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PHOTOCHEMISTRY OF 1,1,3-TRIPHENYL-2-INDANONE. SPONTANEOUS AND PHOTOCHEMICAL DECAY OF *ORTHO*-XYLYLENES[1]

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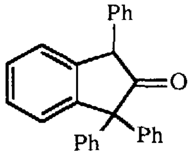
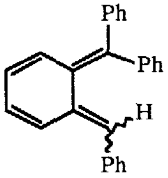
Summary: The photochemistry of the title compound leads to the formation of a long lived *ortho*-xylylene which decays by two competing cyclization pathways leading to benzocyclobutene and dihydroanthracene ring systems. The ratio of products **V** and **VI** is different for one and two-photon processes, thus providing another example where the products can be controlled by the type of photoexcitation used.

There are now many examples where lamp and laser photoexcitation of organic compounds lead to different consequences[3-5]. Many of these examples have been examined from a spectroscopic point of view (e.g., laser-specific luminescence from excited reaction intermediates); however, only in a few cases have the differences in products been examined in any detail. We report here that the photochemistry of 1,1,3-triphenyl-2-indanone (I) leads to very different product ratios depending on whether the decay of the intermediate xylylene **II** occurs spontaneously or photochemically.



I



II

Experimental.

Indanone **I** was prepared by a literature procedure [6]and its spectroscopic properties agree with the proposed structure.

Laser flash photolysis experiments were carried out with the system described earlier [7, 8]. The samples of **I** were excited with the pulses from a Lumonics TE-860/2 excimer laser (308 nm, ~5 ns, ~20 mJ/pulse). In experiments involving excitation of **II** by a second laser, a Candela flash pumped dye laser tuned to 480 nm (Coumarin 480 dye) was used.

Lamp irradiations were performed in Pyrex tubes with a set of nine RPR-3000 lamps. Product yields were determined by GC and GC/MS. UV-Vis spectra were recorded with a Hewlett-Packard model 8451-A diode array spectrometer.

Results and Discussion.

Laser flash photolysis of **I** in benzene or acetonitrile at room temperature lead to a readily detectable transient absorption spectrum with λ_{max} 460 nm, Figure 1. This species is very long lived (e.g. $\tau \sim 230\ \mu s$ in acetonitrile) and decays by first order kinetics. Within the time resolution of these experiments (ca. 20 ns) the formation of this transient appears instantaneous. Neither its yield, nor its lifetime are significantly affected by oxygen (≤ 0.01 M) or by 1,3-cyclohexadiene (≤ 0.1 M), suggesting that all the intermediates involved in the formation of the 460 nm transient must be very short lived, including most likely, the triplet state of **I**.

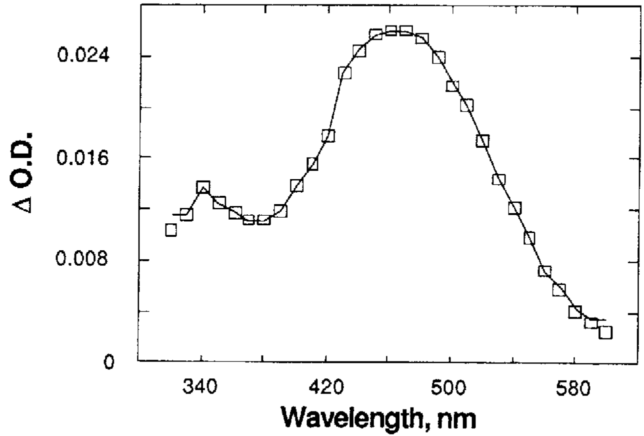
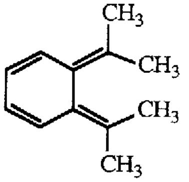
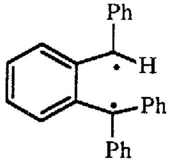


Figure 1. Transient spectrum recorded 1μs following 308 nm laser excitation of **I** in benzene

The spectrum of Figure 1 is attributed to **II** and bears similarities to other *ortho*-xylylenes and related photoenols[9, 10]. The spectrum is red shifted with respect to simpler species, such as tetramethyl-*ortho*-xylylene (**III**), for which we have obtained λ_{max} 360 nm[11]. Interestingly, the expected biradical precursor for **II**, i.e. **IV** must also be very short lived, since **II** would otherwise show a grow-in time profile. For comparison, the biradical precursor to **III** has a lifetime of 580 ns[11].

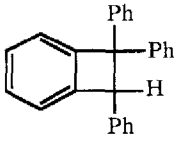


III

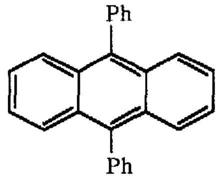


IV

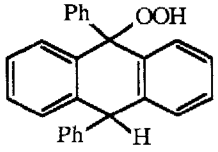
Lamp photolysis of **I** in benzene leads to two main products, **V** and **VI** and a minor product, which from the GC/MS data is probably **VII** or **VIII**, presumably derived from **VI** or its precursors. We believe that **VI** is not a primary product, but rather that it results from **IX**, which is the product of cyclization of **II**. Under lamp irradiation the ratio VI/V[12] is ~0.9 in benzene. Interestingly, this ratio is quite different when laser excitation is employed. These data are summarized in Table 1.



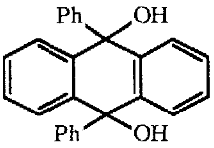
V



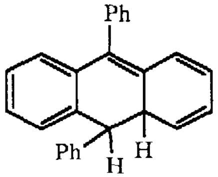
VI



VII



VIII



IX

Table 1. Relative yields of anthracene–to–benzocyclobutene products in the photolysis of **I** in benzene.

Light Source	Wavelength, nm	**VI/V**
Lamp	300-320	0.94[a]
Laser	308	2.54
Two-laser[b]	308 + 480	3.93

[a] Average for six samples between 5 and 50 % conversion: 0.94 ± 0.14

[b] The dye laser (480 nm) was pulsed 2 μs after the excimer laser.

We believe that the change in product ratio in the two top lines in Table 1 is due to photoexcitation of reaction intermediates during the laser pulse; e.g. that photochemical decomposition of **II** leads predominantly to anthracene products. In order to test this hypothesis we carried out two-laser, two-color experiments in which **II** was irradiated with the pulses from a dye laser tuned at 480 nm, so as to selectively excite the xylylene. Figure 2 shows a representative trace which illustrates well the high yield of the photobleaching of **II**. In contrast, in the 320-410 nm region we observe positive transient absorptions concurrent with the bleaching mentioned above; these broad absorptions do not match the spectrum of **VI** and are attributed to the initial product, **IX**. The effect on the product yields has been included in Table 1, and clearly shows a substantial increase in anthracene-products. Their presence was readily detected by UV-Vis spectroscopy, although the yields in the Table are based on GC analysis against authentic samples. There is precedent in the literature for a number of photorearrangements of this type[5,13]. An elegant example involving o-methylbenzophenone was recently reported by Wilson *et al.* [14]; these results are in line with earlier reports[13,15-17]. We were concerned with the possible **IX**→**V** photoconversion under lamp irradiation, based on related work by Quinkert[13]. We find that **VI/V** shows only a very minor dose dependence which extrapolates to *ca.* 1.2 at zero conversion, suggesting that the **IX**→**V** process does not contribute significantly to the changes in Table 1.

We find the enhancement of VI/V rather dramatic in the case of one-laser excitation; conceivably, the laser may also excite other reaction intermediates, such as biradical **IV**, in spite of their short lifetime.

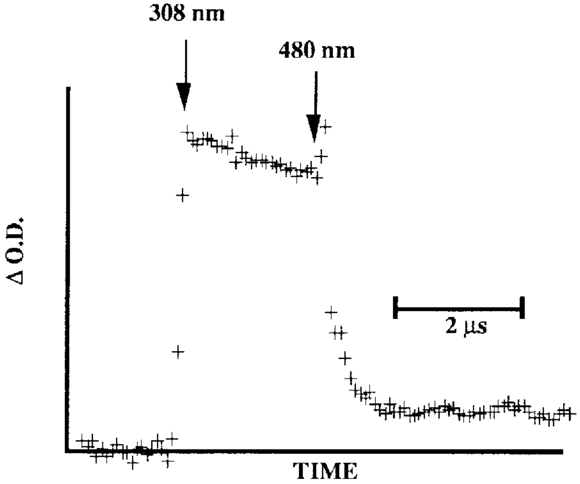


Figure 2. Laser photolysis of **I** in benzene illustrating the photobleaching of **II** by 480 nm dye laser excitation of the xylylene. Monitoring wavelength: 460 nm.

In conclusion, the photochemistry of **I** provides an example of product control in the lamp vs. laser photolysis. The example contrasts with the case of **III**[11] where photochemical and spontaneous decay lead to the same product.

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