Hydroboration of cyclic allenes with disiamylborane

D. S. SETHI, G. C. JOSHI, AND D. DEVAPRABHAKARA
Department of Chemistry, Indian Institute of Technology, Kanpur, India

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It has been shown that 1,2-cyclononadiene and 1,2-cyclotridecadiene undergo 78 and 100% hydroboration respectively, with disiamylborane. 1,2-Cyclononadiene gave products which represented 83% attack of boron at the central carbon atom and 17% attack at the terminal carbon atom. 1,2-Cyclotridecadiene gave 62% central carbon attack and 38% terminal carbon attack. The reactivity and selectivity may be explained mainly in terms of steric effects on a four-centered transition state.

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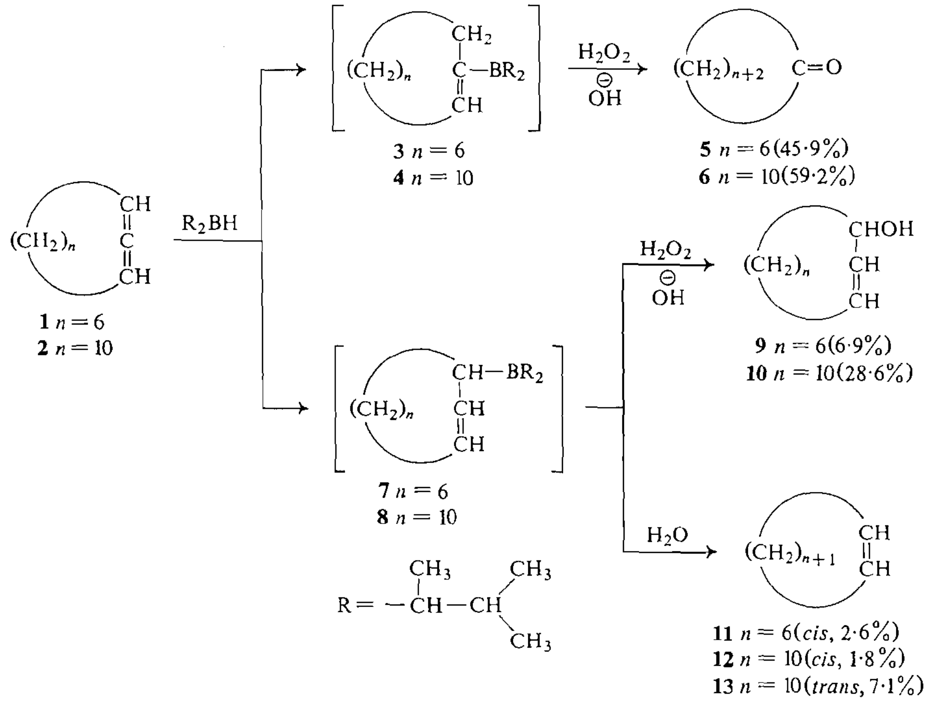
It has been shown that the monohydroboration of 1,2-cyclononadiene (**1**) with diborane results in the attack of diborane, primarily at the central carbon atom of the allenic linkage (1). The object of the present study was to examine the possibility of stereoselective addition of boron to the allenic linkage with disiamylborane (2), which might have revealed some useful and interesting synthetic routes. In particular we were interested to study the effect of the ring size on the reactivity and selectivity in the direction of addition. Since the monohydroboration of allenes might proceed through monoalkyl-, dialkyl-, and trialkylborane stages, the percentage of electrophilic attacks of diborane on the central and terminal carbon atoms of the allenic linkage, will be governed by the cumulative steric effect due to ring size of the allene and the intermediate organoboranes. The percentage electrophilic attacks of disiamylborane are controlled only by the steric effect of ring size of the allene. Accordingly, we undertook the hydroboration of 1,2-cyclononadiene (**1**) and 1,2-cyclotridecadiene (**2**) with disiamylborane which is known to provide greater steric control over diborane (2).

Results and Discussion

Disiamylborane was prepared by hydroboration of 2-methyl-2-butene at −5 to −10 °C under a static pressure of nitrogen (3). A solution of the appropriate allene in diglyme was added within 3 min to the above solution. This reaction mixture was left for approximately 3 h to attain room temperature. After stirring for 6 h at room temperature, the mixture was then hydrolyzed until hydrogen was no longer evolved. The product was oxidized with alkaline hydrogen peroxide in the usual manner. The percentage conversion of the allene to products was determined by gas chromatography (4). The results are summarized in Scheme 1.

The percentage electrophilic attack of boron on the central and terminal carbon atoms of the allenic linkage, as calculated from the percentage yield of the products and also the percentage conversion of the allenes to products, is shown in Table I.

These results suggest that the observed difference in the reactivity and selectivity, in the direction of addition of disiamylborane with 1,2-cyclononadiene (**1**) and 1,2-cyclotridecadiene (**2**), could be dictated solely by difference in steric requirements of the allenes in the Brown's well known postulated transition state for hydroboration (2). The electronic effect seems to be of secondary importance here, since it has been shown that monohydroboration of 1,2-cyclononadiene (**1**) with diborane, followed by oxidation, gives mainly cyclononanone (**5**) (1), while dihydroboration of propadiene yields predominantly 1,3-propanediol (5). The formation of a small quantity of cyclic monoolefins (**11**, **12**) is in complete agreement with our previous investigation (6), in which we have shown that cyclic allylic organoborane intermediates undergo slow hydrolytic cleavage at the boron–carbon bond under the experimental conditions employed. The formation of only *cis*-cyclononene (**11**) from 1,2-cyclononadiene (**1**), and a mixture of *cis*- and *trans*-cyclotridecene (**12** and **13**) containing a major quantity of *trans* isomer (**13**) from 1,2-cyclotridecadiene (**2**), may be attributed to the thermodynamic stabilities of these cyclic monoolefins (**11** and **13**) in 9- and 13-membered rings (7).



SCHEME 1

TABLE I

Percentage electrophilic attack of boron on central and terminal carbon atoms of the allenic linkage

Allene	% electrophilic attack of boron: Central C atom	% electrophilic attack of boron: Terminal C atom	% conversion
1,2-Cyclononadiene (**1**)	83	17	78
1,2-Cyclotridecadiene (**2**)	62	38	100

Experimental

Boiling points are uncorrected. Melting points were performed in open capillaries and are uncorrected. All infrared (i.r.) spectra were recorded on a Perkin-Elmer Infracord model 137B, as films between salt plates. Gas–liquid chromatographic (g.l.c.) analyses were made with an Aerograph model 90P instrument using 6 ft by $\frac{1}{4}$ in. columns. Nuclear magnetic resonance (n.m.r.) spectra were taken on a Varian HR-100 instrument with tetramethylsilane as the internal standard. The following liquid phases were employed (percentages by weight on 60/80 mesh chromosorb W): 15% carbowax 20M–silver nitrate; 15% ucon and 15% carbowax 20M. Samples were collected by g.l.c. for i.r. analysis. Microanalyses were carried out by Mr. A. H. Siddiqui of the Department of Chemistry, Indian Institute of Technology, Kanpur, India.

Materials

Diglyme (Ansul Co.) was first kept over calcium hydride and then distilled from lithium aluminium hydride under reduced pressure. 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 with a few pieces of calcium hydride. Sodium borohydride from Metal Hydrides Inc. (98%) was used without purification. 2-Methyl-2-butene (Aldrich Co.) was used for the preparation of disiamylborane.

1,2-Cyclononadiene and 1,2-cyclotridecadiene were prepared from 9,9-dibromobicyclo[6·1·0]nonane and 13,13-dibromobicyclo[10·1·0]tridecane respectively according to the procedure of Moore and Ward (8). Their properties corresponded well with those reported (8, 9).

Hydroboration of 1,2-Cyclononadiene

Pulverized sodium borohydride (3.2 g, 0.08 mole in 50 ml dry diglyme) and 2-methyl-2-butene (15.4 g, 0.22 mole) were placed in a 250 ml three-necked flask fitted with a condenser, an equilibrating dropping funnel, a thermometer, and an inlet and an outlet for nitrogen. Hydroboration was accomplished by adding boron trifluoride etherate (15.8 g, 0.11 mole) in diglyme (20 ml). The mixture was well-stirred and kept at 0 to −5 °C over a period of 0.5 h. The apparatus was flushed with nitrogen and static nitrogen pressure was maintained throughout the reaction. After allowing the mixture to stand at 0 °C for 1 h, 1,2-cyclononadiene (12.2 g, 0.10 mole) was added in 3 min. The mixture was left for approximately 3 h to attain room temperature. The mixture was then oxidized by adding 3 *N* sodium hydroxide solution, followed by 30% hydrogen peroxide. The products formed were extracted with ether. After drying over anhydrous magnesium sulfate, the samples were analyzed by g.l.c. The percentage conversion of 1,2-cyclononadiene to products as determined by g.l.c. was 78%.

Fractionation of the reaction mixture afforded *cis*-cyclononene (0.25 g, 2.6%), b.p. 60–62 °C at 16 mm, n_D^{25} 1.4748 (lit. (10), b.p. 85–86 °C at 45 mm, n_D^{27} 1.4745); cyclononanone (5 g, 45.9%), b.p. 90–91 °C at 10 mm, n_D^{25} 1.4720 (lit. (11), b.p. 94–95 °C at 13 mm, n_D^{20} 1.4729); and 3-hydroxycyclononene (0.75 g, 6.9%), b.p. 94–96 °C at 3 mm, n_D^{25} 1.4980 (lit. (12), b.p. 100 °C at 3.5 mm, n_D^{32} 1.4965). The identity of the individual products was established by comparing the g.l.c. retention times and i.r. spectra with the authentic samples.

The semicarbazone derivative of **5** had a m.p. and mixture m.p. of 184–185 °C. The m.p. and mixture m.p. of the *p*-nitrobenzoate derivative of **9** was found to be 112–114 °C.

Anal. Calcd. for C_9H_{16}: C, 87.09; H, 12.90. Found: C, 86.94; H, 12.78.

Anal. Calcd. for $C_{10}H_{19}N_3O$: C, 60.91; H, 9.64; N, 21.32. Found: C, 60.65; H, 9.71; N, 21.44.

Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.43; H, 6.54; N, 4.84. Found: C, 66.61; H, 6.44; N, 4.94.

Hydroboration of 1,2-Cyclotridecadiene

The procedure described for 1,2-cyclononadiene was followed without any change. From 1,2-cyclotridecadiene (8.9 g, 0.05 mole), 2-methyl-2-butene (7.7 g, 0.11 mole), sodium borohydride (1.6 g, 0.04 mole), and boron trifluoride etherate (7.9 g, 0.055 mole), there was obtained a mixture of *cis*- and *trans*-cyclotridecene (0.8 g, 8.9%), b.p. 106–114 °C at 3 mm; cyclotridecanone (5.8 g, 59.2%), b.p. 116–119 °C at 3 mm, n_D^{25} 1.4828 (lit. (13), b.p. 78–83 °C at 0.4 mm, n_D^{20} 1.4822); and 3-hydroxycyclotridecene (2.8 g, 28.6%), b.p. 124–130 °C at 3 mm. The percentage conversion of 1,2-cyclotridecadiene to products as established by g.l.c. was 100%. The *cis*-cyclotridecene (20%) and *trans*-cyclotridecene (80%) were separated by g.l.c. and were identified by a comparison of their chromatographic retention times and i.r. spectra with those of authentic samples. The ketone was identified by g.l.c. and i.r. using an authentic sample for comparison, and also through its 2,4-dinitrophenylhydrazone derivative m.p. and mixture m.p. 114–115 °C (lit. (14), m.p. 113.5–114.5 °C). The g.l.c. analysis of the alcohol indicated 8% contamination of the ketone. Its 3,5-dinitrobenzoate derivative melted at 102–103 °C. The i.r. spectrum of the alcohol showed O—H band at 2.94 μ and C=C band at 6.02 μ, and the main signals in n.m.r. spectra were at $J = 4.62$ (multiplet, 2) and $J = 5.52$ (multiplet, 1).

Anal. Calcd. for $C_{13}H_{24}$: C, 86.67; H, 13.33. Found: C, 86.72; H, 13.14.

Anal. Calcd. for $C_{19}H_{28}N_4O_4$: C, 60.64; H, 7.44; N, 14.89. Found: C, 60.80; H, 7.60; N, 14.91.

Anal. Calcd. for $C_{20}H_{26}N_2O_6$: C, 61.54; H, 6.67; N, 7.18. Found: C, 61.46; H, 6.71; N, 7.03.

Acknowledgment

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