activity and stereocontrol in the intramolecular Diels–Alder reaction are currently underway and will be the subject of forthcoming reports from these laboratories.

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**Registry No. 2**, 81095-98-9; **3**, 32775-95-4; **4**, 15484-46-5; **5**, 32775-94-3; **6**, 30982-08-2; **7**, 81095-99-0; **8**, 81096-00-6; **9**, 81096-01-7; **10a**, 81096-02-8; **10b**, 81096-03-9; **12**, 81096-04-0; **13**, 81096-05-1; **14**, 81096-06-2; **15**, 81096-07-3; **16**, 81096-08-4; **17**, 81096-09-5; **18**, 81096-10-8; **19**, 81096-11-9; **20**, 81096-12-0; **21**, 81120-64-1; **22**, 81096-13-1; **23**, 81096-14-2; **24**, 81096-15-3; **25**, 81096-16-4; ii, 81096-17-5; ethyl (*E*)-4-bromocrotonate, 19041-17-9; sorbic acid, 110-44-1; methyl 2-(bromomethyl)acrylate, 4224-69-5; 3,5-hexadien-1-ol, 5747-07-9; bromoacetaldehyde diethyl acetal, 2032-35-1; (2,4-pentadienyl)triphenyl tin, 81096-18-6; 4-bromo-4-pentenal, 36884-29-4.

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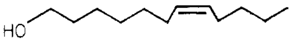
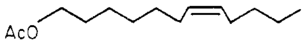
## Pheromone Synthesis via Organoboranes: A Stereospecific Synthesis of (*Z*)-7-Alken-1-ols

*Summary:* Treatment of *trans*-1-alkenylborepanes, obtained via monohydroboration of 1-alkynes with borepane, with iodine in the presence of a base results in the migration of one end of the cycloalkyl chain from boron to the adjacent carbon, producing intermediates containing the eight-membered borocane moiety, which undergoes a rapid deiodoboronation to afford the (*Z*)-7-alkenyl-1-boronate esters. These boronate esters on oxidation produce (*Z*)-7-alken-1-ols, providing a general, one-pot, and stereospecific synthesis of (*Z*)-7-alken-1-ols.

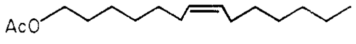
*Sir:* The synthesis[1] of unsaturated alcohols has attracted considerable attention of organic chemists in recent years because such alcohols[2,3] and their acetates[2,4] are known to be insect sex attractants. For example, (*Z*)-7-dodecen-1-ol (**1**) is the pheromone of the male moths of lepidoptera, *Raphia frater* Grt (Noctuidae),[3] and (*Z*)-7-dodecen-1-yl acetate (**2**) is the sex attractant of soybean loopers, *Pseudoplusia includens* (Walker),[5] and also of cabbage looper, *Trichoplusia ni* (Hübner).[6] (*Z*)-7-Tetradecen-1-yl acetate (**3**) is the phermone of the *Amathes c-nigrum* found both in Japan[7] and in Germany.[8] We now report a general, one-pot, and stereospecific synthesis of (*Z*)-7-alken-1-ols, thus providing a simple and very convenient route to the synthesis of pheromones **1**, **2**, and **3** via organoboranes.



**1**

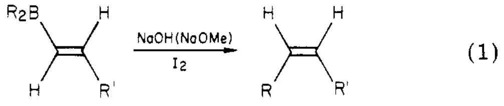


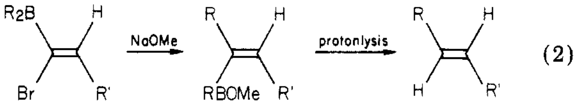
**2**



**3**

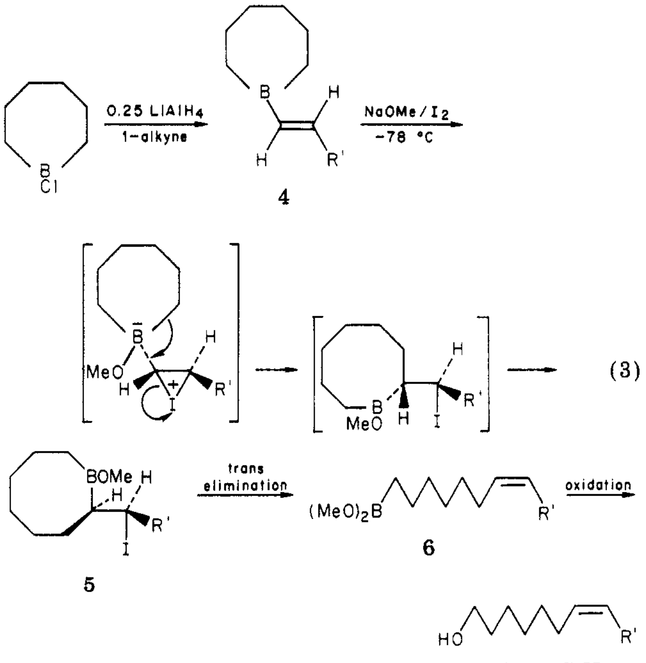
Organoboranes play an important role in bringing latitude to organic synthesis.[9] Highly stereospecific synthesis of cis[10] (eq 1) and trans[11] (eq 2) alkenes via organoboranes is well documented.





99% isomeric purity

It appeared to us that the iodination of the *trans*-1-alkenylborepanes **4**, obtained via the monohydroboration of 1-alkynes with borepane, in the presence of a base should provide (*Z*)-7-alken-1-ols (eq 3). Accordingly, we examined this reaction sequence as a potential route for the synthesis of (*Z*)-7-alken-1-ols.



**1**, R' = $n$-$C_4H_9$
**7**, R' = $n$-$C_6H_{13}$

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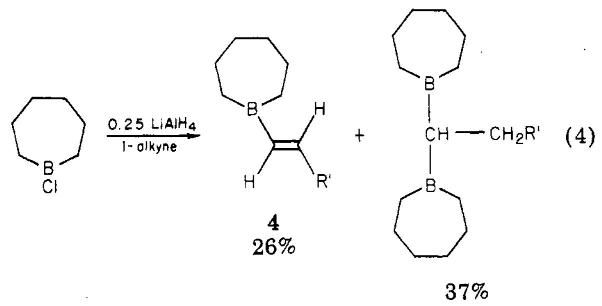
Table I. Synthesis of (*Z*)-7-Alken-1-ols and Their Acetates from 1-Alkyne and Borepane[a]

| 1-alkyne | product[b,c] | % yield | bp, °C (mm) | $n^{20}_D$ |
|---|---|---|---|---|
| 1-hexyne | 1 | 78[d] | 115-117 (0.9)<br>[lit.[15] 74-76 (0.01)] | 1.4549 |
| | 2 | 92[e] | 80-81/0.01<br>[lit.[1a] 85-90 (0.08)] | 1.4432<br>[lit.[1a] $n^{25}_D$ 1.4420] |
| 1-octyne | 7 | 80[d] | 110-112 (0.02)<br>[lit.[15] 94-96 (0.01)] | 1.4566 |
| | 3 | 93[e] | 105-107 (0.01)<br>[lit.[15] 102-104 (0.01)] | 1.4465<br>[lit.[16] $n^{24}_D$ 1.4463] |

[a] All reactions were carried out in 30-mmol scale. [b] Chemical purities of all products are >97% by GC analysis on 6-ft SE 30 column. [c] Isomeric purities are ≃99% by $^{13}$C NMR analysis. [d] Yields of pure products isolated by distillation based on borepane. [e] Isolated yields from corresponding alcohols.

Unfortunately, we encountered one difficulty. The monohydroboration of 1-alkynes with borepane, obtained via the hydridation[12] of *B*-chloroborepane,[13] is accompanied by a competing dihydroboration (eq 4).



4
26%

37%

This difficulty was surmounted by using a large excess of 1-alkyne (12-fold excess), thus providing a clean monohydroboration product **4**. However, the excess alkyne can be recovered quantitatively by distillation from the hydroboration product.

Iodination of the *trans*-1-alkenylborepane (**4**) in the presence of sodium methoxide at −78 °C results in the migration of one end of the cycloalkyl chain from boron to the adjacent carbon, producing the intermediate **5** containing the eight-membered borocane moiety, which undergoes a rapid deiodoboronation to afford (*Z*)-7-alkenyl-1-boronate ester **6**. This intermediate was oxidized in the usual way to provide (*Z*)-7-alken-1-ol (eq 3). Consequently, this reaction sequence was employed for the synthesis of representative insect pheromones belonging to the class of (*Z*)-7-alken-1-ols. Thus, (*Z*)-7-dodecen-1-ol (**1**) and (*Z*)-7-tetradecen-1-ol (**7**) were prepared in high yields (Table I) and were converted into the corresponding acetates **2** and **3**, respectively (Table I). The compounds **1**, **2**, and **3** are natural sex attractants.

It is well-known that in the iodine-induced migration of dialkylvinylboranes, the migrating group from boron becomes attached to the double bond cis to the alkyl group of the original alkyne, as shown in eq 1.[10] Similarly, 7-alken-1-ols, obtained via the iodination of *trans*-1-alkenylborepanes, as in eq 3, should have the same cis stereochemistry. The $^{13}$C NMR chemical shifts of vinylic carbons of cis and trans isomers of disubstituted alkenes are distinctly different.[14] However, in the $^{13}$C NMR spectra of our compounds, no trans isomer was detected.

The following procedure for the synthesis of (*Z*)-7-dodecen-1-ol is representative. To 3.9 g (30 mmol) of *B*-chloroborepane[13] were added 20 mL of THF and 45 mL (390 mmol) of 1-hexyne at −78 °C, followed by a slow addition of $LiAlH_4$ in THF (7.5 mmol) with stirring. The reaction mixture was allowed to warm to 0 °C and stirring was continued for 2 h at 0 °C. Then THF and excess 1-hexyne were distilled off under reduced pressure. The resulting vinylborane was dissolved in THF (40 mL) and the solution was cooled to −78 °C. To this solution at −78 °C was added a solution of NaOMe in MeOH (120 mmol), followed by the addition of 7.62 g (30 mmol) of iodine in THF. After 3 h, any excess iodine was decolorized by adding an aqueous solution of $Na_2S_2O_3$ and the reaction mixture was allowed to warm to room temperature. The reaction mixture was oxidized in the usual way[9] to provide, after distillation, (*Z*)-7-dodecen-1-ol (**1**; 4.3 g, 78%), bp 115–117 °C (0.9 mm), $n^{20}_D$ 1.4549 [lit.[15] bp 74–76 °C (0.01)]. GC analysis showed >97% chemical purity. $^1$H NMR was consistent with the structure. (*Z*)-7-Dodecen-1-yl acetate (**2**) was prepared in 92% yield by reaction with acetyl chloride and pyridine in anhydrous benzene, bp 80–81 °C (0.01 mm), $n^{20}_D$ 1.4432 [lit.[1a] bp 85–90 °C (0.08 mm), $n^{25}_D$ 1.4420].

This reaction sequence represents a very convenient, general, one-pot, and stereospecific synthesis of (*Z*)-7-alken-1-ols, thus providing a simple and convenient route to the synthesis of pheromones **1**, **2**, and **3**. We are presently exploring the possibilities of extending the same strategy using other boracyclanes for the synthesis of insect pheromones containing both *Z* and *E* configurations.

**Registry No.** (*Z*)-**1**, 20056-92-2; (*Z*)-**2**, 14959-86-5; (*Z*)-**3**, 16974-10-0; (*E*)-**4** (R = Bu), 81158-21-6; (*Z*)-**7**, 40642-43-1; *B*-chloroborepane, 60579-52-4; 1-hexyne, 693-02-7; 1-octyne, 629-05-0.

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(17) Postdoctoral research associate on Grant GM 10937 from the National Institutes of Health.