Photochemical Reactions of Alkyl Phenylglyoxylates[1]

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Three new photoproducts, ethyl *O*-benzoyl mandelate (**5a**), ethyl *O*-acetylmandelate (**6a**), and biphenyl triketone (**7a**) are isolated and identified in the reactions of ethyl phenylglyoxylate (**1a**) in benzene. Quantum yields and initial rate constants of product formation are shown to be concentration dependent. For the formation of carbonyl product **3** at lower starting material concentrations (<0.01 M), quantum yields greater than 1 are observed. Variations in the quantum yields as a function of reaction time are due to the accumulation of α-hydroxyphenyl ketene (**D**). The relative reactivities of triplet excited states of phenylglyoxylates **1** and phenyl ketones are compared. A mechanism involving both intramolecular γ-H abstraction and intermolecular H abstraction, which leads to radical chain reaction, is proposed. Rate constants for intramolecular γ-H abstraction (k_N) and intermolecular H abstraction (k_I) of methyl phenylglyoxylate (**1d**) are measured.

Introduction

Photochemical processes occurring at the wavelengths of commercial lasers and releasing species reactive to nucleophiles are potential candidates for sequential processes to be carried out on surfaces.[2] Prior attention has focused on intramolecular reactions of *o*-nitro aromatics[3] (a reaction discovered very early, but developed more recently by Patchornik and co-workers).[4] In an initial employ of a Patchornik-like process, Fodor et al.[5] outlined "light directed spatially addressable parallel chemical synthesis", freeing surface NH_2 which could be subsequentially coupled either to the carboxy terminus of an amino acid or, for detection, to an isothiocyanate (fluorescein isothiocyanate, FITC), see Figure 1.

Alkyl phenylglyoxylate photochemistry is appealing for laser addressable surface reactions because the ester absorbs at 324 nm (the wavelength commercially used in stereolithographic target directed laser chemistry) and the α-hydroxyarylketene produced reacts rapidly with alcohols[6] (Scheme 1), imines,[7] and *vide infra* water. The aryl function is easily converted to polymerizable moieties (i.e., *p*-vinylphenyl), and the polymers formed (i.e., poly-(*p*-vinylphenyl) glyoxylate esters[8]) can be cast or spin-coated to thin films. Further, the eliminated small molecule, an aldehyde or ketone, is soluble in various solvents and is easily removed.

In view of the known photodimerization of aromatic ketones in alcohols,[9] the Norrish type II results for alkyl

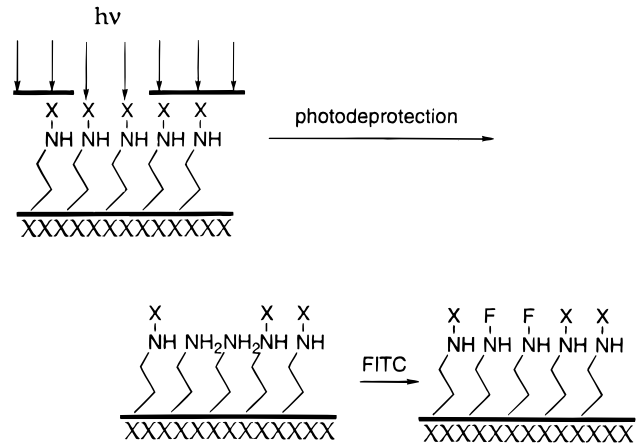
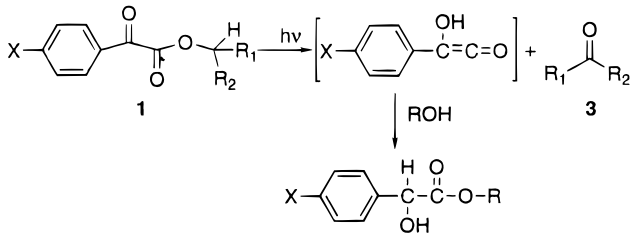


Figure 1.

Scheme 1



phenylglyoxylate esters were initially surprising.[6,10] An intramolecular γ-H abstraction on the alkyl group followed by an α,β cleavage producing α-hydroxyphenylketene along with the carbonyl product (**3**) from the alkyl component of the starting material was postulated. Recent mechanistic studies on a series of alkyl phenylglyoxylates[11] showed little variation in the quantum yields of product formation as a function of ester structure, although the triplet lifetime of the *tert*-butyl ester was substantially longer than that of the esters possessing γ hydrogens. Though the existence of the intermediate

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(9) For a review, see: Neckers, D. C. Mechanistic Organic Photochemistry; Reinhold: 1967; Chapter 7.

(10) Biomolecular photoreduction occurs with phenylglyoxylates as well. See: Schönberg, A.; Latif, N.; Moubasher, R.; Sina, A. *J. Chem. Soc.* **1951**, 1364−1368. As we shall show the process is concentration and solvent dependent.

(11) Encinas, M. W.; Lissi, E. A.; Zanocco, A.; Stewart, L. C.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 386−391.

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formed by Norrish type II reaction (ketene **D**) has been widely accepted, phenylglyoxal, the expected tautomer of α-hydroxyphenylketene (**D**) has never been observed.[11−15] Leermakers reported benzaldehyde and carbon monoxide as products from the photolysis of a concentrated solution of ethyl phenylglyoxylate in benzene and suggested a Norrish type I mechanism for their formation.[16] The analogous alkyl pyruvates have also been studied in detail by Davidson and Goodwin.[17]

The photolysis of alkyl phenylglyoxylates has been used in synthetic applications. Aoyama trapped the ketene intermediate in the synthesis of β-lactams.[15] Kraus utilized the rearrangement of the 1,4-biradical from intramolecular γ-hydrogen abstraction to form cyclic lactones of varying ring sizes.[18] Pyruvate ester photochemistry, analogous to the reported reactions of phenylglyoxylates, was used to convert sensitive alcohols to ketones under mild conditions.[19] Recently, though in modest yield, Tepper and Pirrung employed substituted arylglyoxylates to oxidize alcohols to ketones.[20]

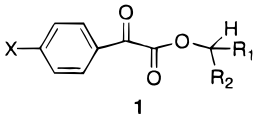
The present study was undertaken to clarify certain mechanistic ambiguities in the n−π* triplet reactions of alkyl phenylglyoxylate esters since the initially formed products from the aromatic residue in nonprotic solvents remained elusive. We now report isolation of several additional products from the photoreaction of various alkyl phenylglyoxylates upon irradiation in benzene. The quantum efficiencies of these reactions under different reaction conditions have been measured, and a mechanism involving both intramolecular γ-H abstraction and an intermolecular radical chain process is proposed. The rate constants of various reactions of the triplet have been measured.

Results

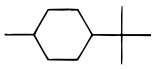
Product Isolation and Identification. The alkyl phenylglyoxylates investigated in this study are summarized in Table 1. All were irradiated at 350 nm in aprotic solvents (chloroform, acetonitrile, and benzene; benzene preferred). Quantitative product analysis of the mixtures were carried out by GC or NMR. The products from the photoreaction of **1a** were isolated and are presented in Scheme 2.[21] Product development as a function of irradiation time is shown in Table 2. Similar results are obtained for other glyoxylates, **1b**−**k**.

No products were obtained from the photolysis of *tert*-butyl phenylglyoxylate (**1l**), and starting material was recovered unchanged even after prolonged irradiation. There is thus no evidence of a Norrish type I reaction as

Table 1. Phenylglyoxylate Esters Studied

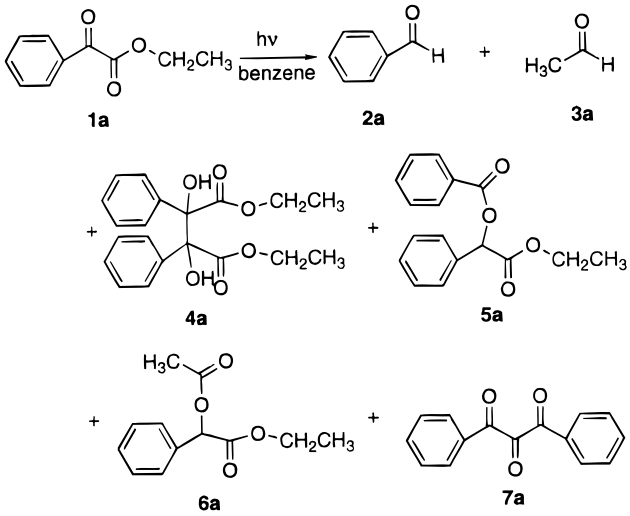


1

Compound	X	−CHR$_1$R$_2$
1a	H	−CH_2CH_3
1b	H	
1c	H	
1d	H	−CH_3
1e	H	−$CH(CH_3)_2$
1f	H	−$CH_2CH_2CH_2CH_3$
1g	H	−$CH(CH_3)CH_2CH_3$
1h	F	−CH_2CH_3
1i	Cl	−CH_2CH_3
1j	Br	−CH_2CH_3
1k	OCH_3	−CH_2CH_3
1l	H	−$CH(CH_3)_3$

[a] **1c** is a mixture of isomers, >95% trans.

Scheme 2[a]



[a] Compound 7a was isolated together with its monohydrate (*ca.* 1:1 ratio) after column chromatography since polyketones are readily interconvertible with their hydrates, see ref 21.

Table 2. Product Distribution with Time: Ethyl Phenylglyoxylate in Benzene

	concentration (M)						
time (mins)	1a	2a	3a	4a	5a	6a	7a
0	0.14	0.000	0.000	0.000	0.000	0.000	0.000
15	0.13	0.013	0.025	a	0.003	0.00	0.002
30	0.08	0.024	0.034	a	0.003	0.001	0.002
45	0.05	0.032	0.045	a	0.003	0.001	0.003
60	0.03	0.039	0.054	a	0.003	0.001	0.003
75	0.01	0.041	0.061	a	0.004	0.001	0.003
90	0.01	0.043	0.063	a	0.004	0.001	0.004
120	0.00	0.046	0.064	0.027	0.006	0.002	0.004

[a] **4a** was formed but not determined qualitatively.

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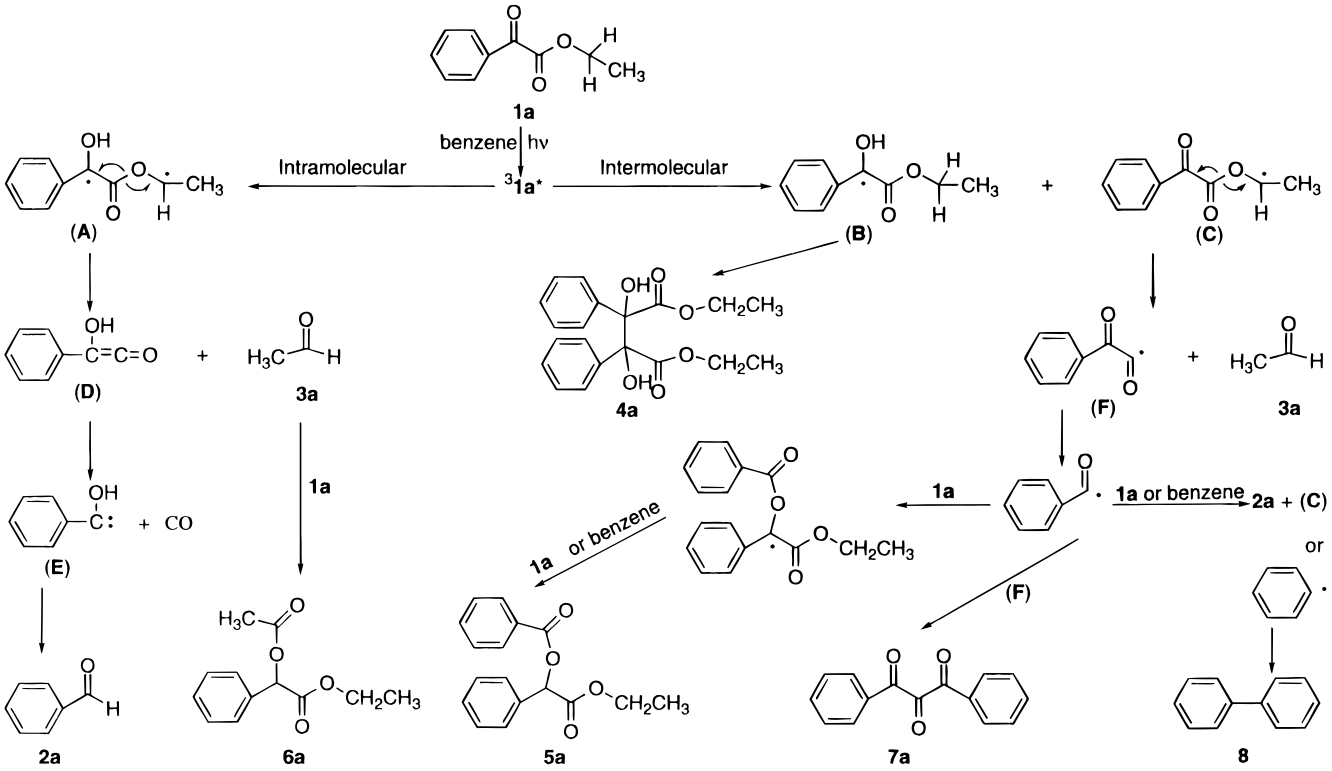
(21) (a) Rubin, M. B. *Chem. Rev.* **1975**, *75*, 177−202 and references cited therein. (b) Wasserman, H.; Fukuyama, J.; Murugesan, N.; Van Duzer, J.; Lombardo, L.; Rotello, V.; McCarthy, K. *J. Am. Chem. Soc.* **1989**, *111*, 371. (c) Lai, J. H.; Pham, H.; Hangauer, D. G. *J. Org. Chem.* **1996**, *61*, 1872−1874.

Scheme 3



proposed by Leermakers to explain the formation of benzaldehyde and CO, nor any evidence for δ-hydrogen abstraction. In comparison with related systems such as aryl ketones,[34] this result indicates that δ-hydrogen abstraction is slow in alkyl phenylglyoxylates.

Proposed Mechanism. A proposed mechanism which accounts for all of the products is shown in Scheme 3.

The proposed intramolecular Norrish type II reaction requires the abstraction of a γ-hydrogen producing biradical **A** followed by α,β cleavage yielding ketene **D** and a carbonyl product **3a**. Since ketene intermediate (**D**) has been proposed to undergo tautomerization to phenylglyoxal,[6] we synthesized phenylglyoxal[22] and compared the NMR spectra of it with that from the photolysis of **1a**. This gives no evidence of phenylglyoxal in the photoreaction mixtures at any degree of conversion. On the other hand, **D** is also expected to readily lose CO to form carbene (**E**),[23] especially under photochemical conditions.[23m] The rearrangement from **E** to benzaldehyde involves a hydrogen migration, and the analogous carbene rearrangement to form olefins has been reported.[24] Attempts to trap **E** with 2,3-dimethyl-2-butene were unsuccessful. Instead, a prior Paternò–Büchi reaction[25] of triplet **1a** with alkene proceeds almost quantitatively. However, ketene **D** may be trapped by adding *N*-benzylidenebenzylamine (**12**) to the reactions of **1a** and **1c**, and a diastereoisomeric mixture of 3,4-diphenyl-1-benzyl-3-hydroxyazetidin-2-one (**13**) is isolated in both cases. Mandelic acid is also isolated from reactions of **1a** in benzene when water is added to trap ketene **D** in this study. The formation of dimer, diethyl 2,3-dihydroxy-2,3-diphenylsuccinate (**4a**), from the reaction of ethyl phenylglyoxylate (**1a**) in nonpolar, non-hydrogen-donating solvents suggests a significant role for the *O*-alkyl function of the starting ester in furnishing a reducing hydrogen atom. Such intermolecular hydrogen abstraction from the ethyl group of **1a** by the triplet of a second molecule of **1a** results in radicals **B** and **C**, and the dimerization of the α-hydroxyphenylcarboxy radicals (**B**) to diethyl 2,3-dihydroxy-2,3-diphenylsuccinate (**4a**) is expected.[6] Fragmentation of **C** yields benzoyl formate radical **F**, which loses CO to form a benzoyl radical which abstracts a hydrogen to regenerate radical **C** or a phenyl radical if the solvent, benzene, is involved. Biphenyl (**8**) is also identified as a product from the dimerization of phenyl radicals. Ethyl *O*-benzoylmandelate (**5a**) forms from the addition of benzoyl radical to the ground state phenylglyoxylate as the first step. A very early paper by Vaughan et al.[26] reported a similar reaction from the decomposition of benzoyl peroxide in benzaldehyde. Ethyl *O*-acetylmandelate (**6a**) is thought to form from the addition of acetyl radicals to **1a** followed by hydrogen

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(25) Paternò –Büchi reaction between alkyl pyruvates and alkenes has been reported. Buhr, S.; Griesbeck, A. G.; Lex, J.; Mattay, J.; Schröer, J. *Tetrahedron Lett.* **1996**, *37*, 1195–1196 and references therein.

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Table 3. Quantum Yields and Initial Rate Constants of Product Formation

compd	initial *C* (M)	temp (°C)	Φ_2[a]	Φ_3[a]	k_2 (s^{-1})	k_3 (s^{-1})	yield of **2** (%)	yield of **3** (%)
1a	0.01	25	0.87	Δ	0.29	Δ	55	Δ
	0.10	25	0.34	Δ	0.06	Δ	23	Δ
	0.01	10	0.60	Δ	0.20	Δ	43	Δ
	0.01	55	0.39	Δ	0.13	Δ	33	Δ
	0.10	55	0.11	Δ	0.04	Δ	Δ	Δ
d_5-**1a**[c]	0.01	25	0.33	Δ	too small	Δ	38	Δ
	0.10	25	0.14	Δ	too small	Δ	6	Δ
1b	0.01	25	0.62	2.9	0.21	0.43	37	57
	0.10	25	0.18	0.62	0.05	0.09	21	35
1c	0.007	25	0.84	3.6	0.31	0.61	39	78
	0.01	25	0.81	2.35	0.19	0.48	Δ	Δ
	0.10	25	0.27	0.63	0.06	0.10	15	32
	0.008	10	0.76	1.5	0.16	0.46	27	32
	0.10	10	0.13	0.40	0.01	0.10	12	32
	0.01	55	0.73	1.5	0.17	0.26	47	57
	0.06	55	0.18	0.67	0.06	0.13	21	36

[a] Quantum yields are the highest value obtained in three or four measurements within 5% of the reactions. [b] Δ denotes that the products are identified but not measured quantitatively. [c] d_5-**1a** is ethyl-d_5 phenylglyoxylate.

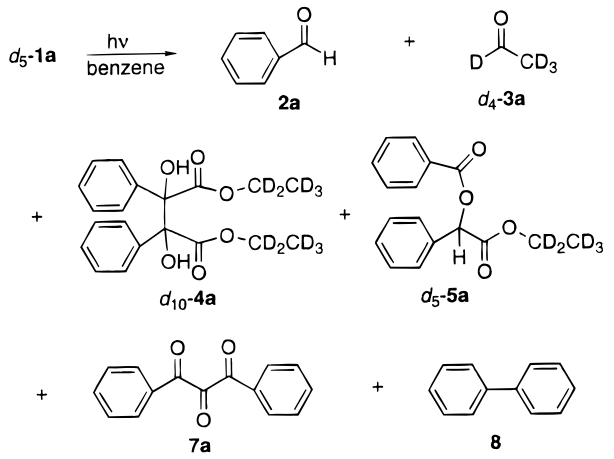
abstraction. Diphenyl triketone (**7a**) results from coupling the benzoyl radical with **F**.

Quantum Yields and Initial Rates of Product Formation. Representative quantum yields of product formation measured in benzene are reported in Table 3. The initial rate constants of product formation (k_2 and k_3) are obtained by assuming the reactions are pseudo zeroth order (rate $= k_{obs}t = k_{2(3)}$[M]t) during the first 5% of the reaction (assuming concentration of starting ester [M] remains constant). Glyoxylates **1d**−**k** behave very similarly to **1a**.

We observed a decrease in the quantum yields of formation of both benzaldehyde (Φ_2) and the corresponding carbonyl product (Φ_3) with irradiation time likely (as Scaiano proposed) because of competitive absorption by the yellow ketene intermediate (**D**).[11] We also noticed that the quantum yield of benzaldehyde formation (Φ_2) first increases and then decreases with time particularly when the concentrations of starting materials are low (<0.01 M) (data not shown). The lower Φ_2 at the onset of the reaction is due to the formation of ketene **D**. If a sample of **1a** is irradiated and then allowed to stand in room light until the yellow color disappears completely, a measurable increase in the concentration of benzaldehyde is observed. Assuming benzaldehyde and CO are the only products derived from ketene **D**, we estimate the concentration upper limit for ketene accumulation to be about 0.0001 M from the increase in benzaldehyde concentration after the yellow color completely disappeared. This low concentration explains why the increasing−decreasing mode in Φ_2 is not obvious in experiments carried out at higher initial concentrations of glyoxylate. Under this condition, the accumulation of **D** (0.0001 M) is negligible when compared to the amount of **2** produced.

As the data in Table 3 show, in the same reaction, Φ_3 and k_3 are higher than the corresponding Φ_2 and k_2. This is partially explained by the formation of products **5** and **7**, which consume benzoyl radicals but not the alkyl moiety of the starting glyoxylate. Quantum yields and initial rate constants vary with the concentration of starting material. Those measured at starting material concentrations of 0.1 M are in the same range as the literature values,[11] but results from reactions with initial concentrations of 0.01 M are substantially higher. Quantum yield, Φ_3, measured at lower initial concentrations is greater than 1, strongly suggesting a radical chain process. The significant decrease in Φ_2, Φ_3 and k_2, k_3 as a function of increasing initial glyoxylate concentration can be understood by the facilitation of intermolecular hydrogen abstraction and coupling of mandelate radicals (**B**) to form **4** at a higher concentration.

Scheme 4



Some temperature dependence on the values of Φ and k is also observed. Decreases in Φ_2, Φ_3 and k_2, k_3 at lower temperatures can be understood according to Arrhenius' equation ($k = A\exp(-E_a/RT)$). However, higher reaction temperatures also somewhat lower Φ and k. This is because the intermolecular reactions are slower at higher temperature, which also agrees with the notion of a intermolecular radical chain reaction mechanism. An increase in both Φ_2, Φ_3 and k_2, k_3 is expected only if just an intramolecular mechanism is operating.

Isotope Effects. Leermakers[16] and Davidson[17] both reported a lack of primary isotope effects in reactions of isopropyl pyruvate esters and similarity of reactivities between primary and secondary esters though they offered different explanations. We studied the photodecomposition of d_5-ethyl phenylglyoxylate (d_5-**1a**) in benzene. The results show a small overall isotope effect since Φ_2 is only about half that of similar reactions of **1a**. Surprisingly, deuteriobenzaldehyde d_1-**2** is detected only when the reaction of d_5-**1a** is carried out in deuteriated benzene. No deuteriobenzaldehyde is obtained when d_5-**1a** is irradiated in benzene, which indicates that benzoyl radical abstracts hydrogen from benzene or other hydrogen sources, see Scheme 4.

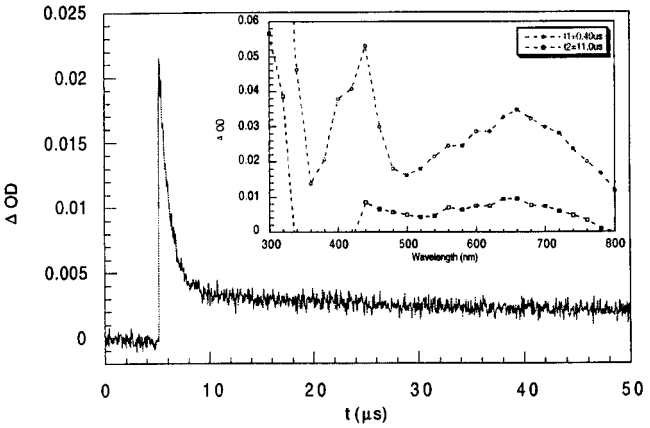


Figure 2. Transient absorption decay trace of **1d** in benzene (0.041 M) monitored at 440 nm. Inset is the transient absorption spectra.

These data suggest a large isotope effect on the intramolecular hydrogen abstraction in that excess solvent is preferred as a locus of atom abstraction over the OCD_2CD_3 moiety even though the solvent is the relatively unreactive benzene. If alkyl pyruvates react by the same mechanism, the apparent lack of isotope effect observed in earlier studies may well be because these authors were unaware of the intermolecular hydrogen abstraction process. It is likely that the acetaldehyde formed from reactions of deuteriated isopropyl pyruvate is CH_3CHO rather than CH_3CDO because the hydrogen is furnished by the solvent especially when solvents other than benzene were used. Since both intermolecular and intramolecular reactions are occurring with compounds containing deuteriated *O*-alkyl functions, the intermolecular mechanism predominates to furnish major products. The existence of intermolecular hydrogen abstraction also explains the similarity in reactivity between primary and secondary esters.

Kinetic Studies. We observe no products from the cyclization of the 1,4-biradical (**A**) produced by the intramolecular hydrogen abstraction. This indicates that the lifetime of biradical **A** is very short, which is characteristic of biradicals with oxygen in their skeletons.[27] They are undetectable by nanosecond flash spectroscopy.[28] In this study, nanosecond laser flash photolysis of benzene solutions of methyl phenylglyoxylate (**1d**) at 355 nm was followed by the appearance of transient absorption at 440 nm, Figure 2. Two distinctive decay patterns were observed. The first decay has a lifetime of 1.2 μs at this condition and is attributed to the glyoxylate triplet. The second decay with a lifetime of 80 μs is assigned to the methyl mandelate radical (corresponding to radical **B** in **1a**). It has the same lifetime as the radical produced by laser flash photolysis of the glyoxylate in 2-propanol (a fast decay with a lifetime of 40 ns followed by a major decay with lifetime of 80 μs). In an earlier study,[11] this slow decay was attributed to residual absorption.

The reactions of phenylglyoxylate photochemistry can be outlined in Scheme 5. In this scheme, reaction (4) involves all unimolecular decay processes other than chemical reaction, (5) is the intramolecular Norrish type

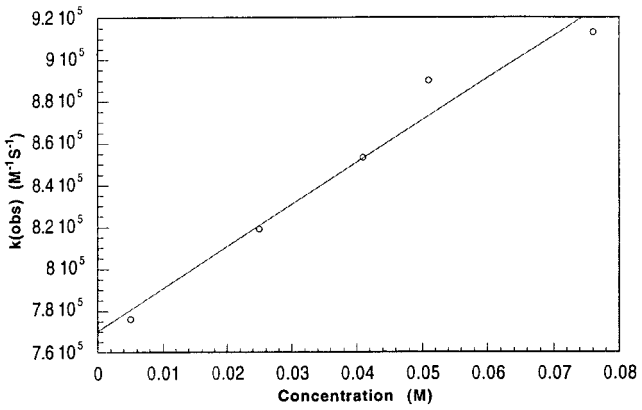


Figure 3. Change of $k_{obs} = 1/\tau'$ with ester concentration [M] for **1d**.

Scheme 5

$$M \xrightarrow{h\nu} {}^1M \quad (1)$$

$${}^1M \longrightarrow M \quad (2)$$

$${}^1M \xrightarrow{ISC} {}^3M \quad (3)$$

$${}^3M \xrightarrow{k_d} M \quad (4)$$

$${}^3M \xrightarrow{k_N} \text{Products} \quad (5)$$

$${}^3M + M \xrightarrow{k_I[M]} \text{Products} \quad (6)$$

$${}^3M + Q \xrightarrow{k_q[Q]} \text{Products} \quad (7)$$

II reaction, (6) is the intermolecular hydrogen abstraction reaction, and (7) is the quenching of triplet by the added quencher (Q). To avoid the involvement of solvent in these reactions, benzene is used as a solvent for the rate constant measurements. Using the methodology of Dalton and Turro et al.[29] for determining Norrish type II rate constants of alkyl ketones, we can determine the rate constants for reactions of methyl ester (**1d**) using the triplet lifetime of the *tert*-butyl ester (**1l**). For **1l**, reaction (4) is the only process that deactivates its triplets and k_d can be obtained from its triplet lifetime, which is measured as 12.7 μs in benzene. This gives a k_d value of 7.88 $\times$ 10^4 s^{-1}, and it can be taken as the unimolecular decay rate (k_d) for the other ester (**1d**).

The triplet lifetime measured at very low concentrations ([M] $\approx$ 0, so that reaction (6) is negligible) of **1d** is $\tau = 1/(k_d + k_N) = 1.38$ μs. Substituting the k_d value gives the rate constant for intramolecular γ-hydrogen abstraction, $k_N = 6.43 \times 10^5$ s^{-1}.

The triplet lifetime of **1d** is dependent on ester concentration. When reactions (4), (5), and (6) all contribute to the decay of the triplet of **1d**, the triplet lifetime

$$\tau' = \frac{1}{k_{obs}} = \frac{1}{k_d + k_N + k_I[M]}$$

A plot of k_{obs} against the ester concentration [M] gives the rate constant for intermolecular hydrogen abstraction, $k_I = 2.0 \times 10^6$ M^{-1} s^{-1}, see Figure 3. If only reactions (5) and (6) compete to give products, when [M] = 0.32 M, $k_N = k_I$[M]. When [M] is about 0.32 M or higher, intermolecular reaction (6) becomes dominant.

As mentioned before, 2,3-dimethyl-2-butene can quench triplets of phenylglyoxylate esters via the Paternò–Büchi

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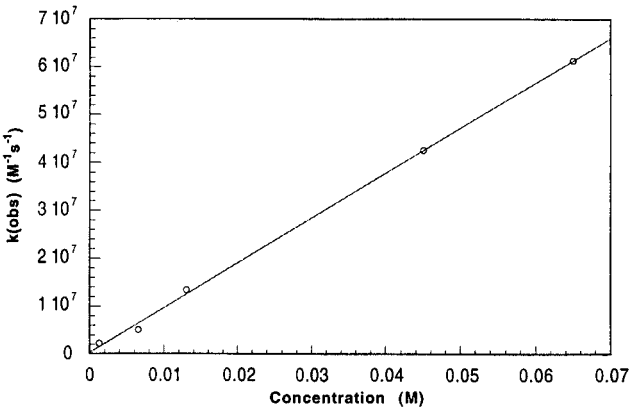


Figure 4. Plots of $k_{obs} = 1/\tau''$ against the concentration of 2,3-dimethyl-2-butene [Q] at constant ester concentration ([M] = 0.025 M) for **1d**.

mechanism. The quenching rate constant k_q is obtained by measuring the triplet lifetime of **1d** when different amounts of this alkene are added to the solution of **1d** in benzene. Reactions (4), (5), (6), and (7) contribute to the decay of the triplet of **1d**, and

$$\tau'' = \frac{1}{k_{obs}} = \frac{1}{k_d + k_N + k_I[M] + k_q[Q]}$$

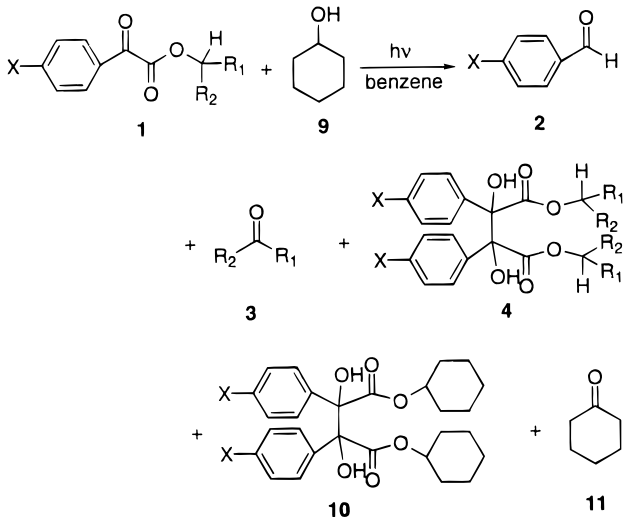
Plotting k_{obs} against the alkene concentration [Q] at constant [M] gives $k_q = 9.39 \times 10^8\ M^{-1}\ s^{-1}$, see Figure 4.

Discussion

Appearance of Dimer and Solvent Dependence. The appearance of dimers, even in a solvent such as benzene, prompted us to consider a mechanism other than just intramolecular γ-H abstraction. Given the intermolecular hydrogen abstraction process, it is obvious that the more easily abstracted the hydrogens of the solvent, the higher should be the yield of dimer. Scaiano et al. observed dimethyl 2,3-dihydroxy-2,3-diphenylsuccinate (**4d**) in reactions of methyl phenylglyoxylate (**1d**) in hydrocarbon solvents. They also noticed the shortening of the triplet lifetime in the hydrocarbon solvent as compared to those measured in benzene but attribute this to impurity quenching.[11] It is more likely that the shorter triplet lifetime obtained in hydrocarbon solvents is due to a larger extent of the solvent quenching the triplet. We have carried out some reactions of ethyl phenylglyoxylate (**1a**) in other solvents such as acetonitrile and deuteriated chloroform. In these solvents, yields of dimer are higher than that from similar reactions in benzene. When the reactions of **1a** are carried out in $CDCl_3$, benzoyl chloride is one of the major products in addition to **2a**, **3a**, **4a**, **5a**, **6a**, and **7a**.

Assessing the Relative Amount of Intra- and Intermolecular Reaction. The relative amounts of intramolecular vs intermolecular hydrogen abstraction can be measured by carrying out an overirradiation of equimolar amounts of phenylglyoxylates (**1a** and **1c**) and cyclohexanol (**9**) in benzene, Table 4. Under conditions where there is no ester exchange in the starting materials in the dark, the yield of dicyclohexyl 2,3-dihydroxy-2,3-diphenylsuccinate (**10**), which must be formed by dimerization of cyclohexyl mandelate [formed by cyclohexanol trapping of α-hydroxyphenylketene (**D**)[6]] after ethyl phenylglyoxylate triplet hydrogen abstraction, and the yield of cyclohexanone (**11**) give the relative amount of

Table 4. Assessment of Percentage of Intramolecular Reaction



entry	cpd 1	concentration (M) 1	9	2	3	4	10	11	intra %	note
1	**1a**	0.02	0.02	0.0	*a*	0.006	0.004	0.001	80	
2	**1a**	0.038	0.045	0.0	*a*	0.010	0.008	0.002	80	
3	**1a**	0.055	0.063	0.0	*a*	0.015	0.012	0.003	80	
4	**1a**	0.076	0.078	0.0	*a*	0.023	0.013	0.003	57	
5	**1a**	0.092	0.107	0.0	*a*	0.023	0.014	0.005	61	
6	**1a**	0.15	0.22	0.0	*a*	0.05	0.03	0.02	60	
7	**1c**	0.03	0.025	0.0	1.9	1.06	1.0	0.05	94	molar ratio

[a] Products are detected but not measured quantitatively.

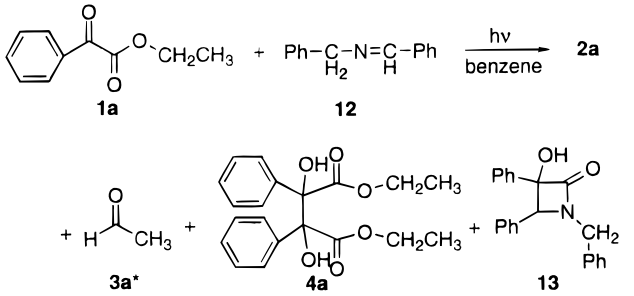
Norrish type II vs intermolecular photoreduction of the starting keto ester. At low starting material concentrations, the Norrish type II reaction predominants, whereas at higher concentrations, the contribution of intramolecular process is substantially lower.

The rate constant for intermolecular hydrogen abstraction between triplets of **1d** and 2-propanol measured by the method as outlined is $1.66 \times 10^6\ M^{-1}\ s^{-1}$. Comparing this value with k_N indicates that the concentration of alcohol has to be 0.26 M to make the rate of intermolecular reaction equal to that of the Norrish type II reaction. Therefore, when the concentration of **9** is less than 0.26 M, Norrish type II reaction dominants.

Additional Evidence for Radical Reactions. Following is further evidence of radical chain processes: When *N*-benzylidenebenzylamine (**12**) is added to trap the α-hydroxyphenylketene (**D**) from reactions of **1a** in benzene, benzaldehyde (**2a**) is also observed, see Table 5. Therefore, aside from decarbonation of ketene **D**, **2a** is also produced by another route. The rate of benzaldehyde formation (and thus Φ_{2a}) is greater than that of a parallel reaction carried out in the absence of **12**. No yellow color is observed when **12** is present, thus confirming that the yellow color produced in the absence of **12** is due solely to α-hydroxyphenyketene (**D**), which can be trapped by **12** immediately upon its formation. The presence of **12** increases the rate of both the intra- and intermolecular hydrogen abstraction by removing the ketene, a competitive absorber of light. The rate of disappearance of the starting material is increased by a factor of 4 in the presence of **12**. The quantitative distribution between ketene formation and intermolecular hydrogen abstraction is given in Table 5.

Effect of Conformation. In reactions of **1b** and **1c**, much less dimer is observed as compared to that of acyclic

Table 5. α-Hydroxyphenylketene Trapped by *N*-Benzylidenebenzylamine[a]



	reactant concentration (M)		product concentration (M)			
entry	1a	12	2a	4a	13	intra %
1	0.012	0.011	0.0004	0.002	0.009	75
2	0.12	0.11	0.005	0.025	0.084	70

[a] **3a** was detected but not measured quantitatively.

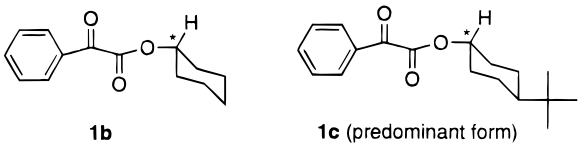


Figure 5.

alkyl phenylglyoxylates (**1a**,**d**−**k**). The Norrish type II reaction, but not the intermolecular reactions, is promoted by a favorable conformation effect at the γ carbon. Since the most stable reactive conformations of **1b** and **1c** are such that bulky substituents assume equatorial positions, the movement of the O−C* bond is restricted, see Figure 5. Using the Norrish type II reactivity of phenyl ketones as a model,[30] **1b** and **1c** are expected to react faster in the intramolecular reaction than the acyclic alkyl phenylglyoxylates because of a less negative entropy of activation.

Comparison of Triplet Reactivity of Glyoxylates and Phenyl Ketones. Pappas studied the photochemistry of *o*-benzyloxyphenylglyoxylates and concluded that the Norrish type II reactivity of phenylglyoxylate is low in the general case.[31] He has suggested that their reactivity is similar to that for aliphatic α-diketones[32] even though the triplet energy of the phenylglyoxylates is about 10 kcal/mol higher. Our observations support this conclusion. The Norrish type II reaction rate constant for **1d** is 6.43×10^5 s^{-1}, whereas those for various δ-substituted valerophenones are all in the range of 0.5 to 20×10^7 s^{-1};[33] Wagner reported that γ,γ-dimethylvalerophenone undergoes a δ-H abstraction with a rate constant of 5×10^5 s^{-1},[34] while we observe no δ-H abstraction in reactions of **1l**. So δ-H abstraction is slower in phenylglyoxylate than in phenyl ketone; *O*-benzyloxyvalerophenone (**14**) undergoes only a Norrish type II reaction, and no δ-H abstraction from the *O*-benzyl group is observed.[35] On the other hand, compounds **15a** and **15b** undergo δ-hydrogen abstraction from the *O*-benzyl group at least an order of magnitude faster than they undergo Norrish type II reactions[31] (Figure 6). Overall, the Norrish type II reaction is sluggish in phenylglyoxylates. It is not surprising that intermolecular hydrogen abstraction competes with the intramolecular γ-hydrogen abstraction process under certain conditions. It has been demonstrated that under ambient temperatures, when abstractable hydrogens are available, the intermolecular abstraction dominants.[6,36]

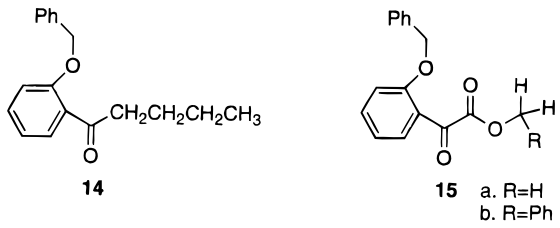
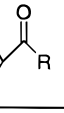
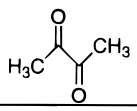


Figure 6.

Table 6. Quenching Rate Constants of Different Excited Triplet Carbonyl Compounds by 2,3-Dimethyl-2-butene[a]

Carbonyl Compds				1d
k_q ($M^{-1}s^{-1}$)	5×10^7 *	4×10^6 *	5×10^8 *	9.39×10^8

[a] An asterisk indicates that data are from ref 37.

On the other hand, phenylglyoxylates react rapidly in the 2 + 2 cycloaddition with alkene as compared to phenyl ketones and α-diketones. Rate constants for the quenching by 2,3-dimethyl-2-butene of different triplet carbonyl compounds are collected in Table 6.[37]

Conclusion. Most synthetic uses of the reactions of phenylglyoxylate triplets result from the intramolecular reaction. Thus, in synthetic applications, conditions must be chosen to avoid competitive intermolecular hydrogen abstraction (i.e., low concentration in benzene). Furthermore, cyclic alkyl phenylglyoxylates show preference for intramolecular reactions over intermolecular radical chain reactions.

We have proposed the first complete mechanism for the photochemical reaction of alkyl phenylglyoxylate based on extensive studies of various glyoxylates. The long-elusive products derived from the phenyl moiety of phenylglyoxylates are isolated and identified. Good material balance is achieved for the first time in the studies of these α-keto esters. Further exploitation in utilizing alkyl phenylglyoxylate photochemistry in combinatorial synthesis is vigorously underway in this laboratory.

Experimental Section

Materials. Benzene (Aldrich) was dried over sodium under N_2. Ethyl phenylglyoxylate (**1a**) was obtained from Aldrich and purified by column chromatography before use. Other chemicals were used as received. Melting points were deter-

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(36) Wang, N. C.; Morduchowitz, A. *J. Org. Chem.* **1964**, *29*, 1654−1655.
(37) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; p 436.

mined with a Thomas Hoover capillary melting point apparatus and were uncorrected. NMR spectra were taken with either a Varian Gemini 200 NMR spectrometer or a Varian Unity Plus 400 NMR spectrometer. Chemical shifts are in ppm with TMS as the internal standard. GC measurements were carried out on a Hewlett-Packard (HP) 5890 gas chromatography. GC/MS were taken on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC, interfaced to an HP 2623A data processor. Infrared spectra were taken with a Galaxy series 6020 FTIR spectrometer. Thin layer chromatography was performed with Whatman silica gel coated TLC plates. Aldrich silica gel 60 Å (70−270 mesh) was used in column chromatography. Elemental analysis was carried out by Atlanta Microlab, Inc. High-resolution mass spectra were taken at the University of Illinois at Urbana−Champaign.

General Procedures for Irradiation of Samples. Alkyl phenylglyoxylates were dissolved in the proper solvent in 16 mm o.d. (L = 125 mm) Pyrex test tubes or 5 mm Pyrex NMR tubes. The tubes were then sealed with a rubber septum bound by sticky parafilm and degassed by bubbling a dry argon gas through the solution for 10−15 min. The tube was then put on a "merry-go-around" in a Rayonet RPR-100 photoreactor equipped with 16 350 nm GE F8T5·BLB UV lamps.

General Procedures for Isolating and Quantifying Photoreaction Products. Several (10 × 100 mL) samples of starting concentration of 0.01 M were irradiated simultaneously in the photoreactor. The samples were immersed in a double-walled Pyrex glass container where water is circulated to maintain constant temperature. The disappearance of starting alkyl phenylglyoxylate was monitored by TLC. When all the starting material was gone, the samples were combined and the solvent was evaporated on a rotary evaporator. The resulting solution was chromatographed under pressure using hexanes:ethyl acetate (40:1 to 20:1) as eluting solvent. Quantitative measurements by NMR were performed as reported.[17a]

Procedure for Trapping α-Hydroxyphenylketene by *N*-benzylidenebenzylamine (12).[15] Phenylglyoxylates and an equimolar concentration of *N*-benzylidenebenzylamine (**12**) were dissolved in 15 mL of dry benzene in a Pyrex test tube and 1.5 g of molecular sieves (Davison, 5 Å, 8−12 mesh) added before the tube was sealed by a rubber septum and degassed by dry argon. The solution was then allowed to sit for at least 8 h before irradiation was carried out.

Quantum Yields. Light intensity was calibrated using the photofragmentation of valerophenone in benzene ($\Phi_{acetophenone} = 0.33$)[38] as an actinometer. Concentrations of glyoxylates and valerophenone were adjusted to ensure that equal amounts of photons were absorbed. Quantities of products produced were monitored by GC. Chlorobenzene was the internal standard in GC calibration and quantitative measurements. Due to competitive absorption by ketene **D**, the values reported in Table 3 are the highest of three−four measurements for each reaction.

Time-Resolved Laser Flash Photolysis. Nanosecond laser flash photolyses were carried out on a setup described by Ford and Rodgers[39] using a Q-switched Nd:YAG laser as a pump light. Argon was bubbled continuously through the sample solution during the measurements.

***Isopropyl* phenylglyoxylate (1e)**[6] (81% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41 (d, J = 7.1 Hz, 6H), 5.32 (septet, J = 7.1 Hz, 1H), 7.50 (t, J = 6.0 Hz, 2H), 7.68 (t, J = 6.0 Hz, 1H), 7.98 (d, J = 6.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.67, 70.66, 128.83, 129.90, 132.42, 134.79, 163.59, 186.70; MS 77 (40), 105 (100), 122 (0.3), 150 (0.3), 192 (0.4, M^+).

***n*-Butyl phenylglyoxylate (1f)**[6] (85% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, J = 7.2 Hz, 3H), 1.45 (qt, J = 7.2 Hz, 7.0 Hz, 2H), 1.75 (tt, J = 7.0 Hz, 6.8 Hz, 2H), 4.40 (t, J = 6.8 Hz, 2H), 7.52 (t, J = 6.0 Hz, 2H), 7.71 (t, J = 6.0 Hz, 1H), 7.99 (d, J = 6.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.56, 18.96, 30.38, 66.04, 128.83, 129.92, 132.37, 134.84, 163.95, 186.44; MS 77 (38), 105 (100), 123 (3), 150 (0.2), 206 (0.5, M^+).

***sec*-Butyl phenylglyoxylate (1g)**[6] (84% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.98 (t, J = 7.4 Hz, 2H), 1.38 (d, J = 7.0 Hz, 3H), 1.72 (qd, J = 7.4 Hz, 7.2 Hz, 2H), 5.17 (tq, J = 7.2 Hz, 7.0 Hz, 1H), 7.52 (t, J = 6.9 Hz, 2H), 7.64 (t, J = 6.9 Hz, 1H), 7.99 (d, J = 6.9 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.58, 19.30, 28.59, 75.10, 128.80, 129.80, 132.38, 134.74, 163.81, 186.74.

Cyclohexyl phenylglyoxylate (1b)[6] (90% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20−2.10 (m, 10H), 5.05 (m, 1H), 7.51 (t, J = 6.0 Hz, 2H), 7.63 (t, J = 6.0 Hz, 1H), 7.89 (d, J = 6.0 Hz, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 23.45, 24.99, 31.26, 75.22, 128.72, 129.73, 134.62, 163.50, 186.61.

Ethyl *p*-Bromophenylglyoxylate (1j).[8] Bromobenzene (2.1 g, 13 mmol), 2.6 g (19 mmol) of ethyl oxalyl chloride, and 25 mL of anhydrous methylene chloride were placed in a 50 mL flask equipped with a magnetic stirrer and suspended in an ice−salt bath. After the solution was stirred for 10 min, 3.4 g (25 mmol) of aluminum chloride was added in small portions over 10 min. When the solution turned red-brown and became homogenous, the ice−salt bath was removed and the mixture was poured over 100 g of crushed ice and 50 mL of concentrated hydrochloric acid. The decomposed mixture was washed with 30 mL of 0.1 N sodium hydroxide three times. After the organic layer was separated and the solvent was evaporated, the crude product was purified by column chromatography using dichloromethane as elution solvent: 2.4 g (72%) pure product was obtained; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.43 (t, J = 7.2 Hz, 3H), 4.44 (q, J = 7.2 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.91 (d, J = 8.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.99, 62.44, 130.38, 131.23, 131.33, 132.18, 163.05, 184.98; MS 75 (33), 77 (33), 155 (45), 256 (2, M^+), 258(2); HRMS m/e measured 255.9735 (Δ = 0.0 mDa); calculated 255.9735.

Ethyl *p*-Fluorophenylglyoxylate (1h). A procedure similar to that described for **1j** produced this compound in 64% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.43 (t, J = 7.2 Hz, 3H), 4.46 (q, J = 7.2 Hz, 2H), 7.20 (t, J = 8.8 Hz, 2H), 8.00−8.15 (dd, J = 8.8 Hz, 5.5 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.92, 62.33, 115.89, 116.32, 128.95, 132.70, 132.91, 163.30, 164.08, 169.22, 184.43; MS 95 (38), 140 (0.9), 168 (2), 196 (1, M^+); HRMS m/e measured 196.0535 (Δ = 0.1 mDa); calculated 196.0536.

Ethyl *p*-Chlorophenylglyoxylate (1i). A procedure similar to that described for **1j** produced this compound in 81% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42 (t, J = 7.2 Hz, 3H), 4.45 (q, J = 7.2 Hz, 2H), 7.28 (t, J = 8.8 Hz, 2H), 7.90−8.16 (dd, J = 8.8 Hz, 5.5 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.01, 62.45, 129.22, 130.86, 131.34, 141.51, 163.13, 184.79; MS 50 (22), 75 (37), 111 (39), 139 (100), 212 (2, M^+); HRMS m/e measured 212.0241 (Δ = −0.1 mDa), calculated 212.0240.

Ethyl *p*-Methoxyphenylglyoxylate (1k). Anhydrous 1,2-dichloroethane (25 mL) and 2.7 g (20 mmol) of aluminum chloride were added to a flask equipped with a magnetic stirrer suspended in an ice−salt bath. Ethyl oxalyl chloride (4.1 g, 30 mmol) was added over 5 min from a syringe while the solution was stirred. Anhydrous anisole (2.2 g, 20 mmol) was also added dropwise over a 30 min period. A brown-red homogenous solution formed as the anisole was added. The mixture was stirred at room temperature for 4 h. Purification was affected in a method similar to that described for **1i** and afforded 2.4 g of pure compound (62% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42 (t, J = 7.1 Hz, 3H), 3.90 (s, 3H), 4.44 (q, J = 7.1 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 8.01 (d, J = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.89, 55.43, 61.99, 114.08,-125.20, 132.34, 164.89, 184.80; MS 50 (4), 77 (17), 92 (20), 107 (8), 135 (100), 208 (4, M^+).

***tert*-Butyl Phenylglyoxylate (1l).** To a stirring solution of 2.5 g (17.3 mmol) of benzoyl formic acid in 40 mL of anhydrous benzene were added 213 mg (1.7 mmol) of 4-(dimethylamino)pyridine (DMAP) and 2.22 g (30 mmol) of *tert*-butyl alcohol. *N*,*N*′-Dicyclohexylcarbodiimide (DCC) was added to the reaction mixture kept in an ice bath. The mixture was stirred in the ice bath for about 10 min and then stirred at room temperature for another 8 h. Precipitated urea was

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filtered out by several vacuum filtrations. The resulting solution was washed with water, 0.5 N HCl, and saturated sodium bicarbonate solution each three times and chromatographed to yield pure product (3.54 g, 92% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.63 (s, 9H), 7.50 (t, J = 6.0 Hz, 2H), 7.64 (t, J = 6.0 Hz, 1H), 7.79 (d, J = 6.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.92, 84.63, 128.74, 129.72, 132.37, 134.54, 163.63, 186.73; MS 77 (35), 105 (100), 123 (3), 206 (0.4, M^+).

4-*tert*-Butylcyclohexyl Phenylglyoxylate (1c). (Isomeric mixture of both cis and trans compounds, with trans isomer predominating.) A procedure similar to that described for **1l** produced this compound in 93% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (s, 9H), 1.00−2.21 (m, 9H), 4.97 (m, 1H), 7.50 (m, 2H), 7.64 (m, 1H), 7.97 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.37, 27.50, 31.83, 46.84, 76.32, 128.77, 129.84, 132.50, 134.66 163.60, 186.64. The ester crystallized upon standing for a prolonged period. It melts at 42−45 °C. Anal. Calcd for $C_{18}H_{22}O_3$: C, 74.97; H, 8.39; O, 16.64. Found: C, 74.78; H, 8.49; O, 16.72.

Ethyl-d_5 Phenylglyoxylate (d_5-1a). A procedure similar to that described for **1l**, starting with ethyl-d_5 alcohol, produced this compound in 95% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.54 (t, J = 6.0 Hz, 2H), 7.62 (t, J = 6.0 Hz, 1H), 7.98 (d, J = 6.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 128.77, 129.86, 132.33, 134.78, 163.94, 186.34; MS 77 (40), 105 (100), 123 (0.5), 155 (0.8), 183 (0.3, M^+); HRMS *m/e* measured 183.0945 (Δ = −0.1 mDa); calculated 183.0944.

Ethyl *O*-Acetylmandelate (6a). This compound was synthesized by adding 2.7 g (15 mmol) of ethyl (±)-mandelate, 1.5 g (19 mmol) of acetyl chloride, and 2.02 g (20 mmol) of triethylamine to 80 mL of chloroform. The mixture was refluxed for 2 h, and 2.9 g of pure product (90% yield) was recovered after column chromatography. One product isolated from the photoreaction of ethyl phenylglyoxylate is identical (^{1}H NMR, ^{13}C NMR, and MS spectra and retention times on two different GC columns) to this compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, J = 7.2 Hz, 3H), 2.20 (s, 3H), 4.10−4.27 (m, 2H), 5.91 (s, 1H), 7.37−7.41 (m, 3H), 7.45−7.49 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.94, 20.69, 61.67, 74.56, 127.58, 128.72, 129.14, 133.85, 168.80, 170.31; MS 77 (16), 79 (15), 107 (100), 149 (35), 176 (14), 222 (1, M^+); IR (neat) 2986.73, 1748.04, 1497.22, 1454.77, 1371.74. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; O,28.88. Found: C,64.79; H, 6.31; O, 28.90.

Ethyl *O*-Benzoylmandelate (5a). A procedure similar to that described for **4a** afforded this compound in 83% yield. One product isolated from the photoreaction of ethyl phenylglyoxylate is identical (^{1}H NMR, ^{13}C NMR, and MS spectra and retention times on two different GC columns) to this compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, J = 7.2 Hz, 3H), 4.22 (m, 2H), 6.14 (s, 1H), 7.44 (m, 5H), 7.58 (m, 3H), 8.13 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.98, 61.72, 74.56, 127.58, 128.78, 129.17,129.26, 129.92, 133.41, 134.05, 165.86, 168.75; MS 77 (24), 105 (100), 162 (3.2), 211(1.2), 238 (4.1), 284 (0.5, M^+); IR (neat) 3067.76, 2982.87, 1751.90, 1724.89, 1601.40, 1454.77, 1257.97. Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67; O, 22.51. Found: C, 71.81; H, 5.63; O, 22.56.

Diethyl 2,3-Dihydroxy-2,3-diphenylsuccinate (4a).[8] Irradiation of a solution of 2.42 g of ethyl phenylglyoxylate in 16 mL of 2-propanol at room temperature for 48 h produced a white crystalline precipitate. Recrystallization from benzene yielded pure compound, 1.46 g. One product isolated from the photoreaction of ethyl phenylglyoxylate is identical (^{1}H NMR, ^{13}C NMR, and MS spectra and retention times on two different GC columns) to this compound. This compound decomposes to ethyl phenylglyoxylate and ethyl (±)-mandelate at temperatures of 100 °C and above. **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (td, J = 7.2 Hz, 2.0 Hz, 6H), 4.25−4.40 (m, 4H), 5.08 (s, 2H), 7.06−7.17 (m, 8H), 7.20−7.26 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.91, 62.75, 81.95, 126.87, 126.93, 127.19, 128.10, 134.74, 175.64.

Diphenyl Triketone (Combined with Its Monohydrate, *ca*. 1:1 Ratio) (7a). Independent synthesis was carried out as reported.[40] One product isolated from the photoreaction of ethyl phenylglyoxylate is identical (^{1}H NMR, ^{13}C NMR, and MS spectra and retention times on two different GC columns) to this compound. **7a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.92 (s, 1H, exchangeable), 7.30−7.40 (m, 2H), 7.45−7.60 (m, 3H), 7.65−7.75 (m, 1H), 7.90−8.00 (m, 2H), 8.05−8.12 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 93.99, 128.75, 129.04, 130.16, 130.19, 134.61, 135.35, 188.19, 192.39, 193.98; MS 51 (19), 77 (50), 105 (100), 210 (1.2), 238 (1.5).

3,4-Diphenyl-1-benzyl-3-hydroxyazetidin-2-one[15] (diastereoisomeric mixture): mp = 99−102 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.86 and 4.94 (q, J = 15 Hz, 2H), 3.95 (s, 1H), 4.54 (s, 1H), 7.00−7.50 (m, 15H).

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