(R = S(*p*-MeOPh)), 123358-94-1; **4** (R = Br), 114597-55-6; **4** (R = OMe), 114597-62-5; **4** (R = OEt), 114597-64-7; **4** (R = CN), 114597-66-9; **4** (R = Me), 127130-18-1; **4** (R = Et), 127130-19-2; **4** (R = *i*-Pr), 127130-20-5; **4** (R = *t*-Bu), 127130-21-6; **6a**, 127130-10-3; **6b**, 127130-11-4; **6c**, 127130-12-5; **6d**, 127130-13-6; **7a**, 127130-22-7; **7b**, 127130-23-8; **7c**, 127130-24-9; **7d**, 127130-25-0; **8a**, 127130-26-1; **8b**, 127130-27-2; **8c**, 127130-28-3; **8d**, 127130-29-4; **9a**, 127130-30-7; **9b**, 127130-31-8; **9c**, 127130-32-9; **9d**, 127130-33-0; $H_3CCH(CH_3)C(OH)(CH_3)C-H_2C(CH_3)_2CH_3$, 5396-09-8; (*Z*)-$HOCD_2C(CH_3)=C(CH_3)CD_2OH$, 70576-51-1; (*Z*)-$ClCD_2C(CH_3)=C(CH_3)CD_2OH$, 127130-34-1; (*Z*)-$D_3CC(CH_3)=C(CH_3)CD_2OH$, 127130-35-2; (*Z*)-$D_3CC(CH_3)=C-(CH_3)CD_2Cl$, 127130-36-3.

The Photocyclization of *o*-Alkoxy Phenyl Ketones

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Abstract: Several *o*-alkoxybenzophenones and *o*-(benzyloxy)benzophenones and -acetophenones photocyclize to 3-hydroxy-2,3-dihydrobenzofurans. Quantum yields generally are quite high, except for *o*-(benzyloxy)acetophenone. The *o*-ethoxy and *o*-benzyloxy ketones form two diastereomeric products, the *Z* isomer being highly preferred in hydrocarbon solvents, the *E* isomer being formed in comparable yield in methanol or with added pyridine. The reaction involves δ-hydrogen abstraction by the ketone triplets followed by cyclization of the 1,5-biradical intermediates. The biradicals have such short lifetimes that they usually cannot be detected by flash spectroscopy or trapped by thiols. Triplet state lifetimes, determined both by steady-state quenching studies and by flash kinetics, reveal that hydrogen abstraction rate constants are quite low. Arrhenius plots for triplet decay indicate activation energies of 3–5 kcal/mol and *A* values of 10^9 for the δ-hydrogen abstraction. MMX calculations and spectroscopic data all indicate that the ketones exist primarily in conformations with the carbon α to the ether oxygen twisted well away from the carbonyl. The low observed rate constants are ascribed to even lower equilibrium populations of conformers in the geometry required for reaction in the triplet state than in the ground state. 2,6-Diacylphenyl ethers show ten times the triplet reactivity of their monoacyl equivalents. In these cases, the ether function is twisted 90° such that the target C–H bond is much closer to a carbonyl. The large solvent effects on the stereochemistry of cyclization despite short biradical lifetimes suggest that bond rotations may induce intersystem crossing of the triplet biradicals. The low cyclization quantum yield from *o*-(benzyloxy)acetophenone and the formation of *o*-benzoylacetophenone as a major side product suggest that the 1,5-biradicals partially cyclize into the benzene ring to generate spiroenol intermediates. Rate constants for quenching of the triplet ketones by 2,5-dimethyl-2,4-hexadiene were measured. The k_q values are $\geq 5 \times 10^9$ M^{-1} s^{-1} for the *o*-methoxy ketones but only $1–3 \times 10^9$ for the *o*-benzyloxy ketones. This rare steric effect on triplet energy transfer is attributed to twisting of the benzoyl chromophores caused by steric congestion.

Over the past decade there has been a growing interest in two questions that, although not generally related, are both involved in intramolecular hydrogen abstraction by triplet ketones: how conformational factors affect intramolecular bifunctional photoreactions;[1-5] and what determines the lifetimes of photogenerated biradicals.[6] Much of the early experimental evidence related to both questions was provided by studies of the Norrish type II reaction of ketones,[7,8] in which γ-hydrogen atom abstraction by n,π* excited states[9] produces 1,4-biradicals.[10]

Since Scaiano first successfully observed type II biradicals by flash spectroscopy,[11] there has developed a realization that intersystem crossing (isc) of triplet-generated biradicals usually determines their lifetimes.[6,11-13] Unfortunately, how (or why) isc varies with structure in 1-hydroxy-1,4-biradicals has not been answered satisfactorily.[13] The early recognition that the type II reaction varies with ketone structure from exclusive cleavage to exclusive cyclization revealed that product formation from biradicals can be subject to strong conformational and stereoelectronic control.[14-19]

As regards conformational effects, there are three extreme boundary conditions that can determine the kinetics of intramolecular excited-state reactions and decay: (1) conformational interconversion being much slower than decay; (2) conformational interconversion being much faster than decay; and (3) reaction of a "reactive" conformation being much faster than rotations to nonreactive geometries, such that the bond rotations that form the "reactive" conformation become rate determining.[1-3] The earliest quantitative examples all involve γ-hydrogen abstraction: Lewis provided the most dramatic example of ground-state conformational control,[20] Alexander and Lewis both considered the ramifications of conformational equilibrium;[20,21] and we provided

(1) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1.
(2) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461–7.
(3) Winnik, M. A. *Chem. Rev.* **1981**, *81*, 491.
(4) Scheffer, J. R. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: New York, 1987; Chapter 1.
(5) de Schryver, F. C.; Boens, N.; Put, J. *Adv. Photochem.* **1977**, *10*, 359.
(6) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819–24; *Acc. Chem. Res.* **1982**, *15*, 252–8.
(7) Norrish, R. G. W. *Trans. Faraday Soc.* **1937**, *33*, 1521.
(8) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.
(9) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.
(10) (a) Yang, N. C.; Yang, D.-H. *J. Am. Chem. Soc.* **1958**, *80*, 2913. (b) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480–8.
(11) (a) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431–4. (b) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126–31.
(12) (a) Zimmt, M. B.; Doubleday, C., Jr.; Gould, I. R.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724–6. (b) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 3618–20.
(13) Caldwell, R. A. *Pure Appl. Chem.* **1984**, *56*, 1167.
(14) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5896–7.
(15) (a) Wagner, P. J.; McGrath, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 3849–51. (b) Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1972**, *94*, 3852–8.
(16) Wagner, P. J.; Zepp, R. G.; Liu, K.-C.; Thomas, M.; Lee, T.-J.; Turro, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 8125–34.
(17) Turro, N. J.; Lewis, F. D. *Tetrahedron Lett.* **1968**, 5845. Turro, N. J.; Lewis, F. D. *J. Am. Chem. Soc.* **1970**, *92*, 311.
(18) Heine, H.-G.; Hartmann, W.; Lewis, F. D.; Lauterbach, R. T. *J. Org. Chem.* **1976**, *41*, 1907–12.
(19) Wagner, P. J.; Thomas, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 241.
(20) Lewis, F. D.; Johnson, R. W.; Johnson, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 6090–9.

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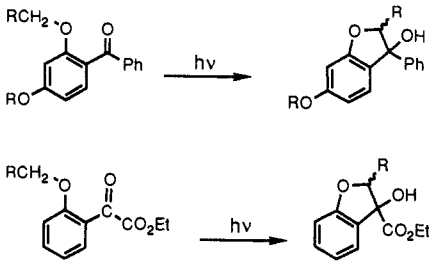
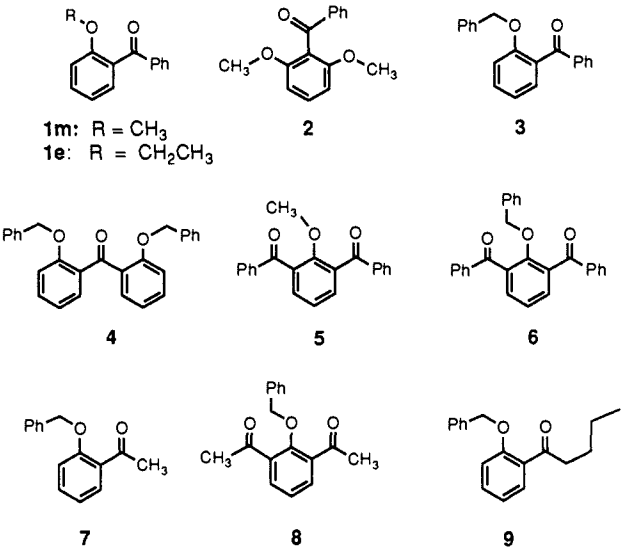
a rare example of rotational control.[22] Other than these 1,5-hydrogen transfers, the only others that have received thorough investigation are the remote transfers typical of benzophenones substituted para with a long alkyl tail,[23] for which Winnik has carefully correlated reactivity with conformational equilibria.[24]

Norrish's original report of his "type II" reaction was actually one of the earliest observations of the strong positional selectivity displayed by intramolecular hydrogen atom transfers. This selectivity has become recognized as a preference for a six-atom cyclic transition state, a preference characteristic of most radical hydrogen-transfer processes.[25-28] In our early studies on the type II reaction, we found that triplet ketones attack γ-hydrogens 20 times faster than otherwise identical δ-hydrogens and interpreted this preference as being both enthalpic and entropic in origin.[29] Houk has since published[30] very revealing calculations on several types of hydrogen atom transfers that indicate a more linear O-H-C geometry in the transition state than we assumed, yet verify our conclusion of comparable[31] influence of entropy and enthalpy in determining the γ/δ preference in triplet hydrogen abstraction by straight chain ketones.

Several examples of efficient photocyclization by ketones to cyclopentanols, presumably via δ-hydrogen abstraction, were scattered in the early literature,[32-35] although only the reaction of phenylglyoxalate esters was given extended mechanistic attention.[36] In recent years there has been a surge of synthetic interest in ring formation involving nonionic intermediates. Given the paucity of knowledge about the formation and reaction of 1,5-biradicals, it was impossible to evaluate the synthetic potential of photoinduced δ-hydrogen abstraction as a source of five-membered rings. Therefore we began a systematic study of various forms of δ-hydrogen abstraction by triplet ketones in order to evaluate conformational control of both triplet and biradical reactivity. The ability to compare 1,5-hydroxy biradicals to the much studied 1,4-biradicals also promised to be of great value, given recent advances in understanding the behavior of different length biradicals generated by triplet α-cleavage of cyclic ketones.[37]



Scheme I

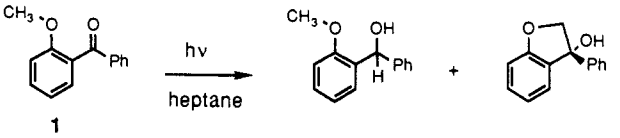


We have already reported studies of *o-tert*-butyl phenyl ketones.[38,39] We have also studied the photocyclizations of α-(*o*-tolyl)acetophenones.[40,41] This paper reports our mechanistic study of the photocyclizations of *o*-alkoxy phenyl ketones,[33] which has produced several surprises, some of which have been communicated.[42,43] Our approach throughout was designed to establish the extent of conformational effects on both triplet and biradical reactivity.

Results

Products. The various *o*-alkoxy ketones listed in Scheme I were irradiated as ~0.02–0.04 M solutions in various degassed solvents; product formation was monitored by gas chromatography (GC), and products were isolated by column chromatography. Their structures were determined by the usual spectroscopic methods, with ^{1}H NMR being especially useful for assigning stereochemistry.

o-Methoxyacetophenone was unreactive when irradiated in benzene. *o*-Methoxybenzophenone (**1m**) produces both the reduction product *o*-methoxybenzhydrol and the cyclization product 3-phenyl-3-hydroxy-2,3-dihydrobenzofuran when irradiated in alkane or alcohol solvents, only the latter in benzene.



Both *o*-methoxyvalerophenone[9] and *o*-benzyloxyvalerophenone (**9**) yield only the *o*-alkoxyacetophenones when irradiated in benzene; **7** formed from **9** produces secondary products as described below.

The *o*-benzyloxy ketones produce two diastereomeric 2-phenyl-3-hydroxy-2,3-dihydrobenzofuran cyclization products. Irradiation in benzene gave primarily the *Z* isomer, in which the 2-phenyl and 3-hydroxy groups are cis to each other. The two diastereomers were produced in comparable yields when the solvent was methanol or contained pyridine. The two were isolated and

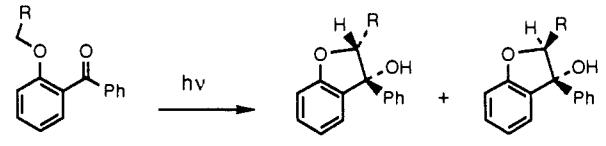
(21) Alexander, E. C.; Uliana, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 5644.
(22) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 239.
(23) Breslow, R.; Winnik, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3083.
(24) Winnik, M. A. *Acc. Chem. Res.* **1977**, *10*, 173.
(25) (a) Corey, E. J.; Hertler, W. R. *J. Am. Chem. Soc.* **1960**, *82*, 1657. (b) Kabasakalian, P.; Townley, E. R. *Ibid.* **1962**, *84*, 2711.
(26) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1597.
(27) Hesse, R. H. *Adv. Free Radical Chem.* **1969**, *3*, 83.
(28) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements of Ground and Excited Molecules*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 251–8.
(29) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7500–6.
(30) Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 2195; *J. Org. Chem.* **1988**, *53*, 1650.
(31) Wagner, P. J.; Zepp, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4958.
(32) (a) Pappas, S. P.; Blackwell, J. E., Jr. *Tetrahedron Lett.* **1966**, 1175. (b) Pappas, S. P.; Zehr, R. D.; Blackwell, J. E., Jr. *J. Heterocycl. Chem.* **1970**, 1215.
(33) Lappin, G. R.; Zannucci, J. S. *J. Org. Chem.* **1971**, *36*, 1805.
(34) (a) Coyle, D. J.; Peterson, R. V.; Heicklen, J. *J. Am. Chem. Soc.* **1964**, *86*, 3850. (b) Yates, P.; Pal, J. M. *J. Chem. Soc. D* **1970**, 553. (c) Stephenson, L. M.; Parlett, J. L. *J. Org. Chem.* **1971**, *36*, 1093.
(35) O'Connell, E. J. *J. Am. Chem. Soc.* **1968**, *90*, 6550.
(36) (a) Pappas, S. P.; Pappas, B. C.; Blackwell, J. E., Jr. *J. Org. Chem.* **1967**, *32*, 3066. (b) Pappas, S. P.; Zehr, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 7112. (c) Pappas, S. P.; Alexander, J. E., Jr.; Zehr, R. D., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6928.
(37) Doubleday, C.; Turro, N. J.; Wang, J.-F. *Acc. Chem. Res.* **1989**, *22*, 199.
(38) Wagner, P. J.; Giri, B. P.; Scaiano, J. C.; Ward, D. L.; Gabe, E.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 5483–90.
(39) Wagner, P. J.; Giri, B. P.; Pabon, R.; Singh, S. B. *J. Am. Chem. Soc.* **1987**, *109*, 8104.
(40) Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 4484–6.
(41) (a) Wagner, P. J.; Zhou, B. *J. Am. Chem. Soc.* **1988**, *110*, 611–2. (b) Wagner, P. J.; Zhou, B. *Tetrahedron Lett.* **1989**, 5389.
(42) Wagner, P. J.; Meador, M. A.; Giri, B. P.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1087–8.
(43) Wagner, P. J.; Meador, M. A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7988–9.

Table I. Steady-state Photokinetics of Various *o*-Alkoxy Ketones in Benzene:

ketone	Φ_{cyc}[a]	$k_q\tau$,[b] M^{-1}
1m	0.30	2580 ± 230
1e	0.62	560 ± 20
3	0.94 (0.46)[c]	101 ± 2
4	0.46	69 ± 3
5	0.77	266 ± 20
6	1.0	12 ± 1.5
7	0.023 (0.20)[d]	1720 (2200)[d]
8	0.17	73 ± 3
9	0.30[e] (0.53)[d,e]	300 ± 60

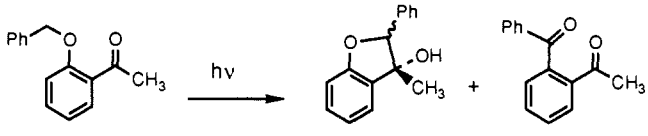
[a] Total benzofuranol. [b] Stern–Volmer slope with 2,5-dimethyl-2,4-hexadiene. [c] In dioxane. [d] With 1 M pyridine. [e] *o*-(Benzoyloxy)acetophenone.

used to calibrate the HPLC for later quantitative measurements. The stereochemistries of the *Z* and *E* isomers were established from the chemical shifts of the 3-methyl or 3-hydroxy groups. There is a good deal of precedent in the literature that the resonances for such groups appear at higher field when they are cis to a phenyl on an adjacent carbon than when they are trans.[15,32,44] Such positioning of course puts the CH_3 or OH partially in the shielding cone of the benzene ring. *o*-Ethoxybenzophenone (**1e**) showed exactly the same diastereoselectivity, giving an 11:1 *Z*/*E* ratio in benzene.



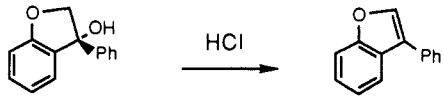
1e (R=CH_3)
3 (R=Ph) **Z** **E**

Irradiation of the *o*-benzyloxybenzophenones in benzene provided quantitative yields of cyclization products. When pyridine was present in solution, a third product that could not be isolated was formed from **3** in a yield comparable to that of each furanol. This product could be detected by HPLC and was not *o*-hydroxybenzophenone. Irradiation of 0.002 M **4** in benzene produced a persistent large increase in near-UV absorption, with a λ_{max} at 360 nm, despite the high yield of cyclization. In the case of *o*-(benzyloxy)acetophenone (**7**), *o*-acetylbenzophenone was obtained as a major photoproduct both with and without added pyridine in the solvent.



7

The mass spectra of the 3-hydroxy-2,3-dihydrobenzofuran products showed prominent M-18 dehydration peaks, as would be expected. Treatment of the products with hydrochloric acid induced dehydration, as previously observed by Pappas,[32] yielding benzofurans whose mass spectra agreed with those of authentic samples. The hydroxy products were stable to HPLC analysis, less so to GC analysis.



The products formed from the diacylphenyl ethers undergo secondary photoreactions. Product structures were not determined, although it was assumed that further cyclization occurs. Special care was taken to keep conversion low during quantitative measurements on these diketones.

Table II. Effect of Added Pyridine on Cyclization Quantum Yields in Benzene

ketone	{pyridine}, M	Φ_Z[a]	Φ_E[b]	Φ_{DK}[c]
1m	0	0.30[d]		
1m	1.2	0.16		
1m	2.5	0.15		
3	0	0.83	0.11	
3	1.2	0.36	0.29	
3	2.5	0.32	0.29	
7	0	0.023	0	0.059
7	0.5	0.060	0.030	0.067
7	1.1	0.087	0.053	0.058
7	1.6	0.10	0.067	0.052
7	2.2	0.12	0.081	0.046

[a] (*Z*)-Furanol. [b] (*E*)-Furanol. [c] 2-Acetylbenzophenone. [d] Only one product.

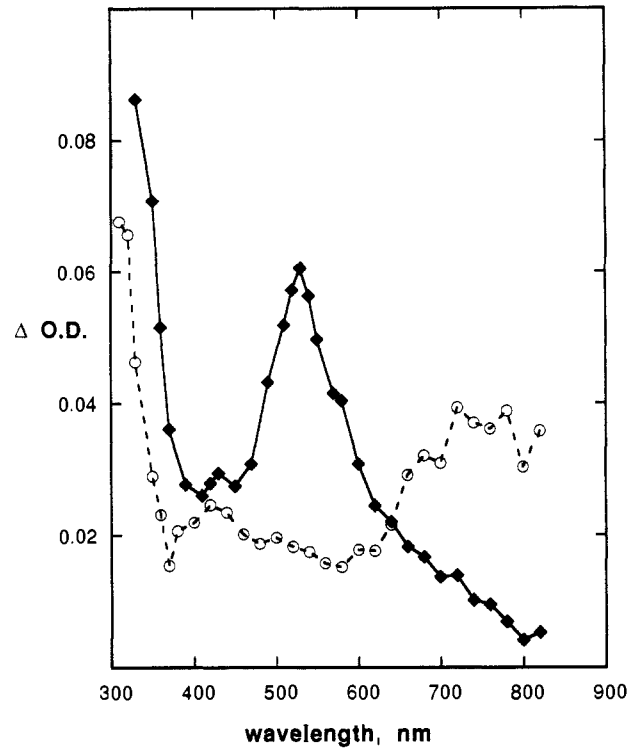


Figure 1. Transient spectra recorded at room temperature following 337-nm laser pulse (8 ns): (◆) *o*-methoxybenzophenone in benzene, monitored 40–90 ns after pulse and (O) 2,6-dimethoxybenzophenone in benzene, monitored 27–42 ns after pulse.

Steady-State Kinetics. Quantum efficiencies for product formation were determined by 313-nm irradiation of degassed solutions 0.02–0.04 M in ketone to low conversion and analysis of product formation by HPLC. Values are listed in Table I. Benzene solutions (0.1 M) in valerophenone were irradiated in parallel as actinometers. The effects of added pyridine on the quantum yields of three of the ketones are listed in Table II. Substitution of dioxane for benzene halves the quantum yield for **3**, an effect very similar to that of added pyridine.

Stern–Volmer quenching studies[45] were conducted as follows: 0.02 M ketone solutions containing various concentrations of 2,5-dimethyl-2,4-hexadiene were irradiated in parallel; yields of product were then measured by GC or HPLC. The $k_q\tau$ values listed in Table I represent the slopes of plots of ϕ^0/ϕ values vs quencher concentrations. Octanethiol was found to quench product formation from **3** with a Stern–Volmer slope of 0.56 M^{-1}.

Flash Kinetics. The ketones in Scheme I also were studied by nanosecond laser spectroscopy. Nitrogen laser excitation (337 nm, 8 ns) of deaerated solutions (~0.003 M) in ketone produced strong transient absorbances above 500 nm (e.g., Figure 1), which

(44) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506–12.

(45) Wagner, P. J. In *Creation and Detection of the Excited State*; Lamola, A. A., Ed.; Marcel Dekker: New York, 1971; pp 174–212.

Table III. Flash Kinetics Data for Various *o*-Alkoxy Ketones

ketone	solvent	τ, ns	k_q, 10^9 M^{-1} s^{-1}	E_a, kcal	log A
1m	benzene[a]	1080	4.8	4.2 ± 0.6	9.2 ± 0.5
1m	methanol	115 ± 5	9.2	3.0 ± 0.1	9.1 ± 0.1
1m	CH_3CN	1500		5.6 ± 0.3	9.9 ± 0.3
1e	benzene	190	3.0[b]		
1e	methanol	180			
2	benzene	1910 ± 8	2.8		
2	methanol	157	5.4	3.1 ± 0.3	9.1 ± 0.2
2	CH_3CN	1450			
3	benzene[a]	53 ± 4	1.9	2.8 ± 0.7	9.2 ± 0.6
3	methanol	50	5.6		
4	benzene[a]	70 ± 3	0.84	3.1 ± 0.5	9.3 ± 0.4
4	methanol	128	5.7		
5	benzene	124	2.1		
5	methanol	115			
7	benzene[a]	455 ± 15	2.9	3.7 ± 0.6	9.0 ± 0.5
7	methanol	590	9.4		
8	benzene	40	1.8		
8	methanol	272			
9	benzene[a]	83	2.9	4.8 ± 0.4	10.4 ± 0.3
9	methanol	246	5.3	4.7 ± 0.1	10.0 ± 0.1

[a] Arrhenius plots in chlorobenzene. [b] Derived from $k_q\tau$ value in Table I.

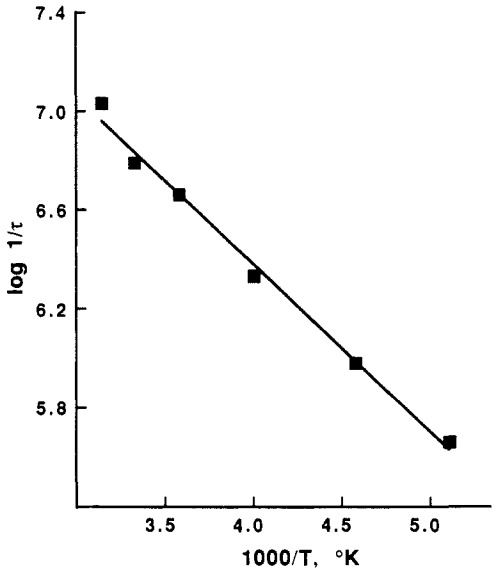


Figure 2. Temperature dependence of decay of triplet 2,6-dimethoxybenzophenone in methanol, monitored at 700 nm.

absorbances showed cleanly exponential decays at various monitoring wavelengths > 400 nm. The lifetimes of these transients were shortened by typical triplet quenchers. When 1-methylnaphthalene was used, the characteristic strong T–T absorption of naphthalene at 425 nm[46] was observed. Plots of reciprocal lifetimes as a function of 2,5-dimethyl-2,4-hexadiene concentration provided direct measures of k_q values ($1/\tau = 1/\tau_0 + k_q[Q]$). The lifetimes and k_q values are listed in Table III. Diketone **6** gave a transient with a lifetime too short to be measured accurately (<20 ns).

Triplet lifetimes of some of the ketones were measured as a function of temperature in methanol and chlorobenzene. For each ketone, at least six temperatures covering a 90° range between 195 and 350 K were studied. Figure 2 shows a representative Arrhenius plot. The resulting activation parameters are listed in Table III.

In some cases, notably **3** and **4**, strong new absorption grew in below 400 nm, as illustrated in Figure 3. Careful analysis of **3** revealed a long-lived byproduct with an absorption profile in the near-UV very similar to those of the LATs formed by ortho and para coupling of benzyl radicals during the photoreduction of ketones.[47]

In an attempt to detect triplet biradical intermediates, solutions of **3** containing enough quencher to shorten triplet lifetimes to <5 ns were flashed. No transients could be detected from simple

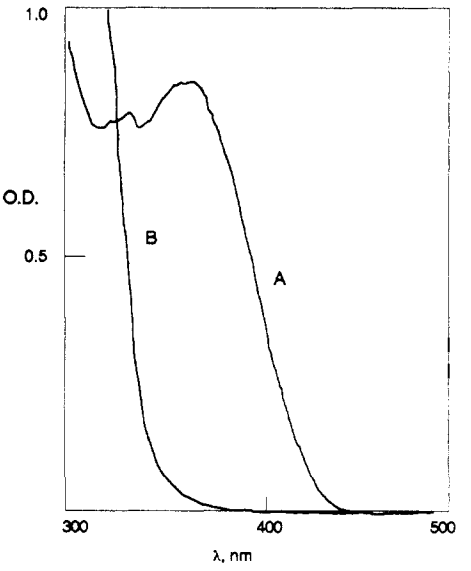


Figure 3. UV spectra of 0.0047 M 2,2′-bis(benzyloxy)benzophenone in benzene before (B) and after (A) irradiation.

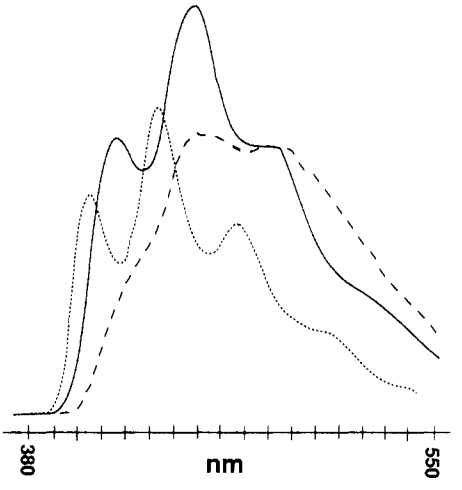


Figure 4. Phosphorescence spectra for several *o*-alkoxyphenyl ketones: (—), **7**; (···), **3**; (– –), **2**.

Table IV. Absorption and Emission Energies of *o*-Alkoxy Ketones

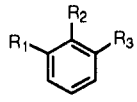
ketone	λ_{La}^{max},[a] nm	λ_{n,π^*}^{max},[a] nm	0.0,[b] nm	E_T, kal
Ph_2CO			417	68.6
1m	239 (12700)	344	416	68.8
2	241 (15600)		420	68.1
3	234 (9440)	343	414	69.1
4	253 (7020)		418	68.4
5	247 (15000)		415	68.9
6	248 (15900)	340	417	68.6
7	230 (5200)	~325[c]	403	71.0
8	218 (2800)	~325[c]	404	70.8
9	240 (11800)		403	71.0
PhCOMe (AP)	238[d]		388	73.7
o-MeO-AP	243[d]		393	72.6[d]

[a] In heptane; extinction coefficient in parentheses. [b] Phosphorescence in 2-methyl-THF. [c] Obscured by strong L_b band. [d] Reference 9.

(46) Bays, J. P.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 727–34.

(47) (a) Schenck, G. O.; Cziesla, M.; Eppinger, K.; Matthias, G.; Pae, M. *Tetrahedron Lett.* **1967**, 193. (b) Chilton, J.; Giering, L.; Steel, C. *J. Am. Chem. Soc.* **1976**, *98*, 1865. (c) Scaiano, J. C.; Abuin, E. B.; Stewart, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.

Table V. ^{13}C NMR Chemical Shifts for *o*-Alkoxy Ketones and *o*-Alkyl Anisoles[a]



R_1	R_2	R_3	ketone	δ_{OCH_2R}	$\delta_{C=O}$
H	OCH_3	H		54.0[b]	
CH_3	OCH_3	CH_3		57.9[b]	
i-Pr	OCH_3	*i*-Pr		61.2[b]	
t-Bu	OCH_3	*t*-Bu		63.7[b]	
OCH_3	PhCO	H	1m	55.3	196.2
OCH_2CH_3	PhCO	H	1e	63.9	197.2
OCH_3	PhCO	OCH_3	2	55.7	195.2
PhCO	OCH_3	PhCO	5	61.6	195.5
PhCO	H	H			196.3
PhCO	*t*-Bu	H			200.2
pMeOPhCo	H	H			195.3
PhCO	$PhCH_2O$	H	3	68.6	196.6
o-($PhCH_2O$)-PhCO	$PhCH_2O$	H	4	70.0	195.5
PhCO	OCH_2Ph	PhCO	6	77.1	195.5
CH_3CO	OCH_2Ph	H	7	70.6	199.8
CH_3CO	OCH_2Ph	CH_3CO	8	79.4	200.0
CH_3CO	H	H			197.0
CH_3CO	*t*-Bu	H			208.6[c]

[a] In $CDCl_3$. [b] Reference 49. [c] Reference 50.

Table VI. Rate Constants for δ-Hydrogen Abstraction in Benzene

ketone	k_H, 10^6 s^{-1}	$1/\tau$,[a] 10^6 s^{-1}	$1/\tau$,[b] 10^6 s^{-1}
1m	0.6	1.8	0.9
1e	5.3		5.3
2	0.2		0.5
3	19.0	19.0	19.0
4	14.0	12.0	14.0
5	8.0	~8.0[c]	8.0
6	150.0	150.0[d]	
7	2.0	1.7	2.2
8	25.0	~25.0[c]	25.0
9		10.0	12.0

[a] From $k_q\tau$ values in Table I. [b] Direct flash measurement. [c] k_q not measured directly. [d] k_q assumed to equal 1.8×10^9 M^{-1} s^{-1}.

benzene solutions. However, when 0.5 M pyridine was present, a weak absorbance with λ_{max} at 550 nm (characteristic of diphenylhydroxymethyl radical centers[48]) and a decay time of 13 ns was observed.

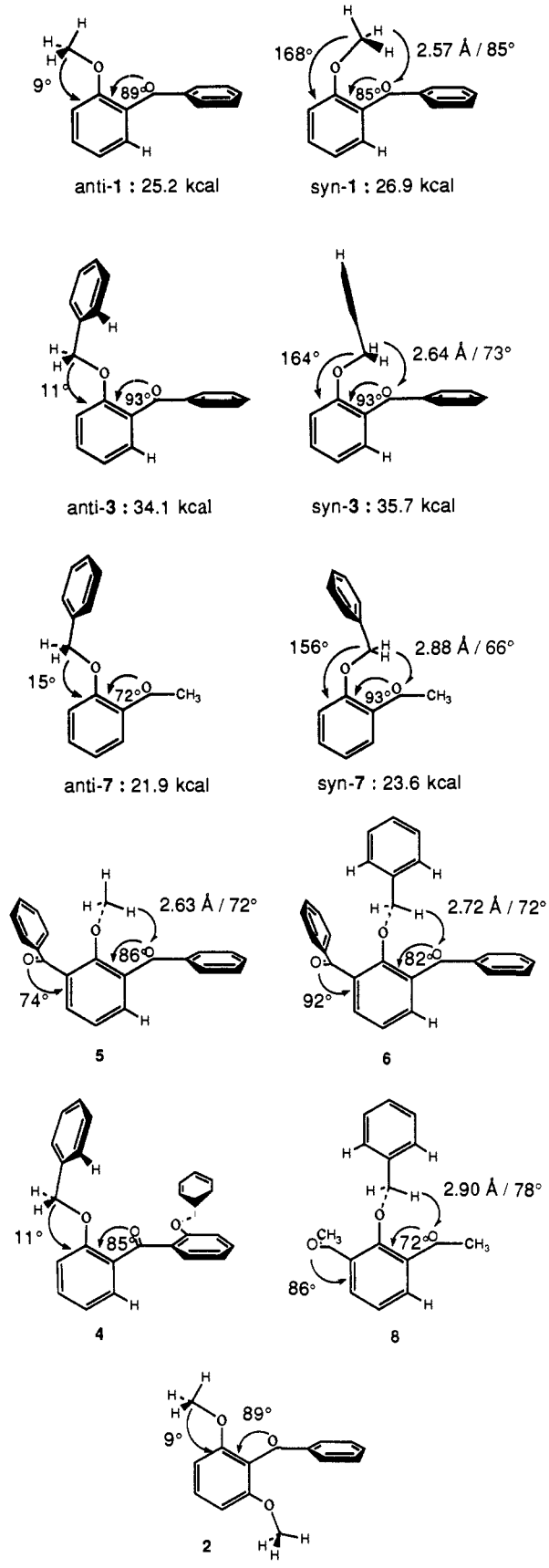
Spectroscopy. Phosphorescence spectra of the ketones in 2-methyltetrahydrofuran glasses were recorded at 77 K; 0,0 band energies are listed in Table IV, which also contains UV λ_{max} values. Some representative emission spectra are shown in Figure 4.

It has been known for some time that ^{13}C chemical shifts of carbonyl groups in phenyl ketones are strongly sensitive to the degree of coplanarity of the benzoyl group[49] and that the ^{13}C chemical shift of the methyl carbon in anisoles is sensitive to the geometry of the ring-methoxy bonding.[50] In both cases, twisting of the carbonyl or alkoxy group out of planarity with the benzene ring increases δ. Table V lists some NMR chemical shifts of the CO and OCH_2R carbons in some of these ketones and in model compounds.

2,6-Disubstitution, both alkyl and acyl, that prevents the alkyl group of anisole from lying in the plane of the benzene ring increases the chemical shift of the methyl carbon. We see that the δ values of **1m** and **2** are not much larger than that for anisole, whereas the value for **5** indicates a large degree of twisting out of plane. The same is true for the benzyl ether; both **6** and **8** show δ values for the CH_2Ph carbon almost 9 ppm larger than the respective monoketones **3** and **7**.

(48) (a) Beckett, A.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2038. (b) Topp, M. R. *Chem. Phys. Lett.* **1975**, *32*, 144.
(49) Liebfritz, D. *Chem. Ber.* **1975**, *108*, 3014.
(50) Strothers, J. B.; Dahmi, K. S. *Can. J. Chem.* **1966**, *44*, 2855.
(51) Serena Software, Bloomington, IN.

Scheme II

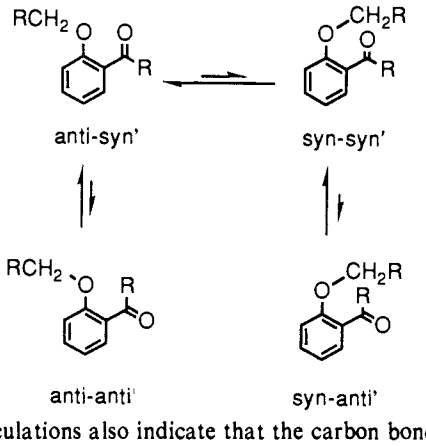


The CO chemical shifts of the benzophenones do not vary much. Twisting of the *o*-alkoxyphenyl ring is offset by increased conjugation of the unsubstituted benzene ring with the carbonyl. Ketones **7–9** do show higher δ values than acetophenone but not nearly as high as 2,4-*tert*-butylacetophenone. We therefore conclude that the benzoyl groups in these compounds are twisted but not nearly perpendicular.

Molecular Mechanics Calculations. Scheme II depicts the lowest energy geometries of the various ketones, as calculated with the MMX treatment resident in PC Model.[51] Energies were minimized with respect to rotations around the benzene–acyl bonds and around the benzene–ether oxygen bonds. For the monoketones, rotation around the ether function provides distinct syn and anti local minima with energy differences between 1.5–2.0 kcal/mol. (The terms "syn" and "anti" here do not imply 0 or 180° dihedral angles but rather 0 < syn < 90 and 90 < anti < 180.) Scheme II notes the distance between the closest reactive hydrogen atom and the carbonyl oxygen as well as the angle θ which the line connecting that hydrogen and oxygen makes with respect to the nodal plane of the carbonyl π-orbital.

One important facet of the calculations involves the degree of coplanarity of the various benzoyl groups in these ketones. (Scheme II indicates twist angles for rotations around the various acyl–benzene and alkoxy benzene bonds.) For example, in **1m** and **3** a nearly perfectly coplanar benzoyl group is predicted to be twisted 90° with respect to the *o*-(benzyloxy)phenyl group. That this geometric estimate is reliable for the benzophenones is borne out by the NMR spectra, in particular the chemical shift of the proton ortho to the benzoyl group and meta to the alkoxy group: 7.35 ppm in **1m** and 7.19 ppm in **3** as opposed to 7.71 ppm in **7**. Obviously, that proton is shielded by the benzene ring of a twisted benzoyl group in **1m** and **3**. Likewise, the ortho protons of the benzyloxy group(s) in **3** and **4** are shielded by the twisted benzoyl group, appearing near 7.0 ppm, in contrast to 7.3 ppm in **7** and **8**. The 70–90° twists calculated for **7** and **8** probably are exaggerated, given the small variations in carbonyl ^{13}C chemical shifts.

Figure 5 plots the calculated energy of the syn and anti rotamers of **7** as a function of the dihedral angles θ for twisting around the acetyl–benzene bond. These are rough fixed rotor calculations, but both rotamers behave like *o*-alkyl phenyl ketones, which exist in equilibrium mixtures of syn′ and anti′ rotamers favoring the former.[22] (We henceforth use primes to distinguish rotamers around the acyl–benzene bonds from rotamers around the alkoxy–benzene bond.) Each rotamer has two minima 160–170° apart, one favored by only 0.2–0.8 kcal/mol over the other. Each syn and anti rotamer has maxima at 0° and 180°, where the carbonyl is coplanar with the benzene ring. Thus **7** has four major conformers with respect to rotations around the alkoxy and acetyl bonds: anti–anti′, anti–syn′, syn′–anti′, and syn–syn′. The predicted energy of the anti rotamer varies by less than 1 kcal/mol for 35° on either side of its minimum at $\theta' = 72°$; the syn rotamer has a much narrower valley around its minimum at $\theta' = 93°$. A slight increase in π-conjugation energy, as must obtain in the triplet state, would produce much more coplanar benzoyl moieties, especially in the anti rotamer.



The calculations also indicate that the carbon bonded to the alkoxy oxygen lies nearly in the plane of the benzene ring in the anti geometry of the 2-alkoxyacylbenzenes. In the 2,6-diacyl compounds, however, the O–CH_3 or O–Bzyl bond is nearly perpendicular to the plane of the center benzene ring. The ^{13}C NMR spectra verify this conclusion, since 2,6-diacyl substitution moves the resonance of the ether carbon to lower field, consistent with more electron density on the oxygen because of decreased conjugation with the benzene ring.[50] Another manifestation of the twisting in **6** is the chemical shift of the ortho protons on the benzyl group: only 6.6 ppm. These protons are held in the shielding cone of the 90° twisted benzoyl groups on each side of the benzyloxy group.

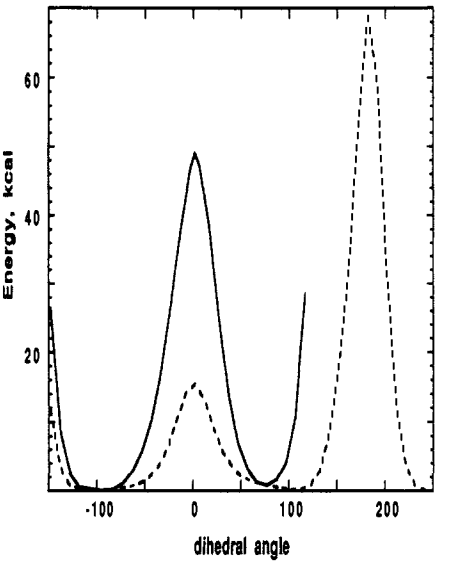
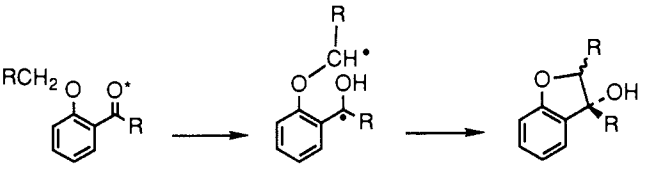


Figure 5. MMX energies for twisting about the acetyl–alkoxyphenyl bond: (···), *anti*-**7**; (—), *syn*-**7**.

Scheme III



Discussion

Mechanism of Photocyclization. The triplet nature of the reaction is indicated by the facile quenching of product formation by typical triplet quenchers such as conjugated dienes and naphthalene. Moreover, we could detect by flash spectroscopy triplet transients with lifetimes comparable to those gleaned from our steady-state product quenching (see below). Sensitization experiments indicated intersystem crossing yields of unity for **3** and **7**.

The attempt to trap a biradical from **3** with added thiol failed. Thiols are known to quench triplet ketones with rate constants $\sim 1 \times 10^7$ M^{-1} s^{-1},[52] so the measured $k_q\tau$ value corresponds to quenching the 50 ns triplet of **3**. Although we could detect a likely biradical intermediate in only one flash spectroscopic experiment, we presume that all of the photoreactions of these *o*-alkoxy ketones involve triplet state δ-hydrogen abstraction followed by cyclization and/or disproportionation of the resulting very short-lived 1,5-biradical, as depicted in Scheme III.

Nature of Ketone Triplets. *o*-Alkoxyphenyl alkyl ketones such as *o*-methoxyacetophenone **13** are known to have π,π^* lowest triplets.[9] Compounds **7** and **8** have L_a absorption bands at considerably higher energy than does **13** (243 nm[9]). These shifts presumably indicate the large twist of the acetyl groups out of coplanarity with the benzene ring. Since the relative energies of aryl ketone π,π^* triplets generally correlate with their L_a band energies,[9] but **7** and **8** have triplet energies even lower than that of **13**, it is likely that the benzoyl chromophore is more nearly coplanar in their excited states than in their ground states. Figure 5 supports this view. In its preferred anti conformation, **7** can twist 40° around the acetyl–benzene bond without undergoing

(52) Zepp, R. G.; Wagner, P. J. *J. Chem. Soc., Chem. Commun.* **1972**, 167–8.

much destabilization. *syn*-**7** can also twist but only by 20°. Therefore *anti*-**7** can achieve near coplanarity of its benzoyl group in both its n,π^* and π,π^* triplets much more readily than can *syn*-**7**.

The phosphorescence and UV spectra of the *o*-alkoxybenzophenones, like those of *p*-methoxybenzophenone,[53] indicate n,π^* lowest triplets. For example, the L_a absorption band of **3** occurs at the same energy as that of **13**, while the n,π^* absorption and the phosphorescence occur at lower energies.

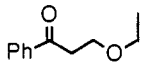
Triplet Reactivity: Determination of Rate Constants for Hydrogen Abstraction. Equation I describes how k_H is determined from experimentally measured factors. ϕ_{isc} equals 1. P_{BR} represents the fraction of 1,5-biradicals that produce product rather than disproportionate to ground-state ketone.[45] Unfortunately,

$$k_H = \phi/\phi_{isc}\tau P_{BR} \quad (1)$$

these biradicals have not been trapped, so P_{BR} values cannot be measured. In the case of **3** and **6**, P_{BR} must be almost 1 since ϕ is almost 1. Since there are no known physical decay reactions of triplet phenyl ketones with rate constants $>10^6$ s^{-1} and no indications of competing chemical reactions of the triplets, we have assumed that $k_H = 1/\tau$ whenever $1/\tau > 10^7$ s^{-1} (i.e., $P_{BR} = \phi$). In the case of **7**, added pyridine increases the cyclization quantum yields significantly, and P_{BR} can be assigned the value of 1 under such conditions.

The long-lived transients detected from the *o*-alkoxy ketones clearly are triplets since they are quenched by triplet quenchers with near diffusion-controlled rate constants producing, in the case of naphthalene, the characteristic absorption of triplet naphthalene. The $k_q\tau$ values obtained by multiplying the separately measured k_q and τ values agree well with those obtained by our steady-state Stern–Volmer quenching of product formation. Table VI lists k_H values and two sets of lifetime values: those measured directly by flash kinetics and those derived from the $k_q\tau$ values in Table I and the directly measured values of k_q, which are lower than the usual "diffusion-controlled" values. In most cases, the two measurements agree well. In cases of significant difference, the k_H values were derived from the flash measurements. The lifetime of **6** was too short for reliable flash measurement; its value was determined from the Stern–Volmer slope and by assuming that $k_q = 1.8 \times 10^9$, the same as for **8**, which was calculated from the $k_q\tau$ value in Table I and the flash measurement of τ. Only **1m**, **2**, and **7** have long enough triplet lifetimes that direct decay could compete with δ-hydrogen abstraction.

Triplet Reactivity: Comparison to Acyclic Ketones. The acyclic ketones β-ethoxypropiophenone (**10**)[54] and γ,γ-dimethylvalerophenone[29] (**11**) undergo triplet state δ-hydrogen abstraction with rate constants of 2×10^7 and 5×10^5 s^{-1}, respectively. The factor of 40/1 by which attack at a secondary ether C–H bond is faster than attack at an unactivated methyl is in accord with known alkoxy radical[55] and triplet ketone[8,56] reactivities. The conformational flexibility of the acyclic ketones permits the intrinsic reactivity of C–H bonds to determine relative reactivities.



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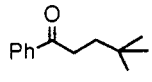

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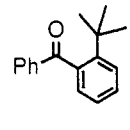
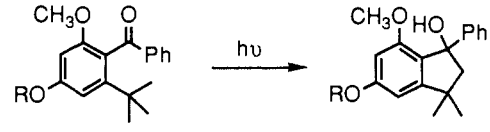


12

In contrast to the just cited "normal" relative reactivities, we see the triplet **1e** abstracts δ-hydrogens only 1/200 as rapidly as does triplet *o*-*tert*-butylbenzophenone (**12**), which displays a rate constant $\geq 1 \times 10^9$ s^{-1}.[38] The ensuing discussion concludes that the factors responsible for this four order of magnitude (200×40) inversion of relative reactivity are primarily conformational rather than electronic.

The k_H value for **3** is comparable to that reported for the corresponding *o*-(benzyloxy)phenyl glyoxalate ester, which gave a $k_q\tau$ value of 116 M^{-1} in benzene.[36] Both types of carbonyl have n,π^* lowest triplets; the ester group apparently is comparable to the phenyl in its effect on triplet reactivity. Interestingly, Pappas recognized the low reactivity of the glyoxalates, but, not suspecting the low reactivity of **3**, he concluded that triplet glyoxalates are intrinsically less reactive than are triplet benzophenones.

There are other consequences of the slow δ-hydrogen abstraction from *o*-alkoxy groups. One is the selective photocyclization of 2,4-dialkoxy-6-*tert*-butylbenzophenones.[35] Another is our finding that *o*-(benzyloxy)valerophenone (**9**) undergoes only Norrish type II reaction. Triplet **9** is six times more reactive than triplet **7**, reacting at the same rate as *o*-methoxyvalerophenone.[9] Likewise, **1m** undergoes primarily photoreduction in alkane solvents, where rates of hydrogen abstraction are $\sim 5 \times 10^6$ s^{-1}.[57] It has been reported that **1m** and other *o*-methoxybenzophenones undergo radical cleavage of the benzyloxy C–O bond in CCl_4 to yield phenols.[58] This could be considered another competing reaction, but it is not clear whether the competition occurs at the triplet level or later.



Triplet Reactivity: Electronic Factors. We must examine how the acylphenyl group affects the intrinsic reactivity of an ether C–H bond and how the *o*-alkoxy group affects the intrinsic reactivity of a n,π^* triplet ketone. The latter effect is relatively easy; the electron-donating inductive effect of an ortho alkoxy group, like one para,[57] should reduce the reactivity of triplet benzophenone but only by a factor of 2–3. Thus 4-(dodecyloxy)-2-(benzyloxy)benzophenone is quenched with a $k_q\tau$ value of 400 M^{-1} in benzene;[33] its triplet apparently is only 1/4 as reactive as triplet **3**.

The first effect is more complicated. It is well-known that phenoxy groups do not provide as much kinetic stabilization of α-radical sites as do alkoxy groups. For example, triplet γ-hydrogen abstraction in γ-methoxybutyrophenone is 2.5 times faster than in γ-phenoxybutyrophenone, which is only twice as fast as in valerophenone itself.[56] Moreover, the triplet reactivity of γ-(*p*-cyanophenoxy)butyrophenone is only half that of valerophenone.[59] *p*-Cyanophenyl presumably has an inductive effect comparable to that of *o*-acylphenyl. However, in choosing such a model, we are in fact asking how much of an inductive effect a functional group can have on its own reactivity. Since the carbonyl function in these *o*-alkoxy ketones presumably is not as strong an electron-withdrawing group in its ^{3}n,π^* state as in its ground state, we feel that we can ignore the effect of the acyl group on the reactivity of the C–H bond.

In summary, the overall depression of reactivity that can be ascribed to inductive effects amounts to no more than one order of magnitude. That leaves a factor of 1000 yet to be explained.

The low triplet reactivity of the *o*-alkoxyacetophenones reflects their π,π^* lowest triplets, *o*-methoxyvalerophenone being only 1/8 as reactive as valerophenone itself in γ-hydrogen abstraction.[9] Thus the 10-fold lower reactivity of the *o*-alkoxyacetophenones **7** and **8** relative to the corresponding *o*-alkoxybenzophenones **3** and **6** is separate from, and in addition to, the three order of magnitude gap noted above.

The three 2,6-diacylphenyl ethers undergo triplet reaction ten times faster than do the corresponding monoacyl compounds. Very little of this rate enhancement is electronic in origin, since *m*CF_3, -CN, -CO_2R and acyl substituents enhance rate constants for triplet hydrogen abstraction by factors of only 1.4–2.4.[57,60]

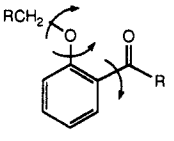
(53) Kearns, D. R.; Case, W. A. *J. Am. Chem. Soc.* **1966**, *88*, 5087.
(54) Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134–5.
(55) Walling, C.; Mintz, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 1515.
(56) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495–9.
(57) Wagner, P. J.; Truman, R. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 7093–7.
(58) Leary, G.; Oliver, J. A. *Tetrahedron Lett.* **1968**, 299.
(59) Frerking, H. W. Ph.D. Thesis, Michigan State University, 1978.
(60) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329–35.

Triplet Reactivity: Conformational Factors. Lewis demonstrated an important conformational principle when he showed that rate constants for triplet γ-hydrogen abstraction can be significantly larger for cyclic ketones than for straight chain ketones because of the less negative entropy of activation associated with the smaller number of degrees of rotational freedom in the cyclic ketones.[61] The large triplet reactivity of **12** is a good example. These *o*-alkoxy ketones also have decreased conformational freedom relative to that enjoyed by acyclic ketones such as **10**, but triplet **1m** is only 1/30, and **1e** only 1/4, as reactive as **10**. Unlike **12**, which exists in a conformation ideal for reaction,[38] the *o*-alkoxy ketones must exist primarily in conformations unsuitable for δ-hydrogen abstraction.

We have always analyzed rate constants for intramolecular hydrogen abstraction as reflecting the relative population(s) of conformations that require little or no bond rotation in order to reach the transition state,[1,2] in accord with the Winstein–Holness principle.[62] In other words, normal conformational interconversions precede reaction, such that the reaction coordinate can be considered to include only bond stretches and distortions of the conformer(s) that has a geometry closest to that required for reaction. Scheffer has recently provided support for this view.[63] Since the triplet is the reactant, it is important to consider how closely excited-state geometries match ground-state geometries. The lengthening of the carbonyl C–O bond in the triplet certainly must change some key interatomic distances and angles from their ground-state values. Fortunately, n,π* excitation is strongly localized on the carbonyl group, such that significant changes in rotational barriers elsewhere in the molecule are unlikely. Therefore we feel secure in using various ground-state measurements and calculations in order to estimate conformational preferences in the excited triplet, especially since we are comparing relative reactivities.

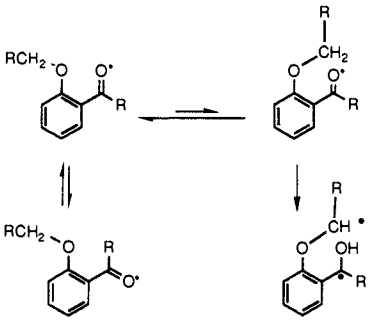
There are two basic conformational requirements for reaction: that the H and O be within bonding distance and that the orientation of bonds and orbitals be proper. Scheffer has found that ~2.9 Å is the maximum ground-state distance that allows bonding, at least for hydrogen abstraction in crystalline ketones.[4] The various orientational requirements are not as clear experimentally,[4,41] although they are the subject of active theoretical interest.[30,64]

In terms of getting an H atom within bonding distance of the carbonyl oxygen, there are three significant rotations in these *o*-alkoxy ketones: about the benzene–carbonyl bond, the benzene–ether oxygen bond, and the ether oxygen–α-carbon bond. The third cannot be involved in the low reactivity of these *o*-alkoxy ketones, since it does not really affect the symmetric methoxy group. In order to determine which of the first two rotations affects reactivity, we studied the three 2,6-diacylphenyl ethers as well as **2** and **4**.



Since **4** is less reactive than **3**, and **2** is less reactive than **1m**, simple anti′ → syn′ rotations around the benzene–acyl bond cannot determine k_H values as they do in *o*-alkyl ketones.[22] In fact, the anti′ → syn′ rotation in triplet *o*-methylacetophenone is much faster than the decay of triplet **7**. Therefore we can assume equilibration of the syn′ ↔ anti′ rotation in the *o*-alkoxy ketones. As noted above, NMR spectra confirm that the benzoyl groups are highly twisted in the ground state.[65] It is very likely that the triplet benzophenones have the same rotational preference, since n,π* excitation should be centered on the benzoyl rather than the more electron-rich alkoxybenzoyl group.[66] Hoffman has calculated that triplet benzophenone has (only) one coplanar benzoyl group,[67] unlike the 30° propeller twist of the ground state.[68] The *o*-alkoxyacetophenones, however, probably are less twisted in their triplet states, as noted below.

Scheme IV



Each of the three 2,6-diacyl ether triplets **5**, **6**, and **8** is about ten times more reactive than its monoacyl counterpart **1m**, **3**, or **7**, respectively. We conclude that anti conformers (rotation around the alkoxy–benzene bond) are favored for **1m**, **3**, and **7** (as well as **2** and **4**), such that the observed rate constants for hydrogen abstraction incorporate an unfavorable anti → syn equilibrium constant.[1,2,43]

The molecular mechanics calculations support this picture. For all of the monoketones, the anti rotatamer is predicted to be of lowest energy and to have a dihedral angle near 0°. NMR data show that ortho-substituted anisoles exist primarily in such an anti conformation.[50] The benzyloxy group would be expected to show an even larger steric preference for the anti geometry. Interestingly, the calculations predict syn conformers only 1.6 kcal/mol above the anti conformers for the monoketones.

There is no doubt that the measured reactivities of **3** and **7** are governed by excited-state rotational equilibria. If anti → syn rotations were rate-determining, there could not be a 35-fold rate difference between *o*-methoxy and *o*-benzyloxy ketones, which reflects the intrinsically more reactive benzylic C–H bonds.[69] Likewise, reactivity cannot be controlled by ground-state equilibria, otherwise **3** in its favored anti conformation could not react with a quantum efficiency of nearly 100%. Scheme IV depicts the conformational equilibria that are concluded to influence reactivity in the *triplet* states of the monoketones. As explained above, however, these equilibria are based on those for the ground state.

If the calculations are correct, the ground-state equilibria produce about 6% of the syn conformer for both **1m** and **3**, in which the methyl or benzyl group is twisted only 12–15° out of the plane of the benzene ring, but the benzoyl group is perpendicular to the *o*-alkoxyphenyl group. Some further factor is required to explain the very low *o*-alkoxy/*o*-*tert*-butyl rate ratios. There do appear to be two unfavorable stereoelectronic features of the syn conformers. The presumably reactive hydrogen is 2.6 Å from the carbonyl oxygen in both cases; the line connecting it to the oxygen makes an angle of 72° with the long axis of the oxygen's n-orbital. Such an orbital orientation should provide an order of magnitude decrease in reactivity.[41] Moreover, in the transition state for hydrogen transfer, the breaking C–H bond is almost perpendicular to the lone pair on the ether oxygen, which

(61) Lewis, F. D.; Johnson, R. W.; Kory, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 6100–6.
(62) Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 5562.
(63) Ariel, S.; Evan, S.; Omkaram, N.; Scheffer, J. R.; Trotter, J. *J. Chem. Soc., Chem. Commun.* **1986**, 375.
(64) (a) Severance, D.; Pandey, B.; Morrison, H. *J. Am. Chem. Soc.* **1987**, *109*, 3231. (b) Sauers, R. R.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1989**, *30*, 527.
(65) Montaudo, G. A.; Finnocchio, P.; Maravigna, P. *J. Am. Chem. Soc.* **1971**, *93*, 4214.
(66) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301.
(67) Hofmann, R.; Swenson, J. R. *J. Phys. Chem.* **1970**, *64*, 415.
(68) (a) Bradley, R.; LeFevre, R. J. W. *J. Chem. Soc.* **1962**, 56. (b) Gore, P. H.; et al. *J. Chem. Soc. B* **1967**, 741. (c) Jones, R. N. *J. Am. Chem. Soc.* **1965**, *67*, 2127. (d) Rekker, R. E.; Nauta, W. Th. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 764. (e) Rekker, R. E.; Nauta, W. Th. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 969.
(69) Encina, M. V.; Lissi, E. A.; Lemp, E.; Zanocco, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1856–60.

is conjugated with the benzene ring. Therefore the developing radical site is not strongly conjugated to the oxygen. However, we pointed out above that a phenoxy group does not activate a C–H bond that much anyway.

We believe that the remaining factor of 10–100 depression of reactivity reflects a much lower equilibrium population of the syn conformer *in the triplet state* than exists in the ground state. As discussed above, the carbonyl in the syn conformer cannot achieve as much conjugation with the benzene ring as in the anti conformer. Such π-conjugation is known to be more important in the excited state than in the ground state.[67,70]

Arrhenius Parameters. The ketones studied undergo three different triplet reactions, which are reflected in the Arrhenius parameters. **9** reacts primarily by γ-hydrogen abstraction and has a relatively high A factor similar to those for valerophenone and *p*-methoxyvalerophenone ($10^{11.2}$).[71] Its activation energy is intermediate between those for valerophenone (4.0 kcal) and *p*-methoxyvalerophenone (6.9 kcal), reflecting reaction from a n,π^* triplet about 0.8 kcal above the lowest π,π^* state. It has been known for two decades now that alkoxy-substituted phenyl alkyl ketones have reduced radical-like reactivity because of their π,π^* lowest triplets.[9,72]

There is a large solvent effect on **1m**; the lower Arrhenius parameters in methanol reflect the large amount of bimolecular hydrogen abstraction from solvent that competes with δ-hydrogen abstraction. It is not clear why the E_a value is higher in acetonitrile than in benzene. CT quenching by solvent benzene probably contributes to overall decay. Dipolar stabilization of an unreactive conformation with a high dipole moment also may occur in acetonitrile.

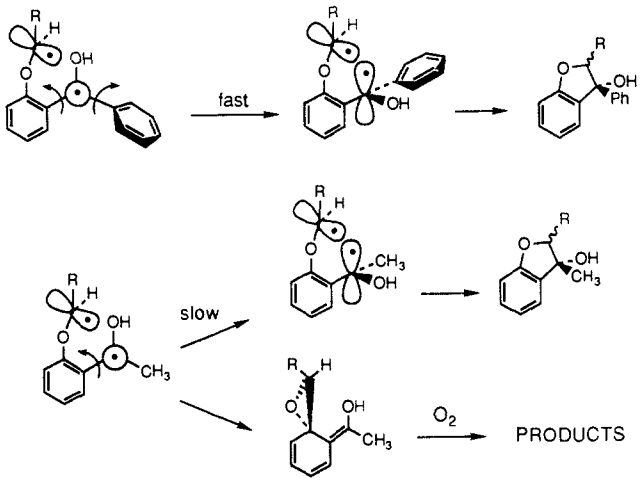
Ketones **3–8** undergo only δ-hydrogen abstraction; all investigated have A values of 10^9 s^{-1}. The benzophenones **3** and **4** have activation energies near 3.0 kcal/mol. The higher value for **1m** reflects the less reactive methoxy C–H bond. The higher value for **7** reflects the π,π^* lowest triplet, as already noted.

What is most interesting is a comparison between **1m** and *o-tert*-butylbenzophenone **12** (E_a = 2.5 kcal; log A = 10.5).[38] The three order of magnitude difference in reactivity appears in a 30-fold lower A factor and a 1.7 kcal higher E_a value for **1m**. Even **3**, with its intrinsically more reactive benzylic C–H bonds, has a slightly higher E_a value than **12**. Since the C–H bond energies of both methoxy and benzyloxy are lower than that for *tert*-butyl,[73] the transition state for δ-hydrogen abstraction in these *o*-alkoxy ketones must be subject to strain not present in **12**. In short, the Arrhenius parameters support our conclusions regarding the higher energy and lower probability of the reactive syn conformations in **1m**, **3**, and **7** realtive to the anti conformations.

Triplet Reactivity: 2,6-Diacylphenyl Ethers. The sterically congested 2,6-diacyl compounds have geometries significantly different from those of the monoketones. The two acyl groups show twist angles near 90 and −90° with respect to the center benzene ring. The alkoxy group is also twisted such that the *O*-methyl or *O*-benzyl bond is nearly perpendicular to the central benzene ring. This places a δ-hydrogen within 2.7–2.9 Å of one carbonyl oxygen. As in the syn conformers of the monoketones, the O–H orientation makes a large angle with respect to the carbonyl n-orbital. Although the order of magnitude increase in reactivity nicely matches the calculated energy difference between syn and anti conformers of the monoketones, we cannot conclude that the diketones coincidentally have "reaction" geometries similar to that of the *syn*-monoketones. One large difference is a C–H–O angle of only 120° in **5**, **6**, and **8**, as opposed to a value of ~150° in the *syn*-monoketones.

The n,π^* triplets of **5** and **6** again would not be expected to differ much from the ground states in geometry except for a longer carbonyl C–O bond. The low triplet energy of **8** suggests that the alkoxy and at least one acyl function are twisted back into partial conjugation with the center benzene ring for stabilization of the π,π^* triplet. Highly twisted aryl ketones are now known to show very low reactivity.[74] Whatever the exact conformation and electronic configuration of **8**, a "reactive" geometry is maintained.

Scheme V



Biradical Behavior. There are four aspects of these 1,5-biradicals' behavior that require discussion: (1) the generally high efficiency of cyclization of the *o*-alkoxybenzophenones; (2) the low efficiency of cyclization for *o*-alkoxyacetophenones; (3) the large solvent effects on quantum efficiencies and on cyclization diastereoselectivity; and (4) the short lifetimes of the biradicals.

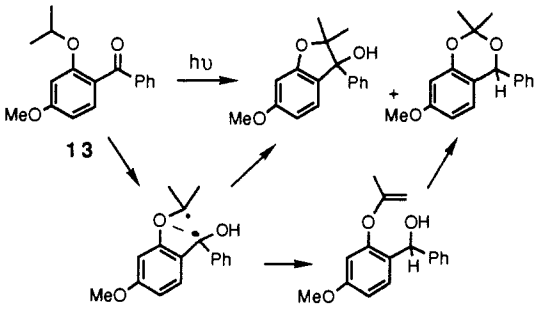
The high cyclization quantum yields for **3** and **6** indicate that the 1,5-biradical intermediates undergo no competing reactions. The same fact was noted for the early examples of this photocyclization.[33,36] Disproportionation back to ground-state ketone is the only simple reaction that can compete with cyclization. However, a 1,6-hydrogen shift might not be expected to compete well with five-membered ring formation. Even in the acyclic 1,5-biradical formed from **10**, disproportionation directly to ketone is a minor reaction.[54] The large disproportionation/cyclization ratio common for most type II 1,4-biradicals[44] does not appear to be the norm for larger biradicals.[40,75]

Lewis base additives or solvents such as pyridine or alcohols produce large changes in both cyclization efficiency and diastereoselectivity. The latter effect is well-known for both 1,4-biradicals[15b,17,44] and for 1,5-biradicals.[36,54] Product quantum yields from 1,4-biradicals generally are maximized by such solvents, since hydrogen bonding suppresses disproportionation back to ketone.[76] However, the large cyclization quantum yields of the *o*-alkoxybenzophenones, like those of *o*-benzyloxyphenyl glyoxalates,[36] are reduced by such solvents, as originally noted.[33] Disproportionation presumably is still suppressed, so some other reaction must begin to compete with five-membered ring formation. The benzophenones are known to produce phenols.[34] We could not observe them as primary products and suspect that they result from oxidative degradation during workup and analysis as well as from secondary photochemistry.[33]

Ketone **7** is unique in cyclizing in very low quantum efficiency and in producing a diketone as the major product in benzene. Formation of the diketone obviously requires an oxidation process. Interestingly, the presence of pyridine increases the cyclization efficiency by a factor of 10 but also destroys the diastereoselectivity. For some reason, diastereoselective cyclization of the unsolvated 1,5-biradical formed from **7** competes very poorly with disproportionation as well as with whatever process forms the

(70) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820–5.
(71) Encina, M. V.; Lissi, E. A.; Lemp, E.; Zanocco, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1856–60.
(72) Yang, N. C.; Dusenbery, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 5899.
(73) Griller, D.; Kanabus-Kaminska, J. M. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 361.
(74) Turro, N. J.; Gould, I. R.; Liu, J.; Jenks, W. S.; Staab, H.; Alt, R. *J. Am. Chem. Soc.* **1989**, *111*, 6378.
(75) Zhou, B.; Wagner, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6796.
(76) Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.

Scheme VI



diketone. The solvated biradical presumably can no longer disproportionate and therefore cyclizes in greater yield, as happens with the 1,5-biradical formed from **12**.

We believe that Scheme V explains solvent effects on quantum yields and on the formation of side products. The key element is the suggestion that the 1,5-biradicals can cyclize at the ortho position to form spiroenols. Of course benzyl radicals, especially hindered ones, are well-known to couple at the ortho and para positions.[77] There is independent evidence that *o-tert*-butylacetophenone undergoes similar spirocyclization,[39] **4** produces a byproduct with λ_{max} = 360 nm, and our flash spectroscopic studies indicate the formation of acid-sensitive enols from **3**, presumably in low yield. The photoenol forms of *o*-alkyl ketones are known to react very rapidly with oxygen,[78] so the spiroenols might be expected to undergo facile oxidation.

Why do the benzophenone-derived biradicals cyclize with nearly 100% efficiency, while those derived from acetophenones cyclize very inefficiently? We believe that the answer lies in different geometries of the biradicals, specifically the degree of conjugation of the p-orbital of the benzylic center with the *o*-alkoxyphenyl ring. In the benzophenone-derived biradical, the benzylic radical center can twist 90° and still remain conjugated with the other benzene ring. Such a twist is required for cyclization. Given the twisted geometry of the reactant, a large bond rotation may not be necessary.

We have already pointed out that the triplet acetophenones probably possess a much more coplanar benzoyl chromophore than do the benzophenones. The benzylic radical center of the biradical also would be stabilized by conjugation with the benzene ring. Consequently, product formation requires more conjugation-breaking bond rotation than is the case for the benzophenone-derived biradicals. We have measured a rate constant of 10^7 s^{-1} for anti′ → syn′ rotation of triplet acetophenone,[22] which may be a close model to this system. A rate constant as slow as 10^3 s^{-1} has been suggested to explain line-broadening in the EPR of benzaldehyde ketyl radicals.[71]

Schem V does not address why solvation would change the partitioning of the biradical. The solvation-induced loss of stereoselectivity in hydroxy-biradical cyclization has commonly been explained as steric recognition that an OH hydrogen-bonded to solvent is much larger than a free OH.[80] If this increased bulk around the reaction center slows down cyclization, then reactions not subject to comparable steric effects would compete better. That rate constants for bimolecular coupling of radicals decrease as the radical centers become more sterically crowded has been recognized for years.[81] Two model examples of $k_{coupling}$ values are as follows: for $PhC(OH)CH_3$ radicals,[82] 2×10^9 M^{-1} s^{-1} in benzene; for $Ph_2C(OH)$ radicals,[83] 6×10^8 M^{-1} s^{-1} in benzene, 1×10^8 in acetonitrile. These values are all slower than diffusion.

The reported behavior of the *o*-isopropoxybenzophenone **13** provides one more example of how steric crowding diminishes cyclization of this type of 1,5-biradical. A ketal becomes a major product along with the expected benzofuranol.[33] Scheme VI indicates what we consider the most likely mechanism for ketal formation: disproportionation of the biradical followed by electrophilic addition of the alcohol group to the enol ether. (The photochemistry of 2,4-di-*tert*-butylacetophenone also demonstrates the important of such disproportionation reactions.[39])

Biradical Lifetimes. The above discussion of solvent and structural effects on biradical partitioning ignores an important question, namely the timing of intersystem crossing and product formation from triplet biradicals. The preponderance of evidence indicates that triplet biradical lifetimes are determined by their intersystem crossing rates.[6,12,13] These 1,5-biradicals are very short-lived when unsolvated; their rates of decay are comparable to bond rotation rates in biradicals.[84]

If one assumes that product formation from singlet biradicals follows rapidly after lifetime-determining intersystem crossing, then product partitioning in fact represents solvent and structural effects on intersystem crossing rates of different triplet biradical conformations.[6] However, the partitioning of these 1,5-biradicals is fully explicable in terms of steric and stereoelectronic effects, as presented in the last section. It seems too much of a coincidence that solvent and structural effects on intersystem crossing rates of various biradical conformations would match so perfectly with their anticipated effects on bond formation unless intersystem crossing occurs mainly or solely in geometries that are close to those of the transition states for product formation. Therefore it has been suggested[85] that intersystem crossing in fact occurs along the reaction coordinates for product formation. Thus steric crowding, including that caused by solvation of the OH, retards bond movement along a coupling coordinate but may not impede coupling into the benzene ring. The 13-ns transient that we ascribe to the presumed 1,5-biradical intermediate from **3** can be detected only in the presence of pyridine, which also causes a 6-fold drop in the stereoselectivity of coupling. This change might suggest a 2-ns lifetime for the unsolvated biradical. In fact, the well-characterized 1,5-biradical from OTBBP also is subject to large solvent effects.[38] Both of these ortho-substituted benzophenone systems form biradicals in geometries that can readily form five-membered rings. The internal oxygen effect on 1,4-biradicals has usually been attributed to a spin-orbit effect,[86] but we agree with Scaiano[87] that it more likely reflects the greater ease of bringing together the ends of a four-membered ring when one carbon atom is replaced with oxygen. (This explanation was originally offered to explain the high cyclization efficiency of α-alkoxyacetophenones.[14,17]

Doubleday and Turro's work establishes that spin-orbit coupling is the dominant mechanism inducing intersystem crossing in short biradicals, probably by through-space interaction of the unpaired electrons.[12,37] How better to bring the two half-occupied orbitals close than when they begin to bond? As noted above, rotation about a benzylic bond is required for product formation in these 1,5-biradicals. Not only does this allow the two half-occupied orbitals to overlap in the proper alignment for bonding, but rotation itself is known to induce spin-orbit coupling.[88] The observed cyclization diastereoselectivity thus may reflect rotation kinetics as well as conformational equilibria.

Low k_q Values. The *o*-alkoxy ketones provide the first extended example of what appears to be steric hindrance to triplet energy transfer. The rate constant for quenching of triplet acetophenone

(77) (a) Nelson, S. F.; Bartlett, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 137. (b) Langais, H.; Fischer, H. *Chem. Ber.* **1978**, *111*, 543.
(78) Findley, D. M.; Tchir, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 514.
(79) Conradi, M.; Zeldes, H.; Livingston, R. *J. Phys. Chem.* **1979**, *83*, 2180.
(80) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898–901.
(81) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.
(82) Scaiano, J. C. Unpublished data.
(83) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048.
(84) Dervan, P. B.; Uyehara, T.; Santilli, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 2069.
(85) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83–89.
(86) (a) Freilich, S.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6255. (b) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 630.
(87) Barton, D. H. R.; Charpiot, B.; Ingold, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. *J. Am. Chem. Soc.* **1985**, *107*, 3607.
(88) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

or benzophenone by conjugated dienes in chlorobenzene is 5×10^9 M^{-1} s^{-1}. We have already reported that this value is not subject to some kinds of steric effects. For example, *tert*-alkyl ketones[89,90] and **12**[39] are quenched with this "normal" rate constant. A single *o*-methoxy group does not affect this value, but 2,6-dimethoxy substitution cuts it in half. A single *o*-benzyloxy group also halves the observed k_q value, while one on each benzene ring cuts the rate by a factor of six. The 2,6-diacylphenyl ethers **5** and **8** have k_q values only 40% of normal.

It has been known for two decades now that observed rate constants for exothermic triplet energy transfer from n,π^* ketones to dienes are typically about half the "diffusion-controlled" value in light solvents.[91] This phenomenon is explained by rates for energy transfer within a solvent cage (k_{et}) and for diffusion apart (k_{-dif}) being comparable ($5-10 \times 10^{10}$ s^{-1}). The decreases in the observed rate constant for **2**, **3**, **5**, and **7–9** all reflect decreases in k_{et} by factors of 3–4. 2,2′-Dibenzyloxy substitution produces a factor of 11 decrease in k_{et}.

$$k_q = k_{dif}k_{et}(k_{et} + k_{-dif})^{-1} \qquad (2)$$

One of us pointed out long ago[90] that exothermic energy transfer is so rapid at van der Waals separation of donor and acceptor as to preclude large steric effects of the type that prevent close approach of nuclei and orbitals. However, proper orientation of orbitals is also necessary, as has become more evident recently.[92,93] Therefore steric hindrance that blocks approach of donor to acceptor from a preferred orbital orientation still leaves other, less favorable approaches open. Unfortunately, it is not yet possible to quantify the relationship between k_{et} values and orbital overlap angles. However, it seems clear than one ortho substituent can block only one face of the carbonyl, whereas in **2** and **4** both faces may be blocked.

Stereoelectronic factors that produce twisted π systems can cause really large decreases in k_{et} values[89,94] as well as in the chemical reactivity of triplet ketones.[74] No such large effects occur here, since all of the benzophenones have one reasonably coplanar benzoyl group and the acetophenones tend to be more planar in their excited states anyway. It is instructive to ponder why an ortho *tert*-butyl group on benzophenone does not slow down energy transfer quenching, whereas an *o*-benzyloxy group does. We believe that the explanation must lie in the floppy benzyl group being able to block a broader arc around the carbonyl than can the "round" *tert*-butyl group.

Summary

o-Alkoxy ketone triplets such as **1e** undergo δ-hydrogen abstraction only 1/200 as rapidly as *o-tert*-butylbenzophenone **12**, whereas β-ethoxypropiophenone is 40 times more reactive than β-*tert*-butylpropiophenone. This large inversion of relative reactivity is shown to reflect primarily conformational factors, especially an unfavorable syn–anti equilibrium for rotation around the benzene–ether oxygen bond, which is concluded to be even worse in the triplet state than in the ground state. In the anti conformer, no C–H bond is anywhere near within bonding distance of the carbonyl, whereas the syn geometry is suitable for hydrogen transfer. This picture is supported by MMX calculations, by NMR and UV spectra, and by the measured Arrhenius factors for triplet reaction. The 1,5-biradical intermediates formed by δ-hydrogen abstraction generally cyclize efficiently to dihydrobenzofuranols, except in the case of *o*-(benzyloxy)acetophenone, in which rotation around the benzene–(reduced)acetyl bond is slow in the biradical. The large variations in product distribution from these biradicals, which are very short lived (≤13 ns), suggest that triplet–singlet intersystem crosssing occurs from geometries close to that of the transition states for the product-forming reactions.

Experimental Section

Solvents were purified by distillation of pretreated reagent-grade materials, with the first and last 10% of distillate being discarded. Benzene was first washed with sulfuric acid and distilled from P_2O_5. Pyridine was first refluxed over barium oxide. 2-Methyltetrahydrofuran was refluxed over cuprous chloride for 12 h, distilled, and then redistilled from lithium aluminum hydride.

Internal standards were various alkanes from C_{15} to C_{24} that were washed with sulfuric acid and then either distilled or recrystallized.

Quenchers. 1,3-Pentadiene (Chemical Samples) and *trans*-stilbene (Fisher) were used as received; 2,5-dimethyl-2,4-hexadiene (Chemical Samples) was allowed to sublime in the refrigerator.

Preparation of Ketones. Valerophenone was prepared by Friedel-Crafts acylation of benzene with valeryl chloride. ***o*-(Benzyloxy)benzophenone.** 2-Hydroxybenzophenone (10 g, Aldrich) was added to 3 g of sodium methoxide (Fisher) in 100 mL of methanol and stirred under nitrogen for 1 h. Benzyl bromide (6.6 mL, Eastman) in 25 mL of methanol was added dropwise; the solution was refluxed overnight. Standard workup and crystallization from chloroform–hexane afforded 6.6 g (45%) of pure white needles, mp 65–67 °C (lit. 62 °C):[95] IR (CCl_4) 1675, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.88 (s, 2 H), 6.96 (m, 2 H), 7.01 (dd, J = 9.0, 0.8 Hz, 1 H), 7.05 (td, J = 7.5, 1.0 Hz, 1 H), 7.16–7.20 (m, 3 H), 7.41 (t, J = 7.5 Hz, 2 H), 7.43 (t, J = 7.0 Hz, 2 H), 7.53 (tt, J = 7.5, 1.2 Hz, 1 H), 7.80 (dd, J = 7.5, 1.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 70.0, 112.7, 120.9, 126.5, 128.2, 129.5, 129.7, 131.9, 132.7, 138.3, 156, 196.1; MS m/z 77, 91 (base), 105, 197, 288 (M^+).

***o*-Methoxybenzophenone.** The sodium salt of 5 g of 2-hydroxybenzophenone was reacted as above but with 3.8 g dimethyl sulfate (Mallinkrodt). The product was recrystallized from ethanol to afford 3.2 g (60%) of white needles, mp 36–38 °C (lit. 39 °C):[96] IR (CCl_4) 1680, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.71 (s, 3 H), 6.98 (br d, J = 8.3 Hz, 1 H), 7.03 (td, J = 7.4, 0.9 Hz, 1 H), 7.35 (dd, J = 7.4, 1.6 Hz, 1 H), 7.41 (t, J = 7.5 Hz, 2 H), 7.45 (ddd, J = 8.3, 7.4, 1.7 Hz, 1 H), 7.54 (tt, J = 7.4, 1.8 Hz, 1 H), 7.80 (dd, J = 8.3, 1.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 55.5, 111.2, 120.3, 128.0, 128.6, 129.3, 129.5, 131.7, 132.7, 137.6, 157.1, 196.2; MS m/z 77, 92, 105, 135 (base), 195, 212 (M^+).

***o*-Ethoxybenzophenone.** 2-Ethoxybromobenzene was first prepared by treating 2-bromophenol in DMF with potassium carbonate and then heating with ethyl bromide. The Grignard reagent was prepared in ether; 1 equiv of benzonitrile was added, and the mixture was refluxed for 5 h. After acid hydrolysis at 0 °C, the aqueous layer was boiled; the separated ketone was then collected and purified. Vacuum distillation (128–130 °C at 0.5 Torr) produced a clear liquid which was recrystallized from 95% ethanol, mp 38.5–39.0 °C: IR (CCl_4) 1668, 1452, 1244; ^1H NMR ($CDCl_3$) δ 1.01 (t, J = 8 Hz, 3 H), 3.93 (quar, J = 8 Hz, 2 H), 6.94 (br d, J = 8.4 Hz, 1 H), 7.02 (td, J = 7.1, 0.9 Hz, 1 H), 7.36–7.46 (complex m, 4 H), 7.52 (tt, J = 7.4, 1.2 Hz, 1 H), 7.78 (dd, J = 8.4, 1.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 63.9, 112.6, 120.6, 128.2, 129.2, 129.7, 129.9, 132.2, 132.8, 138.5, 157.1, 197.2; MS m/z 226, 211, 208, 197, 181, 149, 121 (base), 105, 77.

***o*-(Benzyloxy)acetophenone.** 2-Hydroxyacetophenone (4 g, Aldrich) was stirred with 2.5 g of potassium hydroxide in 100 mL of methanol for 1 h; 5 mL of benzyl chloride (Fisher) were added, and the solution was refluxed overnight. Normal workup afforded 5.6 g (83%) of white crystals, mp 39–41 °C: IR (CCl_4) 1260, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.59 (s, 3 H), 5.15 (s, 2 H), 7.00 (td, J = 6.4, 1.0 Hz, 1 H), 7.01 (d, J = 8.2 Hz, 1 H), 7.33–7.46 (complex m, 6 H), 7.73 (dd, J = 8.0, 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 32.5, 70.6, 112.7, 120.8, 127.5, 128.2, 129.6, 130.4, 133.5, 136.1, 158.0, 199.8; MS m/z 77, 91 (base), 107, 121, 183, 208, 226 (M^+).

***o*-(Benzyloxy)valerophenone.** *o*-Hydroxyvalerophenone was prepared by a Fries rearrangement: 16.5 g of phenyl valerate and 24.7 g of aluminum chloride, each in 100 mL of petroleum ether, were mixed with stirring and refluxed under nitrogen for 3 h. The cooled solution was poured onto ice. Normal workup followed by vacuum distillation bp 60–90 °C at 1 Torr afforded 6.0 g (36%) of liquid with appropriate spectroscopic properties:[97] ^1H NMR ($CDCl_3$) δ 1.0 (t, 3 H), 1.5–2.0 (m, 4 H), 2.9 (t, 2 H), 6.5–7.5 (m, 4 H), 12.2 (s, 1 H); MS m/z 65, 93, 121 (base), 136, 149, 178 (M^+).

The potassium salt of 10 g of the acylphenol was refluxed with 6.7 mL of benzyl chloride in methanol for 2 h. Normal workup and vacuum

(89) Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5806–7.
(90) Wagner, P. J.; McGrath, J. M.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 6883.
(91) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232–8.
(92) Wagner, P. J.; Leventis, N. *J. Am. Chem. Soc.* **1987**, *109*, 2188–90.
(93) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652.
(94) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820.
(95) Bonnard, Y.; Meyer-Oulif, J. *Bull. Chem. Soc. Fr.* **1931**, *49*, 1303.
(96) Stoermer, R.; Frederici, E. *Chem. Ber.* **1918**, *41*, 332.
(97) Ogata, Y.; Tabuchi, H. *Tetrahedron* **1964**, *20*, 1661.

distillation provided 8 g (53%) of an oil that was recrystallized from hexane to afford 6.7 g of white platelets, mp 26–28 °C: IR (CCl_4) 1270, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H, J = 7.3 Hz), 1.22 (sextet, J = 7.2 Hz, 2 H), 1.60 (quintet, J = 7.3 Hz, 2 H), 2.94 (t, 2 H, J = 7.3 Hz, CO-CH_2), 5.12 (s, 2 H, OCH_2Ph), 6.98 (d, J = 8.0 Hz, 1 H), 7.01 (t, J = 8.0 Hz, 1 H), 7.41 (m, 6 H), 7.66 (dd, J = 1.3, 8.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 26.5, 43.7, 70.7, 112.7, 120.9, 127.7, 128.2, 128.7, 129.3, 130.3, 133.0, 136.2, 157.5, 203.4; MS m/z 77, 91 (base), 121, 211, 268 (M^+).

2,2'-Bis(benzyloxy)benzophenone. The potassium salt of 2,2'-dihydroxybenzophenone (5.0 g, Aldrich) was prepared and reacted with 5.6 mL of benzyl bromide in methanol as described for *o*-(benzyloxy)-acetophenone. Recrystallization from ethanol afforded 2.6 g (28%) of off-white needles, mp 98–99.5 °C: IR (CCl_4) 1280, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.7 (s, 4 H), 6.6–7.5 (complex, 12 Ar aromatic H); ^{13}C NMR ($CDCl_3$) δ 70.0, 112.5, 120.8, 126.5, 127.3, 128.1, 130.4, 132.5, 136.3, 157.2, 195.5; MS m/z 77, 91 (base), 183, 211, 303, 376, 394 (M^+).

2,6-Dimethoxybenzophenone was prepared as described by Levine and Sommers;[98] *m*-dimethoxybenzene was reacted with *n*-butyllithium and then with methyl benzoate. After workup, the product was vacuum distilled and recrystallized from methanol, mp 98–100 °C (lit. 97.5–98 °C):[99] IR (CCl_4) 1290, 1310, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.65 (s, 6 H), 6.60 (d, J = 8.5 Hz, 2 H), 7.33 (t, J = 8.5 Hz, 1 H), 7.40 (t, J = 7.5 Hz, 2 H), 7.52 (tt, J = 7.5, 1.2 Hz, 1 H), 7.83 (d, J = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 55.7, 103.9, 117.8, 128.3, 129.2, 133.0, 137.5, 157.5, 195.2; MS m/z 77, 91, 105, 151, 165 (base), 225, 242 (M^+).

Anisole-2,6-dicarboxylic Acid. 2,6-Dimethylanisole was prepared by alkylating the potassium salt of 2,6-dimethylphenol with methyl sulfate in methanol. It was heated for 3 h at 80 °C in a vigorously stirred solution of 18 g of potassium hydroxide and 104 g of potassium permanganate in 700 mL of water. After cooling and filtration, the solution was acidified with HCl. The crystallized product was air dried, mp 219–221 °C; MS m/z 77, 91, 105, 120, 132, 149, 165, 178, 196 (M^+).

2,6-Dibenzoylphenol. The dicarboxylic acid (15 g) was refluxed with 100 mL of thionyl chloride until all the acid was dissolved. Distillation (0.8 Torr, 105–110 °C) gave 9.5 g (42%) of the diacyl chloride. This was refluxed with 10 g of aluminum chloride in 150 mL of benzene for 8 h. Normal workup provided an orange oil, which was triturated with hexane to afford 7.2 g (61%) of the crystalline phenol: ^1H NMR ($CDCl_3$) δ 6.7–8.0 (m, 13 H), 13.8 (s, 1 H).

2,6-Dibenzoylphenyl Benzyl Ether. 2,6-Dibenzoylphenol (3 g) was alkylated with benzyl bromide and potassium hydroxide in methanol as described for *o*-(benzyloxy)acetophenone. The crude product was triturated with hexane to yield 3.0 g (41%) of colorless needles, mp 104–105 °C: IR (CCl_4) 1250, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.69 (s, 2 H), 6.64 (d, J = 8 Hz, 2 H), 7.06 (m, 3 H), 7.32 (t, J = 8.2 Hz, 1 H), 7.43 (t, J = 8.2 Hz, 4 H), 7.56 (t, J = 7.8 Hz, 4 H), 7.85 (d, J = 8.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 77.5, 123.5, 127.8, 127.9, 128.3, 129.9, 131.9, 133.4, 133.8, 135.5, 137.0, 154.4, 195.5; MS m/z 77, 91 (base), 105, 181, 286, 315, 392 (M^+).

2,6-Dibenzoylanisole. 2,6-Dibenzoylphenol (12 g) was alkylated with 4 mL of dimethyl sulfate in alkaline methanol as described above. The oil obtained from workup was chromatographed on 200 g of alumina with 9:1 hexane/methylene chloride eluent. Crystallization from carbon tetrachloride gave 3.0 g (24%) of a white powder, mp 37–38 °C: IR (CCl_4) 1250, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.43 (s, 3 H), 7.28 (t, J = 8.2 H, 1 H), 7.43–7.60 (m, 8 H), 7.86 (d, J = 8.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 61.6, 123.1, 128.5, 129.8, 131.8, 133, 133.4, 136.4, 195.5; MS m/z 77, 91, 105 (base), 147, 181, 211, 225, 239, 285, 299, 316 (M^+).

2,6-Diacetylanisole. The anisole-2,6-dicarboxylic acid above was reacted with 2 equivs of *n*-butyl mercaptan in ether containing 2 equivs of pyridine to give the dithioester.[100] This was dissolved in 50 mL of anhydrous THF, which was stirred at −50 °C for 3 h with 50 mL of THF containing freshly prepared lithium dimethylcuprate.[101] Normal workup followed by vacuum distillation (1 Torr, 125–130 °C) gave 6 g (70%) of the diacetyl product:[100] ^1H NMR ($CDCl_3$) δ 2.6 (s, 6 H), 3.8 (s, 3 H), 7.1 (t, J = 8.2 Hz, 1 H), 7.7 (d, J = 8.2 Hz, 2 H).

2,6-Diacetylphenol. The anisole (5 g) was refluxed under nitrogen for 20 h with 10 g of sodium iodide and 8.5 mL of chlorotrimethylsilane (Aldrich) in 70 mL of acetonitrile.[102] Workup provided 7 g (69%) of a brown oil which soon crystallized. It was recrystallized from methanol: ^1H NMR ($CDCl_3$) δ 2.6 (s, 6 H), 6.8 (t, 1 H), 7.8 (d, 2 H), 13.1 (s, 1 H).

2,6-Diacetylphenyl Benzyl Ether. The phenol (8.2 g) was alkylated with 6 mL of benzyl bromide in 100 mL of alkaline methanol, as described above. Workup and recrystallization from methanol provided white crystals, mp 69–70 °C: IR (CCl_4) 1240, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.59 (s, 6 H), 4.91 (s, 2 H), 7.25 (t, J = 8.1 Hz, 1 H), 7.36 (br s, 5 H), 7.71 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.7, 79.4, 124.3, 128.0, 128.3, 128.6, 132.8, 135.1, 135.4, 156.2, 200.0; MS m/z 77, 91 (base), 147, 225, 235, 253, 268 (M^+).

Identification of Photoproducts. In general, 500 mL of ketone solutions 0.01–0.1 M in spectroscopic grade cyclohexane or heptane were irradiated in a standard preparative well, under nitrogen. An immersion well in the center housed a Hanovia 450-W medium pressure arc which was filtered with a uranium glass sleeve. Alternatively, test tubes containing 200 mg of ketone in 10 mL of benzene were degassed, sealed, and irradiated at 313 nm as described below. After complete reaction, products were isolated by flash chromatography[103] on ICN silica gel (0.032–0.063 mm) with 95:5 (by vol) hexane/ethyl acetate eluent. OH groups were identified in ^1H NMR spectra by their change upon addition of D_2O.

***o*-(Benzyloxy)benzophenone** was irradiated as a 0.1 M solution in heptane containing 2 M pyridine. HPLC revealed three products, one of which did not survive flash chromatography. The other two were identified as the expected oxaindanols, listed in their order of elution.

(*Z*)-2,3-Diphenyl-3-hydroxy-2,3-dihydrobenzofuran: IR (CCl_4) 1275, 2910, 2960, 3030, 3060, 3080, 3500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95 (br s, 1 H, OH), 5.66 (s, 1 H, O*CH*Ph), 6.6–7.9 (m, 14 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 83.2, 95.3, 110.8, 122, 125.5, 126.8, 127.0, 127.6, 127.7, 128.3, 128.5, 128.8, 129.6, 130.7, 134, 142.9, 160.3; MS m/z 77, 84, 91 (base), 105, 121, 181, 270, 288 (M^+).

(*E*)-2,3-Diphenyl-3-hydroxy-2,3-dihydrobenzofuran: IR (CH_2Cl_2) 1225, 2945, 3010, 3570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.62 (br s, 1 H, OH), 5.77 (s, 1 H, O*CH*Ph), 6.9–7.46 (m, 14 H, aromatic); MS virtually the same as for the *Z* isomer.

***o*-(Benzyloxy)acetophenone** was reacted in the same way, also giving three products listed in order of their elution.

(*Z*)-2-Phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran: IR (neat) 1260, 2870, 2910, 2960, 3030, 3060, 3080, 3470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (br s, 1 H, OH), 1.7 (s, 3 H, CH_3), 5.3 (s, 1 H, O*CH*Ph), 6.98 (d, 7.4 Hz, 1 H), 7.26–7.45 (m, 8 H); MS m/z 77, 91 (base), 105, 121, 208, 266 (M^+).

(*E*)-2-Phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran: IR (CCl_4) 1260, 2950, 2970, 3030, 3060, 3580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (s, 3 H, CH_3), 2.48 (s, 1 H, OH), 5.52 (s, 1 H, O*CH*Ph), 6.99 (d, 7.5 Hz, 1 H), 7.25–7.45 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 78.2, 92.9, 110.7, 121.5, 123.9, 127.1, 128.6, 128.8, 130.4, 132, 134.9, 159.4; MS m/z 77, 91, 105, 121, 208 (base), 226 (M^+).

2-Acetylbenzophenone: mp 78–80 °C (lit. 99 °C[104]); IR (CCl_4) 1660, 1680 (lit. 1660, 1680[105] cm^{-1}); ^1H NMR ($CDCl_3$) δ 2.52 (s, 3 H), 7.40 (t, J = 8 Hz, 3 H), 7.52 (d, J = 8 Hz, 1 H), 7.60 (t, J = 8 Hz, 2 H), 7.74 (d, J = 8 Hz, 2 H), 7.89 (d, 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.4, 112.7, 120.4, 128.4, 128.5, 129.3, 129.4, 129.8, 132.2, 133, 137.3, 137.7, 141, 197.9, 198.6; MS m/z 77, 105, 147, 181, 209, 224 (M^+).

***o*-Methoxybenzophenone** was reacted in heptane as above and furnished two products.

***o*-Methoxybenzhydrol**: mp 177–8 °C (lit. 141 °C);[106] IR (CCl_4) 3500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.35 (s, 3 H, OCH_3), 5.45 (s, 1 H, *CH*OH), 6.7–8.1 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 82.7, 113.4, 120, 125.6, 126.1, 127.9, 129.2, 132.3, 134.9, 145.5, 157.7, 167.1; MS m/z 77, 105, 121, 135, 195 (base), 213 (M^+).

3-Phenyl-3-hydroxy-2,3-dihydrobenzofuran: IR (neat) 1225, 2890, 2950, 2980, 3030, 3060, 3080, 3430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (br s, 1 H, OH), 4.48 and 4.66 (AB quar, 2 H, J = 10.29 Hz, OCH_2–), 6.88–7.50 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 82.6, 86.1, 110.8, 121.4, 124.4, 126.1, 127, 128.3, 130.6, 132.2, 142.5, 166.8; MS m/z 77, 91, 105, 121, 165, 181, 194, 212 (M^+, base).

(*Z*)-2-Phenyl-3-methyl-7-acetyl-3-hydroxy-2,3-dihydrobenzofuran was the only significant product obtained from irradiation of 2,6-diacetylphenyl benzyl ether to 50% conversion in cyclohexane. It was assigned the *Z* stereochemistry based on the chemical shifts of the methyl and hydroxy groups: IR (CCl_4) 1260, 2970, 3050, 3560 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (br s, 1 H, OH), 1.77 (s, 3 H, C(OH)CH_3), 2.69 (s, 3 H, $COCH_3$), 5.46 (s, 1 H, O*CH*Ph), 7.08 (t, J = 8 Hz, 1 H), 7.45 (br s, 5 H), 7.57 (d, J = 8 Hz, 1 H), 7.90 (d, J = 8 Hz, 1 H); ^{13}C NMR

(98) Levine, R.; Sommers, J. R. *J. Org. Chem.* **1974**, *39*, 3559.
(99) Fletcher, P.; Marlow, W. *J. Chem. Soc. C* **1970**, 937.
(100) Anderson, R. J.; Hendrick, C. A.; Rosenblum, C. D. *J. Am. Chem. Soc.* **1974**, *96*, 3654.
(101) Whitesides, G. M.; Et al. *J. Am. Chem. Soc.* **1969**, *91*, 4871.
(102) Olah, G. A.; et al. *J. Org. Chem.* **1979**, *44*, 1247.
(103) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(104) Vecchionacci, J. P.; Canevet, J.; Graff, Y. *Bull. Chim. Soc. Fr.* **1974**, Pt. 2, 1683.
(105) Niimi, J.; *Yakugaku Zasshi* **1960**, *80*, 451; see *Chem. Abstr.* **1960**, *54*, 19739d.
(106) Kahil, A. I. M.; Nierenstein, M. *J. Am. Chem. Soc.* **1924**, *46*, 2557.

($CDCl_3$) δ 25.4, 31.3, 77.3, 93.6, 121.6, 125.7, 126.9, 128.7, 128.8, 129, 130.6, 132.9, 134.1, 159.5, 196.5; MS *m/z* 43, 77, 91, 105, 119, 147 (base), 225, 253, 268 (M^+).

***o*-Ethoxybenzophenone** was studied only by NMR analysis. Degassed benzene solutions were irradiated, after which the benzene was replaced with chloroform-*d*. The only detectable products were the (*Z*)-dihydrofuranol and 15% 2-methyl-3-phenylindene. The chloroform was later found to contain trace water and HCl, which catalyzed the dehydration. When irradiation and analysis were performed in benzene-d_6 in an argon-flushed NMR tube, the two isomeric dihydrofuranols, in an 11:1 ratio (based on integration), were the only products. Similar irradiation in methanol-d_4 produced the two isomers in comparable yields, together with about 20% of unidentified byproducts.

(*Z*)-2-Methyl-3-phenyl-3-hydroxy-2,3-dihydrobenzofuran: ^1H NMR ($CDCl_3$) δ 1.45 (d, *J* = 6.3 Hz, 3 H), 4.56 (quar, *J* = 6.3 Hz, 1 H), 6.90–6.95 (complex m, 1 H), 7.07 (dt, *J* = 7.0, 1.2 Hz, 1 H), 7.26–7.40 (complex m, 5 H), 7.50 (dd, *J* = 6.6, 2.1 Hz, 2 H); (C_6D_6) 1.23 (br s, 1 H, OH), 1.28 (d, *J* = 6.3 Hz, 3 H), 4.44 (quar, *J* = 6.6 Hz, 1 H), 6.69 (td, *J* = 7.2, 1.5 Hz, 1 H), 6.84 (br d, *J* = 7.2 Hz, 1 H), 6.90 (br d, *J* = 7.5 Hz, 1 H), 7.00–7.14 (complex m, 4 H), 7.40 (dd, *J* = 7.8, 2.1 Hz, 2 H); (CD_3OD), 1.38 (d, *J* = 6.6 Hz), 4.50 (quar, *J* = 6.6 Hz).

(*E*)-2-Methyl-3-phenyl-3-hydroxy-2,3-dihydrobenzofuran: ^1H NMR (C_6D_6) δ 0.80 (d, *J* = 6.9 Hz, 3 H), 4.58 (quar, *J* = 6.6 Hz, 1 H), 6.74 (td), 7.27 (dd); (CD_3OD), 0.83 (d, *J* = 6.6 Hz), 4.72 (quar, *J* = 6.6 Hz).

2,6-Dibenzoylphenyl benzyl ether was irradiated at 313 nm in a sealed, degassed test tube. Two products (9:1 ratio) were separated from unreacted ketone.

(*Z*)-2,3-Diphenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran: IR (CH_2Cl_2) 1270, 2880, 2900, 3000, 3010, 3550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.19 (br s, 1 H, OH), 5.69 (s, 1 H, O*CH*Ph), 7.0–7.63 (m, 16 H), 7.94 (d, *J* = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 82.2, 95.8, 121.6, 126.5, 127.8, 127.9, 128.2, 128.3, 128.4, 128.6, 128.8, 129.9, 131.7, 132.8, 133, 134.5, 138, 142.3, 195.0; MS *m/z* 77, 91, 105, 181, 285 (base), 374, 392 (M^+).

(*E*)-2,3-Diphenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran: IR (CH_2Cl_2) 1240, 2900, 2960, 3020, 3570 cm^{-1}; ^1H NMR (acetone-d_6) δ 5.70 (s, 1 H, OH), 5.81 (s, 1 H, O*CH*OH), 6.9–7.6 (m, 16 H), 7.90 (d, *J* = 8 Hz, 2 H); MS *m/z* 77, 91, 105, 181, 285, 374 (base), 392 (M^+).

3-Phenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran was the only product obtained by irradiation of 2,6-dibenzoylanisole to 50% conversion in cyclohexane: IR (CH_2Cl_2) 1260, 2950, 3045, 3570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (br s, 1 H, OH), 4.55 and 4.74 (AB quar, 2 H, *J* = 10.5 Hz, OCH_2–), 7.01 (t, *J* = 8 Hz, 1 H), 7.25–7.60 (m, 10 H), 7.86 (d, *J* = 8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 81.8, 86.8, 121.2, 122.2, 122.3, 126, 127.8, 128.2, 128.3, 128.4, 129.9, 130.2, 132.1, 132.8, 137.8, 157.8, 194.1; MS *m/z* 77, 91, 105, 165, 221 (base), 298, 316 (M^+).

***o*-(Benzyloxy)acetophenone** was the only product formed from irradiation of *o*-(benzyloxy)valerophenone at 313 nm in benzene. It was identified by the correspondence of its GC retention time and mass spectrum to those of authentic material.

General Procedures. Samples for quantitative study were prepared in volumetric glassware; 2.8-mL aliquots were placed in clean, constricted 13 × 100 Pyrex tubes, which were subjected to three or four freeze–pump–thaw degassings with a diffusion pump and then sealed. The samples were irradiated in parallel on a merry-go-round apparatus[107] in a room-temperature water bath. A 450-W Hanovia medium pressure mercury arc served as the light source, with a 1-cm path of 0.002 M potassium chromate in 1% aqueous potassium carbonate serving as a filter solution for 313 nm and a set of Corning 7-83 filters for 365 nm.

Light intensity was measured by parallel irradiation of at least three identically prepared sample tubes containing 0.1 M valerophenone in benzene. The quantum yield for acetophenone formation is 0.33.[76]

Gas chromatograph analysis was performed on Varian Model 1400 GC's with flame ionization detectors and digital integrators. Most analyses were done by on-column injection onto 6′ × 1/8″ columns containing either 3% QF-1 or 3% OV-101 on Chromosorb G, with nitrogen carrier gas (40 mL/min). HPLC analysis was performed on a Beckman Model 332 gradient system with Altex 100A pumps, a Perkin-Elmer LC-75 UV detector. Altex Ultrasphere ODS-18 reverse phase or Si absorption phase columns were used. In both cases, product and reactant concentrations were determined relative to known concentrations of internal standards, with premeasured calibration factors.

NMR spectra were recorded on a Bruker WM-250 or a Varian VXR300 Fourier transform spectrometer, with tetramethylsilane as internal standard, IR spectra on a Perkin-Elmer Model 237B spectrometer, mass spectra on a Finnigan 4000 GC/MS spectrometer (direct inlet mode), UV spectra on a Varian-Cary 219 spectrophotometer, and melting points (uncorrected) on a Thomas-Hoover capillary apparatus.

Flash Spectroscopic Measurements. Samples 10^{-3}–10^{-2} M in ketone, such that optical densities at 337 nm equalled approximately 0.6, were placed in 7 × 7 or 7 × 3 mm square Supracil cells fitted with a serum cap. They were deoxygenated by bubbling purified nitrogen through them for several minutes. The laser appartus and analysis procedures are described elsewhere.[108] Excitation was provided by a Molectron UV-24 nitrogen laser (337 nm, 8 ns pulse, ~8 mJ). Lifetimes were monitored at wavelengths that produced the smallest amount of residual absorption, such that single exponential decays were reproducible to a few percent.

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Registry No. 1e, 127154-52-3; **1m**, 2553-04-0; **3**, 93254-81-0; **4**, 74697-53-3; **5**, 127154-53-4; **6**, 127154-54-5; **7**, 31165-67-0; **8**, 127154-55-6; **9**, 127154-56-7; (*Z*)-2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran, 93254-82-1; (*E*)-2,3-diphenyl-3-hydroxy-2,3-dihydrobenzofuran, 93254-83-2; (*Z*)-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran, 93254-84-3; (*E*)-2-phenyl-3-methyl-3-hydroxy-2,3-dihydrobenzofuran, 93254-85-4; *o*-methoxybenzhydrol, 22788-49-4; 3-phenyl-3-hydroxy-2,3-dihydrobenzofuran, 127154-57-8; (*Z*)-2-phenyl-3-methyl-7-acetyl-3-hydroxy-2,3-dihydrobenzofuran, 127154-58-9; 2-acetylbenzophenone, 18019-57-3; 2,5-dimethyl-2,4-hexadiene, 764-13-6; (*Z*)-2-methyl-3-phenyl-3-hydroxy-2,3-dihydrobenzofuran, 127154-59-0; (*E*)-2-methyl-3-phenyl-3-hydroxy-2,3-dihydrobenzofuran, 127154-60-3; (*Z*)-2,3-diphenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran, 127154-61-4; (*E*)-2,3-diphenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran, 127154-62-5; 3-phenyl-7-benzoyl-3-hydroxy-2,3-dihydrobenzofuran, 127154-63-6.

(107) Moses, F. G.; Liu, R. S. H.; Monroe, B. H. *Mol. Photochem.* **1969**, *1*, 245.

(108) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.