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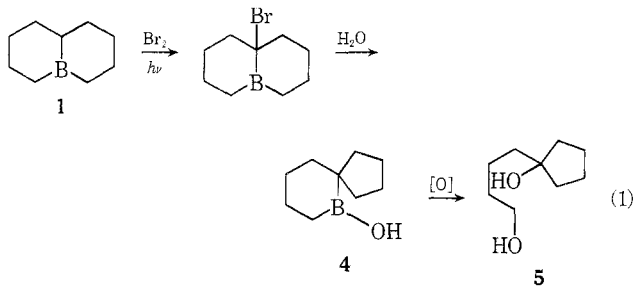
## Synthetic Approach to New Organoborane Structures *via* the α-Bromination of Borapolycyclanes

*Summary:* The light-induced reaction of bromine with borapolycyclanes (**1**, **2**, **3**) in the presence of water provides an entry into polycyclic organoborane intermediates with interesting new structures and to the organic derivatives into which they may be converted.

*Sir:* A simple six-membered boracyclane can undergo ring contraction to produce a five-membered carbocyclic boron intermediate by photochemical reaction with bromine in the presence of water.[1] The reaction proceeds through a rapid, selective α-bromination, followed by a facile migration of the B–C bond from boron to carbon.[2] This development makes possible the synthesis of carbocyclic structures from the corresponding straight-chain dienes.

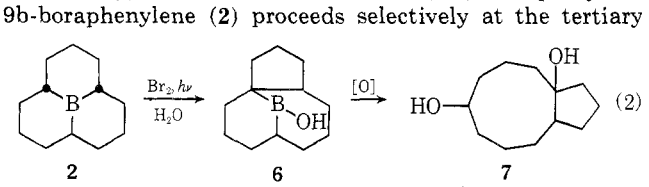
We now wish to report that the reaction is applicable to much more complex systems. Thus, its application to representative borapolycyclanes (**1**, **2**, **3**)[3] proceeds satisfactorily and provides an entry to interesting new organoborane structures (**4**, **6**, **8**) and to the organic derivatives into which such boron compounds can be converted (**5**, **7**, **9**).

For example, treatment of 9-boradecalin (**1**) with bromine in the presence of light and water provides 6-hydroxy-6-boraspiro[4.5]decane (**4**). The structure of **4** was confirmed by oxidation with alkaline hydrogen peroxide to 1-(4-hydroxybutyl)cyclopentanol[4] (eq 1), in an overall yield of 50%. It is evident that the α-bromination occurs selectively at the α tertiary hydrogen atom, rather than at the α secondary position.




1 4 5 (1)

Similarly, the α-bromination of *cis,cis,trans*-perhydro-9b-boraphenylene (**2**) proceeds selectively at the tertiary

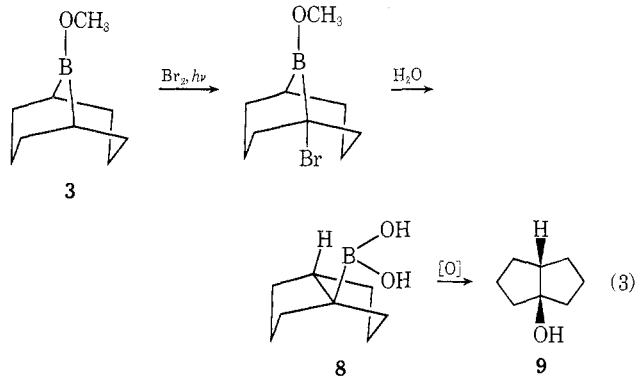



2 6 7 (2)

position. Hydrolysis–oxidation in the usual manner provides bicyclo[7.3.0]dodecane-1,5-diol[4] in 70% yield *via* the polycyclic borane intermediate, 13-hydroxy-13-boratricyclo[7.3.1.0$^{1,5}$]tridecane (**6**) (eq 2).

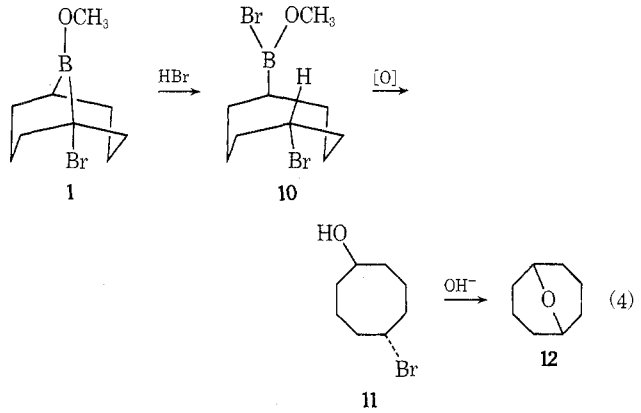
The case of 9-methoxy-9-borabicyclo[3.3.1]nonane (**3**) is of special interest. It was recently established that the α-bromination of *B*-isopropyl-9-borabicyclo[3.3.1]nonane occurs almost exclusively at the α position of the isopropyl group.[5] No significant attack occurs at the α bridgehead positions. Consequently, it was uncertain whether α-bromination in **3** would be feasible.

In fact the bromination, albeit somewhat more sluggish than the other cases, proceeds satisfactorily, producing the *cis*-bicyclo[3.3.0]octane-1-boronic acid (**8**), readily oxidized to *cis*-bicyclo[3.3.0]octan-1-ol[6] (**9**) in a yield of 65% (eq 3). Although the bromo intermediate was not isolated, it is evident that bridgehead substitution must have taken place in view of the structures of the products (**8**, **9**).




3 8 9 (3)

The reaction is accompanied by the formation of cyclooctane 1,5-epoxide[7] (**12**) in 22% yield. This product may arise from a competing attack of hydrogen bromide on the bromination intermediate to form **10** (eq 4). Pmr examination of the reaction mixture reveals the presence of a methine proton (4.05–4.50 ppm in $CCl_4$) assigned to **10**. The integral area ratio of the spectrum reveals that the reaction proceeds 70% through path 3 and 30% through path 4.

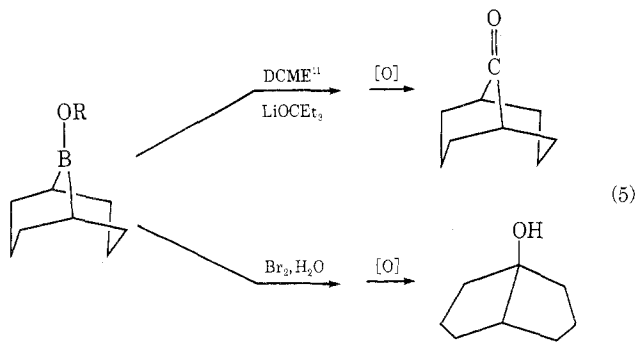



1 10 11 12 (4)

The following procedure for the preparation of *cis*-bicyclo[3.3.0]octan-1-ol is representative. A dry 300-ml flask, equipped with a septum inlet, thermometer well, pressure-equalizing dropping funnel, reflux condenser, and magnetic stirrer, was flushed with dry nitrogen and maintained under a positive nitrogen pressure. The flask was cooled to 0–5° and charged with 4.56 g (30 mmol) of pure 9-methoxy-9-borabicyclo[3.3.1]nonane,[8] 40 ml of methylene chloride, and 30 ml of water. Bromine (1.65 ml, 30 mmol) in 20 ml of methylene chloride was slowly added at 0–5° over 1.5 hr. After the bromine color disappeared, sodium hydroxide solution (6 *N*, 15 ml), ethanol (60 ml), and aqueous hydrogen peroxide (30%, 10 ml) were added at 0–5°. The mixture was then refluxed for 1 hr. The or-

ganic layer was separated and dried over anhydrous potassium carbonate. Glpc analysis revealed a 65% yield of *cis*-bicyclo[3.3.0]octan-1-ol and a 22% yield of cyclooctane 1,5-epoxide. Distillation gave 2.07 g (55%) of *cis*-bicyclo[3.3.0]octan-1-ol: bp 82–83° (15 mm), *p*-nitrobenzoate mp 123.5–124.5° (lit.[6] 124–124.8°).

The carbonylation[9] and dichloromethyl methyl ether (DCME) reactions[10] convert such polycyclic organoboranes to other structures. The difference in these alternative synthetic routes is indicated by eq 5. Consequently, it




(5)

is now possible to proceed from the same intermediate to different boron derivatives and to the organic structures to which they can be converted.

## References and Notes

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