

Hydrolytic cleavage of cyclic allylic organoboranes

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It has been shown that cyclic allylic organoborane intermediates obtained from monohydroboration of some 1,2- and 1,3-cyclic dienes with diborane generated *in situ* undergo slow hydrolysis with oxygen-free water to yield monoolefins.

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It is generally known that organoboranes do not undergo cleavage at carbon-boron bond by water at room temperature (1); however, it has been shown that trisallylborane is unusual in its hydrolysis even at or below room temperature (2). In this connection, we have studied the behavior of certain cyclic allylic organoboranes with oxygen-free water under nitrogen atmos-

phere to establish the generality of this reaction. We undertook the study with cyclopentadiene, 1,3-cyclohexadiene, 1,3-cyclooctadiene, 1,2-cyclononadiene, and 1,2-cyclodecadiene. Our results with these substrates establish that slow hydrolysis of cyclic allylic organoboranes takes place but not as rapidly as does trisallylborane (2).

Results and Discussion

Monohydroboration was carried out by diborane generated *in situ* (3) by the addition of boron trifluoride etherate to the stirred solution of sodium borohydride and diene in dry diglyme under inert atmosphere of nitrogen at 0 to -5° . The resulting mixture of organoboranes was stirred with a known excess of oxygen-free water at 5 to 10° for 2 h only since the increase of hydrolysis time from 2 to 4 h did not affect the yield of the cyclic monoolefin appreciably. A flash distillation of the resulting product under vacuum gave a mixture of organic and water layers. The organic layer was analyzed by vapor-phase chromatography (v.p.c.) for the residual cyclic diene and the cyclic monoolefin. Under these conditions cyclopentadiene, 1,3-cyclohexadiene, 1,3-cyclooctadiene, 1,2-cyclononadiene, and 1,2-cyclodecadiene gave cyclopentene, cyclohexene, *cis*-cyclooctene, *cis*-cyclononene, and *cis*-cyclodecene respectively. The yield of the cyclic monoolefin was estimated based on the amount of the cyclic diene used in the reaction by v.p.c. technique in each case (4). The results are summarized in Table I.

TABLE I
Percentage yield (by weight) of olefin by vapor-phase chromatography

Diene	Olefin	Yield of olefin
Cyclopentadiene	Cyclopentene	5
1,3-Cyclohexadiene	Cyclohexene	21
1,3-Cyclooctadiene	<i>cis</i> -Cyclooctene	35
1,2-Cyclononadiene	<i>cis</i> -Cyclononene	18
1,2-Cyclodecadiene	<i>cis</i> -Cyclodecene	16

Each cyclic monoolefin was separated by v.p.c. and its identity was established thoroughly by comparison of v.p.c. retention times on carbowax-silver nitrate and ucon columns and infrared spectra using an authentic sample.

The formation of cyclic monoolefins from cyclic dienes may be summarized as follows.

The poor yield of cyclopentene from cyclopentadiene is in agreement with the results of Winsten and co-workers (5) who have observed the predominant formation of 3-cyclopenten-1-ol (94%) in the monohydroboration of cyclopentadiene with diborane. It has been reported by Brown and co-workers (6) that the monohydroboration oxidation of 1,3-cyclohexadiene

with diborane gives 34% yield of a mixture of 2-cyclohexen-1-ol (60%) and 3-cyclohexen-1-ol (40%). The lower yield reported may be attributed partly to the competing side reaction of the intermediate allylic organoborane under the hydrolytic experimental conditions. The results with 1,2-cyclononadiene and 1,2-cyclodecadiene further confirm our previous results on monohydroboration oxidation of allenes (7).

We have further confirmed that no other unsaturated organoborane (vinylic or non-allylic) undergoes carbon-boron bond cleavage by water. In support of this we subjected monohydroboration products from 3-hexyne and 1,4-cyclohexadiene to similar study and found no monoolefin formation.

Experimental

All infrared spectra were recorded on a Perkin-Elmer Infrared model 137B with sodium chloride optics. Vapor-phase chromatographic analyses were made with Aerograph model 90P instrument using 6 ft by $\frac{1}{8}$ in. columns. The following liquid phases were employed (percentage by weight on 60/80 mesh chromosorb W): 15% carbowax-silver nitrate and 15% ucon. Cyclic monoolefinic samples were collected by v.p.c. for infrared analysis.

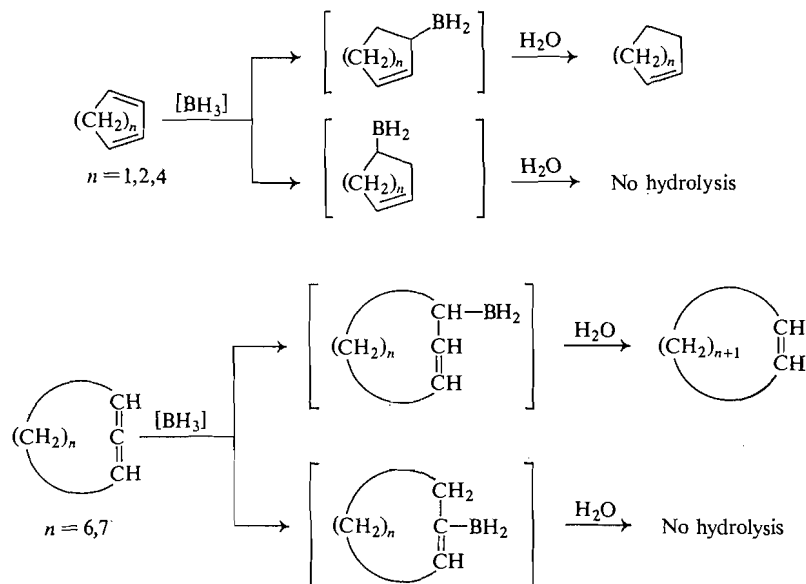
Materials

Diglyme (Ansul Co.) was distilled from lithium aluminium hydride. In order to inhibit peroxidation, 0.01% of sodium borohydride was added. Boron trifluoride ethyl etherate (Eastman) was treated with a small quantity of ethyl ether (to ensure an excess of this component) and distilled under reduced pressure from a few pieces of calcium hydride. Sodium borohydride from Metal Hydrides Inc. (98%) was used without purification.

1,3-Cyclohexadiene (Aldrich), 1,3-cyclooctadiene (Columbia), 1,4-cyclohexadiene (Aldrich), and 3-hexyne (K & K) were used without any purification. Freshly distilled cyclopentadiene from its dimer (Aldrich) was used. 1,2-Cyclononadiene and 1,2-cyclodecadiene were prepared from 9,9-dibromobicyclo[6.1.0]nonane and 10,10-dibromobicyclo[7.1.0]decane according to the procedure of Moore and Ward (8). Their properties corresponded well with those reported.

General Procedure for Monohydroboration and Hydrolysis

In a 250 ml three-necked flask fitted with a condenser, an equilibrating dropping funnel, a thermometer, and an inlet and an outlet (top of the condenser) for nitrogen, was placed pulverized sodium borohydride (2.09 g, 0.055 mole, 10% excess) in dry diglyme (50 ml) and an appropriate cyclic diene or alkyne (0.20 mole). Boron trifluoride etherate (10.28 g, 0.072 mole 10% excess) in diglyme (20 ml) was added dropwise with stirring over a period of 1 h under a slight static pressure of nitrogen while maintaining the temperature of the reaction mixture between 0 to -5° . The stirring was continued for an additional hour at room temperature in order to complete the hydro-



boration. Excess of sodium borohydride was destroyed carefully by dropwise addition of oxygen-free water at 5 to 10° and further 10 ml of oxygen-free water was added and stirred for 2 h.

The resulting mixture was then flash distilled under vacuum to obtain a mixture of water and organic layers. The organic layer was separated, dried, and weighed.

Quantitative measurements of the cyclic monoolefin formed and the unreacted cyclic diene in each case were determined using vapor-phase chromatographic absolute method (4), which involves the direct comparison of a ratio of the areas of the unknown in a mixture with calibration curve obtained from synthetic mixtures containing varying amounts of the components. The yield (percentage by weight) of the cyclic monoolefin was calculated based on the amount of cyclic diene used in the reaction. The identity of each cyclic monoolefin was established by comparison of chromatographic retention times on carbowax-silver nitrate and ucon columns using authentic samples. This was further supported by collecting each cyclic monoolefin by v.p.c. and comparing its infrared spectrum with that of an authentic sample.

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