

Lamp versus Laser Photolysis of a Bichromophoric Dichloroalkane: Chemical Evidence for the Two-Photon Generation of the 1,5-Diphenylpentanediyl Biradical

Julia Pérez-Prieto,^{*,†} Miguel Angel Miranda,^{*,‡} Hermenegildo García,[‡] Klára Kónya,[§] and J. C. Scaiano^{*,§}

Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, Vicent Andrés Estelles s/n, Burjasot, 46100 Valencia, Spain, Instituto de Tecnología Química, Universidad Politécnica de Valencia, Camino de Vera s/n, Valencia, 46071 Spain, and Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5

Received January 3, 1996[®]

Low intensity (lamp) photolysis of 1,5-dichloro-1,5-diphenylpentane (**1**) leads to the formation of the 1-chloro-1,5-diphenylpentyl radical (**7**) through C–Cl bond cleavage. Radical **7** leads to the final products through typical free radical reactions. No cyclopentanes are formed under low intensity conditions. In contrast, high intensity laser irradiation leads to C–Cl photocleavage of radical **7** to yield the 1,5-diphenylpentanediyl biradical (**11**), which results in the formation of isomeric *cis*- and *trans*-1,2-diphenylcyclopentanes; the behavior of these biradicals agrees well with that observed when their precursor is 2,6-diphenylcyclohexanone. Two-color two-laser experiments suggest that both singlet and triplet biradicals are formed, even if only the latter are detectable with nanosecond techniques.

Introduction

Photolysis of monohalogenated organic compounds is known to induce carbon–halogen (C–X) bond cleavage, to give products from either heterolysis or homolysis, depending on the structure of the compound, the nature of the leaving group, and the polarity and nucleophilicity of the solvent.¹ In the case of homolytic cleavage, the final products result from radical reactions.

In many respects the photobehavior of geminal dihalides resembles that previously observed for monohalides. Both reduction and elimination products are formed, which is consistent with initial homolytic cleavage of one of the carbon–halogen bonds, to afford a radical pair. Hydrogen abstraction from the solvent is common and in polar media can be followed by deprotonation or electron transfer reactions.²

Vicinal dibromides undergo photodecomposition to yield bromine atoms. The cleavage is frequently followed by hydrogen abstraction from the solvent to yield HBr.^{3–5} Comparatively little is known about the photobehavior of organic dihalides in which the C–X bonds are separated by two or more carbon atoms. The few examples found in the literature show that photolysis frequently gives rise to isomerization products.⁶ In principle, simultaneous or sequential excitation of both chromophores

with high-intensity light may lead to a difunctional reactive intermediate from which completely different set of products may be formed. For example, our earlier work with 1,5-diiodo-1,5-diphenylpentane revealed the formation of new products by photoexcitation of the intermediate hypervalent iodine intermediate.⁷

In the case of the photolysis of 1,8-bis(chloromethyl)naphthalene and 1,8-bis(bromomethyl)naphthalene it is possible to achieve the double-activation of dihalides.^{8–10} Irradiation of these compounds with a high-intensity KrF excimer laser (248 nm) gives acenaphthene via biphotonic generation of a biradical intermediate and successive radical coupling. However, the yields reported for acenaphthene are very low and decrease upon further irradiation. This has been attributed to secondary reactions of the primary photoproduct.^{8–10} In these substrates the C–X bonds are connected through a single naphthyl group and therefore are not fully independent chromophores.

To our knowledge, no photochemical study of this type has been reported on dichloro derivatives where the C–Cl bonds are separated by a fully saturated carbon skeleton, which would ensure the true bichromophoric nature of the substrates. This has prompted us to undertake a systematic study on 1,5-dichloro-1,5-diphenylpentane (**1**), in order to compare the results of conventional lamp photolysis with those obtained with KrF (248 nm) excimer laser excitation, with two-photon two-color techniques, and with the laser-drop method. Our results clearly show that 1,2-diphenylcyclopentanes are exclusively formed using the high intensity laser source and can be safely assigned as two-photon products.

Results

In this work we have taken advantage of a range of techniques that allowed us to establish the nature and

[†] Universidad de Valencia.

[‡] Universidad Politécnica de Valencia.

[§] University of Ottawa.

[®] Abstract published in *Advance ACS Abstracts*, May 1, 1996.

(1) (a) Kropp, P. J.; Adkins, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2709. (b) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918. (c) Slocum, G. H.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 2177. (d) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131. (e) For a review of the photobehavior of alkyl halides see: Sammes, J. P.; *Chemistry of the Carbon-Halogen Bond*; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

(2) Kropp, P. J.; Pienta, N. J. *J. Org. Chem.* **1983**, *48*, 2084.

(3) Scaiano, J. C.; Barra, M.; Krzywinski, M.; Sinta, R.; Calabrese, G. *J. Am. Chem. Soc.* **1993**, *115*, 8340.

(4) Gannon, T.; McGimpsey, W. G. *J. Org. Chem.* **1993**, *58*, 913.

(5) Weldon, D.; Barra, M.; Sinta, R.; Scaiano, J. C. *J. Org. Chem.* **1995**, *60*, 3921.

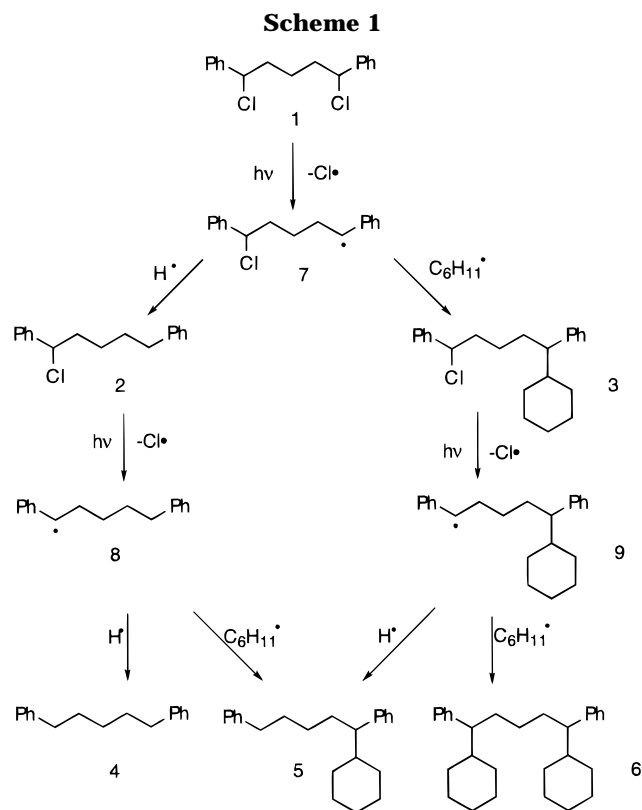
(6) Golub, M. A. *J. Am. Chem. Soc.* **1972**, *92*, 2615.

(7) Banks, J. T.; García, H.; Miranda, M. A.; Pérez-Prieto, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1995**, *117*, 5049.

(8) Ouchi, A.; Yabe, A. *Tetrahedron Lett.* **1992**, *33*, 5359.

(9) Adam, W.; Ouchi, A. *Tetrahedron Lett.* **1992**, *33*, 1875.

(10) Ouchi, A.; Yabe, A.; Adam, W. *Tetrahedron Lett.* **1994**, *35*, 6309.



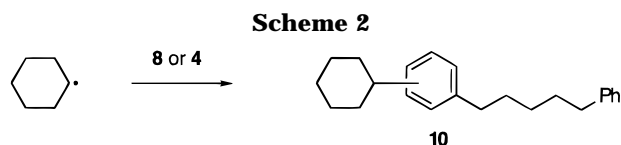
mechanism of a range of mono- and two-photon processes involved in the photodecomposition of 1,5-dichloro-1,5-diphenylpentane (**1**). The results are grouped according to the type of technique employed.

Lamp Irradiation. Photolysis of 1,5-dichloro-1,5-diphenylpentane (**1**) was performed in deaerated cyclohexane solution (ca. 10^{-2} M) for 1 h. Analysis of the photolysate by GC/MS revealed the presence of six products, whose structures were assigned as the following: 1-chloro-1,5-diphenylpentane (**2**), 1-chloro-5-cyclohexyl-1,5-diphenylpentane (**3**), 1,5-diphenylpentane (**4**),¹¹ 1-cyclohexyl-1,5-diphenylpentane (**5**), 1,5-dicyclohexyl-1,5-diphenylpentane (**6**) and cyclohexylcyclohexane.¹²

This structural assignment was confirmed by unambiguous synthesis of the products, using well-established procedures (see Experimental Section), or by comparison with available authentic samples. Minor amounts of two other compounds with m/z 306 for the molecular ion were also detected.

The product distribution can be explained through homolytic cleavage of C–Cl bond(s) to give benzylic radicals (**7–9**) and a chlorine atom (Scheme 1). No disproportionation products were detected, due to efficient hydrogen abstraction from the solvent by chlorine,^{13,14} which yields cyclohexyl radicals. The formation of compounds **3**, **6**, and cyclohexylcyclohexane must occur through recombination of the intermediate benzylic and cyclohexyl radicals, while compounds **2** and **4** can be accounted for through hydrogen abstraction from the medium. Compound **5** could arise via a combination of both routes.

In order to check the feasibility of the proposed mechanistic scheme, compounds **2** and **3** were photolyzed



under conditions similar to those used for compound **1**. Thus, 1-chloro-1,5-diphenylpentane (**2**) was converted into a mixture of 1,5-diphenylpentane, 1-cyclohexyl-1,5-diphenylpentane, and two other isomeric cyclohexane-derived products (m/z 306 for the molecular ion). Since intermediate **8** has a delocalized unpaired electron, the later photoproducts could in principle result from the attack of a cyclohexyl radical to different positions of the aryl ring (Scheme 2).

Unambiguous synthesis of 1-(*p*-cyclohexylphenyl)-5-phenylpentane (**10a**) showed that this compound was identical to one of the minor photoproducts from **1** with a molecular weight of 306. Minor amounts of 1-(*o*-cyclohexylphenyl)-5-phenylpentane (**10b**) were also obtained during the synthesis of **10a**. This allowed us to compare its retention time and fragmentation pattern with those of the other minor photoproduct of **1**, which was clearly different. Thus, the latter may be the third possible isomer: 1-(*m*-cyclohexylphenyl)-5-phenylpentane (**10c**). The formation of products of meta substitution is surprising and suggests that these photoproducts may be formed through radical alkylation¹⁵ of the aryl ring of **4**.

Likewise, irradiation of 1-chloro-5-cyclohexyl-1,5-diphenylpentane (**3**) led to 1-cyclohexyl-1,5-diphenylpentane (**5**) and 1,5-dicyclohexyl-1,5-diphenylpentane (**6**). In this case, no alkylation products were observed.

In summary, C–Cl homolysis of compound **1** takes place as a monophotonic process upon conventional lamp photolysis. No dimerization products (i.e., containing two **1** moieties) were obtained, probably as a consequence of the low substrate concentration, low light intensity, and relatively reactive solvent.

High Intensity Product Studies. Two different conditions of high intensity laser irradiation were employed. The laser drop technique^{7,16} provides a way of performing high intensity photolysis, while minimizing the amounts of secondary products. The products of 266 nm excitation revealed the formation of *cis* and *trans* isomers of 1,2-diphenylcyclopentane in approximately an equimolar ratio. Interestingly, no products of radical recombination or products containing the cyclohexyl moiety were detected. While conversions were small (<10%), the results suggest that radical **7** was quantitatively photodecomposed to biradical **11**, which in turn undergoes predominant cyclization (Scheme 3).

Laser irradiations were also conducted with deaerated 10^{-2} M solutions of **1** in cyclohexane, using a KrF excimer laser (248 nm) and with the sample contained in a quartz spectrometer cell. Compounds **2–6** were again obtained, but in this case significant amounts of *cis*- and *trans*-1,2-diphenylcyclopentane (**12a/12b**), ca. 1/1 ratio, were also found in the photolysis mixtures (Scheme 3). It is noticeable that these compounds are also formed during conventional lamp irradiation of 2,6-diphenylcyclohexanone (**13**) which is known to yield the 1,5-diphenylpentanediyl biradical (**11**).¹⁷ Formation of the diphenylc-

(11) Borsche, W.; Wollemaun, J. *Chem. Ber.* **1912**, *45*, 3713.

(12) *Beilstein Handbuch der Organische Chemie H*, *5*, 71.

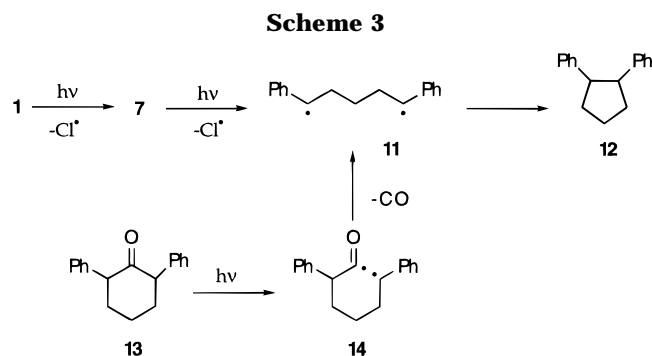
(13) Reported bond energies (kcal/mol): H–Cl, 103.2; H–C₆H₁₁, 95.5; Weast, R. C. *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL; 1976; pp F-221, F-231.

(14) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Luszyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464.

(15) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1981; pp 730.

(16) Scaiano, J. C.; Banks, J. T. *J. Brazil Chem. Soc.* **1995**, *6*, 211.

(17) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *Chem. Phys. Lett.* **1987**, *134*, 549.



cloptane derivatives was therefore a fingerprint for the two-photon chemistry of 1,5-dichloro-1,5-diphenylpentane (**1**) by means of laser photolysis. Clearly, a mixture of mono- and multiphoton processes occur under these conditions, in contrast with the clear dominance of two-photon processes in the laser drop experiments.

Laser Flash Photolysis. Laser flash photolysis of deaerated 1 mM solutions of **1** in cyclohexane at 266 nm were carried out using two different excitation geometries. Front face irradiation of the sample with a highly concentrated beam, in a geometry that tends to favor multiphoton processes, and 90° excitation using a quartz beam diffuser in front of the sample; this avoids hot spots in the beam and tends to promote monophotonic processes.

In the case of front face excitation we observed the formation of an intermediate with λ_{\max} 320 nm which decays with a first-order kinetics and a lifetime of ~600 ns. This is in agreement with the known properties of biradical **11**,¹⁷ a result that is further confirmed by our two-color two-laser experiments (*vide infra*). In contrast, this short lived transient is not detected under the low intensity (monophotonic) conditions, where a much longer lived intermediate ($\geq 2 \mu\text{s}$) showing typical monoradical behavior was detected. In the case of cyclohexanone **13**, we monitored a biradical lifetime of ca. 800–900 ns in cyclohexane; it is possible that its somewhat shorter biradical lifetime when **1** is the precursor is related to the need to carry out these experiments under conditions (high laser intensity) that favor two-photon processes. It is known that under these conditions even very short lived biradicals can undergo biradical–biradical reactions that will lead to a shortening of the experimental lifetimes.¹⁸

These data suggest the formation of the biradical in the first case, since the front-face irradiation favors biphotonic processes. Laser-drop experiments agree well with the conclusions of front-face laser flash experiments. The long lived transient in the 90° irradiation is assigned to the benzylic radical **7**. An investigation of the effects of light intensity on the lifetime of this transient and the size of the signal was carried out by attenuating the laser beam with a set of calibrated neutral density filters. The power dependence of the signal with a diffuse laser beam at 90° showed a linear relationship between transient absorption and laser power, consistent with the behavior anticipated for monophotonic processes.

Two-Laser Two-Color Laser Flash Photolysis. This technique allows the direct examination of the effect of laser excitation on the behavior of reaction intermediates. A first laser pulse (referred to as *synthesis* laser) produces the intermediate of interest (e.g., the monoradical), while the second laser pulse from the *photolysis*

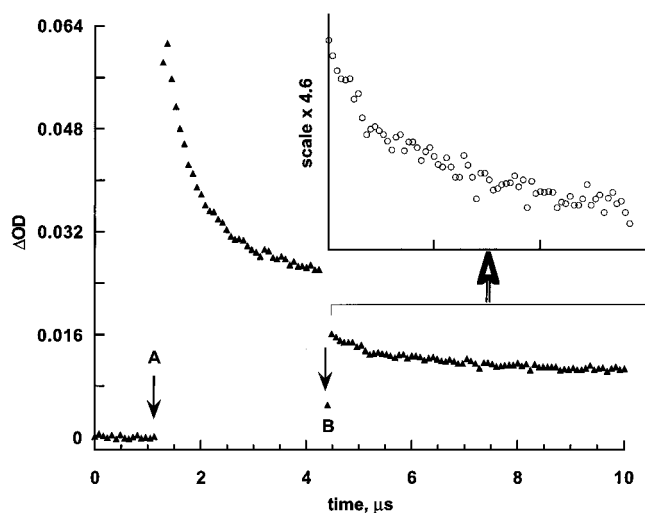


Figure 1. Two-laser two-color experiment showing excitation of **1** in cyclohexane at 266 nm (see A), followed by excitation at 308 nm (B) (monitoring wavelength at 320 nm). The insert shows an enlargement of the signal following excitation by the second laser.

laser excites the reaction intermediate.¹⁹ The wavelength of the *photolysis* laser is usually selected so as to match the optical absorption of the intermediate of interest. Thus, a 1 mM solution of 1,5-dichloro-1,5-diphenylpentane in cyclohexane was excited using 266 nm pulses (Nd: YAG laser, fourth harmonic) to produce the transient, while a second laser with 308 nm pulses to photolyze it;¹⁹ both lasers were incident from the front face. Photolysis of the transient derived from 1,5-dichloro-1,5-diphenylpentane at 308 nm led to permanent and irreversible bleaching of the transient signal as monitored at 320 nm (Figure 1). The low point near the B marker are due to scattered light from the second laser. Interestingly, the small component of fast decay observed following the 308 nm pulse decays with the same lifetime as the initial fast component (~600 ns). We believe that the same biradical (**11**) is produced by two-photon processes at 266 nm or by 308 nm excitation of the monoradical **7**.

We have also analyzed the reaction mixture (3 mL, 1 mM deaerated solution of **1**) from a two-laser experiment in which the sample was irradiated with a 500 pulse series using both lasers, 266 and 308 nm, with the pulses separated by 3 μs . GC/MS analysis showed that more than 50% of the starting material had been photolyzed and mainly 1,2-diphenylcyclopentane products were formed (0.58/0.42, *cis/trans* ratio). Minor amounts of monoradical products were also identified.

Discussion

It is clear from our experiments that the low intensity photolysis of 1,5-dichloro-1,5-diphenylpentane (**1**) can be understood using the same conceptual framework as in the case of simple monochloro compounds. Under these conditions the second chlorine atom is not involved in the primary cleavage step, and the intermediate radical appears to have no tendency for the formation of hyper-valent intermediates of the type recently detected⁷ for the 1,5-diphenyl-5-iodo-1-pentyl radical. This is probably not surprising given the reduced tendency toward bridging in the case of chlorine. Thus, the reaction intermediates observed under attenuated laser excitation, and the

(18) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819.

(19) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* **1988**, *21*, 22.

products characteristic of lamp irradiation, can be readily explained on the basis of Scheme 1. This form of irradiation does not lead to the formation of any 1,2-diphenylcyclopentanes.

In contrast, high intensity laser irradiation leads to the formation of *cis*- and *trans*-1,2-diphenylcyclopentanes with approximately equimolar yields. It is interesting that laser excitation in bulk (i.e. in a spectrometer cell) leads to good conversions to diphenylcyclopentanes, but the presence of monophotonic products (from Scheme 1) is unavoidable under these conditions. Thus, it is clear that many radicals **7** do not undergo photodecomposition under these conditions. While the products under laser-drop conditions also reveal the importance of two-photon processes, the complete absence of monophotonic products indicates that while conversion on the starting material **1** is low, the radical **7** undergoes quantitative photodehalogenation.

It is interesting to examine the structure of radical **7**. Clearly, the dominant chromophore will be the radical center, rather than the intact chlorobenzyl moiety; this will be particularly true at the 308 nm laser wavelength, which is quite close to the absorption maximum for **7** (~320 nm). Thus, the efficient photodecomposition of the radical must require energy transfer from the excited radical (which is expected to have a short excited state lifetime)²⁰ to the C–Cl bond.

Another interesting question relates to the multiplicity with which **11** is formed by photoinduced C–Cl bond cleavage of radical **7**. In principle, we expect the statistical ratio of 3:1 triplets-to-singlets. Our results can only provide a qualitative indication on this question. Note that in Figure 1 308 nm laser excitation of the radical leads to *bleaching*. Yet, one could have anticipated an *enhanced* absorption, since excitation transforms a monochromophoric radical (**7**) into a bichromophoric biradical (**11**), both chromophores being expected to maintain their spectroscopic characteristics.²¹ We believe that the reason for this apparent discrepancy may reflect that biradicals produced in the singlet state undergo rapid decay, in time scales too short for detection with nanosecond techniques. On the other hand triplet biradicals survive long enough for easy detection. Interestingly, the ratio of *cis*- and *trans*-1,2-diphenylcyclopentanes (**12**) is essentially the same reported for the photolysis of **13**.²²

Experimental Section

General Procedure. IR spectra were run in a Perkin-Elmer 843 spectrometer. ¹H and ¹³C NMR spectra were recorded in a Bruker AC 250 spectrometer; chemical shifts (δ) are reported in ppm relative to TMS. GC/MS measurements were made on a Trio 1000 quadrupole mass selective detector connected to a Fisons Series 8000 HRGC gas chromatograph equipped with DB-1 capillary column (15 m, film thickness 1 mm i.d. 0.25 mm). Combustion analysis were performed at the Instituto de Química Bio-Organica of the CSIC in Barcelona. High-resolution mass spectra were conducted on a VG AUTOSPEC instrument.

Conventional Lamp Irradiation. A degassed 10⁻² M cyclohexane solution of the corresponding chloro compound in a quartz tube was irradiated for 1 h with a 125-W medium-pressure mercury lamp inside a quartz immersion well, under continuous magnetic stirring. After evaporation of the solvent, the irradiated mixture was analyzed by GC/MS.

Laser-Drop Photolysis.^{7,16} The beam from a Continuum Surelite Nd-YAG laser using the fourth harmonic (266 nm, <10ns, \leq 20 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 earlier.⁷ Drops of deaerated 2 mM solution of 1,5-dichloro-1,5-diphenylpentane were irradiated by the focused output from the 266 nm laser. GC/MS analysis showed that *cis*- and *trans*-1,2-diphenylcyclopentane were formed in nearly equimolar amounts. The efficiency of transformation was very low (<10%), but interestingly no mono-radical products were detected.

Laser Flash Photolysis. These experiments were carried out using either a Continuum Surelite Nd-YAG laser using the fourth harmonic (266 nm, <10ns, \leq 16 mJ/pulse) or a Lumonics EX-530 excimer laser operated with HCl/Xe/Ne gas mixtures (308 nm, ca. 6 ns, \leq 50 mJ/pulse). Transient signals were captured with a Tektronix-2440 digital oscilloscope which was interfaced to a PowerMacintosh 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.^{23,24} The two-laser two-color experiments were performed by sending a trigger pulse to a Stanford Research Systems Model DG 535 delay generator which then sent TTL pulses which fired the lasers at the desired sequence. All experiments were carried out using flow cells constructed from 7 \times 7 mm Suprasil quartz tubing. Samples were contained in a 100 mL reservoir tank which was purged with a slow stream of either nitrogen or oxygen, as required.

Synthesis of 1,5-dichloro-1,5-diphenylpentane (1). 1,5-Diphenylpentane-1,5-diol²⁵ (0.66 g, 2.6 mmol) was added to concentrated hydrochloric acid (15 mL), and the mixture was stirred for 12 h at room temperature. Afterwards, the solution was neutralized with NaOH, extracted with ether, and dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure to give an oil (0.70 g, 92%). The product was purified by HPLC chromatography (hexane). ¹H NMR (CDCl₃): 1.1–1.9 (m, 2H), 2.1 (m, 4H), 4.8 (dd, $J = 8$, 6Hz, 2H), 7.2–7.4 (m, 10H). ¹³C NMR (CDCl₃): 141.4 (s), 128.2 (d), 128.1 (d), 126.8 (d), 63.2 (d), 39.1 (t), 24.6 (t). MS m/z M⁺ (292, 0), 221 (3), 220 (13), 142 (14), 129 (100), 128 (42), 117 (30), 115 (46), 104 (22), 92 (38), 91 (65). Anal. Calcd for C₁₇H₁₈Cl₂: C, 69.63; H, 6.19; Cl, 24.18. Found: C, 69.69; H, 6.10; Cl, 24.09.

Synthesis of 1-Chloro-1,5-diphenylpentane (2). 1,5-Diphenyl-1-pentanol²⁶ (0.40 g, 1.8 mmol) was added to concentrated hydrochloric acid (10 mL), and the mixture was stirred for 12 h at room temperature. The workup procedure was analogous to that previously described. An oil (0.40 g, 82%) was obtained and purified by HPLC (hexane). ¹H NMR (CDCl₃): 1.4–1.8 (m, 4H), 2.0–2.3 (m, 2H), 2.5 (t, $J = 7$ Hz, 2H), 3.9 (t, $J = 7$ Hz, 1H), 7.2–7.6 (m, 10H). ¹³C NMR (CDCl₃): 142.3 (s), 141.9 (s), 128.6 (d), 128.3 (d), 128.2 (d), 126.9 (d), 125.7 (d), 63.7 (d), 39.9 (t), 35.7 (t), 30.9 (t), 26.7 (t). MS m/z M⁺ (258, 0), 222 (11), 131 (70), 118 (22), 117 (73), 115 (49), 105 (30), 104 (66), 92 (41), 91 (100). Anal. Calcd for C₁₇H₁₉Cl: C, 78.90; H, 7.40; Cl, 13.70. Found: C, 79.07; H, 7.43; Cl, 13.32.

Synthesis of 1-Chloro-5-cyclohexyl-1,5-diphenylpentane (3). 5-Oxo-5-phenylpentanoic acid (1.92 g, 10 mmol) was added dropwise to a 2 M degassed solution of cyclohexylmagnesium chloride (10 mL, 20 mmol) in cyclohexane. After the addition was complete, the mixture was stirred for 12 h at room temperature and quenched by adding ice–water. The reaction mixture was acidified with HCl, extracted with ether, and dried over magnesium sulfate. Solvent was removed to give an oil which was dissolved in acetic acid (67 mL) and perchloric acid (3.4 mL). After addition of 10% palladium on charcoal (0.50 g) the reaction mixture was stirred under

(20) Meisel, D.; Das, P. K.; Hug, G. L.; Bhattacharyya, K.; Fessenden, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 4706.

(21) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431.

(22) Peyman, A.; Beckhaus, H. D.; Rüdhardt, C. *Chem. Ber.* **1988**, *121*, 1027.

(23) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

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

(25) *Beilstein Handbuch der Organische Chemie H*, 6, 1015.

(26) Henbest, H. B.; Trocha-Grimshaw, J. *J. Chem. Soc., Perkin Trans. 1* **1974**, 601.

pressure (12 kg/cm²) during 2 h. The mixture was extracted with ether and dried over magnesium sulfate. Solvent was removed to give 5-cyclohexyl-5-phenylpentanoic acid (**15**) (1.27 g, 49%) which was used without further purification. IR (CCl₄): 1710 (C=O). ¹H NMR (CDCl₃): 0.6–2.0 (m, 15H), 2.1–2.4 (m, 3H), 7.0–7.4 (m, 5H), 10.5 (bb, 1H). ¹³C NMR (CDCl₃): 180.0 (s), 143.8 (s), 128.3 (d), 127.9 (d), 125.8 (d), 51.8 (d), 43.1 (d), 34.0 (t), 31.8 (t), 31.3 (t), 30.9 (t), 26.8 (t), 22.9 (t). HRMS Calcd for C₁₇H₂₄O₂: 260.1776. Found: 260.1780.

To a solution of acid **15** (1.27 g, 4.9 mmol) in anhydrous diethyl ether (30 mL), a 2 M solution of phenyllithium (5 mL, 9.8 mmol) was added dropwise over ca. 20 min. After the addition was complete the mixture was stirred for 1 h at room temperature and quenched by adding ice–water. The organic phase was separated and the alkaline aqueous phase was further extracted with two 10 mL portions of ether. The combined ethereal extracts were washed with brine and dried over magnesium sulfate. Solvent was removed to give an oil (1.07 g, 68%). Purification of the residue by column chromatography (hexane/ethyl acetate, 10/1) left 5-cyclohexyl-1,5-diphenyl-1-pentanone (**16**). White solid (mp 90 °C). IR (CCl₄): 2924, 1690 (C=O), 1214. ¹H NMR (CDCl₃): 0.6–2.0 (m, 15H), 2.3 (m, 1H), 2.9 (m, 2H), 7.1–7.6 (m, 10H), 7.9 (d, *J* = 6 Hz, 5 H). ¹³C NMR (CDCl₃): 200.3 (s), 144.1 (s), 136.9 (s), 132.8 (d), 128.5 (d), 128.4 (d), 127.9 (d), 125.8 (d), 52.0 (d), 43.2 (d), 38.6 (t), 32.1 (t), 31.3 (t), 30.9 (t), 26.5 (t), 22.7 (t). HRMS Calcd for C₂₃H₂₈O: 320.2140. Found: 320.2129.

To a solution of 2.14 g (6.7 mmol) of ketone **16** in 20 mL of ethanol was added sodium borohydride (0.28 g, 7.4 mmol) in small portions over 5 min. The mixture was stirred at room temperature for 20 min and then cooled by means of an ice bath. Subsequently, 40 mL of water was added and then 1 mL of 6 M hydrochloric acid. The reaction mixture was extracted with ether and dried with anhydrous sodium sulfate. Solvent was removed to give an oil to which concentrated hydrochloric acid (20 mL) was added. The mixture was stirred for 12 h at room temperature. Then, the solution was neutralized with NaOH, extracted with ether, and dried with anhydrous sodium sulfate. Solvent was removed to give an oil (1.50 g, 66%). The product was purified by column chromatography (hexane/ethyl acetate, 10/1) to leave 1-chloro-5-cyclohexyl-1,5-diphenylpentane (**3**). ¹H NMR (CDCl₃): 0.6–1.0 (m, 2H), 1.0–2.1 (m, 14 H), 2.3 (m, 2H), 4.7 (m, 1H), 7.0–7.5 (m, 10H). ¹³C NMR (CDCl₃): 142.1 (s), 141.8 (s), 128.5 (d), 128.1 (d), 128.0 (s), 126.9 (d), 126.8 (d), 125.8 (d), 63.7 (d), 63.5 (d), 51.9 (d), 51.8 (d), 43.3 (d), 43.2 (d), 40.0 (t), 39.9 (t), 31.8 (t), 31.8 (t), 31.4 (t), 31.0 (t), 29.7 (t), 26.9 (t), 26.6 (t), 26.5 (t), 25.3 (t), 25.2 (t). MS *m/z* M⁺ (340, 0), 304 (2), 221 (12), 171 (28), 131 (15), 129 (18), 118 (19), 117 (100), 115 (36), 105 (18), 104 (31), 92 (16), 91 (87), 83 (17). Anal. Calcd for C₂₃H₂₉Cl: C, 81.03; H, 8.57. Found: C, 81.21; H, 8.68.

Synthesis of 1-Cyclohexyl-1,5-diphenylpentane (5). 1,5-Diphenyl-1-pentanone (2.38 g, 10 mmol) in anhydrous diethyl ether (40 mL) was added dropwise to a 2 M solution of cyclohexylmagnesium chloride (5 mL, 10 mmol) in cyclohexane. After the addition was complete, the mixture was stirred for 30 min at room temperature and quenched by adding 20 mL of ice–water. The reaction mixture was extracted with ether and dried over magnesium sulfate. Solvent was removed to give a yellow oil to which acetic acid (40 mL), perchloric acid (2 mL), and 10% palladium on charcoal (0.30 g) were added. The reaction mixture was stirred under pressure (12 kg/cm²) during 2 h. Then, the mixture was extracted with ether and dried over magnesium sulfate. Solvent was removed to give 1-cyclohexyl-1,5-diphenylpentane (0.75 g, 50%). The product was purified by HPLC chromatography (hexane). ¹H NMR (CDCl₃): 0.6–1.0 (m, 3H), 1.0–2.0 (m, 14H), 2.3 (m, 1H), 2.5 (m, 2H), 7.0–7.3 (m, 10H). ¹³C NMR (CDCl₃): 144.2 (s), 142.4 (s), 128.5 (d), 128.3 (d), 128.1 (d), 127.9 (d), 125.6 (d), 125.5 (d), 52.1 (d), 43.2 (d), 35.8 (t), 32.3 (t), 31.6 (t), 31.4 (t), 31.1 (t), 27.5 (t), 26.9 (t), 26.5 (t). MS *m/z* M⁺ (306, 3), 224 (8), 145 (41), 131 (26), 117 (9), 105 (9), 104 (14), 92 (18), 91 (100), 83 (6). Anal. Calcd for C₂₃H₃₀: C, 90.13; H, 9.87. Found: C, 89.90; H, 10.01.

Synthesis of 1,5-Dicyclohexyl-1,5-diphenylpentane (6).

1,5-Diphenyl-1,5-pentanedione (1.26 g, 5 mmol) in anhydrous diethyl ether (20 mL) was added dropwise to a 2 M solution of cyclohexylmagnesium chloride (5 mL, 10 mmol) in cyclohexane. After the addition was complete, the mixture was stirred for 30 min at room temperature and quenched by adding 20 mL of ice–water. The reaction mixture was extracted with ether and dried over magnesium sulfate. Solvent was removed to give an oil which was dissolved in 40 mL of acetic acid. Perchloric acid (2 mL) and 0.30 g of 10% palladium on charcoal were added. Hydrogenation was performed under pressure (12 kg/cm²) during 2 h. The workup procedure was analogous to that previously described. An oil (0.65 g, 34%) was obtained and purified by HPLC (hexane). ¹H NMR (CDCl₃): 0.6–1.0 (m, 6H), 1.0–1.3 (m, 6H), 1.3–1.5 (m, 4H), 1.5–2.0 (m, 12H), 2.2 (m, 2H), 7.0–7.4 (m, 10H). ¹³C NMR (CDCl₃): 144.7 (s), 144.6 (s), 128.5 (d), 127.7 (d), 125.5 (s), 125.4 (d), 125.8 (d), 51.7 (d), 51.6 (d), 43.4 (d), 42.9 (t), 32.3 (t), 32.2 (t), 31.4 (t), 31.3 (t), 31.0 (t), 30.7 (t), 26.6 (t), 26.5 (t), 25.6 (t), 25.4 (t). MS *m/z* M⁺ (388, 1), 306 (4), 224 (6), 145 (35), 131 (50), 117 (23), 105 (14), 104 (14), 92 (12), 91 (100). Anal. Calcd for C₂₉H₄₀: C, 89.62; H, 10.37. Found: C, 89.66; H, 10.47.

Synthesis of 1-(*p*-Cyclohexylphenyl)-5-phenylpentane (10a).

Thionyl chloride (1.2 mL, 16.8 mmol) was added to 5-phenylpentanoic (1.99 g, 11.2 mmol), and the mixture was heated under reflux for 1 h. The excess of thionyl chloride was removed in a rotary evaporator to leave the acid chloride, which was used for the following step. To a mixture of cyclohexylbenzene (1.14 g, 7.1 mmol) and the acid chloride was added aluminum chloride (1.50 g, 11.2 mmol) in three portions. After heating on a boiling water bath for 20 min, the reaction mixture was poured onto ice–water, made alkaline by the addition of a 10% NaOH solution, extracted with ether and dried over magnesium sulfate. Solvent was removed to give a reddish oil. Purification of the residue by column chromatography (hexane/ethyl acetate, 10/1) left 1-(*p*-cyclohexylphenyl)-5-phenyl-1-pentanone (**17**) (0.29 g, 13%). IR (CCl₄): 1686 (C=O). ¹H NMR (CDCl₃): 1.2–1.5 (m, 5H), 1.6–2.0 (m, 9H), 2.5–2.8 (m, 1H), 2.7 (t, *J* = 7 Hz, 2H), 3.1 (t, *J* = 7 Hz, 2H), 7.1–7.4 (m, 7H), 7.9 (d, 2H). ¹³C NMR (CDCl₃): 200.1 (s), 153.4 (s), 142.2 (s), 134.8 (s), 128.3 (d), 128.2 (d), 126.9 (d), 125.6 (d), 44.6 (d), 38.2 (t), 35.7 (t), 34.0 (t), 31.1 (t), 26.7 (t), 26.0 (t), 24.0 (t). HRMS Calcd for C₂₃H₂₈O: 320.2140. Found: 320.2133.

To a solution of ketone **17** in 20 mL of ethyl acetate, several drops of perchloric acid and 0.30 g of palladium–carbon catalyst were added. Hydrogenation was performed under pressure (12 kg/cm²) during 2 h. The mixture was extracted with ether and dried over magnesium sulfate. Solvent was removed to give 1-(*p*-cyclohexylphenyl)-5-phenylpentane as a colorless oil (0.25 g, 89%), which was further purified by HPLC (hexane). ¹H NMR (CDCl₃): 1.1–1.5 (m, 7H), 1.5–1.9 (m, 9H), 2.5–2.7 (m, 5H), 7.0–7.2 (m, 7H), 7.2–7.3 (m, 2H). ¹³C NMR (CDCl₃): 145.4 (s), 143.0 (s), 140.1 (s), 128.4 (d), 128.2 (d), 126.6 (d), 125.6 (d), 44.1 (d), 35.9 (t), 35.5 (t), 34.5 (t), 31.4 (t), 29.1 (t), 27.0 (t), 26.2 (t). MS *m/z* M⁺ (306, 26), 173 (21), 159 (48), 145 (22), 131 (16), 117 (25), 105 (10), 92 (15), 91 (100). Anal. Calcd for C₂₃H₃₀: C, 90.13; H, 9.87. Found: C, 89.98; H, 10.04.

Acknowledgment. Financial support by the Natural Science and Engineering Council of Canada through an operating Grant (J.C.S.) and Spanish DGICYT (M.A.M., Project no. PB94-0539; HG, Project no. PB93-0380 and JPP Project no. PR95-289) are gratefully acknowledged. J.C.S. is the recipient of a Killam Fellowship awarded by the Canada Council. Thanks are also due to Dr. J. T. Banks for his contribution to some of the early experiments.