The Crystal Structure of (+)-*cis*-Carvone Tribromide

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THE formation of carvone tribromide from carvone was first reported by Wallach.[1] More recently Wolinsky, Hamsher, and Hutchins[2] have shown this product to have the 2,3-diaxial structure, resulting from *trans*-addition of bromine. They further report it isomerizes to the 2-axial,3-equatorial (*cis*) form in the presence of HBr and acetic acid at 0°. We report the confirmation of the configuration of the new isomer (+)-*cis*-carvone tribromide by *X*-ray crystallographic analysis.

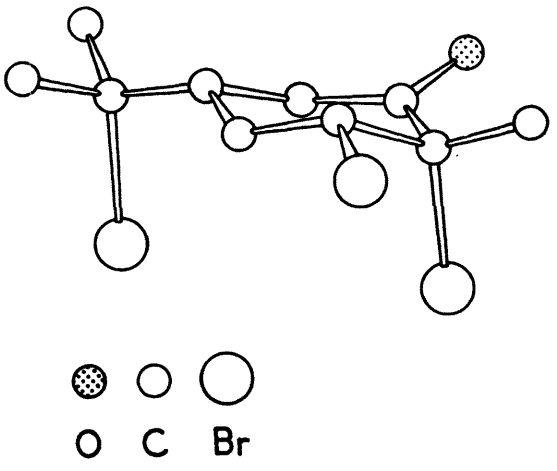

FIGURE. *Absolute configuration of* (+)-cis-*carvone tribromide.*

The crystals are orthorhombic, $a = 18{\cdot}40 \pm 0{\cdot}02$, $b = 11{\cdot}12 \pm 0{\cdot}02$, $c = 6{\cdot}32 \pm 0{\cdot}02$ Å, space group $P2_12_12$, $Z = 4$ molecules of $C_{10}H_{15}OBr_3$ per unit cell. The observed density of 1·98 g./ml. determined by flotation compares well with the calculated value of 2·01 g./ml. Several crystals were used to collect the data since they suffered serious radiation damage within 100 hr. exposure. Photographs were taken on the precession camera using Zr-filtered Mo radiation, and intensities were obtained from densitometer tracings of the films.

The structure was solved by the heavy-atom method using bromine positions determined from a Patterson synthesis. The light atoms appeared immediately in the first electron-density map, and refinement was carried out using Fourier methods and six cycles of full-matrix least-squares analysis. The current *R*-value is 0·106 for 583 observed reflections using isotropic light atoms and anisotropic bromine atoms.

A view of the molecule is given in the Figure and shows unequivocally the 2-axial,3-equatorial (*cis*) bromine configuration. Comparison of observed and calculated differences for anomalous pairs allowed an assignment of absolute configuration, which is that shown.

R.W.S. received financial support from the National Institutes of Health.

Crystals of (+)-*cis*-carvone tribromide were supplied by Professor J. Wolinsky of the Chemistry Department, Purdue University.

(*Received, May 12th,* 1969; *Com.* 652.)

[1] O. Wallach and C. Ohligmacher, *Annalen*, 1899, **305**, 245; O. Wallach, 1918, **414**, 240.
[2] J. Wolinsky, J. Hamsher, and R. O. Hutchins, submitted to *J. Org. Chem.*