Photochemical Reactions of Alkenyl Phenylglyoxylates

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Received May 22, 1997[⊗]

The photochemical reactions of alkyl phenylglyoxylate esters whose ester function contains double bonds of differing substitution, situated at varying distances from the carbonyl group, have been studied. The intramolecular Paternò−Büchi reaction is the dominating photoreaction when an electron rich alkenyl group is situated at the proper distance as in 1′,5′-dimethylhex-4′-enyl phenylglyoxylate (**6**). When the distance between the excited carbonyl group and the same alkenyl function is increased, as it is in 3′,7′-dimethyl-6′-octenyl phenylglyoxylate (**7**), intramolecular γ-hydrogen abstraction (Norrish type II) products, as well as the products of intramolecular photocycloaddition, are observed. We suggest this to be the result of a competitive distant dependent electron transfer reaction between the excited carbonyl group and the alkene. A longer distance of separation between these two reactive functions decreases the efficiency of formation of the cycloaddition product. When the separation of the same alkene from the glyoxylate is shortened as in 4′-methylpent-3′-enyl phenylglyoxylate (**5**), electron transfer-induced remote proton abstraction leading to cyclol formation occurs, in addition to the Paternò−Büchi reaction. Further reducing the distance as in 3′-methylbut-2′-enyl phenylglyoxylate (**3**) results in only the normal intramolecular (Norrish type II) and intermolecular hydrogen abstraction products. At a distance where both oxetane and cyclol formation are possible as in **5**, decreasing the electron richness of the alkenyl group as in *cis*-3′-hexenyl phenylglyoxylate (*cis*-**4**) eliminates the oxetane product. Formation of cyclol is shown to be conformationally controlled in that a similar product is not observed to be formed from *trans*-3′-hexenyl phenylglyoxylate (*trans*-**4**). If both the electron richness of the alkenyl group and the distance of separation are decreased as in 2′-hexenyl phenylglyoxylate (**2**), only γ-hydrogen abstraction products result. *Cis*−*trans* isomerization of the olefin is not observed in either **2** or **4**.

Introduction

Photochemical reactions for formation of macrocyclic ring systems represent an area of intense interest,[2] and cycloadditions are among the most utilized synthetic photoreactions. An important example is the de Mayo reaction[3] used in the construction of the skeleton of taxane.[4] Another photocyclization that has found its way into the synthetic approaches of macrocycles is the intramolecular Paternò−Büchi reaction.[5]

We have studied the Paternò−Büchi reaction of alkyl phenylglyoxylates and found that it proceeds rapidly affording high chemical yields of oxetanes[6] despite potential competition from intramolecular (Norrish type II) and intermolecular hydrogen abstraction processes.[7] Alkenyl phenylglyoxylates in which the double bond is relatively electron rich and suitably located with respect to the carbonyl group undergo the reaction with production of bicyclic oxetanes.[6] To better understand this intramolecular process and explore its application in synthesis, we have studied the photochemical reactions of double-bond-containing alkyl phenylglyoxylates.

The Norrish type II and the intermolecular hydrogen abstraction are common with normal alkyl phenylglyoxylates. These reactions and their mechanism have been extensively studied[8] and will be referred to as intra- and intermolecular hydrogen abstractions. The intramolecular Paternò−Büchi reaction proceeds exclusively when an alkenyl group is electron rich and properly situated. A mechanism involving either the interaction of an exciplex or a radical ion pair prior to product formation is proposed. Abstraction of remote protons and subsequent cyclization produces cyclols.

Results

Photochemical Reactions. The compounds studied are grouped in Table 1. Compounds **1**−**3** are a group in which the alkyl chains are of the same length but the substitution pattern of the alkene differs. Compounds **4** and **5** are paired similarly. Compounds **3** and **5**−**7** contain identical alkene functions, but the length of the alkyl chain from the carbonyl group increases from top to bottom.

Irradiation of dilute (0.01−0.05 M) benzene solutions of **1**−**7** produces very different reaction products, Table 2.[9] Benzaldehyde, alkenyl aldehydes, and dimers are typical of both intra- and intermolecular hydrogen abstraction reactions.[9] Cyclol **8** was isolated as a single diasteromer (45%) from reaction of *cis*-**4**.[10] Oxetane **9**

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

(1) Contribution No. 324 from the Center for Photochemical Sciences, BGSU.

(2) For a recent review, see: Griesbeck, A. G.; Henz, A.; Hirt, J. *Synthesis* **1996**, 1262−1276.

(3) (a) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41. (b) de Mayo, P. *Pure Appl. Chem.* **1964**, *9*, 597.

(4) (a) Begley, M. J.; Mellor, M.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1905−1912. (b) Winkler, J. D.; Hey, J. P.; Williard, P. G. *J. Am. Chem. Soc.* **1986**, *108*, 6425−6427. (c) Winkler, J. D.; Hong, B.-C.; Hey, J. P.; Williard, P. G. *J. Am. Chem. Soc.* **1991**, *113*, 8839−8846.

(5) (a) Carless, H. A. J.; Fekarurhobo, G. K. *J. Chem. Soc., Chem. Commun.* **1984**, 667−668. (b) Carless, H. A. J.; Beanland, J.; Mwesigye-Kibende, S. *Tetrahedron Lett.* **1987**, *28*, 5933−5936. (c) Bichan, D.; Winnik, M. *Tetrahedron Lett.* **1974**, 3857−3860. (d) Nicolaou, K. C.; Hwang, C.-K.; Nugiel, D. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1362−1364. (e) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Carroll, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 3801−3802.

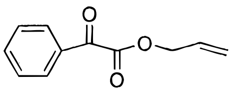
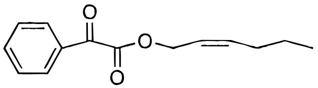
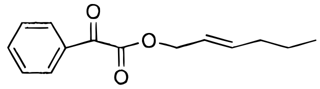
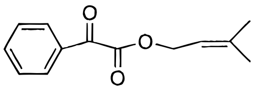
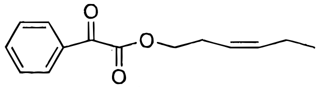
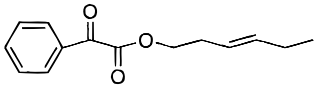
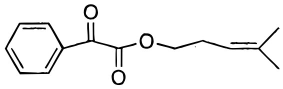
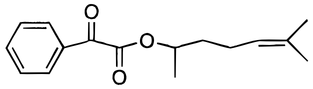
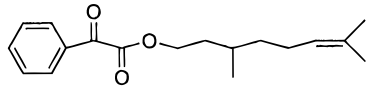
(6) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1997**, *62*, 564−567.

(7) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1996**, *61*, 6407−6415.

(8) See ref 7 and references cited therein.

S0022-3263(97)00912-2 CCC: $14.00

Table 1. Compounds Studied

 **1**	 *cis* - **2**  *trans* - **2**	 **3**
	 *cis* - **4**  *trans* - **4**	 **5**
		 **6**  **7**

(44%) and cyclol **10** (30%) were isolated from reaction of **5**.[11] Oxetane **11** was the only product (92%) produced from the photolysis of **6**. **12** was formed (70%) in competition with intra- and intermolecular abstraction products as shown in an earlier study.[12] A critical observation was that no *cis*–*trans* isomerization occurred upon irradiation of either **2** or **4**.

Discussion

Mechanisms. Oxetanes **9**, **11**, and **12** resulted from intramolecular Paternò–Büchi processes, the regioselectivity of which is opposite to that predicted based on the biradical hypothesis[13] which states that in a $2\pi + 2\pi$ cycloaddition, the excited carbonyl group attacks the π bond of the alkene forming the C–O bond that generates the more stable biradical intermediate. The absence of products expected from the more stable biradical intermediate has important mechanistic implications in this study.

Since the triplet energy of alkyl phenylglyoxylates is about 66 kcal/mol[14] and well below the triplet excitation energies of simple monoalkenes,[15] energy transfer from triplet phenylglyoxylate to alkenes of this study is expected to be endothermic, accounting for, among other things, the lack of excited phenylglyoxylate-sensitized *cis*–*trans* isomerization of the alkene moieties of **2** and **4**. When triplet energy transfer is endothermic, alkenes have been shown to quench excited ketones by a charge transfer process leading to an exciplex.[16] This exciplex subsequently collapses to form the product oxetanes.

A mechanism consistent for the photoreactions of compounds **1**–**7** is proposed in Scheme 1. Ground states (G) are promoted via their singlet states to the corresponding triplet states (T). Charge transfer (k_{ct}) between the alkene and triplet carbonyl group, T, is in competition with the hydrogen abstractions (k_H) and leads to the formation of an exciplex (CP). CP may revert directly to G (k_1) or collapse to one of several different biradicals (k_2, k_3, k_4). Theoretically, two kinds of oxetane-deriving biradicals are possible: stable biradicals (SB) and less stable biradicals (LB). Cyclol precursor (B) results from a regiospecific proton transfer.

In fact, the observed product oxetanes are derived only from LB_a. That there are no products resulting from SB_a (R = Me) occurs either because this biradical always reverts to G (k_r) or because SB does not form. Were reversion of SB to G a significant pathway, one would expect isomerism of **2** or **4**. Since no *cis*–*trans* isomerism is observed, one must conclude the formation of SB is unlikely. This is likely due to the position of the functional groups in the exciplex which favors only LB formation.

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[9] Benzaldehyde and most of the alkenyl aldehydes were not isolated independently. They were identified by GC/MS analyses and by coinjection of the authentic sample with the reaction mixture into GCs using two different columns. The dimers, dialkenyl 2,3-dihydroxy-2,3-diphenyl succinates, were generally isolated and characterized by NMR only. They were not stable under most MS analytical conditions. Products deriving from the intra- and intermolecular hydrogen abstractions have been previously studied.[8] We also conducted exhaustive characterizations of the elusive dimers in an earlier study on the sulfide-containing alkyl phenylglyoxylates; see: Hu, S.; Neckers, D. C. *Tetrahedron* **1997**, *53*, 7165–7180.

[10] **8** with unidentified stereochemistry has been isolated in a comparable yield (49%). Kraus, G. A.; Wu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 8705–8707.

[11] Only cyclol **10** was isolated in comparable yield (31%) from reaction of **5** in an earlier study by Kraus *et al.*[10]

[12] See ref 6. The NMR data fit the structure **12** better than that reported earlier.

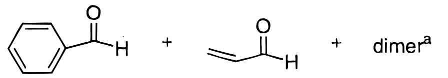
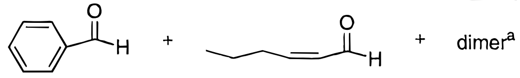
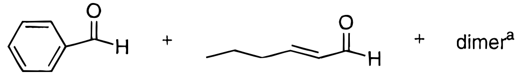
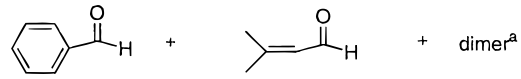
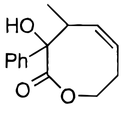
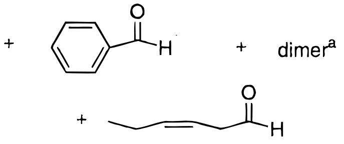
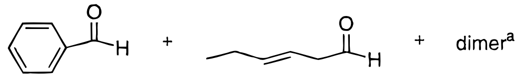
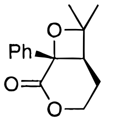
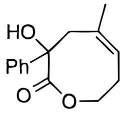
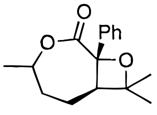
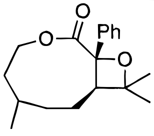
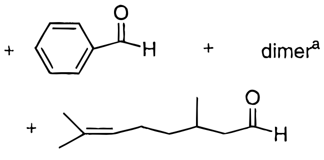
[13] Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; pp 432–442.

[14] Pappas, S. P.; Alexander, J. E.; Zehr, R. D., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6927–6931.

[15] Merer, A. J.; Mulliken, R. S. *Chem. Rev.* **1969**, *69*, 639–656.

[16] (a) Kochevar, I. E.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859–3865. (b) Morrison, H.; Tisdale, V.; Wagner, P. J.; Liu, K.-C. *J. Am. Chem. Soc.* **1975**, *97*, 7189–7191. (c) Schore, N. E.; Turro, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 2482–2488. (d) Caldwell, R. A.; Sovocool, G. W.; Gajewski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549–2557.

Table 2. Photolysis Results

substrate	photoproducts
1	 + dimer[a]
cis-**2**	 + dimer[a]
trans-**2**	 + dimer[a]
3	 + dimer[a]
cis-**4**	 **8**  + dimer[a]
trans-**4**	 + dimer[a]
5	 **9**  **10**
6	 **11**
7	 **12**  + dimer[a]

[a] See ref 9.

Oxetanes are only observed from the isobutylene-like olefins **5**−**7**. In these cases the more stable biradicals SB_a could not be detected even when they only revert to ground state G. In olefins in which R = H, the exciplex (CP_b) no longer collapses to SB_b and LB_b as does CP_a. This is deduced from the absence of both an oxetane product (the product derived from LB_b) and the geometrically isomerized starting materials (*i.e.*: *trans*-**4**, the product from the reversion of SB_b) from *cis*-**4**. That acyclic disubstituted olefins are not sufficiently electron rich to form 2 + 2 adducts with the triplet state of alkyl phenylglyoxylate was observed earlier.[6] The absence of k_2 and k_3 for CP_b reduces k_{ct} from T_b as compared to that of T_a. This leads to k_H of T_b being comparable to its k_{ct}, which accounts for the hydrogen abstraction products observed in addition to **8** when *cis*-**4** is irradiated.

Only one pair of enantiomers is observed for oxetanes **9**, **11**, and **12**, and their stereochemistry is assigned[6] based on the Salem−Rowland rules.[17]

Formation of cyclols **8** and **10** was attributed to long range hydrogen atom abstractions by Kraus *et al.*[10,18] Considering the existence of the exciplex prior to product formation suggests hydrogen atom abstraction is not completely responsible for the formation of cyclols. It is well known that both intermolecular[19] and intramolecular[20] adducts can be formed between excited carbonyl compounds and alkenes by electron transfer-induced proton abstraction. Therefore, we proposed that a pure charge transfer exciplex (contact radical ion pair) followed by a proton transfer leading to B is responsible for the formation of cyclols.

The regioselectivity in the proton transfer step is surprising. Exclusive transfer of a proton η to the excited carbonyl group (α to the double bond on the remote side) forms the 8-membered ring cyclol (**8**, **10**) from both *cis*-**4** and **5**. We propose that the specific orientation of the double bond and the carbonyl triplet in the exciplex favors the closing of the radical resulting from η proton transfer in both *cis*-**4** and **5**. Closing of the biradical resulting from δ proton transfer must not be favored by the configuration adopted by the exciplex. The existence of a specific conformation in the exciplex also explains why only one stereoisomeric cyclol (**8**) is formed.

That the regioselectivity of deprotonation is not controlled by the stability of the resulting product is further confirmed by noting that η proton transfer (the proton at the nearer side, α to the double bond) which could result in an 8-membered ring cyclol from **7** is not observed.

Kinetic Study. Nanosecond laser flash photolysis of benzene solutions of **3**, *cis*-**4**, *trans*-**4**, and **5**−**7** have been carried out to probe the dependence of the triplet reactivities on both the structure of the alkenyl group and the chain length between the excited carbonyl group and alkenyl group. A transient absorption with a maximum at 440 nm was detected for all the compounds studied and attributed to the triplet excited state in agreement with earlier flash photolysis results.[7,9,21] A typical transient decay trace and the transient absorption spectrum are displayed for *cis*-**4** in Figure 1. The absorption decays exponentially, and the triplet lifetimes can be derived. Triplet lifetimes (τ) are collected in Table 3 along with that of a typical alkyl analog, methyl phenylglyoxylate (**13**), and that of the photoinert (in benzene) *tert*-butyl phenylglyoxylate (**14**).[7] The triplet lifetime of **7** is too short to be measured accurately on the nanosecond time scale.

For compounds containing the same alkenyl group (**3**, **5**−**7**), triplet lifetimes depend on the chain length connecting the alkene and the excited carbonyl group, and a longer chain shortens the triplet lifetime. This is interpreted to mean that the quenching complex has a specific requirement with the alkenyl group approaching within a short distance of the excited carbonyl group. A longer chain length makes the chain more flexible, and the required quenching geometry is more easily accessible.[22]

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(17) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

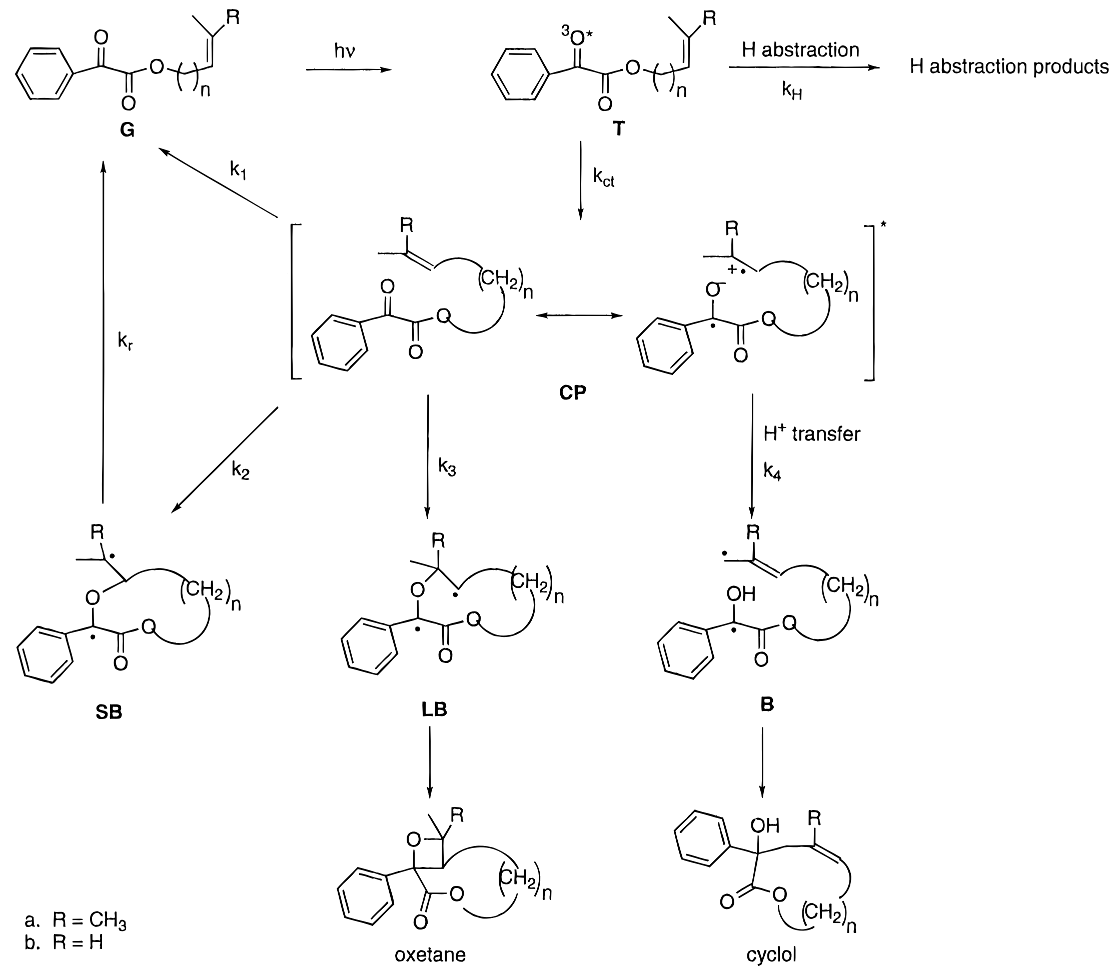
(18) Kraus, G. A.; Zhang, W.; Wu, Y. *Chem. Commun.* **1996**, 2439−2440.

(19) (a) Kubo, Y.; Suto, M.; Araki, T.; Mazzocchi, P. H.; Klingler, L.; Shook, D.; Somich, C. *J. Org. Chem.* **1986**, *51*, 4404−4411. (b) Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1985**, *50*, 1426−1435. (c) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *J. Org. Chem.* **1985**, *50*, 2681−2684.

(20) (a) Maruyama, K.; Kubo, Y.; Machida, M.; Oda, K.; Kanaoka, Y.; Fukuyama, K. *J. Org. Chem.* **1978**, *43*, 2303−2304. (b) Kubo, Y.; Asai, N.; Araki, T. *J. Org. Chem.* **1985**, *50*, 5484−5487. (c) Mazzocchi, P. H.; Fritz, G. *J. Am. Chem. Soc.* **1986**, *108*, 5362−5364.

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

Scheme 1



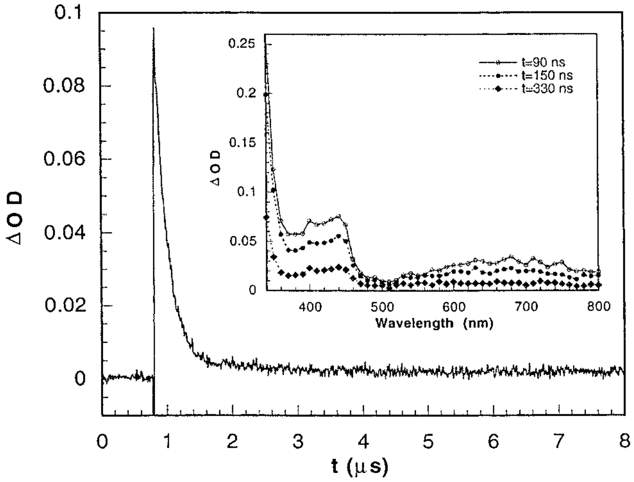
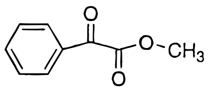
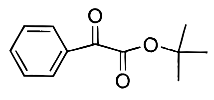


Figure 1. Triplet decay trace of *cis*-**4** in benzene (0.025 M) monitored at 440 nm. Inserted are the transient absorption spectra.

Table 3. Triplet Lifetimes Detected



13



14

	compound							
	3	*cis*-**4**	*trans*-**4**	**5**	**6**	**7**	**13**	**14**
τ (ns)	260	230	470	170	30	<7	1380	12700
k_{ct} (10^6 s^{-1})	3.1	3.6	1.4	5.2	32.6	>142		

The triplet lifetime of **3** is significantly shorter than that of **13** even though only hydrogen abstraction products result. Significant charge transfer quenching of the triplet state of **3** exists, and the rate constant, k_{ct} (3.1 × 10^6 s^{-1}), is obtained by assuming the rates of physical decay and of the hydrogen abstractions of **3** are equal to those of **13**. The k_{ct} values for the other compounds (Table 3) are obtained similarly. That significant quenching of the triplet of **3** prevents oxetane formation is attributed to reversion to ground state from both the exciplex and the biradical intermediate. It is noted that the LB of **3** could form, but the cyclization of this biradical is not favored for the *Z* conformation of the ester functionality.[23] As the ring size becomes larger as in **5**–**7**, closure of the more flexible lactone ring becomes favorable and oxetane products produced.

Quenching rate constants of phenyl ketones by various olefins have been shown to be conformation dependent.[16a] Electron transfer quenching rates of *cis*- and *trans*-**4** are quite different with the *cis* isomer quenched more than

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[22] For similar observations in other excited carbonyl systems, see: (a) Winnik, M. A.; Hsiao, C.-K. *Chem. Phys. Lett.* **1975**, *33*, 518–521. (b) Mar, A.; Winnik, M. A. *Chem. Phys. Lett.* **1981**, *77*, 73–76. (c) Mar, A.; Fraser, S.; Winnik, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 4941–4843. (d) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7335–7337. (e) See ref 9.

[23] Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1994; Chapter 10.

Table 4. Quantum Yields Measured in Benzene

	compound								
	3	*cis*-**4**	*trans*-**4**	**5**	**9**	**10**	**6**	**11**	**7**
$\Phi_{\text{disappearance}}$	0.20	0.36	0.27	0.26			0.11		0.04
$\Phi_{\text{appearance}}$					0.11	0.11		0.10	

twice as rapidly as the *trans*. The isomeric alkenes in **4** result not only in a change in the triplet quenching rate but also in different reaction products. The more rapid quenching in *cis*-**4** leads to a proton transfer and formation of cyclol **8**. The absence of cyclol product in *trans*-**4** is explained by both its unfavorable conformation for cyclol formation in the exciplex and a slower charge transfer rate in the triplet state.

The trisubstituted alkene in **5** is a better triplet quencher than the disubstituted alkenes in **4**. This is attributed to a difference in the oxidation potentials of the different alkenes.[20c] It is also interesting to note that products putatively from hydrogen abstractions disappeared in photoreactions of **5** and **6**, while the k_{ct} value is increased over those of **3** and **4**. These products appear again in **7**, when the k_{ct} value is further increased due to the flexible chain in **7**. Back-electron transfer in the exciplex (CP) is also made efficient by the flexible chain, and reversion of CP to ground state **7** (k_1) competes vigorously with its collapse to LB (k_3). Therefore, the efficiency of the oxetane formation is reduced, and hydrogen abstraction processes become visible.[24]

Thermodynamics. The Gibbs free energy change associated with a full electron transfer from an alkene to phenylglyoxylate can be calculated using the Weller equation:[25]

$$\Delta G_{\text{ET}} = 23.06(E_{\text{D}}{}^{\text{ox}} - E_{\text{A}}{}^{\text{red}}) - E_{\text{T}} - C$$

where ΔG_{ET} is the free energy change for electron transfer, $E_{\text{D}}{}^{\text{ox}}$ and $E_{\text{A}}{}^{\text{red}}$ are the oxidation and reduction potentials of the donor (alkene) and acceptor (phenylglyoxylate), respectively, E_{T} is the triplet energy of the acceptor, and C is the Coulombic interaction term.[25]

The reduction potential of methyl phenylglyoxylate (**13**) was measured as −1.23 V vs SCE in acetonitrile. The value of the triplet energy of phenylglyoxylate is taken as 66 kcal/mol.[14] From the Weller equation, a full electron transfer from an alkene with oxidation potential of 1.7 V and below (vs SCE) is energetically favorable. The oxidation potentials of alkenes vary with their structures, with most of the measured values around 1.7 V.[26]

Quantum Yield. The quantum yields for the disappearance of **3**−**7** and the appearance of **9**−**11** were measured in benzene solutions, Table 4. Quantum yields for the disappearance of **3** and **5** are comparable, while those of **6** and **7** are lower. The trend is observed such that as the length of the chain connecting the alkene and the excited carbonyl group increases, the quantum yield of starting material disappearance decreases. This agrees with the notion that longer chains promote both electron transfer and back-electron transfer between the acceptor and donor (*vide supra*). When more photons are dissipated through this electron transfer process, the quantum yield decreases.

Table 5. Product Ratios of 5 in Different Solvents

	solvents				
	dichloromethane	benzene	2-propanol	methanol	acetonitrile
ϵ^a	0.893	2.275	19.92	32.70	37.5
9/10	1.4	1.1	*b*	1.7^c	1.9

[a] Dielectric constant of solvents from ref 27. [b] Reductive dimer is the only product. [c] Reductive dimer is produced in 50% yield.

The quantum yields for the appearance of **9** and **10** are almost equal, while their summation is slightly less than the quantum yield of the disappearance of **5**. The difference is attributed to hydrogen abstraction processes since an amount of products derived from intra- and intermolecular hydrogen abstraction reactions was also observed when **5** was irradiated. The quantum yield for the appearance of **11** is close to that for the disappearance of **6**, agreeing with the fact that **11** is the only photoproduct derived from **6**.

Solvent Dependence. The ratios of oxetane **9** to cyclol **10** produced when **5** is irradiated in solvents of differing polarities are collected in Table 5.[27] **9** is the favored product in all solvents. Polar solvents were expected to stabilize polar intermediates and promote the formation of cyclol **10**. This is not observed. Therefore, the exciplex from which both **9** and **10** are derived is likely to be short-lived and insensitive to solvent polarity.

The predominant formation of the reductive dimer in the good hydrogen-donating solvent (2-propanol) suggests that the bimolecular hydrogen transfer reaction between **5** and solvent is faster than the unimolecular electron transfer process between the alkene and carbonyl groups in **5**. When the hydrogen-donating ability of the solvent is decreased as it is in methanol, the intramolecular electron transfer reaction becomes competitive with the intermolecular hydrogen abstraction, and products **9** and **10** are observed.

Conclusions

Hydrogen abstraction reactions of alkyl phenylglyoxylates have been used synthetically on several occasions.[8] This study of photochemical reactions of alkenyl phenylglyoxylate reveals the mechanism of several different reactions and enables their better utilization. The formations of both the oxetanes and cyclols are attractive routes for the construction of macrocyclic compounds. The chemistry revealed in this study is comparable with that of the intramolecular quenching of phenyl ketones by olefins[16b,22] and intramolecular photoreactions of phthalimide−alkene systems.[28]

Experimental Section

Materials. Benzene (Aldrich) was dried over sodium benzophenone ketyl under argon. Other chemicals were obtained from commercial sources and used as received. NMR spectra were taken with either a Varian Gemini 200 NMR spectrom-

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(24) Exactly the same results were observed in the study of sulfide-containing alkyl phenylglyoxylates.[9]

(25) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259−271.

(26) Tsuchiya, M.; Akaba, R.; Aihara, S.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1986**, 1727−1730. Since the oxidation potentials of simple alkenes are very sensitive to structural modifications, we propose that the oxidation potentials of the alkenyl groups in compounds studied herein differ significantly from those of simple alkenes and are likely to be lower. A partial or full electron transfer is feasible.

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eter 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. Infrared spectra were taken with a Galaxy series 6020 FTIR spectrometer. Thin layer chromatography was performed with Whatman silica gel-coated TLC plates. Silica gel (60 Å, 60−200 mesh) used in column chromatography was from J. T. Baker Chemical Co. Cyclic voltammograms were recorded on an BAS 100A electrochemical analyzer with platinum as both the working and counter electrodes and Ag/AgCl as the reference electrode. The redox potentials obtained were corrected to vs standard calomel electrode (SCE) by measuring ferrocenium/ferrocene reference (+0.425 V in acetonitrile vs SCE)[29] at identical conditions. The solutions were purged with argon when necessary. 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 ($\Phi_{\text{acetophenone}} = 0.33$)[30] was always irradiated parallel to the sample solution on a "merry-go-round". The disappearance of starting alkenyl phenylglyoxylate was monitored by NMR since dimers resulting from hydrogen abstractions decompose in the GC. The signals from the aromatic hydrogens of the reaction mixture were used as the internal standard since the total number of such hydrogens are conserved in the reaction process. The disappearance of starting alkenyl phenylglyoxylate was monitored by its distinctive downfield (≈8.00 ppm) aromatic hydrogen signals. The appearance of acetophenone in the actinometer and of products **9**−**11** was conveniently monitored by GC. The GC was calibrated against these compounds using chlorobenzene as the internal standard. Quantum yields reported are averages of three measurements.

Time-Resolved Laser Flash Photolysis. Nanosecond laser flash photolysis was carried out on a setup described by Ford and Rodgers[31] using the third harmonic of a Q-switched Nd:YAG laser (Continuum, YG660) as excitation source. The sample solution in a quartz cuvette was purged with argon for 5 min before and during the experiment. The samples were excited with 355 nm pulses (pulse width *ca.* 7 ns).

Allyl Phenylglyoxylate (1). After passing through dry HCl (generated *in situ* by adding concentrated H_2SO_4 to NaCl) for 2 h, 20 mL of allyl alcohol was added to 1.5 g (10 mmol) of benzoylformic acid, and the mixture was refluxed for 2 h. The resulting solution was extracted three times with dichloromethane, and the combined organic layers were washed with saturated $NaHCO_3$ solution and water each three times and dried over anhydrous $MgSO_4$. Evaporating solvent under vacuum left 1.5 g of the title compound as a slightly yellowish oil: yield 85%; ^{1}H NMR (400 MHz) δ 4.88 (dt, $J_1 = 6$, 1.2 Hz, 2H), 5.35 (dq, $J_1 = 10.4$, 2.4 Hz, 1H), 5.46 (dq, $J_1 = 17.2$, 1.2 Hz, 1H), 5.98−6.07 (m, 2H), 7.50−7.54 (m, 2H), 7.64−7.68 (m, 1H), 8.00−8.02 (m, 2H); ^{13}C NMR (50 MHz) δ 66.57, 120.02, 128.90, 130.03, 130.74, 132.39, 134.94, 163.42, 186.04; MS 51 (12), 77 (39), 105 (100), 162 (0.2), 190 (0.3); HRMS *m*/*z* calcd for $C_{11}H_{10}O_3$ 190.0630, found 190.0629.

General Procedure for DCC Esterification (Synthesis of compounds 2−7). Similar procedures to that described earlier[9] produced these α-keto esters in yields better than 85%.

***cis*-2′-Hexenyl phenylglyoxylate (*cis*-2):** hexanes:ethyl acetate = 15:1; ^{1}H NMR (400 MHz) δ 0.93 (t, $J = 7.2$ Hz, 3H), 1.43 (sexet, $J = 7.2$ Hz, 2H), 2.15 (qd, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 2H), 4.94 (dd, $J_1 = 6.8$ Hz, $J_2 = 0.8$ Hz, 2H), 5.63−5.70 (m, 1H), 5.73−5.79 (m, 1H), 7.48−7.52 (m, 2H), 7.63−7.67 (m, 1H), 7.98−8.01 (m, 2H); ^{13}C NMR (50 MHz) δ 13.57, 22.41, 29.51, 61.77, 122.00, 128.79, 129.92, 132.39, 134.81, 136.91, 163.67, 186.20; MS 41 (11), 55 (15), 77 (34), 83 (18), 105 (100), 123 (1.8), 151 (0.1), 205 (0.1); IR (film) 2963.57, 2870.96, 1736.47, 1690.16, 1597.55, 1196.23, 910.68; HRMS *m*/*z* calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1096.

***trans*-2′-Hexenyl phenylglyoxylate (*trans*-2):** hexanes:ethyl acetate = 15:1; ^{1}H NMR (400 MHz) δ 0.91 (t, $J = 7.2$ Hz, 3H), 1.43 (sexet, $J = 7.2$ Hz, 2H), 2.06 (q, $J = 7.2$ Hz, 2H), 4.83 (dq, $J_1 = 6.4$ Hz, $J_2 = 1.2$ Hz, 2H), 5.67 (dtt, $J_1 = 15.6$ Hz, $J_2 = 6.4$ Hz, $J_3 = 1.6$ Hz, 1H), 5.91 (dtt, $J_1 = 15.6$ Hz, $J_2 = 6.4$ Hz, $J_3 = 1.2$ Hz, 1H), 7.48−7.52 (m, 2H), 7.63−7.67 (m, 1H), 7.99−8.02 (m, 2H); ^{13}C NMR (50 MHz) δ 13.53, 21.84, 34.22, 66.83, 122.53, 128.79, 129.95, 132.39, 134.81, 138.42, 163.58, 186.24; MS 41 (14), 55 (22), 77 (38), 83 (26), 105 (100), 122 (0.3); IR (film) 2963.57, 2874.82, 1736.47, 1690.16, 1597.55, 1196.23, 910.68; HRMS *m*/*z* calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1096.

3′-Methylbut-2′-enyl phenylglyoxylate (3): hexanes:ethyl acetate = 15:1; ^{1}H NMR (400 MHz) δ 1.78 (d, $J = 1.2$ Hz, 3H), 1.79 (d, $J = 1.2$ Hz, 3H), 4.88 (d, $J = 7.6$ Hz, 2H), 5.47 (tq, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 7.48−7.52 (m, 2H), 7.63−7.67 (m, 1H), 7.99−8.01 (m, 2H); ^{13}C NMR (50 MHz) δ 18.08, 25.74, 62.90, 117.25, 128.79, 129.94, 132.45, 134.76, 141.07, 163.80, 186.35; MS 41 (45), 57 (19), 69 (99), 77 (52), 105 (100); HRMS *m*/*z* calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0942.

***cis*-3′-Hexenyl phenylglyoxylate (*cis*-4):** hexanes:ethyl acetate = 15:1; ^{1}H NMR (400 MHz) δ 0.95 (t, $J = 7.6$ Hz, 3H), 2.07 (quintet of triplets, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 2H), 2.55 (qt, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 2H), 4.39 (t, $J = 7.6$ Hz, 2H), 5.36 (dtt, $J_1 = 10.8$ Hz, $J_2 = 7.6$ Hz, $J_3 = 1.2$ Hz, 1H), 5.55 (dtt, $J_1 = 10.8$ Hz, $J_2 = 7.6$ Hz, $J_3 = 1.2$ Hz, 1H), 7.27−7.53 (m, 2H), 7.64−7.68 (m, 1H), 7.99−8.02 (m, 2H); ^{13}C NMR (50 MHz) δ 14.09, 20.59, 26.56, 65.55, 122.78, 128.81, 132.37, 134.85, 135.30, 163.78, 186.29; MS 41 (6.9), 55 (11), 67 (8.5), 77 (29), 82 (34), 105 (100), 152 (0.1), 187 (0.1); HRMS *m*/*z* calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1096.

***trans*-3′-Hexenyl phenylglyoxylate (*trans*-4):** hexanes:ethyl acetate = 15:1; ^{1}H NMR (400 MHz) δ 0.97 (t, $J = 7.6$ Hz, 3H), 2.02 (quintet of triplets, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 2H), 2.48 (qt, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 2H), 4.40 (t, $J = 7.6$ Hz, 2H), 5.41 (dtt, $J_1 = 15.0$ Hz, $J_2 = 7.6$ Hz, $J_3 = 1.2$ Hz, 1H), 5.62 (dtt, $J_1 = 15.0$ Hz, $J_2 = 7.6$ Hz, $J_3 = 1.2$ Hz, 1H), 7.27−7.53 (m, 2H), 7.64−7.68 (m, 1H), 7.99−8.02 (m, 2H); ^{13}C NMR (50 MHz) δ 13.47, 25.48, 31.71, 65.65, 123.17, 128.75, 129.90, 132.34, 134.76, 135.74, 163.76, 186.31; MS 41 (6.3), 55 (10), 77 (27), 82 (31), 105 (100), 127 (0.3), 152 (0.1), 187 (0.1); IR (film) 2967.53, 2878.67, 1736.47, 1690.16, 1597.55, 1200.09, 910.68; HRMS *m*/*z* calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1099.

4′-Methylpent-3′-enyl phenylglyoxylate (5): hexanes:ethyl acetate = 15:1; ^{1}H NMR (400 MHz) δ 1.64 (s, 3H), 1.72 (d, $J = 1.2$ Hz, 3H), 2.48 (qt, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 2H), 4.37 (t, $J = 7.2$ Hz, 2H), 5.15 (triplet of quintets, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.49−7.53 (m, 2H), 7.63−7.67 (m, 1H), 7.99−8.01 (m, 2H); ^{13}C NMR (50 MHz) δ 17.77, 25.68, 27.47, 65.70, 118.45, 128.81, 129.95, 132.41, 134.81, 135.45, 163.86, 186.40; MS 41 (11), 55 (19), 67 (14), 77 (32), 82 (58), 105 (100), 187 (0.2), 232 (0.4); HRMS *m*/*z* calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1099.

1′,5′-Dimethylhex-4′-enyl phenylglyoxylate (6): hexanes:ethyl acetate = 15:1; ^{1}H NMR (400 MHz) δ 1.40 (d, $J = 6.0$ Hz, 3H), 1.60 (d, $J = 0.4$ Hz, 3H), 1.69 (d, $J = 1.2$ Hz, 3H), 1.79 (q, $J = 7.2$ Hz, 1H), 1.83 (t, $J = 6.4$ Hz, 1H), 2.09 (q, $J = 7.2$ Hz, 2H), 5.11 (triplet of quintets, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 2H), 5.18−5.26 (m, 1H), 7.49−7.53 (m, 2H), 7.63−7.67 (m, 1H), 7.98−8.01 (m, 2H); ^{13}C NMR (50 MHz) δ 17.52, 19.86, 23.88, 25.63, 35.73, 73.58, 122.91, 128.84, 129.90, 132.61, 134.76, 163.78, 186.69; MS 41 (30), 55 (16), 69 (92), 77 (41), 95 (46), 105 (100), 110 (69), 155 (2.5); HRMS *m*/*z* calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1412.

General Procedures for Irradiation of Samples and Isolating Products. Samples were dissolved in the proper solvent and sealed with a rubber septum bound by sticky

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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, solvent was evaporated on a rotary evaporator and the resulting solution was chromatographed under pressure using hexanes: ethyl acetate as eluting solvent.

3-Hydroxy-4-methyl-3-phenylcyclooct-5-ene lactone (8): hexanes:ethyl acetate = 12:1 to 5:1; ^{1}H NMR (400 MHz) δ 0.92 (d, J = 6.8 Hz, 3H), 2.11 (ddt, J_1 = 14.4 Hz, J_2 = 8.4 Hz, J_3 = 1.6 Hz, 1H), 2.75−2.85 (m, 1H), 3.60 (s, 1H), 3.58−3.66 (m, 1H), 4.21 (ddd, J_1 = 10.8 Hz, J_2 = 4.0 Hz, J_3 = 1.6 Hz, 1H), 4.68 (ddd, J_1 = 12.4 Hz, J_2 = 10.8 Hz, J_3 = 1.6 Hz, 1H), 5.64 (ddd, J_1 = 10.8 Hz, J_2 = 11.2 Hz, J_3 = 2.0 Hz, 1H), 5.79 (dddd, J_1 = 11.2 Hz, J_2 = 8.4 Hz, J_3 = 7.2 Hz, J_4 = 1.2 Hz, 1H), 7.27−7.31 (m, 1H), 7.34−7.39 (m, 2H), 7.75−7.78 (m, 2H); ^{13}C NMR (50 MHz) δ 13.38, 29.52, 41.78, 70.56, 84.32, 126.17, 127.02, 127.68, 128.13, 138.11, 138.31, 179.76; MS 41 (9.4), 51 (10), 67 (81), 77 (39), 82 (100), 105 (69), 147 (2.1), 187 (1.2), 232 (3.6); HRMS *m/z* calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1096.

7,7-Dimethyl-2-oxo-1-phenyl-3,8-dioxabicyclo-[4.2.0]octane (9): hexanes:ethyl acetate = 12:1 to 1:1, two enantiomers; ^{1}H NMR (400 MHz) δ 1.44 (s, 3H), 1.48 (s, 3H), 2.03 (ddt, J_1 = 14.4 Hz, J_2 = 7.6 Hz, J_3 = 2.0 Hz, 1H), 2.24−2.34 (m, 1H), 3.37 (t, J_1 = 9.6 Hz, 1H), 4.31 (ddd, J_1 = 13.2 Hz, J_2 = 11.2 Hz, J_3 = 2.4 Hz, 1H), 4.49 (dq, J_1 = 11.2 Hz, J_2 = 2.4 Hz, 1H), 7.32−7.35 (m, 1H), 7.38−7.42 (m, 2H), 7.51−7.54 (m, 2H); ^{13}C NMR (50 MHz) δ 23.45, 24.72, 30.22, 48.41, 67.36, 67.39, 82.61, 125.08, 128.48, 128.66, 139.98, 172.99; MS 41 (9.4), 51 (7.0), 77 (25), 105 (100), 115 (11), 145 (8.2), 159 (9.7), 188 (5.1), 232 (0.2); HRMS *m/z* calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1096.

3-Hydroxy-5-methyl-3-phenylcyclooct-5-ene lactone (10): hexanes:ethyl acetate = 12:1 to 1:1; ^{1}H NMR (400 MHz) δ 1.94 (s, 3H), 2.06 (ddt, J_1 = 10 Hz, J_2 = 8.4 Hz, J_3 = 1.6 Hz, 1H), 2.40 (d, J = 12.8 Hz, 1H), 2.61−2.67 (m, 1H), 3.50 (d, J = 12.8 Hz, 1H), 3.84 (s, 1H), 4.12 (ddd, J_1 = 10.4 Hz, J_2 = 4.0 Hz, J_3 = 1.6 Hz, 1H), 4.59 (ddd, J_1 = 12.8 Hz, J_2 = 10.4 Hz, J_3 = 1.6 Hz, 1H), 5.64 (dd, J_1 = 8.8 Hz, J_2 = 7.6 Hz, 1H), 7.24−7.35 (m, 1H), 7.36−7.40 (m, 2H), 7.64−7.66 (m, 2H); ^{13}C NMR (50 MHz) δ 27.69, 29.80, 43.06, 69.83, 83.52, 123.00, 125.84, 128.08, 128.37, 139.31, 140.29, 179.85; MS 51 (11), 67 (100), 77 (46), 82 (97), 105 (92), 159 (2.0), 187 (0.9), 232 (5.1); HRMS *m/z* calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1096.

8,8-Dimethyl-2-oxo-1-phenyl-3,9-dioxabicyclo-[5.2.0]nonane (11): hexanes:ethyl acetate = 5:1, two enantiomers; ^{1}H NMR (400 MHz) δ 1.13 (d, J = 6.4 Hz, 3H), 1.39 (s, 3H), 1.44 (s, 3H), 1.62−1.71 (m, 1H), 1.79−1.84 (m, 1H), 1.85−1.93 (m, 1H), 2.04−2.17 (m, 1H), 3.28 (dd, J_1 = 13.6 Hz, J_2 = 4.0 Hz, 1H), 4.22−4.31 (m, 1H), 7.37−7.47 (m, 3H), 7.57−7.60 (m, 2H); ^{13}C NMR (50 MHz) δ 20.81, 22.37, 24.06, 30.43, 31.96, 45.34, 72.20, 81.55, 84.68, 126.21, 129.14, 129.19, 137.83, 173.15; MS 43 (6.7), 77 (22), 105 (100), 115 (7.1), 134 (45), 159 (6.4), 214 (0.8); HRMS *m/z* calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1412.

Acknowledgment. We thank the National Science Foundation (DMR-9013109) and the Office of Naval Research (Navy N00014-91-J-1921) for financial support of this work. The NMR spectrometers were purchased with funds from NSF (CHE9302619), the Ohio Board of Regents, and Bowling Green State University. We acknowledge their support. Conversations with Dr. G. S. Hammond are gratefully acknowledged. We thank Dr. M. A. J. Rodgers for making the laser flash photolysis facilities available to us. Private correspondence with Dr. G. A. Kraus is also gratefully acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR (APT) spectra for all new compounds (24 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.

JO970912S