

Flash Photolysis of (*E*)-1,2-Bis(1-chloro-1-phenylmethyl)cyclopropane. Generation of 1,5-Diphenylpentadienyl Radical and 1,5-Diphenylpentadienylum Cation

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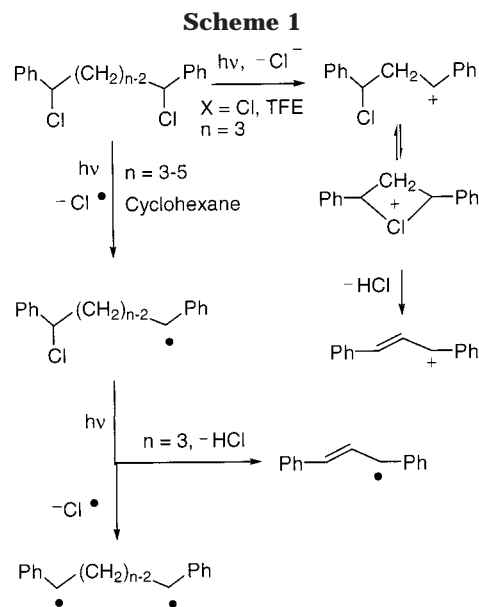
Received August 1, 2001

The 1,5-diphenylpentadienyl radical (**5**) is generated from (*E*)-1,2-bis(1-chloro-1-phenylmethyl)cyclopropane (**1**) via a two-photon process, either in cyclohexane or in acetonitrile as solvent. Two-laser two-color flash photolysis experiments show that excitation of the benzylic radical generated by homolysis of the first C–Cl bond leads, after ring-opening and proton loss, to the stabilized radical **5**. This radical is also generated by photolysis of either (1*E*,3*E*)-5-chloro-1,5-diphenyl-1,3-pentadiene (**6**) or (1*E*,4*E*)-1,5-diphenyl-1,4-pentadiene (**7**) via one-photon or two-photon processes, respectively. On the other hand, laser flash photolysis of **1** in acetonitrile also produces some 1,5-diphenylpentadienylum cation (**10**) generated via a one-photon process. Its formation can be explained as due to competitive photoheterolysis leading to a benzylic cation which thermally ring-opens and dehydrohalogenates. Species **10** is more efficiently generated by photolysis of **6** in acetonitrile and undergoes photoisomerization after laser excitation.

Introduction

Photolysis of monohalogenated organic compounds is known to induce carbon–halogen (C–X) bond cleavage, giving products from either heterolysis or homolysis. Their ratio depends on the structure of the compound, the nature of leaving group, and the polarity and nucleophilicity of the solvent.^{1,2}

The photochemistry of dihalides, in which the C–X bonds are separated by two or more carbon atoms, is a subject of recent interest. They can be photochemical precursors of carbenes, *n*-haloalkylradicals, haloalkyl- and allyl- cations, biradicals, biradicaloids, and allyl radicals. The nature of the photogenerated intermediates depends on the intensity of the irradiation and the polarity of the solvent (Scheme 1).^{3–7} Thus, 1,3-dichloro-1,3-diphenylpropane photolyzes in polar solvents giving rise to 3-chloro-1,3-diphenylpropylum cation, which thermally eliminates HCl to produce the stabilized 1,3-



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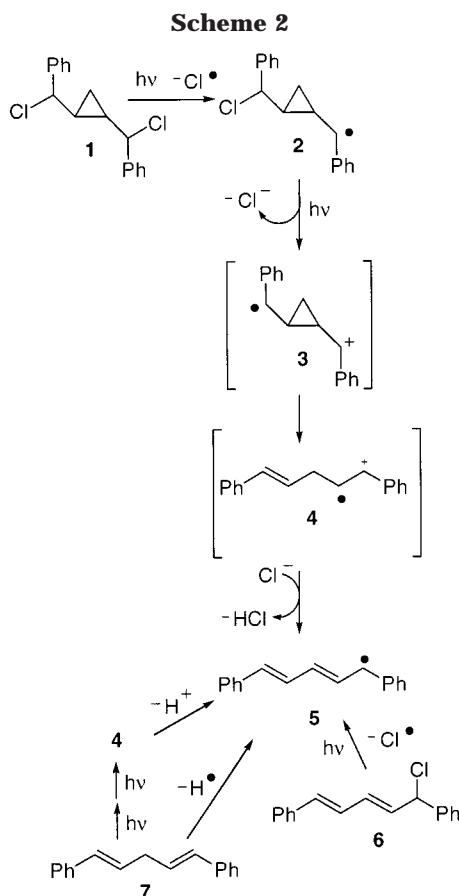
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diphenylpropenylum cation.⁷ On the other hand 1,*n*-biradicals are formed in low polarity solvents; thus, homolytic cleavage of the first C–Cl bond in 1,*n*-dichloro-

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To gain further insight into the stereoelectronic requirements for intramolecular electron transfer between radicals and halides, we decided to perform laser flash photolysis (LFP) studies on the bichromophoric (*E*)-1,2-bis(1-chloro-1-phenylmethyl)cyclopropane (**1**), a rigid analogue of 1,4-dichloro-1,4-diphenylbutane (Scheme 2). This substrate appeared suitable for such studies, since cyclopropyl-substituted benzyl radicals can be detected by LFP;⁹ hence, photolysis of the first C-Cl bond in **1** would lead to the benzylic radical **2**, whose behavior upon irradiation could be studied.

Actually, LFP of **1** generates 1,5-diphenylpentadienyl radical (**5**) via a two-photon process. This demonstrates that light absorption by the benzylic radical in **2** induces cleavage of the remaining C-Cl bond.

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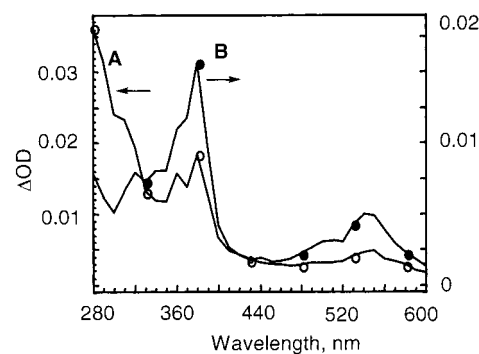


Figure 1. Transient absorption spectra recorded following laser excitation (266 nm) of **1** in acetonitrile 0.32 μ s after the laser pulse, under nitrogen (A; left scale) or oxygen (B; right scale) atmosphere.

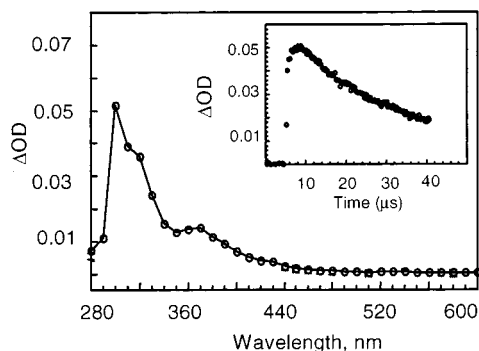


Figure 2. Transient absorption spectrum recorded following laser excitation (308 nm) of benzylcyclopropane/*tert*-butyl peroxide mixtures in benzene 0.16 μ s after the laser pulse. The insert shows the decay as monitored at 320 nm.

Results and Discussion

Laser flash photolysis (266 nm) of deaerated 0.6 mM solutions of (*E*)-1,2-bis(1-chloro-1-phenylmethyl)cyclopropane (**1**) in acetonitrile yielded a transient with a broad absorption band extending from 280 to 350 nm, together with two bands at 360/380 nm and a weak signal around 540 nm (curve A, Figure 1). Similar experiments in cyclohexane produced only a broad absorption centered around 290 nm and extending to 400 nm (spectrum not shown).

The transient absorption between 280 and 350 nm seemed to decay with uniform kinetics, with a lifetime of around 30 μ s in acetonitrile. It was quenched by oxygen at close to the diffusion control limit (curve B, Figure 1).

It is known that photolysis of dichlorodiphenylalkanes in cyclohexane ensues with homolysis of one carbon-halogen bond to produce chloroalkyl radicals which are readily quenched by oxygen at close to diffusion controlled limit.⁸ Thus, the transient absorbing at 280-350 nm in Figure 1 can be ascribed to the benzylic radical **2** (Scheme 2). This type of species has been obtained by hydrogen abstraction from benzylcyclopropane.⁹ To secure the assignment a solution containing di-*tert*-butylperoxide/benzylcyclopropane mixture in benzene was irradiated at 308 nm; the spectrum showed a band absorbing at 300-350 nm with a lifetime of 25 μ s (Figure 2).

On the other hand, the decay of the absorption at 380 nm in acetonitrile (Figure 1) exhibited two distinct components. The short-lived component (not observed

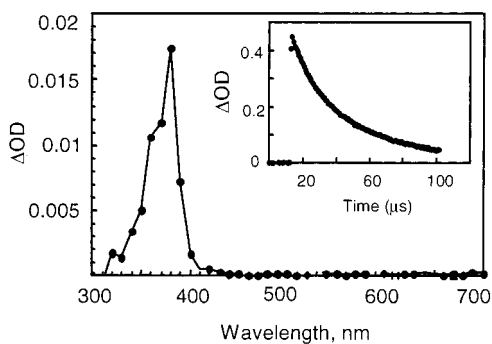
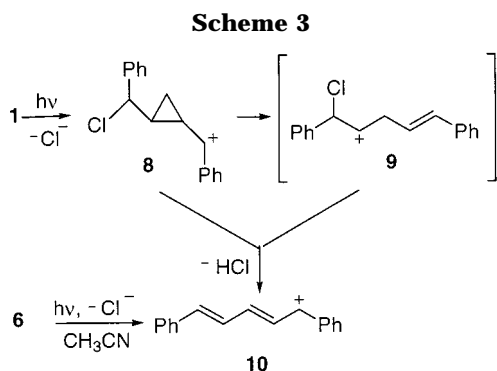


Figure 3. Transient absorption spectrum recorded following laser excitation (266 nm) of 0.06 mM solutions of chloride **6** in cyclohexane under nitrogen atmosphere 2.8 (●) μ s after the laser pulse.



when cyclohexane was the solvent) decayed with a lifetime of 200 ns; it was quenched upon addition of nucleophiles, such as water and methanol, but it was unaffected by oxygen. This is compatible with a carbocationic species. Cyclopropyl-substituted benzyl cations have been detected in the LFP of (*E*)-2,3-diphenylaziridinimines of aryl cyclopropyl ketones.¹⁰ The absorption maximum of the corresponding cation appears at 345 nm with a lifetime around 600 ns in trifluoroethanol. Thus, the short-lived component of the 380 nm band in the LFP of **1** in acetonitrile is ascribed to photoheterolysis (Scheme 3).

On the other hand, the long-lived component at 380 nm had a lifetime around 40 μ s, that was reduced to 25 μ s in oxygen saturated solutions. The absorption at relatively long wavelength, its long lifetime, and its reactivity toward oxygen suggested a stabilized 1,5-diphenylpentadienyl radical (**5**). The spectrum and lifetime of this radical have not been reported yet but LCI-SCF studies of radical **5** predict an absorption maximum close to the observed value.¹¹ In an attempt to confirm the nature of this transient, LFP of 0.06 mM solutions of (*1E,3E*)-5-chloro-1,5-diphenyl-1,3-pentadiene (**6**) in cyclohexane was carried out (Scheme 2). The absorption maxima (at 360 and 380 nm) and the lifetime of the detected transient were similar to those assigned to the pentadienyl radical **5** (Figure 3). The same spectrum was obtained when a 3 mM solution of (*1E,4E*)-1,5-diphenyl-1,4-pentadiene (**7**) in di-*tert*-butyl peroxide was irradiated at 355 nm. Here the *tert*-butoxy radical formed abstracts the allylic hydrogen atom from the olefin **7** and provides also a clean source of **5** (Scheme 2).

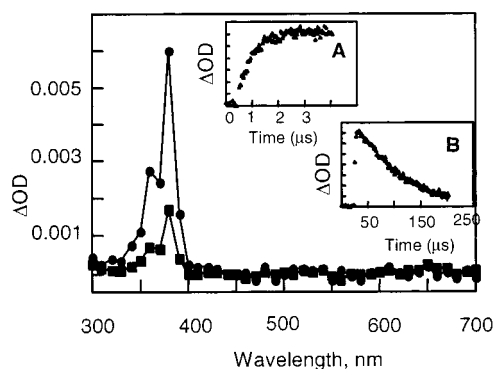


Figure 4. Transient absorption spectra recorded following laser excitation (266 nm) of 0.07 mM solutions of 1,5-diphenyl-1,4-pentadiene in acetonitrile under nitrogen atmosphere 22.4 (●) and 136 (■) μ s after the laser pulse. The inserts shows the growing (A) and the decay (B) as monitored at 380 nm.

Styrene radical cations have been generated by two-photon ionization of the parent olefin in polar solvents.¹² These transients show one strong band at wavelengths from 350 to 380 nm and another one near 600–680 nm. Furthermore, it is known that deprotonation is a common process for these species.¹³ The intensity of the signal at 380 nm was enhanced when **1** was irradiated in acetonitrile as compared to cyclohexane. To confirm the possibility that the radical cation **4** is the precursor of the pentadienyl radical **5**, laser flash photolysis of 0.07 mM solutions of olefin **7** was performed at 266 nm in acetonitrile. The spectroscopic data, as well as the time-dependence, agreed well with formation of the pentadienyl radical **5** (Figure 4). No other band was observed in the region between 280 and 700 nm. When the kinetic trace was studied at short lifetime, a rapid growth ($k = 1.5 \times 10^6 \text{ s}^{-1}$) of the 380 nm absorption was observed (insert A, Figure 4). This growth was not affected by oxygen but reacted with water at diffusion controlled rate ($k = 3.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). We attribute this growing to the deprotonation of the olefin radical cation **4** leading to radical **5** (Scheme 2).

When the effects of light intensity on the 380 nm signal generated by photolysis of **1** in acetonitrile were investigated it was clear that the relationship between the laser power and the top OD fitted with a parabola, which was consistent with a multiphotonic process. To know whether the benzylic radical **2** is the precursor of **5**, two-laser two-color flash photolysis experiments were performed in cyclohexane and acetonitrile. This technique allows direct examination of the effect of the laser excitation on the behavior of reaction intermediates. A first laser pulse (synthesis laser) produces the intermediate of interest while the second laser pulse from the photolysis laser excites this intermediate.¹⁴ Thus, a solution of **1** was photolyzed using 266 nm pulses to produce the transient **2** and a second 308 laser pulse to irradiate it. A permanent and irreversible bleaching of the transient absorption at 290–350 nm was concomitant with formation of more radical **5** (Figure 5); this clearly

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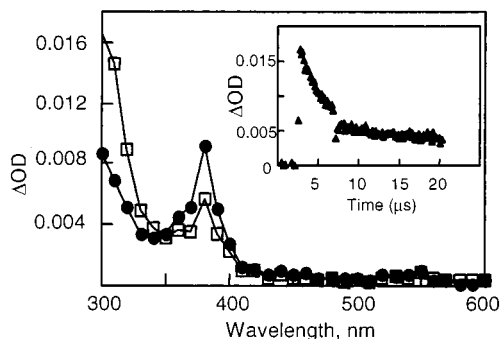


Figure 5. Transient absorption spectra recorded following laser excitation (266 nm) of **1** in acetonitrile under nitrogen atmosphere 1.36 μ s after the laser pulse (\square). Two-laser two-color excitation at 308 nm 5 μ s (\bullet) after the first laser pulse. The inserts shows the kinetic trace at 290 nm.

confirms the two-photon origin of such transient and the intermediacy of benzylic radical **2** in its formation.

Photolysis of **2** with the 308 nm laser pulse might involve intramolecular quenching of the excited radical by the benzylic chloride. This process could give rise to the radical ion **3** which could open to a new radical ion **4** and finally undergo deprotonation to the pentadienyl radical **5** (Scheme 2). Related precedents on quenching of the excited state of benzylic radicals by C–Cl bond can be found in the literature.^{15,8b}

On the other hand, the transient with absorption at 540 nm detected in the LFP of **1** in acetonitrile (Figure 1) was quenched by sodium azide but showed low reactivity toward oxygen. This species, with lifetime of 3 μ s under our conditions, was assigned to the 1,5-diphenylpentadienyl cation (all-*E*)-**10** by comparison of its UV spectrum with that previously obtained for this intermediate. Generation of (all-*E*)-**10** has been reported under different conditions, including $\text{BF}_3/\text{CH}_2\text{Cl}_2$ solution at low temperature¹⁶ (through the ionization of 1,5-diphenylpenta-1,4-dien-3-ol) or zeolite cavities (via adsorption of the 1,5-dichloro-1,5-diphenylpentane).^{6c} Further confirmation for this assignment was obtained by its generation in nonacidic solution from a different precursor, such as chloride **6**. LFP of **6** in acetonitrile led to a spectrum with two signals: a band at 380 nm ascribed to the pentadienyl radical **5** and another band at 540 nm, which was readily quenched by sodium azide, clearly assigned to cation **10** (Figure 6). Generation of the same isomer in the photolysis of dichloride **1** and chloride **6** supports the stereochemical assignment of **10** as all-*E*. In acetonitrile/benzene mixtures, similar transient spectra were observed. However, the relative intensities of the bands assigned to intermediates **5** and **10** were different. As expected, highest amount of cation was formed in pure acetonitrile; based on the relative extinction coefficients of the two species,¹⁷ both homolysis and heterolysis occur to similar extent. By contrast, only

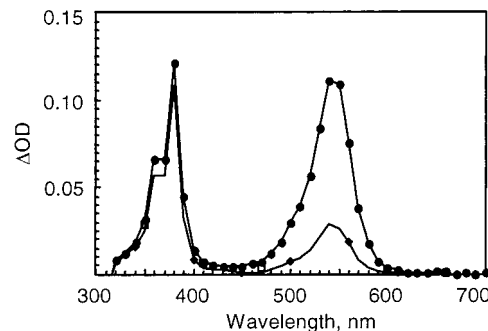


Figure 6. Transient absorption spectra recorded following laser excitation (266 nm) of **6** in acetonitrile under nitrogen atmosphere 0.8 (\bullet) and 7.2 (\blacklozenge) μ s after the laser pulse.

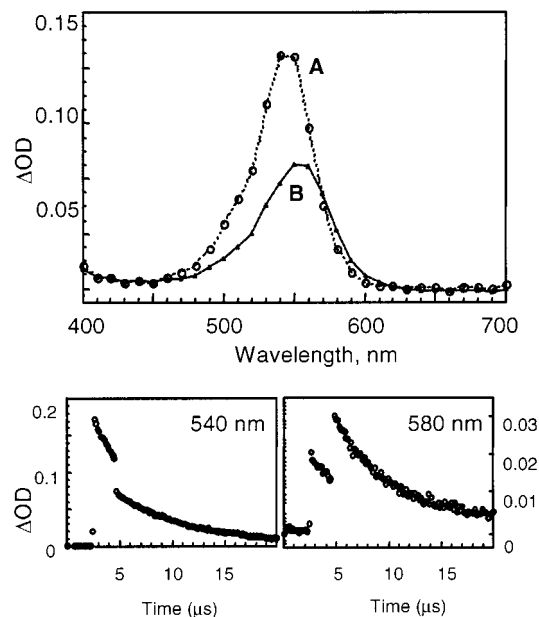


Figure 7. Top: (A) Transient absorption spectrum recorded following laser excitation (266 nm) of **6** in acetonitrile under nitrogen atmosphere 0.4 μ s after the laser pulse. (B) Transient absorption spectrum obtained upon two laser-two color excitation of **7**. The intermediate generated by means of a 266 nm laser pulse is photolyzed after 2.56 μ s by a second laser at 532 nm. Bottom: Kinetic trace at 540 nm (left) and 580 nm (right); the bleaching at 540 nm corresponds to the *Z,E*-isomerization of **10**.

the radical arising from the homolytic process was detected in pure benzene.

Formation of cation **10** from dichloride **1** could be explained as due to its photolysis followed by thermal loss of hydrogen chloride, either via a concerted mechanism or through the intermediacy of a rearranged open cation **9** (Scheme 3).

Cation **10** is expected to show *Z–E* photoisomerism; this process has already been observed in restricted media but not in solution.^{6c} To study such process in solution, two-laser two-color laser flash photolysis experiments of (all-*E*)-**10** were carried out. Thus, an acetonitrile solution of the (1*E*,3*E*)-5-chloro-1,5-diphenyl-1,3-pentadiene (**6**) was excited using a 266 nm pulse to produce the transient **10** which was then photolyzed using a second pulse at 532 nm. Partial bleaching of the signal at 540 nm was concomitant with the rise of a new signal at 550 nm (Figure 7). The new signal could be confidently

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(17) It has been reported that delocalized radicals and the corresponding cation have extinction coefficients of the same order (see ref 18). This agrees with the observation that upon addition of different amounts of benzene to acetonitrile, the decrease of the 540 nm band is very similar to the increase of the 380 nm band.

ascribed to the *Z,E*-isomerization product by comparison with the spectrum of this cation in zeolite media.

Conclusion

Photoinduced intramolecular electron transfer between the benzyl radical and the C–Cl bond of **2** can actually take place, despite their (*E*)-relationship. This has allowed the first detection of the 1,5-diphenylpentadienyl radical, providing a further example of the versatility of dichloro compounds as precursors of interesting intermediates. In polar solvents, formation of the 1,5-diphenylpentadienyl cation, arising from photoheterolysis of dichloride **1**, is also observed as a minor process.

Experimental Section

General Procedure. ¹H and ¹³C NMR spectra were recorded in a 300 MHz spectrometer; chemical shifts (δ) are reported in ppm relative to TMS. Combustion analyses were performed at the Instituto de Química Bio-Orgánica of the CSIC in Barcelona. High-resolution mass spectra were conducted at SCSIE in Valencia.

Reagents and Products. (*E*)-1,2-dibenzoylcyclopropane, (1*E*,3*E*)-1,5-diphenyl-1,4-pentadien-3-one, and benzylcyclopropane are commercially available.

Synthesis of (*E*)-1,2-Bis(1-chloro-1-phenylmethyl)cyclopropane (1**).** Sodium borohydride (0.32 g, 8.4 mmol) was added in small portions over 5 min to a solution of (*E*)-1,2-dibenzoylcyclopropane (0.70 g, 2.8 mmol) in 50 mL of ethanol. The mixture was stirred at room temperature for 3 h and then cooled in an ice bath. After water addition (100 mL), the reaction mixture was extracted with ether and dried with anhydrous sodium sulfate. Solvent was removed, and the solid was washed with 10 mL of diethyl ether to give (*E*)-1,2-bis(1-hydroxy-1-phenylmethyl)cyclopropane¹⁹ as a mixture of diastereoisomers (0.29 g, 42%): ¹H NMR (CDCl₃, 300 MHz): 0.65 and 0.75 (m + m, 2 H), 1.20 and 1.35 (m + m, 2 H), 1.80 (bb, 2 H), 4.05 and 4.20 [d + d (*J* = 7.9 Hz) + m, 2 H], 7.10–7.40 (m, 10 H). ¹³C NMR (CDCl₃, 75.5 MHz): 143.7 (s), 143.6 (s), 129.0 (d), 128.8 (d), 128.7 (d), 128.2 (d), 128.0 (d), 126.3 (d), 126.2 (d), 77.2 (d), 77.0 (d), 26.0 (d), 24.7 (d), 9.0 (t). Anal. Calcd for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.35; H, 7.10.

Chlorotrimethylsilane (0.9 mL) was added to a deaerated solution of (*E*)-1,2-bis(1-hydroxy-1-phenylmethyl)cyclopropane (0.26 g, 1.0 mmol) in 15 mL of anhydrous dichloromethane. The reaction mixture was stirred for 2 h, quenched by water (10 mL), and extracted with ether. The combined organic layers were washed with a saturated solution of sodium hydrogen carbonate, dried over anhydrous sodium sulfate, and concentrated under vacuum to give (*E*)-1,2-bis(1-chloro-1-phenylmethyl)cyclopropane as mixture of stereoisomers (0.26 g, 89%): ¹H NMR (CDCl₃, 300 MHz): 0.70, 0.90 and 1.00 (m + m + m, 2 H) 1.55 and 1.70 (m + m, 2 H), 4.30, 4.40, 4.45 and 4.50 (d + d + d + d, *J* = 8.2 Hz, 2 H), 7.10–7.50 (m, 10 H). ¹³C NMR (CDCl₃, 75.5 MHz): 140.8 (s), 140.7 (s), 140.6

(s), 140.5 (s), 128.6 (d), 128.5 (d), 128.4 (d), 128.3 (d), 127.3 (d), 127.25 (d), 127.1 (d), 127.0 (d), 66.5 (d), 66.4 (d), 66.2 (d), 66.0 (d), 27.9 (d), 27.7 (d), 27.6 (d), 13.95 (t), 13.3 (t), 13.25 (t). HRMS Calcd for C₁₇H₁₆Cl₂: 290.0629. Found: 290.0632. Anal. Calcd for C₁₇H₁₆Cl₂: C, 70.11; H, 5.54. Found: C, 70.64; H, 5.73.

Synthesis of (1*E*,3*E*)-5-Chloro-1,5-diphenyl-1,3-pentadiene (6**).** (1*E*,4*E*)-1,5-Diphenyl-1,4-pentadien-3-ol was prepared from 1,5-diphenyl-1,4-pentadien-3-one following a literature procedure.²⁰ A solution of (1*E*,4*E*)-1,5-diphenyl-1,4-pentadien-3-ol (2.00 g, 8.5 mmol) and sodium chloride (0.07 g, 1.0 mmol) in acetyl chloride (20 mL) were stirred at room temperature for 2 h. The mixture was filtered, and the excess of acetyl chloride was removed under vacuum. The residue was recrystallized from hexane/ether to give (1*E*,3*E*)-5-chloro-1,5-diphenyl-1,3-pentadiene (0.41 g, 19%): ¹H NMR (CDCl₃, 300 MHz): 5.50 (d, *J* = 7.5 Hz, 1 H), 6.10 (dd, *J* = 14.4 Hz, 7.5 Hz, 1 H), 6.50 (d, *J* = 15.5 Hz, 1 H), 6.70 (dd, *J* = 15.5 Hz, 10.2 Hz, 1 H), 7.20–7.40 (m, 10 H). ¹³C NMR (CDCl₃, 50.3 MHz): 134.5 (s), 132.5 (s), 128.9 (d), 128.5 (d), 128.4 (d), 127.9 (d), 127.3 (d), 126.5 (d), 63.7 (d). HRMS Calcd for C₁₇H₁₅Cl: 254.0862. Found: 254.0873.

Synthesis of (1*E*,4*E*)-1,5-Diphenyl-1,4-pentadiene (7**).** 1,5-Diphenyl-1,5-pentanedio²¹ was dehydrated following a published procedure²² to give (1*E*,4*E*)-1,5-diphenyl-1,4-pentadiene.²³

Laser Flash Photolysis. In general, these experiments were carried out with either a Nd:YAG laser using the fourth harmonic (266 nm, <10 ns, ≤20 mJ/pulse) or an excimer laser operated with HCl/Xe/Ne gas mixtures (308 nm, ca. 6 ns, ≤90 mJ/pulse). For specific purposes (see text), the second (532 nm) or the third (355 nm) harmonic of the Nd:YAG laser were used. Transient signals were captured with a Tetrionix-2440 digital oscilloscope, which was interfaced to a computer, which also controlled the experiment. The system was operated with software written in the LabVIEW 3.1.1 environment from National Instruments. Other aspects of this instrument are similar to those described earlier.²⁴ 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.

Acknowledgment. Financial support by the Spanish DGES (M.A.M., Project no. PB97-0339) and by the Natural Sciences and Engineering Research Council of Canada through an operating Grant (J.C.S.) is gratefully acknowledged.

JO010776Y

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