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A REINTERPRETATION: EVIDENCE FOR THE EXCLUSION OF CORNER BROMINATED CYCLOPROPANE IN THE BROMINATION OF trans-CYCLOPROPANE-1,1,2,3-d_4

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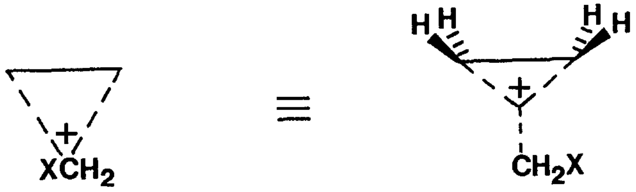
Abstract: The results of bromination of trans-cyclopropane-1,1,2,3-d_4 have been reinterpreted and require an unsymmetrical reaction pathway thereby excluding the formation of a corner brominated reaction intermediate.

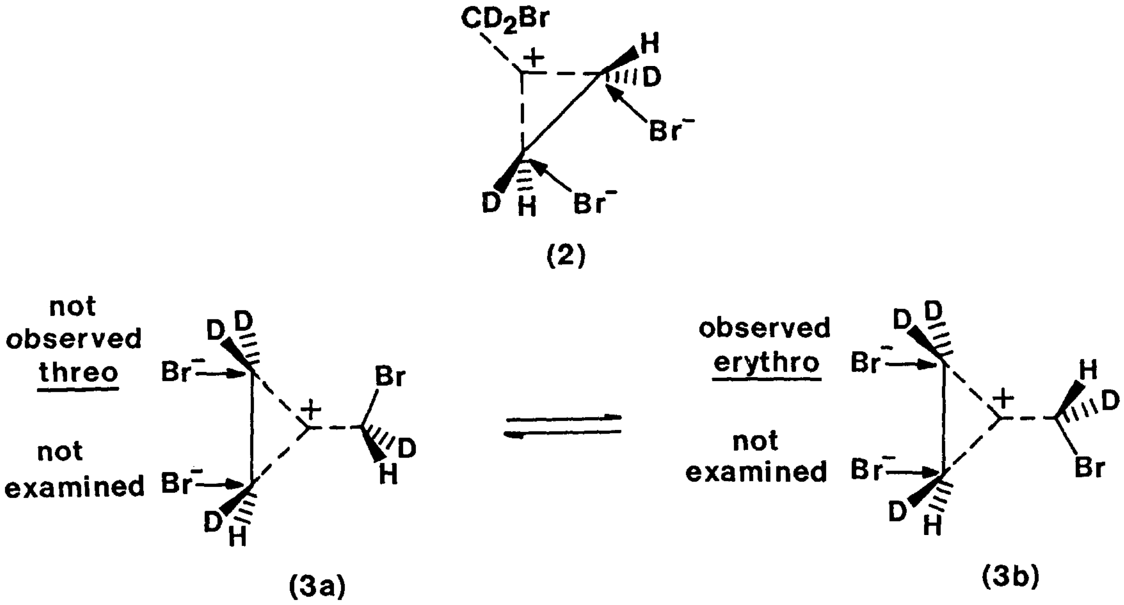
The recent report by Lambert et al.,[1] of the bromination of trans-cyclopropane-1,1,2,3-d_4 in a 85:15 mixture with cis-isomer to give stereospecifically erythro (85%) product dictates inversion of stereochemistry at both the site of electrophilic and nucleophilic attack. From this elegant experiment, however, the authors report, "The observed stereospecificity of the reaction requires an intermediate of type (1) which contains a formally pentavalent carbon."



(1)

Such a species, formally analogous to the non-classical norbornyl cation[2], is a corner brominated cyclopropane.[3] Contrary to the authors' conclusions, this experiment does not dictate the reaction to require a corner brominated cyclopropane intermediate, in fact, the result specifically excludes this possibility.

The two possible corner brominated cyclopropyl cations (2) and (3) are shown in Scheme 1 and ignoring any isotope effect are formed in the ratio 1:2. Cation (2) can collapse by nucleophilic attack with inversion at C2 or C3 to erythro product, the stereochemistry dictated by attack of nucleophile. Cation (3) will be formed equally in



Scheme 1

configurations (3a) and (3b). The intermediacy of corner brominated cyclopropanes (1) require rotation of the pentacoordinated carbon in (3) to be slow with respect to the rate of nucleophilic attack and also requires the initial configuration of the species to dictate which of the adjacent sites is attacked by nucleophile.

The stereoselective formation of *erythro* product requires an unsymmetric reaction pathway[4] and is consistent with the symmetric 3e' orbital or both the degenerate HOMO's of the cyclopropane[5,6] interacting with the electrophile. The latter is analogous to the pathway simulated by Wiberg[7] for proton attack at the corner of 1,2,3-trimethylcyclopropane where both adjacent bonds increased in length but the one on the side away from the proton increased in length more rapidly leading to inversion of configuration.

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