On the [2 + 2] Thermal Cyclodimerization of *cis,trans*-1,3-Cyclooctadiene[1]

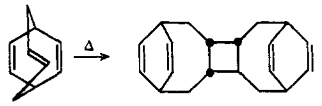
Albert Padwa,*[2a,b] William Koehn,[2b,c] Joseph Masaracchia,[2b]
C. L. Osborn,[3] and D. J. Trecker[3]

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214,
and the Research and Development Department, Union Carbide Corporation,
So. Charleston, West Virginia 25303. *Received October 30, 1970*

Abstract: When heated, neat or in hydrocarbon solvent, *cis,trans*-1,3-cyclooctadiene underwent both dimerization and isomerization. The structures of the 2 + 2 cyclodimers were assigned as the trans,cis, trans,trans, and cis,cis dimers. The ratio of the three dimers was found to be independent of the reaction temperature. The reaction followed good second-order kinetics and has $\Delta H^{\ddagger} = 19$ kcal/mol and $\Delta S^{\ddagger} = -10$ eu. The results have been rationalized on the basis of a stepwise mechanism for dimer formation.

The concerted, suprafacial, thermal fusion of two olefins to form a cyclobutane ring is a symmetry-forbidden process.[4] In accord with this prediction, thermal "1,2" cycloadditions of simple olefins have been shown to involve diradical intermediates.[5] Thermal cycloaddition can, in theory, proceed in a concerted symmetry-allowed fashion by a ($\pi^2s + \pi^2a$) combination of the two π bonds.[4] The high degree of stereospecificity in the 2 + 2 cycloaddition of olefins with allenes,[6-12] ketenes,[13-19] and reactive isocyanates[20,21] points toward the possibility that these reactions are concerted. It appears that a cumulative π-bond system can function more readily as a π^2a donor than an isolated double bond. Orbital symmetry theory applied to the concerted fragmentation of cyclobutane demands that the process occur *via* the ($\sigma^2s + \sigma^2a$) pathway.[4] Relevant studies on the pyrolysis of simple cyclobutanes, however, have been interpreted in terms of a stepwise decomposition involving an intermediate tetramethylene diradical.[22-28] It seems that the thermodynamically unfavorable transition state needed for concerted fragmentation is too difficult to be attained with simple cyclobutanes. In contrast, it has been argued that the high stereospecificity observed in the pyrolytic cleavage of β-lactones[29-31] and β-lactams[27] is the result of a concerted retrogression where the developing carbonyl group functions as the antarafacial site. It would appear as though the majority of thermal [2 + 2] cycloaddition and retrogression reactions of simple systems proceeds through a stepwise mechanism involving 1,4-diradical intermediates. Presumably this is because steric hindrance and angle strain factors develop to prohibitive levels as the two π bonds attempt to attain the requisite geometry for a ($\pi^2s + \pi^2a$) process.

While most of the experimental literature seems to favor a nonsynchronous process for [2 + 2] cycloaddition of olefins, there is one notable case where the evidence seemingly points to a concerted mechanism. The very interesting work of Kraft and Koltzenburg[32] on the stereoselective dimerization of bicyclo[4.2.2]-deca-*trans*-3,*cis*-7,9-triene (**1**) has been put forward by Woodward and Hoffmann[4] as an example of a concerted ($\pi^2s + \pi^2a$) cycloaddition.



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The ($\pi^2s + \pi^2a$) combination of π bonds predicts that the stereochemical relationships at three of the four carbon atoms of the cyclobutane ring will be retained

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[1] For a preliminary report of this work see C. L. Osborne, D. J. Trecker, A. Padwa, W. Koehn, and J. Masaracchia, *Tetrahedron Lett.*, 4653 (1970).

[2] (a) Alfred P. Sloan Foundation Fellow, 1968–1970; (b) State University of New York at Buffalo; (c) NSF Cooperative Fellow, 1968–1970.

[3] Union Carbide Corp.

[4] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

[5] (a) P. D. Bartlett and L. K. Montgomery, *J. Amer. Chem. Soc.*, **86**, 628 (1964); (b) P. D. Bartlett, *Science*, **159**, 833 (1968); (c) J. S. Swenton and P. D. Bartlett, *J. Amer. Chem. Soc.*, **90**, 2056 (1968); (d) P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, **91**, 409 (1969).

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[7] R. Huisgen, L. Feiler, and G. Binsch, *Angew. Chem.*, 76, 892 (1964).

[8] R. Montaigne and L. G. Ghosez, *ibid.*, **80**, 194 (1968).

[9] W. R. Dolbier and S. H. Dai, *J. Amer. Chem. Soc.*, **90**, 5028 (1968).

[10] J. E. Baldwin and J. A. Kapecki, *ibid.*, **91**, 3106 (1969); **92**, 4874 (1970).

[11] W. R. Moore, R. D. Bach and T. M. Ozretich, *ibid.*, **91**, 5918 (1969).

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[13] W. T. Brady, E. F. Hoff, R. Roe, Jr., and F. H. Parry, *J. Amer. Chem. Soc.*, **91**, 5679 (1969).

[14] T. DoMinh and O. P. Strausz, *ibid.*, **92**, 1766 (1970).

[15] R. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Lett.*, 4485 (1969).

[16] R. Huisgen and P. Otto, *ibid.*, 4491 (1968).

[17] W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 612 (1967).

[18] W. T. Brady and E. F. Hoff, *J. Amer. Chem. Soc.*, **90**, 6256 (1968).

[19] N. S. Isaacs and P. S. Stanbury, *Chem. Commun.*, 1061 (1970).

[20] E. J. Mariconi and J. F. Kelly, *Tetrahedron Lett.*, 1435 (1968).

[21] H. Bestian, H. Biener, K. Clauss, and H. Heyn, *Justus Liebigs Ann. Chem.*, 718, 94 (1968).

[22] H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147 (1966).

[23] H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

[24] A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969).

[25] A. T. Cocks and H. M. Frey, *J. Chem. Soc. A*, 1671 (1969).

[26] J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, 91, 7192 (1969).

[27] L. A. Paquette, M. J. Wyuratt, and G. R. Allen, *ibid.*, **92**, 1763 (1970).

[28] L. A. Paquette and J. A. Schwartz, *ibid.*, **92**, 3215 (1970).

[29] D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, 31, 4043 (1966).

[30] O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **90**, 2333 (1968).

[31] M. U. S. Sultanbawa, *Tetrahedron Lett.*, 4569 (1968).

[32] K. Kraft and G. Koltzenburg, *ibid.*, 4357, 4723 (1967).

while one carbon will be inverted. The isolation of the trans,cis dimer **2** as the major product from the thermolysis of **1** is thus compatible with a concerted, symmetry-allowed, $(\pi^2s + \pi^2a)$ combination. It should be emphasized that although orbital symmetry control is implicated in this dimerization, the mere isolation of **2** does not prove such control, especially since two additional cyclodimers were also formed. The formation of dimer **2** could easily be attributed to a multistep process involving diradical intermediates. In order to shed new light on the mechanism of [2 + 2] cycloadditions of distorted olefins, we have examined the thermal dimerization of *cis,trans*-1,3-cyclooctadiene (**3**). The trans double bond present in **3** is sufficiently strained to serve as a general model for the thermal dimerization of distorted π bonds devoid of activating substituents.

Results

cis,trans-1,3-Cyclooctadiene (**3**) was prepared by the method of Liu[33] and isolated following the procedure described by Cope.[34] Heating **3** in a sealed tube under a nitrogen atmosphere in the dark gave a mixture of *cis,cis*-cyclooctadiene (**4**), bicyclo[4.2.0]oct-7-ene (**5**), and three cyclobutane dimers, **6**, **7**, and **8**.[34a] The material balance of the reaction mixture after standing at room temperature for 40 hr was 97% so that no more than 3% of the cis,trans diene went to polymer.

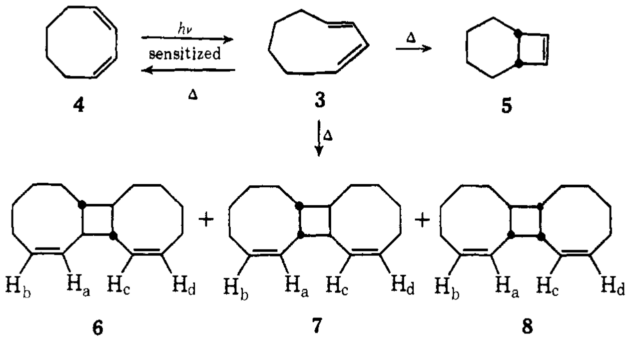

Table I shows the results of two experiments in which the composition percentages of the product were determined at different temperatures. It is interesting to note that an insignificant amount of bicyclo[4.2.0]oct-7-ene (**5**) is formed at 25°. Fonken and coworkers have reported that when *cis,trans*-1,3-cyclooctadiene is heated at temperatures of 80° or higher it is converted to **5** in quantitative yield[35] by a conrotatory[36] electrocyclic ring closure. We have found that *cis,trans*-1,3-cyclooctadiene undergoes both isomerization and dimerization in the neat and that at 25° the major path involves combination of two trans double bonds to afford three [2 + 2] cyclodimers.

Table I. Thermolysis of *cis,trans*-1,3-Cyclooctadiene (3)

Temp, °C	Time, hr	Composition, % 3	4	5	6	7	8
25	40	14	7	2	16	6	53
90	0.5	12	2	14	17	5	51

The ratio of the dimers was found to be practically independent of the reaction temperature over the range −20 to +90° (see Table II). The reaction followed good second-order kinetics in cyclohexane and the second-order rate constants were determined from three runs each at three different temperatures. Kinetic data on the dimerization of **3** are given in Table III. An Arrhenius plot of the second-order rate constants gives $\Delta H^{\ddagger} = 19.0 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -10$ eu. The rate of formation and the proportions of dimers are independent of light, catalytic effects, and solvent polarity.

Table II. Per Cent Composition of Cyclodimers from the Thermolysis of *cis,trans*-1,3-Cyclooctadiene[a]

Temp, °C	% dimer[b] 6	7	8
−20.0	22	12	66
4.0	21	10	69
28.0	21	8	71
40.0	22	8	70
65.0	22	7	70
90.0	24	7	69

[a] Dimerization carried out in the neat. [b] Represents per cent of total dimer formed.

Table III. Summary of Kinetic Parameters for the Thermal Dimerization of *cis,trans*-1,3-Cyclooctadiene in Cyclohexane[a]

Temp, °C	kmol^{-1} min^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
30.2	0.041		
48.0	0.299	19.0	−10
76.0	2.54		

[a] 1.0 M cyclohexane.

The mixture of dimers could be separated by a careful spinning band distillation followed by preparative vapor-phase chromatography. The mass spectra of all three dimers exhibit small parent peaks at 216 and base peaks at 108 with a cracking pattern very similar to 1,3-cyclooctadiene. The infrared spectrum of each isomer is void of bands in the trans double bond stretching frequency region. Hydrogenation of the dimer mixture required 2 mol equiv of hydrogen and afforded three saturated hydrocarbons. The relative amount of each saturated dimer corresponded to the same ratio of the three dimers originally present in the sample prior to hydrogenation. This observation requires that the three dimers be stereochemically or structurally dissimilar.

The structure of the major dimer **8** was assigned on the basis of spectral and hydrogenation data as the trans,cis (syn double bond) dimer. Hydrogenation of **8** afforded a single product, **9** (mp 55–56°), which was identical with the product obtained from both the catalytic reduction of tricyclo[8.6.0.0^{2,9}]hexadeca-2,16-

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(33) R. S. Liu, *J. Amer. Chem. Soc.*, **89**, 112 (1967).

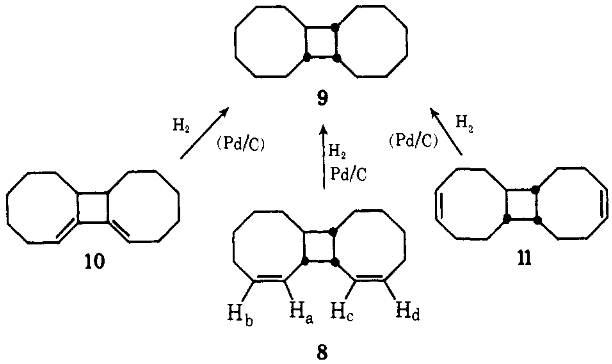
(34) A. C. Cope and C. L. Bumgardner, *ibid.*, **78**, 2812 (1956).

(34a) Note Added in Proof. Dr. J. J. Bloomfield has informed us that he has also noted the formation of three dimers from the thermolysis of neat *cis,trans*-cyclooctadiene. The structures of the dimers were not established but were suggested to be cyclobutane derivatives. See J. J. Bloomfield and J. S. McConaghy, *Tetrahedron Lett.*, 3723 (1969).

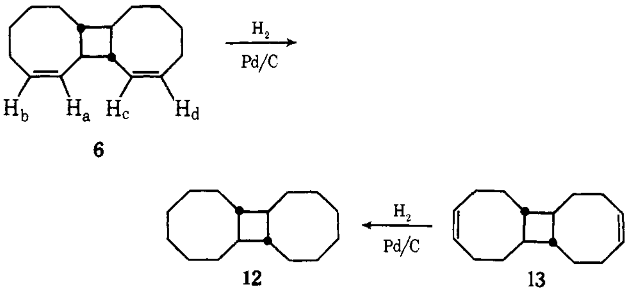
(35) K. M. Shumate, P. N. Neuman, and G. J. Fonken, *ibid.*, **87**, 3996 (1965).

(36) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

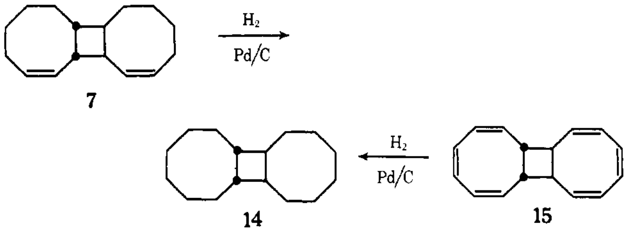
diene (**10**)[37–39] and the trans,cis dimer **11** of 1,5-cyclooctadiene.[40] The 100-MHz nmr spectrum of **8** (pyridine-d_6) shows three groups of absorptions for the four vinyl hydrogens: a doublet of doublets (J = 11.0 and 4.2 Hz) centered at τ 4.23 (H_a), a multiplet centered at 4.50 (H_b and H_d), and another doublet of doublets (J = 11.0 and 1.8 Hz) at 4.75 (H_c). The remaining portion of the spectrum consists of a complex set of lines between τ 7.15 and 8.90 (20 H). When H_a was saturated with an external field, the doublet of doublets at τ 4.75 (H_c) was unaffected. The upfield shift of H_c (relative to H_a) can be attributed to long-range shielding by the π electrons of the neighboring double bond. The fact that $J_{AB} = J_{CD}$ = 11.0 Hz indicates that the two double bonds present in **8** must be cis substituted.[41] The magnitude of three-bond vinyl–allylic proton coupling is known to follow a cos $^2 \phi$ relationship, where ϕ is the dihedral angle between the vinylic and allylic carbon–hydrogen bonds.[42] From a consideration of the dihedral angle between the methine hydrogen and H_c (95° as measured from Dreiding models) the small coupling constant (J = 1.8 Hz) of the upfield vinyl hydrogen (H_c) is to be expected. The combined nmr data are consistent with **8** as the structure of the major dimer.[43]



Catalytic hydrogenation of dimer **6** (mp 34–35°) gave a saturated hydrocarbon, **12**, which was found to be identical with the product obtained from the reduction of the trans,trans (anti) dimer **13** of *cis,trans*-1,5-cyclooctadiene.[40] The 100-MHz nmr spectrum of **6** (pyridine-d_6) showed that H_a and H_c were equivalent, both appearing as a doublet of doublets (J = 11.0, 1.8 Hz) at τ 4.25. Protons H_b and H_d appeared as a two-proton multiplet centered at τ 4.50. The remaining portion of the spectrum consists of a complex set of lines between τ 7.4 and 9.0 (20 H). All this is consistent with structure **6**.

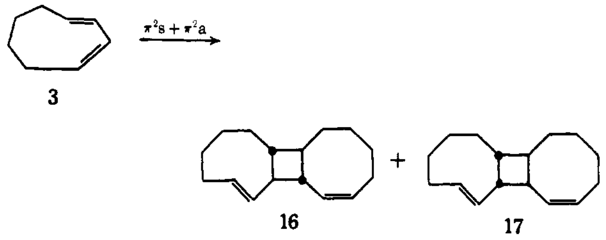


Elucidation of the structure of the minor dimer **7** was hampered by the fact that we were not able to completely separate it from the other dimers and also because it is an air-sensitive compound. The nmr of an enriched sample of **7** (*ca.* 80%) showed the four vinyl protons as a multiplet centered at τ 4.40. Catalytic reduction of **7** gave a hydrocarbon, **14**, mp 58–59°, that possesses a different vpc retention time than the saturated stereoisomers **9** and **12**. It also proved to be different from the saturated trans,trans (syn) dimer obtained by Ziegler[44] and the cis,cis (syn) dimer obtained by Schroder[45] but was identical with the saturated dimer obtained from the reduction of the cis,cis (anti) dimer of cyclooctatetraene,[46] **15**. The syn assignment of the double bonds is the most likely on the basis of analogy and mechanistic considerations.



Discussion

The isolation of the trans,cis (syn) dimer **8** as the major dimer from the thermolysis of **3** indicates that the predominant portion of the reaction occurs in a stereochemical sense compatible with orbital symmetry theory. In line with the explanation previously offered, the high yield of **8** could result from the combination of two trans double bonds *via* the concerted ($\pi^2s + \pi^2a$) pathway. A ($\pi^2s + \pi^2a$) cycloaddition involving the cis and trans double bonds of **3** would be expected to give two dimers, **16** and **17**, related to **6** and **7** but possessing a trans double bond in one of the rings.



In order to demonstrate that **6** and **7** are primary products and are not derived by isomerization of **16** and **17** on work-up, we have carried out the dimerization of **3** in the presence of a 20 mol excess of *cis*-cyclooctene. Under these conditions, the ratio of dimers **6**, **7**, and **8** was unchanged.[47] Similarly, when the crude dimer mixture was treated with an aqueous silver nitrate solution, the ratio of dimers remained

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(37) W. J. Ball and S. R. Landor, *J. Chem. Soc.*, 2298 (1962).

(38) E. T. Marguis and P. D. Gardner, *Tetrahedron Lett.*, 2793 (1966).

(39) G. Wittig, H. L. Dorsch, and J. M. Schuller, *Justus Liebigs Ann. Chem.*, 711, 55 (1968).

(40) J. Leitich, *Angew. Chem., Int. Ed. Engl.*, 909 (1969).

(41) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 280.

(42) E. W. Garbisch, *J. Amer. Chem. Soc.*, 86, 5561 (1964).

(43) An X-ray crystal-structure determination of a derivative of dimer 8 is currently under investigation and will be reported at a later date.

(44) K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kuhlhorn, and J. Schneider, *Justus Liebigs Ann. Chem.*, 589, 122 (1954).

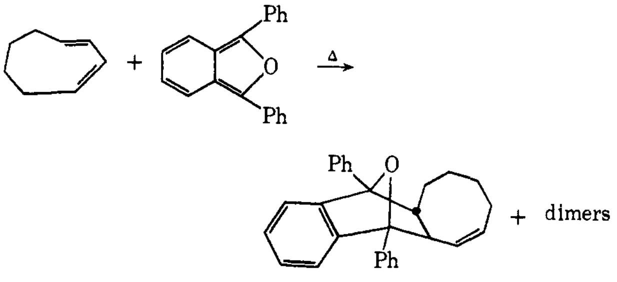
(45) G. Schroder and W. Martin, *Angew. Chem.*, 78, 117 (1966).

(46) A. G. Anastassiou and R. M. Lazarus, *Chem. Commun.*, 373 (1970).

(47) When the dimerization of 3 was carried out in the presence of excess *trans*-cyclooctene, the ratio of the three dimers was also unchanged.

the same. These experiments indicate that **6** and **7** are primary products and are formed by a nonsynchronous stepwise mechanism involving the trans double bonds. At this point it could be argued that **6** and **7** are the result of a two-step process whereas the formation of **8** proceeds in a concerted symmetry-allowed ($\pi^2s + \pi^2a$) fashion. Although this could be the case we feel that the available evidence is more compatible with a stepwise mechanism for the formation of all the dimers.

One might anticipate that a dual mechanism for dimerization would be characterized by a variation in the product ratio as a function of temperature. The dimer ratio, however, was found to be independent of temperature over the range -20 to $+90°$ (see Table II). When the dimerization was carried out in the presence of limited quantities of 1,3-diphenylisobenzofuran, a mixture of the three dimers and the Diels–Alder adduct **18** was produced. Most importantly, the product distribution of the dimers did not change under conditions where the Diels–Alder reaction predominated. The dimerization reaction was also allowed to occur in the presence of maleic anhydride. Again, no change in the dimer ratio occurred under conditions where adduct formation predominated. We suggest that this behavior is consistent with a two-step mechanism for dimer formation.



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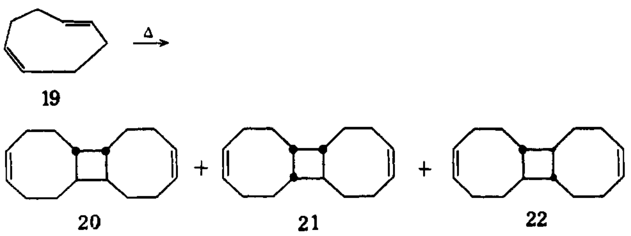
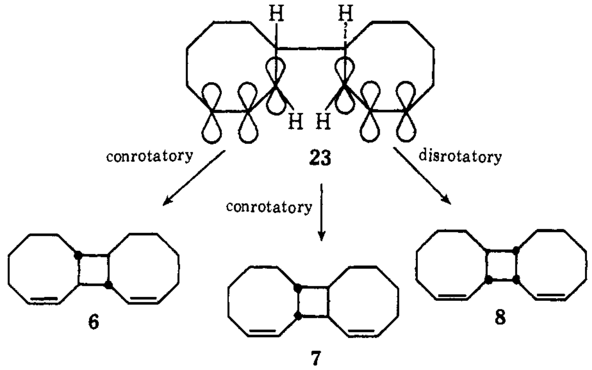
At this point it is worthwhile to compare the dimerization of **3** with that of racemic *cis,trans*-1,5-cyclooctadiene (**19**). Ziegler originally reported that the thermal dimerization of **19** gave a single cyclodimer.[44] More recent work by Leitich showed that three cyclodimers were formed.[40] The structures were assigned as the trans,trans (syn) (**20**), the trans,cis (**21**), and the trans,trans (anti) (**22**) dimers in the ratio of 10:4:1.

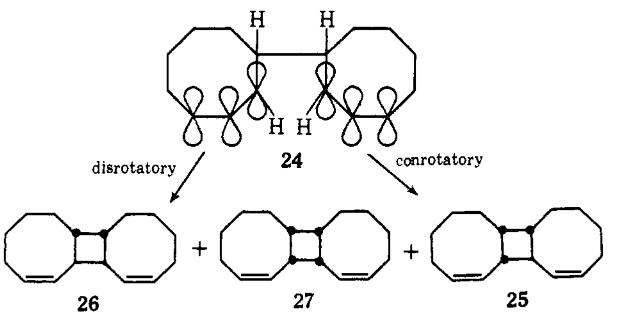


Most noteworthy is the fact that the major dimer **20**, formed from the thermal dimerization of racemic *cis,trans*-1,5-cyclooctadiene, is not the one predicted from orbital symmetry considerations.[48] The reaction followed second-order kinetics, and the thermodynamic functions for dimerization were $\Delta H^{\ddagger} = 17.0$ kcal/mol and $\Delta S^{\ddagger} = -31$ eu. These values are very similar to those obtained for the dimerization of *cis,trans*-1,3-cyclooctadiene (**3**) (see Table III). The kinetics and stereochemistry of the thermal dimerization of racemic **19** can best be interpreted in terms of an intermediate tetramethylene diradical. Since the dimerization of **3** has very similar thermodynamic parameters to that of **19**, it would appear as though both dimerizations proceed through a nonsynchronous multistep process.

It is assumed that the first step in the thermally induced cyclodimerization of **3** involves the formation of a transient biradical or at least proceeds through a transition state of considerable biradical character. Any stabilizing effect on the biradical is expected to be an important factor in determining the direction of addition. The structures of the dimers isolated suggest that the initial step involves combination of the two trans double bonds and the formation of biradical **23** which is stabilized by allylic resonance. Disrotatory closure of **23** will produce **8** while conrotatory closure would be expected to give rise to a mixture of **6** and **7**. Since **8** is the dominant dimer, it would appear that the energy barrier for disrotatory closure is slightly less than that for conrotatory closure. The mild preference for disrotatory closure may be related to the fact that coplanarity of the allyl system can be maintained during the disrotatory motion. On the other hand, the allyl system is twisted away from coplanarity during the conrotatory closure step and consequently this motion leads to an increase in the transition-state energy for bond closure.



We believe that the only rational way to arrive at dimers **6**, **7**, and **8** is by way of diradical **23**. The alternate cis diradical **24** would be expected to produce dimers **25** (conrotatory), **26**, and **27** (disrotatory) upon bond closure. Since these dimers were not detected, it would appear that there is a marked preference for the formation of diradical **23**. This may be related to



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[48] It is worthy to note that the thermal dimerization of (*R*)-(−)-*cis,trans*-1,5-cyclooctadiene gives (+)-*trans,cis*-**21** and (+)-*trans,trans*-(anti)-**22** in a ratio of 1:2.9, with no detectable quantities of the trans,-trans (syn) (**20**) dimer.[40] A comparison of the thermal dimerization of **3** with **19** is therefore valid only when the starting *cis,trans*-1,5-cyclooctadiene is racemic.

steric approach control since nonbonded interactions between two diene molecules are minimized in the transition state for the formation of diradical **23**. One might also argue that the selectivity of diradical formation is based on thermodynamic control.

In conclusion, the results obtained are in accordance with previous experience that thermal cyclobutane-forming reactions proceed *via* a multistep mechanism.

Experimental Section[49]

cis,trans-**1,3-Cyclooctadiene (3)** was prepared by the method of Liu[33] and isolated following the procedure described by Cope.[34]

Thermal Dimerization of ***cis,trans*-1,3-Cyclooctadiene (3).** A sample of 0.0935 g of **3** and 0.0554 g of diethyl phthalate (internal standard) was degassed by bubbling nitrogen at 10° and then sealed in a small test tube with a rubber serum cap. The sample was allowed to warm to room temperature and then kept in the dark for 40 hr. Samples were removed at 20-, 30-, and 40-hr intervals. At the end of 20 hr, 70% of the starting diene had reacted to give 67 wt % dimers, 2% *cis,cis*-1,3-cyclooctadiene, and 1% bicyclo[4.2.0]oct-7-ene. After 40 hr, 86% was reacted giving 75% dimers, 7.5% *cis,cis*-1,3-cyclooctadiene, and 1% bicyclooctene. The remaining 2.5% was presumably polymer. Another sample containing 0.0751 g of *cis,trans*,1,3-cyclooctadiene and 0.055 g of diethyl phthalate was heated to 90° for 35 min. At the end of this period the reaction mixture consisted of 11.5% starting diene, 73% dimers, 1.5% *cis,cis*-1,3-cyclooctadiene, and 14% bicyclooctene. The gas-chromatographic analysis was carried out with a 20 ft × $^1/_8$ in. SE-30 HyPak column at 210°.

Preparative Scale Isolation of the [2 + 2] Cyclodimers. The easiest way to isolate large quantities of the thermal dimers involved the sensitized irradiation of *cis,cis*-1,3-cyclooctadiene at 45°. A solution of 100 g of *cis,cis*-1,3-cyclooctadiene, 2.7 g of acetophenone, and 200 ml of heptane was irradiated at 45° under nitrogen for 110 hr. At the end of this time a white polymer began to deposit on the walls of the reactor. Filtration of the reaction mixture gave 0.6 g of polymer, mp 145–180°. The filtrate was stripped of solvent and monomers *in vacuo* leaving 72 g of a slightly yellow oil. Flash distillation of this residue at 130° (0.3 mm) gave 64 g of a colorless liquid composed of three dimers, **6**, **7**, and **8**, bp 110–115° (0.5 mm), in the ratio of 3:1:7 according to retention time through a 15 ft × $^1/_8$ in. 10% SE-30 column on Chromosorb G at 210°. Preparative gas chromatography through 20 ft × $^3/_8$ in. 20% NPG succinate on Chromosorb W afforded pure samples of each dimer.

The structure of the first dimer eluted from the vpc column was assigned as the trans,trans (anti) (syn double bond) dimer **6**, mp 32–33°.

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18: Found: C, 88.67; H, 11.10.

The infrared spectrum of dimer **6** had bands at 3.31, 3.41, 3.45, 6.85, 6.89, 6.94, 7.01, 12.34, 12.50, 13.07, 13.70, and 14.08 μ. The mass spectrum showed a small parent peak at 216 and a base peak at 108 mass units. The 100-MHz nmr spectrum of **6** (pyridine-d_6) showed a doublet of doublets (J = 11.0, 1.8 Hz) at τ 4.25, a two-proton multiplet centered at 4.50, and a complex set of lines between 7.4 and 9.0 (20 H).

The structure of the second dimer eluted from the column was assigned as the cis,cis (anti) (syn double bond) dimer **7**. Elucidation of the structure of this dimer was hampered by the fact that it was not completely separated from the other dimers and also because it is an air-sensitive liquid. The nmr spectrum of an enriched sample of **7** (*ca.* 80%) showed the four vinyl protons as a multiplet centered at τ 4.40. The mass spectrum showed a parent peak at *m/e* 216 and a base peak at 108. The infrared spectrum of dimer **7** had bands at 3.31, 3.41, 3.44, 3.49, 3.52, 6.85, 6.90, 12.82, 12.98, and 13.89 μ.

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.76; H, 11.31.

The structure of the last dimer eluted from the column was assigned as the trans,cis (syn double bond) dimer **8**. The colorless liquid had an infrared spectrum which showed bands at 3.13, 3.41, 3.48, 6.85, 6.89, 6.94, 12.64, 13.15, 13.60, 13.79, and 14.28 μ. Its mass spectrum showed a small parent peak at 216 and a base peak at 108. The 100-MHz nmr spectrum of **8** (pyridine-d_6) shows three groups of absorptions for the four vinyl hydrogons: a doublet of doublets (J = 11.0 and 4.2 Hz) centered at τ 4.23, a doublet of doublets (J = 11.0 and 1.8 Hz) at 4.75, and a multiplet centered at 4.50. The remaining portion of the spectrum consists of a complex set of lines between τ 7.15 and 8.90 (20 H).

Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.91; H, 11.15.

Formation of Bicyclo[4.2.0]oct-7-ene (5). A solution of 100 g of *cis,cis*-1,3-cyclooctadiene, 2.7 g of acetophenone, and 200 ml of heptane was irradiated at 85° under nitrogen for 110 hr until the reaction had gone to 98% completion (based on unreacted starting material). Distillation of the product through a 3-ft spinning band column gave 126 g of forerun (bp 80–132°), 36 g of bicyclo[4.2.0]oct-7-ene, bp 132°, and 36 g of residue composed of 10 g of **5** and 20 g of dimers. The infrared spectrum of the bicyclooctene was identical with that reported.[35] In subsequent preparative runs the yield of bicyclooctene was increased to 85% by using heptane solvent at 90°.

Catalytic Hydrogenation of the [2 + 2] Cyclodimers. Catalytic hydrogenation of 0.1 g of **6** in 60 ml of methanol containing 10% Pd/C at 26° gave 0.1 g of reduced dimer **12** as a colorless oil. The infrared spectrum (neat) had bands at 3.45, 3.71, 5.76, 6.90, 7.37, and 14.31 μ. The nmr spectrum (CCl_4) had multiplets at τ 8.31 and 8.82. Hydrogenation of 0.1 g of the trans,trans (anti) dimer **13** of *cis,trans*-1,5-cyclooctadiene[40] yielded 0.095 g of **12** identical with the sample prepared above.

Anal. Calcd for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found: C, 87.05; H, 12.89.

Catalytic hydrogenation of 0.2 g of dimer **7** in 30 ml of glacial acetic acid with 10% Pd/C catalyst gave 0.19 g of reduced dimer **14**, mp 58–59°. The infrared spectrum (KBr) had bands at 3.48, 6.87, 6.95, 10.51 and 13.40 μ. The mass spectrum showed the parent ion at *m/e* 220 and a base peak at 110. Catalytic hydrogenation of 0.05 g of the cis,cis (anti) dimer of cyclooctatetraene, **15**, in 50 ml of methanol yielded 0.048 g of **14** identical with the sample prepared from the reduction of dimer **7**.

Anal. Calcd for $C_{16}H_{28}$: C, 87.19; H, 1.81. Found: C, 87.32; H, 12.94.

Catalytic hydrogenation of 0.2 g of dimer **8** in 30 ml of glacial acetic acid with 10% Pd/C catalyst gave 0.2 g of reduced dimer **9**, mp 55–56°. This material was identical with an authentic sample of *trans,cis*-tricyclo[8.6.0.0^{2,9}]hexadecane (**9**) prepared by the catalytic reduction of tricyclo[8.6.0.0^{2,9}]hexadeca-2,16-diene (**10**)[38] or from the catalytic reduction of the trans,cis dimer **11** of 1,5-cyclooctadiene.[40,50]

Anal. Calcd for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found: C, 87.24; H, 12.86.

Dimerization of ***cis,trans*-1,3-Cyclooctadiene in the Presence of** ***cis*- and *trans*-Cyclooctene.** A solution of 0.05 g of **3** in 1 ml of *cis*-cyclooctene was allowed to stand at room temperature for 6 days. At the end of this time the mixture of dimers was analyzed by vapor-phase chromatography on a 15 ft × $^1/_8$ in. 10% SE-30 column on Chromosorb G at 210°. The ratio of the three dimers was unchanged. Similar results were obtained when *trans*-cyclooctene was used as the coreagent.

Dimerization of ***cis,trans*-1,3-Cyclooctadiene in the Presence of 1,3-Diphenylisobenzofuran.** A solution of *cis,trans*-1,3-cyclooctadiene (0.23 g) and 1,3-diphenylisobenzofuran (0.29 g) in 5 ml of benzene was heated at reflux for 10 min. Evaporation of the solvent gave an oily residue which was analyzed by vapor-phase chromatography on a 15 ft × $^1/_8$ in. 10% SE-30 column on Chromosorb G at 210°. The ratio of the three dimers was unchanged. Preparative thick-layer chromatography of the residue resulted in the separation of three distinct bands, which were taken up in chloroform. A white solid was isolated from the middle band,

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(49) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer infracord spectrophotometer, Model 137 The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associates high-resolution spectrophotometer. Tetramethylsilane was used as an internal standard. All irradiations were carried out in a tubular photoreactor using a 200-W Hanovia mercury vapor arc.

(50) The authors would like to thank Dr. J. Leitich and Dr. P. D. Gardner for supplying spectra of the saturated dimers and Dr. A. G. Anastassiou for providing us with a sample of the anti 2 + 2 dimer of cyclooctatetraene.

which, after recrystallization from 95% alcohol, afforded a white, crystalline solid, mp 153–155°. This material was assigned as the Diels–Alder adduct **18** on the basis of the following data. The infrared spectrum was characterized by bands at 3.50, 6.95, 7.45, 7.68, 9.85, 10.20, 13.31, and 14.40 μ. The mass spectrum showed a parent peak at m/e 378 and had peaks at 360 and 270 (base). The nmr spectrum (CCl_4) had multiplets at τ 2.3–3.20, 6.91–7.21, and 7.61–8.90.

Anal. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 88.62; H, 6.92.

Dimerization of *cis,trans*-1,3-Cyclooctadiene in the Presence of Maleic Anhydride. A solution of 0.08 g of *cis,trans*-1,3-cyclooctadiene and 0.2 g of maleic anhydride in 5 ml of toluene was heated at reflux for 1 hr. During this time a white solid precipitated from the reaction mixture. Vapor-phase chromatographic analysis of the solution showed the dimers present in the normal ratio. Evaporation of the solvent left a white solid, mp 305–325°. The infrared spectrum (KBr) of this material showed bands at 3.5, 5.4, 5.6, 6.7, 8.2, 9.2, and 10.9 μ. The material was insoluble in all solvents and resisted sublimation and therefore was not characterized further.

Kinetic Runs. A measured amount of *cis,trans*-1,3-cyclooctadiene and diethyl phthalate (internal standard) was placed in a 10-ml Pyrex test tube that had been thoroughly cleansed and dried in an oven. The mixture was diluted with pure cyclohexane to give 1.0 *M* solutions. A Neslab Instruments constant temperature apparatus, accurate to ±0.01°, was used for the high-temperature runs. A Wilkens-Anderson Lo-Temp refrigeration unit was used to control the bath at the lower temperatures. Thermolysis mixtures were analyzed by vpc. At the end of each time interval the tubes were quenched prior to gas-chromatographic analysis. The reciprocal of the difference between original concentration of diene and amount of dimers produced was plotted against time to give the rate. The results are summarized in Table III.

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Electron and Energy Transfer between Bicyclo[2.2.2]octane Bridgehead Moieties

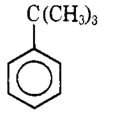
Howard E. Zimmerman* and Ronald D. McKelvey

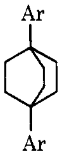
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received September 1, 1970

Abstract: 1,4-Diphenylbicyclo[2.2.2]octane, 1,4-bis(*p*-cyanophenyl)bicyclo[2.2.2]octane, 1,4-bis(*p*-nitrophenyl)-bicyclo[2.2.2]octane, and 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane were synthesized for energy and electron-transfer studies. Introduction of an odd electron into one aromatic ring of the symmetrical diaryl derivatives led to radical anions in which the odd electron was localized in one of the two rings. This result is analyzed as a tunneling problem consisting of a single potential energy barrier corresponding to the bicyclic ring structure. In contrast, the study of energy transfer in the naphthyl–benzoyl derivative provided evidence for singlet transfer from naphthyl to benzoyl and triplet transfer from benzoyl to naphthyl. The singlet transfer is considered to involve a dipole–dipole mechanism. The triplet–triplet transfer provides evidence that close approach is not invariably required.

Related to our studies on the problem of electron transfer between orthogonal π systems[1] was the question of the facility of transfer of electrons and electronic excitation through saturated hydrocarbon insulators. For this study, 1,4-disubstituted bicyclo[2.2.2]octane derivatives were selected, since the bicyclo[2.2.2]octane moiety provides a symmetrical and convenient framework assuring lack of approach of orbitals of the separate π systems.[2]

Also, it is observed experimentally[3,4] that line broadening occurs in the esr spectra of *tert*-butyl aromatic radical anions due to appearance of odd electron density in the β carbon–hydrogen bonds. If there is similar penetration to β carbon–carbon bonds in a 1,4-disubstituted bicyclo[2.2.2]octane derivative as **1**, then this would suggest the ability to delocalize odd electron density to the second ring, since three carbon–carbon bonds are β to both rings.[5]





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Similarly, extended Hückel calculations (*vide infra*) show weighting of the bicyclooctane σ orbitals in the first antibonding MO along with both of the aromatic rings. Hence, there seemed to be the *a priori* possibility of both electron and energy delocalization between rings.

Synthetic Aspects. A synthesis[6] which promised to be of general use began with cyanoethylation of an aryl acetone (**2**), aryl being phenyl or naphthyl as shown in Chart I. Hydrolysis, cyclization, and internal acid-catalyzed aldolization led to **6**. Wolff–Kishner reduction, conversion to the bridgehead chloride (**8**), and Friedel–Crafts reaction with benzene afforded 1,4-diphenylbicyclo[2.2.2]octane (**9**).[7] Nitra-

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[1] H. E. Zimmerman and J. R. Dodd, *J. Amer. Chem. Soc.*, **92**, 6507 (1970).

[2] Recent examples of excitation transfer in rigid systems include: (a) R. A. Keller and L. J. Dolby, *ibid.*, **91**, 1293 (1969); (b) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid*, 87, 995 (1965); (c) A. A. Lamola, *ibid.*, **91**, 4786 (1969).

[3] J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

[4] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963).

[5] Similar studies on the *p*-cyclophanes have been done: F. Gerson and W. B. Martin, Jr., *J. Amer. Chem. Soc.*, **91**, 1883 (1969); S. I. Weissman, *ibid.*, **80**, 6462 (1958).

[6] The initial steps of the synthesis were patterned after the preparation of 4-methoxy-1-phenylbicyclo[2.2.2]octan-2-one and 1-chloro-4-methylbicyclo[2.2.2]octane as described by K. Morita and T. Kobayashi, *J. Org. Chem.*, 31, 229 (1966); Z. Suzuki and K. Morita, *ibid.*, 32, 31 (1967).

[7] After completion of this research, a similar synthesis of 1,4-diphenylbicyclo[2.2.2]octane was published by N. B. Chapman, S. Sotheeswaran, and K. J. Toyne, *ibid.*, **35**, 917 (1970).