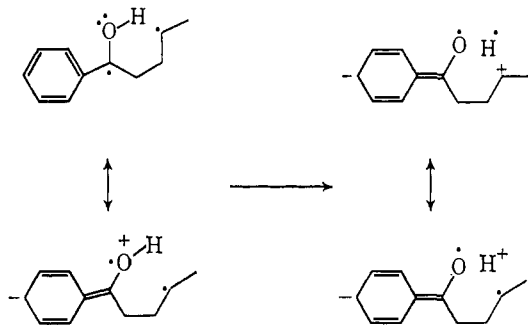


although examples of such effects in biradicals are rare.¹¹ Alkyl radicals display distinct nucleophilic properties.¹² In particular, methyl radicals abstract hydrogen from HCl much faster than from hydrocarbons.¹² If such behavior can be expected of the γ -alkyl radical site in the type II biradical, we can conclude that the proton character of the hydroxyl hydrogen is responsible for the large proportion of disproportionation. The transition state for disproportionation is probably stabilized by a charge-separated resonance form as shown.



The results deserve two additional comments. First, the chloro-, methyl-, and methoxy-substituted valerophenones all display long-lived phosphorescence and therefore have low-lying π, π^* triplets. The lower-than-unity maximum quantum yields indicate some direct radiationless decay competing with chemical reaction of these triplets. Such is not the case with valerophenone or the pyridyl ketones, which have n, π^* lowest triplets. Second, very high concentrations of alcohol begin to decrease the quantum yields, especially for the *p*-methoxy ketone, as might be expected when π, π^* participation is involved. This effect is much more noticeable in methanol than in *t*-butyl alcohol. Solvent effects on type II photoelimination efficiencies thus depend both on the nature of the reacting triplet^{3a} and on the intermediate biradical's lifetime.¹ Consequently, a mere comparison of quantum yields in neat hydrocarbon with those in neat alcohol can be confusing,¹³ and experiments such as plotted in Figure 1 are needed routinely.¹⁴

(11) D. Bryce-Smith and A. Gilbert, *Chem. Commun.*, 1701 (1968).

(12) See Tables in A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth & Co. (Publishers) Ltd., London, 1955, and in A. F. Trotman-Dickenson, "Advances in Free-Radical Chemistry," Vol. 1, G. H. Williams, Ed., Logos Press Ltd., London, 1965, p 1.

(13) N. J. Turro and F. D. Lewis, *Tetrahedron Letters*, 5845 (1968).

(14) This work is being supported by a National Science Foundation grant.

(15) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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Pseudorotation in $(\text{CH}_3)_2\text{NPF}_4^1$

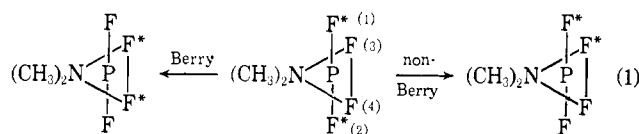
Sir:

The rapid intramolecular interchange of axial and equatorial fluorine atoms observed² for compounds of

(1) Supported by the National Institutes of Health, Grant GM 16020.

(2) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963); E. L. Muetterties, W. Mahler, K. J. Packer, and R.

the formula XPF_4 is commonly believed to occur by a mechanism proposed by Berry,³ in which isomerization of one ground-state trigonal bipyramid to another (pseudorotation) takes place by a transition state or intermediate of square-pyramidal geometry. The simplicity and high symmetry of this mechanism make it attractive. However, a number of distinct mechanistic alternatives for the process which results in fluorine interchange can be envisioned,^{4,5} and clear experimental distinctions between these alternatives have not been reported. We wish to describe ³¹P nmr studies of $(\text{CH}_3)_2\text{NPF}_4^6$ (**1**) which confirm a fundamental prediction of the Berry mechanism, *viz.* that pseudorotation of this compound results in *simultaneous* interchange of both axial fluorine atoms with equatorial fluorines, rather than in interchange of only one pair of axial and equatorial fluorine atoms. In what follows, we will arbitrarily refer to *any* exchange reaction resulting in interchange of both pairs of fluorines as a "Berry" pseudorotation, and to any reaction interchanging only one pair as a "non-Berry" pseudorotation (eq 1), without implying further details of the interchange.



The ³¹P nmr spectrum of **1** at -100° is the triplet of triplets ($J_{\text{P,F}} = 768$ Hz, $J_{\text{P,F}'} = 904$ Hz) expected for a static trigonal-bipyramidal structure having the $(\text{CH}_3)_2\text{N}$ - group in an equatorial position (Figure 1).² At -50° pseudorotation is rapid on the nmr time scale, and the spectrum shows a 1:4:6:4:1 quintet resulting from coupling of ³¹P to four magnetically equivalent fluorines. The slow-exchange spectrum can be considered as the summation of resonances of ³¹P nuclei in the characteristic magnetic environments of the fluorine nuclear spin configurations represented by the 16 possible ¹⁹F spin eigenfunctions of **1**; as a result of degeneracies, these 16 fluorine spin configurations give rise to only nine distinct ³¹P resonances (Figure 2). For the purposes of this discussion, these spin eigenfunctions can be approximated by the symmetrized spin functions for four nuclei in C_{2v} symmetry.⁷ The problem of describing the ³¹P spectral behavior of **1** in the region of intermediate pseudorotation rates can then be treated as a problem of describing the transfer of magnetization between these nine lines and 16 sites by the pseudorotation process.

Schmutzler, *ibid.*, 3, 1298 (1964); R. Schmutzler in "Halogen Chemistry," Vol. 2, V. Gutman, Ed., Academic Press, New York, N. Y., 1967, pp 33 ff.

(3) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960).

(4) E. L. Muetterties, *J. Amer. Chem. Soc.*, 91, 1636, 4115 (1969), and references therein.

(5) For infrared studies pertinent to this problem, see L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, 46, 2402 (1967); R. R. Holmes and R. M. Deiters, *Inorg. Chem.*, 7, 2229 (1968).

(6) D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc.*, A, 171 (1966).

(7) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, Oxford, 1965, Chapter 8. The chemical shift difference between axial and equatorial fluorine atoms ($\delta\nu = 1660$ Hz at 23 kG) and the fluorine-fluorine coupling constant ($J = 62$ Hz) of **1** are such that mixing of these functions is small. Use of the correct eigenfunctions for **1** in the following discussion does not quantitatively change our conclusions, but does obscure their physical foundation.

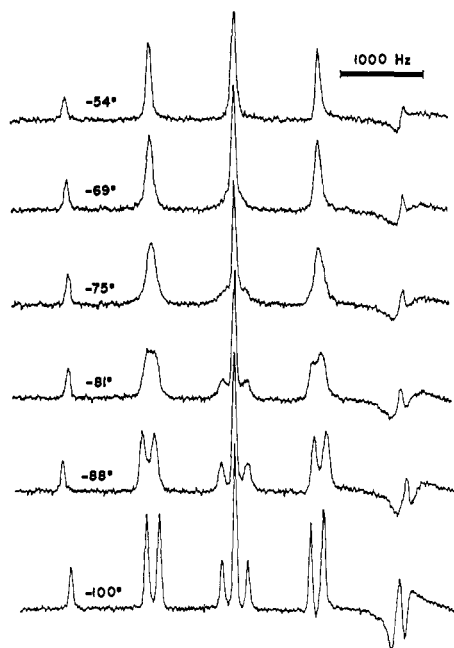


Figure 1. ^{31}P nmr spectra of $(\text{CH}_3)_2\text{NPF}_4$ as a function of temperature (nonspinning sample containing $\sim 10\%$ TMS). These spectra were taken using 2.5-kHz audiomodulation; the shapes of the three highest field lines (lines 7, 8, and 9) are distorted by superposition on center-band resonances. Lines 1-6 are undistorted.

The influence of pseudorotation on the ^{31}P resonances is determined by the extent to which the magnetic environment "seen" by the phosphorus is changed by the fluorine interchange. If pseudorotation results in isomerization of a starting configuration of fluorines to a final configuration which is magnetically indistinguishable from the vantage of the ^{31}P nucleus, no broadening will be observed for the phosphorus transition characteristic of this configuration. If, on the other hand, pseudorotation converts the starting configuration of fluorine nuclei to a final configuration characterized by a different ^{31}P resonance frequency, the two (or more) slow-exchange phosphorus lines coupled by the exchange will broaden and coalesce as the pseudorotation rate increases. The final configurations of fluorine nuclei obtained from a particular starting configuration following pseudorotation by Berry and non-Berry mechanisms are easily determined by inspection, and representative examples are given in Table I.

Table I. Representative Starting and Final Fluorine Spin Configurations for Pseudorotation of **1**

Berry		Non-Berry	
Final	Start-ing	Start-ing	Final
ϕ_1	$\leftarrow \phi_1 \rightarrow$	ϕ_1	
ϕ_4	$\leftarrow \phi_2 \rightarrow$	$1/4\phi_2 + 1/4\phi_3 + 1/4\phi_4 + 1/4\phi_5$	
ϕ_5	$\leftarrow \phi_3 \rightarrow$	$1/4\phi_2 + 1/4\phi_3 + 1/4\phi_4 + 1/4\phi_5$	
ϕ_{11}	$\leftarrow \phi_6 \rightarrow$	$1/4\phi_7 + 1/4\phi_8 + 1/4\phi_9 + 1/4\phi_{10}$	
ϕ_7	$\leftarrow \phi_7 \rightarrow$	$1/4\phi_6 + 1/8\phi_7 + 1/8\phi_8 + 1/8\phi_9 + 1/8\phi_{10} + 1/4\phi_{11}$	
ϕ_9	$\leftarrow \phi_8 \rightarrow$	$1/4\phi_6 + 1/8\phi_7 + 1/8\phi_8 + 1/8\phi_9 + 1/8\phi_{10} + 1/4\phi_{11}$	

In these examples, the axial and equatorial fluorine sites are labeled using the numbering scheme of eq 1, and, e.g., $\phi_2 \rightarrow 1/4\phi_2 + 1/4\phi_3 + 1/4\phi_4 + 1/4\phi_5$ indicates that a molecule of **1** whose fluorines are originally described

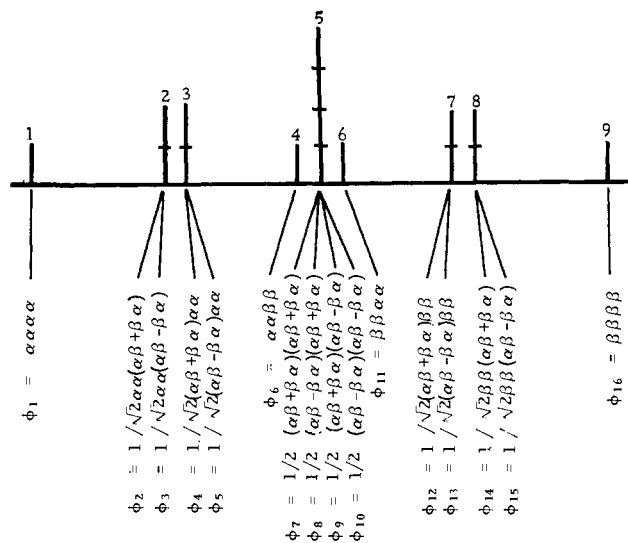


Figure 2. Spectral assignments for the ^{31}P spectrum of $(\text{CH}_3)_2\text{NPF}_4$.

by the spin function $1/\sqrt{2}\alpha(1)\alpha(2)[\alpha(3)\beta(4) + \beta(3)\alpha(4)]$ will be converted on pseudorotation to the configurations $1/\sqrt{2}\alpha\alpha(\alpha\beta + \beta\alpha)$, $1/\sqrt{2}\alpha\alpha(\alpha\beta - \beta\alpha)$, $1/\sqrt{2} \cdot (\alpha\beta + \beta\alpha)\alpha\alpha$, and $1/\sqrt{2}(\alpha\beta - \beta\alpha)\alpha\alpha$ with equal probabilities.⁸

By identifying the sets of transitions which are kinetically coupled by fluorine interchange, the entries in Table I, together with parallel descriptions for the starting configurations not explicitly listed in this table, make it possible to calculate the influence of pseudorotation by either mechanism on the shapes of the lines in the ^{31}P spectrum of **1**. Thus, qualitatively, the configuration ϕ_1 is transformed into itself by Berry or non-Berry pseudorotations; consequently, line 1 of the spectrum is not affected by pseudorotation, regardless of mechanism. Both mechanisms transfer magnetization between lines 2 and 3; however, the rate constant for this transfer by a Berry mechanism is twice that by a non-Berry mechanism, since half of the non-Berry pseudorotation events do not change the phosphorus precession frequency.

A Berry mechanism transfers magnetization between lines 4 and 6, but does not couple any of the transitions making up line 5 with transitions of different frequency; in contrast, a non-Berry mechanism transfers magnetization between lines 4 and 5, and between 5 and 6, but not directly between 4 and 6. Thus, in a Berry mechanism lines 4 and 6 should broaden and coalesce in the intermediate exchange region, while line 5 remains sharp. In a non-Berry mechanism lines 4, 5, and 6 should all broaden in the intermediate exchange region.

These arguments can be used as the basis for quantitative calculations of line shapes using unexceptional procedures.⁹ The kinetic exchange matrices **K** describing transfer of magnetization between the lines of the observed spectra are given by eq 2 and 3. The rows and columns of these matrices are numbered to

(8) These relative probabilities are based on the assumption that the transition from starting to final configurations is instantaneous. The spectral consequences of an intermediate of C_{4v} nuclear symmetry and finite lifetime along the pseudorotation coordinate will be discussed in a full paper.

(9) C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965); G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 2245 (1969), and references in each.



Figure 3. Spectra calculated for pseudorotation by Berry and non-Berry mechanisms. To save space, only the kinetic behavior of lines 1-6 is shown.

correspond with the lines of the observed static spectrum. Spectra calculated for a range of preexchange lifetimes τ are given in Figure 3.

$$K_{\text{Berry}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (2)$$

$$K_{\text{non-Berry}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1/2 & 1/2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/2 & -1/2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/4 & -1/2 & 1/4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1/2 & 1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1/2 & -1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (3)$$

Comparisons of two features of these calculated and observed spectra clearly demonstrate that a Berry mechanism is responsible for pseudorotation in **1**. First, in agreement with spectra calculated assuming this mechanism, line 5 of the observed spectra remains sharp throughout the temperature range responsible for the broadening and complete collapse of lines 4 and 6; by contrast, line 5 is appreciably broadened for intermediate non-Berry exchange rates. Second, the relative rates of broadening and collapse of lines 2, 3, 4, and 6 are compatible with those calculated on the basis

of a Berry mechanism, but are incompatible with relative rates based on a non-Berry process.

(10) National Institutes of Health Predoctoral Fellow, 1966-1969.

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The Solvolysis of Highly Unreactive Substrates Using the Trifluoromethanesulfonate (Triflate) Leaving Group

Sir:

Although it has been realized for some time that trifluoromethanesulfonates (triflates)¹ are remarkably reactive compounds¹⁻⁴ (ethyl triflate is capable of alkylating ether!) their solvolytic behavior has been studied in only a few primary cases. Methyl⁴ and ethyl¹ triflates are approximately $10^{4.4}$ times more reactive than the corresponding tosylates, and the solvolysis of ethyl triflate has been shown to be an S_N2 process.¹ We report in this paper and in a companion study from these laboratories^{5a} kinetic results using the triflate leaving group in a variety of normally highly unreactive systems. We find that use of this extremely reactive leaving group extends significantly the spectrum of compounds whose reactivities can be examined solvolytically.

The triflates employed in this study (Table I) were prepared and purified using the usual procedure for tosylates;⁶ equimolar amounts of the alcohol and trifluoromethanesulfonic acid anhydride⁷ were mixed in pyridine solution at 0°. All of the derivatives prepared were liquids and were stable for several weeks at 5°. On solvolysis, all displayed good first-order kinetics to about 85% reaction.

Table I summarizes the results of our kinetic investigations on I-V. Included are the results previously reported for methyl⁴ and ethyl¹ triflates, and data for the corresponding tosylates, where available. The triflate/tosylate rate ratios can be seen to fall in the range $10^{4.3}$ - $10^{5.3}$; they are remarkably constant considering the variety of systems studied.^{5b,9}

The rate constants presented here for *exo*-bicyclo[3.1.0]hex-6-yl triflate (I, X = OTf) and for 1-nortricyclyl triflate (II, X = OTf) represent the first measurable solvolytic reactivity reported for these systems. Although the thermal and solvolytic behavior of bicyclo[3.1.0]hex-6-yl derivatives has been investigated

(1) Trivial name suggested by A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1968).

(2) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957).

(3) J. Burdon and V. C. R. McLoughlin, *Tetrahedron*, **21**, 1 (1965).

(4) R. L. Hansen, *J. Org. Chem.*, **30**, 4322 (1965).

(5) (a) P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, **91**, 4600 (1969); (b) also cf. W. M. Jones and D. D. Maness, *ibid.*, **91**, 4314 (1969).

(6) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 1180.

(7) Prepared by treatment of barium trifluoromethanesulfonate with fuming sulfuric acid, followed by dehydration with P_2O_5 .⁸ We are indebted to Dr. R. L. Hansen of the Minnesota Mining and Manufacturing Co. for the generous gift of barium trifluoromethanesulfonate and for supplying detailed procedures.

(8) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957).

(9) This essential constancy in going from primary to tertiary bridge-head systems shows that OTf/OTs ratios, unlike OTs/Br ratios,¹⁰ are not sensitive to changes in mechanism.

(10) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965).