Results for IIIb are also summarized in the Discussion. Because diazooctane was stable under reaction conditions, only one deuterium quench was carried out.

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Organoboron Compounds. II. The Preparation of Ethyl-Substituted Boranes by Hydrogenation of 2-Chlorovinyl- and 2-Chlorovinylethylboranes[1a]

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The 2-chlorovinyl- and 2-chlorovinylethylboranes have been hydrogenated to the corresponding ethyl-substituted boranes with the liberation of hydrogen chloride. The reaction takes place at 50–100° in the gas phase with palladium black as catalyst. Reduction to the desired product becomes more difficult with increasing number of chlorovinyl groups in the molecule.

Although the preparation and reactions of 2-chlorovinyl-substituted compounds have been examined in some detail,[2–7] hydrogenation of the 2-chlorovinyl group has never been reported. In connection with our studies into the preparation of alkylboranes without metallic reagents,[7] the catalytic hydrogenation of 2-chlorovinyl- and 2-chlorovinylethylboranes was investigated as a method for preparing 2-chloroethyl-substituted boranes.

This reaction did not yield the expected products but gave instead the corresponding ethyl-substituted boranes and hydrogen chloride. Thus, hydrogenation of (2-chlorovinyl)dichloroborane (I), bis(2-chlorovinyl)chloroborane (II), and tris(2-chlorovinyl)borane (III) was found to give ethyldichloroborane (IV), diethylchloroborane (V), and triethylborane (VI), respectively, in yields of 97, 51, and 25%. Presumably reduction to the desired products becomes more difficult as the number of chlorovinyl groups in the molecule increases. This was confirmed by the hydrogenation of (2-chlorovinyl)ethylchloroborane (VII) and bis(2-chlorovinyl)ethylborane (VIII), which give diethylchloroborane and triethylborane, respectively, in 90 and 30% yields.

The reaction, which was found to be very exothermic, occurs readily at 50 to 100° in the gas phase with palladium black as catalyst. Degradative side reactions occur owing to the liberated hydrogen chloride. These side reactions increase above 100°, especially with the more highly substituted chlorovinyl compounds. Thus, hydrogenation of I at 150 to 200° gives ethane and boron trichloride primarily while ethyldichloroborane is the major product at 50°. Although better yields were obtained for II, III, and VIII at the lower temperatures, side reactions could not be eliminated.

Other reaction conditions were investigated in order to improve the yields. Hydrogenation in the liquid phase resulted in extensive disproportionation of the starting materials. The use of ethylboranes as solvents produced no improvement in the yields. The inclusion of granular zinc for the purpose of removing hydrogen chloride as formed did not result in any improvement. A solution of tris(2-chlorovinyl)borane in bis(2-methoxyethyl) ether containing sufficient 2,6-lutidine to react with all the liberated hydrogen chloride resulted only in the formation of unidentified black tars. Pressures up to 100 psi permitted the reaction to proceed at temperatures below 50°, but the yields were not improved because of the increased solubility of hydrogen chloride in the reactants and products. Of the many catalysts investigated, palladium black was the most active at low temperatures and furthermore was unaffected by hydrogen chloride. It is interesting to note that the attempted platinum-catalyzed hydrogenation of these compounds was unsuccessful.

One can visualize the side reactions that might take place, as outlined in Scheme I, according to known reactions of alkylboranes with hydrogen chloride.[8,9] Moreover, we have been able to isolate and identify all these products. Using this diagram, the best yields can be expected with I, VII, and IX, since these compounds contain only one chlorovinyl group. In fact, we found this to be true experimentally.

Hawthorne, *et al.*,[10] have found that chloroethylboranes are exceedingly unstable, giving ethylene and other products. We were unable to find any chloroethylboranes or ethylene. We did, however,

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(1) This research was performed under Contract AF 33(600)-33920 for the Wright Air Development Center. (b) To whom correspondence should be sent: IBM Research Laboratory, San Jose, Calif.

(2) W. L. Lewis and G. A. Perkins, *Ind. Eng. Chem.*, **15**, 290 (1923).

(3) W. E. Jones, R. J. Rosser, and F. N. Woodward, *J. Soc. Chem. Ind.* (London), **68**, 258 (1949).

(4) H. R. Arnold, U. S. Patent 2,402,589 (1946); *Chem. Abstr.*, **40**, 5769 (1946).

(5) A. E. Borisov, *Izv. Akad. Nauk SSSR, Odt. Khim. Nauk*, 402 (1951); *Chem. Abstr.*, **46**, 2995*d* (1952).

(6) M. F. Lappert, *Chem. Rev.*, **56**, 959 (1956).

(7) E. Gipstein, P. R. Kippur, M. A. Higgens, and B. F. Clark, *J. Org. Chem.*, **26**, 943, 2947 (1961).

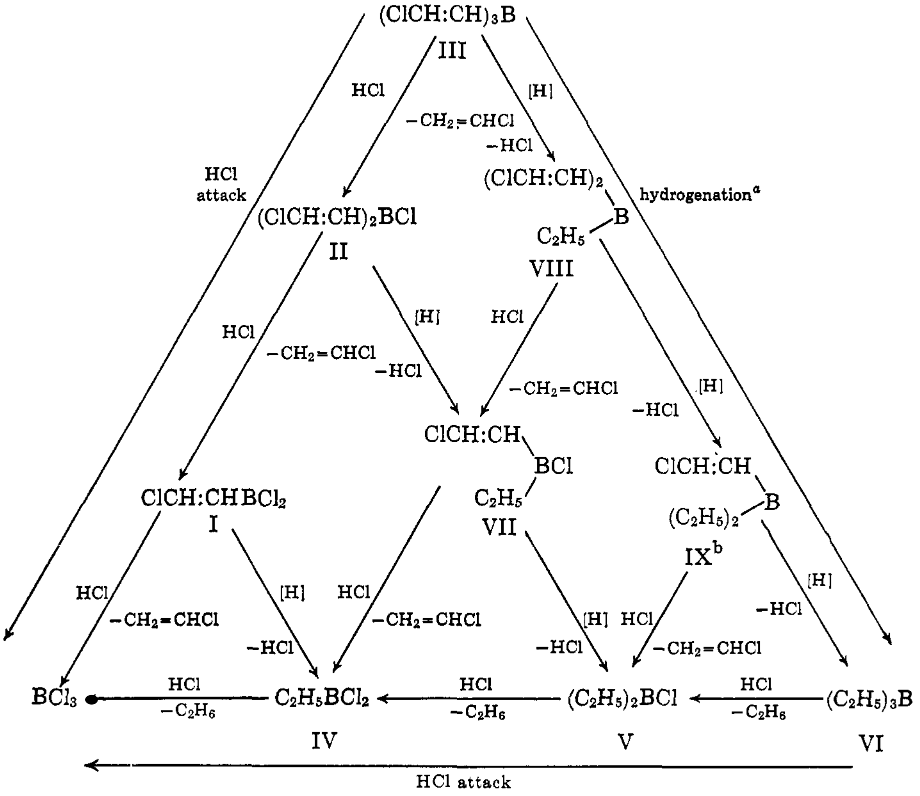
(8) Dialkylboron halides have been prepared by the reaction of hydrogen chloride with trimethyl- and triethylboranes at 150–180° for 1 hr: E. Wiberg, A. Boltz, and P. Bucheit, unpublished work cited by J. Goubeau, *FIAT Rev. Ger. Sci., Inorg. Chem.*, **1**, 218 (1948).

(9) The reaction of hydrogen chloride with tri-*n*-butylborane in the presence of aluminum chloride has been used to prepare *n*-butyldichloroborane. Two-thirds of the alkyl groups are lost as hydrocarbon: R. C. Booth and C. A. Kraus, *J. Am. Chem. Soc.*, **74**, 1415 (1952).

(10) M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5830 (1958).

SCHEME I

HYDROGEN CHLORIDE ATTACK OF ALKYLBORANES



[a] The corresponding vinylboranes were isolated. [b] Compound IX was not isolated or prepared.

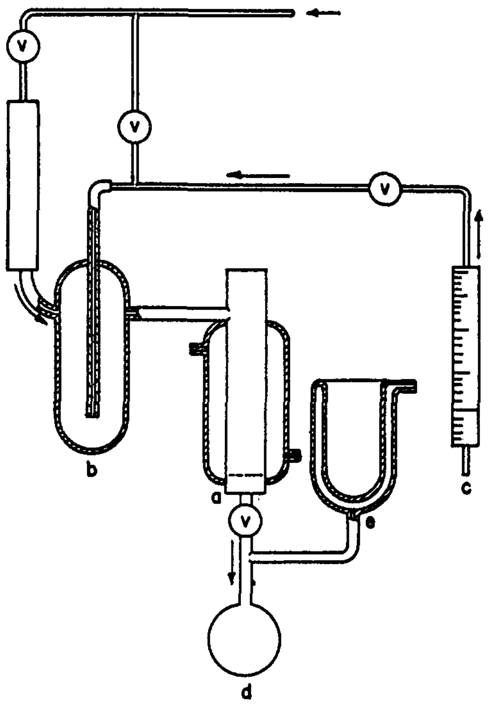


Figure 1.—Hydrogenation apparatus.

find vinylboranes in each reaction that we ran. These facts seem to indicate that chloroethylborane cannot be an intermediate but that a vinylborane must be an intermediate in the reaction. Thus, the reaction must involve removal of the chlorine atom initially, followed by subsequent hydrogenation of the vinylborane.

Experimental Section

Hydrogenation of the 2-Chlorovinylboranes.—All experiments were carried out in the apparatus shown in Figure 1. The entire system was assembled to permit manipulation under a nitrogen atmosphere. The reaction chamber (a) consisted of a tube 1 in. in diameter, 8 in. long, surrounded by a heating jacket. A coarse-glass disk sealed into the lower end of the reactor supported the catalyst. Above the catalyst was a layer of glass beads to distribute the entering liquid and to prevent movement of the catalyst. The liquid was fed into the reactor by a Corson-Cerveny microbellows pump or vaporized by passage of hydrogen through the liquid (b). Dry hydrogen, measured by a Rotameter (c), was passed down over the catalyst bed concurrently with the reactant. The temperature of the catalyst bed was measured by a thermocouple inserted in a central well. The products were condensed in an ice-cooled receiver (d) which was attached to the bottom of the reactor and by a Dry Ice-acetone condenser (e). A water scrubber containing a known amount of standardized sodium hydroxide solution was used to measure the hydrogen chloride evolved. A gas-collecting tube was used to sample the gaseous products when desired. The pyrophoric products were fractionally distilled under nitrogen through a 48-in. glass helix-packed column to give the desired products.

Analysis.—Sampling for analysis was carried out in a drybox. Carbon and hydrogen were determined by the procedure of Scheule and McNabb.[11] Total chlorine was determined by the Volhard method on aqueous alkaline hydrolysates. Where the samples contained chlorovinyl impurities, the potentiometric method of Nadeau, Oaks, and Buxton[12] was used to determine chlorine bound to boron. Total boron was determined by Parr bomb combustion followed by titration with carbonate-free sodium hydroxide in the presence of mannitol. Infrared and gas chromatographic methods of analysis, which were of original development, will be published separately at a later date.[12]

Some typical experimental results are given in Table I.

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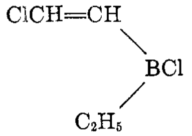
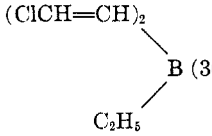
(11) W. J. Scheule and W. M. McNabb, Technical Research Report MCC-1023-TR317, University of Pennsylvania, Philadelphia, Pa.

(12) H. G. Nadeau, D. M. Oaks, and R. D. Buxton, *Anal. Chem.*, **33**, 341 (1961).

TABLE I

HYDROGENATION OF THE 2-CHLOROVINYL- AND 2-CHLOROVINYLETHYLBORANES[a]

Expt	Compd (g)	Temp, °C	Pressure, psi	Ethylborane expected	Bp, °C	Yield, %	Other ethylboranes produced
1	$ClCH{=}CHBCl_2$ (81.5)	50	Atm	$C_2H_5BCl_2$	50.8[b]	97	None
2	$(ClCH{=}CH)_2BCl$ (98.0)	80	Atm	$(C_2H_5)_2BCl$	78.5[c]	51	$C_2H_5BCl_2$
3	$(ClCH{=}CH)_3B$ (85.0)	55	Atm	$(C_2H_5)_3B$	95.0[d]	25	$C_2H_5BCl_2$ $(C_2H_5)_2BCl$
4[e]	$(ClCH{=}CH)_3B$ (13.0)	40	30	$(C_2H_5)_3B$	95.0[d]	0	None
5	$(ClCH{=}CH)_3B$ (15.0)	20	50	$(C_2H_5)_3B$	95.0[d]	13	$C_2H_5BCl_2$ $(C_2H_5)_2BCl$
6	$(ClCH{=}CH)_3B$ (8.5)	20	100	$(C_2H_5)_3B$	95.0[d]	7.5	$C_2H_5BCl_2$ $(C_2H_5)_2BCl$
7	 $(ClCH{=}CH)(C_2H_5)BCl$ (16.0)	60	Atm	$(C_2H_5)_2BCl$	78.5[c]	90	$C_2H_5BCl_2$
8	 $(ClCH{=}CH)_2(C_2H_5)B$ (36.0)	82	Atm	$(C_2H_5)_3B$	95.0[d]	30	$(C_2H_5)_2BCl$

[a] Palladium black was used as the catalyst in these experiments. [b] L. Lynds and D. Stern [*J. Am. Chem. Soc.*, **81**, 5006 (1959)] reported bp 50° (745 mm). [c] V. W. Buls, O. L. Davis, and R. I. Thomas, *ibid.*, **79**, 337 (1957). [d] R. S. Aries [U. S. Patent 3,053,871 (Sept 11, 1962); *Chem. Abstr.*, **58**, 12602*a* (1964)] reported bp 95.0°. [e] A diluent, CH_2Cl_2, was used in this experiment.

Anal. Calcd for $C_2H_5BCl_2$: C, 21.67; H, 4.55; B, 9.77; total Cl, 64.01. Found: C, 21.55; H, 4.50; B, 9.88; total Cl, 64.12.

Anal. Calcd for $C_4H_{10}BCl$: C, 46.02; H, 9.65; B, 10.36; Cl on B, 33.97. Found: C, 46.15; H, 9.54; B, 10.21; Cl on B, 34.08.

Anal. Calcd for $C_6H_{15}B$: C, 73.53; H, 15.43; B, 11.04. Found: C, 73.68; H, 15.22; B, 10.89.

Small amounts of volatile and pyrophoric materials, boiling at temperatures below those of the respective ethylboranes, were also isolated during distillation. These compounds were identified by infrared analysis and from their boiling points as boron trichloride; vinyldichloroborane, bp 45–47.5° (lit.[13] bp 45.4°); divinylchloroborane, bp 66–68° (not reported); and trivinylborane, bp 80–83° (lit.[14] bp 75–85°).

Liquid-Phase Hydrogenation.—(2-Chlorovinyl)dichloroborane (I, 31.4 g, 0.22 mole), and 0.313 g, of platinum oxide were placed in a 500-ml, three-neck flask equipped with heating mantle, stirrer, and reflux condenser. Hydrogen, 13 cc/min, was passed into the reaction mixture at 55–60° for 10 hr. Fractional distillation of the reaction mixture gave 12.5 g (0.087 mole of unchanged starting material), 10.0 g (0.059 mole) of bis(2-chlorovinyl)chloroborane, 5.5 g (0.044 mole) of boron trichloride, and trace amounts of ethyl dichloroborane.

Similarly, 38.3 g (0.27 mole) I and 6 ml of a slurry of Raney nickel in petroleum ether (bp 60–90°) were mixed and hydrogen was passed into the mixture for 10 hr. No hydrogenation occurred and the starting materials were recovered. Other attempts using palladium black as catalyst were also unsuccessful.

Reaction of Tris(2-chlorovinyl)borane (III) with Hydrogen Chloride.—Tris(2-chlorovinyl)borane, 22.0 g (0.11 mole), and 1.0 g of palladium black were placed in a flask connected to a reflux condenser and a Dry Ice–acetone trap. Gaseous hydrogen chloride was slowly bubbled into the liquid at 60°. After 13 hr 5.9 g (0.095 mole) of vinyl chloride had collected in the cold trap. The pot residue contained 16.1 g (0.095 mole) of bis(2-chlorovinyl)chloroborane and 2.8 g (0.014 mole) of unchanged starting material.

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(13) F. E. Brinckman and F. G. A. Stone, *Chem. Ind.* (London), 254 (1959).

(14) A. V. Topchiev, Ya. M. Paushkin, and A. A. Prokhorova, *Dokl. Akad. Nauk SSSR*, **129**, 598 (1959); *Chem. Abstr.*, **54**, 7533*e* (1960).