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STEREOCHEMISTRY OF THE STEREOSELECTIVE EPOXIDATION AND HYDROBORATION OF HEXAMETHYL (DEWAR BENZENE)

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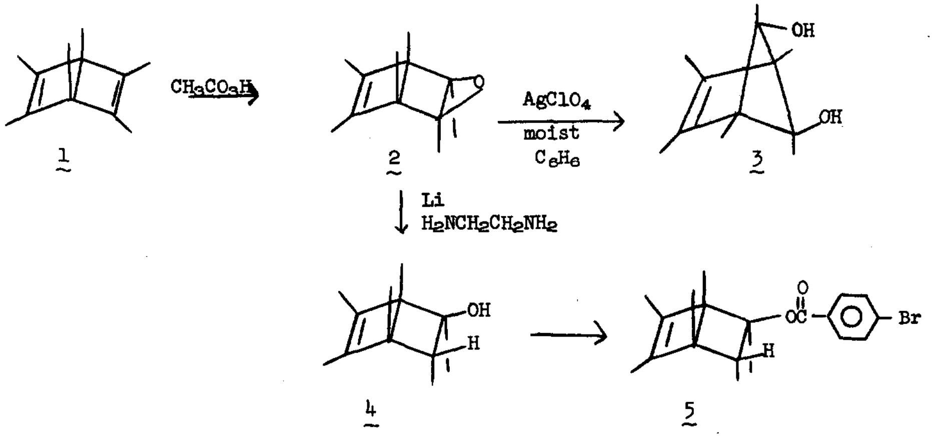
Recently, we outlined briefly the electronic, steric, and torsional strain effects which likely affect the stereochemical course (endo or exo) of electrophilic additions to hexamethyl (Dewar Benzene) (1).[2] The cycloadditions of carbenes[3] and azides[4] to 1 are now recognized to proceed by means of exo bonding without skeletal rearrangement. In those cases where structural bond reorganizations obtain, information concerning the preferred direction of initial attack is not revealed because of the capability of certain intermediate cations for rapid epimerization.[5] The lack of a sufficient number of bona fide examples of established stereochemistry prompted a detailed study of the epoxidation, hydroboration, and oxymercuration of 1.

Upon oxidation with buffered peracetic acid in methylene chloride solution, 1 was converted[6] into epoxide 2. When treated with silver perchlorate in moist benzene, 2 underwent rapid and near-quantitative rearrangement to diol 3 of established structure.[7] In contrast, careful reduction of 2 with lithium in ethylenediamine[8] gave a monoalcohol (4),



mp 53-55° (50% yield); $\delta_{TMS}^{CDCl_3}$ 1.87 (q, J=7 Hz, 1), 1.57 (s, 6), 1.08, 1.07, 1.02 (s, 3 each) and 0.91 (d, J=7 Hz, 3). Little information is available concerning the mechanism of epoxide ring cleavages with lithium-amine combinations. In the lone stereochemically revealing example know to us,[9] thermodynamically-controlled protonation of the intermediate dianion appeared operative. However, such behavior need not be general. That the relative stereochemical disposition of the ring proton and the hydroxyl group was cis followed from the isolation of 4 (70% yield) from hydroboration-oxidation of 1. Detailed knowledge of the absolute stereochemistry of this molecule was gained by conversion to its *p*-bromobenzoate (5), mp 116-118°, with *n*-butyllithium and *p*-bromobenzoyl chloride. The single crystal X-ray diffraction analysis of 5 (Figure 1) reveals clearly that the two substituents in question are both positioned exo on the bicyclo[2.2.0]hexene nucleus.[10] Accordingly, epoxidation and hydroboration of 1 exhibit a marked preference for exo addition in stereochemical conformity with the other cyclic addition processes[11] mentioned above.

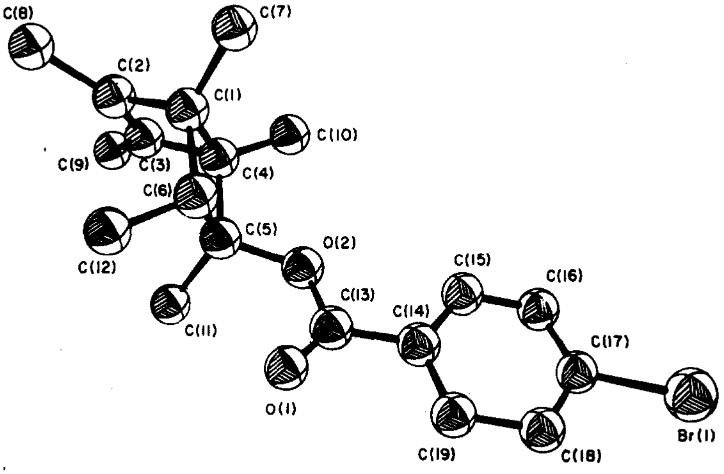
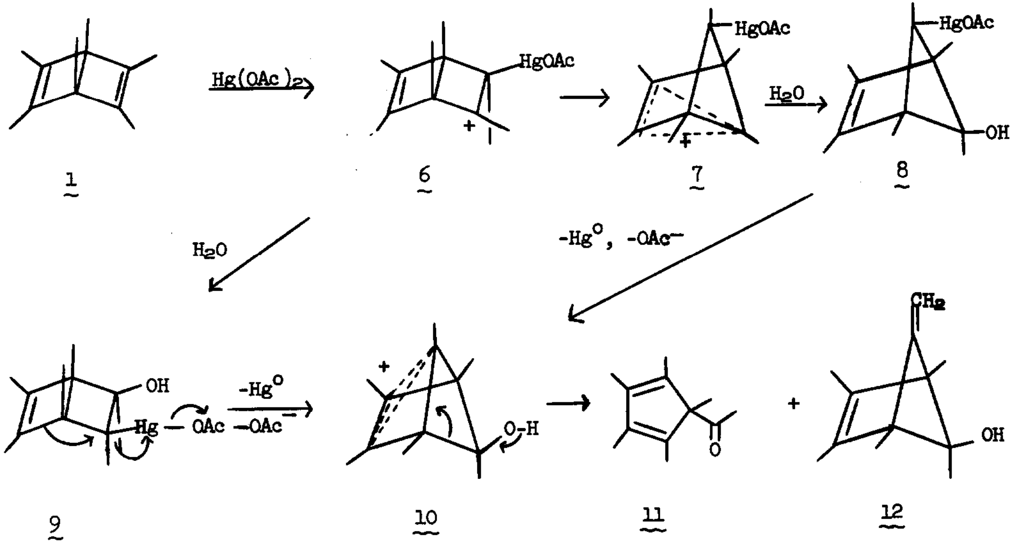


Figure 1. A structural view of 5 as determined by X-ray analysis.

Treatment of 1 under a nitrogen atmosphere with an equimolar amount of mercuric acetate in 50% aqueous tetrahydrofuran according to established procedures[12] (25°, 12 hr) resulted in unexpected rapid deposition of elemental mercury. Acetylpentamethylcyclopentadiene (11)[6b,7] was produced in high yield admixed with a small quantity of an isomeric, as yet incompletely characterized, alcohol which is perhaps 12.[13] Generally speaking, organomercurials are stable to these reaction conditions; however, reversion to olefin does occur in certain cases when the medium is acidic.[14] The differing behavior of **1** would appear to be the result of facile carbonium ion generation in this system, a property which lends itself to ready heterolysis of the C-Hg bond.[12b,14] Thus, stepwise electrophilic attack of $Hg(OAc)_2$ on **1** (from an assumed exo direction) can give rise either to **8** or **9** depending upon the timing of the skeletal rearrangement. Either intermediate is constructed such that homoallylic anchimeric assistance to demercuration can be provided by a neighboring π bond. The resulting poorly solvated cation **10** can ultimately lead to both **11** and **12** rather than **3**.



FOOTNOTES AND REFERENCES

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