Novel Di-isopropylamino Derivatives of Trivalent Phosphorus

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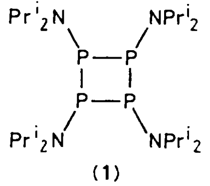
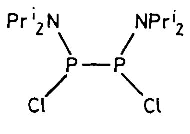
Reduction of $(\text{Pr}^i_2\text{N})_2\text{PCl}$ with LiAlH_4 in diethyl ether gives $(\text{Pr}^i_2\text{N})_2\text{PH}$; reaction of $\text{Pr}^i_2\text{NPCl}_2$ with Mg in boiling tetrahydrofuran gives either the cyclotetraphosphine $(\text{Pr}^i_2\text{N})_4\text{P}_4$ or the 1,2-dichlorobiphosphine $\text{Pr}^i_2\text{NP(Cl)–P(Cl)NPr}^i_2$ depending upon the $\text{Mg:Pr}^i_2\text{NPCl}_2$ mole ratio.

Several years ago we demonstrated that many polyphosphorus compounds containing phosphorus–nitrogen bonds could be obtained from dimethylamino phosphorus derivatives.[1] This communication describes the preparation of the P–H compound $(\text{Pr}^i_2\text{N})_2\text{PH}$, the cyclotetraphosphine $(\text{Pr}^i_2\text{N})_4\text{P}_4$ (**1**) and the 1,2-dichlorobiphosphine $\text{Pr}^i_2\text{NP(Cl)P(Cl)NPr}^i_2$ (**2**).

Trivalent phosphorus derivatives of the type $(\text{R}_2\text{N})_2\text{PH}$ in which the phosphorus is bonded only to nitrogen and hydrogen are rare, being limited to various $\text{C}_3\text{N}_2\text{P}$ heterocycles of the type[2] $\overline{\text{RNCH}_2\text{CH}_2\text{CHR'N(R)P}}\text{H}$ and the silylphosphine $(\text{Me}_3\text{Si})_2\text{NP(H)–N(H)SiMe}_3$.[3] We have now found that $(\text{Pr}^i_2\text{N})_2\text{PH}$, the first acyclic $(\text{R}_2\text{N})_2\text{PH}$ derivative without Si–N bonds, can be prepared by reduction of $(\text{Pr}^i_2\text{N})_2\text{PCl}$[4] with LiAlH_4. In a typical experiment a mixture of $(\text{Pr}^i_2\text{N})_2\text{PCl}$ (75 mmol), LiAlH_4 (105 mmol), and 300 ml of diethyl ether was stirred at room temp. for 72 h. Removal of solvent followed by extraction with pentane and distillation of the filtered pentane solution gave a 60—70% yield of $(\text{Pr}^i_2\text{N})_2\text{PH}$, m.p. 24—25 °C, b.p. 58—59 °C/0.2 mmHg; i.r. ν(PH): 2220 cm^{-1};


(1)


(2)

^{13}P n.m.r.: δ 42.1 p.p.m. [$|^1J$(P–H)$|$ 254 Hz]; ^{1}H n.m.r.: δ 5.8 (1 H, *J* 253 Hz), 3.25 (4 H, m), and 1.1 (24 H, app. q); major ions in mass spectrum: $(\mathrm{Pr^i_2N})_2\mathrm{PH}^+$, $\mathrm{Pr^i_2NPH}^+$, and $\mathrm{Pr^iNH\text{-}PH}^+$. As expected $(\mathrm{Pr^i_2N})_2\mathrm{PH}$ is very air-sensitive and paper impregnated with liquid $(\mathrm{Pr^i_2N})_2\mathrm{PH}$ ignites upon exposure to air.

The cyclotetraphosphine (**1**) and the 1,2-dichlorobiphosphine (**2**) are the first examples of compounds of these types which do not contain phosphorus–carbon bonds. They are both obtained by the reaction of $\mathrm{Pr^i_2NPCl_2}$[5] with magnesium in tetrahydrofuran (THF) solution, the product being determined by the Mg : $\mathrm{Pr^i_2NPCl_2}$ mole ratio. For the preparation of (**1**), a mixture of $\mathrm{Pr^i_2NPCl_2}$ (0.2 mol), magnesium turnings (0.3 g at.), a crystal of iodine, and 400 ml of THF was stirred mechanically at the boiling point for 16 h. Hydrolysis of the reaction mixture with an ice-cold deoxygenated solution of 64.2 g of ethylenediaminetetra-acetic acid and 37.0 g of sodium hydroxide in 400 ml of water followed by evaporation of the dried ($\mathrm{Na_2CO_3}$) THF layer gave crude pale yellow $(\mathrm{Pr^i_2N})_4\text{-}\mathrm{P_4}$ (**1**), yield 40—57%. The pure product was obtained as apparently air-stable white crystals by sublimation at 140 °C/0.025 mmHg, m.p. 197—198 °C, ^{31}P n.m.r.: δ 18.7 p.p.m.; major ions in mass spectrum: $(\mathrm{Pr^i_2N})_4\mathrm{P_4}^+$, $(\mathrm{Pr^i_2N})_2\mathrm{P_3}^+$, $(\mathrm{Pr^i_2N})_2\mathrm{P_2}^+$, $(\mathrm{Pr^i_2N})_2\mathrm{P}^+$, $\mathrm{Pr^i_2NPH}^+$, and $\mathrm{Pr^i_2N}^+$. Reaction of (**1**) with an excess of sulphur in boiling benzene gives white crystalline $(\mathrm{Pr^i_2NPS_2})_2$, m.p. 118—120 °C, similar to the reported[6] reaction of $(\mathrm{Me_3C})_4\mathrm{P_4}$ with sulphur to give the corresponding $(\mathrm{Me_3CPS_2})_2$.

For the preparation of (**2**), a lower Mg : $\mathrm{Pr^i_2NPCl_2}$ mole ratio was used and hydrolysis was avoided. In a typical experiment a mixture of $\mathrm{Pr^i_2NPCl_2}$ (0.2 mol), magnesium turnings (0.1 g at.), and 400 ml of THF was stirred mechanically for 24 h at the boiling point. Removal of the solvent followed by low-temperature crystallization of the residue from pentane gave a 40% yield of white (**2**), m.p. 90—91 °C; ^{31}P n.m.r.: δ 127.7 p.p.m.; major ions in mass spectrum: $(\mathrm{Pr^i_2N})_2\mathrm{P_2Cl_2}^+$, $(\mathrm{Pr^i_2N})_2\mathrm{P_2Cl}^+$, $\mathrm{Pr^i_2NP_2ClH}^+$, $\mathrm{Pr^i_2NPCl}^+$, $\mathrm{Pr^i_2NP}^+$, $\mathrm{Pr^i_2NPHCl}^+$, $\mathrm{Pr^i_2N}^+$, and $\mathrm{Pr^iNP}^+$. A related 1,2-dichlorobiphosphine, $\mathrm{Me_3CP(Cl)\text{–}P(Cl)CMe_3}$, was recently reported.[7]

A large dialkylamino group seems to be essential for the isolation of stable $(\mathrm{R_2N})_2\mathrm{PH}$, $(\mathrm{R_2N})_4\mathrm{P_4}$, and $(\mathrm{R_2N})_2\mathrm{P_2Cl_2}$ derivatives. Thus, the reactions of $(\mathrm{Me_2N})_2\mathrm{PCl}$ with $\mathrm{LiAlH_4}$ and of $\mathrm{Me_2NPCl_2}$ with Mg using reaction conditions similar to those described above for the di-isopropylamino analogues gave $(\mathrm{Me_2N})_3\mathrm{P}$ as the only soluble, volatile organophosphorus derivative with no evidence for the formation of $(\mathrm{Me_2N})_2\mathrm{PH}$, $(\mathrm{Me_2N})_4\mathrm{P_4}$, and $(\mathrm{Me_2N})_2\mathrm{P_2Cl_2}$ in appropriate reactions.

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References

1 R. B. King and W. F. Masler, *J. Am. Chem. Soc.*, 1977, **99**, 4001.

2 E. E. Nifantiev, S. F. Sorokina, A. A. Borisenko, A. I. Zavalishina, and L. A. Vorobjeva, *Tetrahedron*, 1981, **37**, 3183.

3 E. Niecke and G. Ringel, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 486.

4 J. J. S. Gynane, A. Hudson, M. F. Lappert, and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1980, 2428.

5 Z. M. Ivanova, *Zh. Obshch. Khim.*, 1965, **35**, 164.

6 M. Baudler, C. Gruner, G. Fürstenberg, B. Kloth, F. Saykowski, and U. Özer, *Z. Anorg. Allg. Chem.*, 1978, **446**, 169.

7 M. Baudler, J. Hellmann, and J. Hahn, *Z. Anorg. Allg. Chem.*, 1982, **489**, 11.