

Tetrakis(dialkylamino)cyclotetraphosphines and Bis(dialkylamino)dihalobiphosphines^{1,2}

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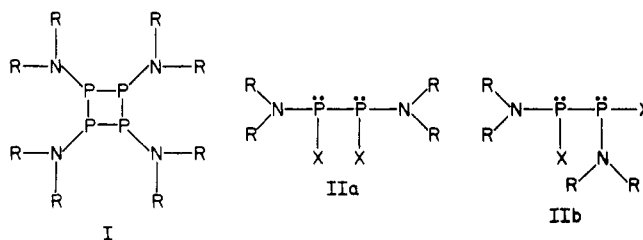
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Dehalogenation of R_2NPCl_2 (R = isopropyl or cyclohexyl) with magnesium in tetrahydrofuran gives the corresponding cyclotetraphosphines $(R_2N)_4P_4$; the corresponding biphosphines $(i-Pr_2N)_2P_2X_2$ (X = Cl and Br) can be isolated from reactions of $i-Pr_2NPX_2$ with more limited quantities of magnesium. Dehalogenations with magnesium of R_2NPCl_2 derivatives having R_2N groups smaller than diisopropylamino lead to redistribution of the dialkylamino groups giving $(R_2N)_2P-P(NR_2)_2$ (R_2N = piperidino) or $(R_2N)_3P$ (R_2N = diethylamino or dimethylamino). Such redistribution reactions can be suppressed but not eliminated by using the homogenous dehalogenating agent $(Me_3Si)_2Hg$ in hydrocarbon solvents. The steric bulk of the diisopropylamino groups in $(i-Pr_2N)_4P_4$ reduces its chemical reactivity relative to other cyclotetraphosphines; thus $(i-Pr_2N)_4P_4$ is unreactive toward oxygen, carbon disulfide, potassium metal, and various metal carbonyls [e.g., $Cr(CO)_6$, $Mo(CO)_6$, and $Fe_2(CO)_9$] under conditions where other cyclotetraphosphines react with these reagents. However, the P_4 ring in $(i-Pr_2N)_4P_4$ is cleaved under mild conditions by hydrogen chloride as well as by bromine and iodine.

Cyclopolyphosphines of the type R_nP_n having exocyclic phosphorus-carbon bonds are well-known.^{3,4} However, at the time this research was initiated little was known about cyclopolyphosphines having exocyclic bonds from the ring phosphorus atoms to atoms other than carbon. The objective of this research was to study the preparation of per(dialkylamino)cyclopolyphosphines, $(R_2N)_nP_n$, by the dehalogenation of (dialkylamino)dihalobiphosphines, R_2NPX_2 . Such per(dialkylamino)cyclopolyphosphines are of interest both for reagents in synthetic organophosphorus chemistry because of the potential reactivity of their phosphorus-nitrogen and phosphorus-phosphorus bonds as well as for ligands in transition metal coordination chemistry because of the potential availability of donor electron pairs on both their phosphorus and nitrogen atoms.

In a preliminary communication¹ we reported the preparation of tetrakis(diisopropylamino)cyclotetraphosphine, $(i-Pr_2N)_4P_4$ (I, R = isopropyl), by the dehalogenation of $i-Pr_2NPX_2$ with magnesium. At about the same time Niecke and Rüger⁵ reported the preparation of tetrakis[bis(trimethylsilyl)amino]cyclotetraphosphine (I, R = Me_3Si) from the 2 + 2 cyclodimerization of the corresponding diphosphene $(Me_3Si)_2NP=PN(SiMe_3)_2$. This paper presents the details of the preparation and properties of the tetrakis(dialkylamino)cyclotetraphosphines, $(R_2N)_4P_4$ (I, R = isopropyl and cyclohexyl), as well as the bis(diisopropylamino)dihalobiphosphines $(i-Pr_2N)_2P_2X_2$ (II, X = Cl and Br, R = isopropyl) which are intermediates in the magnesium dehalogenations of $i-Pr_2NPX_2$. In addition a systematic study is presented on reactions of R_2NPCl_2 derivatives having R_2N groups of diverse sizes with both the heterogeneous dehalogenating agent magnesium and the homogeneous dehalogenating agent $(Me_3Si)_2Hg$.⁶



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 with proton decoupling for the phosphorus-31 and carbon-13 spectra. Chemical shifts (δ) are reported in ppm downfield 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 by using the ions containing ³⁵Cl and ⁷⁹Br for the chlorine- and bromine-containing ions, respectively.

All reactions were carried out in an efficient hood by using aqueous calcium hypochlorite traps to decompose noxious material 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 $(Me_3Si)_2Hg$; (c) filling evacuated vessels containing potentially air-sensitive materials. When necessary Schlenk ware⁷ or a polyethylene glove bag was used to provide the nitrogen atmosphere. Before use all solvents were distilled under nitrogen over appropriate drying agents (Na/benzophenone or metal hydrides except for chlorinated solvents).

The (dialkylamino)dihalobiphosphines, R_2NPX_2 , were prepared from commercially available secondary amines and phosphorus trihalides by using procedures described elsewhere.⁸ Samples used for this work were distilled and their purities and identities were checked by phosphorus-31 NMR and gas chromatography/mass spectrometry before use. The mercury reagent $(Me_3Si)_2Hg$ was freshly prepared from sodium amalgam and trimethylchlorosilane by the published procedure.^{9,10}

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(2) Portions of this work were presented at the 185th National Meeting of the American Chemical Society, Seattle, WA, March, 1983; the International Conference on Phosphorus Chemistry, Nice, France, September, 1983, and the 188th National Meeting of the American Chemical Society, Philadelphia, PA, August, 1984.

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Preparation of (*i*-Pr₂N)₄P₄. A suspension of 9.72 g (400 mmol) of magnesium turnings in 250 mL of tetrahydrofuran containing a crystal of iodine was treated dropwise over 90 min with mechanical stirring with a solution of 50.5 g (250 mmol) of *i*-Pr₂NPCl₂ in 150 mL of tetrahydrofuran. The color of the solution became light yellow. The reaction mixture was then boiled overnight under reflux with mechanical stirring thereby becoming dark yellow. After cooling to room temperature the reaction mixture was poured into a deoxygenated ice-cold solution of 80.2 g (275 mmol) of ethylenediaminetetraacetic acid and 46.2 g (1156 mmol) of sodium hydroxide in 500 mL of water. After stirring for 15–20 min, the tetrahydrofuran layer was separated. The aqueous layer was washed with two 50-mL portions of fresh tetrahydrofuran. The combined tetrahydrofuran solutions were dried over anhydrous sodium carbonate. Concentration of the filtered tetrahydrofuran solution gave 18.6 g (57% yield) of crude (*i*-Pr₂N)₄P₄. Sublimation of the crude product at 135–140 °C (0.025 mm) gave 13.3 g (41% yield) of pure (*i*-Pr₂N)₄P₄ as a white crystalline solid: mp 195–198 °C; mass spectrum (*i*-Pr₂N)₄P₄⁺ (31), (*i*-Pr₂N)₂P₄H⁺ (5), (*i*-Pr₂N)₂P₃⁺ (7), (*i*-Pr₂N)₂P₂⁺ (33), (*i*-Pr₂N)₂P⁺ (51), *i*-Pr₂NPH⁺ (57), *i*-Pr₂N⁺ (100); phosphorus-31 NMR in CDCl₃ δ 18.7; proton NMR in CDCl₃ δ 3.59 (multiplet, *J* = 7 Hz., 8 CH), 1.17 (doublet, *J* = 7 Hz, 16 CH₃); proton decoupled carbon-13 NMR in CDCl₃ δ 49.5 (8 CH), 24.2 (16 CH₃); IR spectrum in CH₂Cl₂ solution 2955 (s), 2920 (m), 2860 (w), 1460 (w), 1450 (w), 1380 (m), 1371 (w), 1356 (m), 1186 (m), 1170 (s), 1150 (m), 1113 (m), 1012 (w), 955 (s), 860 (w), 842 (w), cm⁻¹. Anal. Calcd for C₂₄H₅₆N₄P₄: C, 54.9; H, 10.8; N, 10.7; M_r, 524. Found: C, 55.0; H, 10.8; N, 10.7; M_r, 519 (osmometry in benzene).

A similar reaction with *i*-Pr₂NPBr₂ rather than *i*-Pr₂NPCl₂ gave a 56% yield of (*i*-Pr₂N)₄P₄.

Preparation of (*i*-Pr₂N)₂P₂Cl₂. A suspension of 2.43 g (100 mmol) of magnesium turnings in 300 mL of tetrahydrofuran containing a crystal of iodine was treated dropwise with mechanical stirring with a solution of 40.4 g (200 mmol) of *i*-Pr₂NPCl₂ in 100 mL of tetrahydrofuran. The reaction mixture was then boiled under reflux for 24 h. Solvent was removed at 25 °C (25 mm) from the resulting yellow solution containing a white precipitate. The resulting yellow solid was extracted with 200 mL of dry pentane. Removal of pentane from the filtered extract at 25 °C (25 mm) gave crude (*i*-Pr₂N)₂P₂Cl₂ as a yellow solid. Crystallization of the crude product from dry pentane at -78 °C gave 13.2 g (40% yield) of pure (*i*-Pr₂N)₂P₂Cl₂ as a light yellow solid: mp 90–91 °C; mass spectrum (*i*-Pr₂N)₂P₂Cl₂⁺ (5), (*i*-Pr₂N)₂P₂Cl⁺ (3), *i*-Pr₂NP₂HCl⁺ (9), *i*-Pr₂NPCl⁺ (100), *i*-Pr₂NP⁺ (17), *i*-PrNPHCl⁺ (42), *i*-Pr₂N⁺ (21), *i*-PrNP⁺ (94); phosphorus-31 NMR in CH₂Cl₂ δ 127.7; proton NMR in CDCl₃ δ 3.5 (broad, 4 CH), 1.3 (multiplet, 8 CH₃); proton decoupled carbon-13 NMR in CDCl₃ CH resonances at δ 55.4 (triplet), 47.6 (singlet), and 46.1 (triplet) of relative intensities 10, 23, and 13, respectively, and CH₃ resonances at δ 26.3, (singlet), 24.5 (triplet), 21.8 (singlet), and 19.3 (singlet) of relative intensities 16, 15, 51, and 35, respectively. Anal. Calcd for C₁₂H₂₈Cl₂N₂P₂: C, 43.2; H, 8.5; Cl, 21.3; N, 8.4. Found: C, 43.0; H, 8.6; Cl, 21.0; N, 8.3.

Preparation of (*i*-Pr₂N)₂P₂Br₂. A suspension of 1.4 g (58 mmol) of magnesium turnings in 100 mL of tetrahydrofuran containing a crystal of iodine was treated dropwise with a solution of 16.8 g (58 mmol) of *i*-Pr₂NPBr₂ in 50 mL of tetrahydrofuran. The reaction mixture was stirred at room temperature for 7 days. Solvent was removed from the reaction mixture at 25 °C (25 mm). The residue was extracted with 200 mL of pentane. Concentration of the filtered pentane extract gave a total of 6.2 g (51% yield) of light yellow (*i*-Pr₂N)₂P₂Br₂. Sublimation of the crude product at 130–135 °C (0.01 mm) gave the pure product as a white solid: mass spectrum (*i*-Pr₂N)₂P₂Br₂⁺ (2), (*i*-Pr₂N)₂P₂Br⁺ (10), *i*-Pr₂NP₂HBr⁺ (5), *i*-Pr₂NPBr⁺ (70), *i*-PrNPHBr⁺ (22), *i*-Pr₂N⁺ (63), *i*-PrNP⁺ (100), C₃H₅NP⁺ (90); phosphorus-31 NMR in CDCl₃ δ 136.1; proton NMR in CDCl₃ δ 3.8 (broad, 4 CH), 1.3 (multiplet, 8 CH₃); proton decoupled carbon-13 NMR in CDCl₃ CH resonances at δ 56.9 (triplet, *J* = 7 Hz.), 47.9 (singlet), and 46.6 (triplet, *J* = 12 Hz) of relative intensities 36, 55, and 36, respectively, on the unsublimed product and 42, 32, and 44, respectively, on the sublimed product and CH₃ resonances at δ 24.8 (triplet, *J* = 7 Hz.), 21.1 (singlet), and 19.2 (singlet) of relative intensities 55, 100, and 38, respectively, on the unsublimed product and 59, 100, and 78, respectively, on the sublimed product. Anal. Calcd for

Table I. Products from the Reduction of (Dialkylamino)dichlorophosphines

R ₂ NPCl ₂ ^a	reduction products	
	Mg/THF ^b	(Me ₃ Si) ₂ Hg ^c
Me ₂ NPCl ₂	(R ₂ N) ₃ P (70%)	(R ₂ N) ₂ PCl (70%) (R ₂ N) ₃ P (30%)
(CH ₂) ₅ NPCl ₂	(R ₂ N) ₄ P ₂ (66%)	(R ₂ N) ₃ P _n (85%) (R ₂ N) ₃ P (15%)
Et ₂ NPCl ₂	(R ₂ N) ₃ P (74%)	(R ₂ N) ₂ PCl (10%) (R ₂ N) ₃ P (10%) (R ₂ N) ₄ P ₄ (80%)
(CH ₂) ₃ (CHMe) ₂ NPCl ₂	(R ₂ N) _n P _n (78%)	(R ₂ N) _n P _n
<i>i</i> -Pr ₂ NPCl ₂	(R ₂ N) ₄ P ₄ (56%)	(R ₂ N) ₄ P ₄
Cx ₂ NPCl ₂	(R ₂ N) ₄ P ₄ (77%)	(R ₂ N) ₄ P ₄

^a Me = methyl, (CH₂)₅N = piperidino, Et = ethyl, (CH₂)₃-(CHMe)₂N = 2,6-dimethylpiperidino, *i*-Pr = isopropyl, Cx = cyclohexyl. ^b Yields of the indicated products are given in parentheses. ^c The compositions of the product mixture as determined by the relative intensities of the phosphorus-31 NMR peaks are indicated in parentheses.

C₁₂H₂₈Br₂N₂P₂: C, 34.1; H, 6.7; Br, 37.8; N, 6.6. Found: C, 33.1; H, 6.8; Br, 36.2; N, 6.4.

Preparation of (C_xN)₄P₄ (C_x = cyclohexyl). A suspension of 1.7 g (70 mmol) of magnesium turnings in 150 mL of tetrahydrofuran containing a crystal of iodine was treated dropwise with a solution of 16.0 g (57 mmol) of Cx₂NPCl₂ in 100 mL of tetrahydrofuran. The reaction mixture was boiled under reflux for 48 h. After cooling to room temperature the reaction mixture was hydrolyzed with an ice-cold solution of 18.2 g (62 mmol) of ethylenediaminetetraacetic acid and 10.5 g (263 mmol) of sodium hydroxide in 120 mL of water. The tetrahydrofuran layer was separated and the aqueous layer was washed with two 50-mL portions of diethyl ether. The combined tetrahydrofuran/diethyl ether solutions were dried over anhydrous sodium carbonate. Removal of solvent from the filtered solution gave 9.7 g (81% yield) of crude (C_xN)₄P₄ as a yellow solid. Recrystallization of the crude product from diethyl ether gave 5.6 g (47% yield) of pure (C_xN)₄P₄ as a white solid: mp 226–228 °C; phosphorus-31 NMR in CDCl₃ δ 25.1; proton NMR in CDCl₃ δ 2.9 (broad, CH), 1.7 (broad, 5 CH₂); proton decoupled carbon-13 NMR in CDCl₃ δ 59.9, 35.4, 26.7, 26.0. Anal. Calcd for C₄₈H₈₈N₄P₄: C, 68.2; H, 10.5; N, 6.6; M_r, 845. Found: C, 68.6; H, 10.7; N, 6.4; M_r, 833 (osmometry in benzene). Upon attempted sublimation at 170–180 °C (0.05 mm) (C_xN)₄P₄ decomposed; for this reason a reliable mass spectrum could not be obtained under conditions available to us.

General Procedure for the Reactions of (Dialkylamino)dichlorophosphines with Magnesium (Table I). The (dialkylamino)dichlorophosphine was stirred with a 20–30% excess of magnesium turnings in tetrahydrofuran solution for at least overnight by using the same general techniques as described above for the preparations of (*i*-Pr₂N)₄P₄ and (C_xN)₄P₄. The reaction was followed by phosphorus-31 NMR spectroscopy of the crude reaction mixture. After all of the R₂NPCl₂ derivative had reacted, the tetrahydrofuran was removed at 25 °C (25 mm). The residue was extracted with pentane. Solvent was removed from the filtered pentane extract. The residue was analyzed by gas chromatography/mass spectrometry.

General Procedure for the Reactions of (Dialkylamino)dichlorophosphines with (Me₃Si)₂Hg (Table I). A pentane solution of (Me₃Si)₂Hg was treated dropwise at -78 °C with an equimolar amount of the R₂NPCl₂ derivative. The reaction mixture was allowed to warm slowly to room temperature and then analyzed by phosphorus-31 NMR spectroscopy. After removal of solvent from the filtered pentane solution, the residue was analyzed by gas chromatography/mass spectrometry. Similar results were also obtained by mixing equimolar amounts of R₂NPCl₂ and (Me₃Si)₂Hg in benzene solution at ambient temperature in an NMR tube and then taking the phosphorus-31 NMR spectrum.

Properties of (Et₂N)_nP_n: light yellow semisolid which could not be crystallized; mass spectrum (Et₂N)₄P₄⁺ (49); (Et₂N)₂P₃⁺ (5), (Et₂N)₂P₂⁺ (13), (Et₂N)₂P⁺ (100), Et₂NP⁺ (64), Et₂N⁺ (51); proton decoupled phosphorus-31 NMR in pentane δ 55.0 (in-

completely resolved triplet), 45.6 (sharp singlet).

Properties of $[(\text{CH}_2)_3\text{N}]_n\text{P}_n$: viscous liquid; ions $(\text{C}_5\text{H}_{10}\text{N})_3\text{P}_3^+$, $(\text{C}_5\text{H}_{10}\text{N})_2\text{P}_2^+$, and $\text{C}_5\text{H}_{10}\text{NP}^+$ found in the mass spectrum; phosphorus-31 NMR spectrum in pentane δ 40.8.

Properties of $[(\text{CH}_2)_3(\text{CHMe})_2\text{N}]_n\text{P}_n$: yellow noncrystalline solid; mp 84–86 °C; decomposes upon attempted sublimation at 200 °C (0.005 mm); product from the $(\text{CH}_2)_3(\text{CHMe})_2\text{NPCl}_2/\text{Mg}$ reaction gives the ions $(\text{R}_2\text{N})_2\text{P}_2^+$, $(\text{R}_2\text{N})_2\text{P}_2^+$, $(\text{R}_2\text{N})_2\text{P}_2^+$, R_2NP^+ , and $\text{R}_2\text{N}^+ = (\text{CH}_2)_3(\text{CHMe})_2\text{N}^+$ in the direct inlet solid mass spectrum; phosphorus-31 NMR in pentane δ 50.3.

Properties of $[(\text{CH}_2)_5\text{N}]_4\text{P}_2$: colorless air-sensitive liquid; bp 133–135 °C (0.6 mm); solidifies in a –10 °C freezer; mass spectrum $(\text{C}_5\text{H}_{10}\text{N})_4\text{P}_4^+$ (2), $(\text{C}_5\text{H}_{10}\text{N})_3\text{P}_3\text{H}^+$ (3), $(\text{C}_5\text{H}_{10}\text{N})_3\text{P}^+$ (30), $(\text{C}_5\text{H}_{10}\text{N})_2\text{P}^+$ (92), $\text{C}_5\text{H}_{10}\text{NPH}^+$ (100); phosphorus-31 NMR in pentane δ 117.0. This compound is also obtained in 67% yield from the reaction of $[(\text{CH}_2)_5\text{N}]_2\text{PCL}$ with magnesium in boiling tetrahydrofuran.

Chemical Reactivity of $(i\text{-Pr}_2\text{N})_4\text{P}_4$. (1) **Alcohols.** Treatment of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ with excess methanol at ambient temperature or with excess *tert*-butyl alcohol at its boiling point for 24 h did not result in any reaction; the presence of unchanged $(i\text{-Pr}_2\text{N})_4\text{P}_4$ as the only phosphorus compound in the reaction mixture was shown by phosphorus-31 NMR and/or product isolation.

(2) **Water.** Water does not react with $(i\text{-Pr}_2\text{N})_4\text{P}_4$ under ambient conditions as indicated by the use of an aqueous workup for its isolation.

(3) **Halogens.** Treatment of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ with bromine in dichloromethane solution in a 1:4 $(i\text{-Pr}_2\text{N})_4\text{P}_4/\text{Br}_2$ mole ratio resulted in quantitative conversion to $i\text{-Pr}_2\text{NPBr}_2$ as shown by the phosphorus-31 NMR spectrum. Furthermore a phosphorus-31 NMR spectrum of a dichloromethane solution containing $(i\text{-Pr}_2\text{N})_4\text{P}_4$ and Br_2 in a 1:2 mole ratio exhibited only resonances for $i\text{-Pr}_2\text{NPBr}_2$ and unreacted $(i\text{-Pr}_2\text{N})_4\text{P}_4$ with no evidence for any $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{Br}_2$. Iodine reacts readily with $(i\text{-Pr}_2\text{N})_4\text{P}_4$ in dichloromethane solution at ambient temperature to give a product, possibly $i\text{-Pr}_2\text{NPI}_2$, exhibiting a phosphorus-31 resonance at δ 153.7; intermediates exhibiting phosphorus-31 resonances at δ 166.2 and –21.3 are also found in phosphorus-31 NMR spectra of a dichloromethane solution of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ and I_2 in a 1:2 mole ratio.

(4) **Hydrogen Chloride.** Treatment of a pentane solution of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ at 0 °C with gaseous hydrogen chloride for 15 min gave an immediate yellow precipitate. A gas chromatography/mass spectrometry analysis of the supernatant pentane solution indicated a mixture of $i\text{-Pr}_2\text{NPCl}_2$ and $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{Cl}_2$.

(5) **Carbon Disulfide.** Treatment of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ with boiling carbon disulfide for 24 h followed by evaporation of the resulting solution resulted in the recovery of unchanged $(i\text{-Pr}_2\text{N})_4\text{P}_4$ in nearly quantitative yield.

(6) **Potassium.** Treatment of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ with metallic potassium in boiling tetrahydrofuran for 6 days gave a light yellow solution containing a black precipitate. The phosphorus-31 NMR spectrum indicated $(i\text{-Pr}_2\text{N})_4\text{P}_4$ to be the only phosphorus compound in the solution.

(7) **Photolysis.** Ultraviolet irradiation of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ in diethyl ether solution gave a yellow precipitate which did not have the stoichiometry $(i\text{-Pr}_2\text{NP})_n$ expected for a polymer generated from a diphosphene or phosphinidine. In an attempt to trap any diphosphene or phosphinidene intermediates as a more stable adduct, the ultraviolet irradiation was repeated in the presence of 2,3-dimethylbutadiene. However, the same yellow precipitate was obtained.

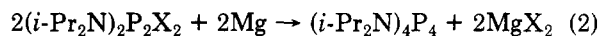
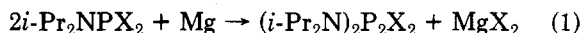
(8) **Metal Carbonyls.** Phosphorus-31 NMR spectra of the dichloromethane-soluble products obtained from $(i\text{-Pr}_2\text{N})_4\text{P}_4$ and the following metal carbonyl systems indicated that unchanged $(i\text{-Pr}_2\text{N})_4\text{P}_4$ was the only phosphorus compound present in significant quantities: (a) $\text{Cr}(\text{CO})_6$ in boiling methylcyclohexane for 48 h. (b) $\text{Mo}(\text{CO})_6$ in boiling methylcyclohexane for 48 h. (c) $\text{Fe}_2(\text{CO})_9$ in diethyl ether at room temperature for 48 h.

Results and Discussion

The reactions of excess magnesium turnings in tetrahydrofuran solution with (dialkylamino)dihalophosphines having sufficiently bulky dialkylamino groups (e.g., *i*-

Pr_2NPCl_2 and $\text{C}_x\text{N}_2\text{NPCl}_2$) provide convenient routes to the corresponding tetrakis(dialkylamino)cyclotetraphosphines, $(\text{R}_2\text{N})_4\text{P}_4$ (I). Since these $(\text{R}_2\text{N})_4\text{P}_4$ derivatives are stable toward water, pure products can be isolated from these reaction mixtures after hydrolysis with aqueous tetrasodium ethylenediaminetetraacetate to remove magnesium salts as well as any halophosphine byproducts. The ring sizes of these new cyclotetraphosphines are established by osmometric molecular weight determinations in benzene solution. In addition, the vacuum sublimable derivative $(i\text{-Pr}_2\text{N})_4\text{P}_4$ (I, R = *i*-Pr) gives the molecular ion $(i\text{-Pr}_2\text{N})_4\text{P}_4^+$ as the highest *m/e* ion in its mass spectrum.

A more detailed study on the reactions of the diisopropylamino derivatives $i\text{-Pr}_2\text{NPX}_2$ (X = Cl and Br) with magnesium suggests the following two-step reaction for the formation of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ (I, R = *i*-Pr):



The intermediate biphosphines $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{X}_2$ (II, X = Cl or Br, R = isopropyl) can be isolated by reactions of $i\text{-Pr}_2\text{NPX}_2$ with a deficiency of magnesium followed by pentane extraction after removal of the tetrahydrofuran solvent. Since the biphosphines $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{X}_2$ are very sensitive toward hydrolysis, the hydrolysis step must be omitted if they are the desired products. The biphosphines $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{X}_2$ (X = Cl and Br) can be purified by vacuum sublimation and give the correct molecular ions in their mass spectra.

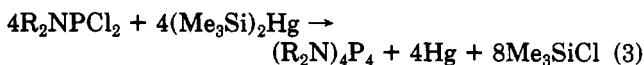
Reactions of the less hindered (dialkylamino)dichlorophosphines Et_2NPCl_2 and Me_2NPCl_2 with magnesium in tetrahydrofuran solution fail to give the corresponding tetrakis(dialkylamino)cyclotetraphosphines. Instead redistribution of the dialkylamino groups on the phosphorus occurs to give the corresponding tris(dialkylamino)phosphines in good yields based on the available dialkylamino groups. Related redistribution reactions were observed by Nöth and Vetter¹¹ in 1961 such as the formation of appreciable quantities of $(\text{Me}_2\text{N})_3\text{P}$ from the reaction of $(\text{Me}_2\text{N})_2\text{PCL}$ with a sodium dispersion in hexane. Presumably dialkylamino redistribution on phosphorus is inhibited for steric reasons in the cases of the bulkier diisopropylamino and dicyclohexylamino derivatives thereby allowing formation of the corresponding tetrakis(dialkylamino)cyclotetraphosphines.

Dialkylamino redistribution on phosphorus also occurs in the reaction of piperidinodichlorophosphine with magnesium but in this case only as far as the formation of tetrapiperidinobiphosphine, $[(\text{CH}_2)_5\text{N}]_2\text{P}-\text{P}[\text{N}(\text{CH}_2)_5]_2$, which was shown to be identical with the product from dipiperidinochlorophosphine, $[(\text{CH}_2)_5\text{N}]_2\text{PCL}$, and magnesium. Reaction of the more hindered 2,6-dimethylpiperidinodichlorophosphine with magnesium did not appear to result in dialkylamino redistribution but instead gave a noncrystalline product. This appeared to be a *per*(2,6-dimethylpiperidino)cyclopolyphosphine on the basis of its phosphorus-31 resonance at δ 50.3 and the observation of the ion $[(\text{CH}_2)_3(\text{CHMe})_2\text{N}]_2\text{P}_3^+$ in its mass spectrum. Unfortunately, this product could not be obtained in the pure state.

In an attempt to suppress dialkylamino redistribution reactions in the dehalogenation of (dialkylamino)dichlorophosphines, the homogeneous dehalogenating agent $(\text{Me}_3\text{Si})_2\text{Hg}^6$ was used instead of the heterogeneous dehalogenating agent magnesium. Use of this reagent to dehalogenate related halophosphines was recently reported

(11) Nöth, H.; Vetter, H.-J. *Chem. Ber.* 1961, 94, 1505.

by Markovski, Romanenko, and Kirsanov.⁶ Such homogeneous reactions of (dialkylamino)dichlorophosphines with $(\text{Me}_3\text{Si})_2\text{Hg}$ in hydrocarbon solvents such as pentane and benzene could form tetrakis(dialkylamino)cyclo-tetraphosphines according to the following equation:



These reactions proceed under mild conditions and therefore can be followed readily by phosphorus-31 NMR spectroscopy with the results indicated in Table I. The use of this milder reagent suppressed diethylamino redistribution in the dehalogenation of Et_2NPCL_2 so that the major product was the cyclotetraphosphine $(\text{Et}_2\text{N})_4\text{P}_4$ as indicated by the ion $(\text{Et}_2\text{N})_4\text{P}_4^+$ as the highest *m/e* ion in the mass spectrum of the crude product. However, pure $(\text{Et}_2\text{N})_4\text{P}_4$ could not be crystallized or sublimed from this crude product. Reaction of Me_2NPCL_2 with $(\text{Me}_3\text{Si})_2\text{Hg}$, however, still resulted only in redistribution of the dimethylamino groups, but the major product was $(\text{Me}_2\text{N})_2\text{PCL}$ rather than the $(\text{Me}_2\text{N})_3\text{P}$ formed as the major product from Me_2NPCL_2 and magnesium. These observations support the greater extent of dialkylamino redistribution on phosphorus with smaller dialkylamino groups but also indicate a lesser extent of dialkylamino redistribution with the homogeneous reagent $(\text{Me}_3\text{Si})_2\text{Hg}$ than the heterogeneous reagent magnesium.

The availability of relatively large quantities of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ from the reaction of $i\text{-Pr}_2\text{NPCL}_2$ with magnesium prompted a study of its chemical reactivity. In most cases the steric hindrance of the diisopropylamino groups in $(i\text{-Pr}_2\text{N})_4\text{P}_4$ reduced its chemical reactivity relative to that of the relatively well-known cyclotetraphosphines having alkyl or aryl substituents. Thus $(i\text{-Pr}_2\text{N})_4\text{P}_4$ is apparently complete stable toward atmospheric oxygen under ambient conditions. It appears to be unreactive toward metal carbonyls under conditions where Et_4P_4 and Ph_4P_4 give metal carbonyl complexes.¹²⁻¹⁵ Furthermore, $(i\text{-Pr}_2\text{N})_4\text{P}_4$ does not form any soluble anionic derivatives upon treatment with excess metallic potassium in boiling tetrahydrofuran for several days in contrast to cyclotetraphosphines such as Et_4P_4 and Ph_4P_4 which form interesting and preparatively useful anionic derivatives.¹⁶⁻¹⁹ The

dialkylamino groups in $(i\text{-Pr}_2\text{N})_4\text{P}_4$ are not solvolyzed by water or by alcohols under conditions where $(i\text{-Pr}_2\text{N})_2\text{PH}$ reacts with alcohols to form the corresponding $(i\text{-Pr}_2\text{N})\text{(RO)PH}$ derivatives.²⁰

The major exception to the low reactivity of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ occurs upon treatment with halogens and hydrogen halides. We hoped that hydrogen chloride under mild conditions would cleave the exocyclic phosphorus-nitrogen bonds in $(i\text{-Pr}_2\text{N})_4\text{P}_4$ to form the interesting tetrachlorocyclo-tetraphosphine, P_4Cl_4 . However, the major products from the treatment of $(i\text{-Pr}_2\text{N})_4\text{P}_4$ with hydrogen chloride at 0 °C are $i\text{-Pr}_2\text{NPCL}_2$ and $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{Cl}_2$ indicating that the P_4 ring in $(i\text{-Pr}_2\text{N})_4\text{P}_4$ is more readily cleaved than the exocyclic phosphorus-nitrogen bonds. Halogens (e.g., bromine and iodine) also readily cleave the P_4 ring in $(i\text{-Pr}_2\text{N})_4\text{P}_4$ forming the corresponding $i\text{-Pr}_2\text{NPX}_2$ derivative as the major product.

The NMR spectra of the $(\text{R}_2\text{N})_4\text{P}_4$ derivatives (I, R = isopropyl and cyclohexyl) are relatively simple indicating the expected equivalence on the NMR time scale of all four phosphorus atoms and all eight alkyl groups. The NMR spectra of solutions of the $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{X}_2$ derivatives (II, X = Cl and Br) indicate only one type of phosphorus atom but several types of isopropyl groups. Since $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{X}_2$ derivatives have two asymmetric phosphorus atoms, meso and *dl* diastereomers (IIa and IIb, respectively) are possible as has been reported for $(\text{Me}_3\text{C})_2\text{P}_2\text{Cl}_2$.²¹ The complexity of the carbon-13 NMR spectra of both $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{X}_2$ derivatives (X = Cl and Br) may be an indication of different isopropyl groups in the meso and *dl* isomers with the possibility on the NMR time scale of one type of isopropyl group in the meso isomer but two types of isopropyl groups in the less symmetrical *dl* isomer. However, it is interesting that the two diastereomers of $(\text{Me}_3\text{C})_2\text{P}_2\text{Cl}_2$ have phosphorus-31 resonances differing by ~7 ppm,²¹ whereas only a single phosphorus NMR resonance is found in each $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{X}_2$ derivative. Possibly phosphorus-31 NMR is less sensitive than carbon-13 NMR to the subtle changes of environment in the meso and *dl* diastereomers of the $(i\text{-Pr}_2\text{N})_2\text{P}_2\text{X}_2$ derivatives.

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Selective Indirect Oxidation of Phenol to Hydroquinone and Catechol

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The introduction of a hydroxyl function into phenol to give hydroquinone and catechol can be achieved in high yields by the reaction of hydrogen peroxide with alkenylphenols. These alkenylphenols are obtained by thermolysis of bisphenol A, alkylation of phenol with cyclopentadiene followed by isomerization, and alkylation of phenol with mesityl oxide followed by thermolysis to give 4-isopropenylphenol, 2- and 4-(cyclopenten-1-yl)phenol, and 2,2,4-trimethyl-1,2-chromene, respectively.

Introduction of hydroxyl functions into aromatic hydrocarbons by known oxidation methods is often burdened

by low conversion, byproduct formation, and difficult separation of reaction products. For instance, in the in-