X-Ray Structure of *threo*-1-Bromomercuri-2-t-butylperoxy-1,2-diphenylethane, a Crystallographic Proof of the Stereochemistry of the Peroxymercuration of *cis*-Stilbene

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Summary The configuration of the title compound has been determined; it is shown that there is intramolecular co-ordination between mercury and the t-butylperoxy group with Hg–O 2·68(4)Å.

INVESTIGATION of the stereochemistry of the peroxymercuration of acyclic alkenes has suggested that a determining factor is the presence of intramolecular mercury–oxygen co-ordination. A comparison of the vicinal coupling constants (J_{AB}) of the *cis*- and *trans*-derived diastereoisomers of the compounds $RCH^AX \cdot CH^B(HgY)R$ (X = $OOBu^t$), formed from but-2-ene (R = Me) or stilbene (R = Ph) with Y = CF_3CO_2 or Br was made[1,2] using the

criterion $J_{erythro} > J_{threo}$. These results could only be reconciled with the expected *trans* mode of addition to the parent alkenes if attractive interaction between mercury and the t-butylperoxy group was sufficient to overcome the repulsion expected to prevail between the R groups.

The evidence was more favourable for the but-2-ene derivatives than those from stilbene and less favourable for the bromides as against the trifluoroacetates. The title compound, the only one available for crystal structure determination, derived from *cis*-stilbene with R = Ph and Y = Br, was therefore regarded, on the n.m.r. evidence, as being least likely to involve intramolecular co-ordination.

Crystal data: $C_{18}H_{21}BrHgO_2$, monoclinic, $P2_1/c$, $a =$ 11·48(1), $b = $ 10·53(1), $c = $ 17·66(2) Å, $\beta = $ 120·5(1)°, $Z = $ 4, $D_m = $ 1·92, $D_x = $ 1·99 g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = $ 101·8 cm^{-1}. In spite of careful recrystallisation crystals were of poor quality and upon irradiation gave a high background intensity with spot broadening as decomposition progressed. The intensity data were measured on a Stoe STADI-2 two circle diffractometer with graphite monochromatised Mo-K_α radiation. Absorption corrections were made using the program SHELX-76; 1486 unique reflexions for which $4° < 2\theta \leqslant 40°$ and $I > 3\sigma(I)$ were used for structure determination. Using the X RAY 72 system the mercury and bromine atom positions were obtained from Patterson maps; the remaining atoms apart from hydrogens were found on (F_0-F_c) Fourier maps phased on the heavy atoms. Refinement of all co-ordinates, anisotropic U_{ij} values for mercury and bromine, and isotropic U for the remaining atoms gave a final R value of 0·098.†
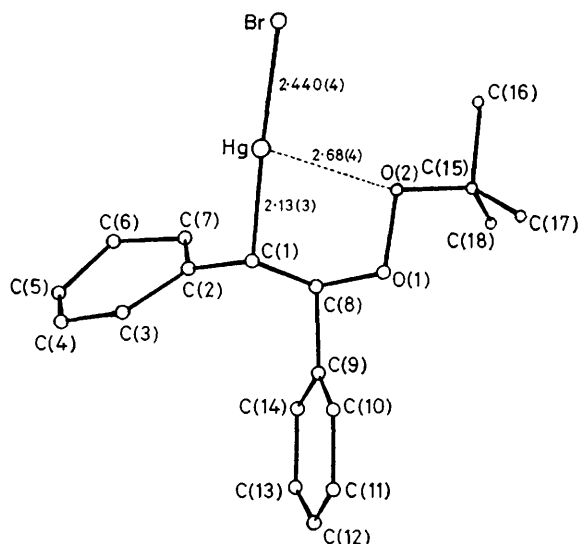

FIGURE 1. View of *threo*-1-bromomercuri-2-t-butylperoxy-1 2-diphenylethane showing Hg co-ordination.

The molecule is shown in Figure 1. The Hg–C and Hg–Br bond lengths have typical covalent values and the C–Hg–Br angle is 177(1)°. The Hg–O contact distance shown is appreciably greater than the covalent distance, typically 2·10 Å, but is less than the van der Waals distance, the lowest estimate[3] of which is 2·90 Å. There is thus strong evidence of intramolecular Hg–O attraction. The torsion angles about the bond C(1)–C(8) are shown in Figure 2. It will be noted that the configuration is indeed *threo*, the conformation being a rotamer derived from *trans* addition to *cis*-stilbene with *anti* disposed protons.
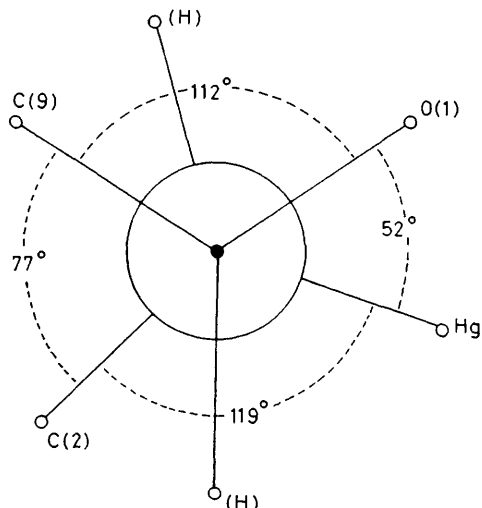

FIGURE 2. Configuration about C(8)–C(1) of *threo*-1-bromomercuri-2-t-butylperoxy-1,2-diphenylethane showing torsion angles.

There are no short intermolecular contacts involving the mercury atom. The averaged standard deviation of the bonds between light atoms is 0·07 Å; within this limit there are no deviations from the expected dimensions for the remainder of the molecule.

[1] A. J. Bloodworth and I. M. Griffin, *J.C.S. Perkin I*, 1975, 195.
[2] A. J. Bloodworth and I. M. Griffin, *J.C.S. Perkin II*, 1975, 531.
[3] D. Grdenić, *Quart. Rev.*, 1965, 303.