

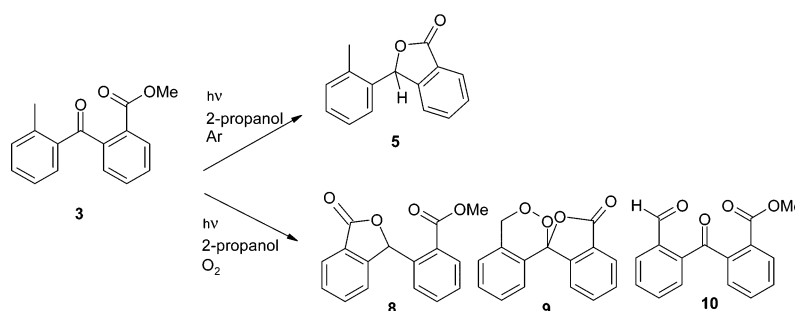
Photoenolization of 2-(2-Methyl Benzoyl) Benzoic Acid, Methyl Ester: Effect of E Photoenol Lifetime on the Photochemistry

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Photolysis of **3** in argon-saturated 2-propanol led to formation of **5** via intermolecular H-atom abstraction followed by lactonization. Irradiation of **4** in 2-propanol gave compounds **6** and **7** that also come from intermolecular H-atom abstraction. In contrast, photolysis of an oxygen-saturated solution of **3** in 2-propanol yields products **8**, **9**, and **10**, which were all formed from intramolecular H-atom abstraction and trapping of the corresponding biradical with oxygen. Laser flash photolysis of **3** in methanol showed formation of biradical **3BR** ( $\lambda_{\text{max}}$  330 nm, and  $\tau = 50$  ns) via intramolecular H-atom abstraction as the main photoreactivity of **3**. Biradical **3BR** decayed into photoenols **3Z** and **3E** ( $\lambda_{\text{max}}$  390 nm,  $\tau = 6.5 \mu\text{s}$  and  $\tau = 162 \mu\text{s}$ , respectively). In comparison, laser flash photolysis of **4** yielded photoenols **4Z** and **4E** ( $\lambda_{\text{max}}$  390 nm,  $\tau = 15 \mu\text{s}$  and  $\tau = 3.6$  ms, respectively). Thus photoenol **3E** is unusually short-lived, and therefore it does not undergo the intramolecular lactonization as we have observed for the analogous photoenol **1E**. Photoenol **3Z** decays back to **3** via an intramolecular 1,5-H shift, whereas photoenol **3E** reforms **3** efficiently via the solvent with the aid of the ortho ester group. The intramolecular lactonization of photoenols **1E** and **3E** must be a slow process, presumably because the photoenols are rigid and the hydroxyl group is inhibited, by intramolecular hydrogen bonding, from acquiring the correct geometry for lactonization. Thus only photoenols that are resistant to reformation of their ketone via the solvent are long-lived enough to undergo lactonization and release the alcohol moiety.

Photoremovable protecting groups have been used in applications such as photolithography, synthetic organic chemistry and biochemistry.<sup>1–10</sup> We recently reported that **1** liberates alcohols upon exposure to UV or daylight,

independent of the reaction media.<sup>11</sup> Furthermore, the release of the alcohol moiety from ester **1** is not quenched in the presence of molecular oxygen. Thus ester **1**

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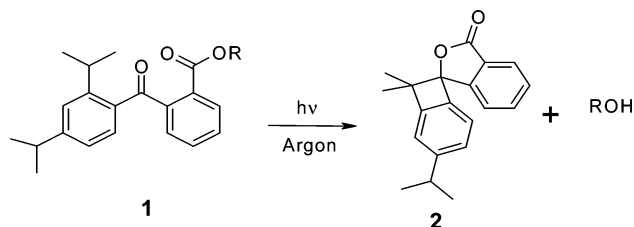
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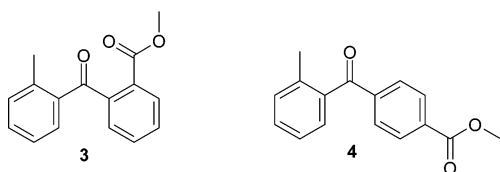
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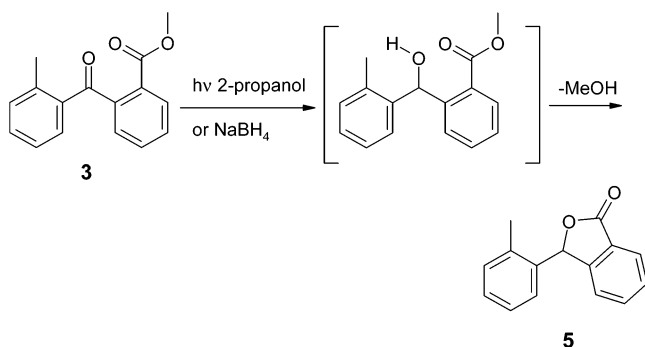


provides a convenient means for slow release of fragrance alcohols in practical applications.<sup>12</sup> In our continuing study of photoremovable protecting groups, we made ester **3**, which is analogous to ester **1** but can be prepared more economically than ester **1**. However, to our surprise **3**, does not release alcohols when irradiated in argon-saturated benzene or dichloromethane solutions.<sup>13</sup> Consequently, we investigated the photoreactivity of **3** and its photokinetics by laser flash photolysis in order to explain why it reacts differently from ester **1**. For comparison, we also studied ester **4**, which is an isomer of **3** that has the ester group in the para position.



## Results

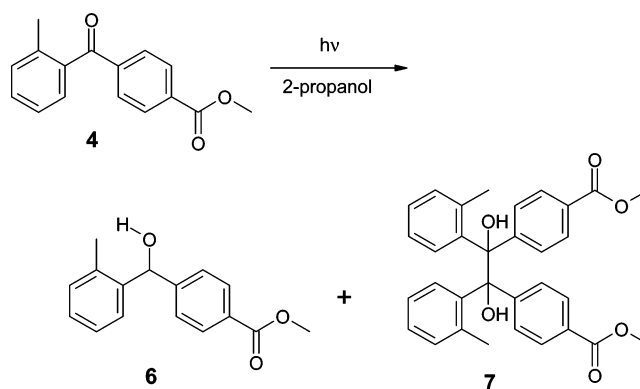
**Product Studies.** Prolonged irradiation of **3** in argon-saturated benzene and dichloromethane did not yield any photoproducts, whereas photolysis of **3** in argon-saturated 2-propanol gave **5** as the major product. Lactone **5**



was isolated in 79% yield and its melting point, IR and NMR spectra match those in the literature.<sup>18</sup> Photoproduct

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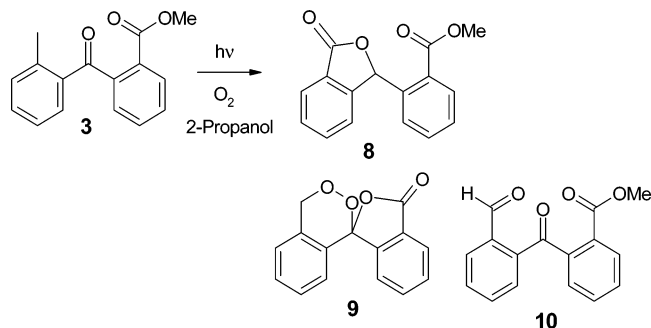
uct **5** must result from intermolecular H-atom abstraction by the triplet excited state of **3** to form 2-(hydroxy-*o*-tolylmethyl) benzoic acid, methyl ester, which undergoes lactonization, whereas photolysis of **3** in argon-saturated benzene or dichloromethane, which do not have easily abstractable H-atoms, does not yield any products. This was further verified by reducing **3** with sodium borohydride, which also yielded **5** as the only product. Similarly, photolysis of **4** in argon-saturated benzene solution did not yield any photoproducts, whereas irradiation of **4** in argon-saturated 2-propanol solutions gave products **6** and **7** in 56% and 17% isolated yields, respectively. The



structures of **6** and **7** were elucidated by obtaining their IR, NMR and MS spectra, which are similar to spectra of the analogous compounds without *o*-methyl substitution.<sup>10,19</sup> The stereochemistry of **7** was determined by X-ray structure analysis to be racemic (RR/SS) at the two chiral centers.

**Product Studies in Oxygen-Saturated Solutions.** We studied the photochemistry of **3** in oxygen-saturated solutions in an attempt to trap any biradicals formed upon intra- and intermolecular H-atom abstraction. Irradiation of oxygen-saturated 2-propanol solutions of **3** to full conversion gave **8** as the major product. Lactone **8** was isolated in 70% yield and its structure was verified by X-ray analysis. When the photolysis of **3** was stopped at low conversions peroxide **9** and aldehyde **10** were the major products. The structure of **10** was verified by

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obtaining its X-ray structure, whereas the characterization of peroxide **9** is based on its IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HRMS spectra. The NMR and IR spectra of **9** are similar to those of an analogous compound that has additional alkyl substituents.<sup>11</sup> We also investigated the photoreactivity of aldehyde **10**. Photolysis of aldehyde **10** in argon-saturated benzene gave **8** as the only product.

**Quantum Yields.** We measured the quantum yields for formation of **5** from **3** by parallel irradiations of sealed tubes containing ester **3** in argon-saturated 2-propanol (see Table 1). Simultaneously, we irradiated an actinometer solution containing 1-(4-methoxy-phenyl)-butan-1-one.<sup>15</sup> The quantum yield for formation of **5** from **3** was 0.02 in argon-saturated 2-propanol. Similarly, we also measured the yield for formation of **8** from **3** in oxygen-saturated 2-propanol solution, which was higher at 0.047. We kept the conversion of **3** below 10% in both argon- and oxygen-saturated 2-propanol. The formation of **8** from **3** is a two-photon process that goes via aldehyde **10**. Thus, it is significant that the quantum yield for the two-photon process of forming **8** is higher than the quantum yield for depletion of **3**. The quantum yield for depletion of **3** is similar to those for formation of products **5** and **8**, which indicates that the reaction is clean without formation of high molecular weight polymers.

**Attempts to Trap Photoenol 3E.** We photolyzed **3** in oxygen-saturated methyl alcohol-*d* ( $\text{CH}_3\text{OD}$ ) solution for 2 h.  $^1\text{H}$  NMR spectra of the reaction mixture showed that the H-atoms on the *o*-methyl group in **3** were fully exchanged with deuterium isotopes without significant formation of any photoproducts.

We were not successful in trapping photoenol **3E** with a dienophile, since photolysis of **3** in argon-saturated benzene or methanol solutions in the presence of maleic anhydride did not yield any new photoproducts.

**Molecular Modeling.** We calculated the minimal energy conformers of **3**, **3Z**, and **3E** (see Figure 1) using Gaussian03.<sup>16</sup> The molecular modeling of **3** reveals that the *o*-methyl group and the carbonyl oxygen of the ester group are lined up with an intramolecular distance of less than 2.6 Å. Thus intramolecular H-atom abstraction is feasible from the ground state conformer of **3**.<sup>20</sup> The minimal energy conformers of photoenols **3E** and **3Z** both show intramolecular H-atom bonding between the hydroxyl group and the carbonyl group of the ester. The distances from the ester carbonyl oxygens to the hydroxyl

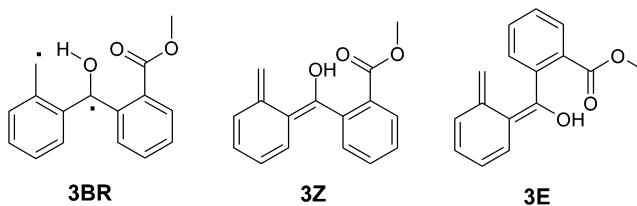
**TABLE 1.** Quantum Yields for Disappearance of **3** and Formation of Products **5** in Argon-Saturated 2-Propanol and **8** in Oxygen-Saturated 2-Propanol

atmosphere	$\Phi_{-3}$ for disappearance of <b>3</b>	$\Phi_5$ for formation of <b>5</b>	$\Phi_8$ for formation of <b>8</b> <sup>a</sup>
Ar	$0.03 \pm 0.003$	$0.02 \pm 0.002$	
O <sub>2</sub>	$0.069 \pm 0.01$		$0.047 \pm 0.01$

<sup>a</sup> The formation of **8** from **3** is a two-photon process, and therefore we used Nikogosyan's definition of quantum yields for two-photon processes.<sup>14</sup>

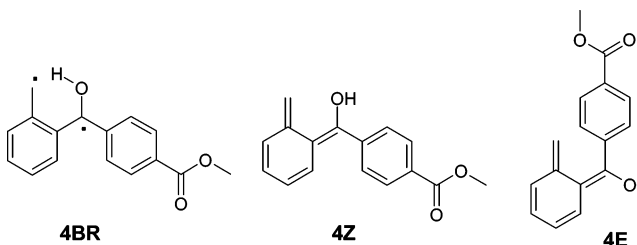
H-atoms are less than 1.77 Å for both **3E** and **3Z**. Our calculations suggest that **3Z** is 2 kcal/mol more stable than **3E**.

**Laser Flash Photolysis.** Laser flash photolysis of **3** in a methanol solution gave a transient spectrum with  $\lambda_{\text{max}} = 330$  nm and  $\tau = 50$  ns, which was formed immediately after the laser pulse (see Figure 2A, Table 2). We assigned this absorption to **3BR** on the basis of its similarity to the transient spectra of analogous 1,4-biradicals and because in oxygen-saturated solutions its lifetime was reduced.<sup>2a,b</sup> The transient spectrum of **3BR**



decayed with the same rate as the formation of a new absorption with  $\lambda_{\text{max}}$  at 390 nm (see Figure 2B). We assigned this new absorption to the mixture of the **3E** and **3Z** photoenols, based on comparison to the transient spectra of similar photoenols.<sup>11</sup> The lifetimes of **3Z** and **3E** in methanol were 6.5 and 162  $\mu\text{s}$ , respectively, as determined from the biexponential decay of the transient at 390 nm for total collection times of 0.1 and 1 ms (see Figure 2C and Table 2). In 2-propanol the lifetimes are 3.5  $\mu\text{s}$  and 44 ms for **3Z** and **3E**, respectively. In dichloromethane the lifetime of **3Z** is reduced to 110 ns and the decay of **3E**, which did not completely follow a monoexponential function, can be estimated to be longer than 10 ms.

For comparison, we did laser flash photolysis of ester **4** in methanol since the lifetime of **3E** was the shortest in this solvent. The transient spectra for **4** are very similar to the spectra obtained for **3**. Immediately after the laser pulse an absorption band was formed that has  $\lambda_{\text{max}}$  at 330 nm, and as before we assigned this band to the 1,4-biradical **4BR**. The absorption at 330 nm decayed



as a new absorption band ( $\lambda_{\text{max}}$  390 nm) was formed, and

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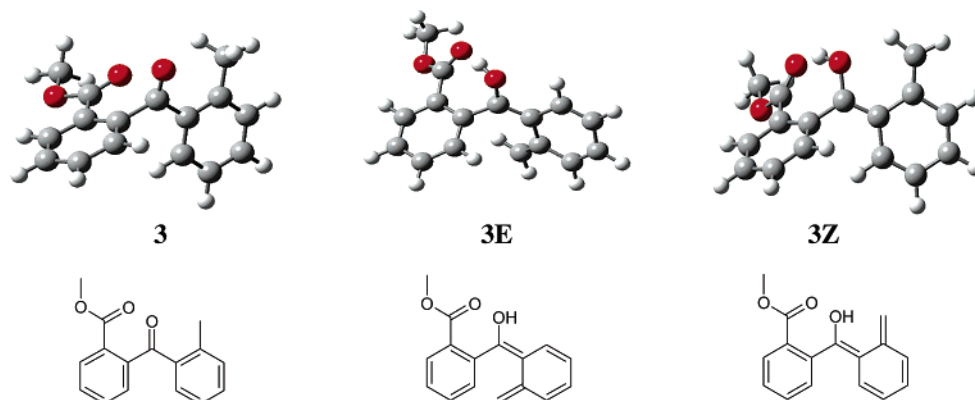


FIGURE 1. Minimal Energy Conformers of **3**, **3Z**, and **3E**.

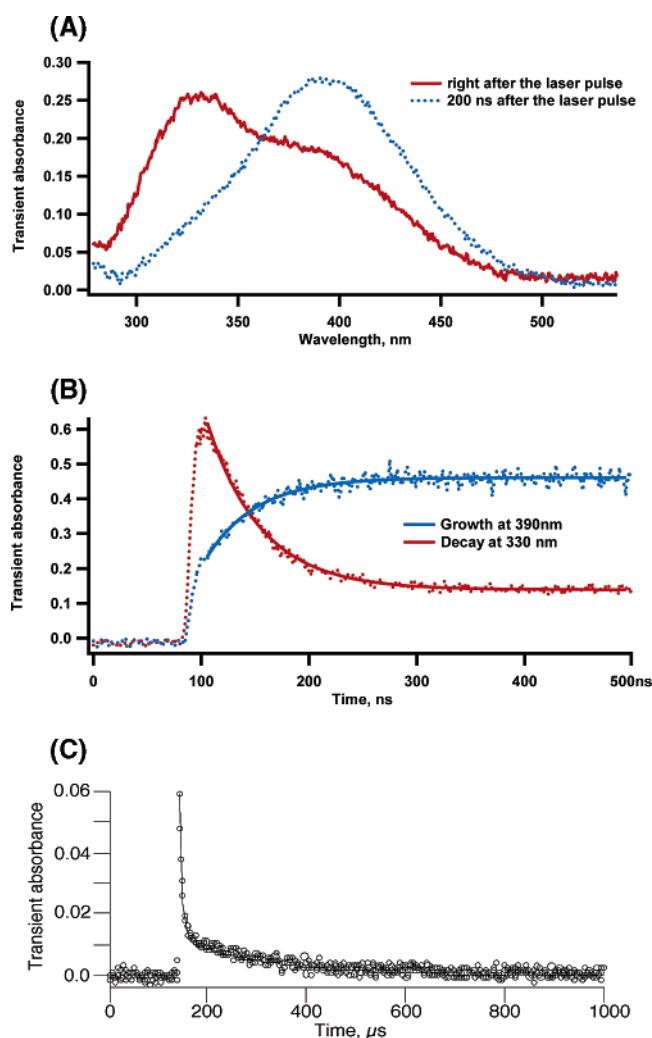


FIGURE 2. Laser flash photolysis of **3**: (A) transient spectra, (B) kinetic traces at 390 and 330 nm, ns timescale, and (C) kinetic trace at 390 nm,  $\mu\text{s}$  timescale.

as previously we assigned the 390 nm band to a mixture of photoenols, **4E** and **4Z**. The lifetime of **4BR** can be estimated to be 60 ns, whereas the lifetimes of **4E** and **4Z** were measured to be  $\tau = 3.6$  ms and 15  $\mu\text{s}$ , respectively. Both esters **3** and **4** yield the **Z** and **E** photoenols in ratios of approximately 80:20, respectively. All the mea-

TABLE 2. Summary of Results of Laser Flash Photolysis Studies

chemical species	solvent	lifetime
<b>1Z</b> <sup>11</sup>	2-propanol	3 $\mu\text{s}$
<b>1E</b>	2-propanol	> 0.2 s
<b>3BR</b>	methanol	50 $\pm$ 5 ns
<b>3Z</b>	methanol	6.5 $\pm$ 0.1 $\mu\text{s}$
<b>3E</b>	methanol	162 $\pm$ 12 $\mu\text{s}$
<b>3Z</b>	2-propanol	3.5 $\pm$ 4 $\mu\text{s}$
<b>3E</b>	2-propanol	44 $\pm$ 8 ms
<b>3Z</b>	dichloromethane	110 $\pm$ 11 ns
<b>3E</b>	dichloromethane	> 10 ms
<b>4BR</b>	methanol	60 $\pm$ 6 ns
<b>4Z</b>	methanol	15 $\pm$ 2 $\mu\text{s}$
<b>4E</b>	methanol	3.6 $\pm$ 0.6 ms
Z photoenol from <i>o</i> -methyl benzophenone <sup>24a</sup>	ethanol	4 $\mu\text{s}$
E photoenol from <i>o</i> -methyl benzophenone <sup>24a</sup>	ethanol	7 ms

sured lifetimes of the **E** and **Z** photoenols and biradicals from esters **3** and **4** are summarized in Table 2.

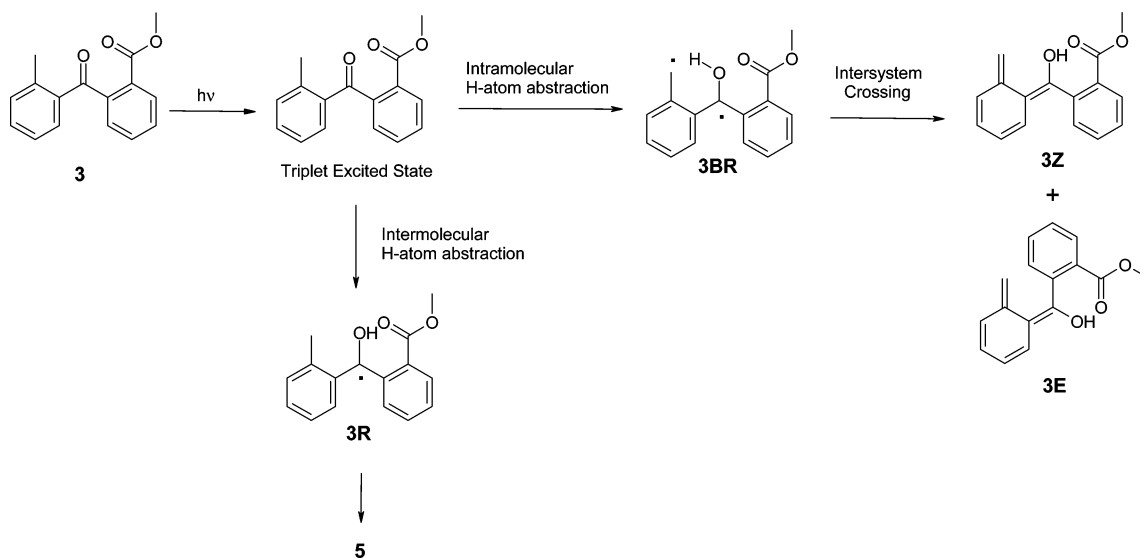
We did not observe the triplet excited states of ketones **3** and **4** because their lifetimes are shorter than the time resolution of the laser flash apparatuses that we used.<sup>17</sup> The triplet excited states of **3** and **4** are expected to be very short-lived because they decay efficiently by intramolecular H-atom abstraction. For comparison, the triplet excited state of the ketone in ester **1** was estimated to have a lifetime of less than 1 ns.<sup>11</sup>

## Discussion

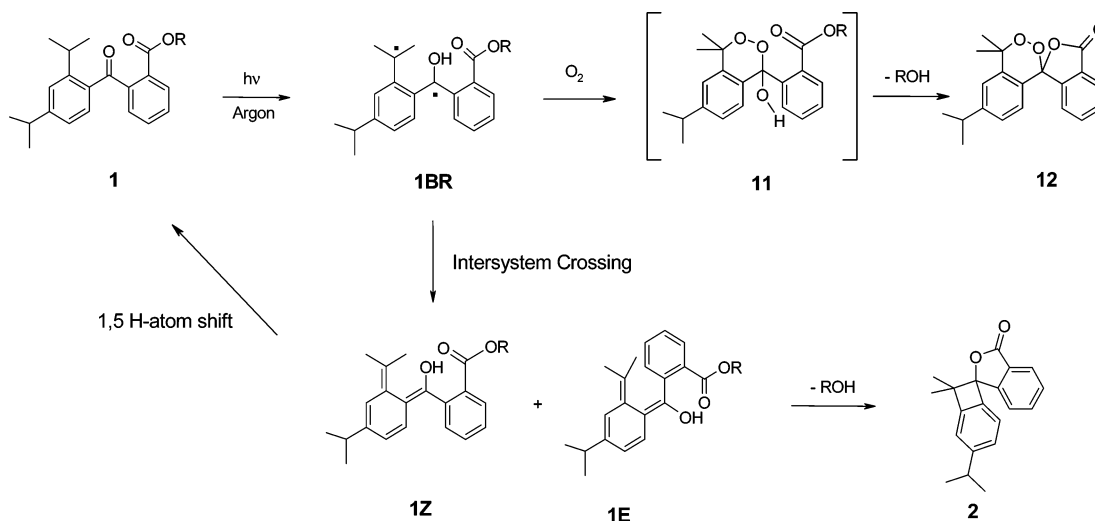
Photolysis of **3** in argon-saturated benzene does not lead to product formation, whereas irradiation of **3** in argon-saturated 2-propanol yields **5**, via an intermolecular H-atom abstraction from the solvent to form radical **3R** (see Scheme 1). We did not observe any dimeric product from photolysis of **3** in 2-propanol as we observed for **4**, presumably because dimerization of **3R** is going to be sterically hindered because of the ortho substituents. The low quantum yield for formation of **5** is similar to the quantum yield for intermolecular photoreduction of *o*-methyl benzophenone, which mainly undergoes intramolecular H-atom abstraction to form photoenols that decay back to the starting material.<sup>21</sup> In comparison, the quantum yields for intermolecular photoreduction and

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## SCHEME 1



## SCHEME 2



lactonization of benzoyl benzoic acid ester derivatives that do not have *o*-alkyl substituents is much higher at 0.62.<sup>11</sup> We did not observe the transient spectrum of the ketyl radical, **3R**. Its transient spectrum can be assumed to be similar to that reported for the *o*-methyl benzophenone ketyl radical which has a  $\lambda_{\max}$  at 530 nm.<sup>22</sup> Thus the laser flash photolysis results and the quantum yield confirm that lactone **5** must be formed via a minor reaction pathway. We did not observe any products from **3** in argon-saturated solutions that could be attributed to intramolecular H-atom abstraction followed by lactonization and release of the alcohol moiety as we have observed for ester **1**.<sup>11</sup> We have shown that the photo-release from ester **1** takes place from the triplet excited state of the ketone chromophore in **1** which undergoes an intramolecular H-atom abstraction to form biradical **1BR**, which in turn decays into photoenols **1Z** and **1E** (see Scheme 2). Photoenol **1Z** is short-lived ( $\tau \approx 3 \mu\text{s}$ ) and reforms **1** via a 1,5 H-atom shift, whereas the longer lived photoenol **1E** ( $\tau > 0.2 \text{ s}$ ) undergoes intramolecular

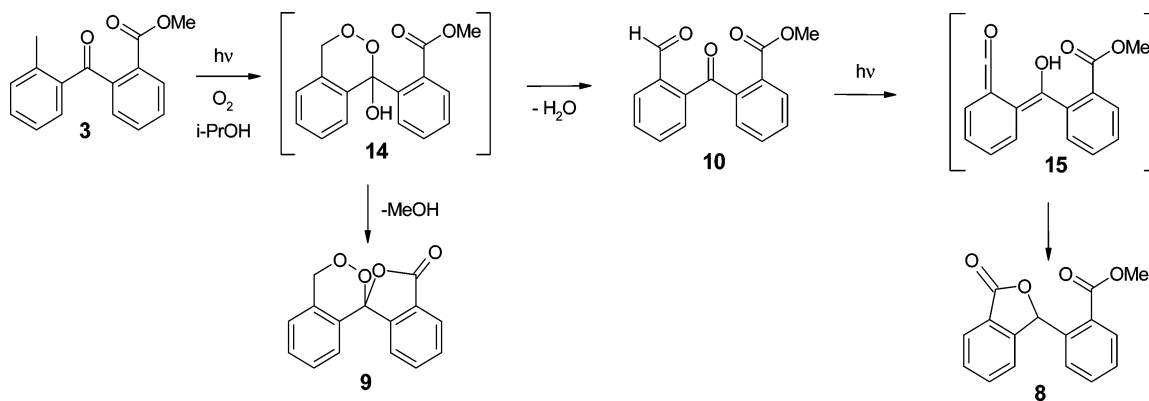
lactonization to release the alcohol moiety and form cyclobutane **2** in the absence of oxygen. Photolysis of ester **1** in the presence of oxygen allows for trapping of **1BR**, and the resulting peroxide, **11**, undergoes lactonization to release the alcohol moiety and form peroxide **12**.

The photoreactivity of **3** leads to the question why **3** does not form photoenols that undergo intramolecular lactonization to release the alcohol moiety as in the case of ester **1** but rather reacts like ester **4** via intermolecular photoreduction. This is particularly intriguing since irradiation of *o*-methyl benzophenone yields Z and E photoenols<sup>23,24</sup> and the E-photoenol is long-lived enough to be trapped with dienophiles.<sup>25</sup> Generally, Z-photoenols are short-lived because they reform the starting material via an intramolecular 1,5-H-atom shift, whereas the E

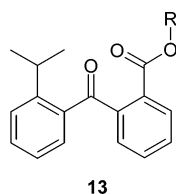
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## SCHEME 3



photoenols are much longer lived, as their reformation of the ketone requires proton transfer via the solvent.<sup>23,26</sup> We have previously demonstrated that ester **13**, which



has only one isopropyl substituent reacts similarly to **1** and releases the alcohol moiety upon exposure to light and thus the difference between the reactivity of **1** and **3** cannot be attributed to the para substituent in **1**.<sup>11,27</sup> Rather, we questioned whether it is possible that **3BR** undergoes efficient reverse H-atom abstraction to reform **3** or if it is possible that photoenol **3E** reverses back to the starting material faster than it can cyclize to form a lactone (see Scheme 1).

Photolysis of **3** in oxygen-saturated solutions allowed for trapping of **3BR** and formation of products **8**, **9**, and **10**. Oxygen must add to biradical **3BR**, and it is possible that photoenols **3E** and **3Z** are also trapped to form endoperoxide **14**, which can undergo intramolecular lactonization to release methanol and form peroxide **9** (Scheme 3). In competition with lactonization, **14** also undergoes dehydration to yield **10**. We demonstrated that aldehyde **10** absorbs another photon and undergoes intramolecular hydrogen abstraction to presumably yield ketene **15**, which then cyclizes to benzofuranone **8**. Thus, the lactonization of the ketene moiety in **15** must be faster than the lactonization of the ester group. The

photochemistry of **10** is comparable to the photolysis of 2-benzoyl-benzaldehyde which yields 3-phenyl-3H-isobenzofuran-1-one.<sup>28</sup> The quantum yield for product formation from **3** in oxygen-saturated 2-propanol solution is higher than in argon-saturated solution (see Table 1). Furthermore, we did not isolate any products by trapping **3R** with oxygen. Thus the majority of the photoreactivity of **3** must take place via intramolecular H-atom abstraction to give **3BR** and in oxygen-saturated solutions some of **3BR** is trapped by reaction with oxygen before the biradical can revert back to the starting material via **3Z** and **3E**. The photooxidations of **3** and **1** differ, since **1** yields only peroxide **12**, from lactonization of endoperoxide **11**.<sup>11</sup> Presumably, endoperoxide **11** is less reactive toward dehydration than **14**, due to the dimethyl substituents. The photooxidation of **3** is similar to that reported by Heindel et al. for photooxygenation of methyl benzophenone.<sup>29</sup>

The lifetimes of the photoenols from *o*-methyl benzophenone and *o*-methyl acetophenones are sensitive to experimental conditions.<sup>2a,30</sup> Addition of bases and acids facilitate the reformation of their starting materials by these photoenols. Photolyses of **3** in argon-saturated CH<sub>3</sub>-OD solution yielded **3** with the *o*-methyl group fully exchanged with deuterium isotopes without significant formation of any photoproducts. Presumably, the deuterium incorporation by **3** comes as **3E** and **3Z** reform **3** via the solvent. It is possible that the hydroxyl group in **3BR** undergoes exchange with the solvent as well. However, photochemically induced hydrogen isotope exchange in the absence of a catalyst requires intermediates with lifetimes much longer than 50 nanoseconds.<sup>31,32</sup> Thus, the deuterium incorporation in **3** and the lack of products formed by intramolecular H-atom abstraction cannot be attributed to efficient reversible H-atom abstraction of **3BR**. Furthermore, we have shown that photolyses of **1** in methyl alcohol-*d* that were stopped at low conversion showed formation of product **2** and

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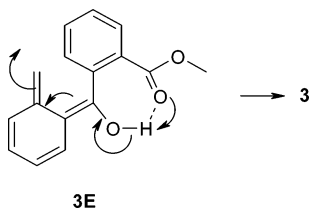
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remaining starting material **1** but with full deuterium exchange of the methine H-atom on the *o*-isopropyl group. Thus we can conclude that the photoenols formed from **1** and **3** reverse back to the ketones efficiently via the solvent.

We were not successful in trapping photoenol **3E** with a dienophile. In contrast, photolysis of **1** under the same conditions in methanol yielded the adduct of **1E** and maleic anhydride in addition to photoproduct **2**.<sup>13</sup> The E-photoenol from *o*-methyl benzophenone can also be trapped with a dienophile. The rate of trapping of the E-photoenol of 2,4-dimethylbenzophenone with dimethyl acetylenedicarboxylate has been measured to be on the order of  $10^3$ – $10^2$  M<sup>-1</sup> s<sup>-1</sup>.<sup>33</sup> We can expect the rates of trapping of **3E** and **1E** to be similar; thus, we can speculate that **3E** must be too short-lived to be trapped with a dienophile.

Laser flash photolysis experiments show that in methanol **3Z** and **4Z** (6.5 and 15  $\mu$ s, respectively) have similar lifetimes as the Z photoenol from *o*-methyl benzophenone in ethanol (4  $\mu$ s).<sup>24a</sup> Generally, the lifetimes of the Z-photoenols from *o*-methyl benzophenone and acetophenone are about a thousand times longer in protic solvents than in nonprotic solvents, because intermolecular H-atom bonding stabilizes the photoenol.<sup>23,26</sup> Accordingly, in dichloromethane, the lifetime of **3Z** is only 110 ns. In contrast, the lifetime of **1Z** does not vary drastically with the solvent presumably because it is stabilized by intramolecular H-atom bonding.<sup>11</sup> Thus the shortening of the lifetime of **3Z** in non-hydrogen bonding solvents indicates that the intramolecular H-atom bonding in **3Z** must be less effective in hindering the reformation of the ketone than in **1Z**. The lifetime of **4E** (3.6 ms) in methanol is comparable to the lifetime of the E photoenol from methyl benzophenone in ethanol (7 ms),<sup>24a</sup> whereas **3E** has a lifetime of only 162  $\mu$ s in methanol. The lifetime of **3E** in 2-propanol is 44 ms and thus 2-propanol is more effective than methanol in retarding the reformation of **3** from **3E**, presumably since it is a better H-atom bonding donor and less acidic. The lifetime of **3E** in



dichloromethane (>10 ms) is almost comparable to its lifetime in 2-propanol. Interestingly, the lifetime of **3E** is much shorter than that of **1E** (>0.2 s in 2-propanol). We expected **1E** to be longer lived than either **3E** or **4E** since reformation of **1** from **1E** involves an isopropylene group which should be less reactive than the methylene substituents of **4E** and **3E**. Similarly, we anticipated that **3E**, **4E** and the E-photoenol from methyl benzophenone would have similar lifetimes since they must reform their ketones via the solvent in a similar manner, but the lifetime of **3E** is much shorter than those of the others. Thus the differences in the photoreactivities of esters **1** and **3** can be attributed to the short lifetime of

**3E**, which prevents it from undergoing intramolecular lactonization. The relatively short lifetime of **3E** compared to that of **1E** must be due to two factors. The methylene group of **3E** is more reactive toward reformation of the ketone by the solvent than the isopropylidene group of **1E** and the ortho ester groups must aid in the reformation of the ketone. Since photoenol **4E** has a lifetime similar to that of the E photoenol of *o*-methyl benzophenone, we conclude that the ester substituent in **3** by itself does not affect the lifetimes of the photoenols. Molecular modeling shows that the lowest energy conformer of the E-photoenol of *o*-methyl benzophenone is similar to that of **3E**, and thus it is unlikely that steric factors are the reason for the efficient reforming of **3** from **3E**. Rather, we propose that the ortho ester group, which is hydrogen-bonded to the alcohol group, must assist in reforming **3** from **3E** as depicted above. In contrast, the reforming of **4** from **4E** cannot be assisted by intramolecular H-atom bonding, and thus it has a much longer lifetime than **3E**. Thus intramolecular lactonization reactions in photoenols **3E** and **1E** are slow processes, presumably since the photoenols are rigid and the hydroxyl group is inhibited, by intramolecular H-atom bonding to the adjacent ester group, from acquiring the correct geometry for lactonization. Consequently, only photoenols that are less reactive toward reforming their starting materials are long-lived enough to undergo intramolecular lactonization.

In summary we have shown that ester **3** undergoes mainly intramolecular H-atom abstraction to form a biradical that intersystem crosses to form E and Z photoenols. Photoenol **3E** and **3Z** are, however, both too short-lived to undergo intramolecular lactonization to release the alcohol moiety as has been observed for ester **1**. We can conclude that the methylene group in photoenol **3E** is too unstable toward reformation of **3** to permit the photoenol to undergo intramolecular lactonization. Thus the realization that methylene groups in photoenols are highly reactive toward reformation of the ketones will aid us in designing new photorelease groups to deliver fragrance in applications.

## Experimental Section

**Molecular Modeling Calculations.** The geometries of all species were optimized by the B3LYP method as implemented in the Gaussian03 programs, using the 6-31G\* basis set.<sup>17</sup>

**Laser Flash Photolysis.** Laser flash photolysis was carried out with an excimer laser (308 nm, 17 ns) and YAG laser (266 nm, 10 ns). These systems have been described in detailed elsewhere.<sup>16</sup>

**Materials and Methods.** Phthalic anhydride, *o*-tolylmagnesium bromide (2 M) solution, methanol, and 2-propanol were obtained from commercial sources and used as received. Benzene and diethyl ether were dried over anhydrous calcium chloride and refluxed over sodium. The Grignard reaction was run under argon in glassware carefully dried in an oven. GC-FID was performed on a gas chromatograph equipped with a type rtx5 column using the following program:  $T_{inj}$  240 °C,  $T_{detection}$  250 °C,  $T_{initial}$  65 °C,  $T_{end}$  320 °C, rate 15 °C/min, total time 22 min, split ratio 5:1, total flow 15 mL/min. Photolysis was carried out using a medium-pressure mercury arc lamp equipped with a Pyrex filter.

**Photolysis of 3.** Ester **3** (37 mg, 0.14 mmol) was dissolved in 2-propanol (15 mL), and the solution was degassed with argon at room temperature for 30 min and irradiated via Pyrex filter for 12 h, when GC analysis of the reaction mixture showed no remaining starting material. The solvent was

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removed under vacuum and the residue was purified using a silica gel column eluted with 10% ethyl acetate in hexane to give of 3-*o*-tolyl-3*H*-isobenzofuran-1-one (**5**) as a white solid, which was recrystallized from hexane/ethyl acetate to yield colorless needles (26 mg, 79%). The melting point,<sup>34</sup> IR and NMR spectra<sup>35</sup> of this compound match those in the literature. Mp: 112–113.5 °C (lit.<sup>34</sup> 113 °C). IR (KBr): 2957, 1760, 1464, 1287, 1212, 1065, 946, 741 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 2.50 (s, 3H), 6.69 (s, 1H), 6.92 (d, 1H), 7.10–7.17 (m, 1H), 7.27 (m, 2H), 7.34 (m, 1H), 7.55–7.71 (m, 2H), 7.98 (d, 1H) ppm.

**Photooxidation of 3.** In a 100 mL Pyrex flask, **3** (0.179 g, 0.70 mmol) was dissolved in 2-propanol (70 mL), and the solution was saturated with oxygen at 0 °C for 30 min and photolyzed for 5 h via a Pyrex filter; the reaction was followed by GC. The reaction mixture was evaporated and the residue was recrystallized from ethyl acetate to give (0.127 g, 71% yield) of methyl 2-(3-oxo-1,3-dihydro-isobenzofuran-1-yl)-benzoic acid methyl ester, **8**. Recrystallization from ethyl acetate yielded **8** as colorless needles. The melting point for this compound matches that reported.<sup>35</sup> The crystals of **8** were triclinic *P*-1, R1 = 0.0639, wR2 = 0.1145. Mp: 156–157 °C (lit.<sup>36</sup> 156 °C). IR (KBr): 3494, 2950, 1759, 1724, 1257, 1064, 986, 750 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 4.01 (s, 3H), 7.25 (m, 1H), 7.37–7.63 (m, 5H), 7.96 (d, 1H), 8.07 (d, 1H) ppm.

Ester **3** (300 mg, 1.2 mmol) was dissolved in benzene, and the resulting 1 × 10<sup>-2</sup> M solutions were placed in 15 mm × 180 mm Pyrex test tubes and purged with oxygen. The solutions were then irradiated (Pyrex sleeve) for 30 min, thus keeping the conversion deliberately low. The solutions were evaporated, and the reaction mixture was separated by silica gel column chromatography to give unreacted **3** (120 mg, 0.48 mmol 40% recovery), **8** (22 mg, 0.08 mmol, 7%), and a mixture of spiro(2,3-benzodioxin-1-isobenzofuran-1-one), **9**, and 2-(2-formyl-benzoyl)-benzoic acid, methyl ester, **10**, (39 mg) in a 2:3 ratio according to <sup>1</sup>H NMR. This mixture was separated by column chromatography to yield aldehyde **10** (20 mg, 0.08 mmol, 6% yield) as colorless crystals that decomposed upon standing and peroxide **9** (5 mg, 0.02 mmol, 2% yield) as a colorless oil. The crystals of **10** were triclinic *P*-1, R1 = 0.0382, wR2 = 0.0994 (see Supporting Information).

**Data for 9.** IR (chloroform): 1784, 1215 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 5.15 (d, 16 Hz, 1H), 5.72 (d, 16, 1H), 6.79–8.02 (m, 8H) ppm. <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>): δ 72.2, 77.4, 122.7, 124.2, 124.6, 125.9, 127.0, 128.1, 129.3, 129.8, 132.0, 133.3, 135.0, 144.9, 187.8 ppm. HRMS: *m/z* calcd for C<sub>15</sub>H<sub>9</sub>O<sub>4</sub> [M - H]<sup>+</sup> 253.0511, found 253.0502.

**Data for 10.** Mp: 101–103 °C. IR (chloroform): 1720, 1697, 1671, 1286 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 3.64 (s, 3H), 7.24–8.02 (m, 8H), 10.43 (s, 1H) ppm. <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>) δ: 52.6, 128.5, 129.0, 130.0, 130.2, 130.8, 132.2, 132.4, 132.5, 137.2, 141.0, 166.6, 192.7, 197.3 ppm. HRMS: *m/z* calcd for C<sub>16</sub>H<sub>12</sub>O<sub>4</sub>Na [M + Na]<sup>+</sup> 291.0633, found 291.0660.

**Photolysis of 3 in CH<sub>3</sub>OD.** An argon-saturated solution of **3** (13 mg, 0.05 mmol) in CH<sub>3</sub>OD (2 mL) was irradiated via Pyrex filter for 2 h. The solvent was removed under vacuum, and the residue was dissolved in CDCl<sub>3</sub> and analyzed by <sup>1</sup>H NMR spectrometer. The *o*-methyl singlet at 3.61 ppm was absent in the <sup>1</sup>H NMR spectrum.

**Photolysis of 4.** A solution of methyl 4-(2-methyl benzoyl)-benzoic acid, methyl ester (258 mg, 1.01 mmol) in argon-saturated 2-propanol (20 mL) was irradiated via Pyrex filter for 18 h. GC analysis of the reaction mixture indicated formation of two photoproducts and some remaining starting material. The solvent was removed under vacuum, and the reaction mixture was separated on a silica column eluted with

10% ethyl acetate in hexane to give recovered starting material (66 mg, 0.26 mmol, 26%), 1,2-bis(2-methylphenyl)-1,2-bis(4-carbomethoxyphenyl)-1,2-ethanediol (**7**), a white crystalline compound (33 mg; 0.065 mmol, 13%), and 4-(2-methyl-benzoyl)-benzoic acid methyl ester (**6**) (108 mg, 0.42 mmol, 42%) as an oil. The crystals of **7** were monoclinic *C*2/*c*, R1 = 0.0483, wR2 = 0.133

**Data for 6.** IR (KBr): 3460, 1723, 1281 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 2.28 (s, 3 H), 3.90 (s, 3 H), 6.05 (s, 1 H), 7.24–7.17 (m, 4 H), 7.41 (d, 8 Hz, 2 H), 7.99 (d, 8 Hz, 2 H) ppm. <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>): δ 19.4 52.2, 73.2, 125.6, 126.4, 126.8, 127.0, 128.0, 128.6, 129.3, 129.8, 130.9, 135.7, 141.0, 148.1, 167.1 ppm. MS (EI) *m/z* (relative intensity): 256 (M+, 4), 241 (14), 225 (12), 197 (10), 179 (54), 163 (32), 152 (9), 137 (100), 119 (42), 105 (38), 91 (56), 77 (46), 65 (20). HRMS: *m/z* calcd for C<sub>16</sub>H<sub>17</sub>O<sub>3</sub>, [M + H]<sup>+</sup> 257.1178, found 257.1248.

**Data for 7.** Mp: 139–142 °C. IR (KBr): 3540, 1724, 1434, 1281, 1111 cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 1.92 (s, 6 H), 3.10 (s, 2 H), 3.90 (s, 6 H), 6.80 (d, 8 Hz, 4 H), 7.00–6.94 (m, 2 H), 7.15–7.08 (m, 4 H), 7.75 (d, 8 Hz, 4 H), 7.90 (d, 8 Hz, 2 H) ppm. <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>): δ 22.4, 52.3, 84.5, 124.0, 127.6, 128.0, 128.1, 129.1, 131.5, 133.3, 138.0, 141.3, 148.2, 167.0 ppm. HRMS: *m/z* calcd for C<sub>32</sub>H<sub>31</sub>O<sub>6</sub>, [M + H]<sup>+</sup> 511.2121, found 511.2048.

**Photolysis of 10.** A degassed solution of **10** (3 mg, 0.01 mmol) in 2-propanol (1 mL) was irradiated via Pyrex sleeve for 30 min. The solvent was evaporated and the residue was dissolved in CDCl<sub>3</sub>. <sup>1</sup>H NMR of the reaction mixture showed clean formation of **8** and no remaining starting material.

**Photolysis of a Mixture of 3 and Maleic Anhydride.** An argon-saturated solution of **3** (0.025 M) in benzene and maleic anhydride (0.25 M) was irradiated via Pyrex sleeve for 24 h. GC analysis showed no product formation. An argon-saturated solution of **3** (0.025 M) and maleic anhydride (0.25 M) in methanol was irradiated for 8 h. GC analysis of the reaction mixture showed only formation of photoproduct **5**.

**Quantum Yields.** Quantum yields for photoreduction and photooxidation of **3** were determined, both for the disappearance of the starting material and formation of products **5** and **8**. 2-Propanol was purified and dried prior to use.<sup>15</sup> The mole-to-area ratio response of the GC was calibrated for compounds **3**, **5**, and **8** and hexadecane. Photolyses were carried out to about 5% conversion in argon-saturated solutions and to 10% conversion in oxygen-saturated solutions. Solutions of **3** (0.05 M) and hexadecane (0.005 M) were irradiated on a merry-go-round apparatus using a 450-W medium-pressure mercury arc lamp and potassium chromate filter to isolate the 3130-Å line. Solutions were analyzed on a Shimadzu GC-17A gas chromatograph equipped with a 15 m × 0.25 mm column with temperature programming between 65 and 320 °C. 1-(4-Methoxy-phenyl)-butan-1-one (Φ<sub>II</sub> = 0.095 in benzene) was used as an actinometer.<sup>13</sup> Each quantum yield was measured three times and averaged.

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**Supporting Information Available:** X-ray structures of **7**, **8**, and **10** in CIF format; <sup>1</sup>H NMR spectra of **4**, **6**, **7**, **8**, and **10**; Cartesian coordinates, no. of imaginary frequencies, and total energy of **3**, **3Z**, and **3E**; and preparation of **3** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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