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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,

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Allene	% yield					
	Ketone		Unsaturated alcohol		Olefins	
	Compound	%	Compound	%	Compound	%
1,2-Nonadiene	2-Nonanone	16.9	2-Nonen-1-ol	38.6	1-Nonene 2-Nonene, <i>cis</i> and <i>trans</i>	5.5 15.8
Phenylpropadiene	1-Phenyl-2- propanone	16.8			Allylbenzene 1-Phenyl-1-propene, <i>cis</i> and <i>trans</i>	22.9 44.1
3-Phenyl-1,2-butadiene	3-Phenyl-2- butanone	10.6			3-Phenyl-1-butene 2-Phenyl-2-butene, <i>cis</i> and <i>trans</i>	19.1 60.3
4,5-Nonadiene	5-Nonanone	60.5	5-Nonen-4-ol	20.4	4-Nonene, cis and trans	8.7
Tetramethylallene	Diisopropyl ketone	73.1				

### TABLE I

Results of the hydroboration-oxidation of the representative acyclic allenes

to examine the relative rates of reaction, and to study the selectivity in the direction of addition.

It has been shown by Brown and Zweifel (2) that the hydroboration of 1-hexene and styrene with disiamylborane followed by alkaline hydrogen peroxide oxidation provides 98-99% primary alcohols. From this observation, the authors have concluded not only the steric equivalence of phenyl and *n*-alkyl groups but also the absence of electrical effect by the phenyl substituent. In view of this, 1,2-nonadiene, phenylpropadiene, 3-phenyl-1,2-butadiene, 4,5-nonadiene, and tetramethylallene were subjected to hydroboration–oxidation under identical conditions, and the nature of the product(s) was explored.

# **Results and Discussion**

Disiamylborane was prepared by the hydroboration of 2-methyl-2-butene under a static pressure of nitrogen (3). A solution of appropriate allene in diglyme was added to the above solution within 3-4 min. The mixture was allowed to attain room temperature (approx. 3 h). After stirring for a further 2 h at room temperature, the mixture was hydrolyzed by careful addition of water till hydrogen was no longer evolved. The resulting organoboranes were oxidized with alkaline hydrogen peroxide in the usual manner. The conversion of the allene to product(s) as determined by gas chromatography (4) was found to be 100% except in the case of tetramethylallene. The latter underwent conversion only to the extent of 30%.

A general scheme for the hydroboration of

acyclic allenes may be represented as follows and the results are summarized in Table I.



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.

The electrophilic attack of boron on the central vs. terminal carbon atom of the allenic linkage in the case of 1,2-nonadiene and phenylpropadiene suggests that the steric requirement of the phenyl group is almost the same as that of *n*-alkyl group, even in acyclic allenes when disiamylborane is used as the hydroborating reagent. The observed difference in the reactivity and selectivity in the

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# TABLE II

Molar ratio of products resulting from the electrophilic attack of boron on terminal and central carbon atoms of the allenic linkage

Allene	Molar ratio (terminal C/central C)
1,2-Nonadiene	3.54
Phenylpropadiene	3.99
3-Phenyl-1,2-butadiene	7.47
4,5-Nonadiene	0.48
Tetramethylallene	0.00

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 90P instrument using 6 ft by  $\frac{1}{4}$  in. columns. The following liquid phases were employed (percentage by weight on 60/80 mesh chromosorb W): 15% silicone rubber, 15% carbowax 20M, 15% ucon, and 15% carbowax 20M – silver nitrate. Samples were collected by g.l.c. for i.r. spectra. 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 kept over calcium hydride for 24 h, decanted, and distilled from slightly excess of lithium

aluminium hydride under reduced pressure. Boron trifluoride ethyl etherate (Eastman) was treated with a small quantity of dry ethyl ether (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-butene (Aldrich Co.) was used for the preparation of disjamylborane.

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-butene (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 etherate (15.8 g, 0.111 mole) in diglyme (20 ml) to the well stirred mixture kept at 0 to  $-5^{\circ}$  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°, 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° at 15 mm, 2.4 g (16.9 % yield) of 2-nonanone with a b.p. 87–90° at 15 mm,  $n_{\rm D}^{30}$  1.4182 (lit. (12), b.p. 195° at 760 mm,  $n_{\rm D}^{20}$  1.4211) and 5.48 g (38.6 % yield) of 2-nonen-1-ol with a b.p. 107–109° at 15 mm,  $n_{\rm D}^{30}$  1.4461 (lit. (13), b.p. 98–99° at 10 mm,  $n_{\rm D}^{19}$  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-dinitrophenylhydrazone derivative with a m.p. 58–59°, did not depress the m.p. of authentic 2-nonanone 2,4-dinitrophenylhydrazone (lit. (12), m.p. 58–59°).

Anal. Calcd. for C<sub>9</sub>H<sub>18</sub>: C, 85.71; H. 14.29. Found: C, 85.64; H. 14.21.

Anal. Calcd. for C<sub>15</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>: C, 55.90; H, 6.83; N, 17.39. Found: C, 55.76; H, 6.58; N, 17.21.

### 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-butene

(15.4 g, 0.22 mole), sodium borohydride (3.2 g, 0.083 mole), and boron trifluoride etherate (15.88 g, 0.111 mole), we obtained 2.7 g (22.9% yield) of allylbenzene with a b.p. 65–66° at 40 mm,  $n_{\rm p}^{32}$  1.5038 (lit. (14), b.p. 72.5–73.5° at 45 mm,  $n_{\rm D}^{25}$  1.5071), 5.2 g, (44.1% yield) of 1-phenyl-1-propenes (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,  $n_D^{32}$  1.5126 (lit. (16), b.p. 122–125° at 50 mm,  $n_D^{28}$ 1.5136). 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 C<sub>9</sub>H<sub>10</sub>: C, 91.53; H, 8.47. Found: C, 91.34: H, 8.38.

Anal. Calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>: 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-butadiene

Following the procedure described for 1,2-nonadiene, from 3-phenyl 1,2-butadiene (9.75 g, 0.075 mole), 2methyl-2-butene (11.5 g, 0.165 mole), sodium borohydride (2.4 g, 0.062 mole), and boron trifluoride etherate (11.8 g, 0.083 mole), there was obtained 7.86 g (79.4% yield) of olefinic mixture containing 3-phenyl-1-butene (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,  $n_{\rm D}^{29}$  1.5060 (lit. (17), b.p. 107–108° at 22 mm,  $n_{\rm D}^{25}$ 1.5074). 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 C10H12: C, 90.91; H, 9.09. Found: C, 90.82; H, 9.21.

Anal. Calcd. for C<sub>11</sub>H<sub>15</sub>N<sub>3</sub>O: C, 64.39; H, 7.32; N, 20.49. Found: C, 64.34; H, 7.21; N, 20.23.

# Monohydroboration of 4,5-Nonadiene

Following the procedure described previously for hydroboration-oxidation, 4,5-nonadiene (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 (7.9 g, 0.055 mole) afforded 0.55 g (8.7% yield) of 4nonene with a b.p.  $50-51^{\circ}$  at 15 mm, 4.3 g (60.5 % yield) of 5-nonanone with a b.p.  $76-78^{\circ}$  at 15 mm,  $n_{D}^{30}$  1.4186 (lit. (18), b.p. 186–187° at 760 mm,  $n_D^{15}$  1.4210), and 1.45 g (20.4% yield) of 5-nonen-4-ol with a b.p.  $85-86^{\circ}$  at 15 mm,  $n_D^{30}$  1.4398 (lit. (19), b.p. 96–100° at 35 mm,  $n_D^{20}$ 1.4405). The g.l.c. analysis of 4-nonene 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-nonanone and 5nonen-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 C<sub>9</sub>H<sub>18</sub>: C, 85.71; H, 14.29. Found: C, 85.61; H, 14.36.

Anal. Calcd. for C<sub>10</sub>H<sub>21</sub>N<sub>3</sub>O: 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 1,2nonadiene, from tetramethylallene (9.6 g, 0.1 mole), 2methyl-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.  $122-124^{\circ}$  at 742 mm,  $n_{\rm D}^{31}$  1.3950 (lit. (20), b.p.  $121-126^{\circ}$  at 760 mm,  $n_{\rm D}^{20}$  1.4001). 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 C<sub>13</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>: C, 53.06; H, 6.12; N, 19.04. Found: C, 52.84; H, 6.10; N, 18.87.

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