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First Determination of Absolute Rate Constants for the Reaction of Aroyl-Substituted Benzyl Carbanions in Water and DMSO

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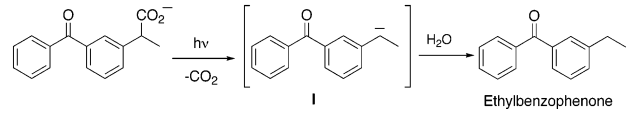
Abstract: The prompt generation of carbanions **II** and **III** within the duration of the nanosecond laser pulse provides a way of evaluating absolute rate constants for their two decay pathways, protonation and cyclization, the latter resulting from an intramolecular nucleophilic carbanion displacement of iodide tethered at the end of the lateral alkyl chain. Absolute rate constants are given for both carbanions (**II** and **III**) and show that the intra-S_N2 reaction is favored in aprotic media, such as dimethyl sulfoxide (DMSO), while protonation is the dominant reaction in basic aqueous media.

Introduction

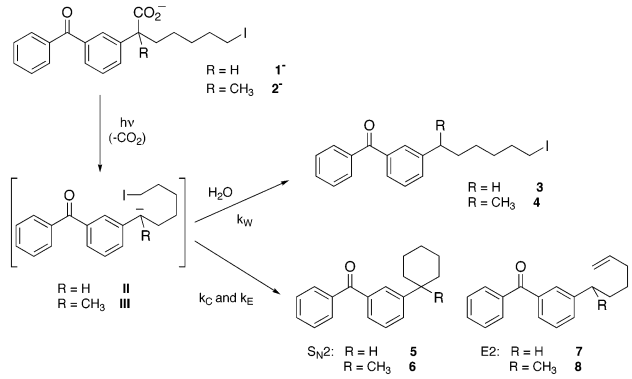
The relative reactivities of carbanions, deeply influenced by the solvent,[1,2] have been extensively studied.[3−7] However, only a few examples of the determination of absolute rate constants for their reactions,[3−6] mostly hydrolysis, have been reported. Competitive product studies are not necessarily under kinetic control and may be influenced by parameters other than the actual reaction of the carbanion, such as protonation−deprotonation, and other pathways contributing to reversibility in product generation. In this paper we report the first absolute rate constants for carbanions participating in nucleophilic reactions other than solvolysis.

Formation of reactive carbanions in solution using pulsed techniques make it possible to observe them directly on a short-time scale and to determine absolute rate constants for many of their elementary reactions. Dorfman et al.[3,4] determined rate constants for protonation reactions of the benzyl anion using pulse radiolysis. A decade ago, Craig et al.[5,6] characterized carbanions derived from the photodecarboxylation of *p*-nitrophenylacetate. Following flash photolysis, they studied the decay modes of the *p*-nitrobenzyl carbanion in aqueous media. More recently, photochemical studies of ketoprofen, a nonsteroidal antiinflammatory drug, have shown that it undergoes decarboxylation to form a carbanion in the subnanosecond time scale.[8−14] This species is responsible for the formation of 3-ethylbenzophenone, as illustrated in Scheme 1.

Scheme 1



Scheme 2



The rapid generation of carbanion **I** provides an interesting intermediate on which to perform mechanistic studies. The decay of this carbanion (**I**) in water is fast (τ = 215 ns), making it unlikely for reactions other than protonation to compete. Suitably substituted carbanions may however undergo intramolecular nucleophilic substitution reactions (see Scheme 2). With this in mind, we examined compounds **1** and **2**, which contain an

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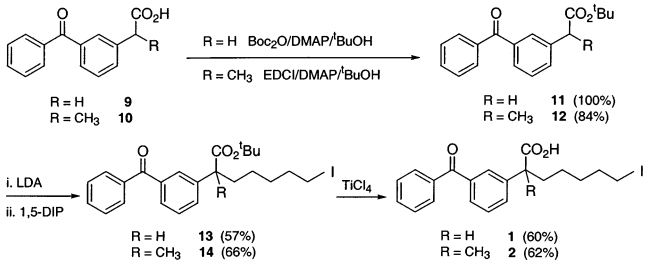
10.1021/ja027624k CCC: $22.00

Scheme 3



iodine atom at the end of an alkyl chain. Upon photoexcitation, and subsequent decarboxylation, they were expected to render their respective carbanions[14] (**II** and **III**) which could either react with water or undergo an intramolecular S_N2 reaction (see Scheme 2).

To gain insight into the reactivity of these carbanions, we carried out comparative studies of the photodecarboxylation of compounds **1** and **2** in a 0.1 M KOH aqueous solution and in dimethylsufoxide (DMSO), to which an excess of NaH was added to generate the corresponding carboxylate forms.

Results and Discussion

Carboxylic acids **1** and **2** were synthesized by α-alkylation of the corresponding *tert*-butyl esters **11** and **12**, followed by hydrolysis of the *tert*-butyl esters **13** and **14** with titanium tetrachloride[15] (see Scheme 3). Ester **12** was prepared by treatment of ketoprofen (**10**) with *tert*-butyl alcohol and 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDCI) in the presence of a catalytic amount of 4-(dimethylamino)-pyridine (DMAP). This methodology did not work for the esterification of acid **9**. Takeda et al.[16] reported novel esterification reagents of the active carbonate type. The reaction of dicarbonates and carboxylic acids in the presence of DMAP as a catalyst gave esters in good yield accompanied by the evolution of carbon dioxide. Indeed, ester **11** was obtained quantitatively by reaction of **9** and di-*tert*-butyl dicarbonate (Boc_2O) in the presence of a catalytic amount of DMAP. The introduction of the alkyl chain was achieved by reaction of enolates from esters **11** and **12**, generated by LDA at low temperature, with 1,5-diodopentane. Removal of the *tert*-butyl group from esters **13** and **14** was performed by titanium tetrachloride at low temperature, yielding acids **1** and **2** in good yields.

The transient absorption spectrum obtained following 355 nm laser excitation of an aqueous 0.1 M KOH solution of compound **1** was similar to that for ketoprofen,[12,14,17] with a broad maximum wavelength at ca. 590 nm (see Figure 1); similar spectra were recorded for **2** (not shown). The decay kinetics for **II**, recorded at 600 nm, appeared first order with a lifetime of 150 ns ($k_{obs} = 6.73 \times 10^6\ s^{-1}$).[18]

Laser excitation of a solution of **1** in DMSO, containing an excess of NaH, gave a transient absorption spectrum with bands around 390 nm and at approximately 800 nm; both bands showed the same kinetics and are assigned to carbanion **II** (see Figure 1).

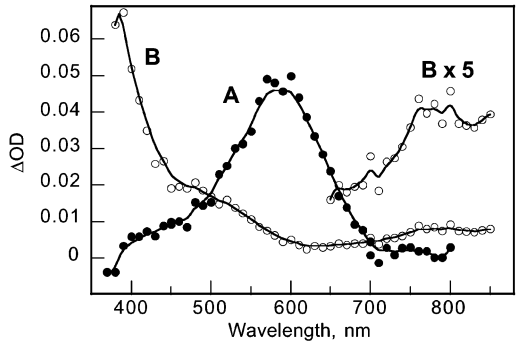


Figure 1. Transient absorption spectra following 355 nm laser excitation of (A) a N_2O-saturated 0.1 M KOH solution of **1** (10 mM) 64 ns after the laser pulse and (B) an Ar-saturated 10 mM solution of **1** in NaH/DMSO 72 ns after the pulse.

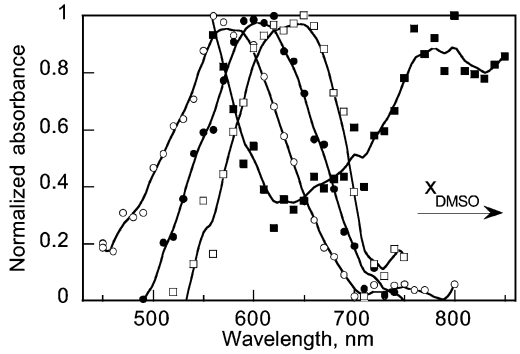


Figure 2. Normalized transient absorption spectra obtained following 355 nm laser excitation of N_2O-saturated 0.1 M KOH solutions of **1** (10 mM): (○) aqueous solution; (●) DMSO mole fraction 0.21; (□) 0.43, and (■) 10 mM **1** in NaH/DMSO solution**,** recorded 64, 32, 24, and 72 ns after laser pulse, respectively.

The red-shift of the carbanion **II** band from 590 nm in water (protic) to 800 nm in DMSO (aprotic) was expected (vide infra). Pronounced solvent effects on carbanion spectra are known.[8,12,19] To verify the shift of carbanion **II** band with solvent, we irradiated 10 mM **1** in basic aqueous solutions with different DMSO mole fractions. Figure 2 illustrates the progressive red-shift with increasing mole fraction of DMSO.

In pure DMSO, the decay was slower than that in aqueous 0.1 M KOH, with a lifetime of 180 ns.[20] The increased lifetime is mainly due to the reduction of carbanion protonation in the anhydrous conditions employed.

When a 0.1 M KOH solution of **2** was excited with a 308 nm laser, the decay of the resulting carbanion (**III**), recorded at 600 nm, was slower than that obtained for carbanion **II**, with a lifetime of 390 ns ($k_{obs} = 2.59 \times 10^6\ s^{-1}$). Thus, introduction of one additional methyl group in structure **1** increases the lifetime of the resulting tertiary carbanion (**III**) by a factor of 2.6, under conditions where protonation is the dominant pathway. We recently reported on these trends in rate constants,[14] which are highly dependent on carbanion substitution. From a series of ketoprofen-derived carbanions, we observed

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(18) This value was measured following 308 nm laser excitation since the signal associated to the carbanion, generated in a basic aqueous solution, is better defined.
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(20) The decay kinetics were recorded at 390 nm because the intensity of the signal at 800 nm was wery weak.

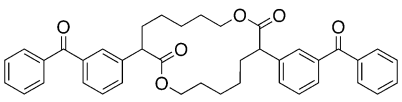
Table 1. Absolute Rate Constants for Protonation and Cyclization of Carbanions **II** and **III**

C⁻	solvent	f_C	f_W	k_{obs} (s^{-1})	k_C (s^{-1})	k_W (s^{-1})[a]
II	DMSO[b]	0.82	0.18	$5.97 \pm 0.06 \times 10^6$	4.9×10^6	(1.1×10^6)
	water[c]	0.07	0.93	$6.73 \pm 0.05 \times 10^6$	4.7×10^5	6.3×10^6
III	DMSO[b]	0.98	0.02	$1.97 \pm 0.02 \times 10^6$	1.9×10^6	(4.0×10^5)
	water	0.03	0.97	$2.59 \pm 0.01 \times 10^6$	7.7×10^4	2.5×10^6

[a] The values of k_W in DMSO are given in parentheses since some variation is anticipated due to day-to-day fluctuations in the water content of "dry" DMSO. [b] Dried with CaH_2, distilled under low pressure, and kept in sieves (base used NaH).

that their reactivities were controlled by the number and size of the alkyl groups attached to the carbanion center, an example of steric control of protonation.

Photolysis of 4 mM **1** and **2** in 0.1 M KOH aqueous solutions gave predominantly the protonated compounds **3** (93%) and **4** (97%), respectively (see Scheme 2). Quantum yields of decomposition were approximately 0.8 for both compounds. The cyclic compounds **5** (7%) and **6** (3%) were obtained in low yields. They are formed by intramolecular cyclization (intra-S_N2). Under these experimental conditions, the intra-E2 products (**7** and **8**) were not detected. To favor intramolecular S_N2 over protonation, we changed the solvent for DMSO, leading to a less solvent-encumbered anion. Further, DMSO cannot stabilize the carbanion by hydrogen bonding, leading to a more nucleophilic anion.[2] When we irradiated a 4 mM solution of **1** in DMSO, in the presence of NaH, to high conversion, the photoproducts contained 82% cyclization (**5**) and the remaining 18% was the protonated compound **3**. Also, we isolated dimer **15**, thermodynamic product of a (dark) nucleophilic substitution between two carboxylic molecules. In one case, with freshly dried DMSO, we were able to completely preclude formation of **3**; this suggests that formation of some **3** in DMSO is due to traces of water. This is further supported by the high reactivity of water in DMSO (vide infra). When a 4 mM solution of **2** in DMSO with an excess of NaH was irradiated, we obtained compound **6** in 98% yield. This shows that the tertiary carbanion center is still capable of an intramolecular S_N2 cyclization. No reactions were observed when basic aqueous or NaH/DMSO solutions were kept in the dark, except for the formation of **15** in solutions of **1** in NaH/DMSO.



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Considering that cyclization and protonation are the only two decay pathways available to carbanions **II** and **III**, the observed decay rate constants can be defined as:

$$k_{obs} = k_W + k_C$$

$$k_W = f_W \times k_{obs} \qquad k_C = f_C \times k_{obs}$$

where k_W is the pseudo-first-order protonation rate constant, k_C is the cyclization rate constant, and f_W and f_C are the fractions of carbanions undergoing protonation and cyclization, respectively. Table 1 gives the observed rate constants as well as the calculated absolute rate constants for protonation (k_W) and cyclization (k_C) of both carbanions (**II** and **III**), according to their respective fractions. To evaluate the water effect on the photolysis of **1** in DMSO, we examined the quenching of carbanion **II** by water. The rate constant for carbanion decay was plotted against the concentration of H_2O or D_2O. The slope of the plot yields a bimolecular rate constant [$k_q(H_2O)$] of 5.1×10^7 M^{-1} s^{-1}. We also determined the rate constant for quenching by D_2O, which led to $k_q(D_2O)$ of 1.1×10^7 M^{-1} s^{-1} (Figure 3). This leads to an isotope effect [$k_q(H_2O)/k_q(D_2O) \sim 5$]. These results show that water (H_2O or D_2O), acts as a proton source, favoring the formation of **3**.

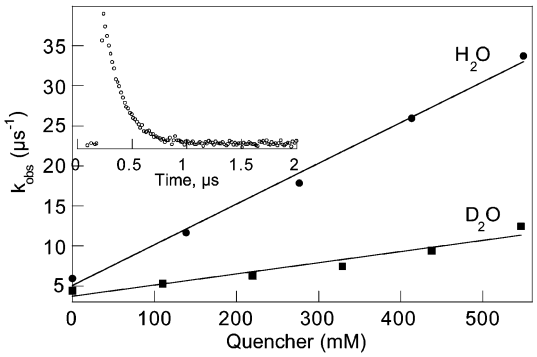

Figure 3. Plot of first-order rate constants for decay of carbanion **II** vs (●) H_2O and (■) D_2O concentrations in DMSO, under N_2 atmosphere. Inset: transient carbanion decay at $[H_2O] = 0$ ($\tau = 180$ ns).

We also examined the quenching of carbanion **III** by water. The slope of the plot (not shown) yields a bimolecular rate constant [$k_q(H_2O)$] of 8.8×10^6 M^{-1} s^{-1}. This low value, in comparison to the one obtained from quenching of carbanion **II**, corroborates again that the steric effect, due to an additional methyl group directly attached to the carbanion center, decreases the reactivity of the carbanion by a factor of 5.8 in DMSO. For comparison, the values of k_W in pure water for both carbanions (**II** and **III**, see Table 1) yield a ratio of 2.5; i.e., hydrogen bonding among water molecules seems to decrease its selectivity.

Extrapolation of the water quenching plot to 55 M water predicts a value for k_{obs} of 2.8×10^9 s^{-1} ($\tau \cong 0.4$ ns). Water is therefore ca. 400-fold more reactive in DMSO than in aqueous media. This, together with the values of k_C in the two solvents, places the well-known fact that S_N2 reactions are faster in polar aprotic than in protic solvents on an absolute rate scale.

The fact that in one case we were able to achieve quantitative cyclization of **1** in DMSO suggests that in the majority of cases, when some protonation was observed, the formation of products **3** and **4** in DMSO is due to traces of water. The slope from Figure 3 and the k_W value in DMSO (e.g., see value in parentheses in the top line of Table 1) allows an estimation of the water content of "dry" DMSO. Thus, the value of 1.0×10^6 s^{-1} suggests a ~0.03% water content.

In conclusion, our studies of **1** and **2** render the first absolute rate constants for reactions of carbanions **II** and **III** in solution. The results provide insights into some established patterns of nucleophilic behavior of carbanions, such as steric and solvent effects. Further, it is clear that photodecarboxylations of carboxylates attached to a suitable chromophore provide a useful probe in this type of studies. Carbanions produced in this manner are formed essentially instantaneously in an irreversible process, thus making their transient decays, and the consequent formation

of products, a kinetically controlled reaction, ideal for mechanistic studies.

Experimental Section

Compound 2-(3-benzoylphenyl)acetic acid was purchased from Karl Industries Inc. (Aurora, OH). All the other starting materials used in this work were purchased from Sigma-Aldrich Canada (Oakville, ON) and used without further purification. Solvents were dried up by the usual methods. DMSO was distilled from CaH_2 and stored over molecular sieves. Column chromatography was carried out with Merck silica gel for flash columns, 230−400 mesh. Analytical thin-layer chromatography (TLC) was performed on E. Merck precoated silica gel 60 F_{254}. All NMR spectra were recorded at 25°C at 300 MHz (^1H and ^{13}C) and chemical shifts are reported relative to internal TMS. All reactions were conducted under an inert atmosphere (N_2 or Ar).

Photoproducts. We prepared 4 mM solutions of acids **1** and **2** in DMSO and an excess of approximately 8 equiv of 95% NaH. After radiation, the mixtures were quenched with water and extracted with diethyl ether. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo.

Product Studies. Steady-state photolysis studies were carried out in a prototype of a Luzchem photoreactor equipped with seven UV lamps. The 4 mM NaH/DMSO solutions of **1** and **2** were deaerated under an Ar atmosphere and irradiated for 20 min at 300 nm. The photolysis mixture was analyzed by HPLC (Varian instrument using a reverse phase 4.6 × 250 mm analytical Zorbax SB-C18 column; the mobile phase used was 15:85 water:methanol, and the flow rate employed was 0.5 mL/min. The detection used a Varian 9065 Polychrom diode array detector). For quantum yield determinations of **1** and **2**, deaerated 4 mM 0.1 M aqueous KOH solutions of **1** and **2** were analyzed in the same conditions for 15 min of radiation. Ketoprofen in 0.1 M KOH was employed as a standard (the quantum yield of photodecarboxylation is 0.75 at pH 7.4).[8] 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.

Nanosecond Laser Flash Photolysis. The laser flash photolysis system has been previously described.[21,22] To obtain kinetics of 0.1 M KOH solutions of **1** and **2**, the samples were excited with a Lumonics EX-530 laser with a Xe−HCl−Ne mixture generating pulses at 308 nm of approximately 6 ns and 100 mJ output at the source. Kinetics from 10 mM NaH/DMSO solutions of **1** and **2**, as well as all the spectra (aqueous and organic samples), were obtained by exciting with the third harmonic of a Surelite Nd:YAG laser generating pulses at 355 nm of 8 ns duration and 20 mJ output. The signals from the monochromator/photomultiplier system were initially captured by a Tektronix 2440 digitizer and transferred to a PowerMacintosh computer that controlled the experiment with a software developed in the LabVIEW 5.1 environment form National Instruments. All the transient spectra and kinetics were recorded by employing 7 × 7 mm^2 Suprasil quartz flow cells. Samples were deaerated by Ar (DMSO) or N_2O (KOH). Use of N_2O eliminates any possible interference from hydrated electrons that are otherwise long-lived in aqueous systems. The quenching rate constants were obtained with static samples.

***tert*-Butyl 2-(3-Benzoylphenyl)acetate (11).**[16] To a solution of di-*tert*-butyl dicarbonate (Boc_2O, 1 g, 4.40 mmol) and 2-(3-benzoylphenyl)acetic acid (**9**, 0.5 g, 2.08 mmol) in t-BuOH (21 mL) was added 4-(dimethylamino)pyridine (DMAP, 76 mg, 0.62 mmol) at room temperature. After 50 min, the solvent was removed in vacuo to give **11** (0.69 g, 99%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.37−7.78 (9H, Ph), 3,56 (s, 2H, CH_2), 1.41 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8 (CO), 170.7 (COO), 138.1 (C quaternary), 138.0 (C quaternary), 135.4 (C quaternary), 128.6−133.7 (Ph), 81.5 (C quaternary), 42.7 (CH_2), 28.4 (CH_3); MS *m*/*z* 296 (M^+, 0.4), 196 ($M^+ - C_5H_9O_2$, 65).

***tert*-Butyl 2-(3-Benzoylphenyl)propionate (12).**[23] A solution of compound **10** (5 g, 20 mmol), DMAP (1.2 g, 9.8 mmol), and t-BuOH (2 mL, 22 mmol) in 80 mL of methylene chloride was cooled with stirring in an ice bath. 1-Ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDCI, 4.2 g. 22 mmol) was added, and the reaction mixture was stirred at 0°C for 2 h and at room temperature overnight. The solution was concentrated to dryness in vacuo, and the residue was taken up in acetyl acetate and water. The organic layer was evaporated, washed with saturated sodium bicarbonate and water, and dried (Na_2SO_4). The solvent was removed in vacuo to yield **12** (5.1 g, 84%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.41−7.80 (9H, Ph), 3.66 (q, J = 7.2 Hz, 1H, CH), 1.45 (d, J = 7.2 Hz, 3H, CH_3), 1.38 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9 (CO), 173.6 (COO), 141.8 (C quaternary), 138.1 (C quaternary), 137.9 (C quaternary), 128.6−132.8 (Ph), 81.1 (C quaternary), 46.7 (CH), 28.4 (CH_3); MS *m*/*z* 210 ($M^+ - C_5H_9O_2$, 25).

***tert*-Butyl 2-(3-Benzoylphenyl)-7-iodoheptanoate (13).** A solution of **11** (500 mg, 1.69 mmol) in anhydrous THF (17 mL) was cooled in a dry ice−acetone bath (−78 °C). To this solution were added LDA (0.93 mL, 1.86 mmol) and 1,5-diodopentane (0.78 mL, 5.08 mmol). After 10 min, the dry ice−acetone bath was removed and the mixture was stirred, warming up to room temperature under an atmosphere of nitrogen for one and a half hour. The reaction mixture was then quenched with water and extracted with ethyl acetate (2 × 25 mL). The organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give a residue, which was purified by flash chromatography column (Si_2O, 95:5 hexane/AcOEt) to furnish **13** (470 mg, 57%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.37−7.77 (9H, Ph), 3.47 (t, J = 7.8 Hz, 1H, CH), 3.11 (t, J = 6.9 Hz, 2H, CH_2I), 2.00 (m, 2H, CH_2), 1.75 (m, 4H, CH_2CH_2), 1.37 (s, 9H, CH_3), 1.27 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9 (CO), 173.1 (COO), 140.3 (C quaternary), 138.1 (C quaternary), 137.9 (C quaternary), 128.7−132.7 (Ph), 81.3 (C quaternary), 52.8 (CH), 33.7 (CH_2), 30.5 (CH_2), 28.3 (CH_3), 26.8 (CH_2), 7.3 (CH_2I); MS *m*/*z* 392 ($M^+ - C_5H_9O_2$, 54).

***tert*-Butyl 2-(3-Benzoylphenyl)-7-iodo-2-methylheptanoate (14).** We followed the same procedure as that for **13**. The ester **12** (1 g, 3.2 mmol) gave compound **14** in a 66% (1.1 g). ^1H NMR (300 MHz, $CDCl_3$) δ 7.37−7.7 (9H, Ph), 3.11 (t, J = 7 Hz, 2H, CH_2I), 1.97 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.48 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.23 (m, 4H, CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1 (CO), 175.1 (COO), 145.3 (C quaternary), 138.0 (C quaternary), 137.9 (C quaternary), 127.9−132.8 (Ph), 82.2 (C quaternary), 51.2 (C quaternary), 39.3 (CH_2), 33.6 (CH_2), 31.3 (CH_2), 28.2 (CH_3), 24.1 (CH_2), 23.3 (CH_3), 7.2 (CH_2I); MS *m*/*z* 406 ($M^+ - C_5H_9O_2$, 43).

2-(3-Benzoylphenyl)-7-iodoheptanoic Acid (1).[15] A stirred solution of ester **13** (470 mg, 1 mmol) in dichloromethane (24 mL) under a nitrogen atmosphere was cooled to −10 °C. Titanium tetrachloride (3.8 mL, 3.8 mmol) was slowly added, and the temperature was brought to 0 °C. After 3 h of stirring, a chilled 2 M solution of HCl (20 mL) was added. The organic phase was separated, washed with 2 M HCl (3 × 25 mL) brine (2 × 25 mL), and concentrated under reduced pressure to yield compound **1** (247 mg, 60%) as yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (s, 1H, Ph), 7.75 (d, J = 1.4 Hz, 2H, Ph), 7.66 (m, 1H, Ph), 7.55 (m, 2H, Ph) 7.45 (t, J = 7.4 Hz, 3H, Ph), 3.61 (t, J = 7.6 Hz, 1H, CH), 3.11 (t, J = 6.9 Hz, 2H, CH_2I), 2.09 (m, 1H, CH_2), 1.76 (m, 3H, CH_2), 1.31 (m, 4H, CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8 (CO), 179.9 (COOH), 139.0 (C quaternary), 138.3 (C quaternary), 137.7 (C quaternary), 128.7−132.7 (Ph), 51.2 (CH), 33.0 (*C*HCH$_2$), 32.8 (*C*H$_2$-CH$_2$I), 30.1 (CH_2), 26.4 (CH_2), 7.2 (CH_2I); MS *m*/*z* 263 (M^+ − I, 9).

2-(3-Benzoylphenyl)-7-iodo-2-methylheptanoic Acid (2). We followed the same procedure as that for **1**. The ester **14** (1 g, 3.2 mmol)

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gave compound **2** in a 66% (1.1 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.83 (s, 9H, Ph), 3.11 (t, J = 6.9 Hz, 2H, CH_2I), 1.99 (m, 2H, CH_2), 1.77 (q, J = 7.5 Hz, 2H, CH_2), 1.59 (s, 3H, CH_3), 1.38 (m, 2H, CH_2), 1.23 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0 (CO), 182.4 (COOH), 143.5 (C quaternary), 138.0 (C quaternary), 137.8 (C quaternary), 128.2−132.9 (Ph), 50.4 (CH), 39.1 (CH_2), 33.5 (CH_2), 31.2 (CH_2), 24.0 (CH_2), 7.3 (CH_2I); MS *m*/*z* 450 (M^+, 1.7), 406 ($M^+ - CO_2H$, 10), 373 ($M^+ - I$, 1); HRMS *m*/*z* calcd for $C_{21}H_{23}O_3I$ 450.0692, found 450.0679.

3-(6-Iodohexyl)phenyl Phenyl Ketone (3). This compound was formed following photodecarboxylation of **1** in a 0.1 M KOH solution. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.80 (m, 9H, Ph), 3.15 (t, J = 7 Hz, 2H, CH_2I), 2.65 (t, J = 7.7 Hz, 2H, CH_2Ph), 1.80 (quin, J = 7 Hz, 2H, CH_2CH_2I), 1.63 (quin, J = 7.7 Hz, 2H, CH_2CH_2Ph), 1.38 (m, 4H, CH_2CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4 (CO), 143.2 (C quaternary), 138.1 (C quaternary), 138.0 (C quaternary), 128.1−133.0 (Ph), 36.0 (α-CH_2), 33.7 (β-CH_2), 31.5 (CH_2CH_2I), 30.7 (γ-CH_2), 7.5 (CH_2I); MS *m*/*z* 392 (M^+, 7); HRMS *m*/*z* calcd for $C_{19}H_{21}OI$ 392.0637, found 392.0637.

3-(6-Iodo-1-methylhexyl)phenyl Phenyl Ketone (4). This compound was formed following photodecarboxylation of **2** in a 0.1 M KOH solution. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.80 (m, 9H, Ph), 3.12 (t, J = 7 Hz, 2H, CH_2I), 2.74 (q, J = 7 Hz, 1H, CH), 1.75 (quin, J = 7 Hz, 2H, CH_2), 1.58 (q, J = 7.3 Hz, 2H, CH_2), 1.2−1.3 (m, 4H, CH_2CH_2), 1.24 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4 (CO), 148.2 (C quaternary), 138.1 (C quaternary), 138.0 (C quaternary), 128.4−132.7 (Ph), 40.2 (CH), 38.4 (CH_2), 33.7 (CH_2), 30.9 (CH_2), 27.0 (CH_2), 22.6 (CH_3), 7.6 (CH_2I); MS *m*/*z* 406 (M^+, 9); HRMS *m*/*z* calcd for $C_{20}H_{23}OI$ 406.0794, found 406.0765.

3-Cyclohexylphenyl Phenyl Ketone (5). This compound was formed following photodecarboxylation of **1** in NaH/DMSO solutions. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (m, 2H, Ph), 7.65 (m, 1H, Ph), 7.56 (m, 2H, Ph), 7.47 (m, 2H, Ph), 7.42 (m, 1H, Ph), 7.37 (m, 1H, Ph), 2.55 (tt, J = 11.6 and 3.3 Hz, 1H, CH), 1.85 (m, 4H, CH_2), 1.73 (bd, J = 13 Hz, 1H, CH_2), 1.40 (m, 5H, CH_2); ^{13}C NMR (225 MHz, $CDCl_3$) δ 196.0 (CO), 148.3 (C quaternary), 137.9 (C quaternary), 137.6 (C quaternary), 127.8−132.2 (Ph), 44.5 (CH), 34.3 (α-CH_2), 26.8 (β-CH_2), 26.0 (γ-CH_2); MS *m*/*z* 264 (M^+, 65); HRMS *m*/*z* calcd for $C_{19}H_{20}O$ 264.1514, found 264.1515.

3-(1-Methylcyclohexyl)phenyl Phenyl Ketone(6). This compound was formed following photodecarboxylation of **2** in NaH/DMSO solutions. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.83 (m, 9H, Ph), 1.99 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 1.19 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6 (CO), 150.7 (C quaternary), 138.2 (C quaternary), 137.8 (C quaternary), 127.8−132.7 (Ph), 38.5 (C quaternary), 38.2 (α-CH_2), 30.1 (γ-CH_2), 26.7 (CH_3), 23.0 (β-CH_2); MS *m*/*z* 278 (M^+, 52); HRMS *m*/*z* calcd for $C_{20}H_{22}O$ 278.1671, found 278.1605.

3,11-Bis-(3-benzoylphenyl)-1,9-dioxa-cyclohexadecane-2,10-dione (15). Thermodynamic byproduct isolated only from a dark reaction of **1** in NaH/DMSO solutions. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.79 (m, 9H, Ph), 4.10 (m, 2H, CH_2O); 3.70 (dt, J = 12 and 3.5 Hz, 1H, CH), 2.26 (m, 1H, $CHCH_2$), 1.23−1.44 (m, 7H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9 (CO), 173.8−173.9 (COO), 140.4−140.5 (C quaternary), 138.2 (C quaternary), 133.8 (C quaternary), 128.7−132.9 (Ph), 64.5−65.0 (CH_2O), 51.4−52.0 (CH), 34.8−35.0 ($CHCH_2$), 28.6−29.2 (OCH_2CH_2), 27.5−27.9 (CH_2), 26.0−26.2 (CH_2); MS *m*/*z* 616 (M^+, 22), 308 ($M^+ - C_{20}H_{20}O_3$, 6); HRMS *m*/*z* calcd for monomer $C_{20}H_{20}O_3$ 308.1412, found 308.1412.

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