hexadiene dimers, but a set of 2,4-hexadiene experiments was also carried out using *n*-tetradecane as internal standard. The detector response ratio was assumed to be the ratio of the number of carbons in the standard to that in the dimer. For the *n*-dodecane–1,3-pentadiene dimer system a response ratio of 1.18 ± 0.02 was measured experimentlly which was in excellent agreement with the expected ratio of 1.20. The 1,3-pentadiene dimers used in this determination were obtained from the benzophenone-sensitized photodimerization of neat 1,3-pentadienes. The benzophenone was removed by chromatography on alumina using *n*-pentane as the eluent and the dimers were distilled prior to use. The distillation step was essential since omitting it gave a *n*-dodecane–dimer response ratio of 1.43, suggesting the presence of higher boiling side products in the dimers.[18] Deviations of independently measured dimer quantum yield values were in most cases $\leq 5\%$ of the average values reported in Table III, and only in one case was the deviation as large as 10%. Diene concentrations were determined using methylcyclohexane as internal standard on a 15 ft × $^1/_8$ in. column packed with 25% Ucon (Polar) on Chromosorb P.

Irradiation Procedures. Irradiations of high diene concentration samples (0.2-ml solution) were performed in a miniature merry-go-round apparatus which has previously been described.[13] Other irradiations, including run 1 in Table II, were performed in a conventional merry-go-round apparatus[31] (3-ml solution) employing 200- or 450-W Hanovia high-pressure mercury lamps. Corning filters CS 7-37 and CS 0-52 were used to isolate the 366-nm mercury line. All irradiations were carried out at 30 ± 1°. Samples were degassed to $<10^{-5}$ Torr using six freeze–pump–thaw cycles and sealed. The benzophenone-sensitized photoisomerization of *cis*-1,3-pentadiene at low diene concentration was used for actinometry.[5] The extinction coefficient of benzophenone at 366 nm in neat 1,3-pentadiene, 69, was found to be the same as in benzene solution.

Acknowledgment. We thank Mr. W. Greene for initial determinations of 1,3-pentadiene dimerization quantum yields and Dr. A. K. Uriarte for measuring the extinction coefficient of benzophenone in 1,3-pentadiene and for helpful discussions.

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(31) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

Cage Effects in the Photochemistry of (*S*)-(+)-2-Phenylpropiophenone[1]

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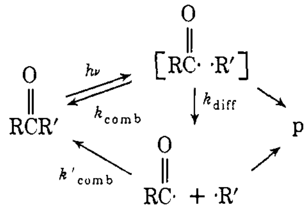
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received January 15, 1973

Abstract: Irradiation of (*S*)-(+)-2-phenylpropiophenone (**1**) in benzene in the presence of dodecanethiol scavenger leads to the formation of benzaldehyde (Φ = 0.44) and racemized ketone **1** (Φ = 0.33). The quantum inefficiency (~20%) is attributed to cage recombination of the benzoyl–1-phenylethyl radical pair prior to loss of chirality rather than to radiationless triplet decay. It is concluded that the rate of radical pair cage reactions is comparable to the rates for diffusion or rotation of the 1-phenylethyl radical with respect to the benzoyl radical.

The photochemical α-cleavage (type I) reaction of ketones in the solution phase normally occurs with quantum efficiencies significantly less than unity.[2–4] For example, we have investigated the α cleavage of a number of *tert*-alkyl[2] and benzyl phenyl ketones[3] and find maximum quantum yields for product formation less than 0.5 in all cases. Such low efficiencies may be due in part to cage (k_{comb}) and noncage (k'_{comb}) recombination of the initially formed radical pair (eq 1). Several recent reports of polarization of the parent ketone nmr spectrum upon irradiation have provided evidence for the cleavage–recombination process.[5]



(1)

However, the extent of cage and noncage recombination cannot be determined from CIDNP spectra. Yang[4c] and Bartltrop[4d] have established the importance of cleavage–recombination for cycloalkanones which undergo photoepimerization at the α carbon as well as isomerization *via* a biradical intermediate. The role of radical pair recombination in acyclic ketone photochemistry is more difficult to assess as both cage and random phase reactions occur.[6] As one approach to this problem, we have investigated the photochemistry of (*S*)-(+)-2-phenylpropiophenone (**1**).[7] This system was chosen because of our interest in benzyl phenyl ketones[3] and, moreover, because the CIDNP results of Müller and Closs[5c] on (±)-**1** qualitatively established the occurrence of cage recombination.

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(1) The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and PPG Industries for support of this research.

(2) (a) F. D. Lewis, *Tetrahedron Lett.*, 1373 (1970); (b) F. D. Lewis and J. G. Magyar, *J. Org. Chem.*, **37**, 2102 (1972); (c) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **94**, 3852 (1972); (d) F. D. Lewis and R. W. Johnson, *ibid.*, **94**, 8914 (1972).

(3) D. R. Kory and R. T. Lauterbach, unpublished results.

(4) (a) N. C. Yang and E. D. Feit, *J. Amer. Chem. Soc.*, 90, 504 (1968); (b) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 6974 (1970); (c) N. C. Yang and R. H.-K. Chen, *ibid.*, **93**, 530 (1971); (d) J. A. Barltrop and J. D. Coyle, *Chem. Commun.*, 1081 (1969); (e) W. K. Robins and R. H. Eastman, *J. Amer. Chem. Soc.*, **92**, 6076 (1970); (f) P. S. Engel and M. A. Schexnayder, *ibid.*, **94**, 4357 (1972).

(5) (a) M. Cocivera and A. M. Trozzolo, *ibid.*, **92**, 1772 (1970); (b) G. L. Closs and D. R. Paulson, *ibid.*, **92**, 7229 (1970); (c) K. Müller and G. L. Closs, *ibid.*, **94**, 1002 (1972); (d) J. A. DenHollander, R. Kaptein, and P. A. T. M. Brand, *Chem. Phys. Lett.*, 10, 430 (1971); (e) T. DoMinh, *Ind. Chim. Belge*, **36**, 1080 (1972).

(6) Engel[4f] has recently observed ~10% recombination of acyl–allyl radical pairs formed upon α-cleavage of a β,γ-unsaturated ketone.

(7) A. McKenzie, R. Roger, and G. O. Wills, *J. Chem. Soc.*, 779 (1926).

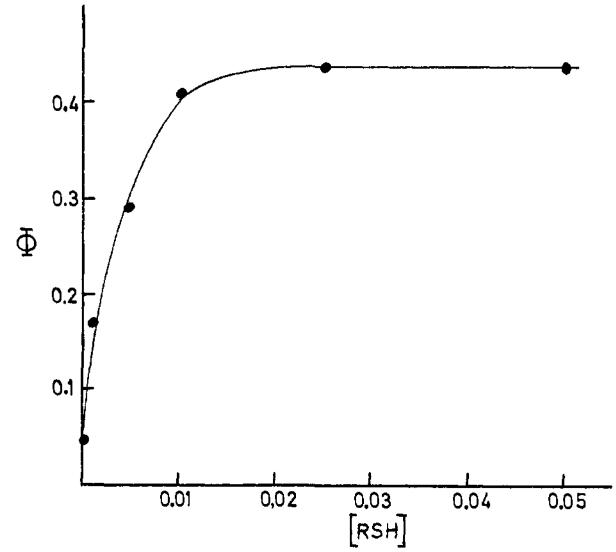
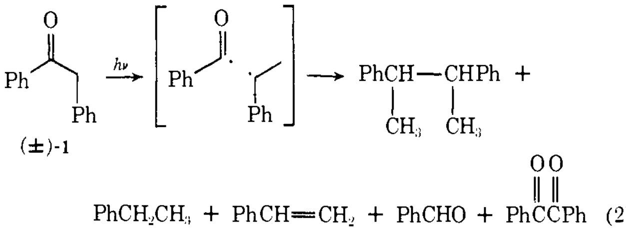


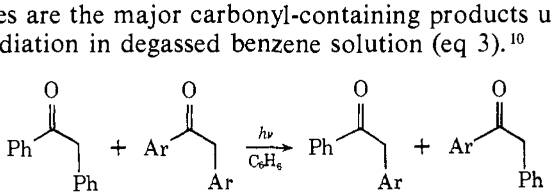
Figure 1. Variation in quantum yield of benzaldehyde formation with 1-dodecanethiol concentration.

Results

Irradiation of racemic **1** in degassed benzene solution results in the formation of several products, all of which can be attributed to an initially formed benzoyl-1-phenylethyl radical pair (eq 2).[8] The yields of these products are dependent on the duration of photolysis and light intensity. Analysis of the photolysis mixtures was greatly simplified by including low concentrations of 1-dodecanethiol (RSH) which acts as a scavenger for noncage benzoyl radicals.[2b,9] The variation in quantum yield for benzaldehyde formation with thiol concentration at <1% conversion is shown in Figure 1. The ability of 0.03 *M* RSH to completely scavenge all noncage benzoyl radicals was established by irradiating mixtures of 2-phenylacetophenone and 2-*p*-tolyl-*p*-methylacetophenone. The crossover ketones are the major carbonyl-containing products upon irradiation in degassed benzene solution (eq 3).[10] Addition of 0.03 *M* RSH completely suppresses crossover ketone formation and benzaldehyde becomes the sole carbonyl-containing product. 1-Phenylethyl and benzyl radicals are not efficiently scavenged even at much higher RSH concentrations.[9] The low concentrations of RSH used in the remainder of our studies preclude competitive photoreduction[11] or scavenging of cage benzoyl radicals. In the presence of 0.03 *M* RSH the quantum yields for loss of ketone and benzaldehyde formation were identical at 5 and 10% conversion.



$$\longrightarrow \underset{CH_3}{PhCH}-\underset{CH_3}{CHPh} + PhCH_2CH_3 + PhCH{=}CH_2 + PhCHO + Ph\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Ph \quad (2)$$



(3)

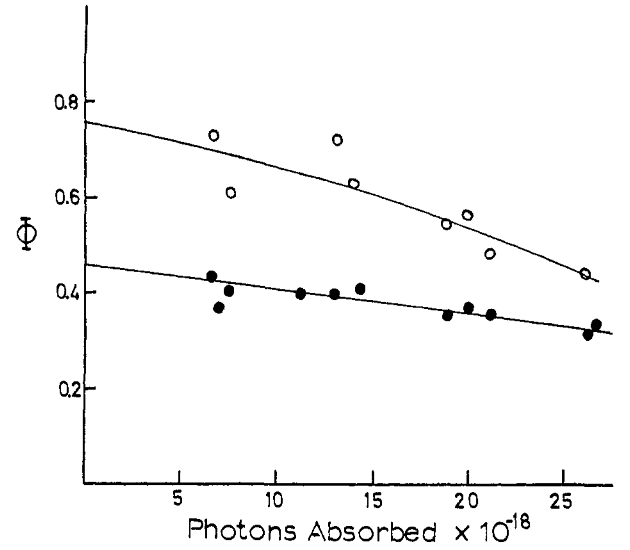


Figure 2. Dependence of quantum yields for loss of optical activity (○) and benzaldehyde formation (●) upon total 365-nm irradiation absorbed.

The triplet lifetime (τ) of racemic **1** was determined by the usual Stern–Volmer method using naphthalene as the triplet quencher. The slope of the Stern–Volmer plot ($k_q\tau$) is given in Table I along with the value of $1/\tau$ obtained by assuming $k_q = 5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.[12] Values for two related ketones are included in Table I.[13]

Table I. Quantum Yields and Kinetic Data for Benzyl Phenyl Ketones

Ketone	Φ^a	$k_q\tau^b$	$1/\tau = k_\alpha$, sec^{-1}
$PhCOCH_2Ph$	0.44	3100	1.6×10^6
$PhCOCH(CH_3)Ph$ ((±)-**1**)	0.44	240	2.1×10^7
$PhCOC(CH_3)_2Ph$	0.45	42	1.2×10^8

[a] Quantum yield for benzaldehyde formation at zero conversion.
[b] Slope of linear Stern–Volmer plots, naphthalene quenching.

Quantum yields for benzaldehyde formation and loss of optical activity for (+)-**1** in 0.03 *M* RSH-benzene were determined as a function of absorbed 365-nm irradiation. The results are given in Figure 2. Maximum conversions correspond to 10% loss of optical activity. The quantum yield for benzaldehyde formation extrapolated to zero conversion is identical with that for racemic **1**.

Discussion

Interpretation of the results for the irradiation of optically active ketone **1** is based on Scheme I. That α cleavage occurs from the triplet state[5c] is confirmed by naphthalene quenching (*vide infra*). Benzaldehyde

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[8] J. Kenyon, A. Rassoul, and G. Soliman, *J. Chem. Soc.*, 1774 (1956).

[9] R. M. Kellogg, *Methods Free-Radical Chem.*, **2**, 107 (1969).

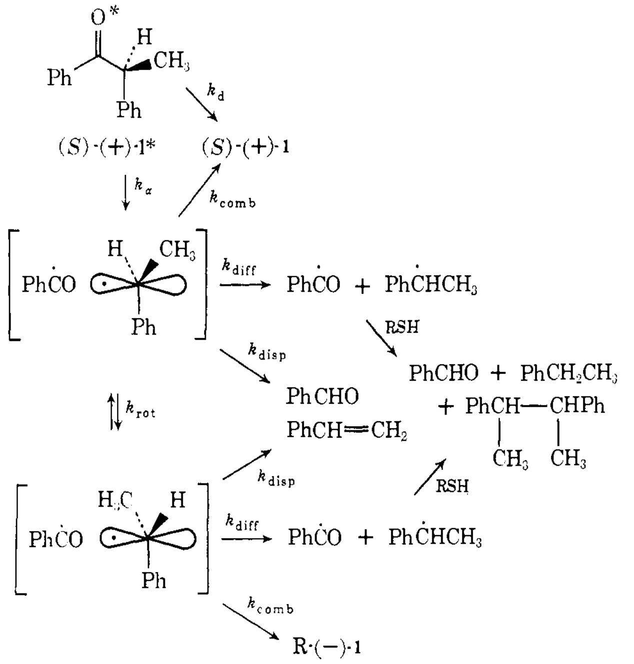
[10] Polarized nmr spectra have been observed for crossover ketones formed upon irradiation of benzoin ethers.[5e]

[11] J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **33**, 1271 (1968).

[12] P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

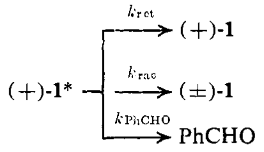
[13] Similar values of $1/\tau$ for the ketones in Table I have recently been reported: H.-G. Heine, *Tetrahedron Lett.*, 3411 (1972).

Scheme I



formation occurs *via* cage disproportionation[14] and diffusion followed by benzoyl radical scavenging. An upper limit for disproportionation can be established from the yield of benzaldehyde in the absence of scavenger ($\Phi_{disp} \leq 0.04$, Figure 1). Thus the majority of benzaldehyde formation is due to diffusion ($\Phi_{diff} = 0.44 \pm 0.02 - 0.04 = 0.40$). Loss of optical activity results from cage recombination with racemization as well as from product formation. The dependence of optical activity upon conversion of ketone can be derived from a simplified mechanism (Scheme II).

Scheme II



$$\Phi_{rac}^0 = k_{rac}\tau = k_{rac}(k_{rac} + k_d + k_{PhCHO})^{-1} \qquad (4)$$

$$\Phi^0_{PhCHO} = k_{PhCHO}\tau \qquad (5)$$

$$\log(\alpha^0/\alpha) = (1 + \Phi^0_{rac}/\Phi^0_{PhCHO})\log([1]^0/[1]) \qquad (6)$$

For a kinetically equivalent scheme, Wagner[15] has derived eq 6, where α is the optical rotation, [1] the total ketone concentration, Φ_{rac} the photoracemization quantum yield (eq 4), Φ_{PhCHO} the total quantum yield for benzaldehyde formation (eq 5), and the superscript denotes values at zero conversion. When our results are plotted according to eq 6, a line with a slope of 1.75 ± 0.23 is obtained (Figure 3). From the slope and benzaldehyde quantum yield, the quantum yield for racemization is obtained ($\Phi_{rac} = 0.33 \pm 0.04$).

The sum of the quantum yields for benzaldehyde formation and racemization is 0.77 ± 0.06. Thus approximately 20% of the ketone excited states return to unracemized ketone (k_{ret}). In terms of Scheme I, retention can result from either nonradiative decay of the triplet state (k_d) or recombination of the radical pair (k_{comb}) prior to loss of chirality (k_{rot}). Although our results cannot distinguish between these retention mechanisms, we favor the latter explanation for several reasons. Naphthalene quenching of benzaldehyde formation from (±)-**1** gives a linear Stern–Volmer plot from which a value of $1/\tau = k_\alpha + k_d = 2.1 \times 10^7$ sec^{-1} is obtained (Table I). If nonradiative decay is responsible for retention, then $k_d \sim 5 \times 10^6$ sec^{-1}. This value is considerably larger than previously reported decay rate constants for aromatic ketones in benzene solution.[2b] Furthermore, the benzyl phenyl ketones in Table I have nearly identical quantum yields for benzaldehyde formation, yet have lifetimes which vary by a factor of 75.[3] It is highly unlikely that nonradiative decay rate constants for ketones of such similar structure would also show such large variation. Thus we conclude that α cleavage of ketone **1** is totally efficient and that retention of optical activity results from cage recombination prior to rotation.

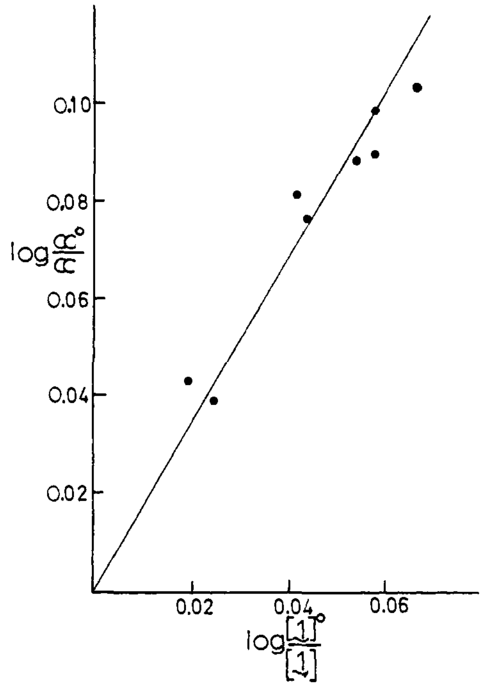


Figure 3. Optical activity of (*S*)-(+)-2-phenylpropiophenone as a function of conversion.

Relative rate constants for the cage reaction of the benzoyl and 1-phenylethyl radicals can be obtained from the quantum yields and the usual steady-state approximation.[16] From the results in Table II several

Table II. Relative Rates for Radical-Pair Reactions

Process	Φ	k_{rel}
$k_{comb}{}^a$	0.56	1
k_{diff}	0.40	0.72
k_{disp}	0.04	0.072
$k_{rot}{}^b$		1.3

[a] $\Phi_{comb} = \Phi_{rac} + \Phi_{ret}$. [b] Obtained from the steady-state approximation as derived in ref 16.

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(14) Müller and Closs have obtained evidence for cage disproportionation based on nmr emission from the vinyl protons of styrene: K. Müller, private communication.

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

(16) (a) K. R. Kopecky and T. Gillian, *Can. J. Chem.*, **47**, 2371 (1969); (b) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970); (c) J. P. Engstrom and F. D. Greene, *J. Org. Chem.*, **37**, 968 (1972).

important conclusions can be drawn. First, the rate of cage reactions ($k_{\mathrm{comb}} + k_{\mathrm{disp}}$) is comparable to that for diffusion.[17] Second, the rate of cage recombination is comparable to that for rotation (k_{rot}) of the 1-phenylethyl radical. Finally, since α cleavage occurs from the triplet state, it follows that spin flipping in the initially formed triplet radical pair must be at least as fast as diffusion. The effect of spin on the stereoselectivity of 1,4-biradical[18] and radical-pair[19] reactions is a topic of current controversy. The lower stereoselectivity of triplet *vs.* singlet biradicals ("spin correlation") has been attributed to the longer lifetime of the triplet species, which must undergo spin inversion prior to bond formation.[18a] Recently, Stephenson[18c] has suggested that higher rotational barriers in the singlet biradical may be responsible for the differences in stereoselectivity. In contrast to the large spin effects observed for biradical reactions, the effect of spin on the extent of radical pair cage reactions is either small or nonexistent.[19]

The conclusion that the rates of cage combination and rotation of the 1-phenylethyl radical are comparable ($k_{\mathrm{rot}}/k_{\mathrm{comb}} = 1.3$) is based on the assumption that α cleavage of the ketone excited state is totally efficient. If radiationless triplet decay is responsible for part of the quantum inefficiency, then a larger $k_{\mathrm{rot}}/k_{\mathrm{comb}}$ ratio would be obtained. For example, if it is assumed that radiationless decay is responsible for half of the inefficiency, then $k_{\mathrm{rot}}/k_{\mathrm{comb}} = 2.3$. Even this value is much smaller than those obtained for thermal decomposition of acyclic esters and azo compounds ($k_{\mathrm{rot}}/k_{\mathrm{comb}} \sim 14$).[16] This difference may be due to the absence of an inert molecules (N_2 or CO_2) separating the radical pair and/or the lower temperature in our experiment.[16,20,21] Finally, quantum yields for α cleavage product formation from ketones will be determined by the competition between cage recombination and product forming reactions. This competition is probably not a simple function of ketone structure or radical stabilities.

Experimental Section

Materials. Racemic 2-phenylpropiophenone was synthesized *via* alkylation of 2-phenylacetophenone (Aldrich) using the method of Meyer and Oelkers.[22] Recrystallization from hexane followed by vacuum sublimation gave crystals of >99% purity by vpc, mp 49° (lit.[20] mp 53°). (*S*)-(+)-2-Phenylpropiophenone was synthesized by the method of McKenzie, *et al.*,[7] starting with L-alanine, and purified by vacuum sublimation, mp 31–32° (lit.[7] mp 34–35°), $[\alpha]^{25}\mathrm{D}$ + 257° (lit.[7] $[\alpha]^{25}\mathrm{D}$ +260°). 2-Phenylacetophenone, 2-(*p*-tolyl)-*p*-methylacetophenone, 2-*p*-tolylacetophenone, and 2-phenyl-*p*-methylacetophenone were synthesized *via* standard Grignard procedures using benzyl chlorides and benzaldehydes followed by Jones oxidation of the resulting alcohols. Dodecanethiol (Aldrich) was distilled prior to use. Naphthalene (Baker Photograde) was used as received. Benzene (Fisher Spectranalyzed) was distilled from phosphorus pentoxide prior to use.

Quantum Yields and Kinetics. Quantum yields were determined on degassed benzene solutions containing 0.1 *M* ketone and 0.03 *M* dodecanethiol contained in Pyrex ampoules. The ampoules were irradiated at 25° on a merry-go-round apparatus using a 200-W medium-pressure mercury lamp and Corning filters 7-54 and 0-52 to isolate the 365-nm irradiation. Yields of benzaldehyde formation and loss of ketone were determined by vpc analysis on a calibrated 7 ft × 0.125 in. column of 10% FFAP on DMSC-treated Chromosorb G. Light intensities were determined using both benzophenone–benzhydrol[23] and potassium ferrioxalate actinometry.[24] Optical rotations were measured from 600 to 460 nm using a Cary 60 spectrometer. Rotations at 15 wavelengths were used to obtain average values for the loss of rotation of each sample.

Crossover Experiment. Irradiation of an equiabsorbing mixture of 2-phenylacetophenone and 2-(*p*-tolyl)-*p*-methylacetophenone in degassed benzene to ~5% conversion results in the formation of 2-*p*-tolylacetophenone ($\Phi = 0.027$) and 2-phenyl-*p*-methylacetophenone ($\Phi = 0.023$) as well as 1,2-diphenylethane ($\Phi = 0.015$), 1,2-di-*p*-tolylethane ($\Phi = 0.015$), 1-phenyl-2-*p*-tolylethane ($\Phi = 0.029$), and smaller amounts of benzils and benzaldehyde. The addition of 0.03 *M* dodecanethiol prior to irradiation completely supresses the formation of ketones and benzils, has little effect on 1,2-diarylethane formation, and greatly enhances benzaldehyde formation.

Acknowledgment. The authors thank Dr. K. Müller for helpful discussion and the referees for constructive suggestions.

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(17) This conclusion is independent of any assumptions as to the origin of retention of optical activity.

(18) (a) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968); (b) N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969); (c) L. M. Stephenson and T. A. Gibson, *ibid.*, **94**, 4599 (1972).

(19) (a) J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964); (b) S. A. Weiner, *ibid.*, **93**, 425 (1971); (c) T. Koenig and J. A. Hoobler, *Tetrahedron Lett.*, 1803 (1972).

(20) H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967), and references therein.

(21) A recent report by R. A. Johnson and S. Seltzer [*J. Amer. Chem. Soc.*, **95**, 939 (1973)] provides a value of $k_{\mathrm{rot}}/k_{\mathrm{comb}} = 0.94$ for the cage recombination of a thermally generated azophenyl-9-methylfluorenyl radical pair.

(22) V. Meyer and L. Oelkers, *Chem. Ber.*, **21**, 1297 (1888).

(23) W. M. Moore and K. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).

(24) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).