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DIHYDROBORATION OF 1,2-CYCLOTRIDECADIENE

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We have shown earlier that monohydroboration of cyclic allenes with diborane[1] or disiamylborane[2] provides mainly vinyl organoborane intermediate. In fact our results have been further confirmed by Fish[3] using 4,4,6-trimethyl-1,3-dioxa-2-borinane. Now we wish to report our interesting results obtained. with 1,2-cyclotridecadiene (1) on dihydroboration-oxidation.

Dihydroboration was achieved using a standard solution of diborane in THF.[4] There was obtained a white precipitate on allowing the reaction mixture to stir for sufficient time (12-14 hr). The resulting organoboranes were oxidized under different conditions and worked up in the usual manner. The mixture of products was carefully analyzed by TLC and then subjected to column chromatographic separation. Our results are summarised in Table 1.

TABLE 1

Products≠	% Yield		
	DHB-H_2O_2-NaOH	DHB-NaOH-H_2O_2*	DHB-CrO_3
cis-Cyclotridecene (10A) *trans*-Cyclotridecene (10B) Bicyclo(10.1.0)tridecane (4)	5 (10A:10B:4=1:7:2)	7 (10A:10B=17:83)	50 (10A:10B=3:17)
Cyclotridecanone (12)	1.5	-	3
Cyclotridecanol (5)	27	60	-
cis-1,2-Cyclotridecane diol (7A)	14	-	-
trans-1,2-Cyclotridecane diol (7B)	15	-	-
1,3-Cyclotridecane diol (6)	3.5	-	-

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* The mixture of organoboranes was hydrolyzed with sodium hydroxide at 80° for 24 hr before oxidation; ≠ The identity of all the products except 6 was established unambiguously using authentic samples. A mixture of *cis* and *trans*-1,3-cyclotridecane diol (6) obtained in the reaction was compared with the mixture of diols prepared by hydroborating 3-hydroxycyclotridecene.

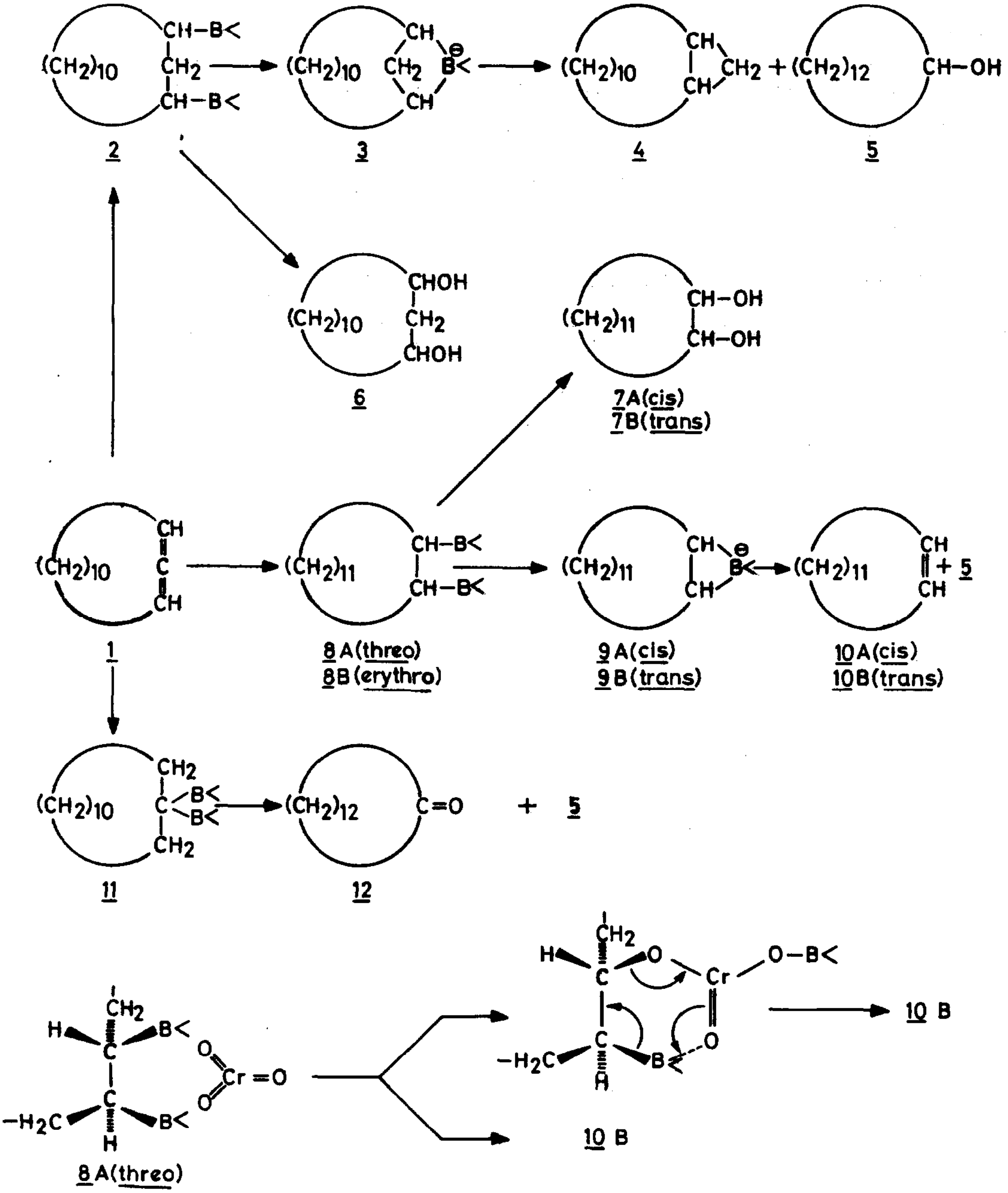
In principle, two successive cis-additions of B-H bond to two orthogonal double bonds of 1 could give rise to 1,3-, vic- and gem-diboro organoboranes (2, 8 and 11) as shown in the Scheme 1. We suggest that the formation of the interesting bicyclo(10.1.0)tridecane (4) is possibly occurring from 2 via the bridged anion (3). Since it has been shown that 1,2-cyclononadiene undergoes monohydroboration to give mainly cis-vinyl organoborane,[3] it is reasonable to assume that the second B-H bond cis-addition should lead predominantly to the formation of vic-diboro organoborane (8A) with threo configuration. However, the formation of erythro-vic-diboro organoborane (8B) from trans-vinyl organoborane intermediate is also possible to some extent. Now the trans-cyclotridecene (10B) as the major product in the mixture of hydrocarbons can be visualized via 9B by direct elimination in accordance with Pasto's mechanism.[5] The exclusive path for the formation of the anion 9B seems to be from 8A with retention in configuration.

There are three possible routes for the genesis of cyclotridecanol (5). The dihydroboration study of diphenyl acetylene suggests that the monoalcohol is exclusively formed by hydrolysis of the vic-diboro organoborane followed by oxidation. The observed increase in the amount of cyclotridecanol (5) formed when the hydrolysis time was enhanced, is in agreement with Pasto's observation,[5] that the vic-diboro organoborane undergoes hydrolysis faster than the monoboro-organoborane. The formation of cyclotridecanone (12) is visualized via 11, whereas 2 and 8 can give rise to isomeric 1,3- and 1,2-cyclotridecane diols (6 and 7) respectively.

Brown and coworkers[4] have shown that organoboranes can be converted to the corresponding ketones by chromic acid oxidation. In view of this, an attempt was made to find the relative amounts of various organoboranes formed in the dihydroboration of 1. To our surprise chromium trioxide-pyridine oxidation of the intermediate organoboranes gave mainly cyclotridecene (10). The exclusive formation of 10B from 8A can be explained via a two-step path or/and one-step path as shown in the Scheme 1.

SCHEME 1

Possible mechanistic pathways for product formation:



Currently studies with other cyclic allenes and the synthetic utility of the new reaction of *vic*-diboro organoboranes with chromium trioxide are in progress.

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