Anal. Calcd for $C_{23}H_{23}NO$: C, 83.85; H, 7.04; N, 4.25. Found: C, 83.69; H, 6.97; N, 4.42.

The infrared spectrum of this material in a potassium, bromide pellet had bands at 5.95, 6.24, 8.42, 8.85, 10.45, 10.55, 12.39, 13.30, and 14.25 μ. The ultraviolet spectrum in 95% ethanol had a maximum at 253 mμ (ϵ 19,400).

A solution of 0.5 g of XVII in 200 ml of 95% ethanol was irradiated with an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Pyrex filter to eliminate wavelengths below 280 mμ. The reaction was followed by glpc of aliquots withdrawn during the reaction, and product assignments were made by comparison of infrared spectra and glpc retention times with authentic samples. The analytical gas chromatography was performed on an Aerograph 350-B instrument with helium as the carrier gas on a column of SE-30 (0.1% on glass beads) at a flow rate of 66 cc/min and at a temperature of 160°. Analysis of the crude photolysis mixture showed two major components with retention times of 1 and 6 min. Comparison of retention times and infrared spectra with those of authentic samples of 4-methylbenzalacetophenone and N-benzylbenzalimine established the identity of the two major products.

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Photosensitized Isomerization of 1,3-Cyclooctadienes and Conversion to Bicyclo[4.2.0]oct-7-ene

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Abstract: The near-quantitative photosensitized cyclization reaction of *cis,cis*-1,3-cyclooctadiene to bicyclo-[4.2.0]oct-7-ene at 80° has been shown to involve first isomerization of the diene to its *cis,trans* isomer, which cyclizes under the reaction conditions. The highly strained *cis,trans* isomer has been isolated in good yield. Photostationary state compositions of the diene isomers were determined.

The generality of the photochemical conversion of conjugated dienes to cyclobutenes has been amply demonstrated by several research groups.[1] Evidence seems to indicate that this valence isomerization is not a triplet-state reaction since the reaction can neither be sensitized nor quenched.[1a,2] There are, however, two exceptional cases in the literature—1,3-cyclooctadiene and the recently reported 1,1′-bicyclohexenyl.[3] This report summarizes the results of our reexamination of the former case.

The conversion of *cis,cis*-1,3-cyclooctadiene (I, COD) to bicyclo[4.2.0]oct-7-ene (II) was reported independently by at least three research groups.[1a,b,4] A similar conversion under photosensitized conditions was indirectly reported by Schenck, *et al.*,[5] in a review article. The latter experiment, however, could not be reproduced successfully by others.[6] It appears to us that the recent observation by Fonken, *et al.*,[7] of the quantitative, facile thermal isomerization of *cis,trans*-COD to II at 80° offers an alternative mechanism for the sensitized reaction. The reaction may involve photosensitized isomerization to the *cis,trans* isomer, which cyclizes to II. Efficiency of the reaction would, therefore, depend upon the reaction temperature. Furthermore, since photosensitized isomerizations can conceivably provide a simple route to strained medium-size ring olefins, such as *cis,trans*-COD,[8] the system was reinvestigated in some detail.

Results

Irradiation of a solution of *cis,cis*-COD with acetophenone as sensitizer in *refluxing* benzene (or *n*-heptane at 80–90°) in a Pyrex immersion apparatus with a 550-w Hanovia medium-pressure mercury lamp for 12 hr led to complete disappearance of the diene with formation of one product. By fractional distillation, the photoproduct was isolated in 85% yield. Its infrared spectrum is identical with that reported for bicyclo[4.2.0]oct-7-ene (II).[10] Irradiation of a similar solution at 15° for the same period gave virtually no II. Instead, formation of a new product, III, was detected by vapor phase chromatography. The compound is apparently unstable under the analysis conditions since lowering the column temperature increased the size of the corresponding peak. At 50° or lower, thermal degradation of the labile photoproduct on the column apparently becomes negligible. Prolonged irradiation of this solution only results in the establishment of a photostationary state between I and III.

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(1) (a) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962); (b) K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965); (c) W. G. Dauben, *Pure Appl. Chem.*, **9**, 539 (1964), and literature cited therein.

(2) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(3) W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Am.*, *Chem. Soc.*, **88**, 2742 (1966).

(4) R. L. Cargill and W. G. Dauben, *J. Org. Chem.*, **27**, 1912 (1962); *Chem. Ind.* (London), **62**, 1198 (1962).

(5) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 785 (1962).

(6) Private communication: A. A. Lamola and G. S. Hammond, unpublished results.

(7) K. M. Shumate, P. N. Neuman, and G. J. Fonken, *J. Am. Chem. Soc.*, **87**, 3996 (1965).

(8) The compound was prepared by a four-step synthesis in 6.0% over-all yield.[9]

(9) A. C. Cope and C. L. Baumgardner, *J. Am. Chem. Soc.*, **78**, 2812 (1956), and previous papers in the series.

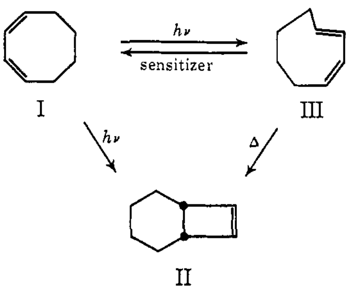
(10) M. V. Evans and R. C. Lord, *ibid.*, **83**, 3411 (1961).

The labile photoproduct has been isolated successfully. Reaction of silver nitrate solution with a pentane solution of *cis,cis*-COD, irradiated at room temperature with acetophenone as sensitizer, gave a crude white solid in 82% yield (based on reacted COD). After one recrystallization, the crystalline solid melted at 125–127° with decomposition. The product has been identified as the silver nitrate complex of *cis,trans*-1,3-cyclooctadiene by its melting point and analysis.[9] On reaction with ammonia the solid gave an olefin, the infrared spectrum of which is identical with that reported for *cis,trans*-1,3-cyclooctadiene.[9] On heating in refluxing benzene the olefin rearranges quantitatively to II, in agreement with Fonken's observation.[7]

The photostationary state composition of 1,3-cyclooctadienes are dependent upon the sensitizer employed. High-energy sensitizers give mixtures richer in the *cis,trans* isomer. Efficiency of the isomerization also appears to vary with sensitizers such that for lower energy sensitizers (E_T = 55–65 kcal/mole[11]) longer periods of irradiation are needed in order to reach the photostationary states. 9-Fluorenone (E_T = 52.5 kcal/mole) failed to sensitize the isomerization. Results with nine sensitizers are shown graphically in Figure 1. It is worth noting that the pattern of variation is almost monotonic and, as the sensitizers increase in energy, the ratio of I:III approaches a constant value of approximately 2.2.

In an attempt to generalize this reaction we have irradiated solutions of 1,3-cycloheptadiene in the presence of photosensitizer at 20 and 80°. Formation of new isomeric products was not detected.

We have also repeated the experiment of conversion of I to II by direct irradiation, but failed to detect any III during the reaction.[12] This would suggest that under these conditions the conversion of I to II does not involve III as an intermediate. The photochemistry of 1,3-cyclooctadiene can be summarized as follows.



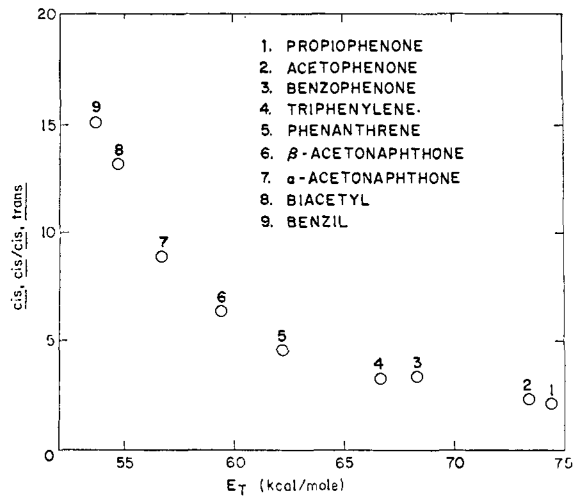


Figure 1. Photostationary state compositions of 1,3-cyclooctadienes.

Discussion

The pattern of variation of the photostationary state compositions of the 1,3-cyclooctadienes is interesting, particularly in comparison with that of the 1,3-pentadiene (piperylene) system, which was studied in considerable detail by Hammond, *et al.*[13] In the latter case a constant composition of *trans*:*cis* = 1.25 was obtained for sensitizers with energy greater than 60 kcal/mole. With lower energy sensitizers the stationary-state composition becomes even richer in *trans*-piperylene. To account for the variation it was suggested that the excitation energy of *trans*-piperylene is higher than that of the *cis* isomer, with a value close to 60 kcal/mole.[13] Variation of stationary-state compositions is, therefore, a reflection of preferential energy transfer to the *cis* isomer. Spectroscopic evidence, later reported by Kellogg and Simpson,[14] is in agreement with the chemical assignments. The curve in Figure 1 also allows us to make approximate assignments of the triplet-state energies of the two isomers of COD: 70–73 kcal/mole for *cis,cis*-COD and <70 kcal/mole for *cis,trans*-COD. We have attempted to obtain spectroscopic evidence in support of this assignment, but were not successful. A 30% solution of *cis,cis*-COD in ethyl iodide (10-cm path length) only gives weak and structureless absorption between 4000 and 5000 A.

Triplet excitation energies obtained by the chemical method have been shown in several systems[13,15] to agree well with the 0–0 band of the $T_1 \leftarrow S_0$ transition, determined spectroscopically. The value assigned in the COD system, however, is considerably higher than the known values of dienes (13 in all including two cyclic dienes, cyclohexadiene and cyclopentadiene)[14,16] which fall within the range of 52–61 kcal/mole. Since *s-cis* dienes are known to have lower excitation energies[17] and hyperconjugation effects by 1,4 substitution should lower the $T_1 \leftarrow S_0$ excitation energy,[14] other unique factors must be contributing here to the large deviation (E_T for butadiene = 59.5 kcal/mole). Examination of a model of the compound, which shows that the diene moiety is far from being planar,[18] suggests a possible explanation. Since the triplet-state energy of an isolated double bond is considerably higher (82 kcal/mole for ethylene[16]), an increase in triplet-state energy is expected as a diene unit loses conjugation by rotation around the central bond into configurations where the

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(11) W. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, 4537 (1965).

(12) We were informed by Professor Fonken that, under these conditions, a photostationary state between I and III can be established; however, the composition is essentially 100% I.

(13) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. D. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964), and previous papers in the series.

(14) R. E. Kellogg and W. T. Simpson, *ibid.*, 87, 4230 (1965).

(15) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *ibid.*, 87, 3406 (1965).

(16) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(17) See ref 15 for a discussion on triplet excitation energies of cisoid and transoid dienes.

(18) Based on Dreiding models a value of 64° was reported for the dihedral angle between the two π systems.[19]

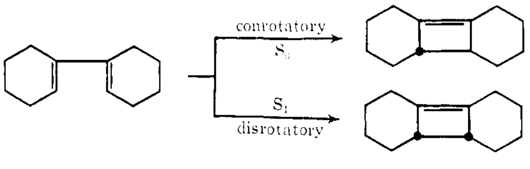
(19) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **86**, 2814 (1964).

double bonds are close to orthogonal. Unfortunately, there are no available theoretical results correlating triplet-state energies of dienes with the dihedral angle between the planes containing the two π bonds to support this explanation.

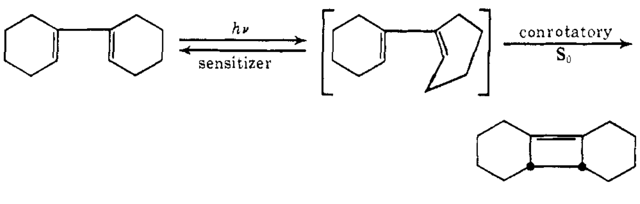
The behavior of the curve in the low-energy region is in direct contrast with the complex pattern reported for the piperylene system.[13] The difference, however, is not surprising. In the piperylene system, the complex behavior was attributed to the presence of *s-cis* and *s-trans* isomers as well as geometric isomers.[13] This complication does not exist in the COD system, for the geometry of the molecule does not allow the diene moiety to exist in the transoid configuration. Furthermore, examination of the model immediately suggests that *trans,trans*-COD is too strained even to be considered.

The evidence presented clearly shows that the photosensitized conversion of I to II is a two-step reaction with light only enhancing the geometric isomerization. Bicyclohexenyl is, therefore, now the only remaining example in the literature of a photosensitized reaction of diene to the corresponding cyclobutene.

Dauben, *et al.*, in their discussion of the valence isomerization of bicyclohexenyl brought about by direct irradiation, considered two mechanisms[3] which are



The conrotatory process was later rejected because of the stereochemistry of the product. Although a similar discussion was not presented for the sensitized reaction, their description of the structure of the triplet and the Woodward–Hoffman rule[20] are only consistent with the mechanism of reaction directly from an excited state, in this case the triplet state. In view of our findings, we wish to postulate an alternative mechanism for the sensitized reaction which involves the highly strained *cis,trans*-bicyclohexenyl intermediate, thermal (from S_0 state) cyclization of which will provide a prod-



uct with the correct stereochemistry.[21] A convenient and related system to test this postulation is the 1,1′-bicycloheptenyl system, where the *cis,trans* isomer may be sufficiently stable for direct detection.[23]

Experimental Section

Photosensitized Cyclization of 1,3-Cyclooctadiene. Preparation of Bicyclo[4.2.0]-7-octene. In a typical run, a solution of 300 g of *cis,cis*-1,3-COD, 10 g of acetophenone, and 600 ml of *n*-heptane was added to a Pyrex immersion apparatus. With the temperature maintained between 80 and 90°, the solution was irradiated with a 550-w Hanovia medium-pressure mercury lamp. After 68 hr a 90% conversion was reached. For complete conversion an additional 40 hr of irradiation was necessary. At the end of the irradiation period a small amount of polymeric material began to coat the well. The irradiated solution was filtered and then distilled through a 2-ft spinning-band column. The fraction boiling at 76–77° (130 mm) (182 g) was greater than 98% pure, and a forerun, 74–76° (130 mm) (42 g), containing 5% *n*-heptane, was also obtained. The infrared spectrum of the product is identical with that reported for bicyclo[4.2.0]-7-octene.[10]

Elevated temperature is a necessary condition for efficient conversion to the product; *e.g.*, irradiation of a similar solution at 20° for a similar period virtually gave no bicyclooctene. Benzene has also been used as solvent. Other compounds which are effective in sensitizing the reaction are propiophenone, benzophenone, triphenylene, and β-acetonaphthone. 9-Fluorenone was not effective.

***cis,trans*-1,3-Cyclooctadiene.** A solution of 60 g of *cis,cis*-1,3-COD and 2 g of acetophenone in 500 ml of *n*-pentane was irradiated in a Pyrex immersion apparatus with a medium-pressure lamp until a photostationary state between the *cis,cis* and the *cis,trans* isomers was reached (17 hr). The temperature of the solution was maintained below 20°. Glpc analysis showed that at such temperatures no bicyclo[4.2.0]oct-7-ene was formed. At 0° 200 ml of 20% silver nitrate solution was added to the irradiated mixture. Precipitation occurred immediately. After stirring vigorously for 2 hr at 0° the solution was filtered. The white solid weighed 41.5 g (82% yield based on reacted COD), mp 90–98°. After one recrystallization from methanol 24 g of white crystalline solid, mp 125–127° dec, was obtained.[9]

Anal. Calcd for $C_8H_{12}AgNO_3$: C, 34.19; H, 4.32; N, 5.03. Found: C, 34.28; H, 4.42; N, 5.16.

A procedure similar to that described by Cope was used to liberate the diene from the silver nitrate complex. To a stirred suspension of 5.0 g of silver nitrate complex in 20 ml of pentane, 20 ml of concentrated ammonia was added dropwise. The white solid gradually dissolved with some decomposition as shown by the presence of brownish solid between layers. The mixture was filtered and separated, and the water layer was washed with 50 ml of pentane. The combined pentane solution was dried over anhydrous sodium sulfate. Pentane was removed by distillation under vacuum, leaving a colorless liquid. Flash distillation yielded 1.2 g of colorless liquid (62% yield) which showed infrared absorption identical with that reported for *cis,trans*-1,3-cyclooctadiene. The diene thus obtained is not contaminated with the *cis,cis* isomer (shown by glpc) and is stable when stored under N_2 at Dry Ice temperature. On heating in refluxing benzene solution, the diene was found to convert quantitatively to bicyclo[4.2.0]oct-7-ene.

Determination of Photostationary-State Composition of 1,3-Cyclooctadienes. The following general procedure was used in preparation of solutions and analysis of photostationary-state compositions of 1,3-cyclooctadienes. Pentane solutions of 10% *cis,cis*-1,3-COD–0.1 *M* sensitizer were degassed and sealed in Pyrex tubes. The solutions were irradiated until a constant ratio between the *cis,cis* and *cis,trans* isomers was reached. Glpc was employed for analysis of the mixtures. To keep the column temperature below 50°, a short (3-ft) 20% tris(cyanoethoxy)propane column was used. A solution with benzil as sensitizer was decolorized on prolonged irradiation. With 9-fluorenone, the solution darkened upon prolonged irradiation, but no detectable amount of the *cis, trans* isomer was formed.

Acknowledgment. The author wishes to thank Drs. H. E. Simmons and J. R. Edman for helpful discussions.

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

[21] Corey, *et al.*,[22] have presented experimental evidence for the existence of *trans*-cycloheptene, produced *via* a thermal reaction. In this photosensitized reaction, intersystem crossing of triplet bicyclohexenyl will produce a vibrationally highly excited ground-state molecule which could overcome the strain energy possessed in our postulated intermediate.

[22] E. J. Corey, F. A. Carey, and R. E. Winter, *J. Am. Chem. Soc.*, **87**, 1934 (1965).

[23] After having completed the preparation of this manuscript, a communication on photosensitized double bond migration in substituted cyclohexenes appeared in the literature.[24] Among other possible mechanisms, the author favors one which involves *trans*-cyclohexene intermediates.

[24] P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 409 (1966); see also J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).