Substitution at 4-Position in 1,2,3σ^2-Diazaphosphole by Phosphorus Trichloride

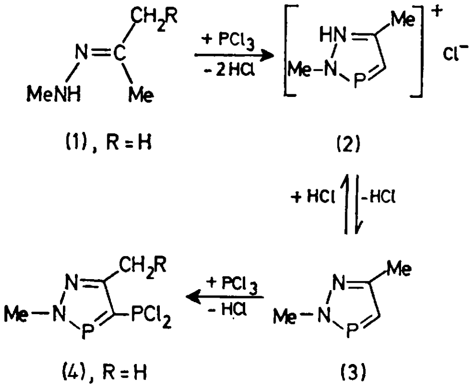
By JÖRG LUBER and ALFRED SCHMIDPETER*

(*Institut für Anorganische Chemie, Universität München, Meiserstrasse* 1, 8000 *München* 2, *Germany*)

Summary 2-Methyl-1,2,3σ^2-diazaphospholes are obtained as hydrochlorides from methylhydrazones and an excess of PCl_3 which, with longer reaction times, give the 4-dichlorophosphino-derivatives; 4-alkyl substituted diazaphospholes may be separated from their mixture with 4-unsubstituted compounds by the use of this reaction.

The title compounds[1,2] may be considered as σ^2-phospha derivatives of pyrazoles. Until now, however, there have been no observations which would show them to parallel the pyrazoles chemically. Their reaction with PCl_3 reported here is reminiscent of an electrophilic aromatic substitution.

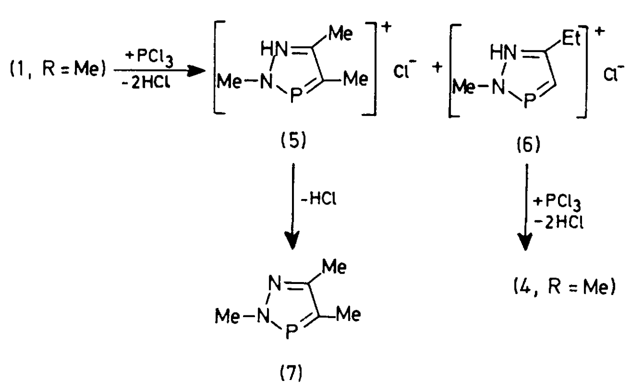
N-Methylhydrazones, possessing in the α-position a methyl or methylene group, react with an excess of PCl_3 to give crystalline 2-methyl-1,2,3σ^2-diazaphospholium chlorides. Thus, PCl_3 and acetone methylhydrazone (**1**, R = H) give, after 2 h, the chloride (**2**) in 60% yield.[2] If the reaction is allowed to proceed for a longer period, the yield of (**2**) decreases, and almost no (**2**) is obtained after 6 h. With the increase in the time of reaction, increasing amounts of another product, an oil, are found which can be distilled and which, by elemental analysis and its n.m.r. spectrum, is identified as 4-dichlorophosphino-2,5-dimethyl-1,2,3σ^2-diazaphosphole (**4**, R = H). It obviously originates from (**2**) by substitution at the carbon atom neighbouring phosphorus either directly or *via* (**3**) after the loss of HCl.[2]



(1), R = H (2) (3) (4), R = H

When unsymmetrical methyl ketones are used, a mixture of 4-unsubstituted and 4-substituted 1,2,3σ^2-diazaphospholes is obtained[1] from which the latter can be separated in pure form by the use of this reaction. Thus, the reaction of (**1**, R = Me) with PCl_3 gives the isomeric diazaphosphole hydrochlorides (**5**) and (**6**), initially in comparable amounts. If the reaction is continued for a longer period, the 4-unsubstituted isomer (**6**) gives the dichlorophosphino-diazaphosphole (**4**, R = Me), while the 4-methyl substituted isomer (**5**) is preserved which can be separated and deprotonated to give the diazaphosphole (**7**).

The n.m.r. data of the new compounds (**5**) and (**7**) correspond well to those of the 4-unsubstituted analogues (**2**) and (**3**), respectively, as do those of the 4-dichlorophosphinodiazaphospholes (**4**). Compounds (**4**, R = H or Me) show in their ^{31}P n.m.r. spectra, besides the low-field signal (−247 and −248 p.p.m., respectively) assigned to the ring phosphorus, a signal at higher field (−158 and −157 p.p.m., respectively), and a signal splitting (70·7 and 60·5 Hz, respectively) for *geminal* phosphorus–phosphorus coupling. Both phosphorus nuclei also split the signals due to the methyl or α-ethyl protons in the 5- and even in the 2-position. The mass spectrum of (**4**, R = H) shows that peaks due to the ions M^+ and $(M - Cl)^+$ are the most intense.



(5) (6) (7) (4, R = Me)

The compounds (**4**) are prepared by heating 50 mmol of the hydrazone (**1**) in 250 mmol of PCl_3 to reflux, as described[2] for the preparation of (**2**), except that the reaction is carried out for 8 h. On cooling the solution, crystalline (**5**) when R = Me, but only a very small amount of unchanged (**2**) when R = H, separates out. The excess of PCl_3 is removed from the filtrate and the oily residue containing (**4**) is distilled *in vacuo*, (**4**, R = H), b.p. 89–90 °C at 10^{-2} Torr, 63%; (**4**, R = Me), b.p. 97–99 °C at 0·5 Torr, 34%.

The crude hydrochloride (**5**) is washed with ether and sublimed at 40–60 °C under reduced pressure (it also sublimes slowly at atmospheric pressure) to give pure (**5**), m.p. 140–142 °C, 30% from which the 4-methyl-1,2,3σ^2-diazaphosphole (**7**), b.p. 75 °C at 45 Torr, 58%, is obtained as described for (**3**).[2]

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[2] J. Luber and A. Schmidpeter, *Angew. Chem.*, 1976, **88**, 91; *Angew. Chem. Internat. Edn.* 1976, **15**, 111.