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Laser Flash Photolysis of [3,*n*]Paracyclophan-2-ones. Direct Observation and Chemical Behavior of 4,4′-(1,*n*-Alkanediyl)bisbenzyl Biradicals

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The 4,4′-(1,*n*-alkanediyl)bisbenzyl biradicals (**2b**−**d**) have been generated from the Norrish type-I reaction of [3,*n*]paracyclophan-2-ones (**1b**−**d**) giving the paracyclophanes **3b**−**d** as the only reaction products. The behavior of biradicals **2b**−**d** has been studied in detail and compared with the previously reported biradical **2a**. The lifetimes increase as the chain length decreases and are affected by the solvent viscosity, thus showing the effect of the length of the chain on the conformations of the biradicals. Quenching with persistent radicals such as TEMPO resulted in length-dependent rate constants. Finally, the study of the magnetic field effects on the biradical lifetimes suggest that ISC control determines biradical lifetimes for long-chain systems.

Introduction

Biradicals have been postulated as reactive intermediates in numerous thermal and photochemical reactions.[1−3] Their direct detection by time-resolved techniques has allowed the study of their spectral properties and chemical behavior. The lifetimes of triplet biradicals are usually controlled by intersystem crossing (ISC), which is sensitive to the different biradical conformations.[4−9] While ISC can occur by two major pathways, spin−orbit coupling (SOC) and electron−nuclear hyperfine coupling (HFC), the latter is only expected to be important when the triplet−singlet energy gap is very small, as for example, when there is large separation between the two radical centers.

Recent interest has been focused on the study of interactions between the radical termini in long-chain acyl−alkyl biradicals.[10,11] One of the main limitations in the study of biradicals is the availability of suitable photochemical precursors, since unambiguous assignment of the reaction products is only possible when they can be clearly distinguished from starting substrates. In this respect, alkanediyl biradicals have been generated from acyl alkyl biradicals obtained in the photolysis of the readily accessible cycloalkanones through thermal or photochemical loss of carbon monoxide.[9,12,13] It is known that their lifetimes increase with increasing distance between the radical centers, showing the SOC contribution to ISC.[14]

We have previously reported the generation of 4,4′-(1,2-ethanediyl)bisbenzyl biradical (**2a**) from [3,2]paracyclophan-2-one (**1a**).[13] This methodology could be extended to (1,*n*-alkanediyl) homologues with longer tethers whose chemical behavior has not been reported (Scheme 1). Further, to the best of our knowledge, the synthesis and photochemical behavior of [3,*n*]paracyclophan-2-ones **1b**−**d** have not been described.

Results

Ketones **1b**-**d** were synthesized by the reaction of *p*-toluenesulfonylmethyl isocyanide with the corresponding 1,*n*-bis(4-bromomethylphenyl)alkanes[15] under phase-

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(1) Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker Inc.: New York, 1985; Vol. 7, pp 339−465.

(2) Johnston, L. J. *Chem. Rev.* **1993**, *93*, 251−266.

(3) Scaiano, J. C.; Johnston, L. J. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1989; Vol. 10, pp 309−356.

(4) Barton, D. H. R.; Charpiot, B.; Ingold, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. *J. Am. Chem. Soc.* **1985**, *107*, 3607−3611.

(5) Johnston, L. J.; Scaiano, J. C.; Sheppard, J. W.; Bays, J. P. *Chem. Phys. Lett.* **1986**, *124*, 493−498.

(6) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819−823.

(7) Tanaka, R.; Kuriyama, Y.; Itoh, H.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1993**, *8*, 1447−1450.

(8) Zimmt, M. B.; Doubleday: C.; Gould, I. R.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6724−6726.

(9) Miranda, M. A.; Font-Sanchis, E.; Perez-Prieto, J.; Scaiano, J. C. *J. Org. Chem.* **1999**, *64*, 7842−7845.

(10) Suzuki, I.; Tanaka, R.; Yamaguchi, A.; Maki, S.; Misawa, H.; Tokumaru, K.; Nakagaki, R.; Sakuragi, H. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 103−113.

(11) Tsentalovich, Y. P.; Morozova, O. B.; Avdievich, N. I.; Ananchenko, G. S.; Yurkovskaya, A. V.; Ball, J. D.; Forbes, M. D. E. *J. Phys. Chem. A* **1997**, *101*, 8809−8816.

(12) Weiss, D. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker Inc.: New York, 1981; Vol. 3, pp 347−420.

(13) Miranda, M. A.; Font-Sanchis, E.; Perez-Prieto, J.; Scaiano, J. C. *J. Org. Chem.* **2001**, *66*, 2717−2721.

(14) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92−111.

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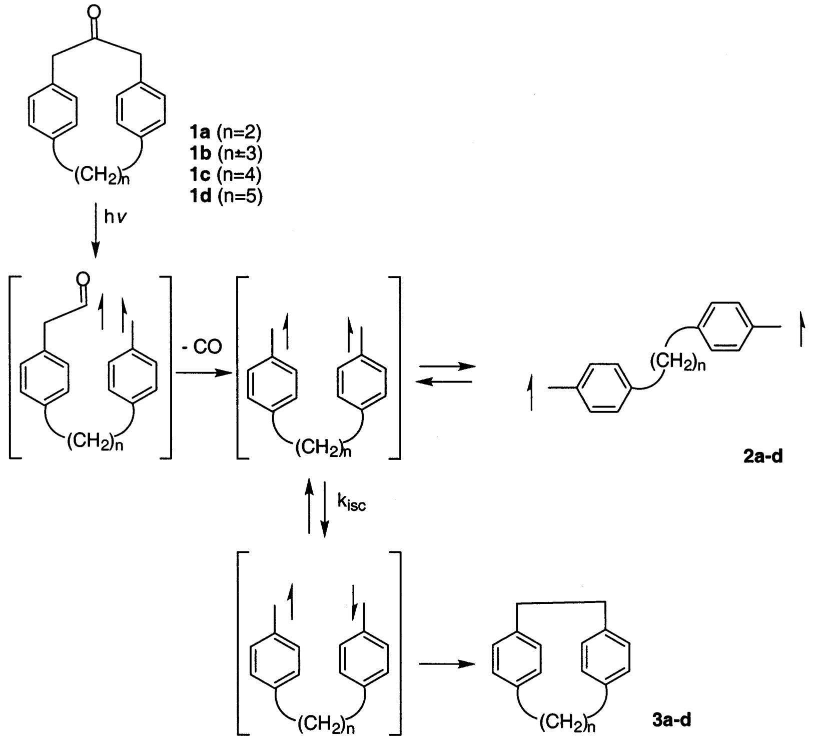
SCHEME 1



transfer conditions followed by acid hydrolysis. Lamp irradiations of deaerated solutions of **1b**−**d** were performed at 254 nm. Analysis of the photolyzate by ^{1}H NMR and GC/MS shows the presence of the decarbonylated cyclophanes (**3b**−**d**) as the only reaction products (Scheme 1).[16,17] No disproportionation or fragmentation products are detected.

Laser flash photolysis (LFP) of deaerated 1 mM solutions of **1c**,**d** in cyclohexane at 266 nm (Nd:YAG laser, fourth harmonic, <10 ns, ≤20 mJ pulse^{-1}) yield narrow absorptions with maxima at ~320 nm (Figure 1). These species have lifetimes ≥1 μs and are quenched by oxygen at close to the diffusion-controlled limit. We have previously reported that photolysis of [3,2]paracyclophan-2-one in solution at room temperature produces 4,4′-(1,2-ethanediyl)bisbenzyl biradical (**2a**) ($\lambda = 320$ nm, $\tau = 8.6$ μs) by thermal decarbonylation of the initially generated acyl−alkyl biradicals.[13] Thus, the long lifetimes of the transient absorbing at 320 nm and its high reactivity toward oxygen support their assignment to the 4,4′-(1,*n*-alkanediyl)bisbenzyl biradicals.

On the other hand, LFP of **1b** yield a broad band at 440 nm with a lifetime of 0.6 μs, together with the signal at 320 nm belonging to the biradical **2b** (Figure 2). Both transients are readily quenched by oxygen. However, these species show different behavior toward a triplet quencher. Photolysis of nitrogen-saturated solutions of **1b** in cyclohexane containing *cis,cis*-1,3-cyclooctadiene shows that the 320 nm band decreases in intensity (though its lifetime remain essentially unchanged) while the transient absorbing at 440 nm is readily quenched. Thus, the band at 440 nm should be ascribed to the triplet state of **1b**; the long wavelength absorption could be probably due to transannular charge-transfer reflecting the interaction between the aromatic rings. As expected, quenching of the triplet by diene leads to a decrease in the yield of biradical formation.

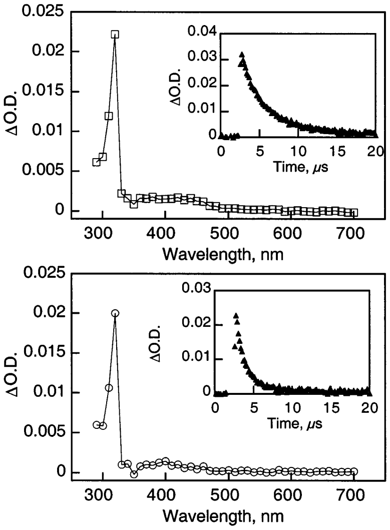


FIGURE 1. Top: transient absorption spectrum recorded following laser excitation of **1c** in cyclohexane under nitrogen (□) 1.20 μs after the laser pulse. Bottom: transient absorption spectrum recorded following laser excitation of **1d** in cyclohexane under nitrogen (○) 0.32 μs after the laser pulse. The insets show the decays as monitored at 320 nm.

Additional support for the above triplet assignment was obtained by LFP experiments with [3,3]paracyclophane (**4**) and [3,3]paracyclophan-2,11-dione (**5**) (Scheme 2). The photolysis of **4** under nitrogen at 266 nm shows

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(15) Wagner, J.; Bendig, J.; Kreysig, D. *Z. Chem.* **1983**, *23*, 407−408.

(16) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3517−3526.

(17) Miyahara, Y.; Shiraishi, T.; Inazu, T.; Yoshino, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 953−954.

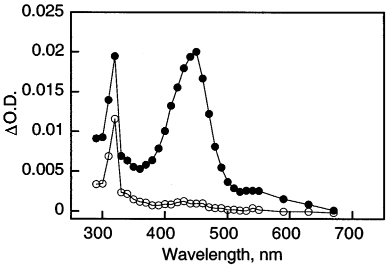


FIGURE 2. Transient absorption spectra recorded following 266 nm laser flash photolysis of a sample containing [3,3]-paracyclophan-2-one **1b** in cyclohexane under nitrogen (●) 2.48 μs and (○) 6.72 μs after the laser pulse.

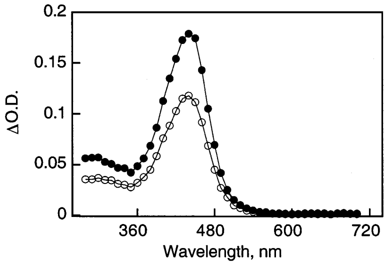
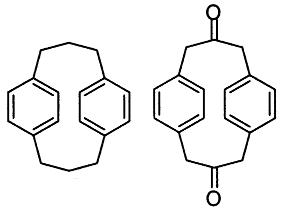


FIGURE 3. Transient absorption spectra recorded following laser excitation of [3,3]paracyclophane **4** in cyclohexane under nitrogen (●) 0.64 μs and (○) 2.24 μs after laser pulse (266 nm).

SCHEME 2



4 **5**

a broad absorption with maximum at 440 nm that decays with the same kinetics over the entire spectrum, thus supporting that only one species is responsible for this transient absorption (Figure 3). The photolysis of the dione **5** under the same conditions yield a broad spectrum with maxima at 320 and 440 nm that decay with different kinetics (Figure 4). Both transients are extremely reactivity toward oxygen, but only the latter species was quenched by *cis,cis*-1,3-cyclooctadiene. Therefore, it was clear that the absorption at 440 nm, observed in the photolysis of **1b**, **4**, and **5** could be due to $\pi-\pi^*$ interactions in the corresponding triplet states.

The biradical lifetimes measured for **2a**−**d** were surprisingly long for benzyl-centered biradicals at room temperature (see Table 1). These results suggested that a comparison of the half-lives of the 4,4′-(1,*n*-alkanediyl)bisbenzyl biradicals with their monoradical analogues could be informative; we note that the decay of monoradicals occurs largely by second-order kinetics, making half-lives a more useful comparative parameter. We chose **7** as a representative monoradical system. Thus, the chloroalkane 1-(4-chloromethylphenyl)-2-(4-methylphenyl)ethane (**6**) was used as precursor of **7** (Scheme 3). LFP of deaerated 1 mM solutions of **6** in cyclohexane gave a transient with maximum at 320 nm and a half-life of 10.6 μs that was quenched by oxygen at close to the diffusion-controlled limit; thus, this transient was assigned to the benzyl radical **7**. For comparison the lifetime of **2a** is 8.6 μs under comparable experimental conditions. This, and the fact that no magnetic field effect was observed for **2a**,**b**, suggests that in this case, the lifetime could be controlled by the encounter of the benzyl moieties, rather than by the dynamics of intersystem crossing.

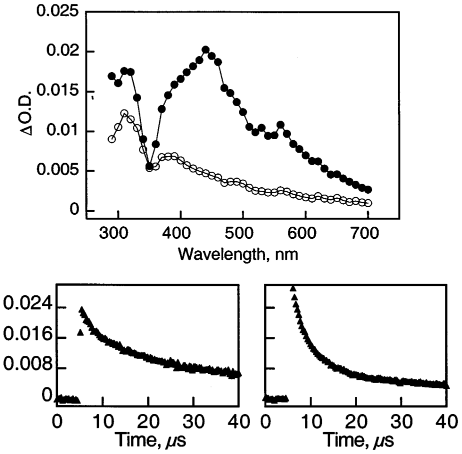
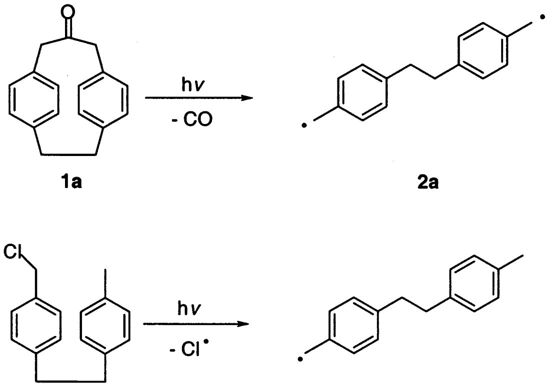


FIGURE 4. Top: transient absorption spectra recorded following laser excitation of **5** in cyclohexane under nitrogen (●) 4.16 and (○) 13.4 μs after laser pulse (266 nm). Bottom: traces monitored at 320 nm (left) and 480 nm (right).

TABLE 1. Lifetimes of Biradicals in Cyclohexane (τ_C) and Ethylene Glycol (τ_E). Rate Constants (k_T) for the Reaction of TEMPO with Biradicals at Room Temperature in Acetonitrile

biradical	τ_C (μs)	τ_E (μs)	k_T (10^8 M^{-1} s^{-1})
2a	8.6	60.7	2.4
2b	3.9	16.4	6.6
2c	3.0	3.6	22
2d	1.3	1.6	21

SCHEME 3

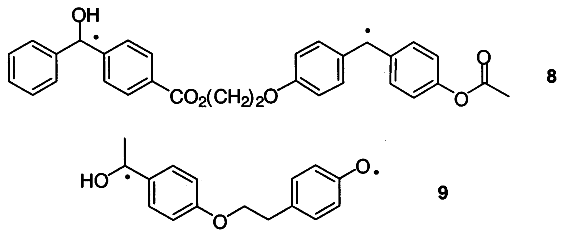


1a **2a**

6 **7**

Conformational motions of biradicals can be slowed-down by increasing the viscosity of the solvent. Table 1 shows the increase in biradical lifetimes when cyclohexane was replaced by ethylene glycol as the solvent; the most dramatic effect was observed for short biradicals (with $n \leq 3$).

SCHEME 4



Triplet biradicals are readily quenched by paramagnetic substrates such as nitroxide radicals.[18-20] To study the reactivity of biradicals **2a**−**d** toward TEMPO, LFP of 1 mM solutions of [3,*n*]paracyclophan-2-ones in acetonitrile were carried out in the presence of various amounts of TEMPO (0−2 mM) (see Table 1). The rate constants obtained for the biradicals with long chain **2c**,**d** are not unexpected (values around 2×10^9 $M^{-1}s^{-1}$ have been reported for α,α,ω,ω-tetraphenyl-α,ω-diyl biradicals in benzene at 300 K).[4] However, the values for **2a**,**b** are slightly low for biradicals; in fact, a similar rate constant (9.5×10^7 $M^{-1}s^{-1}$) has been reported for benzyl radical generated from dibenzyl ketone under the same conditions.[21] TEMPO can react with biradicals via assisted intersystem crossing what is accompanied by shortening of biradical lifetime. However, analysis of the lamp photolysate of **1d** in the presence of TEMPO by ^{1}HNMR reveals the generation of the product arising from the trapping of the acyl−alkyl biradical.[22]

The singlet−triplet energy gaps (E_{ST}) for **2a**−**d** biradicals are unknown. However, for benzyl−benzyl biradicals there is an inverse relation between E_{ST} and spatial separation between the radicals centers.[23,24] Thus, the lifetime for biradical **8** increases when the applied magnetic field was increased.[25] However, more interaction between the radical centers, and therefore a much larger singlet−triplet energy gap has been proposed to explain the lack of magnetic field effects in biradical **9** (Scheme 4).[26]

The relatively large singlet−triplet energy gap for **2a**,**b** probably underlies the low reactivity toward TEMPO for biradicals $n \leq 3$. To gain further insight into this aspect magnetic field effects were studied by application of a 0−3000 G; no effect on the lifetime of 4,4′-(1,*n*-alkanediyl)bisbenzyl biradicals with $n \leq 3$ was observed. However, long chain biradicals show a slight increase in their lifetimes as magnetic field increased until the asymptotic value of 2000 G (Figure 5). Under these conditions, the $k_{isc}/k_{isc}{}^0$ ratio is 0.93 and 0.72 for **2c** and **2d**, respectively.

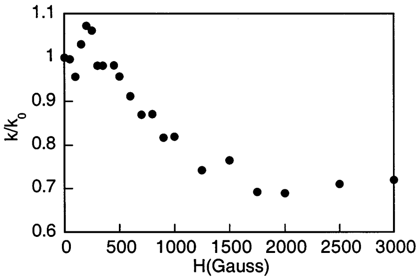
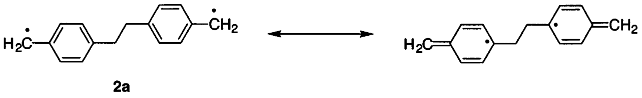


FIGURE 5. Magnetic field effect on the transient decay trace at 320 nm upon 266 nm laser flash photolysis of a 1 mM solution of [3,5]paracyclophan-2-one **1d** in cyclohexane. *k* represents the ISC rate constant in a magnetic field H and k_O the ISC rate constant in the earth's field.

SCHEME 5



Calculations were performed at the UB3LYP/6-31g* level for biradicals **2a** and **2d**. The calculations correctly predict very small ST gaps in the 2−4 cal/mol range and a low-lying singlet state. The relative values for **2a** and **2d** seemed unreliable. For example the ST gap for **2a** was predicted to be smaller than for **2d**. This is contrary to chemical intuition, but more important to the fact that **2d** is subject to magnetic field effects, while **2a** is not, implying that the latter has a larger ST separation.

Discussion

Laser flash photolysis of ketones **1b**−**d** leads to biradicals **2b**−**d** with predictable spectroscopic properties, dominated by the benzyl radical chromophore, and spectroscopically indistinguishable from those of biradical **2a**, or the corresponding monoradical, $PhCH_2^{\bullet}$. This suggests that the relaxed conformation is a stretched one, with minimal interaction between the chromophores.

The negligible magnetic field effects for **2a**,**b** suggest a singlet−triplet energy gap sufficiently large that cannot be overcome by Zeeman splitting of the triplet sublevels in the range of magnetic fields available to us. It appears that resonance places enough spin density at the para positions of **2a**, that behaves as a relatively short biradical (See Scheme 5). In contrast, biradicals **2c** and **2d** are affected by an external magnetic field in much the same way as confined radical pairs, although the fields required are higher than for true radical pairs; this shows that for these long biradicals the lifetimes are controlled by ISC.

The decrease in biradical lifetimes with increasing tether length, combined with the effect of viscosity, suggest that for short biradicals attaining a folded conformation (for at least **2a** and **2b**) controls their decay. It would be hard to rationalize the 7-fold increase in lifetime between cyclohexane and ethylene glycol observed for **2a** with a different hypothesis. While lifetime enhancements are also observed for all other biradicals,

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[18] Adam, W.; Bottle, S. E. *Tetrahedron Lett.* **1991**, *32*, 1405−1408.

[19] Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521−547.

[20] Grissom, J. W.; Gunawardena, G. U. *Tetrahedron Lett.* **1995**, *36*, 4951−4954.

[21] Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983−4992.

[22] The lamp irradiation (Luzchem photoreactor equipped with eight UV lamps, Pyrex filter) of a deaerated 10 mM benzene solution of **1d** for 3 h was carried out in the presence of TEMPO (25 mM) at 300 nm. The reaction mixture was concentrated, and the resulting residue purified by chromatography (CH_2Cl_2). Analysis by NMR showed the generation of the trapping product: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9−1.7 (m, 42 H), 2.6 (t, J = 6 Hz, 4 H), 3.6 (s, 2H), 4.8 (s, 2 H), 7.1−7.3 (m, 8 H).

[23] Wang, J.; Doubleday: C.; Turro, N. J. *J. Phys. Chem.* **1989**, *93*, 4780−4782.

[24] Doubleday: C.; Turro, N. J.; Wang, J.-F. *Acc. Chem. Res.* **1989**, *22*, 199−205.

[25] Mori, Y.; Sakaguchi, Y.; Hayashi, H. *Chem. Phys. Lett.* **1999**, *301*, 365−371.

[26] Scaiano, J. C.; McGimpsey, W. G.; Leigh, W. J.; Jakobs, S. *J. Org. Chem.* **1987**, *52*, 4540−4544.

the effects are dramatically smaller for **2c** and **2d**, suggesting that lifetimes are controlled by a different parameter. This, combined with the detection of magnetic field effects for **2c** and **2d** makes a compelling case for ISC as the key parameter for these systems.

In conclusion, laser flash photolysis of ketones **1b**−**d** has allowed the generation, detection and study for the first time of the 4,4′-(1,*n*-alkanediyl)bisbenzyl biradicals (**2b**−**d**) in solution at room temperature. Conformations of the biradicals, and the factors that determine their decay dynamics, have been found to be affected by the length of the chain linking the benzyl radical moieties. This is reflected in the chemical behavior of the biradicals; with longer tethers leading to behavior approximating that of true radical pairs.

Experimental Section

General Procedure. ^1H and ^{13}C NMR spectra were recorded in a 200 MHz spectrometer; chemical shifts (δ) are reported in ppm relative to TMS. GC/MS measurements were made on a quadrupole mass selective detector connected to a gas chromatography equipped with DB-5 capillary column (30 m × 0.32 mm i.d.; film thickness 0.25 μm). Combustion analyses were performed at M−H−W Laboratories, Phoenix, AZ. The external magnetic field source was a “homemade” magnet that can achieve fields of up to 3000 G. Continuous variation in the magnetic field was possible through the use of a Hewlett-Packard 6282A DC power supply.

Reagents. TEMPO and *cis,cis*-1,3-cyclooctadiene were commercially available. The substrates **4**[27] and **5**[28] were prepared following procedures described in the literature.

Synthesis of 1-(4-Chloromethylphenyl)-2-(4-methylphenyl)ethane (6).[29] 1-(4-Hydroxymethylphenyl)-2-(4-methylphenyl)ethane[30] was added to thionyl chloride (10 mL), and the solution was allowed to stand at room temperature for 12 h; after this time, thionyl chloride was removed under reduced pressure. The residue was submitted to semipreparative HPLC using hexane as eluent to obtain the chloro compound **6** (92%): ^1H NMR ($CDCl_3$) δ 2.3 (s, 3 H), 2.9 (s, 4 H), 4.6 (s, 2 H), 7.2 (d, $J = 8$ Hz, 4 H), 7.3 (d, $J = 8$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 142.1 (s), 138.3 (s), 135.2 (s), 134.8 (s), 128.9 (d), 128.7 (d), 128.5 (d), 128.1 (d), 46.1 (t), 37.6 (t), 37.2 (t), 20.9 (q); MS *m/z* 244 (M^+, 95), 209 (42), 139 (38), 105 (100), 77 (65).

Synthesis of [3.2]Paracyclophan-2-one (1a).[31] This compound was obtained upon photolysis of [3.3]paracyclophane-2,11-dione (**5**): ^1H NMR ($CDCl_3$) δ 3.0 (s, 4 H), 3.7 (s, 4 H), 6.4 (d, $J = 8$ Hz, 4 H), 6.7 (d, $J = 8$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 207.0 (s), 140.0 (s), 133.3 (s), 133.1 (d), 131.0 (d), 51.5 (t), 33.7 (t); MS *m/z* 236 (M^+, 85), 208 (72), 104 (100), 77 (28).

Synthesis of [3.*n*]Paracyclophan-2-ones 1b−d. These compounds were synthesized in low yield (9−15%) by the reaction of *p*-toluenesulfonylmethyl isocyanide (TosMIC) with the corresponding 1,*n*-bis(4-bromomethylphenyl)alkanes. Thus, to a refluxed mixture of *n*-Bu_4NBr (1.6 g, 5 mmol) in CH_2Cl_2 (500 mL) and 30% aqueous NaOH solution (60 mL) was added a mixture of the corresponding 1,*n*-bis(4-bromomethylphenyl)-alkane (2 mmol) and TosMIC (0.4 g, 2 mmol) in CH_2Cl_2 (60 mL) over a period of 2 h. After the solution was refluxed for an additional 3 h and allowed to cool, water (100 mL) was added. The organic layer was concentrated under vacuum. To the residue in CH_2Cl_2 (10 mL) was added concentrated hydrochloric acid (10 mL) and the mixture stirred for 10 min at room temperature. After the usual workup, the residue was chromatographed on silica gel with CH_2Cl_2 to afford the ketones **1b**−**d**.

[3,3]Paracyclophan-2-one **(1b)**: ^1H NMR ($CDCl_3$) δ 2.0−2.2 (m, 2 H), 2.7 (t, $J = 5$ Hz, 4 H), 3.7 (s, 4H), 6.7 (d, $J = 8$ Hz, 4 H), 6.8 (d, $J = 8$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 208.2 (s), 140.0 (s), 133.3 (s), 130.2 (d), 129.9 (d), 51.9 (t), 36.0 (t) 29.2 (t); MS *m/z* 250 (M^+, 90), 222 (18), 117 (100), 91 (22). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.33; H, 7.12.

[3,4]Paracyclophan-2-one **(1c)**: ^1H NMR ($CDCl_3$) δ 1.5−1.7 (m, 4 H), 2.3 (t, $J = 5$ Hz, 4 H), 3.7 (s, 4 H), 6.6 (d, $J = 8$ Hz, 4 H), 6.7 (d, $J = 8$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 207.0 (s), 140.4 (s), 131.4 (s), 129.5 (d), 129.0 (d), 51.4 (t), 35.5 (t), 29.0 (t); MS *m/z* 264 (M^+, 100), 236 (18), 208 (22), 104 (70). Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.51; H, 7.69.

[3,5]Paracyclophan-2-one **(1d)**: ^1H NMR ($CDCl_3$) δ 0.6−0.8 (m, 2 H), 1.3−1.5 (m, 4 H), 2.4 (t, $J = 6$ Hz, 4H), 3.7 (s, 4 H), 6.7 (d, $J = 8$ Hz, 4 H), 6.9 (d, $J = 8$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 207.0 (s), 140.0 (s), 130.9 (s), 128.9 (d), 128.6 (d), 51.2 (t), 33.8 (t), 28.7 (t), 22.5 (t); MS *m/z* 278 (M^+, 100), 250 (12), 117 (46), 104 (50), 91 (28), 77 (18). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.20; H, 7.76.

Conventional Lamp Irradiation of Compounds 1b−d. Deaerated 1 mM cyclohexane or benzene solutions of **1b**−**d** were irradiated for 1 h at 254 nm with a prototype of a Luzchem photoreactor equipped with eight UV lamps. The photolysis mixture was analyzed by GC−MS and ^1H NMR.

Laser Flash Photolysis. These experiments were carried out using a Nd:YAG laser using the fourth laser harmonic (266 nm, <10 ns, <20 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 4.1 environment from National Instruments.[32] Other aspects of this instrument are similar to those described earlier.[33] All experiments were carried out using Luzchem cuvettes constructed from 7 × 7 mm quartz tubing. Samples were purged with a slow stream of either nitrogen or oxygen, as required.

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(27) Otsubo, T.; Kitasawa, M.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1515−1520.

(28) Kurosawa, K.; Suenaga, M.; Inazu, T.; Yoshino, T. *Tetrahedron Lett.* **1982**, *23*, 5335−5338.

(29) Amatore, C.; Gaubert, F.; Jutand, A.; Utley, J. H. P. *J. Chem. Soc., Perkin Trans. 2* **1996**, *11*, 2447−2452.

(30) Camaioni, D. M.; Franz, J. A. *J. Org. Chem.* **1984**, *49*, 1607−1613.

(31) Isaji, H.; Sako, K.; Takemura, H.; Tatemitsu, H.; Shinmyozu, T. *Tetrahedron Lett.* **1998**, *39*, 4303−4304.

(32) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747−7753.

(33) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396−4403.