Laser Flash, Laser-Drop, and Lamp Photolysis of 1,3-Dichloro-1,3-diphenylpropane. One- *versus* Two-Photon Reaction Pathways

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Low intensity irradiation of 1,3-dichloro-1,3-diphenylpropane (**1**) in cyclohexane leads to the formation of 3-chloro-1,3-diphenylpropyl radical (**2**) through homolytic C−Cl bond cleavage. Radical **2** gives rise to final products typical of free radical reactions. Neither 1,2-diphenylcyclopropanes (**6**) nor 3-cyclohexyl-1,3-diphenylpropene (**20**) are obtained under these conditions. Nevertheless, high intensity laser irradiation of the initially formed monoradical **2** leads to the 1,3-diphenylpropenyl radical (**3**) detected with nanosecond techniques. This intermediate is completely trapped by the cyclohexyl radicals generated in the medium to yield **20**. Photolysis of **1** with the laser-drop technique leads to the cyclopropanes **6** as major photoproducts.

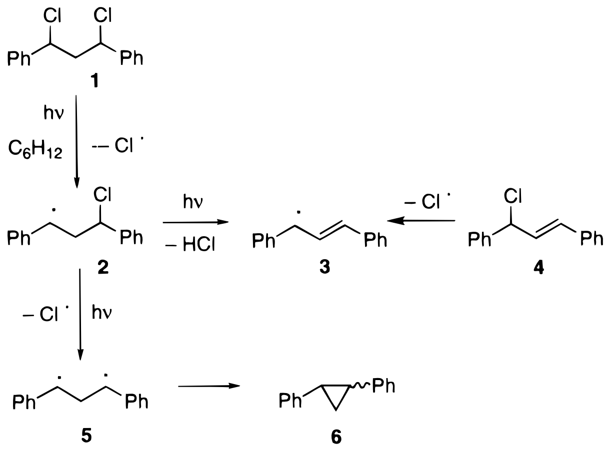
Introduction

The photochemistry of dihalides in which the C−X bonds are separated by two or more carbon atoms is a subject of recent interest.[1−4] We have demonstrated the intermediacy of a hypervalent iodine radical in the photolysis of 1,5-diodo-1,5-diphenylpentane in cyclohexane,[1] while in the case of the dichloro analogue the typical benzyl radical is formed.[4] By contrast, we and others have demonstrated that excitation of dihalides with high-intensity light can lead to difunctional intermediates, biradicals, from which a completely different set of products can be formed. For instance, high intensity irradiation of 1,5-dichloro- and 1,5-diiodo-1,5-diphenylpentane leads to *cis* and *trans*-1,2-diphenylcyclopentanes by a two-photon route. The 1,5-biradical intermediate has been detected with nanosecond techniques.

Futhermore, we have already communicated[5] that different products are obtained when 1,3-dichloro-1,3-diphenylpropane (**1**) is submitted to low or high intensity irradiation. Thus, *cis*- and *trans*-1,2-diphenylcyclopropanes (**6**) are only formed when using the latter conditions. However, in this case the difunctional biradical precursor **5** has not been observed probably because of its very short lifetime;[6,7] instead a longer lived monofunctional 1,3-diphenylpropenyl radical intermediate (**3**) arising from a two-photon procces has been detected.

In this paper we report in full our results on the photochemistry of 1,3-dichloro-1,3-diphenylpropane in cyclohexane. A systematic study on this dihalide was undertaken in order to compare the results of conventional lamp photolysis with those obtained upon laser excitation [Nd: YAG (266 nm), or KrF (248 nm)] and with the laser-drop method. Furthermore, since **3** can be generated from irradiation of 3-chloro-1,3-diphenylpropene (**4**), product studies on the lamp irradiation of this compound were performed to clarify which products arise from the propenyl radical **3** in the high-intensity irradiation of the 1,3-dichloride.

Scheme 1



Our results clearly show that the propenyl radical **3** is not involved in the formation of the 1,2-diphenylcyclopropanes. Instead, it is trapped by the cyclohexyl radicals formed after reaction of chlorine atoms with the solvent. Moreover a mechanism involving intramolecular electron transfer from the excited benzylic radical to the benzylic chloride is proposed for the formation of radical **3** in the high intensity irradiation of the 1,3-dichloride.

Results and Discussion

Low Intensity Irradiations. 1,3-Dichloro-1,3-diphenylpropane (**1**) was prepared from 1,3-diphenyl-1,3-propanedione by sodium borohydride reduction and subsequent exchange of the hydroxyl group by chlorine,

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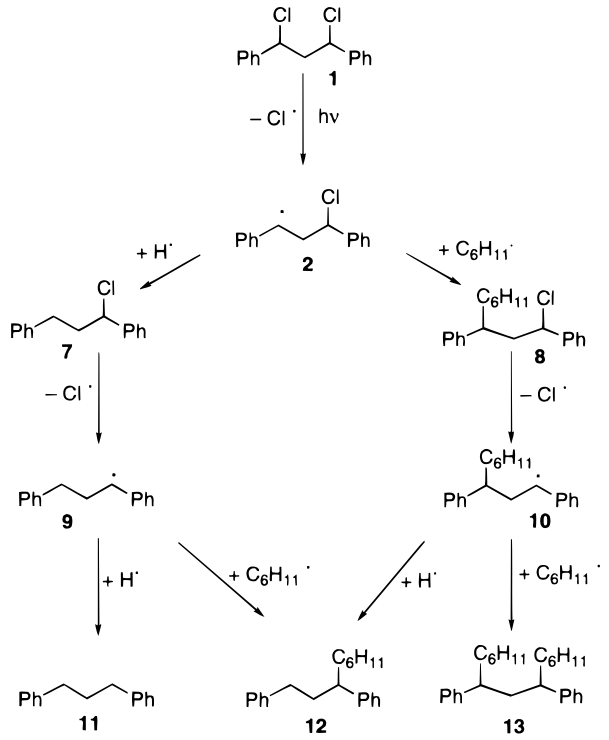
Scheme 2

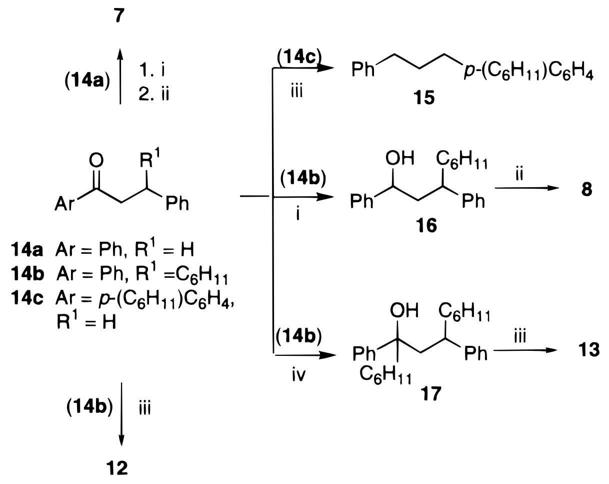


using HCl. Lamp irradiation (medium pressure mercury, quartz filter, 1 h) of a deaerated 10 mM cyclohexane solution of the dichloride led to complete consumption of the starting material. Analysis of the photolysate by GC/MS revealed the formation of 1-chloro-1,3-diphenylpropane (**7**, 5%), 1-chloro-3-cyclohexyl-1,3-diphenylpropane (**8**, 26%), 1,3-diphenylpropane (**11**, 5%),[8] 1-cyclohexyl-1,3-diphenylpropane (**12**, 29%), 1,3-dicyclohexyl-1,3-diphenylpropane (**13**, 17%), and two minor products with *m*/*z* 278 for the molecular ion (7%). The product of coupling of cyclohexyl radicals, cyclohexylcyclohexane,[9] was also detected.

The product distribution can be explained through homolytic cleavage of C−Cl bond(s) from the excited singlet state(s) to give benzylic radicals (**2**, **9**, and **10**) and a chlorine atom. No disproportionation products were detected, due to efficient hydrogen abstraction from the solvent by chlorine,[10,11] which yields cyclohexyl radicals. Similar behavior has been earlier observed in the photochemistry of 1,5-dichloro-1,5-diphenylpentane.[4] Photoproduct formation can be explained from the intermediate benzylic radicals by either hydrogen abstraction from the medium (**7**, **11**), or coupling with cyclohexyl radicals (**8**, **13**), or a combination of both processes (**12**).

Chloro compounds 1-chloro-1,3-diphenylpropane (**7**) and 1-chloro-3-cyclohexyl-1,3-diphenylpropane (**8**) were irradiated under similar conditions. Thus, 1-chloro-1,3-diphenylpropane was partially converted into **11** (13%) and **12** (32%) along with minor amounts of products with *m*/*z* 278 for the molecular ion (7%). Similarly, GC/MS analysis of the photolysate from 1-chloro-3-cyclohexyl-1,3-diphenylpropane showed the formation of **12** (39%) and **13** (32%).

Scheme 3



i. NaBH$_4$, EtOH; ii. HCl; iii. H$_2$ /Pd-C; iv. C$_6$H$_{11}$MgCl

The formation of other products with *m*/*z* 278 in the irradiation of 1,3-dichloro-1,3-diphenylpropane (**1**) is in agreement with radical alkylation of the aryl ring by the cyclohexyl radicals.[12] This type of compound was also found in the photolysis of 1,5-dichloro-1,5-diphenylpentane. Unambiguous synthesis of 1-(*p*-cyclohexylphenyl)-3-phenylpropane (**15**) showed that this compound was identical to one of these minor products.

The structural assignment of photoproducts was confirmed by unambigous synthesis of the products, using well-established methods, or by comparison with available authentic samples. The chloro compounds **7** and **8** were prepared from the corresponding ketones, **14a** and **14b**, respectively, by sodium borohydride reduction and subsequent exchange of the hydroxyl group by chlorine, using HCl. Compounds **12** and **15** were obtained by hydrogenation of the corresponding carbonyl compound **14b** and **14c** in presence of palladium on charcoal. Addition of cyclohexylmagnesium chloride to the carbonyl group of **14b** followed by hydrogenation afforded compound **13**. The above synthetic routes are outlined in Scheme 3. Details and appropriate references are provided in the Experimental Section.

Laser Flash Photolysis. LFP of deaerated 1 mM solutions of **1** in cyclohexane at 266 nm yielded a narrow spectrum, with maxima at 320 (weak), 340 (weak), and 360 nm (strong), see Figure 1. The lifetime of this species was around 10 μs under our experimental conditions. Oxygen saturated solutions of **1** in cyclohexane led to a reduced lifetime of 0.6 μs at 360 nm.

This intermediate does not appear to be a benzylic radical, which would be expected to absorb at ca. 320 nm;[13] thus, the possibility of an interaction between the benzylic radical center and the distant β-phenyl group was first considered, in order to interpret the spectrum. To check this hypothesis, LFP of deaerated 1 mM solutions of **7** in cyclohexane at 266 nm were obtained. However, a spectrum typical of a benzylic radical ($\lambda = 320$ nm) was obtained in this case, see Figure 2.

In view of the absorption at relatively long wavelengths and the long lifetime, the intermediate formed upon LFP of **1** was thought to be the stabilized 1,3-diphenylpropenyl

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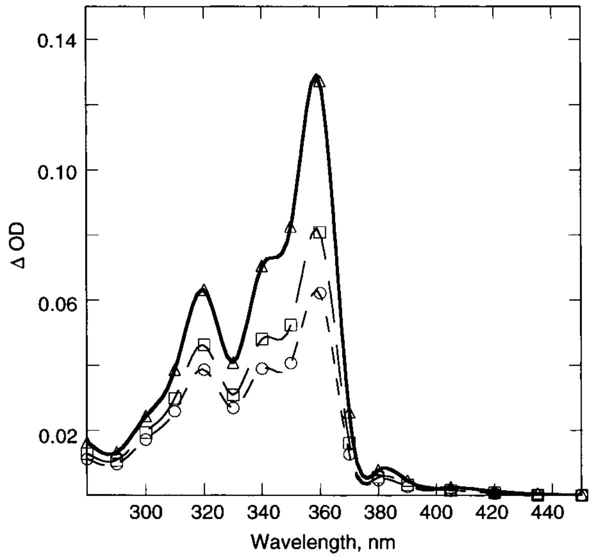

Figure 1. Transient absorption spectra recorded following laser excitation (266 nm) of **1** under nitrogen 0.72 μs (△), 8.48 μs (□), and 15 μs (○) after the laser pulse.

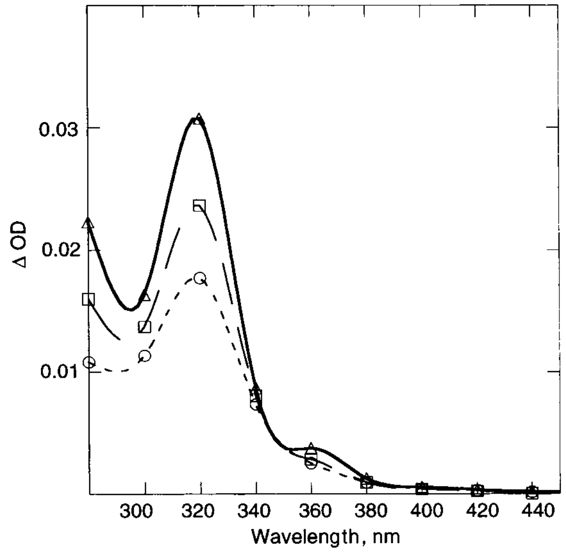

Figure 2. Transient absorption spectra recorded following laser excitation (266 nm) of **7** under nitrogen 4.16 μs (△), 13.4 μs (□), and 31.4 μs (○) after the laser pulse.

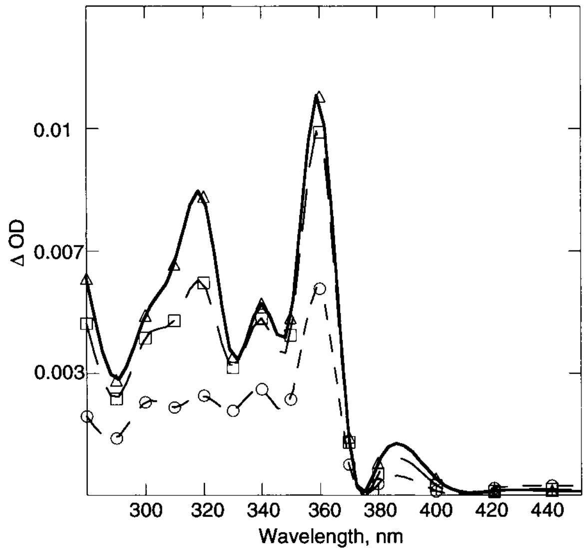

Figure 3. Transient absorption spectra recorded following laser excitation (266 nm) of **1** under nitrogen 0.64 μs (△), 5.76 μs (□), and 34.1 μs (○) after the laser pulse.

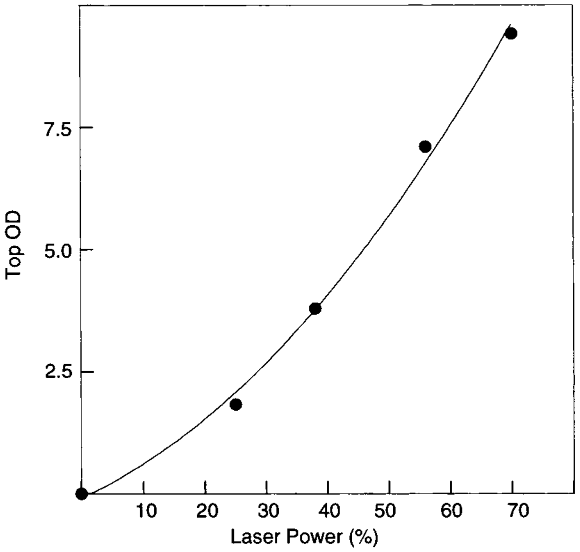

Figure 4. Effect of laser power on signal intensity following 266 nm laser flash photolysis of **1** (monitored at 360 nm). 100% laser power corresponds to ca. 20 mJ/pulse.

radical **3**. To confirm this assignment, the laser flash photolysis of 0.5 mM solutions of 3-chloro-1,3-diphenylpropene (**4**) was carried out. This gave rise to transient **3**, whose absorption matched that described above. The same spectrum was obtained when a 50/50 di-*tert*-butyl peroxide/benzene mixture was irradiated (355 nm, Nd: YAG laser) in presence of 1,3-diphenylpropene. Here allylic hydrogen abstraction[14] by *tert*-butoxy radicals should provide a clean source of **3**.

The formation of propenyl radical **3** was not consistent with the products obtained by lamp irradiation, thus suggesting that a two-photon process was taking place under laser excitation. Accordingly, a different transient spectrum was obtained by placing a beam diffuser made with a frosted quartz plate in front of the sample, in order to minimize multiphoton processes in the laser flash experiments. The main spectral features were a stronger band at 320 nm, together with a less prominent 360 nm band (see Figure 3). In this case the decay of both bands did not follow the same kinetics. Time-resolved absorption spectra at 320 nm showed a short-lived part (τ = 2−3 μs) and a long-lived one (τ = 10 μs). Moreover the fast component was readily quenched by oxygen at close to the diffusion-controlled limit. These data allowed us to assign confidently this transient to the benzylic radical **2**.[13] An investigation of the effects of light intensity on the size of the signal at 360 nm was carried out by attenuating the laser beam with a set of calibrated neutral density filters. Figure 4 has been fitted with a parabola, consistent with all the evidence pointing to a two-photon process.

Two-laser two-color laser flash photolysis of 1,5-dichloro-1,5-diphenylpentane[4] has already been performed. The synthesis laser (266 nm) produces the benzylic monoradical which is the only absorbing chromophore at the photolysis laser wavelength (308 nm). Bleaching of the monoradical by the second laser was accompanied by

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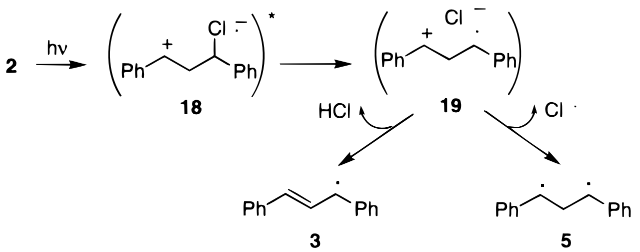
(14) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

Scheme 4



photodecomposition of the remaning chlorobenzyl moiety and formation of 1,2-diphenylcyclopentanes. In the case of the 1,3-dichloro analogue, we assume that photodecomposition of radical **2** might also involve intramolecular quenching of its excited state by the benzylic chloride.[15−19]

This process could give rise to the radical ion pair **19**,[20] which would undergo deprotonation to the propenyl radical **3**. Alternatively, geminate electron transfer from the chloride anion to the 1,3-radical cation within **19** would ultimately result in the formation of 1,2-diphenylcyclopropane (Scheme 4). Related precedents on quenching of cyclopropyl radical cations by chloride can be found in the recent literature.[21]

In principle, the possibility of an alternative intramolecular energy transfer in **2*** was also envisaged; however, it was ruled out in view of the endothermicity of the process. Thus, the excitation energy of the radical (around 62 kcal mol^{-1}) was insufficient to populate the S_1 (107 kcal mol^{-1}) or T_1 (73 kcal mol^{-1}) states of the excited benzylic chloride.[22,23]

High Intensity Product Studies. 1,3-Dichloro-1,3-diphenylpropane was irradiated under different high-intensity conditions. The laser-drop technique[1,24] provides a way of performing high intensity photolysis while minimizing the amounts of products arising from irradiation of (thermally) nonreactive photoproducts.[25] When drops of deaerated solutions of compound **1** in cyclohexane were irradiated by the focused output from a 266 nm laser (1 cycle) only a 10% conversion was observed. The major products were *cis*- and *trans*-diphenylcyclopropanes (**6**) (*cis*/*trans* ratio: 1/2) and significant amounts of 1,3-diphenylpropene, 1-phenylindane, and 3-cyclohexyl-*trans*-1,3-diphenylpropene (**20**) were also obtained. As in the lamp photolysis experiment, minor amounts of 1-chloro-1,3-diphenylpropane and products containing the cyclohexyl moiety were also detected.

Though the laser-drop technique might be more efficient in the conversion of the dihalide than the laser irradiation of a flowing sample, the former technique is not suitable to perform the irradiations under oxygen atmosphere.[24] Thus, in order to compare results under both conditions, deaerated and oxygenated samples running through the cell were irradiated using a 266 nm laser excitation. The dihalide conversion was even lower, but GC/MS analysis of the photolyzed deaerated solutions revealed the formation of the same products as the case of the laser-drop experiment. By contrast, irradiations of oxygenated samples gave rise to lower amounts of cyclohexyl derivatives, without affecting the formation of 1,2-diphenylcyclopropanes.

These results ruled out any role of the propenyl radical in the formation of the 1,2-diphenylcyclopropanes, since the formation of these compounds is not affected by oxygen, while the propenyl radical is scavenged under these conditions. However, the intermediacy of biradical **5** in their formation is easily understood in view of the short lifetime of this intermediate ($\tau = 15$ ns)[6,7] that could preclude its quenching by oxygen. Futhermore, the formation of 1-phenylindane is also rationalized through the involvement of **5**,[26] while 1,3-diphenylpropene could arise either from **5** (H shift) or from **3** (hydrogen abstraction). By contrast, 3-cyclohexyl-*trans*-1,3-diphenylpropene is clearly a product arising from coupling of cyclohexyl and 1,3-diphenylpropenyl radicals. As the later intermediate is formed *via* a two-photon process, the formation of **20** in the laser-drop experiment and its quenching by oxygen can be explained.

Laser irradiations were also performed with deaerated 10 mM solutions of **1** in cyclohexane, using a KrF excimer laser (248 nm) and with the sample contained in a quartz spectrometer cell. Compounds **7**, **8**, and **11**−**13** were obtained, but significant amounts of cyclopropanes were also formed. Clearly, in contrast with the clear dominance of two-photon products arising from irradiation of (thermally) reactive intermediates in the laser-drop experiments other products arising from irradiation of (thermally) nonreactive photoproducts were also formed under these conditions.

Lamp Photolysis of 3-Chloro-1,3-diphenylpropene. At this point it was neccesary to determine which products originate from the propenyl radical generated in the high intensity irradiation experiments. Homolysis of the C−Cl bond of 3-chloro-1,3-diphenylpropene (**4**) generates the propenyl radical as shown in the laser flash photolysis of this compound. Low intensity irradiation (Pyrex filter) of deaerated 10 mM solutions of **4** in

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(15) Application of the Rehm−Weller equation to the $(PhCHCH_3)^*/PhCH_2Cl$ pair, with excited benzylic radical acting as donor, showed that an electron-transfer reaction is thermodynamically possible for this system.

$$\Delta G° = -23.06(E°_{A/A^{\bullet-}} - E°_{D^{+\bullet}/D}) - e_o^{2}/E_a - \Delta E_{o,o}$$

The value of $\Delta E_{o,o}$ for benzyl radicals has been estimated[16] to be around 62 kcal mol^{-1}. The oxidation potential of 1-phenylethyl radical has been found to be 0.37 V (vs SCE).[17] The reduction potential of benzyl chloride is −2.2 V (vs SCE).[18] These data lead to a $\Delta G°$ value of ca. −3 kcal mol^{-1} without taking into account the favorable Coulombic term. However, it must be taken into account that the redox measurements were performed in acetonitrile or dimethylformamide, which are more polar than cyclohexane. Hence, in this solvent the electron transfer step could be less favored. Anyway, the above calculations are to be taken only as a rough indication on the feasibility of the process. Furthermore, in addition to the negative free energy change, other factors such as the proximity of the two centers or proper orbital overlap could enhance the intramolecular electron transfer process. As a matter of fact, analogous intermolecular quenching of excited diphenylmethyl radicals by carbon tetrachloride involving charge transfer have been reported.[19]

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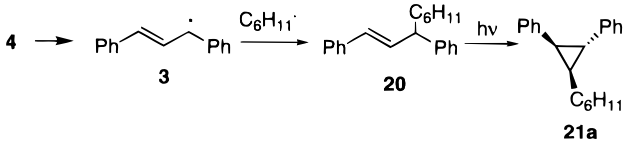
Scheme 5



cyclohexane resulted in the formation of a product with *m/z* 276 for the molecular ion. In principle it could be expected that the intermediate propenyl radical **3** could be trapped by the cyclohexyl radical from the medium to give rise to 3-cyclohexyl-1,3-diphenylpropene (**20**), a product observed in the laser-drop experiment of dichloride **1**. However, NMR data showed that the structure of the photoproduct did not correspond to this compound, but instead to 1-cyclohexyl-*cis,trans*-2,3-diphenylcyclopropane (**21**). The stereochemistry assignment was based on its ^{1}H-NMR spectrum, since **21** is the only geometric isomer with two nonequivalent benzylic hydrogens. These hydrogens gave rise to signals at 2.3 ppm (t, $J = 5.6$ Hz, 1H) and 2.5 ppm (dd, $J_a = 5.6$ Hz, $J_b = 9.3$ Hz, 1H). As expected for vicinal cyclopropyl hydrogens, *cis* coupling was larger than *trans* coupling.[27] The benzylic hydrogen *cis* to the cyclohexyl group was shielded (0.22 ppm) with respect to the benzylic hydrogen with *trans* arrangement.

As compound **21** could arise from a secondary di-π-methane reaction of the *trans*-alkene **20**, the latter compound was irradiated under similar conditions. This led to a clean transformation of *trans*-**20** into the cyclopropane derivative **21** (Scheme 5). A common photoreaction of phenylolefins is *trans*–*cis* isomerization.[28] However, we were not able to detect *cis*-**20** in the photolysate obtained from *trans*-**20**. A reasonable possibility would be that the expected *cis*-**20** also undergoes efficient di-π-methane rearrangement under the irradiation conditions. This was confirmed by an independent photolysis experiment.

Overall, the above results on the photolysis of **4** confirm that the formation of **20** in the laser-drop photolysis of **1** occurs via the intermediacy of radical **3**. The lack of di-π-methane rearrangement under the employed conditions is in agreement with the fact that this high intensity irradiation technique produces almost exclusively primary photoproducts.

Conclusions

It is clear from the above results that monophotonic processes take place in low-intensity irradiations of dichloride **1**. Homolytic cleavage of the first C–Cl bond gives rise to a typical benzylic radical, and no hypervalent intermediate is detected due to the reduced tendency toward bridging in the case of chlorine. Thus, the reaction intermediate observed under attenuated laser excitation and the products characteristic of lamp irradiation can be readily explained on the basis of Scheme 2. No cyclopropanes were obtained under these conditions.

In contrast, high intensity irradiations led mainly to the formation of 1,2-diphenylcyclopropanes (**6**) as major products, together with significant amounts of 1,3-diphenylpropene, 1-phenylindane, and 3-cyclohexyl-*trans*-1,3-diphenylpropene (*trans*-**20**). The 1,3-diphenylpropyl biradical **5** must be the precursor of 1,2-diphenylcyclopropanes, though this intermediate was not observed due to its short lifetime. Formation of 1,3-diphenylpropene and 1-phenylindane can be also explained through the intermediacy of the 1,3-biradical, since they are also obtained during the photoisomerization of 1,2-diphenylcyclopropane.[26] However, 3-cyclohexyl-*trans*-1,3-diphenylpropene must arise from the 1,3-diphenylpropenyl radical **3** detected in the laser flash photolysis experiments. The possibility that the propenyl radical is an intermediate in the formation of 1,2-diphenylcyclopropane can be ruled out because lamp irradiation of 3-chloro-1,3-diphenylpropene (**4**) leads only to *trans*-3-cyclohexyl-1,3-diphenylpropene, which under our irradiation conditions is rapidly transformed into 1-cyclohexyl-2,3-diphenylcyclopropane (**21**). No formation of 1,2-diphenylcyclopropane is observed in this case.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded in a 250 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-1 capillary column (15 m, film thickness 1 mm i.d. 0.25 mm). Combustion analyses were performed at the Instituto de Química Bio-Orgánica of the CSIC in Barcelona. Compound **14a** is commercially available (Aldrich). Compound **4** was synthesized from 1,3-diphenyl-2-propenone following a literature method.[29] High intensity irradiations at 248 nm were realized using a excimer laser (KrF, 248 nm).

Conventional Lamp Irradiation of Chlorides 1, 4, 7, and 8. A degassed 10^{-2} M cyclohexane solution of the corresponding chloro compound either in a quartz tube (**1**, **7**, and **8**) or Pyrex tube (**4**) 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 photomixture was analyzed by GC/MS.

Direct Irradiation of 3-cylohexyl-*trans*-1,3-diphenylpropene (*trans*-20). A degassed solution of *trans*-**20** (10^{-2} M) in cyclohexane was irradiated in a Pyrex tube for 2.5 h with a 125-W medium-pressure mercury lamp inside a quartz immersion well, under continuous magnetic stirring. After evaporation of the solvent, NMR data showed the complete transformation of the alkene in 1-cyclohexyl-*cis,trans*-2,3-diphenylcyclopropane (**21**). ^{1}H NMR ($CDCl_3$): 0.8–1.9 (m, 12H), 2.3 (t, $J = 5.6$ Hz, 1H), 2.5 (dd, $J_a = 5.6$ Hz, $J_b = 9.3$ Hz, 1H), 7.1–7.4 (m, 10H). ^{13}C NMR ($CDCl_3$): 143.1 (s), 138.7 (s), 128.6 (d), 128.4 (d), 128.3 (d), 127.9 (d), 126.35 (d), 125.7 (d), 125.5 (d), 37.15 (d), 36.5 (d), 33.3 (t), 32.4 (t), 32.1 (d), 27.1 (t), 26.4 (t), 26.1 (t), 25.8 (t). MS *m/z* 276 (M^+, 8), 193 (100), 180 (22), 179 (20), 178 (23), 165 (15), 115 (72), 91 (35). Anal. Calcd for $C_{21}H_{24}$: C, 91,25; H 8,75. Found: C, 91,17; H, 8,83.

Laser-Drop Photolysis.[1,24] The beam from a Nd-YAG laser using the fourth harmonic (266 nm, <10 ns, ≤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.[1,24]

Laser Flash Photolysis. These experiments were carried out using a Nd-YAG laser using the fourth harmonic (266 nm, <10 ns, ≤20 mJ/pulse). Transient signals were captured with a 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 enviromment from National Instruments. Other aspects of this instrument are similar to those described earlier.[30,31] All experiments were

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carried out using flow cells constructed from 7 × 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 1,3-Dichloro-1,3-diphenylpropane (1). 1,3-Diphenylpropane-1,3-diol (0.37g, 1.61 mmol), prepared according with the literature,[32] was added to concentrated hydrochloric acid (20 mL). The mixture was stirred for 12 h at room temperature. Afterwards, the solution was neutralized with NaOH, extracted with ether, and dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure to give an oil (0.41 g, 96%). The product was purified by HPLC chromatography (hexane). 1,3-Dichloro-1,3-diphenylpropane was obtained as a diastereoisomeric mixture. ^{1}H NMR ($CDCl_3$): (1*R*,3*S*), 2.65 (dt, $J_a = 15$ Hz, $J_b = 8$ Hz, 1H), 2.95 (dt, $J_a = 15$ Hz, $J_b = 8$ Hz, 1H), 4.8 (t, $J = 8$ Hz, 2H), 7.2−7.3 (m, 10H); (1*R*, 3*R*)/ (1*S*, 3*S*), 2.6 (t, $J = 8$ Hz, 2H), 5.2 (t, $J = 8$ Hz, 2H), 7.2−7.3 (m, 10H). ^{13}C NMR ($CDCl_3$): 140.6 (s), 140.0 (s), 128.8 (d), 128.7 (d), 128.6 (d), 128.5 (d), 127.0 (d), 126.9 (d), 60.7 (d), 60.0 (d), 49.5 (t), 49.4 (t). MS *m/z* 264 (M$^+$, 5), 228 (15), 193 (35), 125 (100). Anal. Calcd for $C_{15}H_{14}Cl_2$: C, 67.94; H, 5.32. Found: C, 67.56; H, 5.34.

Synthesis of 1-Chloro-1,3-diphenylpropane (7). 1,3-Diphenylpropanol (0.40 g, 1.80 mmol), prepared as in the literature,[33] was added to concentrated hydrochloric acid (20 mL), and the mixture was stirred for 12 h at room temperature. The workup procedure was analogous to that previously described. An oil (0.41 g, 95%) was obtained and purified by HPLC (hexane). ^{1}H NMR ($CDCl_3$): 2.2−2.5 (m, 2H), 2.6−2.9 (m,2 H), 4.8 (dd, $J_a = 8$ Hz, $J_b = 6$ Hz, 1H), 7.2−7.4 (m, 10 H). ^{13}C NMR ($CDCl_3$): 141.6 (s), 140.6 (s), 128.7 (d), 128.5 (d), 128.3 (d), 127.0 (d), 126.2 (d), 62.8 (d), 41.4 (t), 33.1 (t). MS *m/z* 230 (M$^+$, 17), 194 (25), 91 (100). Anal. Calcd for $C_{15}H_{15}Cl$: C, 78.12; H, 6.50. Found: C, 78.16; H, 6.58.

Synthesis of 1-Chloro-3-cyclohexyl-1,3-diphenylpropane (8). To a solution of 3-cyclohexyl-1,3-diphenyl-1-propanone[34] (0.18 g, 0.62 mmol) in 20 mL of ethanol was added sodium borohydride (0.03 g, 0.80 mmol) was added in small portions over 5 min. The mixture was stirred at room temperature for 24 h and then cooled by means of an ice bath. Subsequently, 20 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 3-cyclohexyl-1,3-diphenylpropanol (**16**) as a mixture of stereoisomers (0.15 g, 82%). IR (oil): 3354 (OH). ^{1}H NMR ($CDCl_3$): 0.6−2.2 (m, 14H), 2.6−2.75 (m, 1H), 4.1−4.25 (m, 1H), 6.9−7.4 (m, 10H). ^{13}C NMR ($CDCl_3$): 145.7 (s), 143.9 (s), 143.7 (s), 143.6 (s), 128.6 (d), 128.4 (d), 128.3 (d), 128.1 (d), 127.7 (d), 127.10 (d), 126.6 (d), 126.1 (d), 125.4 (d), 73.5 (d), 71.75 (d), 48.4 (d), 43.4 (t), 43.3 (d), 42.7 (t), 41.3 (t), 31.2 (t), 31.1 (t), 30.5 (t), 26.4 (t). MS *m/z* 294 (M$^+$, 85), 276 (47), 193 (100), 174 (97), 107 (81), 92 (31). HRMS Calcd for $C_{21}H_{26}O$: 294.1984. Found 294.1984.

3-Cyclohexyl-1,3-diphenylpropanol (0.15 g, 0.51 mmol) was added to concentrated hydrochloric acid (20 mL). The mixture was stirred for 12 h at room temperature. The solution was then neutralized with NaOH, extracted with ether, and dried over sodium sulfate. The solvent was removed to give an oil (0.14 g, 88%). The product was purified by column chromatography (hexane/ethyl acetate, 10/1) to give 1-chloro-3-cyclohexyl-1,3-diphenylpropane as a diastereoisomeric mixture. ^{1}H NMR ($CDCl_3$): 0.6−2.2 (m, 24 H), 2.5−2.9 (m, 4 H), 4.4 (dd, $J_a = 11$ Hz, $J_b = 2$ Hz, 1 H), 4.5 (dd, $J_a = 11$ Hz, $J_b = 5$ Hz, 1 H), 7.0 (m, 2 H), 7.2−7.3 (m, 18 H). ^{13}C NMR ($CDCl_3$): 142.8 (s), 142.6 (s), 142.4 (s), 140.6 (s), 128.6 (d), 128.5 (d), 128.4 (d), 128.3 (d), 128.2 (d), 128.0 (d), 127.4 (d), 126.6 (d), 126.3 (d), 62.5 (d), 61.5 (d), 49.3 (d), 43.5 (d), 43.1 (d), 43.0 (t), 42.7 (t), 31.25 (t), 31.0 (t), 30.7 (t), 26.5 (t), 26.4 (t). MS *m/z* 312 (M$^+$, 0), 276 (10), 193 (100), 115 (63), 91 (20). Anal. Calcd for $C_{21}H_{25}Cl$: C, 80.66; H, 7.99. Found: C, 81.01; H, 8.16.

Synthesis of 1-Cyclohexyl-1,3-diphenylpropane (12). To a solution of 3-cyclohexyl-1,3-diphenyl-1-propanone[34] (0.10 g, 0.34 mmol) in 20 mL of ethyl acetate were added perchloric acid (1 mL) and 0.10 g of palladium-carbon catalyst. Hydrogenation was performed under pressure (12 kg/cm^2) during 1 h. The mixture was filtered, extracted with ether, and dried over magnesium sulfate. Solvent was removed to give 1-cyclohexyl-1,3-diphenylpropane as a colorless oil (0.06 g, 64%), which was further purified by HPLC (hexane/ethyl acetate, 10/1). ^{1}H NMR ($CDCl_3$): 0.7−1.8 (m, 11 H), 1.8−2.0 (m, 2 H), 2.0−2.2 (m, 1 H), 2.2−2.5 (m, 2 H), 7.1-7.4 (m, 10 H). ^{13}C NMR ($CDCl_3$): 144.2 (s), 142.8 (s), 128.6 (d), 128.3 (d), 128.2 (d), 128.0 (d), 125.8 (d), 125.5 (d), 51.7 (d), 43.3 (d), 34.5 (t), 34.0 (t), 31.3 (t), 31.0 (t), 26.5 (t). MS *m/z* 278 (M$^+$, 13), 196 (13), 117 (50), 91 (100). Anal. Calcd for $C_{21}H_{26}$: C, 90.65; H, 9.34. Found: C, 90.67; H, 9.38.

Synthesis of 1,3-Dicyclohexyl-1,3-diphenylpropane (13). 3-Cyclohexyl-1,3-diphenylpropanone[34] (0.58 g, 2.00 mmol) in anhydrous diethyl ether (20 mL) was added dropwise to a 2 M solution of cyclohexylmagnesium chloride (1 mL, 2.00 mmol) in cyclohexane. After the addition was complete, the mixture was stirred for 1 h 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 1,3-dicyclohexyl-1,3-diphenylpropanol (**17**) as an oil (0.62 g, 83%). IR (oil): 3574 (OH). ^{1}H NMR ($CDCl_3$): 0.5−2.6 (m, 26H), 6.7−6.8 (m, 1H), 6.85−6.95 (m, 1H), 7.0−7.35 (m, 8H). ^{13}C NMR ($CDCl_3$): 145.3 (s), 144.8 (s), 144.0 (s), 128.7 (d), 128.5 (d), 127.5 (d), 127.0 (d), 126.4 (d), 126.0 (d), 125.9 (d), 125.8 (d), 125.6 (d), 125.1 (d), 79.7 (s), 79.0 (s), 49.7 (d), 48.0 (d), 47.4 (d), 47.0 (d), 44.1 (d), 43.7 (d), 43.0 (t), 41.6 (t), 31.7 (t), 31.1 (t), 30.4 (t), 30.2 (t), 27.4 (t), 26.9 (t), 26.6 (t), 26.5 (t), 26.4 (t). MS *m/z* 376 (M$^+$, 8), 375 (21), 356 (19), 294 (78), 209 (100), 190 (81), 120 (84), 92 (79), 83 (48). HRMS Calcd for $C_{27}H_{36}O$: 376.2766. Found 376.2737.

1,3-Dicyclohexyl-1,3-diphenylpropanol (0.62 g, 1.64 mmol) was disolved in 20 mL of acetic acid. Perchloric acid (1 mL) and 0.10 g of 10% palladium on charcoal were added. Hydrogenation was performed under pressure (12 kg/cm^2) during 2 h. Then, the mixture was filtered, extracted with ether, and dried over magnesium sulfate. Solvent was removed to give 1,3-dicyclohexyl-1,3-diphenylpropane (0.46 g, 78%). The product was purified by HPLC (hexane/ethyl acetate, 10:1) and obtained as a diastereoisomeric mixture. ^{1}H NMR ($CDCl_3$): 0.6−2.1 (m, 24H), 2.3−2.5 (m, 2H), 6.9−7.0 (m, 4H), 7.1−7.4 (m, 6H). ^{13}C NMR ($CDCl_3$): 144.8 (s), 144.3 (s), 128.8 (d), 128.7 (d), 127.8 (d), 127.6 (d), 125.6 (d), 125.5 (d), 49.5 (d), 49.3 (d), 43.7 (d), 42.5 (d), 35.9 (t),35.0 (t), 31.9 (t), 31.2 (t), 29.9 (t), 26.8 (t), 26.6 (t), 26.5 (t). MS *m/z* 360 (M$^+$, 9), 278 (8), 173 (70), 91 (100). Anal. Calcd for $C_{27}H_{36}$: C, 90.00; H, 9.99. Found: C, 90.03; H, 10.08.

Synthesis of 1-(*p*-Cyclohexylphenyl)-3-phenylpropane (15). To a mixture of cyclohexylbenzene (1.20 g, 7.50 mmol) and 3-phenylpropanoyl chloride (2.00 g, 11.86 mmol) was added aluminum chloride (1.59 g, 11.86 mmol) in three portions. After stirring 1 h at room temperature, the reaction mixture was poured onto ice−water, extracted with ether, and dried over anhydrous sodium sulfate, and then solvent was removed. Purification of the residue by column chromatography (hexane/ethyl acetate, 10/1) left 1-(*p*-cyclohexylphenyl)-3-phenyl-1-propanone (**14c**) (0.33 g, 15%). IR (oil): 1680 (C═O). ^{1}H NMR ($CDCl_3$): 1.2−1.5 (m, 5H), 1.7−1.9 (m, 5H), 2.5 (m, 1H), 3.1 (t, $J = 8$ Hz, 2H), 3.3 (t, $J = 8$ Hz, 2H), 7.2−7.3 (m, 7H), 7.9 (d, $J = 8$ Hz, 2H). ^{13}C NMR ($CDCl_3$): 198.8 (s), 153.6 (s), 141.3 (s), 134.6 (s), 128.4 (d), 128.3 (d), 128.2 (d), 127.0 (d), 126.0 (d), 44.6 (d), 40.3 (t), 34.0 (t), 30.1 (t), 26.6 (t), 25.9 (t). MS *m/z* 292 (M$^+$, 15), 209 (55), 187 (100), 91 (22). HRMS Calcd for $C_{21}H_{24}O$: 292.1827. Found 292.1831.

To a solution of 1-(*p*-cyclohexylphenyl)-3-phenylpropanone (0.10 g, 0.34 mmol) in 20 mL of ethyl acetate were added several drops of perchloric acid and 0.10 g of palladium-carbon catalyst. Hydrogenation was performed under pressure (12 kg/cm^2) during 1 h. The mixture was extracted with ether and dried over magnesium sulfate. Solvent was removed to give

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1-(*p*-cyclohexylphenyl)-3-phenylpropane as a colorless oil (0.08 g, 85%), which was further purified by HPLC (hexane:ethyl acetate, 10:1). ^{1}H NMR ($CDCl_3$): 1.1−1.4 (m, 5H), 1.6−1.9 (m, 7H), 2.3−2.5 (m, 1H), 2.5−2.6 (m, 4H), 7.0−7.3 (m, 9H). ^{13}C NMR ($CDCl_3$): 145.5 (s), 142.4 (s), 139.6 (s), 128.4 (d), 128.3 (d), 126.7 (d), 125.7 (d), 44.1 (d), 35.5 (t), 35.0 (t), 34.5 (t), 33.0 (t), 26.9 (t), 26.2 (t). MS *m*/*z* 278 (M^+, 50), 187 (17), 173 (20), 159 (25), 131 (20), 117 (42), 91 (100). Anal. Calcd for $C_{21}H_{26}$: C, 90.65; H, 9.34. Found: C, 90.63; H, 9.50.

Synthesis of 3-Cyclohexyl-*trans*-1,3-diphenylpropene (*trans*-20). 3-Cyclohexyl-1,3-diphenylpropanol was dehydrated following a literature procedure[35] to give 3-cyclohexyl-*trans*-1,3-diphenylpropene, (solid). ^{1}H NMR ($CDCl_3$): 0.8−2.0 (m, 11H), 3.1 (m, 1H), 6.4 (m, 2H), 7.2−7.5 (m, 10H). ^{13}C NMR ($CDCl_3$): 144.0 (s), 137.6 (s), 133.2 (d), 130.2 (d), 130.0 (d), 128.4 (d), 128.1 (d), 128.0 (d), 126.9 (d), 126.1 (d), 126.0 (d), 56.7 (d), 43.7 (d), 31.5 (t), 26.5 (t), 26.4 (t). MS *m*/*z* 276 (M^+, 17), 193 (100), 178 (33), 165 (12), 115 (95), 91 (46). Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 90.91; H, 9.07.

Synthesis of 3-Cyclohexyl-*cis*-1,3-diphenylpropene (*cis*-20). A degassed 10^{-2} M acetone solution of 3-cyclohexyl-*trans*-1,3-diphenylpropene in a Pyrex tube was irradiated during 2.5 h with a 125-W medium-pressure mercury lamp inside a quartz immersion well, under continuous stirring. After evaporation of the solvent, the ^{1}H NMR spectrum showed a mixture of isomeric olefins (*cis*-**20**/*trans*-**20**, ratio 72/28). Both isomers were separated by preparative chromatography. Data for *cis*-**20**: ^{1}H NMR ($CDCl_3$): 0.7−2.0 (m, 11H), 3.5 (dd, J_a = 9 Hz, J_b = 11 Hz, 1H), 5.9 (t, J = 11 Hz, 1 H), 6.5 (d, J = 11 Hz, 1H). ^{13}C NMR ($CDCl_3$): 144.3 (s), 137.6 (s), 135.1 (d), 129.1 (d), 128.7 (d), 128.4 (d), 128.0 (d), 126.5 (d), 125.9 (d), 50.2 (d), 43.9 (d), 31.0 (t), 30.9 (t), 26.4 (t), 26.35 (t). MS *m*/*z* 276 (M^+, 10), 193 (100), 178 (24), 165 (9), 115 (100), 91 (37). Anal. Calcd for $C_{21}H_{24}$: C, 91,25 ; H, 8,75. Found: C, 91,30; H, 8,71.

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