photometer. A phosphorescence value was determined for each sample by subtracting the emission intensity of the aerated sample from that just recorded for the degassed, sealed sample.

Acknowledgment. This work was assisted by a National Science Foundation grant. We are grateful to Professors Peter Yates for helpful discussions and Mark Green for insisting that we investigate the extent of δ-hydrogen abstraction.

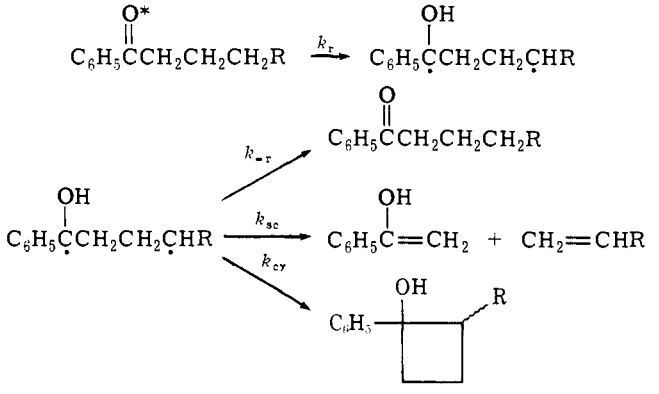
Type II Photoprocesses of Phenyl Ketones. A Glimpse at the Behavior of 1,4 Biradicals

Peter J. Wagner,*[1a] P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott,[1b] and R. G. Zepp

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. *Received August 17, 1971*

Abstract: Electron-donating groups on the benzene ring and electron-withdrawing groups at the δ, ε, and even ζ positions enhance quantum yields of type II photoreactions of phenyl alkyl ketones, whereas electron-withdrawing groups on the benzene ring and electron-donating groups at the γ and δ positions have the opposite effect. These effects are interpreted to reflect charge transfer from the γ-alkyl position to the oxygen in the transition state for reverse transfer of hydrogen back to the γ carbon, the major reaction of most 1-hydroxy 1,4 biradicals. Comparison of nonanophenone-γ,γ-h_2 with nonanophenone-γ,γ-d_2 indicates a k_H/k_D value of 1.35 for reverse hydrogen transfer in the biradical. Ring substituents and the length of the alkyl chain have little effect either on relative yields of cyclization and elimination or on cis/trans cyclobutanol ratios except where intramolecular hydrogen bonding can occur. For example, only *trans*-1-phenyl-2-(methoxymethyl)cyclobutanol is obtained from irradiation of δ-methoxyvalerophenone in benzene. In all cases the stereoselectivity of cyclization is lower in alcohol solvent than in benzene. As γ-alkyl substituents increase in size, the cis/trans cyclobutanol ratio surprisingly increases. α-Dimethyl substitution increases the cyclization/elimination ratio by a factor of ten, while β-dimethyl substitution decreases the ratio by a factor of ten. Kinetic analysis suggests that α-dimethyl substitution slows the rate of cleavage of the biradical while β-dimethyl substitution slows the rate of cyclization. These steric effects on biradical behavior are interpreted as reflecting restricted rotation in the biradical, such that cleavage and cyclization occur before rotational equilibrium is established. Pyridine and alcohols apparently do not enhance type II quantum yields in a kinetically controlled process. Rather a rapid equilibrium must be established between solvated and unsolvated biradicals.

For the majority of phenyl alkyl ketones, quantum yields of type II photoelimination and photocyclization are determined solely by the behavior of the 1,4-biradical intermediate.[2,3] In terms of eq 1, $\Phi_{isc} = 1$ and $k_r\tau_t = 1$. The characteristic quantum inefficiency of type II reactions in the gas phase and in hydrocarbon solvents is always partially and sometimes solely due to reverse hydrogen transfer in the biradical.



$$\Phi_{-k} = \Phi_{isc} k_r \tau_t P_p \quad (1)$$

$$P_p = k_p \tau_{BR} = \frac{k_{sc} + k_{cy}}{k_{sc} + k_{cy} + k_{-r}} \quad (2)$$

In our other papers in this series, we concerned ourselves primarily with the effects of various structural changes on excited state reactivity; quantum yields were discussed only insofar as their values indicated the absence or presence of other excited state reactions competing with γ-hydrogen abstraction. In this paper we consider structural effects on type II quantum yields and thus on the behavior of 1,4 biradicals. There have been two recent, speculative papers regarding 1,4 biradicals.[4,5] Hopefully a unified presentation of all our results pertaining to 1,4 biradicals will best aid understanding of these species and the many other reactions in which they are thought to intervene.

Results

Our results allow some discussion of substituent effects on the following features of 1,4-biradical behavior: (1) competition between cyclization and cleavage; (2) stereochemistry of cyclization; (3) competition between reverse hydrogen atom transfer and product formation; (4) biradical lifetimes (τ_{BR}).

(1) (a) Alfred P. Sloan Fellow, 1968–1972; (b) NDEA Title IV Fellow, 1968–1970.

(2) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 7480 (1972).

(3) P. J. Wagner and A. E. Kemppainen, *ibid.*, **94**, 7495 (1972).

(4) R. Hoffman, S. Swaminathau, B. G. Odell, and R. Gleiter, *ibid.*, **92**, 7081 (1970).

(5) L. M. Stephenson and J. I. Braunman, *ibid.*, **93**, 1988 (1971).

Table I. Percentages of Cyclobutanol Formation for Various Aryl Alkyl Ketones,[a] $ZC_6H_4COCX_2CY_2CHR_1R_2$

Z	X	Y	R_1	R_2	Benzene[b]	Alcohol[c]
H	H	H	H	H	12	
H	H	H	H	CH_3	18 (4/1)	12 (2/1)
H	H	H	CH_3	CH_3	11	6
H	H	H	H	CH_2CH_3	20	
H	H	H	H	$CH(CH_3)_2$	23 (3/1)	17 (3/2)
H	H	H	H	$C(CH_3)_3$	28 (2/1)	17 (1/1)
H	H	H	H	n-C_5H_{11}	20	12
H	H	H	H	C_6H_5	10	
H	H	H	H	OCH_3	28 (7/1)	
H	H	H	H	$CH_2CO_2CH_3$	23	
H	H	H	H	CH_2OCH_3	23 (>20/1)[d]	15 (4/1)
H	H	CH_3	H	H	<3[e]	
H	CH_3	H	H	CH_3	68 (4/3)	64 (4/5)
p-OCH_3	H	H	H	CH_3	20	15
p-OCH_3	H	H	CH_3	CH_3	13	7
p-Cl	H	H	H	CH_3	16	12
p-CH_3	H	H	H	CH_3	18	14
m-CF_3	H	H	H	CH_3	24	23

[a] 0.10 M ketone, irradiated at 3130 Å. [b] Cyclobutanol/(acetophenone + cyclobutanol) in benzene; trans/cis cyclobutanol ratios noted in parentheses. [c] Values obtained in *tert*-butyl alcohol or in wet acetonitrile. [d] No cis isomer detectable. [e] Although we could detect none, a 2.7% yield of cyclobutanol has been isolated; M. E. Mathews, Ph.D. Thesis, University of Toledo, 1969.

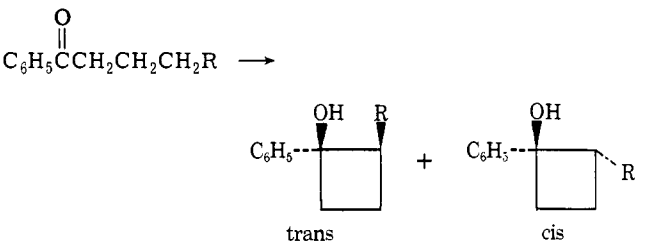
By measuring quantum yield enhancements as a function of added Lewis bases, we can determine maximum values of type II quantum yields, Φ_{max}, at which point $P_p = 1$.[2,6] The value of P_p for a given ketone in a given solvent can be determined merely by dividing the quantum yield observed in that solvent by Φ_{max} for the ketone. For the majority of phenyl alkyl ketones, Φ_{max} equals unity so that quantum yields are a direct measure of P_p. Relative values of k_{cy} and k_{sc} can be determined from product ratios, which generally are readily measurable by vpc analysis. Our trapping experiments[2] even allow us to estimate absolute rate constants for biradical reactions.

Cyclization *vs.* Elimination. Table I compares the actual chemical yields for elimination and for cyclization of various different aryl alkyl ketones. For almost all ketones, only three or four product peaks are observable in vpc traces: one each for olefin and (substituted) acetophenone, and one or two, with characteristic retention times with respect to the parent ketones, which were assumed to correspond to cyclobutanols. Because cyclobutanols have been identified as coproducts in so many laboratories, we specifically isolated and identified the cyclobutanols only from γ-methylhexanophenone,[2] δ-methoxyvalerophenone,[7] and γ-methoxy- and γ-*tert*-butylbutyrophenone.

In general, the competition between cyclization and cleavage of the biradical is not particularly sensitive to substitution either at the γ position or in the benzene ring. There is a definite trend toward increased cyclization with increasing size of γ-alkyl groups and in the γ- and δ-methoxy ketones. The most dramatic changes in cyclization/cleavage ratios are produced by α-dimethyl and β-dimethyl substitution. In all cases, polar solvents which enhance type II quantum yields also depress the amount of cyclization relative to cleavage.

For several ketones, in particular γ-hydroxy-, γ-cyano-, and γ-carbomethoxybutyrophenones, we were unable to detect any cyclobutanol products. It is quite possible that some of these products are unstable to vpc analysis. For all the ketones listed in Table I, with the exception of butyrophenone and δ-methoxyvalerophenone, acetophenone plus cyclobutanols account for all reacted ketone. Cyclopentanols are also formed from δ-methoxyvalerophenone.

Stereochemistry of Cyclization. In all cases where products have been isolated and characterized, *trans*-cyclobutanol is the major isomer formed in hydrocarbon solvents and is characterized by a vpc retention time shorter than that of the cis isomer.



In all cases, polar solvents reduce the trans/cis ratio. It is noteworthy that the trans/cis ratio for the γ-methoxy ketone is double that for valerophenone, that no *cis*-cyclobutanol is formed from the δ-methoxy ketone in benzene, and that large γ-alkyl groups decrease rather than increase the trans/cis ratio. We find it rather remarkable that so much of the highly strained *cis*-2-*tert*-butyl-1-phenylcyclobutanol is formed from γ-*tert*-butylbutyrophenone. Finally, there is hardly any stereoselectivity in the cyclization of the α,α-dimethyl ketone.

Revertibility. Tables II and III list the probabilities P_p that the biradicals derived from the various ketones we have studied go on to products rather than reverting to starting ketone. In particular, Table II compares quantum yields in benzene with maximum quantum yields obtained upon addition of *tert*-butyl alcohol for ring-substituted valerophenones, while Table III shows the effects mainly of γ and δ substituents on the quantum yields of phenyl alkyl ketones. Note that in both tables about half the P_p values are estimates based on observed quantum yields for elimination (extrapolated to zero ketone concentration)[6] and *as-*

(6) P. J. Wagner, I. Kochevar, and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **94**, 7489 (1972).
(7) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, and R. G. Zepp, *ibid.*, **94**, 7500 (1972).

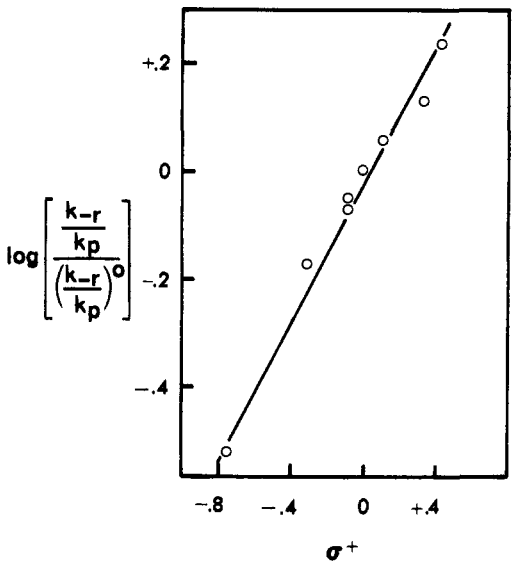


Figure 1. Hammett plot of effect of ring substituents on internal disproportionation of biradicals formed from valerophenone.

Table II. Effects of Ring Substituents on Biradicals Derived from Ring-Substituted Phenyl *n*-Butyl Ketones[a]

Substituent	—Φ, C_6H_6[b]—	Φ_{max}[c]	P_p[d]	k_{-r}/k_p
p-OCH_3	0.18	0.26[e]	0.69	0.45
o-OCH_3	0.18	0.25	0.72	0.39
p-CH_3	0.50	1.0	0.50	1.0
m-CH_3	0.34		~0.42	1.33
p-F	0.36		~0.44	1.27
H	0.40	1.0	0.40	1.50
o-Cl	0.45		~0.55	0.82
m-Cl	0.33		~0.40	1.50
p-Cl	0.35	0.94	0.37	1.70
m-F	0.27		~0.33	2.00
p-CF_3	0.26		~0.32	2.12
m-CF_3	0.23		~0.28[f]	2.58
o-CF_3	0.20		~0.25	3.00
p-(N)[g]	0.31	1.0	0.31	2.23
m-(N)[g]	0.29	1.0	0.29[f]	2.45
o-(N)[g]	0.18	1.0	0.18	4.50

[a] 0.10 *M* ketone irradiated at 3130 Å. [b] Quantum yields in benzene; left column represents only acetophenone; right column represents total of acetophenone and cyclobutanols. All values are averages of several measurements, with precision of ±3%. [c] See text. [d] $\Phi(C_6H_6)/\Phi_{max}$; approximate values based on assumption of usual 18% cyclization. [e] Same value obtained upon addition of *tert*-butyl alcohol, methanol, or pyridine. [f] Another reaction of biradical probably competes with cleavage and cyclobutanol formation (P. J. Wagner and G. Capen, *Mol. Photochem.*, **1**, 173 (1969)). [g] Pyridyl ketones (see reference in footnote *f*).

sumed 18% yields of cyclobutanols. Such estimates are probably good to ±0.02; even larger errors would not affect our semiquantitative comparison of results.

It is apparent that electron-donating substituents on the benzene ring increase the percentage of biradicals which go on to products rather than reverting to ketone, while electron-withdrawing substituents produce the opposite effect. Table II also lists k_{-r}/k_p ratios derived from the measured and estimated P_p values. The value of this ratio varies by a factor of ten between the strongest electron-donating and the strongest electron-accepting substituents. Figure 1 displays a Hammett plot of relative log (k_{-r}/k_p) values *vs.* σ^+ constants for those meta and para substituents for which σ^+ substituents are known. The slope yields a ρ^+ value of +0.60. Correlation with σ constants is very poor.

Table III. Biradical Revertibilities for $C_6H_5COCX_2CY_2CHR_1R_2$

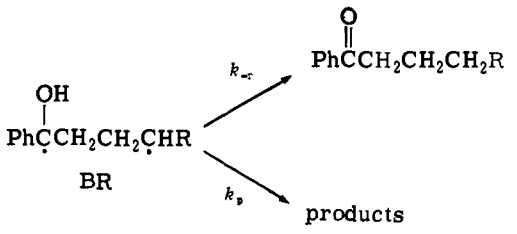
X	Y	R_1	R_2	Φ_{II}^0 (C_6H_6)[a]	P_p[b]
			Primary γ-C		
H	H	H	H	0.36	0.40
H	CH_3	H	H	0.19	0.20
			Secondary γ-C		
H	H	H	CH_3	0.30	0.36
CH_3	H	H	CH_3	0.04	0.16
H	H	H	*n*-C_5H_{11}	0.24	0.31
H	H	D[c]	*n*-C_5H_{11}	0.25[d]	0.37
H	H	H	*t*-C_4H_9	0.22	0.30
H	H	H	C_6H_5	0.47[e]	~0.55
H	H	H	$CH{=}CH_2$	0.24[e,f]	~0.35[f]
H	H	H	OCH_3	0.21	0.29
H	H	H	OH	0.25	~0.34
H	H	H	OC_6H_5	0.29	~0.35
H	H	H	CO_2CH_3	0.47[e]	~0.55
H	H	H	CN	0.30[e]	~0.36
H	H	H	CH_2OCH_3	0.33[g]	0.86
H	H	H	$CH_2CO_2CH_3$	0.58	~0.75
H	H	H	CH_2COOH	0.55	~0.70
H	H	H	CH_2Cl	0.55[h]	0.80
H	H	H	CH_2CN	0.45	~0.50
H	H	H	$(CH_2)_2Cl$	0.44	~0.52
H	H	H	$(CH_2)_2CN$	0.45	~0.53
H	H	H	$(CH_2)_3CN$	0.37	~0.44
			Tertiary γ-C		
H	H	CH_3	CH_3	0.22	0.25
H	H	CH_3	OCH_3	0.18	~0.23

[a] Quantum yield for acetophenone formation in benzene, extrapolated to zero ketone concentration (ref 6); all values reproducible to ±3%. [b] Approximate values estimated on basis of 18% cyclization. [c] Nonanophenone-γ,γ-d_2. [d] Φ_{max} = 0.82. [e] Extrapolated to zero conversion. [f] Other biradical reactions compete; A. Padwa and D. Eastman, *J. Amer. Chem. Soc.*, **91**, 462 (1969). [g] Φ_{max} = 0.47. [h] Φ_{max} = 0.80.

Trends are not so obvious for the data in Table III. Values of P_p definitely decrease as the γ carbon goes from primary to secondary to tertiary. Strong electron-withdrawing groups in the ε, δ, and even ζ positions increase P_p, the magnitude of the increase dropping as the substituent becomes more remote. The effects of γ substituents vary considerably. Large alkyl groups and alkoxy groups seem to lower P_p slightly. Of the four substituents which lead to conjugated olefin products in type II elimination, phenyl and carbomethoxy enhance P_p considerably while vinyl and cyano produce no change. Finally, for the biradicals derived from nonanophenone-γ,γ-h_2 and -γ,γ-d_2, reverse hydrogen transfer displays a primary isotope effect of 1.35 (corrected for incomplete deuteration of the latter ketone).

Biradical Solvation. The enhancement of type II quantum yields produced by Lewis bases can be treated as quenching of reverse hydrogen transfer in the biradical.[6] Such quenching can consist either of a kinetically controlled competition between bimolecular solvation and the various unimolecular reactions of the biradical or of an equilibration between solvated biradicals which do not revert to ketone and unsolvated biradicals which do.

Equation 5 is the Stern–Volmer expression for quenching of biradical reversal by added Lewis base B. Figure 2 depicts the linear adherence to eq 5 displayed by several ketone–*tert*-butyl alcohol systems and for valerophenone–pyridine. The linearity sug-



$$BR + B: \underset{k_{-sol}}{\overset{k_{sol}}{\rightleftharpoons}} BR\cdots B$$

$$BR\cdots B \xrightarrow{k_p'} \text{products}$$

$$\Phi^0/\Phi_{max} = P_p = k_p\tau_{BR} \quad (3)$$

$$\frac{\Phi_{max} - \Phi^0}{\Phi_{max}} = k_{-r}\tau_{BR} \quad (4)$$

$$\frac{\Phi_{max} - \Phi^0}{\Phi_{max} - \Phi} = 1 + K_q[B] \quad (5)$$

kinetic control ($k_p' > k_{-sol}$) $\quad K_q = k_{sol}\tau_{BR}$ (6)

equilibrium ($k_{-sol} > k_p'$) $\quad K_q = K_{sol} = \frac{k_{sol}}{k_{-sol}}$ (7)

gests that solvation of the biradical can be treated kinetically as a normal bimolecular reaction which competes with the biradical's various unimolecular reactions, but it does not differentiate between equilibrium or kinetic control.

If free and hydrogen-bonded biradicals do equilibrate, the hydroxyl protons might exchange with protic solvents. In fact, such an exchange could explain the γ deuteration by deuteriothiol.[2,8] Nonanophenone-γ,γ-d_2 was irradiated to 50% conversion in benzene containing 0.3 *M* *tert*-butyl alcohol. This concentration of alcohol quenches almost half the biradical reversal; if exchange occurred, unreacted starting material would be enriched with hydrogen specifically at the γ position. Mass spectrometric analysis of recovered ketone indicated no loss of deuterium either in the molecular ion or in the acetophenone enol formed by MacLafferty rearrangement. Since there is no exchange with alcohol solvents, exchange with thiol solvent seems unlikely.

Discussion

Biradical Lifetimes. The kinetic factors which determine the stereochemistry of 1,4-biradical reactions are still not fully understood. Probably the only assumption which meets with general acceptance is that, in solution, excess vibrational energy is lost to the medium in 10^{-11}–10^{-12} sec, before any spin inversions or bond rotations can occur. Spin correlation in a 1,4 biradical should be weak enough that triplet–singlet interconversions would be fairly rapid, 10^9–10^{10} sec^{-1}. Stephenson and Brauman[5] have suggested that in triplet-derived biradicals spin inversion is much faster than chemical reactions, so that the stereochemistry of product formation is determined by how well coupling and cleavage compete with bond rotations rather than by the competition between spin inversion and bond rotations. The same assumption is implicit in some interpretations of substituent effects on the competition between cyclization and cleavage.[9,10]

(8) P. J. Wagner and R. G. Zepp, *J. Amer. Chem. Soc.*, 94, 287 (1972).

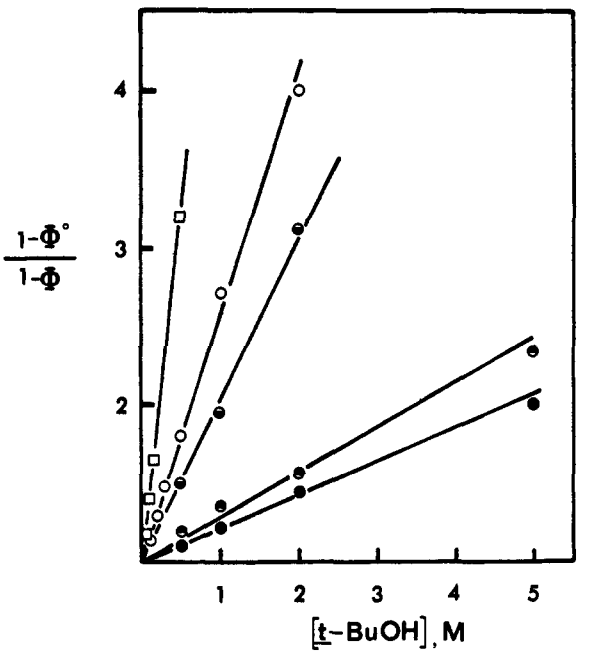


Figure 2. Quenching of biradical disproportionation by added *tert*-butyl alcohol: (○) valerophenone; (●) β,β-dimethylbutyrophenone; (◒) γ-methylvalerophenone; (◓) γ-hydroxybutyrophenone; (□) valerophenone by added pyridine.

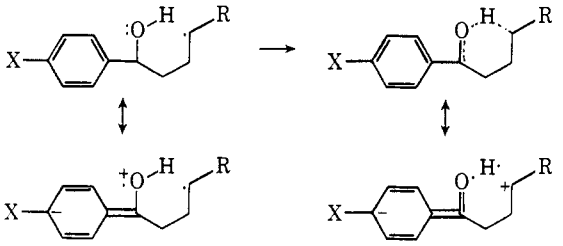
Our separately reported trapping experiments[2,8] suggest lifetimes $\sim 10^{-6}$ sec for *solvated* type II biradicals and $< 2 \times 10^{-7}$ sec for *unsolvated* biradicals. The combined rate of 10^6 sec^{-1} for cyclization and cleavage is reasonably consistent with the activation barriers of 6–8 kcal deduced from cyclobutane pyrolyses.[11]

The stereochemistry of cleavage[12] and of cyclization[2,13,14] observed for triplet-generated 1,4 biradicals indicates that the biradicals do not establish complete rotational equilibrium before reacting. This fact indicates rates for rotation about the 3,4 (β,γ) C–C bond of 1,4 biradicals in the range 10^7–10^9 sec^{-1}. Unfortunately, calculating rotational rates is not straightforward, but the indicated range of values is not unreasonable.[15] We feel that the evidence is convincing that bond rotations and chemical reactions are competitive in type II biradicals, such that substitutional factors which would affect rotation rates must be considered in any discussion of biradical behavior.

Reverse Hydrogen Transfer. The return of the hydroxylic hydrogen to the γ carbon can be considered an intramolecular radical–radical disproportionation reaction. One striking feature of the chemistry of 1-hydroxyl 1,4 biradicals is that this disproportionation is their major reaction, whereas it is at best a minor reaction of hydrocarbon 1,4 biradicals.[13] This reaction primarily determines biradical lifetimes, apparently having a rate $\geq 10^7$ sec^{-1} for valerophenone. Perhaps

(9) (a) P. J. Wagner and A. E. Kemppainen, *ibid.*, 90, 5896 (1968); (b) P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971).
(10) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, 92, 6672 (1970).
(11) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968).
(12) L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *J. Amer. Chem. Soc.*, 93, 1984 (1971).
(13) P. D. Bartlett and N. C. Porter, *ibid.*, 90, 5317 (1968).
(14) (a) N. J. Turro and T-J. Lee, *ibid.*, 92, 7467 (1970); (b) R. G. Zepp and P. J. Wagner, manuscript in preparation; see ref 9b.
(15) (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 71, 2903 (1967); 72, 1866 (1968); (b) R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, 91, 7411 (1969).

the most consistent, clear-cut structure–reactivity relationship that we find for these hydroxy biradicals is that electron-withdrawing groups on the benzene ring increase the probability for reversion of biradical to ground-state ketone while electron-withdrawing groups at the δ and ϵ positions decrease that probability. Consequently, the transition state for disproportionation very likely is stabilized by charge transfer from the γ-radical site to the incipient carbonyl, as pictured below. There is ample evidence in the free-radical literature that alkyl radicals are electron donors.[16] Electron-withdrawing groups near the γ carbon apparently reduce the electron-donating ability of the γ radical site. In particular, such δ substituents cause the elimination quantum yield to rise to 60%, indicating total product quantum yields of 70–80%, even in benzene solvent.



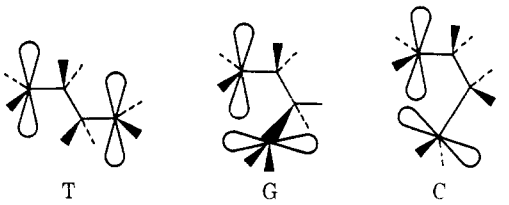
We have assumed that δ, ϵ, and ring substituents do not greatly alter k_{sc} or k_{cy}, the majority of the change in P_p values being due to changing k_{-r} values. Such an assumption clearly cannot be valid for γ substituents. The opposite effects of γ-alkoxy and γ-carbomethoxy groups on P_p may reflect chiefly inductive effects on the γ-radical site. While the increase in P_p caused by a γ phenyl may be due to formation of a conjugated olefin in the cleavage reaction, the lack of any such effect by γ-cyano and γ-vinyl substituents is puzzling. (These values were obtained by extrapolation to zero conversion, a lengthy extrapolation for the γ-cyano ketone.)

The low k_H/k_D value for disproportionation of the biradical from nonanophenone deserves some comment. Such a low value might easily be interpreted to indicate a more rapid reaction, such as the 10^9 M^{-1} sec^{-1} rate constants observed for hydrogen abstraction by chlorine atoms.[17] The small isotope effect does suggest that most of the increase in type II quantum yield of 2-hexanone induced by γ deuteration is due to increased intersystem crossing.[18]

Substituent Effects on Cleavage. The decrease in P_p as the γ carbon goes from primary to secondary to tertiary is probably due largely to increasing electron-donating properties of the γ-radical site. Steric effects may be involved also, since large γ-alkyl groups tend to decrease P_p. In our preliminary report[9] we pointed out that cleavage of a 1,4 biradical can occur efficiently only in a conformation in which the two p orbitals are parallel to the C–C σ bond being broken. Hoffman's calculations[4] indicate that such a conformation optimizes the mixing of π and σ levels which promotes cleavage.

(16) E. S. Huyser, "Free Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, pp 79–81.
(17) K. B. Wiberg and L. H. Slaugh, *J. Amer. Chem. Soc.*, 80, 3033 (1958).
(18) D. R. Coulson and N. C. Yang, *ibid.*, 88, 4511 (1966); N. C. Yang, S. P. Elliot, and B. Kim, *ibid.*, **91**, 7551 (1969).

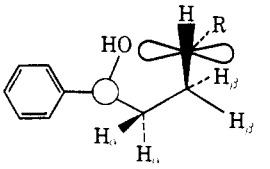
In excellent agreement with this notion, type II cleavage is very inefficient for several cyclic ketones in which the 1,4 biradicals cannot assume such a conformation.[19] Below are pictured various such conformations, ranging from transoid through gauche to cisoid, which suffers from eclipsing interactions about the middle C–C bond. In T and C, all four carbon atoms are coplanar; in G, C_4 is rotated out of the plane of the other three carbons so as to relieve any eclipsing about the middle C–C bond.



T G C

Interestingly, the decrease in P_p caused by large γ groups such as *tert*-butyl reflects lower relative k_{sc} values, since k_{cy}/k_{-r} ratios barely differ for valerophenone and γ-*tert*-butylbutyrophenone, while k_{sc}/k_{-r} decreases from 0.48 to 0.31. Likewise, α-dimethyl substitution has little effect on the k_{cy}/k_{-r} ratio but lowers k_{sc}/k_{-r} to 0.05. β-Dimethyl substitution on butyrophenone lowers both k_{sc}/k_{-r}, from 0.60 to 0.25, and k_{cy}/k_{-r}, from 0.07 to 0.006. The small effect of β- and δ-methyl substituents on k_{sc}/k_{-r} ratios may be largely an inductive effect on k_{-r}, since δ-CO_2Me and δ-Cl raise k_{sc}/k_{-r} to 2.3 and 3.3, respectively.

Our considerations of steric and conformational effects in type II reactions[7] suggest that the initial conformation of the biradical is as pictured below, with the γ p orbital almost parallel to and the benzylic p orbital perpendicular to the α,β C–C bond.



In order for the biradical to attain conformation G, it must rotate 90° about the carbonyl and α-carbon bond; it must also rotate about the C_α–C_β bond to attain conformation T. In either case, α-methyl groups would undergo severe nonbonded interactions with the ortho hydrogens of the benzene ring, thus impeding the crucial rotation enough to lower k_{sc} by the observed order of magnitude. Cleavage probably occurs from a compromise conformation involving small nonbonded interactions and only partial orbital overlap. As Lewis has pointed out,[10] cyclization of 1,4 biradicals most likely produces a puckered cyclobutane ring, for which not as much bond rotation is necessary as for cleavage.

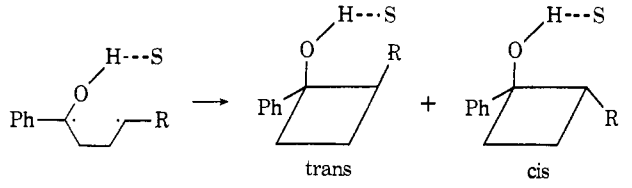
Substituent Effects on Cyclization. Whereas α-dimethyl substitution enhances the yield of cyclization apparently by impeding cleavage, β-dimethyl substitution clearly impedes cyclization of the biradical. Developing 1,3-pseudodiaxial interactions probably destabilize the transition state for cyclization. The stereoselectivity displayed in the preferential formation

(19) (a) A. Padwa and D. Eastman, *ibid.*, **91**, 462 (1969); (b) R. B. Gagosian, J. C. Dalton, and N. J. Turro, *ibid.*, **92**, 4752 (1970).

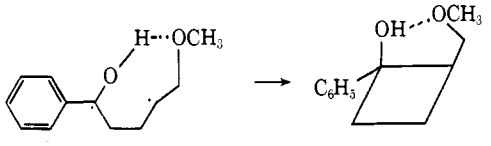
of *trans*-cyclobutanols by γ-substituted butyrophenones shows that the transition states for cyclization of 1,4 biradicals are somewhat sensitive to developing nonbonded interactions. The lowered k_{sc}/k_{cy} ratio for γ-methylvalerophenone relative to valerophenone probably has the same cause.

That the stereoselectivity of cyclization decreases with increasing size of γ-alkyl groups is especially revealing. If, as we suggested above, δ-methyl substitution slightly increases k_{-r}, it also slightly increases k_{cy}, all of which increases involve the formation of the sterically unhappy *cis*-cyclobutanol. There is no way to rationalize this result in terms of the biradicals' reaching rotational equilibrium before proceeding to products. Decreased stereoselectivity with increasing barriers to bond rotation strongly suggests that rates of bond rotation are competitive with chemical reactions of the biradical, as discussed above. In the biradical derived from γ-*tert*-butylbutyrophenone, rotation about the C_β–C_γ bond probably occurs no more than twice before product formation.

The polar solvents which increase P_p also decrease the yield and stereoselectivity of cyclization. In fact, the relative yields of *cis*-cyclobutanol and acetophenone do not vary with solvent for several ketones; the relative yield of *trans*-cyclobutanol is usually halved by alcohols. Presumably the same hydrogen bonding which suppresses reverse hydrogen transfer increases the steric bulk of the hydroxy group, thus impeding specifically trans cyclization.

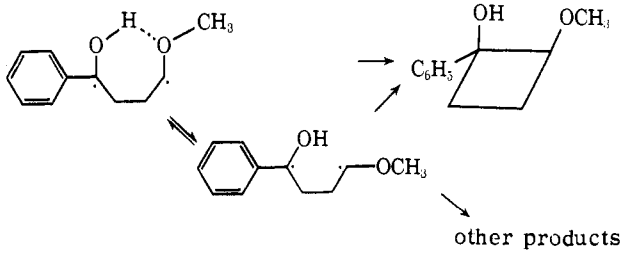


Intramolecular Hydrogen Bonding. There are several cases in which intramolecular hydrogen bonding apparently affects the behavior of the biradical. The near unity value for P_p as well as the negligible amount of *cis*-cyclobutanol obtained for δ-methoxyvalerophenone probably reflect intramolecular hydrogen bonding, even though an eight-membered ring is involved. Such



a structure has enough flexibility to achieve conformations suitable for both cleavage and cyclization. In alcohol solvent, the intramolecular hydrogen bonding is presumably replaced with intermolecular solvation, and a more normal trans/cis cyclobutanol ratio is observed. Interestingly, γ-alkoxy substitution does not enhance P_p values. Models show that the seven-membered ring hydrogen-bonded structure cannot easily achieve a conformation suitable for cleavage. The biradical does undergo extra cyclization to yield the hydrogen-bonded *trans*-cyclobutanol.

The large enhancements in P_p caused by δ-carboethoxy, carboxy, and cyano substituents might be interpreted as being due to intramolecular hydrogen bonding, except for the following observations: (1) ε-



and ζ-cyano substitutions also enhance P_p, but intramolecular hydrogen bonding would require ten- and 11-membered rings; (2) δ- and ε-chloro substitutions enhance P_p even though *n*-butyl chloride produces absolutely no solvent effect on P_p.[6] Consequently, we interpret these effects as being primarily inductive, and note that much of the enhancement in P_p caused by the δ-methoxy group must also be inductive in nature. Neither *o*-methoxy nor *o*-pyridyl ketones[20] show evidence for enhanced P_p values, even though intramolecular hydrogen bonding could occur in both biradicals.

Biradical Solvation. The K_Q value in Figure 2 for pyridine–valerophenone is 4.4 M^{-1}. If solvation were kinetically controlled, the minimum value of τ_{BR} would be 0.5 nsec, since k_{sol} cannot exceed the rate constant for diffusion. However, since the solvated biradicals can be trapped with thiols, it would appear that biradical lifetimes are much longer than 1 nsec. Either hydrogen bonding occurs at rates much slower than diffusion controlled, or, more likely, an equilibrium is established between solvated and unsolvated biradicals before they react further.

The differing slopes observed in Figure 2 for added *tert*-butyl alcohol apparently indicate variations in K_{sol} as a function of biradical structure. Generally, we observed that the efficiency of solvation is little affected by γ substituents, but there are exceptions. For example, intramolecular hydrogen bonding may well lower K_{sol} in γ-hydroxybutyrophenone. Dimethyl substitution at the α or β carbons lowers K_{sol} an order of magnitude. These effects seem best interpreted as simple steric hindrance to solvation. Although the tenfold variation in K_{sol} with biradical structure is not really very large, it certainly affects the ease of experimentally measuring maximum quantum yields.[6] The threefold variation in K_{sol} between pyridine and *tert*-butyl alcohol reflects a billion-fold difference in basicities, and it seems surprising that K_{sol} for pyridine is not much larger. However, another example has just been reported of hydrogen bonding by pyridines being much weaker than might be predicted from basicities.[21] K_{sol} values for bases weaker than alcohols are well below unity.

Experimental Section

Quantum Yields. As described in the other papers in this series,[2,3] sealed Pyrex tubes containing degassed samples were irradiated in parallel on a merry-go-round apparatus. All quantum yields reported in this paper were measured relative to a 0.10 *M* valerophenone actinometer. Product yields were measured by vpc analysis on machines with flame ionization detectors. Tetradecane was invariably used as internal standard for acetophenone and an appropriate *n*-alkane from hexadecane up to eicosane for the cyclobutanols and the ring-substituted acetophenones. On a column packed with 4% QF-1 and 1% Carbowax 20M on acid-washed

(20) P. J. Wagner and G. Capen, *Mol. Photochem.*, **1**, 173 (1969).
(21) E. M. Arnett and E. J. Mitchell, *J. Amer. Chem. Soc.*, **93**, 4052 (1971).

Chromosorb G, the cyclobutanols invariably have retention times a few minutes shorter than their parent ketones. Since cyclobutanol retention times increase with increasing Carbowax loading faster than do ketone retention times, we occasionally analyzed samples on each of two columns containing different amounts of Carbowax to ensure that no cyclic alcohols were eluting under the ketone peak. Since flame detectors effectively count carbons, we assumed that cyclobutanols produce the same response as their parent ketones. All acetophenone–standard responses were calibrated with known mixtures of pure materials.

Cyclobutanols from γ-*tert*-Butylbutyrophenone. The ketone (2 g) in 25 ml of pentane was irradiated to 95% conversion with a 450-W medium-pressure mercury arc filtered by a Pyrex sleeve. Solvent was removed on a flash evaporator and the two products presumed to be cyclobutanols were collected by preparative vpc on a Carbowax 20M column.

Both products displayed similar ir, nmr, and mass spectra, including OH stretches at 3600 cm^{-1} and the M − 18, M − 28, and *m/e* 120 peaks characteristics of 1-phenylcyclobutanols. The product with the shorter retention time had the following nmr spectrum (very dilute in CCl; Varian T-60; chemical shifts relative to TMS) consistent with the *trans*-2-*tert*-butyl-1-phenylcyclobutanol structure: δ 7.2–7.6 (m, 5 H, phenyl), 1.7–2.7 (complex, 5 H, ring protons), 1.45 (s, 1 H, OH), 0.95 (s, 9 H, CMe_3). This product shows *no* hydrogen-bonded O–H stretches in the ir. The product with the longer retention time was assigned as the cis isomer on the basis of both free and H-bonded OH stretches in the ir and the upfield shift of the *tert*-butyl signal in the nmr (δ 0.5, s, (9 H)) which would be caused by the *tert*-butyl group being held in the shielding region of the neighboring benzene ring.

Acknowledgment. This work was partially supported by National Science Foundation grants.

Type II Photoreactions of Phenyl Ketones. Competitive Charge Transfer in α-, γ-, and δ-Dialkylamino Ketones

Peter J. Wagner,*[1] Allen E. Kemppainen, and Thomas Jellinek

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. *Received January 5, 1972*

Abstract: α-Dimethylaminoacetophenone (I), γ-dimethylaminobutyrophenone (II), and δ-pyrrolidinovalerophenone (III) all undergo photoelimination in solution to yield acetophenone. Intersystem crossing yields are lower than unity for all three ketones, decreasing in the order III > II > I. For all three ketones, Φ_{isc} values are higher in methanol than in benzene or acetonitrile. Analysis of quantum yields and lifetimes suggests that all the photoelimination of II and III arises by direct triplet state γ-hydrogen abstraction. Rapid charge transfer quenching by the remote amino group is a competitive triplet reaction, being 3.5 times faster for II than for III and five times faster in benzene or acetonitrile than in methanol, but does not lead to photoelimination products. Triethylamine and dimethyl *tert*-butylamine quench triplet valerophenone at equal rates in a given solvent, the absolute rate constants being ten times higher in benzene and acetonitrile than in methanol. This behavior indicates a bimolecular charge transfer process which leads efficiently to radicals. The lack of a sizable rate increase in acetonitrile indicates that amine–triplet ketone interactions involve charge transfer but not full electron transfer. The decreases afforded by methanol reflect the decreased availability of hydrogen-bonded lone-pair electrons. The lack of biradical formation from the corresponding CT complexes formed from II and III reflects geometric restraints to transfer of a proton to oxygen in the cyclic complex. I is unusual in that all of its photoelimination in benzene and acetonitrile, two-thirds in methanol, arises from an unquenchable singlet state. This observation invalidates the suggestion that π,π* triplets of α-dialkylamino ketones might be highly reactive. The singlet reaction of I may involve either singlet CT complexation or the fact that the ^{1}n,π* state of I has n(O),σ*(C–N) character, causing expulsion of the dimethylamide anion. Triplet I is formed only in methanol or by sensitization and is unusual in that it does not seem to undergo the rapid CT quenching noted for II and III but proceeds to product in high yields.

Photoreduction of ketones by amines has received considerable attention.[2,3] Cohen first proposed that amines *reduce* ketone triplets and that the resulting radical ions collapse either to radicals by a proton shift or to ground states of reactants by a reverse electron shift.[2]

$$R_2C{=}O^* + R_2\ddot{N}CH_2R \longrightarrow R_2\dot{C}{-}\bar{O} + R_2\dot{\ddot{N}}^+{-}CH_2R \longrightarrow R_2\dot{C}OH + R_2\ddot{N}{-}\dot{C}HR$$

In our study of substituent effects on intramolecular hydrogen abstraction by triplet phenyl ketones, we have investigated the photochemistry of α-, γ-, and δ-dialkylamino substituted phenyl alkyl ketones with the hope of establishing how well intramolecular charge transfer interactions compete with intramolecular hydrogen abstraction, in particular, how the competition depends on the distance between the two groups and on the polarity of the solvent.

Results

We have studied three ketones: α-dimethylaminoacetophenone (Im), γ-dimethylaminobutyrophenone (II), and δ-pyrrolidinovalerophenone (III), as well as some ammonium salts of II and III. In all cases, the ketones and their salts undergo type II photoelimination to yield acetophenone. Small peaks presumably corresponding to cyclobutanols appear in vpc traces of II and III photosylates, but not from I. Acetophenone

(1) Alfred P. Sloan Fellow, 1968–1972.

(2) (a) S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, 89, 3741 (1967); (b) S. G. Cohen and H. M. Chao, *ibid.*, 90, 165 (1968); (c) S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, 90, 521 (1968); (d) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, 72, 3782 (1968).

(3) (a) R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 1265 (1967); 511 (1968); (b) S. G. Cohen and G. Parsons, *J. Amer. Chem. Soc.*, 92, 7603 (1970).