absence of such nucleophiles X undergoes intramolecular cyclization at the tertiary ring position to yield XI. A similar rearrangement has also been used to explain the photochemical formation of β-methylglutaconic anhydride from triacetic acid lactone.[23] Electronic rearrangement in XI leads directly to IV.

(23) C. T. Bedford, J. M. Forrester, and T. Money, *Can. J. Chem.*, 48, 2645 (1970).
(24) ACS-PRF Undergraduate Research Participant, 1971–1972.

James W. Pavlik,* Edward L. Clennan[24]

*Department of Chemistry, University of Wisconsin—River Falls
River Falls, Wisconsin 54022*

Investigation of the Conformational Equilibrium of 1-Methylphosphorinane by Low-Temperature ^{31}P and ^{1}H Nuclear Magnetic Resonance Spectroscopy[1]

Sir:

Substantial differences are known to exist in the ^{31}P and ^{1}H nmr spectra of the conformationally biased phosphorinane derivatives I and II[2] [respectively,

I (cis)   II (trans)
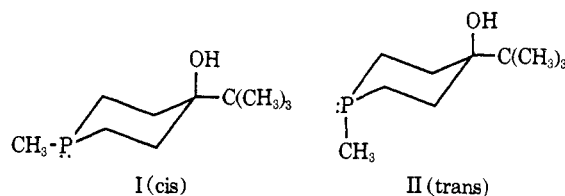
$\delta(^{31}P)$ +57.7 and +64.6 ppm; $\delta(PCH_3)$ 0.95 ($^2J_{PH}$ = 2.1) and 0.89 ppm ($^2J_{PH}$ = 4.0 Hz)], whose structures are known with certainty from X-ray analysis.[3] In the absence of a *tert*-butyl group, *P*-methylphosphorinanes should undergo rapid equilibration between conformers with axial and equatorial methyl and give nmr spectra at room temperature that are time averaged. At very low temperatures, however, it would be expected that equilibration would be so slow that the conformers could be detected by the same ^{31}P and ^{1}H nmr differences seen for I and II. This has proved to be the case and has led to the first determination of some of the energetic parameters for conformational equilibration in a phosphorinane. Qualitative indications[2] that 1,3-nonbonded interactions involving the *P*-methyl group are weak and do not result in a strong preference by the substituent for the equatorial position are confirmed.[4–9]

(1) Supported by Public Health Service Research Grant CA-05507, National Cancer Institute. Purchase of the Bruker spectrometer was made possible in part by a grant from the National Science Foundation (Grant No. GP-10301).
(2) L. D. Quin and J. H. Somers, *J. Org. Chem.*, 37, 1217 (1972).
(3) A. T. McPhail, P. A. Luhan, S. I. Featherman, and L. D. Quin, *J. Amer. Chem. Soc.*, 94, 2126 (1972).
(4) Related systems have also shown some unusual conformational properties. Single-crystal X-ray analysis reveals that 1-phenyl-4-phosphorinanone[5] and its dimethyl ketal[6] have the phenyl group axially oriented. Nmr studies show the same preference for the proton of phosphorinane at −50°[7] and for P substituents of dioxa-[8] and dithia-phosphorinanes.[9]
(5) A. T. McPhail, J. J. Breen, and L. D. Quin, *J. Amer. Chem. Soc.*, 93, 2574 (1971).

The proton-decoupled ^{31}P nmr signal for neat 1-methylphosphorinane (III, bp 144–147°; prepared from methylphosphonous dichloride and $BrMg(CH_2)_5$-MgBr and analyzed as the methiodide, decomposition without melting) was a sharp singlet at room temperature at +53.7 ppm. In a vinyl chloride solution prepared at −40°, the singlet was also present. On lowering the temperature, the peak broadened and finally at −80° separated into two sharp signals spaced 3.1 ppm apart. In accord with I and II, the upfield signal is assigned to the axial conformer (IIIa) and the downfield signal to the equatorial conformer (IIIb). The
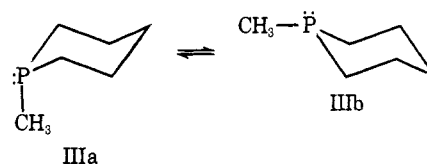
sharpness of the proton-decoupled signals permitted estimation of the equilibrium composition by peak height measurement.[10] At the lowest temperature reached (−130°), the equatorial conformer predominated over the axial (2.0 to 1). This is a remarkably low equatorial preference when compared to methylcyclohexane (99% equatorial at −110° [11]) or *N*-methylpiperidine (95% or more equatorial at −150° [12]), but this result nevertheless suggests that repulsive 1,3 interactions do prevail in the phosphorinane system. The variation in the peak height ratio with temperature gave the following additional vaues for K: −125°, 1.8; −120°, 1.7; −115°, 1.5; −110°, 1.5; −105°, 1.4. A plot of log K against $1/T$ was linear (Figure 1) and on extrapolation gave a constant for the conformational equilibrium at 25° of 0.56. Thus, *the axial form predominates at room temperature.*

We believe this to be the first instance of the use of ^{31}P nmr spectroscopy to explore conformational equilibration in a cyclic system. The technique offers considerable advantage over the use of proton spectra (*vide infra*); the signals are clearly separated and sharp even at very low temperatures. That they are of quite different chemical shift causes coalescence to be reached at higher temperatures.

The methyl proton signal for III, a doublet ($^2J_{PH}$ = 3.0 Hz) at room temperature for the averaged conformation, broadened into a single peak at −100° in either trimethylethylene or vinyl chloride; in the latter, it was possible to lower the temperature further, whereupon the singlet separated into two doublets, somewhat broad and in slight overlap. That the two signals were indeed due to the two P–CH$_3$ doublets was established by decoupling ^{31}P from the protons, which caused the two doublets to collapse to two singlets. At −144°, the upfield doublet had J = 1.8, the lowfield 3.2 Hz, with separation of 8 Hz (0.09 ppm). Based on J values for

(6) A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, Jr., and L. D. Quin, *Chem. Commun.*, 1020 (1971).
(7) J. B. Lambert and W. L. Oliver, Jr., *Tetrahedron*, 27, 4245 (1971).
(8) W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *J. Amer. Chem. Soc.*, 93, 797 (1971).
(9) R. O. Hutchins and B. E. Maryanoff, *ibid.*, 94, 3266 (1972).
(10) The equilibrium constants and thermodynamic values are subject to refinement with the use of more accurate peak measuring techniques.
(11) F. A. L. Anet, C. H. Bradley, and G. W. Buchanan, *J. Amer. Chem. Soc.*, 93, 258 (1971).
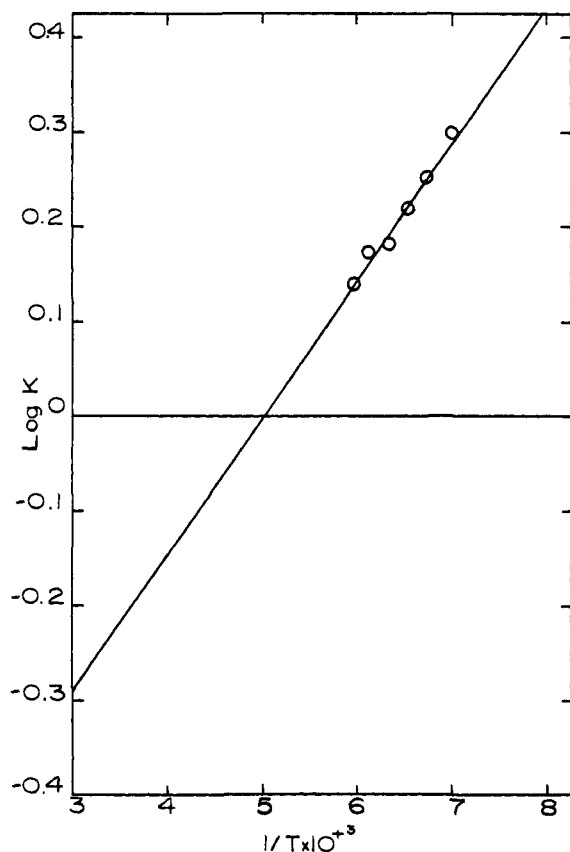(12) J. B. Lambert, W. L. Oliver, Jr., and B. S. Packard, *ibid.*, 93, 933 (1971).

Figure 1. Log K vs. $1/T$ for the equilibrium IIIa $\rightleftarrows$ IIIb in vinyl chloride. Values of K were determined from ^{31}P nmr spectra.

I and II as standards, the signals are assigned to the equatorial (IIIb) and the axial (IIIa) conformers, respectively. Also, the upfield doublet had an area ratio of about 2:1 to the downfield, in accord with the equatorial–axial ratio found from the low-temperature ^{31}P spectrum. The overlap of the peaks, as well as some interference of the downfield signal with the ring CH_2 signals, prevented accurate determination of the variation of K with temperature, but an approximate value (0.2) from extrapolation to room temperature supports the conclusion from the ^{31}P nmr experiment that the axial conformer predominates. Confirmation of the axial predominance is also found in the proximity of the time-averaged J_{PH} value (3.0 Hz) at room temperature to that (3.2 Hz) of the "frozen" axial form IIIa.

As in the methylcyclohexanes,[13] axial methyl protons in the methylphosphorinane system are now seen to absorb downfield of equatorial ones When examined in benzene solution, tertiary 4-phosphorinanols show the opposite relation of P-methyl signals.[2,14] This may be explained on the basis of a deshielding effect associated with the OH group in aromatic solvents;[15] the effect is stronger on the equatorial methyl of the cis isomer[14] and causes a shift sufficient to place the signal slightly downfield of that of the axial methyl of the trans isomer.

The $\Delta G^{\ddagger}$ value for ring inversion calculated by the

(13) F. Johnson, N. A. Starkovsky, and W. D. Gurowtiz, *J. Amer. Chem. Soc.*, **87**, 3492 (1965).

(14) H. E. Shook, Jr., and L. D. Quin, *ibid.*, **89**, 1841 (1967).

(15) P. V. Demarco, E. Farkas, D. Doddrell, B. L. Mylaii, and E. Wenkert, *ibid.*, **90**, 5480 (1968).

coalescence temperature method using the ^{31}P signals was 9.2 kcal/mol at $-75°$. This value is quite similar to that for inversion of the cyclohexane ring (10.5 kcal/mol at $-67°$ [16]). Other thermodynamic functions for the conformational equilibrium in the two systems were considerably different, however. The $\Delta H°$ value, obtained from a van't Hoff plot, was small (-0.67 kcal/mol) and reflects the fact that 1,3 repulsive interactions are weaker than in cyclohexanes. Bond lengths and angles, as well as torsion angles, are quite different in the two systems; as noted elsewhere,[2,14] these differences can account for the diminution of the repulsive forces acting on a P-methyl group. The entropy change, calculated at $-130°$, was -3.3 eu. The combination of a small $\Delta H°$ value and a nonnegligible entropy difference between the isomers results in a substantial dependence of $\Delta G°$ on temperature and happens to be accompanied by a change in sign (at $-130°$, $\Delta G° = -0.20$; at $25°$, $\Delta G° = +0.34$ kcal/mol). Thus the important conclusion is reached that, under these special circumstances for $\Delta H°$ and $\Delta S°$, the $\Delta G°$ value at room temperature does not reveal the true nature of the 1,3 interactions; the low-temperature studies imply, however, that these are repulsive, and that there is no need to invoke an explanation for the predominance of the axial form at room temperature on the premise of attractive interactions in this conformer. Such interactions may, however, be important in other systems, as has recently been discussed for the silacyclohexanes.[17]

All spectra were obtained on a Bruker HFX-10 spectrometer; ^{31}P spectra were obtained at 36.4 MHz and are referenced to external 85% H_3PO_4, while ^1H spectra were obtained at 90 MHz. For low-temperature work, 15% solutions of III were used; TMS was employed as lock in trimethylethylene and CCl_2F_2 in vinyl chloride. Mr. Antonio Castillo is thanked for his skilled technical assistance with these experiments.

(16) F. A. Bovey, F. P. Hood, III, E. W. Anderson, and R. L. Kornegay, *J. Chem. Phys.*, **41**, 2041 (1964).

(17) M. T. Tribble and N. L. Allinger, *Tetrahedron*, **28**, 2147 (1972); R. J. Ouellette, D. Baron, J. Stolfo, A. Rosenblum, and P. Weber, *ibid.*, **28**, 2163 (1972).

Sidney I. Featherman, Louis D. Quin*

Paul M. Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706
Received October 20, 1972

The Equilibrium between 2-Hydroxypyridine and 2-Pyridone in the Gas Phase

Sir:

The equilibrium between 2-pyridone (1) and 2-hydroxypridine (2) is representative of a large number of protomeric equilibria which have been extensively investigated in solution[1] and are of interest to studies of thermodynamic stabilities and, for the heteroaromatic bases of the nucleic acids, to hypotheses about base pairings. It is clear that 1 is strongly favored over 2 in solution,[2] but some reservation has been expressed

(1) A. Albert, "Heterocyclic Chemistry," Athlone Press, London, 1968, pp 369–375; A. R. Katritzky, *Chimia*, **24**, 134 (1970), and references cited therein.

(2) A. R. Katritzky and J. M. Lagowski, *Advan. Heterocycl. Chem.*, **1**, 347 (1963); R. H. Cox and A. A. Bothner-By, *J. Phys. Chem.*, **73**, 2465 (1969), and references cited therein.