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Pseudo-Rotation in *o*-Isopropylphenylbis(*p,p'*-bitolyl)phosphorane[1]

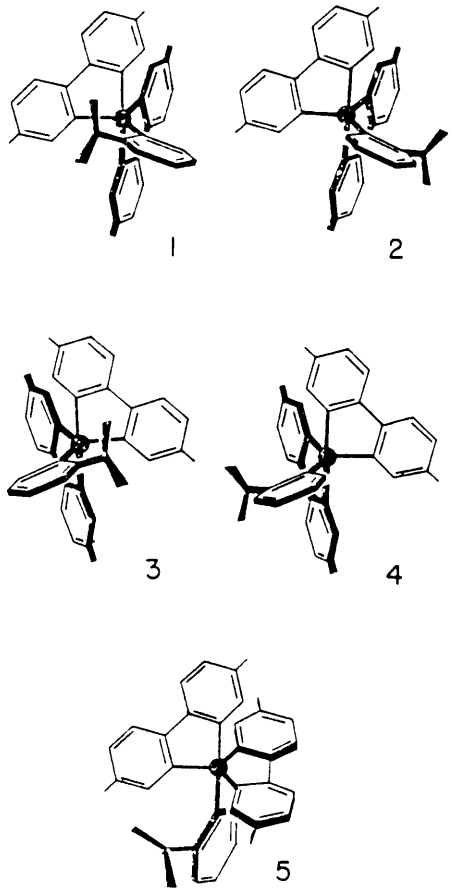
Sir:

The facile intramolecular interchange of aryl groups between the axial and equatorial positions of pentaarylphosphoranes provides an important example of the stereochemical flexibility which characterizes a variety of pentacoordinate compounds.[2,3] The mechanism of this interchange is generally believed to be that originally suggested by Berry for phosphorus pentafluoride, in which the transition state for the pseudo-rotation of one ground-state trigonal bipyramid into another is a tetragonal pyramid.[4] However, other less symmetrical mechanisms for axial–equatorial exchange seem possible, particularly for compounds containing bulky or chelating ligands.[3] We wish to report the results of an nmr study of pseudo-rotation in *o*-isopropylphenylbis(*p,p'*-bitolyl)phosphorane (**1**), which support the applicability of the Berry mechanism to this more complicated system.

Compound **1** was prepared by the tosylimine procedure developed by Wittig and coworkers.[2,5] Its spectrum at 33° in bromobenzene solution consists of three lines at δ 2.60 (3 H), 2.52 (3 H), and 2.46 (6 H) for the bitolyl methyl protons,[6] and two doublets (J = 6.6 Hz) at δ 0.98 and 1.82 for the isopropyl methyl protons. On warming the sample to 130°, the bitolyl methyl signals collapse to a single line,[7] and the isopropyl resonances to a sharp doublet.

The magnetic nonequivalence of the four bitolyl methyl groups is consistent with the expected[8] trigonal bipyramidal structure **1**, with the restriction that rotation of the *o*-isopropylphenyl group (*e.g.*, **1** → **2**) is slow on the nmr time scale. The magnetic nonequivalence of the diastereomeric isopropyl methyl groups reflects their proximity to the chiral environment provided by the bis(*p,p'*-bitolyl)phosphorus center. This latter type of nonequivalence can be averaged only by reversing the sense of the chirality of the molecule (**1** → **3** or **4**); simple rotation of the *o*-isopropylphenyl group (**1** → **2**) leaves it unchanged.[9] Thus the lines shapes of the bitolyl methyl peaks in the exchange-broadened region provide a measure of the rate of interchange of axial and equatorial positions of **1**; the shapes of the isopropyl resonances provide an independent measure of the rate of interconversion of enantiomers. Comparison of these two rates provides a delicate probe with which to examine details of the pseudo-rotation process.

We have carried out kinetic analyses of the temperature dependence of the isopropyl and bitolyl methyl line shapes using standard techniques[10] and find that



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(2) G. Wittig, *Bull. Soc. Chim. France*, 1162 (1966).

(3) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967).

(4) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960). An infrared and Raman study of PF_5 has recently indicated that fluorine interchange does *not* take place along normal vibrational modes of the molecule: L. C. Hoskins and R. C. Lord, *ibid.*, **46**, 2402 (1967).

(5) D. Hellwinkel, *Ber.*, **99**, 3628, 3642, 3660 (1966). This work provides convincing evidence that the rate of racemization of optically active bis(biphenyl)phenylphosphoranes is too large to be amenable to polarimetric measurement.

(6) In nitrobenzene solution four lines are clearly resolved.

(7) Hellwinkel has reported similar observations: D. Hellwinkel, *Angew. Chem. Intern. Ed. Engl.*, **5**, 725 (1966); see also D. G. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 2762 (1967).

(8) Good precedent for this structure is provided by an X-ray examination of bis(biphenyl)phenylantimony: J. Weiss, unpublished results quoted in ref 2; see also P. J. Wheatley, *J. Chem. Soc.* 2206 (1964); W. C. Hamilton S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965), for related structures.

(9) For examples of magnetic nonequivalence in dissymmetric systems, see W. L. Meyer and R. B. Meyer, *ibid.*, **85**, 2170 (1963); F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *ibid.*, **86**, 3576 (1964).

(10) R. Kubo, *Nuovo Cimento Suppl.*, **6**, 1063 (1957); R. A. Sack, *Mol. Phys.*, **1**, 163 (1958); C. S. Johnson, Jr., *Advan. Magnetic Resonance* **1**, 33 (1965).

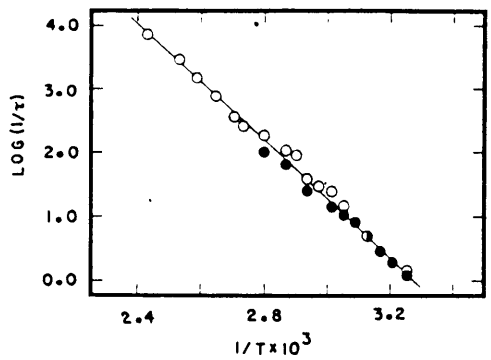

Figure 1. Arrhenius plot of rate data from the isopropyl resonances (open circles) and the bitolyl methyl resonances (filled circles) of **1**. The Arrhenius parameters derived from a least-squares fitting to all the points are $E_a = 20.8 \pm 0.4$ kcal/mole; $\log A = 15.0 \pm 0.3$.

we can obtain excellent agreement between calculated and observed spectra for each group of lines, using an exchange scheme in which pseudo-rotation converts each one of the conformations **1**, **2**, **3**, or **4** with equal probability into the other three. Specifically, the kinetic exchange matrix K[10] used for this problem had elements $K_{ij} = -1$, $i = j$, and $K_{ij} = {}^1/_3$, $i \neq j$, for the four bitolyl methyl peaks, and $K_{ij} = -{}^2/_3$, $i = j$, and $K_{ij} = {}^2/_3$, $i \neq j$, for the isopropyl methyl doublets, and implies that the rate constants k_{12}, k_{13}, and k_{14} describing conversion of **1** to **2**, **3**, and **4**, respectively, are equal.[11] Although spectra calculated on the assumption that $k_{12} = k_{14}$ and $k_{13} = 0$ were in equally close agreement with the spectra observed for the bitolyl methyl protons, spectra calculated assuming either that $k_{12} \geq 2k_{14}$ or that $k_{14} \geq 2k_{12}$ had line shapes which were qualitatively distinguishable from those observed.[12]

An Arrhenius plot of the rate data obtained by comparison of the observed spectra with those calculated using the assumption that $k_{12} = k_{13} = k_{14}$ (Figure 1) indicates that within our experimental error the points obtained from the isopropyl resonances fall along the same line as those from the bitolyl methyl resonances and implies that the interchange of axial and equatorial positions on the bridging bitolyl groups occurs at the same rate as the interconversion of enantiomers. This observation strongly suggests that axial–equatorial interchange and racemization share a common mechanism and is entirely consonant with the Berry mechanism.

Although this result in no sense establishes the correctness of the Berry mechanism, it does argue against certain other mechanistic possibilities. For example, a plausible alternative mechanism, which would involve an intermediate such as **5** in the exchange process, would be expected to result in a rate of interchange of enantiomers approximately twice that of interchange of axial and equatorial bitolyl methyl groups. The data of Figure 1 indicate that the rates of these two processes are in fact equal, and, although the difference between this observed rate equality and the twofold difference in rates predicted to result from the intermediacy of **5** is small, it is probably outside the experimental error in our measurements.

(11) The symmetry of this exchange matrix makes it unnecessary to assign chemical shifts to the individual bitolyl methyl groups.

(12) The particular limiting exchange scheme in which $k_{12} = 0$ leads to a doublet for the bitolyl methyl protons in the fast-exchange limit, rather than the observed singlet.

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