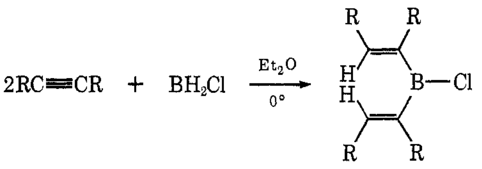
See Editorial, *J. Org. Chem.*, **38**, No. 19, 4A (1972)

Reaction of Representative Alkynes with Monochloroborane Diethyl Etherate. A Simple Convenient Synthesis of Dialkenylchloroboranes *via* Hydroboration

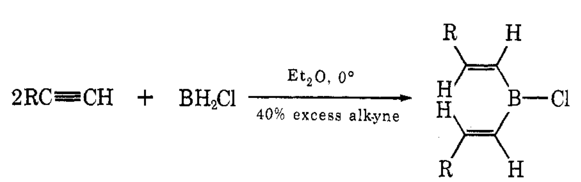
Summary: Monochloroborane diethyl etherate ($BH_2Cl \cdot OEt_2$) reacts with alkynes to give dialkenylchloroboranes which are easily isolated and, if desired, readily converted into the corresponding dienes, alkenes and carbonyl compounds.

Sir: The reaction of monochloroborane diethyl etherate ($BH_2Cl \cdot OEt_2$) with alkynes can be controlled to provide the hitherto difficultly accessible dialkenylchloroboranes. These dialkenylchloroboranes are easily isolated by simple distillation under reduced pressure. They can be protonolyzed to the alkenes, oxidized to aldehydes or ketones, or converted into cis,trans dienes on treatment with sodium hydroxide and iodine. Consequently, this development provides a remarkably simple route to such cis,trans dienes.

$BH_2Cl \cdot OEt_2$ in ethyl ether solution readily hydroborates a variety of olefins providing a simple synthesis of dialkylchloroboranes.[1] Investigation of the reaction of this reagent with representative alkynes revealed that internal alkynes, such as 3-hexyne and 1-phenylpropyne, undergo monohydroboration rapidly at 0° by the reagent used in stoichiometric amounts to form the dialkenylchloroboranes cleanly, as shown in eq 1. In the case of terminal alkynes, the reaction involving stoichiometric amounts of the reagent produces only 60–70% of the monohydroboration product.[2] However, essentially quantitative formation of the desired dialkenylchloroborane can be achieved in these cases by using excess alkyne (~40%) (eq 2). All of the terminal alkynes tested behaved in the same manner. The dialkenylchloroboranes are easily isolated by distillation under low pressure. A few representative dialkenylchloroboranes were synthesized, isolated, and characterized by pmr and elemental analysis (Table I).



(1)



(2)

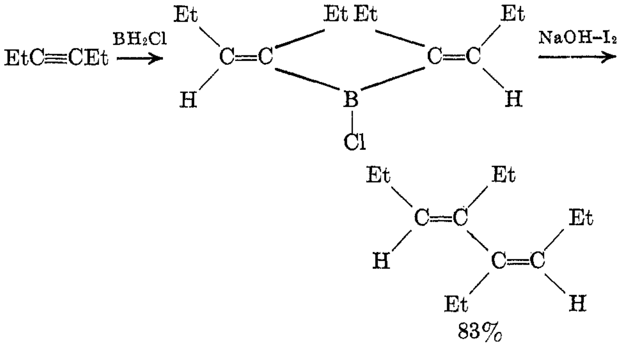
TABLE I

SYNTHESIS OF DIALKENYLCHLOROBORANES BY THE MONOHYDROBORATION OF ALKYNES WITH MONOCHLOROBORANE DIETHYL ETHERATE

Alkyne	Dialkenylchloroborane[a]	Isolated yield, %	Bp, °C (mm)
1-Hexyne	Bis(*trans*-1-hexenyl)-chloroborane	81	79–81 (0.05)
3,3-Dimethyl-1-butyne	Bis(*trans*-3,3-dimethyl-1-butenyl)chloroborane	80	52–53 (0.09)
Cyclohexylethyne	Bis(*trans*-2-cyclohexyl-1-ethenyl)chloroborane	76	122–124 (0.025)
3-Hexyne	Bis(*cis*-3-hexenyl)-chloroborane	88	66–68 (0.10)

[a] The stereochemistry of the products were determined by pmr. The isolated dialkenylchloroboranes all gave correct elemental analyses.

Zweifel and coworkers have reported that thexyl dialkenylborinates, obtained by the oxidation of thexyldialkenylboranes with trimethylamine oxide, are converted into cis,trans dienes on treatment with NaOH–I_2.[3] The dialkenylchloroboranes can be directly transformed into cis,trans dienes by Zweifel's procedure (eq 3 and 4). Consequently, this development now provides a remarkably simple route to such dienes.



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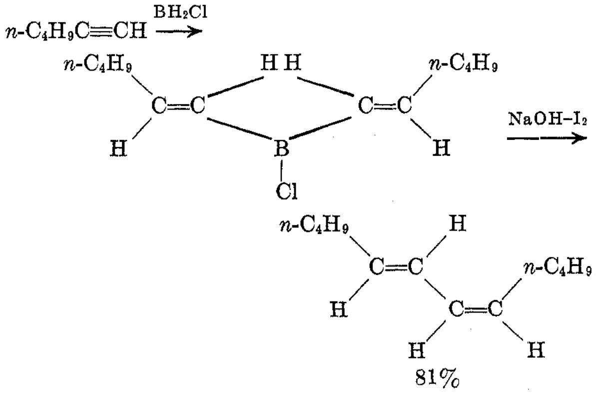

(4)

Like the other alkenylboranes,[4] the dialkenylchloroboranes undergo protonolysis with acetic acid in tetra-

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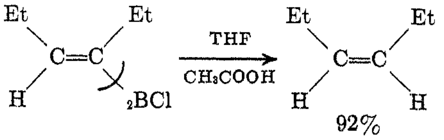
[1] H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, **94**, 2112 (1972).

[2] In this case, the alkyne underwent considerable dihydroboration. The nature of the dihydroboration product is currently under investigation.

[3] G. Zweifel, N. L. Polston, and C. C. Whitney, *J. Amer. Chem. Soc.*, **90**, 6243 (1968).

[4] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 3834 (1961).

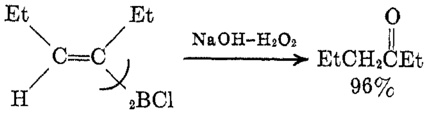
hydrofuran to give stereochemically pure olefins (eq 5 and 6). Oxidation of dialkenylchloroboranes with



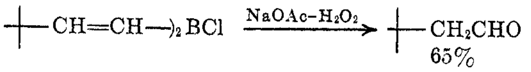
(5)

$$n\text{-}C_4H_9CH{=}CH{-})_2BCl \xrightarrow[CH_3COOH]{THF} \underset{90\%}{n\text{-}C_4H_9CH{=}CH_2} \quad (6)$$

alkaline hydrogen peroxide gives the corresponding carbonyl compounds (eq 7 and 8).



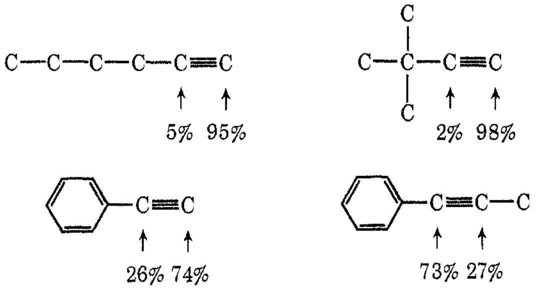
(7)



(8)

The directive effect in the monohydroboration of representative alkynes with $BH_2Cl \cdot OEt_2$ was examined. Analysis of the hydroboration mixture for residual alkyne and hydride established that quantitative conversion to the dialkenylchloroborane was achieved. The reaction mixture was then oxidized and the resulting carbonyl products were reduced to the alcohols with alkaline sodium borohydride. The alcohols were analyzed by gc. In the case of terminal alkynes, the amount of the internal alcohols found corresponds to the fraction of boron in the internal position. Since the formation of dialkenylchloroborane was quantitative, the remainder of the boron must have gone to the terminal position. (Oxidation of terminal vinylboranes to aldehydes in quantitative yield is more difficult.) The results are presented in Chart I. The results reveal that the directive effect in the hydroboration of terminal acetylenes with $BH_2Cl \cdot OEt_2$ is less than that observed in the hydroboration of olefins with this reagent.[5] However, it is not possible to compare the directive effects achieved with $BH_2Cl \cdot OEt_2$ with those of borane itself, because the latter reagent converts terminal acetylene predominantly to the dihydroboration product.[4,6] The greater control of monohydroboration of acetylenes provided by chloroborane represents a major advantage of this reagent.

CHART I
DISTRIBUTION OF BORON IN THE MONOHYDROBORATION OF ALKYNES WITH $BH_2Cl \cdot OEt_2$



The following experimental procedures for the synthesis and reactions of bis(*cis*-3-hexenyl)chloroborane are representative. To a solution of 100 mmol of 3-hexyne in 15 ml of ethyl ether was added dropwise 50 mmol of BH_2Cl in ethyl ether[1] (37 ml) at 0° and this mixture was stirred under nitrogen for 2 hr. The ether was removed using a water aspirator and the bis(*cis*-3-hexenyl)chloroborane was distilled at 66–68° (0.1 mm). The product, obtained in 88% yield, was characterized by pmr and elemental analysis. In the experiment involving terminal alkynes, the procedure was identical except that 140 mmol of alkyne (40% excess) was used instead of the stoichiometric amount.

For the synthesis of diene, 50 mmol of bis(*cis*-3-hexenyl)chloroborane (ether removed, but not distilled) was dissolved in 40 ml of tetrahydrofuran. Aqueous sodium hydroxide (3 *M*, 200 mmol) was then added at 0°, followed by dropwise addition of tetrahydrofuran solution of iodine until a slight color of iodine persisted. The excess iodine was destroyed by stirring with excess sodium thiosulfate solution at 25°. The diene was extracted into pentane, washed with dilute thiosulfate solution, dried, and distilled at 62–64° (8 mm). The *cis,trans*-4,5-diethyl-3,5-octadiene, obtained in 83% yield, was characterized by pmr.[3]

To achieve the protonolysis, 4 mmol of bis(*cis*-3-hexenyl)chloroborane was dissolved in 2 ml of tetrahydrofuran and stirred with 2 ml of glacial acetic acid at 25° for 3 hr. The yield of *cis*-3-hexene formed was 92% (gc analysis).

Oxidation of 10 mmol of bis(*cis*-3-hexenyl)chloroborane in 10 ml of ether was carried out by adding, at 0°, 20 mmol of aqueous sodium hydroxide (3 *M*), followed by 2 ml of 30% hydrogen peroxide (dropwise) and 10 ml of ethanol, and stirring at 25° for 30 min. The yield of 3-hexanone was 96% (gc analysis).

The present development provides, for the first time, a general convenient procedure for the synthesis of dialkenylchloroboranes.[7] The ready availability of these compounds by the present simple procedure should facilitate the exploration of the chemistry of this interesting class of compounds. Diene formation, protonolysis, and oxidation are synthetically useful reactions of these compounds, and other interesting applications may be anticipated.

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[5] H. C. Brown and N. Ravindran, *J. Org. Chem.*, **38**, 182 (1973).

[6] G. Zweifel and H. Arzoumanian, *J. Amer. Chem. Soc.*, **89**, 291 (1967).

[7] The only compound of this class reported to date is the diethenylchloroborane obtained in 35% yield by the fractionation of a mixture of products from the reaction of tetraethenyltin with boron trichloride at 60°: F. E. Brinckman and F. G. A. Stone, *J. Amer. Chem. Soc.*, **82**, 6218 (1960).

[8] Postdoctoral research associate on National Science Foundation Grant No. 27742X.

RICHARD B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA 47907

HERBERT C. BROWN*
N. RAVINDRAN[8]

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Conformational Effect on Observable Magnetic Nonequivalence of Diastereotopic Protons.

III. 3-Axial Alkyl Effect[1]

Summary: The diastereotopic, benzylic protons of a substituted 1-benzylpiperidine appear as an AB quartet in the nmr spectrum if a 3-alkyl substituent is either axially oriented or is a branched chain and equatorial.

Sir: The diastereotopic relationship of two hydrogens is a necessary but not a sufficient requirement for