Hydroboration of acyclic allenes with disiamylborane

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The present investigation demonstrates the hydroboration of 1,2-nonadiene, phenylpropadiene, 3-phenyl-1,2-butadiene, 4,5-nonadiene, and tetramethylallene with disiamylborane. All the allenes except tetramethylallene underwent 100% conversion. Examination of the products indicated preferential electrophilic attack of boron on the least substituted terminal carbon atom in the case of 1,2-nonadiene, phenylpropadiene, 3-phenyl-1,2-butadiene, and on the central carbon atom in 4,5-nonadiene. In tetramethylallene boron, attack was exclusively on the central carbon atom. These results have been explained in terms of steric effects on a four-centered transition state.

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In our preceding publication (1), the effect of ring size on hydroboration of cyclic allenes with disiamylborane has been demonstrated. In continuation of this study we undertook the hydroboration of representative acyclic allenes with disiamylborane, to achieve monohydroboration,
TABLE I
Results of the hydroboration-oxidation of the representative acyclic allenes

<table>
<thead>
<tr>
<th>Allene</th>
<th>Ketone Compound</th>
<th>Ketone %</th>
<th>Unsaturated alcohol Compound</th>
<th>Alcohol %</th>
<th>Olefins Compound</th>
<th>Olefins %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Nonadiene</td>
<td>2-Nonanone</td>
<td>16.9</td>
<td>2-Nonen-1-ol</td>
<td>38.6</td>
<td>1-Nonene</td>
<td>5.5</td>
</tr>
<tr>
<td>Phenylpropadiene</td>
<td>1-Phenyl-2-propanone</td>
<td>16.8</td>
<td></td>
<td></td>
<td>2-Nonene, cis and trans</td>
<td>15.8</td>
</tr>
<tr>
<td>3-Phenyl-1,2-butadiene</td>
<td>3-Phenyl-2-butanone</td>
<td>10.6</td>
<td></td>
<td></td>
<td>Allylbenzene</td>
<td>22.9</td>
</tr>
<tr>
<td>4,5-Nonadiene</td>
<td>5-Nonanone</td>
<td>60.5</td>
<td>5-Nonen-4-ol</td>
<td>20.4</td>
<td>1-Phenyl-1-propene, cis and trans</td>
<td>44.1</td>
</tr>
<tr>
<td>Tetramethylallene</td>
<td>Diisopropylketone</td>
<td>73.1</td>
<td></td>
<td></td>
<td>3-Phenyl-1-butene</td>
<td>19.1</td>
</tr>
</tbody>
</table>

The identity of each product was established by comparison of gas liquid chromatographic (g.l.c.) retention times (using several columns) and infrared spectra (i.r.) with those of an authentic sample. Wherever necessary, elemental analysis and preparation of known derivatives were also used in the characterization of products.

The ratio of electrophilic attack of boron on the terminal and central carbon atoms of the allenic linkage as calculated from the molar ratio of the products for each allene is shown in Table II.

A general scheme for the hydroboration of acyclic allenes may be represented as follows and the results are summarized in Table I.
direction of addition of disiamylborane to these acyclic allenes could solely be dictated by the difference in steric requirements of the allenes in the Brown’s well-known postulated transition state for hydroboration (5). The electronic effect seems to be of minor importance here. Our result with tetramethylallene suggests that complete selectivity in the hydroboration of a tetrasubstituted allene is possible using disiamylborane.

The formation of olefins is in complete agreement with our previous observation (6), where we have shown that allylic organoboranes undergo slow hydrolytic cleavage at the boron–carbon bond. The ready hydrolysis of allylic organoboranes from phenylpropadiene and 3-phenyl-1,2-butadiene may be interpreted through the formation of an extensive stabilized carbanion, which in turn picks up a proton to give a mixture of possible olefins. The most thermodynamically stable isomer was found to be the major product in each olefinic mixture. In particular it is interesting to know that the predominant formation of cis-2-phenyl-2-butene over its trans isomer is in complete agreement with Cram’s observation (7).

### Experimental

Boiling points are uncorrected. Melting points were performed in open capillaries and are uncorrected. All infrared spectra were recorded on a Perkin–Elmer model 521 spectrophotometer from compounds as films between salt plates or in cells. Gas chromatographic analyses were made with Aerograph model 900 instrument using 6 ft by ⅛ in. columns. The following liquid phases were employed (percentage by weight on dry ethyl silicate ethyl (to ensure an excess of this component) and distilled under reduced pressure from calcium hydride. Sodium borohydride from Metal Hydrides Inc. (98%) was used without purification. 2-Methyl-2-butenic (Aldrich Co.) was used for the preparation of disiamylborane.

Tetramethylallene (K & K Co.) was used for hydroboration. It showed no detectable impurities by g.l.c. 1,2-Nonadiene, phenylpropadiene, 3-phenyl-1,2-butadiene, and 4,5-nonadiene were prepared by two-step sequence starting from a suitable olefin in each case according to the procedure of Moore and Ward (8). Their properties corresponded well with those reported (9–11).

### Monohydroboration of 1,2-Nonadiene

Pulverized sodium borohydride (3.2 g, 0.083 mole) in dry diglyme (50 ml), and 2-methyl-2-butenic (15.4 g, 0.22 mole) were placed in 250 ml three-necked flask equipped with a condenser, an equilibrating dropping funnel, a low temperature thermometer, and an inlet and outlet for dry nitrogen gas. Hydroboration was achieved by adding boron trifluoride ethereal (15.8 g, 0.111 mole) in diglyme (20 ml) to the well-stirred mixture kept at 0 to −5°C over a period of 0.5 h. Throughout the reaction a static pressure of nitrogen gas was maintained. After leaving the reaction mixture for 1 h at 0°C, 1,2-nonadiene (12.4 g, 0.10 mole) was added in 3 min. The reaction mixture was allowed to attain the room temperature (approx. 3 h). The excess of the hydride was destroyed by careful addition of water until hydrogen was no longer evolved. The oxidation of the intermediate organoboranes was accomplished in the usual manner by adding 3 N sodium hydroxide (pH 9–10) followed by 30% hydrogen peroxide. The products were extracted with ether, dried over anhydrous magnesium sulfate and ether distilled over. At this stage the percentage conversion of allene to products was determined by g.l.c.

Fractionation of the reaction mixture afforded 2.68 g (21.3% yield) of olefinic product with a b.p. 40–42°C at 15 mm, 2.4 g (16.9% yield) of 2-nonanone with a b.p. 87–90°C at 15 mm, 6 g 1,4182 (lit. (12), b.p. 195°C at 760 mm, nD20 1.421) and 5.48 g (38.6% yield) of 2-nonen-1-ol with a b.p. 107–109°C at 15 mm, nD20 1.4461 (lit. (13), b.p. 98–99°C at 10 mm, nD20 1.4480). Gas chromatographic analysis of the olefinic product on a carbowax–silver nitrate column indicated the presence of 1-nonene (26%), cis-2-nonene (4%), and trans-2-nonene (70%). The identity of the individual product(s) was established by comparison of g.l.c. retention times and i.r. spectra with those of the authentic samples. The 2,4-dinitrophenylhydrazones derivative with a m.p. 58–59°C, did not depress the m.p. of authentic 2,4-dinitrophenylhydrazone (lit. (12), m.p. 58–59°C).


### Monohydroboration of Phenylpropadiene

The procedure described for monohydroboration of 1,2-nonadiene was followed without any change. From phenylpropadiene (11.6 g, 0.1 mole), 2-methyl-2-butenic

<table>
<thead>
<tr>
<th>Allene</th>
<th>Molar ratio (terminal C/central C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Nonadiene</td>
<td>3.54</td>
</tr>
<tr>
<td>Phenylpropadiene</td>
<td>3.99</td>
</tr>
<tr>
<td>3-Phenyl-1,2-butadiene</td>
<td>7.47</td>
</tr>
<tr>
<td>4,5-Nonadiene</td>
<td>0.48</td>
</tr>
<tr>
<td>Tetramethylallene</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**TABLE II**

Molar ratio of products resulting from the electrophilic attack of boron on terminal and central carbon atoms of the allenic linkage.
(15.4 g, 0.22 mole), sodium borohydride (3.2 g, 0.083 mole), and boron trifluoride etherate (15.88 g, 0.11 mole), we obtained 2.7 g (22.9 % yield) of allylbenzene with a b.p. 65-66° at 40 mm, nD15.038 (lit. (14), b.p. 72.5-73.5° at 45 mm, nD1.5071), 5.2 g (44.1 % yield) of 1-phenyl-1-propanes (cis and trans) with a b.p. 58-60° at 10 mm (lit. (15), b.p. 53° at 8 mm), and 2.25 g (16.8 % yield) of 1-phenyl-2-propanone with a b.p. 96-97° at 10 mm, nD1.5126 (lit. (16), b.p. 122-125° at 50 mm, nD1.5136). Gas chromatographic analysis of the olefinic mixture showed 6 % of cis isomer and 94 % of trans isomer. The identity of each product was established on the basis of the comparison of g.l.c. retention times and i.r. spectra with those of authentic samples. The 2,4-dinitrophenylhydrazone of the ketone had m.p. and mixture m.p. 152-153° (lit. (16), 152-153°).


Anal. Calcd. for C13H14N2O4: C, 57.32; H, 4.46; N, 17.84. Found: C, 57.21; H, 4.42; N, 17.68.

**Monohydroboration of 3-Phenyl-1,2-butanediene**

Following the procedure described for 1,2-nona diene, from 3-phenyl 1,2-butanediene (9.75 g, 0.075 mole), 2-methyl-2-butene (11.5 g, 0.165 mole), sodium borohydride (2.4 g, 0.062 mole), and boron trifluoride etherate (1.18 g, 0.083 mole), there was obtained 7.86 g (79.4 % yield) of olefinic mixture containing 3-phenyl-1-butenes (24 %), cis-2-phenyl-2-butene (62 %), and trans-2-phenyl-2-butene (14 %) with a b.p. 65-75° at 20 mm and 1.18 g (10.6 % yield) of 3-phenyl-2-butanone with a b.p. 103° at 20 mm, nD1.5060 (lit. (17), b.p. 107-108° at 22 mm, nD1.5074). The products were identified by comparison of their g.l.c. retention times and i.r. spectra with those of authentic samples. The semicarbazone derivative of the ketone had m.p. and mixture m.p. 169-170° (lit. (17), m.p. 173°).


Anal. Calcd. for C11H14N2O: C, 64.39; H, 7.32; N, 20.49. Found: C, 64.34; H, 7.21; N, 20.23.

**Monohydroboration of 4,5-Nona diene**

Following the procedure described previously for hydroboronation-oxidation, 4,5-nona diene (6.2 g, 0.05 mole), 2-methyl-2-butene (7.7 g, 0.11 mole), sodium borohydride (1.6 g, 0.041 mole), and boron trifluoride etherate (7.3 g, 0.055 mole) afforded 0.55 g (8.7 % yield) of 4- nonene with a b.p. 50-51° at 15 mm, 4.3 g (60.5 % yield) of 5-nonenone with a b.p. 76-78° at 15 mm, nD11.4186 (lit. (18), b.p. 186-187° at 760 mm, nD1.4210), and 1.45 g (20.4 % yield) of 5-nonen-4-ol with a b.p. 85-86° at 15 mm, nD11.4398 (lit. (19), b.p. 96-100° at 35 mm, nD11.4405). The g.l.c. analysis of 4-nonenone showed 97 % trans isomer and only 3 % cis isomer. Only trans isomer was separated by g.l.c. and identified by comparison of i.r. spectra with that of an authentic sample. The cis isomer was identified only by comparison of g.l.c. retention times with those of an authentic sample. On the basis of i.r. and g.l.c. analysis data of the authentic samples, the ketone and the alcohol were shown to be 5-nonenone and 5- nonen-4-ol respectively. The semicarbazone derivative of the ketone had m.p. and mixture m.p. 89-90° (lit. (18), m.p. 89-90°).


Anal. Calcd. for C10H12N2O: C, 60.3; H, 10.55; N, 21.10. Found: C, 60.21; H, 10.41; N, 20.93.

**Monohydroboration of Tetramethylallene**

Following the procedure described previously for 1,2-nona diene, from tetramethylallene (9.6 g, 0.1 mole), 2-methyl-2-butene (15.4 g, 0.22 mole), sodium borohydride (3.2 g, 0.083 mole), and boron trifluoride etherate (15.8 g, 0.111 mole), there was obtained only 2.5 g (73.1 % yield based on consumed starting material) of diisopropyl ketone with a b.p. 122-124° at 742 mm, nD11.390 (lit. (20), b.p. 121-126° at 760 mm, nD11.4001). The percentage conversion of tetramethylallene to the products as established by g.l.c. was 30 %. The identity of the ketone was established by comparison of g.l.c. retention times and i.r. spectra with those of an authentic sample. The m.p. and mixture m.p. of the 2,4-dinitrophenylhydrazone of the ketone was observed to be 88-89° (lit. (20), m.p. 87-88°).

Anal. Calcd. for C13H18N2O4: C, 53.06; H, 6.12; N, 19.04. Found: C, 52.84; H, 6.10; N, 18.87.

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