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Solvent-Dependent Photochemistry of 2,2,2-Tribromoethyl-(2′-phenylacetate)

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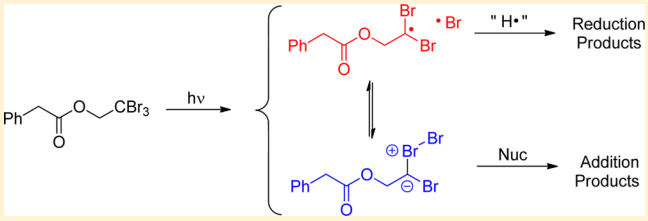
Supporting Information

ABSTRACT: Photolysis (254 nm) of the title compound **1** produces a variety of stable products, which vary significantly with the nature of the solvent. Solvents that serve as efficient H atom donors (methanol, ethanol, isopropyl alcohol) favor products arising from a net reduction of one or more of the C−Br bonds. These include 2,2-dibromoethyl-(2′-phenylacetate) **2** and 2-bromoethyl-(2′-phenylacetate) **3**. In the presence of nucleophiles, products such as 2-(2′-phenylacetoxy)acetic acid **5a** and/or its ester derivatives are produced. Phenylacetic acid **6** is formed in some cases but under the conditions studied appears to be a minor product. The results are interpreted in terms of a general mechanism that features formation of an iso-tribromo intermediate **9** and/or a geminate radical-atom pair.



INTRODUCTION

The photochemistry of organohalogen compounds has attracted much interest over the years. Halogenated compounds have been used in refrigerants, flame retardants, pesticides, and other products.[1−3] Concerns about the environmental fates of such compounds has motivated many mechanistic photochemical studies designed to identify environmental degradation pathways for such compounds. Organohalides have also been studied for use as free radical photoinitiators[4] as well as photoacid generators.[5−7] Finally, there is fundamental interest in understanding the factors that affect homolytic versus heterolytic scission of C−X bonds in the excited state.[8−12]

The current work focuses on the direct photochemical decomposition of the 2,2,2-tribromoethoxy group. This functional group has been used as an electrolytically removable protecting group for carboxylic acids, alcohols, amines, and thiols.[13−16] We have had a longstanding interest in identifying protecting groups that can be removed via photoinduced electron transfer. However, the current study focuses on the direct photochemistry of the 2,2,2-tribromoethoxy group. The behavior of this group under conditions of photoinduced electron transfer will be described in a subsequent report.

There appear to be few, if any, experimental studies on the photochemistry of the 2,2,2-tribromoethoxy group in particular. However, two areas of research into related species are relevant. First, Kropp and others examined product distributions from the solution photolysis of various alkyl monohalides. In general, it was concluded that the initial event is C−X bond homolysis. For alkyl iodides in polar protic solvents, it is possible to observe solvolysis products that result from nucleophilic trapping of the corresponding carbenium ion. These products were attributed to an electron transfer process in the geminal radical pair, which in favorable cases predominates over cage escape. In the case of bromides, the general trend was to observe mixtures of products resulting from radical as well as cation formation.[17−21]

Recent time-resolved studies on the photolysis of geminal di- and tribromides have identified an additional intermediate: the so-called isodi(or tri)-bromomethyl species, wherein one halogen atom dissociates from the carbon atom and reattaches to a remaining halogen. This iso species forms within a few picoseconds of photolysis and decays on a subnanosecond time scale via three competing pathways: homolytic dissociation to form radical species, addition of solvent nucleophiles to form products of OH bond insertion, and reversion to the starting di- or trihalide species.[22−27]

Experiments described below show that, unlike the monobromo species, photolysis of 2,2,2-tribromoethyl-(2′-phenylacetate) **1** can provide clean products that strongly depend on the solvent. In CH_3CN/H_2O mixtures, photolysis results in clean formation of a product of hydrolysis. In contrast, when good H atom donors are employed, photolysis produces excellent yields of mono- and didehalogenation products. A mechanism incorporating reversible formation of an iso-trihalo intermediate, competing homolysis, and nucleophilic displacement reactions is proposed.

RESULTS AND DISCUSSION

The title compound **1** was prepared by coupling 2,2,2-tribromoethanol and phenylacetyl chloride using standard esterification methods as outlined in Scheme 1.[28] The resulting ester shows a maximum absorption in the UV at 210 nm along with a shoulder or tail that, at high concentrations, extends

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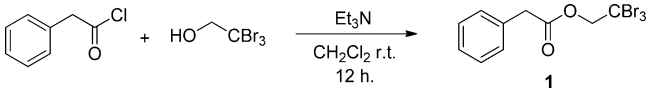
Scheme 1. Synthesis of 1



above 300 nm. These can be attributed to a superposition of the n−σ* absorption related to the C−Br bond (ca. 210 nm) and the typical absorption bands of the phenyl chromophore. The compound shows little, if any, fluorescence. Attempts to detect fluorescence from **1** (CH_3CN λ_{ex} = 254 nm) resulted in negligible signals, lower in comparison to the fluorescence quantum yield of benzene (Φ = 0.05),[29] that did not differ significantly from background.

Ester **1** was dissolved in various solvents and subjected to 254 nm photolysis, and the product distributions were determined by ^{1}H NMR analysis of the crude photolysis mixtures. In most cases, product identities were further confirmed by GC−MS analysis. The latter method, being much more sensitive, could also detect trace products whose yields were too low to be determined by ^{1}H NMR. These are also indicated in Table 1. Products **1**, **2**, and **3** have not been previously reported, and limited characterization data can be found on **5a** and **5b**, the methylated analogue of **5a**, so these species were either independently synthesized or purified from the photolysis mixtures. Full characterization data are available in the Supporting Information. The results of the photolysis studies are summarized in Table 1 (see also Figure 1).

It was expected that direct photolysis of ester **1** would result in homolytic C−Br bond fragmentation providing a radical atom pair that could either escape the initial solvent cage and form radical products or else form the isotribromo intermediate **9**. Studies of similar species suggest that the latter would either react with hydroxylic nucleophiles to form products of OH bond insertion or isomerize back to form the starting material. The dibromo alkyl radical **10** could form a variety of coupling, H atom abstraction, and/or disproportionation products. There is a specific interest in the possibility that this radical might expel a carboxylate ion by way of β-bond scission leading to formation of phenylacetic acid **6**.[30−32] Such a pathway would be useful in the further development of photoreleasable protecting groups. As will be apparent from the discussion below, this

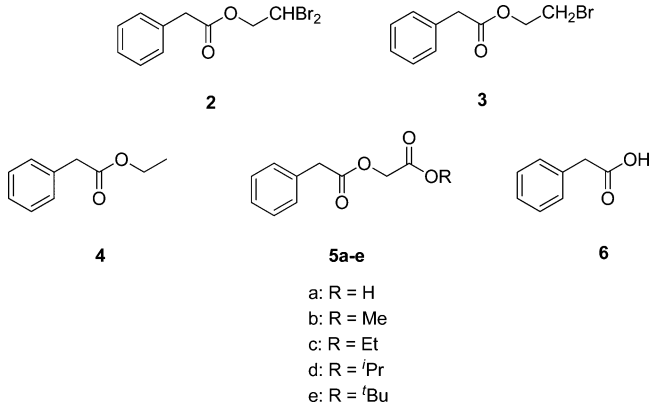


Figure 1. Major products observed in the photolyses of **1** in various solvents.

product does form, but we have not been able to identify conditions where it is the exclusive product from 254 nm direct photolysis.

Acetonitrile, being both polar and relatively non-nucleophilic, was expected to optimize formation of radical **7** (Scheme 3) (any isotribromo intermediate would presumably revert back to starting material in the absence of a nucleophile) and subsequent elimination to form phenylacetic acid **6** (Scheme 3 (a)). It was therefore somewhat surprising that the photolysis of **1** in this solvent generates primarily 2-(2′-phenylacetoxy)-acetic acid **5a** with only minor amounts of the radical product phenylacetic acid **6**.

We hypothesized that the major product from these photolyses, **5a**, was the result of trapping the isohalo intermediate **9** by trace amounts of water in the acetonitrile solvent (Scheme 2), while the minor product, **6**, could be construed as resulting from heterolysis of the initially formed radical **8**. Reid et al. have argued, on the basis of computational studies, that an ion-pair ($RCBr_2^+\cdots Br^-$) resonance structure is a significant contributor for **9** in the condensed phase and that H-bonding solvents such as water should help stabilize this species.[27] This is certainly consistent with our observations of significant products formed via **9** when water and other H-bonding species (see below) are added. Adding water to the

Table 1. Product Ratios from Photolysis of 1 in Various Solvents

entry	solvent	[1] (mM)	time (min)	1	2	3	4	5a−e	6
T1	MeCN	15.13	60	61.7				31.2 **a**	7.1
T2	MeCN	15.13	120	26.9				62.4 **a**	10.7
T3	MeCN	15.13	180	10.2				75.1 **a**	14.7
T4	MeOH	15.88	30	61.0	22.4			16.6 **b**	
T5	MeOH	15.88	60	3.7	44.9	*a*	*a*	27.9 **b**	23.5
T6	MeCN-d_3	20.12	90	59.9				40.1 **a**	
T7	MeOH-d_4	27.61	90	23.3				76.7 **b**	
T8	MeCN (16.7% H_2O)	13.80	60	8.6				71.4 **a**	20.0
T9	ethanol	22.70	60	0	*a*	(<45)	55[b]	**c**[a]	
T10	2-propanol	19.87	60	0	*a*	88	12[b]	**d**[a]	*a*
T11	*tert*-butyl alcohol	16.50	60	4.9	*a*			48.7 **a**, **e**[a]	46.4
T12	cyclohexane	13.47	60	0	*c*				
T13	THF (no BHT)	18.54	60	0	*c*				
T14	THF (with BHT)	18.96	30	0	(<100)[d]				

[a]Minor amounts of this product were detected by GC−MS. [b]Based on reported chemical shifts.[33] [c]Only product identified by ^{1}H NMR accompanied by numerous unidentified major products. [d]Major product identified by ^{1}H NMR accompanied by numerous unidentified minor products.

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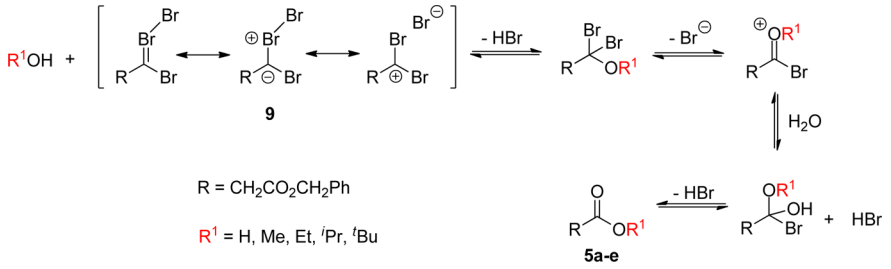
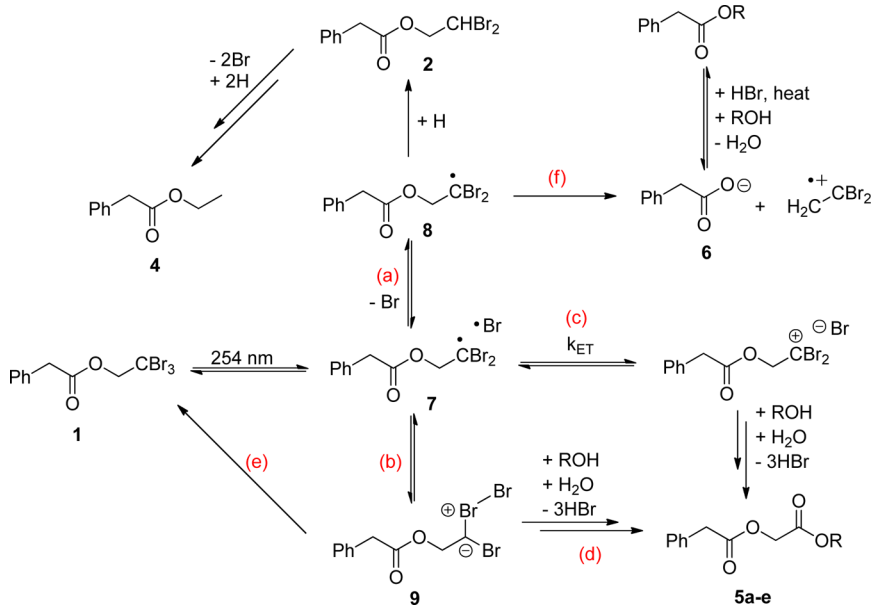
Scheme 2. Proposed Mechanism for the Solvent Trapping of Isohalo Intermediate 9



Scheme 3. Proposed Reaction Pathways for the Observed Photolysis Products of 1



acetonitrile increased the rate of conversion but did not significantly affect the yield of phenylacetic acid **6**. The ^{1}H NMR spectrum of the unpurified photolysis mixture indicates that the two products form cleanly with negligible byproducts (entries T1−T3 in Table 1). Indeed in our hands, this photochemical route proved to be a more practical method for generating isolable quantities of 2-(2′-phenylacetoxy)acetic acid than a previously published procedure.[34]

The latter results are consistent with the mechanism shown in Scheme 3. Excited state homolysis provides a geminate radical pair and the latter partitions between recombination to form the isotrihalo intermediate **9** and cage escape (reversibly) forming a free dibromoalkyl radical and bromine atom. The isotrihalo intermediate either combines with water, eventually forming 2-(2′-phenylacetoxy)acetic acid **5a**, or isomerizes back to form the reactants. Phenylacetic acid could form through a secondary heterolysis of the dibromoalkyl radical **8**, although given the low yields of this product, it is apparently not a particularly fast process relative to competing reactions such as radical recombination and H atom abstraction (which will be described subsequently). While recent ultrafast spectroscopic studies on related systems cause us to favor **9** as the key intermediate, the alternative pathway wherein electron transfer would form a carbenium ion intermediate as suggested by Kropp et al. (pathway c in Scheme 3) cannot be excluded on the basis of the data from the current study.

The competition between nucleophlic trapping (pathway d) and reversion to starting material (pathway e) is supported by our observation that the photochemical conversion rate increases when water is added to the acetonitrile. For example, 60 min of photolysis in nominally dry acetonitrile converts <40% of the starting material compared to >90% in acetonitrile with 17% water (entries T1 and T8 in Table 1). It is interesting that the ratio of phenylacetic acid **6** to **5a** is not significantly affected upon addition of water. This observation implies that the heterolysis step leading to the formation of phenylacetic acid **6** (step f) is also promoted by the addition of water. The latter effect is presumably due to water increasing the polarity of the solvent and thus accelerating the heterolytic bond cleavage (pathway d) to approximately the same extent it accelerates the nucleophilic trapping of **9** leading to **5a** (pathway e).

Also notable is the solvent isotope effect when comparable runs were carried out in CD_3CN (entry T6 in Table 1). In this case only **5a** can be detected in the photolysis mixture, and the homolysis/elimination product **6** falls below the limit of detection. This can be attributed to a kinetic isotope effect on the trapping of the Br atom in the geminate radical pair **8**. The latter can either recombine to form the isotribromo intermediate **9** or, if free radicals are formed through cage escape or H atom transfer to the Br atom, through elimination of phenylacetate ion. The deuterated solvent is slower to trap the Br atom, resulting in fewer free radicals and thus low (<5%) yields of **6**.

Photolysis in methanol provides two significant products: a monodebrominated product **2** and a substitution product **5b**

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(entries T4 and T5 in Table 1). The major product **2** results from a net reduction of the C−Br bond. This presumably arises through H atom transfer from the solvent to the intermediate dibromoalkyl radical **8**. Unlike in CH_3CN, where this radical eliminates the phenylacetoxy ion, radical **8** is apparently able to abstract a H atom from the solvent. While CH_3CN and CH_3OH have similar bond dissociation energies (96.0 and 96.1 kcal/mol, respectively)[35] previous work has shown that electron-poor radicals similar to **8** react more rapidly with electron-rich C−H bonds in substrates such as CH_3OH compared with electron-deficient C−H bonds in substrates such as CH_3CN.[36,37] This mechanism is supported by a significant kinetic isotope effect. The use of CD_3OD suppresses formation of reduction product **2**, and the substitution product, **5a**, is the only product detected by ^{1}H NMR (entry T7 in Table 1).

The minor product in CH_3OH, **5b**, presumably arises from the analogous methanol trapping of the isotrihalo intermediate **9**. The resulting α,α-dibromoether would rapidly hydrolyze. This process would lead to the formation of **5b**. The identity of **5b** was further confirmed by comparison to a ^{1}H NMR spectrum of an independently synthesized sample as well by HPLC analysis.

Similar C−Br bond reduction is observed in ethanol, a solvent that is a stronger H atom donor (C−H BDE = 94.8 kcal/mol).[35] However, in this case, the two major products observed were ethyl phenylacetate **4** and 2-bromoethyl-(2′-phenylacetate) **3** (entry T9 in Table 1). These products obviously result from multiple C−Br bond reductions. We note that control experiments showed that **4** can also form from (thermal) Fischer esterification of the phenylacetic acid product **6** in cases where HBr (the presumed byproduct of reduction or substitution reactions) is added to a solution of **6** in ethanol. Thus, there is some uncertainty as to how much of product **4** results from a Fischer esterification pathway as compared to the sequential reduction of **1**. However, as will be described below, the formation of **4** in comparable experiments using isopropyl alcohol as the solvent suggests that Fischer esterification of **6** is only a small contributor to its overall yield.

It is not clear at this time why NMR-detectable amounts of the singly reduced species **2** are not observed (trace amounts of this product are in fact detected by GC−MS). One possibility is that the newly formed 1-hydroxyethyl radical can further serve as a one electron reducing agent leading to the formation of acetaldehyde and compound **3** upon further hydrogen abstraction.

Photolysis of **1** in 2-propanol (C−H BDE = 91.0 kcal/mol)[35] provides results similar to those observed in ethanol. The doubly debrominated compound **3** is the major component in the photolysis mixture (entry T10 in Table 1). Presumably, the isopropyl radical formed from the first hydrogen abstraction can serve as a reducing agent leading to the formation of acetone. Smaller amounts of the completely debrominated product **4** are also detected. In this case, **4** clearly forms through sequential C−Br bond reductions as Fischer esterification of **6** would lead to isopropyl phenylacetate rather than **4**. The more sensitive GC−MS shows that in fact trace amounts of the isopropyl ester do form, along with minor amounts of substitution product **5d**.

Omission of a good hydrogen donating source such as when *tert*-butyl alcohol is used as the photolysis solvent, provides results consistent with the findings of no reduction products identifiable by ^{1}H NMR. Instead, the major products were found to be phenylacetic acid and 2-(2′-phenylacetoxy)acetic (entry T11 in Table 1). It would appear that the *tert*-butyl alcohol is too sterically hindered to allow for efficient trapping of the isohalo intermediate, conceding to the addition of trace amounts of water. The formation of **4** under these conditions was also confirmed by mass spectrometry.

In solvents that are less polar and non-nucleophilic, such as cyclohexane and THF, the singly reduced species **2** is the only product that can be detected in the ^{1}H NMR of the crude photolysis mixture. However, these photolyses were not clean. The spectra showed that numerous unidentified minor products also accompanied **2**. However none were individually formed in sufficient yield to permit complete characterization. In contrast, when photolyses were carried out in THF that had 0.025% of the preservative BHT, then **2** was clearly the major product and preparative quantities could be generated and isolated under these conditions (entries T12−14 in Table 1).

■ CONCLUSION

Direct photolysis of **1** provides a variety of products that are strongly dependent on the solvent used in the experiments. Despite this diversity of outcomes, all of the product studies reported here are consistent with the general mechanism depicted in Scheme 3. An initial C−Br homolysis step creates a radical atom pair. The latter can form an isotribromo intermediate **9**. This intermediate either reverts to starting material or is trapped by nucleophiles to form **5a−e**. Alternatively, the radical pair **8** can either proceed through a series of steps to form reduction products such as **2−4** or undergo heterolysis to form elimination product **6**. The ratio of these products depends on the ability of the solvent to serve as an H atom donor or nucleophile. Strong H atom donors favor the reductive pathways. Indeed, with BHT it is possible to achieve preparatively useful yields of the dibromo product **2**. Likewise when water, but no good H atom donor, is provided, preparatively useful yields of **5a** can be obtained. While **6** is formed under many conditions, we are unable to identify conditions where it is the major product. Our data suggest that the challenge is competing formation of the isotribromo species from the geminate radical pair. This provides an intermediate that is apparently sufficiently long-lived to be trapped by trace amounts of nucleophiles. One potential solution to this problem would be photochemical electron transfer, which ought to provide the desired radical **8**, accompanied by the bromide rather than a bromine atom and circumventing formation of **9**. Such an approach is the subject of our current investigations.

■ EXPERIMENTAL SECTION

General Experimental Conditions. All reagents were acquired through commercial sources and used without further purification. Solvents were used directly from commercial sources and stored in sealed amber bottles with 4 Å molecular sieves. MeCN was distilled from CaH_2 and stored in a similar fashion as previously stated. NMR data was collected on a 400 MHz spectrometer in $CDCl_3$ or CD_3CN and chemical shifts (δ) are reported in ppm relative to the solvent peak. ^{1}H NMR spectra are reported as follows: chemical shift (ppm), multiplicity (m, multiplet; t, triplet; d, doublet; s, singlet), integration and coupling constants (Hz). Product purification by flash chromatography was done using silica gel, 40−63 μm. Reactions were monitored by GC equipped with an FID detector.

General Photolysis Procedure. Photolysis experiments were done in a capped quartz cuvette purged with nitrogen gas for 15 and 3 min for the solution head space. Isolation reactions were carried out in

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a capped 120 mL quartz test tube and were purged with nitrogen gas for a minimum of 20 and 10 min for the head space. Irradiations were conducted on an 8-bulb Rayonet reactor using 253.7 nm light bulbs. After a certain amount of irradiation time, the photolysis mixture was transferred to a vial, and the solvent was removed under reduced pressure. The unpurified products were redissolved in $CDCl_3$ and subjected to ^1H NMR analysis.

Synthesis of 2,2,2-Tribromoethyl-(2′-phenylacetate) (1). 2,2,2-Tribromoethanol (2.00 g, 7.07 mmol), triethylamine (1.97 mL, 14.1 mmol), phenylacetyl chloride (1.87 mL, 14.1 mmol), and dry CH_2Cl_2 (30 mL) were stirred at room temperature overnight. After 12 h a GC trace of the mixture confirmed consumption of the starting material. The reaction mixture was transferred to a 125 mL separatory funnel, and the organic layer was washed with deionized H_2O (3 × 50 mL) and cold 1 M HCl (3 × 50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford an orange watery oil. Purification of the ester was done by flash column chromatography with 1:1 hexanes/CH_2Cl_2 as eluent. The ester was obtained as a very faint peach colored watery oil (2.19 g, 77.0%). ^1H (400 MHz, $CDCl_3$): δ 7.32 (m, 5H), 4.94 (s, 2H), 3.79 (s, 2H). ^{13}C (400 MHz, CD_3CN): δ 171.3, 135.1, 131.0, 129.9, 128.6, 77.9, 41.7, 37.1. FT-IR (ATR): neat, 1748.19 cm^{-1}. HRMS (ESI-TOF) m/z: [M]+ calcd for $C_{10}H_9Br_3O_2$ 400.8211; found 400.8214.

Isolation of 2,2-Dibromoethyl-(2′-phenylacetate) (2). Compound **1** (98.3 mg, 0.245 mmol) was added to a 120 mL quartz test tube with 30 mL of THF containing 0.025% BHT. The solution was irradiated for 90 min, and the solvent was removed under reduced pressure. A NMR of the crude photolysis mixture confirmed the loss of starting material and the formation of **2**. The crude product was transferred to a 125 mL separatory funnel with 30 mL of CH_2Cl_2. The organic layer was washed with deionized water (3 × 30 mL) and saturated $NaHCO_3$ solution (2 × 30 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The still crude mixture by NMR proved difficult to purify, but this was accomplished by flash column chromatography using a gradient of 95:5, hexanes/ethyl acetate followed by 90:10, hexanes/ethyl acetate as the eluent. Ester **2** was obtained as a watery clear oil (7.70 mg, 9.75%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 5H), 5.70 (t, 1H, J = 6.4 Hz), 4.58 (d, 2H, J = 6.4 Hz), 3.71 (s, 2H) ^{13}C (400 MHz, CD_3CN): δ 171.9, 135.3, 130.9, 129.9, 128.5, 70.6, 42.0, 41.6. FT-IR (ATR): neat, 1740.82 cm^{-1}. HRMS (ESI-TOF) m/z: [M]+ calcd for $C_{10}H_{10}Br_2O_2$ 322.9106; found 322.9116.

Isolation of 2-Bromoethyl-(2′-phenylacetate) (3). Compound **1** (73.7 mg, 0.184 mmol) was added to a 120 mL quartz test tube with 30 mL of 2-propanol. The solution was irradiated for 90 min and the solvent was removed under reduced pressure. A NMR of the crude photolysis mixture confirmed the loss of starting material and the formation of **3**. The crude mixture proved difficult to purify but was accomplished by flash column chromatography using a gradient of 95:5, hexanes/ethyl acetate followed by 90:10, hexanes/ethyl acetate as the eluent. The remaining product appeared to be a clear watery oil (4.90 mg, 11.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 5H), 4.42 (t, 2H, J = 6.0 Hz), 3.68 (s, 2H), 3.51 (t, 2 H, J = 6.0 Hz). ^{13}C (400 MHz, $CDCl_3$): δ 171.3, 133.8, 129.5, 128.8, 127.4, 64.3, 41.3, 28.7. FT-IR (ATR): neat, 1735.81 cm^{-1}. HRMS (ESI-TOF) m/z: [M]+ calcd for $C_{10}H_{11}BrO_2$ 243.0021; found 243.0033.

Isolation of 2-(2′-Phenylacetoxy)acetic acid (5a). Compound **1** was added to a 120 mL quartz test tube with 40 mL of acetonitrile. The reaction was monitored by ^1H NMR until the loss of starting material could be confirmed. The solvent was removed under reduced pressure, and the resulting product was characterized. ^1H (400 MHz, $CDCl_3$): δ 7.32 (m, 5 H), 4.68 (s, 2H), 3.76 (s, 2H). ^{13}C (400 MHz, CD_3CN): δ 172.3, 169.7, 135.3, 130.7, 129.7, 128.3, 61.9, 41.2. FT-IR (ATR): CH_3CN subtracted: 3235 cm^{-1}, 1745.39 cm^{-1}, 1655.18 cm^{-1}. HRMS (ESI-TOF) m/z: [M]− calcd for $C_{10}H_9O_4$ 194.0535; found 194.0503.

Synthesis of 2-Methoxy-2-oxoethyl-(2′-phenylacetate) (5b).[34] Phenylacetic acid (3.03 g, 22.2 mmol), potassium carbonate (2.80 g, 20.2 mmol), methyl bromoacetate (2.30 mL, 24.3 mmol), and acetone (30 mL) were added to a flask was equipped with a condenser. The mixture was heated under reflux (70 ± 5 °C) for 5 h with stirring. The reaction mixture went from chalky white to clear upon the duration of heating. After 5 h, the reaction was concentrated under reduced pressure and the contents were transferred to a 125 mL separatory funnel using 50 mL of deionized H_2O. The aqueous layer was extracted with 150 mL of diethyl ether. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield a clear watery oil (4.22 g, 91.1%). ^1H (400 MHz, $CDCl_3$): δ 7.32 (m, 5H), 4.63 (s, 2H), 3.746 (s, 2H), 3.740 (s, 3H). ^{13}C (400 MHz, CD_3CN): δ 172.4, 169.6, 135.4, 130.7, 129.8, 128.4, 62.2, 53.1, 41.4. FT-IR (ATR): neat, 1740.97 cm^{-1}. HRMS (ESI-TOF) m/z: [M]+ calcd for $C_{11}H_{12}O_4$ 209.0814; found 209.0803.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H NMR, ^{13}C NMR, IR, and MS spectra for all synthesized and isolated compounds. ^1H NMR spectra for the aforementioned photolysis reactions of **1** (Table 1). GC−MS data and specifications for selected photolysis reactions as well as HPLC chromatograms for confirmation of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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