Preparation of (2-Chlorovinyl)ethylchloroborane and Bis(2-chlorovinyl)ethylborane[1]

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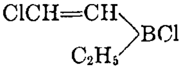
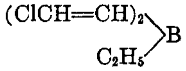
During the investigation to develop methods for the preparation of 2-chlorovinyl- and 2-chlorovinylethylboranes, (2-chlorovinyl)ethylchloroborane (I) and bis(2-chlorovinyl)ethylborane (II) were prepared for the first time. Both compounds are stable and have been fractionally distilled many times *in vacuo* without decomposition, rearrangement or disproportionation.



$ClCH{=}CH(C_2H_5)BCl$

I



$(ClCH{=}CH)_2(C_2H_5)B$

II

Compound I was prepared in two ways: (a) in 25% yield by the interaction of ethyldichloroborane and tris(2-chlorovinyl)borane[2] and (b) in 90% yield by the reaction of ethyldichloroborane with acetylene (vinylation) with activated carbon as catalyst.

Compound II was prepared in 90% yield by the thermal disproportionation of I at atmospheric pressure. Preparation of II by vinylation of I was unsuccessful.

Attempts to prepare (2-chlorovinyl)diethylborane by the interaction of diethylchloroborane and (2-chlorovinyl)dichloroborane, by vinylation of diethylchloroborane and by disproportionation of II were also unsuccessful.

EXPERIMENTAL[3]

Preparation of (2-chlorovinyl)ethylchloroborane (I). (a) *Interaction of ethyldichloroborane and tris(2-chlorovinyl)borane.* A mixture consisting of 111.0 g. (1.00 mole) of ethyldichloroborane and 195.0 g. (1.00 mole) of tris(2-chlorovinyl)borane was refluxed under nitrogen for 4 hr. in a 500-ml. round-bottomed flask fitted with reflux condenser. The mixture was fractionally distilled under nitrogen to give 34.1 g. (0.25 mole) of I, b.p. 35° at 30 mm., and 42.1 g. (0.25 mole) of bis(2-chlorovinyl)chloroborane. The unconverted starting materials were recovered.

(b) *Vinylation of ethyldichloroborane.* All vinylation experiments were performed using the following apparatus and procedures. The entire system was assembled to permit manipulation under a nitrogen atmosphere. The reaction chamber consisted of a Pyrex tube 1 inch in diameter, 30 inches long, surrounded by a heating jacket. A coarse sintered glass disk sealed into the lower end of the tube supported the catalyst which was 150 cc. of activated carbon. The liquid was fed into the reactor either by a Corson-Cerveny microbellows pump or vaporized by passage of acetylene through the liquid. The products were condensed in an ice-cooled receiver which was attached to the bottom of the reactor and by a Dry Ice–acetone condenser. At the conclusion of each experiment the pyrophoric products were fractionally distilled under nitrogen. Some typical experimental results are given in Table I.

TABLE I

VINYLATION OF ETHYLDICHLOROBORANE

Expt. No.	Temp.	Time, Hr.	Mole Ratio $C_2H_5BCl_2/C_2H_2$	Yield, %
1	70	11	1/1.5	90
2	100	11	1/1.5	90
3	130	17.5	1/1.5	50[a]

[a] The low yield is due to disproportionation of (2-chlorovinyl)ethylchloroborane to give equimolar quantities of ethyldichloroborane and bis(2-chlorovinyl)ethylborane. This disproportionation begins at a temperature of about 115°.

Anal. Calcd. for $C_4H_7BCl_2$: C_2H_2, 19.03; B, 7.91; Total Cl, 51.82; Cl on B, 25.91. Found: C_2H_2, 19.00; B, 7.80; Total Cl, 51.73; Cl on B, 25.81.

Preparation of bis(2-chlorovinyl)ethylborane (II). (a) *By disproportionation of (2-chlorovinyl)ethylchloroborane* (I). Compound I, 136.0 g. (1.00 mole), was subjected to fractional distillation at atmospheric pressure. During the disproportionation ethyldichloroborane began to distill (50.8°). When the temperature of the mixture reached 152°, a sharp rise in the temperature of the vapor occurred, indicating the completion of the disproportionation. The pressure was reduced and 85 g. (0.45 mole) of II, yield 90%, was recovered at 77–78° at 15 mm. The infrared spectrum indicated no B-Cl absorption.[3]

Anal. Calcd. for $C_6H_9BCl_2$: C_2H_2, 31.97; B, 6.64; Total Cl, 43.54. Found: C_2H_2, 31.90; B, 6.50; Total Cl, 43.56.

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

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

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

A Spectral Study of the Reaction between Iodine and *N,N*-Dimethylaniline in Cyclohexane

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Although the iodination of arylamines in aqueous medium has been extensively investigated, there is little data in the literature concerning the iodination of arylamines in nonpolar solvents. The studies reported to date of the interaction of iodine with Lewis bases in nonpolar media have been concerned with the formation of charge transfer complexes. The observation and determination of the charge transfer complex of benzene

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[1] Taken in part from a thesis submitted in partial fulfillment of the requirements for the M.S. degree.

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