path of electrophilic additions. However, in general this treatment is an oversimplification and it is still impossible at this time to present an overall theory that adequately treats all such electrophilic additions.

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Mechanistic Photochemistry of γ-Hydroxy-γ-phenylbutyrophenone. The Nature of the 1,4-Biradical Intermediate

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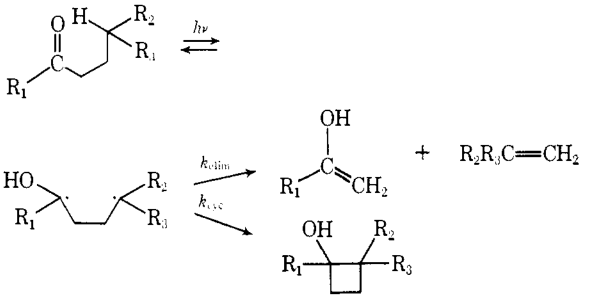
Abstract: The mechanistic photochemistry of γ-hydroxy-γ-phenylbutyrophenone (**1**) and its β,γ-dideuterio derivative (**2**) has been investigated. The presence of a biradical intermediate formed by γ-deuterium abstraction upon photolysis of **2** has been established by the formation of deuterium–hydrogen exchanged ketone **3**. A deuterium isotope effect on the rate constant for γ-hydrogen abstraction of 1.7 is observed. A kinetic analysis shows that bond rotations in the biradical are about five times slower than reabstraction of hydrogen or elimination to give acetophenone.

Reactions postulated to proceed through 1,4-biradical intermediates[1] have attracted considerable attention. Among the better known examples of such reactions are the thermal[2] and photochemical[2b,3] 2 + 2 addition of haloethylenes to dienes, the thermal and photochemical decomposition of cyclic azo compounds,[4] the 2 + 2 photoaddition of ketones[5] and thioketones[6] to olefins, the isomerization of olefins by "energy transfer" from carbonyl excited states,[5c,f,7] and the type II photoelimination and cyclization reactions of carbonyl compounds having a γ-hydrogen.[8-19] Previous investigations have established that the biradical intermediates formed by γ-hydrogen abstraction by the n,π* carbonyl excited state of dialkyl and aryl alkyl ketones give rise to both elimination and cyclization products (eq 1). Early evidence for the biradical intermediate was provided by (1) the formation of both a vinylcyclobutanol and a cyclohexenol from 6-hepten-2-one,[8] (2) observation of an inverse deuterium isotope effect on the quantum yield of dialkyl ketone photoelimination,[9,10] and (3) the formation of cyclization and elimination products with identical rate constants for a number of ketones.[10-12] The fact that some carbonyl compounds optically active at the γ-carbon form cyclization or elimination products with some retention of configuration[13,14] has caused speculation that a concerted reaction mechanism might be involved in these reactions. However, small amounts of retention of configuration during cyclization are compatible with the formation of a short-lived biradical for which cyclization occurs faster than bond rotation.[15] The recent study of dialkyl ketone photochemistry by Yang and Elliott[16] has shown that whereas triplet alkanones react with concurrent racemization at the γ-carbon, singlet alkanones do not. Thus, the triplet biradical undergoes



(1)

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[1] Unfortunately, the terms biradical and diradical have been used loosely and interchangeably.

[2] (a) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964); (b) P. D. Bartlett, *Science*, **159**, 833 (1968); (c) P. D. Bartlett and G. E. H. Wallbillich, *J. Amer. Chem. Soc.*, **91**, 409 (1969); (d) P. Lomas and P. Tarreut, *J. Org. Chem.*, **34**, 323 (1969).

[3] N. J. Turro and P. D. Bartlett, *ibid.*, **30**, 1849 (1965).

[4] P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

[5] (a) D. A. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (b) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **90**, 6863 (1968); (c) N. C. Yang, *Photochem. Photobiol.*, **7**, 767 (1968); (d) E. Albone, *J. Amer. Chem. Soc.*, **90**, 4663 (1968); (e) S. H. Schroeter, *Chem. Commun.*, 12 (1969); (f) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970).

[6] A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 161 (1969); 238 (1969); *J. Amer. Chem. Soc.*, **90**, 7038 (1968).

[7] J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

[8] N. C. Yang, A. Marduchowitz, and D. H. Yang, *ibid.*, **85**, 1017 (1963).

[9] A. Padwa and W. Bergmark, *Tetrahedron Lett.*, 5795 (1968).

[10] D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

[11] J. A. Barltrop and J. D. Coyle, *ibid.*, **90**, 6584 (1968).

[12] F. D. Lewis and N. J. Turro, *ibid.*, **91**, 311 (1970); *Tetrahedron Lett.*, 5845 (1968).

[13] K. H. Schulte-Elte and G. Ohloff, *ibid.*, 1143 (1964).

[14] J. E. Gano, *ibid.*, 2549 (1969).

[15] J. Orban, K. Schaffner, and O. Jeger, *J. Amer. Chem. Soc.*, **85**, 3033 (1963).

[16] (a) N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969); (b) N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969).

[17] (a) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966); (b) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

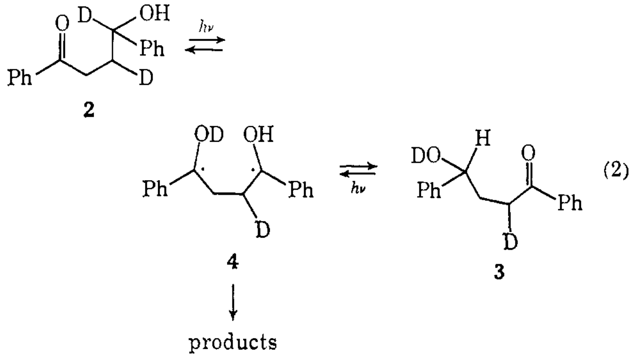
[18] P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5898 (1968).

[19] P. J. Wagner and H. N. Schott, *ibid.*, **91**, 5383 (1969).

extensive bond rotation prior to further reaction; however, the singlet biradical, if formed, does not do so. Unfortunately no information on the optical activity of the cyclization products was reported.

Wagner[17–19] originally proposed that the inefficiency of product formation from simple phenyl alkyl ketones in nonpolar solvents ($\varphi < 0.5$) was due to reversion of the biradical to the ground-state ketone on the basis of two major lines of reasoning. First, inefficiency due to competition of triplet decay with γ-hydrogen abstraction would require rate constants for triplet decay comparable to those for hydrogen abstraction ($k_r \gtrsim 10^8\ \text{sec}^{-1}$). As the n,π* triplet states of aromatic ketones without γ-hydrogens decay with rate constants on the order of $10^6\ \text{sec}^{-1}$ [20] such an explanation is considered unreasonable.[17b] Second, polar solvents increase the quantum yield of product formation to near unity for phenyl alkyl ketones.[17–19,21] This effect is explained[17b] as being due to the formation of a strong hydrogen bond from the hydroxyl proton of the biradical to the solvent which retards back transfer of the proton but not cyclization or elimination.

In spite of the extensive investigations of the type II reactions of aromatic ketones, little is known about the factors which govern the reactions of the 1,4-biradical intermediates. This situation is due, at least in part, to the fact that γ-hydrogen abstraction is the rate-determining step in these reactions so that biradical reactivity can only be inferred from product studies. As part of a study designed to provide information about the lifetime and behavior of 1,4-biradical intermediates, the photochemical behavior of γ-hydroxy-γ-phenylbutyrophenone (**1**) and its β,γ-dideuterio derivative (**2**) have been investigated. Compound **1** has a unique structure which leads to a totally symmetric biradical intermediate. The biradical intermediate (**4**) from **2** can undergo hydrogen or deuterium reabstraction to give either **2** or the hydrogen–deuterium exchanged product **3** (eq 2) depending on whether bond rotations precede reabstraction or not.



Results

Products and Quantum Yields. γ-Phenyl-γ-hydroxybutyrophenone (**1**) and its β,γ-dideuterio derivative (**2**) were prepared by reduction of dibenzoylethylene with lithium aluminum hydride[23] or lithium aluminum deuteride (99% D). The deuterated compound is presumably formed as a tetradeuterio derivative, but aqueous acid work-up removes the hydroxyl and α-deuteriums. The nmr spectrum of **2** shows a two-proton doublet at δ 3.08 and a one-proton triplet at 2.15 whereas **1** has a two-proton triplet at 3.08, a two-proton quartet at 2.15, and a one-proton triplet at 4.8. The mass spectrum of **2** shows it to be 97.7% d_2 (*m/e* 242) and 2.3% d_1 (*m/e* 241). If the deuterium is equally distributed between the β- and γ-carbons, then each position is 98.8% deuterated. The major fragments in the mass spectrum of **2** correspond to loss of water, α cleavage, and β cleavage (McLafferty rearrangement) in agreement with the assigned structure. The infrared spectra of **1** and **2** were essentially identical having free O–H stretching at 3630 cm^{-1} and intramolecular hydrogen-bonded O–H stretching at 3470 cm^{-1} with $\epsilon(\text{OH})^b/\epsilon(\text{OH})^f = 0.45$. Ketones **1** and **2** have normal aromatic carbonyl ultraviolet absorption spectra with ϵ_{3200} 58 and ϵ_{2780} 880. The emission spectrum of **2** at 77°K in an EPA glass was similar in appearance to that of acetophenone except that each major band was split into two components. This may be due to emission from intramolecularly hydrogen bonded and nonhydrogen bonded molecules.

Photolysis of **1** or **2** in degassed benzene solution results in the formation of 2 mol of acetophenone for each mole of consumed starting material. A zero-order rate plot for the formation of acetophenone (Figure 1) is linear to over 50% conversion. The mass balance is excellent (Figure 1) and no evidence for a cyclic product (*cis*- or *trans*-1,2-diphenylcyclobutane-1,2-diol) was obtained by either vpc or nmr analysis of the photolysis mixtures. All quantum yields were determined at 3130 Å on degassed solutions irradiated in parallel with benzophenone–benzhydrol actinometer solutions.[24] The quantum yields for acetophenone for-

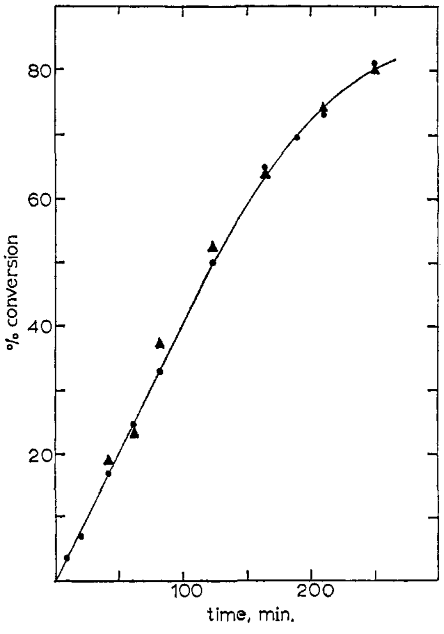


Figure 1. Acetophenone formation (●) and loss of ketone **1** (▲) as a function of length of irradiation.

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(20) (a) W. C. K. Clark, A. D. Litt, and C. Steel, *Chem. Commun.*, 1087 (1969); (b) P. J. Wagner, *Mol. Photochem.*, **1**, 71 (1969); (c) F. D. Lewis, *Tetrahedron. Lett.*, 1373 (1970).

(21) Exceptions to such solvent dependent behavior have been noted for aryl alkyl ketones with electron-withdrawing substituents[19] and for α-alkoxyacetophenones[12] as well as esters.[22]

(22) P. Ausloos, *J. Amer. Chem. Soc.*, **80**, 1310 (1958).

(23) R. E. Lutz and J. S. Gillespie, *ibid.*, **72**, 2002 (1950).

(24) W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962).

mation from **1** and **2**, normalized for formation of 2 mol of acetophenone per mole of hydroxy ketone, are 0.49 ± 0.02 and 0.50 ± 0.02, respectively. The quantum yield for acetophenone formation from **1** and **2** is independent of the initial concentration of hydroxy ketone (0.03–0.12 *M*) and the volume per cent of added *t*-butyl alcohol (1–67%). The effect of temperature on the quantum yield of acetophenone formation from **1** was also investigated. The results are given in Table I along with those for valerophenone photoelimination run as a control. The agreement of the valerophenone quantum yields with literature results[11,18] is indicative of the accuracy of the method used for quantum yield determination.

Table I. Temperature Dependence of Quantum Yields for Acetophenone Formation from γ-Hydroxy-γ-phenylbutyrophenone and Valerophenone

Temp, °C	Φ_{II} for **1**	Φ_{II} for PhCOBu-*n*
20	0.49	0.33
33	0.49	
43	0.47	0.33
55	0.49	0.31

Intersystem crossing efficiencies (Φ_{ST}) of **1** and **2** were determined by the method of Lamola and Hammond.[25] The 1.0 *M cis*-piperylene used for triplet counting is sufficient to quench 88% of the triplets of **1** and 93% of the triplets of **2**, based on the kinetic results given below.[26] Thus the observed extents of sensitized piperylene isomerization relative to acetophenone (Φ_{ST} = 1.0)[25] for **1** = 0.86 and **2** = 0.93 correspond to intersystem crossing ratios of 1.0 ± 0.05 for both **1** and **2**.

Rate Constants. Photolysis of **1** and **2** in degassed benzene solution in the presence of varying amounts of *trans*-piperylene resulted in the linear Stern–Volmer plots (φ_0/φ *vs.* [quencher]) shown in Figure 2. The slopes of the Stern–Volmer plots equal $k_q\tau$ where k_q is the rate constant for quenching of the ketone triplet by piperylene and τ is the ketone triplet lifetime. Assumption of the value 5×10^9 M^{-1} sec^{-1} for k_q[17] allows calculation of τ or $1/\tau$. Table II gives the pertinent kinetic data.

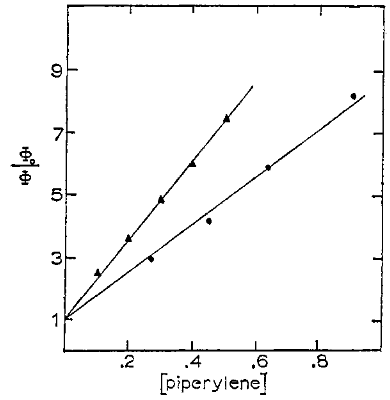

Figure 2. Stern–Volmer plots for quenching of acetophenone formation from **1** (●) and **2** (▲).

Table II. Kinetic Data for γ-Hydroxy-γ-phenylbutyrophenones

Ketone	Φ_0	$k_q\tau$, M^{-1}	$1/\tau$, sec^{-1}
1	0.49 ± 0.02	7.7	6.7×10^8
2	0.50 ± 0.02	12.8	3.9×10^8

Deuterium–Hydrogen Exchange. Degassed benzene solutions of **2** were irradiated for increasing intervals of time. After vpc analysis for the extent of conversion, the samples were washed with water to remove any deuterium bound to oxygen which would result from disproportionation of the biradical intermediate to the deuterium exchanged hydroxy ketone **3** (eq 2). The residual hydroxy ketone was then isolated and recrystallized prior to mass spectral analysis for loss of deuterium. A control sample was treated in an identical manner except that it was not irradiated. The abundances of **3** (*m/e* 241) relative to **2** (*m/e* 242 = 100%) corrected for the natural isotopic abundance of ^{13}C are given in Table III. The values are the average of two or more scans of the molecular ion region of each sample. Knowing the amount of acetophenone formed in each run, the percentage composition for each component can be calculated. Since the quantum yield for acetophenone formation was previously shown to be independent of extent conversion (Figure 1), the quantum yields for formation of **3** can be calculated from the percentage compositions. With the exception of the highest conversion run, the quantum yields are within experimental error of the average value φ_3 = 0.040 ± 0.005.

Table III. Deuterium Exchange Analysis for the Photolysis of the γ-Deuterio Ketone **2**

Run	Abundance of **3**, %	Acetophenone, %	% **2**	% **3**	Φ_3
0	2.33 ± 0.25	0	100	0	0
1	3.45 ± 0.18	11.8	87.2	0.99	0.042
2	5.05 ± 0.25	22.5	75.4	2.08	0.046
3	6.61 ± 0.50	35.5	61.9	2.64	0.037
4	8.77 ± 0.12	46.6	50.1	3.30	0.036
5	10.6 ± 0.50	60.3	36.6	3.06	0.025

Discussion

Discussion of the preceding results for the γ-hydroxy-γ-phenylbutyrophenones **1** and **2** is best accomplished in terms of eq 3–9 where A is the ketone, Q an added quencher, Bi_3 is the initially formed triplet biradical, and Bi the singlet biradical which cleaves to form acetophenone or disproportionates to the ground-state ketone (A_0) or, in the case of **2**, to the deuterium exchanged ketone (A_0'). The observed quantum yield for product formation (φ_{obsd}) can be expressed as the product of the efficiencies of formation of the

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(25) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(26) Use of piperylene concentrations greater than 1 *M* was purposely avoided; see R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 211 (1970).

$$\mathrm{A_0} \xrightarrow{h\nu} \mathrm{A_1} \xrightarrow{k_{\mathrm{ST}}} \mathrm{A_3} \tag{3}$$

$$\mathrm{A_3} \xrightarrow{k_{\mathrm{d}}} \mathrm{A_0} \tag{4}$$

$$\mathrm{A_3} + \mathrm{Q} \xrightarrow{k_{\mathrm{q}}} \mathrm{A_0} + \mathrm{Q_3} \tag{5}$$

$$\mathrm{A_3} \xrightarrow{k_{\mathrm{r}}} \mathrm{Bi_3} \tag{6}$$

$$\mathrm{Bi_3} \xrightarrow{k_{\mathrm{ST'}}} \mathrm{Bi} \tag{7}$$

$$\mathrm{Bi} \xrightarrow{k_{\mathrm{II}}} 2\mathrm{PhCOCH_3} \tag{8}$$

$$\mathrm{Bi} \xrightarrow{k_{-\mathrm{r}}} \mathrm{A_0} \tag{9}$$

$$\mathrm{Bi} \xrightarrow{k_{-\mathrm{r}'}} \mathrm{A_0}' \tag{10}$$

triplet state (φ_{ST}), formation of the biradical intermediate (φ_{Bi}) by γ-hydrogen abstraction, and formation of products from the biradical (φ_{P}). The triplet

$$\varphi_{\mathrm{obsd}} = \varphi_{\mathrm{ST}}\varphi_{\mathrm{Bi}}\varphi_{\mathrm{P}} \tag{11}$$

counting studies showed that the triplets of **1** and **2** are formed with unit efficiency. Hence the observed quantum yield is the product of φ_{Bi} and φ_{P} (eq 12).

$$\varphi_{\mathrm{obsd}} = \varphi_{\mathrm{Bi}}\varphi_{\mathrm{P}} = \left(\frac{k_{\mathrm{r}}}{k_{\mathrm{r}} + k_{\mathrm{d}}}\right)\left(\frac{k_{\mathrm{II}} + k_{-\mathrm{r}}'}{k_{\mathrm{II}} + k_{-\mathrm{r}} + k_{-\mathrm{r}}'}\right) \tag{12}$$

The quantum yield for acetophenone formation from **1** and **2** is 0.50 and the quantum yield for deuterium exchange from **2** is 0.040 ± 0.005 (Table III). Hence the total observed quantum yield for product formation from **2** (0.54 ± 0.02) is substantially less than unity. The inefficiency of the overall reaction can be due to either inefficiency in the formation of the biradical ($\varphi_{\mathrm{Bi}} < 1$) or inefficiency in the formation of products from the biradical ($\varphi_{\mathrm{P}} < 1$).

The quantum yield for biradical formation is of crucial importance to further discussion and hence merits comment. The values for $1/\tau$ given in Table II represent the sum of all processes leading to destruction of the ketone triplet states. A number of aromatic ketones which do not have γ-hydrogens have apparent unimolecular triplet decay rate constants of less than 10^6 sec^{-1} in benzene solution.[20] Values of k_{d} three orders of magnitude greater than this would be required for φ_{Bi} to be less than unity. Such a possibility has been considered and rejected for phenyl alkyl ketones.[12,17] However for the γ-hydroxy ketones **1** and **2** the possibility of triplet deactivation *via* interaction with the γ-hydroxyl group exists. The plausibility of such interaction is demonstrated by the infrared spectra of **1** and **2**. Using the absorbtivities of free and bonded hydroxyl to obtain a rough estimate of relative concentrations of these species[27] shows that about 30% of ground-state **1** and **2** are intramolecularly hydrogen bonded. The strength of the 1,4-intramolecular hydrogen bond is reflected by the large difference in frequency between the free and bonded absorptions. Thus, there is substantial interaction between the carbonyl ground state and the γ-hydroxyl proton. However, several lines of evidence indicate this hydrogen bonding does not affect the quantum yield for biradical formation. First, alcoholic solvents increase the quantum yield for photoelimination from simple phenyl alkyl ketones.[11,17-19,21] Thus hydrogen bonding of the carbonyl ground state does not necessarily diminish triplet-state reactivity. Second, adding *t*-butyl alcohol to the benzene solutions of **1** or **2** does not alter the quantum yield. Since the added *t*-butyl alcohol should compete with the γ-hydroxyl group in hydrogen bonding to the carbonyl, an increase in quantum yield would be expected with added *t*-butyl alcohol if intramolecular hydrogen bonding reduced the quantum yield for γ-hydrogen abstraction. Finally, since $\varphi_{\mathrm{II}} = 0.50 \pm 0.02$ for both **1** and **2** while their $1/\tau$ values differ by nearly a factor of two, inefficiency in the biradical formation would require that k_{d} change in going from **1** to **2** by exactly the amount required to keep φ_{Bi} constant (eq 12). Since deuteration on the β- and γ-carbons should not alter intramolecular hydrogen bonding, such a likelihood is highly improbable. We thus conclude that the inefficiency of product formation is due to reversion of the 1,4-biradical intermediate to starting material rather than to inefficient formation of the biradical.

If the triplet state reacts predominantly through γ-hydrogen abstraction, then the $1/\tau$ values given in Table II are the rate constants for γ-hydrogen abstraction. The rate constant for **1** (6.7×10^8 sec^{-1}) is slightly greater than that for γ-phenylbutyrophenone (4.0×10^8 sec^{-1} [28]). The ability of an α-oxygen to stabilize the biradical intermediate[12] probably accounts for the slightly enhanced rate constant. The deuterium isotope effect on the γ-abstraction reaction is $k_{\mathrm{H}}/k_{\mathrm{D}} = 1.7$. Although deuterium labeling has been widely used in mechanistic studies of type II photoelimination,[10,13-15,29] only the study of Coulson and Yang[10] on 2-hexanone and 2-hexanone-5-*d* provides data on the relative rate constants for hydrogen and deuterium abstraction. Their results indicate that $k_{\mathrm{H}}/k_{\mathrm{D}} = 2.7$ for singlet abstraction and $k_{\mathrm{H}}/k_{\mathrm{D}} = 5.7$ for triplet abstraction. The lower deuterium isotope effect observed for **1** *vs.* **2** probably reflects the greater ease of abstraction of a secondary benzylic hydrogen *vs.* a secondary aliphatic hydrogen. Free-radical hydrogen abstraction reactions are known to show decreasing deuterium isotope effects as the strength of the carbon–hydrogen bond undergoing homolysis is decreased.[30] A fair estimate of exothermicity of biradical formation from excited-state ketones can be obtained, knowing the ketone excited-state energies, by calculating the heat of formation of the ground-state ketone and the biradical.[31] Such a calculation predicts that biradical formation from triplet **1** is ~20 kcal/mol exothermic whereas biradical formation from singlet and triplet 2-hexanone is ~15 kcal/mol and ~10 kcal/mol exothermic, respectively. The greater exothermicity of biradical formation from **1** is thus in accord with the smaller kinetic isotope effect for γ-hydrogen abstraction.

Whereas a positive deuterium isotope effect is observed for the γ-abstraction reaction of **1** and **2**, there is no measurable isotope effect on the quantum yield of product formation. Negative deuterium isotope effects on the quantum yields of type II photoelimination have been observed for dialkyl ketones[9,10]

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(27) M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965).

(28) P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5896 (1968).

(29) (a) R. Srinivasan, *ibid.*, **81**, 5061 (1959); (b) R. P. Borkowski and P. Ausloos, *J. Phys. Chem.*, **65**, 2257 (1961).

(30) K. B. Wiberg and E. L. Motell, *Tetrahedron*, **19**, 2009 (1963).

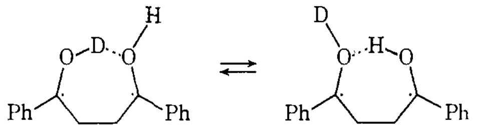
(31) See ref 12 for a description of these calculations.

and arylaroylazetidines.[32] The usual explanation[32] for the increased quantum yield for the deuterated ketones is that reversion of the biradical to the ketone is slower when deuterium rather than hydrogen is being reabstracted. Yang[16] has recently advocated an alternative explanation that deuteration increases the intersystem crossing quantum yield for dialkyl ketones rather than retarding the reabstraction process. Since both **1** and **2** undergo intersystem crossing with unit efficiency, the lack of an isotope effect upon the quantum yield is in best accord with Yang's proposal.

The quantum yields for acetophenone formation from **1** and **2** (Table II) are larger than those for simple phenyl alkyl ketones, but similar to that for γ-phenylbutyrophenone ($\varphi_{II} = 0.49$).[18] Elimination may be more favored relative to disproportionation to starting material for **1** and **2** than for ketones such as valerophenone ($\varphi_{II} = 0.33$) due to the formation of thermodynamically more stable elimination products (2 mol of acetophenone *vs.* acetophenone plus olefin).[12,18] The unusual absence of a cyclization product deserves comment. *trans*-1,2-Diphenylcyclobutane-1,2-diol is a solid with mp 148–150°[33] and should be stable under the photolysis conditions. However no nmr signals with appropriate chemical shifts[33] could be observed in the photolysis mixtures, thus ruling out its formation in greater than 1–2% yield. Factors which determine cyclization to elimination ratios are not well understood; however, steric requirements and radical stabilities have been observed to be important.[11,12]

The quantum yields for acetophenone formation and loss of γ-hydroxy ketone are constant to greater than 50% conversion (Figure 1). Since acetophenone absorbs significant amounts of the 3130-Å irradiation even at moderate conversions, this result implies that energy transfer from acetophenone to the γ-hydroxy ketone is highly efficient. Otherwise a falloff in the quantum yield at lower conversions would be observed. The lack of temperature effect on the quantum yield for photoelimination of **1** indicates that the efficiency of product formation from the biradical is insensitive to temperature. Barltrop and Coyle[11] have attributed the lack of a temperature effect on valerophenone photoelimination to similar activation energies for the elimination and disproportionation reactions.

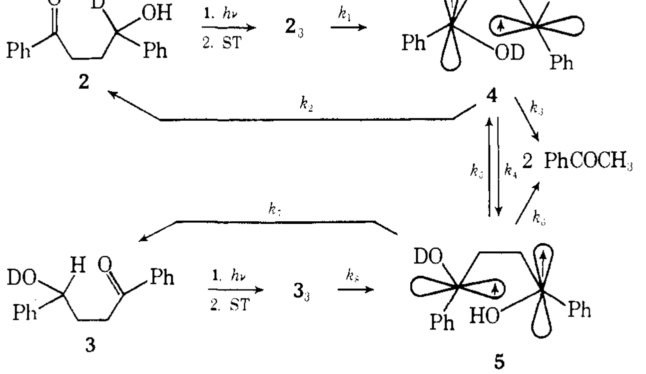
The effects of solvent polarity on the quantum yield for photoelimination have provided considerable information about the nature of biradical intermediates. Although the polar solvent effect is not the same for all carbonyl compounds, the conclusion that the origin of the effect is hydrogen bonding of the biradical seems generally agreed upon.[11,12,17–19,21] Wagner[18,19] has used the variation in quantum yield with alcohol concentration to assign the quantum yield for biradical formation (φ_{Bi}) by assuming that φ_{Bi} equals the maximum observed quantum yield for product formation. This assumption has only been applied to substituted valerophenones and γ-methylvalerophenones. It clearly cannot apply to **1** and **2** since there is no variation in quantum yield with increased *t*-butyl alcohol concentration. This would require that $\varphi_{Bi} = 0.50$, in obvious disagreement with the observation of deuterium–hydrogen exchange from **2** and the arguments given above for biradical formation with unit efficiency. The lack of solvent sensitivity shown by hydroxy ketones **1** and **2** may be due to the fact that intramolecular hydrogen bonding of the biradical is more favorable than intermolecular hydrogen bonding. Intramolecular hydrogen bonding of 1,4-diols is known to be strong in spite of the unfavorable entropy for seven-membered ring formation.[27] Intramolecular hydrogen bonding of the 1,4-biradical intermediates from α-alkoxyacetophenones has been postulated to explain the solvent dependence of the photochemistry of these compounds.[12] The lack of ketone concentration dependence rules out the unlikely possibility that intermolecular hydrogen bonding between hydroxy ketone molecules is important in the photochemistry of **1** and **2**.



(13)

The formation of the deuterium-exchanged product **3** upon photolysis of **2** demonstrates unequivocally the presence of a 1,4-biradical intermediate. In spite of the extensive investigation on the mechanism of aryl alkyl ketone photochemistry, this is the first direct evidence for a biradical intermediate. The per cent of deuterium-exchanged material (Table III) increases with the extent of conversion to acetophenone. This is as expected since the zero-order rate constants for disappearance of **1** and **2** are the same as are their molar absorbances at 3130 Å. The most striking aspect of our results is how little deuterium–hydrogen exchange is observed. If the argument that all the inefficiency in the photolysis of **1** and **2** is due to reversion to the starting ketone is accepted, then the results indicate that the quantum yield for biradical reabstraction to form the original ketone (**2**) is 0.46 while the quantum yield for formation of the deuterium-exchanged ketone (**3**) is only 0.04. Since bond rotations must occur in the biradical in order for **3** to be formed, the relative yields of **2** and **3** are indicative of the relative rate constants for biradical hydrogen abstraction and bond rotation. This is best illustrated by Scheme I. Spin-inversion steps have been left out, but it is assumed that spin inversion must precede either reabstraction (k_2 or k_7) or acetophenone formation (k_3 or k_6). The rather

Scheme I



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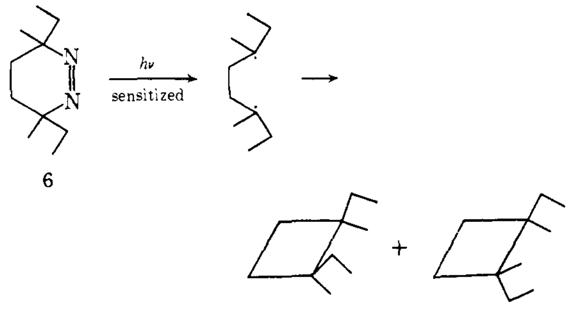
(32) A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, **92**, 107 (1970).
(33) G. W. Griffin and R. B. Hagar, *J. Org. Chem.*, **28**, 599 (1963).

complex kinetic scheme can be greatly simplified.[34] First, the rate constants for interconversion of the biradicals **4** and **5** must be identical ($k_4 = k_5$) since the same partial bond rotations are required going in either direction. Second, the zero-order rate constants for formation of **4** and **5** from **2** and **3** must be the same ($k_1 = k_8$) as must the rate constants for acetophenone formation ($k_3 = k_6$) in view of the identical quantum yields for acetophenone formation from **2** and **1**.[35] Finally, reabstraction and elimination must both occur with approximately the same rate constants ($k_2 \sim k_3$ and $k_6 \sim k_7$) which must be larger than the rate constant for bond rotation in order to explain the acetophenone quantum yield of 0.50 and the small amount of **3** formed by photolysis of **2**. Since $k_6 \cong k_7$ only half of the biradical **5** will give the deuterium-exchanged starting material (**3**). Thus the quantum yield for formation of **5** from **4** is 0.080. This makes the quantum yield for formation of acetophenone from **4** equal to 0.46, in agreement with the assumption that $k_2 = k_3 > k_4$. From these results, the ratio of rate constants for bond rotation and reabstraction (k_4/k_2) is 0.17. A similar result can be obtained by simulating the kinetics with a TR-20 analog computer[36] varying the rate constant k_4 to obtain the best fit for the experimental data. The curves shown in Figure 3 were obtained for values of $k_4/k_2 = 0.20$ and 0.16.

The result that the rate constant for bond rotation in the biradical is about five times slower than that for hydrogen reabstraction is at first surprising. Yang and Elliott's recent study on optically active 5-methyl-2-heptanone showed that the rate constant for bond rotation of their triplet biradical is much faster than the rate constant for hydrogen reabstraction.[16] On the other hand, Bartlett and Porter[4] find that the biradical formed by triplet sensitized decomposition of the *meso* and *d,l* cyclic azo compounds **6** form cyclobutanes with 61 and 65% retention of configuration, respectively (eq 14). This indicates that bond rotations in their



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(14)

biradicals are somewhat slower than the rates of cyclization. Bergman[37] has discussed in considerable detail much of the experimental data on 1,3 and 1,4 biradicals. He observes that there are wide differences in the behavior of biradicals generated in different manners and that the ratio of rate constants for rotation and cyclization decreases as substitution at the radical centers is increased. Clearly the often used assumption that rotational barriers in free radicals are small[2a,5f] (~3 kcal/mol) is a gross oversimplification. Norman and Gilbert[38] have reviewed a number of cases in which rotation about radical centers is clearly hindered. In addition to steric hindrance to rotation in the biradical (**4**), intramolecular hydrogen bonding of the type shown in eq 13 could substantially lower the rate of rotation of the biradical. Such hydrogen bonding is not possible for biradicals formed by γ-hydrogen abstraction from ketones not possessing a γ-hydroxyl group This factor may thus explain the difference between our observations and those of Yang and Elliott.[16]

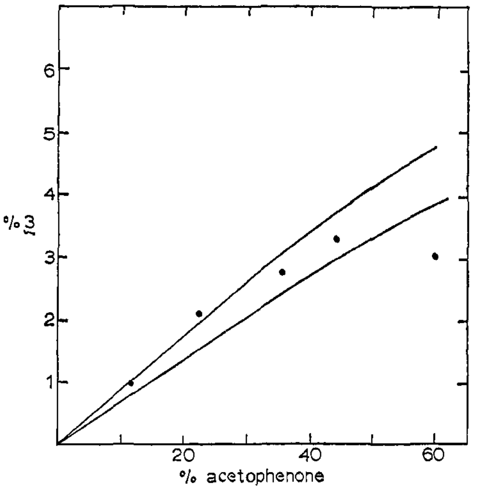

Figure 3. % deuterium exchange *vs.* % acetophenone formation; experimental points and simulated kinetics with $k_4/k_2 = 0.20$ (upper curve) and $k_4/k_2 = 0.16$ (lower curve).

In summary, the existence of a biradical intermediate formed by abstraction of a γ-hydrogen by a triplet phenyl alkyl ketone has been unequivocally established. The biradical was found to undergo elimination and reabstraction of hydrogen approximately five times faster than bond rotation at the radical centers. The unique structural features of ketones **1** and **2** which were essential to the present study, namely the γ-hydroxyl group, make any attempt at generalizing our results to all aryl alkyl ketones hazardous. For example, bond rotations in biradical intermediates from simple aryl alkyl ketones may be more rapid than those observed in this study. One conclusion that may be drawn is that bond rotations in biradicals need not necessarily be faster than the reactions of the biradical. Thus the formation of cyclization and elimination products from optically active carbonyl compounds with partial retention of configuration[13-15] is not inconsistent with a biradical mechanism. Further investigations of 1,4-biradical intermediates designed to extend the present study are currently in progress.

Experimental Section

Preparation of Ketones. γ-Phenyl-γ-hydroxybutyrophenone (**1**) was prepared using the method of Lutz and Gillespie[23] by reduction of dibenzoylethylene with a small excess of lithium aluminum

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(34) This simplification is possible because the rate of bond rotation is slow relative to elimination and reabstraction. A complete steady-state analysis of a similar kinetic scheme is given in R. C. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

(35) Compound **3** should have the same zero-order rate constant for acetophenone formation as **1** since γ-hydrogen abstraction is involved in both cases.

(36) Electronic Associates, Inc., W. Long Branch, N. J.

(37) See Bergman and Carter, ref 34.

(38) R. O. C. Norman and B. C. Gilbert, *Advan. Phys. Org. Chem.*, **5**, 53 (1967).

hydride (mp 87-89°, lit.[23] 92-93°). The deuterated compound (**2**) was prepared by reduction of dibenzoylethylene with lithium aluminum deuteride-d_4 99% D (Alfa Inorganics, mp 84-85°). Melting points are uncorrected. Infrared spectra were recorded on a Beckman IR 10 spectrophotometer, ultraviolet spectra on a Cary 15 spectrophotometer in cyclohexane, emission spectra on a Perkin-Elmer MPF-2A with phosphorescence attachment in an ether-isopentane-ethanol (EPA) glass, and mass spectra on a CEC 21-104 mass spectrometer with an ionization voltage of 15 eV. The structures assigned to **1** and **2** are in agreement with their ir, uv, nmr, and mass spectra.

Quantum Yields. Solutions 0.05 *M* in ketone and about 0.005 *M* in tetradecane internal standard were degassed and sealed under vacuum in 13 mm o.d. Pyrex tubes. The tubes were photolyzed on a merry-go-round apparatus at 25 ± 2° using a Hanovia 450-W medium pressure mercury lamp and a potassium chromate filter solution to isolate 3130-Å irradiation. Photolyses were carried to less than 10% except when dependence on extent of conversion was studied. The photolyzed solutions were analyzed for acetophenone formation and loss of starting material on a Hewlett-Packard 5750 dual flame gas chromatograph with a calibrated 5 ft × $^{1}/_{8}$ in. column of 4% QF 1 and 1% Carbowax 20 M on Chromosorb G. Vpc traces were analyzed with a Gelman planimeter. Benzophenone-benzhydrol actinometers[24] were photolyzed simultaneously and analyzed at 3600 Å using a Beckman DU spectrophotometer with Gilford attachment Model 222. Variable-temperature studies employed the same apparatus immersed in a water bath thermostated to ±1°. Reported quantum yields are the result of multiple vpc analyses of one or more solutions, overall accuracy ±5%. Light intensities of approximately 5 × 10^{-6} Einstein l.$^{-1}$ sec^{-1} were used in all cases.

Quenching Studies. Samples were prepared and analyzed as for quantum yield determination except that varying amounts of *trans*-piperylene (Chemical Samples) were added to the solutions. Five concentrations of piperylene, in addition to blanks containing no piperylene, were used for each Stern-Volmer plot.

Intersystem Crossing Quantum Yields. The method of Lamola and Hammond[25] was used. Degassed benzene solutions of 0.05 *M* acetophenone and **1** and **2** each 1.0 *M* in *cis*-piperylene (Chemical Samples) were irradiated for 6 hr at 3130 Å. Analysis for piperylene isomerization was on a 10 ft × $^{1}/_{8}$ in. column of 25% sulfolane on Chromosorb P at 40°.

Mass Spectra Samples. Samples were prepared, degassed, irradiated for varying periods, and analyzed in the same way as for quantum yield determination. The benzene solutions were then washed twice with 10 ml of water and dried with magnesium sulfate, and the benzene was removed. The residue was recrystallized at 0° from chloroform-pentane and the crystalline product analyzed on a CEC 21-104 mass spectrometer with an ionization voltage of 15 eV. The molecular ion region was scanned several times for each sample and the isotopic composition calculated as an average value corrected for the natural abundance of ^{13}C.

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Mechanisms of SNi Reactions. Ion Pair Return in the Decomposition of Aralkyl Thiocarbonates[1a]

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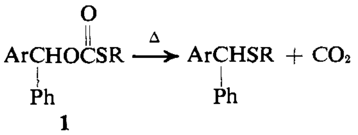
Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received February 5, 1970*

Abstract: On being heated at elevated temperatures in inert solvents *p*-chlorobenzhydryl S-alkyl or S-aryl thiocarbonates decompose to give carbon dioxide and a *p*-chlorobenzhydryl sulfide (eq 1). Use of both optically active and ^{18}O-labeled esters and recovery of the thiocarbonate remaining after partial decomposition show that this reaction is accompanied by some racemization of the thiocarbonate and also by equilibration of the ^{18}O label between the alkyl and acyl oxygens of the ester. Since other evidence indicates the involvement of ion pair intermediates in the decomposition, measurements of the rate of ^{18}O equilibration (k_{eq}) and of loss of optical activity (k_α) can be compared with rates of decomposition (k_d) to determine both the importance of ion pair return to reactants under various conditions and also the stereochemistry of the return process. The results reveal that the fraction of ion pairs undergoing return to thiocarbonate is somewhat larger in bromobenzene (89% for the S-phenyl ester) than it is for the same ester in the better ionizing solvent benzonitrile (77%), and also that in benzonitrile the percentage return from either the S-methyl or S-cyclohexyl ester is larger (90%) than for the S-phenyl compound. Although return with retention of configuration predominates for all three esters, it accounts for a smaller percentage of the total return in the case of the S-alkyl and cycloalkyl esters, return with racemization being almost nonexistent for the S-phenyl ester. The significance of these results and their interpretation in terms of both current theories of ion pair behavior and the mechanism (eq 2) of the thiocarbonate decomposition are discussed.

On being heated in inert solvents at 130-170° aralkyl thiocarbonates (**1**) undergo decomposition to an aralkyl sulfide and carbon dioxide (eq 1).[2] The dependence of the rate of this reaction on solvent ionizing power and on the structure of the aralkyl group indicates that the reaction involves heterolysis of the aralkyl-O bond and ion pair intermediates.[2] Furthermore, the variation in the rate of decomposition with



$$\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{ArCH}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR} \xrightarrow{\Delta} \underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{ArCH}}\mathrm{SR} + \mathrm{CO_2} \qquad (1)$$

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (b) To whom inquiries should be addressed at the Department of Chemistry, University of Vermont, Burlington, Vt. (c) Participant, National Science Foundation Research Participation for College Teachers Program, Summer 1967.

[2] J. L. Kice, R. A. Bartsch, M. A. Dankleff, and S. L. Schwartz, *J. Amer. Chem. Soc.*, **87**, 1734 (1965).