

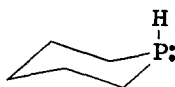
THE CONFORMATIONAL PREFERENCE OF THE PROTON ON PHOSPHORUS IN  
PHOSPHACYCLOHEXANE

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Phosphacyclohexane (pentamethylenephosphine or phosphorinane) can exist in conformations in which the proton on phosphorus is either axial (I) or equatorial (II). Determination of the



I



II

conformational preference of this proton bears on the similar problem in the nitrogen analogue, piperidine.<sup>1</sup> We wish to report from coupling constant data that phosphorinane exists almost entirely in the conformation with the phosphorus proton (the "P-proton") axial (I).

Phosphorinane has four distinct advantages over piperidine in a study of the conformational properties of the substituent proton.<sup>2</sup> (1) The proton on phosphorus exchanges with the medium more slowly than the corresponding proton on nitrogen, so that couplings with the ring protons can be observed. Analogous experiments<sup>3</sup> with piperidine have failed to discern H-N-C-H couplings, even at  $-80^\circ$  with irradiation of nitrogen-14. (2) The phosphorus atom is configurationally stable. Consequently, the substituent on phosphorus cannot convert from the axial to the equatorial position, or vice versa, once ring inversion has been frozen out. In contrast, nitrogen inversion will interconvert axial and equatorial N-methylpiperidine at  $-50^\circ$ .<sup>4</sup>

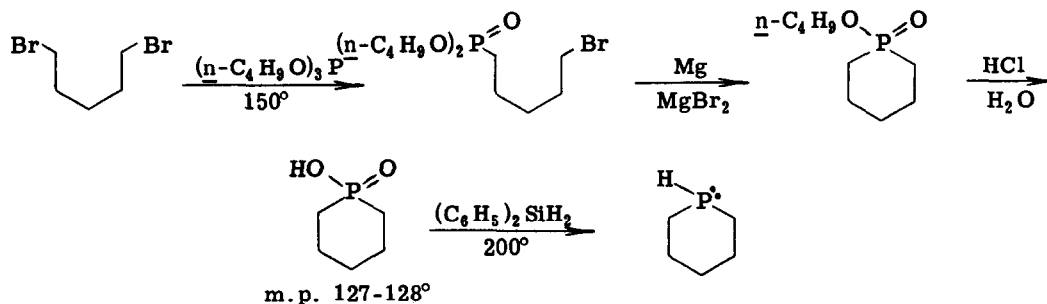
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(3) Since  $^{31}\text{P}$  has a spin of  $1/2$ , no quadrupolar effects are present. Because the directly-bonded  $^{31}\text{P}$ -H coupling constant is quite large,<sup>4</sup> the P-proton subspectra corresponding to spins  $+1/2$  and  $-1/2$  of  $^{31}\text{P}$  are well separated. All of the information concerning the coupling between the P-proton and the ring protons can be obtained from either subspectrum. (4) The phosphorus atom is nearly  $p$  hybridized, so the nonbonding electron pair resides in an orbital of very high  $g$  character.<sup>4</sup> The lone pair must therefore have little or no directionality, and the concept of steric requirements is wholly inapplicable. The properties and interactions of the proton alone must determine its conformational preference. In the piperidine case, for which the lone pair is highly directional, properties of both the lone pair and the proton have been considered to be conformationally important, but have never been experimentally separated. Phosphorinane thus offers an ideal system for determination of the inherent preference of the proton.

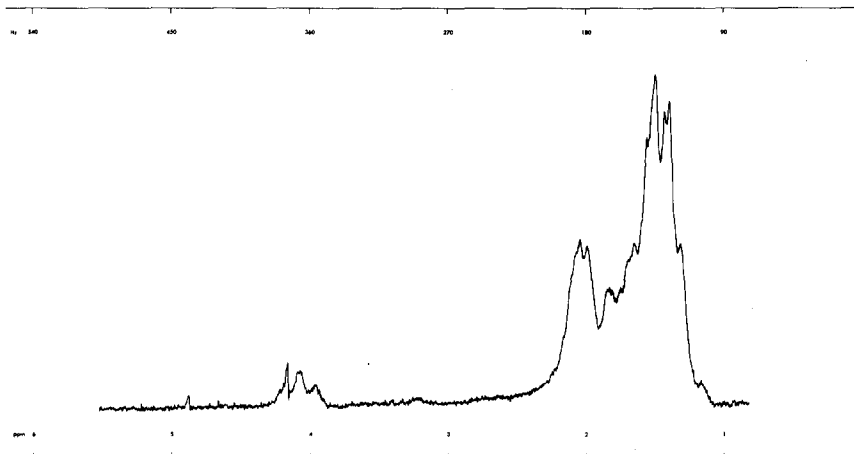
Phosphorinane was prepared by the following route:<sup>5, 6</sup>



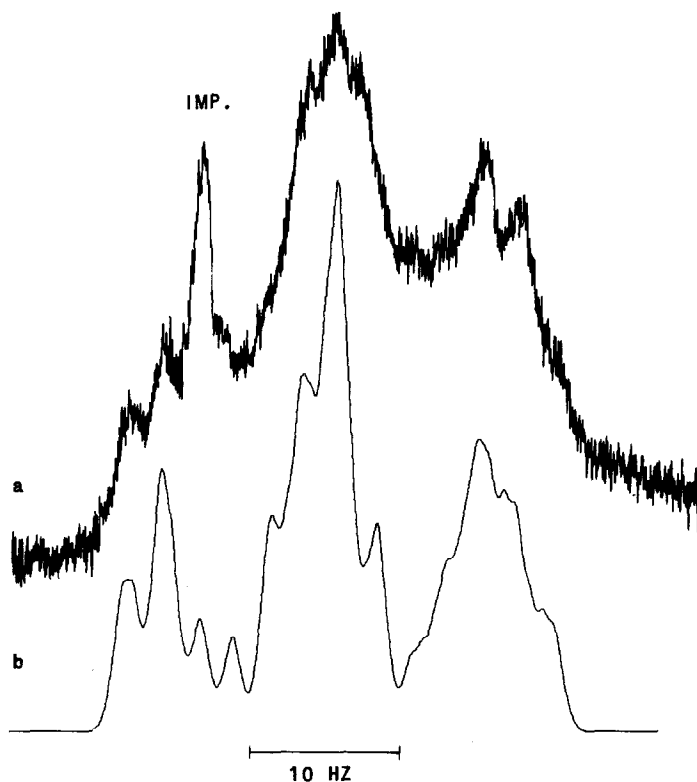
The final step was carried out on a vacuum line. The product was distilled directly into a cooled nmr tube. After dry, degassed trichlorofluoromethane (Freon 11) was introduced as solvent, the tube was sealed under vacuum.

At  $-50^\circ$ , the nmr spectrum of phosphorinane (Figure 1) consists of a multiplet between 1.2 and 2.2 ppm (10.5 protons) and a set of peaks centered at 4.1 ppm (0.5 proton). The spectrum of the P-proton is split into two portions by the large  $J_{31\text{P-H}}$ . One portion appears at 4.1 ppm and the other falls under the resonances of the ring protons. Because the P-proton clearly exhibits couplings to  $^{31}\text{P}$  and to the ring protons, exchange with the medium must be nmr-slow at this temperature. Irradiation at the  $^{31}\text{P}$  frequency brings about the disappearance of the multiplet at 4.1 ppm and the appearance of a nearly identical multiplet 100 Hz to higher field. The magnitude of  $J_{31\text{P-H}}$  must therefore be  $200 \pm 10$  Hz.

The location of the proton on phosphorus may be determined from its coupling pattern with the  $\alpha$  protons. An axial P-proton would give a triplet of triplets, because of coupling with



**Figure 1.** The 90-MHz spectrum of phosphorinane at  $-50^\circ$ . All nmr spectra in this study were taken on the Bruker HFX-10 spectrometer.



**Figure 2.** The low-field subspectrum of the P-proton in phosphorinane at 90 MHz and  $-50^\circ$ : (a) observed; (b) calculated by LAOCN3. The sharp resonance ("imp.") is caused by an impurity; at 60 MHz, this peak is sufficiently displaced from the P-proton resonance to reveal the obscured fine structure.

two adjacent axial ( $J_{aa}$ ) and two equatorial ( $J_{ae}$ ) protons.<sup>2,7,8</sup> An equatorial P-proton resonance would approximate to a quintet ( $J_{ae} \sim J_{ee}$ ) or a multiplet with a small bandwidth. The observed pattern for the P-proton in phosphorinane can only arise from a proton that is axial (Figure 2a). The multiplet is somewhat complicated by virtual coupling with the  $\beta$  protons. A seven-spin system including the P-proton, the four  $\alpha$  protons, and the two axial  $\beta$  protons accurately simulates the observed spectrum (Figure 2b). The derived couplings,  $J_{aa} = 12$  Hz and  $J_{ae} = 2.5$  Hz, may be explained only in terms of a P-proton that is almost entirely axial. No more than 10% of the equatorial isomer could have been present but not detected.

We may conclude from these results that the proton has an inherent preference for the axial position. An explanation for this observation has been offered by Allinger and co-workers in terms of attractive axial-axial interactions between protons.<sup>9</sup>

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