J. Org. Chem. **1994**, *59*, 8023–8029

Photogeneration of the Xanthyl Cation: β-Cleavage from Excited State Ketones

Mary Frances Clifton,[†] David J. Fenick,[‡] Susan M. Gasper,[†] Daniel E. Falvey,[‡] and Mary K. Boyd[*,†]

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626, and Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Received June 13, 1994[®]

Irradiation of 9-xanthylacetone or 9-xanthylacetophenone in dilute acidic aqueous solution results in facile formation of the xanthyl cation. This cation photogeneration is not subject to acid catalysis over the acid range of 5–30% H_2SO_4. In contrast, the thermal reaction requires considerably stronger acidic media, and its rate shows a strong dependence on acid concentration. Laser flash photolysis studies demonstrate that the excited-state mechanism proceeds through an initial homolytic carbon–carbon β-bond cleavage to generate the xanthyl radical. The xanthyl cation is produced from the xanthyl radical in a subsequent step, with oxygen acting as the oxidizing agent. The intermediacy of the xanthyl radical in the mechanism is also supported by the isolation of the radical coupling product bixanthyl from preparative irradiations. Triplet sensitization and quenching experiments demonstrate that the reaction proceeds through an excited triplet state of the ketone substrates.

Introduction

Carbocations are important intermediates in an array of organic chemical reactions resulting in extensive investigations of their ground-state chemistry.[1] Recent advances in techniques to detect photogenerated transient carbocations have permitted the direct measurement of cation reactivity at very short time scales.[2] Measurements of ground-state carbocation electrophilic reactivity have provided valuable data regarding the kinetics and mechanisms of numerous reactions including nucleophilic reactions and cationic polymerization.[2] Prominent methods for the photogeneration of carbocations include the formation and oxidation of radicals,[3,4] photoheterolysis of carbon–heteroatom bonds,[5–11] photoprotonation of carbon–carbon multiple bonds,[12,13] and heterolysis of radical cations.[14] Cations generated by these methods include xanthyl,[6] fluorenyl,[7] dibenzosuberyl,[8] di- and triarylmethyl,[9] and vinyl[10] cations. Disadvantages encountered in the use of these methods include the competitive formation of radicals through homolytic cleavage rather than photoheterolysis,[2,6c] high concentrations required for bimolecular oxidation of initially formed radicals,[3] and the requirement for acidic or aqueous solutions for photoprotonation.[12]

Relatively few instances of carbocation photogeneration involve carbon–carbon bond cleavage. Examples include the one electron oxidation of acetals $PhCH_2CR(OR')_2$, with subsequent rapid heterolytic carbon–carbon bond cleavage of the acetal radical cations giving α-dialkoxymethyl carbocations,[14] and the direct photoheterolysis of a carbon–carbon bond in nitrobenzyl acetals generating a carbanion and carbocation.[15] Novel methods for carbon–carbon bond cleavage are of particular interest to the fossil fuel industry, where new techniques for the selective breakdown of macromolecules (such as coal) may replace current, unfavorable pyrolytic procedures.[16]

We were intrigued by a report of Deno's which demonstrated that the xanthyl cation is produced in a thermal reaction from protonated xanthyl alcohols and xanthyl ketones in strongly acidic solutions.[17] Mechanistic studies by Keeffe on 9-xanthylacetone (**1**) and 9-xanthylacetophenone (**2**) suggest an A1 mechanism involving initial protonation on the carbonyl oxygen, with subsequent heterolytic carbon–carbon bond cleavage generating the xanthyl cation (Scheme 1), although a concerted mechanism could not be ruled out.[18] Triphenylmethyl derivatives were also studied,[17] but failed to eject the corresponding triphenylmethyl cation, even

---

[†] Loyola University of Chicago.

[‡] University of Maryland.

[®] Abstract published in *Advance ACS Abstracts*, November 15, 1994.

(1) Olah, G. A.; Schleyer, P. v. R. *Carbonium Ions*; Wiley: New York, 1970; Vols. I–IV.

(2) Das, P. K. *Chem. Rev.* **1993**, *93*, 119.

(3) Faria, J. L.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 1277.

(4) (a) Steenken, S.; Buschek, J.; McClelland, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 2808. (b) McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 5860.

(5) For earlier work in carbocation generation via photosolvolysis see: Cristol, S.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327.

(6) (a) Wan, P.; Yates, K.; Boyd, M. K. *J. Org. Chem.* **1985**, *50*, 2881. (b) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929. (c) Minto, R. E.; Das, P. K. *J. Am. Chem. Soc.* **1989**, *111*, 8858.

(7) (a) Wan, P.; Krogh, E. *J. Am. Chem. Soc.* **1989**, *111*, 4887. (b) Krogh, E.; Wan, P. *Tetrahedron Lett.* **1986**, 823. (c) Wan, P.; Krogh, E. *J. Chem. Soc., Chem. Commun.* **1985**, 1207. (d) Krogh, E.; Wan, P. *Can. J. Chem.* **1990**, *68*, 1725. (e) McClelland, R. A.; Mathivanan, N.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 4857.

(8) Johnston, L. F.; Lobaugh, J.; Wintgens, V. *J. Phys. Chem.* **1989**, *93*, 7370.

(9) (a) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918. (b) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 3966. (c) Spears, K. G.; Gray, T. J.; Huang, D. *J. Phys. Chem.* **1986**, *90*, 779.

(10) (a) Kobayashi, S.; Schnabel, W. *Z. Naturforsh.* **1992**, *47b*, 1319. (b) Kobayashi, S.; Zhu, Q.; Schnabel, W. *Z. Naturforsch.* **1987**, *43b*, 825. (c) Kobayashi, S.; Kitamura, T.; Taniguchi, H.; Schnabel, W. *Chem. Lett.* **1983**, 1117. (d) VanGinkel, F. I. M.; Visser, R. J.; Varma, C. A. G. O.; Lodder, G. *J. Photochem.* **1985**, *30*, 453.

(11) Pienta, N. J.; Kessler, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 2419.

(12) Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157.

(13) (a) Shizuka, J. *Acc. Chem. Res.* **1985**, *18*, 141 and references cited therein. (b) Wan, P.; Wu, P. *J. Chem. Soc., Chem. Commun.* **1990**, 822. (c) Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 9648.

(14) Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 4967.

(15) (a) Wan, P.; Muralidharan, S. *J. Am. Chem. Soc.* **1988**, *110*, 4336. (b) Wan, P.; Muralidharan, S. *Can. J. Chem.* **1986**, *64*, 1949.

(16) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344.

(17) Deno, N. C.; Sacher, E. *J. Am. Chem. Soc.* **1965**, *87*, 5120.

(18) (a) Trudell, M. B. M.Sc. Thesis, San Francisco State University, 1988. (b) Keeffe, J. R. Personal communication.

0022-3263/94/1959-8023$04.50/0

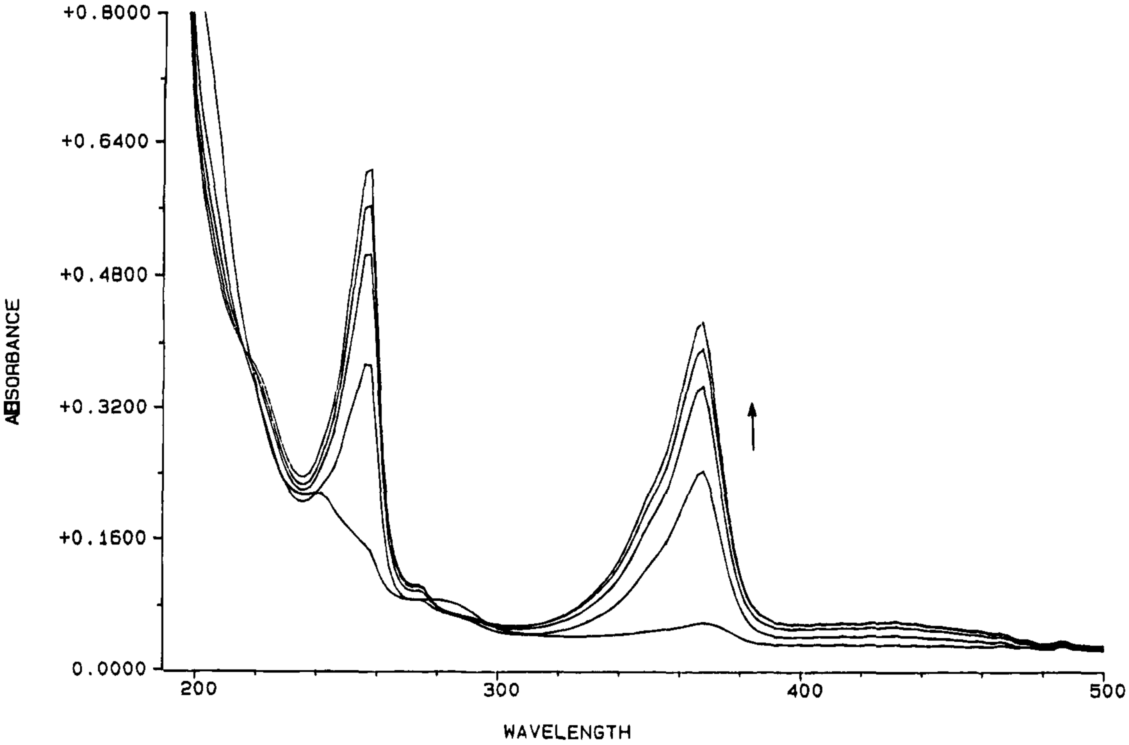
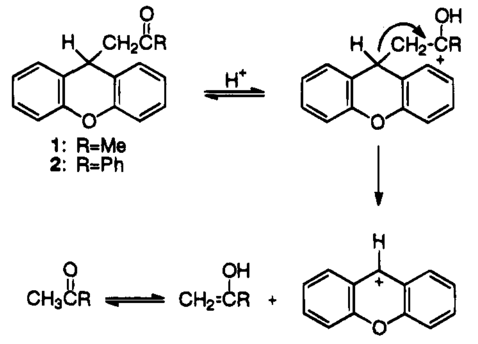


Figure 1. Absorption spectra measured following irradiation of **1** in 30% H_2SO_4 (with 33% acetonitrile cosolvent) with an excitation wavelength of 300 nm. Spectra were measured at 1 min irradiation time intervals and show growth of the xanthyl cation peaks.

Scheme 1



when treated with stronger acids at higher temperatures. The differences in reactivity between the xanthyl and triphenylmethyl compounds were attributed to the greater stability of the xanthyl cation.

Xanthyl cations are produced adiabatically following irradiation of 9-substituted xanthen-9-ols, indicating an enhanced excited-state stability of the xanthyl cation.[6a] Thus we reasoned that the bond cleavage reaction of **1** and **2** generating the xanthyl cation might be promoted by irradiation. Specifically, we wished to determine whether the same bond cleavage reaction to generate the xanthyl cation would occur photochemically under less acidic conditions than required for the thermal reaction. We report here that the xanthyl cation is generated photochemically from 9-xanthylacetone and 9-xanthylacetophenone in mildly acidic aqueous solutions, under conditions where no thermal reaction occurs. The photogeneration of the xanthyl cation from these substrates proceeds via a different mechanism than that of the thermal reaction. Preparative photolyses and laser flash photolysis studies support a mechanism involving initial homolytic carbon–carbon bond cleavage to generate the xanthyl radical, with subsequent oxidation to the xanthyl cation.

Results

9-Xanthylacetone (**1**) and 9-xanthylacetophenone (**2**) were prepared by a two-step procedure.[18a,19] Acid-catalyzed reaction of xanthydrol with ethyl acetoacetate or ethyl benzoylacetate gave the β-keto esters ethyl 2-(9-xanthyl)-3-oxobutanoate (**3**) and ethyl 2-(9-xanthyl)-2-phenyloxopropanoate (**4**), respectively. Base hydrolysis of **3** yielded ketone **1**, while hydrolysis of **4** gave ketone **2**.

Preparative Photolyses. Solutions were prepared of **1** and **2** in aqueous acidic solution (5–30% H_2SO_4) with acetonitrile cosolvent for solubility reasons (aqueous/acetonitrile 2:1 for **1** and 1:2 for **2**). The sulfuric acid percentages have not been corrected for the cosolvent (see Experimental Section for details). Irradiations were performed at 300 or 254 nm in a Rayonet RPR-100 photoreactor. The reaction progress was monitored by UV/vis absorption spectroscopy, since the absorption characteristics of the substrates and the xanthyl cation are quite different. Solutions of **1** and **2** were irradiated for 1–4 min. A spectrum corresponding to the xanthyl cation (absorption maximum of 374 nm) was observed to grow cleanly over the entire acid range examined, with a decrease in the absorption peaks corresponding to **1** and **2**. Clean isosbestic points were observed for growth of the xanthyl cation absorption spectra for irradiation of both **1** and **2** in each acid concentration studied. Figure 1 illustrates a series of absorption spectra obtained from irradiation of **1** in 30% H_2SO_4. The reaction is obviously very fast, since the spectra were obtained at 1 min irradiation times using only two lamps in the Rayonet reactor. A control dark reaction, also monitored by absorption spectroscopy, was used to ensure that no thermal reaction occurred in these acidic solutions over the time scale of the irradiations.

---

[19] Fosse, R. *Bull. Soc. Chim. Fr.* **1906**, *35*, 1005.

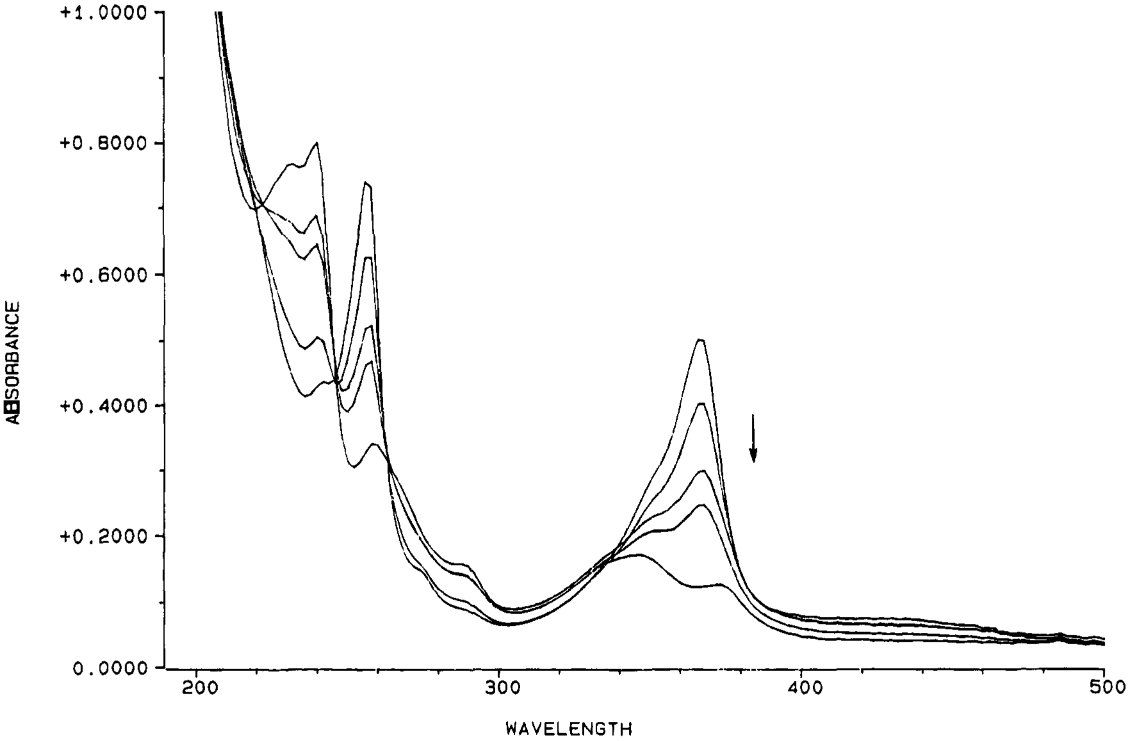


Figure 2. Absorption spectra measured following irradiation of xanthyl cation solutions produced from photolysis of **1** in 30% H_2SO_4 (with 33% acetonitrile cosolvent) with an excitation wavelength of 300 nm. Spectra were measured at 4 min irradiation time intervals and show xanthyl cation peaks decreasing with concomitant formation of xanthone.

Continued irradiation resulted in a decrease in xanthyl cation absorbance, with the concomitant increase in the absorption spectrum of a peak with absorption maximum of 340 nm. Formation of this photoproduct was observed upon irradiation of the xanthyl cation solutions produced from photolyses of **1** and **2** over the entire acid range of 5–30% aqueous sulfuric acid. Figure 2 illustrates absorption spectra obtained following further irradiation of the xanthyl cation produced from irradiation of **1** in 30% H_2SO_4. This secondary photoproduct was identified as xanthone by comparison to the absorption spectrum of an authentic sample of xanthone. Further confirmation of xanthone as the secondary photoproduct came from its isolation following exhaustive irradiation of **1**. A yield of 75% for the formation of xanthone was obtained from GC analysis. Aqueous workup and product isolation followed by GC analysis also identified acetophenone and bixanthyl as minor photoproducts (yields of approximately 2–3% were observed for both photoproducts) from the irradiation of **2** in 5% H_2SO_4.

The initially formed xanthyl cation was stable indefinitely in the aqueous acidic solutions without further irradiation, according to absorption spectra. A control experiment was performed to determine the source of the xanthone. Xanthydrol was dissolved in the same acidic media (5–30% aqueous H_2SO_4, with acetonitrile cosolvent). UV/vis spectroscopy showed that the xanthyl cation was thermally generated, although the xanthyl cation was in partial equilibrium with xanthydrol in these dilute acid concetrations. Irradiation of the argon-purged cation/alcohol solutions at 254 nm also yielded xanthone. No xanthone was produced in a control dark experiment.

Acid Catalysis. Earlier studies established that formation of the xanthyl cation from the thermal cleavage of **1** and **2** was strongly acid dependent.[17,18] As described in the previous section, the xanthyl cation is produced from irradiation of **1** and **2** over a wide range of acid concentrations. In order to determine whether this photochemical generation of the xanthyl cation is subject to acid catalysis, we irradiated **1** in solutions of varying acidity (5–30% aqueous H_2SO_4, with acetonitrile cosolvent). Aliquots were removed after irradiation times of 1 min, 2 min, and 4 min. The relative amounts of xanthyl cation produced in the varying acid solutions were obtained from the absorption intensity at 374 nm. However, under these dilute acid concentrations, the xanthyl cation is in partial equilibrium with its corresponding alcohol, xanthydrol.[20] In order to account for this, sufficient acid was added to each aliquot in order to shift the cation–alcohol equilibrium completely to the cation side prior to analysis by UV/vis spectroscopy.

The cation absorbance at 374 nm was identical for each acid solution at a particular photolysis time, showing that the amount of xanthyl cation formed is independent of acid concentration (Figure 3). The amount of xanthyl cation generated in the photochemical experiments varied from 10% after 1 min irradiation to 60% after 4 min irradiation time. Carrying out the irradiations to higher conversion was not attempted due to a secondary photochemical reaction producing xanthone. Control dark experiments ensured no thermal generation of the cation from **1** under either the experimental or analysis conditions.

Triplet Sensitization and Quenching Studies. In order to determine the multiplicity of the reactive state, sensitization experiments were carried out with benzophenone as the triplet sensitizer. Sufficient benzophenone was added to an aqueous acidic (5% H_2SO_4) solution of **1** or **2** to ensure that the sensitizer absorbed at least 90% of the incident light (λ_{max} = 300 nm). Acetonitrile was again used as cosolvent for solubility purposes. The high concentration and strong absorbance of benzophenone did not allow us to use absorption spectroscopy to

---

[20] Boyd, M. K. Ph.D. Thesis, University of Toronto, 1988.

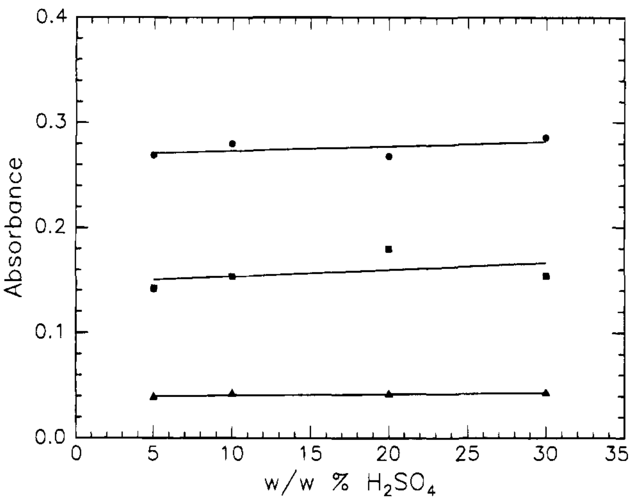


Figure 3. Plot of absorption intensity of xanthyl cation (at 374 nm) versus percent aqueous H_2SO_4 (acid concentration not corrected for cosolvent). The xanthyl cation was produced from irradiation of **1** with irradiation times of 1 min (▲), 2 min (■), and 4 min (●). These times correspond to cation conversions of 10, 32, and 60% respectively.

analyze the amount of xanthyl cation formed. Instead, the photolysis solutions were analyzed by GC for both reactant disappearance and product formation. GC analysis of the reaction mixture following neutralization and extraction showed that the amounts of both **1** and **2** decreased, with the formation of the same photoproducts obtained from the direct irradiation. Reaction of both **1** and **2** in the presence of the sensitizer suggest the involvement of the triplet excited state for these compounds.

Triplet quenching experiments were performed using potassium sorbate or oxygen as quenchers. The effect of these triplet quenchers on the reaction was determined by comparison of the absorption intensity at 374 nm (corresponding to xanthyl cation) for the quenched versus unquenched irradiations. For both quenchers, solutions of **1** or **2** were prepared in aqueous acidic (5% H_2SO_4) acetonitrile. As previously described, sufficient acid was added to the photolyzed solutions to shift the cation/alcohol equilibrium completely over to the cation side prior to analysis. For the experiments using oxygen as a triplet quencher, solutions of **1** and **2** were purged with argon or oxygen for 30 min. For identical irradiation times, the solutions purged with oxygen gave absorption intensities approximately 35% lower at 374 nm, compared to the argon-purged solutions.

Irradiation at 300 nm of **1** and **2** in in the presence of potassium sorbate (10^{-3} M) similarly gave lower absorbance values for the amount of cation formed, when compared to irradiated solutions lacking the diene quencher. Higher concentrations of potassium sorbate could not be used, since the diene would then absorb the incident light (λ_{ex} = 300 nm). The oxygen and potassium sorbate quenching experiments showed that less cation was formed in the presence of the triplet quenchers, providing further support for the triplet state mechanism.

Laser Flash Photolysis Studies. Laser flash photolysis studies were performed on **1** and **2** in aqueous acidic acetonitrile using a XeCl excimer laser (λ_{ex} = 308 nm). The acetonitrile:H_2O:acid ratio was 90:8:2 by volume. The larger amount of acetonitrile was necessary for substrate solubilities at the higher concentrations required for laser studies. The transient spectra obtained following laser flash photolysis of either **1** or **2** in oxygen or nitrogen purged solutions show formation of an intermediate with an absorption maximum of 345 nm, within the rise time of the laser pulse (10 ns). The spectrum of the primary photoproduct is shown in Figure 4a, as the trace obtained 10 μs after laser excitation of **2**. The xanthyl radical was identified as the primary photoproduct by comparison to literature reports[6c,21] and by independently generating the radical from irradiation of xanthene in the presence of *tert*-butyl peroxide. Reference to literature spectra eliminated the 9-xanthylidene carbene as a possible intermediate, since its absorption spectrum exhibits broad maxima at 374, 383, and 393 nm.[22]

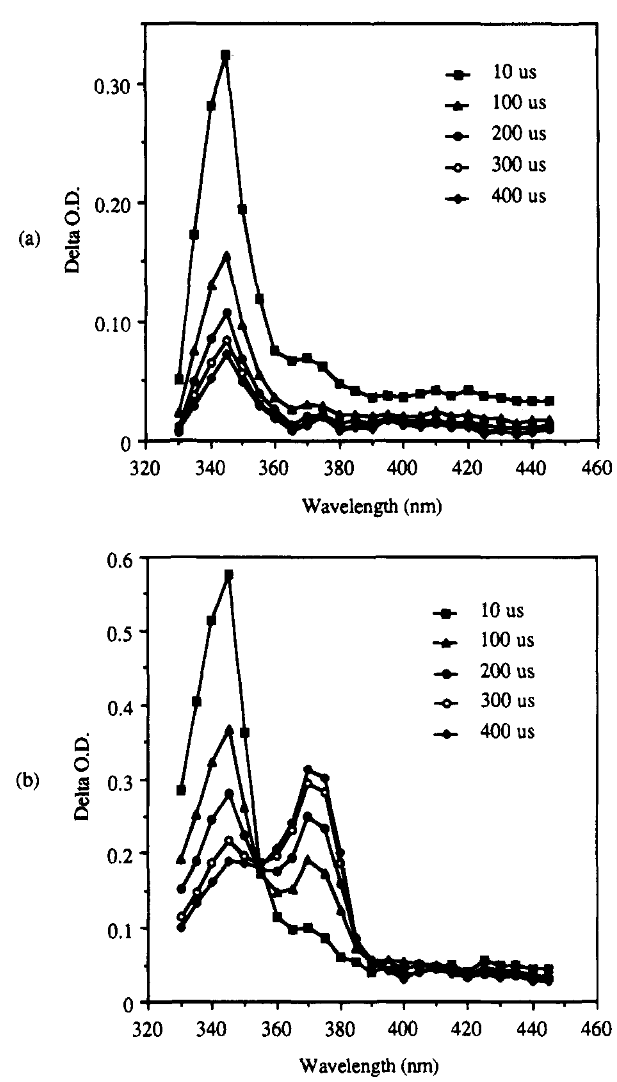


Figure 4. Transient spectra obtained following photolysis of xanthylacetophenone in 90:8:2 CH_3CN:H_2O:H_2SO_4. Figure 4a was obtained from substrate solutions purged with nitrogen and shows decay of the initially formed xanthyl radical. Figure 4b was obtained from substrate solutions purged with air. The exclusive formation of the xanthyl cation from the xanthyl radical is indicated by the isosbestic point at 355 nm.

In nitrogen-saturated solutions, the absorbance corresponding to the xanthyl radical decays slowly (Figure 4a), whereas in oxygen-saturated solutions the xanthyl radical absorption spectrum decay is accompanied by the growth of a new spectrum with an absorption maximum

---

[21] Samanta, A.; Gopidas, K. R.; Das, P. K. *J. Phys. Chem.* **1993**, *97*, 1583.

[22] Lapin, S. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *107*, 4243.

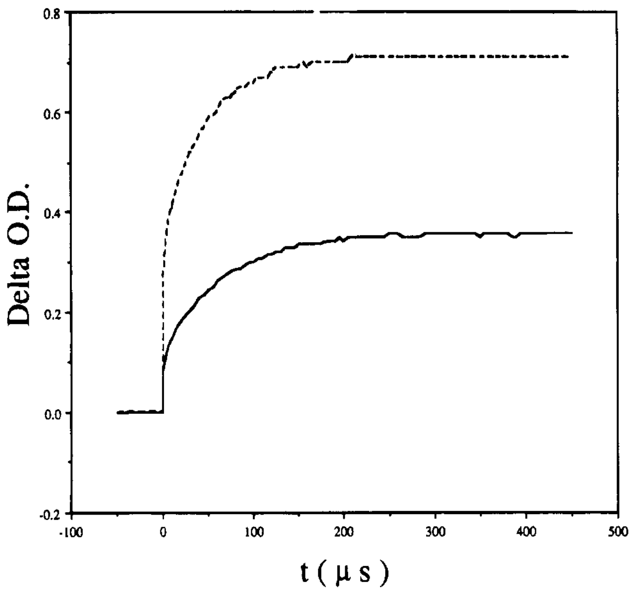


Figure 5. Transient absorption waveforms of xanthylacetophenone (solid) and xanthylacetone (dotted) at 370 nm in 90:8:2 CH_3CN:H_2O:H_2SO_4 purged with air.

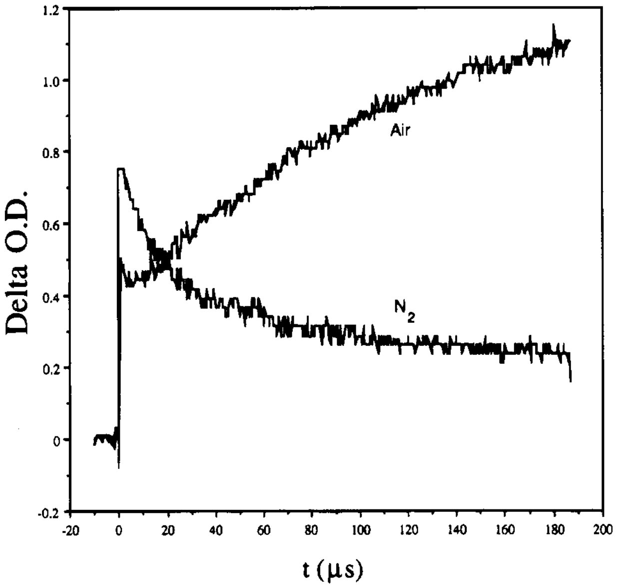
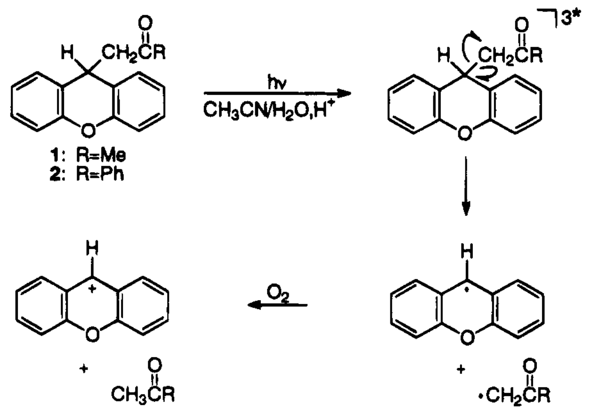


Figure 6. Transient absorption waveforms for xanthylacetophenone in 90:8:2 CH_3CN:H_2O:H_2SO_4 purged with nitrogen and purged with air.

at 370 nm. This secondary photoproduct was identified as the xanthyl cation, by comparison to its characteristic UV/vis spectrum (Figure 1). Both **1** and **2** show the initial formation of the xanthyl radical with subsequent conversion to the xanthyl cation, with clean isosbestic points. Figure 4b illustrates this clean conversion of the xanthyl radical to the xanthyl cation for irradiation of **2**. Growth of the 370 nm absorbance, corresponding to xanthyl cation formation, is a pseudo-first-order process for both **1** and **2** (Figure 5). Least squares analysis gave rate constants for growth of the cation of 1.5×10^4 s^{-1} for **1** and 2.1×10^4 s^{-1} for **2**.

In solutions that were rigorously purged with nitrogen, no absorptions due to the xanthyl cation were detected, and only the decay of the xanthyl radical was observed. Figure 6 compares the behavior of oxygen- and nitrogen-purged samples of **2** by monitoring the absorption at 370 nm. This wavelength is the absorption maximum for the xanthyl cation. The xanthyl radical also absorbs at this wavelength, but with less intensity. In oxygen-saturated solution there is an initial jump in the absorption intensity resulting from formation of the radical within the duration of the laser pulse, followed by a slower pseudo-first-order growth resulting from conversion of the radical into the more strongly absorbing cation. In nitrogen-purged solutions the same initial jump due to radical formation is detected; however, in this case the absorption decays in a second-order process as the radical recombines and reacts to form stable products other than the cation. These results indicate that the presence of oxygen is necessary for xanthyl cation formation. The magnitude of the initial jump differs for **1** and **2** (Figure 5), which can be attributed to differences in quantum efficiency for formation of the radical.

Scheme 2



To examine the role of acid on radical and cation formation, **1** and **2** were irradiated in 100% acetonitrile and in a solution of acetonitrile/water (90:10 by volume). Transient spectra obtained following laser flash photolysis show that the xanthyl radical is produced from both substrates within the rise time of the laser pulse, but no peaks corresponding to xanthyl cation formation were observed to grow in. Apparently the presence of acid is required to observe efficient cation formation. Preparative irradiation of **2** in acetonitrile resulted in formation of xanthone.

Discussion

The results reported above demonstrate that the xanthyl cation can be generated from **1** and **2** photochemically under less acidic conditions than required for the thermal reaction. Formation of the xanthyl cation in the ground-state reaction is strongly acid dependent.[17,18] In contrast, preparative irradiations of **1** and **2** in aqueous acidic acetonitrile showed no acid dependence on the amount of xanthyl cation formed, over an acid range of 5–30% H_2SO_4. No acid catalysis was observed in the photochemical reaction for conversions of 10–60% cation. Acid concentrations higher than 30% H_2SO_4 could not be studied in the irradiations due to competing thermal reactions.

The lack of acid catalysis in the photochemical generation of the xanthyl cation, combined with the observation from laser flash photolysis experiments that the xanthyl radical is the primary photoproduct, indicate a different mechanism operating in the excited state. We propose the two-step mechanism for the cation photogeneration illustrated in Scheme 2. The first step involves initial homolytic carbon–carbon bond cleavage of **1** or **2** to generate the xanthyl radical and the corresponding α-acyl radical. This bond cleavage process would be independent of the acid concentration and is in accord with the experimental finding. The radical coupling product bixanthyl was isolated from preparative irradiations of **2** and supports the intermediacy of the xanthyl radical in the mechanism. Acetophenone was also confirmed as a product from photolysis of **2**. Its formation can be attributed to hydrogen abstraction by the precursor α-acyl radical.

The second step of the proposed mechanism for cation photogeneration involves oxidation of the xanthyl radical to generate the xanthyl cation. Laser flash photolysis studies show that the initially formed xanthyl radical is cleanly converted to the xanthyl cation in the presence of oxygen. Oxygen has a reduction potential of 0.682 V vs NHE,[23] while the oxidation potential of the xanthyl radical is -0.002 V vs SCE (or 0.24 V vs NHE).[16] Thus, oxygen can act as the oxidizing agent to produce the xanthyl cation, since the electron transfer process is calculated to be exothermic by 0.44 V.

Oxidation of the xanthyl radical to the xanthyl cation may occur via a one-step (outersphere) electron transfer pathway or by a two-step (innersphere) process in which oxygen adds to the xanthyl radical followed by heterolytic carbon−oxygen bond cleavage.[24] Both the innersphere and outersphere mechanisms would generate the xanthyl radical and superoxide. Our experiments are incapable of distinguishing between these two mechanisms regarding the role of oxygen.

The laser flash photolysis experiments demonstrate that no cation is formed in rigorously deoxygenated solutions. Rather, the observed decay of the radical absorption in the absence of oxygen is likely due to secondary chemical reactions of the xanthyl radical, such as the formation of the radical coupling product, bixanthyl. We were unable to fully inhibit xanthyl cation formation in the preparative irradiations solely by purging the photolysis solutions with argon. Apparently, small amounts of adventitious oxygen are sufficient to oxidize the xanthyl radical, due to the low substrate concentrations (10^{-5} M) used in the preparative irradiations.

The initial bond cleavage is proposed to proceed through an excited triplet state of **1** and **2**. Triplet sensitization experiments using benzophenone showed that both **1** and **2** underwent the same bond cleavage process in the presence of the sensitizer as in the direct irradiation. Triplet quenching experiments using potassium sorbate resulted in a decreased efficiency of formation of the xanthyl cation produced from **1** and **2**. Both the sensitization and triplet quenching experiments implicate a reactive triplet state in the mechanism. Oxygen was also observed to act as a quenching agent in the preparative irradiations. Irradiation of **1** and **2** in oxygen-purged solutions resulted in less xanthyl cation produced compared to the amount of cation produced in argon purged solutions. While oxygen is presumed to act as the oxidizing agent to generate the xanthyl cation, it may also act as a triplet quencher.[25]

Detection of the xanthyl cation following laser flash photolysis of **1** and **2** requires the presence of aqueous acid. Irradiation of **1** or **2** in 100% acetonitrile with oxygen or nitrogen purging resulted in formation of the xanthyl radical, as detected by transient absorption spectroscopy. No xanthyl cation peaks were observed to grow in. The absorption spectrum corresponding to the xanthyl radical decayed over time, presumably through secondary radical reactions. The xanthone photoproduct isolated from preparative irradiation of **2** in acetonitrile supports the idea that radical chemistry dominates under these conditions, presumably due to a slower rate constant for cation formation in the less polar solvent.

Laser flash photolysis of **1** and **2** in solutions of acetonitrile/water (90:10) similarly showed formation of the xanthyl radical, although no cation peaks were detected in either oxygen- or nitrogen-purged solutions. In deoxygenated solutions the xanthyl radical is not oxidized, and likely undergoes the secondary radical reactions previously described. In the presence of oxygen, the radical presumably is oxidized to the xanthyl cation. This cation would then be rapidly trapped by water to give xanthydrol. McClelland and co-workers generated the xanthyl cation via laser flash photolysis of xanthydrol in 1:4 acetonitrile/water. A rate constant of 2.3×10^4 s^{-1} was measured for reaction of the cation with solvent.[6b] The presence of acid is thus required to stabilize the cation for transient detection in our experiments.

Carbonyl compounds are well known to undergo photochemically induced α-cleavage (Norrish Type I) reactions to give two radical fragments.[25] Cleavage of the β-bond is considerably rarer and occurs with compounds containing relatively weak $C_\alpha-C_\beta$ bonds, such as cyclopropyl ketones[26] and γ,δ-unsaturated ketones.[27] α,β-Epoxy ketones similarly undergo photochemically induced β-cleavage, due to the weak $C_\alpha-O_\beta$ bond.[28] Bromoacetyl chloride undergoes β-cleavage of the C−Br bond as well as α-cleavage of the C−Cl bond.[29] In the case of **1** and **2**, the facile β-homolytic bond cleavage is attributed to the stability of the xanthyl radical. Alternatively, the reaction can also be viewed as a benzylic-type cleavage, as opposed to β-cleavage.

In summary, we report a new photochemical route for carbocation formation. Homolytic cleavage of the benzylic bond in **1** and **2** gives the xanthyl radical. Facile oxidation of the initially formed radical results in cation formation. The ability to generate both radical and cation, depending on the reaction conditions, may have applications in concurrent radical/cation photoinitiator systems.[30] We are continuing our studies on related systems, including efforts to generate carbocations through direct photoheterolysis of carbon−carbon bonds.

Experimental Section

Materials. Ethyl acetoacetate was obtained from Fisher and distilled prior to use. Methylene chloride and concentrated sulfuric acid were obtained from Fisher and used as received. Ethyl benzoylacetate (tech 90%), 9-hydroxyxanthene, trifluoroacetic acid (TFA), acetonitrile (reagent grade), and deuterated chloroform were obtained from Aldrich and used as received. Merck silica gel, grade 60, 230−400 mesh, was used for flash column chromatography. All ^{1}H NMR and ^{13}C

---

[23] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; Wiley: New York, 1980.

[24] Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987

[25] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, 1978.

[26] (a) Hess, L. D.; Jacobson, J. L.; Schaffner, K.; Pitts, J. N. *J. Am. Chem. Soc.* **1967**, *89*, 3684. (b) Dauben, W. G.; Shaffer, G. W.; Deviny, E. J. *J. Am. Chem. Soc.* **1970**, *92*, 6273.

[27] (a) Padwa, A. *Org. Photochem.* **1967**, *1*, 91. (b) Johnson, C. K.; Doming, B.; Reusch, W. *J. Am. Chem. Soc.* **1963**, *85*, 3894.

[28] Crandall, J. K.; Mayer, C. F.; Arrington, J. P.; Watkins, R. J. *J. Org. Chem.* **1974**, *39*, 248.

[29] Person, M. D.; Kash, P. W.; Butler, L. J. *J. Chem. Phys.* **1992**, *97*, 355.

[30] Timpe, H. J. *Pure Appl. Chem.* **1988**, *60*, 1033.

NMR spectra were taken in $CDCl_3$, and all absorption spectra were taken in aqueous acidic solutions using acetonitrile as a cosolvent.

General Methods. NMR spectra were obtained on a Varian VXR300 instrument with ^1H NMR signals reported in parts per million (δ) from TMS internal standard. ^{13}C NMR chemical shifts (δ) were reported using 77.0 ppm ($CDCl_3$) as a reference peak. UV and visible absorption spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. GC analyses were performed using a Hewlett-Packard 5890 series II chromatograph with FID detector and fitted with an HP 1 capillary column (crosslinked methyl silicone gum) measuring 25 m × 0.2 mm × 0.33 μm film thickness. The gas chromatograph was equipped with a Hewlett-Packard 3396 series II integrator. Temperature programming starting at 120 °C for 6 min, increasing at 3 °C/min, and holding at 250 °C for 10 min was used. Injector and detector temperatures were held at 275 °C. Sulfuric acid densities were determined at 25.0 °C with an Anton-Paar DMA 48 digital precision density meter. Sulfuric acid solutions were prepared from distilled water and reagent grade acid. Solution densities were determined and converted to weight percent acid from literature tables.[31]

General Photolysis Procedure. Stock solutions of **1** and **2** were prepared at 4×10^{-4} M in acetonitrile. Solutions for irradiation were prepared by combining 5 mL of these stock solutions with acetonitrile (29 mL for **1**, 66 mL for **2**) and aqueous sulfuric acid (5–30% H_2SO_4, 66 mL for **1** and 29 mL for **2**). Solutions were purged with dry argon for 30 min using a fritted glass rod and then transferred to 20 mL or 200 mL quartz tubes. The solutions were irradiated at an excitation wavelength of 254 nm or 300 nm using from 2–6 lamps in a Rayonet photoreactor. A merry-go-round device (in the case of 20mL cuvettes) provided equivalent irradiation to each solution. The total time of irradiation was varied, with aliquots being removed at one minute intervals. Samples wrapped in foil served as dark controls. The solutions were either directly analyzed by UV/vis spectroscopy or the photoproducts were initially isolated through aqueous workup followed by GC analysis.

Triplet Sensitized Photolysis: General Method. Benzophenone was used as the triplet sensitizer in the photolysis of **1** and **2**. Solutions (100 mL total volume) were prepared containing benzophenone (4×10^{-4} M), **1** or **2** (4×10^{-5} M), dodecane (5 mg), and aqueous acidic (5% H_2SO_4) acetonitrile, with the same relative amounts of aqueous acid to acetonitrile as described in the General Photolysis Procedures. The concentration of benzophenone was chosen in order that benzophenone absorb at least 90% of the incident light. Dodecane was added to each solution to serve as an internal standard for GC response factors. Solutions were transferred to 200 mL quartz cuvettes and photolyzed (as described above) for 10 min using two lamps of 254 nm wavelength. Dark reactions of the solutions were also tested. Direct irradiation control experiments of **1** and **2**, as well as benzophenone, were conducted. In order to isolate unreacted starting materials and possible photoproducts from the aqueous acidic solution, the photolyzed solutions were washed with 1 M NaOH, extracted using methylene chloride, and dried over anhydrous $MgSO_4$. The solutions were gravity filtered and solvent removed in vacuo. GC analyses were then performed as described above.

Triplet Quenching. The potassium salt of 2,4-hexadienoic acid (potassium sorbate) was used as a triplet quencher at a concentration of 10^{-3} M in aqueous acidic (5% H_2SO_4) acetonitrile (acid/acetonitrile 1:9 by volume). **1** or **2** was added to the stirred solution to give a concentration of 10^{-3} M, and the solutions were purged with dry argon for 30 min. UV/vis spectra of the solutions were recorded with and without addition of quencher, before and after purging. The solutions were then photolyzed for 0, 4, or 8 min using two lamps of 300 nm wavelength. The irradiated solutions were analyzed by UV/vis spectra following the addition of sufficient sulfuric acid to shift the xanthyl cation/xanthydrol equilibrium completely to the cation side.

Oxygen was also used as a triplet quencher of **1** and **2** in aqueous acidic (5% H_2SO_4) acetonitrile (aqueous/acetonitrile 2:1 for **1** and 1:2 for **2**). Solutions of **1** and **2** (2×10^{-5} M) were purged using a fritted rod with either dry argon or oxygen for 30 min. These solutions were then irradiated for 0 or 4 min using two lamps of 254 nm. Sulfuric acid was added to the irradiated solutions prior to analysis by UV/vis spectroscopy, as described above.

Laser Flash Photolysis. These experiments were performed using a Questek 2120 excimer laser as the excitation source. All of the spectra and kinetic runs reported here were done with XeCl reagent gas which provides UV pulses at 308 nm with a duration of 6–10 ns and a pulse energy of 30–50 mJ. Transient UV/vis absorption signals were monitored using a CW 500 W Xe lamp beam which was passed through the sample perpendicular to the excitation beam. Single wavelength transient waveforms were digitized using a LeCroy 9420 350 MHz digital oscilloscope and transferred to an IBM PS 2/286 computer for storage and spectral analysis.

Sample solutions were placed in an all glass flow cell[32] which was sealed with a rubber serum cap and purged with nitrogen (or oxygen where noted) for 10–15 min prior to the experiment. Sample concentrations were adjusted such that their optical densities were 1.0–1.5 at the excitation wavelength.

Syntheses. Ethyl 2-(9-Xanthyl)-3-oxobutanoate (3). Ethyl acetoacetate (1.54 mL, 12.1 mmol) was alkylated with 9-hydroxyxanthene (2.0 g, 10.1 mmol) using TFA (3 drops) as a catalyst. The reaction mixture was heated at reflux for 2 h. The crude β-keto ester was recrystallized from 95% ethanol giving a white solid: mp 86–87 °C (lit.[18a] mp 87–88 °C); ^1H NMR δ 7.31 (m, 8H), 4.89 (d, 1H), 4.05 (q, 2H), 3.83 (d, 1H), 1.95 (s, 3H), 1.13 (t, 3H).

9-Xanthylacetone (1). β-Keto ester **3** (0.20 g, 0.65 mmol) was hydrolyzed using 5% NaOH (5.2 mL) by heating at reflux for 5 h. Acidification followed by recrystallization from 95% EtOH gave a white solid: mp 93–94 °C (lit.[18a] mp 93–94 °C); ^1H NMR δ 7.24 (m, 8H), 4.70 (t, 1H), 2.87 (d, 2H), 2.04 (s, 3H); ^{13}C NMR δ 206.24, 152.12, 128.52, 127.60, 125.19, 123.41, 116.53, 54.43, 34.54, 31.16.

Ethyl 2-(9-Xanthyl)-2-phenyloxopropanoate (4). Ethyl benzoylacetate (2.08 mL, 12.1 mmol), 9-hydroxyxanthene (2.0 g, 10.1 mmol) and TFA (2 drops) were heated at reflux for 5 h. The crude β-keto ester was purified using silica gel column chromatography (CH_2Cl_2 eluant). Recrystallization from 95% EtOH gave a white solid: mp 74–75 °C (lit.[18a] mp 81–85 °C); ^1H NMR δ 7.73 (d, 2H), 7.24 (m, 11H), 5.05 (d, 1H), 4.60 (d, 1H), 3.91 (q, 2H), 0.99 (t, 3H).

9-Xanthylacetophenone (2). β-Keto ester **4** (0.25 g, 0.67 mmol) was hydrolyzed using 5% NaOH (5.4 mL) by heating at reflux for 5 h. Acidification and extraction with methylene chloride, followed by recrystallization from 95% EtOH, yielded a white solid: mp 82–85 °C (lit.[18a] mp 82–85 °C); ^1H NMR δ 7.26 (m, 13H), 4.85 (t, 1H), 3.35 (d, 2H); ^{13}C NMR δ 197.94, 152.36, 133.14, 128.84, 128.54, 128.11, 127.88, 125.55, 123.49, 116.58, 49.74, 34.70.

Acknowledgment. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research (to M.K.B.). D.E.F. thanks the NSF (Grant CHE-9119998) and the NIH (Grant GM45856) for financial support. M.F.C. thanks the Department of Education for a GAANN fellowship. We are grateful to J. R. Keeffe for many helpful discussions.

---

[31] *International Critical Tables*; McGraw-Hill: New York, 1930; Vol. 3, p 35.

[32] Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381.