Vinylic Organoboranes. 2. Improved Procedures for the Protonolysis of Alkenyldialkylboranes Providing a Simplified Stereospecific Synthesis of (Z)-Alkenes

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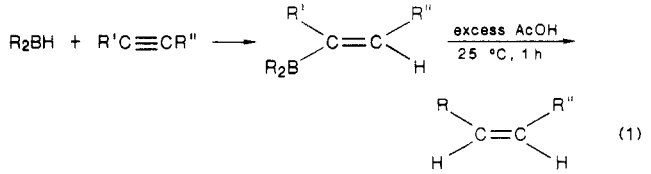
Extremely mild, essentially neutral conditions have been developed for the rapid protonolysis of a representative sampling of alkenyldialkylboranes. Thus, both *B*-alkenyl-9-borabicyclo[3.3.1]nonanes and alkenyldicyclohexylboranes are readily protonolyzed to the corresponding *cis*-alkene and methyl dialkylborinate by 1 equiv of methanol. The sterically more hindered alkenyldisiamylboranes, on the other hand, require a catalytic amount of organic acid for efficient protonolysis. The yield of alkene in all cases is ≥86%. This hydroboration–protonolysis sequence thus promises to be an efficient, economical method for the synthesis of *cis*-alkenes from alkynes, since the methyl dialkylborinate formed can be recycled back to the corresponding dialkylborane hydroborating reagent.

In connection with our continued interests in the application of boron chemistry for organic synthesis, protonolysis of organoboranes appeared to be a convenient method for the synthesis of the corresponding hydrocarbons.[1,2] It also appeared that the protonolysis of alkenylboranes, readily available via hydroboration of alkynes, would provide a general method for the synthesis of *cis*-alkenes.

Recently, we initiated a program on the synthesis of insect pheromones via boranes. Although the stuctures of many insect sex attactants are quite simple, the compounds must be very pure for maximum effectiveness. Therefore, procedures utilized for their synthesis must possess unusually severe requirements for high regio- and stereospecificity. An extraordinarily large number of recognized insect sex attractants contain one or more cis-olefinic linkages.[3] Previously these compounds have often been synthesized from the corresponding alkynes by careful hydrogenation with a special catalyst.[4] Isomeric purities no greater than 97% could be achieved in this manner.

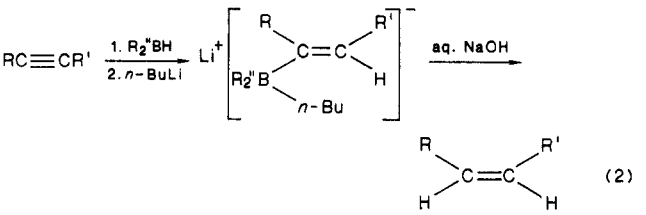
The hydroboration of internal alkynes, followed by protonolysis of the intermediate alkenylborane, routinely provides *cis*-alkenes of >98% purity.[1,2] Since a number of functional groups can be tolerated by the hydroboration reaction,[5] the method is widely applicable to a variety of substrates carrying such functional groups. Thus the hydroboration–protonolysis sequence appears ideal for the synthesis of cis-olefinic pheromones.

However, while the hydroboration of alkynes by various reagents has been quite well-studied,[6] conditions for the protonolysis have received little attention. Generally, protonolysis with a seven- to ninefold excess of acetic acid had been utilized for alkenyldialkylboranes (eq 1).[2]



(1)

Because of the incompatibility of this procedure with various acid-sensitive functional groups, Negishi and Chiu developed a novel procedure to protonolyze alkenylboranes effectively under basic conditions.[7] It involved treatment of the readily available alkenyltrialkylborates with aqueous sodium hydroxide to provide the corresponding alkenes in excellent yields and purity (eq 2).

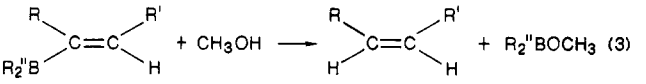


(2)

We sought a mild, neutral protonolyzing reagent that could be utilized for substrates containing either acid- or base-sensitive functional groups. In addition, we wanted a process that would be as economical as possible. Therefore, methods were considered that involved recycling of the organoboranes. Accordingly, we undertook a study of the protonolysis of representative alkenyldialkylboranes with methanol as a method to prepare *cis*-alkenes to be utilized in our pheromone research.

Results and Discussion

Unlike the protonolysis of trialkylboranes,[1,8] the protonolysis of alkenyldialkylboranes is a facile process, proceeding at room temperature in a matter of minutes with glacial acetic acid.[2] This indicated to us that the protonolysis might occur even under mild, neutral conditions, utilizing a reagent such as methanol (eq 3).



(3)

This method might also have an economic advantage over previously utilized methods. The methyl dialkylborinates formed are volatile liquids that could be readily recovered by distillation. In one instance, that for *B*-methoxy-9-borabicyclo[3.3.1]nonane (*B*-methoxy-9-BBN), the methyl dialkylborinate has been reconverted to the original hydroborating agent by simple treatment with borane–methyl sulfide.[9] This would then allow for effi-

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(3) (a) Jacobson, M., Ed. *Insecticides of the Future*; Marcel Dekker, Inc.: New York, 1980. (b) Mayer, M. S.; McLaughlin, J. R. *An Annotated Compendium of Insect Sex Pheromones*; Florida Agricultural Experiment Stations Monograph Series No. 6, University of Florida, Gainesville, August 1975.
(4) (a) Hendrick, C. A. *Tetrahedron* **1977**, *33*, 1845. (b) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446.
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(6) Brown, H. C.; Campbell, J. B., Jr. *Aldrichimica Acta* **1981**, *14*, 3.
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(9) (a) Unpublished results with J. A. Sinclair. (b) Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.* **1979**, *168*, 281.

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Table I. Protonolysis of Terminal Alkenyldialkylboranes[a]

borane	conditions	time, h	yield,[b] %
B-(1*E*)-(1-octen-1-yl)-9-BBN	CH_3OH/25 °C	6	96
(1*E*)-(1-octen-1-yl)dicyclohexylborane	CH_3OH/65 °C	1.5	91
(1*E*)-(1-octen-1-yl)disiamylborane	CH_3OH/65 °C	36	31[c]
	5 mol % $NaOCH_3/CH_3OH$/65 °C	3	<1[c]
	5 mol % CH_3CO_2H/CH_3OH/25 °C	6	90
	1 mol % CH_3CO_2H/CH_3OH/65 °C	1.5	83

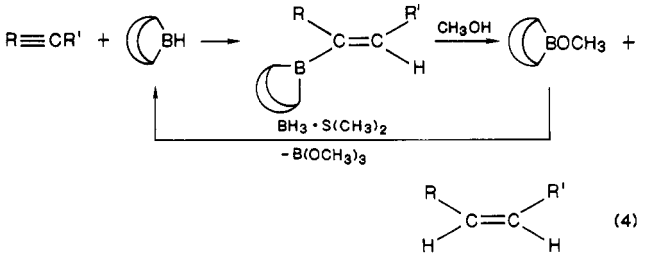
[a] All reactions were run as 1 M solutions in THF using 1 equiv of protonolyzing agent. [b] Yield of 1-octene by VPC. Yield of olefin in 9-BBN compound is based on distilled alkenyl-9-BBN. Yields for alkenyldicyclohexyl- and -disiamylboranes are based on starting alkyne. Unless otherwise indicated, the yields of olefin were maximized at the time period indicated, and longer reaction times did not significantly increase the yield. [c] Reaction was terminated at time indicated. Yields are therefore not maximized.

Table II. Protonolysis of Internal Alkenyldialkylboranes[a]

borane	conditions	time	$t_{1/2}$	yield,[b] %
B-(1*Z*)-(4-octen-4-yl)-9-BBN	CH_3OH/30 °C	22 h		(<60)[c,d]
	CH_3OH/65 °C	2 h		98
	1 mol % CH_3CO_2H/CH_3OH/25 °C	<15 min		99
(4*Z*)-(4-octen-4-yl)dicyclohexylborane	CH_3OH/65 °C	2 h		86
(4*Z*)-(4-octen-4-yl)disiamylborane	CH_3OH/65 °C	72 h		32[d]
	5 mol % $NaOCH_3/CH_3OH$/65 °C	3 h		<1[d]
	5 mol % CH_3CO_2H/CH_3OH/30 °C	48 h		(100)[c]
	1 mol % CH_3CO_2H/CH_3OH/65 °C	9 h	3 h	79
	1 mol % $(CH_3)_3CCO_2H/CH_3OH$/65 °C	2 h	40 min	86
	1 mol % $[(CH_3)_2CH]_3CCO_2H/CH_3OH$/65 °C	57 h	24 h	77
	1 mol % $[(CH_3)_3C]_2CHCO_2H/CH_3OH$/65 °C	35 h	35 h	50
	1 mol % $PhCO_2H/CH_3OH$/65 °C	3 h	1.25 h	79
	1 mol % *p*-CH_3OPhCO_2H/CH_3OH/65 °C	2.5 h	45 min	86
	1 mol % *p*-$ClPhCO_2H/CH_3OH$/65 °C	4 h	1.5 h	76
	1 mol % Ph_3CCO_2H/CH_3OH/65 °C	20 h	3 h	81
	1 mol % $MesCO_2H/CH_3OH$/65 °C	12 h		72

[a] All reactions were run as 1 M solutions in THF using 1 equiv of protonolyzing agent. [b] Yield of *cis*-4-octene by VPC. Yield of olefin in 9-BBN compound is based on distilled alkenyl-9-BBN. Yields for alkenyldicyclohexyl- and -disiamylboranes are based on starting alkyne. Unless otherwise indicated, the yields of olefin were maximized at the time period indicated, and longer reaction times did not significantly increase the yields. [c] Yield based on disappearance of alkenyldialkylborane and appearance of methyl dialkylborinate, as monitored by ^{11}B NMR. [d] Reaction was terminated at time indicated. Yields are therefore not maximized.

cient recycling of the borane for industrial production of *cis*-alkenes (eq 4).



(4)

With these goals in mind, we set out to explore the protonolysis of alkenyldialkylboranes with methanol.

Protonolysis of Terminal Alkenyldialkylboranes. The alkenyldialkylboranes obtained by the hydroboration of 1-octyne by 9-BBN, dicyclohexylborane, and disiamylborane were chosen as representative examples of terminal alkenylboranes, and the results of this study are shown in Table I.

Thus, of the terminal alkenylboranes, only the more sterically hindered alkenyldisiamylborane requires a catalytic amount of organic acid for efficient protonolysis.[10] Both *B*-1-octenyl-9-BBN and 1-octenyldicyclohexylborane are protonolyzed rapidly with 1 equiv of methanol. The yield of olefin in each case is ≥90%. Finally, it is interesting to note that basic conditions (5 mol % $NaOCH_3/CH_3OH$) inhibit protonolysis of the 1-octenyldisiamylborane.

(10) Köster, R.; Amen, K.-L.; Bellut, H.; Fenz, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 748.

Protonolysis of Internal Alkenyldialkylboranes. The results of our study utilizing internal alkenyldialkylboranes are summarized in Table II. Once again, *B*-4-octenyl-9-BBN and 4-octenyldicyclohexylborane require no acid catalysts for rapid and efficient protonolysis, although, as expected, the conditions required were somewhat more vigorous than those needed for the terminal alkenyldialkylboranes. The yield of *cis*-4-octene is again quite high, ≥86%.

A thorough study for the most efficient catalyst for the protonolysis of the highly hindered (4-octenyl)disiamylborane was undertaken. Basic conditions were found to be ineffective. However, a variety of acid catalysts could be utilized, and an interesting series was developed. Thus, while the more hindered pivalic acid and benzoic acid (and benzoic acid derivatives) were clearly more efficient than acetic acid, as the acid became even more hindered, the efficiency of protonolysis declined rapidly. To understand this phenomenon, some knowledge of the mechanism of the protonolysis is required.

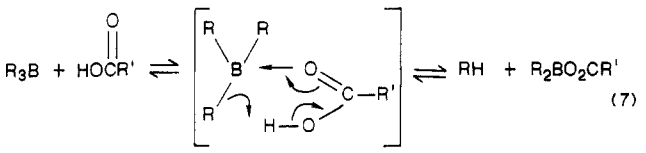
Köster has proposed that the acid catalyst protonolyzes trialkylboranes and is then displaced in an equilibrium reaction by the large amount of alcohol present (eq 5 and 6).[10] It has also been established that in the protonolysis

$$R_3B + HO_2CR' \rightarrow RH + R_2BO_2CR' \quad (5)$$

$$R_2BO_2CR' + HOR'' \rightleftharpoons R_2BOR'' + HO_2CR' \quad (6)$$

of organoboranes by carboxylic acids, a pre-rate-determining coordination of the acid with the boron atom occurs that simultaneously polarizes and weakens the carbon–boron bond and increases the electrophilic character of the proton.[11] The protonolysis thus proceeds most efficiently

through a six-membered transition state where the nucleophilic and electrophilic sites are in proper geometric relationship to one another (eq 7).[12] Like acetic acid,



(7)

pivalic acid allows complexation with the borane. However, the *tert*-butyl group of pivalic acid is bulky enough that it prefers to remain far away from the reaction center. This allows the proper strain-free geometry in the transition state to be attained and results in a rapid protonolysis. It is probable that with the more hindered carboxylic acids, the initial complex is highly sterically strained, driving the equilibrium in eq 7 to the left and thereby causing the protonolysis to be slowed considerably.

Conclusions

It has been determined that a number of alkenyldialkylboranes can be protonolyzed cleanly in high yields utilizing only methanol as the protonolyzing reagent. In those cases where steric hindrance slows the protonolysis, a catalytic amount (1 mol %) of pivalic acid appears to be most effective in bringing about efficient protonolysis. Thus the hydroboration–protonolysis procedure promises to be the method of choice for the efficient, economical synthesis of insect pheromones containing cis double bonds.

Experimental Section

General Comments. The techniques employed extensively during this study are described elsewhere.[13] All glassware was oven-dried at 140 °C for at least 4 h before use, assembled hot, and allowed to cool under a stream of prepurified nitrogen. The transfers of all liquids and solutions were carried out by using oven-dried nitrogen-flushed hypodermic syringes fitted with stainless steel needles. All reactions were carried out under a static pressure of nitrogen.

Materials. THF was distilled under nitrogen from lithium aluminum hydride and then stored under nitrogen in a large ampule with a Teflon stopcock. All alkenyldialkylboranes were prepared according to published procedures.[13] The *B*-alkenyl-9-BBN compounds were distilled materials, while the alkenyldicyclohexyl- and -disiamylboranes were simply used after the volatiles had been removed in vacuo. Reagent grade methanol was deoxygenated,[13] but otherwise used as obtained from J. T. Baker. Triisopropylacetic acid and di-*tert*-butyl acetic acid were kindly provided by Professor M. S. Newman; all other acids were commercial samples and were used as obtained.

Analyses. Gas chromatographic analyses were carried out on a Hewlett-Packard 5750 dual-thermal conductivity chromatograph using a 6 ft × 0.25 in. o.d. column filled with 10% SE-30 on 60/80 AW-DMCS Chromosorb W, using the internal standard technique.

The ^{11}B NMR spectra were recorded on a Varian FT-80A spectrometer operating at 23.267 MHz. The spectra were run on samples in 5-mm tubes held coaxially in 10-mm tubes containing deuteriochloroform lock sample. The spectra were ^{1}H decoupled at 3.5 W.

Protonolysis of Alkenyldialkylboranes. All of the reactions indicated in Table I and II were run as follows: To a dry, nitrogen-flushed, 25-mL flask equipped with a septum inlet and Teflon-coated stirring bar and capped with a condenser was added 5 mmol of the alkenyldialkylborane. Then, 4 mmol of *n*-decane was added, followed by ~2.5 mL of THF. Finally, 5 mmol of the appropriate protonolyzing reagent was added. Those reactions that required heating were heated by a heating mantle at a gentle reflux. Aliquots were taken at various time periods and the appearance of alkene was monitored by GLC analysis. It was previously determined that the alkenyldialkylboranes do not liberate free alkene when injected on the gas chromatograph.

Acknowledgment. We thank Professor Melvin S. Newman of The Ohio State University for samples of triisopropylacetic acid and di-*tert*-butylacetic acid, which were utilized in this study, and to Albany International for their financial support of this work.

(11) Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. *J. Am. Chem. Soc.* **1965**, *87*, 1236.
(12) Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. *Inorg. Chem.* **1965**, *4*, 1649.
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Vinylic Organoboranes. 3. Pheromones via Organoboranes. 1. Stereospecific Synthesis of Straight-Chain *Z*-Monoolefinic Insect Pheromones via Lithium (1-Alkynyl)trialkylborates

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Various insect pheromones with straight-chain *Z*-monoolefinic structures have been prepared from lithium (1-alkynyl)trialkylborates. Treatment of lithium (1-alkynyl)trialkylborates, readily prepared from lithium acetylides and trialkylboranes, with iodine under mild conditions produces the corresponding alkynes in essentially quantitative yield. Monohydroboration of the resultant alkyne with 9-borabicyclo[3.3.1]nonane yields the corresponding (*Z*)-olefin after protonolysis. The combination of these two reaction sequences provides a general route for the synthesis of (*Z*)-olefins. The position of the double bond and the carbon-chain length are easily controlled by properly choosing the initial reactants. The incorporation of functional groups is also easily achieved because of the mild reaction conditions and the tolerance of hydroboration to many functional groups. High yield and purity of the products are obtained.

The study of insect pheromones has recently attracted great attention.[2] This is due to their interesting structures and their potential applications for the control of pest insects.[2a,3] Various synthetic methods have been rapidly

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