

# Photochemistry of the Biradicals Derived from the Photodecomposition of 2,2,6,6-Tetraphenylcyclohexanone<sup>1</sup>

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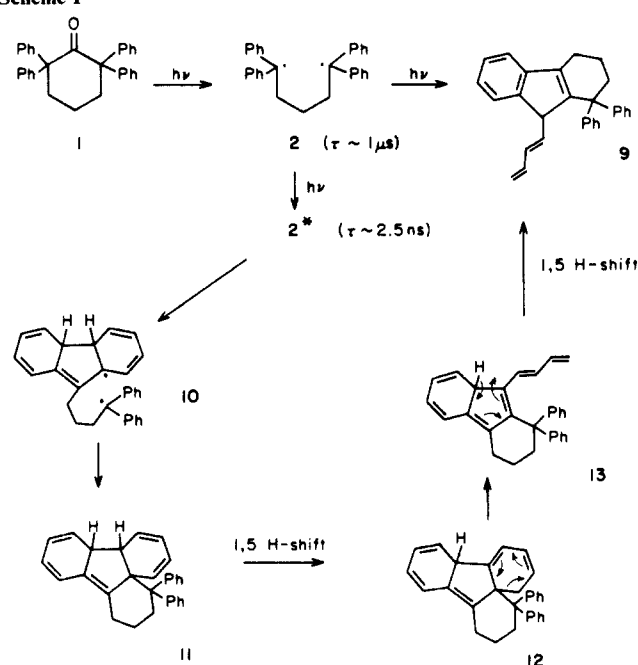
**Abstract:** Laser photolysis of 2,2,6,6-tetraphenylcyclohexanone leads to biradical **2** following Norrish type I cleavage and decarbonylation. Excitation of **2** in one- or two-laser experiments leads to a new photoproduct, characterized as **9**. Transient studies of the photochemistry of **2** reveal a very short lived excited state for the biradical ( $\tau \sim 2.5$  ns in benzene at room temperature) which decays leading to one of the intermediates in the reaction path to **9**. This intermediate absorbs strongly at 480 nm and has lifetimes of 0.9 and 1.1  $\mu$ s in acetonitrile and benzene, respectively; this intermediate has been tentatively assigned structure **10**, produced via cyclization at one of the biradical termini. The dramatic difference between the one- and two-photon photochemistry of **1** illustrates well the way in which laser chemistry can differ from photoprocesses initiated by conventional light sources.

The photoexcitation of short-lived reaction intermediates is an improbable process when conventional, low-intensity light sources are utilized to carry out a photochemical reaction. In contrast, these processes can be easily induced when high-power pulsed lasers are used for irradiation. The reasons for this difference are twofold. In the case of the conventional source (frequently a lamp) the steady-state concentration of intermediates is usually quite low (typically  $10^{-6}$ – $10^{-12}$  M) and the low photon flux makes the absorption of a photon by a short-lived intermediate a very unlikely event. These conditions are reversed in the case of pulsed laser sources capable of generating transient concentrations of ca.  $10^{-4}$  M in a few nanoseconds. These intermediates can be exposed to a high photon flux towards the end of the laser pulse. A few examples of isolation of products derived from biphotonic processes (i.e., transient photochemistry) of this type have been reported;<sup>3–6</sup> in addition, processes of this type have been known (and, indeed, a cause for concern) among those using laser photolysis for research on reaction intermediates.

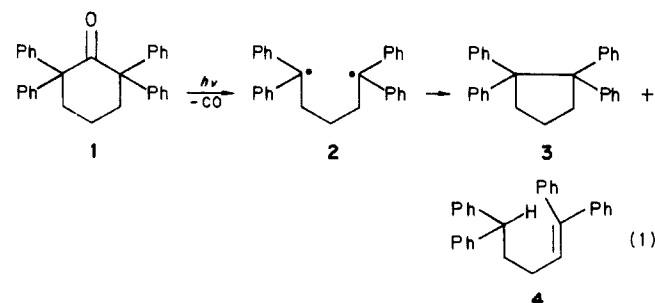
In the last few years we have seen a dramatic increase in the application of lasers in a wide range of fields; many of these applications (medicine, graphics, photoresists) involve very specifically the interaction of the laser beam with organic materials. These photoprocesses must involve different degrees of "laser specific" chemistry resulting from the photolysis of short-lived species. This new chemistry is not only different from "lamp photochemistry" but in many cases it cannot be predicted on the basis of our current knowledge of "one-photon photochemistry". We have undertaken a detailed study of photoprocesses in short-lived reaction intermediates, including species as diverse as free radicals,<sup>5,7</sup> carbenes,<sup>8</sup> ylides,<sup>9</sup> and biradicals.<sup>3</sup> For this purpose we have a laser photolysis system (described in detail elsewhere)<sup>5</sup> which allows the use of two lasers in a carefully controlled sequence. The first pulse from the "synthesis laser" is used to produce the reaction intermediate under study; this is followed by a second "photolysis pulse", within the lifetime of the intermediate of interest. This pulse is of an appropriate wavelength to favor absorption by the intermediate and is ideally at a wavelength where its precursor is completely transparent.

In this paper we report a study of the photochemistry of **2**,

Scheme I



produced from 2,2,6,6-tetraphenylcyclohexanone (**1**). Conventional lamp photolysis of **1** leads to **3** and **4**,<sup>10</sup> i.e.,



The photoprocesses leading to **2** are extremely fast ( $\leq 1$  ns);<sup>10</sup> this combines with the intense absorptions from **2** to make excitation of the biradical (even with one laser pulse) a highly probable process. The photoreactions of **2** were examined with the use of one- and two-laser sources, and the transient phenomena have been combined with detailed studies involving product iso-

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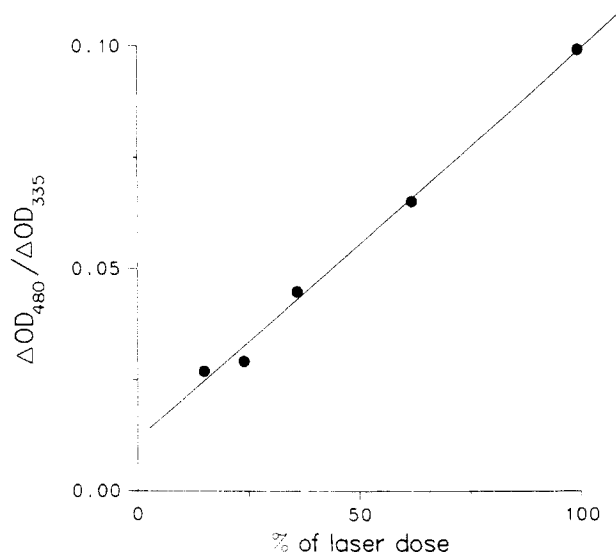
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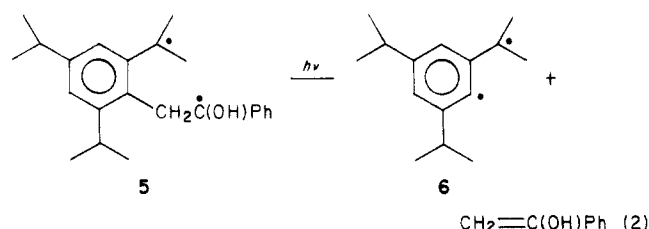
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**Figure 1.** Plot of the ratio of the transient optical densities at 480 and 335 nm in 1:3 benzene/methanol ( $\Delta OD_{480}/\Delta OD_{335}$ ) as a function of the 308 nm laser intensity.

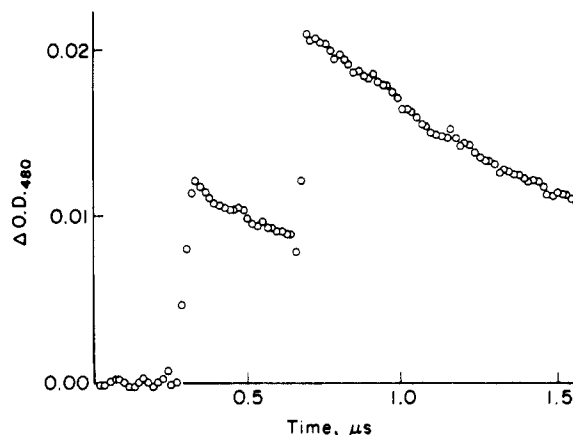
lation and characterization. Of particular relevance to this study are various recent reports on the photolysis and photochemistry of excited diphenylmethyl<sup>4,5,11</sup> and related radicals,<sup>4,7,11-13</sup> as well as our report on the photocleavage of a 1,5-biradical,<sup>3</sup> i.e.,



## Results and Discussion

Unless otherwise indicated, experiments were carried out at room temperature in samples deaerated by bubbling oxygen-free nitrogen.

**Evidence for Two-Photon Processes from Single-Pulse Experiments.** Laser flash photolysis of **1** with the 308-nm pulses from an excimer laser in benzene or benzene-methanol mixtures led to intense transient absorptions with  $\lambda_{\max}$  334 and 480 nm. Our earlier experiments in this area indicated that the latter band was largely the result of a two-photon process.<sup>10</sup> A clear indication of this effect can be obtained from the following experiment: A 0.003 M solution of **1** in 1:3 benzene/methanol was photolyzed with the attenuated 308-nm pulses. Attenuation was achieved by using a calibrated set of neutral density filters. The transient optical densities were monitored at 480 and 335 nm and for the latter covered the 0.3 to 0.08 range. A plot of the ratio  $\Delta OD_{480}/\Delta OD_{335}$  of the two transient optical densities as a function of the transmission of the neutral density filters (Figure 1) shows a clear dependence, indicating that the 480-nm band is of a higher order in light intensity than the 335-nm band. In fact, the plot follows a good linear dependence, this being the expected behavior in the limit of low optical densities and "instantaneous" processes (in the time scale of the laser pulse duration). The intercept in Figure 1 is approximately 0.01, indicating that the "monophotonic" intensity in the visible region is only about 1% of that for the UV band. This intensity ratio agrees well with that observed for other benzylic radical centers.<sup>14,15</sup>



**Figure 2.** Transient absorption at 480 nm obtained by two-laser photochemistry of **1** in 1:3 benzene/methanol; the 308-nm pulse precedes the 337-nm pulse by ca. 400 ns and the 308-nm laser has been attenuated to 24%.

While this experiment does not identify the species responsible for the 480-nm absorption, it does indicate that it originates in a biphotonic process.

**Intensity Dependence of the Signals Produced by a Sequence of Two Laser Pulses.** The strong absorption band from biradical **2** at 334 nm is ideally located for excitation using the 337-nm pulses from a nitrogen laser. In these experiments the concentration of **1** (typically 0.001 M) in 1:3 benzene/methanol was selected so as to achieve significant absorption at 308 nm, while maintaining an essentially transparent solution at 337 nm. Figure 2 illustrates the result of such an experiment, in which the 337-nm pulse follows the 308-nm one after ca. 400 ns. The two "jumps" observed with 480 nm as the monitoring wavelength are due to two-photon excitation at 308 nm (**2** also absorbs strongly at this wavelength) and to excitation of **2** by the 337-nm pulse. It should be noted that the jump induced by the 337-nm laser is not observed when it is not preceded by 308-nm excitation of the sample, clearly indicating that this signal is due to excitation of an intermediate produced by the 308-nm laser.

If we assume that the transient absorption at 480 nm due to monophotonic processes can be neglected, then the following equations will hold:

$$A_{308} = aI_{308}^2 \quad (3a)$$

$$A_{337} = bI_{308}I_{337} \quad (3b)$$

where  $A_{308}$  and  $A_{337}$  are the absorbances at 480 nm induced by the 308 and 337 nm laser pulses, respectively, and  $I_{308}$  and  $I_{337}$  are the corresponding laser doses in arbitrary units. The parameters  $a$  and  $b$  are proportionality constants incorporating the corresponding extinction coefficients ( $b$  also incorporates  $a^{1/2}$ ). Dividing eq 3a and 3b gives eq 4. Thus, if  $I_{337}$  is constant, the

$$A_{308}/A_{337} = (a/b)(I_{308}/I_{337}) \quad (4)$$

ratio of the 308 and 337 nm induced signals should be a linear function of the laser dose at 308 nm. Figure 3 illustrates a plot according to eq 4, for 308 nm laser doses between 15 and 100%, adjusted by using neutral density filters.

**Spectroscopy and Lifetime of the Intermediate Generated by Excitation of Biradical 2.** We have already indicated in an earlier publication<sup>10</sup> that the spectrum in the 480-nm region is largely due to a two-photon process. We have now recorded a detailed spectrum in a two-laser experiment, using a sequence similar to that described for Figure 2 with a delay of 450 ns between the two laser pulses. The detection was triggered about 100 ns before the 337-nm pulse. The spectrum obtained in 1:3 benzene/methanol is shown in Figure 4. It should be noted that as usual spectra of this type record  $\Delta OD$ , not OD, that is, the difference spectrum between a transient and its precursor. However, in the time scale of the experiment the actual precursor is the biradical **2**, not the ketone **1**. Thus, the bleaching at ca. 330 nm is due to

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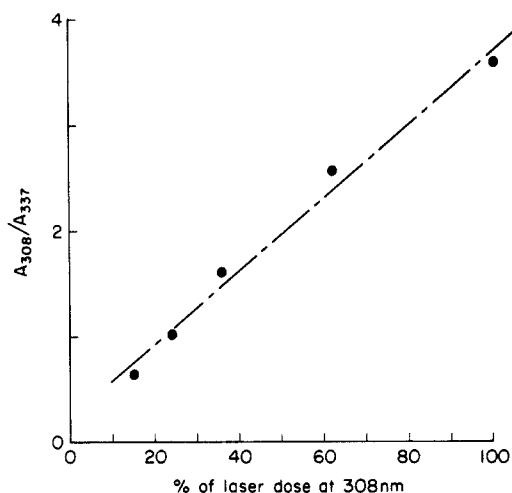


Figure 3. Plot of the ratio of the absorbances at 480 nm induced by the 308 and 337 nm laser pulses ( $A_{308}/A_{337}$ ) as a function of the 308 nm laser intensity.

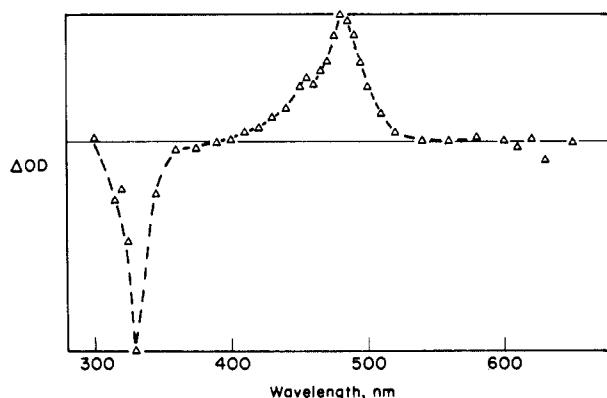


Figure 4. Spectrum obtained by two-laser photochemistry of **1** in 1:3 benzene/methanol; the 308-nm pulse precedes the 337-nm pulse by 450 ns and the detection system was triggered 100 ns before the latter.

the depletion of the biradical **2** upon excitation and provides an excellent indication that the precursor of the 480-nm band is indeed biradical **2**.

Interestingly, the bleaching at 330 nm does not recover after excitation, clearly showing that the photolysis of **2** leads to irreversible chemical changes.

The lifetime of the 480-nm species was monitored in a two-laser experiment, free from the interference that is inherent to the one-laser experiment. The decay in 1:3 benzene/methanol followed clean first-order kinetics with a lifetime of  $1.3 \pm 0.1 \mu\text{s}$ . Similarly, in benzene and acetonitrile the lifetimes were  $1.1 \pm 0.1$  and  $0.9 \pm 0.1 \mu\text{s}$ , respectively.

**Lifetime and Fluorescence from Excited Biradical 2.** The lifetime of the 480-nm band ( $>1 \mu\text{s}$ , vide supra) seems too long to be due to the excited biradical **2**. This is supported by several arguments: (i) Excited diphenylmethyl radicals have lifetimes of ca. 260 ns and even these are long for excited radicals;<sup>4,5</sup> while many factors could shorten this lifetime in the case of the biradical, it is hard to see what factors could lengthen the lifetime by a factor of 4. (ii) Biradicals generally show the same spectral characteristics as the same sites in monoradicals; here, the 480-nm band is quite different from those of excited diphenylmethyl [ $\lambda_{\text{max}}$  355 (strong) and 430 nm].<sup>4,5</sup> (iii) Excited diphenylmethyl radicals are strongly fluorescent,<sup>4,5</sup> while no luminescence with the lifetime for the 480-nm transient could be detected. (iv) Fluorescence from excited diphenylmethyl radicals is readily quenched by radicals such as nitroxide radicals.<sup>16</sup> A similar intramolecular interaction

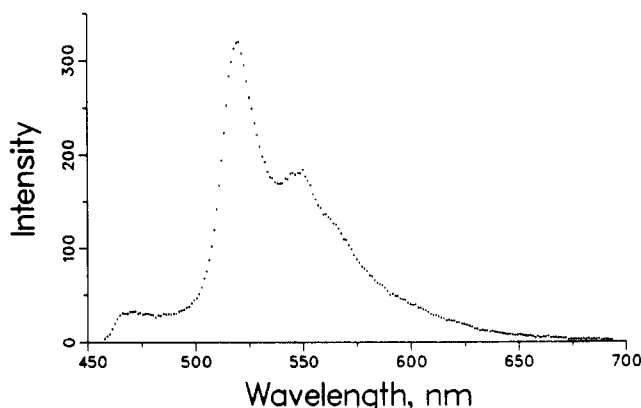
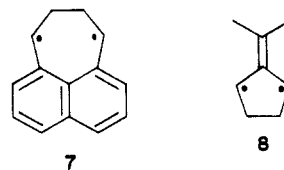


Figure 5. Fluorescence spectrum obtained by two-laser photochemistry of **1** in benzene.

in excited biradicals should lead to very short lived excited states. (v) Biradical **7** has been reported to fluoresce at 77 K with  $\lambda > 512 \text{ nm}$  with a lifetime of  $190 \pm 10 \text{ ns}$ . The lifetime is, however, much shorter at room temperature.<sup>17</sup> A fluorescence lifetime of 280 ps has been observed for the singlet biradical **8** at room temperature.<sup>18</sup>



We felt that if excited **2** (**2\***) had a measurable lifetime, we should be able to detect and characterize its luminescence. This expectation proved correct. When the sample luminescence was monitored in very short time scales (two-laser experiment, 337 nm following 308 nm pulse) we readily detected a weak but characteristic luminescence at  $\sim 520 \text{ nm}$ , Figure 5. This fluorescence compares well with that observed for diphenylmethyl radicals, for which  $\lambda_{\text{max}} = 530 \text{ nm}$ .<sup>5</sup> The spectrum of Figure 5 was obtained with use of an Optical Multichannel Analyzer. For the kinetic measurements the pulses from a PRA nitrogen laser (600-ps pulses, 1 mJ/pulse) instead of the higher energy Molelectron laser ( $\sim 8$ -ns pulses) were used. The shorter pulses allowed us to measure a fluorescence lifetime of  $\sim 2.5 \text{ ns}$ , i.e., two orders of magnitude shorter than that of the excited monoradical.<sup>5</sup>

We are confident that this is the true lifetime of the excited biradical. This result confirms that the 480-nm absorption band cannot be due to the excited biradical **2**.

**Quenching of the 480-nm Absorption.** A number of quenching studies were carried out on the 480-nm band in attempts to establish the origin of these signals. It was easier to carry out these measurements using one-laser (308 nm) excitation; this is due to the fact that some of the quenchers which interact efficiently with the 480-nm band also quench the ground-state biradical. These quenchers (such as oxygen) make the two-laser experiment difficult because of the depletion of ground-state biradical in the time interval between the two laser pulses. In any event, the experiments described before (vide supra) clearly demonstrate that the 480-nm signal is almost exclusively due to a biphotonic process, regardless of the mode of generation.

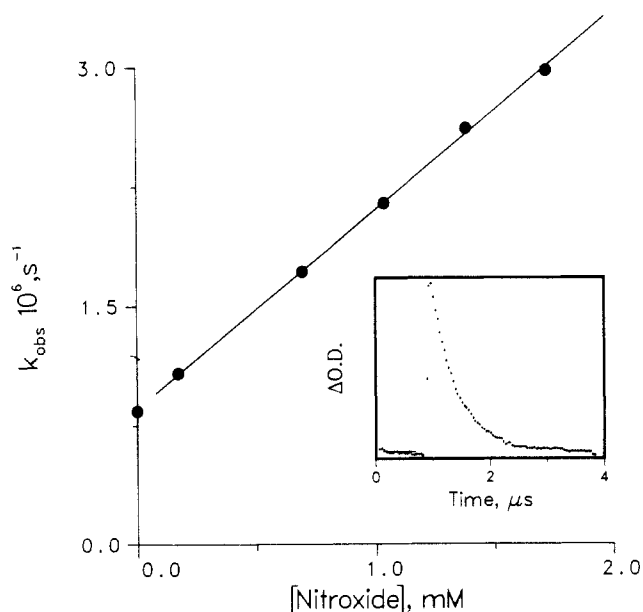
In an air-saturated solution of **1** in benzene the lifetime at 480 nm was 93 ns, suggesting  $k_{\text{O}_2} \sim 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

Quenching by di-*tert*-butyl nitroxide (DTN) in benzene (Figure 6) led to  $k_{\text{DTN}} = (1.25 \pm 0.04) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The decay traces at all nitroxide concentrations followed clean pseudo first-order kinetics (see insert in Figure 6).

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**Figure 6.** Plot of the decay of the 480-nm transient in benzene as a function of the di-*tert*-butyl nitroxide concentration and (insert) a representative decay trace monitored at 480 nm.

Addition of 2,5-dimethyl-2,4-hexadiene, a well-known triplet quencher, in concentrations of up to 0.05 M (in 1:4 benzene:methanol) did not lead to any detectable change in the lifetime monitored at 480 nm.

The experiment described above only proves that if the 480-nm signal is due to an excited triplet, its triplet energy cannot exceed ca. 55 kcal/mol (typical triplet energies for dienes are around 58 kcal/mol<sup>19</sup>). In order to test for lower energies we also carried out a series of experiments with  $\beta$ -carotene as an acceptor (triplet energy  $\sim 23$  kcal/mol<sup>20</sup>). These experiments are substantially more difficult than those with dienes due to competing absorption at 308 nm by  $\beta$ -carotene (which limits the concentration range to  $<0.005$  M). In any event, we found no evidence for sensitized formation of triplet  $\beta$ -carotene as a result of energy transfer from the 480-nm species.

**Product Isolation and Characterization.** Capillary gas chromatographic analysis of the products of lamp or two-laser photolysis unequivocally showed the formation of a new product, characteristic of the two-laser photolysis. The same product was also formed in the one-laser, 308-nm photolysis of the sample, but in substantially reduced yields. The absence of this product in the lamp photolysis and the one- vs. two-laser dependence of its yield leave no doubt that it is the result of the two-photon (biradical photochemistry) process characterized in the study of transient phenomena (vide supra). At high laser doses and short delays between lasers ( $\sim 100$  ns) this new product accounted for  $\sim 12\%$  of the total products. In addition, two substantially smaller new products with similar retention times were also observed in the GC traces, but were not characterized in any detail.

GC-MS of the main product showed  $M^+$  at  $m/e$  374, consistent with an isomer of **3** and **4**. The product was isolated by preparative HPLC following irradiation of a sample containing 24 mg of **1** (more details in the Experimental Section) with 9000 pairs of laser pulses with the use of a 100-ns delay between pulses and with the lasers operated at 2 Hz. About 1 mg of a product sample that was  $>90\%$  pure by capillary GC was obtained.

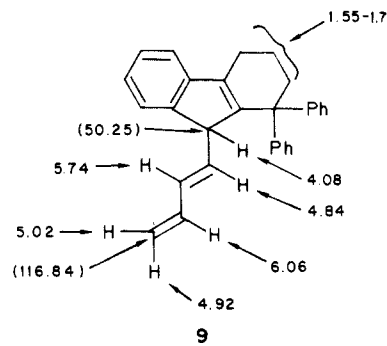
The IR spectrum of the product indicates the presence of monosubstituted ( $760, 702 \text{ cm}^{-1}$ ) and ortho-disubstituted ( $740 \text{ cm}^{-1}$ ) aromatic rings, as well as terminal  $=\text{CH}_2$  groups ( $910, 1000 \text{ cm}^{-1}$ ).

Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained for the isolated product. Proton NMR shows 6  $\text{CH}_2$  groups, 1 CH, 5 olefinic

protons, and 14 or 15 aromatic protons. Analysis of the coupling constants for the olefinic and methane protons as well as decoupling experiments conclusively show the presence of a  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CH}<$  moiety. Relaxation times for the two terminal olefinic protons are shorter than for the other olefinics, as expected for vicinal protons.

A  $^{13}\text{C}$  NMR DEPT experiment shows the presence of 3  $-\text{CH}_2-$ , 1  $-\text{CH}$ , and one terminal  $=\text{CH}_2$  groups.

The spectral data (more in the Experimental Section) are fully consistent with structure **9**. The structure of **9** is shown below along with some chemical shifts (brackets used for  $^{13}\text{C}$ , others for  $^1\text{H}$ ).



An NMR spectrum of the photolysis mixture showed that **9** was present before the isolation procedure and so was not produced by rearrangement of an initial photoproduct during chromatography.

**Mechanism of Reaction. Correlation of Data from Product Studies and Laser Experiments.** It is clear that **9** itself or its triplet state cannot be responsible for the transient signals observed at 480 nm. Triplet **9** would be expected to be shorter lived than the 480-nm transient and would most likely absorb at shorter wavelengths.<sup>21</sup> Scheme I shows a tentative reaction mechanism. Product **9** and biradical **2** and its excited state are well-characterized, but the reaction path from **2**\* leading to **9** does involve some degree of speculation. The cyclization leading to **10** is a reaction for which there is considerable precedent,<sup>12,13,22-24</sup> although, not surprisingly, reported examples do not include highly excited precursors comparable to **2**\*. This rearrangement is presumably followed by cyclization of the biradical which at some point must cross to the singlet manifold. A 1,5 H-shift in **11** gives **12** which may then rearrange to **9** by ring opening to **13** followed by a second 1,5 H-shift or by a direct 1,13 H-shift.

An alternative mechanism can probably be written, starting with the zwitterionic form of **2**. Indeed, not only are excited diphenylmethyl radicals good electron donors and acceptors<sup>5</sup> but also theoretical treatments of biradicals suggest that their excited states may have zwitterionic character.<sup>25</sup> One can only speculate that in such a mechanism proton, rather than hydrogen, migration may be a more favorable route ultimately leading to **9**.

Which of the intermediates in Scheme I should be assigned to the 480-nm species? The only apparent candidate is biradical **10** which retains a diphenylmethyl terminus and has a radical center conjugated with a system of five double bonds, the latter being presumably responsible for the visible absorption. Similar absorptions have been detected by Meisel et al.<sup>4</sup> in the photochemistry of substituted diphenylmethyl radicals. In addition, our quenching experiments seem to support a biradical, rather than an excited state. While the failure to sensitize  $\beta$ -carotene is not a conclusive experiment due to the difficulties associated with this measurement, the result is certainly the expected one if the 480-nm species is a biradical.

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## Conclusion

Our results clearly show the ease with which two photon processes can be induced in the photochemistry of **1** and presumably in many other systems. Interestingly, while laser applications have increased dramatically in the last few years, only a few rather isolated studies of transient photochemistry have been carried out. Perhaps more worrying than our lack of knowledge in this area is our lack of awareness that processes of this type may play a crucial role in many laser applications.

The study reported herein includes one of the first determinations of the lifetime of an excited biradical in fluid solution and a rather dramatic example of the differences in products between one- and two-photon processes (compare **3** and **4** with **9**). It also provides considerable insight into the sorts of measurements that can be used to examine processes of this type.

## Experimental Section

Infrared spectra were recorded on a Digilab FTS-11 infrared spectrometer. A Perkin-Elmer 8320 gas chromatograph equipped with a 12-m BP1 on vitreous silica capillary column was used for all GC analysis. GC-MS spectra were recorded on a Hewlett-Packard 5995 instrument equipped with a 10-m Ultra 1 (OV-101) capillary column. Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-500 spectrometer. A Perkin-Elmer Series 10 liquid chromatograph equipped with a Lobar Silica Gel 60 prepacked column (Merck, Size A, 1 cm  $\times$  24 cm) was used for all liquid chromatographic separations.

2,2,6,6-Tetraphenylcyclohexanone<sup>10</sup> was a generous gift from Professor D. H. R. Barton. 2,5-Dimethyl-2,4-hexadiene (Aldrich) was distilled before use.  $\beta$ -Carotene was recrystallized from diethyl ether/petroleum ether. Benzene and methanol (Aldrich, Gold Label) and di-*tert*-butyl nitroxide were used as received.

**Laser Flash Photolysis.** Samples of **1**, 0.001–0.003 M in the appropriate solvent, were contained in  $7 \times 7$  mm<sup>2</sup> quartz cells and were deaerated by nitrogen purging. A Lumonics TE-860-2 excimer laser (Xe-HCl, 308 nm,  $\sim 5$ -ns pulses;  $\leq 80$  mJ/pulse) and a Moletron nitrogen laser ( $\sim 8$ -ns pulses, 337 nm,  $\leq 10$  mJ/pulse) or a PRA LN 1000 nitrogen laser (0.6-ns pulses,  $\leq 1.5$  mJ/pulse) were used for excitation. Further details of the laser flash photolysis facility<sup>26</sup> and the modifications required for two laser experiments<sup>5</sup> have been described. An Optical Multichannel Analyzer with an E.G. & G. 1420 detector recently has been incorporated in the laser system.

**Preparative Photolysis of 1.** A degassed sample of **1** (24 mg in 25 mL of benzene) was irradiated in a two-laser experiment with the excimer laser pulse followed ca. 100 ns later by the Moletron nitrogen laser pulse and with both lasers operating at 2 Hz. The sample was stirred by

bubbling nitrogen through the cell during the irradiation period. The progress of the reaction was followed by GC analysis of a small aliquot of the solution. A total of 9000 shots, delivered in units of 1000 with 10–20 min intervals between units, was required to obtain ca. 90% conversion. Preliminary experiments indicated that inadequate sample mixing and  $>90\%$  conversion led to decreased yields of the biphotonic product.

The irradiated reaction mixture was concentrated to 0.5 mL and separated by liquid chromatography with  $\text{CH}_2\text{Cl}_2$ /hexane solvent mixtures. The biphotonic product had a retention time of 22 min and was isolated in  $>90\%$  purity as determined by GC analysis of the isolated material (ca. 1 mg). The material was an oil, and several attempts to crystallize it were unsuccessful.

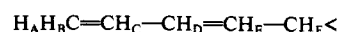
Structure **9** was assigned to the isolated material on the basis of the following spectral data and as discussed above. MS,  $m/e$  375 ( $M^+ + 1$ ), 32.8%; 374 ( $M^+$ ), 100.0%; 297, 17.3%; 253, 23.1%; 181, 17.4%. IR (thin film deposited from  $\text{CHCl}_3$ ) 3085, 1640, 1600, 910, 760, 740, 702  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.26–7.23 (m, 14 H), 6.06 (ddd,  $J_{A,C} = 10.3$  Hz,  $J_{B,C} = 16.5$  Hz,  $J_{C,D} = 10.8$  Hz, 1 H), 5.74 (dd,  $J_{C,D} = 10.8$  Hz,  $J_{D,E} = 10.6$  Hz, 1 H), 5.02 (d,  $J_{B,C} = 16.5$  Hz, 1 H), 4.92 (d,  $J_{A,C} = 10.3$  Hz), 4.84 (dd,  $J_{D,E} = 10.6$  Hz,  $J_{E,F} = 10.4$  Hz, 1 H), 4.08 (d,  $J_{E,F} = 10.4$  Hz, 1 H), 2.66–2.50 (m, 3 H), 2.36–2.31 (m, 1 H), 1.70–1.55 (m, 2 H).<sup>27</sup>  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  132.4, 130.1, 129.8, 129.3, 127.9, 127.3, 126.8, 125.9, 125.1, 123.6, 118.3, 116.8, 50.25, 39.7, 22.6, 18.1. Proton decoupling experiments for protons A–F were used to establish the coupling patterns of the olefinic protons. A  $^{13}\text{C}$  DEPT experiment confirmed the presence of one  $=\text{CH}_2$  (116.8), one C–H (50.2), and three  $\text{CH}_2$  (18.1, 22.6, 39.7) carbon atoms.

A 500-MHz NMR spectrum of the photolysis mixture showed conclusively that **9** was present in the original mixture and was therefore not formed during the chromatographic separation. The NMR spectrum also showed the presence of additional olefinic signals which were not due to **9** or **4**; these are presumably due to the two minor products of the biphotonic reaction.

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**Registry No.** **1**, 83576-30-1; **2**, 95935-53-8; **9**, 100858-14-8.

(27) Subscripts refer to the butadiene group:



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## Nonlinear Effects in Asymmetric Synthesis. Examples in Asymmetric Oxidations and Aldolization Reactions

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**Abstract:** It has been shown in three experiments that there is a strong departure from the linear relationship usually assumed between the enantiomeric excess of a chiral auxiliary and the extent of the asymmetric synthesis. This gives useful information on the reaction mechanisms. Asymmetric oxidation of methyl *p*-tolyl sulfide or asymmetric epoxidation of geraniol in the presence of various chiral titanium complexes, as well as the proline-catalyzed Hajos–Parrish reaction, is investigated in detail.

Horeau and Guetté<sup>1</sup> discussed the importance of diastereomeric interactions of a mixture of enantiomers in the liquid phase. These interactions are responsible for some *unusual physical properties*

of mixtures of enantiomers such as the nonequivalence of the enantiomeric excess and the optical purity<sup>2</sup> or the different NMR spectra for a racemic mixture or a pure enantiomer.<sup>3–6</sup> The

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(2) Horeau, A. *Tetrahedron Lett.* **1969**, 3121–3124.