Tetrahedron Letters No.53, pp. 4653-4656, 1970. Pergamon Press. Printed in Great Britain.

THE THERMAL DIMERIZATION OF *cis,trans*-1,3-CYCLOOCTADIENE

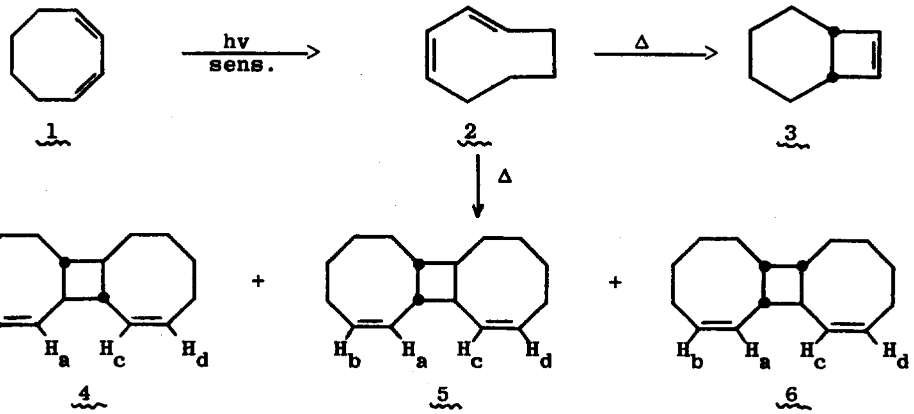
C. L. Osborn and D. J. Trecker
Research and Development Department, Union Carbide Corporation
Chemicals and Plastics, South Charleston, West Virginia 25303

Albert Padwa,* William Koehn, and Joseph Masaracchia
Department of Chemistry, State University of New York at Buffalo,
Buffalo, New York 14214

(Received in USA 31 August 1970; received in UK for publication 19 October 1970)

The photosensitized conversion of *cis,cis*,-1,3-cyclooctadiene (**1**) to bicyclo[4.2.0]oct-7-ene (**3**) has been shown to be a two-step process involving initial sensitized isomerization of the diene to its *cis,trans*-isomer[1] (**2**), followed by conrotatory thermal closure of **2** to **3**.[2,3] Fonken has reported that when **2** is heated at temperatures of 80° or higher, it is converted to **3** in quantitative yield.[2] At this time we wish to report that **2** undergoes both isomerization and dimerization and that at 25° the major path involves combination of two *trans* double bonds to afford three (2 + 2) cyclodimers.

cis,trans-1,3-Cyclooctadiene (**2**) was prepared by the method of Liu[1] and isolated following the procedure described by Cope.[4] Heating **2** in a sealed tube under a nitrogen atmosphere in the dark gave a mixture of **1**, **3**, and three cyclobutane dimers **4**, **5**, and **6**.



1 **2** **3**

4 **5** **6**

---

* Fellow of the Alfred P. Sloan Foundation, 1968-1970

Table I shows the results of two experiments in which the composition percentages were determined at different temperatures. It is interesting to note that an insignificant amount of **3** is formed at 25°.

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

Temperature, °C	Time, hours	Composition, %					
		1	**2**	**3**	**4**	**5**	**6**
25	40.0	7	14	2	16	6	53
90	0.5	2	12	14	17	5	51

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 that of 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 two mole equivalents 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 (**6**) was assigned on the basis of spectral and hydrogenation data as the *trans*-*cis* (*syn* double bond) dimer.[5] Hydrogenation of **6** afforded a single product (**7**) (mp 55-56°) which was identical to the product obtained from both the catalytic reduction of tricyclo-$[8.6.0.0^{2,9}]$hexadeca-2,16-diene (**8**)[6,7,8] and the *trans*-*cis*-dimer (**9**) of 1,5-cyclooctadiene.[9] Catalytic hydrogenation of dimer **4** (mp 34-35°) gave a saturated hydrocarbon (**10**) which was found to be identical with the product obtained from the reduction of the *trans*-*trans* (anti) dimer (**11**) of *cis*,*trans*-1,5-cyclooctadiene. Catalytic reduction of **5** gave a hydrocarbon (**12**), mp 58-59°, that possesses a different vpc-retention time than the saturated stereoisomers **7** and **10**. It also proved to be different from the saturated trans,trans (syn) dimer obtained by Ziegler[10] and the cis,cis (syn) dimer obtained by Schroder[11] but was identical to the saturated dimer obtained from the reduction of the cis,cis (anti) dimer of cyclooctatetraene.[12] The syn assignment of the double bonds in the three dimers is the most likely on the basis of their nmr spectra[5] and mechanistic considerations.

The concerted, suprafacial, thermal fusion of two olefins to form a cyclobutane ring is a symmetry-forbidden process.[13] This transformation, can in theory, proceed in a concerted symmetry allowed fashion by a ($\pi 2s$ + $\pi 2a$) combination of the two π-bonds. This combination predicts that the stereochemical relationships at three of the four carbons of the cyclobutane ring will be retained while one carbon will be inverted. The isolation of the trans-cis (syn) dimer as the major isomer from the thermolysis of **2** indicates that the predominant portion of the reaction occurs in a stereochemical sense compatible with orbital symmetry theory. It is interesting to note that the dimerization of cis, trans-1,5-cyclooctadiene also gives three dimers.[9] Most noteworthy is the fact that the major dimer in that case is not the one predicted from orbital symmetry considerations. Further discussion on the differences between the two systems will be postponed until a more thorough study of the dimerization can be undertaken.

Acknowledgement: One of us (A.P.) acknowledges the support of this work by the National Science Foundation (Grant GP-9385). The authors would also like to thank Dr. J. Leitich and Dr. P. D. Gardner for supplying spectra of several of the saturated dimers and Dr. A. G. Anastassiou for providing us with a sample of the anti 2 + 2 dimer of cyclooctatetraene.

References

1. R. S. Liu, J. Amer. Chem. Soc., **89**, 112 (1967).
2. K. M. Schumate, P. N. Neuman, and G. J. Fonken, ibid., **87**, 3996 (1965).
3. R. B. Woodward and R. Hoffman, ibid., **87**, 395 (1965).
4. A. C. Cope and C. L. Bumgardner, ibid., **78**, 2812 (1956).
5. All compounds analyzed satisfactorily. Complete spectroscopic and degradative details will be given in our full manuscript.
6. W. J. Ball and S. R. Landor, J. Chem. Soc., 2298 (1962).

7. E. T. Marquis and P. D. Gardner, Tetrahedron Letters, 2793 (1966).

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

9. J. Leitich, Angew Chem. Int. Ed., 909 (1969).

10. K. Ziegler, H. Sauer, L. Bruns, H. Froitzheim-Kuhlhorn, and J. Schnieder, Liebigs Ann. Chem., 589, 122 (1954).

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

12. A. G. Anastassiou, R. P. Cellura, and J. H. Gebrian, Chem. Commun., 375 (1970).

13. R. B. Woodward and R. Hoffmann, Angew. Chem. Int. Ed., 781, (1969).