selected for additional testing against selected human tumors implanted in nude mice. The biological data resulting from these studies will be reported in a separate publication.

Photoinduced Electron Transfer to a Carbenium Ion[1]

H. Al-Ekabi, H. Kawata,[2] and P. de Mayo*

Photochemistry Unit, Department of Chemistry, University of Western Ontatio, London, Ontario, Canada, N6A 5B7

Irradiation ($\lambda > 430$ nm) of the cation obtained by protonation of 1,1-di-*p*-anisylethylene (1) in the presence of excess 1 in benzene–trifluoroacetic acid solution results in electron transfer from the neutral ethylene and the formation of the corresponding radical and radical cation. These have been identified by the aid of flash photolysis and quenching experiments with an electron donor and by the nature of the final products. The radical cation was also prepared, for comparison, by using 9,10-dicyanoanthracene as the electron acceptor. The quantum yields of the photoproducts, derived from both radical and radical cation, are very low ($\sim 10^{-3}$), which suggests the occurrence of an efficient back-electron-transfer process between radical and radical cation to regenerate 1 and the ground-state cation.

Introduction

As part of our work on semiconductor mediated organic reactions we had occasion to study the reactions of 1,1-di-*p*-anisylethylene (1) in the presence of two pure samples of CdS.[3] A difference in behavior between them was observed in that while both samples gave the dimeric products 10–13, believed to be derived from the radical cation 1·+, one sample gave, in addition, a substance believed to be 6. A further difference found was that the CdS sample which produced 6 gave, in a "dark" reaction, another dimeric product identified as 3 and known to be formed[4] by simple acid catalysis from 1. The other sample of CdS underwent no "dark" reaction whatsoever. From these observations we were led to suspect that 6 arose by the combined action of acid and light on 1—despite the fact that washing the CdS did not remove its "acid" properties—and one possibility that presented itself was that 6 was generated by the action of light on the cation derived from 1, i.e., 2.

The photochemistry of carbenium ions has been largely restricted to that of those derived from unsaturated carbonyl compounds and to instances of valence tautomerism or geometrical isomerism.[5,6] There have been, also, a few reports of the photochemical reduction of cations where the products isolated are complex, and where the source

Table I. Quantum Yields of Photoproducts

| [acid],[a] M | C_A/C_0[b] | quantum yield (×10³)[e] | | | |
		10	11	6	7
0	(1.0)				
0.13[c]	0.99	0.34	2.9	0.25	0.12
0.52[c,d]	0.95	0.45	2.4	0.22	0.15
1.03[c]	0.68	0.85	1.7	0.16	0.41
1.62[c]	0.36	0.90	1.0	0.05	0.70
2.34[c]	0.16	0.63	0.6	~ 0	0.57

[a] Trifluoroacetic acid. [b] The ratio of the concentration of olefin (C_A) to initial concentration of olefin (C_0; 4.2×10^{-2} M) was calculated from UV spectra. [c] The quantum yields, at these acid concentrations, were determined on a PTI "Quantacount" equipped with a 150-W xenon lamp: 3 h irradiation at 480 nm. [d] Solution was irradiated at 480 nm, determined on JASCO spectroirradiator, calibrated with thermopile and potassium ferrioxalate (at 360 nm). [e] Error, ±15%.

of the "reducing" electron is unknown.[7,8] More relevant to the present study is the work of Barton, Haynes, and their co-workers who showed that simple Lewis acids efficiently catalyze the insertion of triplet oxygen into conjugated dienes to yield cyclic peroxides.[9] A model for this reaction was proposed involving the formation of a diene cation radical. A consequence of this model was that oxygenation of substrates other than dienes should have been possible, provided that the reaction of the cation radical with oxygen (or superoxide) were thermodynamically favored. Diphenylethylene and its derivatives were exam-

(1) Publication No. 394 from the Photochemistry Unit, University of Western Ontario.

(2) On leave from College of Humanities and Social Sciences, Iwate University, Japan.

(3) Al-Ekabi, H.; de Mayo, P. *J. Org. Chem.* **1987**, *52*, 4756.

(4) (a) Evans, A. G.; Jones, N.; Jones, P. M. S.; Thomas, J. H. *J. Chem. Soc.* **1956**, 2757. (b) Tadros, W.; Sakla, A. B.; Abdou, S. E. *Ibid.* **1972**, 2839.
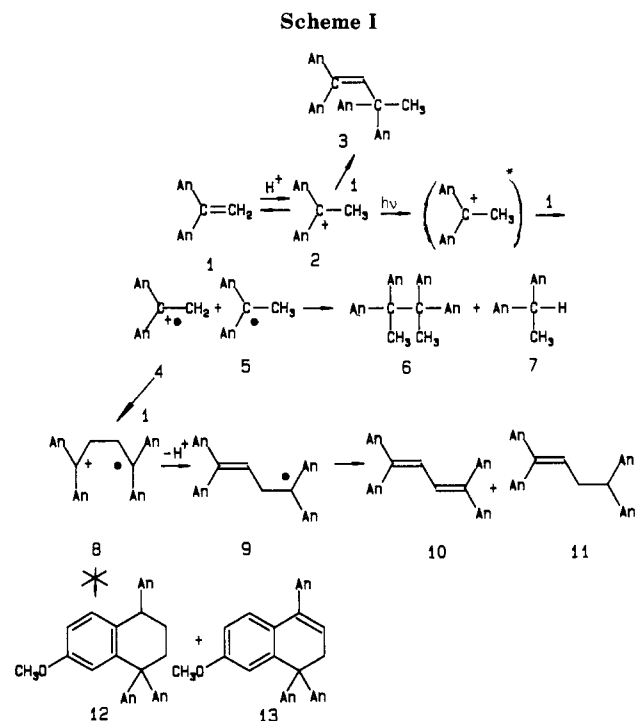
(5) Childs, R. F. *Rev. Chem. Intermed.* **1980**, *3*, 285.

(6) Cabell-Whiting, P. W.; Hogeveen, H. *Adv. Phys. Org. Chem.* **1973**, *10*, 129.

(7) (a) Van Tamelen, E. E.; Cole, P. M. *J. Am. Chem. Soc.* **1971**, *93*, 6158. (b) Owen, E. D.; Allen, D. M. *J. Chem. Soc., Chem Commun.* **1973**, 95.

(8) Van Tamelen, E. E.; Greelaw, R. H.; Schumacher, H. *J. Am. Chem. Soc.* **1971**, *93*, 6151.

(9) Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans.* **1975**, 2055.

Scheme I

ined, and 1,2-dioxanes were obtained.[10] It was proposed that the olefin radical cation, formed upon irradiation of the CT complex of the olefin with SbCl$_5$, reacts with another molecule of olefin to give the dimer radical cation **8**. The latter reacts with oxygen to give the tetraaryl-1,2-dioxane. The species **8** is also that responsible for product formation in the 9,10-dicyanoanthracene-sensitized dimerization of **1**,[11-13] as well as in the CdS-mediated process.[3] In all three cases it is the molecule of **1** (neutral) which is acted upon and which is converted to the reactive radical cation **1**$^{\bullet+}$.

Results and Discussion

Steady-State Irradiation. The foregoing suggested that the irradiation of **1** be attempted in homogeneous acid medium. Solution of **1** in various concentrations of trifluoroacetic acid in benzene gave a deep orange color (λ_{max} 500 nm, ϵ 9.5 × 10^4 M^{-1} cm^{-1}) attributed to the ion **2**. Irradiation of **1** (4.2 × 10^{-2} M) with light λ >430 nm under these acid conditions gave five products analyzed by GLC and HPLC and identified spectroscopically after isolation by flash chromatography on silica gel.[3] No reaction occurred under these conditions when the acid was omitted, which implicated **2** as the species excited. The products were the "acid-catalyzed" dimer **3** together with (Table I) **6, 7, 10**, and **11**. The first two products strongly suggested that a radical **5** was involved, leading to Scheme I as the overall process for the formation of all products. In this scheme the original molecule of **1** acted upon does not generate the radical ion directly, as indicated in the three previous examples cited, but acts as a reagent. In this respect the process more resembles the interesting work of Moutet and Reverdy,[14] in which a zinc tetraphenyl-

porphyrin radical ion is excited and abstracts an electron from 1,1-diphenylethylene (DPE) to give the radical cation of that species which reacts with a further molecule of DPE to give dimeric products.

The analysis for **6** was complicated by the observation that its decomposition took place on GLC to give **1** and **7**, in what appeared to be 1:1 ratio. The identity of the products and that the ratio was indeed 1:1 was shown by controlled thermolysis above the mp in a sealed tube. The estimation of **6** and **7** by HPLC presented no problems. It was further shown the yield of **3** obtained was unchanged at low conversion whether in the presence of light or not.

The quantum yields for **6, 7, 10** and **11** at 3% conversion were very low at 480 nm (Table I), indicating the occurrence of an energy-wasting process. Since no fluorescence (Φ_F < 10^{-3}) could be observed the most likely rationalization is the participation of the ubiquitous back electron transfer,[15] in this case regenerating ground-state **2** and **1**. Table I also shows the effect of acid concentration on the quantum yields of the products at 480 nm. Since increase in acid concentration required a shift in the ethylene-cation equilibrium toward the protonated ethylene, and hence a concomitant *decrease* in neutral ethylene concentration, for clarity the ratios of the concentrations of **1** to its initial concentration are given in Table I.[16]

If the formation of **10** and **11** were to proceed only through a common intermediate, such as indicated in eq 1 and 2 for **8** then **10** and **11** should have the same dependence on the concentration of

$$4 + 1 \rightarrow 8 \rightarrow 9 \tag{1}$$

$$9 + 9 \rightarrow 10 + 11 \tag{2}$$

pendence on the concentration of **1** (and **4** which depends on [**1**]) and also, at a particular original concentration of **1**, on the concentration of acid. This is not the case, and hence some other process must be involved. The dimerization of **4** is conceivable, which, with the loss of two protons, would give **10** (eq 3). Disproportionation of **5** would give **1** and **7** (eq 4), but disproportionation of **5** and **9** may lead to **7** and **10** (eq 5) or **1** and **11** (eq 5a).

$$4 + 4 \rightarrow 10 \tag{3}$$

$$5 + 5 \rightarrow 1 + 7 \tag{4}$$

$$5 + 9 \rightarrow 10 + 7 \tag{5}$$

$$5 + 9 \rightarrow 1 + 11 \tag{5a}$$

Since we have found that the quantum yield for **11** is larger than that for **10**, we interpret this as indicating that eq 5a is more important than eq 2-5 at relatively low concentrations of acid. The tentative inclusion of eq 5a rationalizes why the sum of the quantum yields of **10** and **11** (derived from **4**) is greater than that of **6** and **7** (derived from **5**). Though the concentration of **4** and **5** decreases with increasing concentration of acid, increasing importance of eq 3 and 4 would lead to an increase in **10** and **7** at the expense of **11**. Since the formation of **6** is doubly dependent on the concentration of **5** (and hence of **1** and of acid), the sharp decrease with acid is not surprising.[17] Furthermore, the amount of acid-catalyzed dimer **3** de-

(10) Haynes, R. K.; Probert, M. K. S.; Wilmot, I. D. *Aust. J. Chem.* **1978**, *31*, 1737.

(11) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356.

(12) Mizuno, K.; Ishii, M.; Otsuji, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5570 (footnote 8).

(13) (a) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. (b) Mattes, S. L.; Farid, S. *Ibid.* **1983**, *105*, 1386.

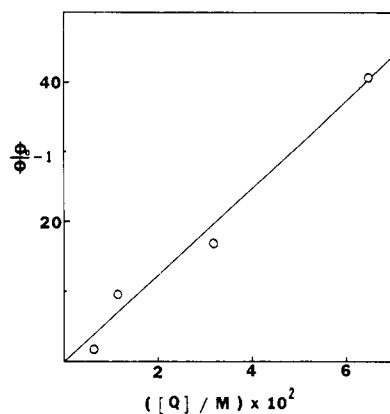(14) Moutet, B. G.; Galland, B.; Reverdy, G. *Electrochim. Acta* **1987**, *32*, 175.

(15) Mattes, S.; Farid, S. In *Organic Photochemistry*; Padwa, A.; Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233.

(16) The concentrations of **2** is independent of the concentration of **1** and of acid in these experiments, because only **2** is absorbing the light, and at all concentrations used essentially all the light at 480 nm was absorbed. The concentration of **2** thus depends only on the light intensity.

(17) The situation is further complicated by the acid-catalyzed decomposition of **6** to give **1** and **7**: a solution (1.29 × 10^{-3} M) of **6** in benzene-trifluoroacetic acid (1.62 M) decreased by 10% in 4 h at room temperature.

Figure 1. Effect of 1,2,4-trimethoxybenzene, as quencher, on the quantum yield of 6 (r = 0.992, slope 6.5 × 10^2 M^{-1}): [DAE] = 4.2 × 10^{-2} M, [TFA] = 1.62 M.

Table II. Quenching of 10, 11, and 7 with TMB^a

10^2[quencher], M	$10^3\Phi^b$		
	10	11	7
0	0.90	1.0	0.41
0.65	0.65	0.49	0.30
1.3	0.40	0.27	0.20
3.2	0.23	0.08	0.09
6.5	0.16	0.07	0.04

^{a}[DAE] = 4.2 × 10^{-2} M, [TFA] = 1.62 M. ^{b}Error, ±15%.

creases to 40% by increasing the concentration of TFA from 0.13 to 1.62 M. These results show the concentration of the neutral molecule 1 in acidic solution has an important role both in the dark and in the photoreaction.

Quenching Experiments. One method of demonstrating the participation of an electron-transfer process involves the quenching of that process by the addition of an electron-transfer agent.[14] In the present instance an electron donor better than 1 is indicated and 1,2,4-trimethoxybenzene (TMB, $E_{1/2}^{ox}$ = 1.12 V vs SCE[18]) appeared suitable. Quenching of the singlet or triplet of 2 appeared to be thermodynamically prohibited, but two species might be expected to be susceptible to quenching by electron transfer: 2* and the radical cation 4. In competing with 1 for 4, or in interfering with other processes involving 4, TMB is unambiguously a quencher, but in competing with 1 for 2* (eq 6a or 7a) the situation is more complex. Trapping of 2* by TMB still produces 5

$$2^* + 1 \longrightarrow 4 + 5 \longrightarrow 2 + 1 \quad (6)$$
$$\longrightarrow \text{products} \quad (6a)$$
$$2^* + \text{TMB} \longrightarrow 5 + \text{TMB}^{\bullet+} \longrightarrow 2 + \text{TMB} \quad (7)$$
$$\longrightarrow \text{products} \quad (7a)$$

though not 4 and so is not directly a quencher for 5. But as has been pointed out the quantum yield of 6 is very low, which strongly suggests that back electron transfer (eq 6 and 7) is important. That quenching by TMB is observed for 6 indicates that eq 7 is relatively more important than eq 6. If the mode of formation of 6 be as indicated in Scheme I then its quenching should give a linear Stern–Volmer, as is the case (Figure 1). Predictions concerning the quenching of 10, 11, and 7 (Table II) are not possible since the routes to these products are not yet precisely defined.[19]

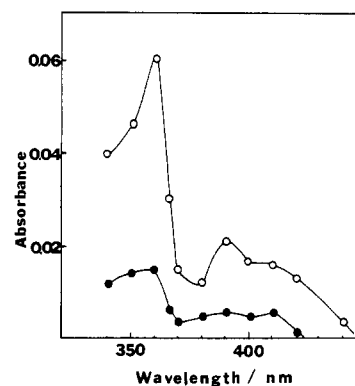(18) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* 1964, *86*, 4124.

Figure 2. Transient absorption spectra produced in argon-saturated benzene solution containing 2.4 × 10^{-4} M of 1 and 0.52 M of trifluoroacetic acid: (a) 100 μs after flash (O); (b) 200 μs after flash (●).
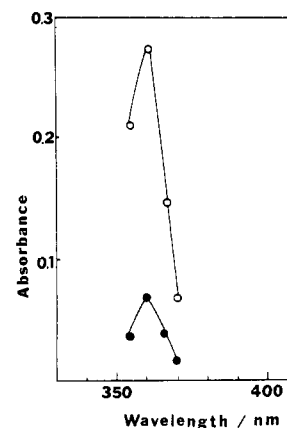

Figure 3. Transient absorption spectra observed on flash photolysis of 4.2 × 10^{-3} M of 1 and 2.5 × 10^{-5} M of DCA: (a) 100 μs after flash (O); (b) 200 μs after flash (●).

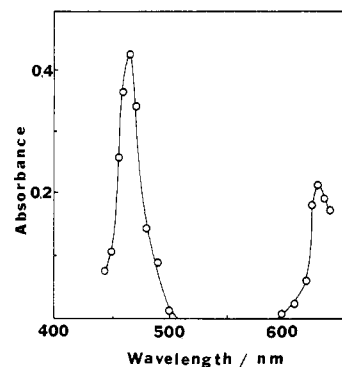**Figure 4.** Transient absorption spectrum observed after 3 ms of flash photolysis of 4.2 × 10^{-3} M of 1 and 2.5 × 10^{-5} M of DCA.

Flash Photolysis. The nature of the products from the irradiation of 2 was strong evidence for the electron

(19) A new product was obtained by the acid-catalyzed reaction of 1 with TMB: this dark reaction was not accelerated by irradiation. On the basis of spectroscopic evidence it is assigned the structure i. ^{1}H NMR:
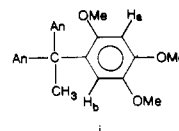
7.04 (4 H, d, J = 9.08 Hz), 6.77 (4 H, d, J = 8.78 Hz), 6.53 (1 H, s, H_b), 6.31 (1 H, s, H_a), 3.88 (3 H, s, OMe), 3.93 (6 H, s, 2 O*Me*), 3.57 (3 H, O*Me*), 3.43 (3 H, s, O*Me*), and 2.17 ppm (3 H, s, CH_3). Precise mass calcd for $C_{25}H_{28}O_5$ 408.1937, found 408.1934.

transfer and the formation of the radical **5** and the radical ion **4**. The complex nature of the electron-transfer quenching of the reaction, however, made it desirable to seek other evidence for the participation of **4**. Flash photolysis (xenon) of a solution (2.4×10^{-4} M) of **1** in benzene containing 0.52 M trifluoroacetic acid generated a transient absorption shown in Figure 2 after 100 and 200 μs after flashing. The absorption extended from ~340 to 440 nm, where the absorption of **2** is comparatively weak, but the region 450–510 nm was not accessible. No transient could be observed >510 nm. The decay of this transient appeared to be second order ($k/\epsilon = 5.5 \times 10^5$ cm s^{-1}) at 360 nm. No transient was observed when the solution was air-saturated or when the trifluoroacetic acid was omitted. This transient appeared to have the properties of the radical ion, and confirmation was sought in another mode of generation of the same species.

9,10-Dicyanoanthracene (DCA) has been frequently used as a photochemically induced electron acceptor.[15] When a solution of **1** (4.2×10^{-3} M) in benzene containing DCA (2.5×10^{-5} M) was flashed two transients could be observed (Figure 3, after 100 and 200μs; Figure 4, after 3 ms). The decay of both transients appeared to be second order (k/ϵ 1.3×10^5 cm s^{-1} at 360 nm; $k/\epsilon = 4.8 \times 10^3$ cm s^{-1} at 465 nm). These transients were not observed when **1** or DCA were flashed separately. The transient shown in Figure 3, attributed to the radical ion **4**, is very similar to that shown in Figure 2 and confirms the scheme proposed. The transient shown in Figure 4 is attributed to the DCA radical anion formed concomitantly in the electron transfer.[20,21]

Addition of the quencher TMB (2.4×10^{-3} M) to a solution of **1** (2.4×10^{-4} M, actual concentration of **2** is 1.2 $\times 10^{-5}$ M) containing trifluoroacetic acid (0.52 M) completely quenched the transient in Figure 2. Instead, there was observed the growth of a different species. Since this was produced under similar conditions, but in the absence of **1** it was presumably derived from TMB, and its nature was not further investigated.

Conclusions. The irradiation of the ion **2** is believed to induce electron transfer from **1** to **2***. The nature of the products **10** and **11**, produced by the irradiation of **1** in acidic medium, has provided evidence that the radical ion **4** is involved as an intermediate. This has been confirmed by the direct observation of an intermediate, identified as the species **4**, which has also been generated using DCA as the acceptor. This supports the view that **1** is acting as the donor in the reaction of **2***. That the latter is acting as the acceptor and so generates **5** is indicated by the formation of **6** and to a lesser extent that of **7**. It was under the conditions available to us not possible to detect **5** directly. The reduction of an excited carbenium is a process expected to have some generality.[22]

Experimental Section

Chemicals. Compounds **1** and **7** were prepared according to the literature method.[4] Benzene (spectral grade, BDH), methanol (HPLC grade, BDH), and acetonitrile (HPLC grade, BDH) were used without further purification. Trifluoroacetic acid was Baker Analyzed Reagent.

General Irradiation Procedure. Irradiations of trifluoroacetic acid containing solutions of **1** in benzene (4.2×10^{-2} M) were carried out in the absence of oxygen (four freeze–pump–thaw cycles) using a 150-W xenon lamp together with a Corning glass filter 3-72. In all cases a known amount of *n*-hexadecane as calibrant was added to the mixture. After irradiation, the solution was washed with water to remove the acid and dried (anhydrous magnesium sulfate). The photoproducts (except **7**) were analyzed with a Varian 3700 gas chromatograph equipped with a flame ionization detector, which was connected to a Hewlett-Packard 3390A integrator. Analysis was performed on a 2 m × 2 mm column packed with OV-101 (3%) on Chromosorb W (H.P.), 80–100 mesh. For determination of the amount of **7**, analysis was performed with a Varian 5000 Liquid Chromatograph. In the HPLC a radial pack cartridge (8C1810μ, Water) was used. The detector was a Lambda-Max Model 481 LC spectrophotometer (Waters), which was connected to a Hewlett-Packard 3390A integrator. The solvent used for HPLC was a mixture of methanol, acetonitrile, and water in a volume ratio of 100:110:90. Since the dimer **6** was converted into equimolar amounts of **1** and **7** at the high temperatures required for GLC, the amount of **6** could be estimated by subtracting the true amount of **7** (obtained from HPLC) from the total amount indicated by GLC. Since the peaks for **6** and the acid dimer **3** overlap in HPLC it was necessary to use both GLC and HPLC techniques to determine the yields of photoproducts.

Quantum Yield. A JASCO spectroirradiator and a PTI Quantacount apparatus were used for the quantum yield determination. Potassium ferrioxalate was used as an actinometer (360 nm) calibrated at 480 nm with a thermophile.

Flash Photolysis. Flash photolysis was carried out with a FP1000 flash photolysis system (PRA). The flash energy was 50 J and full width at half-maximum was about 10 μs. An unfiltered 75-W high-pressure Xe lamp was used as the monitoring lamp. The monitoring beam was focused through the quartz sample cell (10 cm path) into a Model 1700-II Czerny-Turner monochromater (slits set for 2-nm resolution). The monochromater output was detected by an RCA 1P28 photomultiplier. All the samples for flash photolysis were saturated with argon.

Photochemical Preparation of 6, 7, 10, and 11. Solutions of **1** in benzene (250 mg in 6 mL) were irradiated in the presence of trifluoroacetic acid (1.6 M) at λ > 430 nm under argon for 2 h. After irradiation, the solution was washed with water to remove the acid, and the filtrate from two identical experiments were combined and separated by flash chromatography on silica gel (230–400 mesh) using methylene dichloride–hexane (3:1) as eluent. Further separation was achieved by thin-layer chromatography using the same solvent combination. The products **6, 7, 10,** and **11**, after separation, were identified by spectral data.[3]

Registry No. **1**, 4356-69-8; **2**, 25836-80-0; **3**, 39117-63-0; **6**, 110173-91-6; **7**, 10543-21-2; **10**, 54655-89-9; **11**, 110173-90-5; TFA, 76-05-1; TMB, 135-77-3; DCA, 1217-45-4.

(20) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391.
(21) Davis, H. F.; Lohray, B. B.; Gopidas, K. R.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 3685.

(22) The formation of triphenylmethyl *radicals* in the study of the photolytic generation of the corresponding cation may be an example: McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1986**, *108*, 7023.