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SYNTHESIS AND X-RAY ANALYSIS OF NEW SPIROPHOSPHORANES

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Abstract 2- and 3-hydroxyalkyliminophosphoranes and their valencetautomeric pentacoordinated phosphoranes are deprotonated by KH to give anionic pentacoordinated phosphoranes. Upon methylation the latter are converted into N-methyl derivatives. The geometries of these compounds are determined by X-ray analysis and n.m.r. spectroscopy.

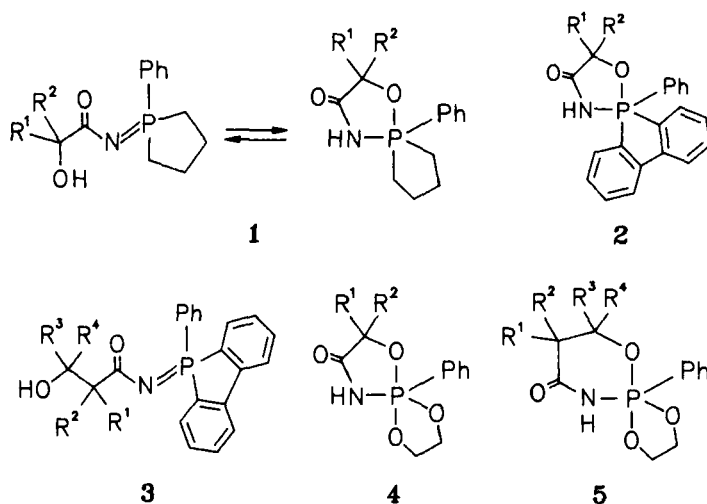
The Staudinger reaction¹ of 2- and 3-hydroxycarboxylic acid azides with phosphorus(III) compounds - leading to iminophosphoranes and/or pentacoordinated phosphoranes - is the field in which we have been researching over the last few years. The resulting products are interesting not only from a theoretical point of view, but also with regard to related compounds involved in the Mitsunobu synthesis². As published recently^{3,4}, pentacoordinated phosphoranes are obtained as the only products in the reaction of 2- and 3-hydroxycarboxylic acid azides with 2-phenyl-1,3-dioxaphospholane, whereas acyclic phosphines or 1-phenylphospholane yield iminophosphoranes or mixtures of ring-chain tautomeric products, respectively.

Continuing our studies, we synthesized the 1-phenylphospholane derivatives **1a** ($R^1=Ph$, $R^2=H$), **1b** ($R^1=R^2=CH_3$), **1c** ($R^1-R^2=-(CH_2)_4-$) and **1d** ($R^1-R^2=-(CH_2)_5-$) to investigate the ring-chain-tautomerism of 2-hydroxyacyliminophosphoranes.

By means of ³¹P n.m.r., the influence of the solvent on the equilibrium was studied. The degree of cyclization⁵ varies from 0.2 in CH₂Cl₂ to 0.8 in toluene; the amount of the spirocyclic form is even enlarged by amines. Thus it was possible to determine the full spectroscopic data of both isomers by choosing a proper solvent. In most cases the pentacoordinated form crystallizes from solutions containing the equilibrium mixtures.

However, the analogous 5-phenyldibenzophosphole derived compounds **2a** ($R^1=Ph$, $R^2=H$), **2b** ($R^1=R^2=CH_3$) and **2c** ($R^1-R^2=-(CH_2)_4-$) showed no iminophosphorane species at all. Reaction of 5-phenyldibenzophosphole with 3-hydroxycarboxylic acid azides leads to the compounds **3a** ($R^1=R^2=Ph$, $R^3=R^4=H$) and **3b** ($R^1=R^2= R^3=H$, $R^4=Ph$), which exclusively occur as phosphoranylidenamides.

On treatment with strong bases, the compounds **1** -where ring-chain tautomerism is observed - as well as **2** and the 2-phenyl-1,3-dioxaphospholane derived compounds **4a** ($R^1=Ph$, $R^2=H$)⁴, **5a** ($R^1=R^2=Ph$, $R^3=R^4=H$) and **5b** ($R^1=R^2=R^3=H$, $R^4=Ph$)³ yield anions which according to ³¹P n.m.r. exist in the spirocyclic form. The kind of cation exhibits a pronounced effect and favours the spirocyclic anions in the order $K^+ > Na^+ > Li^+$.



Interestingly, deprotonation of the "noncyclic" compounds **3** by KH leads also to solutions of spirocyclic anions ($\delta^{31}P < -50$). Complete assignment of all carbon atoms in the ¹³C n.m.r. spectrum of the K salt of **3a** ($R^1=R^2=Ph$, $R^3=R^4=H$) proves the structure without any doubt: the three quaternary aromatic carbons exhibiting large ¹³C-³¹P coupling constants ($\delta=161.9$, $^1J=64$ Hz, $\delta=146.0$, $^1J=143$ Hz, $\delta=138.1$, $^1J=149$ Hz) are characteristic for an equatorial-apical position of the phosphole moiety and an equatorial position of the phenyl ligand.

Addition of methylating agents to all of the phosphorane anions gave N-methylspiroposphoranes **6-9** regiospecifically. The n.m.r. spectra of these derivatives differed remarkably from those of the nonalkylated compounds, especially by having some extremely broadened resonance lines in ¹³C n.m.r.; in addition, the value of the ³J_{PNCH} was unexpectedly small, indicating an apical position of the N-methyl group.

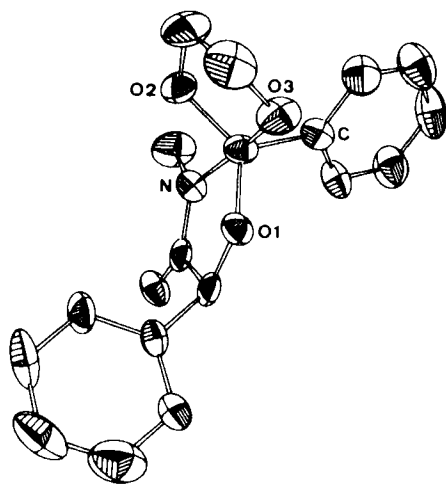


FIGURE 1 ORTEP drawing of molecule **6a**. Selected bond lengths: P-C 1.799(12), P-O¹ 1.608(5), P-O² 1.629(5), P-O³ 1.662(5), P-N 1.797(6).

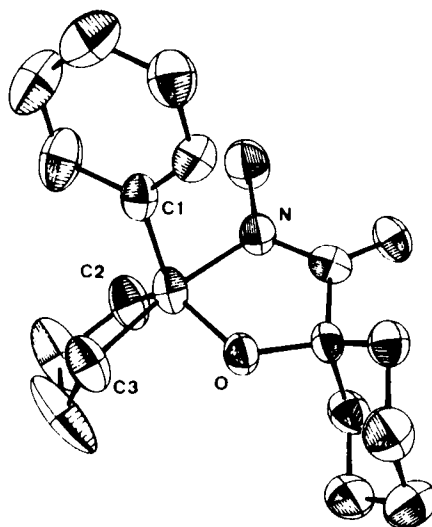


FIGURE 2 ORTEP drawing of molecule **6b**. Selected bond lengths: P-C¹ 1.822(7), P-C² 1.837(9), P-C³ 1.878(10), P-O 1.617(4), P-N 1.887(6).

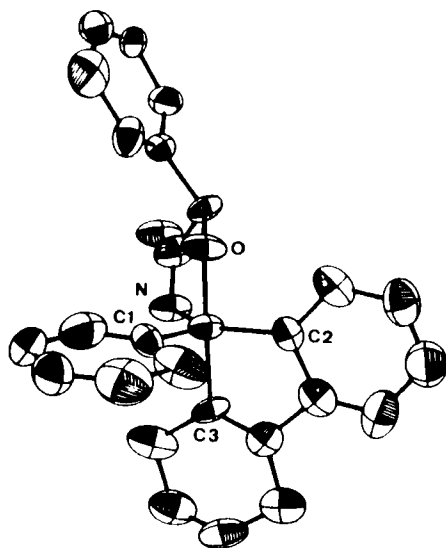


FIGURE 3 ORTEP drawing of molecule **2a**. Selected bond lengths: P-C¹ 1.822(14), P-C² 1.814(12), P-C³ 1.862(16), P-O 1.756(8), P-N 1.675(10).

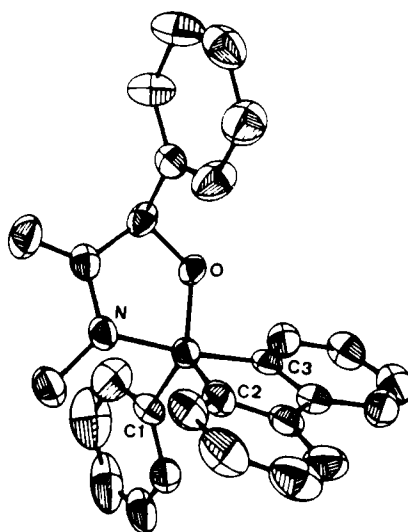
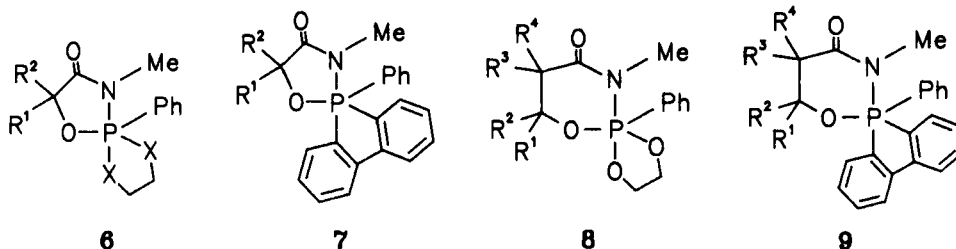


FIGURE 4 ORTEP drawing of molecule **7a**. Selected bond lengths: P-C¹ 1.832(7), P-C² 1.836(8), P-C³ 1.887(8), P-O 1.604(5), P-N 1.859(7).



To verify the presumed geometry which is in contrast to the rule of relative apicophilicity⁶, single X-ray analyses of the N-methyl derivatives **6a** ($R^1=Ph$, $R^2=H$, $X=O$), **6b** ($R^1-R^2=-(CH_2)_5-$, $X=CH_2$)⁷, **7a** ($R^1=Ph$, $R^2=H$)⁸ and of the nonalkylated compounds **1b**⁷ and **2b**⁹ were performed.

By these analyses, direct evidence for the change of molecular geometry of N-methylated species in respect to nonalkylated spirophosphoranes is given. According to the method of Holmes and Deiters¹⁰, the following geometries were found: **1b** ($R^1=R^2=CH_3$) square pyramidal; **2b** ($R^1=Ph$, $R^2=H$) trigonal bipyramidal; **6a** ($R^1=Ph$, $R^2=H$) trigonal bipyramidal; **6b** ($R^1-R^2=-(CH_2)_5-$) trigonal bipyramidal; **7a** ($R^1=Ph$, $R^2=H$) trigonal bipyramidal; all of the N-methyl derivatives have the N-atom in the apical and the O-atom in the equatorial position of the tbp.

Recording the n.m.r. spectra of **6a** and **7a** under slow exchange conditions proved that the preferred geometry in solution is also trigonal bipyramidal.

REFERENCES

1. H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919).
2. O. Mitsunobu, *Synthesis*, **1** (1981).
3. P. Pöchlauer, W. Petter, P. Peringer and E.P. Müller, *J. Chem. Soc., Chem. Commun.*, **1985**, 1764.
4. P. Pöchlauer, Ch. Himmer, P. Peringer, E.P. Müller, Th. Jenny and W. Petter, *Phosphorus Sulfur*, **30**, 455 (1987).
5. H.B. Stegmann, R. Haller and K. Scheffler, *Chem. Ber.* **110**, 3817 (1977).
6. S. Trippett, *Phosphorus Sulfur*, **1**, 89 (1976).
7. B. Köll, E.P. Müller, M. Fischer, W. Petter, *Z. Kristallogr.*, **185**, 229 (1988).
8. K. Totschnig, E.P. Müller, M. Fischer, W. Petter, *Z. Kristallogr.*, **185**, 252 (1988).
9. E.P. Müller, W. Petter, will be published elsewhere.
10. R.R. Holmes and J.A. Deiters, *J. Am. Chem. Soc.*, **99**, 3318 (1977).