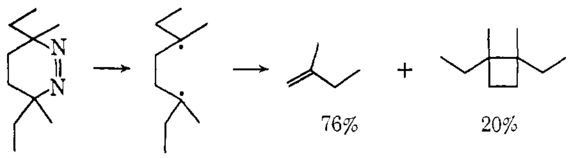
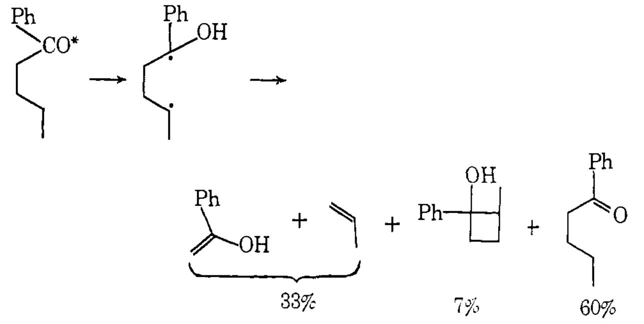
Polar Substituent Effects in the Reactions of 1,4 Biradicals

Sir:

Rather compelling evidence has been accumulated that the type II photoelimination of ketones proceeds through 1,4-biradical intermediates, the behavior of which determines the quantum efficiency of the reaction.[1-3] Such intermediates are assumed to occur in many photocycloaddition reactions[4] and in some thermal cycloadditions.[5] Bartlett and Porter recently described the behavior of the 1,4 biradical which presumably intervenes in the decomposition of a cyclic azo compound.[6] Although evidence for disproportionation reactions of presumed biradical intermediates does exist,[7] it would appear from Bartlett's work[6] that coupling and β scission are generally favored in simple hydrocarbon biradicals. The behavior of the 1,4 biradicals postulated in photoelimination is then unusual in that their *major* reaction seems to be disproportionation involving the hydroxyl hydrogen. The following reactions exemplify the difference.[1,6]





Since we are studying the effects of ring substituents on the nature and reactivity of the triplet states of phenyl ketones undergoing photoelimination,[8,9] we have checked whether any substituent effects can be detected on the behavior of the presumed biradical intermediates. Figure 1 depicts the response of several *n*-butyl aryl ketones to addition of various concentrations of *t*-butyl alcohol. The rapidly rising unlabeled line represents our earlier report[1] that the total quantum yield for disappearance of valerophenone rises to unity, most likely indicating that hydrogen bonding by the biradical impedes its disproportionation back to ketone. Pyridyl ketones respond identically, although their type II quantum yields in benzene are considerably lower than that of valerophenone. The quantum yields for disappearance of the *p*-methyl, *p*-chloro, and *p*-methoxy ketones, however, rise only so far, and then level off to values considerably below unity. With *p*-methoxyvalerophenone, added pyridine produces the same effect as *t*-butyl alcohol; added methanol also produces the same maximum Φ. Table I summarizes the quantum yield values. The ϕ_P values describe the probability that the biradicals proceed on to products in benzene rather than revert back to ketone by disproportionation. The basic assumption is that once the quantum yield levels off to a constant value, there is enough alcohol present to ensure that *all* biradicals proceed on to products.

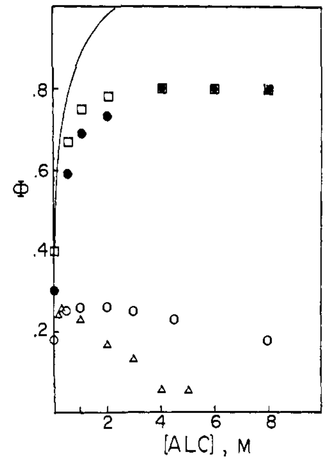


Figure 1. Effects of added *t*-butyl alcohol on quantum yields for reactions of substituted valerophenones: □, *p*-methyl; ●, *p*-chloro; ○, *p*-methoxy; △, methanol added to *p*-methoxy; line at upper left represents valerophenone itself.

Table I. Quantum Efficiencies for Substituted *n*-Butyl Phenyl Ketones[a]

Substituent	Φ(benzene)[b]	Φ(alc)[b,c]	ϕ_P
p-MeO	0.18	0.26, 0.26,[d] 0.25[e]	0.69
p-Me	0.39	0.80	0.50
None (H)	0.40	1.00	0.40
p-Cl	0.30	0.80	0.37
3-(N)	0.29	1.00	0.29
2-(N)	0.18	1.00	0.18

[a] Irradiations were performed on 0.10 *M* ketone solutions at 3130 Å to <5% conversion. [b] Total quantum yields for reaction of ketone. [c] Maximum value in Figure 1. [d] Methanol added. [e] Pyridine added.

The trend of substituent effects on ϕ_P is clear: disproportionation of the biradical is favored by electron-withdrawing groups. Such behavior suggests very strongly that the disproportionation reaction is sensitive to the acidity of the hydroxyl group. Polar effects in free-radical reactions are of classic importance,[10]

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(1) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5898 (1967).

(2) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(3) (a) R. D. Rauh and P. A. Leermakers, *ibid.*, **90**, 2246 (1968); (b) P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968); (c) J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5900 (1968).

(4) For reviews, see O. L. Chapman and G. Lenz, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 283; P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(5) L. K. Montgomery, K. Schneller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

(6) P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968).

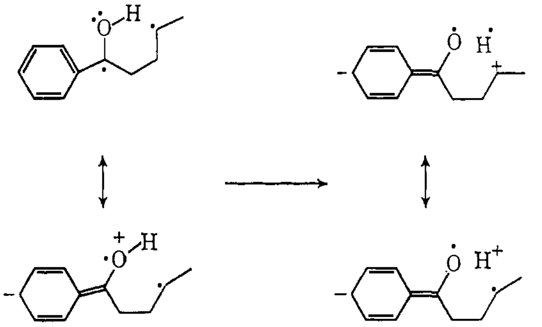
(7) E. J. Corey, J. D. Bass, R. LeMahieu, and P. B. Mitra, *ibid.*, **86**, 5570 (1964); R. C. Cookson, J. Hudac, S. A. Knight, and B. Whitear, *Tetrahedron Letters*, 79 (1964); W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

(8) P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **90**, 5898 (1968).

(9) N. C. Yang and R. L. Dusenbery, *ibid.*, **90**, 5899 (1968); J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5902 (1968).

(10) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 132.

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]

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(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).

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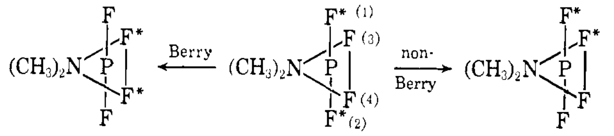
Pseudorotation in $(CH_3)_2NPF_4$[1]

Sir:

The rapid intramolecular interchange of axial and equatorial fluorine atoms observed[2] for compounds of 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 ^{31}P nmr studies of $(CH_3)_2NPF_4$[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.



(1)

The ^{31}P nmr spectrum of **1** at $-100°$ is the triplet of triplets ($J_{P,F} = 768$ Hz, $J_{P,F}' = 904$ Hz) expected for a static trigonal-bipyramidal structure having the $(CH_3)_2N$- 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 ^{31}P to four magnetically equivalent fluorines. The slow-exchange spectrum can be considered as the summation of resonances of ^{31}P nuclei in the characteristic magnetic environments of the fluorine nuclear spin configurations represented by the 16 possible ^{19}F spin eigenfunctions of **1**; as a result of degeneracies, these 16 fluorine spin configurations give rise to only nine distinct ^{31}P 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 ^{31}P 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.

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(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. 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.