

# Multiple-Photon Chemistry of 9-(Phenoxymethyl)- and 9,10-Bis(phenoxymethyl)anthracenes in the Laser-Jet: Generation, Photochemistry, and Time-Resolved Laser-Flash Spectroscopy of Anthracenylmethyl Radicals and Pulse Radiolysis of 9-(Bromomethyl)anthracene

Waldemar Adam,<sup>\*,†</sup> Katrin Schneider,<sup>†</sup> Marion Stapper,<sup>‡</sup> and Steen Steenken<sup>\*,‡</sup>

Contribution from the Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany, and Max-Planck-Institut für Strahlenchemie, D-45470 Mülheim, Germany

Received October 18, 1996<sup>⊗</sup>

**Abstract:** In the high-intensity laser-jet (LJ) photolysis of 9-(phenoxymethyl)anthracene (**1a**) and 9,10-bis(phenoxymethyl)anthracene (**1b**) multiple-photon chemistry was observed. Thus, while the [4 + 4] photodimer **8a** was formed as the one-photon product in the low-intensity conventional photolysis of monoether **1a**, the high-intensity irradiation in the laser-jet yielded 1,2-bis(9-anthracenyl)ethane (**3a**), lepidopterene (**4a**), biplanene (**5a**), 9-(chloromethyl)anthracene (**6a**), and 9-(methoxymethyl)anthracene (**7a**) as main products. The product distribution depended on the solvent used: after C–O homolysis of the ether **1a**, for which at least two photons are required, the resulting arylmethyl radical **2a** dimerizes in benzene, in methylene chloride it engages in photoinduced electron transfer, while in methanol it undergoes photoionization. With the help of time-resolved laser-flash photolysis of the monoether **1a** it was confirmed that the homolysis of the C–O bond leads to the 9-anthracenylmethyl radical **2a**. The authentic radical **2a** was generated independently by time-resolved pulse radiolysis and laser-flash photolysis of 9-(bromomethyl)anthracene. Analogous to the monoether **1a**, the bisether **1b** gave under the high intensity conditions of the laser-jet irradiation tetrabenzo[2.2]paracyclophane (**3b**), its photodimer (**5b**), 9,10-(bischloromethyl)anthracene (**6b**), and 9-(chloromethyl)-10-(phenoxymethyl)anthracene (**9b**); their distribution depended also on the solvent used. Mechanistic pathways are offered for these multiple-photon processes.

## Introduction

The 9-anthracenylmethyl radical (**2a**) has been the subject of recent photophysical and photochemical studies.<sup>1–4</sup> Tokumura and Itoh<sup>1</sup> reported its absorption band at ca. 420 nm on 248-nm photolysis of 9-chloromethylanthracene. 9-Anthracenylmethyl radicals (**2a**) were reported to show a doublet–doublet fluorescence emission ( $\lambda_{\text{max}} = 545$  nm,  $\tau_{\text{F}} = 21$  ns).<sup>1,2</sup> Furthermore, upon irradiation of arylmethyl derivatives with two pulsed lasers (two-color experiments), excited arylmethyl radicals and even aryl cations were detected by UV spectroscopy.<sup>5</sup>

Besides the generation of the radicals **2a** on photolysis of 9-halomethylanthracene derivatives, their formation on 313-nm photolysis of 9-anthracenylmethyl 9'-fluorenyl ketone<sup>3</sup> and 1-(9-anthryl)hexan-2-one<sup>4</sup> was described by Guillet *et al.* Detailed studies of the radical **2a** products were performed after photolysis or pyrolysis of 9-AnthCH<sub>2</sub>SePh.<sup>6</sup> Dependent on the reaction conditions, different product ratios of the dimers **3a**, **4a**, and **5a** were found.

The 9-anthracenylmethyl radical (**2a**) constitutes a good substrate for laser-jet experiments since its absorption characteristics match the emission lines of the argon-ion laser (333, 351, 364 nm).<sup>1</sup> We report herein novel results on the formation of the 9-anthracenylmethyl radical (**2a**) in the laser-jet photolysis of 9-(phenoxymethyl)anthracene (**1a**). Furthermore, for mechanistic support, we have detected the radical **2a** intermediate by means of time-resolved laser-flash spectroscopy of the ether **1a** and of 9-(bromomethyl)anthracene, and the pulse radiolysis of the latter. In addition we report the electronic absorption spectrum of the anthracene triplet state. Also the product studies of the laser-jet photolyses of 9,10-bis(phenoxymethyl)anthracene (**1b**) in various solvents are presented. With this study we demonstrate that the laser-jet mode of operation constitutes a valuable complementary technique for time-resolved laser-flash photolysis and pulse radiolysis.

## Results

**Laser-Jet and Conventional Photolyses.** On photolysis of monoether **1a** [extinction coefficients (log  $\epsilon$ ) at the emission wavelengths of the lasers at 248, 333, 351, and 364 nm are 4.945, 3.408, 3.620, and 3.785, respectively], the products in Scheme 1 were observed, namely the dimers **3a**, **4a**, and **5a**, the chloride **6a**, the ether **7a**, the photodimer **8a**, and phenol.

A strong dependence of the product composition was observed on the light intensity. Phenol was formed quantitatively in all LJ photolyses of monoether **1a** but none at the low intensity of the conventional photolysis. The products **3a**, **4a**, **5a**, **6a**, and **7a** were found in appreciable amounts at the high intensities of the laser-jet photolysis, but only in traces at the low intensities of the conventional irradiation. Instead, the latter

<sup>†</sup> University of Würzburg.

<sup>‡</sup> Max-Planck-Institut für Strahlenchemie.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, March 15, 1997.

(1) Tokumura, K.; Mizukami, N.; Udagawa, M.; Itoh, M. *J. Phys. Chem.* **1986**, *90*, 3873–3876.

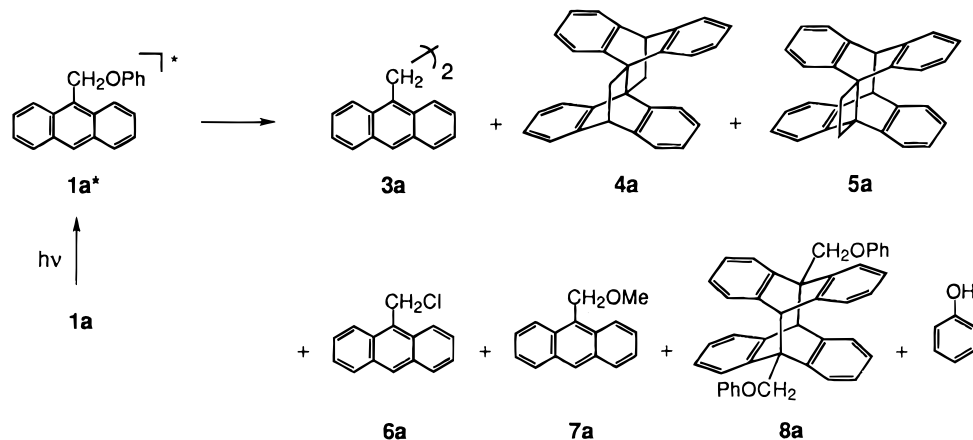
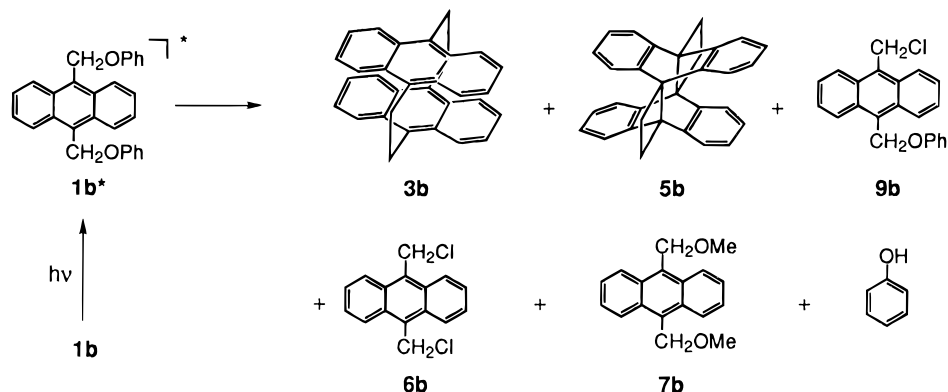
(2) Weir, D.; Johnston, L. J.; Scaiano, J. C. *J. Phys. Chem.* **1988**, *92*, 1742–1746.

(3) Modi, P. J.; Guillet, J. E.; Scaiano, J. C.; Wintgens, V. *J. Photochem. Photobiol. A: Chem.* **1994**, *81*, 87–91.

(4) Modi, P. J.; Guillet, J. E. *J. Photochem. Photobiol. A: Chem.* **1994**, *84*, 213–220.

(5) Faria, J. L.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 1924–1930.

(6) Higuchi, H.; Sakata, Y.; Misumi, S.; Otsubo, T.; Ogura, F.; Yamaguchi, H. *Chem. Lett.* **1981**, 627–630.

Scheme 1. Photolysis Products of the Anthracene Monoether **1a**Scheme 2. Laser-Jet Photolysis Products of the Anthracene Bisether **1b**

**Table 1.** Product Studies of the Laser-Jet (High Intensity) Photolysis of Anthracene Monoether **1a**

entry	solvent <sup>c</sup>	conv <sup>a</sup> [%]	mb <sup>a</sup> [%]	product distribution <sup>a,b</sup> [%]				
				<b>3a</b>	<b>4a</b>	<b>5a</b>	<b>6a</b>	<b>7a</b>
1	benzene (3.9 W)	25	78	traces	65	35		
2	<i>n</i> -hexane (3.6 W)	47	72	traces	69	31		
3	CH <sub>2</sub> Cl <sub>2</sub> (3.6 W)	46	78	traces	traces	traces	100	
4	MeOH (3.3 W)	19	90		9	traces		91

<sup>a</sup> Conversion (conv) of monoether **1a**, mass balance (mb) of products, and product distribution were determined by <sup>1</sup>H NMR spectroscopy, error 5% of stated value; phenol was formed quantitatively. <sup>b</sup> Normalized to 100%. <sup>c</sup>  $c = 3.52 \times 10^{-3}$  M, 50- $\mu$ m capillary, 1 cycle, flow rates of 0.8 (entries 1, 3) and 1.0 mL/min (entries 2, 4); in parentheses is given the laser power of all UV lines (333, 351, and 364 nm).

photolysis of monoether **1a** in benzene on the preparative scale gave the corresponding photodimer **8a** in about 42% yield. At room temperature, the photodimer **8a** is quite insoluble in all solvents used and precipitates during the photolysis. This product was not detected at the high-intensity conditions of the laser-jet photolysis.

As the quantitative data of the laser-jet photolyses in Table 1 reveal, the distribution of products is highly dependent on the solvent employed. Thus, in nonpolar, aprotic benzene and *n*-hexane as solvents, the dimers **4a** and **5a** were formed in a ratio of ca. 66:33 (Table 1, entries 1 and 2) at the high intensities. A control experiment confirmed that the dimer **5a** was observed exclusively (>99%) on irradiation of dimer **3a** in CDCl<sub>3</sub>. The structure of dimer **5a** was established by its <sup>1</sup>H NMR spectrum, which matched that in the literature.<sup>7</sup>

In the aprotic but more polar, halogen-containing solvent methylene chloride, the chloride **6a** (Table 1, entry 3) was

**Table 2.** Laser-Jet Photolysis of Anthracene Monoether **1a** in a 1:4 Mixture of Methylene Chloride and Methanol

entry	laser power <sup>a</sup> [W]	product ratio <sup>b</sup> <b>7a/6a</b>
1	2.5	1.3 ± 0.1
2	3.5	2.2 ± 0.1
3	4.5	3.2 ± 0.2

<sup>a</sup>  $c = 3.50 \times 10^{-3}$  M, 50- $\mu$ m capillary, flow rate of 0.8 mL/min, all UV lines (333, 351, and 364 nm), 1 cycle. <sup>b</sup> <sup>1</sup>H NMR spectroscopy, error 5% of stated value.

obtained essentially quantitatively, while the dimers **3a**, **4a**, and **5a** were observed only in traces at the high-intensity conditions. Contrastingly, in the protic, polar methanol (Table 1, entry 4) the ether **7a** was the major product (91%), but appreciable (9%) amounts of dimer **4a** were observed.

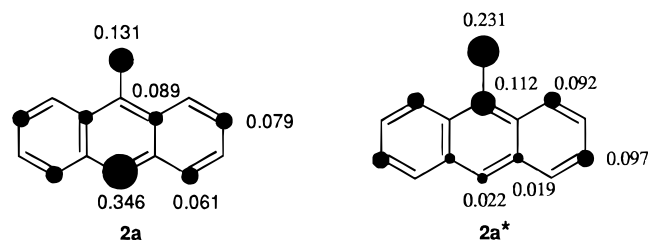
Of mechanistic relevance in the LJ photolysis is the influence of the light intensity on the product distribution (Table 2). In a 1:4 mixture of CH<sub>2</sub>Cl<sub>2</sub> and MeOH, the product ratio of 9-anthracenylmethyl methyl ether (**7a**) versus 9-(chloromethyl)-anthracene (**6a**) increased with the laser power.

The photolysis products of bisether **1b** are outlined in Scheme 2 and the product studies of the LJ photolyses are listed in Table 3. Like the monoether **1a**, at the low intensities of the conventional irradiation, bisether **1b** gave an insoluble precipitate; but unlike for the former, it could not be characterized. The dimers **3b** and **5b**, the chloro ether **9b**, the bischloride **6b**, and the bisether **7b** were identified as the high-intensity products of the laser-jet photolysis. Their amounts depended on the solvent employed. Thus, the dimer **3b** was formed exclusively in benzene (Table 3, entry 1), while in methylene chloride (Table 3, entry 2) the chloride **9b** was obtained as the major product. The dimer **3b** and bischloride **6b** were minor products and the dimer **5b** was observed only in traces. A control experiment

**Table 3.** Product Studies of the Laser-Jet (High Intensity) Photolysis of Anthracene Bisether **1b**

entry	solvent <sup>c</sup>	conv <sup>a</sup> [%]	mb <sup>a</sup> [%]	product distribution <sup>a,b</sup> [%]				
				<b>3b</b>	<b>5b</b>	<b>9b</b>	<b>6b</b>	<b>7b</b>
1	benzene	41	60	100				
2	CH <sub>2</sub> Cl <sub>2</sub>	84	53	16	traces	57	27	
3	MeOH	19	81	100				traces

<sup>a</sup> Conversion (conv) of bisether **1b**, mass balance (mb) of products, and product distribution were determined by <sup>1</sup>H NMR spectroscopy, error 5% of stated value; phenol was formed quantitatively. <sup>b</sup> Normalized to 100%. <sup>c</sup>  $c = 3.52 \times 10^{-3}$  M, 50- $\mu$ m capillary, 1 cycle, flow rates of 0.8 mL/min, 3.9 W MLUV (333, 351, and 364 nm).

**Figure 1.** The  $\pi$  spin densities ( $\rho$ ) for the ground (**2a**) and the excited (**2a\***) state radicals, calculated by the AM1 method.

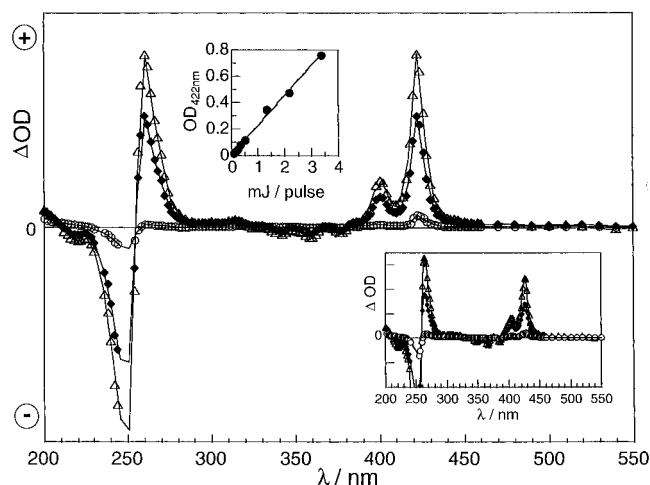
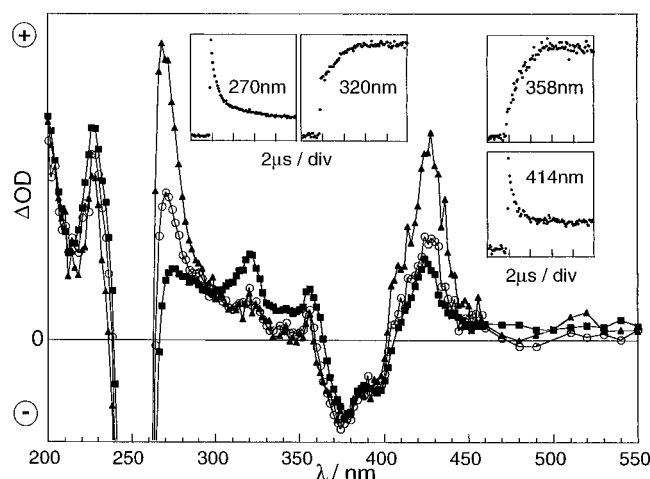
showed that the latter was formed exclusively (>99%) on irradiation of dimer **3b** in CDCl<sub>3</sub>. The photolysis of bisether **1b** in methanol (Table 3, entry 3) led to the dimer **3b** essentially exclusively, with only traces of the corresponding bisether **7b**. Finally, in analogy to the monoether **1a**, phenol was formed quantitatively from the bisether **1b** at the high intensity in all solvents, but none in the conventional photolysis.

**AM1 Calculations.** The spin densities ( $\rho$ ) of the 9-anthracenylmethyl radical [ground state (**2a**) and excited (**2a\***) states], calculated by the AM1 method,<sup>8</sup> are shown in Figure 1. For the ground-state radical **2a**, the  $\pi$  spin density is almost three times higher at the *para* position than at the  $\alpha$  position, i.e. 0.346 versus 0.131, and both are significantly larger than at the remaining sites. In contrast, for the excited-state radical **2a\***, the  $\alpha$  position shows the largest  $\pi$  spin density, i.e. 0.231 versus 0.022 in the *para* position.

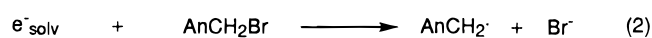
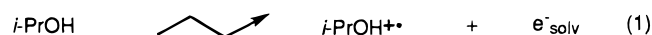
**Time-Resolved Laser-Flash Photolyses.** Upon 248-nm photolysis of anthracene (model compound) in MeCN under an Ar atmosphere, absorption bands at 270, 404, and 424 nm were observed (Figure 2), whose intensity increased linearly with increasing laser power (see upper inset). The last two maxima match those reported,<sup>9</sup> and the one at 270 nm has not been previously observed. Since all bands decay exponentially with the same rate constant ( $k = 5 \times 10^4$  s<sup>-1</sup>) and since the O<sub>2</sub> and ferrocene quenching effect was the same for all bands, these absorptions are assigned to the triplet state of anthracene. This assignment is in agreement with the reactivity of the species with the triplet quenchers O<sub>2</sub> and ferrocene, namely  $k_q(\text{O}_2) = 1 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> and  $k_q(\text{ferrocene}) = 7.3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. The negative signals at ca. 340, 357, and 376 nm (Figure 2) are due to depletion of ground state anthracene, which absorbs at these wavelengths. Analogous observations were made with 9-(hydroxymethyl)anthracene and 9-(methoxymethyl)anthracene (**7a**), whose triplet absorption spectra are very similar to that of anthracene itself (see the lower inset of Figure 2).

(8) For the AM1 method, cf.: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909. The VAMP 5.0 program (Rauhut, G.; Chandrasekhar, J.; Clark, T. University of Erlangen, FRG, 1993) was used by employing a Silicon Graphics Iris Indigo workstation. Geometry optimizations were carried out by using the AUHF method.

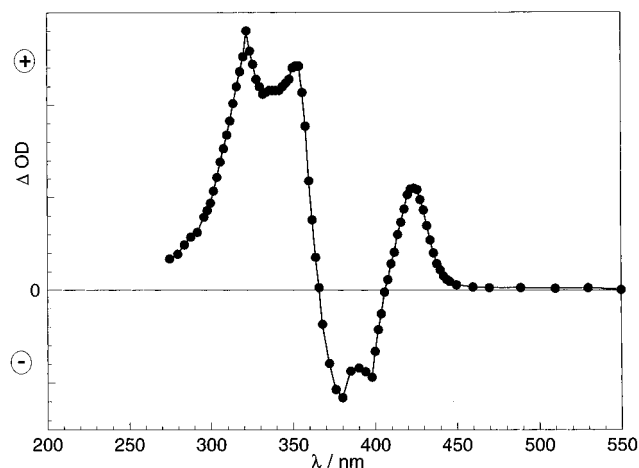
(9) Scaiano, J. C.; Sugamori, S. E. *Speclib 4.0, Compilation of Transient Spectra*, National Research Council of Canada, 1991.

**Figure 2.** Time-resolved absorption spectra observed on 248-nm photolysis of anthracene ( $2.00 \times 10^{-5}$  M) in MeCN saturated with Ar gas (triangles, squares, and circles represent spectra recorded at 2, 11, and 170  $\mu$ s after the 3.4-mJ pulse). In the upper inset is shown the dependence of the yield of the anthracene triplet on the laser pulse power. The lower inset exhibits the spectrum of the triplet of AnCH<sub>2</sub>-OMe in MeCN as recorded at 0.6 (triangles), 12 (diamonds), and 170  $\mu$ s (circles) after the 2.7-mJ pulse.**Figure 3.** Time-resolved absorption spectra observed on 248-nm photolysis of 9-(bromomethyl)anthracene ( $3.00 \times 10^{-5}$  M) in MeCN saturated with Ar gas (triangles, circles, and squares represent spectra recorded at 0.1, 0.7, and 7  $\mu$ s after the 2.1-mJ pulse). In the insets are shown the decay of the triplet as monitored at 270 and 424 nm and the concomitant buildup of radical **2a** at 320 and 358 nm.

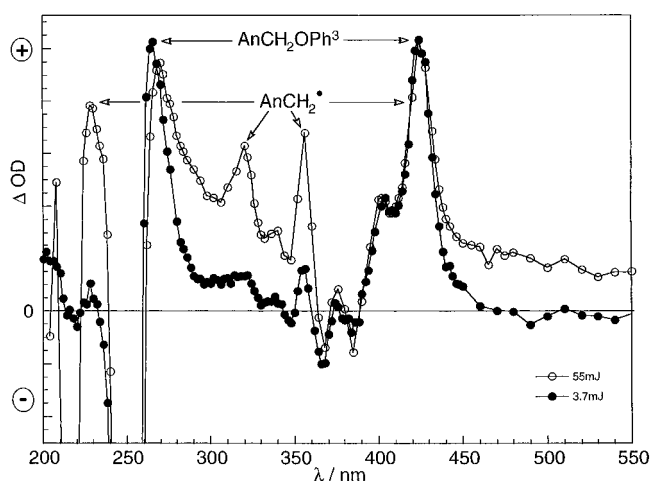
As a further model compound, 9-(bromomethyl)anthracene was studied. At low pulse power of the 248-nm laser light (<10 mJ/pulse), a spectrum was observed with bands at 426 and 270 nm (see Figure 3), which is assigned to its triplet state. The latter was quenched by ferrocene with a rate constant of  $4.4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. Additional bands at 226, 320, and 356 nm are visible. The 226-, 320-, 356-, and broad 426-nm bands are assigned to the 9-anthracenylmethyl radical (**2a**), produced by homolysis of the CH<sub>2</sub>-Br bond in the 9-(bromomethyl)anthracene photolysis. This assignment was confirmed by performing pulse-radiolysis experiments in the solvent *i*-PrOH, in which radical **2a** was produced by reaction with the solvated electron, cf. eqs 1 and 2. As seen in Figure 4, the observed



transient for the radical **2a** has absorption maxima at 320, 356,



**Figure 4.** Time-resolved absorption spectra observed on pulse radiolysis of 9-(bromomethyl)anthracene (0.12 mM) in *i*-PrOH saturated with Ar gas recorded at 1.3 ms after the pulse.



**Figure 5.** Time-resolved absorption spectrum of transients observed on 248-nm photolysis of monoether **1a** ( $1.20 \times 10^{-5}$  M) in MeCN saturated with Ar gas and recorded at 200 ns after the 3.7-mJ (filled circles) and the 55-mJ pulse (open circles).

and 424 nm. The last band matches that reported<sup>1</sup> for the radical **2a**, and the bands at 320 and 356 nm are described here for the first time. From the insets it is seen that there is a delayed formation of **2a** (monitored at 320 and 358 nm) as the triplet decays (at 270 and 414 nm), with apparently mixed-order kinetics. This indicates that additional  $\text{CH}_2\text{Br}$  bond homolysis occurs probably as a result of triplet-triplet annihilation to yield the singlet excited state from which the C-Br bond cleavage takes place.

On photolysis of monoether **1a** in MeCN at 248 nm in the absence of  $\text{O}_2$ , very similar signals as for anthracene were found (Figure 5, closed circles). In addition, a species characterized by three bands at  $\lambda_{\text{max}}$  ca. 226, 320, and 356 nm was observed. This species was identified as the radical **2a**, which was particularly visible at the higher laser-pulse powers (Figure 5, open circles). The spectra in Figure 5 are normalized to the peak at 424 nm. It is clearly evident that the proportion of radical **2a** to triplet **1a** is much larger at the higher pulse power, which indicates conversion of the triplet into the radical by absorption of an additional photon.

## Discussion

**Time-Resolved Laser-Flash Photolyses and Pulse Radiolyses.** On photolysis of the monoether **1a**, the transient with the three absorption bands (Figure 5) at  $\lambda_{\text{max}}$  270, 404, and 424

nm is assigned to the triplet of **1a**.<sup>9</sup> The additional bands at  $\lambda_{\text{max}}$  320, 356, and ca. 425 nm (Figure 5) are due to the radical **2a**.<sup>1</sup> Consequently, comparison of the spectra of the photolysis of monoether **1a** with those of the photolysis and the pulse radiolysis of  $\text{AnCH}_2\text{Br}$  confirms that the radical **2a** had been formed in these photochemical processes.

**Laser-Jet and Conventional Laser Photolyses.** In benzene, as expected for anthracene derivatives,<sup>10</sup> [4 + 4] cycloaddition of monoether **1a** to the corresponding photodimer **8a** (Scheme 3) is observed under the low-intensity conditions of the conventional laser photolysis. In contrast to this conventional anthracene photochemistry, for the high-intensity photolysis, novel phototransformations of the monoether **1a** can be witnessed. Thus, instead of [4 + 4] cycloaddition, in all employed solvents the LJ photolysis products are those derived from the intermediary 9-anthracenylmethyl radical (**2a**), the latter generated on homolysis of the  $\text{CH}_2\text{-O}$  bond in the monoether **1a** (Scheme 3). These multiple-photon products, all observed exclusively under the high-intensity photolysis conditions of the laser-jet mode, are the dimers **3a-5a** in benzene and *n*-hexane, the chloro derivative **6a** in methylene chloride, and the ether **7a** besides dimer **4a** in methanol (Scheme 1, Table 1). These results clearly implicate multiple-photon chemistry in the formation of the radical **2a** on photolysis of ether **1a** under the laser-jet conditions. Sufficient conversion was achieved to afford enough multiple-photon products for complete characterization and quantitative analysis.

In benzene or *n*-hexane as solvent, only coupling products of radical **2a**, i.e. the dimers **3a-5a**, were obtained in the LJ photolyses of monoether **1a**. Dimer **3a**, detected only in traces, results from coupling of two  $\alpha$  radicals of **2a**, and its further photolysis affords dimer **5a** by intramolecular [4 + 4] cycloaddition (Scheme 3). The formation of dimer **4a** was suggested by Becker *et al.* to involve the  $\alpha$ /*para* dimer of the radical **2a** through thermal intramolecular Diels-Alder reaction (see Scheme 3), a facile process even at room temperature.<sup>11</sup>

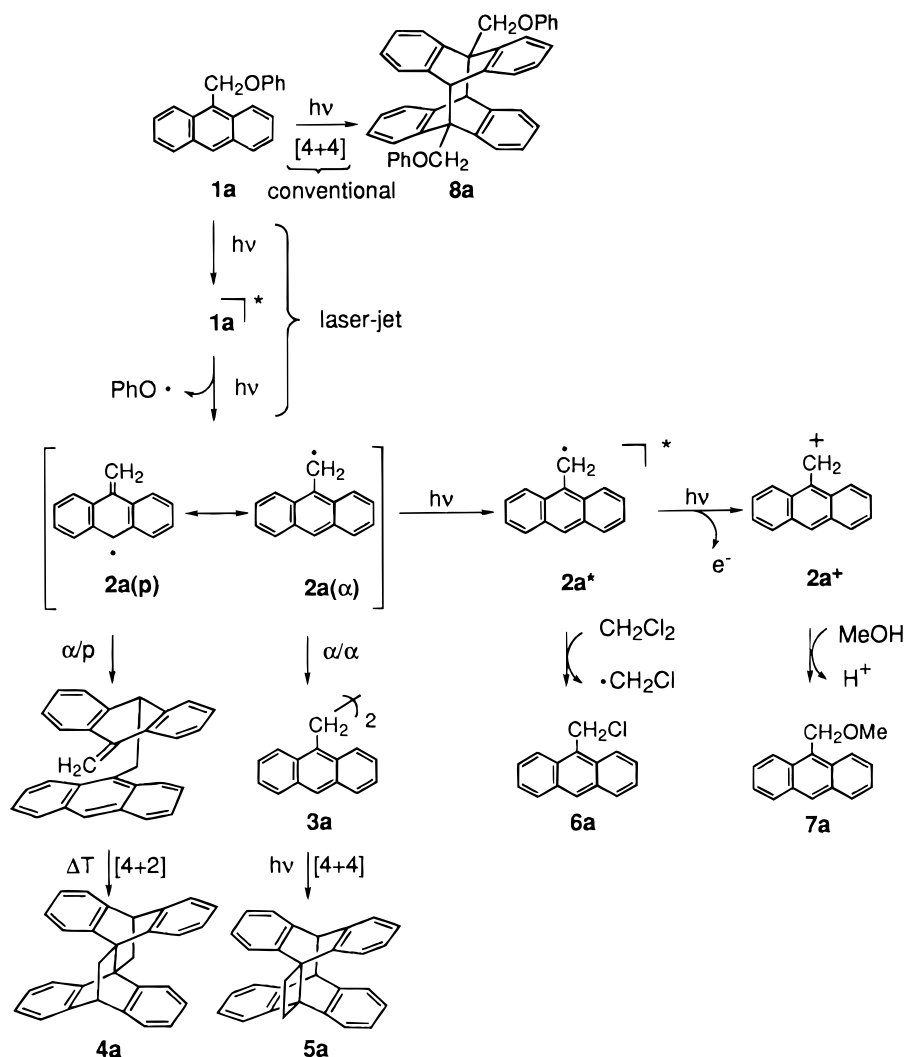
The product ratios of the dimers **4a** and **5a** in both solvents are similar (Table 1, entries 1 and 2), i.e. ca. 33:66 in favor of dimer **4a**. The AM1 calculations for the ground state of radical **2a** (Figure 1) reveal a ca. 3-fold higher spin density in the *para* rather than  $\alpha$  position and, thus, account for the preferred  $\alpha$ /*para* rather than  $\alpha$ / $\alpha$  coupling. Steric factors (*peri* strain) are presumably the reason why the expected *para/para* dimer is not formed.<sup>1,11</sup> That the ground state radical **2a** is the likely precursor to the coupling products **4a** and **5a** rather than its excited state **2a\*** is suggested by the reversal in the spin densities for these two electronic configurations. A much higher value resides at the  $\alpha$  than at the *para* position (Figure 1) for the excited radical **2a\*** and, thus, the  $\alpha$ / $\alpha$  products **3a** and **5a** should have prevailed, which clearly contradicts our experimental findings (Table 1, entries 1 and 2).

In contrast, for the laser-jet photolysis of monoether **1a** in methylene chloride the exclusive product was the chloride **6a** (Table 1, entry 3). Only traces of the dimers **3a**, **4a**, and **5a** were detected. Furthermore, neither under our low-intensity photolysis conditions of monoether **1a** nor in the conventional photochemistry of 9-anthracenylmethyl 9'-fluorenyl ketone by Guillet *et al.*<sup>3</sup> in methylene chloride was the 9-(chloromethyl)-anthracene (**6a**) observed as product. These facts suggest that multiple-photon chemistry is responsible for the formation of **6a** in the photolysis of **1a**.

To account for the formation of chloride **6a** from monoether **1a** in the LJ photolysis in  $\text{CH}_2\text{Cl}_2$ , we recall the relevant results

(10) Becker, H.-D. *Chem Rev.* **1993**, *93*, 145-172.

(11) Becker, H.-D.; Andersson, K.; Sandros, K. *J. Org. Chem.* **1980**, *45*, 4549-4555.

**Scheme 3.** Pathways of the Conventional (Low Intensity) and Laser-Jet (High Intensity) Photolyses of the Anthracene Monoether **1a**

reported by Scaiano<sup>12</sup> for the time-resolved laser-flash photolysis of the benzhydryl or 1-naphthylmethyl radicals, whose excited states are efficiently quenched by chlorinated solvents like  $\text{CCl}_4$  through electron-transfer chemistry. The propensity of these excited radicals to engage in electron-transfer reactions was shown by their quenching with methyl viologen.<sup>12</sup> Consequently, in view of these facts and in analogy to our previous LJ studies<sup>13</sup> on the benzhydryl radical, we propose a similar pathway (Scheme 3) for the efficient formation of 9-(chloromethyl)anthracene (**6a**) in the LJ photolysis of monoether **1a** in  $\text{CH}_2\text{Cl}_2$ . The more usual  $\text{CCl}_4$  was not employed for this purpose because anthracene derivatives undergo facile photo-induced electron transfer (PET) in this solvent already during conventional (low intensity) photolysis.<sup>14</sup> The resulting monoether **1a** radical cation would preclude observation of the searched for multiple-photon chemistry of the radical **2a**. Thus, the chlorine abstraction from  $\text{CH}_2\text{Cl}_2$  is rationalized in terms of electron transfer by the excited 9-anthracenylmethyl radical **2a**<sup>\*</sup> to generate first the pair of anthracenylmethyl cation **2a**<sup>+</sup> and  $\text{CH}_2\text{Cl}_2^{\bullet-}$  radical anion, followed by chloride-ion transfer to afford the chloro product **6a** and chloromethyl radicals.

(12) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368–6372.

(13) Adam, W.; Schulte Oestrich, R. *J. Am. Chem. Soc.* **1992**, *114*, 6031–6034.

(14) Workentin, M. S.; Johnston, L. J.; Wayner, D. D. M.; Parker, V. D. *J. Am. Chem. Soc.* **1994**, *116*, 8279–8287.

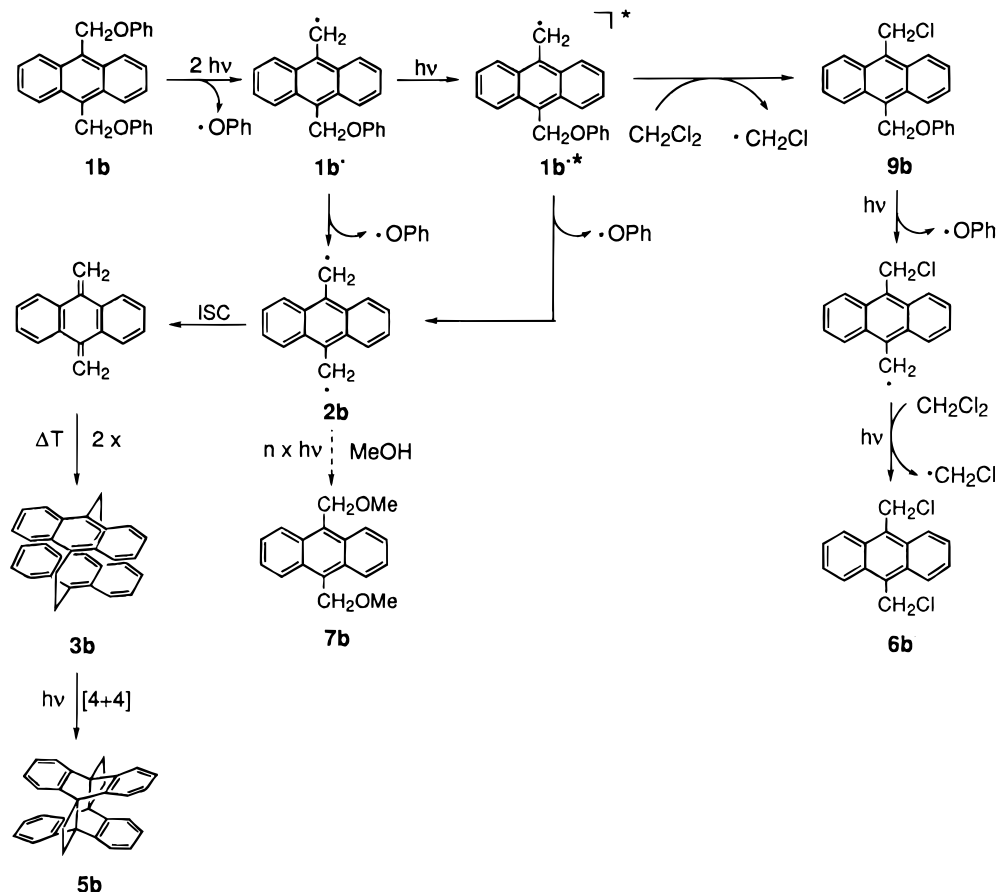
Unfortunately, we found no evidence for the latter; presumably due to the volatility of the products, they are buried by the solvent.<sup>15</sup> Furthermore, the alternative pathway of direct chlorine atom abstraction by the electronically excited aromatic radical is unlikely for excited arylmethyl radicals in chlorinated hydrocarbons.<sup>16</sup> Therefore, since the chloro product **6a** is not observed in the low-intensity photolysis of monoether **1a** in  $\text{CH}_2\text{Cl}_2$  and excited arylmethyl radicals are essential for electron transfer, the present multiple-photon process engages at least three photons in the high-intensity irradiations, i.e. two photons for C–O cleavage in the monoether **1a** and a third photon to excite the resulting radical **2a** to **2a**<sup>\*</sup> (Scheme 3).

In methanol as solvent, a different product composition is obtained, in which now ether **7a** is the main product (Table 1, entry 4). In contrast to  $\text{CH}_2\text{Cl}_2$ , electron transfer from the excited radical **2a**<sup>\*</sup> to the alcohol is not feasible, as inferred from similar behavior of the excited benzhydryl radical in ethanol.<sup>17</sup> Thus, analogous to our previous study on the benzhydryl radical,<sup>13</sup> we postulate that photoionization to generate the cation **2a**<sup>+</sup> competes with the  $\alpha/para$  coupling of the radical **2a** to dimer **4a**, the preferred coupling process for the ground state radical **2a** (Figure 1). The cation **2a**<sup>+</sup> is

(15) Schmitt, G.; Comes, F. J. *J. Photochem. Photobiol. A: Chem.* **1987**, *41*, 13–30.

(16) Faria, J. L.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 1924–1930.

(17) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1984**, *106*, 3056–3057.

**Scheme 4.** Pathways of the Laser-Jet Photolysis of the Anthracene Bisether **1b**

subsequently nucleophilically trapped by methanol (Scheme 3) to produce the ether **7a**. Such photoionization of aryl-substituted methyl radicals has been documented<sup>16,18</sup> and provides experimental support for this mechanism.

The mechanistically relevant question arises, whether in methanol the photoionization of the radical **2a**, like the benzhydryl radical,<sup>13</sup> requires more than one photon. Indeed, the results of the competition experiment in Table 2 support also for the photoionization of the radical **2a** the multiple-photon pathway (Scheme 3). Thus, for the LJ photolysis of the substrate **1a** in a mixture of  $\text{CH}_2\text{Cl}_2$  and MeOH, the product ratio of 9-anthracenylmethyl methyl ether (**7a**) versus 9-(chloromethyl)anthracene (**6a**) increases at the higher laser power. Consequently, the excited radical **2a\*** competes between photons (ionization) and  $\text{CH}_2\text{Cl}_2$  (electron transfer) so that at the higher photon densities photoionization of **2a\*** proportionally increases and the ether **7a** is favored. Thus, the formation of the ether **7a** requires overall at least four photons—two photons are necessary to generate the radical **2a** by C–O cleavage of the substrate **1a** and at least two photons for photoionization of the radical **2a** (Scheme 3).

By analogy, the above discussed photochemistry of the monoether **1a** is helpful to explain the photolysis products of the bisether **1b** (Table 3). Thus, C–O bond homolysis is exclusively observed under the high-intensity conditions of the LJ mode and constitutes again a multiple-photon process.

In benzene as solvent (Table 3, entry 1), the dimer **3b** of the 9,10-anthraquinodimethane (Scheme 4), i.e. the intermediate produced by double C–O cleavage, was obtained in the LJ photolysis of bisether **1b**. The mechanistic alternative of, first, one C–O bond homolysis, dimerization, and, second, a double

C–O cleavage followed by cyclization is unlikely because the dimer of the 9-(10-phenoxymethyl)anthracenylmethyl radical should have been detected, analogous to the dimer **3a** observed in the LJ photolysis of monoether **1a** through  $\alpha/\alpha$  coupling of two 9-anthracenylmethyl radicals **2a** (Scheme 3).

The major product in the laser-jet photolysis in methylene chloride is the chloro ether **9b**, while the bischloride **6b** and dimer **3b** were formed in smaller amounts, and dimer **5b** was detected only in traces (Table 3, entry 2). The latter derives from further photoreaction of dimer **3b** by intramolecular [4 + 4] cycloaddition (Scheme 4). For the chlorides **9b** and **6b** we propose a pathway analogous to the formation of chloride **6a** in the LJ photolysis of the monoether **1a** in  $\text{CH}_2\text{Cl}_2$  (Scheme 3). Consequently, the generation of chlorides **9b** and **6b** from diether **1b** by Cl transfer from  $\text{CH}_2\text{Cl}_2$  through electron-transfer chemistry must involve at least three photons, of which two are required for the first C–O bond homolysis to the radical **1b'** as common intermediate. Absorption of another photon to generate the electronically excited radical **1b'\*** is necessary for chlorine atom abstraction to afford the monochloride **9b**. Whether excitation of the radical **1b'** is essential for the second C–O homolysis to generate the diradical **2b** is uncertain, but two additional photons are presumably required for the sequential double Cl abstraction from the solvent  $\text{CH}_2\text{Cl}_2$  to yield the bischloride **6b**! To form the latter, 9,10-anthraquinodimethane cannot be the intermediary precursor because this anthracene derivative shows no absorption within the available argon-ion laser lines;<sup>19</sup> therefore, excitation of 9,10-anthraquinodimethane and subsequent chlorine abstraction is not feasible. Presumably, the bischloride **6b** results from photolytic C–O bond cleavage of the chloride **9b** and further chlorine abstraction from

(18) Faria, J. L.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 1277–1279.(19) Tardieu, P. *Ann. Chim. (Paris)* **1961**, *6*, 1445–1502.

$\text{CH}_2\text{Cl}_2$  by the electronically excited radical intermediate, a mechanistic speculation that requires at least three additional photons in analogy to the formation of **6a** from **1a** (Scheme 3).

In methanol as solvent, the dimerization of 9,10-anthraquinodimethane to the paracyclophane **3b** is the exclusive pathway (Table 3, entry 3). The bisether **7b** expected to be formed by sequential double photoionization of the diradical **2b** and methanol trapping is observed only in traces. While this route is effective in the laser-jet photolysis of monoether **1a** to afford **7a** (Scheme 3), for the formation of **7b** from bisether **1b** the photon densities are just about at the limits of the possible for the laser-jet technique in observing such a demanding multiple-photon process.

Both examples, the photolyses of monoether **1a** (Table 1) and bisether **1b** (Table 3) show similar multiple-photon chemistry in terms of C–O bond homolysis and ionization of the resulting arylmethyl radical intermediates under the high-intensity conditions of the laser-jet, with a pronounced solvent dependence. Thus, in benzene the C–O bond cleavage engages at least two photons to afford the dimers **3a** and **4a** from **1a** and **3b** from **1b**. While the [4 + 4] photocycloaddition of **3a** leads efficiently to **5a**, such that only traces of dimer **3a** remain, the dimer **3b** persists and no corresponding [4 + 4] photoadduct **5b** was detectable. Since the double C–O bond photolysis requires already several photons to generate the dimer **3b** from the bisether **1b**, the photon density is not high enough during the total residence time (ca. 50  $\mu\text{s}$ ) in the laser focus to effect the further [4 + 4] cycloaddition of dimer **3b** to **5b**. In contrast, in methylene chloride the chloride **6a** results efficiently from the monoether **1a** and the chlorides **6b** and **9b** from the bisether **1b** at the expense of the respective photodimers **3a** (**5a**) and **3b** in benzene. For both chlorinated photoproducts **6a** and **6b** (**9b**), their photolytically generated precursor arylmethyl radicals require subsequent excitation for the electron transfer with methylene chloride. Finally, for methanol, in which the corresponding ether products **7a** and **7b** are formed through ionization of the intermediary arylmethyl radicals, for the latter bisether the laser-jet technique is at its limits of the possible as concerns the photon density essential for such a multiple-photon process. Thus, while the monoether **1a** leads to the ether product **7a** highly efficiently, for the bisether **1b** only traces of **7b** are produced because the latter multiple-photon process requires probably as many as four or more photons. Nevertheless, the anthracene substrates **1a** and **1b** have been very valuable to demonstrate the efficacy of the laser-jet mode to explore high-intensity photochemistry through product studies, which nicely complements the time-resolved laser-flash studies for the mechanistic elucidation of multiphoton processes.

## Experimental Section

**Materials and General Aspects.** The solvents benzene, *n*-hexane, methanol, acetonitrile, and methylene chloride were distilled and the latter was passed immediately before photolysis through an alumina column to remove traces of acid. 2-Propanol (reagent grade) was used as purchased. All solutions were degassed by purging with a slow stream of dry argon gas for 45 min before irradiation. NMR spectra were recorded on a Bruker AC 200 or a Bruker AC 250 spectrometer. Quantitative product studies were determined by  $^1\text{H}$  NMR analysis ( $\text{CDCl}_3$ ) of the identified products directly on the photolysates after removal of the solvent under reduced pressure (ca. 20  $^\circ\text{C}$ , 18 Torr). The IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrophotometer. The known ethers **1a**,<sup>20a</sup> **7a**,<sup>20f</sup> and **7b**,<sup>20g</sup> dimers **3a**,<sup>20b</sup> **3b**,<sup>20c</sup> and **4a**,<sup>11</sup> and chlorides **6a**<sup>20d</sup> and **6b**<sup>20c</sup> were prepared according to reported procedures. Chloride **9b** was identified by comparison of  $^1\text{H}$  NMR data.

**9,10-Bis(phenoxymethyl)anthracene (1b).** A solution of 942 mg (10.0 mmol) of phenol, 1.32 g (9.57 mmol) of potassium carbonate,

and 400 mg (1.45 mmol) of 9,10-bis(chloromethyl)anthracene (**6b**) in 40 mL of dry acetone was allowed to reflux for 20 h. The solvent was removed under reduced pressure (ca. 20  $^\circ\text{C}$ , 18 Torr) and 10 mL of distilled water was added. The aqueous solution was extracted with methylene chloride (3  $\times$  10 mL), the combined organic phases were washed with saturated, aqueous  $\text{Na}_2\text{CO}_3$  solution (2  $\times$  10 mL) and with saturated aqueous  $\text{NaCl}$  solution (2  $\times$  10 mL) and dried over  $\text{MgSO}_4$ , and the solvent was removed under reduced pressure (ca. 20  $^\circ\text{C}$ , 18 Torr). After recrystallization from ethanol, 410 mg (72%) of bisether **1b** was obtained as pale yellow needles, mp 242–244  $^\circ\text{C}$  dec. IR (KBr) 3040, 2890, 1570, 1460, 1200, 1010, 835  $\text{cm}^{-1}$ ; UV ( $\text{CH}_3\text{-CN}$ )  $\lambda$  (log  $\epsilon$ ) 259 (4.13), 356 (2.82), 373 (3.06), 394 nm (3.06);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  5.99 (s, 4 H), 7.07 (m, 2 H), 7.18 (m, 4 H), 7.41 (m, 4 H), 7.56 (m, 4 H), 8.36 (m, 4 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50.3 MHz)  $\delta$  62.6 (t), 114.8 (d), 121.2 (d), 124.7 (d), 124.9 (d), 126.2 (d), 129.6 (s), 130.8 (s), 159.1 (s). Anal. Calcd for  $\text{C}_{28}\text{H}_{22}\text{O}_2$  (390.5): C, 86.13; H, 5.68. Found: C, 86.16; H, 5.69.

**Photodimer of 9-(Phenoxymethyl)anthracene (8a).** A solution of 284 mg (1.00 mmol) of monoether **1a** in 10 mL of benzene was degassed as described above and irradiated for 15 h under an argon gas atmosphere in a Rayonet Photochemical Reactor [RPR (800 W, 110 V)], which was equipped with 350-nm lamps. During the photolysis a solid precipitated, which was collected by filtration, and after recrystallization from benzene, 120 mg (42%) of dimer **8a** was obtained as colorless needles, mp 275–276  $^\circ\text{C}$ ; IR (KBr) 3000, 2880, 2820, 1560, 1450, 1270, 1200, 1040, 840  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $d_6$ -DMSO, 200 MHz, 100  $^\circ\text{C}$ )  $\delta$  4.32 (s, 2 H), 5.15 (s, 4 H), 6.8–7.3 (m, 26 H). Anal. Calcd for  $\text{C}_{42}\text{H}_{32}\text{O}_2$  (568.7): C, 88.70; H, 5.67. Found: C, 88.91; H, 5.48.

**Laser-Jet Irradiations.** The previously described experimental setup<sup>21ab</sup> was employed. The beam of the argon-ion laser (3.3–3.9 W over the 333-, 351-, and 364-nm UV lines) was focused by means of a quartz lens ( $f = 80$  mm) onto a free-falling liquid jet of the photolysis solution. The free-falling liquid jet was generated by passing the substrate solution to be irradiated through a 50- $\mu\text{m}$  capillary and maintained by means of a Bischoff 2200 HPLC pump. The irradiation chamber was kept under a positive argon gas pressure and the substrate solution was passed once through the focal region of the laser beam for the irradiation.

**Control Experiments. (a) Normal Laser Irradiations.** These were carried out in a Schlenk tube by irradiation at the 333-, 351-, and 363-nm lines of the Coherent INNOVA 100 argon-ion laser (3.0 W over all UV lines), supplied with quartz optics. The beam was widened with a quartz lens ( $f = 50$  mm) to the size of ca. 1 cm in diameter and the 10-mL sample was irradiated for 5 min (benzene, *n*-hexane, methylene chloride) or 10 min (methanol) under an argon gas atmosphere.

**(b) Photolysis of Dimer 3a.** A solution of 5.00 mg (13.1  $\mu\text{mol}$ ) of **3a** in 0.7 mL of  $\text{CDCl}_3$  was irradiated for 5 min at the 333-, 351-, and 363-nm lines of the Coherent INNOVA 100 argon-ion laser (3.0 W over all UV lines) under an argon gas atmosphere. NMR analysis showed complete conversion and the dimer **5a** was obtained (>99%).

**(c) Competition Experiments.** A solution of monoether **1a** (3.50  $\times 10^{-3}$  M) in 4:1  $\text{MeOH}/\text{CH}_2\text{Cl}_2$  was irradiated in the LJ apparatus at different light intensities, the solvent was removed under reduced pressure (ca. 20  $^\circ\text{C}$ , 18 Torr), and the residue was analyzed by  $^1\text{H}$  NMR spectroscopy. The results are summarized in Table 2.

**(d) Photolysis of Dimer 3b.** A solution of 5.00 mg (12.2  $\mu\text{mol}$ ) of **3b** in 0.7 mL of  $\text{CDCl}_3$  was irradiated for 2 min at the 333-, 351-, and 363-nm lines of the Coherent INNOVA 100 argon-ion laser (2.0 W over all UV lines) under an argon gas atmosphere. NMR analysis showed complete conversion and the dimer **5b** was obtained (>99%).

(20) (a) Kornblum, N.; Lurie, A. P. *J. Am. Chem. Soc.* **1959**, *81*, 2705–2715. (b) Schreiber, K. C.; Emerson, W. J. *Org. Chem.* **1966**, *31*, 95–99. (c) Golden, J. H. *J. Chem. Soc.* **1961**, 3741–3748. (d) Rohrbach, W. D.; Gerson, F.; Möckel, R.; Boekelheide, V. *J. Org. Chem.* **1984**, *49*, 4128–4132. (e) Fieser, L. F.; Novello, F. C. *J. Am. Chem. Soc.* **1940**, *62*, 1855–1859. (f) Mancilla, J. M.; Nonhebel, D. C.; Russell, J. A. *Tetrahedron* **1975**, *31*, 3097–3101. (g) Kruyt, W.; Veldstra, H. *Landbouwk. Tijdschr.* **1951**, *63*, 398–403.

(21) (a) Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figley, T. M. *Spectrochim. Acta, Part A* **1990**, *46A*, 551–558. (b) Wilson, R. M.; Adam, W.; Schulte Oestrich, R. *Spectrum* **1991**, *4*, 8–17.

**Time-Resolved Laser Flash Photolyses.**<sup>22</sup> Solutions of monoether **1a** or anthracene [optical density (OD) ca. 1–2, ca.  $10^{-5}$  M] in acetonitrile were allowed to pass (ca. 1–2 mL/min flow rate) through a Suprasil quartz cuvette (2 mm  $\times$  4 mm) and photolyzed with 20-ns pulses of 248-nm radiation (ca. 2–40 mJ/pulse) from a Lambda-Physik EMG103MSC excimer laser. The light-induced optical transmission changes corresponded typically to peak optical density changes ( $\Delta$ OD) of 0.01 to 0.1, which depended on substrate concentration and pulse power; the rise time was 1–2 ns. Digitization of these data was achieved with the help of Tektronix 7612 and 7912 transient recorders, interfaced with a DEC LSI11/73<sup>+</sup> computer, which also process-controlled the operation of the apparatus and on-line preanalyzed the data. Final data analysis was performed on a Microvax I, which was connected to the LSI computer.

---

(22) Verbeek, J.-M.; Stapper, M.; Krijnen, E. S.; van Loon, J.-D.; Lodder, G.; Steenken, S. *J. Phys. Chem.* **1994**, *98*, 9526–9536.

**Pulse Radiolyses.**<sup>23</sup> A solution of 9-(bromomethyl)anthracene ( $1.20 \times 10^{-4}$  M) in *i*-PrOH was irradiated with 3-MeV electron pulses of 0.1–0.4- $\mu$ s duration with doses such that 0.2–1  $\mu$ M radical concentrations were produced. The optical transmission was digitized with a Tektronix 7612 transient recorder interfaced with a DEC LSI11/73<sup>+</sup> computer.

**Acknowledgment.** We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support and Dipl.-Chem. H. M. Harrer for the AM1 calculations.

JA963643G

---

(23) Jagannadham, V.; Steenken, S. *J. Am. Chem. Soc.* **1984**, *106*, 6542–6551.