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HYDROBORATION OF MEDIUM-RING DIENES - A CONVENIENT STEREOSPECIFIC SYNTHESIS OF *CIS*-1,5-CYCLIC DIOLS

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The organoboranes as synthetic intermediates have created immense interest since the discovery of the reaction of diborane with alkenes and related unsaturated compounds[1,2]. Brown and Knight[3] have shown that the reaction of *cis,cis*-1,5-cyclooctadiene with borane in THF can be controlled to provide a convenient synthesis of 9-borabicyclo(3.3.1)nonane which on oxidation yields *cis*-1,5-cyclooctane diol. However, the synthetic utility of this valuable reaction has not yet been investigated. The following communication will indicate the application of such cyclic hydroboration to the synthesis of *cis*-1,5-cyclic diols.

We now report that the hydroboration-isomerization-oxidation of *cis,cis*-1,3-cyclooctadiene, *cis,cis*-1,5-cyclononadiene[4] and *cis,cis*-1,6-cyclodecadiene proceeds preferentially to the *cis*-1,5-cyclic diols. The results are summarized in the TABLE.

TABLE

Diene	Product[e]	m.p.	Yield (%)
cis,cis-1,3-Cyclooctadiene	*cis*-1,5-Cyclooctane diol[b,6]	73-74°	75
cis,cis-1,5-Cyclononadiene	*cis*-1,5-Cyclononane diol[b,c]	70-71°	80
cis,cis-1,6-Cyclodecadiene[a]	*cis*-1,5-Cyclodecane diol[b,d]	135-136°	82

a. We are very grateful to Professor P.D. Gardner for a generous gift of *cis,cis*-1,6-cyclodecadiene.

b. Molecular ion-18 has been observed for all *cis*-1,5-cyclic diols (unpublished work).

c. We thank Professor V. Prelog for suggesting that our diol is a polymorphic modification of his diol A (reported m.p. 82-84°) since the m.p. and mixed m.p. of *bis-p*-nitrobenzoate of our diol and the *bis-p*-nitrobenzoate of diol A are identical (182°)[7].

d. *Bis-p*-nitrobenzoate, m.p. 140°.

e. The purity of each product was checked by careful t.l.c.

The procedure used follows essentially that described by Brown and Knight[3] except for the time of isomerization (~4 hr at 70°). In the case of a nine-membered cyclic diene, we have observed the formation of *cis*-1,5-cyclononane diol starting from either *cis,cis*-1,3- or *cis,cis*-1,4-cyclononadiene[5]. Hydroboration-oxidation of *cis,cis*-1,3-cyclooctadiene gave *cis*-1,3-(23%) and *cis*-1,4-cyclooctane diol[6] (77%), whereas *cis,cis*-1,5-cyclononadiene yielded a 1:4 mixture of *cis*-1,4- and *cis*-1,5-cyclononane diol. The result with *cis,cis*-1,6-cyclodecadiene was essentially the same with or without isomerization.

The identity of all the new products has been established by elemental analyses, i.r., n.m.r., mass spectrometry, preparation of *bis*-*p*-nitrobenzoate and unequivocal synthesis.

Prior to this synthesis of *cis*-1,5-cyclononane diol, the formation of epimeric 1,5-cyclononane diols has been described by Prelog and co-workers[7]. Thus the utilization of the hydroboration-isomerization-oxidation provides a convenient stereospecific synthesis of *cis*-1,5--cyclic diols in nine- and ten-membered rings for the first time.

On the basis of thermodynamic consideration our results show that six-, seven- and eight-membered rings fused to a six-membered ring are the most stable boron bridged bicyclic organoboranes. Furthermore, this demonstrates the preference for six-membered boron heterocyclic rings in isomerization reactions.

Currently work is in progress with other medium-ring dienes.

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