

Fig. 4.—Electron density in the plane of the benzene ring atoms. All spurious peaks decreased and practically disappeared in both  $\rho_2$  and  $\rho_3$ .

The two peaks ignored in  $\rho_1$  as being too close to a 2-fold axis ( $\sim 1.2$  Å.) persisted and increased in height in  $\rho_2$  and  $\rho_3$ . It now became apparent that the benzene molecules were on 2-fold axes (multiplicity two in C2) thus accounting for a half of a mole of solvent.

Refinement continued through conventional electron and difference density considerations employing individual isotropic thermal parameters. The sixth and final structure factor computation gave  $R = 0.146$ . The density based on these phases is shown in Fig. 3; that of the benzene is shown in Fig. 4.

In addition to confirming the structure deduced by chemical means, this determination revealed the stereochemistry of the molecule; the bridgehead methoxy is *trans* to the carbamoyloxymethyl group and the aziridine. Moreover, the methyl and methoxy functions on the quinone are established with certainty. The pyrrolizine nitrogen in this molecule was known to be non-basic<sup>3</sup>; in the solid, this nitrogen is planar within the accuracy of its determination ( $\pm 0.03$  Å.). And finally, the nitrogen and oxygen atoms of neighboring carbamate groups are intermolecularly hydrogen bonded along the  $b$  axis.

A more detailed account of this determination will appear elsewhere.

(3) Lederle Laboratories, private communication.

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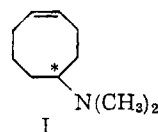
**OPTICALLY ACTIVE *cis-trans*-1,5-CYCLOÖCTADIENE FROM AN ASYMMETRIC HOFMANN ELIMINATION<sup>1</sup>**  
Sir:

The labile 1,5-cycloöctadiene obtained from N-methylgranatanine by two successive Hofmann

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exhaustive methylation reactions<sup>2</sup> must differ from the stable *cis-cis*-1,5-cycloöctadiene by the geometric configuration of one or both of the double bonds.<sup>3,4</sup> The *trans-trans*-configuration was considered most probable for the labile diene because of the smaller amount of steric strain indicated by molecular models.<sup>4</sup>

We have obtained unequivocal evidence that the compound is *cis-trans*-1,5-cycloöctadiene. The product of the first Hofmann exhaustive methylation of N-methylgranatanine proved to be *cis*-4-cycloöcten-1-yl dimethylamine, identical with a sample prepared from *cis*-4-cycloöcten-1-yl brosylate<sup>5</sup> and dimethylamine. This amine (I) has an asymmetric carbon atom, and has been resolved



by fractional crystallization of the *d*-10-camphor-sulfonic acid salts from diisobutyl ketone. The less soluble form had m.p. 144.0–145.5°,  $[\alpha]^{27D} - 1.88^\circ$  (*c* 13.0, water), and the more soluble form had m.p. 142.5–143.5°,  $[\alpha]^{26D} + 30.71^\circ$  (*c* 13.0, water). (Anal. Calcd. for  $C_{20}H_{35}NO_4S$ : C, 62.29; H, 9.15; N, 3.63. Found for the (–) isomer: C, 62.42; H, 9.17; N, 3.83. Found for the (+) isomer: C, 62.43; H, 9.20; N, 3.61.) The salts were converted to the tertiary amines I,  $[\alpha]^{25D} - 59.5^\circ$  (*c* 7.0, acetone) (obtained from levorotatory salt) and  $[\alpha]^{25D} + 61.5^\circ$  (*c* 2.4, acetone) (obtained from the dextrorotatory salt). The amines were characterized by conversion to picrates and methiodides. The methiodide obtained from the (–) amine had m.p. 258° (dec.),  $[\alpha]^{25D} - 14.92^\circ$  (*c* 6.0, water), while that obtained from the (+) amine had m.p. 262° (dec.),  $[\alpha]^{25D} + 14.30^\circ$  (*c* 2.7, water). (Anal. Calcd. for  $C_{11}H_{22}NI$ : C, 44.75; H, 7.51; N, 4.75. Found for the (–) isomer: C, 43.58; H, 7.19; N, 4.86. Found for the (+) isomer: C, 44.44; H, 7.64; N, 4.80.)

The optically active methiodides were converted separately to the corresponding methohydroxides with suspensions of silver hydroxide in water. The solutions were concentrated, and then distilled under reduced pressure under the usual conditions of the Hofmann elimination. The (–) methiodide yielded (+)-*cis-trans*-1,5-cycloöctadiene,  $n^{25D} 1.4893$ ,  $[\alpha]^{25D} + 121.3^\circ$  (*c* 2.0, pentane), while the (+) methiodide formed the enantiomer,  $n^{25D} 1.4885$ ,  $[\alpha]^{25D} - 120.5^\circ$  (*c* 2.0, pentane).

This demonstration of optical activity confirmed the fact that the labile diene must be different from the symmetrical *cis-cis*-1,5-cycloöctadiene. The *trans-trans* structure for the labile diene is ruled out by the *cis* geometry of the double bond in amine I. This double bond would not change to *trans* geometry during the second Hofmann elimination since the *cis* double bond is highly favored

(2) R. Willstätter and H. Veraguth, *Ber.*, **38**, 1975 (1905).

(3) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

(4) K. Ziegler, H. Sauer, L. Burns, H. Froitzheim-Kühlhorn and J. Schneider, *ibid.*, **589**, 122 (1954).

(5) A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959).

in the eight-membered ring.<sup>6</sup> This leaves *cis-trans*-1,5-cyclooctadiene as the only possible structure for the labile diene. The fact that the enantiomeric methoxyhydroxides lead to enantiomeric *cis-trans*-1,5-cyclooctadienes shows that the asymmetry characteristic of the bases is preserved in the transition states leading to the olefins. This is the first case in which a cyclic *trans* olefin has been shown to be asymmetric. The rigid structure of the ring and the non-bonded hydrogen interactions prevent rotation of the *trans*-CH=CH— unit with respect to the rest of the ring, which would result in racemization.

(6) R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957).

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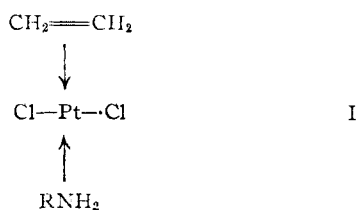
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RESOLUTION OF *trans*-CYCLOÖCTENE;  
 CONFIRMATION OF THE ASYMMETRY OF *cis-trans*-  
 1,5-CYCLOÖCTADIENE<sup>1</sup>

Sir:

Optically active stereoisomers of *trans*-cycloalkenes should be capable of existence provided the ring is sufficiently small to preclude rotation of the —CR=CR— unit relative to the rest of the molecule. This expectation has been realized by partial resolution of *trans*-cycloöctene.

Complexes with square planar geometry (formula I) can be prepared from "ethylene platinumous chloride" [1,3-diethylene-2,4-dichloro- $\mu$ -dichloro-diplatinum(II)], or Zeise's acid [H(PtC<sub>2</sub>H<sub>4</sub>Cl<sub>3</sub>)] derived from it, and an amine such as *p*-toluidine.<sup>2</sup>



Displacement of ethylene by other olefins in platinum(II) complexes is well known,<sup>3</sup> and one case involving an olefin amine platinum(II) complex has been reported.<sup>4</sup>

The method of resolution was to prepare a complex using optically active (+)-1-phenyl-2-aminopropane ("Dexedrine," dex) (I, where R is C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)—) and then to displace the ethylene by *trans*-cycloöctene, forming *trans*-dichloro-*trans*-cycloöctene "Dexedrine" platinum(II) (II). If *trans*-cycloöctene is capable of existence in optically active forms, this complex II would constitute a mixture of diastereomers.

The reaction of H(PtC<sub>2</sub>H<sub>4</sub>Cl<sub>3</sub>) with "Dexedrine" led to the complex I, C<sub>2</sub>H<sub>4</sub>PtCl<sub>2</sub>dex, m.p. 120–121°, [α]<sup>25D</sup> +20.5° (*c* 2.5, methylene chloride). (Anal. Calcd. for C<sub>11</sub>H<sub>17</sub>NPtCl<sub>2</sub>: C, 30.76; H,

3.99; N, 3.27; Pt, 45.74. Found: C, 30.54; H, 4.00; N, 3.31; Pt, 45.74.)

Reaction of *trans*-cycloöctene<sup>5</sup> with I in methylene chloride<sup>6</sup> gave the expected complex C<sub>8</sub>H<sub>14</sub>PtCl<sub>2</sub>dex, II. Fractional crystallization from hexane at –20° gave as the least soluble material IIa, a viscous oil at room temperature (crystalline at –20°), [α]<sup>25D</sup> +24° (*c* 2.5, methylene chloride); and as the most soluble material IIb, a viscous oil also crystalline at lower temperatures, [α]<sup>25D</sup> +4° (*c* 2.5, methylene chloride). (Anal. Calcd. for C<sub>17</sub>H<sub>27</sub>NPtCl<sub>2</sub>: C, 39.91; H, 5.32; N, 2.75; Pt, 38.17. Found for IIa: C, 39.90; H, 5.26; N, 2.82; Pt, 38.04. Found for IIb: C, 40.28; H, 5.41; N, 3.03; Pt, 37.95.)

The olefin and amine were liberated by shaking a solution of each complex (IIa and IIb) in methylene chloride with 10% aqueous potassium cyanide solution. The methylene chloride solutions were washed with water, 5% hydrochloric acid (to remove the amine), 5% sodium bicarbonate and water. After drying over sodium sulfate, the solvent was evaporated at room temperature and the residues were distilled, yielding *trans*-cycloöctene, identified by comparison of infrared spectra with the spectrum of an authentic sample. From IIa the *trans*-cycloöctene had [α]<sup>25D</sup> –21° (*c* 2, pentane); from IIb [α]<sup>25D</sup> +18.5° (*c* 2, pentane).<sup>7</sup> Each sample was hydrogenated over prerduced platinum oxide in acetic acid to optically inactive cycloöctane (m.p. 11°) with the uptake of 95% of the theoretical amount of hydrogen.

Application of the same method to *cis-trans*-1,5-cycloöctadiene also resulted in partial resolution, confirming the asymmetry of the molecule (*cf.* the preceding communication). Reaction of *cis-trans*-1,5-cycloöctadiene with I gave a complex (III), C<sub>8</sub>H<sub>12</sub>Pt<sub>2</sub>Cl<sub>4</sub>dex<sub>2</sub>, which was fractionally crystallized from benzene-cyclohexane yielding as the most soluble material IIIa, m.p. 106–108° (after further recrystallization from carbon tetrachloride), [α]<sup>25D</sup> +55.2° (*c* 2.5, methylene chloride); and as the least soluble material IIIb, m.p. 155–157°, [α]<sup>25D</sup> –18.3° (*c* 2.5, methylene chloride). (Anal. Calcd. for C<sub>26</sub>H<sub>38</sub>N<sub>2</sub>Pt<sub>2</sub>Cl<sub>4</sub>: C, 34.28; H, 4.20; N, 3.08; Pt, 42.87. Found for IIIa: C, 34.42; H, 4.05; N, 2.75; Pt, 43.22. Found for IIIb: C, 34.10; H, 4.33; N, 3.06; Pt, 42.46.) Treatment of IIIa and IIIb in the manner described for IIa and IIb gave samples of *cis-trans*-1,5-cycloöctadiene, identified by comparison of infrared spectra with the spectrum of an authentic sample. The diene from IIIa had [α]<sup>25D</sup> –26° (*c* 1.3, pentane); the diene from IIIb had [α]<sup>25D</sup> +34° (*c* 1.2, pentane).

This method of resolution should be general for olefins forming sufficiently stable pi complexes with platinum. It is being extended to other cyclic olefins with molecular asymmetry, and rates

(5) A. C. Cope, R. A. Pike and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(6) For one of many similar examples see J. R. Joy and M. Orchin, *ibid.*, **81**, 305, 310 (1959).

(7) NOTE ADDED IN PROOF.—(–)-*trans*-Cycloöctene completely resolved through the complex C<sub>8</sub>H<sub>14</sub>PtCl<sub>2</sub>C<sub>8</sub>H<sub>6</sub>CH(NH<sub>2</sub>)CH<sub>3</sub> has [α]<sup>19D</sup> –411° (*c* 0.27, methylene chloride) (A. C. Cope and T. V. Van Auken, unpublished results).

(1) Presented at the Carl S. Marvel Honorary Symposium, Tucson, Arizona, December 28, 1961.

(2) J. Chatt, *J. Chem. Soc.*, 3340 (1949).

(3) J. S. Anderson, *ibid.*, 971 (1934).

(4) A. H. Gelman, *Compt. rend. Acad. Sci. URSS*, **32**, 347 (1941).