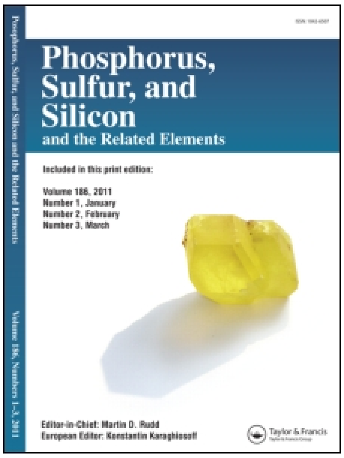

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# New Dialkylamino Derivatives of Trivalent Phosphorus

R. B. King[a]; N. D. Sadanani[a]; P. M. Sundaram[a]
[a] Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.

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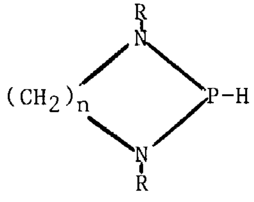
# NEW DIALKYLAMINO DERIVATIVES OF TRIVALENT PHOSPHORUS

R. B. KING, N. D. SADANANI, P.M. SUNDARAM
Department of Chemistry, University of Georgia, Athens,
Georgia 30602, U. S. A.

Abstract Recent developments in the chemistry of $(R_2N)_2PH$, $(R_2N)(R'O)PH$, $(R_2N)_4P_4$, and $R_2NP(Cl)$-$P(Cl)NR_2$ derivatives are discussed.

Previous studies[1] on cyclic derivatives of the type $(R_2N)_2PH$ have used the reaction of $nBu_3SnH$ with the corresponding $(R_2N)_2PCl$ derivative for their synthesis. We have now found that treatment of $(R_2N)_2PCl$ derivatives with $LiAlH_4$in diethyl ether in some cases can yield the corresponding $(R_2N)_2PH$ derivatives and we have used this method for the preparation of the first silicon-free acyclic $(R_2N)_2PH$ derivatives.[2] The course of this reaction appears to be very dependent upon the size of the $R_2N$ group. Thus the reduction of $(iPr_2N)_2PCl$ with $LiAlH_4$ in diethyl ether gives a 60-70% yield of $(iPr_2N)_2PH$, m.p. 24-25°C, b.p. 58-59°C/0.2mm., IR $\nu$(PH): 2225cm.$^{-1}$; $^{31}P$ NMR:$\delta$42.1 ($^1J_{PH}$=254 Hz.), with no evidence by GC/MS for the formation of any $(iPr_2N)_3P$. An analogous reaction of $(Et_2N)_2PCl$ with $LiAlH_4$ gives a mixture of $(Et_2N)_3P$ and $(Et_2N)_2PH$ from which pure $(Et_2N)_2PH$ can be separated in 30% yield by vacuum distillation as a very air-sensitive liquid, b.p. 50-55°C/1.2mm., IR $\nu$(PH): 2272cm.$^{-1}$; $^{31}P$ NMR: $\delta$76.3 ($^1J_{PH}$=259 Hz.). An analogous reaction of $(Me_2N)_2PCl$ with $LiAlH_4$ gives only $(Me_2N)_3P$ in nearly quantitative yield with no evidence (even by GC/MS) for the formation of any $(Me_2N)_2PH$ as an isolable product.

This synthetic approach can also be used to prepare cyclic $(R_2N)_2PH$ derivatives similar to the previously[1] reported compounds. Thus reduction of $(CH_2)_n(NCMe_3)_2PCl$ with $LiAlH_4$ in diethyl ether or tetrahydrofuran gives 50-60% yields of the corresponding P-H compounds $(CH_2)_n(NCMe_3)_2PH$(I:n=2 and 3; R=tert-butyl). However, this reaction



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also requires significant steric hindrance at the phosphorus since an analogous reduction of the less sterically hindered $(CH_2)_2(NMe)_2PCl$ with $LiAlH_4$ under similar conditions failed to give any evidence by $^{31}P$ NMR for the formation of the corresponding P-H derivative I (n=2, R=methyl).

The diisopropylamino groups in $(iPr_2N)_2PH$ appear to be susceptible towards alcoholysis without destruction of the P-H bond. Thus treatment of $(iPr_2N)_2PH$ with methanol in toluene or pentane solution appears to form successively $(iPr_2N)(MeO)PH$ ($^{31}P$ NMR: $\delta$ 106.5, $^1J_{PH}$=244 Hz.) and $(MeO)_2PH$ ($^{31}P$ NMR: $\delta$ 172.0, $^1J_{PH}$=195 Hz.) as indicated by the $^{31}P$ NMR spectrum of the crude reaction mixture. Distillation of the reaction mixture results in decomposition of the $(MeO)_2PH$ but allows isolation of the $(iPr_2N)(MeO)PH$ as a very air-sensitive liquid, b.p. 34-36°C/2.5-2.6mm., which gives a correct GC/MS. Analogous reactions of $(iPr_2N)_2PH$ with ethanol, isopropanol, and tert-butanol also give the corresponding $(iPr_2N)(R'O)PH$ and $(R'O)_2PH$ derivatives (R' = ethyl, isopropyl, tert-butyl) identified by their $^{31}P$ NMR spectra. In each case the $(iPr_2N)(R'O)PH$ derivative can be isolated by vacuum distillation as a liquid which rapidly turns brown upon exposure to air and which gives the correct mass spectrum.

Preliminary experiments indicate that in some cases the $(R_2N)_2PH$ derivatives are useful reagents for the preparation of polyphosphines through appropriate addition reactions. Thus reaction of $(Et_2N)_2PH$ with $(Et_2N)_2PCH=CH_2$ in boiling tetrahydrofuran for 9 days in the presence of potassium hydride gives a 75% yield of liquid $(Et_2N)_2PCH_2CH_2P(NEt_2)_2$, b.p. 135-140°C/0.005-0.025mm., $^{31}P$ NMR: $\delta$ 91.1. However, a corresponding reaction of the more sterically hindered $(iPr_2N)_2PH$ with $(iPr_2N)_2PCH{=}CH_2$ using either KH at temperatures up to 100°C or azobis(isobutyronitrile) at temperatures up to 160°C does not give the corresponding adduct $(iPr_2N)_2PCH_2CH_2P(N\text{-}iPr_2)_2$ thereby indicating the significance of steric factors in this reaction.

Other chemistry of $(iPr_2N)_2PH$ relates to the apparent difficulty of its deprotonation to form the $(iPr_2N)_2P^-$ anion. Thus attempted metallation of $(iPr_2N)_2PH$ with n-butyllithium in tetrahydrofuran followed by addition of methyl iodide failed to give any evidence for the formation of $(iPr_2N)_2PMe$ thereby suggesting that the lithium derivative $(iPr_2N)_2PLi$ is not formed from the reaction of $(iPr_2N)_2PH$ with butyllithium. Also reaction of $(iPr_2N)_2PCl$ with potassium metal in boiling tetrahydrofuran failed to give any $(iPr_2N)_2PK$ as indicated by the failure to obtain any $(iPr_2N)_2PMe$ after quenching the reaction mixture with excess methyl iodide.

The reactions of $R_2NPCl_2$ with magnesium can be used for syntheses of the cyclotetraphosphines $(R_2N)_4P_4$ and the biphosphines $R_2NP(Cl)\text{-}P(Cl)NR_2$. Again this chemistry appears to require a relatively large $R_2N$ group such as diisopropylamino.[2] Thus boiling a mixture of $iPr_2NPCl_2$ and magnesium metal in a 1:1.5 mole ratio in boiling tetrahydrofuran followed by hydrolysis with concentrated aqueous tetrasodium EDTA gives a 40-57% yield of white volatile $(iPr_2N)_4P_4$, m.p. 197-198°C, sublimes 140°C/0.025mm., $^{31}P$ NMR: $\delta$ 18.7. For the preparation of $iPr_2NP(Cl)\text{-}P(Cl)N\text{-}iPr_2$ a lower $Mg/iPr_2NPCl_2$ ratio is used and hydrolysis is avoided. Thus reaction of $iPr_2NPCl_2$ with magnesium in a 2:1 mole ratio in boiling tetrahydrofuran for 24 hr. followed by removal of the solvent and low temperature crystallization from pentane gives up to 40% of white $iPr_2NP(Cl)\text{-}P(Cl)N\text{-}iPr_2$, m.p. 90-91°C, $^{31}P$ NMR: $\delta$ 127.7. Similar reactions of $Me_2NPCl_2$ and $Et_2NPCl_2$ with magnesium failed to give the corresponding $(R_2N)_4P_4$ or $R_2NP(Cl)-P(Cl)NR_2$ derivatives and instead gave only ill-defined air-sensitive yellow polymeric solids and the corresponding $(R_2N)_3P$ derivatives.

The large diisopropylamino groups in $(iPr_2N)_4P_4$ appear to shield the $P_4$ ring from many chemical reactions that are characteristic of $R_4P_4$ cyclopolyphosphines containing phosphorus-carbon bonds.[3] Thus $(iPr_2N)_4P_4$ is unreactive towards oxygen and is not converted to anionic derivatives with potassium metal in boiling tetrahydrofuran as indicated by the $^{31}P$ NMR spectrum. Furthermore, $(iPr_2N)_4P_4$ appears to be relatively unreactive towards metal carbonyls although there is some infrared $\nu(CO)$ spectroscopic evidence for the formation of cis-$L_2Mo(CO)_4$ and $LFe(CO)_4$ derivatives from its reactions with $Mo(CO)_6$ (boiling methylcyclohexane) and $Fe_2(CO)_9$ (boiling diethyl ether), respectively. Reaction of $(iPr_2N)_4P_4$ with excess sulfur in boiling benzene gives white crystalline $(iPr_2NPS_2)_2$, m.p. 118-120°C, similar to the reported[4] reaction of $(Me_3C)_4P_4$ with sulfur to give the corresponding $(Me_3CPS_2)_2$. Hydrogen chloride, bromine, and iodine appear to cleave the $P_4$ ring in $(iPr_2N)_4P_4$ at room temperature or below to form the corresponding $iPr_2NPX_2$ (X=Cl, Br, and I) derivatives.

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