

It has been observed by Chapman that the irradiation of tropone afforded benzene in low yield.¹⁰ The difference between these results seems to arise from the solvent effect on the excited state. Since in a polar solvent such as water¹¹ or acidic media the $\pi-\pi^*$ transition of tropone, the absorption of which appears at around $310\text{ m}\mu$,¹² is stabilized compared to $n-\pi^*$ transition, the $\pi-\pi^*$ transition may contribute to the $(6+6)$ π -type cycloaddition of tropone.

This $(6+6)$ π -type photodimerization process is in good contrast to the $(6+4)$ π -type cycloaddition of tropone with cyclopentadiene, which occurred in the dark.¹³ Although the formation of the *exo* adduct of the latter reaction is rationalized by Hoffmann and Woodward's molecular orbital consideration for Diels-Alder reaction,¹⁴ the specific formation of *trans* photodimer Ia may be reasonably explained in the same fashion as proposed by Chapman for the photodimerization process of 2-phenoxy-4,5-benzotropone.¹⁵ The ground-state dipole of tropone which is directed from the tropone ring to the carbonyl oxygen may arrange two tropone molecules in an *exo* orientation as shown in Chart I, giving the dimer directly upon excitation.

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(10) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

(11) Dimer I was also obtained in low yield on irradiation of tropone in water.

(12) Proof that this absorption band is due mainly to $\pi-\pi^*$ transition is as follows: (i) this band shows no hypsochromic shift but bathochromic shift, and does not change its intensity greatly with a change in solvent from polar to nonpolar: cf. T. Mukai, *Nippon Kagaku Zasshi*, **79**, 1547 (1958); (ii) ASMO calculation of tropone supports the assumption that this band arose from $\pi-\pi^*$ transition. Details will be published by Y. Amako, H. Yamaguchi, and T. Azumi, Tohoku University.

(13) R. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, **15** (1966); S. Ito, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Japan*, **39**, 1351 (1966).

(14) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1965).

(15) O. L. Chapman, H. G. Smith, R. W. King, D. J. Pasto, and M. R. Stoner, *ibid.*, **85**, 2031 (1963).

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The Course of Tropone Photodimerization in Acetonitrile

Sir:

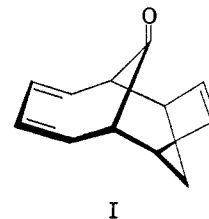
The recent report¹ that tropone and cyclopentadiene undergo *thermal* cycloaddition to give the crystalline adduct I marks the first demonstration of $(6+4)$ cycloaddition, a process which, in general, is allowed a concerted course by the Hoffmann-Woodward rules.² We now describe a *photochemical* process whereby tropone is converted to three crystalline dimers formally corresponding to $(6+4)$, $(6+2)$, and $(4+2)$ modes of cycloaddition, respectively.^{3,4}

(1) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, **15** (1966).

(2) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(3) The thermal $(2+2)$ addition of diphenylketene to tropone has recently been reported by C. Jutz, I. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, **22**, 1809 (1966).

(4) The thermal $(4+2)$ adduct of tropone with maleic anhydride is described by T. Nozoe, T. Mukai, T. Nagase, and V. Toyooka, *Bull. Chem. Soc. Japan*, **33**, 1247 (1960). As determined in our laboratories, the diester XI in this series has $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 227, 339 $\text{m}\mu$ (ϵ_{max} 7800, 144); $\nu_{\text{C=O}}^{\text{CHCl}_3}$ 1748, 1666 cm^{-1} .



I

Whereas the photochemistry of tropolones has been intensively studied,⁵ that of tropone has been limited to the cursory report that benzene plus a "complex mixture of products" are produced.⁶ We have observed that exposure for 28 hr of a dilute solution of tropone in acetonitrile to a 140-w high-pressure mercury source, using cooled glass vessels, results in clean conversion to a mixture containing approximately 50% tropone photodimers, in addition to some 30% unchanged tropone. Careful silica gel chromatography, followed by fractional crystallization, produced as major products three dimers, mp 141–142°, 124–125°, and 118–119°, in approximately equal yields.⁷ The complex nmr spectra of each of these substances revealed their lack of molecular symmetry and, moreover, indicated that each contained four protons bound to saturated carbon and eight protons bound to unsaturated carbon. Therefore, each photodimer had resulted from two tropone molecules by formal loss of two double bonds and generation of one new ring.

The 141–142° dimer [$\nu_{\text{max}}^{\text{CHCl}_3}$ 1698, 1670 cm^{-1} ; $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 225, 256, 266, 285 (sh) $\text{m}\mu$ (ϵ_{max} 9400, 4200, 4350 1900 (sh))] was unique in that it underwent ready thermal retrogression to tropone at 95°.⁸ The presence of the grouping $-\text{C}(\text{H}_B)=\text{CH}_A\text{C}(=\text{O})-$ in a six-membered or larger ring was indicated by the 225- $\text{m}\mu$ and 1670- cm^{-1} maxima and by the nmr signals of H_A (τ 4.2) and H_B (τ 3.8), with $|J_{AB}| = 12$ cps. The maxima at 256 and 266 $\text{m}\mu$, as well as the 1698- cm^{-1} carbonyl band, were similar to the values cited by Cookson¹ for the cycloheptadienone system of model I.⁹ All of our data were consistent with gross structure II or III for the 141–142° dimer. Further stereochemical definition was derived from complete catalytic hydrogenation of the dimer over 10% Pd-C to an octahydro diketone (IV, $\nu_{\text{C=O}}^{\text{CHCl}_3}$ 1697 cm^{-1}), which on standing in cold dilute base was rapidly converted to a crystalline isomeric hydroxy ketone, mp 80–82°, having in addition to hydroxyl absorption a sharp carbonyl maximum at 1736 cm^{-1} . This latter transformation must involve formation of a five-membered ring through an internal aldol reaction (IV \rightarrow V) facilitated by the proximity of the two carbonyl bridges, and thus defines not only the *syn* relation but also the relative positions of the carbonyl groups. Stereochemistry at the ring

(5) Reviewed by K. S. Koch, *Advan. Alicyclic Chem.*, in press.

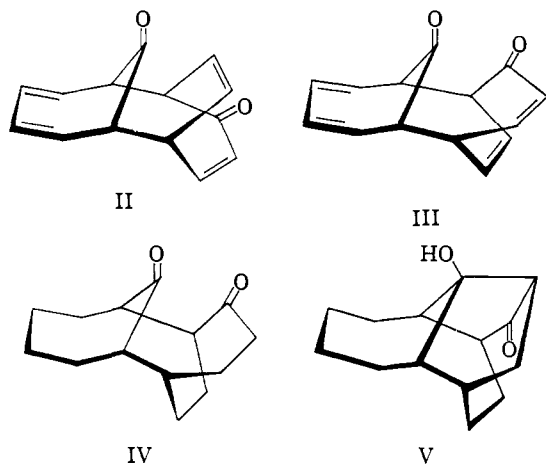
(6) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

(7) All compounds for which melting points are cited have been fully characterized by satisfactory spectra, carbon-hydrogen analyses, and mass-spectrometric or vapor pressure thermistor molecular weights. We are indebted to Messrs. L. Brancone and W. Fulmor of these Laboratories, Dr. R. Pitcher of Varian Associates, and the services of the Morgan-Shaffer Corporation (Montreal) for the determinations. Valuable discussions with Dr. J. Karliner (Lederle) are gratefully acknowledged.

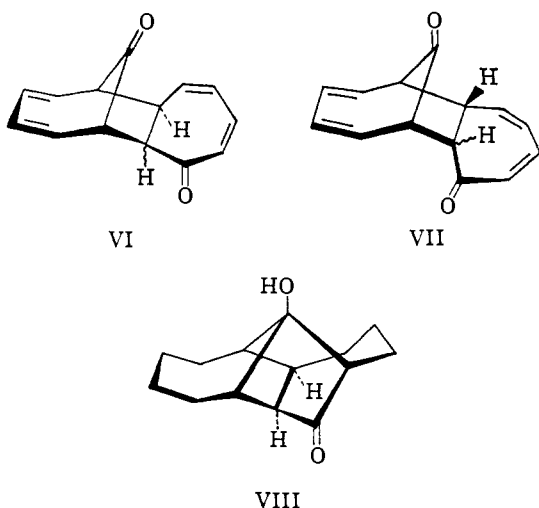
(8) The other two dimers undergo complex transformations above 100° to give mixtures which have not been resolved to date.

(9) A related bridged diene, 9-hydroxy-9-methyl-bicyclo[4.2.1]-nonatriene, is reported to have $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 260 $\text{m}\mu$ (ϵ_{max} 6300) [T. S. Cantrell and H. Shecter, *J. Am. Chem. Soc.*, **85**, 3300 (1963)].

junction carbon atoms adjacent to the bridging carbonyl in III remains unspecified.



The 124–125° tropone photodimer ($\nu_{\max}^{\text{CHCl}_3}$ 1745, 1660 cm^{-1} ; $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 267, 292 $\text{m}\mu$ (ϵ_{\max} 6520, 5300)) possesses the 267- $\text{m}\mu$ ultraviolet absorption of the cycloheptadiene system of compound III, but differs from III in that it displays a structurally diagnostic strained-ring carbonyl infrared maximum at 1745 cm^{-1} . The remaining 1660- cm^{-1} band and 292- $\text{m}\mu$ maximum are both indicative of a 2,4-cycloheptadienone grouping.¹⁰ These observations point to gross structure VI or VII for the 124–125° photodimer, and these structures are in turn consistent with the data obtained for the corresponding octahydro derivative, mp 73–74° ($\nu_{\max}^{\text{CHCl}_3}$ 1731, 1692 cm^{-1}). Although no further stereochemical definition is presently available, it may be significant that *prolonged* treatment of the 73–74° octahydro derivative with dilute base gave no evidence for the formation of the relatively unstrained internal aldol VIII.



Finally, the spectrum of the 118–119° dimer ($\nu_{\max}^{\text{CHCl}_3}$ 1665 cm^{-1} ; $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 224, 291 $\text{m}\mu$ (ϵ_{\max} 8900, 4500)) suggests the presence of both the $-\text{CH}=\text{CHC}(=\text{O})-$ chromophore and the 2,4-cycloheptadienone groupings.

(10) For 2,4-cycloheptadienone itself, the ultraviolet spectrum, λ_{\max} 292 $\text{m}\mu$ (ϵ_{\max} 6160), has been reported by E. E. van Tamelen and G. T. Hildahl, *J. Am. Chem. Soc.*, **78**, 4405 (1956). In the case of the diphenylketene-tropone adduct³ the values cited were λ_{\max} 290 $\text{m}\mu$ (ϵ_{\max} 2200), ν_{CO} 1655 cm^{-1} .

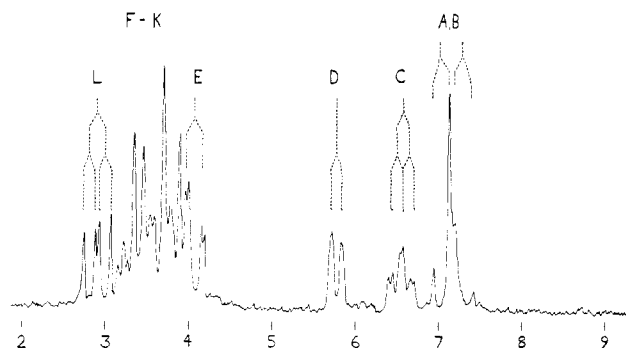
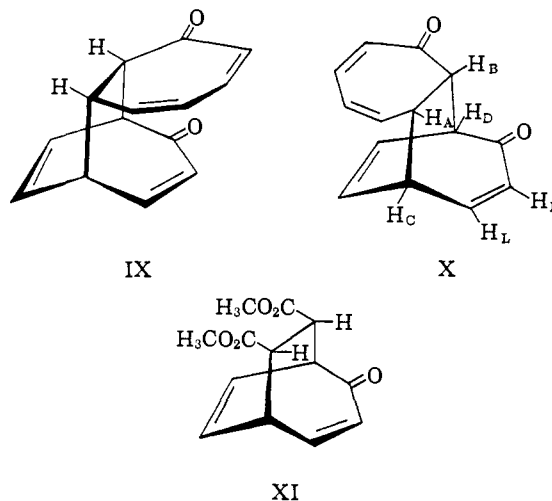


Figure 1. Nmr spectrum of the 118–119° dimer X in CDCl_3 solution at 60 Mc; protons assigned as in formula X.

These features are best accommodated in terms of a (4 + 2) adduct in which the 2,3 double bond of one tropone molecule has added to the diene system of a second in a Diels–Alder fashion. Eight such adduct isomers are possible, of which four are immediately precluded by the 6.2-D. dipole moment measured¹¹ for the 118–119° dimer in benzene solution; this value requires a head-to-head rather than head-to-tail orientation. Of the two remaining *cis* adducts IX and X, the latter is favored by the 60-Mc nmr spectrum (Figure 1) of the dimer, in which the chemical shifts of the protons labeled H_E (τ 4.11) and H_L (τ 2.96) are precisely the same as those of the corresponding olefinic protons in the simple model diester XI.⁴ Catalytic hydrogenation of the 118–119° dimer produced the corresponding octahydro diketone, mp 98–99° ($\nu_{\max}^{\text{CHCl}_3}$ 1698 cm^{-1}), which was stable to the *prolonged* action of cold base, an observation consistent with structure X. However neither of the two possible *trans* isomers is excluded by our data.



More complex transformations of these photodimers, their mass spectra, and further discussion of their genesis will be presented in our full paper.

(11) We are indebted to Mr. R. Murray (Stamford Research Laboratories, American Cyanamid Co.) for this determination.

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