

Two-Photon Generation of the 1,4-Diphenyl-1,4-butanediyl Biradical: Direct Detection and Product Studies

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The 1,4-diphenyl-1,4-butanediyl biradical (**3**) is generated from 1,4-dichloro-1,4-diphenylbutane (**1**) or 2,5-diphenylcyclopentanone (**8**) under several irradiation conditions. The products resulting from this intermediate are styrene (**4**), 1,2-diphenylcyclobutane (**5**), and 1-phenyl-1,2,3,4-tetrahydronaphthalene (**6**). The formation of tetrahydronaphthalenes appears to be a fingerprint for the intermediacy of 1,4-biradicals having a phenyl group attached to one of the radical centers as corroborated in the high-intensity irradiation of 2-phenylcyclopentanone (**12**). The yield of **6** depends on the substrate and irradiation conditions; this is rationalized as due to a conformational memory effect of the nascent biradical.

Introduction

1,4-Diaryl-1,4-butanediyl biradicals have been detected in the laser flash photolysis of sulfones¹ or cyclobutanes² via inter- or intramolecular energy-transfer processes. Moreover, they have been postulated as intermediates in a wide range of thermal and photochemical reactions, such as the light-induced N₂ and SO₂ loss from cyclic azoalkanes^{3,4} and sulfones,¹ the geometric isomerization of cyclobutanes⁵ and the dimerization of styrenes.^{2,6–8}

However, studies on the products arising from this type of biradicals have only been carried out for the dimerization of styrenes, the cycloreversion of cyclobutanes, and the N₂ extrusion from cyclic azoalkanes. These studies suggest that 1,4-diaryl-1,4-biradicals undergo two competitive reactions: fragmentation to styrenes and cyclization to cyclobutanes. The fact that both types of photoproducts are also in some cases the starting reagents further complicates the interpretation of product studies. On the other hand, it has been observed that the photolysis of diarylcyclobutanes leads to 1-aryl-1,2,3,4-tetrahydronaphthalene as an additional photoproduct,^{2,5} but it has not been made clear whether this compound results from direct rearrangement of the excited diarylcyclobutane or from α to ortho coupling in the 1,4-biradical, followed by 1,3-hydrogen shift. Fur-

thermore, minor amounts of 1-aryl-1,2,3,4-tetrahydronaphthalene have been detected in the photodimerization of styrenes, which has been rationalized as due to a secondary process of the initially obtained cyclobutanes.² By contrast, not even traces of this compound appear to be formed in the photolysis of the cyclic azoalkane 3,6-diphenyl-3,4,5,6-tetrahydropyrazine, which is thought to proceed via identical 1,4-biradical intermediates.⁹

Oxygen trapping of biradicals is a well-established method¹⁰ to demonstrate their participation; however, the only attempts to observe oxygenation products in the above series of experiments were done in the photolysis of the cyclic azo compound in solution, under a continuous stream of oxygen, but they were not successful.

Altogether, these data show some inconsistencies; hence, it appeared interesting to generate the 1,4-diphenylbutanediyl biradical by alternative methods where the final products could be easily distinguished from the starting substrates, thus facilitating the unambiguous assignment of the products arising from this intermediate.

We have previously reported that phenyl-substituted linear alkanediyls can be generated by a two-photon process from acyclic dichlorodiphenylalkanes¹¹ or by a one-photon process from 2,*n*-diphenylcycloalkanones.¹² In this context, we report here the detection of the 1,4-diphenyl-1,4-butanediyl biradical (**3**) generated from 1,4-dichloro-1,4-diphenylbutane (**1**) via a two-photon process (Scheme 1). The products resulting from this intermedi-

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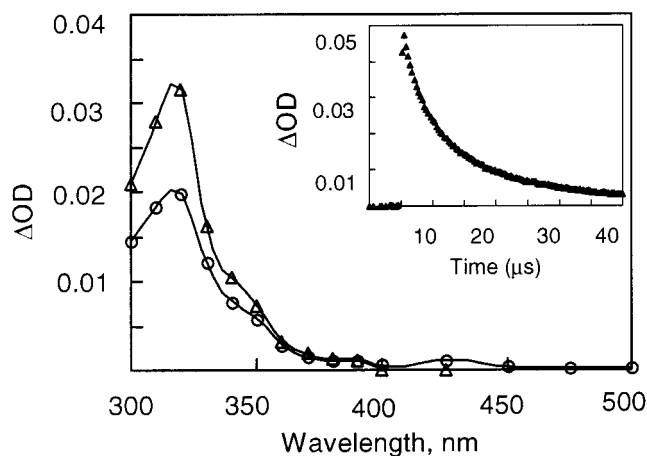
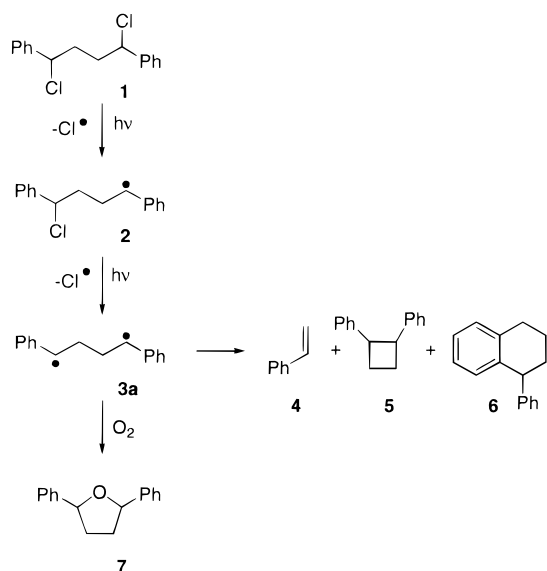


Figure 1. Transient absorption spectra recorded following laser excitation of **1** in cyclohexane under nitrogen 3.12 μs (Δ) and 17.0 μs (\circ) after the laser (266 nm) pulse. The insert shows the decay as monitored at 320 nm.

Scheme 1



ate are established by laser drop photolysis of **1**, and the results are compared with those obtained in the photolysis of *trans*-2,5-diphenylcyclopentanone. On the basis of this information, the previous mechanisms thought to involve biradical **3** are discussed.

Results

Photolysis of 1,4-Dichloro-1,4-diphenylbutane.

Laser flash photolysis of deaerated 0.4 mM solutions of 1,4-dichloro-1,4-diphenylbutane (**1**) in cyclohexane at 266 nm (Nd:YAG laser, fourth harmonic, <10 ns, 16 mJ/pulse) yielded a narrow absorption, with maximum at 320 nm (see Figure 1). The lifetime of this species was around 4 μs under our experimental conditions. This signal was quenched by oxygen at close to the diffusion-controlled limit. Hence, it was assigned to be the benzylic radical **2** obtained through homolytic cleavage of one of the two C–Cl bonds.¹³ Photolysis of this transient at 308 nm (HCl/Xe/Ne gas mixtures, excimer laser, ~6 ns, 50

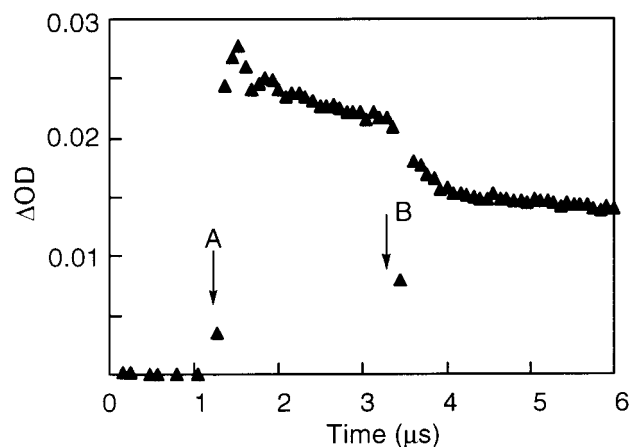


Figure 2. Two-laser–two-color experiment showing excitation of 1,4-dichloro-1,4-diphenylbutane in cyclohexane at 266 nm (see A), followed by excitation at 308 nm (B) (monitoring wavelength at 320 nm).

mJ/pulse) led to permanent and irreversible bleaching of the signal as monitored at 320 nm (Figure 2). The decay observed following the 308 nm pulse had two components, one of them coincident with that of the benzylic radical and a second, faster one corresponding to a more reactive transient species with lifetime of 200 ns. The absorption spectrum after the 308 nm pulse was indistinguishable from that of the benzylic radical **2**; however, as its lifetime was in agreement with those reported for 1,4-diaryl-1,4-butanediyl biradicals,^{1,2} the structure **3** was assigned to the fast-decaying species.

To establish the nature of the primary photoproducts arising from biradical **3**, laser-drop photolysis was used. This technique provides a way of performing high-intensity photolysis^{14,15} while minimizing the amounts of products arising from irradiation of (thermally) nonreactive photoproducts. When drops of 2 mM deaerated solutions of **1** in cyclohexane were irradiated by the focused output from a 266 nm laser (one cycle) only a 10% conversion was observed (Table 1, Scheme 1). The photoproducts detected were styrene (**4**, 79%), *cis*- and *trans*-diphenylcyclobutanes (**5**, 10%, *cis/trans* ratio: 46/54), and 1-phenyl-1,2,3,4-tetrahydronaphthalene (**6**, 11%).¹⁶ The formation of these compounds can be accounted for in terms of competition between fragmentation, cyclization, and α to ortho coupling of the 1,4-diphenyl-1,4-butanediyl biradical. Laser irradiations were also performed with deaerated and oxygenated 10 mM cyclohexane solutions of **1**, using a 266 nm laser, with the sample contained in a quartz spectrometer cell. Analysis of the photolyzed deaerated solutions by GC/MS revealed the formation of the same products as in the case of the laser-drop experiment (see Table 1, footnote d). When

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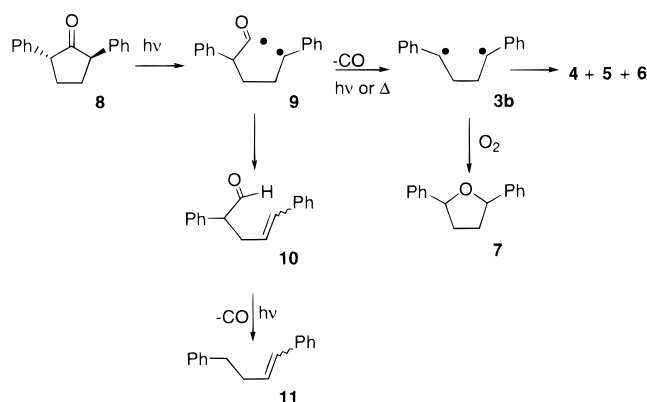
(16) By contrast, lamp irradiation (medium-pressure mercury, quartz filter, 2 h) of deaerated 10 mM cyclohexane solution of **1** led to complete consumption of the starting material. Analysis of the photolysate by GC/MS revealed the formation of products arising from the expected homolytic cleavage of a carbon–chlorine bond followed by hydrogen abstraction from solvent by chlorine atoms, radical–radical recombination, and some secondary photolysis of monochlorinated products. Not even traces of styrene, 1,2-diphenylcyclobutane, and 1-phenyl-1,2,3,4-tetrahydronaphthalene were detected in the photolysate.

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Table 1. Comparative Studies of the Photochemistry of 1, 8 and 12 in Deaerated Solutions

condns	conversn (%)	relative product distribution ^{a,b} (%)					
		5					
		4 ^c (cis/trans)	6	10	11	14	16 17
1 laser-drop	10	79	10 (46/54)	11			
1 laser	50 ^d	80	14 (40/60)	6			
8 lamp	84	50	38 (15/85)	4	7	1	
8 laser	20	40	20 (25/75)	40			
12 lamp	28						>99
12 laser	40	12					47 12 27

^a Control experiments showed that styrene did not react significantly under the employed irradiation conditions. The cyclobutanes **5** were formed in very low yield (less than 5%), and the cis/trans ratio was ca. 10:1. On the other hand, compound **6** was detected only as traces. ^b The structural assignment of known photoproducts **5**, **6**, **8**, **10**, **11**, **14**, **18** and **16**²⁴ was confirmed by comparison with authentic samples. ^c Part of the styrene could have been evaporated when rotaevaporating the photolyzate before analysis. ^d Roughly 25% of the reacted material consisted of two-photon products (**4–6**); the rest were the typical monophotonic products mentioned in ref 16.

Scheme 2

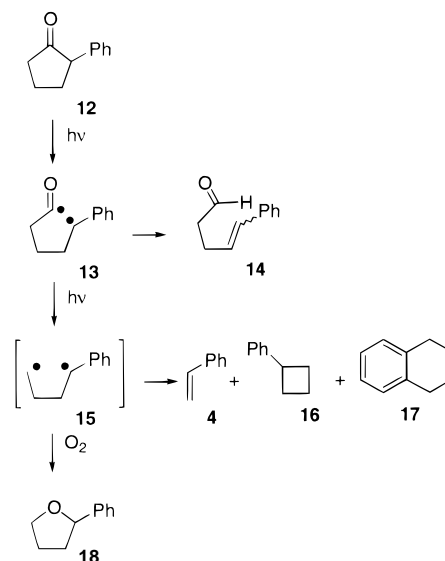
oxygenated samples were laser-photolyzed, the oxygen trapping product 2,5-diphenyltetrahydrofuran (**7**)¹⁷ was detected.

Photolysis of *trans*-2,5-diphenylcyclopentanone.

To the best of our knowledge, the photochemical behavior of this ketone has not been the subject of any previous report. Lamp irradiation (Pyrex filter) of **8** in deaerated cyclohexane for 1 h led to styrene (**4**, 50%), 1,2-diphenylcyclobutane (**5**, 38%, cis/trans ratio, 15/85), 1-phenyl-1,2,3,4-tetrahydronaphthalene (**6**, 4%), 2,5-diphenyl-4-pentenal (**10**, 7%), and 1,4-diphenyl-1-butene (**11**, 1%). A small amount of the starting ketone (16%) was recovered unchanged (Table 1, Scheme 2).

The formation of enal **10** demonstrated that, in contrast with the case of the 2,6-diphenylcyclohexanone, H-abstraction by the initially generated acyl-alkyl biradical **9** competes with thermal decarbonylation to biradical **3**. This easily explains the formation of compounds **4–6** and **10**. To ascertain the origin of 1,4-diphenyl-1-butene, enal **10** was photolyzed under the same conditions. Analysis of the photolysate by ¹H NMR and GC/MS evidenced its partial transformation into **11**. On the other hand, photolysis of ketone **8** in oxygenated cyclohexane solution gave rise to the oxygen-trapping product **7**¹⁷ (50/50 cis/trans mixture).

A deaerated 1 mM cyclohexane solution of **8** was also irradiated at 266 nm (Nd:YAG). Under these conditions,

Scheme 3

the photoproduct distribution was quite different from that obtained in the low-intensity irradiation. Thus, enal **10** and alkene **11** were not formed, which agrees with the acyl-alkyl biradical **9** being photolyzed within the laser pulse. However, the most dramatic feature was the sharp increase of 1-phenyl-1,2,3,4-tetrahydronaphthalene (40%) under high-intensity irradiation (see Table 1).

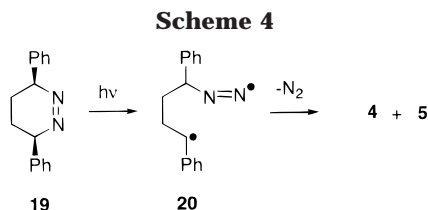
In view of the diverging results obtained in the photolysis of ketone **8** as a function of the light intensity, the monosubstituted analogue **12** was also studied under different conditions.

It is known¹⁸ that lamp irradiation ($\lambda = 313$ nm) of **12** leads to the unsaturated aldehyde **14**, through intramolecular H abstraction in the primary acyl alkyl biradical (**13**). Under our irradiation conditions, **14** was also the only photoproduct. Hence, we wondered whether biradical **13** can be further photolyzed if generated by means of a high-intensity laser source. Actually, laser (266 nm) irradiation of a 1 mM cyclohexane solution of **12** gave rise to significant amounts of styrene, phenylcyclobutane (**16**), and 1,2,3,4-tetrahydronaphthalene (**17**) (Scheme 3, Table 1). These results revealed that acyl-alkyl biradical **13** is photolyzed within the laser pulse (10 ns), photodecarbonylating to the dialkyl biradical **15**. Its disproportionation, cyclization, or α to ortho-coupling generates **4**, **16**, and **17**, which are the fingerprints for two-photon processes. Finally, laser photolysis of ketone **12** in oxygenated cyclohexane solution gave rise to the oxygen-trapping product of the biradical, namely 2-phenyltetrahydrofuran (**18**).¹⁹

Discussion

From the above results, it is clear that in the 1,4-diphenyl-1,4-butanediyl biradical fragmentation to styrene and cyclization to 1,2-diphenylcyclobutane compete with α to ortho coupling, leading to 1-phenyl-1,2,3,4-tetrahydronaphthalene (**6**). If one takes also into account the results obtained with the cyclopentanones **8** and **12**, the formation of tetrahydronaphthalenes seems to be a fingerprint for the intermediacy of 1,4-biradicals having

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a phenyl group attached to one of the radical centers. This observation can be a useful tool for the reexamination of previous mechanisms thought to involve 1,4-diaryl-1,4-butanediyl biradicals. Thus, the tetrahydronaphthalenes detected in the sensitized photolysis of styrenes and 1,2-diarylcyclobutanes would be actually direct products formed from the biradical intermediates rather than secondary photoproducts. Hence, their detection constitutes further support for the advanced mechanistic proposals. By contrast, the lack of formation of **6** in the photolysis of 3,6-diphenyl-3,4,5,6-tetrahydropyrazine (**19**) appears to be against the involvement of biradical **3** as a key intermediate in this reaction. Instead, it can be suggested that in this case photolysis of the first C–N bond could lead to a diazenyl biradical (**20**), from which 1,2-diphenylcyclobutane and styrene could be formed through nitrogen elimination (Scheme 4).²⁰ This is also consistent with the failure to detect oxygen-trapping products in the photolysis of **19**, in contrast with the observed formation of tetrahydrofuran derivatives in the two-photon transformation of the dichloride **1** and in the decarbonylation of the cyclic ketones **8** and **12** in aerated solutions.

Finally, the fact that quite different yields of tetrahydronaphthalenes are obtained depending on the starting substrate and the irradiation conditions deserves a further comment. Thus, while **6** was a minor product in the two-photon photolysis of the dichloride **1** or in the one-photon decarbonylation of the ketone **8**, it was obtained in much higher yield upon high-intensity irradiation of the ketone. This points to differences in the chemical behavior of biradical **3** linked to the predominance of different biradical conformations.²¹ It can be envisaged that the preferred conformation will be different for fragmentation, cyclization, and α to ortho coupling. The nascent biradical could have a lifetime shorter than that required for rotational equilibration, thus collapsing by the reaction path associated with the least motion requirement. The data here obtained suggest that the formation of 1,2,3,4-tetrahydronaphthalenes is favored when the biradical is initially generated in a conformation, such as **3b**, with a short distance between the radical termini.

Experimental Section

Synthesis of 1,4-Dichloro-1,4-diphenylbutane (1). Preparation of dichloride **1** was accomplished following a procedure describe in the literature.²⁵

(20) This mechanism has been found to operate in a number of cases. See, for example: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99–150. Adam, W.; Harrer, H. M.; Nau, W. M.; Peteres, K. *J. Org. Chem.* **1994**, *59*, 3786–3797. Simpson, C. J. S. M.; Wilson, G. J.; Adam, W. *J. Am. Chem. Soc.* **1991**, *113*, 4728–4732.

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1 (mixture of stereoisomers): ¹H NMR (CDCl₃, 250 MHz) δ 1.9–2.3 (m, 4 H), 4.7 (m, 2 H), 7.2 (m, 10 H); ¹³C NMR (CDCl₃, 141.2 (s), 128.7 (d), 128.4 (d), 126.8 (d), 63.0 (d), 62.7 (d), 37.5 (t), 37.2 (t); HRMS calcd for C₁₆H₁₆Cl₂ 278.0629, found 278.0623.

Synthesis of trans-2,5-Diphenylcyclopentanone (8). Preparation of ketone **8** was accomplished following a procedure described in the literature.²⁶ Thus, a mixture of α,α' -diphenyladipic acid (3.50 g, 11.74 mmol) and finely powdered barium hydroxide (0.25 g) was heated under a stream of nitrogen, at 300–320 °C, until evolution of carbon dioxide (about 2 h). Addition of hexane to the crude mixture precipitated 1.5 g (6.35 mmol, 54% yield) of **8**.

8: ¹H NMR (CDCl₃, 250 MHz) δ 2.2 (m, 2 H), 2.6 (m, 2 H), 3.5 (m, 2 H), 7.2–7.4 (m, 10 H); ¹³C NMR (CDCl₃, 62.5 MHz) δ 215.3 (s), 138.4 (s), 128.6 (d), 128.1 (d), 127.0 (d), 55.8 (d), 29.5 (t); MS *m/z* 236 (M⁺, 12), 208 (7), 117 (7), 104 (100); HRMS calcd for C₁₇H₁₆O 236.1201, found 236.1205.

Conventional Lamp Irradiation of Compounds 1, 8 10, and 12. A cyclohexane solution of the compound either in a quartz (**1**) or Pyrex tube (**8**, **10**, and **12**) 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.

Laser-Drop Photolysis. The beam from a Nd:YAG laser using the fourth harmonic (266 nm, <10 ns, \leq 16 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 previously.¹⁴

Laser Flash Photolysis. These experiments were carried out using either a Nd:YAG laser using the fourth harmonic (266 nm, <10 ns, \leq 20 mJ/pulse) or an excimer laser operated with HCl/Xe/Ne gas mixtures (308 nm, ca. 6 ns, \leq 50 mJ/pulse). Transient signals were captured with a Tetrionix-2440 digital oscilloscope that was interfaced to a computer that 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 previously. The two-laser two-color experiments were performed by sending a trigger pulse to a delay generator, which then sent TTL pulses which fired the lasers at the desired sequence. All experiments were carried out using 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.

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