Light-induced Reaction of Boracyclanes with Bromine in the Presence of Water. Ring Contraction of Boracyclanes to Produce Carbocyclic Structures

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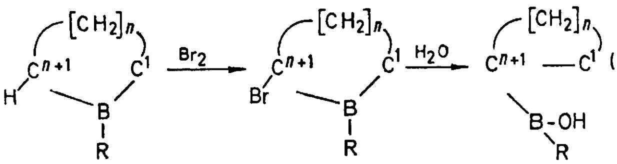
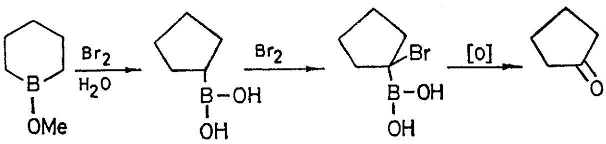
Summary Six-membered boracyclanes undergo ring contraction to produce the corresponding five-membered carbocyclic compounds by treatment with bromine in the presence of water.

The light-induced α-bromination of trialkylboranes, dialkylborinic acids, and thexyldialkylboranes in the presence of water provides a convenient method for the synthesis of new carbon–carbon bonds.[1] Various types of straight-chain or branched carbon structures are now available *via* this procedure.



(1)

If bromine attacks hydrogen α to the boron atom of boracyclanes to produce the α-bromo-derivatives, and if the B–C¹ bond rearranges from boron to C^{n+1}, ring contraction of boracyclanes to achieve the formation of carbocyclic structures would be possible [equation (1)].

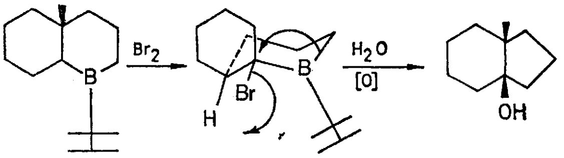


(2)

(I)

Accordingly, the representative boracyclanes (I), (II), and (III) were prepared *via* hydroboration of the corresponding dienes.[2] These boranes were treated with bromine in the presence of water under normal laboratory light, and then oxidized with alkaline hydrogen peroxide.

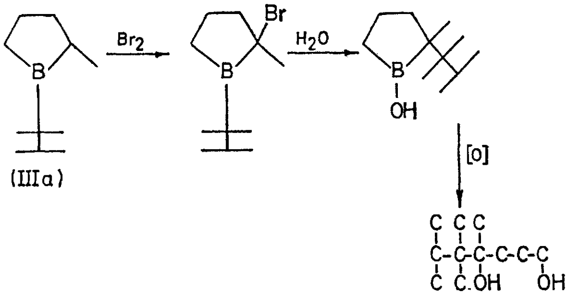
The six-membered boracyclanes (I) and (II) undergo ring contraction to the five-membered carbocyclic compounds. The bromination–oxidation of (I) affords cyclopentanone in 48% yield [equation (2)]. This conversion requires 2 mol. equiv. of bromine, presumably because of a competing α-bromination of the cyclopentylboronic acid.



(3)

(II)

The bromination–oxidation of (II) yields *cis*-8-hydrindanol in 60% yield [equation (3)]. The predominant formation of *cis*-isomer might be due to the preferred formation of *cis*-9-bromo-1-thexyl-1-boradecalin in the α-bromination stage, followed by migration of the B–C² bond.



(IIIa)

(4)

(IV)

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The versatility of this new development is indicated by the fact that the same borane (II) is converted by carbonylation–oxidation into pure *trans*-1-decalone.[3]

Five-membered boracyclanes (IIIa,b) fail to undergo this ring contraction, but in the case of (IIIa) undergo instead preferential migration of thexyl group to produce the diol (IV) in 55% yield [equation (4)]. This result is presumably a reflection of the large ring strain involved in a contraction to the cyclobutane structure, forcing the migration to take another path. Bromination of 2-methyl-1-boracyclopentan-1-ol (IIIb) was also tried, but here also the ring contracted product, 1-methylcyclobutanol, was not detected.

The present results provide the first example of a new type of ring contraction of cyclic boranes. A number of cyclic boranes is available from dienes and trienes *via* hydroboration.[4] Consequently, the present results may also provide a convenient and general procedure for the synthesis of carbocyclic structures from the corresponding polyenes.

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[1] H. C. Brown and Y. Yamamoto, *Synthesis*, **1972**, **699**, and references cited therein.

[2] For preparation of (I), see H. C. Brown, E. Nagishi, and S. K. Gupta, *J. Amer. Chem. Soc.*, 1970, **92**, 6648; (II), H. C. Brown and C. D. Pfaffenberger, *ibid.*, 1967, **89**, 5475; (III), H. C. Brown, E. Negishi, and P. L. Burke, *ibid.*, 1972, **94**, 3561.

[3] H. C. Brown and E. Negishi, *Chem. Comm.*, 1968, 594.

[4] H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, 1972, **94**, 3567.