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HYDROBORATION OF CYCLODECADIENES

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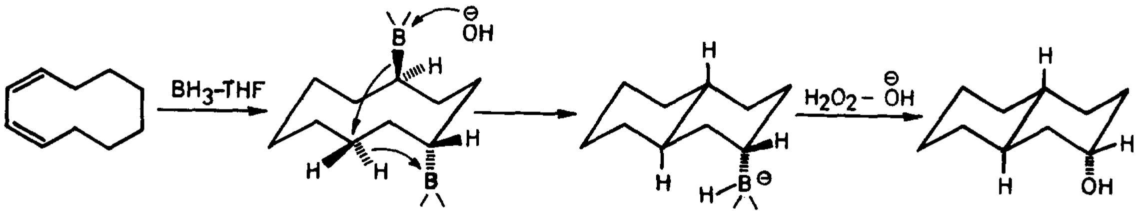
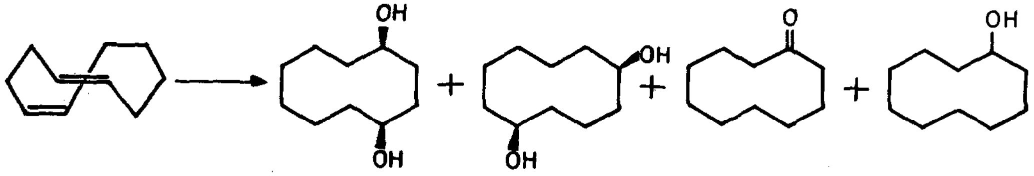
It has recently been shown that *cis,cis*-1,5-cyclooctadiene[1] and *cis,cis*-1,5-cyclononadiene[2] on cyclic hydroboration-oxidation give a mixture of *cis*-1,4- and *cis*-1,5-cyclic diol whereas *cis,cis*-1,6-cyclodecadiene[2] results in the formation of only *cis*-1,5-cyclodecane diol. This difference in behaviour prompted us to examine the cyclic hydroboration of *cis,cis*-1,3-cyclodecadiene[3] and *cis,trans*-1,5-cyclodecadiene. The following communication demonstrates the interesting diversity observed in cyclic hydroboration of isomeric cyclodecadienes.

Hydroboration-oxidation of *cis,cis*-1,3-cyclodecadiene (1) gave *trans,cis*-2-decalol (4)[4] in 42% yield, along with cyclodecanone (8) (6%) and two isomeric cyclodecane diols[5] (27%). There was no change in the product distribution on isomerization-oxidation of the intermediate organoboranes. In our opinion, one of the reasonable pathways for the formation of the major product 4 is *via* *trans*-1,4-diborocyclodecane (2) as shown below:



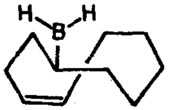
1 2 3 4

Hydroboration-oxidation of *cis,trans*-1,5-cyclodecadiene (5) afforded *cis*-1,4-cyclodecane diol (6),[6] *cis*-1,5-cyclodecane diol (7),[2] cyclodecanone (8) and cyclodecanol (9) in the yields 61, 10, 4 and 4% respectively. However, the isomerization of the intermediate organoboranes followed by oxidation, resulted mainly in a 1:1 mixture of 8 and 9 in 72% yield.



5 6 7 8 9

It has been shown that monohydroboration-protonolysis of cis,trans-1,5-cyclodecadiene (5) gives cis-cyclodecene.[7] This result suggests that the highly reactive trans-double bond adds to B-H bond in preference to the cis-double bond. Since cis-1,4-cyclodecane diol (6) is formed as the major product during hydroboration-oxidation of 5, we tentatively propose that the initial boron attack is probably controlled by the conformation of the diene to give 10 as the major product. The predominant formation of 11 from 10 seems to arise from a kinetically controlled process dictated by the conformation of 10. The isomerization experiment clearly implies the instability of 11. A rationale for this can be offered in terms of isomerization of 11 to 12 which can arise either by several elimination addition steps or in a single step. The vinylborane (12) can act as the hydroborating agent to form 13 and/or 14 which are known to produce 8 as well as 9.[8]



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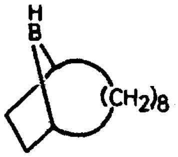

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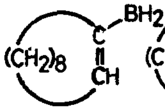

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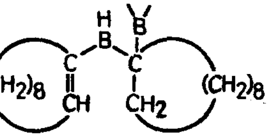

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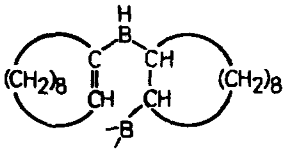

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In conclusion, the results of the present investigation clearly brings forth the configurational and conformational effects in cyclic hydroboration and isomerization studies.

REFERENCES AND FOOTNOTES

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4. W.G. Dauben, R.C. Tweit and C. Mannerskantz, J. Amer. Chem. Soc., 76, 4420 (1954).
5. The isomeric diols (9% A and 18% B) have not been characterised. But the diols were separated by column chromatography on basic alumina. The diol A had m.p. 66-68°; bis-p-nitrobenzoate, m.p. 84-84°. The diol B had m.p. 89-91°; bis-p-nitrobenzoate, m.p. 164-156°.
6. It had m.p. 116°; bis-p-nitrobenzoate, m.p. 145-146°.
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