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The Reaction of *cis*-1,2-Dichloroethylene with Borane in Tetrahydrofuran. The Supply of Monochloroborane in a Tetrahydrofuran Solution

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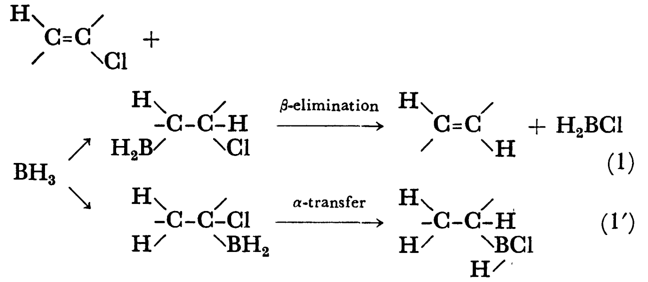
Synopsis. In the reaction of *cis*-1,2-dichloroethylene with borane in THF at 20 °C for 2 h, about 94% of borane was converted to monochloroborane. The resulting solution was stable at 0 °C for several hours.

Monochloroborane (H_2BCl), which has a strongly electronegative chlorine atom, can be expected to show some different properties from borane. For example, the boron atom of H_2BCl adds more selectively to the terminal carbon atom of 1-alkene than does borane.[1,2] The method for the preparation of H_2BCl in a THF solution includes the reaction of hydrogen chloride with BH_3 in THF[3] and the reaction of boron trichloride with BH_3 in THF.[4]

In the course of our study of the reaction using substituted boranes, we needed a less expensive, ready method for the preparation of H_2BCl in a THF solution. It has been reported that, in the hydroboration of alkenyl chloride with BH_3, the boron atom which was once introduced on to a vicinal position of chlorine atom was eliminated rapidly with the chlorine atom to form an olefinic double-bond and H_2BCl. Thus, we tried to prepare H_2BCl in a THF solution utilizing the above elimination reaction.

Polychloroethylenes, bearing chlorine atoms on both doubly bonded carbon atoms, were subjected to the reaction with BH_3 in THF in order to achieve an effective formation of H_2BCl by a β-elimination reaction (1) and to avoid an α-transfer reaction, which would prevent the formation of H_2BCl (1′).



Polychloroethylene (4 mmol) was added to BH_3 (2 mmol) in THF at 0 °C, and the solution was stirred at 20 °C. After the reaction, the solution was hydrolyzed. The amounts of residual hydride and chloroborane were estimated by measuring the volume of hydrogen gas evolved and by titrating the hydrochloric acid in the solution with a standardized aqueous 0.1 mol dm^{-3} $NaHCO_3$ solution, using Methyl Orange as the indicator. The results are shown in Table 1.

Tetrachloroethylene and trichloroethylene did not show signs of reaction having occured. However, in the cases of *cis*-1,2-dichloroethylene (*c*-DCE) and *trans*-1,2-dichloroethylene (*t*-DCE), the reaction did proceed. In these cases, it was observed that the hydrogen atom on the boron atom (hydride) was consumed in the reaction, and that nearly an equal amount of hydrochloric acid was formed on the hydrolysis of the reaction mixture. On the other hand, an appreciable amount of vinyl chloride was collected in

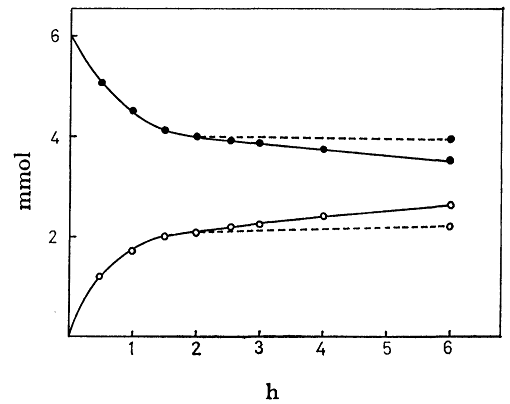


Fig. 1. The amount of hydrogen evolved and hydrochloric acid formed by the hydrolysis in the reaction[a] of *cis*-1,2-dichloroethylene and BH_3 in THF. ●: Hydrogen, ○: hydrochloric acid.
a) 4 mmol of *cis*-1,2-DCE was added to 2 mmol of BH_3 in THF.

Table 1. The reaction of polychloroethylenes or vinyl chloride with BH_3 or H_2BCl in THF at 20 °C

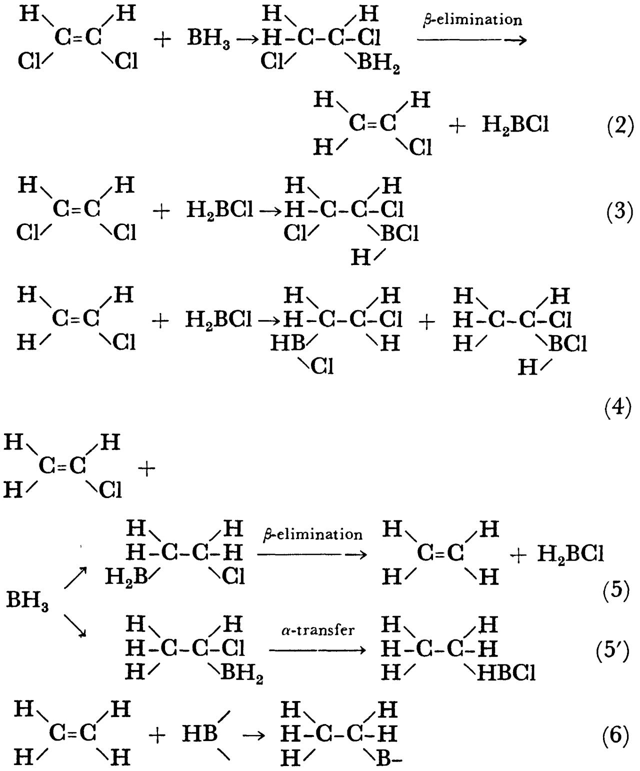
Borane 2 mmol	Chloroethylene 4 mmol	Reaction time h	Hydrogen mmol	Hydrochloric acid mmol
BH_3	Tetrachloroethylene	12	6.00	0
BH_3	Trichloroethylene	12	6.00	0
BH_3	*t*-DCE	2	4.05	2.02
BH_3	*c*-DCE	2	4.01	2.01
BH_3	*c*-DCE	6	3.44	2.52
BH_3	*c*-DCE	6[a]	3.94	2.19
H_2BCl	*c*-DCE	2	4.00	1.98
H_2BCl	Vinyl chloride	2	3.99	1.99

a) After a reaction at 20 °C for 2 h, the reaction temperature was maintained at 0 °C.

a cold trap. As *t*-DCE had the disadvantage in this operation owing to its low boiling property, *c*-DCE was employed for further examinations.

As is shown in Fig. 1, the reaction of the first of the three hydrogen atoms of BH_3 reacted rapidly, but the second and the third did so slowly. When the solution was cooled to 0 °C after a reaction at 20 °C for 2 h, at which point the first hydrogen atom of BH_3 seemed just to have been consumed, the reaction was virtually stopped, as is shown by the dotted line.

The possible reactions which occur upon the addition of *c*-DCE to BH_3 in THF are thought to be as below. However, as is shown in Table 1, H_2BCl in a THF solution, prepared from boron trichrolide and BH_3 in THF,[4] hardly reacted with *c*-DCE or vinyl chloride under the same reaction conditions (20 °C, 2 h). Accordingly, the contributions of Reactions 3 and 4 must be negligible. Thus, the source of the hydrochloric acid in the hydrolysed solution is regarded as H_2BCl formed in Reaction 2 and/or 5 and chloroethylborane formed in Reaction 5′. Further, in the reaction of *c*-DCE with BH_3 in THF at 20 °C for 2 h, 0.12 mmol of ethanol was formed by an alkaline–hydrogen peroxide oxidation. This amount corresponds to a 3% loss of the hydride, probably caused by the α-transfer reaction and/or by the hydroboration of ethylene, as is shown in Reactions 5′ and 6. On the other hand, by careful examinations of the reaction mixture and its oxidation product, no compounds were found other than vinyl chloride and ethanol.



These results show that about 94% of BH_3 is converted to H_2BCl in the present reaction. The resulting H_2BCl solution showed nearly the same properties as the H_2BCl solution (THF) obtained by the other established method.[4] For example, the ^{11}B NMR spectrum of the solution showed a triplet at −4.58 ppm (relative to boron trifluoride etherate), with $J=129$ Hz (lit,[4] −4.59 ppm, $J=131$ Hz), and no other signals which should result from BH_3 and H_2BCl[4] were observed. In addition, quite similar results were obtained, both in the yield and in the isomer distribution, on the hydroboration of 1-alkene using such a solution, prepared by a reaction at 20 °C for 2 h.

Experimental

Materials. Commercial tetrachloroethylene, trichloroethylene, *c*-DCE, and *t*-DCE were dried over molecular sieve-5A and distilled before use. BH_3 in a THF solution was prepared as has been described in the literature.[6]

Procedure. A dry, 25-ml flask equipped with a magnetic stirring bar, a septum inlet and an outlet, connected to a cold trap (−70 °C), was flushed with argon. In the flask, 2 mmol of BH_3 in THF was then placed, after which 4 mmol of *c*-DCE was introduced at 0 °C. Then the solution was hydrolyzed with 2 ml of water, and hydrogen evolved was measured by means of a gas meter, connected to an end of the cold trap. On the other hand, hydrogen chloride in the solution was titrated by the use of 0.1 mol dm^{-3} aqueous $NaHCO_3$ solution, using Methyl Orange as the indicator. The solution was then oxidized with alkaline hydrogen peroxide, and the organic layer was analyzed by GLC.

The reaction of vinyl chloride with H_2BCl was examined in a similar manner. In this reaction, a THF solution (5 ml) of vinyl chloride (6 mmol) was added to a THF solution (1.5 ml) of H_2BCl (2 mmol) prepared by the method in Ref. 4.

The ^{11}B NMR spectrum was recorded by means of a Hitachi R-20A spectrometer.

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