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Comparative Study of the Reactivities of Substituted 3-(Benzoyl)benzyl Carbanions in Water and in DMSO

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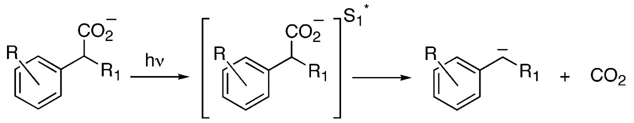
Received May 8, 2004

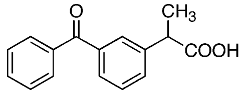
Benzyl-substituted carbanions produced by photodecarboxylation of ketoprofen derivatives have been examined in basic aqueous and DMSO solutions. Product studies, combined with kinetic measurements from laser flash photolysis, have allowed the determination of absolute rate constants for protonation and intra-S_N2 reactions leading to five- and six-membered ring cyclizations; the former are significantly faster. Many of the well-known trends in carbanion reactivity are placed on an absolute rate basis; thus, intra-S_N2 are favored in polar nonprotic solvents, and the effect is larger for the more hindered carbanion centers. Protonation by water is slightly dependent on the nature of the carbanion center and is ~400 times faster in nonhydroxylic solvents, compared with bulk water. As expected, the reactivity for halide leaving groups follows the usual order of decreasing bond strengths, i.e., $I^- > Br^- > Cl^-$.

Introduction

The possibility of generating carbanions or other reactive intermediates within the duration of a nanosecond laser pulse provides a very powerful method to perform mechanistic studies and learn about their reactivity.[1−10] Laser excitation of suitable precursors leads to essentially instantaneous carbanion formation in an irreversible process, thus making their transient decays, and the formation of photoproducts, a kinetically controlled reaction. Employing picosecond and nanosecond flash photolysis techniques, Craig et al.[1,2] investigated the dynamics of the photodecarboxylation of the *p*-nitrophenylacetate in aqueous media. Similarly, Wan et al.[7,11] studied the photodecarboxylation of aroyl-substituted phenylacetic and diarylacetic acids, giving in most cases the corresponding carbanion. In recent reports,[8,9] we explored the reactivities of aroyl-substituted benzyl carbanions formed following photodecarboxylation of a series of ketoprofen-derived compounds in protic and aprotic solvents.

SCHEME 1. Mechanism of the Heterolytic Photodecarboxylation





Ketoprofen

Mechanistically, these photodecarboxylations involve C−C bond heterolysis from the excited state, giving rise to a benzylic carbanion intermediate (see Scheme 1). We have proposed that this reaction involves the singlet state.[6,12]

Following decarboxylation, this ionic intermediate reacts promptly with its microenvironment. In the systems studied here, this leads to protonation or cyclization, although in the presence of other scavengers it can lead to the formation of a wide variety of final products.[13] In this paper, we examine the ability of photogenerated aroyl-substituted benzyl carbanions to cyclize in protic and aprotic media, via an intramolecular nucleophilic

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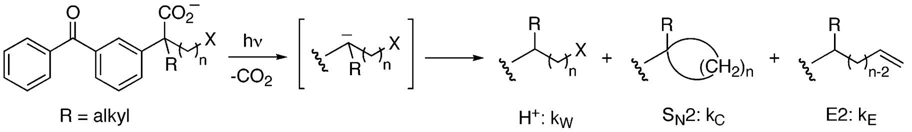
10.1021/jo049224g CCC: $27.50

SCHEME 2. Reaction of Photogenerated Aroyl-Substituted Benzyl Carbanions



SCHEME 3. Synthesis of the Aroyl-Substituted Benzylcarboxylic Acids

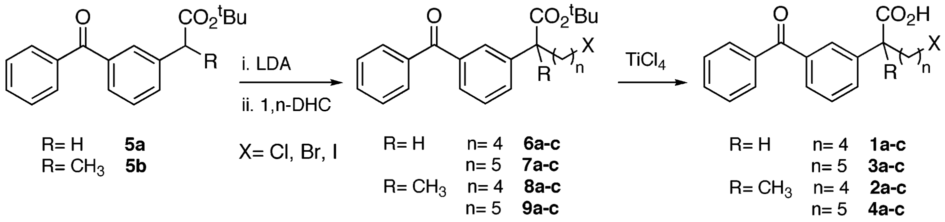
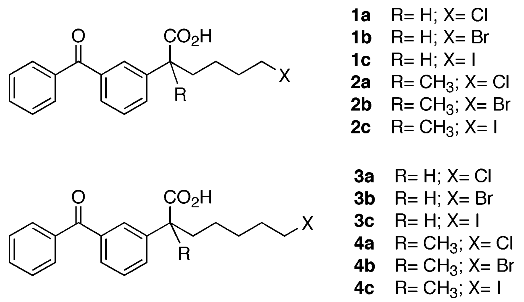


CHART 1. Set of Molecules Studied



attack of the carbanion to an eletrophilic center, as illustrated in Scheme 2.

When the leaving group (X) was iodide (I) and $n = 5$, we observed that the intra-S_N2 reaction was favored in aprotic media, such as dimethyl sulfoxide (DMSO), while protonation was the dominant reaction in basic aqueous media; elimination was not observed.[9] The goal of this paper is to quantify structure−reactivity trends in carbanion chemistry in systems where the direct determination of kinetic data is feasible; our studies are based on the photodecarboxylation for a series of ketoprofen-derived compounds (Chart 1).

To study the nucleophilic behavior of the photogenerated carbanions, and given the fast protonation of these species in water,[9] we compared hindered (by a methyl group) to unhindered nucleophilic sites to evaluate steric effects and different leaving groups (I, Br, and Cl) attached at the end of the alkyl chain, which are likely to have a major influence on the reaction dynamics. Further, we analyzed the effect of the length of the lateral alkyl chain on the cyclization reaction. All the experiments were carried out in aqueous solutions containing 0.1 M potassium hydroxide (to ensure only the carboxylate is present) or in dry, basic DMSO.

Results

Carboxylic acids **1**−**4** were prepared in high yields in two steps: alkylation of esters **5a**,**b** with the corresponding 1,*n*-dihalocompound (1,*n*-DHC, $n = 4$ or 5) to give the intermediate *tert*-butylcarboxylic esters **6**−**9**, followed by removal of the *tert*-butyl group by titanium tetrachloride (see Scheme 3).[9]

The transient absorption spectra obtained following 308 nm laser excitation of aqueous 0.1 M KOH solutions of compounds **1b**, **1c**, **2a**, and **4b** were similar to that for the well-characterized carbanion from ketoprofen (see Figure 1).[6,8,10,14] The visible part of the spectrum was common to all species, with a broad band located at ca. 590 nm.

TABLE 1. Quantum Yields of Photodecarboxylation of 1−4 and Decay Rate Constants for the Photogenerated Carbanions of 1-4 in 0.1 M KOH Solutions

compd	Φ_{photodec}	k_{obs}/s^{-1}
1a (X = Cl; $n = 4$)	0.78	$(6.99 \pm 0.04) \times 10^6$
1b (X = Br; $n = 4$)	0.70	$(6.9 \pm 0.1) \times 10^6$
1c (X = I; $n = 4$)	0.82	$(7.61 \pm 0.07) \times 10^6$
2a (X = Cl; $n = 4$)	0.82	$(2.57 \pm 0.02) \times 10^6$
2b (X = Br; $n = 4$)	0.77	$(2.77 \pm 0.02) \times 10^6$
2c (X = I; $n = 4$)	0.78	$(3.20 \pm 0.04) \times 10^6$
3a (X = Cl; $n = 5$)	0.68	$(5.98 \pm 0.05) \times 10^6$
3b (X = Br; $n = 5$)	0.62	$(6.25 \pm 0.08) \times 10^6$
3c[a] (X = I; $n = 5$)	0.5	$(6.73 \pm 0.05) \times 10^6$
4a (X = Cl; $n = 5$)	0.6	$(2.76 \pm 0.01) \times 10^6$
4b (X = Br; $n = 5$)	0.75	$(2.62 \pm 0.01) \times 10^6$
4c[a] (X = I; $n = 5$)	0.8	$(2.59 \pm 0.01) \times 10^6$

[a] From ref 9.

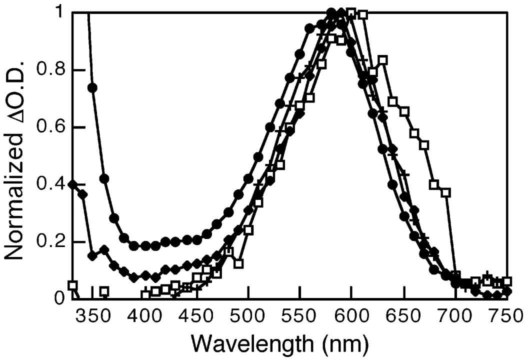


FIGURE 1. Transient absorption spectra following 308 nm laser excitation of N_2O-saturated 0.1 M KOH solution of 0.4 mM **1b** (+), **2a** (□), and **4b** (◆) 64 ns after the laser pulse and **1c** (●) 32 ns after the pulse.

The decay for the resulting carbanions from **1** to **4**, recorded at 600 nm, followed first-order kinetics and led to the rate constants listed in Table 1. Quantum yields for photodecarboxylation for compounds **1**−**4** were estimated using the reaction of ketoprofen as relative acti-

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CHART 2. Photoproducts of Carboxylic Acids 1a–c, 2a–c, 3a–c, and 4a–c

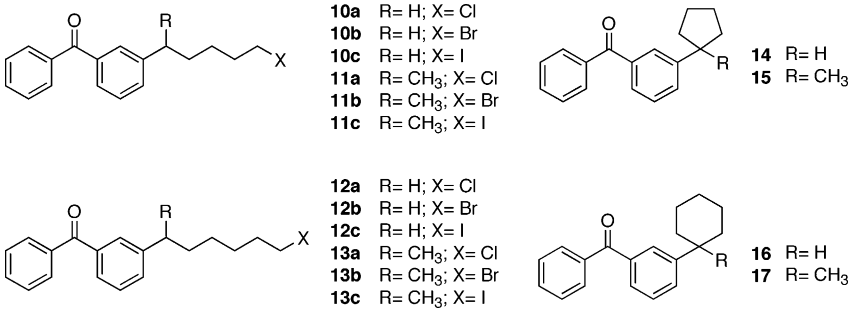

TABLE 2. Absolute Rate Constants for Protonation (k_W) and Cyclization (k_C) of Photogenerated Carbanions from 1–4 in DMSO and Quenching Rate Constants by Water (k_{Quen}) in Solutions of 1–4 in DMSO[a]

compd[b]	f_C[c]	f_W[c]	k_{obs} (s^{-1})	k_C (s^{-1})	k_W (s^{-1})[d]	k_{quen} ($M^{-1}\ s^{-1}$)
1a (X = Cl; n = 4)	13 (**14**)	87 (**10a**)	$(2.2 \pm 0.1) \times 10^6$	2.8×10^5	(1.9×10^6)	3.3×10^7
1b (X = Br; n = 4)	100 (**14**)		$(3.6 \pm 0.1) \times 10^7$	3.6×10^7	$(<7.3 \times 10^5)$[d]	
1c (X = I; n = 4)	100 (**14**)			$>5 \times 10^7$		
2a (X = Cl; n = 4)	43 (**15**)	57 (**11a**)	$(9.2 \pm 0.1) \times 10^5$	4.0×10^5	(5.2×10^5)	7.8×10^6
2b (X = Br; n = 4)	100 (**15**)			$>5 \times 10^7$		
2c (X = I; n = 4)	100 (**15**)			$>5 \times 10^7$		
3a (X = Cl; n = 5)		100 (**11a**)	$(3.0 \pm 0.1) \times 10^6$	$<6.0 \times 10^4$[e]	(3.0×10^6)	6.9×10^7
3b (X = Br; n = 5)	17 (**16**)	83 (**11b**)	$(3.6 \pm 0.1) \times 10^6$	6.1×10^5	(3.0×10^6)	5.5×10^7
3c[f] (X = I; n = 5)	82 (**16**)	18 (**11a**)	$(6.0 \pm 0.1) \times 10^6$	4.9×10^6	(1.1×10^6)	5.1×10^7
4a (X = Cl; n = 5)	–	100 (**13a**)	$(5.5 \pm 0.1) \times 10^5$	$<1.1 \times 10^4$[e]	5.5×10^5	1.0×10^7
4b (X = Br; n = 5)	42 (**17**)	58 (**13b**)	$(7.4 \pm 0.1) \times 10^5$	3.1×10^5	(4.3×10^5)	8.3×10^6
4c[f] (X = I; n = 5)	98 (**17**)	2 (**13c**)	$(2.0 \pm 0.1) \times 10^6$	1.9×10^6	(3.9×10^4)	8.8×10^6

[a] Dried with CaH_2, distilled under low pressure and kept in 4 Å sieves (base used NaH). [b] In general, the samples were measured as soon as possible following preparation, given their reduced stability in the presence of NaH. [c] Percent fraction of cyclization and protonation. [d] The values of k_W are given in parentheses since some variation is anticipated due to day-to-day fluctuations in the water content of "dried" DMSO. [e] Estimated values, considering that a 2% of photoproduct is the lower limit detectable by our HPLC. [f] Data from ref 9.

nometer ($\Phi = 0.75$ at pH 7.4[15]), and the photolysis was limited to less than 10% conversion to minimize light absorption and reaction of photoproducts. The high values of these quantum yields (Table 1) confirm that decarboxylation of ketoprofen and derivatives is a very efficient photochemical reaction. The decay rate constants can be essentially regarded as protonation rate constants, since this is the dominant carbanion decay process.

When 4 mM **1–4** in 0.1 M KOH aqueous solutions were irradiated, we quantitatively obtained the corresponding protonated photoproducts **10–13** (see Chart 2), with the exception of compounds **3c** and **4c**, which also gave the cyclic photoproducts **16** (7%) and **17** (3%), respectively, formed by intramolecular nucleophilic attack (intra-S_N2).[9] Taking into consideration the overall rate constant for carbanion decay, the rate constants for cyclization for **3c** and **4c** were estimated as 4.7×10^5 and 7.7×10^4 s^{-1}, respectively (vide infra).

Kinetics studies of compounds **1–4** in DMSO solutions, containing an excess (8:1 equiv) of sodium hydride (NaH), were measured following 355 nm excitation using a front-face geometry, since the signal associated with the carbanion, generated in an aprotic medium, was better resolved under these exposure conditions. Considering both the structural similarity and reactivity of carboxylic acids **1–4** (shown above), we used compound **2a** as a model. Laser excitation of a solution of **2a** in DMSO gave a transient absorption spectrum with bands around 390 nm and at approximately 800 nm (weak), similar to those observed in this solvent following laser flash photolysis of ketoprofen and **3c**[9] (see Figure 2). There is literature precedent for solvent-induced shifts in the carbanion spectra.[9]

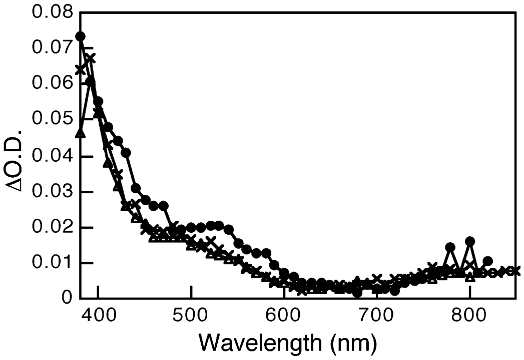

FIGURE 2. Transient absorption spectra following 355 laser excitation of Ar-saturated 10 mM solutions in NaH/DMSO of **2a** (●), **3c** (×), and ketoprofen (△), recorded at 200, 72, and 72 ns after the laser pulse.

The decay for carbanions photogenerated from 10 mM **1–4** solutions in NaH/DMSO, recorded at 390 nm, followed first-order kinetics (see Table 2). They were recorded at this wavelength since the intensity of the signal at 800 nm was very weak. A few control experiments showed that the 390 and 800 nm signals followed the same kinetics.

Product studies were carried out under extremely dry conditions (water < 0.03%[9]). The short lifetimes associated with transient carbanions, generated from photo-

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decarboxylation of compounds **1**−**4**, usually include a contribution from reaction with traces of water, in addition to the expected cyclization. Photolysis of 4 mM **1**−**4** in DMSO to high conversion (10%), in the presence of an excess of NaH, gave mixtures of cyclic and protonated photoproducts (see Table 2). It is likely that the excess NaH also behaves as a sacrificial drying agent helping reduce the concentration of traces of water. Considering that cyclization and protonation are the only two decay pathways available to the photogenerated carbanion, the cyclized and protonated absolute rate constants, k_C and k_W, respectively, were calculated considering cyclized and protonated carbanion fractions (f_C and f_W) determined by HPLC and the observed rate constant (k_{obs}), as defined eqs 1 and 2:

$$k_{obs} = k_C + k_W \tag{1}$$

$$k_C = f_C k_{obs} \quad k_W = f_W k_{obs} \tag{2}$$

Values of k_W in Table 2 are given in parentheses, since this value is influenced by variations in the trace amounts of water contained in the “dry” solvent.

As illustrated in Table 2, formation of cyclic products **14**−**17** was enhanced in DMSO, confirming that S_N2-type reactions are favored in aprotic polar solvents, compared to protic solvents (see values for water in Table 1). In cases such as **1c**, **2b**, and **2c**, the cyclization took place so fast that the nanosecond laser system response was too slow to measure the kinetics for the corresponding carbanion reactions.

To evaluate the water effect on the photolysis of **1**−**4** in DMSO, we examined the quenching of the carbanions by water, expanding earlier work[9] where we also had determined the kinetic isotope solvent effect when we measured the quenching rate constant for compound **3c** by H_2O and D_2O.

Discussion

It is well-known that factors such as the nature of the nucleophile, solvent, and leaving group directly affect the rate of the bimolecular nucleophilic substitution (S_N2) reactions; yet, in the case of carbanions, little has been documented with absolute rate constants. The rapid and efficient decarboxylation of ketoprofen and related substituted benzophenones offers a simple photochemical route to benzyl carbanions in solution. While there has been some discussion in the literature as to whether the decarboxylation pathway is singlet- or triplet-mediated, there is no doubt that the carbanion is formed in the subnanosecond time scale and the observable species is the singlet ground-state carbanion. In addition to fast time-resolved experiments, recent studies show that it is possible to lengthen the carbanion lifetime to many minutes in tetrahydrofuran,[12] thus confirming that the species observed is the ground state.

Laser flash photolysis of substrates **1**−**4** takes advantage of the fast decarboxylation of the corresponding carboxylates under strong basic conditions; this provides a nearly-instantaneous source of carbanions suitable for detailed kinetic and mechanistic studies.

In earlier studies,[9] we showed that steric effects were important in carbanion protonation reactions, that the spectroscopy of the carbanions was largely unaffected by remote halogen substitution, and for precursors **3c** and **4c**, that cyclization could be favored over protonation by use of dry DMSO in the presence of NaH as a strong base. Our results in this paper greatly expand the reactions examined, in particular by examining the role of different leaving groups and by exploring the formation of five- and six-membered rings. The results are consistent with our earlier reports where the data overlap.

Photodecarboxylation in aqueous solutions gave predominantly the protonated product. As observed in earlier studies,[8,9] protonation rate constants were influenced by steric effects. Cyclization yields were very low, reflecting rapid carbanion protonation. The only cases where cyclization was detected in aqueous solution were compounds **3c** and **4c**, which yielded the corresponding cyclic products in a 7% (**16**) and 3% (**17**), respectively. In contrast, when photodecarboxylation was carried out in DMSO, the main process was cyclization through an intra-S_N2 reaction.

We have estimated the rate constants for cyclization in DMSO using eqs 1 and 2. In those cases where cyclization was too fast to prevent detection of the carbanion, a lower limit of $>5 \times 10^7$ s^{-1} was estimated for the rate constant. In the cases of compounds **3c** and **4c**, it was possible to determine and compare cyclization rate constants in both aqueous and DMSO solutions. For **3c**, the values were 4.7×10^5 and 4.9×10^6 s^{-1}, respectively, and for **4c** 7.7×10^4 and 1.9×10^6 s^{-1}, respectively. These values showed a reduction of the cyclization rate constant in hydrogen-bonding solvents. The effect was larger for **4c**, the more sterically encumbered carbanion. Thus, the decrease in the importance of cyclization in protic media is not just the result of the competition with the solvent (55 M water in our case) but also the result of a significant reduction in the value of the cyclization rate constant.

The ease with which carbanions were scavenged even by trace amounts of water provided an indication that water was a much better quencher in DMSO than in bulk water, as already determined in comparison of water-quenching rates in bulk water and in nonprotic media.[9]

Considering the cyclization as an intra-S_N2 reaction (i.e., while an intramolecular reaction, mechanistically equivalent to the S_N2 process), the nature of the leaving group is expected to have a significant effect on the rate constants. When the intra-S_N2 reaction involved chloride as the leaving group, protonation was systematically favored, despite our effort to obtain truly dry DMSO; in earlier work we estimated the water content of “dry” DMSO at around 0.03%, or approximately 16 mM, under our experimental conditions. Remarkably, the photoreaction of compounds **1a** and **2a** yielded the five-membered ring products **14** and **15** in a 13% and 43%, respectively. Not surprisingly, when bromide or iodide were the leaving groups, the cyclization reaction was favored with iodide giving highest cyclization yields. Thus, the reactivity order for the halide leaving groups was $I^- > Br^- > Cl^-$, with differences of approximately 1 order of magnitude between pairs (see Table 2).

Considering the data from Table 2, cyclization to form a five-membered ring (compounds **1** and **2**) was at least 1 order of magnitude faster than for six-membered rings (compounds **3** and **4**). Entropy and stereoelectronic effects probably favors five-membered ring closure. According to Ruzicka's hypothesis,[16] (a) the probability of end-to-end interaction in a bifunctional linear precursor, which diminishes as the chain grows longer, and (b) ring strain are two independent factors in determining the ease of cyclization. In terms of entropy, these processes involve negative $\Delta S^{\ddagger}$ contributions due to reduction of internal rotation freedom around the single bonds of the molecular backbone when the open-chain precursor converts to the ring-shaped transition state. In our case, there was an additional loss of one internal rotation in order to achieve the transition state for the six-membered ring, compared with a five-membered ring. Ring strain was not a key factor in our reaction system since cyclization of the five-membered ring, which should have a more strained ring, was favored over the six-membered ring.

In a previous paper,[9] we pointed out that the presence of a methyl group attached directly to the carbanion center hindered the cyclization reaction. Interestingly, in the case of a five-membered ring closure addition of a methyl group at the carbanion center led to a modest increase in the intra-S_N2 reaction rate constant (compare k_C of series **1** and **2**). Clearly, the enhanced nucleophilicity of the carbanion center is more important than steric contributions in some cases. In contrast, the presence of the methyl group in the formation of a six-membered ring caused the cyclization rate constant to decrease by approximately a factor of 2. We speculate that this may force the halide to leave from a near-axial orientation.

Conclusion

The kinetic and mechanistic studies presented here provide absolute kinetic parameters for intra-S_N2 and protonation reactions of benzyl carbanions. Many of the concepts that are normally taught in introductory organic chemistry can now be illustrated with absolute rate constants. Thus, intra-S_N2 reactions are favored in polar nonprotic solvents, and the effect is larger for the more hindered carbanion centers. Protonation by water is slightly dependent on the alkyl groups attached directly on the carbanion center. In addition, the water protonation rate constant is about 400 times faster in nonhydroxylic solvents, compared with bulk water. As expected, the reactivity for halide leaving groups follows the usual order of decreasing bond strengths, i.e., $I^- > Br^- > Cl^-$.

Photoinduced decarboxylation of suitable substituted carbanions provides a route for the formation of substituted cycloalkanes that proceeds in high yields in nonhydroxylic solvents and with good leaving groups such as bromide and iodide.

Experimental Section

General Methods. All reactions were conducted in an inert atmosphere (N_2 or Ar). Photoreactions were carried out in Pyrex glassware. Combined organic extracts were dried over anhydrous Na_2SO_4. Solvents were removed from the reaction mixture or combined organic extracts by using a rotary evaporator. Reactions were monitored by thin-layer chromatography (TLC) on precoated E. Merck silica gel 60 F_{254} plates. Column chromatography was carried out with silica gel for flash columns, 230−400 mesh. Melting points were measured on a MELT-TEMP II apparatus. ^{1}H NMR spectra were obtained in $CDCl_3$ at 300 MHz, with TMS as an internal standard, and ^{13}C NMR spectra were obtained at 75.5 MHz, unless otherwise noted. IR spectra were recorded as films on NaCl plate. Elemental analyses were performed by MHW laboratories (Phoenix, AZ).

Nanosecond Laser Flash Photolysis. Similar laser flash photolysis systems have been previously described.[17,18] The laser flash photolysis systems used a Lumonics EX-530 laser (Xe-HCl-Ne mixture, 308 nm, ca. 6 ns and <100 mJ/pulse), or the third harmonic of a Surelite Nd:YAG laser generating 355 nm pulses of 8 ns duration and 20 mJ/pulse output. The signals from the monochromator/photomultiplier system were initially captured by a Tektronix 2440 digitizer and transferred to a Power Macintosh computer that controlled the experiment with software developed in the LabVIEW 5.1 environment from National Instruments. All the transient spectra and kinetics were recorded by employing 7×7 mm^2 Suprasil quartz cells. Samples were usually deaerated by bubbling Ar (DMSO) or N_2O (KOH); the latter (N_2O) was used to eliminate possible interference from hydrated electrons that are otherwise long-lived in aqueous systems. Samples that contained NaH were first flushed for 15 min with argon just before DMSO was added. To have a good signal in laser experiments, the concentration of the samples was ca. 8 mM in DMSO (355 nm excitation) and 0.4 mM in aqueous solution (308 nm excitation). The quenching rate constants were obtained using static samples.

The stability of samples of substituted benzophenones in the presence of NaH has been discussed in a recent publication.[12] Briefly, while sample aging eventually leads to reduction, these samples are sufficiently stable for laser and product studies to be conducted.

Materials. Commercially available organic compounds (from Aldrich unless otherwise indicated) were used without further purification except for the solvents. Tetrahydrofuran (THF, Omnisolv) was freshly distilled from sodium, CH_2Cl_2 from calcium hydride, and DMSO from calcium hydride at reduced pressure and stored on 4 Å molecular sieves. Starting materials (3-benzoylphenyl)acetic acid (Karl Industries) and ketoprofen [2-(3-benzoylphenyl)propionic acid] (Sigma) were commercially available. Compounds **3c**, **4c**, **5a**, **5b**, **7c**, and **9c** were prepared according to reported methods.[9] Photoproducts **12c**, **13c**, **16**, and **17**,[1] as well as **14**,[8] were known. Details of synthesis and characterization are provided in the Supporting Information.

Product Studies. Steady-state photolysis studies were carried out in a Luzchem photoreactor, employing 7 LZC-UVB lamps (300 nm).[19] The Ar-deaerated 4mM NaH/DMSO and N_2-deaerated 4 mM 0.1 M KOH solutions of **1a**−**c**, **2a**−**c**, **3a**,**b**, and **4a**,**b** were irradiated for 15 min at ~300 nm. Argon or N_2 were used to eliminate oxygen; the choice of either one was based on availability in different laboratories. To identify the starting material, as well as the photoproducts produced, the eluent absorbances at 254 nm were compared before and after photolysis, given that both products and starting materials have the same molar absorptivity. The photolysis mixture was analyzed by a Varian HPLC system, equipped with a reversed-phase 4.6 × 250 mm analytical Zorbax SB-C18 column. The mobile phase was 15:85 water/methanol and the flow rate 0.5 mL/min. The detection used a Varian 9065 Polychrom diode array detector.

Quantum Yield Determination. The N_2-deaerated 4 mM 0.1 M KOH solutions of **1a**−**c**, **2a**−**c**, **3a**,**b**, and **4a**,**b** were irradiated at 300 nm for 1 min to ensure conversions lower than or equal to 10%. A 0.1 M KOH solution of ketoprofen

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[16] Galli, C.; Mandolini, L. *Eur. J. Org. Chem.* **2000**, 3117−3125.

[17] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

[18] Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

[19] For detailed lamp spectral information, see: http://www.luzchem.com/handbook/exp_standards.html.

was employed as a standard (the quantum yield of photodecarboxylation is 0.75 at pH 7.4).[15] To quantify the starting material, as well as the photoproducts, a calibration curve was made in the HPLC with different KP standard solutions, registering the signal at 254 nm.

Acknowledgment. J.C.S. thanks NSERC (Canada) and Ontario's Premier's Research Excellence Award program for generous financial support. G.C. thanks the Ontario Graduate Scholarship Program for a postgraduate scholarship.

Supporting Information Available: Details of synthetic methodology. ^{1}H and ^{13}C NMR spectra of **1a**–**c**, **2a**–**c**, **3a**,**b**, **4a**,**b**, **6a**–**c**, **7a**,**b**, **8a**–**c**, **9a**,**b**, **10a**–**c**, **11a**–**c**, **12a**,**b**, **13a**,**b**, **14**, and **15** and additional data for some known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049224G