

shown previously that not only does *trans*-1-phenyl-1,3-butadiene go to a photostationary mixture containing the *cis* and *trans* isomers but longer photolysis time results in electrocyclic ring closure to 3-phenylcyclobutene.⁶ The difference may arise as a result of different conformations allowed in I and not in the phenylbutadiene or as a result of the hydrogen shift being the preferred pathway when feasible.

(6) M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966).

Martin Pomerantz, Gerald W. Gruber

Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received September 26, 1967

Pseudo-Rotation in *o*-Isopropylphenylbis(*p,p'*-bitolyl)phosphorane¹

Sir:

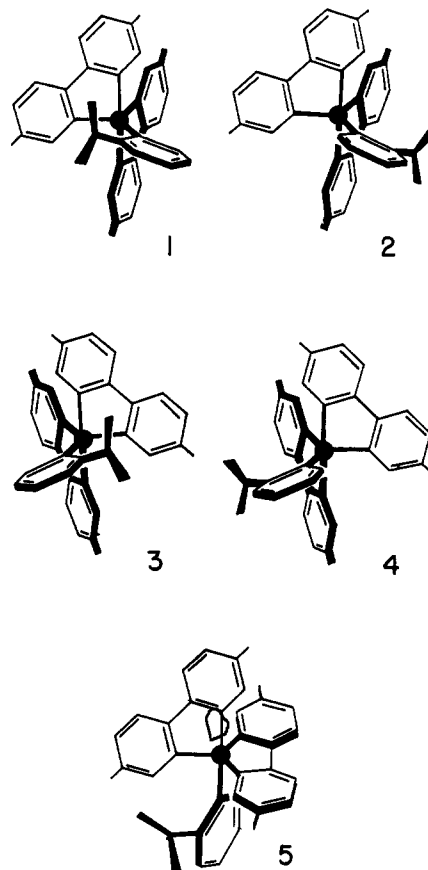
The facile intramolecular interchange of aryl groups between the axial and equatorial positions of pentarylphosphoranes provides an important example of the stereochemical flexibility which characterizes a variety of pentacoordinate compounds.^{2,3} The mechanism of this interchange is generally believed 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 expected⁸ trigonal bipyramidal structure **1**, with the restriction that rotation of the *o*-isopropylphenyl group (e.g., **1** \rightarrow **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** \rightarrow **3** or **4**); simple rotation of the *o*-isopropylphenyl group (**1** \rightarrow **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 techniques¹⁰ and find that



(1) Supported in part by the U. S. Army Research Office (Durham), Grant ARO-D-31-124-G691, and by Eli Lilly and Co.

(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 PF₅ 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).

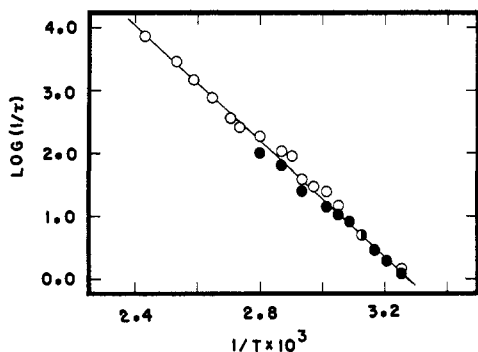


Figure 1. Arrhenius plot of rate data from the isopropyl resonances (open circles) and the bitolyl methyl resonances (filled circles) of **1**. The Arrhenius parameters derived from a least-squares fitting to all the points are $E_a = 20.8 \pm 0.4$ kcal/mole; $\log A = 15.0 \pm 0.3$.

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

(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.

small, it is probably outside the experimental error in our measurements.

George M. Whitesides, William M. Bunting

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received September 15, 1967

Rapid Rotation about Carbon-Carbon Bonds in Alkyl Diradicals. Mixtures of Singlet and Triplet Methylene

Sir:

Triplet methylene reacts with olefins to form alkyl diradicals, as in the addition to $RCH=CHR$ to form $R\dot{C}H-CHR-\dot{C}H_2$; the diradicals undergo various further reactions leading to stable products, including the ring-closure reaction to form the substituted dimethylcyclopropanes (DMC).¹⁻⁵ Stereospecificity in the formation of the *cis*- and *trans*-DMC molecules from the corresponding 2-butenes has been widely used as a criterion for identification of the reactions of singlet methylene, assuming complete retention of orientation of the methyl groups.⁶ The absence of complete stereospecificity for some methylene reactions, and therefore evidence for the presence of an appreciable fraction of triplet methylene, has been demonstrated in several systems, most prominently the photosensitization reactions of ketene by $Hg(6^3P_1)$ in the gas phase,⁷ of diazomethane by benzophenone in the liquid phase,⁸ and the collisional deactivation of methylene in excess Ar or N_2 .⁹

The degree of nonstereospecificity in triplet methylene reactions depends directly upon the relative rate constant, k_1 , of the ring-closing reaction in competition with the rate of rotation, k_2 , about the C-C bonds in the diradical. If $k_1 \gg k_2$, the triplet reactions would also be completely stereospecific. If $k_1 \ll k_2$, the same distribution of DMC molecules would be anticipated from either 2-butene as the reaction partner. We present here evidence for the latter: rotation is much more rapid than ring closure, at least in the gas phase, and the resulting DMC molecules are formed in the same ratio, within the errors of measurement, from triplet methylene reaction with either 2-butene as the precursor.

Our experimental procedure has involved the formation of CHT by photolysis of CHTCO in the presence of (a) 2-butene alone; (b) 2-butene + O_2 ; and (c) 2-butene + CH_3X ($X = I$ or Br). The O_2 serves as a total scavenger for all triplet products;¹⁰⁻¹² CH_3I pre-

(1) H. M. Frey, *Progr. Reaction Kinetics*, **2**, 131 (1964).

(2) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, including chapters by H. M. Frey and P. P. Gaspar and G. S. Hammond.

(3) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

(4) J. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964).

(5) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

(6) R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 3383 (1959); **78**, 4496 (1956).

(7) F. J. Duncan and R. J. Cvetanović, *ibid.*, **84**, 3593 (1962).

(8) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **83**, 2397 (1961); **84**, 1015 (1962).

(9) H. M. Frey, *ibid.*, **82**, 5947 (1960).

(10) R. W. Carr Jr., and G. B. Kistiakowsky, *J. Phys. Chem.*, **70**, 118 (1966).

(11) C. McKnight and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 3179 (1966).

(12) C. McKnight, E. K. C. Lee, and F. S. Rowland, *ibid.*, **89**, 469 (1967).