phenyl-1-benzoylcyclopropane (258.0 mg, 0.800 mmol), $[\alpha]^{25}{}_{325}$ 920 ± 15°; 43.1 mg (0.133 mmol) of cis-2-p-cyanophenyl-trans-3-phenyl-1-benzoylcyclopropane, $[\alpha]^{25}{}_{343}$ −2980 ± 80°; 6.8 mg (0.021 mmol) of trans-2-p-cyanophenyl-cis-3-phenyl-1-benzoylcyclopropane, $[\alpha]^{25}{}_{345}$ −104 ± 8°.

Thermal and Photochemical Interconversions of Cyclooctatetraenes and Semibullvalenes. Exploratory Organic Photochemistry. LII[1,2]

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Abstract: Irradiation of cyclooctatetraene at −60° in isopentane with an acetone sensitizer afforded semibullvalene and benzene as the major volatile products. Nmr and vpc assay indicated ca. 42% of semibullvalene based on reacted cyclooctatetraene; despite vpc overlap with cyclooctatetraene, semibullvalene could be isolated by silver nitrate liquid partition chromatography with 26% recovery. Bicyclo[4.2.0]octa-2,4,7-triene, independently prepared, was irradiated under typical conditions and found to afford only benzene, thus establishing that this compound was not an intermediate in the semibullvalene formation. Low-temperature irradiations were monitored by low-temperature infrared analysis, and evidence was obtained for the direct formation of semibullvalene. In related efforts 1,3,5,7-tetramethylcyclooctatetraene was found to be only slightly reactive on irradiation under similar conditions and the tetramethylsemibullvalenes were not among the products. Contrariwise, pyrolysis of 1,3,5,7-tetramethylcyclooctatetraene afforded $\beta,\beta',\gamma,\gamma'$-tetramethylsemibullvalene and presumably $\alpha,\alpha',\alpha'',\alpha'''$-tetramethylsemibullvalene. Photolysis of the former semibullvalene was investigated and found to give 1,3,5,7-tetramethylcyclooctatetraene.

In an attempt to delineate both the excited and ground state pathways interrelating the (CH)₈ hydrocarbons, we have investigated the photochemistry of cyclooctatetraene (**1**). Although cyclooctatetraene has been obtained[2,3] on irradiation of two of its (CH)₈ isomers, namely barrelene[2] and semibullvalene (**2**),[3] and similar behavior has been found for the benzo[4] and naphtho[5] derivatives of barrelene and semibullvalene, the photochemistry of cyclooctatetraene has not been extensively studied. There are reports of the formation of benzene and acetylene,[6] and also, the valence tautomer bicyclo-[4.2.0]octa-2,4,7-triene (**3**)[7] from the photolysis of cyclooctatetraene.

Low-Temperature Photolysis of Cyclooctatetraene. Results. In pursuing our study of the low-temperature photochemistry of cyclooctatetraene, we began with exploratory irradiation of small samples (ca. 100 mg) under different conditions in sealed quartz tubes kept

at temperatures ranging from −65 to −30°. Nmr analysis used to follow the direct irradiation of cyclooctatetraene (i.e., without sensitizer) strikingly revealed approximately equal amounts of semibullvalene and benzene. Above −30°, the formation of benzene predominated and the inside wall of the tube was badly coated with opaque polymeric material. In the presence of acetone sensitizer the conversion was somewhat accelerated, suggesting that triplet sensitization is occurring. With large concentrations of acetone, the

$$(1)$$
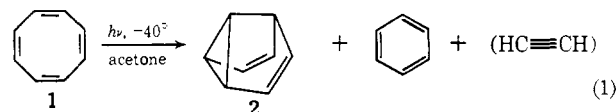
efficiency diminished slightly perhaps due to self-quenching. Acetophenone and benzophenone, however, were found ineffective in sensitizing the reaction. The results are summarized in Table I.

Preparative Low-Temperature Photolysis of Cyclooctatetraene. Results. Hitherto semibullvalene had been obtained by laborious multistep syntheses with limited overall yield.[3] In view of the single step formation of semibullvalene from easily available cyclooctatetraene, our attention was turned toward the matter of preparative utility. A low-temperature photolysis assembly (note Figure 1) utilizing a vacuum chamber between a Hanovia immersion well and the surrounding flask was found convenient. In a typical run irradiation of 11.4 g (0.109 mol) of cyclooctatetraene and 16.6 g of acetone in 500 ml of isopentane at −60° with a 450-W medium-pressure lamp with a

(1) For paper LI, see H. E. Zimmerman and C. M. Moore, *J. Amer. Chem. Soc.*, **92**, 2023 (1970).

(2) Preliminary communication of the present results: H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968).

(3) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

(4) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

(5) H. E. Zimmerman and C. O. Bender, *ibid.*, **91**, 7516 (1969).

(6) (a) I. Tanaka, S. Miyakawa, and S. Shida, *Bull. Chem. Soc. Jap.*, **24**, 119 (1951); I. Tanaka and M. Okuda, *J. Chem. Phys.*, **22**, 1780 (1954); H. Yamazaki and S. Shida, *ibid.*, **24**, 1278 (1956). (b) 1,2,4,7-Tetraphenylcyclooctatetraene has been reported to afford p-terphenyl and tolane on irradiation: E. H. White and R. L. Stern, *Tetrahedron Lett.*, 193 (1964).

(7) (a) G. J. Fonken, *Chem. Ind.* (London), 1625 (1963); (b) E. Migirdicyan and S. Leach, *Bull. Soc. Chim. Belges*, **71**, 845 (1962).

Table I. Low-Temperature Photolyses under Different Conditions; Low Conversion Runs

Run	Concn of COT, mol	Filter	Sensitizer concn, mol	Time, hr	T, °C	Semibull-valene, %	Benzene, %
1	0.62 (P)[a]	Vycor		12	−30	2.0	2.0
2	0.87 (P)	Corex		21	−65	1.4	0.8
3	0.50 (P)	Vycor	Acetone, 1.50	3	−40	1.8	1.4
4	0.50 (P)	Vycor	Acetone, 1.50	5	−40	2.2	1.5
5	0.50 (P)	Vycor	Acetone, 1.50	8	−40	3.1	2.2
6	0.50 (P)	Vycor	Acetone, 1.50	12	−40	4.0	3.5
7	0.27 (P)	Corex	Acetone, 11.6[c]	6	−45	1.2	0.8
8	0.28 (THF)[b]	Pyrex	Acetophenone, 0.76	9	−40	0	0
9	0.39 (THF)	Pyrex	Benzophenone, 1.15	10	−40	0	0

[a] Isopentane solvent. [b] Tetrahydrofuran solvent. [c] More than 95% of the incident light absorbed by acetone.

Vycor filter for 50 hr afforded a mixture which was shown by nmr and vpc analysis to contain 9.27 g (81.5%) of cyclooctatetraene, 0.845 g (7.4%) of semibullvalene, and 0.34 g (4.0%) of benzene. Semibullvalene could be concentrated by fractional crystallization of cyclo-
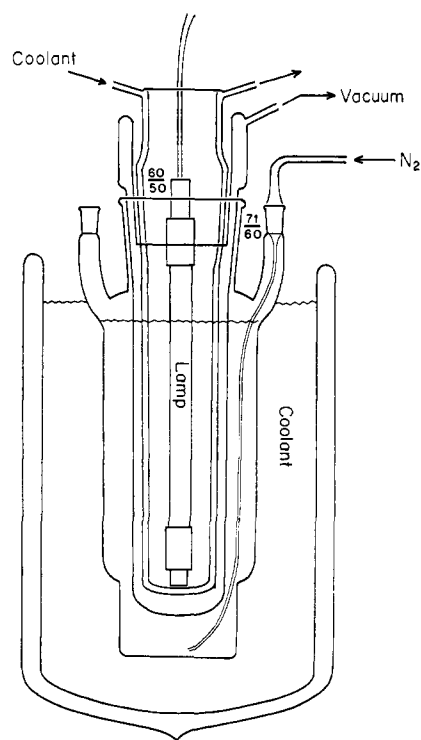

Figure 1. Low-temperature photolysis apparatus.

octatetraene from the mixture with isopentane solvent at −78°. Vpc was found ineffective in separating semibullvalene from cyclooctatetraene, but aqueous silver nitrate–ether liquid–liquid partition chromatography proved efficient. A 220-mg yield of semibullvalene was isolated, and this corresponds to 5% based on 38% unrecovered cyclooctatetraene. Isolation techniques are further described in the Experimental Section.

Low-Temperature Infrared Studies of the Cyclooctatetraene Photolysis. Results. Low-temperature ir

studies of photochemical reactions have proven instructive in elucidating the intermediacy of thermally unstable species. It seemed wise to look for possible intermediates in the cyclooctatetraene to semibullvalene conversion. A solution of cyclooctatetraene in THF–n-propyl ether (2:1 v/v) was irradiated at −78° and the course of the reaction was followed by ir spectroscopy at this temperature. After 2 hr irradiation, a decrease in the intensity of bands characteristic of cyclooctatetraene was noticeable. The spectrum obtained after 10 hr irradiation at −78° revealed shoulders at 6.82, 12.20, 12.68, and 14.50 μ. The first three correspond to the strongest bands of semibullvalene while the last one to that of benzene. The solution was warmed up to room temperature in the dark for 1 hr. The ir spectrum run, again at −78°, was identical with that obtained just before warming. Both the 6.4- and 10.5-μ regions where absorptions due to cyclobutenes and $trans$-double bonds are expected to appear, respectively, were transparent during the photolysis. Hence no evidence could be adduced for thermally unstable photolysis intermediates.

Test of a Potential Intermediate. Photolysis of Bicyclo[4.2.0]octa-2,4,7-triene. Results. As an operational test of the potential intermediacy of bicyclo-[4.2.0]octa-2,4,7-triene (**3**) in the formation of semibullvalene, which seemed a real possibility ($vide\ infra$) at the beginning of this work and is presented as mechanism I in the Discussion ($vide\ infra$), the bicyclooctatriene (**3**) was independently prepared following the method of Vogel, Kiefer, and Roth[8] and photolyzed at −65° with monitoring by low-temperature nmr. The nmr showed the formation of benzene but not semibullvalene. Benzene was formed in 87% yield and separated by vpc in 70% yield.

$$(2)$$
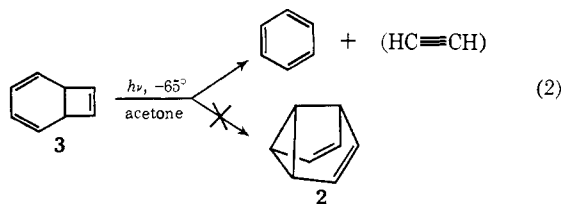
(8) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

Photochemical Behavior of 1,3,5,7-Tetramethylcyclooctatetraene. Results.

In view of the interesting photochemistry of cyclooctatetraene itself, it seemed of interest to explore the generality of the reaction. For this purpose the irradiation of 1,3,5,7-tetramethyl-cyclooctatetraene (4) was selected. It was found that neither at low temperature (to −65°) nor at room temperature was there any observable conversion to tetramethylsemibullvalene. The reactant seemed particularly unreactive, despite acetone sensitization. However, at room temperature a slow conversion to mesitylene was encountered. In all these experiments the mass balance was excellent and no scrambling of the methyl groups was detected.

Thermal Behavior of 1,3,5,7-Tetramethylcyclooctatetraene. Results.

With the lack of photochemical reactivity of the tetramethylcyclooctatetraene in mind and the knowledge[9] that octamethylcyclooctatetraene undergoes a thermal rearrangement to give octamethyl-semibullvalene,[9] it appeared likely that whether the thermal *vs.* photochemical conditions are required for the cyclooctatetraene to semibullvalene conversion is a function of substitution. Accordingly, the thermal behavior of 1,3,5,7-tetramethylcyclooctatetraene (4) was investigated. It was found that at 250° there was a slow conversion to β,β′,γ,γ′-tetramethylsemibull-valene (5, 1,3,5,7-tetramethyltricyclo[3.3.0.0²,⁸]octa-3,6-diene) and also mesitylene (*ca.* 2% each after 15 hr). Additionally, the nmr suggested the presence of the isomeric α,α′,α′′,α′′′-tetramethylsemibullvalene (6) but this could not be isolated. The remaining material proved to be reactant tetramethylcyclooctatetraene (4). It appears that the thermal reaction of the tetramethyl-cyclooctatetraene is appreciably slower than that of the octamethyl analog described by Criegee.[9]
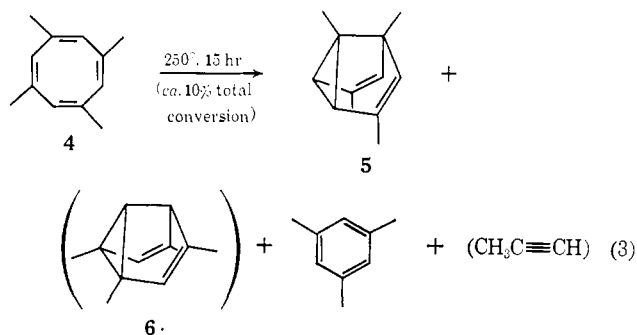

Irradiation of β,β′,γ,γ′-Tetramethylsemibullvalene. Results.

There existed the possibility that the lack of photochemical reaction of the 1,3,5,7-tetramethyl-cyclooctatetraene (4) derived merely from a very unfavorable steady state. Actually, in the case of cyclooctatetraene itself (*vide supra*) the steady-state concentration of semibullvalene is by no means large and cyclooctatetraene predominates at a photoequilibrium.

Hence it seemed important to determine whether a photochemical route from β,β′,γ,γ′-tetramethylsemi-bullvalene (5) to 1,3,5,7-tetramethylcyclooctatetraene (4) existed. Irradiation of 5 did indeed afford 1,3,5,7-tetramethylcyclooctatetraene (4) in 58% yield.

Interpretative Discussion of Results. The Gross Mechanism of the Cyclooctatetraene to Semibullvalene Photolysis.

One possible mechanism, mentioned

(9) R. Criegee and R. Askani, *Angew. Chem.*, 80, 531 (1968).
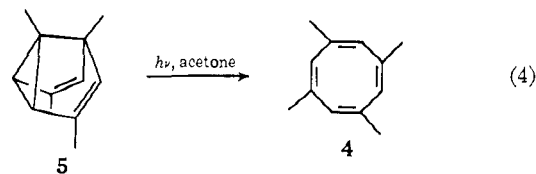

above, seemed quite reasonable when the cyclooctatetraene to semibullvalene reaction was first encountered. This was the photochemical formation of bicyclo[4.2.0]-octa-2,4,7-triene (3)[7,10] followed by secondary irradiation of this intermediate. Irradiation of 3 might reasonably be expected to give semibullvalene through a di-π-methane rearrangement[11] (eq 5). However, the
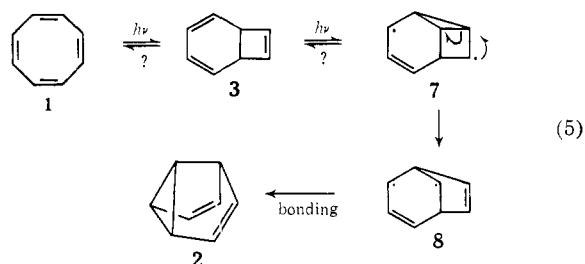
finding that independently prepared bicyclo[4.2.0]octa-2,4,7-triene (3) did not give semibullvalene under reaction conditions provides strong evidence against 3 as a reaction intermediate in semibullvalene formation.

A second mechanism which seemed reasonable is the formation of the tricyclic diene (9, tricyclo[3.3.0.0²,⁶]-octa-3,7-diene) by a photochemical cycloaddition. This mechanism is especially reasonable since this tricyclic diene (9) has been found in these laboratories[12] to afford semibullvalene thermally at room temperature (eq 6). However, again the evidence argues negatively, since even at −70° no trace of additional absorption for such an intermediate (*i.e.*, 9) could be detected in the ir during photolysis at a time when semibullvalene peaks were developing and easily discernible. At these low temperatures the tricyclic diene 9 should be stable.[12]
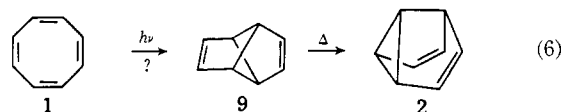
The observation that semibullvalene is developing during the low-temperature photolysis argues against any large accumulation of a ground-state intermediate which slowly, or later on warming, proceeds onward to semibullvalene. One possibility involves 1,5 + 4,6 bonding directly from the excited state of some cyclooctatetraene stereoisomer (10). It has already been noted[13] that 1,5 bonding in the excited state of polyene systems is especially favorable energetically and that 1,3 bonding (here 4,6) is just somewhat less likely. Mechanistic versions in which 1,5 and 4,6 bonding are developing simultaneously may turn out to be energetically favorable or not depending on electronic factors (*vide infra*). The 1,5 + 4,6 mechanism is considered in

(10) In the present study no evidence could be found for the photochemical formation of 3; one possibility is that this derives from a difference in conditions compared to ref 7.

(11) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, 91, 1718 (1969), and papers cited therein.

(12) Unpublished results of H. E. Zimmerman and J. D. Robbins.

(13) H. E. Zimmerman, *J. Amer. Chem. Soc.*, 88, 1566 (1966); *Science*, 153, 837 (1966).

|	Hückel (0,2,4, etc. inversions)	Möbius (1,3,5, etc. inversions)
$(4N + 2)e$	Allowed (aromatic)	Forbidden (antiaromatic)
$(4N)e$	Forbidden (antiaromatic)	Allowed (aromatic)

Figure 2. Summary of Hückel-Möbius stability situation for ground state. Excited state results are the reverse.

detail below following discussion of further evidence; however, for the present it may be seen that of the possible gross mechanisms considered this seems to be the most likely candidate.

10
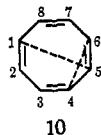
Interpretative Discussion of the Thermal and Photochemistry of 1,3,5,7-Tetramethylcyclooctatetraene. Turning now to the tetramethylcyclooctatetraene results, we note that the lack of photochemical reactivity of the tetramethylcyclooctatetraene must derive from an intrinsically difficult pathway or from an unfavorable photochemical steady state. The observation that $\beta,\beta',\gamma,\gamma'$-tetramethylsemibullvalene reverts to 1,3,5,7-tetramethylcyclooctatetraene on photolysis (eq 7) shows that a pathway is available in one direction and provides permissive but not definitive evidence for the unfavorable steady-state rationale. Also in connection with the tetramethyl series and its photochemistry, we note that, since 1,3,5,7-tetramethylcyclooctatetraene (4) is the product of photolysis of $\beta,\beta',\gamma,\gamma'$-tetramethyl-semibullvalene (5), the reaction in which cyclooctatetraenes are formed from semibullvalenes involves a simple $\alpha,\alpha' + \gamma,\gamma'$ fission (eq 7).

Another aspect of interest is that photolysis of 1,3,5,7-tetramethylcyclooctatetraene not only gives no semibullvalene but also gives unscrambled reactant back. This means that if there is any unfavorable steady state established, the forward and return routes to the semibullvalene must be skeletally identical.

$$(7)$$

5   4
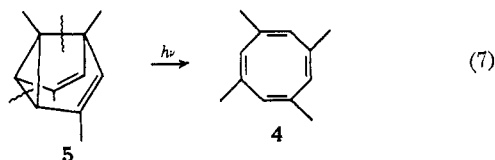
Interpretative Discussion of the Molecular Details of Cyclooctatetraene to Semibullvalene Reactions. With respect to the molecular mechanism of formation of semibullvalene from cyclooctatetraene, it is convenient to focus attention on three of the double bonds of the tetraene system. This is reasonable since the corresponding 1,3,5-cyclooctatriene undergoes a similar 1,5 + 4,6 photochemical closure to dihydrosemibullvalene[14] and the fourth double bond can be considered

to be a perturbation affecting triene mechanisms. Chart 1 lists the stereoisomers of 1,3,5-cyclooctatriene and whether in each case 1,5 + 4,6 closure is thermal or photochemically allowed. It is interesting that of the different geometric isomers of 1,3,5-cyclooctatriene, those having zero or an even number of *trans* double bonds lead to thermally allowed 1,5 + 4,6 closure while those with an odd number of *trans* double bonds should have photochemically allowed 1,5 + 4,6 closures. The question of "forbiddenness or allowedness" is not obtainable simply in the usual way described by Woodward and Hoffmann[15] since the molecules lose any symmetry they have as the reaction proceeds. However, a simple method not requiring symmetry and depending on the number of sign inversions in a cyclic array of orbitals in a transition was described by us some years ago.[11,13b,16,17] Recently a new nomenclature for counting sign inversions has been suggested.[18] While the present discussion will use the original designation, the 2a–2s equivalent[18] is also included in Chart I to help clarify the similarity in the modes of counting inversions. Our approach made use of the generalization that systems having zero or an even number of sign inversions between orbitals were "Hückel-like" in being low energy if containing $4N + 2$ electrons and that systems with an odd number of such sign inversions were "Möbius-like" and were stable with $4N$ electrons.[11,13b,16,17] The situation is summarized in Figure 2. In Chart I those reaction pathways will be thermally allowed which have a zero or even number of i's (or 2a's) indicated between orbitals since this is a $4N + 2$, i.e., six electron cyclic system of orbitals. In the chart the cycle of orbitals is given by the letter sequence a, b, c, d, e, and f. The photochemically allowed pathways have an odd number of i's or 2a's.[19] Although our method does not require that pairs of 2π components be arranged so that like signs overlap between these components, as long as each inversion is counted, Chart I has these arranged in this fashion to allow comparison of the method counting inversions and the method counting 2a's.

(15) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(16) H. E. Zimmerman, *ibid.*, **88**, 1564 (1966).

(17) H. E. Zimmerman, *Angew. Chem.*, **81**, 45 (1969).

(18) (a) Recently R. Hoffmann, 21st National Organic Chemistry Symposium, Salt Lake City, Utah, June 19, 1969, has suggested the use of the designation 2a to represent each sign inversion. However, there is no disagreement with the current approach which differs only in nomenclature. (b) In the counting of single inversions (*i.e.*, i's in our convention) the cyclic array of orbitals can be chosen with arbitrary sign orientations without changing the even or odd nature of the total sum of inversions.

(19) An interesting reactivity index[20] can be defined as half of the number of orbitals in a cyclic array which are not involved in plus–minus overlap. When r is odd, the reaction is thermally allowed and when r is even, the reaction is thermally forbidden. This is just a convenient way of determining whether one is dealing with the "allowed diagonal" or "forbidden diagonal" of Figure 2. This rule is identical with our reasoning as given earlier. One can see that r, as defined, also equals one-half of the total number of orbitals minus the number of inversions, since two orbitals involved in plus–minus overlap result from each inversion. To be on the "allowed diagonal" of Figure 2 when the total number of electrons is $4N + 2$, $r = 2N + 1$ – (an even number of inversions). The index r is then the difference between an odd and an even number and is odd. Similarly when the total number of electrons is $4N$, Figure 2 shows that for allowedness a Möbius system (*i.e.*, a system with an odd number of i's) is required. Then $r = 2N$ – (an odd number of inversions) and r is odd. For neutral systems N also represents the number of orbitals.

(20) The r index treatment was given at a lecture presented to the Annual Joint Meeting of the Chemical Society and the Royal Institute of Chemistry, Nottingham, April 14–18, 1969, by H. E. Zimmerman.

(14) (a) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964); (b) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Amer. Chem. Soc.*, **86**, 2660 (1964); (c) W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964).

In the case of the present chemistry then, the decision of whether each pathway is forbidden or allowed must result from counting inversions and the dependence on the number of *trans*-double bonds derives from this type of analysis.

Inspection of Chart I suggests that it is the *trans,-cis,cis* stereoisomer which can undergo photochemical 1,5 + 4,6 bonding. The same conclusion is valid for a cyclooctatetraene with this stereochemistry but, of course, with the fourth double bond. We note that White[21] has recently reported a cyclooctatetraene having similar stereochemistry, namely the *trans,cis,-cis,cis* product from the photolysis of 1,2,4,7-tetraphenylcyclooctatetraene.

Chart I. Stereoisomeric 1,3,5-Cyclooctatrienes and Allowedness for Closure[a]
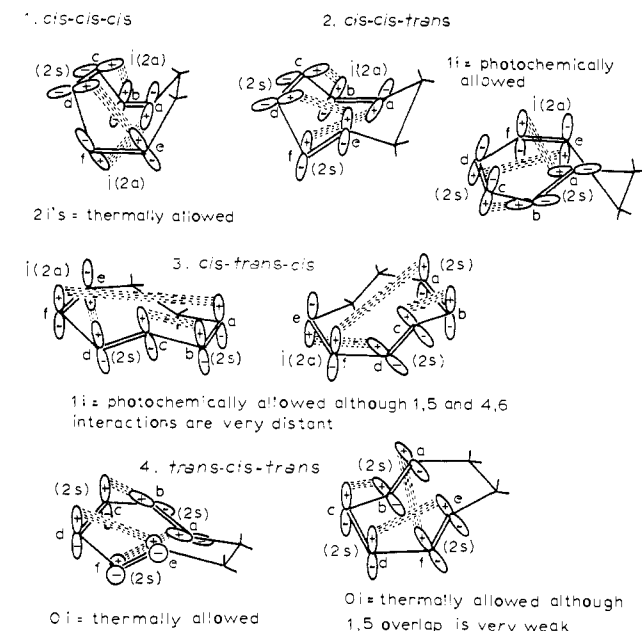
[a] Dotted lines represent interactions leading to dihydrosemibullvalene and increasing for the given pathway.

This seems to be a reasonable candidate as an intermediate in the photochemical cyclooctatetraene to semibullvalene transformation. This would require a two quantum process with the *trans,cis,cis,cis*-cyclooctatetraene, formed initially photochemically, absorbing the second photon and reacting more rapidly than it is formed since no evidence for accumulation of such an intermediate could be found in the low-temperature infrared studies. This seems reasonable in view of the strained nature of the intermediate (note Figure 3).

Such a postulate would also accommodate the observation that the tetra- and octamethylcyclooctatetraenes are unreactive, since in these derivatives severe methyl–methyl interaction is anticipated.

The thermal reactions seem most likely to proceed *via* the allowed processes beginning with all-*cis* or *trans,-cis,trans,cis* (chiral conformer) stereoisomers in view of the considerations in Chart I.

Low-Temperature Photolyses under Different Conditions. All the photolyses were carried out in 0.8-cm i.d. quartz tubes.[22] Solutions of cyclooctatetraene were degassed, sealed under vacuum, and placed under the di-

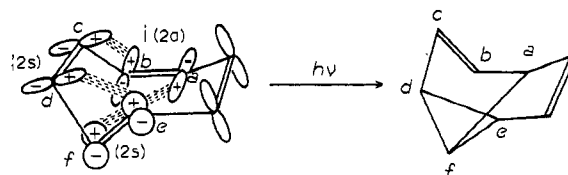(21) E. H. White, E. W. Friend, Jr., R. L. Stern, and H. Maskill, *J. Amer. Chem. Soc.*, 91, 523 (1969).

Figure 3. Perspective view of closure of *trans,cis,cis,cis*-cyclooctatetraene.

rected stream of cold nitrogen produced by boiling liquid nitrogen with a nichrome heater immersed in a dewar reservoir. A calibration curve giving solution temperature *vs.* the heater voltage was obtained. The tube was mounted parallel to a quartz immersion well containing a 450-W medium-pressure Hanovia mercury lamp. After a desired time of irradiation, the tube was opened in the cold and the photolysate was diluted with isopentane to *ca.* 10 ml. The solution was washed with three 5-ml portions of water to remove most of acetone and dried over anhydrous sodium sulfate. The acetophenone and benzophenone sensitizers were removed by passing the mixture through a 2 × 6 cm column packed with deactivated silica gel. The solution was concentrated by distillation through a 25 cm × 10 mm column packed with stainless steel helices. The nmr spectrum of the residue was examined to determine the composition. It was found to be advisable to use ^{13}C satellites of cyclooctatetraene which appear at τ 3.05 and 5.65 and have 1.108% intensity of the total cyclooctatetraene as the internal standard for integration of the photoproducts, semibullvalene and benzene, which were obtained in the range of 0–10% yield. Specific data for individual determinations are listed below. In run 1, 137.8 mg of cyclooctatetraene was irradiated for 12 hr in 2.0 ml of isopentane at −30° with Vycor filter without sensitizer to give 2.0% semibullvalene and 2.0% benzene; run 2, 200 mg of cyclooctatetraene, 21 hr, 2.0 ml of isopentane, −65°, Corex filter, without sensitizer, 1.4% semibullvalene and 0.8% benzene; run 3, 120 mg of cyclooctatetraene, 3 hr, 2.0 ml of isopentane, −40°, Vycor filter, 200 mg of acetone sensitizer, 1.8% semibullvalene and 1.4% benzene; run 4, 120 mg of cyclooctatetraene, 5 hr, 2.0 ml of isopentane, −40°, Vycor filter, 200 mg of acetone sensitizer, 2.2% semibullvalene and 1.5% benzene; run 5, 120 mg of cyclooctatetraene, 8 hr, 2.0 ml of isopentane, −40°, Vycor filter, 200 mg of acetone sensitizer, 3.1% semibullvalene and 2.2% benzene; run 6, 120 mg of cyclooctatetraene, 12 hr, 2.0 ml of isopentane, −40°, Vycor filter, 200 mg of acetone sensitizer, 4.0% semibullvalene and 3.5% benzene; run 7, 93 mg of cyclooctatetraene, 6 hr, 1.0 ml of isopentane, −45°, Corex filter, 2.26 g of acetone sensitizer, 1.2% semibullvalene and 0.8% benzene; run 8, 98 mg of cyclooctatetraene, 9 hr, 3.0 ml of tetrahydrofuran, −40°, Pyrex filter, 310 mg of acetophenone sensitizer, 0% semibullvalene and 0% benzene; run 9, 102 mg of cyclooctatetraene, 10 hr, 2.0 ml of tetrahydrofuran, −40°, Pyrex filter, 546 mg of benzophenone sensitizer, 0% semibullvalene and 0% benzene.

Preparative Low-Temperature Photolysis of Cyclooctatetraene. The low-temperature photolysis assembly described above and in Figure 1 was used. A solution of 11.37 g (0.109 mol) of cyclooctatetraene and 16.55 g

(22) All melting points were taken on a calibrated hot-stage apparatus.

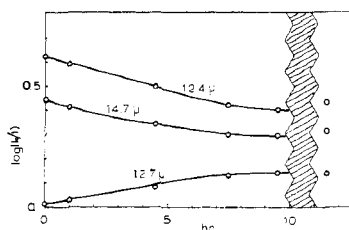*Zimmerman, Iwamura / Exploratory Organic Photochemistry*

Figure 4. Plots of the ir absorbances of the cyclooctatetraene and semibullvalene bands vs. irradiation time. The shaded area corresponds to sitting in the dark at room temperature.

of acetone in 500 ml of isopentane was irradiated with a 450-W Hanovia medium-pressure uv lamp through a Vycor glass filter for 50 hr with Dry Ice–acetone cooling. An equilibrium temperature of -60 to $-65°$ was reached; it was necessary to add Dry Ice every 2 hr. The solution was purged with nitrogen to effect stirring of the solution. At the end of the irradiation, the inside wall of the flask was covered with a film of insoluble polymeric material. After washing with three 20-ml portions of cold water to remove most of the acetone and drying over anhydrous sodium sulfate, the yellow photolysis solution was concentrated to 50 ml by distillation through a 42 cm $\times$ 20 mm column packed with stainless steel helices. Gas chromatography[23] and the nmr spectrum[3] of the residue showed the presence of 9.27 g (81.5%) of cyclooctatetraene, 0.845 g (7.4%) of semibullvalene, and 0.340 g (4.0%) of benzene. On cooling the concentrate to $-78°$, yellow needles of cyclooctatetraene precipitated. The mother liquor was siphoned off and the residue was recrystallized from 10 ml of isopentane to give 4.27 g of cyclooctatetraene. The combined mother liquor was dried over sodium sulfate and concentrated to 10 ml by distillation through the aforementioned column. Nmr analysis of the concentrate indicated 13% semibullvalene and 5.3% benzene with the remaining material being cyclooctatetraene. A 1.0-ml portion of the above mixture was put on a 3.6 cm $\times$ 150 cm column packed with 400 g of Celite impregnated with a solution of 24 g of silver nitrate in 136 g of water. Elution was with ether saturated with water in 40-ml fractions; benzene[24] eluted in fractions 32–37, cyclooctatetraene in fractions 97–150, and semibullvalene in fractions 148–190. The combined ether solution of the last fractions, amounting to 2 l. in volume, was washed with five 5-ml portions of 60% aqueous silver nitrate. To the ice-cooled aqueous extract was added with stirring 50 ml of 30% ammonium hydroxide in 5 min. The mixture was extracted with five 5-ml portions of ether.[25] From ten batches of the silver nitrate liquid–liquid partition chromatography, a 200-ml ether solution of 540 mg of pure semibullvalene was obtained, as indicated by nmr,

(23) Their respective retention times on a 6.5 ft $\times$ 0.25 in. stainless steel column packed with Chromosorb P coated with 15% Apiezon L (at 75° under 15 psi of N_2) were 5.2 (benzene) and 23.5 min (cyclooctatetraene and semibullvalene).

(24) Traces of biacetyl from the photolysis of acetone and acetaldehyde monoethyl acetal, presumably an impurity in ether, were also detected in this fraction.

(25) A major problem in the preparative procedure was in the step of enrichment of the semibullvalene solution obtained as the elute of the silver nitrate liquid–liquid partition chromatography. The concentration was ca. 0.004%. Fractional distillation of ether, even through an efficient column, lost a considerable portion of the material due both to inefficiency of the fractionation and thermal decomposition under prolonged heating. Also the small amount of impurities, e.g., ethanol, in ether was no longer negligible.

which lacked cyclooctatetraene and benzene peaks. The ether solution was concentrated to 20 ml, and 1 ml each was injected into the preparative vpc[26] to afford 220 mg of semibullvalene. From the combined cyclooctatetraene fractions of the liquid–liquid partition chromatography was recovered additional 2.80 g of cyclooctatetraene. The yield of semibullvalene based on 38% unrecovered cyclooctatetraene was 5%.

Ir Monitored Low-Temperature Photolysis of Cyclooctatetraene. In a Beckman Model VLT-2 variable-temperature ir cell of 0.085 mm optical thickness with NaCl windows (catalog no. 195793) was placed a 0.387 M solution of cyclooctatetraene in THF–n-propyl ether (2:1 v/v). A beam of uv light from a 200-W high-pressure Hg arc (Osram HBO) was passed through a 2.0-cm-long water cell serving as an infrared filter onto the window of the ir cell which was kept at $-78°$. After a fixed time of irradiation, the cell was mounted on a Perkin-Elmer Infracord ir spectrometer and the ir spectrum was obtained against the solvent background.

At $-78°$ cyclooctatetraene shows characteristic ir bands at 6.7 (w), 11.5 (w), 11.9 (w), 12.4 (s), 13.1 (w), and 14.7 μ (s). After a 2 hr irradiation, a decrease in the intensity of these bands was noticeable. The spectrum obtained after 4.5 hr irradiation showed absorption bands at 6.82, 12.2, 12.68, and 14.5 μ. The first three coincide with those of the strongest bands of semibullvalene while the last with that of benzene. After 10 hr these absorptions were clearly identified as shoulders of the strong bands at 12.4 and 14.7 μ of the starting cyclooctatetraene. The cell was then warmed up to room temperature and kept at the ambient temperature in the dark for 1 hr. The ir spectrum was run again at $-78°$ and reproduced[27] the last one which had been obtained just before warming the solution.

There was no absorption peak which disappeared after warming to room temperature, indicating no accumulation of thermally unstable intermediates as bicyclo[4.2.0]octa-2,4,7-triene. Second, the 10.5-μ region was transparent throughout the irradiation where the band characteristic of the trans-double bond should appear.[28] Also transparent was the 6.4-μ region where $\nu_{C=C}$ of cyclobutenes is generally expected to appear.[8]

Low-Temperature Photolysis of Bicyclo[4.2.0]octa-2,4,7-triene. Bicyclo[4.2.0]octa-2,4,7-triene was prepared from trans-7,8-dibromobicyclo[4.2.0]octa-2,4-diene according to the method of Vogel, et al.[8] The nmr spectrum[29] revealed contamination of the sample

(26) Preparative vpc was carried out using a Model 776 Prepmaster Jr., Hewlett Packard, F & M Scientific Division, equipped with a 5.7 ft $\times$ 1 in. column packed with 11% Apiezon L on Chromosorb P (nonacid washed). The retention time was 9.4 min at 75°, 11 psi of N_2. Preferential decomposition and inefficient trapping of semibullvalene during the preparative vpc could not be avoided.

(27) Actually there was observed a slight (10–15%) increase in the intensity of the 12.4- and 14.7-μ bands and decrease of the 12.7-μ band as shown in Figure 4. The phenomenon seems, however, more likely to be due to the circulation of the photolysis solution within the cell with the result of moving the less effectively photolyzed portion of the solution to the optical path than indication of the disappearance of the unstable intermediates.

(28) A. C. Cope and C. L. Bumgardner, J. Amer. Chem. Soc., 78, 2812 (1956); A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, ibid., 89, 4024 (1967); G. M. Whitesides, G. L. Goe, and A. C. Cope, ibid., 91, 2608 (1969).

(29) All the nmr spectra were measured on a Varian HA-100 spectrometer at -42 to $-47°$, care being taken not to raise the temperature during transfer. Vpc analyses were on a 6.5 ft $\times$ 0.25 in. stainless steel column packed with Chromosorb P coated with 15% Apiezon L at 85°, the retention times being 2.5 and 9.2 min for benzene and cyclooctatetraene, respectively, under the nitrogen head pressure of 15 psi.

with 10% cyclooctatetraene, 8% benzene, and 2% dimethyl ether. A solution of 2.0 g of this sample in 250 ml of precooled isopentane containing 2.3 g of acetone was irradiated at −65° with a 450-W Hanovia medium-pressure immersion lamp through a Vycor glass filter. The progress of the reaction was monitored by examining the nmr spectra and vpc of aliquots. The composition *vs.* time was as follows: 0 time, 1600 mg of bicyclooctatriene, 210 mg of cyclooctatetraene, 160 mg of benzene; 3 hr, 920, 220, and 580 mg, respectively; 5 hr, 856 mg of the first two components and 795 mg of benzene; 8 hr, 240, 240, 1020 mg; 15 hr, 0 mg of bicyclooctatriene, 250 mg of cyclooctatetraene, and 1214 mg of benzene.

After the desired number of aliquots had been taken the reaction mixture was removed from the cooling bath, washed with two 50-ml portions of water, and concentrated to 5 ml by distillation through a 42 cm × 20 mm column packed with stainless steel helices. Separation by preparative vpc afforded 850 mg of benzene and 210 mg of cyclooctatetraene as identified by comparison of vpc retention time, and ir and nmr spectra with those of authentic samples. Benzene was formed in 87% yield and separated in 80% efficiency.

1,3,5,7-Tetramethylcyclooctatetraene. This was prepared according to the method of de Mayo and Yip[30] and purified by recrystallization from methanol and final sublimation under vacuum.[31] The colorless prisms, mp 69.5∼70.0° (lit.[30,31] mp 69–70°), showed a shoulder at 275 nm (ϵ 403) in cyclohexane.

Low-Temperature Photolysis of 1,3,5,7-Tetramethylcyclooctatetraene. In a low-temperature photolysis flask described in Figure 1 was irradiated a solution of 2.55 g (0.0159 mol) of 1,3,5,7-tetramethylcyclooctatetraene and 9.6 g of reagent grade acetone in 500 ml of isopentane at −70° for 23 hr. The solvent and acetone were removed under reduced pressure. Both in the nmr spectrum and on the vpc chart there was no peak observed other than those of the starting material. From short-path distillation of the residue at 45° under 0.5 mm was recovered 2.52 g (98.8%) of 1,3,5,7-tetramethylcyclooctatetraene, mp 69–70°.

Irradiation of 1,3,5,7-Tetramethylcyclooctatetraene at Room Temperature. A solution of 10.1 g (0.0631 mol) of 1,3,5,7-tetramethylcyclooctatetraene and 35.2 g of reagent grade acetone in 180 ml of cyclohexane was purged with nitrogen and irradiated at room temperature with a 450-W Hanovia medium-pressure uv lamp through a Vycor glass filter for 48 hr. The solvent was removed by distillation under reduced pressure. The nmr spectrum in carbon tetrachloride of the pale yellow crystalline residue showed weak ill-defined absorptions at τ 8.8, 7.05, and 5.0. A pair of singlets at 7.79 and 3.32 were also observed other than two peaks at τ 8.35 and 4.60 of the starting cyclooctatetraene and 8.57 of the solvent cyclohexane. The pair of the new peaks were identified as those of mesitylene by comparison with an authentic sample and estimated by integration to be formed in 3.5% yield. This figure was also confirmed by vpc analysis on a 8.5 ft × 0.25 in. column packed with 15% diethylene glycol succinate on Chromosorb P at 110°, the retention times being 5.5 and 8.2 min for mesitylene and 1,3,5,7-tetramethyl-

cyclooctatetraene, respectively. The first three signals were assigned to those of polymeric material formed during the photolysis because of the fact that they were not found in the sample which was obtained by short-path distillation of the crude photolysate at 45° (0.1 mm). Actually 9.13 g (90.4% recovery) of the cyclooctatetraene was recovered as pale yellow prisms.

Pyrolysis at 250° of 1,3,5,7-Tetramethylcyclooctatetraene. A solution of 3.3 g (0.0206 mol) of the cyclooctatetraene in 15 ml of Nujol was degassed, sealed in a Pyrex tube (2 mm thick wall) under vacuum, and heated at 250° for 15 hr. From the mixture, 2.9 g of volatile material was obtained by heating gradually to 150° (0.5 mm). By repeated fractional crystallization of the distillate from isopentane, 2.0 g of the cyclooctatetraene was recovered as colorless plates. The orange mother liquors of crystallization were concentrated to 1.5 ml. The nmr spectrum of the mixture showed 87% 1,3,5,7-tetramethylcyclooctatetraene, 5.3% 1,3,5,7-tetramethyltricyclo[3.3.0.0^{2,8}]octa-3,6-diene, 5.0% mesitylene, and 2.6% 2,4,6,8-tetramethyltricyclo[3.3.0.0^{2,8}]octa-3,6-diene by integration. No isomeric tetramethylcyclooctatetraene was detected.[32]

The attempted separation of the cyclooctatetraene and the semibullvalenes was unsuccessful by vpc on a 5.7 ft × 1 in. column packed either with 11% Apiezon L on Chromosorb P (NAW) or with 20% diisodecyl phthalate on Chromosorb P (AW). An ether–aqueous silver nitrate liquid–liquid partition chromatography which had been applied successfully to the separation of the parent hydrocarbons was also ineffective.

The mixture was charged on a 90 cm × 35 mm column packed with silica gel (Davison Chemical, Grace MIL-D-3716, mesh 60–200) impregnated with 10% (w/w) silver nitrate and dried overnight at 100°. Elution with 20-ml fractions of hexane–ether (9:1 v/v) gave a yellow oil rich in mesitylene in fractions 20–80. Continued elution with hexane–ether (8:2) gave the cyclooctatetraene in fractions 100–150 which was followed by 1,3,5,7-tetramethyltricyclo[3.3.0.0^{2,8}]octa-3,6-diene (fractions 180–240). The last fractions were concentrated to *ca.* 5 ml through a 20 cm × 1.5 cm helipack column and then to *ca.* 200 μl under reduced pressure and separated by preparative vpc on a 8.5 ft × 0.25 in. column packed with 15% diethylene glycol succinate on Chromosorb P at 110° and 10.5 psi of nitrogen. Collection in a U-tube cooled in a Dry Ice–acetone bath afforded 30 mg of the semibullvalene. This represents a 3.8% yield based on unrecovered tetramethylcyclooctatetraene and a 38% loss during the process of separation. Nmr and uv spectral data are summarized in Table II; ir (CCl$_4$) 3.33, 3.37, 3.42, 3.51, 6.10, 6.23, 6.92, 6.99, 7.30, 8.70, 9.79, 11.15, 12.0, 14.57, and 15.6 μ.

Anal. Calcd for C$_{12}$H$_{16}$: C, 89.94; H, 10.06. Found: C, 89.46; H, 9.80.

From the cyclooctatetraene fractions of the chromatography, 510 mg of the pure sample was recovered as colorless prisms, mp 69–70°.

The yellow oil fractions of five batches of pyrolysis were combined and rechromatographed on the same silver nitrate–silica gel column. Fractions 20–37, 38–54, and 55–80 were collected separately. Mesitylene

(30) P. de Mayo and R. W. Yip, *Proc. Chem. Soc.*, 84 (1964).
(31) F. A. Cotton, J. W. Faller, and A. Musco, *J. Amer. Chem. Soc.*, 90, 1438 (1968).

(32) R. Criegee, W. Eberius, and H. A. Brune, *Chem. Ber.*, 101, 94 (1968).

Table II. Spectral Data for Semibullvalenes

	τ_H			τ_{CH_3}				
	α	β	γ	α	β	γ	Uv sh, nm (ϵ)	Ref
$R_\alpha = R_\beta = R_\gamma = H$	5.83	4.92	7.03[a]				225, 235 (2400)	3
$R_\alpha = R_\beta = R_\gamma = CH_3$				8.75	8.75	9.08[a]	240 (3980)	9, c
				8.58	8.52	9.10[b]		
$R_\alpha = R_\beta = H; R_\gamma = CF_3$	5.28	4.62a						d
$R_\alpha = H; R_\beta = R_\gamma = CH_3$	6.33				8.40	9.04[a]	238 (3200)	This work
$R_\alpha = CH_3; R_\beta = R_\gamma = H$		5.39	7.29	8.40[a]				This work

[a] CCl_4. [b] Pyridine–CCl_4 (9:1). [c] R. Criegee, W. D. Wirth, W. Engel, and H. A. Brune, *Chem. Ber.*, **96**, 2230 (1963). [d] R. S. H. Liu, *J. Amer. Chem. Soc.*, **90**, 215 (1968); R. S. H. Liu and C. G. Krespan, *J. Org. Chem.*, **34**, 1271 (1969).

was concentrated in the first fraction. In the last fractions were the peaks which had been present in the initial pyrolysis mixture and assigned to the $\alpha,\alpha',\alpha'',\alpha'''$-tetramethylsemibullvalene detected; this seemed due to decomposition during the chromtography. The middle fraction was found to be rich in a component whose nmr spectrum consisted of τ 8.35 (s), 7.3 (m), 4.98 (m), and 4.35 (m) in the ratio of 3:1:2:1 and which had a vpc retention time of 11.5 min (*cf.* mesitylene, 5.5 min).

Acetone-Sensitized Photolysis of $\beta,\beta',\gamma,\gamma'$-Tetramethylsemibullvalene. A quartz tube of 22 mm i.d. containing a solution of 70 mg of the tetramethylsemibullvalene and 120 μl of acetone in 2 ml of isopentane was degassed, sealed under vacuum, strapped to a quartz immersion well containing a 450-W medium-pressure Hanovia mercury lamp, and irradiated for 3 hr with external ice–water cooling. At the end of irradiation, the inside wall of the quartz tube was slightly

opaque due to a deposit of colorless insoluble material. The solution was concentrated by distillation and shown by nmr to contain 1,3,5,7-tetramethylcyclooctatetraene. No peaks due to the starting material and isomeric cyclooctatetraene were detected. Formation of the pentacyclic isomer 1,3,5,7-tetramethylpentacyclo-[3.3.0.0²,⁴.0³,⁷.0⁶,⁸]octane, the octamethyl homolog of which had been obtained by direct irradiation of the corresponding semibullvalene,[9] was also ruled out based on the fact that the high field region τ 9–9.5 of the nmr spectrum was transparent. Trituration of the residue with 100 ml of methanol gave 40 mg (58% yield) of 1,3,5,7-tetramethylcyclooctatetraene, mp 69–70°.