Mr. P. C. Lauterbur and Mr. J. J. Burke of the Mellon Institute for the determination and interpretation of the NMR spectra, and Dr. A. L. Smith and Mr. N. C. Angelotti foi interpretation of the infrared absorption spectra.

MIDLAND, MICH.

[CONTRIBUTION FROM THE ENERGY DIVISION, OLIN MATHIESON CHEMICAL CORP.]

Organoboron Compounds. I. The Preparation of 2-Chlorovinyl- and 2-Chlorovinylethylboranes by Vinylation, Disproportionation and Exchange Reactions[1]

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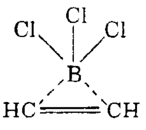
2-Chlorovinyl- and 2-chlorovinylethylboranes have been prepared by synthetic routes which do not require the use of metals, metal alkyls or Grignard reagents. These routes comprise vinylation, disproportionation, and exchange reactions. The methods of preparation and mechanisms are discussed.

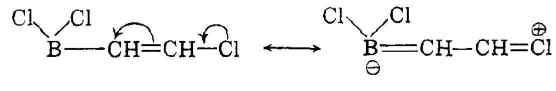
The alkylhaloboranes are versatile intermediates which can be utilized for the preparation of many organoboron compounds containing one, two, or three boron-carbon bonds. The halides are very reactive and readily undergo reactions in which the halogen is replaced without affecting the boron-carbon bonds. In general, synthetic routes to alkylhaloboranes require the use of metals, metal alkyls, or Grignard reagents.[2] It was the purpose of this investigation to prepare alkylhaloboranes from boron halides without metallic compounds.

The present investigation has developed a synthesis of 2-chlorovinyl- and 2-chlorovinylethylboranes by vinylation (reaction with acetylene), disproportionation, and exchange reactions. The vapor-phase reaction of boron trichloride with acetylene in the presence of typical vinylation catalysts has been found to give (2-chlorovinyl)-dichloroborane (I) primarily and very small quantities of bis(2-chlorovinyl)chloroborane (II) and tris(2-chlorovinyl)borane (III).[3] Further investigation of this reaction to obtain better yields of $ClCH{:}CHBCl_5$ (I), $(ClCH{:}CH)_2BCl$ (II), $(ClCH{:}CH)_3B$ (III), bis(2-chlorovinyl)chloroborane, and tris(2-chlorovinyl)borane indicated that acetylene could not be added easily to compounds containing the chlorovinyl group.

Presumably this reaction proceeds through an intermediate complex.



While the electrophilic character of the boron atom in boron trichloride is high, the electrophilicity of the boron atom attached to the chlorovinyl group is decreased by the following resonance form:



Thus a second chlorovinyl group was added to (2-chlorovinyl)dichloroborane with difficulty in poor yields (6%) while no addition occurred with either (2-chlorovinyl)ethylchloroborane[4] or bis(2-chlorovinyl)chloroborane. It is interesting to note that acetylene adds readily to ethyldichloroborane and not to diethylchloroborane.[4] The formation of the π-complex with acetylene is apparently prevented by the inductive effect of the ethyl groups and by steric hinderance.

In an attempt to find other methods for preparing bis- and tris(2-chlorovinyl)boranes, the disproportionation of (2-chlorovinyl)dichloroborane was investigated. Hennion *et al.*[5] found that alkyldichloroboranes disproportionate into dialkylchloroboranes in the presence of trialkylboranes as catalyst. They also found that dialkylchloroboranes could be disporportionated into trialkylboranes and alkyldichloroboranes by slow fractional distillation at atmospheric pressure at temperatures above 100°. We found that when (2-chlorovinyl)dichloroborane was refluxed without catalyst no disproportionation occurred. Upon addition of activated carbon, disproportionation occurred between 100–125° to give equimolar quantities of bis(2-chlorovinyl)chloroborane and boron trichloride.[6] Activated carbon inhibited the disproportionation of bis(2-chlorovinyl)chloroborane into tris(2-chloro-

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[1] This research was performed under Contract AF 33(600)-33920 for the Wright Air Development Center.

[2] For a review of this subject see M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

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

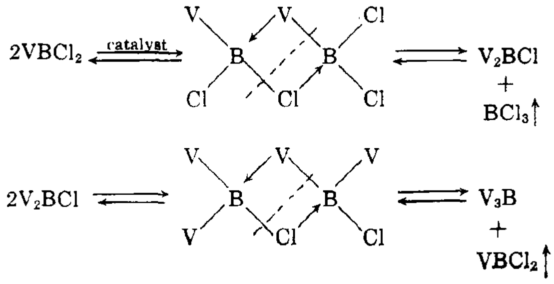
[4] E. Gipstein, P. R. Kippur, M. A. Higgins, and B. F. Clark, *J. Org. Chem.*, **26**, 943 (1961).

[5] G. F. Hennion, P. A. McCusker, and E. C. Ashby, *J. Am. Chem. Soc.*, **79**, 5192–5194 (1957).

[6] B. F. Clark, E. Gipstein, M. A. Higgins, and P. R. Kippur, U. S. Patent **2,919,291**, Dec. 29, 1959; *Chem. Abstr.*, **54**, 7506 (1960).

vinyl)borane and (2-chlorovinyl)dichloroborane and in its absence the reaction proceeded readily.[7]

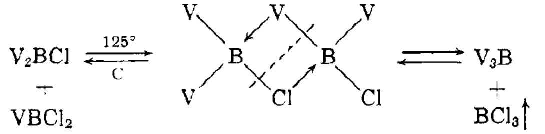
The mechanism which is postulated for the disproportionation involves two steps[5,8]: (1) Dimerization of two reactant molecules in the liquid phase and (2) cleavage of the dimer to give the products:


(1)

(2)

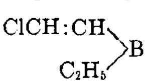
V = ClCH:CH

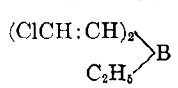
Attempts to carry these reactions to completion have been unsuccessful. The disproportionation of (2-chlorovinyl)dichloroborane when carried above 125° resulted in reduced yields of bis(2-chlorovinyl)chloroborane, a more than theoretical evolution of boron trichloride and the formation of tris-(2-chlorovinyl)borane. Presumably an exchange reaction occurs between product and reactant:

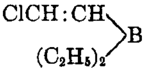

(3)

Similarly, bis(2-chlorovinyl)chloroborane when refluxed above 185° began to distill out of the reaction mixture and the product began to decompose.

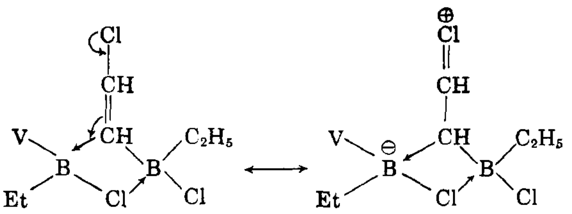
The disproportionation of (2-chlorovinyl)ethylchloroborane[4] was of interest since either a chlorovinyl or ethyl group in the intermediate could result in two different products; bis(2-chlorovinyl)ethylborane(V) or (2-chlorovinyl)diethylborane (VI) respectively. In the formation of the intermediate


$\begin{matrix}\text{ClCH:CH}\\ \text{C}_2\text{H}_5\end{matrix}\!\!>\!\text{BCl}$ (IV);


$\begin{matrix}(\text{ClCH:CH})_2\\ \text{C}_2\text{H}_5\end{matrix}\!\!>\!\text{B}$ (V);


$\begin{matrix}\text{ClCH:CH}\\ (\text{C}_2\text{H}_5)_2\end{matrix}\!\!>\!\text{B}$ (VI)

steric factors are not significant. The electrophilic boron atom would be expected to attract the chlorovinyl group in preference to the ethyl group with its high electron density. The following resonance forms would tend to stabilize the intermediate with the chlorovinyl group in the bridged position. As expected (2-chlorovinyl)ethylchloroborane disproportionated into bis(2-chlorovinyl)ethylborane and ethyldichloroborane in 90% yield.[4] It is interesting to note that although unsymmetrical trialkylboranes disproportionate readily,[9] disproportionation of bis(2-chlorovinyl)ethylborane into (2-chlorovinyl)diethylborane did not occur.



Borisov prepared (2-chlorovinyl)dichloroborane and bis(2-chlorovinyl)chloroborane by the exchange of boron trichloride with (2-chlorovinyl)-chloromercury and bis(2-chlorovinyl)mercury respectively in hydrocarbon solvents.[10] These compounds were also obtained by treating bis(2-chlorovinyl)chloroborane or tris(2-chlorovinyl)borane with boron trichloride. The redistribution of equimolar quantities of tris(2-chlorovinyl)borane and ethyldichloroborane gave approximately equivalent quantities of (2-chlorovinyl)ethylchloroborane and bis(2-chlorovinyl)chloroborane.[4] Some disproportionation occurred when (2-chlorovinyl)-dichloroborane and diethylchloroborane were refluxed together; however, (2-chlorovinyl)diethylborane was not obtained.

The 2-chlorovinyl- and 2-chlorovinylethylboranes are colorless fuming liquids which undergo rapid oxidation and hydrolysis in air. (2-Chlorovinyl)-ethylchloroborane ignites spontaneously in air while the hot vapors of all these compounds flash in the presence of oxygen.

These compounds, when treated with a 10% solution of sodium hydroxide, liberate acetylene quantitatively.

EXPERIMENTAL

Materials. Boron trichloride, technical grade (The Matheson Co.) was used directly without purification. *Acetylene*, "Prestolite" grade (Union Carbide Corp.), was freed of acetone vapor by passage through two traps at −65°.

Catalysts. Mercuric chloride on activated carbon (Davison Chemical Co.), *activated carbon*, "Columbia" brand, CXA, 4 × 6 mesh (National Carbon Co.)

Analysis. Characterization of all compounds was accomplished with the use of the following analytical tools: Infrared spectra, vapor phase chromatography, mass spectra, freezing point depression, refractive index, and wet analysis.[11]

(2-Chlorovinyl)dichloroborane (I). *Vinylation of boron trichloride.* Using the procedures described in the literature,[3,4] a 90% yield of (2-chlorovinyl)dichloroborane was obtained. The mixture was separated by fractional distillation under nitrogen, first at atmospheric pressure to remove boron trichloride and finally at reduced pressure to give the prod-

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[7] B. F. Clark, E. Gipstein, M. A. Higgins, and P. R. Kippur, U. S. Patent **2,918,498**, Dec. 22, 1959; *Chem. Abstr.*, **54**, 7560 (1960).

[8] T. D. Parsons and D. M. Ritter, *J. Am. Chem. Soc.*, **76**, 1710 (1954).

[9] P. A. McCusker, *Congr. intern. chim. pure et appl.*, **16**, Paris (1957), *Mem. Sect. chim. minerale*, 549–554 (1958); *Chem. Abstr.*, **54**, 10833 b,c (1960).

[10] A. E. Borisov, *Izvest. Akad. Nauk S.S.S.R. Odtel. Khim Nauk*, No. 4, 402–408 (1951); *Chem. Abstr.*, **46**, 2995d (1952).

[11] A detailed report of the techniques, apparatus, and methods used is to be published by H. G. Nadeau, D. M. Oaks, Jr., and R. D. Buxton in *Analytical Chemistry.*

TABLE I

DISPROPORTIONATION OF (2-CHLOROVINYL)DICHLOROBORANE

Mole $ClCHCHBCl_2$	Volume Carbon, Ml.	Final Pot Temp.	Reflux Time, Hr.	Product Composition, Mole $CClCHCH)_2BCl$	Product Composition, Mole BCl_3	Recovered Starting Material, $ClCHCHBCl_2$
1.54	20	119	14.0	0.40	0.30	0.62
3.12	150[a]	124	6.0	1.03	1.08	1.00
4.58	200	125	18.0	1.40	1.72	1.42
4.50	200[a]	123	6.0	1.14	1.78	1.56
5.00	200	134	19.4	0.98	2.63	0.72

[a] Carbon recovered from previous runs.

uct, b.p. 34° at 70 mm., d_D^{20} 1.3045, n_D^{25} 1.4768. The residue (8%) consisted primarily of bis(2-chlorovinyl)chloroborane and lesser amounts of tris(2-chlorovinyl)borane.

Bis(2-chlorovinyl)chloroborane. (a) *Vinylation of boron trichloride and (2-chlorovinyl)dichloroborane.* In the same manner above using excess acetylene, slightly increased yields (10–12%) of the di- and trisubstituted chlorovinylboranes were obtained. Excess acetylene and 342 g. (2.39 mole) of (2-chlorovinyl)dichloroborane were passed over a catalyst of mercuric chloride on activated carbon at 100° for 20 hr. Fractional distillation of the mixture under nitrogen gave 25 g. (0.15 mole) 6% yield) bis(2-chlorovinyl)-chloroborane and 8 g. (0.41 mole) tris(2-chlorovinyl)borane.

(b) *Disproportionation of (2-chlorovinyl)dichloroborane.* After refluxing (2-chlorovinyl)dichloroborane for 48 hr. no disproportionation was observed. However, activated carbon catalyzed the disproportionation. In a 1-l. round-bottom flask, (2-chlorovinyl)dichloroborane was refluxed at 100° in the presence of activated carbon through a Vigreux column and water condenser at 15–18°. The evolved vapors of boron trichloride were collected in a cold trap at −65°. When the boiling point of the mixture reached 125° heating was stopped. The mixture was cooled to room temperature under nitrogen then fractionally distilled through a 45-cm. glass helix-packed column to give bis(2-chlorovinyl)-chloroborane, b.p. 32° at 2 mm.; d_4^{20} 1.2759; n_D^{20} 1.5452; m.p. −36.9 (reported[10] for II d_4^{20} 1.2759; n_D^{20} 1.5452). A summary of these experiments is presented in Table I.

Anal. Calcd. for $C_4H_4BCl_3$: C_2H_2, 30.76; B, 6.39, Total Cl, 62.88. Found: C_2H_2, 30.70; B, 6.32; Total Cl, 62.81.

Tris(2-chlorovinyl)borane (III). (a) *Vinylation of bis(2-chlorovinyl)chloroborane.* In the usual manner 3:1 molar ratios of acetylene and bis(2-chlorovinyl)chloroborane were reacted at temperatures of 140–180°. Fractional distillation of the mixture gave only the starting material.

(b) *Disproportionation of bis(2-chlorovinyl)chloroborane.* After refluxing bis(2-chlorovinyl)chloroborane for 36 hr. with activated carbon catalyst no disproportionation occurred. Without carbon disproportionation occurred. In a 3-l.round-bottom flask fitted with Vigreux column and water condenser 609.3 g. (3.12 moles) of bis(2-chlorovinyl)-chloroborane was refluxed at 140° under an atmosphere of nitrogen. After 6 hr., the boiling point of the mixture rose to 185° and 151.8 g. (1.06 moles) of (2-chlorovinyl)dichloroborane was collected in the receiver. The reaction mixture was cooled to room temperature then fractionally distilled through a 45-cm. glass helix-packed column to give 191.4 g. (0.98 mole) (yield 63%) of tris(2-chlorovinyl)borane, *b.p.* 55° at 0.05 mm., d_{20}^{20} 1.2520; n_D^{20} 1.5570.

Anal. Calcd. for $C_6H_6BCl_3$: C_2H_2, 39.94; B, 5.53; Cl, 54.50. Found: C_2H_2, 39.90; B, 5.48; Cl, 54.44.

Thermal decomposition of tris(2-chlorovinyl)borane. In a 500-ml. round-bottomed flask fitted with Vigreux column and water condenser, 195.3 g. (1.0 mole) of tris(2-chlorovinyl)borane was refluxed at 185°. Hydrogen chloride and acetylene were evolved as the temperature rose to 226°. After 4 hr. the temperature of the mixture dropped back to 185°. The mixture was cooled and fractionally distilled to give 109.2 g. (0.64 mole) bis(2-chlorovinyl)chloroborane and 430. g. (0.22 mole) of unchanged tris(2-chlorovinyl)borane.

Bis(2-chlorovinyl)ethylborane (V). *Vinylation of (2-chlorovinyl)ethylchloroborane.* (2-Chlorovinyl)ethylchloroborane, 137 g. (1.0 mole), prepared by the method of Gipstein *et al.*[4] was reacted with 56 g. (2.0 moles) of acetylene over activated carbon as catalyst at 100°. Only the starting compound was recovered by fractional distillation.

Compound V was prepared in 90% yield by disproportionation of 2-chlorovinylethylchloroborane.[4]

(2-Chlorovinyl)diethylborane (VI). (a) *Vinylation of diethylchloroborane.* By the usual procedure 104 g. (1.0 mole) diethylchloroborane and 26 g. (1.0 mole) acetylene were passed over activated carbon for 50 hr. at 100°. Fractional distillation of the mixture gave only the starting compound.

(b) *Exchange of diethylchloroborane and (2-chlorovinyl)-dichloroborane.* Equimolar quantities, 45.0 g. (0.43 mole) diethylchloroborane and 66.5 g. (0.46 mole) (2-chlorovinyl)dichloroborane, were refluxed through a 20-inch vacuum jacketed packed distillation column and cold finger condenser for 4 hr. Fractional distillation of the mixture gave 42.8 g. (0.41 mole) of unchanged diethylchloroborane and a mixture consisting of (2-chlorovinyl)dichloroborane and bis(2-chlorovinyl)chloroborane. A very small amount of boron trichloride was collected in the cold trap at −65°. A disproportionation of (2-chlorovinyl)dichloroborane catalyzed by diethylchloroborane appears to have taken place.

(c) *Disproportionation of bis(2-chlorovinyl)ethylborane.* In a 250-ml. round-bottom flask fitted with Vigreux column and water condenser, 54 g. (0.25 mole) of bis(2-chlorovinyl)-ethylborane was refluxed at 195° for 5 hr. Fractional distillation of the mixture gave products consisting of the starting compound, bis(2-chlorovinyl)chloroborane, and tris(2-chlorovinyl)borane.

Vapor pressures of the chlorovinyl and chlorovinylethylboranes. Representative vapor tensions of these compounds

TABLE II

PHYSICAL PROPERTIES OF 2-CHLOROVINYL- AND 2-CHLOROVINYLETHYL BORANES

Compound	Vapor Pressure Constants[a] A	Vapor Pressure Constants[a] B	B.P., 760 Mm.	ΔH Vap. at B.P., (Kcal./Mole)	Trouton Constant, Cal./Deg. Mole
$ClCH{:}CHBCl_2$	1864	7.900	99	8.53	23.3
$(ClCH{:}CH)_2BCl$	2875	9.748	146[b]	13.24	32.2
$(ClCH{:}CH)_3B$	3876	8.539	226[b]	17.80	36.3
$\left.\begin{matrix}ClCH{:}CH\\ C_2H_5\end{matrix}\right\rangle BCl$	1767	5.911	134[b]	8.13	20.0
$\left.\begin{matrix}(ClCH{:}CH)_2\\ C_2H_5\end{matrix}\right\rangle B$	2529	7.373	195[b]	10.95	24.1

[a] Constants for the equation $\log_{10} p$ (mm.) $= B - A/T$.
[b] Found by extrapolation of vapor pressure equations.

were determined with an isoteniscope. The normal boiling points, the molar heats of vaporization calculated by the Clausius-Clapeyron equation, and Trouton constants were determined from these values and are given in Table II.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, ETHYL CORP.]

Bimetallic Ethyl Compounds as Reagents for the Synthesis of Tetraethyllead from Lead Metal

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Received October 10, 1960

The ethylation of lead metal by reaction with bimetallic ethyl compounds such as sodium tetraethylaluminum and an ethyl halide to produce tetraethyllead has been investigated. Tetraethyllead was obtained using sodium tetraethylaluminum, sodium tetraethylboron, sodium triethylzinc, sodium triethylaluminum fluoride, sodium triethylaluminum methoxide, and sodium ethylaluminum triethoxide as the bimetallic ethyl compounds. Optimum conditions for the reaction of lead metal with sodium tetraethylaluminum and ethyl chloride were explored.

The synthesis of tetraalkyllead by the reaction of lead metal and an alkyl halide with the alkyl derivative of a reactive metal, such as lithium, magnesium, or zinc, has been reported.[1,2] Calingaert and Shapiro also found in unpublished work that the yields of tetraalkyllead are very low when an alkylsodium compound is used. They attributed the poor yields from the alkylsodium compounds to their insolubility in the reaction media and to the tendency of the alkyl halide to alkylate the alkylsodium compound.

$$RNa + R'Cl \longrightarrow RR' + NaCl$$

More recently, it has been discovered in these laboratories that bimetallic alkyl compounds containing sodium, such as sodium tetraethylaluminum, will react with lead metal and alkyl halides to produce tetraalkyllead in high yield. The superiority of these compounds is attributed primarily metal to a reduction in the reactivity of the alkyl compounds with the alkyl halide and also to their increased solubilities.

A characteristic of the reactions of these bimetallic alkyl compounds is the reaction of one alkyl group to produce tetraalkyllead, sodium halide, and the alkyl, alkoxy, or halide compound of the second metal in the bimetallic alkyl compound. For example, sodium tetraethylaluminum reacts with lead metal and ethyl chloride to produce sodium chloride, tetraethyllead, and triethylaluminum, while sodium triethylaluminum fluoride reacts to produce sodium chloride, tetraethyllead, and diethylaluminum fluoride.

$$2NaAl(C_2H_5)_4 + Pb + 2C_2H_5Cl \longrightarrow (C_2H_5)_4Pb + 2NaCl + 2(C_2H_5)_3Al$$

$$2Na(C_2H_5)_3AlF + Pb + 2C_2H_5Cl \longrightarrow (C_2H_5)_4Pb + 2NaCl + 2(C_2H_5)_2AlF$$

This paper reports the results of an investigation of the synthesis of tetraethyllead by the reaction of lead metal and ethyl halides with bimetallic ethyl compounds. Sodium tetraethylaluminum was investigated the most extensively. Sodium tetraethylboron, sodium triethylaluminum fluoride, sodium triethylaluminum methoxide, sodium ethylaluminum triethoxide, and sodium triethylzinc also were found to be reactive but the yields of tetraethyllead were not so high as those obtained with sodium tetraethylaluminum. However, no effort was made with these last materials to define the conditions required for maximum yields. The fact that all these materials react attests to the general reactivity of such bimetallic alkyl compounds. The results are summarized in Table I.

Sodium tetraethylaluminum was found to react readily with lead metal and all the ethyl halides investigated, although the yield of tetraethyllead was less than quantitative. The limitation on yields is attributable to a deactivation of the lead metal surfaces by agglomeration of the finely divided lead metal into larger particles. A highly reactive lead metal surface is advantageous for higher yields, as shown by the relatively low yields which were obtained when lead shot (1%) and commercial lead powder (17%) were used. For this reason, the lead metal employed in the remaining experiments was synthesized by the reaction of sodium-lead alloy with ethyl chloride.

$$4NaPb + 4C_2H_5Cl \longrightarrow (C_2H_5)_4Pb + 3Pb + 4NaCl$$

The lead metal produced in this manner is highly reactive and is pyrophoric under certain conditions. Higher yields of tetraethyllead could be obtained by using an excess of sodium tetraethylaluminum, since the excess promoted complete reaction before the lead metal could become deactivated by agglomeration.

Diethyl sulfate was found to react readily with sodium tetraethylaluminum and lead metal but

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[1] H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **72**, 1760 (1950).

[2] G. Calingaert and H. Shapiro, U. S. Patents **2,535,193** (1950), **2,558,207** (1951), and **2,562,856** (1951).