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*trans,trans*-1,5-Cyclooctadiene

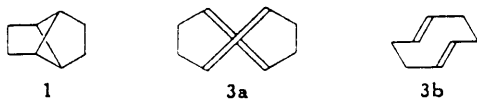
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George M. Whitesides, Gerald L. Goe, and Arthur C. Cope

## *trans,trans*-1,5-Cyclooctadiene<sup>1</sup>

Sir:

Irradiation of *cis,cis*-1,5-cyclooctadiene in an ether solution containing copper(I) chloride yields tricyclo-[3.3.0.0<sup>2,6</sup>]octane (**1**).<sup>2</sup> The mechanism of this reaction is still unclear;<sup>2</sup> however, the fact that the carbon skeleton of **1** can in principle be derived in a simple



manner from the racemic conformation of *trans,trans*-1,5-cyclooctadiene (**3a**) makes the properties of this latter hydrocarbon under the conditions of the photochemical reaction of interest. We wish to report the isolation of both *cis,trans*-<sup>3</sup> and *trans,trans*-1,5-cyclooctadienes from an irradiated pentane suspension of bis[chloro(*cis,cis*-1,5-cyclooctadiene)copper(I)] (**2**).<sup>4</sup>

The crystalline complex **2**, when suspended in pentane, dissociates partially to free cyclooctadiene and a solid nonstoichiometric cyclooctadiene-copper(I) chloride complex containing excess copper(I) chloride. A stirred suspension of **2** (0.5 g, 1.2 mmoles) in 70 ml of degassed pentane was irradiated for 24 hr in a quartz vessel, using a Rayonet reactor equipped with low-pressure mercury lamps. The resulting mixture was filtered, and the solid was washed thoroughly with pentane. The filtrate was shown by vpc to contain **1** (19%, based on the cyclooctadiene originally present in the complex **2**), *cis,cis*-1,5-cyclooctadiene (52%), and small quantities of several other components.<sup>5</sup> The remainder of the olefinic material was bound in the pentane-insoluble copper(I) chloride residue.

The solid residues from several irradiations were combined and treated with aqueous sodium cyanide solution to displace the remaining olefins from their copper(I) complexes. The pentane extract of the resulting mixture contained *cis,cis*-1,5-cyclooctadiene (10% based on **2**), *cis,trans*-1,5-cyclooctadiene (13%; vpc retention time and infrared spectrum identical with those of an authentic sample<sup>3</sup>), and a new compound, **3** (1.5%).<sup>6</sup>

Compound **3** polymerized rapidly in the presence of oxygen or acid, or in concentrated solution, but could be isolated by preparative vpc<sup>6</sup> and stored in dilute pentane solution at  $-20^\circ$  for several hours. Its infrared spectrum ( $\text{CCl}_4$  or  $\text{CS}_2$ ) showed bands at 1615 (olefin) and  $985\text{ cm}^{-1}$  (*trans* olefin), but no bands in the

region  $750\text{--}650\text{ cm}^{-1}$  (*cis* olefin).<sup>7</sup> Its mass spectrum showed a clearly defined molecular ion at  $m/e$  108 ( $\text{C}_8\text{H}_{12}^+$ ) and a fragmentation pattern very similar to that of *cis,cis*- and *cis,trans*-1,5-cyclooctadienes,<sup>8</sup> but easily distinguishable from that of *cis,cis*-1,3- and *cis,cis*-1,4-cyclooctadienes.<sup>9</sup> The nmr spectrum of **3** (1:1 TMS- $\text{CCl}_4$ ,  $-20^\circ$ ) showed structureless peaks at  $\delta$  4.88 (olefinic hydrogen) and 2.43 (allylic hydrogen), with relative areas 1:2. Ozonolysis of **3** and oxidation of the ozonide gave succinic acid in approximately 85% yield, as determined by vpc analysis of its dimethyl ester following esterification with diazomethane. No ( $<0.5\%$ ) glutaric or adipic acid could be detected in the ozonolysis mixture.

Compound **3** could also be prepared, albeit in low yield (2.4%), by the low-temperature Hofmann degradation<sup>10</sup> of a mixture of *cis*- and *trans*-1,5-bis(dimethylamino)cyclooctane dimethiodides<sup>11</sup> with potassium amide in liquid ammonia. The only other hydrocarbon product detectable by vpc in this reaction was *cis,trans*-1,5-cyclooctadiene (1.2%).

These results show unambiguously that **3** is *trans,trans*-1,5-cyclooctadiene. That the *cis,trans*- and *trans,trans*-1,5-cyclooctadienes are found only in the solid residues from the irradiation, rather than free in solution, is consistent with the known high stability of complexes of cyclic *trans* olefins with silver(I).<sup>12</sup>

The ultraviolet spectrum of *trans,trans*-1,5-cyclooctadienes in both isooctane and ether solutions showed an unusual absorption at  $\lambda_{\text{max}}$  246  $m\mu$  ( $\epsilon \sim 1500$ ). This transition must in some manner owe its low energy to the proximity of the  $\pi$  orbitals of the double bonds of **3**.<sup>13</sup> However, neither this observation, nor the other available spectroscopic data, can presently be interpreted to provide a clear answer to the chemically important question of the relative stabilities of the conformations **3a** and **3b**.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 34-57.

(8) The principal differences were small differences in peak intensities. Mass spectra of *cis* and *trans* olefins are usually almost identical (K. Bieman, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 151).

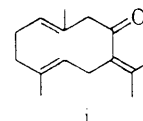
(9) The most intense peak in the mass spectra of **3** and the 1,5-cyclooctadienes occurred at  $m/e$  54, attributable to butadiene molecular ion. There were no intense peaks in this region in the spectra of the other isomers.

(10) G. Wittig and R. Polster, *Ann. Chem.*, **612**, 102 (1958).

(11) Z. Jacura, Ph.D. Thesis, Massachusetts Institute of Technology, 1962. The amine was prepared in a straightforward manner from 1,5-cyclooctanedicarboxylic acid [A. C. Cope, E. S. Graham, and D. J. Marshall, *J. Am. Chem. Soc.*, **76**, 6159 (1954)].

(12) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

(13) The anomalous absorption displayed by germacrone (i) and its derivatives at 213  $m\mu$  ( $\epsilon$  12,600) provides some precedent for the spectrum of **3**: F. Sorm, *Pure Appl. Chem.*, **2**, 533 (1961). Although this



transition was rationalized by an interaction between parallel double bonds, the endocyclic double bonds in the related germacatriene have been shown to possess the "crossed" conformation by X-ray crystallography of its silver nitrate complex: F. H. Allen and D. Rogers, *Chem. Commun.*, 588 (1967).

(1) Supported in part by the U. S. Army Research Office (Durham) Grant ARO(D)-31-124-435, and by the National Science Foundation Grant GP-6222.

(2) R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964); I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

(3) A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *ibid.*, **89**, 4024 (1967).

(4) J. H. van der Hende and W. C. Baird, Jr., *ibid.*, **85**, 1009 (1963); H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963).

(5) See J. Meinwald and B. E. Kaplan, *J. Am. Chem. Soc.*, **89**, 2611 (1967), and ref 2 for discussions of the structures of these products.

(6) Vpc analyses were carried out using glass columns containing 4-nitro-4-methylpimelonitrile or 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P; injection and detector block temperatures of  $80^\circ$  were necessary to avoid thermal decomposition of **3**.

. Irradiation of **3** in pentane gave tricyclooctane **1** in 70% yield, and no other volatile products. We have not been able to convert **3** to **1** thermally under a variety of conditions. The former observation, taken with others which will be published in the complete paper, suggests that *trans,trans*-1,5-cyclooctadiene may be an intermediate in the copper-catalyzed photochemical conversion of *cis,cis*-1,5-cyclooctadiene to tricyclooctane (**1**).

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