Photochemistry of *o*-Benzyloxyphenylglyoxylates. A Case of Favored Intramolecular Hydrogen Abstraction *via* a Seven-Membered Cyclic Transition State[1]

S. Peter Pappas,* James E. Alexander, and Robert D. Zehr, Jr.

Contribution from the Departments of Chemistry, North Dakota State University, Fargo, North Dakota 58102, and Emory University, Atlanta, Georgia 30322.
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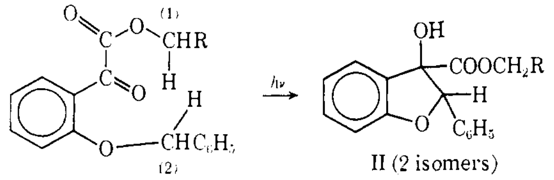
Abstract: The photochemistry of methyl and benzyl *o*-benzyloxyphenylglyoxylate (I) has been investigated. Quantum yield determinations establish that intramolecular hydrogen abstraction occurs at the benzyl ether carbon *via* a seven-membered cyclic transition state in preference to the alkoxy ester carbon *via* a six-membered ring. The results of quenching and sensitization studies define the reactive intermediate as an n,π* triplet and yield a rate constant for abstraction of 10^7 sec^{-1}. The results also provide an upper limit for the rate of abstraction at the alkoxy ester carbon, which is 100-fold less than predicted on the basis of hydrogen "abstractability." This discrepancy and the facility of abstraction *via* a seven-membered cyclic transition state in this system are discussed.

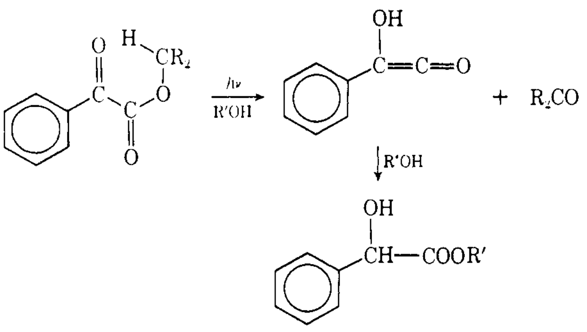
The chemical literature attests to the favored status of reactions with six- as compared to seven-membered cyclic transition states. In photochemistry, this is exemplified by the established preference for intramolecular 1,6-hydrogen abstraction by the oxygen of electronically excited carbonyl compounds.[2] Thus, one might well predict that light-induced hydrogen abstraction would occur at the alkoxy ester carbon-1 in preference to the ether carbon-2 of phenylglyoxylic esters I, since the latter course involves the less-favored seven-membered ring. Indeed, Huyser and Neckers[3] have postulated intramolecular 1,6-hydrogen abstraction from the alkoxy ester carbon of unsubstituted phenylglyoxylate esters to account for the photoproducts (eq 1). However, in the case of methyl ester Ia, the isomeric dihydrobenzofurans IIa were produced in about 90% yield, presumably by 1,7-hydrogen abstraction–cyclization.[4] Nevertheless, this result did not rule out faster, reversible abstraction from the alkoxy ester position. To render the hydrogens more equally "abstractable," the corresponding benzyl ester Ib has been investigated. Herein, we present our results of a mechanistic study which (1) establishes the intramolecularity of the abstraction, (2) precludes the importance of hydrogen abstraction from the alkoxy ester carbon in both Ia and Ib, (3) defines the reactive intermediate, and (4) provides a rate constant which reflects a marked facility for 1,7-hydrogen abstraction in this system.



I

II (2 isomers)

a, R = H
b, R = C$_6$H$_5$



(1)

Results and Discussion

Irradiations of degassed solutions of ester Ia were conducted in a merry-go-round apparatus at ambient temperatures (~33°) and 366 nm (450-W Hanovia mercury lamp and Corning 7-83 filter combination). An internal standard was utilized to monitor the formation of products by glc. The rate of dihydrobenzofuran formation was found to be independent of the initial concentration of Ia for optically dense solutions. For 0.06 *M* Ia, this rate was constant throughout the range of 5–50% conversions. These results established the intramolecularity of dihydrobenzofuran formation. Quantum yield determinations and quenching studies were conducted on 0.06 *M* Ia with conversions generally under 15%.

Quantum yields were determined both by ferrioxalate[5] and benzophenone–benzhydrol (degassed benzene solutions) actinometry[6,7] which provided equivalent results within the range of experimental values (<15%). Average yields for product appearance and their ratios, obtained in benzene, acetonitrile, and *tert*-butyl alcohol, are presented in Table I. The corresponding yields for disappearance of ester Ia, as determined by ultraviolet absorption measurements, were found to be about

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* Address correspondence to this author at North Dakota State University.

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 87 (1968).

(3) E. S. Huyser and D. C. Neckers, *J. Org. Chem.*, **29**, 276 (1964); D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold, New York, N. Y., 1967, pp 179–182.

(4) S. P. Pappas, B. C. Pappas, and J. E. Blackwell, Jr., *J. Org. Chem.*, 32, 3066 (1967).

(5) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y. 1966, pp 783–786.

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

(7) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

Table I. Photoreactivity of Ia[a]

Solvent	cis/ trans[b]	ϕ_{+II}[c]	$k_q\tau$,[d] M^{-1}	τ[e], 10^{-8} sec	k_r,[f] 10^7 sec^{-1}
Benzene	6.7	0.89	116	2.3	3.8
Acetonitrile	1.9	0.56	300	2.7	2.1
tert-Butyl alcohol	1.0	0.47	175	7.6	0.62

[a] 0.06 *M*. Conversions <15%. [b] Ratio of isomeric dihydrobenzofuran products with reference to the geometric relationship of the 2-phenyl and 3-hydroxy groups. [c] Quantum yield for dihydrobenzofuran formation at 366 nm by ferrioxalate actinometry. Estimated error ±8%. [d] From Stern–Volmer quenching of dihydrobenzofuran formation by 1,3-cyclohexadiene. Estimated error ±10%. [e] Calculated from the assumption that $k_q = 5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ in benzene, $11 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ in acetonitrile, and $2.3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ in *tert*-butyl alcohol.[7] [f] The minimum rate constant for 1,7-hydrogen abstraction calculated by multiplying $1/\tau$ by ϕ_{+II}.

5–10% higher, on the average, than for dihydrobenzofuran formation, a discrepancy which could be accounted for by the appearance of at least three additional minor products in the glc traces. Quantum yields for the formation of dihydrobenzofurans IIb from the benzyl ester Ib were also determined in benzene, acetonitrile, and *tert*-butyl alcohol and were found to be within experimental error of the corresponding values for the methyl ester (Table I). Product ratios from the two esters were essentially identical.

The high quantum yields of dihydrobenzofuran formation for both esters effectively rule out the importance of reversible 1,6-hydrogen abstraction from the alkoxy ester carbon in benzene solution. The possibility that this course is competitive in acetonitrile and *tert*-butyl alcohol, which could account for the lower quantum efficiency in these solvents, may also be precluded in view of the equivalent quantum yields of dihydrobenzofuran formation for both esters. In the event that 1,6-hydrogen abstraction from the alkoxy ester carbon were important, it would be expected to compete more effectively in the case of the benzyl ester thereby lowering the quantum yield of dihydrobenzofuran formation relative to that for the methyl ester, which was not observed.

These results preclude the importance of 1,6 abstraction from the alkoxy ester carbon-1, except as a possible step in the formation of the dihydrobenzofurans II. Conceivably, 1,6 abstraction may be followed by hydrogen transfer from C-2 to C-1 (*via* a nine-membered ring) and, thereafter, cyclization to II. However, this possibility has been excluded in the course of studies on isotope effects. Irradiation of Ia, dideuterated at C-2, yielded IIa which contained one deuterium atom (by mass spectral analysis) after aqueous treatment. This result is consistent with 1,7 abstraction whereupon a readily exchangable O–D bond is produced, but not with the alternative two-step process, which is predicted to yield dideuterated IIa, with deuterium bonded to carbon on the ring and the carboxymethyl group. The mass spectral fragmentation pattern also excluded the presence of deuterium on the carboxymethyl group. We conclude, therefore, that 1,7-hydrogen abstraction is the preferred course by at least an order of magnitude in this system.

In view of the remarkable temperature effect reported for phenylglyoxylate esters,[3] whereby intermolecular hydrogen abstraction from solvent is observed at ambient temperature and the intramolecular reaction (eq 1) predominates at 78° in alcohol solutions, the esters Ia and b were also irradiated in *tert*-butyl alcohol at reflux. In both cases, the dihydrobenzofurans II accounted for more than 90% of the products as determined by glc (internal standard) in analogy with the results at ambient temperature.

Quenching studies on the formation of dihydrobenzofurans IIa were conducted with 1,3-cyclohexadiene (E_T = 54 kcal/mol).[8] Linear Stern–Volmer plots of ϕ_0/ϕ_q *vs.* [Q] to ϕ_0/ϕ_q values >10 were obtained in benzene, acetonitrile, and *tert*-butyl alcohol. Essentially all of the quenched reaction could be accounted for by the formation of cyclohexadiene dimers, indicative of triplet quenching.[9] Furthermore, the product ratios (Table I) remained unchanged on sensitization, which satisfies the "fingerprint" method for triplet reaction.[10,11]

The highest energy bands in the phosphorescence spectra of Ia in isopentane and EPA glasses corresponded to 62 and 67 kcal, respectively, a shift indicative of n,π* emission.[12] Accordingly, the formation of dihydrobenzofurans IIa was quenched by *trans*-piperylene (E_T = 59 kcal/mol)[8b] as well as naphthalene (E_T = 61 kcal/mol),[13] but not by biphenyl (E_T = 70 kcal/mol),[14] thereby leaving little doubt as to the identity of the abstracting and phosphorescing states. Thus, it is likely that the reactive intermediate is an n,π* triplet.

Linear Stern–Volmer plots were also obtained with *trans*-piperylene[15] and naphthalene. It is noteworthy that differential quenching was observed. For example, in acetonitrile the relative rates of quenching were found to be 1.0:1.5:7.0 by *trans*-piperylene, naphthalene, and 1,3-cyclohexadiene, respectively; whereas the order of triplet energies is naphthalene > piperylene > cyclohexadiene. Similar results were obtained in benzene. Thus, naphthalene quenches more effectively than piperylene, although it is predicted to be equally or less efficient on the basis of the relative triplet energies. Similar findings, observed previously in the quenching of short-lived excited triplet states of ketones with dienes, have been attributed to an orientation effect.[16]

The lifetimes were determined by utilizing literature values for quenching rate constants (k_q)[7] and slopes ($k_q\tau$) of the Stern–Volmer plots obtained with 1,3-cyclohexadiene. Since the observed quantum yields

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(8) (a) D. F. Evans, *J. Chem. Soc.*, 1735 (1960); (b) R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, 87, 4230 (1965).

(9) D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 1301 (1968).

(10) H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968).

(11) Sensitization studies have also revealed that inefficient intersystem crossing is a significant factor in lowering the overall quantum yields in acetonitrile and *tert*-butyl alcohol relative to benzene. These results and the solvent effects on the stereochemistry of cyclization will be discussed elsewhere.

(12) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 46.

(13) Reference 12, p 132.

(14) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2820 (1967); see also, ref 2, p 53.

(15) Results indicative of two triplet intermediates, including curvilinear Stern–Volmer plots with *trans*-piperylene in acetonitrile have been found to be irreproducible. See J. E. Alexander and S. P. Pappas, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract ORG-87.

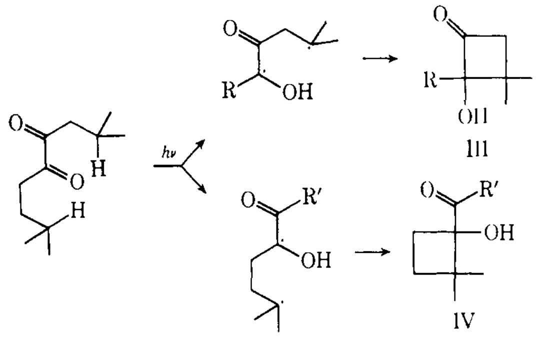
(16) D. I. Schuster, A. C. Fabian, N. P. Kong, W. C. Barringer, W. C. Curran, and D. H. Sussman, *J. Amer. Chem. Soc.*, **90**, 5027 (1968).

define the lower limits of the efficiency of triplet abstraction ($k_r\tau$), minimum values for the rate of triplet abstraction (k_r) may be determined and are of the order 10^7 sec^{-1} (Table I). This value is about two–three orders of magnitude lower than observed for α-alkoxyacetophenones,[17,18] which may reflect the relative ease of hydrogen abstraction *via* a six- and seven-membered cyclic transition state.[19]

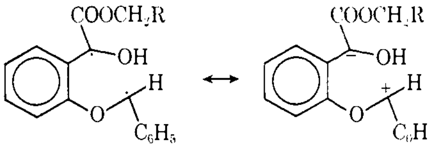
The results provide an upper limit for the rate of intramolecular 1,6-hydrogen abstraction in this system which is relatively low ($k \leqslant 10^6$ sec^{-1}). Thus, it is not surprising that intermolecular abstraction is the favored course for phenylglyoxylate esters at ambient temperatures.[3,20] This finding also correlates with the slow rate of 1,6 abstraction, recently reported for α-diketones.[21] The latter results were attributed to reduced reactivity of the carbonyl grouping as a consequence of the low triplet energy (E_T = 56 kcal/mol) of α-diketones. However, the former may be due to different factors in view of the facility of abstraction from the alkoxy ether carbon which we observe, as well as the higher triplet energy (~65 kcal/mol) of I. Two possibilities are (1) an unfavorable geometry of the triplet for 1,6 abstraction and (2) unusually low reactivity of the hydrogen on the alkoxy ester carbon.

With regard to the latter possibility, *tert*-butoxy radicals exhibit a three- to fourfold preference for alkyl-substituted methylene hydrogens relative to those adjacent to an acetoxy function.[22] Phenyl radicals are reported to exhibit a similar preference for methyl hydrogens of *n*-pentane relative to methyl benzoate.[23] If this selectivity reflects that of n,π^* triplet state ketones, which has been suggested in the case of *tert*-butoxy radicals,[24] the effect does not account for the extrapolated low order of reactivity. For example, based on the reported rate of 4 × 10^8 sec^{-1} for intramolecular 1,6 abstraction by γ-phenylbutyrophenone,[18] it would follow that abstraction from the benzyloxy ester carbon-1 of Ib should approximate 10^8 sec^{-1}, which is two orders of magnitude greater than our results allow.

In a transoid arrangement of the α-dicarbonyl groups of I, the hydrogen on the alkoxy ester carbon is readily accessible to the ketonic oxygen. Consequently, the possibility that an unfavorable geometry is responsible for the extrapolated low rate of 1,6 abstraction would suggest a nontransoid configuration in the reactive triplet of I. In order to account for the apparent 100-fold discrepancy based on hydrogen "abstractability" discussed above, this interpretation would require either (1) that the transoid configuration is 2-3 kcal/mol higher in energy than the favored geometry of the reactive triplet, or (2) that the triplet undergoes the observed hydrogen abstraction from C-2 about 100 times faster than conversion to the transoid form. The structural criterion of unreactivity is readily satisfied. 1,6-Abstraction cannot occur *via* a cisoid configuration and is unfavorable when the carbonyl groups lie in perpendicular planes.[25] However, it is not clear why a cisoid or twisted geometry would be energetically favored over the transoid configuration, particularly to the extent required. Furthermore, a twisted geometry is inconsistent with spectroscopic data on α-diketones[26] and a favored cisoid configuration is not in accord with the photoreactivity of α-diketones, which undergo intramolecular hydrogen abstraction to yield 2-hydroxycyclobutanones III, to the exclusion of 1-acylcyclobutanols IV.[27]



Thus, the extrapolated low rate ($k \leqslant 10^6$ sec^{-1}) of 1,6 abstraction in this system is not reasonably attributable to either the nature of the hydrogen to be abstracted or the geometry of the abstracting triplet, and, consequently, may well reflect a low reactivity of the α-dicarbonyl system of I, as suggested for aliphatic α-diketones,[21] even though the triplet energy of I is about 10 kcal/mol higher. For a system of relatively low reactivity, it follows that 1,7 abstraction, with an observed rate of 10^7 sec^{-1}, is a remarkably facile process, to which several factors may contribute. First, the probability of the 1,7 interaction may be comparable to that of 1,6 abstraction in this system in view of the coplanarity of the ketone with both the phenyl ring and the ester carbonyl. Second, the hydrogen on the benzyl ether carbon is predicted to be more reactive than that on the alkoxy ester carbon. Third, the biradical intermediate V, resulting from 1,7 abstraction, is "formally" conjugated and may be stabilized by delocalization, including polar contribution. Either of the latter two factors might well account for the minimum tenfold preference of 1,7 over 1,6 abstraction in this system.



V, R = H or C_6H_5

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[17] N. J. Turro and F. D. Lewis, *Tetrahedron Lett.*, 5845 (1968); *J. Amer. Chem. Soc.*, **92**, 311 (1970).

[18] P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968).

[19] (a) E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, pp 114–20. (b) The effect of an adjacent phenyl group as compared to alkyl, by which these systems also differ, is expected to be small as evidenced by the threefold rate enhancement of intramolecular abstraction by γ-phenylbutyrophenone relative to propiophenone.[18]

[20] N. C. Yang and A. Morduchowitz, *J. Org. Chem.*, **29**, 1654, (1964).

[21] N. J. Turro and Ta-Jyh Lee, *J. Amer. Chem. Soc.*, **91**, 5651 (1969).

[22] C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960).

[23] R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).

[24] (a) A. Padwa, *Tetrahedron Lett.*, 3465 (1964); (b) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **86**, 3902 (1964); *ibid.*, **87**, 3361 (1965).

[25] For spectroscopic evidence in support of two triplet states of β-naphthyl, assigned as the cisoid and transoid configurations, see W. G. Herkstroeter, J. Saltiel, and G. S. Hammond, *ibid.*, **85**, 182 (1963).

[26] T. R. Evans and P. A. Leermakers, *ibid.*, **89**, 4380 (1967).

[27] W. H. Urry and D. J. Trecker, *ibid.*, **84**, 118 (1962); W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Lett.*, 609 (1962); however, see T. L. Burkoth and E. F. Ullman, *ibid.*, 145 (1970).

We wish to note, in conclusion, that the phototransformation I → II may also involve hydrogen abstraction from C-2 by the ester carbonyl *via* an eight-membered cyclic transition state followed by hydrogen transfer to the ketonic oxygen and cyclization—a course which may not be excluded. However, this route is not available to *o*-benzyloxybenzaldehyde which also provides dihydrobenzofurans on irradiation,[28] or to an *o*-benzyloxybenzophenone derivative,[29] recently reported to undergo an analogous photocyclization.

Experimental Section

Preparation of Phenylglyoxylates I. The preparation and characterization of methyl *o*-benzyloxyphenylglyoxylate (Ia) from *o*-benzyloxybenzaldehyde, *via* the cyanohydrin, has been described.[4] The dideuterio analog was prepared accordingly from dideuterio-*o*-benzyloxybenzaldehyde, derived from salicylaldehyde and *α,α*-dideuteriobenzyl chloride.[30]

Anal. Calcd for $C_{16}H_{12}O_4D_2$: C, 70.6; H, 5.3. Found: C, 70.6; H, 5.1.

Benzyl *o*-benzyloxyphenylglyoxylate (Ib) was prepared from *o*-benzyloxyacetophenone[31] as follows. Oxidation with selenium dioxide, as previously described for a related acetophenone,[32] yielded crystalline *o*-benzyloxyphenylglyoxylic acid, mp 146–147°, which, without further purification, was converted into the desired ester, *via* the acid chloride, as previously described for phenyl glyoxylic acid.[33] The ester was purified by distillation, bp 193–196° (0.15 mm), and redistilled twice to yield a sample homogeneous by glc analysis. This material, which could not be induced to crystallize, exhibited the appropriate spectral properties and was analyzed as the corresponding 2,4-dinitrophenylhydrazone derivative, mp 126–127°, which was recrystallized from 95% ethanol.

Anal. Calcd for $C_{28}H_{22}N_4O_7$: C, 63.9; H, 4.2; N, 10.6. Found: C, 64.0; H, 4.2; N, 10.7.

Solvents and Materials. Reagent grade benzene (Fisher) and *tert*-butyl alcohol (Fisher) were distilled from sodium prior to use. Nanograde acetonitrile (Mallinckrodt) was distilled twice from phosphorus pentoxide, and redistilled from calcium hydride prior to use. Reagent grade benzophenone, benzhydrol, biphenyl, and naphthalene (all from Fisher) were recrystallized and sublimed prior to use. 1,3-Cyclohexadiene (Aldrich), *n*-tetradecane (K and K Laboratories), and *n*-hexadecane (Eastman) were distilled prior to use. *trans*-Piperylene (Aldrich) was used as received.

Identification of the Photoproducts II. Characterization of the isomeric methyl esters IIa has been described.[4] Separation of the isomeric benzyl esters IIb was effected, analogously, by alumina chromatography. Stereochemical assignments are based on the relative positions of the carboxybenzyl hydrogens in the nmr spectra[34] of the isomers. These methylene hydrogens appear as AB quartets from which the chemical shifts may be calculated as τ 4.59 and 4.71 (J_{AB} = 12.0) for one of the isomers, 5.17 and 5.37 (J_{AB} = 12.5 Hz) for the other. This difference is attributed to the relative configuration of the 2-phenyl and 3-carboxybenzyl groups. The isomer exhibiting the high-field resonances is assigned the configuration in which these groups are cis, wherein the methylene hydrogens lie in the shielding cone of the aromatic ring. An analogous effect was observed on the carboxymethyl hydrogen resonances of the isomeric methyl esters IIa.[4]

The isomer which exhibits an AB quartet centered at τ 5.27 also shows a singlet at 4.20, assigned to the ring methine hydrogen, and a broad hydroxyl resonance at 5.5 (10% solution in deuteriochloroform), which disappears on the addition of deuterium oxide. The other isomer with the AB quartet centered at 4.65 also features a singlet at 4.11 ascribable to the methine hydrogen, and a broad hydroxyl resonance at 6.9 (15% solution in deuteriochloroform). The relatively high-field position of the hydroxyl resonance in the latter isomer is attributed, primarily, to a shielding effect by the adjacent *cis*-phenyl group. Thus, the relative chemical shifts of the carboxybenzyl and hydroxyl resonances in each isomer corroborate the assignments. Both isomers yield 2-phenyl-3-carboxybenzylbenzofuran, mp 60–60.5°, on treatment with thionyl chloride and pyridine, as previously described in the methyl series.[4]

Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.5; H, 4.9. Found: C, 80.4; H, 4.9.

Quantum Yields. Solutions 0.03–0.06 *M* in keto ester I and about 0.002 *M* in internal standard in purified solvents (4 ml total volume) were degassed (0.01 mm) by several freeze–thaw cycles and sealed *in vacuo* in 15-mm o.d. Pyrex tubes. The tubes were then irradiated on a merry-go-round apparatus (with 21 tube positions) at ambient temperature (~33°) using a Hanovia 450-W medium-pressure lamp and Corning 7-83 filter combination to isolate the 366-nm band. The solutions were analyzed for product appearance on a Varian 1740 flame ionization gas chromatograph by a 5 ft × 1/8 in. column of 3% SE-30 on 100–120 Varaport 30 with temperature programming between 100 and 200°. The disappearance of keto ester I was monitored on a Beckmann Model DU spectrophotometer with constant temperature control. Actinometers were photolyzed simultaneously. Benzophenone–benzhydrol actinometry was carried out on degassed benzene solutions 0.05 *M* in benzophenone and 0.2 *M* in benzhydrol. The disappearance of benzophenone was monitored spectrophotometrically. The conversions were kept under 15% and ϕ was taken as 0.85.[6,7] Equivalent results were obtained by ferrioxalate actinometry.[5] During the course of the preliminary studies, conversions of keto ester Ia were extended to 50% to establish the intramolecularity of dihydrobenzofuran formation. However, the quantum yield data in Table I represent the average of at least three determinations in each case, with conversions under 15%. The quantum yields for keto ester disappearance were, on the average, 5–10% higher than for dihydrobenzofuran formation. However, the appearance of at least three additional minor products in the glc traces accounted for this discrepancy. The chromatographic analyses were preceded by determination of the relative glc response to internal standard and product IIa, which was found to be 1.49/1.0 in the case of tetradecane and 1.80/1.0 for hexadecane. Quantum yields of formation of dihydrobenzofurans IIb from the benzyl keto ester Ib were determined in the same manner.

Irradiations in *tert*-Butyl Alcohol at Reflux. A "Black Light" source (G.E. H100PSP38-4) was utilized and placed about 5–10 cm from the reaction vessel (a Pyrex round-bottomed flask equipped with a reflux condenser), which contained a *tert*-butyl alcohol solution (120 ml) of the benzyl keto ester Ib (1.3 × 10^{-3} *M*) and an internal standard (8 × 10^{-4} *M* hexadecane). Prior to illumination the solution was heated to a state of reflux, which was sustained during the irradiation by the heat of the light source. After completion of the phototransformation, it was determined (by glc) that the dihydrobenzofurans IIb accounted for more than 90% of the material balance. Equivalent results were obtained with the methyl keto ester Ia.

Quenching Studies. Samples were prepared, irradiated, and analyzed (by glc) in the same way as for quantum yield determinations except that varying amounts of quencher (1,3-cyclohexadiene, *trans*-piperylene, naphthalene, or biphenyl) were added to the solutions which were 0.06 *M* in keto ester I. Four or more concentrations of quencher, in duplicate, were used for each Stern–Volmer plot, which, in each case, was clearly linear both visually and on the basis of linear least-square fits. Repeated determinations agreed within the range of 15%.

Triplet Counting. These experiments were preceded by the preparation of 1,3-cyclohexadiene dimers[35] and determination of the relative glc response to internal standard (hexadecane) and the dimers, which was found to be 1.51/1.0. The necessary information was obtained from the quenching experiments utilizing 1,3-cyclohexadiene. Irradiation of a benzene solution 0.06 *M* in Ia and 0.05 *M* in 1,3-cyclohexadiene yielded 1.65 × 10^{-3} *M* dihydrobenzofurans IIa and 13.6 × 10^{-3} *M* cyclohexadiene dimers, as compared to 19.8 × 10^{-3} *M* IIa, corresponding to a 33% conversion, in the absence of quencher. This represents a quenching efficiency of 74%. The quenching efficiency was 103% for 0.5 *M* cyclohexadiene. In acetonitrile, the quenching efficiency was 66 and 113%

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[28] S. P. Pappas and J. E. Blackwell, Jr., *Tetrahedron Lett.*, 1171 (1966).

[29] G. R. Lappin and J. S. Zannucci, *Chem. Commun.*, 1113 (1969).

[30] S. Meyerson, P. N. Rylander, E. L. Eliel, and J. D. McCollum, *J. Amer. Chem. Soc.*, 81, 2606 (1959).

[31] U. P. Pandit and T. C. Bruice, *ibid.*, 82, 3386 (1960).

[32] G. Hallmann and K. Hagele, *Justus Liebigs Ann. Chem.*, **662**, 147 (1963).

[33] W. G. Dauben, D. F. Dickel, O. Jeger, and V. Prelog, *Helv. Chim. Acta*, **36**, 325 (1953); H. C. Brown and M. S. Kharasash, *J. Amer. Chem. Soc.*, **64**, 329 (1942).

[34] The nmr spectra were obtained in deuteriochloroform solution on a Varian A-60 spectrometer. Chemical shifts are reported in τ units.

[35] D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).

with 0.05 and 0.5 M 1,3-cyclohexadiene, respectively. These values, which represent averages of at least two determinations (estimated error ±10%), are in reasonable accord with the efficiencies of benzophenone-sensitized cyclohexadiene dimerization as a function of cyclohexadiene concentration reported by Vesley.[36]

Sensitization Studies. Samples were prepared, irradiated, and analyzed (by glc) in the same way as for quantum yield determinations except that various sensitizers (benzophenone, *m*-methoxy-, and *p*-methoxyacetophenone) were added to the solutions. In each case, the product ratios did not vary significantly from the values obtained on direct irradiation and recorded in Table I.

Spectra. Phosphorescence spectra of keto ester Ia were taken in isopentane and ether–isopentane–ethanol (EPA) glasses at 77°K using an Aminco-Bowman spectrofluorimeter with a phosphorescence attachment.

Acknowledgment. We wish to thank Dr. Ted Evans for the phosphorescence spectra and helpful discussion.

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[36] G. F. Vesley, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1968.

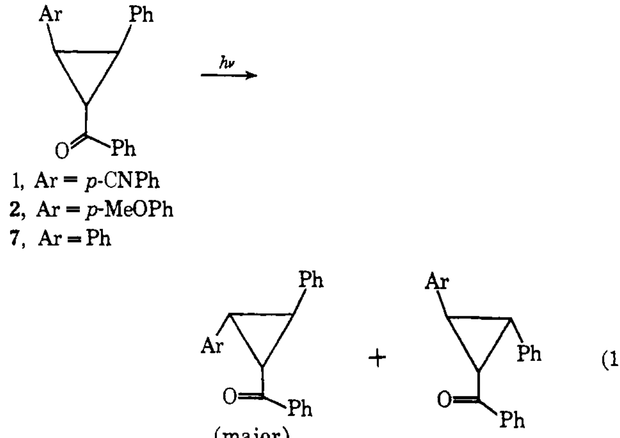
Excited-State Three-Ring Bond Opening in Cyclopropyl Ketones. Mechanistic Organic Photochemistry. LX[1]

Howard E. Zimmerman* and Thomas W. Flechtner

Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706. Received April 6, 1970

Abstract: The photochemistry of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane was investigated for comparison with our previous studies on *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane and *trans*-2-*p*-methoxyphenyl-*trans*-3-phenyl-1-benzoylcyclopropane. On both sensitized and direct irradiation a facile stereoisomerization process to yield *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane was observed. The quantum yield for the direct irradiation was 0.94 and that for the acetophenone sensitized reaction was 1.02. Evidence was obtained that the direct irradiation reaction derived primarily from the triplet excited state. Quenching studies allowed estimation of the rate of triplet ring fission and *trans–trans* to *cis–trans* stereoisomerization as $k_r = 3.0 \times 10^{10}$ sec^{-1}. This proves to be very similar to the rate for *trans*-2-*p*-methoxyphenyl-*trans*-3-phenyl-1-benzoylcyclopropane but considerably lower than the rate for *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane. Hence the conclusion may be drawn that despite *p*-methoxyphenyl facilitating three-ring fission, the energetic stabilization is minor, while that deriving from *p*-cyanophenyl is considerable. Surprisingly, despite the isoenergetic nature of the triplet sensitization, energy transfer proved to be of unit efficiency. Isoenergetic transfer is discussed as a phenomenon and one new hypothesis is discussed.

In our recent investigations of excited state electron distribution in cyclopropyl ketones, we utilized *trans*-2-*p*-cyanophenyl-*trans*-3-phenyl-1-benzoylcyclopropane[2] (**1**) and *trans*-2-*p*-methoxyphenyl-*trans*-3-phenyl-1-benzoylcyclopropane[3] (**2**). In both of these cases, the reactions observed were stereoisomerizations (note eq 1). These studies afforded both relative rates of different bond fission processes as well as absolute rates of triplet excited state ring opening. For an independent assessment of the energetic importance of the different *para* substituents, it was necessary to ascertain the efficiency and rate of ring fission in the parent molecule lacking the *para* substituents. Thus a study of the photochemistry of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane (**7**) was initiated.



1, Ar = *p*-CNPh
2, Ar = *p*-MeOPh
7, Ar = Ph

(1)

(major)
3, Ar = *p*-CNPh
4, Ar = *p*-MeOPh
8, Ar = Ph

(minor)
5, Ar = *p*-CNPh
6, Ar = *p*-MeOPh

Results

Reaction Product, Quantum Yield, Sensitization, and Quenching Studies. Exploratory studies of the irradiation of *trans,trans*-2,3-diphenyl-1-benzoylcyclopropane (**7**) revealed a particularly clean conversion to the *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane stereoisomer (**8**). The structure of this stereoisomer was established firmly by independent synthesis as detailed in the Experimental Section.

Our study began with investigation of the reaction efficiency. Irradiation in benzene at 313 nm in our "black box" apparatus[4] and ferrioxalate actinometry[5]

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* Address correspondence to this author.

[1] For paper LIX see H. E. Zimmerman and V. J. Hull, *J. Amer. Chem. Soc.*, in press.

[2] H. E. Zimmerman, S. S. Hixson, and E. F. McBride, *ibid.*, **92**, 2000 (1970).

[3] H. E. Zimmerman and C. M. Moore, *ibid.*, **92**, 2023 (1970).

[4] (a) Described as apparatus B by H. E. Zimmerman, H. G. Dürr, R. S. Givens, and R. G. Lewis, *ibid.*, **89**, 1863 (1967). (b) The apparent quantum yield decreased with time due to light absorption by-product and very minor but strongly absorbing impurities.