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(14) J. M. Eckert and R. J. W. Le Fèvre, *J. Chem. Soc.*, 3991 (1962).
(15) The end absorption of the amine moiety in **13** would be hidden beneath the 241-nm band.
(16) It should be realized that this explanation is not definitive because the single conformer **11**, in analogy to **10** alone, may give rise to the spectrum of **3**.
(17) Unpublished results from this laboratory indicate that ϕ_f's of acyclic trialkylamines such as triethylamine (fluorescence λ_{max} 282 nm) and dimethylethylamine (fluorescence λ_{max} 292 nm) are in the 0.5–0.6 range.
(18) A. M. Halpern, R. J. Sternfels, and P. Ravinet, to be submitted for publication. Data were obtained in *n*-hexane at 25 °C. Self-quenching rate constants were ca. 2×10^{10} M^{-1} s^{-1}.
(19) A. M. Halpern and D. K. Wong, *Chem. Phys. Lett.*, **37**, 416 (1976).
(20) In the case of tropinone, no emission was detected from the state populated (presumedly carbonyl π, π^*) via the σ-coupled transition because of internal conversion to the n, π^* state.
(21) Fluorescence data for 2-adamantanone, **9**, and norcamphor are reported in ref 5: **9**, $\phi_f = 5.2_4 \times 10^{-3}$, $\tau_f = 7.9$ ns, $k_r = 6.6 \times 10^5$ s^{-1}, fluorescence λ_{max} 427 nm; norcamphor, $\phi_f = 3.3_5 \times 10^{-3}$, $\tau_f = 4.9$ ns, $k_r = 6.8 \times 10^5$ s^{-1}, fluorescence λ_{max} 425 nm.
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(25) The production of a highly fluorescent photoproduct in the 300-nm region would obviously complicate the determination of the intrinsic quantum yield for amine-like fluorescence from the β-amino ketones. Care was taken to determine the ϕ_f's in Table II rapidly and on freshly prepared solution before appreciable photolysis could take place.
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A Photoisomer of 1,3,6,8-Tetraphenylcyclooctatetraene as a 1:1 Mixture of 1,2,4,7-Tetraphenylcyclooctatetraene and 2,5,7,8-Tetraphenylbicyclo[4.2.0]octatriene in Dynamic Equilibrium. A Structural Enigma

Emil H. White,* Robert L. Stern, Thomas J. Lobl, Stephen H. Smallcombe, Howard Maskill, and Earl W. Friend, Jr.

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218.

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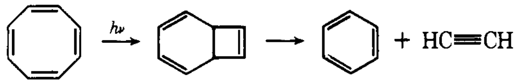
Abstract: The irradiation of 1,3,6,8-tetraphenylcyclooctatetraene (I) yields a photoisomer. This material, which behaves as a single substance in most tests, was ultimately shown to be a 1:1 mixture of 1,2,4,7-tetraphenylcyclooctatetraene (XV) and 2,5,7,8-tetraphenylbicyclo[4.2.0]octatriene (VIII) in mobile equilibrium at 25 °C.

The irradiation of cyclooctatetraene in the solid,[1] liquid,[2,3] and gas[4] phases yields benzene and acetylene, presumably via the valence isomer bicyclo[4.2.0]octatriene. The photochemical addition of an acetylene to benzene to give a 1,2-disubstituted cyclooctatetraene has also been demonstrated, and the bicyclic valence isomer was invoked as a probable intermediate.[5] The bicyclic isomer is also accessible[6] thermally as shown by trapping experiments with dienophiles[7] and by cleavage to give the corresponding acetylene and benzene in the case of a tetracarbethoxycyclooctatetraene.[8] Bicyclo[4.2.0]octatriene has also been synthesized by ground-state reactions;[9] the parent compound is labile, reverting to cyclooctatetraene with a half-life at 0 °C of 14 min.



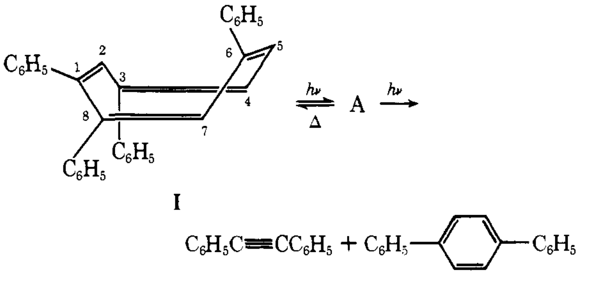
(1)

We report here details of an investigation of the photochemical conversion of 1,3,6,8-tetraphenylcyclooctatetraene (I)[3,10a] into an isomer, A. On the basis of the physical and chemical properties of photoisomer A we conclude that it is a 1:1 mixture of 1,2,4,7-tetraphenylcyclooctatetraene (XV) and 2,5,7,8-tetraphenylbicyclo[4.2.0]octatetraene (VIII) in dynamic equilibrium.[10] The *chemical* evidence gathered in the structure proof was ambiguous, and we suspect that this structural problem could not have been solved on the basis of the chemical results alone.

Results

1,3,6,8-Tetraphenylcyclooctatetraene (I) was prepared by treatment of 1,3-diphenyl-2,4-bis(dimethylamino)cyclobutane dimethiodide with a strong base.[12] Yields of about 30% of I were achieved accompanied by 1,3,5,7-tetraphenylcyclooctatetraene (II, 39%) and smaller amounts of other products.[1,13]

Photochemistry of 1,3,6,8-Tetraphenylcyclooctatetraene (I). The irradiation of compound I under a variety of conditions yielded a photoisomer, A (eq 2). Hexane solutions of I were



$$C_6H_5C{\equiv}CC_6H_5 + C_6H_5{-}C_6H_4{-}C_6H_5 \quad (2)$$

irradiated with 40-W General Electric "Cool White" fluorescent lights, 275-W General Electric sunlamps, and 450-W Hanovia mercury lamps. Whether solutions were degassed and sealed under vacuum or irradiated while open to the atmosphere appeared to make no significant difference. In all cases, the concentration of I decreased during irradiation while the concentration of A increased first (to a maximum of about 58%

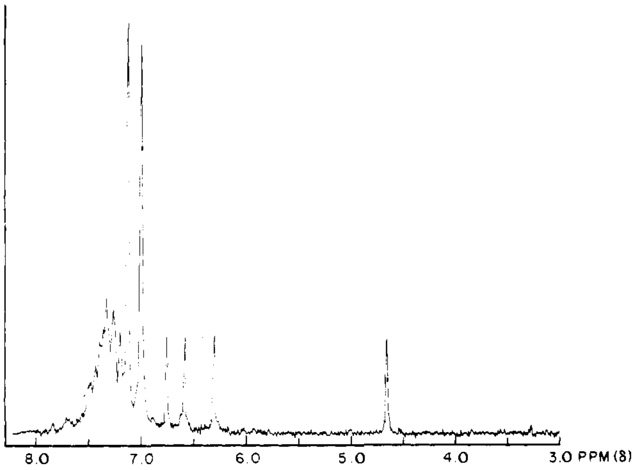


Figure 1. The 60-MHz NMR spectrum of photoisomer A (XV ⇌ VIII) in $CDCl_3$ (ppm from Me_4Si).

conversion), then decreased. The ultimate products of irradiation were tolane and *p*-terphenyl (68–100% depending upon conditions).[3] Similar results were obtained at −80 °C. These changes were monitored by uv and fluorescence spectroscopy, and it appeared that two consecutive first-order processes were being observed: the conversion of I to A and the conversion of A to tolane and *p*-terphenyl (eq 2). Consistent with this view is the observation that in solution at 25 °C and in the solid state at −196 °C, photoisomer A yields diphenylacetylene and *p*-terphenyl on irradiation (albeit slowly in the latter case).

On a preparative scale, 0.04 M solutions of I in hexane were irradiated. Under these conditions the photoisomer precipitates out of solution; since A is relatively photostable in the solid state, this technique minimizes the photodegradation of A.

Photoisomer A. The thermal reversion of A to I was followed by uv, NMR, ir, and fluorescence spectroscopy and also by TLC. Always, the only detectable product was I. By following the reaction spectrofluorometrically at 25 °C, the isomerization was shown to be first order with $k_{(\mathrm{isom})} \approx 10^{-5}\ \mathrm{s}^{-1}$, which corresponds to a half-life of approximately 18 h. When iodine was added to the solution at 25 °C, this rate was increased sevenfold. When the isomerization was followed by uv spectroscopy, isosbestic points were obtained at 240 and 290 nm—as expected if a single compound were being formed from another single compound. In the solid state A is quite stable, and only by heating a potassium bromide disk to 125 °C for 12 h was it possible to effect some conversion to I (followed by ir). There was no evidence for the formation of compounds other than I.

Only fair elemental analyses for $C_{32}H_{24}$ were obtained for photoisomer A (Experimental Section); oxygenation was suspected[14,15] and tested for by treating a solution of A in methylene chloride with oxygen. The only result, however, was partial isomerization back to I; no oxygenated products were observed. It appears that photoisomer A binds solvent on crystallizing. Consistent analyses were obtained after recrystallization from a given solvent, which were different from results obtained after recrystallization from another solvent.

Physical and Spectral Properties of A. The photoisomer was obtained as hairlike, colorless needles, mp 122.5-123 °C.[16] Repeated molecular weight determinations gave results with an average of 449 (theor = 408).[17] The NMR spectrum of A in deuteriochloroform is reproduced in Figure 1; very similar spectra were obtained at 100 MHz and also in deuteriobenzene. There was no significant change in the spectrum when solutions were cooled from 40 to −40 °C, and at 70 °C the only obvious change was the appearance of I due to thermal isomerization of A. In the thermal conversion of A into I, the two singlets at 6.31 and 4.69 ppm decreased at the same rate. It was established by double resonance[18] that there is no detectable coupling between the four upfield singlets of Figure 1.

The uv absorption spectrum of A [255 nm (log ε 4.38), 350 (4.05)] is similar to that of I [263 (4.66), 325 (3.81)]; the long-wavelength maximum clearly indicates the presence of an extensively delocalized system. Like the NMR spectrum, the uv spectrum does not change with temperature (−70 to +25 °C), though at −196 °C some fine structure begins to appear. Unlike I, A is fluorescent [$\lambda_{\max}$ (fluorescence) 445 nm; λ (excit) 365 nm], which indicates an increased measure of rigidity in the molecule.[19] The long wavelength absorption band and the fluorescence maximum are at approximately the same wavelengths as those for dimethyl 1,4-diphenylcyclohexa-1,3-diene-*trans*-5,6-dicarboxylate.[20]

The most significant feature of the ir spectrum of A is that, as in the case of the uv spectrum, it is very similar to that of I. The most significant difference is that A shows more and sharper bands in the fingerprint region. This, like fluorescence, is indicative of a more rigid molecule. Compounds A and I both show weak absorption just below 3000 cm^{-1} in the infrared (2900 cm^{-1} for A and 2920 cm^{-1} for I); the 2920 band for I may be an overtone. There is no change in the ir spectrum of solid A down to −129 °C. Differences were noted in the fingerprint regions of spectra in the solid state and in solution, but it was not known whether these differences were the result of association in the solid state or the selective crystallization of one compound from a mixture. ^{13}C NMR spectra and selective proton NMR spectra, which were obtained late in the structural work, are given in a later section.

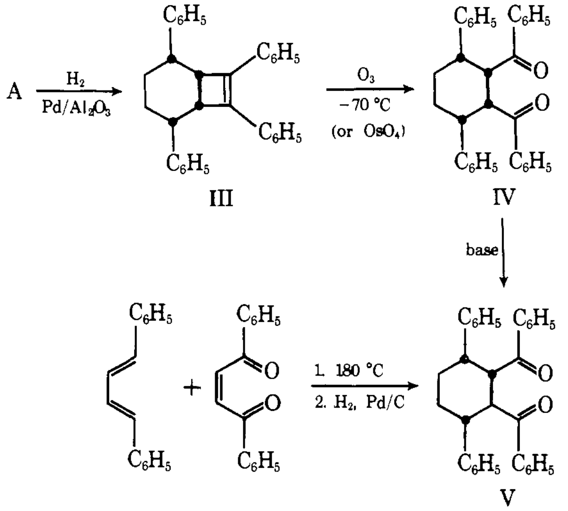
Chemical Properties of A. 1. Hydrogenation. The photoisomer A ($C_{32}H_{24}$) added 2 molar equiv of hydrogen to give a hydrocarbon, $C_{32}H_{28}$. After repeated recrystallization and chromatography this hydrocarbon was shown to be homogeneous by ir, uv, NMR, and fluroescence spectroscopy and by TLC. The electronic spectra [λ_{sh} 228 nm (log ε 4.36), $\lambda_{\max}$ 288 (4.13); $\lambda_{\max}$ (fluorescence) 405 nm ($\lambda_{(\mathrm{excit})}$ 310 nm)] are suggestive of a 1,2-diphenylcyclobutene chromophore.[21] These results and the NMR spectrum [7.13 ppm (s, 10 H), 6.96 (s, 10 H), 3.58 (m, 4 H), 2.05 (m, 4 H)] are consistent with structure III.

Tetrahydro A reacted with ozone at −70 °C to give, after hydrogenolysis, a diketone (IV); chromatography on basic alumina converted IV to an isomeric diketone V. Compound V was independently synthesized by the Diels–Alder reaction of *cis*-1,4-diphenylbut-2-ene-1,4-dione and 1,4-diphenylbuta-1,3-diene, followed by hydrogenation of the initially formed adduct. An alternative to ozonolysis of an olefin is hydroxylation with osmium tetroxide, followed by oxidative cleavage of the vicinal diol to give the corresponding diketone.[23] In the present case the cis,cis,cis diketone (IV) was obtained directly in 57% yield after cleavage of the osmate ester (from III) with hydrogen sulfide. This direct cleavage is not without precedent,[24] and it may be the rule for cyclobutenes. Compound IV was again isomerized to V on chromatography, but if pyridine was used as solvent for the osmium tetroxide cleavage, V was obtained directly. These reactions are shown in Chart I, and they clearly corroborate the spectral evidence suggesting structure III for the hydrogenated photoisomer.

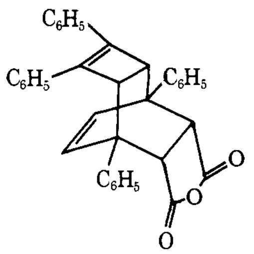
To confirm that direct formation of a diketone from osmium tetroxide cleavage of a cyclobutene is not exceptional, 1,2-diphenylcyclobutene was oxidized by the same procedure; 71% of 1,4-diphenylbutane-1,4-dione was obtained. Tetraphenylethylene also showed some cleavage. These results are in contrast to the reaction of 1,2-diphenylcyclohexene with osmium tetroxide from which Tomboulian[25] obtained 47% of *cis*-1,2-diphenyl-1,2-dihydroxycyclohexane.

2. Reaction of A with Dienophiles. At 25 °C, photoisomer A forms a crystalline, fluorescent adduct ($C_{36}H_{26}O_3$) with

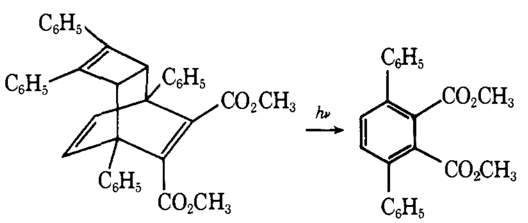
Chart I



maleic anhydride. (It was established that I did not give adducts with maleic anhydride or dimethyl acetylenedicarboxylate at 25 °C.)[26] The adduct gave a uv spectrum, λ_{max} 292 nm (log ϵ 4.11), which is characteristic of a 1,2-diphenylcyclobutene.[21] On the basis of the analysis, the uv spectrum, and the NMR spectrum [7.15 ppm (m, 22 H), 4.27 (s, 2 H), 3.78 (s, 2 H)], structure VI (or a stereoisomer) was assigned to this adduct.



VI

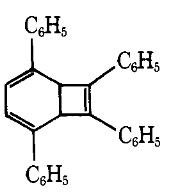


VII

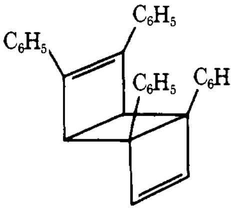
The reaction of A with dimethyl acetylenedicarboxylate at 25 °C also produced a crystalline, fluorescent adduct ($C_{38}H_{30}O_4$). The fluorescence spectrum (384 nm, $\lambda_{(excit)}$ 320 nm) is consistent with a diphenylcyclobutene chromophore;[21] together with the NMR spectrum [7.35 ppm (m, 10 H), 6.96 (m, 10 H), 6.80 (s, 2 H), 3.92 (s, 2 H), 3.22 (s, 6 H)] and the mode of synthesis, structure VII is suggested. The somewhat anomalous absorption in the uv (272 nm, compare with the spectrum of VI) may result from interactions between the three double bonds of the tricyclic system of VII.

Adduct VII (like VI) is thermally stable up to its melting point. When a 10^{-4} M ethanolic solution of it was irradiated, a clean conversion occurred and dimethyl 3,6-diphenylphthalate[27a] was formed in 56% yield. Reduction of VII with lithium aluminum hydride led to an alcohol ($C_{36}H_{32}O_2$) which had virtually the same uv spectrum (λ_{max} 274 nm) and fluorescence spectrum [λ_{max} (fluorescence) 384 nm] as VII. The analysis corresponds to the reduction of a 1,2-dicarbomethoxyethylene moiety to 1,2-bis(hydroxymethyl)ethane.[27b]

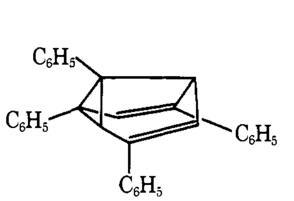
The Possibility of a Single Structure for Photoisomer A. The physical and chemical information we obtained for photoisomer A up to 1974 appeared contradictory. The NMR spectrum (Figure 1) with one uncoupled high field signal for one hydrogen proved impossible to assign to a single structure when consideration was given to the ultraviolet absorption spectrum and other data, yet hydrogenation yielded a single substance (III) by all the tests available and in quantitative yield. The single structures that were considered included the bicyclo[4.2.0]octa-2,4,7-trienes (VIII[3] and four other positional isomers), the tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes (IX and five other positional[12] and geometrical isomers), the tricyclo[5.1.0.0^{4,8}]octa-2,5-dienes (e.g., X),[2,14] the tricyclo[3.3.0.0^{2,6}]octa-3,7-dienes (e.g., XI),[28,29] the tricyclo[4.1.1.0^{7,8}]octa-2,4-dienes (e.g., XII), the dihydrophenanthrenes (e.g., XIII],[30] the *trans,cis,trans,cis*-tetraphenylcyclooctatetraenes, and the mono-*trans*-tetraphenylcycloocta tetraenes. With respect to the latter structure, which we earlier assigned to the photoisomer,[11] one of the five possible isomers (XIV) comes very close to accounting for the physical and chemical properties of the photoisomer,[10,11] but it is inadequate to account for the ^{13}C NMR spectrum and the low-temperature reactions of the photoisomer (vide infra).



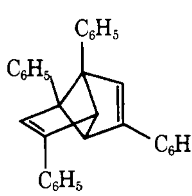
VIII



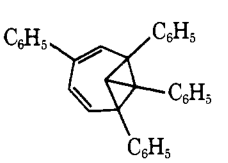
IX



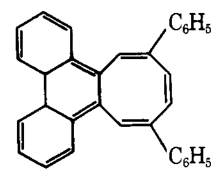
X



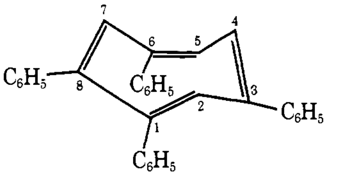
XI



XII



XIII



XIV

Photoisomer A as a Pair of Valence Isomers in Equilibrium. Since no single structure could account for all the properties of the photoisomer, various equilibria were considered. The most successful involving similar structures was an equilibrium between equal amounts of bicyclooctatrienes VIII and VIII′.

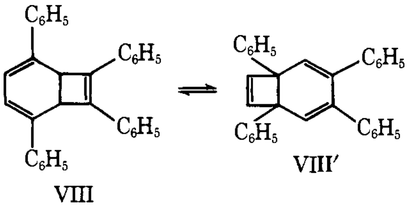


Chart II

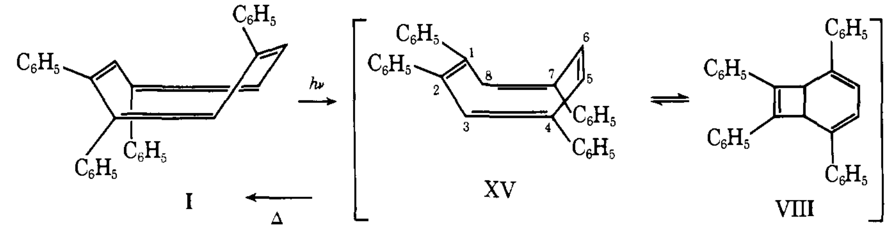
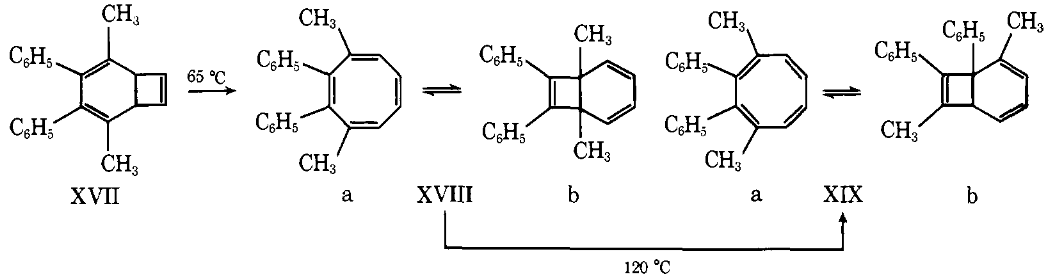


Chart III



Assuming $K = 1$ ($\Delta G° = 0$) and $\Delta H° = 0$, this equilibrium mixture can account for the chemical reactions undergone by the photoisomer and for the NMR, ir, and fluorescence spectra and tolerably well for the uv spectrum. In 1974, ^{13}C NMR spectra and low-temperature spectra were obtained which eliminated equilibrium VIII $\rightleftarrows$ VIII′ from consideration.

Structure of Photoisomer A. The new data show that photoisomer A is an equimolar mixture of 1,2,4,7-tetraphenylcyclooctatetraene (XV)[10a] and 2,5,7,8-tetraphenylbicyclo[4.2.0]octatriene (VIII) in dynamic equilibrium (Chart II).

The ^{13}C NMR spectrum (proton decoupled) shows a single peak at high fields (44.319 ppm from Me_4Si) consistent with the presence of a single kind of sp^3 carbon in XV $\rightleftarrows$ VIII. Gated decoupled spectra show that this carbon is coupled to one hydrogen ($J = 142$ Hz), the coupling constant being consistent with the bridgehead nature of the carbon.[31] The low field range of the decoupled spectrum contains eight sharp signals (144.5–134.6 ppm), which would be expected for the eight different unsaturated quaternary carbons of XV $\rightleftarrows$ VIII. Some of the remaining expected 15 signals in the total spectrum are unresolved (133.3–121.4 ppm). The starting cyclooctatetraene (I, $C_{32}H_{24}$) with a twofold axis of rotation gave the simpler spectrum expected: four low field (143.4–139.6 ppm) and eight higher field (130.2–126.1 ppm) bands (decoupled spectra).

The following low-temperature proton NMR spectra clinch structure XV $\rightleftarrows$ VIII for the photoisomer. A solution of the photoisomer in deuteriochloroform was evaporated under vacuum (probable temperature <0 °C), and the resulting crystals were dissolved in deuteriochloroform at −40 °C; the NMR spectrum of this solution was similar to that of Figure 1.[32] When the crystalline sample was prepared by evaporation at 25 °C and then dissolved at −40 °C, however, the NMR spectrum showed only half the peaks shown in Figure 1. Peaks were present at 4.65, 6.28, and 6.94 ppm, but the peaks at 6.51 and 6.73 were completely missing, and the phenyl peak at 7.05 ppm had disappeared into the multiplet for the remaining phenyl groups. When the sample was allowed to warm to −15 °C, the spectrum reverted within minutes to the familiar spectrum of Figure 1. The addition of 4-phenyl-1,2,4-triazoline-3,5-dione (XVI) at −40 °C to XV $\rightleftarrows$ VIII led to a loss of only the signals at 4.65, 6.28, and 6.94 ppm[33] and the appearance of a signal attributable to the adduct, ~4.07 ppm. Upon warming to 25 °C, the signals of cyclooctatetraene XV also disappeared, presumably via VIII.

These observations are consistent with the view that crystals of photoisomer A—prepared at temperatures where equilibration can occur—consist solely of bicyclic form VIII. The 4.65, 6.28, and 6.94 ppm peaks of Figure 1 are thus assigned to protons on $C_{1,6}$, $C_{3,4}$, and the vicinal phenyls on the cyclobutene ring, respectively; the noncoplanarity of these crowded phenyl rings presumably accounts for the fact that the ring hydrogens appear as a singlet in the spectrum (Figure 1) despite the fact that the rings are attached to a double bond.[34] Similarly, the 6.51 and 6.73 ppm peaks of Figure 1 are assigned to the cyclooctatetraene hydrogens of form XV and the 7.05 peak is assigned to the vicinal phenyl groups.

The reactions and interconversions outlined above are analogues of a parallel set reported by McCay and Warrener[35] involving a dimethyldiphenylcyclooctatetraene (Chart III). Fortunately, in their case the equilibrium constant was not unity, so that the peak heights in the NMR spectra revealed directly that a mixture of two components was involved.[36]

System XV $\rightleftarrows$ VIII for photoisomer A is also consistent with the chemical reactions it undergoes if one allows the reasonable assumption that the hexadiene moiety of form VIII is the most reactive part of system XV $\rightleftarrows$ VIII. Structure XV $\rightleftarrows$ VIII is also consistent with the proton NMR spectrum (Figure 1), noting that forms XV and VIII both have a plane of symmetry and that the dihedral angles for the dissimilar nonphenyl hydrogen atoms of VIII are near enough to 0 °C to ensure undetectable coupling.[37] Lastly, the structure is consistent with the uv absorption spectrum [tetraphenylcyclooctatetraene (see text) + 1,2-diphenylcyclobutene[21] + 1,4-diphenylhexadiene[20]], with the ir spectrum (2900 cm^{-1} absorption), and with the fluorescence spectrum.[20]

The independent existence of cyclooctatetraenes I and XV (also XVIIIa and XIXa) at 25 °C is noteworthy. The barrier between double bond isomers of the parent cyclooctatetraene and monosubstituted cyclooctatetraenes is ~16 kcal, and the rate of interconversion at 25 °C is rapid ($T_{1/2}$ = seconds).[38] The high barrier separating the double bond isomers listed above is undoubtably a result of the increase in nonbonded interactions of adjacent substituents on reaching the planar configuration of the transition state separating the double bond isomers.[35b]

Steric interactions of the vicinal phenyl rings in compounds XV and XVIIIa presumably account for many of the unusual properties of these species. Cyclooctatetraene XVIIIa is in equilibrium with the bicyclic form XVIIIb because of a partial relief of the adjacent phenyl interaction in XVIIIb brought about by the larger Ph—C═C—Ph bond angle in the cyclobutene system.[39,40] A similar explanation accounts for the equilibrium between XV and VIII. No appreciable concentration of the bicyclic form is in equilibrium with cyclooctatetraene I; the adjacent phenyl rings in this case are relatively strain-free because of the natural "tub" shape of the cyclooctatetraene ring which leads to an appreciable dihedral angle for the adjacent phenyl rings. The freedom from strain in cyclooctatetraene I presumably accounts for its greater stability relative to cyclooctatetraene XV [(XV $\rightleftarrows$ VIII) $\xrightarrow{\Delta}$ I]. Photochemical double bond isomerizations have been reported for several 1,2-disubstituted cyclooctatetraenes, but formation of a corresponding bicyclooctatriene was not noted in those cases.[41]

In retrospect, the most unsettling experimental results concerning the structure of our photoisomer (A = XV $\rightleftarrows$ VIII) were the observations from the NMR spectra that $K = 1$ and ΔH° = effectively 0.[32] Coupled with the chemical reactions, these data provided a strong (but erroneous) incentive to devise a single structure for the photoisomer.

The equilibrium between XV and VIII is related to the fluxional processes occurring in molecules such as bullvalene[42] and some organometallic compounds.[43] In the present case, interestingly, nonidentical partners are involved.

Experimental Section

Ozonolysis experiments were run using a Welsbach Laboratory Ozonizer Model T-408 operating with predried air; ir spectra were recorded on Perkin-Elmer Models 137, 337, or 521; uv spectra were recorded on a Cary 14; melting points were determined with a Kofler hotstage apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Varian Models A-60 and HA-100 and on a JEOL Model MH-100. ^{13}C NMR spectra were recorded on a Varian XL-100-15 FT. Proton and carbon chemical shifts are recorded in ppm units relative to internal tetramethylsilane and refer to the center of gravity of the signal. Fluorescence spectra were recorded on either a Perkin-Elmer Hitachi or an Aminco-Bowman apparatus and wavelengths were calibrated by the superposition of the fluorescence spectrum of a standard solution of anthracene. Solvents were reagent grade chemicals. Hexane for spectral and low-concentration photolyses experiments was spectroquality grade and was checked by uv before use. Elemental analyses were done either by Mr. J. Walter of this department or by Galbraith Laboratories (Knoxville, Tenn.).

Preparation of 1,3,6,8-Tetraphenylcyclooctatetraene (I). (a) Heterogeneous Runs. To 350 ml of *tert*-butyl alcohol (freshly distilled from potassium) was added 13.9 g of clean potassium, and the mixture was allowed to react under reflux during 5 h. Then, under nitrogen, 19.5 g (33.8 mmol) of 1,3-diphenyl-2,4-bis(dimethylamino)cyclobutane dimethiodide[12] was added followed by gentle heating to continue the refluxing for 10 h. The flask was cooled, 500 ml of water was added, and the solution was exhaustively extracted with benzene (or ether). The combined organic phase was successively washed with 1% hydrochloric acid, dilute sodium bicarbonate solution, and finally with water. After the solution had been dried with sodium sulfate, evaporation of the solvent in vacuo gave 7.5 g of a yellow solid. This crude product was chromatographed on alumina with hexane-ether, and 2.7 g (6.6 mmol, 39.2%) of compound II was obtained from the fractions containing 15–19% ether. From the fractions of 20–25% ether was obtained 2.0 g (4.9 mmol, 28%) of II. The latter material was recrystallized from hexane to give 1.2 g (2.9 mmol, 17%) of pure cyclooctatetraene I as yellow plates: mp 132–133 °C (lit. 133–134 °C);[12] uv λ_{max} (heptane) 263 nm (log ϵ 4.66), 325 (3.81); NMR 7.33 (m, 20 H), 6.88 (s, 2 H), 6.61 ppm (s, 2 H); ir 3100–3000, 1600, 1500, 1455, 1010, 882, 820, 755, 695, and 530 cm^{-1}.

(b) Homogeneous Runs. A solution of 50 ml of benzene, 2 g (3.46 mmol) of 1,3-diphenyl-2,4-bis(dimethylamino)cyclobutane dimethiodide and 2.74 g (27.0 mmol) of potassium *tert*-butoxide was heated under reflux for 100 h. The mixture was allowed to cool, and it was then extracted with 60 ml of 5% hydrochloric acid. The benzene phase was washed with sodium bicarbonate solution, with water, and then it was dried with sodium sulfate. The benzene was evaporated in vacuo to give 1.75 g of a solid. Chromatography on alumina gave approximately equal amounts of I and II. Recrystallization of I from dichloromethane-ethanol give 171 mg (0.42 mmol, 24%), and the physical and spectral properties were exactly as described above and as reported earlier.[1]

Irradiation of Compound I in Dilute Solution. (a) 275-W Sunlamps. A 2.1 × 10^{-5} M solution of I hexane was placed in a 10-mm o.d. quartz cell with a Pyrex graded joint. It was degassed through five freeze–thaw cycles and sealed under vacuum. The solution was then irradiated through the Pyrex part of the cell with a 275-W General Electric sunlamp placed 30 cm away; the temperature was maintained at 26–28 °C by using a quartz water heat baffle inserted between the sunlamp and the sample. The effect of the irradiation was monitored by following the intensity of the main fluorescence band of A at 445 mm ($\lambda_{(excit)}$ 365 nm). The intensity of the peak increased for ca. 5 min and then began to decrease slowly; the maximum corresponded to 58% conversion to the photoisomer. After 131 min irradiation, only 1.3% of the photoisomer remained; another fluorescence band at 343 nm ($\lambda_{(excit)}$ 295 nm) indicated a yield of 68% of *p*-terphenyl (the spectrum of the other product, tolane, was hidden by the intense *p*-terphenyl fluorescence); a weak fluorescence at 422 nm was also observed.

(b) Intense Irradiation with 275-W Sunlamps. A 2.03 × 10^{-5} M solution of I in hexane was placed in a quartz-Pyrex cell and degassed as above. Then, two 275-W General Electric sunlamps were placed 1 cm from the tube which was maintained at 15 °C by cold, running water (these are the same conditions used in the preparation of A except at much lower concentration). The irradiation was followed in this run by using the ultraviolet spectrum.

In the first 6 min, a band at 340 nm formed, while the original cyclooctatetraene band at 260 nm decreased as expected for formation of the photoisomer; but after 10 min the peak at 340 nm began to decrease and a shoulder appeared at 240 nm on the main peak. After 2 h of irradiation, all absorption above 300 nm disappeared and that below 300 nm showed increased fine structure but decreased overall intensity. The fine structure was probably due to tolane.

(c) Mild Irradiation with 40-W General Electric "Cool White" Fluorescent Lamps. Fluorescent lamps were used to irradiate (at 15 cm) two aliquots of a 1.57 × 10^{-5} M solution of I, one degassed and sealed under vacuum, the other exposed to the laboratory atmosphere. Here the fluorescence bands of the photoisomer and a cleavage product, *p*-terphenyl, were used to monitor the extent of conversion. A maximum of 45% of the photoisomer was formed after 4 h irradiation in the degassed cell; the open cell maximum conversion was 38%. The constant increase of the *p*-terphenyl fluorescence reached the ≈100% mark in 25 h in the degassed cell and 68% in the open cell.

Similarly, irradiation with a 150-W incandescent lamp led to *p*-terphenyl (30%) and photoisomer A (60%), while irradiation with a GE low-pressure mercury lamp (Germicidal Lamp) yielded the photoisomer fairly cleanly.

Photoisomer A. Hexane (4 ml) was added to a 10-mm o.d. Pyrex tube containing 80 mg (0.18 mmol) of I to give a 4.5 × 10^{-2} M solution. The solution was degassed using liquid nitrogen as coolant (through five freeze–thaw cycles), and the tube was sealed under vacuum. It was heated to approximately 80 °C to effect maximum solution of I and then was irradiated for 2 h with two 275-W General Electric sunlamps placed 1 cm away. The tube was maintained at ca. 15 °C during the irradiation by continuously flowing cold water but was removed periodically and warmed to redissolve I. (Unless this was done, a matrix of I and A formed on the inside surface of the tube, and this effectively stopped further conversion of I into A.) Usually, a fluorescent glow appeared after ca. 10 min irradiation, photoisomer A crystallized after ca. 20 min, and the conversion was complete after 1.5–2 h.

The tube was then opened, and the solvent was evaporated in vacuo. Recrystallization from ether (or methylene chloride-ethanol) gave 44 mg (0.11 mmol, 55%) of the photoisomer as fine, colorless needles: mp 121–122 °C; uv λ (hexane) 255 nm (log ϵ 4.38), 350 (4.05); λ_{max} (hexane) (fluorescence) 445 nm, $\lambda_{(excit)}$ 365 nm; ir (KBr) 3080–3000, 2900, 1590, 1495, 1445, 1350, 915, 855, 790, 770, 757, 742, 725, 710, 692, 595, 550, 515, and 490 cm^{-1}; NMR (Figure 1) 7.3 (m, 20 H), 6.79 (s, 1 H), 6.58 (s, 1 H), 6.31 (s, 1 H), 4.69 ppm (s, 1 H) (see text for closely related values obtained with a different spectrometer).[32] Molecular weight[21] (theor 408) 442, 442, 449 (freezing-point depression of benzene solutions), 462 (Merchrolab osmometer), average = 449.

Anal. Calcd for $C_{32}H_{24}$: C, 94.08, H, 5.92. Calcd for $C_{32}H_{24} \cdot 0.25C_4H_{10}O$: C, 92.81, H, 6.25. Found: C, 92.82; H, 6.19 (recryst diethyl ether; C, 93.46; H, 6.19 (hexane–toluene).

Low-Temperature Spectra of A. The NMR spectra at −40 and −20 °C in deuteriochloroform (prepared by cooling solutions from 25 °C) showed slight broadening of the various singlets compared with the spectrum at 25 °C. But the positions were not altered. At least part of the line broadening is due to the crystallization of A.

The uv spectrum of A in a 4:1 methylcyclohexane–ether glass at −196 °C showed increased molar extinctions (ca. 2×) and additional fine structure at 230, 240, 255, 268, 349, 366, and 387 nm. But there was no change in positions of maxima, and the density effect largely accounts for increased absorption. Irradiation of the glass at −196 °C by a General Electric 275-W sunlamp produced very little change, whereas a medium-pressure mercury lamp produced significant changes which were ascribable to the formation of *p*-terphenyl and tolane.

The ir spectrum was recorded in a KBr matrix at −129 °C; it was identical with that obtained at room temperature.

Attempted Spin Decoupling. The NMR spectrum of A (20 mg in 0.4 ml of deuteriochloroform) was recorded at 100 MHz as each of the sharp singlets was irradiated in turn. No effect at all was detected upon the rest of the spectrum, and it was concluded that there is no coupling (or very little) between the hydrogens which give rise to the singlets.

Thermal Conversion of A to I. (a) Ultraviolet Monitoring. The isomerization at 25 °C of a 3.2×10^{-5} M solution of A in diethyl ether was followed by measuring the uv spectrum over an estimated five half-lives; isosbestic points at 240 and 290 nm were observed. A good first-order plot was obtained.

(b) Fluorescence Monitoring. The fluorescence spectra ($\lambda_{(\text{excit})}$ 365 nm) of a 2.1×10^{-5} M solution of A in hexane at 25 °C were recorded over 6 half-lives. A first-order process was observed ($k \approx 10^{-5}$ s^{-1}, $T_{1/2} \approx 18$ h). In another aliquot, a small crystal of iodine was added which subtantially increased the rate of isomerization ($T_{1/2} \approx 2.5$ h).

(c) NMR Monitoring. The isomerization of A in deuteriochloroform was followed over 5 h by measuring the intensity of the NMR singlets at 6.31 and 4.69 ppm. The extrapolated half-life by this method was 10.5 h at ca. 30 °C and ca. 16 min at 60 °C; following the resonances at 6.31 and 4.69 ppm led to the same decay values.

(d) Isomerization of A in the Solid State. A KBr disk of the photoisomer which showed no bands characteristic of I had remained unchanged during 4 months at room temperature. However, when the disk was heated at 125 °C for 12.5 h, significant decreases in the intensities of the bands due to A were noted as well as a corresponding appearance of bands due to I. No bands were observed which are not due to either A or I.

Attempted Addition of Oxygen. A solution of 25 mg (0.061 mmol) of the photoisomer in 5 ml of methylene chloride was stirred at 0 °C for 4.5 h under an atmosphere of dry oxygen. Solution ir spectra showed that at the end of this period no significant change had occurred: infrared bands at 1010 and 755 cm^{-1} changing slightly in intensity and the formation of bands at 890 and 575 cm^{-1} indicated that the only change was the isomerization of the photoisomer into cyclooctatetraene I. The solution was then allowed to warm to ca. 25 °C and was stirred for an additional 5 h under oxygen. The infrared spectrum once more showed further decomposition to compound I but no new compound appeared to be formed. This was corroborated by TLC. Continuing the stirring under oxygen for an additional 32 h followed by standing for 8.5 h at ca. 25 °C once again showed only compound I and A in an approximate ratio of 1:2 by both TLC and ir inspection. It was concluded that under these conditions, oxygen does not add to either A or to I.

Hydrogenation of A. The photoisomer (51.5 mg, 0.126 mmol) was hydrogenated in 7 ml of ethyl acetate (using 25 mg of prereduced 5% palladium on alumina) with the absorption of 2.04 equiv (0.258 mmol) of hydrogen. The catalyst was removed by filtration, and the product was recrystallized from ether–ethanol (hexane is an alternative) to give 52 mg (0.129 mmol, 100%) of colorless, fluorescent needles of compound III: mp 161.5–162 °C; uv λ_{sh} (hexane) 228 nm (log ϵ 4.36), λ_{max} 288 (4.13); λ_{max} (hexane) (fluorescence) 405 nm ($\lambda_{(\text{excit})}$ 310 nm); NMR 7.13 (s, 10 H), 6.96 (s, 10 H), 3.58 (m, 4 H), 2.05 ppm (m, 4 H); ir 3100–3000, 2940, 2900, 1600, 1500, 755, 695, and 515 cm^{-1}.

Anal. Calcd for $C_{32}H_{28}$: C, 93.16; H, 6.92. Found: C, 93.33; H, 6.84.

3,6-*trans*-Diphenyl-4,5-*cis*-dibenzylcyclohexene. A solution of 35 g (0.183 mol) of 1,4-diphenylbuta-1,3-diene[44] and 43 g (0.183 mol) of *cis*-1,4-diphenylbut-2-ene-1,4-dione[45] in 350 ml of triethylene glycol was heated at 180 °C for 24 h. The solution was cooled, 150 ml of water was added, and the mixture was stirred and heated to reflux. The precipitate was filtered from the cooled mixture and was washed with 95% ethanol to give 72 g (92%, mp 183–183.5 °C) of adduct V.

Anal. Calcd for $C_{32}H_{26}O_2$: C, 86.90; H, 5.89. Found: C, 86.40; H, 5.74.

Attempts to prepare all-cis isomer by this route were unsuccessful. Heating the reactants in benzene at 110 °C for 16 days led to a recovery of only starting materials, whereas at 150 °C for 30 days, a 51% yield of compound V was obtained.

To 32 ml of ethanol was added 0.37 g of sodium, followed by 1 g of adduct V. The solution was heated under reflux for 3 h under nitrogen and then cooled. Filtration yielded unchanged adduct (0.8 g, 80% recovery, mp 182.5–183.5 °C).

1,4-*trans*-Diphenyl-2,3-*cis*-dibenzoylcyclohexane (V). A solution of 56 mg (0.127 mmol) of the adduct in ethyl acetate (with 17 mg of 10% palladium on charcoal) was hydrogenated. The uptake of hydrogen was 3.28 ml at 24 °C and 746 mm (0.117 mmol); the filtered solution was then evaporated to dryness. The product was recrystallized from ethanol–water to give a quantitative yield of 1,4-*trans*-diphenyl-2,3-*cis*-dibenzoylcyclohexane (V) (mp 150.5–152.5 °C after a polymorphic transition at 79 °C): ir (KBr) 1669, 1490, 1450, 1207, 1020, 755, and 700 cm^{-1}; uv λ_{max} (methanol) 247 nm (log ϵ 4.36); NMR 7.1 (m, 20 H), 4.5 (m, 2 H), 3.7 (m, 2 H), 2.0 ppm (m, 4 H).

Anal. Calcd for $C_{32}H_{28}O_2$: C, 86.45; H, 6.35. Found: C, 86.36; H, 6.53.

Ozonolysis of III. A solution of 30 mg (0.073 mmol) of III in 5 ml of ethyl acetate was cooled to −78 °C and a calibrated stream of ozone (11.5×10^{-6} mol/min) was bubbled into the solution for 9.5 min through a 2-mm capillary tube. The mixture was hydrogenolyzed after the addition of 20 mg of 10% Pd on charcoal and a further 5 ml of ethyl acetate to give 28 mg of crude product. This material was chromatographed on alumina using hexane–ether and 23 mg (77%) of III and 4 mg of V (53% based on unrecovered III; mp 149.5–151.5 °C; mixture mp 150.5–152.0 °C) were isolated. The sample of V was identical by ir, uv, and TLC as well as by mp with the synthetic material.

In a second run, the crude product (from 44 mg of III) after hydrogenolysis was recrystallized from dichloromethane–methanol (without chromatography) to give 31% of pure IV (mp 209.5–211 °C; uv λ_{max} (methanol) 245 nm (log ϵ 4.31); ir (KBr) 1669, 1500, 1450, 1218, 1020, 1000, 756, 730, 715, and 695 cm^{-1}).

Anal. Calcd for $C_{32}H_{28}O_2$: C, 86.45; H, 6.35. Found: C, 86.18; H, 6.29. IV was then chromatographed on alumina using hexane-ether, and V was isolated from the eluent which was identical with the synthetic sample. In a third run (114 mg of III), the product was chromatographed to yield 32% of IV, with a recovery of 31% III.

Reaction of III with Osmium Tetroxide. (a) To 100 mg (0.243 mmol) of III in 8 ml of anhydrous ether was added 90 mg (0.35 mmol) of osmium tetroxide. The solution was stirred under dry nitrogen for 115 h during which time a brown precipitate formed. Hydrogen sulfide was then bubbled through the reaction mixture for 5 min, and it was stirred for a further 2 h. The solution was evaporated to dryness, and the residue was rapidly percolated through 5 g of silica gel using ether–dichloromethane (to remove inorganic materials). The eluent was evaporated, and the residue was shown by TLC and ir to contain only III and IV. There was no trace of a diol nor of V. After chromatography on alumina using ether–hexane, 26 mg (57% based on unrecovered III) of V was isolated. This material was shown to be identical with that obtained by ozonolysis of III followed by chromatography.

(b) To a solution of 40 mg (0.16 mmol) of osmium tetroxide in 3 ml of anhydrous pyridine was added 50 mg (0.122 mmol) of III in 6 ml of anhydrous pyridine; the mixture was then stirred at ca. 25 °C for 72 h. A solution of 50 mg of sodium metabisulfite in 8 ml of water was added. The mixture became dark red and translucent after 15 min. It was extracted with 50 ml of chloroform, and the chloroform phase was washed with dilute acid, dried, and evaporated in vacuo to give 30 mg of brown-green oil. It was shown by ir that this crude product contained V, but no diol and no IV. Chromatography on alumina gave 12 mg (23%) of V, identical with samples of V obtained by the Diels–Alder synthesis and hydrogenation.

The Adduct of Photoisomer A with Dimethyl Acetylenedicarboxylate. To 26 mg (0.064 mmol) of A were added 1 ml of freshly distilled dimethyl acetylenedicarboxylate and 3 ml of benzene to effect homogeneity. A yellow solution was immediately obtained, though the starting materials are colorless. The mixture was left for 20 h in the dark at ca. 25 °C. Solvent and residual dieneophile were distilled in vacuo to leave a pale-yellow solid. This was triturated four times with 5 ml of cold hexane, which led to the extraction of 18 mg of cyclooctatetraene I and left 8 mg (78% based on unrecovered I) of a colorless solid (VII); NMR 7.35 (m, 10 H), 6.96 (m, 10 H), 6.80 (s, 2 H), 3.92 (s, 2 H), 332 ppm (s, 6 H); mp (recryst ethanol–dichloromethane) 189–189.5; uv λ_{max} (methanol) 272 nm (log ϵ 3.96); λ_{max} (fluorescence) 384 nm ($\lambda_{\text{(excit)}}$ 320 nm); ir (KBr) 1720, 1430, 1295, 1270, 1250, 1220, 1065, 1050, 975, 815, 770, 758, 745, and 695 cm^{-1}.

Anal. Calcd for $C_{38}H_{30}O_4$: C, 82.88; H, 5.49. Found: C, 82.54; H, 5.56.

The Adduct of Photoisomer A with Maleic Anhydride. A solution of 525 mg (5.35 mmol) of maleic anhydride, 28 mg (0.067 mmol) of A, and 5 ml of benzene was stirred under nitrogen in the dark for 48 h at ca. 25 °C. The solution was extracted with water, dried over sodium sulfate, and the solvent was evaporated in vacuo. The residue was recrystallized from ethanol–dichloromethane to give 30 mg (0.061 mmol, 90%) of the adduct VI: mp 237.5–239 °C; uv λ_{max} (methanol) 292 nm (log ϵ 4.11); ir (KBr) 1848, 1770, 1490, 1440, 1205, 1072, 1003, 937, 912, 837, 745, and 687 cm^{-1}; NMR 7.15 (m, 22 H), 4.27 (s, 2 H), 3.78 ppm (s, 2 H).

Anal. Calcd for $C_{36}H_{26}O_3$: C, 85.34; H, 5.17. Found: C, 85.34; H, 5.06.

Reduction of VII. To 33 mg of lithium aluminum hydride (Metal Hydrides Inc., 95%, 0.87 mmol) in 50 ml of dry ether (redistilled from lithium aluminum hydride) was added a solution of 32.6 mg (0.006 mmol) of the adduct in 50 ml of dry ether and 10 ml of dry benzene. The addition was over 5 min, and the mixture was stirred for 30 min at ca. 25 °C before being heated under reflux. The apparatus was protected from atmospheric moisture by silica gel guard tubes. The cooled solution was treated with an excess of moist ether, then several drops of water before being extracted between ether and dilute hydrochloric acid. The ether phase was washed with dilute sodium carbonate solution, dried with sodium sulfate, and filtered. After evaporation of the solvent in vacuo, an oil was left: ir 3400 (broad), 3050, 2900, 1600, 1500, 1450, 1023 (broad), 763, 750, and 695 cm^{-1}; uv λ_{max} (methanol) 274 nm; λ_{max} (fluorescence) 384 nm ($\lambda_{\text{(excit)}}$ 320 nm). After cooling and scratching a solution of this oil in hexane–benzene, crystals were deposited, mp 103–106 °C. Mass spectral analysis (70 eV) showed $P^+ = 496$. Calcd for $C_{36}H_{32}O_2$: $(P + 1)^+/P^+ = 39.6\%$; $(P + 2)^+/P^+ = 8.24\%$. Found: 39.6% and 8.3%, respectively. Major peaks *m/e* = 408 $[M^+ - (HOCH_2CH{=}CHCH_2OH)]$, 306, 230, 204 (base peak, $C_{16}H_{12}^+$), 178 ($C_6H_5C{\equiv}CC_6H_5^+$), and 102 ($C_6H_5C{\equiv}CH^+$).

Dimethyl 1,4-Diphenylcyclohexa-1,3-diene-*trans*-5,6-dicarboxylate. This compound was prepared by the method of Fieser[20] by the Diels–Alder reaction of 1,4-diphenylbuta-1,3-diene and dimethyl acetylenedicarboxylate in refluxing diglyme, followed by isomerization with methanolic potassium hydroxide. Recrystallization from methanol gave colorless needles: mp 169–171 °C (lit.[20] 169–170 °C); uv λ_{sh} (ether) 230 nm (log ϵ 4.06), λ_{max} 330 nm (4.30); λ_{max} (ether) (fluorescence) 445 nm ($\lambda_{\text{(excit)}}$ 350 nm); NMR 7.18 (m, 10 H), 6.27 (s, 2 H), 4.22 (s, 2 H), and 3.36 ppm (s, 6 H).

Dimethyl 3,6-Diphenylphthalate. A solution of 10 mg (0.04 mmol) of dibenzoyl peroxide, 100 mg (0.29 mmol) of dimethyl 1,4-diphenylcyclohexa-1,3-diene-*trans*-5,6-dicarboxylate[20] and 300 mg (1.7 mmol) of *N*-bromosuccinimide in 25 ml of carbon tetrachloride was heated under reflux for 4 h. The cooled solution was filtered and evaporated in vacuo. The residue was extracted twice with 20 ml of cold ether. The colorless crystalline residue (20 mg, 0.06 mmol; 20%), which was shown by TLC to be a single compound, was recrystallized from methanol: mp 188–190 °C (cor) (lit.[27] 189–190 °C); uv λ_{sh} (ethanol) 227 nm (log ϵ 4.39), λ_{max} 260 (4.31); ir (KBr) 1745, 1720, 1450 (complex), 1305, 1250, 1230, 792, 765, and 705 cm^{-1}.

Photolysis of Compound VII. A solution of 8 mg (0.018 mmol) of VII in 100 ml of ethanol was irradiated for 30 min (Rayonet photochemical reactor). The uv spectrum changed from 270 to 254 nm [λ_{max} (ethanol)] and the absorbance increased. The solution was evaporated in vacuo and the residue was chromatographed on alumina using diethyl ether. Dimethyl 3,6-diphenylphthalate (3.5 mg, 0.01 mmol; 56%) was obtained: NMR 7.50 (s, 2 H), 7.39 (s, 10 H), and 3.59 (s, 6 H) ppm; mass spectrum (70 eV) $P^+ = 346$; mp (recryst from diethyl ether) 188–189 °C (cor), mmp 188–189 °C (cor).

^{13}C NMR Spectra. The natural abundance carbon-13 magnetic resonance spectra at 25.14 MHz were taken on a Varian XL-100-15-FT NMR spectrometer which was equipped with a proton noise decoupler that had been modified to allow the decoupler power to be gated (on and off) under computer control. A Varian 16K-620i computer was used to control data acquisition as well as to perform the Fourier transformations of the time averaged free induction decay. The sample which was contaminated with ~20% of compound II was analyzed at 0 °C in a 5-mm NMR tube containing 0.3 ml of a 0.5 M solution of photoisomer A in deuteriochloroform (similar spectra were obtained in deuteriodichloromethane). The deuterium resonance of the solvent was used to provide field/frequency stabilization.

The first spectrum was taken with complete proton decoupling and showed many signals in the "aromatic" region and a single line in the "aliphatic" portion (44.319 ppm) as well as a 1:1:1 triplet for the solvent. A second spectrum was taken of the same sample with the decoupler gated so as to provide full nuclear Overhauser enhancement for hydrogen bearing carbons without loss of C–H coupling information. The aliphatic region now showed a 1:1 doublet at 44.32 ppm with a coupling constant of 141.6 ± 3 Hz. The sample was then heated in a water bath at 50 °C for 1 h and a third spectrum obtained. The spectrum was identical with one obtained earlier of cyclooctatetraene II, and there was no evidence for a resonance in the aliphatic region.

The following sharp signals were observed in the proton decoupled spectra of photoisomer A and assigned to unsaturated quaternary carbons (chemical shifts in ppm from Me_4Si): 134.63, 137.70, 139.13, 139.53, 139.22, 140.80, 141.36, 144.50. The resonances arising from proton-bearing carbons were noticeably broadened by incomplete decoupling under the experimental conditions. Signals were observed at 133.30, 131.99, 129.64, 126.47, 125.94, 125.53, 121.39, 121.31, 44.32 ppm (signals for $CDCl_3$ at 78.27, 76.99, and 75.72). The spectrum of cyclooctatetraene I consisted of signals at 143.369 (073), 141.532 (077), 139.894 (064), 139.591 (060), 130.165 (065), 128.516 (156), 128.363 (169), 127.818 (087), 127.673 (090), 127.394 (071), 126.665 (140), 126.130 (154), ppm rel to Me_4Si.

NMR Spectra of Photoisomer A (XV $\rightleftharpoons$ VIII) Dissolved at −40 °C Treatment with 4-Phenyl-1,2,4-triazoline-3,5-dione. The spectra were measured on a Jeol MH-100 NMR spectrometer using deuteriochloroform solutions. Details and line positions are given in the body of this paper.

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(10) (a) In order to distinguish the cyclooctatetraene double bond isomers (I and XV), we have designated a ring carbon bearing one of the vicinal phenyl groups as no. 1 and have given priority to a double bond over a single bond. (b) Earlier, we had assigned a *cis,cis,cis,trans*-cyclooctatetraene structure to this isomer[11] (see text).

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(21) 1,2-Diphenyl-3,4-bis(acetoxymethyl)cyclobutene: λ_{sh} 228 nm (log ϵ 4.28), λ_{max} 290 (4.12); λ_{max} (fluorescence) 382 nm, $\lambda_{(excit)}$ 309 nm. 1,2-Diphenylcyclobutene:[22] λ_{max} 227 nm (log ϵ 4.38), 297 (4.26); λ_{max} (fluorescence) 380 nm, $\lambda_{(excit)}$ 317 nm. See also: G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **10**, 340 (1971).

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(32) The last set of spectra were run on a Jeol-100 instrument and the bands are sharper than those of Figure 1. The new spectra show a slight enhancement of the bands of form VIII at the expense of those of XV at −40 °C.

(33) In contrast, no reaction was observed between photoisomer A and dimethyl acetylenedicarboxylate at −40 °C during 48 h.

(34) A similar effect is noticed in *o*-terphenyl.

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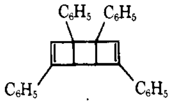

i

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Steric and Spin-Orbital Effects on the Photodimerization of Thianaphthene 1,1-Dioxide[1,2]

William W. Schloman, Jr.,[3] and Benjamin F. Plummer*

Contribution from the Department of Chemistry, Trinity University, San Antonio, Texas 78284.

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Abstract: The quantum yields of dimerization of thianaphthene 1,1-dioxide and 2-bromothianaphthene 1,1-dioxide were measured at 313 nm as a function of substrate concentration in selected solvents. The dimerization of 2-bromothianaphthene 1,1-dioxide was sensitized by the crown ether complex of Rose Bengal and by Michler's ketone, but not by crystal violet. The dimerization of thianaphthene 1,1-dioxide shows reasonable linear Stern–Volmer quenching by cyclooctatetraene. The 2-bromothianaphthene 1,1-dioxide under similar quenching conditions with cyclooctatetraene yields data that produce a curved Stern–Volmer relation. The results of this study indicate that internal heavy atoms show a modest effect on both $T_1 \leftrightarrow S_1$ and $S_0 \leftrightarrow T_1$, but that the former process shows a greater sensitivity to external heavy-atom perturbation. An exciplex mechanism that competes with excited triplet state dimerization of 2-bromothianaphthene 1,1-dioxide is proposed to be consistent with all the available data. Rate constants for the multipathway scheme are derived and steric hindrance to ring closure is suggested as being a contributing factor to the inefficiency of the reaction.

External and internal heavy-atom effects on the photochemical processes of acenaphthylene and its derivatives have been the subject of several recent studies.[4] Because the effects upon acenaphthylene photochemistry have been dramatic, we have initiated studies to seek out and explore other molecules in which the heavy-atom effect might prove to be a viable experimentally detectable phenomenon.

The mechanistic study of the photodimerization of thianaphthene 1,1-dioxide (TND) published by Harpp and Heitner[5] reported data that suggested to us that TND fit the criteria[4e] for a molecule that should manifest a photochemical heavy-atom effect. Indeed, the photodimerization of TND was found to show an external heavy-atom effect,[1b] and this encouraged us to broaden the study to include 2-bromothianaphthene 1,1-dioxide (BrTND).

The fact that the general phenomena of the heavy-atom effect may be more widespread in photochemistry than is generally recognized is illustrated by this study and by recent data reported for quite different structural systems.[6]

Results

A. Photoproducts. The only detectable photoproduct that results from irradiating 2-bromothianaphthene 1,1-dioxide (BrTND) in benzene has been identified as the trans-cyclobutane dimer derived from head-to-tail combination of BrTND (Scheme I). The high melting point of this dimer in conjunction with its extreme insolubility in all organic solvents precluded the use of the common analytical techniques of NMR, GLC, and high-pressure liquid chromatography in its structure proof. By pursuing the chemical approach used by