

# Photochemistry of *trans*-10,11-Dibromodibenzosuberone: A Near-UV Photoacid Generator

T. Gannon and W. G. McGimpsey\*

Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Received July 17, 1992

Pulsed laser irradiation of *trans*-10,11-dibromodibenzosuberone, **I**, in room-temperature benzene and acetonitrile solutions resulted in efficient debromination to yield dibenzosuberone, **II**. In benzene, the transient absorption due to the bromine atom ( $\text{Br}^\bullet$ )-benzene  $\pi$ -complex was observed, while in acetonitrile with added  $\text{Br}^-$  the transient absorption due to  $\text{Br}_2^{\bullet-}$  was detected. In both cases, transient production was instantaneous, indicating that  $\text{Br}^\bullet$  is a primary photoproduct. Transient actinometric experiments using the benzophenone triplet state as a standard and  $\text{Br}_2^{\bullet-}$  as the  $\text{Br}^\bullet$  probe allowed the determination of the quantum yield for  $\text{Br}^\bullet$  production,  $\Phi = 2.4 \pm 0.6$ . In acetonitrile, in the presence of the H-atom donor, 2-propanol,  $\text{Br}^\bullet$ - $\text{Br}^\bullet$  recombination to give  $\text{Br}_2$  competes with H-atom abstraction to yield the acid HBr. Under high-intensity laser irradiation, recombination and H-atom abstraction are competitive, while under low flux laser or UV lamp irradiation, H-atom abstraction is very efficient. In the presence of 1-3 M 2-propanol, acid formation was found to be nearly quantitative.

## Introduction

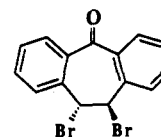
The rate of acid-catalyzed thermal polymerization in the production of photoresists can be controlled by generating the acid photolytically. A variety of photoacid sources, including aryldiazonium, iodonium, and sulfonium salts have been used to produce both positive and negative tone resists. For diazonium salts with complex metal halide anions, irradiation yields a Lewis acid derived from the complex anion which can then react with protic species present to produce a strong acid. Iodonium and sulfonium salts undergo H-atom abstraction to give strong acids.<sup>1,2</sup>

Since diaryliodonium salts and purified triarylsulfonium salts generally have low absorptivity in the near-UV (>300 nm) and visible region of the spectrum, their use as photoacid generators usually requires irradiation in the deep UV. This is a disadvantage due to the absorptivity of the resist material in the same spectral region resulting in direct excitation which may lead to undesirable side reactions. While diazonium salts exhibit varied absorptivity through the near-UV and visible region, thermal instability limits their usefulness.<sup>1</sup>

Recently, Scaiano and co-workers<sup>3</sup> have reported that 266-nm Nd/YAG laser irradiation of a vicinal dibromide—1,2 dibromoethane—in room-temperature acetonitrile solution leads to the production of bromine atoms,  $\text{Br}^\bullet$ , with quantum yield  $\Phi = 2.3 \pm 0.5$ . Thus, photoinduced homolytic carbon-bromine bond cleavage produces the 2-bromoethyl radical which thermally loses a second  $\text{Br}^\bullet$  to form ethylene. When the irradiation was carried out in the presence of a H-atom donor such as 2-propanol (IPA) or methanol, generation of acid was observed presumably as the result of H-atom abstraction by  $\text{Br}^\bullet$ . However, while dibromoethane appears to be an efficient photoacid generator, due to its absorption characteristics, it is still necessary to irradiate in the deep UV.

We have used a combination of CW irradiation and nanosecond laser flash photolysis to study the photo-

chemical generation of  $\text{Br}^\bullet$  and subsequent acid production from *trans*-10,11-dibromodibenzosuberone, **I**, in room-temperature acetonitrile and benzene solutions. Like dibromoethane, **I** is a vicinal dibromide, and it is thermally stable at ambient temperatures, but unlike dibromoethane, it has relatively high absorptivity in the 300-400-nm region.



**I**

Since  $\text{Br}^\bullet$  is not directly detectable by absorption spectroscopy, we have employed two transient "probes" to detect and quantify the extent of photochemical debromination, the  $\text{Br}^\bullet$ -benzene  $\pi$ -complex and the bromine radical anion,  $\text{Br}_2^{\bullet-}$ . We have also shown that acidic solutions are produced when **I** is irradiated in acetonitrile in the presence of IPA.

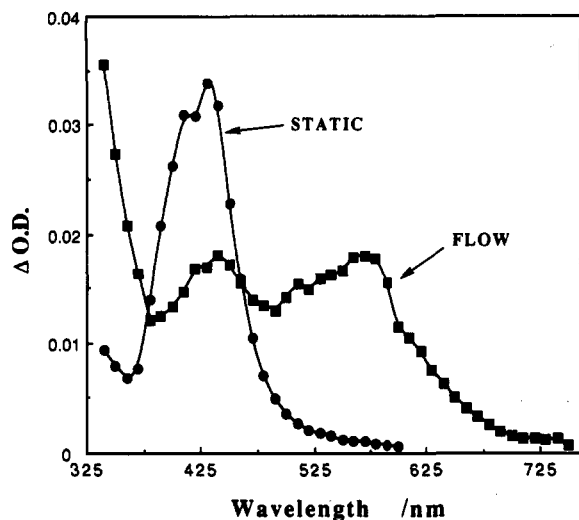
## Experimental Section

**Materials.** **I** and **II** were obtained from Aldrich and were recrystallized twice from methanol prior to use. Benzene and IPA were Aldrich spectrophotometric grade and were used as received. Acetonitrile was Aldrich anhydrous grade and was also used as received. Tetra-*n*-butylammonium bromide (Aldrich 99%) was recrystallized from hexane. Benzophenone (Aldrich 99%) was recrystallized from methanol.

**Product Studies.** For identification of the photolysis products, irradiations were carried out on static, dry nitrogen-degassed 5-mL solutions of **I** in benzene. Samples were irradiated for 20 min through Pyrex in a Rayonet reactor using 300-nm lamps. Solvent was then removed by rotary evaporation, and the residue was resolubilized with 1 mL of benzene. Sample analysis was by reversed-phase HPLC using a Hewlett-Packard 1040 HPLC equipped with a RP18 reversed-phase Hypersil column. The eluent was 85:15 methanol-water.

**Laser Flash Photolysis.** The laser flash photolysis system and experimental technique have been described in detail

(1) Pappas, S. P. *Imaging Tech.* 1985, 11, 146.  
 (2) McKenan, D. R.; Schaedeli, U.; MacDonald, S. A. *J. Polym. Sci., Part A: Polym. Chem.* 1989, 27, 3927.  
 (3) Scaiano, J. C.; Barra, M.; Calabrese, G.; Sinta, R. *Chem. Commun.*, in press.



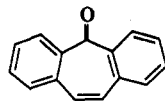
**Figure 1.** Transient absorption spectrum obtained 500 ns after laser photolysis of I in degassed benzene solution: (a) (square symbols) flow sample; (b) (round symbols) static sample.

elsewhere.<sup>4</sup> Briefly, approximately 150-mL solutions of I were degassed with dry nitrogen in a reservoir connected by viton tubing to a specially constructed  $7 \times 7$ -mm<sup>2</sup> quartz flow cell. The cell was connected by viton or silicon tubing to a peristaltic pump with variable flow rate. This flow system ensured that a fresh volume of sample was irradiated by each successive laser pulse. Irradiation was by either a Lumonics EX510 excimer laser (308 nm; 25 mJ/pulse; 8-ns duration) or the frequency tripled output of a Continuum Surelite Nd/YAG laser (355 nm; <50 mJ/pulse; 6 ns duration). The detection system, controlled by a PC, allowed acquisition of time-resolved point-by-point absorption spectra as well as kinetic decays at individual wavelengths.

**Acid Determination.** Acid generation was determined for both laser and UV lamp irradiation. For laser irradiation, continuously degassed 3-mL static samples of I in acetonitrile were irradiated by 400 pulses from the excimer laser. For the lamp irradiation, degassed 3-mL samples were exposed to the Pyrex-filtered output of a 450-W Hanovia medium-pressure mercury arc lamp for 20 min. The absorbance at 308 nm for the laser samples was matched with the absorbance at 350 nm of the lamp samples. IPA concentrations from 0 to 3 M were used. Following irradiation, samples were treated with NaI and titrated with NaOH.

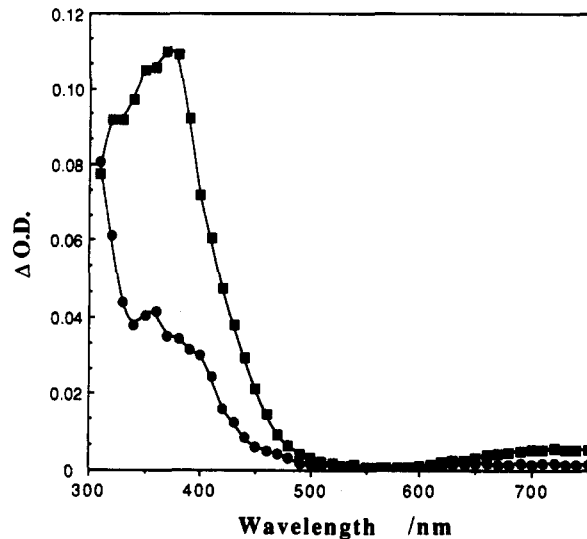
## Results and Discussion

**(a) Debromination of I.** CW lamp irradiation of I in degassed benzene solution yielded only one product which is identified as dibenzosuberone, II, based on a comparison of the HPLC analyses of the reaction mixture and an authentic sample of II.



II

Further support for the photochemical debromination of I to form II is obtained when a degassed 1 mM solution of I in benzene was irradiated by a pulsed 355-nm frequency-tripled Nd/YAG laser or 308-nm excimer laser. The transient absorption spectrum obtained 500 ns after the laser pulse is shown in Figure 1 (square symbols). The



**Figure 2.** Transient absorption spectrum obtained 500 ns after laser photolysis of I in degassed acetonitrile solution: (a) (square symbols) 0.03 M TBAB added; (b) (round symbols) absence of TBAB.

spectrum exhibits three absorption bands at  $\lambda = 560$ , 440, and  $\sim 320$  nm. The 440-nm band is identical to the triplet-triplet absorption spectrum of II.<sup>5</sup> Consistent with the assignment of this band to triplet II is our observation that the intensity of the 440-nm absorption was dependent on the flow rate of the solution of I through the cell, increasing as the flow rate was decreased (in fact, only the 440-nm band was observed when I was irradiated in a static cell, see Figure 1 (round symbols)). This indicates that the absorption was not due to a primary photoproduct. We conclude, then, that ground state II is produced by debromination of I as a result of one laser pulse and then is excited to form the triplet state by a subsequent laser pulse.

A second absorption band observed at 560 nm is identical to that reported for the  $\pi$ -complex formed when Br<sup>\*</sup> is scavenged by benzene<sup>6,7</sup> and is thus assigned to this transient. The 320-nm shoulder in the transient absorption spectrum is tentatively assigned to molecular bromine, Br<sub>2</sub> (formed by Br<sup>\*</sup>-Br<sup>\*</sup> recombination), which absorbs strongly in the 300  $\rightarrow$  400 nm region. However, interference due to the ground-state absorptions of both I and II in the same spectral region does not allow an unambiguous assignment.

There was no transient absorption observed which could be attributed to the triplet state of I, and attempts to observe the triplet by sensitization were unsuccessful. It is likely then, that the observed photochemistry is derived from the singlet manifold.

Figure 2 (round symbols) shows the transient absorption spectrum obtained following irradiation of a solution of I in acetonitrile by the excimer laser. There remains the indication of a large absorption at wavelengths less than 300 nm (Br<sub>2</sub>), and as was expected, the transient absorption assigned to the  $\pi$ -complex was no longer observed. However, a new absorption with a shoulder at 360 nm extending into the visible region was detected. In order to confirm that loss of bromine from I also occurs in acetonitrile, a similar laser experiment was carried out in

(4) Wang, Z.; Weininger, S. J.; McGimpsey, W. G. *J. Phys. Chem.*, in press.

(5) McGimpsey, W. G., unpublished data.

(6) McGimpsey, W. G.; Scaiano, J. C. *Can. J. Chem.* 1988, 66, 1474.

(7) Buhler, R. E. *Rad. Res.* 1972, 4, 233.

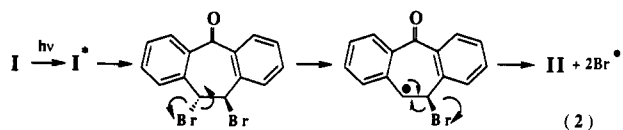
the presence of 0.03 M tetra-*n*-butylammonium bromide (TBAB), a source of Br<sup>-</sup> in polar solvents. Br<sup>-</sup> has been shown to react with Br<sup>•</sup> at a diffusion-controlled rate to form the transient radical anion Br<sub>2</sub><sup>•-</sup>,<sup>3</sup> which absorbs strongly in the 350–400 nm region.<sup>8</sup> Thus Br<sub>2</sub><sup>•-</sup>, like the π-complex in benzene, acts as a probe for the detection of Br<sup>•</sup>. Figure 2 (square symbols) shows the transient spectrum obtained following addition of TBAB, confirming the presence of Br<sub>2</sub><sup>•-</sup> and therefore the debromination of I in acetonitrile. The similarity between the spectrum obtained in the presence of TBAB and the shoulder at 360 nm observed in the absence of TBAB may indicate that Br<sub>2</sub><sup>•-</sup> is also formed in the absence of added bromide.<sup>9</sup>

(b) **Quantum Yield of Debromination.** Br<sub>2</sub><sup>•-</sup> has a well-established extinction coefficient ( $\epsilon_{360}(\text{Br}_2^{\bullet-}) = 9900 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>10</sup> and therefore it can be used with an actinometer to determine the quantum yield of debromination. Benzophenone was selected as an actinometer. The triplet-triplet absorption of benzophenone has  $\lambda_{\text{max}} 525 \text{ nm}$ <sup>11</sup> with  $\epsilon_{525} = 7800 \text{ M}^{-1} \text{ cm}^{-1}$  in benzene<sup>12</sup> and a quantum yield for triplet formation  $\Phi = 1.0$ .<sup>13</sup> Samples of benzophenone in benzene and I in acetonitrile with matched absorbances at the laser wavelength were irradiated, and the absorbances due to benzophenone triplet and Br<sub>2</sub><sup>•-</sup> were measured at the appropriate monitoring wavelengths as a function of laser dose. The quantum yield for Br<sup>•</sup> formation was calculated from eq 1. In this calculation

$$\frac{\Phi_{\text{Br}^{\bullet}}}{\Phi_{\text{BZP}}} = \frac{\Phi_{\text{Br}_2^{\bullet-}}}{\Phi_{\text{BZP}}} = \frac{O.D._{\text{Br}_2^{\bullet-}}}{O.D._{\text{BZP}}} \cdot \frac{\epsilon_{\text{BZP}}}{\epsilon_{\text{Br}_2^{\bullet-}}} \quad (1)$$

it was assumed that all of the Br<sup>•</sup> produced were scavenged by Br<sup>-</sup> and therefore that all of the absorption at 360 nm was due to Br<sub>2</sub><sup>•-</sup>. This is not unreasonable given the large Br<sup>-</sup> concentration and the diffusion-controlled rate of Br<sup>•</sup> scavenging by Br<sup>-</sup>. We found  $\Phi_{\text{Br}^{\bullet}} = 2.4 \pm 0.6$ , in good agreement with the result obtained for 1,2-dibromoethane.<sup>3</sup>

With this quantum yield information, the photochemistry of I can be summarized by eq 2. That is, excitation of I leads initially to loss of one Br<sup>•</sup>. The second Br<sup>•</sup> is subsequently lost in a rapid thermal process which is almost certainly driven by the conjugation gained by proceeding from I to II.



(c) **Photoacid Generation.** Br<sup>•</sup> is a relatively efficient H-atom abstractor. Reaction of Br<sup>•</sup> with methanol and IPA to form HBr was reported to take place with rate constants of  $10^6$ – $10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>3</sup> Thus, we expected that laser irradiation of I in acetonitrile with added IPA would

**Table I. Acid Concentrations Determined Following Irradiation of I in Acetonitrile Solutions in the Presence and Absence of IPA (in mM)**

light source	IPA concn (M)			
	0	1	2	3
laser 308 nm	0.4 ± 0.2	0.8 ± 0.3	0.9 ± 0.3	0.9 ± 0.3
lamps	0.9 ± 0.5	1.6 ± 0.6	2.1 ± 0.5	2.5 ± 0.8

lead to generation of HBr which could then be detected by titration of the irradiated samples with base.

Laser irradiation (400 pulses, 35 mJ/pulse, 308-nm excimer laser) of I in acetonitrile (ca.  $5 \times 10^{-4} \text{ M}$ ) with both 0.03 M TBAB and 0–3 M IPA added gave indirect evidence for the reaction of Br<sup>•</sup> with IPA. It was observed that the transient absorbance at 360 nm due to Br<sub>2</sub><sup>•-</sup> decreased as the IPA concentration increased, indicating that Br<sup>•</sup> undergoes a reaction in competition with the Br<sup>-</sup> scavenging reaction (H-atom abstraction or Br<sup>-</sup>-Br<sup>•</sup> recombination). Product studies also support this conclusion. When degassed samples containing 0–3 M IPA (no TBAB) were irradiated and subsequently titrated with base, more base was required than for titration of identical nonirradiated samples, and furthermore, those samples containing IPA required more base to titrate than those which contained no IPA. Such a result would appear to confirm photogeneration of acid in the presence of IPA. However, considering the strong indication from transient absorption spectra and UV-vis spectra obtained after laser irradiation that Br<sub>2</sub> is produced during irradiation, and considering that Br<sub>2</sub> also reacts with base, this evidence alone does not give conclusive proof for acid generation. Under laser irradiation, high light fluxes lead to high Br<sup>•</sup> concentrations, increasing the rate of Br<sup>-</sup>-Br<sup>•</sup> recombination. At high recombination rates H-atom abstraction will not compete efficiently. In order to avoid possible interference due to Br<sub>2</sub>, irradiations were carried out with a smaller laser dose (400 pulses, <10 mJ/pulse). Under these lower flux conditions, only minor changes were observed in the region of the absorption spectrum where Br<sub>2</sub> absorbs, indicating that recombination is of little significance. As an added precaution, NaI was added to the irradiated samples before titration (in order to reduce Br<sub>2</sub> to Br<sup>-</sup>). Taking these precautions, it can be safely assumed that the difference between titration volumes for irradiated and nonirradiated samples represents the amount of photogenerated acid present. Table I, row 1, gives the acid concentrations found for laser irradiation in the presence of 0–3 M IPA. These values are corrected for the small volume of base required to titrate the nonirradiated samples. The acid concentrations found not only confirm the quantitative debromination of I measured by benzophenone actinometry (vide supra), but that the reaction of Br<sup>•</sup> to form acid is nearly quantitative as well (ca.  $1 \times 10^{-3} \text{ M}$  acid formed vs ca.  $2(5 \times 10^{-4}) \text{ M}$  Br<sup>•</sup> available in the starting material.)<sup>14</sup>

Low flux irradiations of similar samples (ca.  $1 \times 10^{-3} \text{ M}$ ) were also performed using a Pyrex-filtered medium-pressure mercury arc lamp (20 min, 450 W,  $\lambda > 310 \text{ nm}$ ). Sample absorbances at 350 nm were matched to the laser sample absorbance at 308 nm. No UV-vis absorption due to Br<sub>2</sub> was observed. Titration of lamp irradiated samples with base (with added NaI) yielded the same qualitative results as the laser irradiated samples. Table I also gives

(8) Zehavi, D.; Rabani, J. *J. Phys. Chem.* 1972, 76, 312.

(9) It is unclear at this time whether Br<sup>-</sup> is present in solution due to a minor amount of heterolytic cleavage of I competing with homolytic cleavage or as a secondary product formed as a result of H-atom abstraction by Br<sup>•</sup> from trace amounts of H-donors.

(10) Hug, G. L. *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution*; National Bureau of Standards: Washington, 1981; NSRDS-NBS 69, p 160.

(11) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data Suppl.* 1986, 15, 1.

(12) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* 1988, 110, 511.

(13) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* 1965, 43, 2129.

(14) The production of acid in the absence of IPA may be due to H atom abstraction from either acetonitrile solvent or I.

**Table II. Molar Extinction Coefficients for Compounds I and II in Acetonitrile at Commonly Used Laser and Hg Lamp Wavelengths**

$\lambda/\text{nm}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	
	I	II
254	9600	33 000
266	9900	17 800
308	2020	11 200
313	1440	10 100
337	460	2820
355	450	2590
365	340	1900
380	170	500
405	10	10

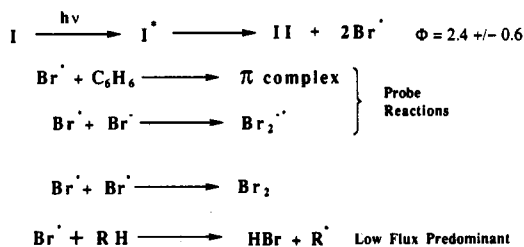
the acid concentrations found for the lamp experiments. Again, acid formation appears to be quantitative. The difference between the acid concentrations calculated for the lamp and laser experiments is simply the result of the higher starting concentration of I in the lamp experiments.

In the experiments which we have described we have not measured the effect which the extent of conversion has on the photoacid quantum yield. Table II lists the molar extinction coefficients of both I and II in acetonitrile at the wavelengths used in this study as well as other wavelengths commonly used. It is clear from these data that as the extent of conversion increases, more of the incident light will be absorbed by the photoproduct II. We are currently measuring photoacid quantum yields as a function of conversion.

### Summary

The photochemistry of I is given in Scheme I. During either laser or lamp irradiation, I undergoes photochemical

### Scheme I



debromination to yield II plus  $2\text{Br}^{\cdot}$ .  $\text{Br}^{\cdot}$  can be scavenged by either (1) benzene, to give the  $\pi$ -complex ( $\lambda$  560 nm), or (2)  $\text{Br}^{\cdot}$  in acetonitrile, to give  $\text{Br}_2^{\cdot-}$  ( $\lambda$  360 nm). Both of these transients act as probes for the generation of  $\text{Br}^{\cdot}$ . Under high flux pulsed laser irradiation, in the presence of H-atom donors,  $\text{Br}^{\cdot}$ - $\text{Br}^{\cdot}$  recombination to give  $\text{Br}_2$  competes with H-atom abstraction. Under low flux laser or lamp irradiation in the presence of H-atom donors, H-atom abstraction to give acid is the predominant decay pathway. It is interesting to note that the production of acid with low flux laser or lamp sources was shown to be nearly quantitative despite the similarity between the ground-state absorption spectra of I and II.

**Acknowledgment.** The authors wish to thank Professor J.C. Scaiano and his co-authors for communication of their results prior to publication. Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. The authors wish to thank Acton Research Corp. for their loan of a monochromator. Acknowledgement is also made to D. Ren for performing some of the preliminary photoacid measurements.