Time-Resolved Studies of the Photogeneration and Photochemistry of Tetramethyl-*o*-xylylene[1]

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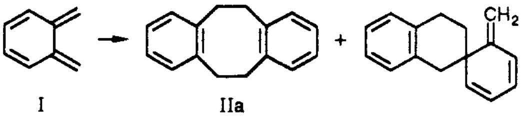
Abstract: The photodecomposition of 1,1,3,3-tetramethyl-2-indanone (V) leads to the formation of tetramethyl-*o*-xylylene (III), which ultimately decays to give *o*-isopropenylcumene (IV) as the only product. The xylylene III shows λ_{max} ~358 nm in benzene and has a remarkably long lifetime, 9.1 min at room temperature. The infrared spectrum of III was recorded in situ at room temperature (in cyclohexane or carbon tetrachloride); characteristic bands were observed at 681 and 1212 cm^{-1}. Laser photolysis studies reveal that the formation of III involves an intermediate with a lifetime of 580 ns, which is attributed to the 1,4-biradical VI; this species is the same as the triplet state of III, and is readily scavenged by oxygen and β-carotene. Two-laser two-color experiments indicate that the photolysis of III yields the same product as its thermal decay (i.e., IV), but the photochemical process is at least 10 orders of magnitude faster than the thermal reaction.

The involvement of *o*-xylylene (I) and some of its derivatives in the photochemistry of 2-indanones has been conclusively established in detailed product studies reported by Quinkert et al.[3] These intermediates have also been characterized in matrix isolation studies at cryogenic temperatures,[4-7] by flow NMR,[8] and by conventional flash photolysis[9] in solution at ambient temperatures.

The photodecomposition of the appropriately substituted 2-indanone provides a clean source of *o*-xylylenes which has been employed at room and lower temperatures.[3,9] Other sources, including those employed for matrix work at cryogenic temperatures, are hydrogen transfer in carbenes[10] (e.g., *o*-tolylmethylene), dichlorides[11] (e.g., 1′,2′-dichloro-*o*-xylene), and sulfones.[12]

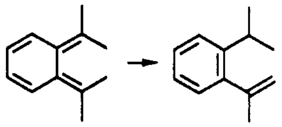
o-Xylylene (I) in solution decays predominantly by dimerization to yield the corresponding dimers, IIa and IIb (i.e., reaction 1).



I IIa IIb (1)

In contrast, tetramethyl-*o*-xylylene (III) decays via an intramolecular 1,5-hydrogen shift to yield *o*-isopropenylcumene[9,13] according to reaction 2.

Xylylene III has been shown[9] to be a very long lived, but photosensitive transient. In this paper we report the results of a study of the generation of III by photodecomposition of indanone V, where we have been able to detect for the first time the biradical/triplet–xylylene precursor to III. Further, we have explored the photochemistry of III using two-laser, two-color techniques.

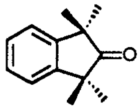


III IV (2)

Results

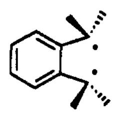
This section is divided according to the type of measurement employed. Samples were normally deaerated by bubbling oxygen-free nitrogen.

Laser Flash Photolysis. Laser excitation (308 nm) of a solution of 1,1,3,3-tetramethyl-2-indanone (V) in benzene (0.3 absorbance at 308 nm for a 7-mm optical path) led to a long-lived intermediate with an absorption band centered at λ_{max} ~358 nm (Figure 1).



V

We assign the spectrum of Figure 1 to tetramethyl-*o*-xylylene (III) on the basis of other experiments described herein and in agreement with earlier studies. The spectrum in polar solvents such as acetonitrile was virtually identical with that of Figure 1. The species absorbing at 358 nm was too long-lived for its decay to be monitored by laser photolysis techniques (vide infra). Examination at short time scales showed that the 358-nm species is not formed immediately after laser excitation, but rather it grows in with first-order kinetics and has a lifetime of ca. 580 ns in benzene at room temperature. Figure 2 (top) shows a representative transient absorption trace monitored at 360 nm. That the precursor to III is an intermediate with this lifetime is clearly demonstrated by the traces recorded in the 320-nm region (see Figure 2, bottom) where a decay concurrent with the growth at 360 nm is readily observed. The fact that the 320-nm traces do not decay to the preexcitation level is an indication that III absorbs at this wavelength. Since the singlet and triplet states of V are very short lived (vide infra), we assign the precursor to III (i.e., the 320-nm transient) to biradical VI.



VI

Biradical VI is the structure resulting from CO elimination in V. However, by analogy with systems involving photo-enols,[14-16]

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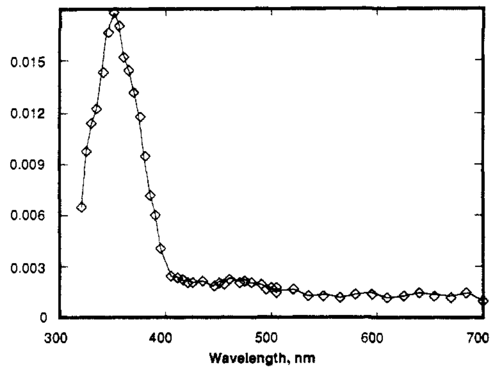

Figure 1. Transient absorption spectrum obtained on 308-nm excitation of 3.0 mM 1,1,3,3-tetramethyl-2-indanone in benzene.

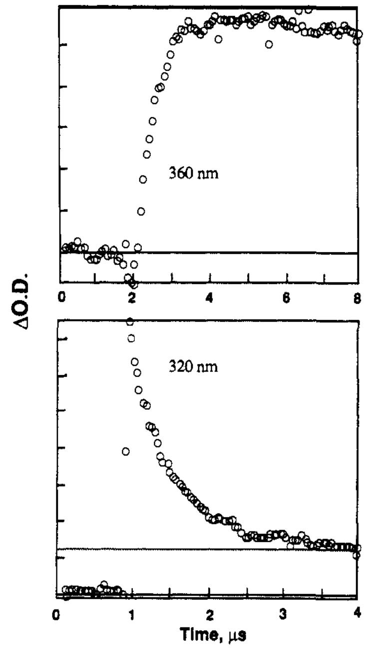

Figure 2. Top: growth of absorption at 360 nm due to tetramethyl-*o*-xylylene generated from indanone V, upon 308-nm excitation. Bottom: decay trace at 320 nm for biradical VI generated as above. Note change in time scale.

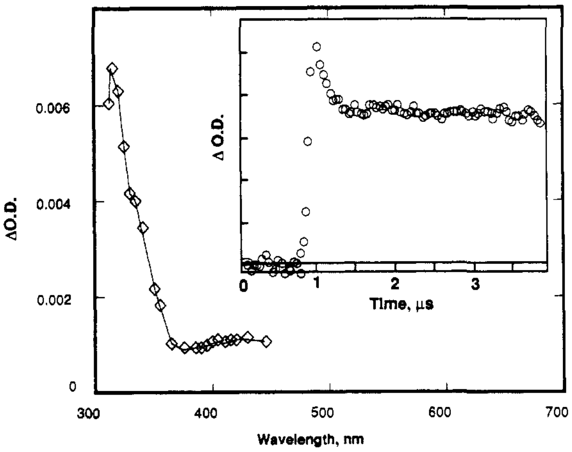

Figure 3. Transient absorption spectrum of the biradical VI obtained on 308-nm excitation of 3.0 mM V in benzene. Insert: decay trace for VI at 320 nm in a sample containing an oxygen concentration of 0.42 mM (compare with Figure 2).

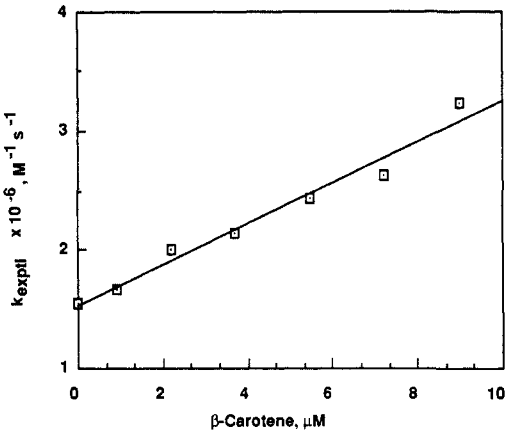

Figure 4. Quenching of biradical VI by β-carotene in benzene following eq 4.

VI and the triplet state of III (^{3}III*) must be one and the same species. Figure 3 shows the absorption spectrum of VI at λ <450 nm.

Our assignment of the 320-nm transient to VI = ^{3}III* is also supported by several experiments outlined below. Oxygen has been shown to be an excellent quencher for VI. The insert in Figure 3 shows one decay trace monitored under 0.42 mM oxygen; quite clearly the biradical lifetimes are greatly reduced in the presence of oxygen, although the effect on the yield of III, as measured by the residual absorption in a matched set of experiments is minimal. This was also confirmed by monitoring the invariance of the xylylene absorption at 360 nm.

The rate constant for the interaction of VI with oxygen was determined from a plot of the reciprocal biradical lifetime against the concentration of oxygen. The value obtained for the rate constant was (1.9 ± 0.2) × 10^{10} M^{-1} s^{-1} in benzene at 20 °C (correlation coefficient 0.987).

Quenching experiments were also carried out with 1,3-cyclohexadiene and with β-carotene (β-C). The former should be an excellent quencher for the carbonyl triplet; in spite of this, addition of up to 1 M 1,3-cyclohexadiene leads to no change in the decay of 320 nm (as expected for a biradical), and the yield of VI decreases only by 20% or less. The inability of the diene to reduce the yield of xylylene means that the triplet state of V, ^{3}V*, must have a lifetime of less than 1 ns.

β-Carotene has also been employed as a quencher. While β-carotene shows some absorption at 308 nm (i.e., the laser wavelength), its intersystem crossing yield is essentially zero, so that β-carotene triplets can only be formed via energy transfer from an appropriate donor.[17] The triplet state of β-C lies only 19 kcal/mol above its ground state,[18] so that it is also a good candidate to quench ^{3}III*, according to eq 3.

$$\text{III}^* + \beta\text{-C} \rightarrow \text{III} + \beta\text{-C}^* \qquad (3)$$

β-C* has a characteristic spectrum (quite distinct from III*) and its formation can be readily monitored at 520 nm; monoexponential analysis of either these growth traces or the decay traces at 320 nm leads to an experimental rate constant, k_{exptl}, which is related to the rate constants of interest according to eq 4, where

$$k_{\text{exptl}} = \tau_B^{-1} + k_3[\beta\text{-C}] \qquad (4)$$

τ_B is the lifetime for VI = ^{3}III* and k_3 is the rate constant for reaction 3. A plot of k_{exptl} vs [β-C] based on the decay traces at 320 nm is illustrated in Figure 4; the value of k_3 obtained from the plot is (1.7 ± 0.1) × 10^{10} M^{-1} s^{-1} in benzene at room temperature (correlation coefficient 0.987).

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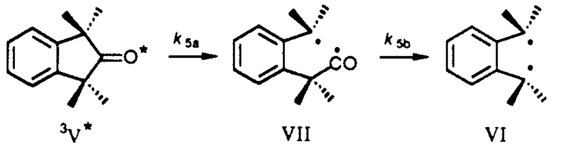
Several experiments were carried out in attempts to scavenge the xylylene with electron-deficient olefins such as fumaronitrile, dimethyl acetylenedicarboxylate, and maleic anhydride. The reactions are too slow for flash techniques (including conventional flash photolysis), and these experiments were unsuccessful. Attempts to detect the quenching from product studies did not yield significant amounts of trapping products under conditions where similar experiments with I yield the corresponding 4 + 2 adduct (e.g., dimethyl acetylenedicarboxylate).

Several attempts to time resolve the formation of the 320-nm transient were unsuccessful. Therefore, we believe that the formation of this species occurs in <20 ns. We expect this process to take place in two steps, according to reaction 5.



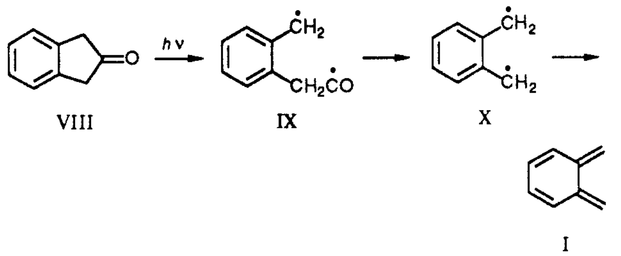
(5)

Our quenching studies (vide supra) indicate that $k_{5a} > 10^9$ s^{-1}, and while we do not have a direct measurement for k_{5b}, we have failed to detect any delayed formation of VI, suggesting that $k_{5b} \geq 5 \times 10^7$ s^{-1}. This should be compared with a decarbonylation rate constant of $>10^7$ s^{-1} for monoradicals with a structure similar to VII.[19,20] We note that while the spectroscopic data for the short-lived intermediate would be consistent with its assignment to either VI or VII, the latter can be ruled out because it would not be expected to have excited-state properties. Thus, the experiments with β-carotene can only be consistent with structure VI (i.e., III*).

A number of experiments were also carried out with 2-indanone (VIII) in an attempt to compare the generation and properties of I with those of III.

Just as in the case of III, we expect X and the triplet state of I (^{3}I*) to be the same species. It was straightforward to obtain intense signals from I upon irradiation of VIII at 308 nm. Essentially the same behavior was observed in benzene and in acetonitrile. The position of λ_{max} (380 nm) is in good agreement with the value reported in a matrix at low temperature (373 nm).[4,5]

We were unable to detect directly the precursors to I (i.e., IX or X), although it was not entirely clear whether this was the result of a kinetic problem (i.e., all steps in reaction 6 being very fast) or of a spectroscopic problem. We had anticipated that at least the decarbonylation step could be slower for IX than for VII.



(6)

Conventional UV-Visible Spectroscopy. We have mentioned before that the decay of III was too slow to be monitored by using laser flash photolysis techniques. In fact III is long-lived, and therefore its decay may be monitored with a conventional UV-visible spectrometer. Figure 5 shows a series of absorption spectra obtained at various times following excitation by 700 laser shots at 308 nm. The insert shows a plot corresponding to a first-order (i.e., monoexponential) analysis of the decay data from which we obtain a lifetime of 9.1 min in benzene at room temperature. We attribute this decay to reaction 2. The lifetime of III appeared to be insensitive to the presence or absence of oxygen.

Product Studies. Irradiation of indanone V in benzene with RPR-3000 lamps leads to IV as the only important product (>95%). Given the long lifetime and photosensitivity (vide infra) of III, we were concerned with the possibility that the "spontaneous" decay of III into IV could actually be a photoprocess triggered by ambient light and/or the same light source that generates III from the indanone, since it is almost impossible to prevent some photoexcitation of III even at wavelengths considerably removed from its absorption maximum (such as 308 or 313 nm). We therefore designed an experiment to test this possibility. Two separate irradiations were carried out on two identical samples (samples A and B) that contained 0.05 M V in benzene. Both samples received a total of 30-min excitation from a set of nine RPR-3000 lamps. Sample A was subjected to uninterrupted irradiation. Sample B was subject to 30 irradiations of 60 s each, with intervals of 10 min between irradiations. During these intervals the lamps were switched off, and the samples were maintained in the dark photolysis chamber; thus, these times allowed for well over 70% of the concentration of III to decay in the dark before the lamps were turned on again for a brief period. Analysis of samples A and B showed no difference in the concentration, or nature of the products, with IV being the only major product, as usual.

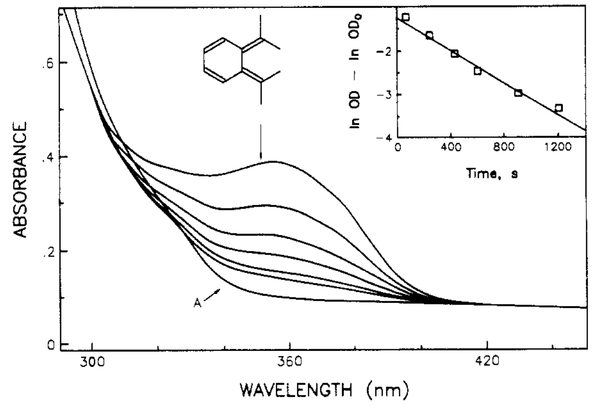


Figure 5. Time dependence of absorption spectra for tetramethyl-*o*-xylylene in benzene. A: absorption of V before irradiation. Insert: first-order analysis of this data.

Infrared Spectroscopy Studies. The infrared and Raman spectra of *o*-xylylene (I) isolated in low-temperature Ar matrices have been reported.[6,7] Even though no detailed structural information was derived from these spectra, a comparison of the infrared spectrum of III with that of I would be useful and would help corroborate our assignments. Given the long lifetime of III as determined by UV-visible spectroscopy, our experiments were carried out in solution at room temperature. The initial concentration of V was 0.04 M in either cyclohexane or CCl_4, in order to achieve adequate IR absorption over the 500-μm optical path of the flow cell (NaCl windows). This is a rather long pathlength for infrared studies and presents the inconvenience that the signals from the solvent are "totally absorbing" and therefore cannot be subtracted properly. Some spectral regions are thus not amenable to study.

The infrared cell was positioned in the open sample compartment of a Bomem Michelson-100 FT-IR spectrophotometer. The spectrophotometer was set up such that the output from the excimer laser could be directed to the infrared cell. The first step of the procedure was to record the infrared spectrum of the solvent. To check for possible interference of the laser with the FT-IR spectrophotometer, spectra of the solvent were recorded with the laser on; i.e., while the FT-IR spectrum was being recorded, the sample was being irradiated with 308-nm radiation. No significant differences were found between spectra recorded with the laser on or off.

For the actual experiments, a deaerated solution of V was flowed into the cell; then the flow was stopped, and the spectrum of the unirradiated solution was recorded. The sample was then exposed to 1000 laser shots at 308 nm. Immediately after photolysis FT-IR spectra were recorded at 4-cm^{-1} resolution; 20 scans were accumulated for each spectrum, corresponding to a time difference

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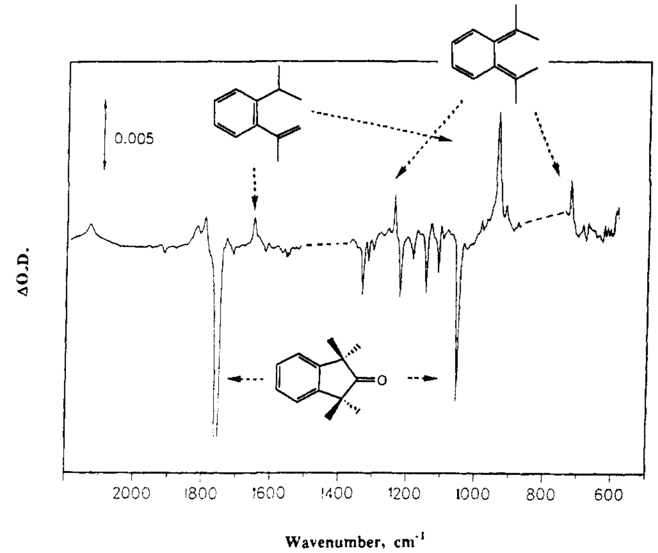

Figure 6. Difference infrared spectrum of a solution of V (0.04 M in CCl_4). The trace shown is the result of subtracting a spectrum recorded ca. 2 min after irradiation (308 nm, 1000 shots) from that recorded before irradiation. The dotted lines correspond to spectral regions masked by solvent bands.

of ~2 min between consecutive spectra. All the spectra were then Fourier transformed and ratioed against the spectrum of the solvent.

Figure 6 shows a representative infrared difference spectrum, resulting from subtracting the spectrum recorded immediately after photolysis from the spectrum collected before photolysis (i.e., that of pure V). In this difference spectrum, negative bands correspond to functional groups disappearing during the reaction, while positive bands correspond to species formed during the reaction. Among the negative peaks, the intense ones at 1745 and 1017 cm^{-1} reflect the depletion of V.

The most prominent positive bands in Figure 6 are at 681, 900, 1212, and 1637 cm^{-1}. Comparison with spectra recorded at longer times from the laser irradiation showed that the bands at 681 and 1212 cm^{-1} decrease in intensity as the time between irradiation and collection increases. Thus, they are assigned to a transient species. The bands at 900 and 1637 cm^{-1} do not decrease with time and are therefore assigned to the stable final product (IV). To corroborate this assignment, the final product, IV, was isolated, and its infrared spectrum was recorded as a thin film deposited on a KBr window. The spectrum shows two strong bands at 1642 and 900 cm^{-1}, which confirm our assignment.

The two bands due to the transient species, at 681 and 1212 cm^{-1}, should be compared with the IR spectra of *o*-xylylene reported previously. In the two reports available[6,7] the spectrum was recorded from Ar matrices at temperatures between 4 and 15 K. In the spectrum of *o*-xylylene a band of medium intensity was observed[7] at 675 cm^{-1} which corresponds well with the one at 681 cm^{-1} observed by us at room temperature and in fluid solution. The IR band observed at 1212 cm^{-1} (Figure 6) corresponds with a series of weak IR bands observed between 1160 and 1300 cm^{-1} in the matrix and also to the band at 1293 cm^{-1} observed in the Raman spectrum.[6] These bands are generally associated with 1,2-substituted aromatic systems.[21] The same infrared spectrum was observed when cyclohexane was used as solvent.

In the IR spectrum of IV there is a strong band at 770 cm^{-1} typical of ortho-disubstituted aromatics. We also compared the IR spectrum of IV with that of *o*-methylstyrene and found the only significant difference to be the frequency of the C=C stretching band. This band is at 1643 cm^{-1} in IV and at 1625 cm^{-1} in *o*-methylstyrene as a consequence of the different substitution patterns at the olefinic group.

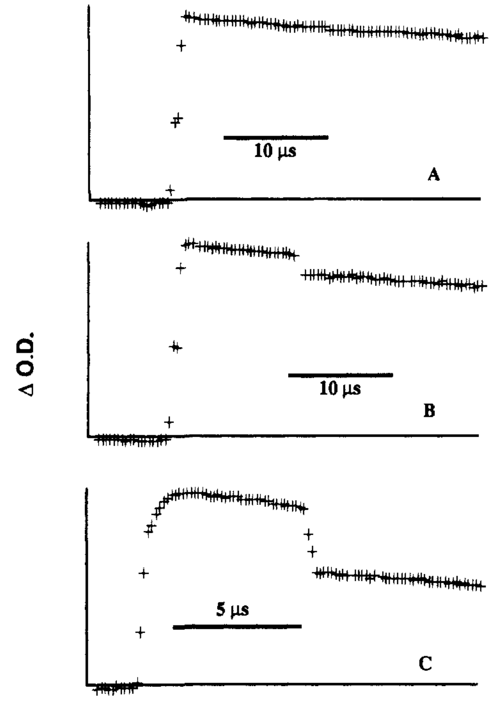

Figure 7. Decay of transients produced from 1,1,3,3-tetramethyl-2-indanone monitored at 360 nm for 308-nm excitation (trace A) and 308 followed by a 337-nm laser pulse in a flow system (trace B) and in a static cell (trace C). Laser frequency, 0.33 Hz. Note that the shorter time scale in trace C starts to reveal the growth that reflects the biradical lifetime. The apparent slow decay in trace A is due to a time constant of the system and not due to decay of III.

Our IR assignments have been included in Figure 6. These IR results confirm that the same species (III) is formed in cyclohexane and CCl_4. As in previous work[6,7] there is no detailed structural information readily obtainable from the spectra, but the similarities in the IR spectra of III and those reported for I confirm our assignments.

Two-Laser, Two-Color Irradiation. The experiments were carried out by using two-laser techniques in which 308-nm excitation was followed by 337-nm pulses after a delay of a few microseconds. The technique has been recently reviewed,[22] and the reader is referred to this article for details of the experiment.

While somewhat removed from the absorption maximum (see Figure 1), III shows significant absorption at 337 nm, where its precursor (V) is transparent. We find that 337-nm laser excitation of III leads to its photobleaching, as illustrated in Figure 7, where trace A shows a normal "one laser" trace monitored at 360 nm. Traces B and C in Figure 7 show the effect of 337-nm excitation on the concentration of III. Trace B, leading to about 10% photobleaching, was obtained in a flow system, where the 337-nm pulse can only bleach the concentration of III generated by the preceding 308-nm laser pulse. In contrast, trace C was obtained in a static cell, where the 337-nm pulse has access to at least some III (diffusion tends to remove it from the excitation region) generated by earlier 308-nm laser pulses. Note that in these experiments the lasers are pulsed at frequencies between 0.3 and 1 Hz. Quite clearly in the static cell about three times as much III is photobleached by each pulse, as compared with the flow cell; this is a consequence of the long lifetime of III.

No evidence for the formation of biradical VI was obtained upon photoexcitation of III. Thus, the direct photolysis of III must involve predominantly (and possibly exclusively) the singlet manifold. We have found that while two-laser experiments lead to the extensive photobleaching of III, they do not lead to any new products, suggesting that III yields IV both thermally *and* photochemically. The photobleaching of III appeared to be complete

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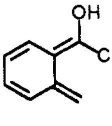
within the duration of the laser pulse.

These experiments show that photolysis of III leads to the formation of IV. In related experiments, McCullough et al.[9] have also observed that the lifetime of III was a function of the monitoring beam intensity in conventional flash photolysis experiments.

Discussion

The results of this study confirm and expand considerably our knowledge of the spectroscopic properties of *o*-xylylenes. Steric effects at the *exo*-CR_2 groups greatly enhance the lifetime of III in comparison with I, but have only minor effects on the UV-visible and IR spectra; thus λ_{max} values are 380 and 358 nm for I and III, respectively. The blue shift of III is probably a reflection of its expected nonplanarity due to the congestion of the methyls which leads to reduced conjugation. The infrared spectrum of III shows characteristic bands at 681 and 1212 cm^{-1}. Comparison with reported data[6,7] for other *o*-xylylenes under conditions of matrix isolation confirms our assignment of the structure of III. Our kinetic data also indicate that the lifetime of III is long enough to make it a useful intermediate in organic reactions.

We have been able to demonstrate for the first time that the photogeneration of III from IV involves the intermediacy of a species with a lifetime of 580 ns in benzene. We have assigned this intermediate to triplet biradical VI. Interestingly, the lifetime is much longer than that for typical photoenols[16] in nonpolar solvents, but it is comparable with those obtained in polar media. For example, for the enol derived from *o*-methylacetophenone,[14] XI, the lifetimes are 300 and 580 ns in methanol and in wet acetonitrile, respectively.



XI

Just as in the case of photoenols, VI shares the properties of biradicals and of excited states; that is, VI and the triplet state of III, $^3III^*$, are the same species. This is exemplified by the energy-transfer quenching by β-C, which occurs with a rate constant approaching diffusion control and leads to the formation of the readily detectable triplet state of β-C. Similarly, oxygen is a very efficient quencher.

Photoexcitation of III does not seem to yield any significant concentration of $^3III^*$, suggesting that intersystem crossing is a minor process in III. However, nitrogen laser irradiation of III does lead to extensive bleaching. This photobleaching does not result in the formation of any new products, indicating that both thermal or photochemical decay of III lead to the same product, generated by a 1,5-hydrogen shift to yield IV. McCullough et al.[9] have suggested that in the case of the nonplanar III the hydrogen shift must be antarafacial. This shift is ground state forbidden and excited state allowed.[9,23] Our results indicate that the photochemical 1,5-hydrogen shift occurs within the duration (~8 ns) of the 337-nm nitrogen laser pulse. When this is compared with the lifetime of 9.1 min for the thermal decay, we conclude that the excited state process in *at least* 10 orders of magnitude faster than the ground-state process, in full agreement with the allowed (excited) and forbidden (ground state) nature of these processes.

The behavior of III contrasts with that of I, which decays via dimerization to generate IIa and IIb. The fact that III does not dimerize is also reflected by its long lifetime.

Experimental Section

Materials. The solvents employed were Spectrograde or Gold Label and used as received. β-Carotene (Aldrich) was used as received. 2-Indanone (Aldrich) was chromatographed on silica gel and recrystallzed twice from hexane. 1,1,3,3-Tetramethyl-2-indanone (V) was synthesized from 2-indanone upon treatment with methyl iodide and powdered potassium hydroxide, in hot toluene, in the presence of catalytic amounts of [18]-crown-6.[24] After purification (chromatography on silica gel, followed by sublimation at low pressure), needles melting at 76–77 °C were obtained (lit.[25] mp 76–77 °C).

General Techniques. UV–visible spectra were recorded with a Hewlett-Packard 8451A diode array spectrometer. Infrared spectra were recorded with a Bomem Michelson-100 FT-IR instrument positioned on the same table on which laser flash photolysis experiments were carried out.

GC analyses were carried out on a Perkin-Elmer Model 8320 capillary gas chromatograph employing a 12-m J&W bonded phase vitreous silica BP1 silicone column. GC–MS analyses were performed on a Hewlett-Packard Model 5995 system.

Proton NMR spectra were recorded with Varian 60-MHz instruments. Melting points were determined in a Mel-Temp apparatus and were not corrected.

Preparative irradiations were carried out in Pyrex cells and in a reactor fitted with 9 RPR-3000 lamps. The temperature in the photolysis chamber was normally 30–35 °C.

Product Studies. In a typical experiment, 1 mL of a 0.03 M solution of V in benzene, contained in a Pyrex tube, was deaerated by bubbling with oxygen-free nitrogen and irradiated in a "merry-go-round" setup employing 9 RPR-3000 Rayonet lamps. The products were analyzed by GC and GC–MS using decane as an internal standard. Product IV was isolated by thin-layer chromatography and characterized by spectroscopic methods. ^1H NMR ($CDCl_3$): δ (ppm) 1.17 (d, 6 H), 1.98 (d, 3 H), 3.12 (sep, 1 H), 4.70 (m, 1 H), 5.08 (m, 1 H), 7.06 (m, 1 H) in accord with literature data.[13] MS *m/z*: 160 (39, M^+), 145 (100), 117 (40), 115 (25), 91 (24), 77 (10), and 63 (11). IR (CCl_4): 1642 and 900 cm^{-1}.

Quenching studies with dimethyl acetylenedicarboxylate were carried out employing concentrations of this scavenger in the 0.016–0.24 M range.

In the two-laser, two-color experiments the samples containing 0.015 M V in benzene were continuously bubbled with nitrogen during the experiment to avoid excessive accumulation of product in the irradiation region. No new products in addition to IV were detected by gas chromatography. The yield of IV was insensitive to the excitation of III by the second (337 nm) laser.

Laser Photolysis. Xylylenes were generated by photolysis of the corresponding indanone precursor with a Lumonics TE860-2 excimer laser (308 nm, ~5 ns, ≤20 mJ/pulse). For the two-laser experiments a Molectron UV-24 nitrogen laser (337 nm, ~8 ns, ≤10 mJ/pulse) was used to excite the xylylene. Our detection system incorporates a monochromator–photomultiplier system; the signals from the RCA-4840 photomultiplier were initially captured by an R-7912 Tektronix digitizer and transferred to a PDP11/23$^+$ computer that controls the system and provides suitable storage and processing facilities. Further details have been reported elsewhere.[26,27]

Some of the transient spectra were obtained with a gated intensified optical multichannel analyzer (Series III, from EG&G), which has been interfaced (EG&G interface Model 1461) to a PDP11/73 computer.

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