Laser Flash, Laser-Drop, and Preparative Photochemistry of 1,5-Diiodo-1,5-diphenylpentane. Detection of a Hypervalent Iodine Radical Intermediate

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Received November 30, 1994[⊗]

Abstract: Studies of the laser flash and laser-drop photolysis of 1,5-diiodo-1,5-diphenylpentane (**4**) support the intermediacy of a cyclic hypervalent iodine radical, **19**. Radical **19** has spectroscopic and chemical properties quite different from those of typical benzylic radicals; for example, the absorption spectrum of **19** is red-shifted and significantly broader than that for the 5-chloro-1,5-diphenylpentyl radical, **14**. In addition, **19** is virtually unreactive toward oxygen. Laser-drop photolysis of **4** led to further decomposition of **19** to yield primarily a mixture of isomeric 1,2-diphenylcyclopentanes (**18**) presumably from the corresponding 1,5-biradical. The differences and similarities between this biradical and that produced in the photolysis of 1,5-diphenylcyclohexanone (**15**) are discussed.

Introduction

The photochemistry of alkyl iodides has been well-studied for many decades,[1,2] and it results mainly in C–I cleavage due to absorption by the relative long-wavelength n → σ^* transition of the carbon–iodine bond (in comparison to other alkyl halides).[3] Homolytic cleavage of the C–I bond produces an alkyl radical and iodine atom. In polar solvents, electron transfer competes efficiently with escape from the solvent cage to produce an ion pair.[4,5] For bicyclic iodides it has been proposed that the nascent ion pair leads to solvolysis at the bridgehead carbon when methanol is used as solvent.[5–8] However, in nonpolar solvents electron transfer becomes unfavorable and escape from the solvent cage leads to radical products.[9,10]

An interesting feature of halogen atoms is their ability to form halonium ions. These are divalent compounds of electron-deficient halogens. Diaryliodonium ions are probably the best understood of the halonium ions because of their synthetic utility in the arylation of nucleophiles under mild conditions[11,12] and their industrial importance as photoinitiators for free radical and cationic polymerization.[13–15]

The mechanism for the arylation of nucleophiles is not clear, but it has generally been accepted to occur by one of two possible mechanisms: (i) trapping of the diaryliodonium ion by the nucleophile to form a trivalent iodine intermediate followed by reductive elimination to form the arylated nucleophile and aryl iodide (Scheme 1),[12] or (ii) one-electron reduction of the diaryliodonium ion to form a divalent iodine radical intermediate which subsequently cleaves to produce an aryl radical and aryl halide—in turn, the aryl radical combines with the oxidized nucleophile to form products (Scheme 2).[16–18]

Support for a divalent iodine radical intermediate was provided in an elegant paper by Tanner et al.[19] in which they showed that the kinetics for the transfer of iodine from an aryl iodide to an aryl radical did not correspond to a simple atom abstraction model. They proposed that a symmetrical transition state with partial bonding between the aryl groups and the iodine atom was not a part of the mechanism, but rather that the divalent iodine radical was an intermediate. Their study also showed the formation of benzene during the arylation of phenoxide with mono-substituted diphenyliodonium ion. A photo-CIDNP study by DeVoe and co-workers[20] gave direct evidence for the involvement of phenyl radicals during the anthracene-sensitized photolysis of diphenyliodonium hexafluorophosphate in acetonitrile-d_3. They concluded that a divalent iodine radical intermediate was formed by electron transfer from the anthracene triplet, ultimately leading to phenylated anthracenes and phenyl iodide as products.

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[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1995.

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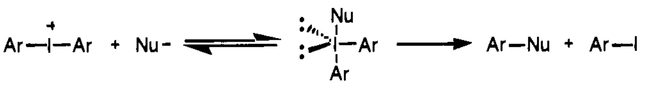
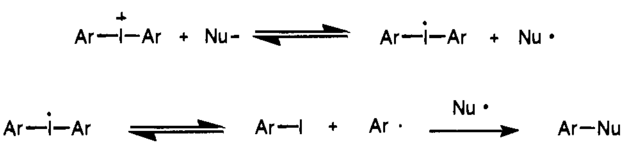
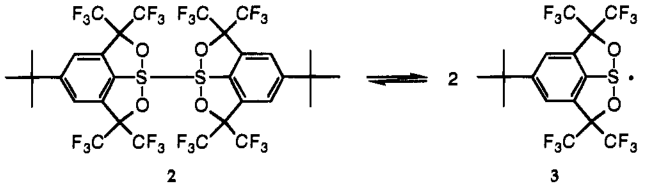
Scheme 1



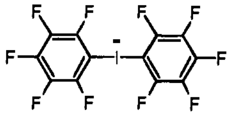
Scheme 2



Scheme 3



A communication by Farnham and Calabrese[21] reported the isolation and X-ray structure for the iodinanide anion **1** (isolated as the lithium salt complexed with 2 equiv of tetramethylethylenediamine). These compounds had been postulated previously by Wittig and Schöllkopf[22] and Reich and co-workers[23] based on kinetic evidence. While iodinanide species are rare, their existence, along with iodonium cations, demonstrates the ability of divalent iodine to exist in two extreme oxidation states. Thus, it could be expected that an intermediate oxidation state of divalent iodine may be observable.



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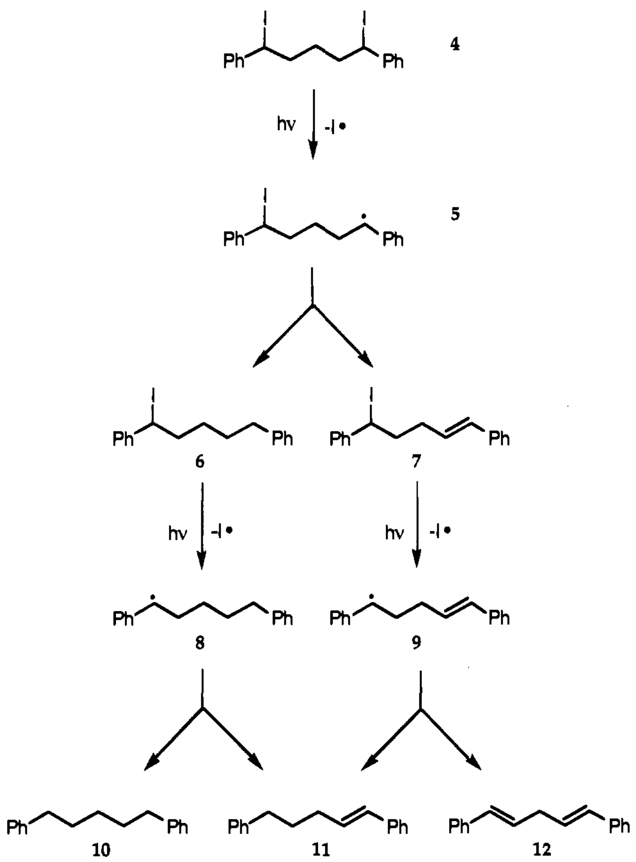
Hypervalent sulfur radicals are well-established.[24,25] Martin and Perkins[26] have shown that sulfuranyl radicals **3** are in equilibrium with their dimers with $K_{eq} = 5.55 \times 10^{-2}$ M at 20 °C (Scheme 3).

To date, there have been no conclusive reports on divalent halogen radicals, although in many cases such complexes have been invoked to explain anomalous results in reactions of haloalkyl radicals. Thaler[27] reported that bromination of bromoalkanes leads to a much higher yield of 1,2-dibromoalkanes than would be expected from thermodynamic considerations. Skell and Shea[28] were able to show that, during the course of bromination of (+)-1-bromo-2-methylbutane with DBr, a significant amount of starting material undergoes hydrogen−deuterium exchange with retention of configuration at the asymmetric carbon. They postulated that a bridged radical intermediate was responsible for this result. McGimpsey et al.[29] recently reported on the relative insensitivity toward oxygen of 1-naphthyl-2-bromoethyl radicals and suggested the involvement of a bridged intermediate.

Scheme 4



Although dialkyliodonium ions are well-known,[30] and one can envisage a divalent iodine radical as the one-electron reduction product of such ions, we could only find one report for the detection of such a radical in the literature.[31] In this article we report evidence for such a radical resulting from the photolysis of 1,5-diiodo-1,5-diphenylpentane (**4**). Our conclusions are based on steady-state photolysis, laser flash photolysis, and laser-drop photolysis (LDP)[32] of **4**.

Results

Low-Intensity Irradiation. Lamp irradiation (medium pressure mercury, Pyrex filter, 1 h) of a 0.50 mM deaerated solution of 1,5-diiodo-1,5-diphenylpentane (**4**) (Scheme 4) led to complete consumption of starting material and the formation of a mixture of 1,5-diphenyl-1-iodopentane (**6**), 1,5-diphenylpentane (**10**), and isomer mixtures of 1,5-diphenyl-1-pentene (**11**), 1,5-diphenyl-5-iodo-1-pentene (**7**), and 1,5-diphenyl-1,4-pentadiene (**12**). Under similar conditions, 1,5-diphenyl-1-iodopentane (**6**) was partially converted into 1,5-diphenylpentane (**10**) and 1,5-diphenyl-1-pentene (**11**).

By contrast, the photolysis of 1,5-dichloro-1,5-diphenylpentane (**13**) led to a complex mixture containing more than 11 products, which can be explained by the expected homolytic cleavage of a carbon−chlorine bond (Scheme 5) followed by hydrogen abstraction from solvent by chlorine atoms, radical−radical recombination, and some secondary photolysis of monochlorinated products.

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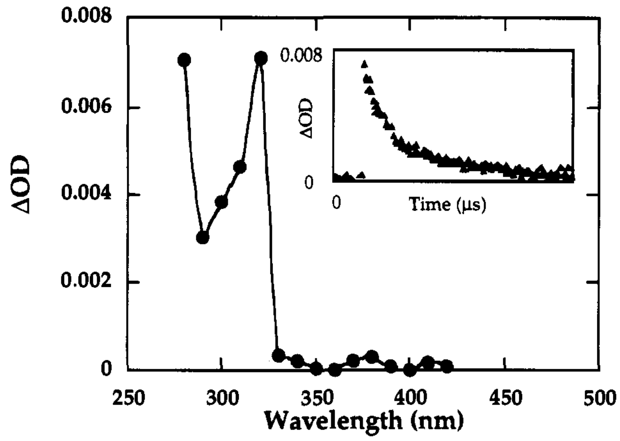


Figure 1. Transient absorption spectrum obtained upon 248 nm laser flash photolysis of **13** in cyclohexane 2 μs after the laser pulse. The inset shows the decay as monitored at 320 nm.

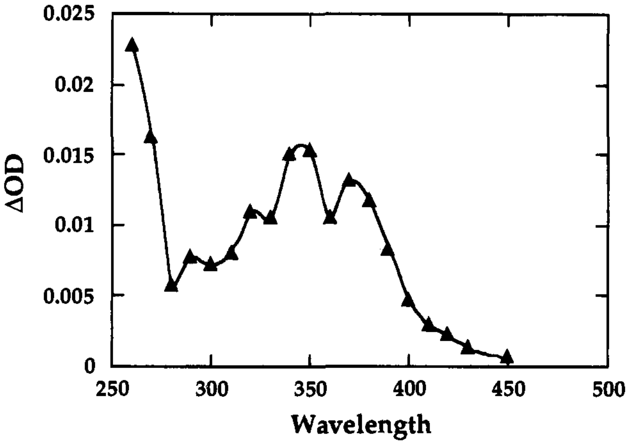
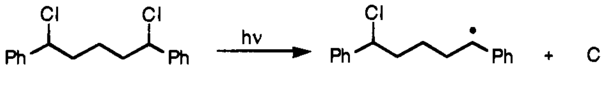


Figure 2. Transient absorption spectrum obtained upon 248 nm laser flash photolysis of **4** in cyclohexane 0.5 μs after the laser pulse. Decay of the transient is shown in Figure 3.

Scheme 5



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Laser Flash Photolysis. Laser flash photolysis at 266 or 248 nm of deaerated solutions of **13**, the dichloro analog of **4**, yields a very narrow spectrum centered at 320 nm (Figure 1) which decays by mixed first- and second-order kinetics. This absorption is readily quenched by oxygen at close to the diffusion controlled limit. In contrast to the spectrum obtained by photolysis of **13**, 248 nm laser flash photolysis of a deaerated, ~50 μM solution of **4** in cyclohexane leads to an instantaneous (in the <20 ns time scale), broad absorption, extending from at least 260 nm to about 450 nm, with local maxima at 290, 320, 350, and 370 nm and a strong band continuing into the deep UV (Figure 2). This absorption decays with the same kinetics over the entire spectrum, and follows first-order (or pseudo-first-order) kinetics with a lifetime of 4.4 ± 0.3 μs under our experimental conditions.

A similar spectrum is obtained upon 308 nm laser flash photolysis of a 0.39 mM solution of **4** in cyclohexane. Oxygen saturated solutions of **4** in cyclohexane lead to a lifetime only slightly shorter than the same solutions deaerated by nitrogen bubbling (2.4 vs 2.9 μs) (Figure 3). The reduced lifetime under 308 nm excitation (compared with 248 nm) is probably due to differences in power between the two lasers (*vide infra*).

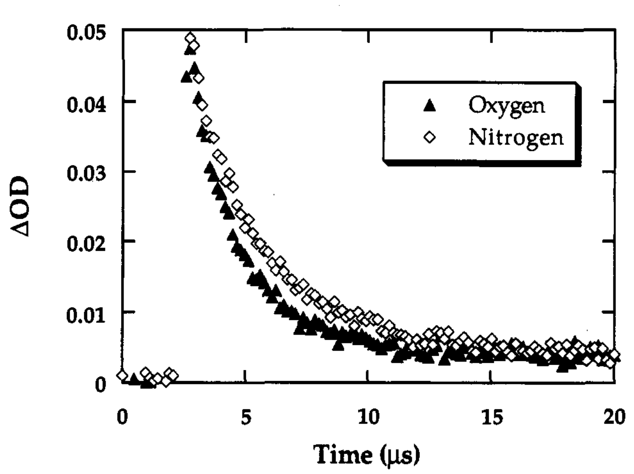

Figure 3. Effect of oxygen on the decay of the transient formed upon 308 nm laser flash photolysis of **4** (monitored at 350 nm).

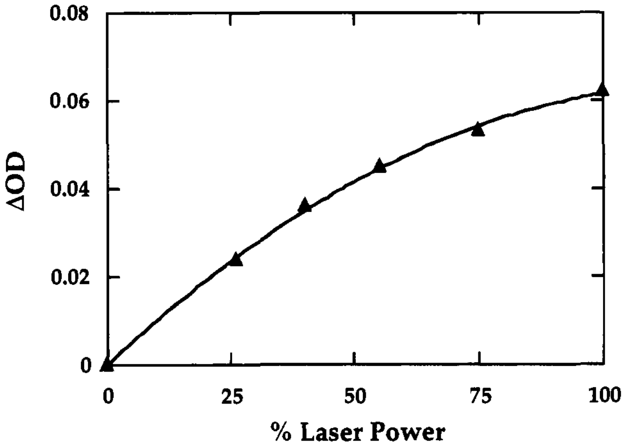

Figure 4. Effect of laser power on signal intensity following 308 nm laser flash photolysis of **4** (monitored at 350 nm). 100% laser power corresponds to ~100 mJ/pulse.

An investigation of the effects of light intensity on the lifetime of the transient and the size of the signal was carried out by attenuating the laser beam with a set of calibrated neutral density filters. We observed that the lifetime increases as the laser power is decreased, suggesting that transient decay incorporates a second-order component. Figure 4 shows a distinct downward curvature in a plot of the absorption signal against the laser power. This type of curvature is common when the initial transient undergoes further photolysis during the laser pulse.[33]

Laser photolysis of 2,6-diphenylcyclohexanone (**15**) in cyclohexane led to biradical **16** (see Scheme 7 below) which had a spectrum similar to that of benzyl radicals, in agreement with similar results reported by Turro and co-workers.[34]

A few preliminary experiments were carried out with 1,5-diiodopentane (**17**) in an attempt to establish the generality of our observations. Laser flash photolysis (248 nm) of a 10 mM solution of **17** in cyclohexane led to the immediate formation of a species with the spectrum given in Figure 5. A weak absorption (due to I_2) grows in at ~570 nm and some residual absorption is observed at ~300 nm following the decay. The UV signals are attributed to the radical formed by loss of an iodine atom and decay by a combination of first- and second-order kinetics. When approximated as a first-order decay, the lifetimes are 4.1 and 3.1 μs under nitrogen and oxygen,

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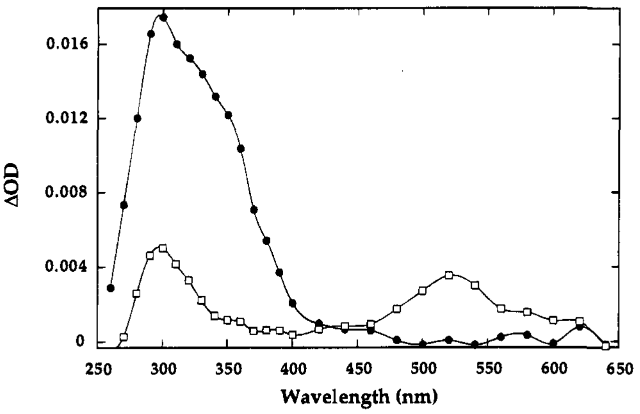


Figure 5. Transient absorption spectra obtained upon 248 nm laser flash photolysis of **17** in cyclohexane 0.6 (●) and 29 μs (□) after the laser pulse.

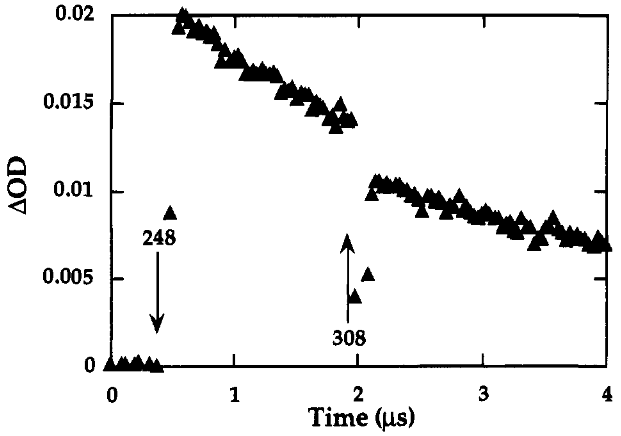


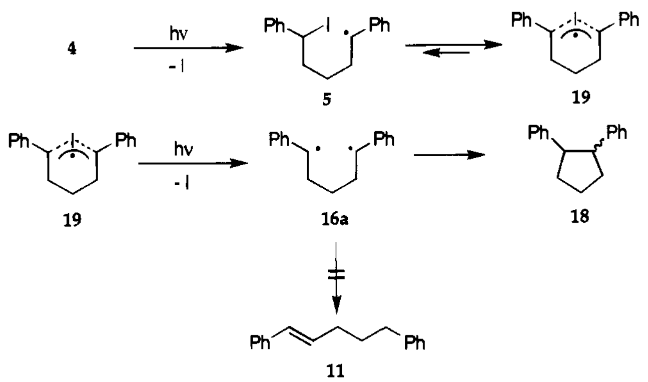
Figure 6. Bleaching at 350 nm of the transient formed upon 248 nm laser flash photolysis of **4** by 308 nm laser pulse. The 308 nm laser was fired ~1.5 μs after the 248 laser.

respectively. The results compare well with those obtained from **4**, except for a blue shift in the absorption signals.

Two-Laser Two-Color Laser Flash Photolysis. This work was carried out in cyclohexane using 248 nm excimer laser pulses to produce the transient and a second excimer laser with 308 nm pulses to photolyze it.[35] Photolysis of the transient derived from **4** at 308 nm leads to permanent and irreversible bleaching as monitored at 320 and 350 nm (Figure 6). The low points near the 2 μs marker are due to scattered light from the second laser.

Laser-Drop Photolysis.[32] These experiments facilitate the product studies that are frequently difficult in two-laser two-color experiments due to the low conversions involved. When drops of deaerated 0.60 mM solutions of **4** in cyclohexane were irradiated by the focused output from a 308 nm laser, the products changed dramatically. The major products are *cis*- and *trans*-1,2-diphenylcyclopentane (**18**) in approximately equimolar amounts, with minor amounts of the olefins **11** (≤15% of products). Product distributions were determined by ^{1}H NMR because **4** undergoes decomposition in the GC injector. These products (see Scheme 6) imply that both iodine atoms are extruded during the laser pulse to produce 1,5-diphenylpentadiyl biradical (**16**). We believe that the processes responsible for the change in products under the high-intensity conditions of LDP are the same as those responsible for the bleaching signals observed under two-laser two-color laser flash photolysis (*vide supra*). An accurate mass balance is sometimes difficult to estimate due to the chromatographic instability of **4**, but at least 75% of the materials were accounted for under conditions where the conversion was ~33%.

Scheme 6



Biradical **16** can be produced alternatively by the photolysis of 2,6-diphenylcyclohexanone (**15**), and it is known to give **11** and **18** as products;[36] under lamp irradiation the olefins accounted for ~50% of the products. G. C. Rüchardt et al.[36] reported that the ratio of cyclic to olefinic products changed dramatically as a function of temperature in *n*-pentane as solvent. We anticipated that a similar temperature dependency would also occur in cyclohexane if the laser-drop experiments caused a significant temperature change. Thus, we carried out a control experiment with **15** to see if the small amount of olefinic products from LDP of **4** could be due to elevated temperatures within the irradiated drop. LDP of **15** in cyclohexane gave approximately the same product distribution as the low-intensity photolysis, with the olefins accounting for 60% of the products. We did not expect a large temperature increase during LDP,[33] and the above results confirm that any temperature increase is less than 20 °C. Table 1 shows the product distributions for the low- and high-intensity photolysis of **4** and **15**.

Discussion

The absorption spectra of benzylic radicals are well-known in the literature.[37] They have a characteristic narrow absorption at around 320 nm. They have been produced from a variety of precursors, including the photolysis of benzyl chlorides.[38-40] This, combined with the quenching of the signal in Figure 1 by oxygen,[41] allows us to assign confidently the transient from photolysis of **13** to the benzylic radical **14** as shown in Scheme 5. There are a number of anomalies which do not allow us to assign the transient in Figure 2 to the corresponding benzylic radical **5**. Thus, (i) the broad absorption is uncharacteristic of benzylic radicals. Iodine substitution four σ carbon−carbon bonds away from the radical center would not be expected to have such an effect on the absorption spectrum. (ii) The decay of this transient is only slightly affected by the presence of oxygen. It is well-known that benzylic radicals react with oxygen at near the diffusion-controlled rate.[41] (iii) Although the products from the photolysis of **4** could all be accounted

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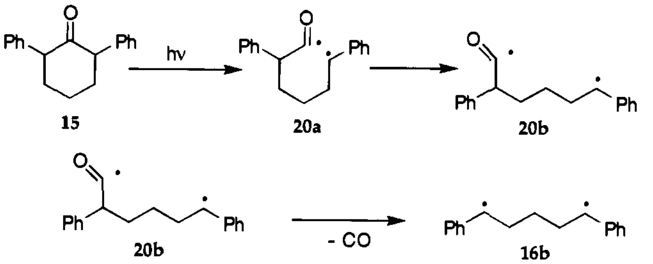
Table 1. Comparative Study of the Photochemistry of **4** and **15** under Various Experimental Conditions

substrate	method	conversion (%)	mass balance	products (%)
4	Hg lamp	100	91	**6** (29), **10** (20), **11** (20), **7** (24), **12** (7)
4	LDP	33	75[a]	**11** (15), **18** (85)
15	Rayonet (300 nm)	25	95	**11** (55), **18** (45)
15	LDP	22	92	**11** (60), **18** (40)

[a] Approximate value, see text.

Scheme 7



for by invoking a benzylic radical intermediate, it would be expected that the reaction mixture would be more complex. Notably missing are radical dimers, which are very common products under high-intensity conditions because high radical concentrations favor radical–radical reactions.[33]

We propose that LDP of **4** results in rearrangement of **5** to yield the divalent iodine radical intermediate **19** which undergoes absorption of a second photon to produce the cyclic product and an iodine atom. It is difficult to ascertain whether absorption of a photon by **19** results in the concerted formation of a carbon–carbon bond along with the extrusion of an iodine atom or formation of the biradical **16a** upon extrusion of iodine. Clearly the biradical cannot be *identical* to that formed by photochemical decarbonylation of **15** (Scheme 7), since much more olefin **11** is formed from **15** than in the LDP of **4**. Spin considerations could be invoked to explain the differences in product distributions in the two experiments. If the cyclopentanes (**18**) were produced by the photolysis of the benzylic radical **5** by way of biradical **16b**, one would expect a significant yield of the olefins **11**. This is because spin statistics determine that three-quarters of the biradicals produced in such a process would have to be triplets and the lowest energy conformation of the benzylic radical would be the "stretched" linear chain. Previous investigations on **15** have shown that the relaxed triplet biradical gives a significant yield of the olefins, along with the cyclopentanes, as products.[36] Thus, one cannot dismiss the biradical as an intermediate because of the lack of olefinic products since the incipient biradical would be in a conformation which favors cyclization and in close proximity to a heavy atom. Turro and co-workers[42,43] have shown that intersystem crossing due to spin–orbit coupling is facilitated by small end-to-end distances of the biradical termini. A similar effect may be induced by the departing iodine atom. Thus, even though spin statistics determine that three-quarters of the biradicals formed in such a process would be triplets, any triplet biradicals may not live long enough to undergo the rotations leading to a conformation which would allow formation of the olefins before intersystem crossing to the singlet state occurs. It has been shown that the photolysis of **15** leads to the biradical **20**, which is followed by decarbonylation to give the triplet biradical **16b** (Scheme 7). Although the lifetime for **20** is short, ~120 ns at 190 K,[42] it lives long enough so that the lowest energy conformation (the linear conformation shown in Scheme 5) is achieved before decarbonylation. Therefore, the incipient biradical is not in a conformation which allows rapid intersystem crossing and cyclization; as a result, both olefins and cyclic products are formed. The mechanism of LDP of **4** is shown in Scheme 6.

Further evidence for formation of **19** as an intermediate can be seen from the two-laser two-color laser flash photolysis of **4**. If the triplet biradical were produced in a linear conformation (i.e. as in the case of **15**), as would be expected from a true benzylic radical, one would not expect instantaneous bleaching of the signal since the triplet biradical also absorbs very strongly at 320 nm with a lifetime of 900 ns in acetonitrile.[42] Although there may not be a jump in the absorption signal (unless the extinction coefficient of the biradical was significantly larger than that of the precursor radical), it would be expected that the decay of the triplet biradical would be resolved after the 308 nm laser pulse. However, the bleaching of the signal at 320 nm is essentially instantaneous.

Experiments with 1,5-diiodopentane (**17**) indicate that a similar hypervalent iodine intermediate is also formed in this case, thus suggesting that these cyclic intermediates may be quite general.

We have shown in this study that the olefins are produced in a 60% yield when the triplet biradical precursor **15** is photolyzed. LDP of **15** shows that the olefins are produced even under these extreme conditions; thus, the virtual absence of olefins in the LDP of **4** cannot be attributed to temperature increases under these experimental conditions.

Conclusion

Laser flash photolysis of 1,5-diiodo-1,5-diphenylpentane (**4**) leads to a transient intermediate with spectroscopic and chemical properties quite distinct from those expected for a simple benzylic radical formed by C–I cleavage. This intermediate is assigned to **19**, a cyclic hypervalent iodine intermediate. Laser-drop photolysis of **4** leads to the expected photodecomposition of **19** to yield an isomeric mixture of 1,2-diphenylcyclopentanes (**18**). It is suggested that photolysis of **19** may involve the intermediacy of biradical **16a** which leads to the same products as the biradical derived from 1,5-diphenylcyclohexanone (**15**) but with a very different cyclopentane/olefin ratio. Either the proximity of the termini in the nascent conformation of **16** (**16a**) or the proximity of the heavy atom may be responsible for the relaxation of spin selection rules allowing an increased yield of cyclized products.

Experimental Section

General Techniques. NMR spectra were recorded in a Bruker AC 250 MHz or a Varian Unity 300 MHz spectrometer, using TMS as internal standard. GC was carried out in a HP 5980A instrument with FID detector and provided with a 25 m capillary column of 5% phenylmethylsilicone. GC-MS were obtained using a Varian Saturn II spectrometer using the same column as for GC. HPLC purifications were carried out using a Waters isocratic equipment and a semipreparative Microporasil column. Chemical analyses were performed at the Instituto de Química Bio-Organica CSIC in Barcelona. **15** was prepared following a literature procedure.[36] 1,5-Diiodopentane was an Aldrich product.

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Synthesis of 1,5-Diiodo-1,5-diphenylpentane (4). Preparation of diiodide **4** was accomplished following the general procedure previously reported by Jung.[44] Trimethylsilyl iodide (1.9 mL) was added to a solution of 1,5-diphenyl-1,5-pentanediol[45] (500 mg) in dichloromethane (20 mL) under an argon stream, and the resulting solution was magnetically stirred at room temperature for 24 h. The reaction was quenched by adding water (2 mL). This mixture was extracted with three aliquots of ethyl ether (25 mL) and the combined organic layers were washed with 10% aqueous sodium thiosulfate and sodium hydrogen carbonate, successively. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography using dichloromethane as eluent to give **4** (840 mg, 90%) as a mixture of both diastereomers.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.5−7.2 (m, 10 H), 5.1 (t, $J = 8$ Hz, 2H), 2.5−2.3 (m, 2H), 2.2−1.9 (m, 2H), 1.8−1.1 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 143.6 (s), 143.5 (s), 128.7 (d), 127.9 (d), 120.9 (d), 40.2 (d), 33.4 (t), 33.1 (t), 30.1 (t), 29.9 (t). Anal. Calcd for $C_{17}H_{18}I_2$: C, 42.88; H, 3.81; I, 53.31. Found: C, 42.96; H, 3.85; I, 53.53.

Synthesis of 1,5-Dichloro-1,5-diphenylpentane (13). 1,5-Diphenyl-1,5-pentanodiol (660 mg) was added to concentrated hydrochloric acid (15 mL) and the solution was allowed to stand at room temperature for 8 h. After this time, the reaction mixture was diluted with cold water (50 mL) and the organic material extracted with ethyl ether (three aliquots, 50 mL). The combined ethereal layers were washed with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residue was submitted to semipreparative HPLC using hexane as eluent to obtain the dichloro compound **13** (700 mg, 92%).

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.5−7.2 (m, 10), 4.8 (dd, $J = 8$, 6 Hz, 2H), 2.4−1.9 (m, 4H), 1.8−1.2 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 141.4 (s), 129.5 (d), 128.2 (d), 126.7 (d), 63.2 (d), 39.1 (t), 24.6 (t). Anal. Calcd for $C_{17}H_{18}Cl_2$: C, 69.93; H, 6.19; Cl, 24.18. Found: C, 69.69; H, 6.10; Cl, 24.09.

Low-Intensity-Irradiation Procedure of Diiodo Compounds 4 and 15. A solution of **4** (ca. 5×10^{-4} M) in cyclohexane (25 mL) was bubbled with argon for 30 min and sealed in a Pyrex cell. Then, the solution was submitted to external photolysis under magnetic stirring using a 125 W medium-pressure mercury lamp for 1 h. After this time, the mixture was analyzed by GC and GC-MS, before the solvent was removed under vacuum. A ^{1}H-NMR spectrum of the reaction mixture was obtained by dissolving the residue in deuterated chloroform. The observed reaction products and their corresponding yields are contained in Table 1. Their structural assignment was corroborated by comparison with authentic samples of these compounds prepared by reported procedures in the case of **10**,[46] **11**,[36] and **12**[45] or by alternative synthesis for compounds **6** and **7**. A solution of **15** (ca. 2×10^{-2} M) in cyclohexane (2 mL) was bubbled with nitrogen for 30 min and sealed in a quartz cell. This was submitted to photolysis in a homemade photochemical reactor equipped with nine Rayonet RPR-300 nm lamps for 1 h. The sample was analyzed by GC and GC-MS. The observed reaction products and their corresponding yields have been included in Table 1.

Alternative Synthesis of 1,5-Diphenyl-1-iodopentane (6). The mono-iodo compound **6** was prepared by treating 1,5-diphenyl-1-pentanol[47] with trimethylsilyl iodide in dichloromethane under argon atmosphere following the same experimental procedure described above for 1,5-diphenyl-1,5-diiodopentane (**4**).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.5−7.1 (m, 10 H), 5.1 (t, $J = 8$ Hz, 1H), 2.6 (t, $J = 8$ Hz, 2H), 2.5−2.0 (m, 2H), 1.7 (m, 2H), 1.5−1.3 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.0 (s), 142.0 (s), 128.6 (d), 128.3 (d), 128.2 (d), 127.8 (d), 127.0 (d), 125.7 (d), 41.2 (d), 35.5 (t), 34.7 (t), 30.4 (t), 29.4 (t). Anal. Calcd for $C_{17}H_{19}I$: C, 58.30; H, 5.47; I, 36.23. Found: C, 58.38; H, 5.57; I, 36.51.

Alternative Synthesis of 1,5-Diphenyl-5-iodo-1-pentene (7). Sodium borohydride (92 mg) was added in small portions over 5 min to a solution of 1,5-diphenyl-4-penten-1-one[48] (50 mg) in ethanol (10 mL). The mixture was stirred at room temperature for 20 min and then cooled by means of an ice bath before water (20 mL) was added. After extraction with ether and drying over anhydrous sodium sulfate the organic solvent was removed under vacuum. The resulting diphenylpentenol was dissolved in dichloromethane. This solution was bubbled with argon for 5 min, before triethylamine (0.4 mL) and trimethylsilyl iodide (1 mL) were added. The subsequent silylation procedure was the same as that previously described for the synthesis of 1,5-diiodo-1,5-diphenylpentane (**4**).

^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.5−7.2 (m, 10H), 6.7 (d, $J = 16$ Hz, 1H), 6.2 (dt, $J = 16$, 7 Hz, 1H), 5.2 (dd, $J = 7$, 6 Hz, 1H), 2.7−2.2 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 143.8 (s), 137.3 (s), 131.3 (d), 128.7 (d), 128.5 (d), 128.1 (d), 128.0 (d), 127.1 (d), 126.0 (d), 40.6 (d), 33.3 (t), 33.0 (t). Anal. Calcd for $C_{17}H_{17}I$: C, 58.63; H, 4.92. Found: C, 58.73; H, 5.07.

Laser Flash Photolysis. These experiments were carried out using either a Lumonics EX-510 excimer laser operated with F_2/Kr/He gas mixtures (248 nm, ~6 ns, ≤100 mJ/pulse), a Lumonics EX-530 excimer laser operated with HCl/Xe/Ne gas mixtures (308 nm, ~6 ns, ≤80 mJ/pulse), or a Continuum Surelite Nd-YAG laser using the fourth harmonic (266 nm, <10 ns, ≤16 mJ/pulse). Transient signals were captured with a Tektronix-2440 digital oscilloscope which was interfaced to a Macintosh IIci computer which also controlled the experiment. The system was operated under LabVIEW 2.2 software from National Instruments. Other aspects of this instrument are similar to those described earlier.[49,50] The two-laser two-color experiments were performed by sending a TTL pulse to a Stanford Research Systems Model DG 535 delay generator which then sent TTL pulses which fired the lasers at the desired time intervals. All experiments were carried out using flow cells constructed from 7 × 7 mm Suprasil quartz tubing. Samples were contained in a 100 mL reservoir tank which was bubbled with slow streams of either nitrogen or oxygen as required.

Laser-Drop Photolysis. The beam from the Lumonics EX-530 excimer laser, with a fresh HCl/Xe/Ne gas mixture to ensure at least 100 mJ/pulse at 308 nm, was focused by means of a quartz lens into a drop of the photolysis solution suspended from a 6-in. syringe needle (20 gauge). Further details for this type of experiment have been described earlier.[32]

Acknowledgment. H.G. acknowledges support from DGICYT of Spain (Grant No. PB93-0747) and the Generalidad Valenciana. J.C.S. thanks the Natural Sciences and Engineering Research Council (Canada) for support under its operating grants program.

JA9438775

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