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Lamp versus Laser Photolysis of 1,3-Dichloro-1,3-diphenylpropane in Cyclohexane. Direct Observation of 1,3-Diphenylpropenyl Radical

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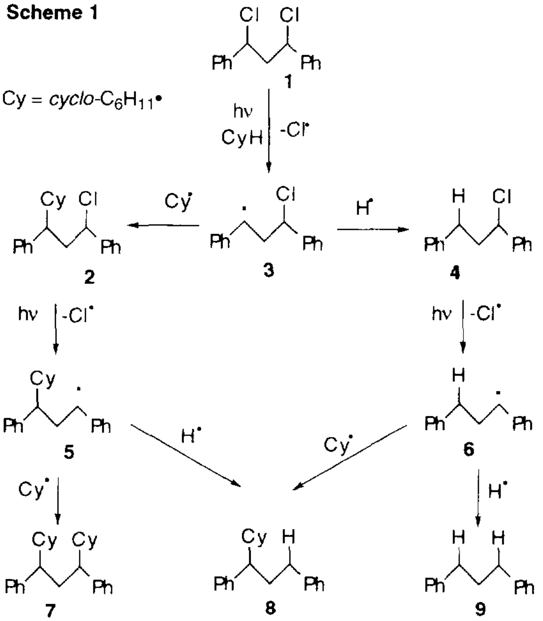
Abstract: Laser photolysis of the title compound leads to two-photon processes indicating the involvement of the 1,3-diphenylpropanediyl biradical (**12**) and the 1,3-diphenylallyl radical (**10**).

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-diiodo-1,5-diphenylpentane in cyclohexane,[1] while in the case of 1,5-dichloro-1,5-diphenylpentane the typical benzyl radical was formed.[4] We and others have demonstrated that excitation of dihalides with high-intensity light can lead to a difunctional reactive intermediates from which a completely different set of products can be formed.[1-5]

We report here a comparative lamp *vs.* laser (Nd-YAG, fourth harmonic, 266 nm) photolysis study of 1,3-dichloro-1,3-diphenylpropane (**1**). Laser flash photolysis (LFP) studies show that a two-photon process is responsible for the formation of 1,3-diphenylpropenyl radicals (**10**) as one of the transients under high intensity conditions. This radical had been prepared earlier from the 1,3-diphenylallyl anion by electron transfer,[6] but neither lifetime nor absorption spectra had been obtained. Further, product studies under low and high intensity conditions show that that *cis*- and *trans*-1,2-diphenylcyclopropanes (**13**) are exclusively formed by a two photon route.

Scheme 1

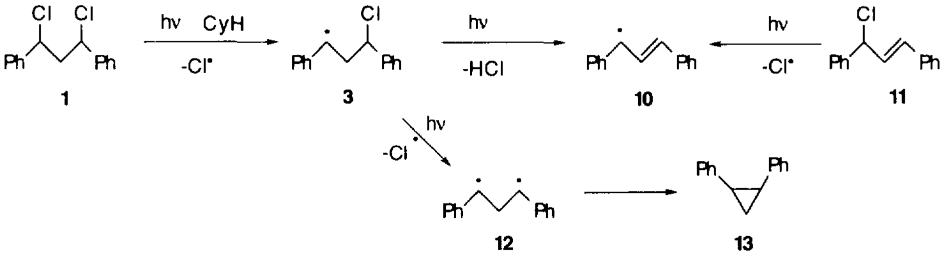


Low-Intensity Irradiation. Lamp irradiation, predominantly in the 254 nm region (Hg medium pressure, quartz filter, 1h), of a 10 mM deaerated solution of **1** (Scheme 1) led to complete consumption of the starting material and the formation of a mixture of 1-chloro-3-cyclohexyl-1,3-diphenylpropane (**2**), 1-chloro-1,3-diphenylpropane (**4**), 1,3-dicyclohexyl-1,3-diphenylpropane (**7**), 1-cyclohexyl-1,3-diphenylpropane (**8**), 1,3-diphenylpropane (**9**), and cyclohexylcyclohexane.[7] Cyclohexyl radicals (see products **2**, **7** and **8**) should be formed by reaction of chlorine atoms with the solvent.[8] All new compounds were fully characterized.[9,10]

Laser Flash Photolysis.[11] LFP of deaerated solutions of **1** at 266 nm yielded a narrow spectrum, with maxima at 320 (weak), 340 (weak) and 360 nm (strong), see Fig. 1A. The decay follows approximately the same kinetics throughout the spectrum with half lives 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.

As this long-lived intermediate could not be the 3-chloro-1,3-diphenylpropyl radical (**3**) (which would be expected to absorb at ~320 nm)[12] we checked the possibility that **3** could lose hydrogen chloride to give the allyl radical **10**, Scheme 2. Thus, experiments were carried out with 3-chloro-1,3-diphenylpropene[13] (**11**) in an attempt to establish the nature of the transient. Laser flash photolysis of a 0.5 mM solution of **11** in cyclohexane gave rise to a transient whose absorption matched that described above. LCI-SCF studies of allyl radical **10** predict an absorption maximum at close to the observed values.[14] Oxygen quenched this transient (i.e. shortened its lifetime), but increased its yield of production; fluorescence measurements under a nitrogen, air or oxygen atmosphere showed that the fluorescence of 3-chloro-1,3-diphenylpropene is quenched by oxygen. We tentatively suggest that oxygen promotes intersystem crossing and enhances triplet formation. Attempts to detect singlet oxygen luminescence were unsuccessful, suggesting the triplet state of **11** is very short lived. Thus, **10** probably originates predominantly from a short lived triplet state. Radical **10** was also obtained when a 50/50 di-*tert*-butyl peroxide/benzene was irradiated (355 nm, Nd:YAG) in presence of 1,3-diphenylpropene. Here allylic hydrogen abstraction[15] by *tert*-butoxy radicals should provide a clean source of **10**.

Scheme 2



The formation of the allyl radical **10** was not consistent with the products obtained by lamp irradiation, thus suggesting that a two-photon process was taking place under laser excitation. In order to minimize multiphoton processes in the laser flash experiments, we placed a beam diffuser (made with a *frosted* quartz plate) in front of the sample; this avoids high intensity regions in the beam and promotes monophotonic behavior. The spectrum obtained under these conditions showed a stronger band at 320 nm, together with a diminished 360 nm band (see Fig. 1C). The 320 nm band had a lifetime of ca. 2-3 μs and was readily quenched by oxygen at close to the diffusion controlled limit. These data allowed us to assign confidently this transient to the benzyl radical **3**.[12]

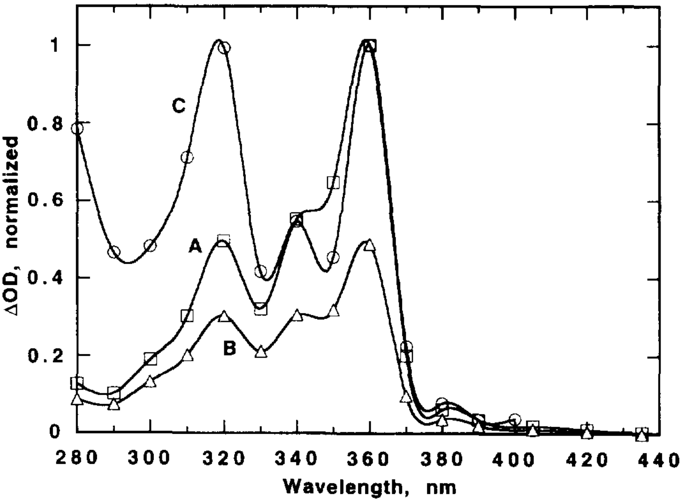


Figure 1. Transient absorption spectra recorded following laser excitation (266 nm) of **1** under nitrogen, without diffuser (**A** and **B**, see text) after 770 ns (**A**, □) and 1500 ns (**B**, Δ), and (**C**) with diffuser 120 ns after laser excitation.

An investigation of the effects of light intensity on the magnitude of the signals at 320 and 360 nm was carried out by attenuating the laser beam with a set of calibrated neutral density filters. At 360 nm the dependence of the signal intensity with laser dose was characteristic of two-photon processes. Interestingly, the formation of allyl radical is consistent with the elimination of hydrogen chloride from radical **3**.

High intensity product studies. Laser irradiations were conducted in 0.01 M solutions of **1** in cyclohexane using 248 or 266 nm laser excitation with the sample in a spectrometer cell. Compounds **2**, **4** and **7-9** were again obtained, but in this case significant amounts of cyclopropanes **13** were also formed. Any role of 1,3-diphenylpropenyl radical in the formation of the cyclopropane derivatives is highly unlikely, since these compounds were also obtained when an oxygenated solution of **1** was photolyzed (Nd:YAG, 266nm), conditions under which **10** is scavenged by oxygen.[16] In contrast, the short lifetime of the biradical **12** ($\tau \sim 15$ ns)[17,18] could preclude its quenching by oxygen No dimerization products[4] derived from the allyl radical were observed, probably as consequence of the low substrate concentration, and the dominance of reaction with other more reactive radicals, such as those derived from the solvent.

We also employed the laser-drop technique[19] since it provides a way of performing high intensity photolysis while minimizing the amounts of secondary products. When drops of deaerated solutions of **1** in cyclohexane were irradiated by the focused output from a 266 nm laser (1 cycle) the product distribution changed dramatically. The efficiency of transformation was very low (<10 %) but the major products were *cis-* and *trans-*diphenylcyclopropanes; minor amounts of 1,3-diphenylpropenes and products containing the cyclohexyl moiety were also observed. The formation of the cyclopropane derivatives implies that both chlorine atoms are extruded during the laser pulse, presumably to produce the 1,3-diphenylpropanediyl biradical **12**

Conclusions

High intensity photolysis of 1,3-dichloro-1,3-diphenylpropane (**1**) leads to an isomeric mixture of *cis-* and *trans-*1,2-diphenylcyclopropanes whose formation is believed to involve the intermediacy of the 1,3-diphenylpropanediyl biradical (**12**). Surprisingly 1,3-diphenylpropenyl radical (**10**) was also formed through a two-photon process. This is likely a *sequential* two-photon process, involving absorption by an excited state of **1**, most likety its triplet state.[20] This allyl radical is not believed to be involved in the formation of the cyclopropane derivatives.[21]

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(9) The synthetic methodologies employed are similar to those employed earlier for the corresponding 1,5-dichloro derivatives.[4] New compounds had the following properties: 1,3-dichloro-1,3-diphenylpropane (**1**): ^{1}H-NMR (200 MHz, CDCl3): δ 2.6-2.7 (m,2H), 5.2 (dd, 2H, J1=7Hz, J2=8Hz), 7.3-7.4 (m,10H) 2.9-3.0 (m,2H), 4.8 (dd, 2H, J1=7Hz, J2=8Hz), 7.3-7.4 (m,10H) ^{13}C-NMR (66 MHz, CDCl3): 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) ppm. Anal. Calc. C: 67.94%, H: 5.32%; Found C: 67.56%, H: 5.345%, mass. spec. (m/z) 264 (5), 228 (15), 125 (100). 1-Chloro-3-cyclohexyl-1,3-diphenylpropane (**2**): ^{1}H-NMR: δ 0.6-2.2 (m,24H), 2.5-2.9 (m, 4H), 4.5 (dd, 1H, J1=5Hz, J2=11Hz), 4.4 (dd,1H, J1=2Hz, J2= 11 Hz), 7.0 (m, 2H), 7.2-7.3 (m, 18H). ^{13}C-NMR: 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),127.9(d), 127.5(d),127.4(d), 126.6(d),126.3(d), 62.5(d), 61.5(d), 49.3(d), 43.4(d), 43.1(d), 42.9(t), 42.7(t), 31.3(t), 31.2(t), 31.0(t), 30.6(t), 26.4(t), 26.3(t). Anal. Calc. C: 80.66%, H: 7.99%; Found C: 81.01%, H: 8.16%, mass. spec. (m/z) 312

(0), 276(10), 193 (100). 1-Chloro-1,3-diphenylpropane (**4**): ^{1}H-NMR: δ 2.2-2.5 (m,2H), 2.6-2.9 (m,2H), 4.8 (dd, 1H, J1=6Hz, J2=8Hz), 7.2-7.4 (m,10H), ^{13}C-NMR: 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). Anal. Calc. C: 78.12%, H: 6.50%; Found C: 78.16%, H: 6.58%, mass. spec. (m/z) 230 (17), 194 (25), 91 (100). 1,3-dicyclohexyl-1,3-diphenylpropane (**7**): ^{1}H-NMR: δ 0.6-2.2 (m,24H), 2.3-2.5 (m,2H), 6.9-7.0 (m,4H), 7.1-7.4 (m,6H), ^{13}C-NMR: 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), 31.8(t), 31.1(t), 29.9(t), 26.7(t), 26.6(t), 26.5(t). Anal. Calc. C: 90.00%, H: 9.99%; Found C: 90.03%, H: 10.08%, mass. spec. (m/z) 360 (9), 278 (8), 91 (100). 1-Cyclohexyl-1,3-diphenylpropane (**8**): ^{1}H-NMR: δ 0.7-1.8 (m,11H), 1.8-2.0 (m,2H), 2.0-2.2 (m,1H), 2.2-2.5 (m,2H), 7.1-7.4 (m,10H),^{13}C-NMR: 144.2(s), 142.7 (s), 128.6 (d), 128.3 (d), 128.1(d), 128.0 (d), 125.8 (d), 125.5 (d), 51.7 (d), 43.34 (d), 34.47 (t), 34.0 (t), 31.3 (t), 31.0 (t), 26.5 (t). Anal. Calc. C: 90.65%, H: 9.34%; Found C: 90.67%, H: 9.38%, mass. spec. (m/z) 278 (13), 196 (13), 91 (100).

(10) Compounds **1**, **2** and **7** are mixtures of two stereoisomers.

(11) The laser system uses Lumonics EX-510 and EX-530 for excitation wavelengths of 248 and 308 nm, Surelite lasers from Continuum for the Nd-YAG wavelengths of 266, 355 and 532 nm and a Molectron UV-24 nitrogen laser for 337 nm. All pulse durations are <10 ns and typical pulse energies between 5 and 50 mJ. The signals from the monochromator/photomultiplier system were initially captured by a Tektronix 2440 digitiger and transfered to a PowerMacintosh computer that controlled the experiment with software developed in the LabVIEW 3.1.1 environment from National Instruments. Other aspects of the system are similar to those described earlier: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747; Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

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(16) Oxygen leads to a complex mixture of products, characteristic of radical processes. 1,3-Diphenyl-propene oxide, the two isomeric chalcones and some dibenzyl ketone are among the products. Attempts to detect singlet oxygen luminescence were unsuccessful, a result that is consistent with the involvement of radicals rather than long lived excited states.

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