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ORGANOBORANES

XV. A SIMPLE CONVENIENT PROCEDURE FOR THE PREPARATION OF ALKYLDICHLOROBORANES VIA HYDROBORATION–REDISTRIBUTION

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SUMMARY

Trialkylboranes derived from terminal, cyclic and bicyclic olefins via hydroboration with 5 mole percent excess borane undergo ready redistribution with boron trichloride at 110° to give the corresponding alkyldichloroboranes, providing a convenient synthesis of such derivatives. On the other hand, trialkylboranes derived from internal olefins, such as 3-hexene, undergo this reaction more sluggishly and produce products in which the boron atom has migrated in part from its original position.

INTRODUCTION

The reaction of boron trichloride with trialkylboranes derived from terminal or cyclic olefins via hydroboration would appear to provide a convenient preparative route to alkyldichloroboranes (eqn. 1).

$$3\ RCH{=}CH_2 + BH_3 \rightarrow (RCH_2CH_2)_3B + 2\ BCl_3 \rightarrow 3\ RCH_2CH_2BCl_2 \quad (1)$$

Thus early workers[1,2] reported the reaction of tri-n-butylborane with boron trichloride at 200° for 20 h to produce a 74% yield of n-butyl dichloroborane (eqn. 2).

$$(n\text{-}C_4H_9)_3B + 2\ BCl_3 \xrightarrow[20\ h]{200°} \underset{(74\%)}{3\ n\text{-}C_4H_9BCl_2} \quad (2)$$

More recent studies have demonstrated the dramatic catalytic effect of hydride on the redistribution of organoboranes with boron trichloride. In this manner Köster[2,3] has reported the synthesis of ethyldichloroborane at 50° using *sym*-tetrabutyldiborane as a catalyst (eqn. 3). The authors state that higher alkyldichloroboranes may also be prepared at ca. 100° but give no experimental details. Zakharkin[4] has reported similar reactions at 125° using sodium borohydride as catalyst.

$$Et_3B + 2\ BCl_3 \xrightarrow[50°]{[n\text{-}Bu_2BH]_2} \underset{(98\%)}{EtBCl_2} \quad (3)$$

The need for representative alkyldichloroboranes in our studies led us to explore the Köster procedure. It appeared to us that the procedure could be simplified by carrying the hydroboration out with a modest excess of diborane. In this way the desired trialkylborane would be produced in the presence of a small quantity of the active catalyst, alkylboron hydride, and there would be no need to prepare and introduce the catalyst in a separate operation. This procedure was tested and proved to be both convenient and successful. The study revealed certain limitations not previously recognized on this synthetic approach to the monoalkyldichloroboranes.

RESULTS AND DISCUSSION

Tri-n-hexylborane, obtained via hydroboration of 1-hexene in THF with excess diborane, reacts at 110° in 4 h with boron trichloride (following removal of the solvent) to give n-hexyldichloroborane. Similar results were obtained for a representative series of olefins and these results are summarized in Table 1.

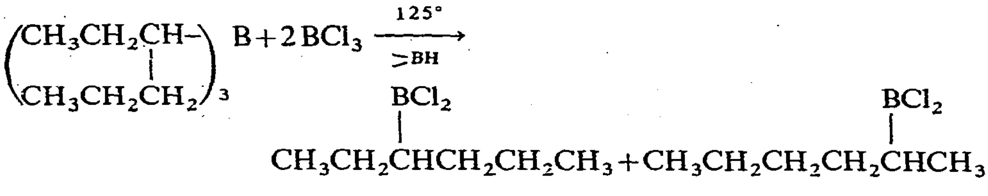
TABLE 1

THE REACTION OF OLEFINS VIA HYDROBORATION–REDISTRIBUTION TO GIVE ALKYLDICHLOROBORANES

Alkene	*Product*[c]	*B.p.* (°C)	*Yield*[b] (%)
1-Butene[a]	n-Butyldichloroborane	105–107 (lit.[5] 104–106)	75
1-Hexene	n-Hexyldichloroborane	155–158 (lit.[6] 157.2)	81
2-Methyl-1-pentene	2-Methyl-1-pentyldichloroborane	146–148	75
Cyclopentene	Cyclopentyldichloroborane	138–140	73
Cyclohexene	Cyclohexyldichloroborane	166–168 (lit.[5] 167)	80
3-Hexene	3- and 2-Hexyldichloroborane[d]	143–146	42
Norbornene	2-Norbornyldichloroborane	181–184	63

[a] In this case commercial tri-n-butylborane was used and 5 mole percent borane added as borane/THF. [b] Isolated yields. [c] All compounds were identified by spectral means, methanolysis, oxidation and comparison with known samples. [d] This reaction required a temperature of 125° for 5 hours.

Surprisingly, the 3-hexyl derivative behaved very sluggishly under the usual conditions. Even raising the temperature to 125° only resulted in an isolated yield of 42%. Furthermore, oxidation of the resultant borane with alkaline hydrogen peroxide produced a 60/40 mixture of 3- and 2-hexanol plus traces of 1-hexanol, indicating the alkyldichloroborane to be a mixture of the 2- and 3-isomers (eqn. 4).

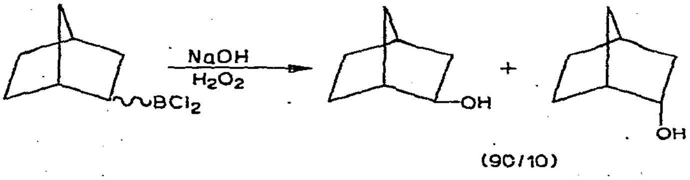


$$\left(\begin{matrix}CH_3CH_2\underset{|}{C}H{-}\\ CH_3CH_2CH_2\end{matrix}\right)_3 B+2BCl_3\xrightarrow[\mathord{>}BH]{125^\circ} CH_3CH_2\overset{\overset{BCl_2}{|}}{C}HCH_2CH_2CH_3+CH_3CH_2CH_2CH_2\overset{\overset{BCl_2}{|}}{C}HCH_3$$

(4)

Presumably the borane is undergoing partial isomerization[7] at these temperatures. The sluggishness of the redistribution reaction in this case is probably a result of the steric bulk of the secondary alkyl moiety. Similar results have been previously noted in other redistribution reactions[8].

Interestingly, the organoboranes from cyclic and bicyclic olefins undergo redistribution with little difficulty. However, oxidation of the 2-norbornyldichloroborane indicated the presence of approximately 10% of the *endo* alcohol (eqn. 5).



(5)

Since the hydroboration of norbornene proceeds to give 99.5% of the *exo* isomer[9], it is clear that isomerization to the *endo* isomer must have occurred at some subsequent stage*.

CONCLUSION

It is evident that the present development makes available a highly convenient route to certain alkyldichloroboranes. For many such derivatives this appears to be the simplest synthetic route available. For others, alternative methods are required. We are presently searching for a solution to these problems.

EXPERIMENTAL SECTION

Materials

All glassware was dried thoroughly in a drying oven, assembled hot and cooled under a stream of nitrogen. Reagent THF was dried over molecular sieves and stored under nitrogen. The borane/THF solution was prepared by the procedure of Brown and coworkers[10,11]. The olefins were distilled from $LiAlH_4$ and stored under nitrogen. Boron trichloride (Matheson, Coleman and Bell) was used directly from the tank, condensed, and measured out volumetrically at ca. 11° as a liquid, then allowed to distill into the reaction vessel as a gas. Commercial tri-n-butylborane was distilled and used without further purification. The NMR spectra were measured on a Varian T-60 NMR spectrometer in deuteriochloroform. TMS was used as an internal standard.

Preparation of alkyldichloroboranes

n-Hexyldichloroborane was prepared by adding to a dry 100 ml flask under nitrogen equipped with a magnetic stirrer, a septum inlet controlled by a Teflon stopcock, and an empty dry ice condenser, 25 ml of THF and 18.75 ml (150 mmoles) of 1-hexene. To this was added dropwise 23.0 ml (52.5 mmoles of BH_3) of a 2.39 *M*

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* The isomerization of tri-*exo*-norbornylborane to the *endo* moiety in the presence of excess diborane has recently been established in these laboratories by Dr. G. Srinivasan.

solution of borane in THF. After allowing the solution to cool, the THF was removed under vacuum produced by a water aspirator. The resulting organoborane was heated to 110° and the condenser filled with dry ice. To the rapidly stirred borane was added 10.6 ml (120 mmoles) of boron trichloride at a rate adequate to maintain the temperature at 110° (approximately 2 h). The solution was stirred for an additional 2 hours and 4 ml of a low boiling olefin such as 1-hexene or cyclopentene was added to the hot reaction mixture to destroy residual hydride. The reaction mixture was cooled and the condenser replaced with a distillation apparatus containing a 6″ Vigreux column. Distillation at atmospheric pressure gave 20.2 g (81%) of n-hexyldichloroborane, b.p. 156–158° (lit.[6] 157.2°). 2-Methyl-1-pentyl, cyclopentyl, cyclohexyl and norbornyldichloroborane were prepared identically to the above. n-Butyldichloroborane was prepared from commercial tri-n-butylborane using a 5% excess of hydride added as BH_3/THF in identical fashion to the above procedure. The 3- and 2-hexyldichloroboranes required temperatures of 125° for 5 hours. Otherwise this reaction was run identically to the above.

Oxidation of alkyldichloroboranes

To a dry 25 ml flask equipped with a magnetic stirring bar, reflux condenser and septum inlet, under nitrogen atmosphere, was added 10 mmoles of the alkyldichloroborane. To this was added 5 ml of THF and 30 ml of 3 *N* NaOH (*caution*: exothermic). Finally, 10 mmoles of 30% hydrogen peroxide was added and the solution was heated to 50° for 20 minutes. After cooling the aqueous layer was saturated with potassium carbonate and the organic layer analyzed for the alcohols on a 12′ Carbowax 20M column, or in the case of norbornyl, by NMR of the isolated material.

Methanolysis of alkyldichloroboranes

To a dry 10 ml flask equipped with a reflux condenser and septum inlet was added 5 mmoles of the dialkylchloroborane and 0.394 ml (10 mmoles) of methanol (*caution*: exothermic). After the liquid cooled, the dimethoxyboronates were analyzed by NMR in $CDCl_3$ and compared to known samples. The crude purity was typically approximately 95% by NMR.

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