Photochemical Reactions of Halo-/Aryl Sulfide-Substituted Alkyl Phenylglyoxylate, an Assessment of the Lifetime of the Intermediate 1,4-Biradical

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Photochemical reactions of several halo/aryl sulfide-substituted alkyl phenylglyoxylates (**1**) were studied. For 2′-bromo- (**1b**), 2′-iodo- (**1c**), 2′-(phenylthio)- (**1d**), and 2′-(phenylsulfinyl)- (**1e**) ethyl phenylglyoxylate, vinyl phenylglyoxylate (**2**), proposed to be the result of β-elimination from the 1,4-biradical formed by triplet state γ-hydrogen abstraction, is the dominant photoproduct. In the cases **1b** and **1d** Norrish Type II products were also observed. Vinyl phenylglyoxylate (**2**) was not observed with 2′-chloroethyl (**1a**), 3′-bromopropyl (**1f**), and 3′-(phenylthio)propyl (**1g**) phenylgly-oxylate. The lifetime of the 1,4-biradical intermediate is deduced from the competition between the β-elimination of the monoradical and the normal biradical decay. The triplet lifetime and the photoreaction efficiency of **1** were not significantly affected by halogen-substitution.

Introduction

Photoreactions of alkyl phenylglyoxylates in aprotic solvents have been proven to be predominantly Norrish Type II processes, eq 1.[2] The intermediate 1,4-biradical resulting from triplet state γ-hydrogen abstraction decays exclusively by α-β cleavage, and no cyclization of this biradical (the Yang reaction) is observed.[3] Though nanosecond laser flash photolysis reveals no transient attributable to the biradical,[2b] the lifetime of this inter-mediate has been estimated using the cyclopropylmethyl radical clock method.[4] Since the rate constant for ring opening of the model cyclopropylmethyl radical is sensi-tive to substituents at the radical center,[5] as well as on the cyclopropyl ring,[6] apparent uncertainties have been introduced in lifetime estimations made by the method.[7] We therefore designed compounds, **1**, based on the reported reactivities of β-elimination from the monoradi-cals[8] and biradicals.[9] It was expected, that after irradia-tion, a 1,4-biradical would derive from γ-hydrogen ab-straction via the triplet state of **1**. Competition between β-elimination and normal decay in this biradical would enable us to deduce the lifetime of this intermediate.
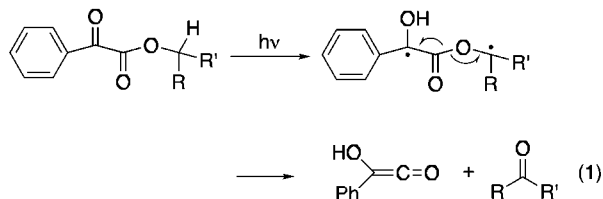

Table 1. Compounds Studied

1	n	X
1a	2	Cl
1b	2	Br
1c	2	I
1d	2	S—C₆H₅ (phenyl)
1e	2	S(=O)—C₆H₅ (phenylsulfinyl)
1f	3	Br
1g	3	S—C₆H₅ (phenyl)

Results

Photoreactions. Halo-/aryl sulfide-substituted alkyl phenylglyoxylates, **1**, were prepared, Table 1, and dilute (*ca.* 0.01 M) benzene solutions irradiated with UV light (365 nm). GC/MS analyses of reaction mixtures during the first 10% reaction[10] revealed the products shown in Table 2. Relative yields of **2** and **5** were obtained from NMR measurements of the reaction mixtures and are the

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

(1) Contribution No. 325 from the Center for Photochemical Sci-ences.

(2) (a) Huyser, E. S.; Neckers, D. C. *J. Org. Chem.* **1964,** *29,* 276−278. (b) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1996,** *61,* 6407−6415 and references therein.

(3) This is likely due to the short lifetime of this biradical and to the unfavorable conformation adopted by this biradical for the closing of a four-membered lactone ring, see Hu, S.; Neckers, D. C. *J. Org. Chem.* **1997,** *62,* 564−567. One such cyclization has been mentioned in a communication: Kraus, G. A.; Zhang, W.; Wu, Y. *Chem. Commun.* **1996,** 2439−2440.

(4) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1997,** *62,* 755−757.

(5) Hollis, R.; Hughes, L.; Bowry, V. W.; Ingold, K. U. *J. Org. Chem.* **1992,** *57,* 4284−4287.

(6) (a) Newcomb, M. *Tetrahedron* **1993,** *49,* 1151−1176 and refer-ences therein. (b) Tadic-Biadatti, M.-H. L.; Newcomb, M. *J. Chem. Soc., Perkin Trans. 2* **1996,** 1467−1473.

(7) Private communications with Dr. Martin Newcomb are gratefully acknowledged.

(8) (a) Skell, P. S.; Shea, K. J. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, p 809. (b) Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1972,** *94,* 6485−6495. (c) Lloyd, R. V.; Wood, D. E. *J. Am. Chem. Soc.* **1975,** *97,* 5986−5992. (d) Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1974,** *96,* 6715−6720.

(9) (a) Wagner, P. J.; Sedon, J. H.; Lindstrom, M. J. *J. Am. Chem. Soc.* **1978,** *100,* 2579−2580. (b) Wagner, P. J.; Lindstrom, M. J.; Sedon, J. H.; Ward, D. R. *J. Am. Chem. Soc.* **1981,** *103,* 3842−3849.

Table 2. Photoproducts and Kinetic Data

| 1	photoproducts	2/5	Φ disappearance of 1	triplet lifetime in benzene
1a	5, 6, 7	0	/	0.65 μs
1b	2, 3, 4, 5, 6, 7	2.6	0.79	1.1 μs
1c	2, 3, 4	infinite	/	1.0 μs
1d	2, 3, 4, 5, 6, 7	24.5	0.47	68 ns
1e	2, 3	infinite	0.72	185 ns
1f	5, 6, 7	0	/	0.95 μs
1g	5, 6, 7	0	/	20 ns

averages of three measurements. Signals from the vinyl protons of **2** and the aldehyde proton of **5** were distinctive (see Supporting Information) and used to quantify the relative yields of **2** and **5** (GC was also used for quantifying purposes. The results from GC are less reproducible than from NMR). Benzaldehyde, **5**, carbonyl product, **6**, and carbon monoxide, **7**, were derived from the Norrish Type II reaction.[11] When irradiated longer, the photosylates from **1b** turned deep yellow and that from **1c** turned red, thus indicating the formation of free bromine and iodine, respectively. These colored species competed with the starting material for the incoming photons making exhaustive irradiation of **1b** and **1c** impossible. Irradiations of **1d** and **1e** to completion formed vinyl phenylglyoxylate, **2**. **2** isolated from a photosylate of **1d** was identical to an authentic sample synthesized independently from benzoylformic acid and vinyl acetate.[12] The identification of **2** in the photosylates of **1b**, **1c**, and **1e** resulted from comparison of MS cracking patterns and GC retention times on two different columns with those of the authentic compound.

Mechanism. A mechanism for the formation of products from **1a**–**e** is proposed, Scheme 1. **1** is promoted to the triplet excited state (**T**) via its singlet state, followed by γ-hydrogen abstraction to form a 1,4-biradical (**R**). β-Elimination from **R** followed by hydrogen transfer in the resulting radical pair produces **2** and HX. White precipitates of pyridinium hydrohalide were obtained when 0.01 M pyridine was added to the reactions of **1b** and **1c** trapping the resulting hydrohalides, HX.[13] Ben-

Scheme 1
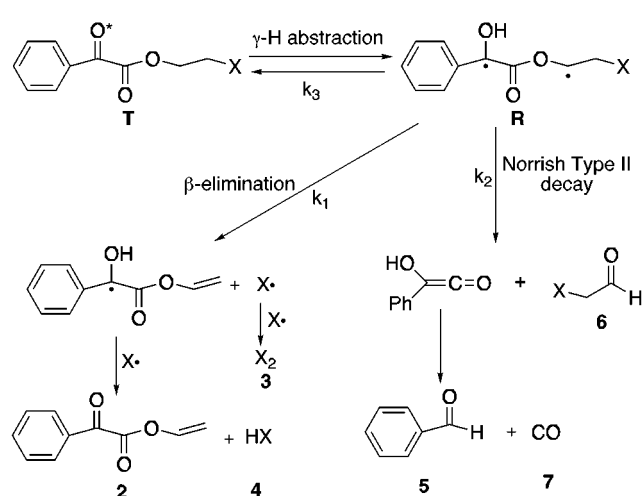
zenethiol (**4d**) was identified by GC and MS analyses.[14] Coupling of radical X$^\bullet$ accounted for the free bromine (**3b**) and iodine (**3c**) observed in the reactions of **1b** and **1c**, respectively, which indicates that there is some diffusion of the initially formed radical pair. Phenyl disulfide (**3d**)[14] was produced from the coupling of two phenylthiyl radicals. The coupling of phenylsulfinyl radicals in the reaction of **1e** produced *S*-phenyl ester of benzenesulfonothioic acid (**3e**)[14] in agreement with earlier reports.[9a,15] Normal Norrish Type II decay of **R** resulted in products **5**–**7**.

With **1f** and **1g**, similar processes lead to biradical **R**′ after irradiation, eq 2. β-Elimination is not possible in **R**′ since the leaving group X is at the γ position of the radical center.[16] The only products observed in reactions of **1f** and **1g** were those derived from the Norrish Type II decay from **R**′.
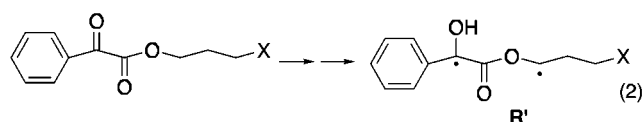
Kinetic Study. The quantum yields of disappearance of **1b**, **1d**, and **1e** in benzene were measured, Table 2. The values for **1b** and **1e** are close to those of other alkyl phenylglyoxylates.[4] That of **1d** was lower as is expected from the quenching of excited carbonyl triplet by sulfide compounds.[17] This electron transfer quenching process also explains the shorter triplet lifetimes measured by laser flash photolysis for the aryl sulfide-substituted alkyl phenylglyoxylate as compared to those of the halogen-substituted compounds, Table 2. Further, the triplet lifetime of **1g** is significantly shorter than that of **1d** in

(10) Since vinyl phenylglyoxylate, **2**, undergoes slow photoreaction, product analyses were carried out during the first 10% of the reaction to avoid complications from secondary photoproducts.

(11) No attempt was made to isolate the Norrish Type II products in this study since they have been adequately documented.[2b]

(12) Swern, D.; Jordan, Jr., E. F. *Organic Syntheses*; Rabjohn, N., Ed.; John Wiley & Sons: New York, 1963; Coll. Vol. IV, pp 977–980.
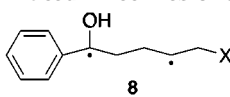
(13) Since both HX and X$_2$ are expected to add to the double bond in **2**,[9b] adding pyridine to the reactions prevents the consumption of **2** by secondary radical reactions. Trapping of HX and X$_2$ also helps to remove the colored photoproducts and makes the exhaustive irradiation of **1** possible. However, pyridine has been shown to react with the triplet excited state of alkyl phenylglyoxylate, Hu, S.; Neckers, D. C. *J. Photochem. Photobiol. A: Chem.*, submitted. Pyridine was not used in any of the quantitative experiments.

(14) Retention times on two different GC columns and the MS fraction patterns are identical to those of an authentic sample.

(15) Topping, R. M.; Kharasch, N. *J. Org. Chem.* **1962**, *27*, 4353–4356.

(16) β-Elimination would be possible from the 1,5-biradicals resulting from δ-hydrogen abstraction in **1f** and **1g**. However, δ-hydrogen abstraction in alkyl phenylglyoxylate is not favored.[2b]

(17) (a) Gutenplan, J. B.; Cohen, S. G. *J. Org. Chem.* **1973**, *38*, 2001–2007. (b) Hu, S.; Neckers, D. C. *Tetrahedron* **1997**, *53*, 2751–2766.

Table 3. Estimated Lifetimes of the 1,4-Biradicals

X	k_1, taken as the rate constants for β-cleavage in **8** $(s^{-1})^a$	$k_2 (s^{-1})$	$k_{total} (s^{-1})$	τ of biradical **R**
Cl	4×10^6	$> 4 \times 10^7$	$> 5.7 \times 10^7$	< 18 ns ^{c,d}
Br	$3 \times 10^{8\ b}$	1.2×10^8	5.3×10^8	2 ns
I	$5.0 \times 10^{11\ b}$	$< 5.0 \times 10^{10}$	$< 6.8 \times 10^{11}$	> 0.001 ns ^{c,e}
S—⟨C₆H₅⟩	4.4×10^8	1.8×10^7	9.7×10^8	10 ns
S(=O)—⟨C₆H₅⟩	2.5×10^9	$< 2.5 \times 10^8$	$< 3.8 \times 10^9$	> 0.4 ns ^{e}

^{a} Data from Ref. 9.
^{b} Minimum value.
^{c} Estimates made by assuming quantum yield of starting material disappearance to be the same as that of **1b**.
^{d} A **2/5** value less than 0.1 was assumed.
^{e} A **2/5** value greater than 10 was assumed.

Figure 1. Transient absorption spectra and decay traces from laser flash photolyses of 0.01 M benzene solutions of **1b** (A) and **1f** (B).

agreement with earlier observations in that a longer, more flexible chain connecting the electron donor with acceptor helps to attain the required electron transfer geometry in which the donor and the acceptor are in close proximity.[18]

Lifetime of 1,4-Biradical Intermediate. The rate constants for β-elimination in 1,4-biradicals, **8**, derived from γ-hydrogen abstraction in valerophenone have been measured,[9] Table 3. By assuming the β-cleavage rate constants of 1,4-biradicals **R**, k_1, to be the same as those of **8**, and measuring the relative yields of **2/5**, the rate constants for normal Norrish Type II decays in **R**, k_2 can be calculated.[19] The quantum yield of starting material disappearance is expressed by $(k_1 + k_2)/(k_1 + k_2 + k_3)$. From the values of k_1 and k_2, $k_{total} = k_1 + k_2 + k_3$ can be derived, as can the lifetimes of the biradical **R** ($\tau = 1/k_{total}$).

The lifetime values for **R** obtained in this study agree well with our earlier results.[4] These values are significantly shorter than those of the 1,4-biradicals with no oxygen in their skeletons ($\tau = 35-40$ ns[9,20]) and are close to those of typical Paternó–Büchi (pre-oxetane) biradicals ($\tau = 1.5-4$ ns).[21]

Discussion

β-Cleavage at 1,4-Biradical. Compounds **1f** and **1g** were studied to confirm that the cleavage of C–X bond occurs only at the 1,4-biradical stage and not in any

excited states. The fact that no C–X cleavage derived products were observed in the reactions of **1f** and **1g** while such products dominated the reactions of **1b** and **1d** suggests that the C–X cleavage is not induced by certain interactions between the excited carbonyl group and the X chromophores. Had this been the case, similar reaction pathways would be expected with **1b** and **1f**, or with **1d** and **1g**, since the interacting chromophores in these two groups are identical.

Further, addition of an equimolar amount of 1-bromopropane or iodoethane to 0.01 M benzene solution of methyl phenylglyoxylate shows no significant alternations to either the triplet-triplet absorption spectrum or the triplet lifetime in laser flash photolysis experiments. Lifetimes (Table 2) and transient absorption spectra (Figure 1) of the triplet excited states of **1b** and **1f** are also very similar, which implies that the difference in reaction pathway between these two compounds is not due to any difference in excited state reactivity, but due to the difference in the structures of the 1,4-biradicals (**R** *vs* **R′**, *vide supra*).

Regioselective Cyclization. We have studied the photochemical reactions of alkylsulfide-substituted alkyl phenylglyoxylates, **9**,[18b] and found that cyclol **10** was produced by an electron transfer mechanism as shown in Scheme 2. For **9a** and **9b**, cyclols **10a** and **10b** were the respective photoproducts derived in almost quantitative yields. When the chain became longer ($n = 4-11$),

(18) (a) Mar, A.; Fraser, S.; Winnik, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 4941−4943 and references therein. (b) Hu, S.; Neckers, D. C. *Tetrahedron* **1997**, *53*, 7165−7180, 12771−12788.

(19) Since both the β-cleavage and the Norrish Type II decay are first order reactions, the ratio of the yields of the resulting products is equal to the ratio of the reaction rate constants. We also assumed that the coupling of the radical pair leading to **2** is a highly efficient in-cage reaction. The diffusion apart of X• from the radical pair is negligible. Although the radical pair is formed as a triplet, the triplet ↔ singlet interconversion is promoted by the free spins residing entirely on a halogen *via* spin-orbit coupling, which results in efficient in-cage reactions producing **2**.[9b]

(20) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126−2131.

(21) (a) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6255−6257. (b) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629−630.
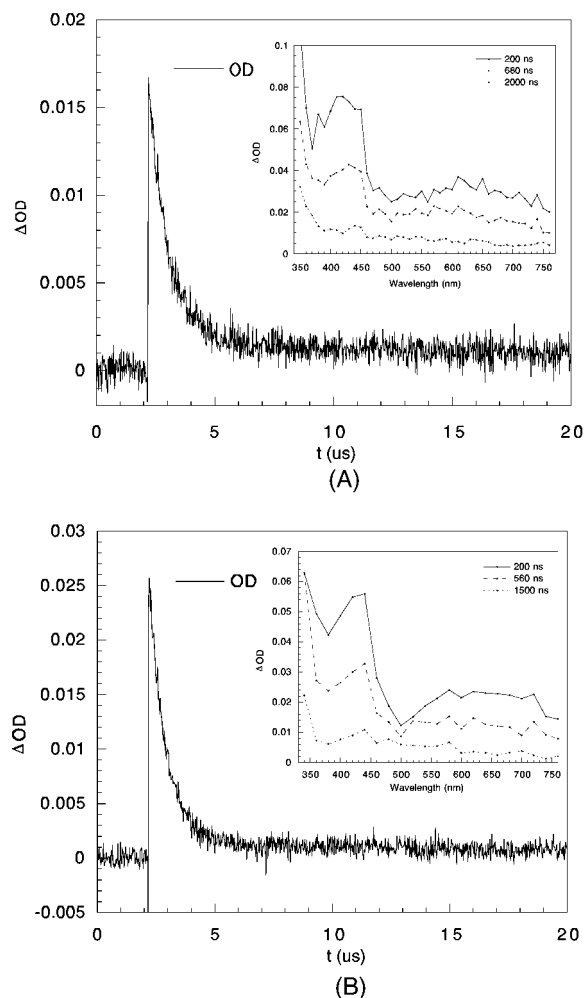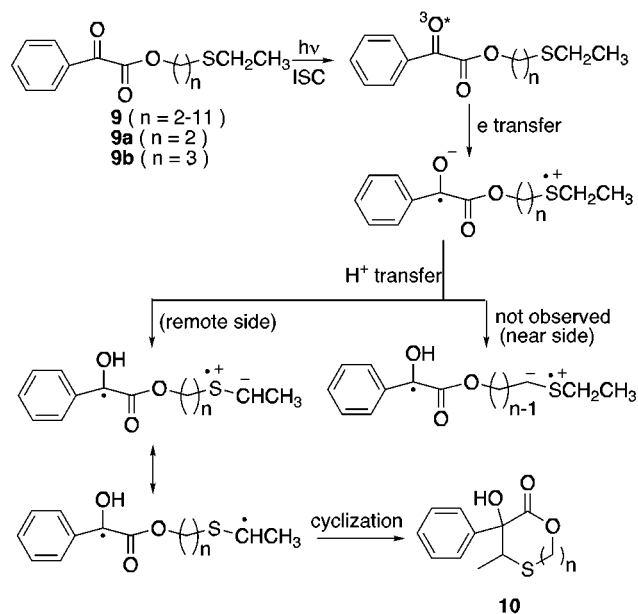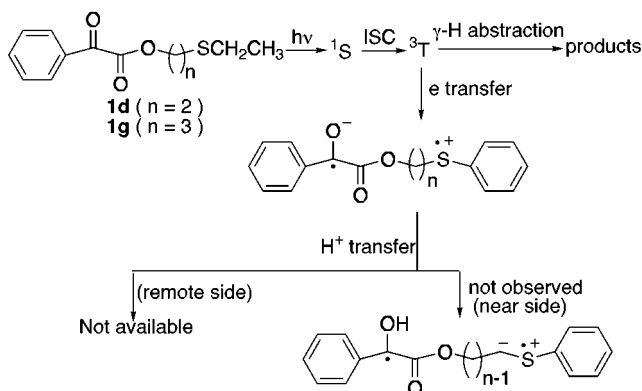
Scheme 2

Scheme 3

hydrogen abstraction derived products appeared in addition to **10**. In each of the compounds studied, cyclization occurred regioselectively from the methylene α to S on the side remote from the excited carbonyl group. No cyclization was observed from the α methylene on the near side of S.

When **1d** and **1g** were irradiated, similar electron transfer processes were expected, Scheme 3. Since there is no proton on the remote α carbon, no cyclization product was anticipated. Indeed, the products observed were derived exclusively from the γ-hydrogen abstraction process. This observation further supports our earlier proposal that proton transfer from α carbon on the near side of S is not productive due to conformational factors.[18b]

Other Halogenated Carbonyl Compounds. Analogous β-elimination reactions in δ-haloalkyl phenyl ketones have been studied.[9] This process produced products from both Norrish Type II cleavage and Yang cyclization in 1,4-biradical **8**. However, the 1,4-biradical derived from γ-hydrogen abstraction in α-bromo-α-diketone (**11**) cyclized to cyclobutanone (**12**) exclusively with the bromine still retained in the product, eq 3.[22] No β-cleavage from the biradical intermediate was observed. This was rationalized by the fact that the lowering of the spin density at the hydroxy radical site caused by the

conjugation with the keto group prevented cleavage of the bromine.[23]
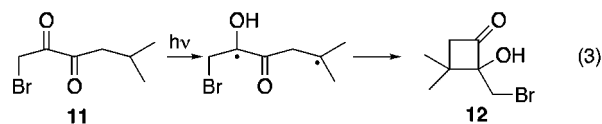
Other α-halo monoketones react rather differently in that fission of the C-halogen bond is the primary process in the excited states of these compounds.[24]

Conclusion

The photochemical reactions of several halo-/aryl sulfide-substituted alkyl phenylglyoxylates in benzene have been studied. The triplet excited state underwent a γ-hydrogen abstraction producing a 1,4-biradical intermediate, which further eliminated β-halogen or aryl sulfide radical. Normal Norrish Type II cleavage competed with the β-elimination process. The relative yields products derived from these two processes depended on the reactivities of the β-leaving groups. The lifetime of the intermediate 1,4-biradical was estimated.

Experimental Section

Material. Benzene (Aldrich) was distilled over sodium benzophenone ketyl immediately before use. Other chemicals were the highest grade obtainable from commercial sources and used as received. NMR spectra were taken with either a Varian Gemini 200 NMR spectrometer or a Varian Unity Plus 400 NMR spectrometer using chloroform-*d* as solvent. Chemical shifts are in ppm with TMS as the internal standard. GC measurements were carried out on a Hewlett-Packard (HP) 5890 gas chromatograph with a 30 m × 0.253 mm i.d. × 0.25 μm film thickness DB-1 column (J & B Scientific) and a flame ionization detector. GC/MS were taken on a Hewlett-Packard 5988 mass spectrometer coupled to a HP 5880A GC with a 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 ms column (J & B Scientific), interfaced to a HP 2623A data processor. Thin layer chromatography was performed with Whatman silica gel coated TLC plates. Silica gel (60 Å, 60−200 mesh, Aldrich) was used in column chromatography. High resolution mass spectra were obtained from the University of Illinois at Urbana−Champaign.

Quantum Yields. A benzene solution (0.1 M) of valerophenone as actinometer ($\Phi_{acetophenone} = 0.33$)[25] was always irradiated parallel to the sample solution on a "merry-go-round". The reactions were monitored by GC except for that of **1e**. The GC was calibrated against these compounds using chlorobenzene as the internal standard. Quantum yields reported are averages of three measurements. In the reactions of **1e**, the disappearance of starting material was monitored by NMR since **1e** was not detectable under normal GC conditions. Signals from aromatic hydrogens in the reaction mixture were used as the internal standard. The disappearance of **1e** was monitored by its down field (≈ 8.00 ppm) signals from the aromatic hydrogens.

Time-Resolved Laser Flash Photolysis. Nanosecond laser flash photolyses were carried out on a setup described by Ford and Rodgers[26] using the third harmonic of a Q-switched Nd:YAG laser (Continuum, YG660) as the excitation source. The sample solution in a quartz cuvette was purged

(22) Hamer, N. K. *J. Chem. Soc., Perkin Trans. 1* **1983**, 61−64.

(23) Wagner, P. J.; Park, B.-S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York, 1991; Vol. 11, pp 227−366.
(24) (a) Jones, II, G.; McDonnell, L. P. *J. Chem. Soc., Chem. Commun.* **1976**, 18−19. (b) Givens, R. S.; Strekowski, L. *J. Am. Chem. Soc.* **1975**, *97*, 5867−5873 and references therein.
(25) Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1972**, *94*, 3852−3857.
(26) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1994**, *98*, 3822−3831.

with argon for 5 min before and during the experiment. The samples were excited with 355 nm pulses (pulse width *ca.* 7 ns). Light from a 200 W xenon lamp was focused into the sample solution and then into a SPEX1680 0.22 mm double spectrometer. A computer controlled kinetic spectrophotometer (Kinetic Instruments) was used in its absorption mode to obtain transient spectra and kinetic data. The spectrometer was interfaced with a digital oscilloscope (Le Croy 9450, 350 MHz bandpass).

General Procedure for the DCC Esterification (syntheses of compound **1**). To the appropriate hydroxyl compound, benzoylformic acid, and 4-(*N*,*N*-dimethylamino)pyridine (molar ratio: 1.0:1.1:0.1) in a round bottom flask was added dry dichloromethane to make an approximate 0.2 M solution. The solution was then placed over ice to cool to 0 °C. An equal molar amount of 1,3-dicyclohexylcarbodiimide (DCC) in dry dichloromethane was added dropwise to the stirred solution. Usually, a white precipitate formed instantly. The mixture was then allow to warm up to room temperature and stirred overnight. The precipitate was filtered and the solvent evaporated in *vacuo*. Purification by flash column chromatography with indicated eluents following the compound name produces **1** in good yields.

2′-Chloroethyl phenylglyoxylate (1a) (hexanes:ethyl acetate = 10:1): R_f in 5/1 (hexanes/ethyl acetate) = 0.32, yellowish oil, yield 90%. δ_H (400 MHz) 3.80−3.83 (m, 2H), 4.63−4.65 (m, 2H), 7.49−7.53 (m, 2H), 7.64−7.68 (m, 1H), 8.01−8.04 (m, 2H). δ_C (APT, 50 MHz) 40.93, 65.21, 128.84, 129.94, 132.03, 135.03, 163.13, 185.58. MS 214 (M$^+$ + 2, 0.05), 212 (M$^+$, 0.1), 105 (100), 77 (48), 51 (21). HRMS *m/e* calculated for C$_{10}$H$_9$ClO$_3$: 212.0240, measured: 212.0241.

2′-Bromoethyl phenylglyoxylate (1b) (hexanes:ethyl acetate = 10:1): R_f in 5/1 (hexanes/ethyl acetate) = 0.30, yellow oil, yield 86%. δ_H (400 MHz) 3.64 (t, *J* = 6.2 Hz, 2H), 4.70 (t, *J* = 6.2 Hz, 2H), 7.49−7.54 (m, 2H), 7.64−7.69 (m, 1H), 8.01−8.04 (m, 2H). δ_C (APT, 50 MHz) 27.70, 64.99, 128.83, 129.94, 132.01, 135.01, 162.96, 185.51. MS (EI): 258 (M$^+$ + 2, 0.08), 256 (M$^+$, 0.07), 105 (100), 77 (57), 51 (26). MS (CI): 259 (M + 2 + 1), 257 (M + 1). HRMS (CI) *m/e* calculated for C$_{10}$H$_{10}$BrO$_3$ (M + 1): 256.9813, measured: 256.9822.

2′-Iodoethyl phenylglyoxylate (1c) (hexanes:ethyl acetate = 10:1): R_f in 5/1 (hexanes/ethyl acetate) = 0.30, yellow oil, yield 85%. δ_H (400 MHz) 3.42 (t, *J* = 7.0 Hz, 2H), 4.65 (t, *J* = 7.0 Hz, 2H), 7.51−7.54 (m, 2H), 7.65−7.70 (m, 1H), 8.02−8.05 (m, 2H). δ_C (APT, 50 MHz) −1.21, 65.90, 128.86, 130.03, 132.07, 135.05, 162.80, 185.53. MS (EI) 304 (M$^+$, 0.09), 155 (14), 105 (100), 77 (41), 51 (20). MS (CI): 305 (M + 1). HRMS (CI) *m/e* calculated for C$_{10}$H$_{10}$IO$_3$ (M + 1): 304.9675, measured: 304.9677.

2′-(Phenylthio)ethyl phenylglyoxylate (1d) (hexanes: ethyl acetate = 10:1): R_f in 5/1 (hexanes/ethyl acetate) = 0.38, yellow oil, yield 81%. δ_H (400 MHz) 3.25 (t, *J* = 7.0 Hz, 2H), 4.51 (t, *J* = 7.0 Hz, 2H), 7.18−7.23 (m, 1H), 7.26−7.31 (m, 2H), 7.40−7.43 (m, 2H), 7.46−7.51 (m, 2H), 7.61−7.66 (m, 1H), 7.99−8.02 (m, 2H). δ_C (APT, 50 MHz) 32.13, 64.08, 126.88, 128.79, 129.06, 129.97, 130.21, 132.16, 134.25, 134.92, 163.27, 185.75. MS 286 (M$^+$, 4.6), 136 (24), 105 (100), 77 (53), 51 (21). HRMS *m/e* calculated for C$_{16}$H$_{14}$SO$_3$: 286.0664, measured: 286.0663.

2′-(Phenylsulfinyl)ethyl phenylglyoxylate (1e) (hexanes:ethyl acetate = 1:1): R_f in ethyl acetate = 0.56, yellow oil, yield 75% (two steps). δ_H (400 MHz) 3.16 (dt, J_1 = 5.6 Hz, J_2 = 14 Hz, 1H), 3.24−3.31 (m, 1H), 4.65 (dt, J_1 = 5.6 Hz, J_2 = 12 Hz, 1H), 4.80−4.86 (m, 1H), 7.47−7.54 (m, 5H), 7.64−7.69 (m, 3H), 7.99−8.01 (m, 2H). δ_C (APT, 50 MHz) 55.18, 58.58, 123.66, 128.81, 129.32, 129.92, 131.25, 131.96, 135.03, 142.78, 162.89, 185.22. MS (EI): 302 (M$^+$, 0.2), 177 (34), 105 (100), 77 (84), 51 (38). MS (CI): 303 (M + 1). HRMS (CI) *m/e* calculated for C$_{16}$H$_{15}$SO$_4$ (M + 1): 303.0691, measured: 303.0684.

3′-Bromopropyl phenylglyoxylate (1f) (hexanes:ethyl acetate = 10:1): R_f in 5/1 (hexanes/ethyl acetate) = 0.31, yellow oil, yield 91%. δ_H (400 MHz) 2.32 (quintet, *J* = 6.4 Hz, 2H), 3.51 (t, *J* = 6.4 Hz, 2H), 4.54 (t, *J* = 6.4 Hz, 2H), 7.50−7.54 (m, 2H), 7.65−7.69 (m, 1H), 7.99−8.02 (m, 2H). δ_C (APT, 50 MHz) 28.87, 31.14, 63.64, 128.88, 129.92, 132.23, 134.98, 163.49, 185.91. MS 272 (M$^+$ + 2, 0.1), 270 (M$^+$, 0.1), 105 (100), 77 (60). HRMS *m/e* calculated for C$_{11}$H$_{11}$BrO$_3$: 269.9892, measured: 269.9890.

3′-(Phenylthio)propyl Phenylglyoxylate (1g). 3-(Phenylthio)-1-propanol was synthesized by a general method described previously.[18b] δ_H (400 MHz) 1.76 (quintet, *J* = 6.4 Hz, 2H), 2.31 (s, 1H), 2.91 (t, *J* = 6.4 Hz, 2H), 3.62 (t, *J* = 6.4 Hz, 2H), 7.05−7.09 (m, 1H), 7.16−7.20 (m, 2H), 7.23−7.25 (m, 2H). δ_C (APT, 50 MHz) 29.96, 31.51, 61.01, 125.81, 128.77, 128.94, 136.10. MS 168 (M$^+$, 44), 123 (12), 110 (100). HRMS *m/e* calculated for C$_9$H$_{12}$SO: 168.0609, measured: 168.0609. Compound **1g**: (hexanes:ethyl acetate = 10:1), R_f in 5/1 (hexanes/ethyl acetate) = 0.40, yellow oil, yield 87%. δ_H (400 MHz) 2.08 (quintet, *J* = 6.4 Hz, 2H), 3.03 (t, *J* = 6.4 Hz, 2H), 4.50 (t, *J* = 6.4 Hz, 2H), 7.15−7.20 (m, 1H), 7.25−7.29 (m, 2H), 7.33−7.36 (m, 2H), 7.47−7.51 (m, 2H), 7.62−7.66 (m, 1H), 7.98−8.00 (m, 2H). δ_C (APT, 50 MHz) 27.85, 29.91, 64.30, 126.26, 128.84, 128.95, 129.52, 129.94, 132.27, 134.90, 135.40, 163.60, 186.04. MS 300 (M$^+$, 4.6), 149 (19), 123 (8.5), 105 (100), 77 (25). HRMS *m/e* calculated for C$_{17}$H$_{16}$SO$_3$: 300.0820, measured: 300.0820.

General Procedures for Irradiation of Samples and Isolating Products. Samples were dissolved in benzene and sealed with a rubber septum bound by sticky parafilm. Degassing was achieved by bubbling dry argon gas through the solution for 10−15 min. Irradiation was carried out in a Rayonet RPR-100 photoreactor equipped with sixteen 350 nm GE F8T5·BLB UV lamps. After irradiation, the solvent was evaporated on a rotary evaporator, and the resulting mixture was chromatographed under pressure.

Vinyl phenylglyoxylate (2) was isolated in a photosylate of **1d** (hexanes:ethyl acetate = 10:1): R_f in 5/1 (hexanes/ethyl acetate) = 0.46, yellow oil, yield 54%. δ_H (400 MHz) 4.85 (dd, J_1 = 6.4 Hz, J_2 = 2.4 Hz, 1H), 5.16 (dd, J_1 = 13.6 Hz, J_2 = 2.4 Hz, 1H), 7.44 (dd, J_1 = 13.6 Hz, J_2 = 6.4 Hz, 1H), 7.50−7.54 (m, 2H), 7.65−7.69 (m, 1H), 8.03−8.06 (m, 2H). δ_C (APT, 50 MHz) 100.93, 128.90, 130.05, 132.08, 135.14, 140.18, 160.02, 184.58. MS (EI): 148 (M$^+$ − 28, 0.8), 105 (100), 77 (60), 51 (27). MS (CI): 177 (M + 1). HRMS (CI) *m/e* calculated for C$_{10}$H$_9$O$_3$ (M + 1): 177.0552, measured: 177.0550. Its structure was confirmed by independent synthesis.[12]

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for the new compounds **1a**−**g**, **2**, and ^{1}HNMR spectra used to quantify **2/5** in the reactions of **1b** and **1d** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.