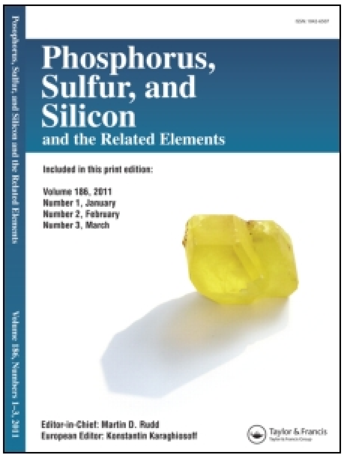

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Preparation, Crystal Structure and Properties of Spirophosphoranes Derived from Hydroxycarboxylic Acid Azides

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PREPARATION, CRYSTAL STRUCTURE AND PROPERTIES OF SPIROPHOSPHORANES DERIVED FROM HYDROXYCARBOXYLIC ACID AZIDES

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Abstract Spirophosphoranes are produced by reaction of 2-phenyl-1,3,2-dioxaphospholane with both 2- and 3-hydroxycarboxylic acid azides, whereas 1-phenylphospholane yields spirophosphoranes only upon reaction with the former. The structures of two spirophosphoranes have been determined by X-ray analysis.

Several papers have appeared in the last years concerning the Staudinger reaction[1] of bifunctional azides with phosphorus(III)compounds to give iminophosphoranes and/or pentacoordinate phosphoranes[2]. In extension of our studies on this topic[3] we investigated the reaction of carboxylic acid azides containing an additional OH group.

α- and β-Hydroxycarboxylic acid azides, easily available from the corresponding acid hydrazides, reacted with triphenylphosphine, trimethylphosphite or 1-phenylphospholane to give phospholanylidene α- and β-hydroxyacylamides, respectively. 1-Phenylphospholane derivatives of α-hydroxycarboxylic acids were found to be in equilibrium with the corresponding spirophosphoranes, whereas the analogous β-hydroxy compounds did not form λ^5-phosphoranes in a detectable extent. By reaction with 2-phenyl-1,3,2-dioxaphospholane, however, α- and β-hydroxycarboxylic acid azides were converted completely into spirophosphoranes.

X-ray analysis of spirophosphorane 1 (Figure 1) showed nearly ideal rpy geometry, the sum of angle deviations calculated with the Holmes and Deiters method[4] is only 18.7°. In contrast, the homologous compound with a six-membered ring was found to possess nearly ideal tbp geometry, the sum of angle deviations being 11.1°[5].

Crystal data: $C_{16}H_{16}NO_4P$, M=317.29, monoclinic, space group $P2_1$, a=9.120(2), b=7.395(5), c=11.744(6) Å, β=106.87(5)°, Z=2, $D_{calc.}$=1.39 g cm^{-3}; 1392 observed reflections with $2\theta \leq 50°$. The final value of R was 0.037; R_w=0.04.

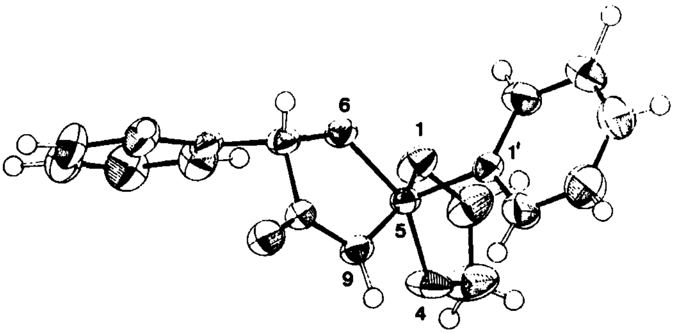

FIGURE 1 ORTEP drawing of the molecule 1. Selected bond lengths: P-C 1.802(1), P-O(1) 1.650(1), P-O(4) 1.644(1), P-O(6) 1.655(1), P-N 1.739(1) Å.

By X-ray analysis, the benzoannulated derivative 2 (Figure 2) was observed in conformation a and b in the asymmetric unit. The two independent molecules show only small differences in their geometries but large differences in the temperature factors. The arrangement of the ligands around the phosphorus is tbp distorted 42% and 33% to rpy along the Berry intramolecular exchange coordinate[4].

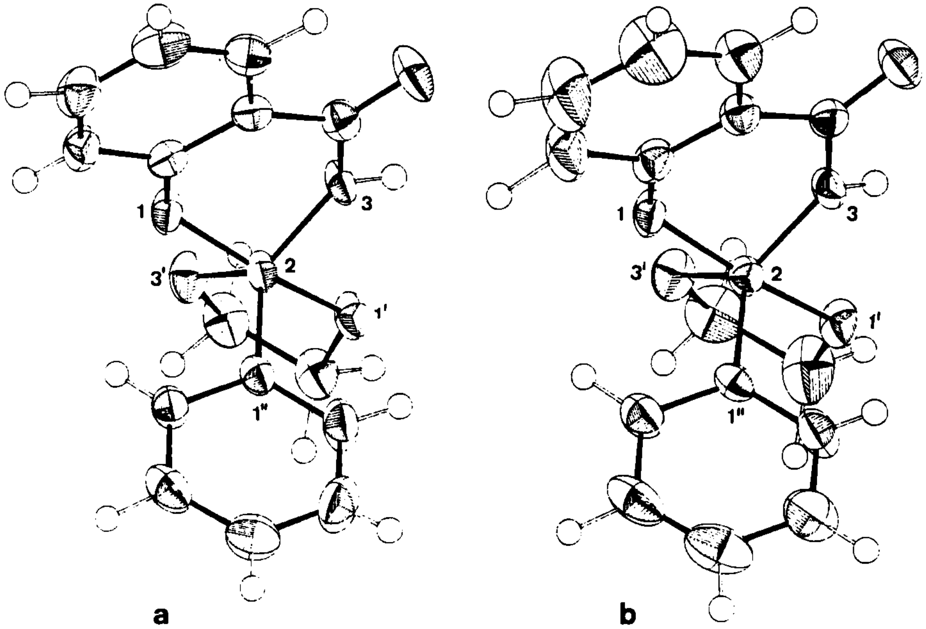

FIGURE 2 ORTEP drawing of the molecule 2 observed in conformation a and b in the asymmetric unit; the P-O(1) and the P-N bond are in the same plane. Selected bond lengths: P-C 1.801(4), P-O(1') 1.686(3), P-O(3') 1.619(3), P-O(1) 1.707(3), P-N 1.704(2) Å (conformation a); P-C 1.807(4), P-O(1') 1.685(3), P-O(3') 1.620(2), P-O(1) 1.714(3), P-N 1.690(3) Å (conformation b).

Crystal data: $C_{15}H_{14}NO_4P$, M=303.25, triclinic, space group $P\bar{1}$, a=11.36(2), b=12.38(1), c=12.73(1) Å, α= 65.73(9), β=75.36(9), γ=63.95(9)°, Z=4 (2 independent molecules), $D_{calc.}=1.38$ g cm^{-3}; 4155 observed reflections with $2\Theta \leq 50°$. The final value of R was 0.059; $R_w=0.074$.

To distinguish between the two possible mechanisms of epimerization on phosphorus - a ring-opening/ring-closure pathway, pseudorotation on phosphorus -, the activation energies and the resulting activation parameters were determined. For the epimerization of 1 and its six-membered ring homologue, the activation entropy was found to be clearly negative (-10.9±3.5 and -14.0±2.0 cal mol^{-1} K^{-1}), a fact which confirms epimerization by pseudorotation; the alternative path should show a positive value of $\Delta S^{\#}$.

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