BARRIERS TO PSEUDOROTATION IN ALKYLPHOSPHORANES

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The first pentaalkylphosphorane, I, homocubyltrimethylphosphorane, was prepared recently, and an interesting feature of its proton nmr spectrum at room temperature is that the chemical shifts of all the methyl protons are identical, even though no structure can be drawn for the molecule in which the methyl protons have identical environments.² If the molecule has a trigonal bipyramidal conformation, one of the methyls should be axial and two equatorial. An averaging process called pseudorotation is known for other pentavalent compounds, ³ but while pseudorotation rates should decrease with temperature, at the lowest temperatures now achievable with most instruments, kinetically unaveraged nmr spectra have usually been observed only for compounds in which the substituents attached to the central atom differ in electronegativity.^{3a,b} Of molecules studied in which phosphorus is surrounded by five identical atoms, only two kinds have had their pseudorotations slowed so



III

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No. 23

that unaveraged spectra are observed. These are the bis-biphenylenephosphoranes, III, some of which exhibit unaveraged proton nmr spectra even at room temperature, ⁴ and some fluorine-substituted pentaalkoxyphosphoranes, which exhibit unaveraged fluorine nmr spectra below -100° . ⁵ In others, averaged spectra were observed down to the lowest temperature reached, -100° for pentaphenylphosphorane^{6,7} and a pentaalkoxyphosphorane,⁸ and about -197° for phosphorus pentafluoride.^{3a}

We have now found that the spectrum of the pentaalkylphosphorane I is the same at -100° as it is at room temperature. But at -158°, while the resonances of the remaining protons and of added tetramethylsilane are not significantly changed, the methyl resonance is broadened. The broadening intensifies as the sample is cooled to the lowest temperature achieved, -184°. Presumably the effect that accounts for these observations is the slowing of the pseudorotation process, but the low temperatures that must be reached before any effect is observed imply that the barrier to pseudorotation is low.

Similarly the proton nmr spectrum of II, which differs from I in that a phenyl replaces a methyl, also shows only one methyl resonance at room temperature, and the spectrum is similar at -100°. However as shown in Figure 1, below -128° the resonances of the methyl protons at δ 1.18 and of the ring protons adjacent to the phosphorus atom at δ 2.74 broaden, while the remaining resonances remain largely unchanged. Down to -172° only further broadening occurs. The implication is that the barrier to pseudorotation, as well as the difference in energy between conformers in which methyl and phenyl are permuted, is small.

Because at the lowest temperatures the spectra were not completely unaveraged, the chemical shifts of the methyls in the different conformational environments are not known. However for I, assuming that the methyls occupy two sites whose population ratio is 2:1, that the difference between the chemical shifts of methyls at these sites is between 0.5 and 1 ppm,⁹ and that both $J_{P,CH_3} = 9.1 \text{ Hz}$,¹⁰ the shape of the methyl resonance at -167°, when it is broadened just to the point at which the phosphorus proton coupling is no longer resolved, could be computer simulated¹¹ and ΔG^{\dagger} calculated to be between 5.1 and 4.9 kcal/mole. The corresponding activation energy for II must be similar.

The spectra were determined in mixtures of $CH_2 = CHC1$ and $CIFC = CF_2$ (33:67 v/v).¹² The lowest temperature at which the experiment could be performed was determined for I by the freezing point of the solvent mixtures and for II by its solubility.

The barriers here are the lowest measured for the pseudorotation of pentasubstituted phosphorus compounds, although for phosphorus pentafluoride the barrier must be lower yet.^{3a} They are much lower than the barriers in III, which for various R vary between 11.9 and 20.8 kcal/mole.⁴



Figure 1. Proton nmr spectra (60 MHz) of II at various temperatures.

Footnotes

- (a) Alfred P. Sloan Research Fellow, 1971-1973;
 (b) Supported by the National Institutes of Health under grant MH08912.
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- (4) (a) D. Hellwinkel, <u>Chimia</u>, 22, 488 (1968); (b) G.M. Whitesides and W.M. Bunting, J. Amer. Chem. Soc., 89, 6801 (1967).
- (5) F. Ramirez, et.al., Phosphorus, 1, 1 (1971).
- (6) E.L. Muetterties, W. Mahler, K.J. Packer, and R. Schmutzler, <u>Inorg. Chem.</u>, 3, 1298 (1964).
- (7) Penta-p-tolylphosphorane shows only one methyl resonance down to -60° [D. Hellwinkel, <u>Angew. Chem. Int. Ed. Engl.</u>, 5, 725 (1966)].
- (8) D. Gorenstein and F.H. Westheimer, J. Amer. Chem. Soc., 89, 2762 (1967).
- (9) Line shapes calculated, assuming that the difference in chemical shifts was less than 0.4 ppm, did not resemble the observed spectra. Satisfactory simulation could be achieved assuming any value between 0.5 and 1.0 ppm for this difference.
- (10) This is the average coupling measured in the spectra at room temperature.
- (11) The program used is DNMR3: D.A. Kleier and G. Binsch, J. Mag. Resonance, 3, 146 (1970).