# Photochemistry of 1,2-Dibromoethyl Arenes

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UV laser photolysis of 2-(1,2-dibromoethyl)naphthalene in benzene and acetonitrile results in C-Br homolytic bond cleavage via the singlet and possibly the triplet manifolds. Cleavage produces a bromine atom, Br, and the 2-bromo-1-(2-naphthyl)ethyl radical. In benzene, the presence of Br\* is indicated by formation of the Br<sup>•</sup>-benzene  $\pi$ -complex, while in acetonitrile with added Br<sup>-</sup>, Br<sub>2</sub><sup>•-</sup> is produced. In addition to these two transient probes, the formation of acidic solutions following photolysis in the presence of a H atom donor is also an indication of Br<sup>•</sup> generation. The debromination quantum yield was determined by quantifying the formation of both Br<sub>2</sub><sup>\*-</sup>  $\Phi_{Br^*} = 0.87 \pm 0.10$ , and acid  $\Phi_{H^*} = 0.85 \pm 0.14$ . The difference between these values and those obtained for other vicinal dibromides ( $\Phi_{Br} > 2$ ) which undergo photochemical debromination followed by facile thermal C-Br cleavage is attributed to the greater stability of the 2-bromo-1-(2-naphthyl)ethyl radical relative to 2-vinylnaphthalene, the product formed by loss of the second Br<sup>•</sup>. Photolysis of the 2-bromo-1-(2-naphthyl)ethyl radical using a second laser pulse leads to further C-Br cleavage resulting in enhanced production of 2-vinylnaphthalene. UV laser photolysis of 2-bromo-9-(1,2-dibromoethyl)anthracene also causes C-Br cleavage resulting in the production of Br\* and the 2-bromo-1-(2-bromo-9-anthryl)ethyl radical. The efficiency of debromination was lower in this compound ( $\Phi_{Br^*} = 0.45 \pm 0.10$ ;  $\Phi_{H^+} = 0.48 \pm 0.11$ ) than for the naphthalene compound because of competition between cleavage from the singlet manifold and intersystem crossing to a low-energy unreactive triplet state. Like the naphthalene analog, laser photolysis of the anthrylethyl radical leads to further debromination. Both radicals exhibit unusual stability in the presence of oxygen.

# Introduction

Efficient photochemical acid generation is of great interest to the photoresist and photolithography industries. To date, the most commonly used photoacid generators have been aryl diazonium, iodonium, and sulfonium salts<sup>1-7</sup> with complex metal halide anions. When irradiated, these compounds produce very strong acids in generally good yields but also suffer from inconvenient absorption characteristics and/or poor thermal stability.

Recently, photoacid generation has been reported for a class of organic compounds called vicinal dibromides.<sup>8-10</sup> Direct photolysis of these compounds in the presence of a H atom donor results in homolytic C–Br bond cleavage to produce bromine atoms, Br<sup>•</sup>. H atom abstraction by Br<sup>•</sup> yields HBr, a strong acid. The potential advantages offered by the use of these compounds include greater thermal stability, tunability of the absorption characteristics, and a high acid quantum yield. For example, 1,2-dibromoethane<sup>9</sup> undergoes debromination (and, therefore, acid production) with a quantum yield of 2.3. We recently reported a similar quantum yield for *trans*-10,11-dibromodibenzosuberone (I).<sup>10</sup>



In each case, the high debromination yield was explained by photoinduced C-Br cleavage followed by facile thermal C-Br

cleavage which is driven by the instability of the intermediate radical relative to the product. For I, conjugation of the two phenyl rings provides a large driving force for the thermal debromination step. In addition to the high acid yield, I has an absorption spectrum which extends to the near UV, making it particularly useful in situations where deep UV irradiation is not desirable.

We undertook the present study in order to (i) determine whether high debromination yields are a general characteristic of vicinal dibromides and (ii) show that debromination and acid production could be achieved in vicinal dibromides with extended aromatic chromophores, i.e., compounds with absorption spectra in the visible range. This paper describes the fluorescence and phosphorescence spectroscopy, and the CW and transient photochemistry of 2-(1,2-dibromoethyl)naphthalene (II) and 2-bromo-9-(1,2-dibromoethyl)anthracene (III) in solution. Included in the transient photochemical results are determinations of the debromination and photoacid quantum yields as well as evidence for two-laser-induced debromination involving an intermediate radical species.



# **Experimental Section**

Materials. Unless otherwise specified, the following materials were obtained from Aldrich. Acetonitrile (MeCN), cyclohexane

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TABLE 1: Emission Parameters for II, III and Model Compounds

	$S_1$ (kcal/mol)	$T_1$ (kcal/mol)	$\Phi_{\rm F}$
II	84.1	60.8	0.010
naphthalene	91.5	60.9	0.230
III	70.6	-	0.003
9-bromoanthracene	73.2	~41	0.030

(CH), benzene (BZN), isopropyl alcohol (IPA), and ethanol (EtOH) were Spectrophotometric grade and were used as received. Bromine (99.5+%) was used as received. 2-Vinylnaphthalene (98%) and 9-vinylanthracene (97%) were recrystallized from ethanol. Benzophenone (BZP)(99%) was recrystallized from methanol prior to use. Anthracene (99.9%), 9-bromoanthracene (96%), and tetra-*n*-butylammonium bromide (TBAB)(99%) were recrystallized from hexane. Naphthalene (99+%) was recrystallized from Lancaster Synthesis and was recrystallized from ethanol and water.

Synthesis of 2-(1,2-Dibromoethyl)naphthalene (II). To a stirred solution of 2-vinylnaphthalene (3.08 g, 20.0 mmol) in CHCl<sub>3</sub> (8 mL) at 0 °C was added dropwise a solution of bromine (3.20 g, 20.0 mmol) in CHCl<sub>3</sub> (5 mL). The reaction mixture was stirred for 1 h, following which the solvent was evaporated. The resulting solid was recrystallized from aqueous EtOH to give the dibromide II (3.26 g, 52% yield), which was identified by NMR and GC-MS: mp 78-79 °C. Anal. Calcd for  $C_{12}H_{10}Br_2$ : C, 45.90; H, 3.21. Found: C, 46.04; H, 3.01.

Synthesis of 2-Bromo-9-(1,2-dibromoethyl)anthracene (III). Bromination of 9-vinylanthracene was carried out exactly as for 2-vinylnaphthalene. In addition to bromination at the vinyl side chain, GC-MS analysis indicated incorporation of a third bromine. The <sup>13</sup>C spectrum confirmed that substitution occurs at the 2 position. III was obtained as a yellow solid and recrystallized from 1:1 ethanol/methanol: 0.88 g, 42% yield, mp 142–143 °C. Anal. Calcd for  $C_{16}H_{11}Br_3$ : C, 43.83; H, 2.50. Found: C, 43.14; H, 2.24.

Fluorescence and Phosphorescence. Fluorescence spectra were obtained using a Perkin Elmer LS-50 spectrofluorimeter. Samples contained in quartz cells were outgassed with dry nitrogen and optical densities were <0.10 at the excitation wavelength. Fluorescence quantum yields were obtained for II and III using naphthalene ( $\Phi_F = 0.23$ )<sup>11</sup> and 9-bromoanthracene ( $\Phi_F = 0.03$  as measured versus anthracene,  $\Phi_F = 0.28^{12,13}$ ), respectively, as standards. Phosphorescence spectra were measured in a 77 K methylcyclohexane glass using the same instrument. Samples were contained in 3 mm i.d. cylindrical quartz cells which were placed in a specially constructed quartz dewar.

Laser Flash Photolysis. The laser flash photolysis system has been described in detail elsewhere.<sup>14,15</sup> Briefly, in the one-laser transient experiments, samples of II were irradiated with the pulses of a Lumonics EX 510 excimer laser (308 nm; 30 mJ/ pulse; 8 ns). In the two-laser experiments, the pulse from a frequency-tripled Continuum "Surelite" Nd/YAG laser (355 nm; 50 mJ; 6 ns) followed the excimer laser pulse by ca. 1-3  $\mu$ s. For the one-laser experiments with III, the 355 nm YAG laser provided the initial excitation pulse, while in the two-laser studies the 355 nm pulse was followed by the pulse from a Candela SLL 250 flashlamp-pumped dye laser (445 nm; 75 mJ; 350 ns). Samples (absorbance was less than 0.7) were contained in a specially constructed  $7 \times 7 \text{ mm}^2$  quartz flow cell. The solution was caused to flow from a reservoir through the cell by the action of a peristaltic pump. The flow ensured that each laser pulse, or pair of pulses, irradiated a fresh volume of sample. In those experiments which were run under deoxygenated conditions, air was removed by constantly bubbling a stream of dry nitrogen through the reservoir. "Air-saturated" experiments were run without nitrogen bubbling.



Figure 1. Transient absorption spectrum obtained 1  $\mu$ s following 308 nm laser photolysis of II in deoxygenated BZN. Insets show the decay kinetics at 320, 370, and 550 nm.

**Product Studies.** One- and two-laser product studies were carried out by irradiating deoxygenated 3 mL static samples of II and III in BZN or CH with 500 pulses from the 308 nm laser (II) or 355 nm laser (III) in the one-laser experiments and 500 pairs of 308 + 355 nm pulses (II) or 355 + 445 nm pulses (III) in the two-laser experiments. Product analysis was by HPLC using a silica column and cyclohexane as the mobile phase. Irradiated samples were compared to authentic samples of II, III, and the corresponding vinyl parent compounds.

**Photoacid Quantum Yield.** Photoacid quantum yields were determined relative to the actinometer, azoxybenzene.<sup>16</sup> A solution of azoxybenzene in EtOH and a deoxygenated solution of II (or III) in MeCN with 3 M IPA added were prepared with matching absorbances at 308 nm ( $\sim$ 1.0 at 308 nm) and irradiated by 500 pulses from the 308 nm laser. The irradiated azoxybenzene was treated according to the literature method described. The solution of II or III was titrated with a dilute solution of NaOH which had been prepared immediately prior to use. In the preparation of the base, care was taken to avoid the formation of carbonates and silicates. An unirradiated sample was also titrated in order to correct for acid formed as a result of any thermal debromination.

### **Results and Discussion**

**Emission Parameters.** Parameters obtained from absorption, fluorescence, and phosphorescence measurements of II and III are given in Table 1. Those obtained for naphthalene<sup>11,17,18</sup> and 9-bromoanthracene<sup>19</sup> standards are shown for comparison. 9-Bromoanthracene was chosen as a standard due to the incorporation of the bromine atom on the aromatic ring in III.

It is clear from the data in Table 1 that the dibromoethyl side chain has a moderate effect on the singlet  $S_1$  energies in both II and III as compared to those of the model compounds. The effect on the  $T_1$  energy of II is much less pronounced. We were unable to obtain a phosphorescence spectrum of III. Presumably, a low triplet energy, characteristic of anthracenes,<sup>18</sup> allows efficient radiationless deactivation. There was a dramatic decrease in the fluorescence quantum yields for both compounds as compared to the standards. This decrease can be attributed to more efficient intersystem crossing (ISC) due to an internal heavy atom effect as well as irreversible chemistry following excitation to  $S_1$ . (See below.)

One-Laser Transient Photochemistry of II: Carbon-Bromine Bond Cleavage. Figure 1 shows the transient absorption spectrum



Figure 2. Transient absorption spectra obtained 1  $\mu$ s following 308 nm laser photolysis of II in deoxygenated MeCN in the absence (round symbols) and presence (square symbols) of 0.1 M TBAB.

obtained 1  $\mu$ s following 308 nm photolysis of II in deoxygenated BZN. The spectrum exhibits three major features: a broad weak absorption band with  $\lambda_{max} = 550$  nm, a shoulder at 370 nm, and a stronger absorption at 320 nm. The decay kinetics at relatively short times (up to 20  $\mu$ s) after the laser pulse gave reasonable first-order fits at all three wavelengths and are shown as insets in the figure. ( $\tau = 0.99 \pm 0.04 \ \mu$ s, 6.58  $\pm 0.04 \ \mu$ s, and 6.47  $\pm 0.05 \ \mu$ s at 550, 370, and 320 nm, respectively.) However, when measured over longer time scales (up to 100  $\mu$ s after the pulse), the kinetics gave good second-order fits. Under air-saturated conditions, the lifetimes at 320 and 370 nm decreased slightly ( $\tau = 5.0 \pm 0.15 \ \mu$ s) while the lifetime at 550 nm and the transient spectrum were essentially unchanged.

This transient behavior is consistent with C-Br homolytic bond cleavage at the carbon which is  $\alpha$  to the naphthyl ring, yielding a bromine atom, Br\*, and a long-lived 2-bromo-1-(2-naphthyl)ethyl radical, hereafter referred to as the naphthylethyl radical. The observed 550 nm absorption band is characteristic of the Br<sup>•</sup>-BZN  $\pi$ -complex ( $\lambda_{max} = 550$  nm) formed when BZN scavenges Br<sup>•,20,21</sup> Figure 2 shows the transient spectrum obtained in deoxygenated MeCN (round symbols). While the 300-400 nm region of the spectrum is similar to that obtained in BZN, no 550 nm band was observed, thus confirming that the 550 nm absorption in BZN is due to the  $\pi$ -complex. Also shown in Figure 2 (square symbols) is the spectrum obtained in MeCN in the presence of 0.1 M TBAB. The 360 and 730 nm maxima in this spectrum are characteristic of Br2\*-, formed by the diffusioncontrolled reaction of Br<sup>•</sup> with Br<sup>-,9,22,23</sup> The formation of both Br\* probes  $-\pi$ -complex and Br<sub>2</sub>\*--confirms that homolytic bond cleavage occurs.

The observed spectra in the 300–400 nm region were similar for both BZN and MeCN and closely resemble the spectra reported for a variety of naphthylmethyl radicals.<sup>24–26</sup> Results of oxygen quenching, triplet sensitization, debromination quantum yield, and acid generation experiments as well as product studies are described below to support the assignment of this absorption to the naphthylethyl radical. We feel it is important to identify the radical as unambiguously as possible because its production and stability (on a microsecond time scale) point to behavior for II which differs significantly from that observed for other vicinal dibromides (for example, I and dibromoethane).

Our evidence for the generation and detection of the naphthylethyl radical is as follows. (i) The absorption spectrum in the 300-400 nm region is not due to a triplet state. The lack of efficient quenching of the lifetime of this absorption observed in air-saturated solution is not consistent with a triplet state, which should be quenched at a diffusion-controlled rate.

(ii) Triplet sensitization experiments were carried out in BZN using benzophenone as the sensitizer in the presence of  $10^{-3}$  M II. In these experiments, the laser wavelength was 355 nm. Efficient quenching of the benzophenone triplet state was accompanied by detection of the 550 nm  $\pi$ -complex absorption as well as concurrent formation of the same 300-400 nm absorption observed in the direct irradiation of II. This indicates that debromination occurs rapidly following formation of the triplet and lends support to our assignment of the 300-400 nm absorption to the naphthyl radical.

(iii) The debromination quantum yield,  $\Phi_{Br^*}$ , was determined using  $Br_2^{*-}$  as a transient probe for  $Br^*$  formation, ( $\epsilon$  (360 nm) = 9900 M<sup>-1</sup> cm<sup>-1</sup>)<sup>27</sup> and the benzophenone triplet, T<sub>1</sub>, state as a transient actinometer ( $\Phi_{ISC} = 1.0$ ).<sup>28</sup> Deoxygenated samples of II (with added TBAB) and benzophenone in MeCN were prepared with matching ground state absorbances at 308 nm. The maximum transient absorbance was measured at 360 nm for the sample of II and at 525 nm for benzophenone T<sub>1</sub> ( $\epsilon$  (525 nm) = 7630 M<sup>-1</sup> cm<sup>-1</sup>)<sup>29</sup> at a series of laser pulse energies. (Energies were adjusted using neutral density filters.) The initial slopes of the transient absorbance versus laser energy plots were calculated and used in eq 1 for the determination of  $\Phi_{Br^*}$ . In eq 1, the

$$\Phi_{Br} = \Phi_{Br_{2}} = \frac{\text{Slope}_{Br_{2}}}{\text{Slope}_{BZP}} \frac{\epsilon_{BZP}}{\epsilon_{Br_{2}}} \Phi_{BZP}$$
(1)

assumption is made that all the Br<sup>•</sup> produced are scavenged by Br<sup>-</sup>. This is reasonable given the diffusion-controlled rate constant for scavenging and the high (0.1 M) TBAB concentration.<sup>9</sup> In the determination of the Br<sub>2</sub><sup>•-</sup> absorbance, a correction was made for the transient absorbance observed at 360 nm in the absence of TBAB. The value of  $\Phi_{Br^*}$  obtained in this manner was 0.87  $\blacksquare$  0.10.

This value of  $\Phi_{Br^*}$  indicates that every excitation event leads to the loss of approximately one Br<sup>•</sup>. If debromination is purely a photochemical process, then this result would imply that the naphthylethyl radical should be sufficiently long-lived to be detected. However, it is important to note that  $\Phi_{Br^*}$  represents the sum of photochemical debromination and any *rapid* thermal debromination which occurs subsequently from the naphthylethyl radical. Thus, a value of  $\Phi_{Br^*}$  close to one may be a result of efficient photochemical debromination and inefficient thermal cleavage of the radical or, alternatively, inefficient photochemical cleavage followed by efficient thermal cleavage.

To determine the importance of thermal debromination, we performed product studies according to the method outlined in the experimental section. The product of thermal debromination of the naphthylethyl radical is expected to be 2-vinylnaphthalene. HPLC analysis of 308 nm laser irradiated samples indicated that 2-vinylnaphthalene was present in minor amounts compared with other products. This result confirms that most debromination is photochemical and supports our identification of the naphthylethyl radical.

(iv) H atom abstraction from IPA and methanol by photogenerated Br<sup>•</sup> produces acidic solutions.<sup>9</sup> The formation of acid was used as a stable probe for C-Br bond cleavage. The photoacid generating efficiency of II was determined qualitatively by base titration of CW-irradiated solutions. Thus,  $6 \times 10^{-4}$  M solutions of II in deoxygenated MeCN in the presence of 3 M IPA (OD at 300 nm ~0.7) were irradiated through Pyrex by 300 nm

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Rayonet lamps for 5–60 min. We have shown previously that, with this concentration of IPA, all the Br<sup>•</sup> produced reacts by H atom abstraction.<sup>10</sup> Titration by dilute NaOH indicated that the solutions irradiated for longer than 15 min were  $(6.0 \pm 1.0) \times 10^{-4}$  M acid, which means that roughly one proton is produced per molecule of II. This result is qualitatively consistent with the value determined for  $\Phi_{Br^{-1}}$ .

Quantitative measurements were performed to determine  $\Phi_{H^+}$ , the quantum yield for acid production. (Since the experiments were carried out under conditions where all Br<sup>•</sup> produced react to form acid,  $\Phi_{H^+}$  is also a measure of the debromination efficiency.) Azoxybenzene was used as an actinometer following the procedure outlined in the experimental section. The value of  $\Phi_{H^+}$  determined in this manner was  $0.85 \pm 0.14$ , in close agreement with  $\Phi_{B^{*+}}$ . It should be noted that the difference between  $\Phi_{H^+}$  and the quantum yield for azoxybenzene chemistry ( $\Phi = 0.02$ ) is quite large and therefore could affect the uncertainty associated with this value.

All of the evidence presented above as well as the two-laser results discussed below support the conclusion that irradiation of II leads to photochemical debromination with a yield close to one and that subsequent thermal debromination is unimportant. This also leads to the conclusion that the 300–400 nm spectrum is that of the naphthylethyl radical.

The absence of thermal debromination from the naphthylethyl radical represents behavior that is significantly different from that observed for other vicinal dibromides. For example, no intermediate was observed following photochemical debromination of  $I^{10}$  Presumably, thermal debromination occurs so rapidly that the lifetime of the intermediate radical is too short to allow detection. Both the naphthylethyl radical and the radical derived from I will be stabilized by resonance interactions with the adjoining aromatic rings. In addition, the unpaired electron of the radical may interact with the d-orbitals of the neighboring Br<sup>•</sup>, causing it to bridge to the radical site.<sup>30</sup>



The stabilizing effect of this interaction on the radical has been suggested as a reason for the increased H atom abstraction rates from carbon atoms which are  $\beta$  to a halogen atom in *n*-butyl halides.<sup>31</sup>

We suggest that the difference in behavior between I and II arises because conjugation of the two phenyl rings in I provides a driving force sufficient to overcome the stabilization of the radical. In II, the driving force due to conjugation is much less important.

The stability of the naphthylethyl radical in the presence of oxygen is unusual and deserves comment. The similar naphthylmethyl radical is quenched rapidly by oxygen  $(k \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}).^{25}$  In fact, benzylic-type radicals in general are easily oxidized. It seems likely that in this case the effect of Br<sup>•</sup> bridging to the radical site provides stabilization not only toward further debromination but toward oxidation as well.

**Two-Laser Photochemistry of II.** Considering the different debromination behavior of II as compared to that found previously for I, we investigated the lability of the C-Br bond in the naphthylethyl radical using two-laser flash photolysis. Figure 3 shows the transient absorption spectrum obtained following two-laser (308 + 355 nm) irradiation of II in deoxygenated BZN (square symbols). The spectrum was obtained  $3.5 \,\mu$ s after the 308 nm pulse and  $0.5 \,\mu$ s after the 355 nm pulse. The spectrum obtained  $3.5 \,\mu$ s after the 308 nm pulse in a one-laser experiment



Figure 3. Transient absorption spectra obtained following one- (308 nm; round symbols) and two-laser (308 + 355 nm; square symbols) photolysis of II in deoxygenated BZN. One-laser spectrum was obtained 3.5  $\mu$ s after the 308 nm pulse. Two-laser spectrum was obtained 3.5  $\mu$ s after the 308 nm pulse and 0.5  $\mu$ s after the 355 nm pulse. Insets show the two-laser kinetic behavior at 370 and 550 nm.

(round symbols) is given for comparison. (In contrast to the spectrum in Figure 1, this one-laser spectrum does not show the 550 nm absorption band because the  $\pi$ -complex has decayed almost entirely at 3.5  $\mu$ s after the laser pulse.) The kinetic decays monitored at 370 and 550 nm are shown as insets. Both the spectrum and kinetics clearly show that irradiation at 355 nm (in the absorption band of the naphthylethyl radical) causes bleaching of the naphthylethyl radical absorption and production of the  $\pi$ -complex. A control experiment in which only the 355 nm laser was used yielded only a minor amount of  $\pi$ -complex absorption (ca. 20% of that observed following the 355 nm pulse in the two-laser experiment), indicating that while there is some direct 355 nm excitation of II, the naphthylethyl radical is the major source of Br\*. Bleaching was also observed in MeCN and CH; however, as expected, no  $\pi$ -complex was observed.

Debromination of the naphthylethyl radical was confirmed by the results of one- and two-laser product studies. Samples of II in CH were irradiated according to the procedure described in the experimental section and analyzed by HPLC. (The 355 nm pulse followed the 308 nm pulse by ca. 500 ns.) In both the oneand two-laser samples, a small amount of the debromination product, 2-vinylnaphthalene, was detected. However, the ratio of 2-vinylnaphthalene produced in the two-laser experiments versus that produced in the one-laser experiments was 1.3 to 1. While additional unidentified products were detected for both the one- and two-laser studies, only the 2-vinylnaphthalene yield was enhanced by the second laser. While it was not possible to unambiguously identify the other photoproducts, it is possible that one product is the naphthylethyl dimer formed by radicalradical recombination. The second-order decay kinetics observed indirectly support this suggestion.

This transient and product evidence confirms that the irradiation of the naphthylethyl radical results in C-Br bond cleavage and, indeed, adds further support to our assignment of the radical. The photofragmentation of a substituted naphthylmethyl radical has been reported previously.<sup>26</sup> Laser irradiation (337 nm) of 1-bromo-2-(bromomethyl)naphthalene yielded a 1-bromo-2methylnaphthyl radical which, when irradiated with a 430 nm laser, underwent further debromination. However, the productoriented evidence in this study was ambiguous.

The one- and two-laser photochemistry of II is shown in Scheme 1.



Figure 4. Transient absorption spectrum obtained 0.5  $\mu$ s following 355 nm laser photolysis of III in deoxygenated BZN. Insets show decay kinetics at 440 and 550 nm.





One- and Two-Laser Transient Photochemistry of III: Carbon-Bromine Bond Cleavage. Figure 4 shows the transient absorption spectrum obtained 0.5 µs following 355 nm laser photolysis of III in deoxygenated BZN. The spectrum exhibits absorption bands at  $\lambda_{max} = 550, 440, and < 320 \text{ nm}$ . The decay kinetics at 440 and 550 nm are shown as insets in the figure. (The spectrum in the 400-420 nm region exhibits negative  $\Delta OD$  values due to bleaching of the ground state absorption.) Analogous to the case for II, the 550 nm band, which was unaffected by the presence of oxygen, is assigned to the Br<sup>•</sup>-BZN  $\pi$ -complex. The absorption band in the 380-460 nm region is due to two transient species, as evidenced by the decay at 440 nm which clearly shows short- and long-lived components. Figure 5 shows the transient decay kinetics obtained at 440 nm under air-saturated and deoxygenated conditions. While the long-lived component is unaffected by oxygen and decays over long time scales with primarily second-order kinetics, the short-lived species was completely quenched, indicating that it is due to the triplet state of III.

The inset in Figure 5 shows the transient absorption spectrum obtained 0.5  $\mu$ s following the 355 nm pulse under air-saturated conditions. The spectrum in the 300-460 nm range is almost identical to that reported previously for the 9-anthrylmethyl radical<sup>32</sup> and therefore, in analogy to that for II, is assigned to



Figure 5. Transient decay kinetics obtained for 355 nm laser photolysis of III in decxygenated (round symbols) and air-saturated (square symbols) BZN. Inset shows the transient absorption spectrum obtained 0.5  $\mu$ s following 355 nm laser photolysis in air-saturated BZN.

the 2-bromo-1-(2-bromo-9-anthryl)ethyl radical (referred to below as the anthrylethyl radical) produced by C-Br cleavage at the 1-position on the ethyl side chain. (While Br• may be produced by cleavage on the aromatic ring, this process is likely much less efficient than cleavage on the side chain due to the lower stability of the aromatic radical produced. In addition, UV irradiation of 9-bromoanthracene and 9,10-dibromoanthracene in BZN has been shown previously not to cause cleavage.<sup>33,34</sup> The anthrylethyl radical is even less sensitive to oxygen than the naphthylethyl radical. Again its stability may possibly be attributed to Br• bridging to the radical site.

Debromination quantum yield experiments were performed in a manner similar to that for II. These measurements yielded  $\Phi_{Br}$ = 0.45 ± 0.10. This value was confirmed by photoacid measurements which gave  $\Phi_{H^*} = 0.48 \pm 0.11$ . These two results, combined with one-laser product studies showing that 9-vinylanthracene is only produced in minor amounts, suggest that, like that of II, the debromination of III is primarily a photochemical event. This result further supports our assignment of the anthrylethyl radical.

The fact that oxygen quenching of the triplet state of III does not decrease the amount of anthrylethyl radical produced (Figure 5) indicates that C-Br cleavage in III does not occur via  $T_1$  and therefore is likely a singlet state process. (However, given that ISC in anthracenes occurs primarily from  $S_1$  to the nearly isoenergetic  $T_2$  state,<sup>19,35-37</sup> we cannot rule out the latter as a precursor to cleavage.)

The lack of  $T_1$  reactivity in III (which accounts for our ability to detect the triplet) contrasts with the cleavage observed from the  $T_1$  state of II. This difference can be understood on the basis of the difference in  $T_1$  energies—60.8 kcal/mol in II compared with ca. 40 kcal/mol in III. The C-Br bond dissociation energy (BDE) in benzyl bromide is ca. 59 kcal/mol.<sup>38,39</sup> Since the BDE for the C-H bond in 9-methylanthracene differs from that in toluene only by approximately 6 kcal/mol.<sup>40-42</sup> by analogy, we do not expect the C-Br BDE's for either II or III to be dramatically lower than 59 kcal/mol. Thus, while the  $T_1$  energy of II is sufficient to facilitate cleavage, in III cleavage from  $T_1$  will be uphill energetically.

The efficiency of debromination of III is considerably less than that observed for II. We attribute this difference to efficient competition between debromination from  $S_1$  and ISC to the lowenergy, unreactive triplet state. (It should be noted that ISC **SCHEME 2** 



may also be important in II. However, since both the singlet and triplet states of II debrominate,  $\Phi_{Br}$  does not provide information about its importance.)

Two-laser photolysis (355 nm + 445 nm) of III in air-saturated BZN yielded the same qualitative results as were observed for II. (Air-saturated BZN was used to eliminate the possibility of exciting the triplet state of III with the second laser pulse.) Thus, the 440 nm anthrylethyl radical absorption was bleached by the second laser while the 550 nm absorption of the  $\pi$ -complex was enhanced concurrently. One- and two-laser product studies confirm that 9-vinylanthracene is a product of anthrylethyl radical irradiation. That is, photolysis of the radical causes debromination. Scheme 2 summarizes the photochemistry of III.

#### Summary

UV laser photolysis of II in BZN, CH, and MeCN results in homolytic C-Br bond cleavage to produce Br\* and a 2-bromo-1-(2-naphthyl)ethyl radical. Transient evidence for Br\* is provided by the Br<sup>•</sup>-BZN  $\pi$ -complex ( $\lambda_{max} = 550 \text{ nm}$ ) in BZN and  $Br_2^{\bullet-}(\lambda_{max} = 360, 730 \text{ nm})$  in MeCN with added TBAB. The broad absorption in the 300-400 nm region is consistent with the naphthylethyl radical. Sensitization using benzophenone also led to formation of the  $\pi$ -complex, indicating that the energy of the triplet state is sufficient to facilitate cleavage. However, due to the lack of triplet absorption, the importance of cleavage from the triplet manifold under direct excitation is unknown.  $\Phi_{Br}$ , the quantum yield of debromination, was determined using Br2<sup>--</sup> as a transient probe. The value obtained,  $\Phi_{Br} = 0.87 \pm 0.10$ , indicates that nearly every excitation event leads to bond cleavage. Since product studies show only minor amounts of 2-vinylnaphthalene produced, we conclude that the majority of debromination is a photochemical process, rather than partially photochemical and partially thermal. The debromination yield was confirmed using acid production as a stable Br\* probe. Br\* formation in the presence of a H atom donor leads to H atom abstraction and HBr production ( $\Phi_{H^+} = 0.85 \pm 0.14$ ). The photochemical behavior of this system is significantly different from that of other vicinal dibromides which have been shown to undergo facile thermal debromination following photochemical debromination. The lack

of thermal debromination in II is attributed to the stability of the intermediate naphthylethyl radical relative to 2-vinylnaphthalene.

Photolysis of the naphthylethyl radical in a two-laser experiment in BZN results in bleaching of the radical absorption and production of the  $\pi$ -complex, indicating that radical excitation causes C-Br cleavage. This is confirmed by one- and two-laser product studies. Enhanced production of 2-vinylnaphthalene was observed in the two-laser experiments.

UV laser photolysis of III also causes C-Br cleavage ( $\Phi_{Br} = 0.45 \pm 0.10$ ,  $\Phi_{H^+} = 0.48 \pm 0.11$ ) yielding Br<sup>•</sup> and a stable 2-bromo-1-(9-anthryl)ethyl radical. Unlike the case for II, the triplet state of III was also observed. Since the triplet energy lies well below the C-Br bond energy, cleavage from the triplet does not occur. This accounts not only for observation of the triplet but also for the reduced debromination efficiency; i.e., ISC to the unreactive triplet competes with debromination from the singlet.

Photolysis of the anthrylethyl radical also leads to debromination as evidenced by bleaching of the radical absorption and, in BZN, formation of the  $\pi$ -complex.

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