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Preliminary communication

The reaction of alkynes with dichloroborane ethyl etherate in the presence of boron trichloride. A simple, general synthesis of alkenyldichloroboranes

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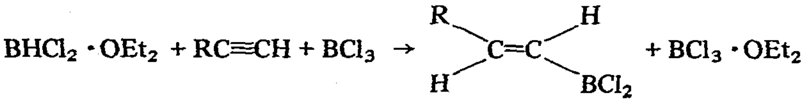
SUMMARY

The hydroboration of alkynes with dichloroborane ethyl etherate induced by boron trichloride in pentane gives alkenyldichloroboranes providing, for the first time, a simple, general synthesis of these compounds and their derivatives.

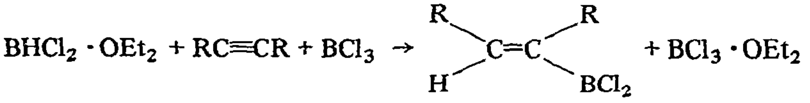
The reaction of alkynes with dichloroborane ethyl etherate ($BHCl_2 \cdot OEt_2$), neat or in pentane, gives a mixture of dialkenylchloroboranes and alkenyldichloroboranes. However, in the presence of boron trichloride, the reaction in pentane yields the alkenyldichloroboranes cleanly. The alkenyldichloroboranes are easily isolated by distillation, after separating the solution from the precipitated solid, boron trichloride ethyl etherate. Therefore, this procedure provides a simple, straightforward and general synthesis of the hitherto difficultly accessible alkenyldichloroboranes in good yields.

Alkenyldichloroboranes are not known widely. The only compound of this class reported so far is the ethenyldichloroborane which was obtained in low yield by the fractionation of a mixture of products from the reaction of BCl_3 with tetraethenyltin[1] or diethenylzinc[2]. In view of our recent work on the chemistry of vinylboron compounds[3], it is apparent that the vinyldichloroboranes and their derivatives are potentially very useful synthetic intermediates in organic and organometallic chemistry. Therefore, a simple route for the general synthesis of vinyldichloroboranes became highly desirable. We decided to explore the hydroboration route in order to develop such a procedure for the preparation of these compounds.

The reaction of 1-octyne with neat $BHCl_2 \cdot OEt_2$ is slow and incomplete at 25°. The reaction goes to near completion in refluxing pentane giving a mixture of the 1-octenyldichloroborane and bis(*trans*-1-octenyl)chloroborane. We encountered a similar difficulty previously when we treated alkenes with $BHCl_2 \cdot OEt_2$. We then circumvented the problem and obtained the desired alkyldichloroboranes cleanly, by conducting the reaction in the presence of BCl_3 in pentane solution[4]. We tried the same approach in the present case also. The presence of BCl_3 in a mixture of the alkyne and the reagent in pentane resulted in a rapid reaction giving the alkenyldichloroboranes cleanly (eqns. 1 and 2). For example, the



$$BHCl_2 \cdot OEt_2 + RC{\equiv}CH + BCl_3 \rightarrow \overset{R}{\underset{H}{>}}C{=}C\overset{H}{\underset{BCl_2}{<}} + BCl_3 \cdot OEt_2 \qquad (1)$$



$$BHCl_2 \cdot OEt_2 + RC{\equiv}CR + BCl_3 \rightarrow \overset{R}{\underset{H}{>}}C{=}C\overset{R}{\underset{BCl_2}{<}} + BCl_3 \cdot OEt_2 \qquad (2)$$

addition of $BHCl_2 \cdot OEt_2$ to a mixture of 1-hexyne and BCl_3* in pentane at 0° resulted in the precipitation of a white solid, $BCl_3 \cdot OEt_2$, on the sides of the flask. Within 15 min after the addition of $BHCl_2 \cdot OEt_2$, 93% of 1-hexyne had undergone the reaction at 0°. On warming up to room temperature, 96% of 1-hexyne disappeared and there was no active hydride left in the reaction mixture. This indicates the formation of 1-hexenyldichloroborane in 92% yield. On distillation of the pentane solution, after the separation from the solid $BCl_3 \cdot OEt_2$, the pure *trans*-1-hexenyldichloroborane was obtained. The reaction appears to be quite general. For example, no difficulty was encountered in the conversion of 3-hexyne to *cis*-3-hexenyldichloroborane in 94% yield. The results are presented in Table 1.

TABLE 1

SYNTHESIS OF ALKENYLDICHLOROBORANES BY THE HYDROBORATION OF ALKYNES WITH DICHLOROBORANE ETHYL ETHERATE INDUCED BY BORON TRICHLORIDE

Alkyne	*Product* [a]	*Yield (%)* [b]	*B.p. (°C/mm Hg)*
1-Hexyne	*trans*-1-Hexenyldichloroborane	69	66–68/18
3-Hexyne	*cis*-3-Hexenyldichloroborane	83	56–58/17

[a] The products were characterized by PMR and protonolysis followed by the identification of the olefin. [b] Isolated yield.

The reagent, $BHCl_2 \cdot OEt_2$, was prepared as described previously[4]. The synthesis of *cis*-3-hexenyldichloroborane is described as the representative procedure. A dry 300-ml round bottom flask, kept under nitrogen, was charged with 77 mmol of 3-hexyne (10% excess), 70 mmol of BCl_3 in pentane (35 ml) and 85 ml of dry pentane. The mixture was cooled in an ice bath and 70 mmol of $BHCl_2 \cdot OEt_2$ (11.2 ml) was added slowly while stirring vigorously the contents of the flask. The stirring was continued for 15 min at 0°

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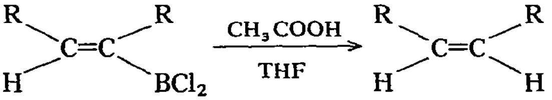
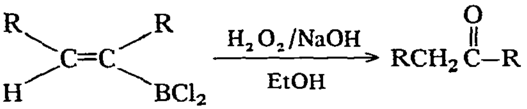
*1-Hexyne was found to be stable to BCl_3 in pentane solution at 0° for short periods of time. However, considerable destruction of 1-hexyne occurred on stirring the mixture at 25° for longer periods of time.

followed by 1 h at 25°. The contents of the flask was cooled to 0° and the pentane solution was siphoned into another flask through a glass tube fitted with fritted disc under a positive pressure of nitrogen. The solid remaining in the reaction flask was washed twice with pentane and the washings were collected along with the main solution. The pentane was then removed using a water aspirator. The *cis*-3-hexenyldichloroborane was obtained in 83% yield by distillation at 56–58° (17 mm). The product was characterized by PMR.

The alkenyldichloroboranes are protonolyzed with acetic acid to obtain the stereochemically pure olefins and oxidized with alkaline hydrogen peroxide to carbonyl compounds (eqns. 3 and 4). The vinyldichloroboranes are converted into vinylboronic acids by water and vinylboronic acid esters by alcohols. These derivatives are converted by treatment with the halogens under appropriate conditions into stereochemically pure vinyl iodides and bromides of opposite configurations[3].



(3)



(4)

The ready availability of the alkenyldichloroboranes by this simple procedure will facilitate the further exploration of the chemistry of these interesting new boron derivatives.

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