PHEROMONE SYNTHESIS *VIA* ORGANOBORANES: A STEREOSPECIFIC SYNTHESIS OF (*E*)-7-ALKEN-1-OLS*

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Abstract - Borepane, obtained *via* hydridation of *B*-chloroborepane, hydroborates 1-bromo-1-alkynes cleanly to provide the *B*-(*cis*-1-bromo-1-alkenyl)borepanes. Treatment of these intermediates with sodium methoxide results in the displacement of bromine by one end of the boracycloalkyl moiety, producing the corresponding vinylboranes, containing the eight-membered borocane moiety. These intermediates, on controlled protonolysis followed by oxidation, provide the (*E*)-7-alken-1-ols. This process constitutes a simple, very convenient, stereospecific and general one-pot synthesis of (*E*)-7-alken-1-ols. Pheromones, (*E*)-7-tetradecen-1-ol, (*E*)-7-tetradecen-1-ol acetate and (*E*)-7-dodecen-1-ol acetate were prepared in excellent yields.

The synthesis[1] of unsaturated alcohols is acquiring considerable importance because several insect sex attractants[2] are acetates of such unsaturated alcohols. For example, (*E*)-7-dodecen-1-ol acetate (1) is the sex pheromone of the moth, *Argyroploce leucotreta* M[2b] and (*E*)-7-tetradecen-1-ol (2) and the corresponding acetate (3) are sex pheromones of the corn earworm, *Heliothis zea* (Boddie).[2c]

(1)

(2)

(3)

Since the presence of minor isomers frequently inhibits the biological activity of such sex attractants,[3] a highly stereospecific synthesis of this class of compounds is desirable. This work describes a very convenient and stereospecific synthesis of (*E*)-7-alken-1-ol, providing a convenient

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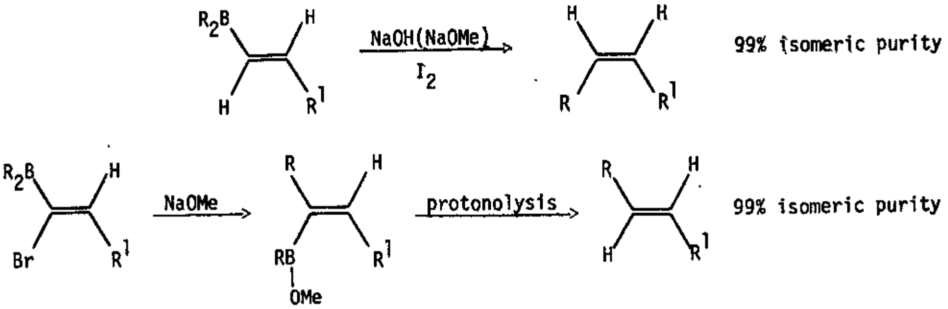
*Dedicated to Professor Herbert C. Brown in recognition of his outstanding contributions to chemistry.

route to the synthesis of pheromones (1), (2) and (3) *via* organoboranes.

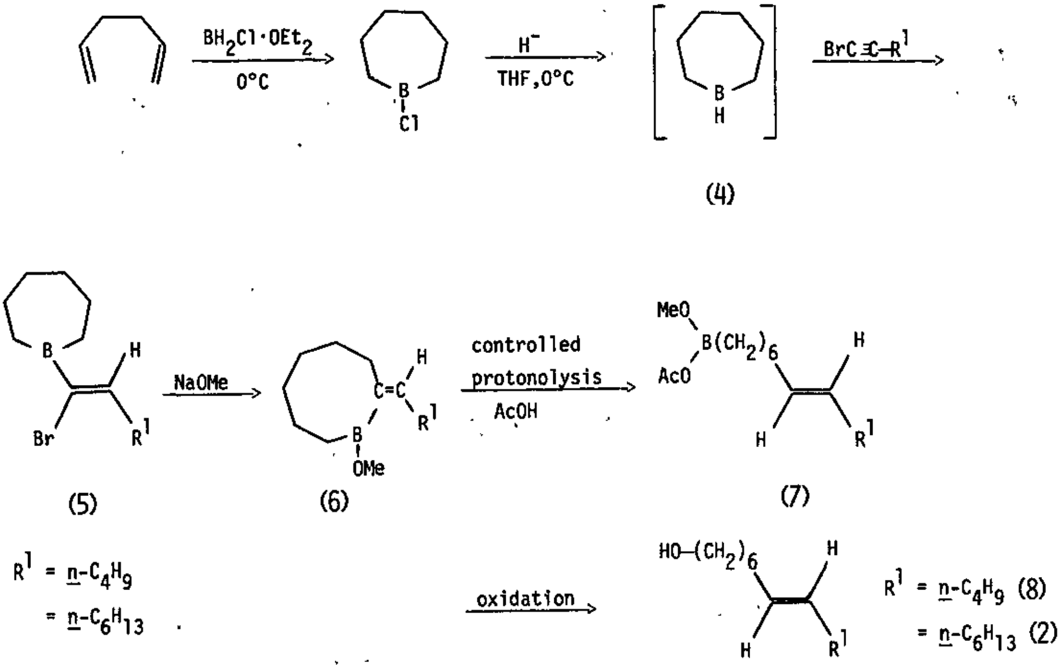
Synthetic applications of organoboranes are widespread in the literature.[4] Highly stereospecific synthetic methods for the preparation of cis[5] and trans[6] alkenes *via* organoboranes (Scheme 1) are well documented.

Scheme 1



The hydroboration of 1-bromo-1-alkyne with borepane (4) generated *in situ via* the hydridation[7] of *B*-chloroborepane,[8] provides the corresponding *B*-(*cis*-1-bromo-1-alkenyl)borepane (5) (Scheme 2), as evidenced by its conversion to 1-bromo-1-alkene (R^1 = *n*-C_4H_9) on protonolysis with acetic acid.

Scheme 2



When B-(cis-1-bromo-1-alkenyl)borepane (5) was treated with sodium methoxide, displacement of bromine by one end of the boracycloalkyl moiety occurs, resulting in the formation of the eight membered ring borocane intermediate (6). Treatment with acetic acid at reflux temperature for two hours led to the protonolysis of the vinylborane, producing the boronate ester (7), which was oxidized in the usual procedure by alkaline hydrogen peroxide to provide (E)-7-alken-1-ol in high overall isolated yields. Consequently, this reaction sequence was employed for the synthesis of representative insect pheromones belonging to the class of (E)-7-alken-1-ols. Thus, (E)-7-dodecen-1-ol (8) and (E)-7-tetradecen-1-ol (2) were prepared in 80% and 78% isolated yields respectively, and converted into the corresponding acetates (1) and (3) in 94% and 93% yields respectively. These acetates (1) and (3) are natural sex attractants.[2c,b]

It has already been established that in the base induced migration of 1-bromo-1-alkenyldialkylboranes the migrating group from boron becomes attached to the double bond trans to the alkyl group of the original alkyne, as shown in Scheme 1.[6] Therefore, the 7-alken-1-ols obtained, as in Scheme 2, should have the trans stereochemistry. The trans stereochemistry was confirmed by the strong ir absorption at ∿ 965 cm^{-1} in each case.[9] The ^{13}C nmr chemical shifts of the vinylic carbons of cis and trans isomers of disubstituted alkenes are distinctly different.[10] However, in the ^{13}C nmr spectra of our compounds, no detectable cis isomer was observed. Consequently, this reaction sequence represents a very convenient, general and stereospecific one-pot synthesis of (E)-7-alken-1-ols.

The following procedure for the synthesis of (E)-7-dodecen-1-ol is representative. To 30 mM of B-chloroborepane[8] in THF at 0°C was added 7.5 mM of $LiAlH_4$ in THF with stirring under nitrogen.[11] After one hour at 0°C, the resulting borepane solution in THF was transferred into the solution of 1-bromo-1-hexyne (4.83 g, 30 mM) in THF at -78°C. The reaction mixture was allowed to warm to 0°C and then stirred for an additional three hours at 0°C. Sodium methoxide (75 mM) in MeOH was added slowly and the contents were stirred at room temperature for one hour. Then 3 ml of acetic acid was added to neutralize any excess sodium methoxide and the solvents and volatile materials were removed under vacuum. Acetic acid, 40 ml, was added and heated under reflux for two hours. The reaction flask was cooled to room temperature and acetic acid was distilled off under vacuum. The reaction mixture was oxidized in the usual way[4] to provide (E)-7-dodecen-1-ol (8) (4.41 g, 80%) bp 100-103°C/0.8 mm, $n^{20}D$ 1.4540 (lit.[1a] bp 78-81°C/0.06 mm, $n^{25}D$ 1.4521). GLC analysis indicated > 97% chemical purity, ^{1}H nmr was consistent with the structure.

Similarly, (E)-7-tetradecen-1-ol (2) was prepared in 78% yield, bp 107-109°C/0.05 mm, $n^{20}D$ 1.4555 (lit.[1c] 110-115°C/0.05 mm).

(E)-7-Dodecen-1-ol acetate (1) was prepared in 94% yield by reaction with acetyl chloride and pyridine in anhydrous benzene, bp 93-95°C/0.15 mm, $n^{20}D$ 1.4420 (lit.[1a] bp 78-82°C/0.05 mm, $n^{25}D$ 1.4410).

Similarly, (*E*)-tetradecen-1-ol acetate (3) was prepared in 93% yield, bp 115-117°/0.1 mm, n^{20}_{D} 1.4460 (lit.[1c] bp 90-95°C/0.01 mm).

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11. For detailed experimental techniques in handling air-sensitive materials, see Ref. 4, Chapter 9.

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