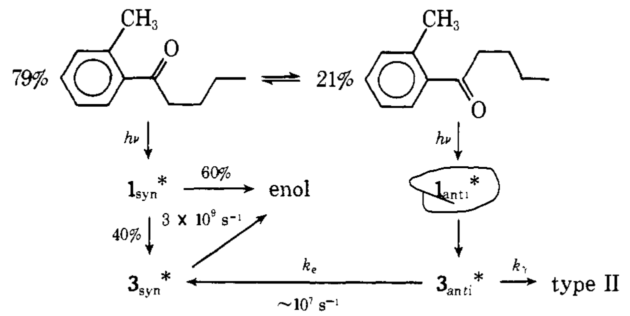
Scheme I



probability for product formation from the diradical intermediate (P = 0.08-0.18), and competing enolization, not just from the latter as previously assumed.[16]

Addition of large concentrations of *tert*-butyl alcohol causes type II yields to maximize, as previously noted.[16] However, the effect represents a combination of P maximizing while ϕ_T, k_γ,[20] and k_e[5] all decrease. Analysis of the data in *tert*-butyl alcohol on the basis that $P = 1$ gives further self-consistent results, in that $\alpha = 0.10$ and $k_e = 0.6 \times 10^7$ for ketones **3–5.**

These type II results are important for two reasons. First, they establish that the long-lived triplet detected by sensitization experiments is a ketone triplet and not, say, a triplet enol,[3,21] which would not be expected to undergo type II elimination. Second, the value of k_e appears to be independent of C-H bond strength! *o*-Ethylvalerophenone (**6**) has the same triplet lifetime as *o*-methylvalerophenone (**4**). In *tert*-butyl alcohol, exact kinetic analysis yields the same value of k_e for both ketones. In benzene, where the value of P cannot yet be ascertained, assumption of comparable k_γ values for **4** and **6** produces comparable values of k_e. Equally interesting is the behavior of ketones **7h** and **7d,** which also display comparable triplet lifetimes in benzene. Since the low type II quantum yields indicate that k_e is a major contributor to triplet decay, it must be concluded that there is no significant isotope effect on k_e. A k_H/k_D value of 4.8 obtains in type II γ-hydrogen abstraction.[22]

Since k_e is independent of C-H bond strength, we must conclude that the rate determining step for enolization of the long-lived triplet is not hydrogen abstraction. This conclusion is almost demanded by the model of discrete syn and anti triplet conformers and does not fit any other scheme that we can think of. Scheme I summarizes what we believe to be the mechanism for photoenolization of *o*-tolyl alkyl ketones. The process competing with normal triplet reactions of the anti triplet is irreversible rotation into a syn conformation which enolizes so rapidly that other reactions cannot compete. The Φ_T values in fact measure the percentage of anti ground states in what is presumably a rapid conformational equilibrium. NMR chemical shift data have been interpreted as indicating that *syn*-**1** predominates over *anti*-**1**,[23] but no quantitative analysis has been reported. The various percentages and rates depend on solvent and on the ortho alkyl group in ways which only further work can explain. The $\sim 10^7\ s^{-1}$ rate which we ascribe to rotation in the triplet would indicate a barrier of some 8 kcal. Because of severe nonbonded interactions in the totally planar forms, this barrier would certainly be expected to be smaller than that in excited benzaldehyde, for which a value of some 20 kcal has been calculated.[15]

Finally, we note that we have purposely ignored some important questions, such as the energetic proximity of n, π* and π,π* triplets in these compounds[20,24] and the possible formation of triplet enols,[3] in order to emphasize the importance of previously unsuspected conformational factors and the rapidity of enolization of triplets with syn conformations. Although the importance of ground-state conformations in photochemical processes is now well documented,[25] this photoenolization is a rare case[26] where an excited-state conformational change appears to be rate limiting.

References and Notes

(1) This work was supported by the National Science Foundation (Grant No. GP-19580).
(2) E. F. Zwicker, L. J. Grossweiner, and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2671 (1963).
(3) K. R. Huffman, M. Loy, and E. F. Ullman, *J. Am. Chem. Soc.*, **87**, 5417 (1965).
(4) G. Porter and M. F. Tchir, *J. Chem. Soc. A*, 3772 (1971).
(5) H. Lutz, E. Breheret, and L. Lindqvist, *J. Chem. Soc., Faraday Trans. I*, 2096 (1973).
(6) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
(7) Corrections were made for the increases in isomerization quantum yield above 1 M diene, R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **92**, 211 (1970).
(8) The kinetics are similar to those derived by J. C. Dalton and J. J. Snyder, *Mol. Photochem.*, **6**, 291 (1974).
(9) $k_q\tau$ = intercept/slope; $k_q = 5 \times 10^9\ M^{-1}\ s^{-1}$. If steric hindrance to energy transfer is significant,[10] all rates listed in Table I would be smaller.
(10) W. G. Herkstroeter, L. B. Jones, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4777 (1966).
(11) We do not imply two planar conformers but rather two rotational minima in which the ortho methyl and the carbonyl oxygen are either on the same side or on opposite sides of the plane perpendicular to the benzene ring and bisecting the para-carbon and the carbonyl carbon.
(12) Inasmuch as enolization resembles type II γ-hydrogen abstraction, the n,π singlet reaction is expected to be some five–ten times faster than the n,π* triplet reaction.[13] Such a rate could compete well with the rapid intersystem crossing of phenyl ketones.[14]
(13) (a) P. J. Wagner, *Acc. Chem., Res.*, **4**, 168 (1971); (b) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).
(14) (a) P. M. Rentzepis, *Science*, **69**, 239 (1970); (b) R. M. Hochstrasser, H. Lutz, and G. W. Scott, *Chem. Phys. Lett.*, **24**, 162 (1974).
(15) R. Hoffmann and J. R. Swenson, *J. Phys. Chem.*, **64**, 415 (1970).
(16) W. R. Bergmark, B. Beckmann, and W. Lindenberger, *Tetrahedron Lett.*, 2259 (1971).
(17) P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **94** 7495 (1972).
(18) We have applied this type of analysis previously: P. J. Wagner and G. Capen, *Mol. Photochem.*, 1, 173 (1969); P. J. Wagner and J. M. McGrath, *J. Am. Chem. Soc.*, **94**, 3849 (1972).
(19) Note that the rate decrease produced by the ortho-methyl is comparable to that produced by a meta-methyl,[20] making us believe that the assumed value of k_q is reasonable.
(20) P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *J. Am. Chem. Soc.*, **95**, 5604 (1973).
(21) G. Porter and M. Tchir, *Chem. Commun.*, 1372 (1970).
(22) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 7480 (1972).
(23) G. Montaudo, P. Finocchiaro, and P. Maravigna, *J. Am. Chem. Soc.*, **93**, 4214 (1971).
(24) The phosphorescence spectrum and lifetime of 1 are very similar to those of its meta and para isomers and indicate that the n,π* and π,π* triplets are almost isoenergetic. Consequently, it is most unlikely that the two triplets observed for **1** represent different electronic states.
(25) (a) J. E. Baldwin and S. M. Krueger, *J. Am. Chem. Soc.*, **91**, 6144 (1969); (b) W. C. Dauben, R. G. Williams, and R. O. McKelvey, *ibid.*, **95**, 3932 (1973); (c) F. D. Lewis and R. W. Johnson, *ibid.*, **94**, 8914 (1972).
(26) Others have noted the need for excited state rotations in photochromic systems: (a) R. Rosenfield, M. Ottolenghi, and A. Y. Meyer, *Mol. Photochem.*, **5**, 39 (1973); (b) E. Migirdicyan, A. Despres, V. Lejeune, and S. Leach, *J. Photochem.*, **3**, 383 (1974).
(27) L. L. Quill Fellow, 1973–1976.

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Enhanced Photocyclization of α-Fluoro Ketones[1]

Sir:

We have studied the photochemistry of α-fluorovalerophenone (**1**) and α,α-difluorovalerophenone (**2**) and find that the α-fluorines greatly enhance the efficiency of type II cyclization, such that a cyclobutanol is the only significant product formed from **2.**

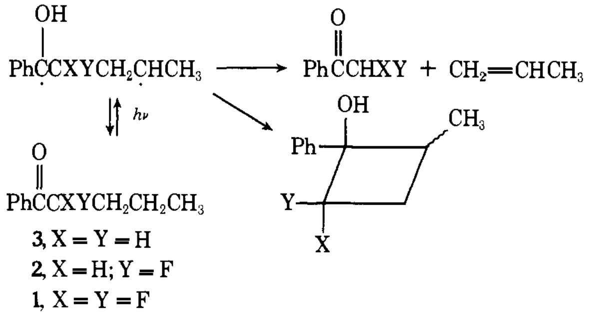
The monofluoro ketone was prepared by treatment of α-bromovalerophenone with potassium fluoride in glycerol;[2]

Table I. Photokinetics of Fluorinated Phenyl Ketones[a]

Ketone	Φ_{elim}[b]	Φ_{cyc}[c]	$k_q\tau$, M^{-1} [d]
1	0.34	0.35	18
2	$\leq$0.01	0.60	36
3[e]	0.31	0.07	40
4	0.41	0.08	780

[a] With 0.04 M ketone irradiated at 313 nm in degassed benzene solutions. [b] (α-Fluoro)acetophenone. [c] Cyclobutanol. [d] Average of duplicate runs with 2,5-dimethyl-2,4-hexadiene as quencher. [e] Data from P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, 94, 7495 (1972).

the difluoro ketone **2** was prepared by similar treatment of α-bromo-**1**. Table I lists product quantum yields and quenching slopes obtained for the two ketones and compares them to the analogous data for valerophenone, **3**.



3, X = Y = H
2, X = H; Y = F
1, X = Y = F

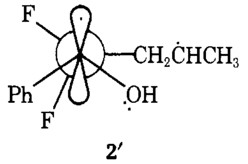
It is now well established that type II photoelimination and cyclization of phenyl ketones proceed from a 1,4-diradical intermediate formed by γ-hydrogen abstraction by the triplet ketone.[3,4] Fluorine substitution does not greatly affect the rate of triplet state hydrogen abstraction, but it does promote an unexpected alteration in the behavior of the intermediate diradical. Cyclization is markedly enhanced at the expense both of cleavage and of disproportionation back to ground state ketone, such that cyclization accounts for 99% of the photoreaction of **2.** This finding not only provides new potential for the synthesis of partially fluorinated cyclobutanols but also provokes in a new form the question of how high-energy intermediates such as 1,4-diradicals can show such selectivity in their reactions.

Enhanced cyclization-cleavage ratios are not unprecedented in type II photoreactions.[3] Cycloalkyl ketones[5,6] and *tert*-alkyl ketones[7] all produce mainly cyclobutanols; α-diketones[8] undergo only cyclization. It was first suggested[8,9] that bond energy differences might affect competing diradical reactions. However, the preferential photocyclization of cycloalkyl and *tert*-alkyl ketones attests to the predominant importance of stereoelectronic effects. 1,4-Diradicals apparently do not cleave readily unless the 2,3 C–C bond can align itself parallel to the two singly occupied p orbitals at carbons 1 and 4.[3,6,7,10,11]

The large effect of the α-fluorines could be ascribed to relative product energies, since fluorine seems to prefer to be bonded to sp^3 rather than sp^2 hybridized carbons.[12] In order to test this possibility, we have prepared and photolyzed γ-fluorobutyrophenone (**4**). As Table I shows, **4** undergoes a "normal" amount of cyclization, even though the two competing reactions of the intermediate diradical offer the fluorine atom the same sp^3 vs. sp^2 bonding option. Consequently, since the very exothermic reactions of diradicals are rarely seriously affected by product energies (although conformational preferences already present in the diradical sometimes parallel product stabilities[7,13]), it seems worthwhile to explore the possibility that α-fluorines might somehow affect the ability of the diradical to attain the conformation required for cleavage.

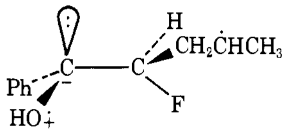
The effect of α-methyl substitution has been interpreted as indicative of steric interference with the bond rotations necessary to bring the diradical into the correct conformation for cleavage.[7] Such an explanation seems inadequate for the much larger effects on product ratios produced by the much smaller fluorine atom. Instead, we suspect that it is hyperconjugative stabilization of the diradical by the α-fluorines which constrains the diradical into a conformation with little of the p–σ overlap required for cleavage.

Although β-chloro and β-bromo radicals are indicated by EPR spectra to be bridged,[14] such is not the case for β-fluoro radicals. Kochi and Krusic very recently have shown that β-fluoroethyl radicals do have preferred conformations.[15] In fact, if the 2,2-difluoroethyl radical can be taken as a model for the diradical **2′** formed from **2**, the preferred

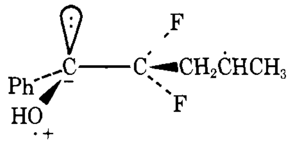


2′

conformation of **2′** would be as shown and would indeed curtail cleavage. However, the barrier to C–C rotation in the difluoroethyl radical is under 2 kcal.[15] Unless the added substituents on **2′** were to significantly increase this value, simple radical hyperconjugation seems an unlikely explanation for the decreased cleavage. However, the 2,2-difluoroethyl radical is not an adequate model for **2′**. α-Hydroxy radicals are known to be stabilized significantly by conjugation with the oxygen lone pair, such that the carbon is significantly carbanionic and sp^3 hybridized.[16] Therefore, any hyperconjugative interactions of α-fluorines in these diradicals would necessarily be largely anionic. A group of theoretists recently summarized the predicted conformational consequences of such hyperconjugation.[17] In particular, an electronegative group such as F attached β to a carbanion is predicted to strongly stabilize the conformation in which the C–F bond is parallel to the nonbonding sp^3 orbital on carbon. The behavior of the diradicals from **1** and **2** can be understood if hyperconjugative interactions stabilize the conformations shown below, drawn in the zwitterionic resonance forms.



1′



2′

Conformer **2′** is exactly the same as described above for purely radical hyperconjugation, with the C_α–C_β bond perpendicular to the sp^3 orbital so as to maximize overlap of that orbital with both C–F bonds. The preferred conformation for γ-hydrogen abstraction probably yields **2′** directly.[18] Likewise, the diradical formed from **1** would initially have a conformation very similar to **1′**. If hyperconjugative interactions in β-fluorocarbanions are as large as recently predicted,[17] the barriers to rotation of diradicals **1′** and **2′** out of the conformations shown could well be large enough to prevent significant overlap between the sp^3 (p) orbital and the α,β C–C bond even in the microsecond lifetime[19] of the diradical.

In summary, the novel alteration in Norrish type II product ratios caused by α-fluorine substitution may well be a unique manifestation of fluorine hyperconjugation. We are currently studying ketones fluorinated elsewhere on the alkyl chain in order to better understand the effects of fluorine substitution on triplet and diradical reactivities.

References and Notes

(1) We gratefully acknowledge support of this work by NSF Grant GP-19850.
(2) D. P. Shirokov, T. V. Smirnova, and A. N. Litvinova, *Zh. Uses. Khim. Ova.*, **14**, 234 (1969); Chem. Abstr., 71, 49463 (1969).
(3) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).
(4) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 7480 (1972).
(5) A. Padwa and E. Alexander, *J. Am. Chem. Soc.*, **89**, 6376 (1967).
(6) (a) R. B. Gagosian, J. C. Dalton, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 4752 (1970); (b) F. D. Lewis, R. W. Johnson, and R. A. Ruden, *ibid.*, **94**, 4292 (1972).
(7) (a) F. D. Lewis and T. A. Hilliard, *J. Am. Chem. Soc.*, **94**, 3852 (1972); (b) P. J. Wagner et al., *ibid.*, **94**, 7506 (1972).
(8) W. H. Urry and D. J. Trecker, *J. Am. Chem. Soc.*, **84**, 718 (1962).
(9) N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, 3671 (1966).
(10) P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **90**, 5896 (1968).
(11) R. Hoffmann, S. Swaminathau, B. G. O'Dell, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 7081 (1970).
(12) (a) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964); (b) J. F. Harrison, *ibid.*, **93**, 4112 (1971); (c) L. M. Sachs, M. Geller, and J. J. Kaufman, *J. Chem. Phys.*, **51**, 2771 (1969).
(13) (a) R. A. Caldwell and P. Fink, *Tetrahedron Lett.*, 2987 (1969); (b) P. J. Wagner and P. A. Kelso, *ibid.*, 4152 (1969).
(14) (a) A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, **5**, 552 (1970); (b) F. Biddle and A. Hudson, *ibid.*, **18**, 45 (1973); (c) A. R. Lyons and M. C. R. Symons, *J. Am. Chem. Soc.*, **93**, 7330 (1971); (d) T. Kawamura, D. J. Edge, and J. K. Kochi, *ibid.*, **94**, 1752 (1972).
(15) K. S. Chen, P. J. Krusic, P. Meakin, and J. K. Kochi, *J. Phys. Chem.*, **78**, 2014 (1974).
(16) A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. A*, 132 (1971).
(17) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221 (1972).
(18) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 7500 (1972).
(19) P. J. Wagner and K. C. Liu, *J. Am. Chem. Soc.*, **96**, 5952 (1974).

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Time Resolved Electron Spin Resonance Spectroscopy. III. Electron Spin Resonance Emission from the Hydrated Electron. Possible Evidence for Reaction to the Triplet State[1]

Sir

In time-resolved ESR experiments carried out on pulse irradiated aqueous solutions we have found that the presence of certain other radicals causes the ESR line of the hydrated electron, e_{aq}^-, to appear in emission. The radical-pair theory of CIDEP[2,3] which is used to explain abnormal ESR intensities in systems of homogeneously reacting radicals, is capable of explaining emission for one radical of an unlike pair (and corresponding enhanced absorption for the other) as a result of differing g factors for the two kinds of radicals. In the present case, however, the sense of the effect—emission for the radical (e_{aq}^-) with the lower g factor—is opposite to that expected on the basis of the usual assumptions (see below). It is the purpose of this paper to describe the experimental results and to offer a tentative explanation for the observed effect.

The ESR spectrum of the hydrated electron was first reported by Avery et al. who found a single ESR line at $g = 2.0002 \pm 0.0002$ in basic methanol solutions.[4] In the course of similar time-resolved ESR studies[5,6] we have examined the ESR signal of e_{aq}^- in a number of chemical systems. Because the radiolysis of water produces approximately equal yields of e_{aq}^- and OH[7] it is necessary to study e_{aq}^- in a mixed radical system. In addition to pure water where OH is the "counter radical" to e_{aq}^-, it is possible to find a number of reactants for OH which do not react rapidly with e_{aq}^- and so can be used to change the nature of the counter radical. As will be described, the behavior of the ESR signal of e_{aq}^- varies considerably depending on the counter radical.

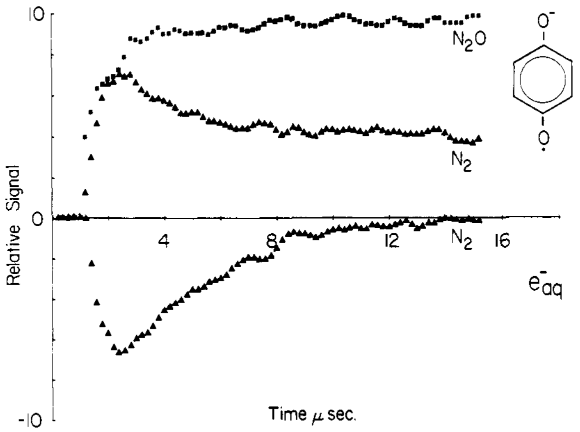

Figure 1. Time dependence of the ESR signals of e_{aq}^- and p-benzosemiquinone ion in a solution of 2 mM hydroquinone (pH 11.9). The lower trace gives the signal for e_{aq}^- in N_2 saturated solution while the center trace shows the central line of the semiquinone ion for the same conditions. The upper trace gives the signal for the semiquinone ion in N_2O saturated solution where the yield is roughly twice as great. Most of the decay of the central trace is relaxation of an enhanced absorption and not chemical decay since the long term level is nearly 50% that in the N_2O solution.

ESR experiments were carried out with an improved version of the fast-response ESR spectrometer described earlier.[5,8] Initial experiments used the OH scavengers methanol and SO_3^{2-}, and in each case a strong ESR signal was found at $g = 2.00033 \pm 0.00003$. This signal is clearly that of e_{aq}^- as is shown by its absence when the solution was saturated with N_2O.[9] The time profile at the center of resonance showed a rise to a maximum at ~4 μsec and a subsequent exponential decay with a half-life of ~6 μsec.[10] The disappearance of e_{aq}^- can be the result of reactions with impurities,[11] radiation induced products, and radicals. That radical-radical reactions are probably involved is shown by the fact that at lower doses (per pulse) both the rise and the decay are somewhat slower.[12] After the ESR signal of e_{aq}^- had been located it was found possible to observe it in basic water with no OH scavenger. Under these conditions the signal maximum was only about 20% as intense.

A number of other reactants for OH were tried with varying results. Methanol and sulfite gave nearly identical curves for e_{aq}^- under the same dose conditions. Ethylene, formate, and *tert*-butyl alcohol also behaved similarly but gave a 40% larger maximum height than sulfite or methanol and a somewhat faster decay. Bromide and ferrocyanide gave smaller signals than sulfite. With the systems of carbonate (counter radical $CO_3\cdot^-$), phosphite ($\dot{P}O_3^{2-}$), hypophosphite ($H\dot{P}O_2^-$), phenol (pH 11, phenoxyl), and hydroquinone (pH 11, benzosemiquinone ion) the ESR signal of the electron appeared in emission. With CO_3^{2-} the maximum amplitude of the emission occurred at 2-3 μsec (a shorter time than for the absorption signals) and was 60% stronger than the signal with sulfite at the same dose rate. The amplitude of the emission curve was approximately linearly dependent on dose rate. Even at the lowest dose rates the curves did not cross into absorption out to at least 20 μsec where the signal was comparable to the noise level. A typical emission curve is shown in Figure 1 for hydroquinone as OH scavenger. Here it was possible to detect the lines of the semiquinone ion counter radical formed by OH. The initial peak and subsequent decay of this radical (center trace) show that, as required by the theory, this ESR signal experiences an enhanced absorption[13] which is complementary to the emission of e_{aq}^-.