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Rate constants for ring openings of 2-phenylcyclobutylcarbinyl radicals

Calvin J. Emanuel, John H. Horner and Martin Newcomb*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

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epoc ABSTRACT: Kinetics of ring openings of 2-phenyl-substituted cyclobutylcarbinyl radicals were studied by laser flash photolysis methods employing *N*-hydroxypyridine-2-thione (PTOC) esters as radical precursors. The radicals studied were (*trans*-2-phenylcyclobutyl)methyl (**1a**), 1-(*trans*-2-phenylcyclobutyl)ethyl (**1b**), 1-methyl-1-(*trans*-2-phenylcyclobutyl)ethyl (**1c**), (*cis*-2-phenylcyclobutyl)methyl (**2a**), 1-(*cis*-2-phenylcyclobutyl)ethyl (**2b**) and (ethoxycarbonyl),(*trans*-2-phenylcyclobutyl)methyl (**13**). Arrhenius parameters for radicals **1** were determined in THF and acetonitrile and those for radicals **2** were determined in THF. Rate constants for ring openings at 20 °C in units of 10^7 s^{-1} are 1.3 (**1a**), 1.0 (**1b**), 0.8 (**1c**), 3.2 (**2a**) and 3.9 (**2b**). These ring openings are more than three orders of magnitude faster than those for the parent cyclobutylcarbinyl radicals lacking the phenyl groups. The family can be used in direct studies of radical substituent effects and as internal reporter groups for other radical reactions. A demonstration of the former application is the measurement of the kinetics of ring openings of radical **13** which rearranges with rate constants nearly equal to those of the analogous methyl-substituted radical **1b** and, unlike radicals **1** displays a polar solvent effect in the kinetics of the fragmentation reaction. Copyright © 2000 John Wiley & Sons, Ltd.
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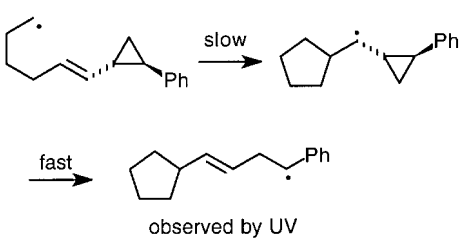
KEYWORDS: radical; kinetics; ring opening; laser flash photolysis; cyclobutylcarbinyl

INTRODUCTION

Determinations of rate constants for radical reactions are often accomplished by indirect competition kinetic methods,[1] but many absolute radical kinetic values ultimately rely on the results of direct measurements of rate constants obtained by laser flash photolysis (LFP) methods employing UV–visible detection. When the reactant and product radicals do not contain useful UV–visible chromophores, LFP studies can be conducted by a 'probe' technique wherein a reaction that produces 'color' (the probe reaction) and the reaction of interest occur simultaneously. Formation of the detectable product from the probe reaction is followed, but the observed rate constant is equal to the sum of the rate constants for the two reactions. Reactions that give benzylic or diphenylalkyl radical products are especially useful for both direct and probe LFP studies because these radicals absorb in the 315 and 330 nm regions, respectively.[2] Intramolecular probe reactions require syntheses, but they are powerful because the first-order probe reaction is independent of concentration.

A limitation of intramolecular probe reactions that directly produce aryl-substituted radicals is that the stabilities of the final product radicals result in kinetic accelerations in these reactions of 2–3 orders of magnitude in comparison with the reactions of the parent radicals lacking the phenyl groups. Accordingly, the reactions can become too fast to be useful for probe applications. In order to attenuate this kinetic effect and maintain the desired chromophore in the product radicals, our group developed a 'reporter group' method[3–5] that employs the ultrafast ring openings of 2-aryl-substituted cyclopropylcarbinyl radicals as exemplified in Scheme 1. In this design, the kinetic accelerating effect of aryl group substitution is avoided by initial production of an alkyl



Scheme 1

**Correspondence to:* M. Newcomb, Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA.
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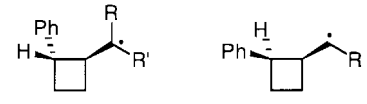
radical instead of a benzylic or diphenylalkyl radical.

An alternative for intramolecular probe design employs an inherently slow radical reaction that is accelerated by formation of aryl-substituted radical products to a rate appropriate for nanosecond-resolution LFP studies. The cyclobutylcarbinyl radical ring opening is such a 'slow' reaction with $k = 5 \times 10^3$ s^{-1} at 25 °C.[6,7] In a previous paper,[8] we reported rate constants for ring opening reactions of the *trans*-2-phenylcyclobutylcarbinyl radicals **1** in THF. Here we report detailed kinetics for ring openings of radicals **1** in THF and acetonitrile and for ring openings of the *cis* isomers (**2**) in THF and details of the syntheses of the radical precursors. Radicals **1** and **2** can be used both in direct LFP studies and in LFP reporter group studies of radicals that react with rate constants of $<1 \times 10^7$ s^{-1} at ambient temperature.



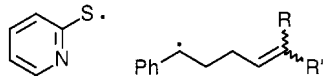
1a: R = R' = H
1b: R = Me, R' = H
1c: R = R' = Me

2a: R = H
2b: R = Me

RESULTS AND DISCUSSION

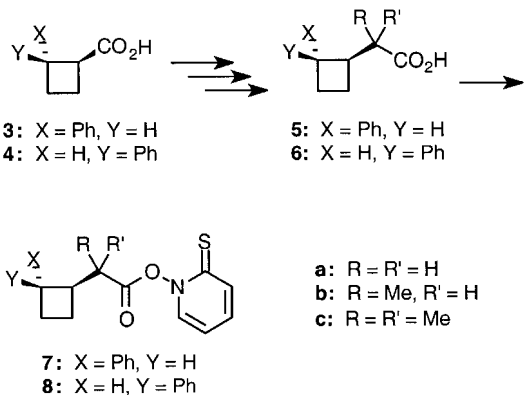
Radicals **1** and **2** were produced in LFP studies by photolyses of the appropriate *N*-hydroxypyridine-2-thione (PTOC)[9] ester precursors. The synthetic sequence for the precursors is shown in Scheme 2. Homologation of the known phenyl-substituted cyclobutanecarboxylic acids **3** and **4** gave the corresponding cyclobutylacetic acids **5a** and **6a**, respectively. Methylation via the ester enolates and saponification gave acids **5b**, **5c** and **6b**. One noteworthy point in the preparation of *trans*-2-phenylcyclobutanecarboxylic acid (**3**) is a base-catalyzed isomerization of the *tert*-butyl ester that proved to be a convenient entry to highly diastereomerically enriched material from a mixture of **3** and **4**. Acid **3** is difficult to separate from the mixture of **3** and **4** produced in the cyclization reaction that gives the cyclobutane ring; acid **4** can be isolated more easily because it will crystallize from a solution containing **3** and **4**. The PTOC esters **7a–c** and **8a** and **b** were prepared by reactions of the corresponding acid chlorides with *N*-hydroxypyridine-2-thione sodium salt.[9]

Photolysis of PTOC esters **7** and **8** with 355 nm light gave acyloxyl radicals that rapidly decarboxylated to give radicals **1** and **2**, respectively, and the by-product pyridine-2-thiyl radical (**9**). Radical **9** has a broad, long-wavelength absorbance with λ_{max} at 490 nm,[10] and it apparently decays mainly by radical–radical coupling because we have observed that its rate of decay is insensitive to oxygen concentration. Ring openings of radicals **1** and **2** gave benzylic radical products **10** with λ_{max} at ca 320 nm.[2]



9 **10**

The kinetics of ring openings of radicals **1** in THF and acetonitrile and of radicals **2** in THF were measured in the range 0–50 °C; the upper temperature limit results from the thermal instability of the PTOC esters. Detailed kinetic results are provided in the Supporting Information, and the results in THF are shown graphically in Fig. 1. The Arrhenius functions obtained from the kinetic data are collected in Table 1. The rate constants for ring openings of radicals **1** and **2** are at the upper limit of the nanosecond-resolution unit, slightly below the point at which instrument response convolution will affect the observed rates. With such fast reactions, radical–radical couplings and reactions of radicals with residual oxygen are too slow ($k < 10^4$ s^{-1}) to contribute to the observed rate constants. The major source of error in the measurements appears to involve temperature control as



3: X = Ph, Y = H
4: X = H, Y = Ph

5: X = Ph, Y = H
6: X = H, Y = Ph

a: R = R' = H
b: R = Me, R' = H
c: R = R' = Me

7: X = Ph, Y = H
8: X = H, Y = Ph

Scheme 2

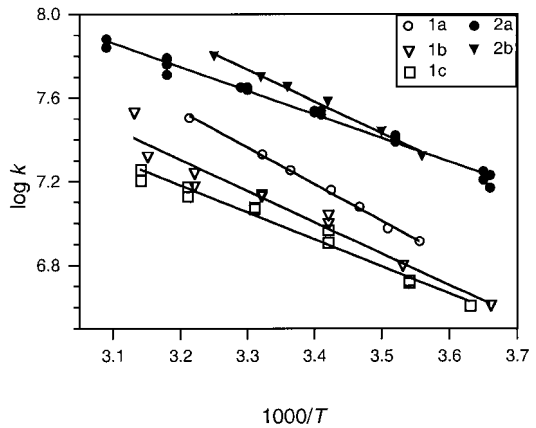


Figure 1. Rate constants for ring opening reactions of radicals **1** and **2** in THF. The lines are the Arrhenius functions listed in Table 1

Table 1. Arrhenius parameters for ring openings of radicals **1** and **2**

Radical	Solvent	Log A[a]	E_a (kcal mol^{-1})[a]	k_{20} (s^{-1})[b]
1a	THF[c]	13.1 ± 0.3	8.0 ± 0.4	1.3×10^7
	CH_3CN	13.7 ± 0.4	8.8 ± 0.6	1.3×10^7
1b	THF[c]	12.1 ± 0.6	6.8 ± 0.9	$1.0_5 \times 10^7$
	CH_3CN	12.6 ± 0.7	7.5 ± 0.9	1.0×10^7
1c	THF[c,d]	11.3 ± 0.4	5.9 ± 0.6	0.8×10^7
	CH_3CN	11.9 ± 0.5	6.6 ± 0.7	0.9×10^7
2a	THF	11.40 ± 0.19	5.21 ± 0.26	3.2×10^7
2b	THF	12.6 ± 0.4	6.7 ± 0.5	3.9×10^7

[a] Errors are at 2σ.
[b] Calculated rate constant at 20 °C.
[c] Previously reported in Ref. 8.
[d] The Arrhenius function for reaction of radical **1c** in THF given in Ref. 8 is actually the function for reaction in CH_3CN.

indicated in some of the plots in Fig. 1 because the random error in a measured rate constant was small. The temperature of the circulating bath was controlled to within ±0.2 °C, but the kinetic studies were conducted with flowing solutions that were temperature-regulated in a storage funnel. We believe that changes in the flow-rates resulted in varying changes from the nominal temperatures. Accordingly, the kinetic measurements in the vicinity of ambient temperature should be more accurate.

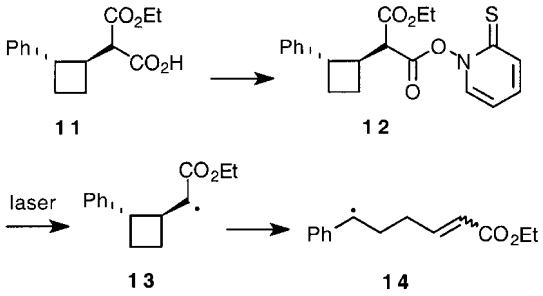
The rate constants for ring openings of radicals **1** were the same in THF and in CH_3CN showing a lack of sensitivity towards solvent polarity (Table 1). A more dramatic demonstration of the absence of solvent effects on the kinetics was found in the rate constants for reaction of radical **1b** obtained in several solvents. Specifically, the observed rate constants at 16 °C in cyclohexane, THF, acetonitrile and ethanol were in the range $(7.3 \pm 0.3) \times 10^6$ s^{-1}. The absence of a kinetic effect due to changes in solvent polarity is consistent with the expectation that the transition states will not be polarized for radical reactions in which both the reactant and product do not contain polar stabilizing substituents.[11]

For each radical **1**, the Arrhenius parameters in the two solvents overlap at the 90% confidence interval, and the apparent increases in log A and E_a in CH_3CN compared with THF are most likely artifactual. The differences in the log A and E_a terms for the series of radicals **1** clearly are outside of experimental uncertainty. The unusual feature in this series is that the decrease in rate constants for ring opening with increasing alkyl substitution at the radical center is not due to radical stabilities. Indeed, the activation energies for ring openings of **1** *decrease* with increasing radical substitution, but reduced log A terms with increasing substitution more than offset the effects in the activation energies. Thus, the reduced rate constants with increasing substitution are due largely to entropic effects instead of enthalpy effects. A similar trend was previously seen in ring openings of a series of cyclopropylcarbinyl radicals where rate constants were determined by LFP methods with high precision.[5] In that work, computational studies of the transition states for ring openings indicated that the secondary radical (analog of **1b**) should have a smaller log A term than the primary radical (analog of **1a**) due to the loss of one low-energy reaction channel for the secondary system. Further, the orientation of methyl groups with respect to the cycloalkane in the ground state for the tertiary radical (analog of **1c**) differed from those in the less substituted radicals. It is likely that similar subtle effects are at play in the case of radicals **1**.

We have no simple rationalization for the difference in rate constants between radicals **2a** and **2b**. The *cis* substitution of the phenyl group with respect to the carbinyl radical center almost certainly is important, and it seems likely that steric compression for the secondary system is greater than that for the primary system resulting in a faster ring opening for **2b**. The small log A term for radical **2a** indicates a higher degree of organization than has been observed in cyclopropylcarbinyl radical ring openings.

In comparison with the parent radical, cyclobutylcarbinyl, the phenyl substitution in radical **1a** results in an acceleration in the ring opening reaction at ambient temperature by a factor of 2600. This is almost exactly the same amount of acceleration observed by *trans*-2-phenyl substitution in the cyclopropylcarbinyl radical (a factor of 2400).[12,13] For the *cis*-substituted radical **2a**, the accelerations in the rate constants for ring opening of the phenyl-substituted radical in comparison with its parent radical was a factor of 6400; this is a larger accelerating effect than found with the *cis*-phenyl group in the analogous cyclopropylcarbinyl radical series,[13] apparently reflecting an increased component of strain for the *cis*-phenyl substituent in the cyclobutylcarbinyl series. As noted above, an increased strain in the *cis* radical **2** series is also suggested by the observation that the rate constant for fragmentation of the secondary radical **2b** is greater than that for the primary radical **2a**.

The results for radical **1a** can be compared with those from an indirect kinetic study of this ring opening previously reported by Hill *et al.* in a work focused on the preparation and reactions of (2-phenylcyclobutyl)methyl Grignard reagents.[14] Reactions of the *cis* and *trans* isomers of (2-phenylcyclobutyl)bromomethane with 0.3 M Bu_3SnH in benzene at 80 °C gave only ring-opened products, but reaction of a 60:40 mixture of *trans* and *cis* isomers with ca 3 M tin hydride at 80 °C gave about 7% yield of the *trans*-cyclobutane product.[14] Using the currently accepted rate constants for reaction of Bu_3SnH with a primary alkyl radical ($k = 2 \times 10^7$ l mol^{-1} s^{-1} at 80 °C),[15] the rate constant for ring opening of radical **1a** at 80 °C would be 1.5×10^8 s^{-1}, in excellent agreement with the values of 1.4×10^8 and 1.8×10^8 s^{-1} extrapolated from the Arrhenius functions for **1a** in THF and acetonitrile, respectively.



Scheme 3

Radicals **1** and **2** react with appropriate rate constants for nanosecond-resolution LFP studies of substituent effects. This was demonstrated by a study of the effect of ethoxycarbonyl substitution at the radical center (Scheme 3). Acid **11**, prepared from acid **5a** by ethoxycarbonylation of the ester enolate and partial hydrolysis of the malonate thus formed, was converted to PTOC ester **12**. As with other α-ethoxycarbonyl-substituted PTOC esters,[16] compound **12** was unstable, but it was obtained in adequate purity for LFP studies. Photolysis of **12** gave radical **13** that rearranged to radical **14**. The rate constants for ring opening of radical **13** at 19.1 °C in THF and acetonitrile were 5×10^6 and 8×10^6 s^{-1}, respectively.

Despite the radical-stabilizing effect of the ester group in **13**, the ring opening in THF was only a factor of 2 less rapid than ring opening of the methyl-substituted analog **1b**, and the rate constants for ring openings of radicals **13** and **1b** in acetonitrile were about the same. The fast opening of stabilized radical **13** seems counterintuitive, but it is consistent with an expected stabilization of the transition state due to polarization. The modest acceleration in the ring opening of **13** on proceeding from THF to the more polar solvent acetonitrile is also consistent with transition state polarization, especially in the light of the consistent kinetic values found for radicals **1** in these two solvents. An acceleration in the ring opening of an ethoxycarbonyl-substituted cyclopropylcarbinyl radical, giving an alkyl radical product instead of a benzylic radical product, was even more pronounced.[5]

In addition to LFP studies of substituent effects on radicals such as that in Scheme 3, radicals **1** and **2** could find applications as internal reporter groups in LFP kinetic studies. LFP reporter group studies in our laboratory to date[3,5,8,17] have used the ultrafast ring openings of 2-phenyl-substituted cyclopropylcarbinyl radicals ($k > 1 \times 10^{11}$ s^{-1} at ambient temperature)[13] as the reporting elements, which will be adequate for many applications, but applications of 2-phenylcyclobutylcarbinyl reporter moieties can provide an advantage in some instances. Whereas 2-phenylcyclobutylcarbinyl radicals fragment rapidly enough to be used as a reporting element in most radical reactions, they do not cleave fast enough to compete with the collapse of radical pairs. Thus, any fragmentation in the 2-phenylcyclobutylcarbinyl series must occur from diffusionally free species, i.e. species that have escaped from radical pair solvent cages.

EXPERIMENTAL

Synthetic procedures for the preparations of carboxylic acids **5a–c**, **6a** and **b** and **11** are described in the Supporting Information.

(trans-2-Phenylcyclobutyl)ethanoic acid 2-thioxo-2H-pyridin-1-yl ester (7a) (general method)[9]. Oxalyl chloride (0.12 ml, 1.41 mmol) was added slowly to a stirred solution of acid **5a** (0.18 g, 0.94 mmol) in benzene containing one drop of DMF. After 1 h, the solvent and excess oxalyl chloride were removed under vacuum. In the following and all subsequent procedures, the reaction vessels were shielded from light. The acid chloride was taken up in benzene and the solution was added to a stirred suspension of the sodium salt of *N*-hydroxypyridine-2-thione[18] (0.17 g, 1.13 mmol) and one drop of DMAP in benzene in an ice-bath. The solution was stirred for 4 h. The reaction mixture was washed with a 10% aqueous solution of $NaHCO_3$ and brine and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude PTOC ester was rapidly chromatographed on silica gel (70:30 hexanes–ethyl acetate) to yield 0.12 g (0.40 mmol, 43%) of **8a** as yellow oil. ^{1}H NMR: δ 1.80 (quin, J = 10.5 Hz, 1 H), 2.03–2.35 (m, 4 H), 2.86–2.97 (m, 2 H), 3.24 (q, J = 8.4 Hz 1 H), 6.44 (td, J = 7.5, 1.8 Hz, 1 H), 6.75 (dd, J = 7.5, 1.8 Hz, 1 H), 7.11 (td, J = 7.5, 1.8 Hz, 1 H), 7.19–7.36 (m, 5 H), 7.60 (dd, J = 9.0, 1.8 Hz, 1 H). ^{13}C NMR: δ 25.02, 26.94, 37.78, 39.46, 47.03, 112.41, 126.48, 127.04, 128.51, 133.48, 137.12, 137.57, 143.45, 167.23, 175.66.

2-(trans-2-Phenylcyclobutyl)propanoic acid 2-thioxo-2H-pyridin-1-yl ester (7b). This was obtained as a yellow oil in 36% yield from 0.12 g of acid **5b** by the general method. ^{1}H NMR: δ 1.34 (d, J = 6.6 Hz, 3 H), 1.74 (quin, J = 9.3 Hz, 1 H), 1.97 (quin, J = 10.2 Hz, 1 H), 2.18 (q, J = 8.4 Hz, 1 H), 2.30 (q, J = 8.5 Hz, 1 H), 2.75–2.93 (m, 2 H), 3.33 (q, J = 9.6 Hz, 1 H), 5.63 (d, J = 6 Hz, 1 H), 6.20 (td, J = 7.2, 1.8 Hz, 1 H), 7.02 (t, J = 7.0 Hz, 1 H), 7.22–7.33 (m, 5 H), 7.55 (dd, J = 8.4, 1.2 Hz, 1 H). ^{13}C NMR: δ 14.0, 23.6, 27.8, 43.8, 45.7, 46.6, 112.0, 126.5, 127.5, 128.7, 133.3, 136.9, 137.6, 143.7, 170.3.

2-Methyl-2-(trans-2-phenylcyclobutyl)propanoic acid 2-thioxo-2H-pyridin-1-yl ester (7c). This was obtained as a yellow oil in 22% yield from 0.06 g of acid **5c** by the general method. ^{1}H NMR: δ 1.39 (s, 3 H), 1.40 (s, 3 H), 1.86–2.04 (m, 3 H), 2.22 (q, J = 8.5 Hz, 1 H), 2.95–3.00 (m, 1 H), 3.35 (q, J = 9 Hz, 1 H), 5.67 (d, J = 6.6 Hz, 1 H), 6.23 (td, J = 7.1, 1.8 Hz, 1 H), 7.03 (ddd, J = 8.8, 7.2,

1.5 Hz, 1 H), 7.21–7.35 (m, 5 H), 7.54 (dd, J = 8.8, 1.7, 1 H). ^{13}C NMR: δ 19.5, 20.1, 23.4, 26.6, 42.6, 43.6, 50.9, 112.1, 126.5, 127.9, 128.5, 128.7, 133.3, 137.1, 137.8, 144.0, 172.1, 175.8.

(cis-2-Phenylcyclobutyl)ethanoic acid 2-thioxo-2H-pyridin-1-yl ester (8a). This was obtained as a yellow oil in 60% yield from 0.32 g of acid **6a** by the general method. ^{1}H NMR: δ 1.81–1.89 (m, 1 H), 2.08–2.12 (m, 1 H), 2.30–2.59 (m, 4 H), 3.22–3.32 (m, 1 H), 3.87 (q, J = 8.4 Hz, 1 H), 6.54 (td, J = 6.6, 1.8 Hz, 1 H), 7.12–7.38 (m, 7 H), 7.62 (d, J = 7.8 Hz, 1 H).

2-(cis-2-Phenylcyclobutyl)propanoic acid 2-thioxo-2H-pyridin-1-yl ester (8b). This was obtained as a yellow oil in 89% yield from 0.15 g of acid **6b** by the general method. ^{1}H NMR: δ 0.97 (d, J = 6.9 Hz, 1.8 H), 1.37 (d, J = 7.2 Hz, 1.2 H), 1.87–1.95 (m, 1 H), 2.15–2.45 (m, 3 H), 2.62–2.72 (m, 1 H), 3.05–3.15 (m, 1 H), 3.75–3.81 (m, 1 H), 6.43 (td, J = 5.7, 1.8 Hz 1 H), 7.07–7.35 (m, 6 H), 7.55 (dd, J = 8.0, 1.8 Hz, 1 H).

Carboxy(trans-2-phenylcyclobutyl)ethanoic acid 2-thioxo-2H-pyridin-1-yl ester (12). This was obtained as a yellow oil in 45% yield from 0.15 g of acid **11** by the general method. ^{1}H NMR: δ 0.97 (t, J = 7.2 Hz, 1.8 H), 1.27 (t, J = 7.2 Hz, 1.2 H), 2.00–2.35 (m, 3 H), 2.65 (q, J = 6.9 Hz, 1 H), 3.12–3.28 (m, 2 H), 3.43–3.49 (m, 1 H), 3.86–3.96 (m, 1 H), 4.10–4.25 (m, 2 H), 6.17 (d, J = 6.6 Hz, 1 H), 6.30 (t, J = 6.3 Hz, 1 H), 6.58 (t, J = 6.9 Hz, 1 H), 7.12–7.65 (m, 3 H), 7.95 (d, J = 7.2 Hz, 1 H), 8.46 (m, 1 H).

Kinetic studies. Kinetic studies were accomplished with an Applied Photophysics LK-50 kinetic spectrometer employing an Nd:YAG laser for production of 355 nm light (ca 40 mJ per pulse). Dilute solutions of the radical precursor were thermally equilibrated in a jacketed storage funnel and allowed to flow through a cell in the spectrometer. Detailed results for radicals **1** and **2** are given in the Supporting Information. Typical errors in the kinetic solutions were $<$5%.

Supporting information

Synthetic procedures for the preparations of acids **5**, **6** and **11** and tables of observed rate constants for reactions of radicals **1** and **2** (13 pages) are available.

Acknowledgements

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