from the filtered reaction mixture at ~25 °C (25 mm). The turbid residual liquid was extracted with 45 mL of pentane. Solvent was removed from the filtered pentane solution at 25 °C (25 mm). Distillation of the liquid residue gave 4.5 g (58% yield) of $(CH_2)_3(NCMe_3)_2PH$: bp 84–87 °C (1.8–1.9 mm); mass spectrum, $(CH_2)_3(NCMe_3)_2PH^+$ (43), $(CH_2)_3(NCMe_3)_2P^+$ (94), $(CH_2)_3N_2(CMe_3)(CMe_2)PH^+$ (32), $(CH_2)_3N_2(CMe_3)PH^+$ (53), $(CH_2)_3N_2PH_2^+$ (100); ^{31}P NMR (Et_2O) δ 49.7 (J_{PH} = 216 Hz [lit.[7] δ 49.6 (J_{PH} = 214 Hz)].

An attempt to take the ^{31}P NMR spectrum of $(CH_2)_3(NCMe_3)_2PH$ in $CDCl_3$ resulted in an exothermic reaction to give $(CH_2)_3(NCMe_3)_2PCl$, as indicated by the chemical shift of the ^{31}P NMR resonance.

Preparation of $(CH_2)_2(NCMe_3)_2PCl$. A solution of 7.0 mL (11.0 g, 80 mmol) of phosphorus trichloride in 200 mL of hexane was treated dropwise at 0 °C with a solution of 27.0 g (78 mmol) of $(CH_2)_2(NHCMe_3)_2$ in 200 mL of hexane. The reaction mixture was then stirred for 18 h at room temperature and boiled under reflux for 24 h. Removal of solvent from the filtered reaction mixture gave 16 g (87% yield) of brownish solid, shown by gas chromatography/mass spectrometry to be essentially pure $(CH_2)_2(NCMe_3)_2PCl$: mp 75–77 °C; mass spectrum, $(CH_2)_2(NCMe_3)_2PCl^+$ (5), $(CH_2)_2(NCMe_3)(NCMe_2)PCl^+$ (27), $(CH_2)_2(NCMe_3)_2PH_2^+$ (60), $(CH_2)_2(NCMe_2)_2P^+$ (100), $(CH_2)_2NCMe_3PCl^+$ (8), $(CH_2)_2N_2(CMe_3)PH^+$ (29), $(CH_2)_2N_2(CMe_2)P^+$ (59), $(CH_2)_2N_2PH_2^+$ (78); ^{31}P NMR $(CDCl_3)$ δ 169.7; ^1H NMR $(CDCl_3)$ δ 3.40 (d, J = 6 Hz, 2 CH_2) δ 1.41 (d, J = 2 Hz, 6 CH_3); proton-decoupled ^{13}C NMR $(CDCl_3)$ δ 53.9 (d, J = 11 Hz, 2 CH_2), 45.6 (d, J = 10 Hz, 2 C), 29.0 (d, J = 12 Hz, 6 CH_3).

Preparation of $(CH_2)_2(NCMe_3)_2PH$. Tetrahydrofuran (200 mL) kept at −78 °C was treated successively with 2.5 g (66 mmol) of solid $LiAlH_4$ and a solution of 15 g (64 mmol) of $(CH_2)_2(NCMe_3)_2PCl$ in 50 mL of tetrahydrofuran. The pale brown reaction mixture was stirred at −78 °C for 5 h. At this point, the ^{31}P NMR spectrum, run both with and without proton decoupling, indicated the presence of an $(R_2N)_2PH$ derivative. The reaction mixture was stirred at room temperature for 18 h. Solvent was then removed from the reaction mixture at ~25 °C (25 mm). The dark brown residue was extracted with 50 mL of pentane by stirring for 2 h. The pentane solution was filtered from the yellow pasty insoluble material. Removal of pentane from the filtrate at ~25 °C (25 mm), followed by vacuum distillation of the dark brown liquid residue (adding glass wool to minimize frothing), gave 7.0 g (54% yield) of very air-sensitive liquid malodorous $(CH_2)_2(NCMe_3)_2PH$: bp 66–68 °C (1.3–1.4 mm); mass spectrum, $(CH_2)_2(NCMe_3)_2PH^+$ (14), $(CH_2)_2(NCMe_3)_2P^+$ (45), $(CH_2)_2(NCMe_3)(NCMe_2)PH^+$ (8), $(CH_2)_2N_2CMe_3PH^+$ (23), $(CH_2)_2N_2CMe_2PH_2^+$ (13), $(CH_2)_2N_2CMe_2P^+$ (14), $(CH_2)_2N_2PH_2^+$ (100); ^{31}P NMR (pentane) δ 57.9 (J_{PH} = 156 Hz); ^1H NMR (C_6D_6) δ 5.67 (d, J = 156 Hz, PH), 2.85 (m, 2 CH_2), 1.18 (s, 6 CH_3); proton-decoupled ^{13}C NMR (C_6D_6) δ 52.7 (d, J = 12 Hz, 2 CH_2), 49.2 (d, J = 8 Hz, 2 C), 28.9 (d, J = 10 Hz, 6 CH_3); IR ν (PH) 2340 cm^{-1}.

Reaction of $(CH_2)_2(NMe)_2PCl$ with $LiAlH_4$. A solution of 20.0 g (131 mmol) of $(CH_2)_2(NMe)_2PCl$ in 50 mL of diethyl ether was added dropwise at −78 °C to a solution of 5.0 g (132 mmol)

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of LiAlH$_4$ in 150 mL of diethyl ether. The resulting mixture was stirred at room temperature for 24 h. At that point, the proton-decoupled ^{31}P NMR spectrum of the reaction mixture indicated the absence of any unchanged (CH$_2$)$_2$(NMe)$_2$PCl but the presence of a singlet resonance at δ 115.6, which did not split into a doublet when the proton decoupling was turned off. The reaction mixture was filtered from a large quantity of a pasty yellow precipitate. Solvent was removed from the filtrate at ~25 °C (25 mm). The residue was stirred with 50 mL of pentane overnight. The very air-sensitive pentane solution was filtered. Since a ^{31}P NMR spectrum again showed only the component at δ 115.6 and no PH derivative, this reaction mixture was not investigated further.

Reaction of (*i*-Pr$_2$N)$_2$PH with Methanol. A solution of 5.0 g (21.5 mmol) of (*i*-Pr$_2$N)$_2$PH in 30 mL of pentane was treated dropwise at −78 °C with a solution of 2.0 mL (1.6 g, 49.5 mmol) of methanol in 10 mL of pentane. The reaction mixture was stirred for 18 h at room temperature, during which time it gradually became dark brown. Examination of the reaction mixture by proton-coupled ^{31}P NMR indicated a major doublet at δ 106.5 ($J_{\rm PH}$ = 247 Hz), assigned to (*i*-Pr$_2$N)(MeO)PH, as well as weak doublets at δ 172.0 ($J_{\rm PH}$ = 195 Hz) and 43.5 ($J_{\rm PH}$ = 222 Hz), assigned to (MeO)$_2$PH and unreacted (*i*-Pr$_2$N)$_2$PH, respectively. After stirring for an additional 24 h at room temperature, the reaction mixture was filtered, and pentane was removed from the filtrate at ~25 °C (25 mm). Vacuum distillation of the remaining liquid into a receiver cooled to −78 °C gave 3.0 g (86% yield) of very air-sensitive (*i*-Pr$_2$N)(MeO)PH: bp 34–36 °C (2.5–2.6 mm); mass spectrum, (*i*-Pr$_2$N)(MeO)PH$_2^+$ (41), (*i*-Pr$_2$N)(MeO)PH$^+$ (64), (*i*-Pr$_2$N)(MeO)P$^+$ (34), (*i*-Pr$_2$N)POH$^+$ (100), (*i*-Pr$_2$N)PH$^+$ (66), *i*-PrNHPOH$^+$ (100); ^{31}P NMR (pentane) δ 106.5 ($J_{\rm PH}$ = 244 Hz); ^{1}H NMR δ 6.31 (d, J = 248 Hz, PH), 3.4 (m, 2 CH), 3.30 (d, J = 12 Hz, CH$_3$O), 1.13 (dd, J_1 = 7 Hz, J_2 = 1 Hz, 4 CH$_3$); IR ν (PH) 2280 cm^{-1}. This product rapidly turned brown at room temperature and, therefore, could not be shipped intact to an analytical laboratory.

Reaction of (*i*-Pr$_2$N)$_2$PH with Ethanol. A solution of 5.0 g (21.5 mmol) of (*i*-Pr$_2$N)$_2$PH in 25 mL of pentane was treated dropwise at −78 °C with a solution of 2.7 mL (2.13 g, 46 mmol) of ethanol in 10 mL of pentane. The reaction mixture was stirred for 40 h at room temperature. Pentane was removed from the filtered reaction mixture, and the residue was distilled into a receiver cooled to −78 °C to give 3.0 g (79% yield) of (*i*-Pr$_2$N)(EtO)PH: bp 35–40 °C (1.2–1.3 mm); mass spectrum: (*i*-Pr$_2$N)(EtO)PH$_2^+$ (62), (*i*-Pr$_2$N)(EtO)PH$^+$ (79), (*i*-Pr$_2$N)(EtO)P$^+$ (35), (*i*-Pr$_2$N)POCH$_3^+$ (100), (*i*-Pr$_2$N)PH$_3^+$ (100), (*i*-Pr$_2$N)PH$^+$ (76), EtOPNH$_2^+$ (100); ^{31}P NMR (pentane) δ 100.9 ($J_{\rm PH}$ = 242 Hz); ^{1}H NMR (C$_6$D$_6$) 6.62 (d, J = 241 Hz, PH), 3.57 (m, CH$_2$), 3.28 (m, 2 CH), 1.12 (d, J = 7 Hz, 5 CH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 64.5 (d, J = 27 Hz, CH$_2$), 52.4 (d, J = 10 Hz, 2 CH), 24.7 (d, J = 6 Hz, 2 CH$_3$), 24.3 (d, J = 6 Hz, 2 CH$_3$), 17.7 (J = 6 Hz, CH$_3$); IR ν (PH) 2280 cm^{-1}. This product rapidly turned brown upon exposure to air.

Reaction of (*i*-Pr$_2$N)$_2$PH with 2-Propanol. A solution of 5.0 g (21.5 mmol) of (*i*-Pr$_2$N)$_2$PH in 10 mL of pentane was treated dropwise at −78 °C with a solution of 3.5 mL (2.75 g, 45.7 mmol) of 2-propanol in 8 mL of pentane. The reaction mixture was stirred at room temperature for 24 h. Examination of the reaction mixture by proton-coupled ^{31}P NMR at this point indicated a major doublet at δ 95.5 ($J_{\rm PH}$ = 242 Hz), assigned to (*i*-Pr$_2$N)(*i*-PrO)PH, as well as a minor doublet at δ 151.2 ($J_{\rm PH}$ = 201 Hz), assigned to (*i*-PrO)$_2$PH. After the mixture was left standing for an additional 72 h at room temperature, the pentane was removed at ~25 °C (25 mm). Distillation of the brown liquid residue into a receiver cooled to −78 °C gave 4.0 g (97% yield) of colorless liquid (*i*-Pr$_2$N)(*i*-PrO)PH, bp 57–58 °C (2.0–2.1 mm); mass spectrum, (*i*-Pr$_2$N)P$_2$H$_2$(O-*i*-Pr)$_2^+$ (4), (*i*-Pr$_2$N)P$_2$H$_3$O(O-*i*-Pr)$^+$ (30), (*i*-Pr$_2$N)(*i*-PrO)PH$_2^+$ (60), (*i*-Pr$_2$N)(*i*-PrO)PH$^+$ (45), (*i*-Pr$_2$N)(*i*-PrO)P$^+$ (32), (*i*-Pr$_2$N)(EtO)P$^+$ (27), (*i*-Pr$_2$N)PH$_2$OH$^+$ (24), (*i*-Pr$_2$N)POH$^+$ (29), (*i*-Pr$_2$N)PH$_3^+$ (100), (*i*-Pr$_2$N)PH$^+$ (67), (*i*-PrNH)POH$^+$ (36), *i*-PrOPH$_2^+$ (64), *i*-PrNPH$_2$ (40); ^{31}P NMR (pentane) δ 95.4 ($J_{\rm PH}$ = 249 Hz); ^{1}H NMR (benzene) δ 6.42 (d, J = 240 Hz, PH), 3.77 (m, CH), 3.30 (m, 2 CH), 1.12 (d, J = 6 Hz, 6 CH$_3$); IR ν (PH) 2350 cm^{-1}.

Reaction of (*i*-Pr$_2$N)$_2$PH with *tert*-Butyl Alcohol. (a) In Pentane at Room Temperature. A solution of 5.0 g (21.5 mmol) of (*i*-Pr$_2$N)$_2$PH in 10 mL of pentane was treated dropwise at −78 °C with a solution of 4.2 mL (3.3 g, 44.7 mmol) of *tert*-butyl alcohol in 10 mL of pentane. The reaction mixture was stirred for a total of 10 days at room temperature, occasionally analyzing the reaction mixture by ^{31}P NMR. After 3 days, the ^{31}P NMR spectrum showed approximately equal amounts of (*i*-Pr$_2$N)(Me$_3$CO)PH and unchanged (*i*-Pr$_2$N)$_2$PH, whereas after 7 days, the observed (*i*-Pr$_2$N)(Me$_3$CO)PH/(*i*-Pr$_2$N)$_2$PH ratio was 6:1. Even after the 10-day reaction period, the reaction mixture did not turn the dark brown color characteristic of (*i*-Pr$_2$N)$_2$PH reactions with less hindered alcohols. After completion of the reaction, the pentane was removed at ~25 °C (25 mm). Distillation of the residual yellow liquid into a receiver cooled to −78 °C gave colorless liquid (*i*-Pr$_2$N)(Me$_3$CO)PH, bp 47–49 °C (1.1–1.2 mm); mass spectrum: (*i*-Pr$_2$N)P$_2$H$_3$O(OCMe$_3$)$^+$ (1), (*i*-Pr$_2$N)(Me$_3$CO)PH$_2^+$ (3), (*i*-Pr$_2$N)PH$_2$OH$^+$ (16), (*i*-Pr$_2$N)PHOH$^+$ (52), (*i*-Pr$_2$N)POH$^+$ (15), (*i*-Pr$_2$N)PH$_3^+$ (100), (*i*-Pr$_2$N)PH$^+$ (35); ^{31}P NMR (pentane) δ 81.0 ($J_{\rm PH}$ = 242 Hz); IR ν (PH) 2280 cm^{-1}.

(b) In Boiling Benzene. A mixture of 6.0 g (25.8 mmol) of (*i*-Pr$_2$N)$_2$PH, 12.0 mL (9.5 g, 128 mmol) of *tert*-butyl alcohol, and 35 mL of benzene was boiled under reflux for 7 days. The ^{31}P NMR spectra of the reaction mixture suggested the presence of a mixture of (Me$_3$CO)$_2$PH [δ 115.0 ($J_{\rm PH}$ = 205 Hz)] and (Me$_3$CO)$_2$P(O)H [δ −3.9 ($J_{\rm PH}$ = 679 Hz); lit.[16] δ −3.8 ($J_{\rm PH}$ = 678 Hz)]. Distillation of the reaction mixture gave a colorless liquid, bp 63–64 °C (2.2–2.3 mm), indicated by its ^{31}P NMR spectrum to contain ~97% (Me$_3$CO)$_2$P(O)H and ~3% (Me$_3$CO)$_2$PH.

Reaction of (Et$_2$N)$_2$PH with Ethanol. A solution of 4.0 g (22.7 mmol) of freshly distilled (Et$_2$N)$_2$PH in 10 mL of pentane at −78 °C was treated dropwise with a solution of 2.6 mL (2.1 g, 44.5 mmol) of ethanol in 10 mL of pentane. Analysis of the reaction mixture after 5 h by ^{31}P NMR indicated the presence of (EtO)$_2$PH [δ 161.1 ($J_{\rm PH}$ = 197 Hz)] and (Et$_2$N)(EtO)PH [δ 121.6 ($J_{\rm PH}$ = 234 Hz)]. Attempts to isolate these products by vacuum distillation into a receiver cooled to −78 °C gave a few drops of liquid, bp 24 °C (1.5 mm), indicated by ^{31}P NMR to be mainly (EtO)$_2$PH and a few more drops of liquid, bp 40 °C (1.5 mm) indicated by ^{31}P NMR to be a mixture of approximately equal quantitites of (EtO)$_2$PH and (Et$_2$N)(EtO)PH. These liquids rapidly turned brown at room temperature and, therefore, were too unstable for detailed study.

Reaction of (Et$_2$N)$_2$PH with *tert*-Butyl Alcohol. A solution of 4.0 g (22.7 mmol) of freshly distilled (Et$_2$N)$_2$PH in 10 mL of pentane at −78 °C was treated dropwise with a solution of 10.0 mL (7.9 g, 107 mmol) of *tert*-butyl alcohol in 10 mL of pentane. After the solution was stirred at room temperature for 24 h, the ^{31}P NMR spectrum indicated that all of the (Et$_2$N)$_2$PH had reacted to form a mixture of (Et$_2$N)(Me$_3$CO)PH [δ 106.7 ($J_{\rm PH}$ = 254 Hz)], (Me$_3$CO)$_2$PH [δ 114.9 ($J_{\rm PH}$ = 205 Hz)], and (Me$_3$CO)$_2$P(O)H [δ −4.1 ($J_{\rm PH} \approx$ 700 Hz)]. Attempts to isolate a pure product by vacuum distillation led to decomposition.

Reaction of (CH$_2$)$_2$(NCMe$_3$)$_2$PH with *tert*-Butyl Alcohol. A solution of 6.0 g (29.7 mmol) of (CH$_2$)$_2$(NCMe$_3$)$_2$PH in 25 mL of pentane was treated dropwise at −78 °C with a solution of 2.6 mL (2.0 g, 27.7 mmol) of *tert*-butyl alcohol in 10 mL of pentane. After the solution was stirred for 18 h at room temperature, the ^{31}P NMR spectrum of the reaction mixture showed unchanged (CH$_2$)$_2$(NCMe$_3$)$_2$PH at δ 58.0 ($J_{\rm PH}$ = 159 Hz), a PH compound at δ 88.9 ($J_{\rm PH}$ = 247 Hz), and a third component without a PH bond at δ 114.1. The reaction mixture was then boiled under reflux for 18 h. The ^{31}P NMR spectrum then showed that almost all of the (CH$_2$)$_2$(NCMe$_3$)$_2$PH had disappeared to give the other two components listed above plus (Me$_3$CO)$_2$PH [δ 115.1 ($J_{\rm PH}$ = 205 Hz)]. Solvent was removed from the filtered reaction mixture, and the residue was distilled under vacuum to give 2.5 g (100% yield based on *tert*-butyl alcohol) of (Me$_3$CO)$_2$PH, bp 55–60 °C (1.9–2.0 mm).

A similar reaction of (CH$_2$)$_2$(NCMe$_3$)$_2$PH with ethanol in C$_6$D$_6$ solution in an NMR tube at ambient temperature clearly gave (EtO)$_2$PH [δ 160.0 ($J_{\rm PH}$ = 195 Hz)] as indicated by its ^{31}P NMR spectrum.

Preparation of (Et$_2$N)$_2$PCH═CH$_2$. A solution of 0.4 mol of vinylmagnesium bromide in 250 mL of tetrahydrofuran was treated dropwise at 0 °C with 58 g (0.275 mol) of (Et$_2$N)$_2$PCl. The reaction mixture was then stirred overnight at room temperature and boiled under reflux for 3 h. The resulting brown mixture was hydrolyzed with a mixture of 130 g (0.44 mmol) of ethylenediaminetetraacetic acid, 75 g (1.87 mol) of sodium hydroxide, 800 mL of deoxygenated water, and 150 mL of diethyl ether. The upper ether layer was washed with aqueous sodium chloride, and the aqueous layer was washed with diethyl ether. The combined diethyl ether solutions were dried over potassium carbonate and then distilled to give 28 g (50% yield) of colorless liquid $(Et_2N)_2PCH{=}CH_2$: bp 65–70 °C (1.4–1.6 mm); mass spectrum, $(Et_2N)_2PCH{=}CH_2^+$ (64), $(Et_2N)_2P^+$ (24), $Et_2NPCH{=}CH_2^+$ (100), Et_2NPH^+ (60); ^{31}P NMR (tetrahydrofuran) δ 89.9; ^1H NMR ($CDCl_3$) $\delta \sim 6.0$ (m, =CH), ~ 5.5 (m, $=CH_2$), 3.05 (quintet, J = 8 Hz, 4 CH_2), 1.04 (t, J = 7 Hz, 4 CH_3); proton-decoupled ^{13}C NMR ($CDCl_3$) δ 139.9 (s, =CH), 123.9 (d, J = 15 Hz, $=CH_2$), 42.8 (d, J = 17 Hz, 4 CH_2), 14.9 (d, J = 4 Hz, 4 CH_3).

Preparation of $(CH_2)_3(NCMe_3)_2PCH{=}CH_2$. A solution of 0.1 mol of vinylmagnesium bromide in 250 mL of tetrahydrofuran was treated dropwise at −78 °C with a solution of 15.0 g (0.06 mol) of $(CH_2)_3(NCMe_3)_2PCl$ in 50 mL of tetrahydrofuran. The reaction mixture was stirred overnight at room temperature and then boiled under reflux for 3 h. Hydrolysis with a mixture of 25 g of sodium hydroxide, 35 g of ethylenediaminetetraacetic acid, 100 mL of diethyl ether, and 150 mL of deoxygenated water, followed by vacuum distillation similar to the procedure given above for the preparation of $(Et_2N)_2PCH{=}CH_2$, gave 5.0 g (34% yield) of colorless liquid $(CH_2)_3(NCMe_3)_2PCH{=}CH_2$, bp 80–85 °C (0.7–0.8 mm); ^{31}P NMR (pentane) δ 56.4.

Preparation of $(i\text{-}Pr_2N)_2PCH{=}CH_2$. A solution of 0.08 mol of vinylmagnesium bromide in 250 mL of tetrahydrofuran was treated dropwise at −78 °C with a solution of 10.0 g (0.038 mol) of $(i\text{-}Pr_2N)_2PCl$ in 50 mL of tetrahydrofuran. The reaction mixture was stirred overnight at room temperature and then boiled under reflux for 6 h. Hydrolysis with a mixture of 18.4 g of sodium hydroxide, 32 g of ethylenediaminetetraacetic acid, 150 mL of deoxygenated water, and 100 mL of diethyl ether, followed by distillation similar to the procedure given above for the preparation of $(Et_2N)_2PCH{=}CH_2$ gave 6.3 g (65% yield) of colorless liquid $(i\text{-}Pr_2N)_2PCH{=}CH_2$: bp 77–80 °C (0.3 mm); mp 26–27 °C; mass spectrum, $(i\text{-}Pr_2N)_2PCH{=}CH_2^+$ (23), $i\text{-}Pr_2NPCH{=}CH_2^+$ (100), $i\text{-}PrNHPCH{=}CH_2^+$ (54); ^{31}P NMR ($CDCl_3$) δ 53.1; ^1H NMR ($CDCl_3$) δ 6.4 (m, =CH), 5.6 (m, $=CH_2$), ~ 3.4 (br, 2 CH), ~ 1.2 (t, J = 7 Hz, 4 CH_3); proton-decoupled ^{13}C NMR ($CDCl_3$) δ 142.4 (d, J = 2 Hz, =CH), 122.5 (d, J = 23 Hz, $=CH_2$), 47.5 (d, J = 11 Hz, 2 CH), 24.6 (d, J = 11 Hz, 2 CH_3), 24.3 (d, J = 12 Hz, 2 CH_3).

Preparation of $(Et_2N)_2PCH_2CH_2P(NEt_2)_2$. A mixture of 5.0 g (28.4 mmol) of freshly distilled $(Et_2N)_2PH$, 0.1 g of potassium hydride, 6.0 mL (5.7 g, 28.2 mmol) of $(Et_2N)_2PCH{=}CH_2$, and 40 mL of tetrahydrofuran was boiled under reflux for 9 days. Solvent was removed from the filtered brown reaction mixture at 25 °C (25 mm). Vacuum distillation of the residual brown liquid gave 8.0 g (75% yield) of pale yellow $(Et_2N)_2PCH_2CH_2P(NEt_2)_2$: bp 135–140 °C (0.005–0.025 mm); mass spectrum, $(Et_2N)_2PCH_2CH_2P(NEt_2)_2^+$ (3), $(Et_2N)_2PCH_2CH_2PHNEt_2^+$ (10), $(Et_2N)_2PCH_2CH_2PNEt_2^+$ (14), $Et_2NPCH_2CH_2PHNEt_2$ (19), $Et_2NPCH_2CH_2PNEt_2^+$ (15), $(Et_2N)_2P^+$ (91), Et_2NPH^+ (100); ^{31}P NMR (pentane) δ 91.1; ^1H NMR (C_6H_6) δ 2.97 (br, 8 CH_2), 1.56 (t, J = 6 Hz, 2 CH_2), 0.98 (t, J = 7 Hz, 8 CH_3); proton-decoupled ^{13}C NMR ($CDCl_3$) δ 42.5 (8 CH_2), 22.8 (t, 2 CH_2), 15.1 (8 CH_3); IR 2960 (s), 2928 (s), 2850 (s), 1460 (m), 1372 (s), 1341 (m), 1290 (m), 1190 (s), 1097 (w), 1054 (m), 1011 (s), 913 (s), 799 (m), 685 (m), 658 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{44}N_4P_2$: C, 57.1; H, 11.7; N, 14.8. Found: C, 57.2; H, 11.7; N, 14.6.

This product solidified upon storage in a −10 °C freezer.

Preparation of $(CH_2)_3(NCMe_3)_2PCH_2CH_2P(NCMe_3)_2(CH_2)_3$. A mixture of 4.8 g (20 mmol) of $(CH_2)_3(NCMe_3)_2PCH{=}CH_2$, 20 mL of tetrahydrofuran, $\sim$0.1 g of ether-washed potassium hydride, and 4.0 g (19 mmol) of $(CH_2)_3(NCMe_3)_2PH$ was boiled under reflux for 8 days. Volatile materials were removed from the reaction mixture by distillation at temperatures up to 115 °C (0.01 mm). The distillation residue was extracted with pentane. Evaporation of pentane from the filtered extract gave 4.0 g (44% yield) of pale yellow $(CH_2)_3(NCMe_3)_2PCH_2CH_2P(NCMe_3)_2(CH_2)_3$. The analytical sample, a colorless solid, mp 89–91 °C, was obtained from this crude product by sublimation at 110 °C (0.01 mm): ^{31}P NMR ($CDCl_3$) δ 61.8; proton-decoupled ^{13}C NMR ($CDCl_3$) δ 54.5 (t, 4 CH_2), 38.6 (s, 4 C), 30.1 (12 CH_3 + 2 CH_2), 20.5 (s, 2 CH_2). Anal. Calcd for $C_{24}H_{52}N_4P_2$: C, 62.8; H, 11.4; N, 12.2. Found: C, 63.0; H, 11.5; N, 12.0.

Reaction of $(i\text{-}Pr_2N)_2PH$ with $(i\text{-}Pr_2N)_2PCH{=}CH_2$. (a) With a Base Catalyst. A mixture of 5.0 g (22 mmol) of $(i\text{-}Pr_2N)_2PH$, $\sim$0.1 g of potassium hydride, 6.0 g (23 mmol) of $(i\text{-}Pr_2N)_2PCH{=}CH_2$, and 70 mL of tetrahydrofuran was boiled under reflux for 7 days. Periodic analysis of the reaction mixture by gas chromatography/mass spectrometry indicated the presence of unchanged starting materials in equal quantities, indicating the absence of significant amounts of addition. Similar results were obtained in boiling dioxane.

(b) With a Free Radial Initiator. A mixture of 0.1 g of 2,2′-azobis[2-methylpropionitrile], 6.0 g (23 mmol) of $(i\text{-}Pr_2N)_2PCH{=}CH_2$, and 5.0 g (22 mol) of $(i\text{-}Pr_2N)_2PH$ was heated in an oil bath at 100–110 °C for 4 days. Analysis of this reaction mixture by gas chromatography/mass spectrometry indicated only the presence of unchanged starting materials. Therefore, an additional 0.3 g of 2,2′-azobis[2-methylpropionitrile] was added, and the reaction mixture was heated in an oil bath at 160–170 °C for 4 days. Again, analysis of the reaction mixture indicated only unchanged starting materials.

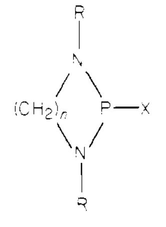
Results and Discussion

Our initial attempts to prepare acyclic silicon-free $(R_2N)_2PH$ derivatives were directed toward $(i\text{-}Pr_2N)_2PH$ with the idea that the bulky isopropyl groups would protect the product from unwanted decomposition reactions. However, an attempt to convert $(i\text{-}Pr_2N)_2PCl$ to $(i\text{-}Pr_2N)_2PH$ with tri-*n*-butyltin hydride similar to the reported procedure[7] for the preparation of the cyclic $R'C_3H_5(NR)_2PH$ derivatives gave $i\text{-}Pr_2NH$ and $n\text{-}Bu_3SnCl$ as the only volatile products, with no spectroscopic evidence for the production of any PH derivatives. The phosphorus introduced into this reaction appeared in an orange solid product insoluble in pentane and of uncertain composition.

In view of the failure to obtain any $(i\text{-}Pr_2N)_2PH$ from the reaction of $(i\text{-}Pr_2N)_2PCl$ with $n\text{-}Bu_3SnH$, we next tried the reaction of $(i\text{-}Pr_2N)_2PCl$ with $LiAlH_4$. This reaction was considerably more successful, leading to the formation of reasonable yields of $(i\text{-}Pr_2N)_2PH$ as an air-sensitive liquid, which could easily be isolated from the reaction mixture by vacuum distillation. Most definitive in the characterization of $(i\text{-}Pr_2N)_2PH$ are its mass spectrum and its ^{31}P NMR spectrum run with and without proton decoupling in order to demonstrate that the observed resonance arises from a phosphorus atom directly bonded to hydrogen.

The reactions between $(R_2N)_2PCl$ and $LiAlH_4$ to give $(R_2N)_2PH$ appear to depend on the size of the R_2N groups. Thus, the reaction of $(Et_2N)_2PCl$ with $LiAlH_4$ gives a relatively small yield (30% maximum) of the corresponding $(Et_2N)_2PH$, with some evidence for the formation of slightly volatile phosphorus–aluminum byproducts (possible $(Et_2N)_3P\cdot AlH_3\cdot nOEt_2$), which have not been fully characterized. The reaction of $(Me_2N)_2PCl$ with $LiAlH_4$ gives no evidence for the formation of any $(Me_2N)_2PH$. Instead, the available dimethylamino groups in this reaction redistribute almost quantitatively to form $(Me_2N)_3P$. We thus suspect that a key to the relatively good yield of $(i\text{-}Pr_2N)_2PH$ from the reaction of $(i\text{-}Pr_2N)_2PCl$ with $LiAlH_4$ is the inability of three relatively bulky diisopropylamino groups to fit easily around a single phosphorus atom to form $(i\text{-}Pr_2N)_3P$, thereby inhibiting redistribution reactions leading to product destruction.

Similar steric effects influence the reactions of the cyclic phosphorus–nitrogen derivatives $(CH_2)_n(NR)_2PCl$ (II, X = Cl; n = 2 and 3) with $LiAlH_4$. Thus, reactions of the relatively hindered *tert*-butyl derivatives $(CH_2)_n(NCMe_3)_2PCl$ (II, X = Cl; R = *tert*-butyl; n = 2 and 3) with



II

$LiAlH_4$ lead to the corresponding $(CH_2)_n(NCMe_3)_2PH$ derivatives (II, X = H; R = *tert*-butyl; n = 2 and 3). The properties of the trimethylene derivative $(CH_2)_3(NCMe_3)_2PH$ are identical with those reported by the Russian group,[7] who obtained this compound from the reaction of $(CH_2)_3(NCMe_3)_2PCl$ with n-Bu_3SnH, as discussed above. The reaction of the much less hindered methyl derivative $(CH_2)_2(NMe)_2PCl$ (II, X = Cl; R = methyl; n = 2) with $LiAlH_4$ failed to give any evidence for the formation of the corresponding $(CH_2)_2(NMe)_2PH$, as indicated by the ^{31}P NMR spectrum of the reaction mixture, which did not show any species containing phosphorus directly bonded to hydrogen.

A characteristic reaction of bis(dialkylamino)phosphines, $(R_2N)_2PH$, is the successive alcoholysis of the two R_2N groups to give $(R_2N)(R'O)PH$ and $(R'O)_2PH$ without destruction of the phosphorus–hydrogen bond. These reactions were followed by ^{31}P NMR with and without proton decoupling so that phosphorus atoms directly bonded to hydrogen could be distinguished from phosphorus atoms not bonded to hydrogen. The most detailed such studies were made on the reactions of $(i\text{-}Pr_2N)_2PH$ with methanol, ethanol, 2-propanol, and *tert*-butyl alcohol. The rates of these reactions appear to decrease as the size of the alcohol increases, as expected. In general, the products $(i\text{-}Pr_2N)(R'O)PH$ [R' = CH_3, C_2H_5, $(CH_3)_2CH$, and $(CH_3)_3C$] can be isolated by distillation as air-sensitive liquids, characterized by their NMR and mass spectra. However, the mass spectra of the $(i\text{-}Pr_2N)(R'O)PH$ derivatives are complicated by an apparent condensation to the diphosphines $(i\text{-}Pr_2N)P_2H(OR')_2$ with diisopropylamine elimination; the possibility of carrying out this condensation on a preparative scale by pyrolysis is currently under investigation. The products $(R'O)_2PH$ decomposed upon attempted isolation and, thus, were identified only from the ^{31}P NMR spectra of the crude reaction mixtures. Attempted reaction of $(i\text{-}Pr_2N)_2PH$ with excess *tert*-butyl alcohol under forcing conditions (boiling benzene for 1 week) in an effort to isolate $(Me_3CO)_2PH$ led instead to its oxidation product $(Me_3CO)_2P(O)H$, identified by comparison of its ^{31}P NMR parameters with those reported[16] in the literature. However, $(Me_3CO)_2PH$ appeared to be distillable as a very air-sensitive liquid from the reaction of $(CH_2)_2(NCMe_3)_2PH$ with excess *tert*-butyl alcohol. Some alcoholysis reactions of $(Et_2N)_2PH$ were also investigated, but these were less successful owing to the lower stability of $(Et_2N)_2PH$ and $(Et_2N)(R'O)PH$ derivatives relative to their diisopropylamino analogues.

One of the original motivations for developing the chemistry of bis(dialkylamino)phosphines as outlined in this paper was the desire for new reagents to prepare poly(phosphines) having phosphorus–nitrogen bonds, which, because of their potential chemical reactivity, could provide sources of novel chelating ligands exhibiting diverse π-acceptor properties. In this connection, the base-catalyzed addition of $(R_2N)_2PH$ to $(R_2N)_2PCH{=}CH_2$ has been shown to give the corresponding diphosphines $(R_2N)_2PCH_2CH_2P(NR_2)_2$, provided that the R_2N groups are not too large [i.e., $(R_2N)_2$ = $(Et_2N)_2$ or $(CH_2)_3(NCMe_3)_2$]. However, the corresponding addition of $(i\text{-}Pr_2N)_2PH$ to $(i\text{-}Pr_2N)_2PCH{=}CH_2$ failed to give any $(i\text{-}Pr_2N)_2PCH_2CH_2P(N\text{-}i\text{-}Pr_2)_2$ under either base-catalyzed (KH) or free-radical-catalyzed (2,2'-azobis[2-methylpropionitrile]) conditions, apparently because of greater effective steric hindrance of the diisopropylamino groups relative to either the diethylamino or $(CH_2)_3(NCMe_3)_2$ group. The lower steric hindrance of the $(CH_2)_3(NCMe_3)_2$ group relative to two diisopropylamino groups is also suggested by the observation that $(CH_2)_3(NCMe_3)_2PH$ (II, X = H; R = *tert*-butyl; n = 2) reacts exothermically with $CDCl_3$ to give $(CH_2)_3(NCMe_3)_2PCl$ under conditions where $(i\text{-}Pr_2N)_2PH$ does not react with $CDCl_3$, as indicated by ^{31}P NMR spectra.

The characterization of new compounds prepared during the course of this research depends largely upon their mass spectra and NMR spectra, since all new compounds, except for the diphosphines $(R_2N)_2PCH_2CH_2P(NR_2)_2$, are too sensitive to be shipped intact to analytical laboratories. During the course of investigating these spectra, the following interesting features were observed. (1) The methyl groups in (diisopropylamino)phosphorus derivatives, such as $(i\text{-}Pr_2N)_2PH$, $(i\text{-}Pr_2N)_2PCH{=}CH_2$, and $(i\text{-}Pr_2N)(EtO)PH$, exhibit three or four ^{13}C NMR peaks. Since coupling of the methyl carbons to the single phosphorus atom can only lead to a doublet, this indicates two different types of methyl groups. However, the limited symmetry around the nitrogen atom in a diisopropylamino group makes the two methyl groups diastereotopic, leading theoretically to four peaks when the diisopropylamino group is bonded to a spin $^1/_2$ phosphorus atom. In some cases, the central two of the theoretical four methyl ^{13}C NMR peaks in a (diisopropylamino)phosphorus group overlap, leading to an apparent "triplet". (2) The $|^1J_{PH}|$ coupling constants are 249–259 Hz in the acyclic $(R_2N)_2PH$ derivatives (R = ethyl and isopropyl) but decrease to 216 Hz in the six-membered ring derivative $(CH_2)_3(NCMe_3)_2PH$ (II, X = H; R = *tert*-butyl; n = 3) and to 156 Hz in the five-membered ring derivative $(CH_2)_2(NCMe_3)_2PH$ (II, X = H; R = *tert*-butyl; n = 2). Apparently, as the size of the C_nN_2P ring decreases from 6 (n = 3) to 5 (n = 2) the s character of the P–H bond decreases, leading to a decrease in the $|^1J_{PH}|$ coupling constant. Such an effect of $|^1J_{PH}|$ on the size of the ring containing the phosphorus atom does not seem to have been previously reported. The $|^1J_{PH}|$ coupling constants fall in the range 241–249 Hz for the derivatives $(i\text{-}Pr_2N)(R'O)PH$ and in the range 195–205 Hz for the derivatives $(R'O)_2PH$. (3) The mass spectra of $(CH_2)_n(NCMe_3)_2PCl$ (II, X = Cl; R = *tert*-butyl; n = 2 and 3) exhibit the ions $(CH_2)_nNCMe_3PCl^+$ in significant abundance, suggesting the facile loss of one of the two ring nitrogens, along with its associated *tert*-butyl group.

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Registry No. $(i\text{-}Pr_2N)_2PCl$, 56183-63-2; $(Et_2N)_2PCl$, 685-83-6; $(Me_2N)_2PCl$, 3348-44-5; $(CH_2)_3(NCMe_3)_2PCl$, 55342-76-2; $(CH_2)_2(NCMe_3)_2PCl$, 89437-94-5; $(CH_2)_2(NMe)_2PCl$, 6069-36-9; $(i\text{-}Pr_2N)_2PH$, 86660-77-7; $(i\text{-}Pr_2N)_2PD$, 89437-93-4; $(Et_2N)_2PH$,

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41291-42-3; $(CH_2)_3(NCMe_3)_2PH$, 55342-78-4; $(CH_2)_2(NCMe_3)_2PH$, 89437-95-6; $(i\text{-}Pr_2N)(MeO)PH$, 89437-96-7; $(MeO)_2PH$, 20502-63-0; $(i\text{-}Pr_2N)(EtO)PH$, 89437-97-8; $(i\text{-}Pr_2N)(i\text{-}PrO)PH$, 89437-98-9; $(i\text{-}PrO)_2PH$, 88542-86-3; $(i\text{-}Pr_2N)(Me_3CO)PH$, 89437-99-0; $(Me_3CO)_2PH$, 2171-76-8; $(Me_3CO)_2P(O)H$, 13086-84-5; $(Et_2N)(EtO)PH$, 89438-00-6; $(EtO)_2PH$, 20502-85-6; $(Et_2N)(Me_3CO)PH$, 89438-01-7; $(Et_2N)_2PCH{=}CH_2$, 89438-02-8; $(CH_2)_3(NCMe_3)_2PCH{=}CH_2$, 89438-03-9; $(i\text{-}Pr_2N)_2PCH{=}CH_2$, 89438-04-0; $(Et_2N)_2PCH_2CH_2P(NEt_2)_2$, 86926-28-5; $(CH_2)_3(NCMe_3)_2PCH_2CH_2P(NCMe_3)_2(CH_2)_3$, 89438-05-1; PCl_3, 7719-12-2; $i\text{-}Pr_2NH$, 108-18-9; Et_2NH, 109-89-7; $(CH_2)_3(NHCMe_3)_2$, 22687-38-3; $(CH_2)_2(NHCMe_3)_2$, 4062-60-6; MeOH, 67-56-1; EtOH, 64-17-5; $i\text{-}PrOH$, 67-63-0; Me_3COH, 75-65-0; $(Me_2N)_3P$, 1008-26-0; $LiAlH_4$, 16853-85-3; $CH_2{=}CHBr$, 593-60-2.

Correct Structures of Montanin C, Teupolin I, and 12-*epi*-Teucvin, Three (12*R*)-Neoclerodan-20,12-olides Isolated from the *Teucrium* Species

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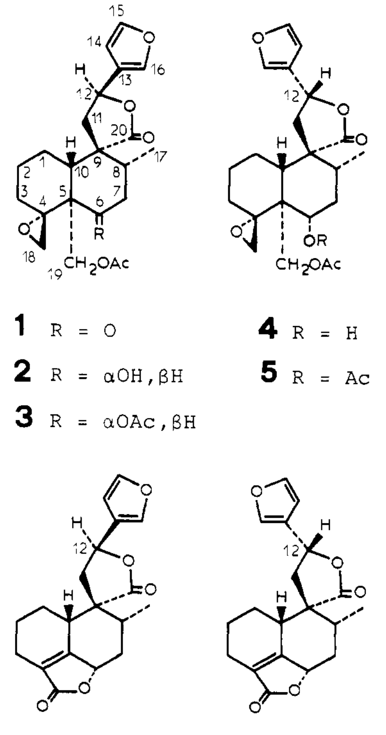
The previously assigned C-12(*S*) configuration for teupolin I (**2**) and montanin C (**3**) must be amended to C-12(*R*) (**4** and **5**, respectively) as the result of extensive ^1H and ^{13}C NMR spectroscopic studies, chemical correlations, and an X-ray diffraction analysis of montanin C which provided only its relative configuration. In addition, the structure of a new diterpenoid, 12-*epi*-teucvin (**7**), which also possesses a C-12(*R*) stereochemistry, has been ascertained. Comparative studies between three pairs of C-12 epimers allowed us to establish some criteria for determining the stereochemistry at C-12 of neoclerodan-20,12-olide derivatives by means of ^1H and ^{13}C NMR spectroscopy. In particular, the compounds with a C-12(*R*) configuration showed a clear NOE between the C-17 and the C-12 protons, which was not observed in the epimers belonging to the C-12(*S*) series.

A large number of diterpenoids with the clerodane skeleton have been isolated from plants in the last few years.[2] Interest in these compounds has been stimulated by their biological activity as insect antifeedants and as antitumor, antimicrobial, and antifungal agents.[3] The *Teucrium* species (family Labiatae) have afforded a number of neoclerodane and 19-norneoclerodane diterpenoids,[4] some with unusual and fascinating structures.[4d-f]

Two years ago[5] we established the structure of the diterpenoid 19-acetylgnaphalin (**1**, Chart I) by means of an X-ray diffraction analysis, and we pointed out that the sodium borohydride reduction of **1** yielded a compound (**2**) which could, in principle, be identical with teupolin I, a diterpenoid previously isolated from *Teucrium polium*,[6] although some of their physical data did not entirely agree. At the same time we pointed out that the acetyl derivative **3** had physical and spectral data which differed from those reported[7] for montanin C, another diterpenoid found in *Teucrium montanum*, to which structure **3** had been repeatedly attributed.[6-8] Shortly afterwards, Miyase and

Chart I



1 R = O

2 R = αOH, βH

3 R = αOAc, βH

4 R = H

5 R = Ac

6

7

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