JOC Article

Photoenolization as a Means To Release Alcohols

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We have designed molecules which release alcohols upon exposure to UV light independent of the reaction media, making it possible to liberate alcohols in a controlled manner in applications. Photolysis of 2-(2-isopropylbenzoyl)benzoate ester derivatives **4** in various solvents and in thin films results in the liberation of the alcohol moiety from the ester. The reaction mechanism for the release of the alcohol has been elucidated by time-resolved laser flash photolysis. Upon irradiation the triplet excited state of ketone, **4** is formed, and its lifetime can be estimated to be between 0.08 and 0.8 ns. The triplet excited state decays by efficient intramolecular H-atom abstraction to form a 1,4-biradical, **8**, that has a lifetime of less than 17 ns and is trapped by molecular oxygen. In the absence of oxygen, biradical **8** intersystem crosses to form photoenols (*Z*)-**9** and (*E*)-**10** in a ratio of 5:2, respectively. Photoenol (*Z*)-**9** has a lifetime of ~3000 ns in protic solvents and returns to the starting material through 1,5 intramolecular hydrogen transfer. The other isomer, (*E*)-**10**, is much longer lived (>1 ms) and releases the alcohol moiety through an intramolecular lactonization.

1. Introduction

Photoremovable protecting groups are of interest since they have demonstrated applications in photolithography, synthetic organic chemistry, and biochemistry.[1−7] Recently, Porter et al. reported that photolysis of 2-benzoylbenzoate esters **1** in 2-propanol yielded the corresponding alcohol and lactone **3**[1] whereas irradiation of **1** in the presence of the electron donor cyclohexylamine also released the alcohol but led to the formation of lactone **2**. Presumably these reactions take place by photoreduction of **1** to form 2-(α-hydroxyphenylmethyl)-benzoic ester, which then undergoes intramolecular lactonization to release the alcohol. This mechanism is supported by the fact that chemical reduction of 2-benzoylbenzophenone esters also yields lactone **2**.[8] The reaction only takes place in the presence of electron donors or H-donating solvents, which are necessary for the initial H-atom abstraction by the ketone chromophore, leading to the photoreduction of the benzoyl benzoate esters.

We are interested in slow release of alcohols since they are used as fragrances in applications such as body care and household cleaning goods.[9] One of the drawbacks of using volatile alcohols in fragrances is that the desired aroma is perceived for a relatively short time in applications. Thus, by forming an ester of a volatile alcohol with 2-benzoylbenzoic acid, it is possible to release the fragrance in a controlled manner over an extended time period by exposure to light. The limitation of this method is that the release of the alcohol takes place only in the presence of an electron-donating molecule or in a solvent that has abstractable H-atoms. Another problem is that molecular oxygen quenches the excited state of the benzophenone chromophore. Consequently we decided to design a protecting group for alcohols that will release the alcohol upon exposure to light, independent of the reaction media, and thus make the photorelease of alcohols feasible in film-type applications. The excited state of the protecting group should be sufficiently short lived that it is not quenched by oxygen, ensuring that

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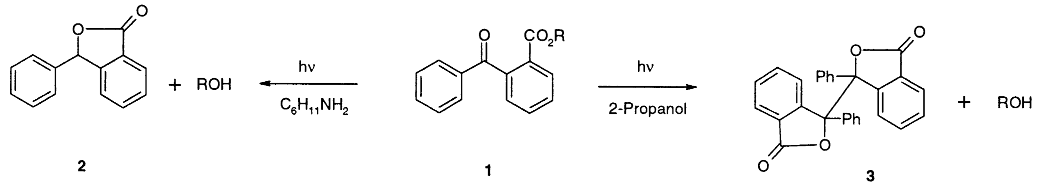
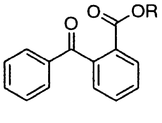
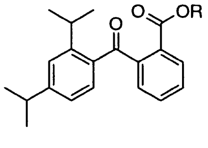


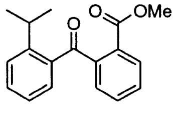
the reaction will take place in air. We have therefore synthesized derivatives of 2-benzoylbenzoate esters **4** with an isopropyl substituent ortho to the ketone that allows for an intramolecular H-atom abstraction. For synthetic reasons we also prepared compounds that contained isopropyl groups in the para position. In this paper we describe the photoreactivity of these compounds, via intramolecular H-atom abstraction to form the *Z* and *E* photoenols, which, theoretically, then can undergo intramolecular lactonization to release the alcohol moiety. We are particularly concerned with how the reactivity of the *Z* and *E* photoenols differs and whether both isomers release the protected alcohol. We used time-resolved laser flash photolysis experiments to elucidate the reaction mechanism. For comparison we performed the laser flash photolysis experiments using the analogous 2-benzoylbenzoate geraniol ester, **1a**, and 2-benzoylbenzoic acid, **1b**, which cannot undergo intramolecular H-atom abstractions.



1a: R=Geranyl
1b: R=H



4a: R=Geranyl
4b: R=CH_3



4c

2. Results and Discussion

2.1. Photodecomposition of 1 and 4. Photolysis of **4a,b** under argon in toluene, 2-propanol, benzene, and chloroform gave the corresponding alcohol and lactone **5**, whereas irradiations of **4a,b** with UV lamps or daylight in air yielded the corresponding alcohol and peroxide **6** (see Figure 1). By comparison, photolysis of **1** in benzene did not yield any detectable products, and irradiation of **1** in chloroform gave only a trace amount of products. Irradiation of acid **1b** in 2-propanol produced **3** in a manner similar to that of the photolysis of **1a** in 2-propanol that gave geraniol and **3** (see Figure 2).[1] Photolysis of **1** in toluene resulted in **7** as the major product. In Figure 3 are plotted the rates of conversion of **1a** and **4a** to their respective photoproducts in toluene, 2-propanol, benzene, and chloroform. The reactivity of **4a** is not affected significantly by the solvent, whereas **1a** only releases geraniol in appreciable amounts in solvents that have abstractable H-atoms, such as toluene and 2-propanol. Quantitative analysis of the photolysis of **4a** in toluene under argon showed that the photoproducts geraniol and **5** are formed in similar amounts (see Figure 4). The depletion of the starting material **4a** is quantitative within experimental error to the formation of the photoproducts, which indicates a clean reaction without formation of polymeric tar.

Thin films of **4a** were prepared in volumetric flasks which were sealed under ambient air and exposed to daylight. After 5 h the contents of the flask were diluted with a solvent and analyzed by GC−FID and GC−MS, which showed geraniol was released. In contrast, irradiation of thin films of **1a** did not release geraniol.

2.2. Quantum Yields. We measured the quantum yields (see Table 1) for the photoreactivities of **4a** and **1a** in 2-propanol using valerophenone as the actinometer.[10] The quantum yields for depletion of the starting materials are similar to those for formation of products,

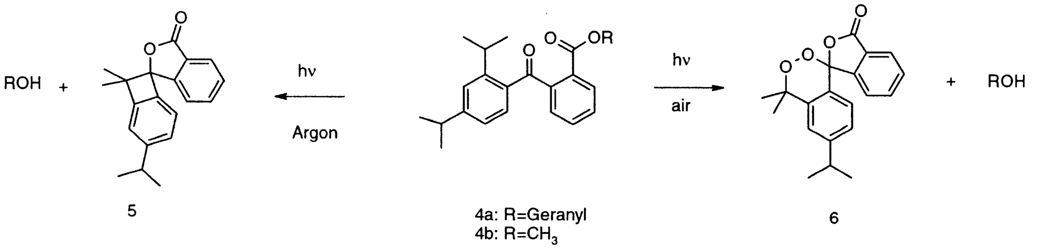


FIGURE 1. Photolysis of **4**.

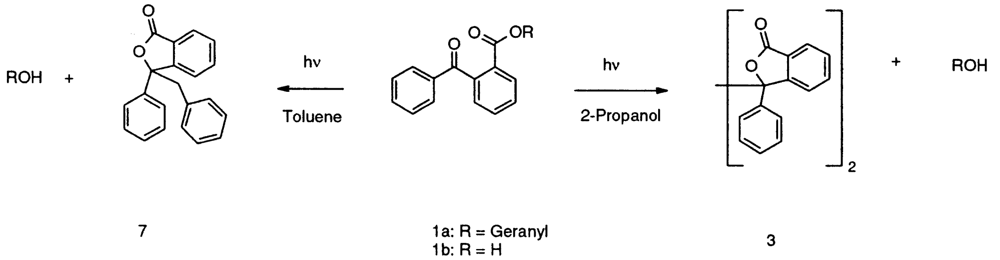


FIGURE 2. Photolysis of **1b**.

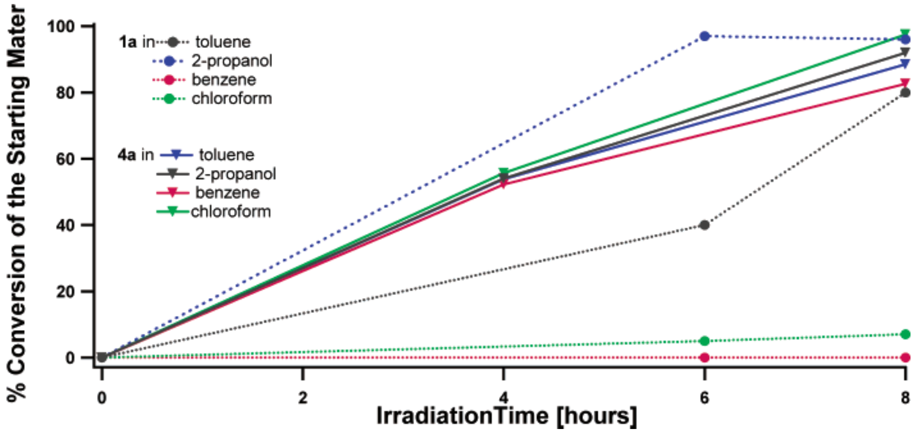


FIGURE 3. Conversions of **1a** (broken lines) and **4a** (solid lines) upon irradiation in various solvents under argon.

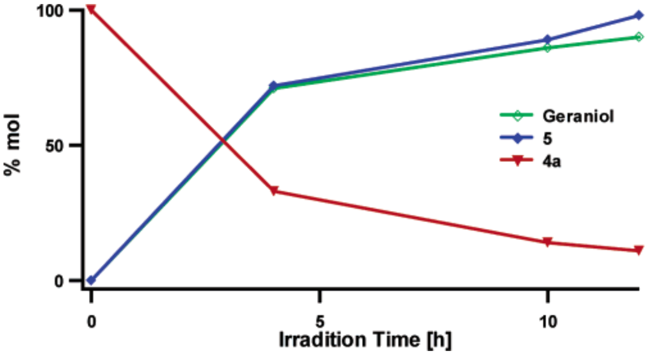


FIGURE 4. Quantitative measurement of formation of geraniol from photolysis of **4a** in toluene under argon.

TABLE 1. Quantum Yields for Formation of Photoproducts from and Depletions of 1 and 4

	1a	4a
Φ for depletion	0.62	0.17 (0.20)[a]
Φ for formation of products	0.62[b]	0.14[c] (0.17)[a,d]

[a] The number in parentheses is the quantum yield measured under an O_2 atmosphere. [b] Quantum yield for formation of **3**. [c] Quantum yield for formation of **5**. [d] Quantum yield for formation of **6**.

indicating that the reaction is very clean without formation of high molecular weight polymers. In 2-propanol, the quantum yields for **1a** depletion are much higher than for **4a**. The quantum yield for product formation from **4a** increased slightly when the solution was bubbled with oxygen prior to photolysis.

2.3. Phosphorescence. The phosphorescence spectra of **1** and **4** were obtained in ethanol glasses at 77 K. The spectra for **1a** and **4a** are displayed in Figure 5. These spectra have vibrational bands as typically observed for triplet excited ketones with n,π* configuration. The 0,0 band can be estimated to be around 406 and 414 nm for **1a** and **4a**, respectively; thus, the triplet energy values of the ketones are 70.4 and 69.1 kcal/mol, respectively, similar to the triplet energy of benzophenone itself.[11] The yield of the phosphorescence emission from **4** is 5 times less than for **1** because it has an additional channel for decay via intramolecular H-atom abstraction that is not available to **1**. The lifetime of the phosphorescence of **4** was shorter than the time resolution of our phosphorescence meter (45 μs). The decay of **1** could be observed but not fitted to a single-exponential function because the compound was frozen in a wide variety of conformations, each having its own specific lifetime.

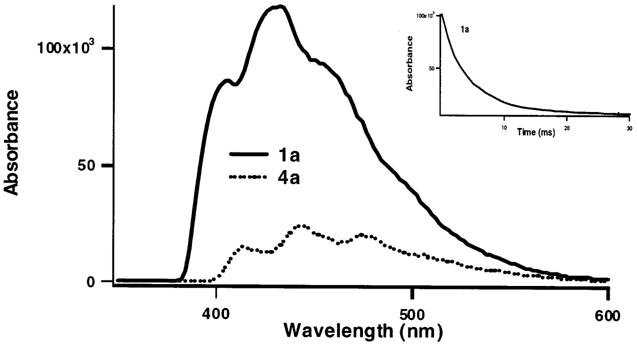


FIGURE 5. Phosphorescence spectra of **1a** and **4a**. The inset shows the decay of the phosphorescence of **1a** measured at 420 nm.

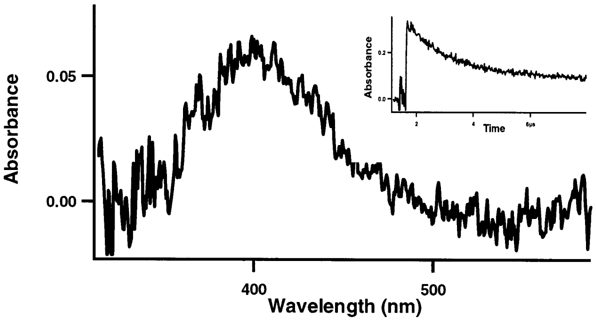


FIGURE 6. Transient spectrum of **4a** in 2-propanol. The inset shows the kinetic trace at 390 nm.

2.4. Laser Flash Photolysis. Laser flash photolysis of **4a** at 308 nm in dichloromethane or ethanol under argon gave a broad transient absorption between 320 and 480 nm with a λ_{max} at 390 nm (see Figure 6). On the basis of the similarity of this spectrum to the transient spectra of *Z* and *E* photoenols of triisopropylbenzophenone and 2-methylbenzophenone,[12,13] we assigned this absorption

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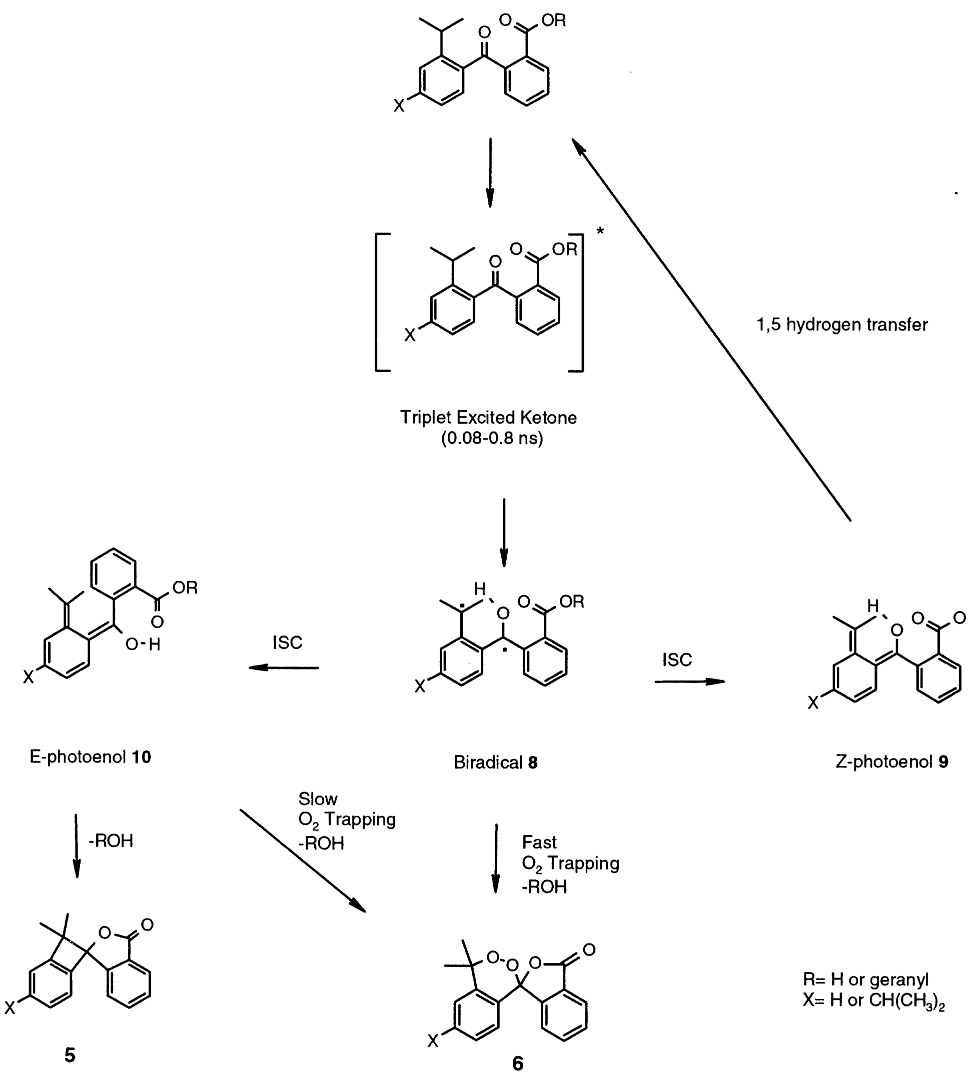
SCHEME 1



to photoenols (Z)-**9** and (E)-**10** (see Scheme 1). The absorption spectrum had two components. Spectra obtained 100 and 5000 ns after the laser pulse were similar except for slightly enhanced absorptions at lower wavelengths at the longer time. In the kinetic mode we followed the decay of the shorter lived component and found that it had a lifetime of ~1300 ns in dichloromethane and accounted for approximately 75% of the absorption. Its lifetime was prolonged to ~3000 ns in hydrogen-bonding solvents such as ethanol and 2-propanol. The longer lived component did not decay significantly over a 100 μs time scale. We proposed that the short-lived component was the (Z)-**9** photoenol that can reketonize through 1,5 hydrogen transfer, whereas the E enol was longer lived since it could only undergo reketonization through proton transfer from the solvent.

We did not detect the absorption of the triplet excited state of ketone **4a**; however, we did succeed in quenching the triplet excited ketone with isoprene. By adding isoprene, we reduced the yield of photoenols (Z)-**9** and (E)-**10**, whereas their lifetimes were not affected. Isoprene did not affect the lifetime of photoenols (Z)-**9** and (E)-**10** since presumably their triplet energies are very low, but reduced their yields by quenching of the triplet excited state of the ketone precursor. Stern–Volmer treatment of the quenching of the absorbance at 390 nm with isoprene in dichloromethane gave a linear plot with a slope of 0.8 (see Figure 7). By assuming that the energy transfer from the triplet excited state of the ketone to isoprene was diffusion controlled, or k_q is between 1×10^9 and 10×10^9 M^{-1} s^{-1}, the lifetime of the triplet ketone could be estimated to be between 0.08 and 0.8 ns.

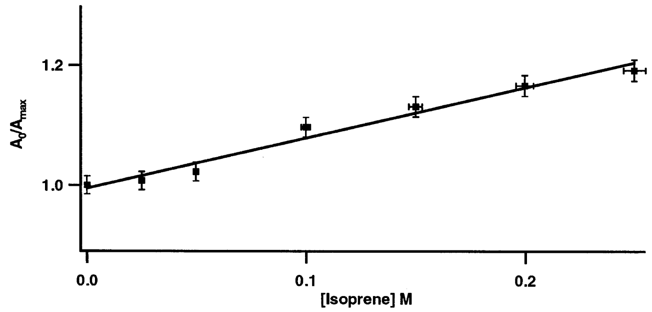


FIGURE 7. Stern–Volmer graph for the quenching of the triplet excited state of **4** with isoprene in 2-propanol.

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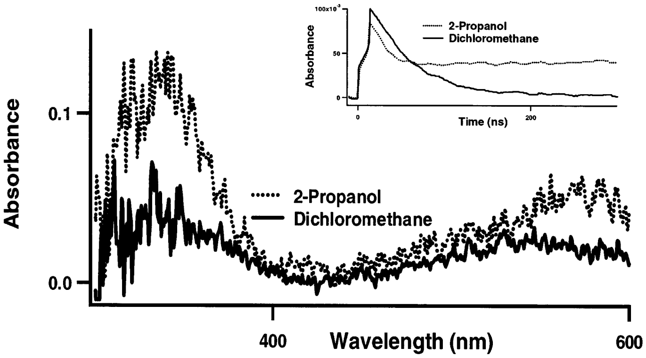
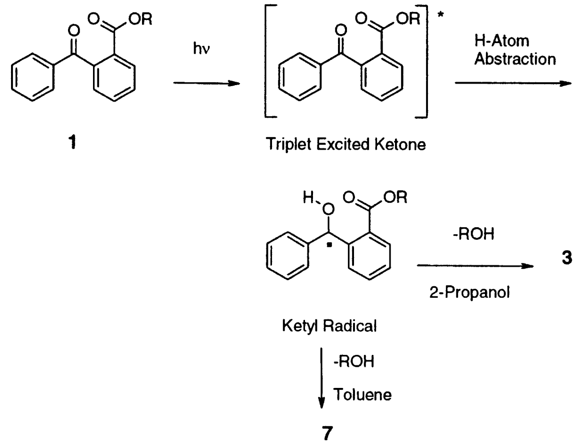


FIGURE 8. Transient spectra of **1a** in 2-propanol and dichloromethane. The inset shows the kinetic trace at 530 nm.

SCHEME 2



Laser flash photolysis of **4** under oxygen gave reduced yields of photoenols (*Z*)-**9** and (*E*)-**10** without shortening the lifetime of (*Z*)-**9**, presumably because we trapped biradical **8** with molecular oxygen. The triplet excited state of **4** is too short lived to be quenched by molecular oxygen, whereas biradicals are known to react with oxygen with a rate constant in excess of 10^9 M^{-1} s^{-1}.[14]

Laser flash photolysis of **1a** and **1b** in dichloromethane under argon yielded transient absorptions with maxima at λ 330 and 530 nm (see Figure 8). We assigned these absorptions to the triplet excited ketones because of their similarity to the triplet excited state of benzophenone.[15] In 2-propanol the absorption maximum was shifted to 590 nm instead of 550 nm, due to the absorption of the ketyl radical that formed upon hydrogen atom abstraction from the solvent (see Scheme 2). In dichloromethane the lifetimes of the triplet excited states of **1a** and **1b** were 100 and 130 ns, respectively. In 2-propanol these lifetimes were reduced to 35 and 50 ns, for **1a** and **1b**, respectively, due to intermolecular H-atom abstraction by the triplet excited ketones. In the kinetic mode the absorption did not decay fully to zero absorbance in 2-propanol because the ketyl radical absorbed in the same region as the triplet excited state of **1**.

2.5. Matrix Isolation of Photolysis of 4c. We synthesized ester **4c** because it is more volatile than ester **4a** or **4b**. We deposited ester **4c** in argon matrices and obtained IR spectra. Upon irradiation the spectra did not change. Presumably, in the matrix, only those conformations where the isopropyl group is located close to the ketone react due to the restrictions imposed on molecular motion by the matrix. Since *o*-alkyl-substituted aryl ketones have been shown to undergo H-atom abstraction at low temperatures via quantum mechanical tunneling,[16] we expected **4c** to react similarly to form biradical **8**. The matrix must restrict the rotation of biradical **8c**, and thus, it could only intersystem cross to form (*Z*)-**9c** but not (*E*)-**10c**.[17] Since the intramolecular lactonization was much slower than reketonization of (*Z*)-**9c**, we did not observe any product formation in the argon matrices.

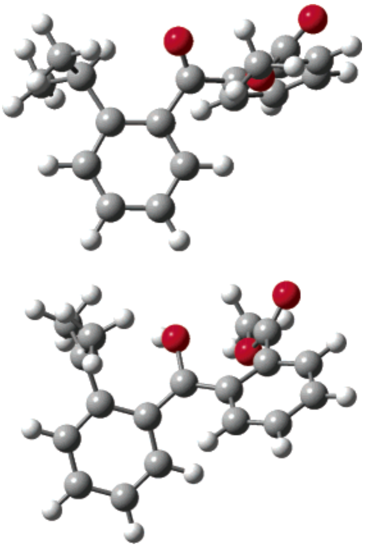


FIGURE 9. Absolute minimal energy conformations of **4c** and biradical **8c**.

2.6. Ab Initio Calculations. We did ab initio calculations using Gaussian 98 and optimized the structures of ester **4c**, biradical **8c**, (*Z*)-**9c**, and (*E*)-**10c**. For reasons of economy we did these calculations only for ester **4c** and its photoproducts and presumed that the minimal energy conformations of **4a,b**, **8a,b**, (*Z*)-**9a,b**, and (*E*)-**10a,b** are very similar. We wanted to confirm that, in the ground state conformation of ester **4**, the *o*-isopropyl group was in close proximity to the ketone chromophore and to determine whether any low-energy conformations of **4** where the *o*-isopropyl group faced away from the ketone existed. In the optimized structure of **4** the phenyl ring bearing the ester group was in conjugation with the ester group, because the torsion angle between the C=O in the ester group and the aromatic ring was ~30° (see Figure 9). The ketone C=O group was more conjugated to the isopropyl-substituted phenyl, since the torsion angle between the ketone C=O and the isopropyl-substituted phenyl group was ~30° whereas the torsion angle between the ketone C=O and the ester-substituted phenyl was ~60°. The methine H-atom of the *o*-isopropyl group was within 2.3 Å of the carbonyl ketone oxygen. We looked for other minimal energy conformations of

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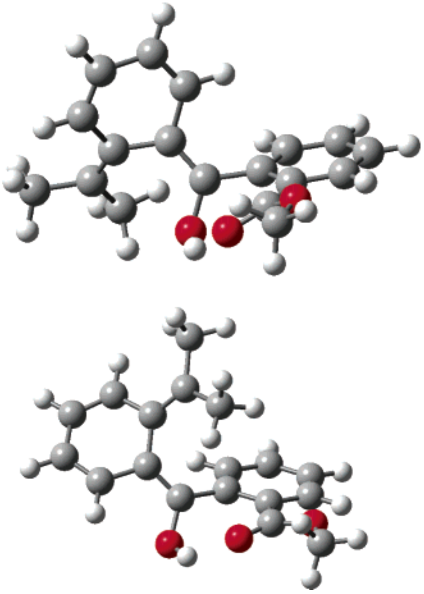

FIGURE 10. Minimal energy conformations of (*Z*)-**9c** and (*E*)-**10c**.

ketone **4c** where the isopropyl group was facing away from the carbonyl group and found one that was 1.5 kcal/mol higher in energy than the absolute minimal energy conformation of **4c**.

We optimized the structure of the triplet biradical **8c**. Its minimal energy conformation was very similar to the one for ester **4c** (see Figure 9). The hydroxyl proton was localized 2.85 Å from the isopropyl carbon radical, which was twisted out of conjugation with the phenyl ring. Both the phenyl groups were rotated approximately 30° out of the plane of the ketyl radical.

We optimized the structures of the photoenols since we were particularly interested in determining whether the minimal energy conformations of (*Z*)-**9** and (*E*)-**10** have intramolecular H-atom bonding and the energy difference between these two isomers. In the optimized structure of photoenol (*Z*)-**9c**, there was H-atom bonding between the hydroxyl group and the carbonyl group of the ester (see Figure 10). The distance between the hydroxyl proton and the ester carbonyl oxygen was 1.96 Å, and the angle O−H···O was 135°. The hydroxyl proton was located 3.66 Å away from the isopropyl vinyl carbon atom, making 1,5 hydrogen transfer feasible with some minor conformational changes of the molecule. By comparison, the optimized structure of (*E*)-**10c** predicted a much lower probability for the 1,5 hydrogen transfer since the distance between the O−H group and the isopropyl vinyl carbon atom was 5 Å. As in the case of (*Z*)-**9c**, the hydroxyl proton and the ester group C═O of (*E*)-**10c** were hydrogen bonded since the distance between them was only 1.90 Å with an O−H···O angle of 137°. Our calculations showed that (*Z*)-**9c** was only 0.6 kcal/mol more stable than (*E*)-**10c**.

3. Discussion

The primary photoreaction of **4** is photoenolization, and the proposed mechanism for the photorelease is shown in Scheme 1. We did not observe the triplet state of ketone **4** with the laser flash photolysis apparatus because it was short lived due to efficient intramolecular H-atom abstraction, but the lifetime was determined to be between 0.08 and 0.8 ns by quenching with isoprene. Since we observed a linear Stern−Volmer plot for the quenching of the triplet excited state of **4** with isoprene, the triplet excited state must be able to reach rotational equilibrium before it reacts. Therefore, any populated conformations of **4** where the *o*-isopropyl group is not in close proximity to the ketone chromophore must be able to rotate in the excited state before decaying. At low temperatures the phosphorescence yields for **4** were 5 times less than for **1**. This is consistent with our calculations which demonstrated that **4** existed mainly in a lowest energy conformation at 77 K that favored efficient intramolecular H-atom abstraction. The intramolecular H-atom abstraction in **4** resulted in biradical **8**, which was trapped by oxygen. Since we did not observe biradical **8** with the laser flash apparatus, we can assume that it has a lifetime less than the time resolution of the laser flash apparatus or 17 ns. The calculated minimal energy conformation of biradical **8** was very similar to the minimal energy conformations of **4** and photoenol (*Z*)-**9**. Biradical **8** was, however, long lived enough to intersystem cross, forming both (*Z*)-**9** and (*E*)-**10**. It is reasonable to assume that the ratio of the *E*/*Z* photoenols must be a reflection of the populations of the various biradical **8** conformations that decay into either the *Z* or *E* photoenol depending on their structure or conformational alignment.

(*Z*)-**9** had lifetimes of ∼3000 and 1300 ns in 2-propanol and dichloromethane, respectively. This was comparable to the lifetime of the *Z* photoenol of methylacetophenone in protic solvents.[3] The main difference between (*Z*)-**9** and the methylacetophenone *Z* photoenol was that the latter was much shorter lived in nonprotic solvents where hydrogen bonding between the solvent and the hydroxy group did not retard reketonization. According to our calculations, (*Z*)-**9** had intramolecular H-atom bonding between the hydroxyl group and the ester carbonyl group which delayed reverse H-atom transfer in nonprotic solvents. The involvement of the hydroxyl group in the intramolecular hydrogen bond was, nonetheless, not sufficient to impede the reverse H-atom transfer long enough to release the alcohol moiety of (*Z*)-**9**. By comparison, (*E*)-**10** was much longer lived than (*Z*)-**9** because it could not revert to **4** through intramolecular 1,5 hydrogen transfer. Presumably, (*E*)-**10** reacted with molecular oxygen, but since this was a ground-state reactivity, it was much slower than the trapping of biradical **8** with oxygen, and we did not observe it under our experimental conditions in the laser flash apparatus. The rate of trapping of the *E* photoenol of 2,4-dimethylbenzophenone with dimethyl acetylenedicarboxylate has been measured to be 10^2 M^{-1} s^{-1}.[18]

Irradiation of **4** in various solvents led to efficient release of the alcohol moiety of the molecule. Similarly, exposure of **4** in thin films to sunlight also released the alcohol. In the absence of air the major photoproduct was **5**, whereas in the presence of oxygen the major product was **6**. Peroxide **6** must be formed by trapping both biradical **8** and (*E*)-**10** with oxygen. The resulting peroxide could then release the alcohol moiety through

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intramolecular lactonization. It is also possible that the oxygen trapping took place after the intramolecular lactonization of (*E*)-**10**. In the absence of oxygen (*E*)-**10** underwent conrotatory electrocyclization and released the alcohol to form cyclobutene **5**.[19] The quantum yields for product formation upon photolysis of **4** were low because the major photoproduct (*Z*)-**9** reversed back to the starting material without releasing the alcohol. Quantum yields for formation of products from **4a** in the presence of O_2 were somewhat higher than in the absence of O_2 because biradical **8** was trapped before it could convert into (*Z*)-**9**, which did not yield any products. Similarly, **4b** did not show any reactivity in argon matrices although the ground-state conformation of this molecule favored H-atom abstraction, presumably because in these matrices only (*Z*)-**9** was formed.

By comparison, irradiation of **1** in dichloromethane or in thin films did not result in significant product formation, but photolysis of **1** in hydrogen-abstractable solvents such as 2-propanol led to release of the alcohol or water. The lifetime of the triplet excited state of **1** was, as expected, much longer than that of ketone **4**. In solvents such as toluene and 2-propanol the triplet excited state of **1** decayed by intermolecular H-atom abstraction to form a ketyl intermediate. In toluene the ketyl radical was intercepted by the benzyl radical formed by intermolecular H-atom abstraction to form **7**, whereas in 2-propanol two ketyl radicals combined to form dimer **3**. In 2-propanol the quantum yield for formation of products from **1** was much higher than from **4**.

4. Conclusion

We have made protective groups that release alcohols upon exposure to UV light independent of the reaction media and are therefore ideal for slow fragrance release in applications. The release takes place through intramolecular H-atom abstraction and formation of biradical **8** that intersystem crosses to form photoenols (*Z*)-**9** and (*E*)-**10**. The shorter lived photoenol (*Z*)-**9** did not result in product formation but reverted back to the starting material through 1,5 hydrogen transfer. In contrast, (*E*)-**10** released the alcohol through an intramolecular lactonization. The quantum yields for release of the alcohol from **4** were low since the major photoenol (*Z*)-**9** did not yield any products. Interestingly, we can trap the 1,4-biradical **8** with molecular oxygen. The trapped biradical released the alcohol, and thus, the photorelease was not decreased in atmospheric air. By comparison the photorelease from **1** was not possible unless the reaction took place in solvents that can undergo hydrogen abstraction. In a solvent such as 2-propanol or toluene the reaction was very efficient. We are currently designing systems that release alcohols through photoenolization but where the intramolecular lactonization is more efficient with the expectation that the *Z* photoenol will yield products as well as the *E* photoenol.

5. Experimental Section

Quantum Yields. Solutions of ester **1** or **4** ($\sim 10^{-2}$ M) and valerophenone in 2-propanol were irradiated simultaneously in a "merry-go-round" apparatus. The light from a mercury arc lamp was filtered through a basic solution in potassium chromate to isolate the 313 nm emission band. The disappearance of the starting material and the formation of photoproducts were analyzed by GC using hexadecane as an internal standard and valerophenone as an actinometer.[8]

Calculations. The geometries of all species were optimized by the Hartree−Fock method as implemented in the Gaussian 98 programs, using the 6-31G basis set.[20]

Phosphorescence. The phosphorescence spectra were obtained on a phosphorometer that has a time resolution of 45 μs.

Laser Flash Photolysis. Laser flash photolysis was carried out with an excimer laser (308 nm, 17 ns). The system has been described in detailed elswhere.[21]

Matrix Isolations. Matrix isolation studies were done using conventional equipment.[22]

Preparation of Starting Materials. 2-Benzoylbenzoic acid is commercially available.

Geranyl 2-Benzoylbenzoate (1a). The geraniol ester of 2-benzoylbenzoic acid was prepared according to the literature.[1] The ^{1}H NMR, IR, and MS spectra of **1a** fit with the ones in the literature.[1] IR (neat): 2925, 1720, 1675, 1450, 1280, 1125 cm^{-1}. ^{1}H NMR (360 MHz, $CDCl_3$): δ 8.06 (dd, 6 Hz, 1H), 7.74 (d, 7 Hz, 2H), 7.56 (m, 3H), 7.42 (m, 3H), 5.07 (m, 2H), 4.53 (d, 9 Hz, 2H), 1.97 (m, 4H), 1.67 (s, 3H), 1.59 (s, 3H), 1.55 (s, 3H) ppm. CILR-MS (NH_3): *m*/*z* 380 $[M + 18]^+$.

2-(2′,4′-Diisopropylbenzoyl)benzoic Acid. Phthalic anhydride (19.3 g, 0.13 mol) was placed in a flame-dried three-neck round-bottom flask under nitrogen. 1,2-Dibromoethane (100 mL) and aluminum chloride (36.0 g, 0.27 mol) were added, and the resulting solution was stirred at room temperature while 1,3-diisopropylbenzene (20.4 g, 0.126 mol) was added dropwise. The reaction mixture was stirred at 100 °C for 2 h and then poured over ice/hydrochloric acid (1:1). The solution was extracted twice with dichloromethane. The organic extract was washed with a saturated aqueous sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated under vacuum to yield an oil which was characterized as being 2-(2′,4′-diisopropylbenzoyl)benzoic acid (isolated yield 36 g, 74%).

IR (neat): 2965, 1695, 1670, 1605 cm^{-1}. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.98 (dd, 1 and 8 Hz, 1H), 7.59 (m, 1H), 7.52 (m, 1H), 7.37 (dd, 1 and 8 Hz, 1H), 7.31 (d, 1 Hz, 1H), 7.09 (d, 8 Hz, 1H), 6.94 (dd, 2, 8 Hz, 1H), 3.82 (m, 1H), 2.91 (m, 1H), 1.25 (m, 12H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$): δ 198.6 (s), 170.9 (s), 153.2 (s), 151.0 (s) 143.8 (s), 133.9 (s), 132.3 (d), 131.7 (d), 130.6 (d), 129.8 (d), 128.9 (s), 128.7 (d), 125.0 (d), 122.7 (d), 34.3 (d), 29.0 (d), 24.1 (q), 23.7 (q) ppm. LREIMS: *m*/*z* (relative abundance) 310 (5, M^+), 265 (43), 249 (45), 221 (100), 149 (32), 84 (41), 49 (35).

Geranyl 2-(2′,4′-Diisopropylbenzoyl)benzoate (4a). 2-(2′,4′-Diisopropylbenzoyl)benzoic acid (1.15 g, 3.7 mmol) was dissolved in dry pyridine (10 mL) in a flame-dried three-neck round-bottom flask. To the solution were added geraniol (0.5 g, 3.6 mmol), 4-(dimethylamino)pyridine (0.10 g, 0.8 mmol), and 1,3-dicyclohexylcarbodiimide (0.76 g, 3.7 mmol). The resulting solution was stirred overnight, poured onto a mixture

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of shaved ice (20 g), hydrochloride acid (32%, 24 g), and ethyl acetate (30 mL), and stirred vigorously for 10 min. This mixture was extracted twice with diethyl ether and the organic layer washed twice with a saturated aqueous sodium bicarbonate solution, twice with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residual oil was purified by silica gel column chromatography eluted with 20% diethyl ether in heptane to yield geranyl 2-(2′,4′-diisopropylbenzoyl)benzoate as a pale yellow oil (isolated yield 1.08 g, 75%).

IR (neat): 2965, 1725, 1670 cm^{-1}. ^{1}H NMR (360 MHz, CDCl$_3$): δ 7.76 (dd, 3, 6 Hz, 1H), 7.51 (m, 2H), 7.37 (dd, 3, 6 Hz, 1H), 7.31 (d, 2 Hz, 1H), 7.18 (d, 8 Hz, 1H), 6.97 (dd, 2, 8 Hz, 1H), 5.22 (m, 1H), 5.04 (m, 1H), 4.64 (d, 7 Hz, 2H), 3.79 (m, 1H), 2.92 (m, 1H), 2.1−1.9 (m, 4H), 1.74 (br s, 3H), 1.62 (br s, 3H), 1.58 (br s, 3H), 1.28 (d, 7 Hz, 6H), 1.25 (d, 7 Hz, 6H) ppm. ^{13}C NMR (90 MHz, CDCl$_3$): δ 198.5 (s), 167.2 (s), 152.9 (s), 150.6 (s), 142.7 (s), 142.4 (s), 134.1 (s), 131.7 (s), 131.2 (s), 131.6 (d), 131.1 (d), 129.9 (d), 129.6 (d), 128.7 (d), 124.7 (d), 123.8 (d), 122.8 (d), 117.9 (d), 62.3 (t), 39.5 (t), 34.3 (d), 29.2 (d), 26.3 (t), 25.7 (q), 24.1 (q), 24.1 (q), 23.7 (q), 23.7 (q), 17.7 (q), 16.4 (q) ppm. LREIMS: *m*/*z* (relative abundance) 446 (M$^+$, $<$0.5), 309 (100), 265 (29), 249 (52), 231 (28), 221 (49), 149 (52), 93 (34), 69 (55), 41 (53). HRMS: *m*/*z* calcd for $C_{30}H_{38}O_3Na$, $[M + Na]^+$, 469.2756, found 469.2719.

Methyl 2-(2′,4′-diisopropylbenzoyl)benzoate (**4b**) was formed by refluxing 2-(2′,4′-diisopropylbenzoyl)benzoic acid (11 g, 0.03 mol) in methanol. The resulting oil was purified by silica gel column chromatography eluted with 20% ethyl acetate in hexane (2.2 g, 22%).

IR (neat): 2962, 1728, 1671, 1605, 1288, 943, 769 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.54 (m, 2H), 7.42 (m, 1H), 7.33 (s, 1H), 7.16 (d, 8 Hz, 1H), 6.98 (d, 8 Hz, 1H), 3.78 (m, 7 Hz, 1H), 3.69 (s, 3H), 2.93 (m, 1H), 7.86 (m, 1H) 1.30 (d, 7 Hz, 6H), 1.26 (d, 7 Hz, 6H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ 198.5, 167.8, 153.2, 150.7, 142.7, 131.6, 131.5, 134.2, 131.0, 130.2, 129.8, 129.1, 124.9, 123.0, 52.5, 34.5, 29.4, 24.3, 23.9 ppm. MS (EI): *m*/*z* (relative intensity) 324 (M$^+$, 6), 309 (14), 292 (11), 265 (33), 249 (58), 231 (20), 221 (100), 193 (16), 178 (18), 163 (52), 115 (13), 91 (14), 77 (22). HRMS: *m*/*z* calcd for $C_{21}H_{24}O_3Na$, $[M + Na]^+$, 347.1618, found 347.1664.

Methyl 2-(2′-Isopropylbenzoyl) benzoate (4c). To a stirred solution of phthalic anhydride (1.69 g, 11.4 mmol) in anhydrous benzene (80 mL) was added 2-isopropylphenylmagnesium iodide, prepared from 2-isopropyliodobenzene (2.80 g, 11.4 mmol), magnesium turnings (0.35 g, 14.4 mmol), and a crystal of iodine in anhydrous ether (50 mL). Over a 15 min period at room temperature, a yellow solid formed. The mixture was refluxed for 12 h and poured onto ice/hydrochloric acid and the resulting mixture extracted with ether (2×50 mL). The organic phase was washed two times with brine, dried over magnesium sulfate, and evaporated to give 2-(2′-isopropylbenzoyl)benzoic acid as a dark oil. Without further purification, the material was dissolved in methanol (50 mL) and titrated with diazomethane in ether and the resulting solution evaporated. The residue was purified by silica gel column chromatography to yield methyl 2-(2′-isopropylbenzoyl)benzoate as a yellow oil which eventually solidified and was recrystallized from hexane (yield after recrystallization 220 mg, 7%).

Mp: 71−72.5 °C. IR (neat): 2965, 1728, 1671, 1287, 931, 762 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.84 (m, 1H), 7.41−7.56 (m, 5H), 7.13−7.26 (m, 2H), 3.70 (m, 7 Hz, 1H), 3.70 (s, 3H), 1.29 (d, 7 Hz, 6H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ 198.7, 167.9, 150.2, 142.1, 136.8, 131.9, 131.4, 130.7, 130.6, 129.8, 129.4, 126.7, 125.2, 52.6, 29.5, 24.3 ppm. MS (EI): *m*/*z* (relative intensity) 282 (M$^+$, 3), 267 (12), 250 (66), 231 (33), 222 (44), 207 (67), 193 (68), 181 (78), 178 (58), 163 (100), 152 (33), 103 (30), 91 (37), 77 (71). HRMS: *m*/*z* calcd for $C_{18}H_{19}O_3$, $[M + H]^+$, 283.1334, found 283.1339.

Isolation of Photoproducts. Spiro (3′-isopropyl-8′,8′′-dimethylbenzodioxin)-3-isobenzofuran-1-one (6). A solution of **4b** (40 mg, 0.12 mmol) in toluene (5 mL) was saturated with oxygen and irradiated with a mercury arc lamp through a Pyrex filter. GC analysis of the reaction mixture showed formation of product **6** and remaining starting material in a ratio of 1:10, respectively. The solvent was removed under vacuum and the resulting mixture purified on silica gel eluted with ethyl acetate/hexane (1:10). Column chromatography yielded a pure fraction of **6** which was crystallized from ethanol to yield colorless needles (23 mg, 68% yield).

Mp: 142−143 °C. IR (neat, gas phase): 2970, 1810, 1290, 940 cm^{-1}. ^{1}H NMR (360 MHz, CDCl$_3$): δ 7.98 (m, 1H), 7.67 (m, 2H), 7.28 (m, 1H), 7.12 (d, 2 Hz, 1H), 7.03 (dd, 2 and 8 Hz, 1H), 6.63 (d, 8 Hz, 1H), 2.92 (m, 1H), 1.81 (s, 3H), 1.63 (s, 3H), 1.25 (d, 7 Hz, 6H) ppm. ^{13}C NMR (90 MHz, CDCl$_3$): δ 168.0 (s), 150.8 (s), 145.2 (s), 141.6 (s), 134.7 (d), 131.6 (d), 128.0 (s), 126.6 (d), 125.6 (d), 125.4 (s), 125.3 (d), 124.0 (d), 121.7 (d), 106.9 (s), 81.3 (s), 34.2 (d), 27.7 (q), 25.1 (q), 23.9 (q), 23.8 (q) ppm. LREIMS: *m*/*z* (relative abundance): 324 (M$^+$, 3), 292 (38), 264 (18), 249 (45), 221 (100), 189 (39). HRMS: *m*/*z* calcd for $C_{20}H_{21}O_4$, $[M + H]^+$, 325.1440, found 325.1447.

Spiro(3′-isopropyl-8′,8′′-dimethylbicyclo[4,2,0]octa-1(b),2,4-triene)-3-isobenzofuran-1-one (5). A degassed solution of **4b** (33 mg, 0.10 mmol) in 2-proponal (3 mL) was irradiated using a medium-pressure mercury arc containing a Pyrex filter at 25 °C for 16 h. The reaction was monitored using thin-layer chromatography (10% ethyl acetate in hexane). After completion of the reaction, the solvent was evaporated and the product was purified using column chromatography. The resulting solid was recrystallized from pentane to yield needles of **5** (yield after recrystallization 18 mg, 62%).

Mp: 104−105 °C. IR (neat): 2961, 2869, 1760, 1466, 1230 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.9 (d, 1H), 7.5 (m, 2H), 7.1 (m, 3H,), 6.9 (d, 1H), 3.0 (septet, 1H), 1.29 (s, 6H), 1.26 (d, 6H) ppm. ^{13}C NMR (60 MHz, CDCl$_3$): δ 170.5, 152.5, 149.0, 138.3, 133.2, 129.1, 127.2, 126.4, 125.2, 124.0, 122.8, 118.2, 92.1, 55.9, 35.0, 24.1, 23.7 ppm. GC−MS: *m*/*z* (relative intensity) 292 (M$^+$, 5), 249 (50), 221 (100). HRMS: *m*/*z* calcd for $C_{20}H_{21}O_2$, $[M + H]^+$, 293.1542, found 293.1536.

3-Benzyl-3-phenyl-3*H*-isobenzofuran-1-one (7). A degassed solution of **1b** (100 mg, 0.44 mmol) in toluene (20 mL) was irradiated with a medium-pressure arc lamp through a Pyrex filter. GC analysis of the reaction mixture showed formation of product **7** and remaining starting material in a ratio of 95:5, respectively. The solvent was removed under vacuum and the resulting oil purified on a silica column eluted with 20% ethyl acetate in hexane. The resulting solid was recrystallized from ethanol (80 mg, 61% yield).

Mp: 95−6 °C (lit.[23] 97−8 °C). IR (CHCl$_3$): 1770, 1287 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.7−7.5 (m, 5H), 7.4−7.2 (m, 4H), 7.1−7.0 (m, 3H), 7.0−6.9 (m, 2H), 3.60 (d, 15 Hz, 1H), 3.40 (d, 15 Hz, 1H) ppm. HRMS: *m*/*z* calcd for $C_{21}H_{16}O_2Na$, $[M + Na]^+$, 323.1048, found 323.1017.

Product Studies from Photolysis of 1 and 4. Photolysis of 4a in Various Solvents under Argon. Solutions of **4a** in chloroform (0.015 M), benzene (0.015 M), and toluene (0.015 M) were placed in test tubes, degassed with argon, and photolyzed simultaneously for 4 h with a mercury arc lamp through a Pyrex filter. The contents of the reaction mixtures were analyzed with a GC chromatograph, and in all instances formation of geraniol and **5** were detected along with some unreacted **5a**. The test tubes were degassed again with argon and photolyzed for an additional 4 h and their contents analyzed with a GC chromatograph to reveal further formation of geraniol and **5**.

Photolysis of 4a in Various Solvents in Air. Solutions of **4a** in toluene (0.01 M) and benzene (0.01 M) were photolyzed using an 8 W 366 nm lamp. After 10 h of irradiation GC analysis of the reaction mixture showed 40% conversion and formation of **6** and geraniol.

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Quantitative Analysis for Formation of Photoproducts from Photolysis of 4a in Solutions. To solutions of **4a** in benzene (0.0067 M) and toluene (0.011 M) was added an external standard, hexadecane. These solutions were degassed with argon and photolyzed with a mercury arc lamp through a Pyrex filter. The quantities of geraniol, **5**, and **4a** were determined after 4, 10, and 12 h of photolysis by using GC analysis.

Photolysis of 1a in Various Solvents. Solutions of **1a** in chloroform (0.017 M), benzene (0.017 M), 2-propanol (0.017 M), and toluene (0.017 M) were placed in test tubes, degassed with argon, and photolyzed simultaneously for 6 h with a mercury arc lamp through a Pyrex filter. The reaction mixtures were analyzed with a GC chromatograph, which revealed that the reaction mixture of **1a** in toluene contained **7**, geraniol, and unreacted starting material. The photolyzed sample of **1a** in 2-propanol showed a small amount of remaining starting material and formation of geraniol and **3**. The irradiated solution of **1a** in benzene did not show any product formation, only unreacted starting material. GC analysis of the photolyzed solution of **1a** in chloroform showed mainly unreacted starting material and formation of dimer **3** and geraniol in trace amounts. The test tubes were degassed with argon and photolyzed for an additional 2 h and their contents analyzed by GC chromatography. The reaction mixtures in 2-propanol, chloroform, and benzene remained similar to those at the earlier time point, whereas photolysis of **1a** in toluene went to further completion.

Photolysis of Thin Films of 4a. Films of **4a** were prepared by adding a pentane solution of **4a** (20 mg, 0.05 mmol) to volumetric flasks and removing the solvent under a stream of nitrogen while turning the flasks slowly to distribute the ester evenly on the surface of the glass. The flasks were then sealed under ambient atmosphere, half of them exposed to daylight for 5 h, and the others kept in the dark. The contents of the flasks were diluted quantitatively with solvent and analyzed for release of geraniol by GC−FID. The quantity of geraniol released was determined by using GC analysis relative to an external standard of geraniol. Films of **4a** that were exposed to daylight for 5 h released 5 mol % geraniol, whereas films kept in the dark did not yield any geraniol.

Photolysis of Thin Films of 1a. Films of **1a** were prepared as described for **4a**. Prolonged photolysis of these films did not lead to any detectable release of geraniol.

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Supporting Information Available: ^{1}H NMR spectra of **4a**, **4b**, **4c**, **5**, and **6** and Cartesian coordinates, number of imaginary frequencies, and total energy of **4c**, **8c**, (*Z*)-**9c** and (*E*)-**10c**. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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