

p-benzoylbiphenyl,⁸ a σ_R value of -0.41 may be calculated by subtraction of the σ_I value of 0.10 .⁵ The fact that this value exceeds the proposed threshold value for resonance parameters supports our contention based on increased resonance interaction for the benzenophenone system.

Acknowledgment. We acknowledge with thanks gifts of samples from Dr. Herbert C. Brown and Dr. Kerry Bowers, and the generous support of this work by the National Science Foundation (GP 4335) and the National Institutes of Health (GM 12755).

(9) To whom requests for reprints should be directed.

Maurice M. Bursey, F. W. McLafferty⁹
 Department of Chemistry, Purdue University
 Lafayette, Indiana 47907
 Received August 8, 1966

Tropone Dimer. A New Type of Photocycloaddition Reaction

Sir:

Recently much attention has been directed toward molecular orbital symmetry considerations for explaining different behavior in photochemical and thermal reactions.¹⁻⁴ Although it is predicted from Woodward and Hoffmann's selection rule² that a concerted cycloaddition of $(6 + 6)$ π -type, $n = 3$ in a $4n$ system, would occur photochemically, this type of photocycloaddition has never been reported. We wish to report the first example of $(6 + 6)$ π -type cycloaddition: the photodimerization of tropone.

Irradiation of tropone in 2 *N* sulfuric acid with a mercury lamp (Toshiba H-400 P) for 140 hr in a Pyrex vessel afforded, on purification using alumina column chromatography, dimer I, mp 220° (7.5%), besides oily product (6.6%), recovered tropone (8%), and a large amount of polymer.

The structure of dimer I was confirmed to be tricyclo[6,4,1,1^{2,7}]tetradeca-3,5,9,11-tetraene-13,14-dione (Ia) from the following physical and chemical evidence. *Anal.* Found for $C_{14}H_{12}O_2$: C, 79.16; H, 5.72; ultraviolet in methanol, 254 $m\mu$ (ϵ 8800)⁵ and 273 $m\mu$ (shoulder); infrared in KBr, 3030 (double bond), 1705 (carbonyl), and 1600 and 723 cm^{-1} (*cis* diene); nmr (100 Mc) in $CDCl_3$, $A_2B_2X_2$ coupling pattern at τ 4.15 (A protons, 2 H), 4.45 (B protons, 2 H), and 6.58 (X protons, doublet, $J = 6.0$ cps, 2 H) shown in Figure 1a. The assignment of these protons was provided by decoupling technique.⁶

As shown in Figure 1b, a typical A_2B_2 coupling pattern appeared centered at τ 4.30 when X was saturated, while on saturation of B a singlet was observed for X. The nmr evidence indicated that the molecule was symmetrical, the A and B protons were olefinic, and X was a methine proton.

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(2) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(3) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

(4) K. Fukui, *Tetrahedron Letters*, 2009 (1965).

(5) Cyclohexa-1,3-diene and cyclohepta-1,3-diene have absorption maxima at 256 $m\mu$ (ϵ 8000) and 248 $m\mu$ (ϵ 7500), respectively (A. I. Scott, "Interpretation of Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, p 48).

(6) The authors thank Dr. M. C. Woods for the measurement and discussion of the nmr spectra.

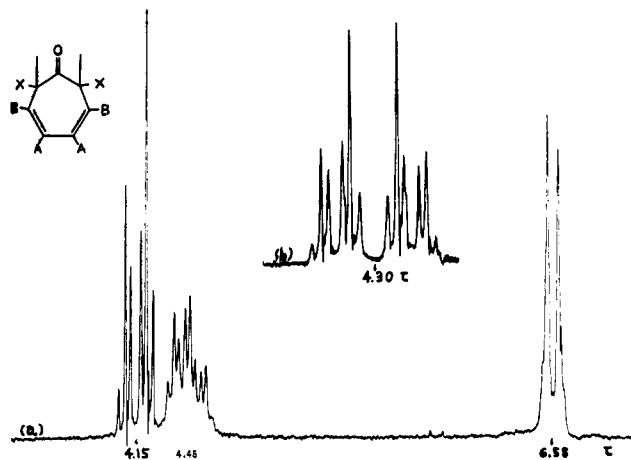


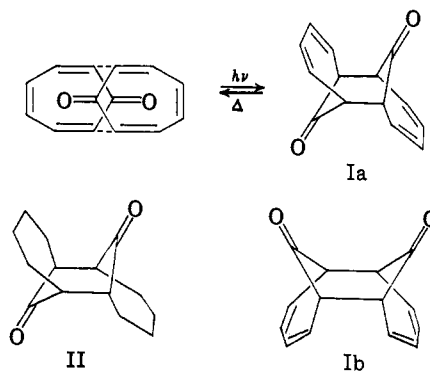
Figure 1.

The mass spectrum of I included peaks with m/e 212 (molecular ion), 149, 141, 106 ($M/2$), and 78 (base peak).⁷ The occurrence of the relatively strong peak of m/e 106 and base peak 78 suggested the cleavage of I to tropone, which exhibits a base peak at m/e 78 corresponding to benzene⁸ on electron impact. The dissociation of I to tropone was also brought about by heating. On pyrolysis at 220° in a sealed tube under nitrogen atmosphere, I gave tropone in 60% yield, which was identified by infrared spectrum and the formation of picrate, mp 99° .

On catalytic hydrogenation over 10% palladium-carbon, I took up 4 mole equiv of hydrogen to give an octahydro derivative (II), mp 93° , in almost quantitative yield, which had the following physical properties. *Anal.* Found for $C_{14}H_{20}O_2$: C, 76.25; H, 9.11; infrared in KBr, 1704 cm^{-1} (carbonyl), and no absorption due to double bond; mass spectrum, peaks with m/e 220 (molecular ion), 110, 81, and 67.

Summarizing the evidence cited above, two possible structures, Ia and Ib, can be deduced for dimer I. Evidence for the *trans* form (Ia) rather than the *cis* form (Ib) came from dipole moment measurements.⁹ The dipole moment of I taken in benzene at 25° was 0.8 D., strongly supporting Ia for the structure of dimer I (see Chart I).

Chart I



(7) Mass spectra were taken at 70 ev by Dr. S. Hishida, Nippon University, Tokyo, whom the authors acknowledge.

(8) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 241.

(9) The authors thank Dr. H. Watanabe, Shionogi & Co. Ltd., for the measurement of the dipole moment.

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.

Acknowledgment. Financial support from Sankyo Co. Ltd. is acknowledged.

(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).

Toshio Mukai, Takahiro Tezuka, Yutaka Akasaki
Department of Chemistry, Faculty of Science
Tohoku University, Sendai, Japan

Received July 20, 1966

The Course of Tropone Photodimerization in Acetonitrile

Sir:

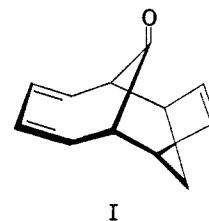
The recent report¹ that tropone and cyclopentadiene undergo *thermal* cycloaddition to give the crystalline adduct I marks the first demonstration of $(6+4)$ cycloaddition, a process which, in general, is allowed a concerted course by the Hoffmann-Woodward rules.² We now describe a *photochemical* process 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°. The presence of the grouping $-\text{C}(\text{H}_\text{B})=\text{CH}_\text{A}\text{C}(=\text{O})-$ 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 $|J_{\text{AB}}| = 12$ 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)].