The 4,4'-(1,2-Ethanediyl)bisbenzyl Biradical: Its Generation, **Detection, and (Photo)chemical Behavior in Solution**

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The 4,4'-(1,2-ethanediyl)bisbenzyl biradical (2) is clearly and efficiently generated by photolysis of [3.2]paracyclophane-2-one (8) in cyclohexane solution. This intermediate is also formed via twophoton processes from [2.2]paracyclophane (3) and 1,2-bis(4-chloromethylphenyl)ethane (4). The products arising thermally from biradical 2 are [2.2]paracyclophane and [2.2.2.2]paracyclophane (11) (under high-intensity conditions). Furthermore, two-laser two-color flash photolysis shows that biradical **2** is photostable in solution at room temperature. Thus, formation of *p*-xylylene (1) from 2 occurs neither thermally nor photochemically.

Introduction

Biradicals have often been postulated as reactive intermediates in thermal and photochemical reactions,¹ such as Cope and di- π -methane rearrangements or cyclopropane isomerization. In some cases, photoinduced generation in matrixes has allowed their detection by increasing the lifetimes to the point that conventional methods can be used for characterization.² As chemical reactivity is inhibited in matrix isolation, its study usually requires generation of the reactive intermediates in fluid solution. Sophisticated time-resolved techniques have allowed the study of the chemical (photo)reactivity of some biradicals in solution by spectroscopic methods.³ One of the main limitations in the study of reactive intermediates is the availability of suitable photochemical precursors, since unambiguous assignment of the reaction products is only possible when they can be clearly distinguished from the starting substrates.

In this respect, dihaloalkanes have been used as precursors of biradicals.⁴ In particular, we have reported the versatility of dichlorodiphenylalkanes to provide linear alkanediyl biradicals through two-photon processes; by using two-laser two-color techniques, the first

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generated *n*-chloroalkyl radicals have been photolyzed to the corresponding biradicals.⁵ On the other hand, these reactive species have also been generated from acyl alkyl biradicals, obtained in the photolysis of the readily accessible 2, n-diphenyl- and 2-phenylcycloalkanones, through thermal or photochemical loss of carbon monoxide.^{6,7}

In this paper, we have focused our attention on the detection, characterization, and chemical reactivity of 4,4'-(1,2-ethanediyl)bisbenzyl biradical (2) in fluid solution. This type of reactive species has been postulated as intermediate in the thermal⁸ and photochemical racemization⁹ of optically active [2.2]paracyclophanes and in the polymerization of p-xylylene (1)¹⁰ (controlled polymerization of 1 leads to compounds of low molecular weight, including $3)^{11}$ (Scheme 1).

Interestingly, matrix isolation techniques have allowed the direct detection of biradical 2 in the photolysis of 3 at 77 K.^{12,13} A two-photon process via the triplet state (lifetime of a few seconds in such media) has been found to produce dissociation of paracyclophane to biradical 2. The formation of *p*-xylylene when irradiating **3** at 83 K has been interpreted as an evidence for the thermal cleavage of 2 to 1.12

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In solution, the lifetime of the T_1 triplet state is very short. Hegelson and Cram have studied the wavelength-dependent photochemistry of **3** in alcoholic solutions. From the analysis of photoproducts they have proposed that the biradical is produced by exciting **3** with light of wavelength shorter than 230 nm, which can be able to populate higher triplet states.¹⁴

On the other hand, **3** has been photolyzed with an ArF laser (193 nm) in the gas phase at 458 K. There has been no indication of $T_n \leftarrow T_1$ absorption, but *p*-xlylene is generated via a two-photon process.¹⁵

Thus, biradical **2** has not been detected in liquid solution, and it is not clear whether it couples to [2.2]-paracyclophane or/and dissociates to *p*-xylylene in this medium. Trying to obtain direct evidences on these issues, we have generated this species from different precursors such as 1,2-bis(4-chloromethylphenyl)ethane (**4**) and [3.2]paracyclophane-2-one (**8**). Photolysis of the latter precursor has clearly shown formation of biradical **2**, which does not cleave to *p*-xylylene but leads mainly to [2.2]paracyclophane under the reaction conditions; traces of the dimerization product, [2.2.2.2]paracyclophane (**11**), were also observed.

Results

Photolysis of 1,2-Bis(4-chloromethylphenyl)ethane 4. Laser flash photolysis (LFP) of deaerated 0.9 mM solutions of 1,2-bis(4-chloromethylphenyl)ethane (**4**)¹⁶ in cyclohexane at 266 nm (Nd:YAG laser, fourth harmonic, <10 ns, \leq 16 mJ/pulse) yielded a narrow transient absorption, with a sharp maximum at 320 nm (see Figure 1). The lifetime of this species was around 9 μ s under our experimental conditions. This signal was quenched by oxygen at close to the diffusion-controlled limit. Hence, it was assigned to be the benzylic radical **5** obtained through homolytic cleavage of one C–Cl bonds¹⁷ (Scheme 2).

Two-laser two-color experiments were performed in order to study the photoreactivity of the benzylic radical 5; thus, a 266 nm laser was used as the synthesis laser,



Figure 1. Top: transient absorption spectra recorded following laser excitation of **4** in cyclohexane under nitrogen 2.40 μ s (\triangle) and 12.2 μ s (\square) after the laser (266 nm) pulse. The insert shows the decay as monitored at 320 nm. Bottom: transient absorption spectra recorded following laser excitation of **6** in cyclohexane under nitrogen 2.40 μ s (\bigcirc) and 8.8 μ s (\square) after the laser (266 nm) pulse.



and a 308 excimer laser (HCl/Xe/Ne gas mixtures, excimer laser, ~6 ns, \leq 90 mJ/pulse) was used to photolyze the generated **5**. Though some bleaching of the signal at 320 nm was observed, spectra (not shown) were not clear enough as to make a safe assignment. GC/MS analysis of the photolyzate obtained after laser drop photolysis evidenced the formation of minor amounts of paracyclophane (**3**) (Scheme 2).¹⁸

To rule out the possibility that photocleavage of the ethane brigde in benzylic radical **5** could occur when using high-intensity irradiation conditions, we performed the laser photolysis of the model compound 1-(4-chloromethylphenyl)-2-(4-methylphenyl)ethane (**6**).¹⁹ LFP of deaerated 10 mM solutions of **6** in cyclohexane at 266 nm gave a spectrum typical of a benzylic radical ($\lambda_{max} =$ 320 nm). Two-laser two-color experiments (266/308 nm) were performed to study the possibility of photocleavage of the ethane bridge in benzylic radical **7** generated upon irradiation of **6** with the synthesis laser at 266 nm; no bleaching of the signal at 320 nm. In agreement

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with these observations, GC/MS analysis of the photolyzate did not show even trace amounts of **3** (Scheme 3). Thus, **7** is photostable; the same could be expected for its analogue **5**, although it cannot be completely ruled out that in the case of **5** the presence of the second chlorine atom could enhance cleavage of the ethane bridge.

Photolysis of [3.2]Paracyclophan-2-one (8). This compound can be obtained in low yield upon photolysis of [3.3]paracyclophane-2,11-dione.²⁰ Although ketone **8** has not previously been used as biradical precursor, it seemed reasonable to expect photocleavage to the acylalkyl biradical **9**, which due to α -phenyl substitution could (photo)decarbonylate^{6,7} to provide biradical **2** (Scheme 4). Lamp irradiation (Rayonet photoreactor, 30 min) at 254 nm of deaerated 2 mM benzene solutions of **8** led to [2.2]paracyclophane (**3**) as the only product; 50% of the starting ketone was recovered unchanged.

Laser flash photolysis of deaerated 1 mM solutions of **8** in cyclohexane at 266 nm yielded a narrow absorption



Figure 2. Transient absorption spectra recorded following laser excitation of **8** in cyclohexane under nitrogen 0.8 μ s (\bigcirc) and 16.5 μ s (\triangle) after the laser (266 nm) pulse. The insert shows the decay as monitored at 320 nm.

with maximum at 320 nm (see Figure 2). Its formation was not instantaneous, and its absorption decayed with the same kinetics over the entire spectrum (see inserts in Figure 2), thus supporting that only one species is responsible for this transient absorption. Its lifetime was around 8.6 μ s under our experimental conditions. The rounded top of the kinetic trace (see insert in Figure 2) probably reflects the decarbonylation in Scheme 4, which is expected to occur in the 100–300 ns time scale.²¹ The species was quenched by oxygen at close to the diffusioncontrolled limit. Hence, it was assigned to biradical **2** obtained through thermal loss of carbon monoxide from the initially generated acyl-alkyl biradical **9** (Scheme 4).

Two-laser two-color flash photolysis of ketone 8 was also performed. The synthesis laser (266 nm) produced biradical 2, which is the absorbing chromophore at the second laser wavelength (308 nm). Neither bleaching of the biradical by the 308 nm laser nor new signals in the UV spectra or emission at longer wavelengths were observed. This is not surprising since for the diphenylmethyl radical, where the excited-state lifetime is 260 ns,²² the lifetime in a biradical is 100 times shorter.²³ For the benzyl radical, the room temperature excited state is only 1 ns.²⁴ If we anticipate a comparable shortening in the case of biradicals, this emission would not be detectable. Product studies on the photolysis under highintensity irradiation provided further evidences against photocleavage of 2 to p-xylylene (1). Thus, deaerated 5 mM solutions of ketone 8 in cyclohexane, with the sample contained in a quartz spectrometer cell, were irradiated with 4000 laser pulses at 266 nm (Scheme 4). Product analysis revealed the formation of [2.2]paracyclophane and minor amounts of [2.2.2.2]paracyclophane (11);²⁵ however, not even traces of [2.2.2]paracyclophane (12) (which would also be formed if xylylene 1 were an intermediate)²⁵ were detected.

These results allow to rule out that biradical **2** thermally or photochemically cleaves to *p*-xylylene in liquid

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Figure 3. Top: transient absorption spectra recorded following laser excitation of **3** in cyclohexane under nitrogen 0.8 μ s (\bigcirc), 2.96 μ s (\square) 7.84 μ s (\blacksquare), and 14.5 μ s (\triangle) after the laser (266 nm) pulse. Bottom: traces monitored at 380 (left) and 290 nm (right).



Figure 4. Transient absorption spectra recorded following laser excitation of **3** in cyclohexane under oxygen 2.96 μ s (\bigcirc) and 7.84 μ s (\diamondsuit) after the laser (266 nm) pulse. The insert shows the decay as monitored at 290.

solution, but supports its coupling to [2.2]paracyclophane. Irradiation under high-intensity conditions generates high concentrations of biradical **2**, which is then able to dimerize giving product **11**, which is not found under conditions of lamp irradiation.

High-Intensity Irradiation of [2.2]Paracyclophane (3) in Solution. The above results motivated a reinvestigation of the photolysis of [2.2]paracyclophane in solution at room temperature.

Laser flash photolysis of deaerated 1 mM solutions of **3** in cyclohexane at 266 nm yielded a broad spectrum with maxima at 290 and 380 nm; a similar spectrum was obtained by irradiation at 308 nm (Figure 3). These signals decayed with different kinetics, showing the different nature of the species absorbing at the two wavelengths (see insets in Figure 3). Thus, while the band at 380 nm decayed with first-order kinetics, the 290 nm band had two components, a fast one with the same kinetics as the signal at 380 nm and a slower one. Oxygen saturated solutions of **3** in cyclohexane led to a narrow absorption spectrum with maximum at 290 nm (Figure 4). The long lifetime of the species, its absorption in this spectral region, and its low reactivity toward oxygen are



Figure 5. Top: (A) transient absorption spectra recorded following laser excitation of **3** in cyclohexane in the presence of cyclooctadiene $1.20 \ \mu s$ (\triangle), $3.76 \ \mu s$ (\bigcirc), and $8.08 \ \mu s$ (\Box) after the laser (266 nm) pulse. The insert shows the decay as monitored at 320 nm. Bottom: Effect of the laser power on signal intensities monitored at 290 (A) and 320 nm (B). 100% corresponds to a laser power of 10 mJ.

characteristic features of *p*-xylylene.²⁶ The oxygenquenchable band at 380 nm (with a component at 290 nm) was assigned to the triplet state of **3** ($T_4 \leftarrow T_1$) absorption (CT band characteristic of the transannular interaction between the aromatic rings).²⁷

Deaerated 3 mM solutions of **3** in cyclohexane containing cyclooctadiene as a triplet quencher were also irradiated at 308 nm. In this case, absorption spectra with two maxima, one at 290 nm and another one centered at 320 nm, were observed (Figure 5). It seems reasonable to assign the first absorption band with a longer lifetime to *p*-xylylene, while that at 320 nm with a shorter lifetime (9.6 μ s) (nondetected under oxygen) should correspond to biradical **2**. This band appeared as a shoulder in Figure 3.

Moreover, in agreement with the above results on the photolysis of **8**, biradical **2** clearly observed upon laser flash photolysis of **3** in the presence of the triplet quencher does not cleave to *p*-xylylene at room temperature. An investigation of the effects of light intensity on the size of the signals at 290 and 320 nm was carried out by attenuating the laser beam with a set of calibrated neutral density filters. The results (Figure 5) agreed with previous evidences supporting that both biradical **2** (in matrix media)¹³ and *p*-xylylene (in gas phase)¹⁵ originate through two-photon processes.

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Finally, deaerated 3 mM solutions of paracyclophane in cyclohexane were irradiated with 4000 laser pulses either at 248 or 266 nm and with the sample contained in a quartz spectrometer cell. Product analysis revealed the formation of [2.2.2]paracyclophane (12)²⁵ and [2.2.2.2]paracyclophane (11) (Scheme 4). While the formation of (11) agrees with the intermediacy of 2, the detection of 12 provided further evidences for the intermediacy of 1, which can couple either to its trimeric or tetrameric products.²⁵

Conclusion

4,4'-(1,2-Ethanediyl)bisbenzyl biradical (2) is detectable at room temperature and does not cleave to *p*-xylylene but cyclizes to [2.2]paracyclophane (3) or dimerizes to [2.2.2.2]paracyclophane (11). Furthermore, biradical 2 is photostable in liquid solution at room temperature.

Experimental Section

Reagents and Products. [2.2]Paracyclophane was commercially available. The required substrates **6**¹⁹ and **8**²⁰ were prepared following procedures described in the literature. Products **11** and **12** were known compounds;²⁵ their identification was based on NMR and MS spectra, by comparison with literature data.

Synthesis of 1,2-Bis(4-chloromethylphenyl)ethane (4).¹⁶ 1,2-Bis(4-hydroxymethylphenyl)ethane^{16b} was added to concentrated hydrochloric acid (15 mL), and the solution was allowed to stand at room temperature for 8 h. After this time, the reaction mixture was diluted with cold water (50 mL) and the organic material extracted with ether, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residue was submitted to semipreparative HPLC using hexane as eluent to obtain the dichloro compound 4 (90%): ¹H NMR (CDCl₃, 250 MHz) & 2.2 (m, 2 H), 2.6 (m, 2 H), 3.5 (m, 2 H), 7.1 (d, J = 6.5 Hz, 4H), 7.3 (d, J = 6.5 Hz, 4H); ¹³C NMR (CDCl₃, 62.5 MHz) & 215.3 (s), 138.4 (s), 128.6 (d), 128.1 (d), 127.0 (d), 55.8 (d), 29.5 (t); MS m/z 236 (M⁺, 12), 208 (7), 117 (7), 104 (100). Anal. Calcd for C₁₆H₁₆Cl₂: C, 68.83; H, 5.78. Found: C, 69.16; H, 5.79.

Conventional Lamp Irradiation of Compounds 4 and 8. A degassed 10 mM cyclohexane solution of **4** in a quartz tube was irradiated for 1 h with a 125 W mediumpressure mercury lamp inside a quartz inmersion well, under continuous magnetic stirring. In the case of compound **8**, a degassed 2 mM benzene solution of the ketone was irradiated for 30 min with a Rayonet photoreactor, seven RPR-253.7 nm lamps. In all cases, after evaporation of the solvent, the photomixture was analyzed by GC-MS and ¹H NMR.

Laser-Drop Photolysis. The beam from a Nd:YAG laser using the fourth harmonic (266 nm, <10 ns, \leq 16 mJ/pulse) was focused by means of a quartz lens into a drop of the photolysis solution suspended from a 2 in. syringe needle (20 gauge). Further details for this experiment have been described previously.²⁸

Laser Flash Photolysis. These experiments were carried out using either a Nd:YAG laser using the fourth harmonic (266 nm, <10 ns, <20 mJ/pulse), an excimer laser operated with HCl/Xe/Ne gas mixtures (308 nm, ca. 6 ns, \leq 90 mJ/pulse), or an excimer laser operated with $F_2/Kr/He$ gas mixtures (248 nm, ca. 6 ns, <100 mJ/pulse). Transient signals were captured with a Tetronix-2440 digital oscilloscope which was interfaced to a computer that also controlled the experiment. The system was operated with software written in the LabVIEW 3.1.1 environment from National Instruments.²⁹ Other aspects of this instrument are similar to those described earlier.²² The two-laser two-color experiments were performed by sending a trigger pulse to a delay generator which then sent TTL pulses which fired the lasers at the desired sequence. All experiments were carried out using cells constructed from 7×7 mm Suprasil quartz tubing. Samples were purged with a slow stream of either nitrogen or oxygen, as required.

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