

## The Stereochemistry of Cyclooctatetraene Dibromide<sup>1</sup>

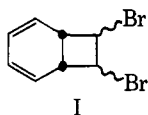
NORMAN L. ALLINGER, MARY ANN MILLER, AND LEONARD A. TUSHAUS

Department of Chemistry of Wayne State University, Detroit 2, Michigan

Received April 1, 1963

The bromines in cyclooctatetraene dibromide are shown to be *trans* to one another.

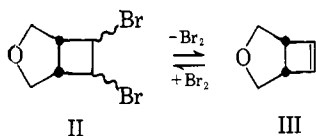
When cyclooctatetraene is treated carefully with one equivalent of bromine, cyclooctatetraene dibromide [7,8-dibromobicyclo[4.2.0]octadiene-(2,4)] (I, shown) is formed in good yield.<sup>2</sup> The *cis* stereochemistry of the



ring juncture was established many years ago on the basis of synthetic and degradative studies,<sup>3,4</sup> but the stereochemistry of the bromine atoms has been debated for some time.<sup>5,6</sup>

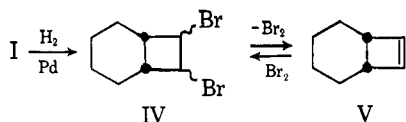
Georgian<sup>5</sup> calculated the dipole moments to be expected for I (1.0 D. if the bromines were *trans*, 2.4 D. if *cis*), and from the experimental moment (2.4 D.) concluded that the bromines were *cis*.

Blomquist and Cook<sup>6</sup> converted I to II by a sequence of reactions, and found that II was debrominated to give III, which added bromine to give back II. Since bromine adds to olefins in a *trans* manner, they assigned a *trans* configuration to the bromines.



Since the two groups of investigators reached opposite conclusions by different methods, both of which seemed to be sound, it appeared worthwhile to try to resolve the question by examining the assumptions made in the two cases.

Blomquist and Cook assumed that the addition of bromine to III would be *trans*. While this assumption appeared safe *a priori*,<sup>7</sup> it seemed under the circumstances desirable to rule out the possibility of neighboring group participation by the oxygen. This was done in the present work by hydrogenation of I to give IV. This compound was debrominated to give V. The addition of bromine gave back IV (superimposable infrared spectra). Since bromine adds in the ordinary



(1) This work was supported by the U. S. Army Research Office under Grant Number DA-20-018-ORD 22743.

(2) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).

(3) A. C. Cope and M. Burg, *J. Am. Chem. Soc.*, **74**, 168 (1952).

(4) E. Vogel, *Angew. Chem.*, **65**, 346 (1953).

(5) V. Georgian, *Chem. Ind. (London)*, 1626 (1959).

(6) A. T. Blomquist and A. G. Cook, *ibid.*, 873 (1960).

(7) No case of preferential ionic *cis* addition of bromine to an olefin appears to be known. See J. A. Berson and R. Swidler, *J. Am. Chem. Soc.*, **76**, 4060 (1954); H. Kwart and L. Kaplan, *ibid.*, 4073 (1954); and references cited.

*trans* fashion to cyclobutene,<sup>8</sup> the conclusions of Blomquist and Cook were confirmed, and the configuration of the bromines in I and the derived compounds is indeed *trans*. This conclusion was confirmed by examination of the proton magnetic resonance spectrum of IV. If the bromines were *cis*, because of the low barriers to inversion in the cyclohexane<sup>9</sup> and cyclobutane rings,<sup>10</sup> the hydrogens on the carbons carrying the bromines are equivalent and should show a first order spectrum corresponding to an A-X system<sup>11</sup> which should consist of a doublet in the 5- $\tau$  region. The *trans* bromines lead, on the other hand, to an ABXY system. A first-order prediction, which may or may not be a very good approximation, suggests that these protons will be seen as an octet. The observed spectrum shows an octet centered at 5.67  $\tau$ , which appears to definitely eliminate the *cis* isomer as a possibility, and is consistent with the *trans*. The *trans* arrangement of the bromines thus appears quite certain, and there remains only to explain the erroneous conclusions reached by Georgian on the basis of the dipole moment measurements.

The dipole moment of IV in benzene solution was determined in the present work as 2.78 D. This value is in good agreement with that reported by Georgian for I (2.4 D.). The erroneous interpretation, therefore, appears to result from the assignment of incorrect theoretical values to the *cis* and *trans* isomers of IV. (Georgian calculated values of 2.8 and 1.4 D. for *cis* and *trans* IV, respectively). Georgian's theoretical values were based on bond moments which were not given, and involved the assumptions that the cyclobutane ring is square and planar. This calculation has been repeated as exactly as possible in the present work, using values for C-Br bonds indicated by the literature,<sup>12</sup> (1.91 D. when the bromines are *cis*, and 2.24 D. when they are *trans*). The theoretical values obtained in the present work assuming a square planar ring are 3.50 D. for the *cis*, and 1.74 D. for the *trans*, neither of which is anywhere near the experimental value of 2.78 D. It has been long known, however, that cyclobutane and its derivatives are nonplanar,<sup>10,13,14</sup> and there is considerable evidence available on the degree of nonplanarity, so an effort was made to obtain better theoretical values

(8) J. Weinstock, S. N. Lewis, and F. G. Bordwell, *ibid.*, **78**, 6072 (1956).

(9) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *ibid.*, **84**, 386 (1962).

(10) G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *ibid.*, **75**, 5634 (1953).

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 91.

(12) (a) P. Bender, D. L. Flowers, and H. L. Goering, *J. Am. Chem. Soc.*, **77**, 3463 (1955); (b) N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czajka, and N. A. LeBel, *ibid.*, **82**, 5876 (1960).

(13) W. G. Rothschild and B. P. Daily, *J. Chem. Phys.*, **36**, 2931 (1962).

(14) (a) J. M. Conia, J. L. Rivol, L. A. Tushaus, C. L. Neumann, and N. L. Allinger, *J. Am. Chem. Soc.*, **84**, 4982 (1962); (b) A. Almennigen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961); (c) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

TABLE I  
 DIPOLE MOMENT DATA<sup>a</sup>

7,8-Dibromobicyclo[4.2.0]octane (IV), mol. ref., 52.03		
$N_2$	$d_{12}$	$\epsilon_{12}$
0.00000000	0.873308	2.2729
.00068752	.874343	2.2806
.00111469	.874963	2.2856
.00237442	.876795	2.3001
.00263129	.877146	2.3029
$\alpha = 11.465$	$\epsilon_1 = 2.2728$	$d_1 = 0.87333$
$\beta = 1.458$	$P_{2\infty} = 215.4$	$\mu = 2.83 \pm 0.02D$
<i>trans</i> -1,2-Dibromocyclobutane, mol. ref., 34.36		
0.00000000	0.873103	2.2729
.00113255	.874624	2.2821
.00242126	.876177	2.2923
.00347876	.877651	2.3010
.00434098	.878738	2.3076
$\alpha = 8.007$	$\epsilon_1 = 2.2730$	$d_1 = 0.87311$
$\beta = 1.296$	$P_{2\infty} = 151.1$	$\mu = 2.39 \pm 0.01D$
<i>cis</i> -1,2-Dibromocyclobutane, mol. ref., 34.36		
0.00000000	0.872478	2.2692
.00036920	.872981	2.2732
.00079314	.873553	2.2785
.00109040	.873932	2.2820
$\alpha = 12.306$	$\epsilon_1 = 2.2686$	$d_1 = 0.87249$
$\beta = 1.332$	$P_{2\infty} = 213.6$	$\mu = 2.91 \pm 0.03D$

<sup>a</sup> Benzene Solution, 25°.

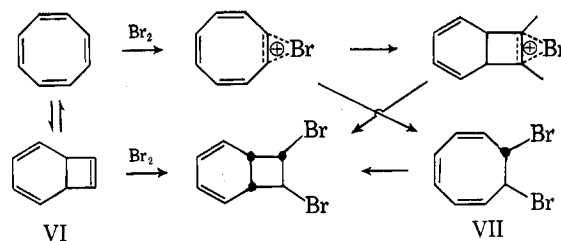
for the moments. The geometry of cyclobutyl bromide is rather accurately known,<sup>13</sup> and taking that geometry and making small adjustments in bond lengths and angles to fit the symmetry properties of the dibromides, it was calculated that the "natural" angles between the dipoles would be 59.0° and 115.6° for the *cis* and *trans* isomers, respectively. Using the previously mentioned values for group moments, the *cis*- and *trans*-1,2-dibromocyclobutanes were calculated to have moments of 3.33 and 2.39 D., respectively. These compounds were then prepared, their dipole moments were measured, and they were found to be 2.91 and 2.39 D., respectively. The theoretical and experimental values agreed well for the *trans* isomer, but not so well for the *cis*, and the cause for the discrepancy in the latter case was sought. From the geometry of the *cis* isomer, the distance apart of the bromines was calculated as 3.41 Å. This is less than the sum of the van der Waals radii of the two bromines, and it is expected that in such a case,<sup>15</sup> since the bending constant of a carbon-bromine bond is low, the bromines will in fact bend apart until they are approximately at the van der Waals distance (3.90 Å.). Such a distortion widens the angle between the dipoles to a calculated value of 68.5° and leads to a calculated resultant moment of 3.15 D., which is in reasonable agreement with experiment. This model with the bromines spread 3.9 Å. apart therefore seems to portray accurately the real molecule.

The experimental moment of IV is in good agreement with the moment of *cis*-1,2-dibromocyclobutane. There is another factor to be considered, however. The dihedral angle between the *cis* hydrogens in a dibromocyclobutane which are replaced by the cyclohexane ring in IV is about 25°, whereas in cyclohexane

it is 60°. Obviously some compromise will be reached, and it will involve the cyclobutane ring puckering more in IV than in the cyclobutane dibromide itself. The distortion required by the fusion of the six-membered ring is such that it will increase the "natural" angle between the dipoles of the *cis* isomer and decrease that of the *trans*. In the *cis* case the bromines will simply stop pushing as hard against one another, but they will not change their position significantly unless the distortion of fusion is exceedingly large. Thus, if the bromines are *cis*, there probably will be little difference between the moments of the simple cyclobutane and IV. If the bromines are *trans*,<sup>16</sup> on the other hand, the fusion of the cyclohexane will push them together, and the moment of *trans* IV will be greater than that of *trans*-1,2-dibromocyclobutane. Just how much greater is difficult to calculate. The observed moment, however, corresponds to a decrease in the angle between the dipoles of some 13°, which is not very large and appears physically quite reasonable. Thus the dipole moment data are in perfectly good agreement with either a *cis* or a *trans* arrangement of the bromines, and they offer no help in the establishment of the correct stereochemistry in IV. It now becomes clear that Georgian's earlier theoretical calculation of the moments of the *cis* and *trans* isomers of IV led to inaccurate values and incorrect conclusions.

All of the available data are now consistent with the *trans* geometry of the halogens, and the stereochemistry of the molecule appears to be established beyond doubt.

Very little can be said about the mechanism of the formation of cyclooctatetraene dibromide. Since the molecule has a normal *trans* arrangement of the bromines, no special mechanism is required by the known facts. Cyclooctatetraene may simply close to the



valence bond tautomer VI, which can then add bromine. This pathway seems unlikely, however, since no evidence for the tautomer VI has ever been reported. More likely paths are formation of the bromonium ion, and then either addition of bromide to give VII, followed by cyclization, or the same steps in reverse order (cyclization of the bromonium ion followed by addition of bromide).

### Experimental

**7,8-Dibromobicyclo[4.2.0]octane (IV).**—Bromine was added to cyclooctatetraene following the usual procedure,<sup>2</sup> and the dibromide (I) was obtained as an almost colorless liquid, b.p. 63–64° (0.1 mm.),  $n_D^{25}$  1.5913; lit.<sup>2</sup> b.p. 90–91°, (1 mm.),  $n_D^{25}$  1.5951. The unsaturated dibromide was reduced with hydrogen using a palladium-on-barium sulfate catalyst. The product obtained was somewhat variable in quality, often contaminated with 5–10% of the starting dibromide, b.p. 74° (0.5 mm.),  $n_D^{25}$

(16) The "diequatorial" conformation is considered to be the predominant one, since axial bromine is very unfavorable here (ref. 13), and the equatorial halogens are sterically comfortable and sufficiently far apart that only a minor electrostatic repulsion is expected.

(15) V. A. Atkinson and O. Hassel, *Acta Chem. Scand.*, **13**, 1737 (1959).

1.5549; lit.<sup>2</sup> b.p. 91° (1.2 mm.),  $n_D^{20}$  1.5583. The infrared spectrum often showed a weak to medium band at 13.8  $\mu$  and a shoulder at 3.3  $\mu$  which were absent in pure samples. The proton magnetic resonance spectrum of the compound in carbontetrachloride with internal tetramethylsilane showed an octet centered at 5.67  $\tau$ . This spectrum was obtained some years after completion of the remainder of the work, and no pure material remained. The spectrum was obtained on a sample that contained about 10% of I, judging from the area of the vinyl hydrogen absorption. Hence some of the finer features of the recorded spectrum may be due to impurity.

**Bicyclo[4.2.0]oct-7-ene (V).**—The olefin was prepared by treating dibromide IV with magnesium, b.p. 131–133°,  $n_D^{25}$  1.4729; lit.<sup>4</sup> b.p. 132.5°,  $n_D^{20}$  1.4761. Addition of bromine to V in methylene chloride at 0° gave an 80% yield of the dibromide IV, a colorless liquid, b.p. 94° (1.2 mm.),  $n_D^{25}$  1.5517. The infrared spectrum (2–15  $\mu$ ) was superimposable upon that of authentic IV.

**cis and trans-1,2-Dibromocyclobutane.**—These compounds were prepared according to standard procedures.<sup>8,17</sup> The *trans*-dibromide had b.p. 93–94° (55 mm.),  $n_D^{25}$  1.5344; lit.<sup>8</sup> b.p. 74–75° (26.5 mm.),  $n_D^{25}$  1.5352. The *cis* isomer, obtained by addition of hydrogen bromide to 1-bromocyclobutene in the presence of benzoyl peroxide, was purified by gas chromatog-

raphy, and was pure by that criterion,  $n_D^{25}$  1.5485; lit.<sup>17</sup>  $n_D^{25}$  1.5478. The infrared spectra were in good agreement with those obtained by Abell and Chiao.<sup>17,18</sup>

**Dipole Moments.**—The moments were calculated by essentially the method of Halverstadt and Kumler,<sup>19</sup> utilizing an IBM 7070 computer programmed as described earlier.<sup>20</sup> The molar refractivities were calculated from tables<sup>21</sup> and atomic polarization was neglected. The apparatus has been described previously.<sup>22</sup>

**Acknowledgment.**—The authors are indebted to Dr. M. A. DaRooge and Mr. C. L. Neumann for the dipole moment determinations, to Dr. M. Emerson and Mr. R. Ford for the n.m.r. spectra, to Dr. N. A. LeBel and Mr. P. M. Subramanian for the sample of *cis*-1,2-dibromocyclobutane, and to Dr. A. T. Blomquist and Dr. V. Georgian for correspondence regarding various aspects of the present work.

(18) Personal communication from Professor Abell.

(19) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(20) N. L. Allinger and J. Allinger, *J. Org. Chem.*, **24**, 1613 (1959).

(21) A. I. Vogel, W. T. Cresswell, G. J. Jeffery, and J. Leicester, *Chem. Ind. (London)*, 358 (1950).

(22) N. L. Allinger, H. Blatter, M. A. DaRooge, and L. A. Freiberg, *J. Org. Chem.*, **26**, 2550 (1961).

(17) P. I. Abell and C. Chiao, *J. Am. Chem. Soc.*, **82**, 3610 (1960).

## The Pulegone Oxides

WILLIAM REUSCH AND CALVIN KEITH JOHNSON

*Kedzie Chemical Laboratory, Michigan State University, East Lansing, Michigan*

Received April 4, 1963

The diastereoisomeric pulegone oxides have been isolated as crystalline solids. These isomers are assigned configurations Ia and IIa on the basis of the n.m.r. spectra, the optical rotatory dispersion curves, the thermal isomerization occurring at 200°, and a consideration of the available conformations.

Over three decades ago, Prileschaev reported<sup>1</sup> the preparation of a crystalline oxide, m.p. 44°, from pulegone by oxidation with perbenzoic acid. This work was recently confirmed by Pigulevsky and Mironova,<sup>2</sup> who also found that this dextrorotatory oxide was converted to a more strongly dextrorotatory liquid modification when heated at 200° for ten hours. On the basis of the Raman spectra and the change in specific rotation the latter workers concluded that isomerization of the crystalline pulegone oxide (Ia or IIa) to its diastereoisomer (IIa or Ia) was taking place, and that no deep structural changes occurred during heating. The lack of convincing evidence for this assertion combined with our interest in the high temperature reactions of oxiranes<sup>3</sup> has led us to re-examine these

facts and interpretations. In this paper we report the isolation of and assignment of configurations to the diastereoisomers Ia and IIa.

Good yields of pulegone oxide mixtures were obtained from pulegone either by oxidation with perbenzoic acid<sup>1,2</sup> or by reaction with alkaline hydrogen peroxide.<sup>4</sup> These mixtures yielded to analysis by vapor phase chromatography (v.p.c.) and proved to be almost identical in composition (33% Ia and 67% IIa). The crystalline modification, m.p. 44°, was readily isolated, but v.p.c. analysis showed this to be a compound consisting of equal proportions of the two diastereoisomers. These isomers were eventually separated by careful distillation at reduced pressure, followed by crystallization from petroleum ether. A survey of appropriate physical properties is given in Table I.

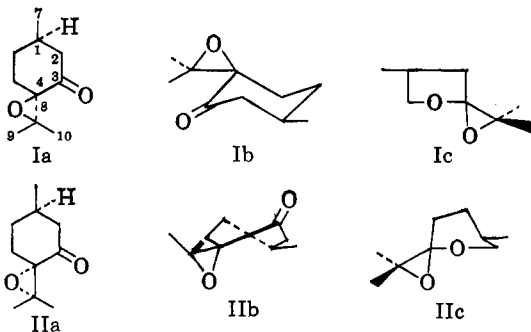


TABLE I

Isomer	M.p., °C.	$\lambda_{max}^{heptane}$	$m\mu$ ( $\epsilon$ )	$\nu_{max}^{CCl_4}$ cm. <sup>-1</sup>	$[\alpha]^{C_2H_5OH}_D$
Ia	59	209	225	1727	+48.0°
			303 (31)		
IIa	55	209	221	1728	-19.6°
			303 (31)		

In contrast to the report by Prileschaev, both Ia and IIa, prepared in this manner, are stable indefinitely under normal laboratory conditions. However, heating either Ia or IIa at 200° in an inert atmosphere does

(1) M. N. Prileschaev, *Bull. soc. chim.*, (iv) **41**, 687 (1927).

(2) G. V. Pigulevsky and I. K. Mironova, *Zh. Obshch. Khim.*, **27**, 1101 (1957).

(3) W. Reusch and C. K. Johnson, *J. Am. Chem. Soc.*, **84**, 1759 (1962).

(4) W. Treibs, *Ber.*, **66**, 1492 (1933).