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Preliminary communication

FACILE DISPLACEMENT OF TETRAMETHYLETHYLENE FROM THEXYLBORANE-TRIETHYLAMINE BY TREATMENT WITH OLEFINS. A CONVENIENT SYNTHESIS OF MONOALKYLBORANE DERIVATIVES

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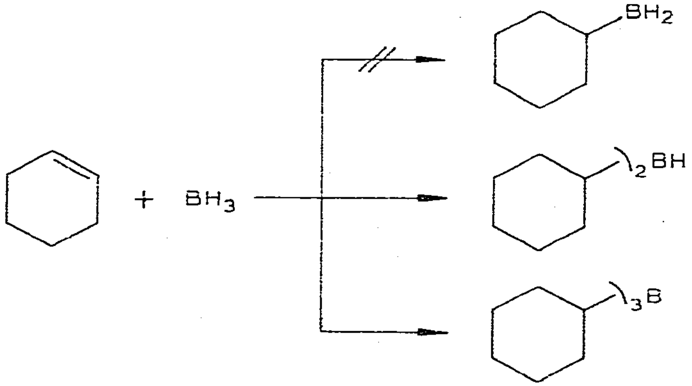
Summary

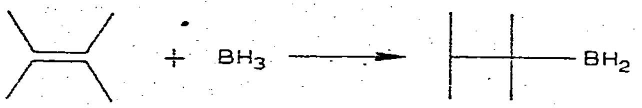
The reaction of thexylborane-triethylamine with representative olefins proceeds readily at 25° with the displacement of tetramethylethylene (TME) and the formation of the corresponding monoalkylborane-triethylamine adduct. This reaction provides a convenient synthesis in high yield of such monoalkylboranes and their derivatives.

Hydroboration of olefins with borane—THF [1] or borane-methyl sulfide [1] generally proceeds rapidly past the monoalkylborane stage to the dialkylborane or trialkylborane stage [2,3]. Consequently, it is generally not possible to synthesize monoalkylboranes by the direct reaction of olefins with borane (eq. 1).



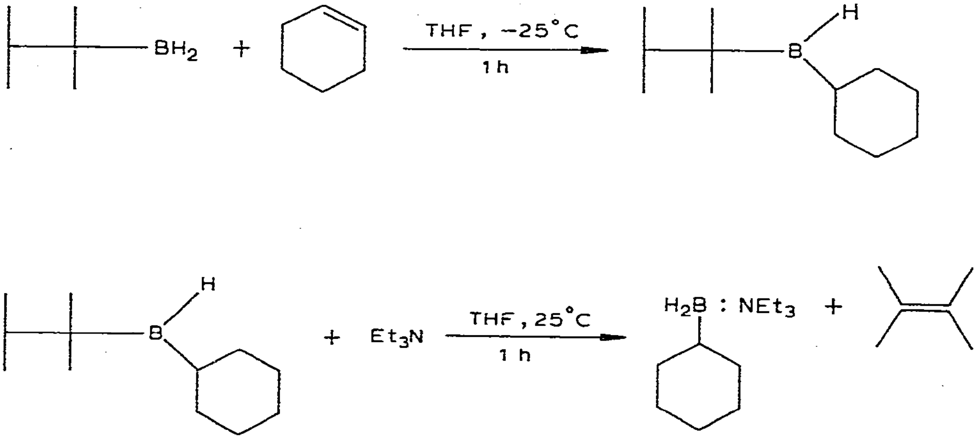
(1)

Only in the case of certain highly hindered olefins, such as tetramethylethylene (TME) is it possible to control the hydroboration so as to achieve the synthesis of the monoalkylborane [2]. In this way, thexylborane is readily prepared [4] (eq. 2).



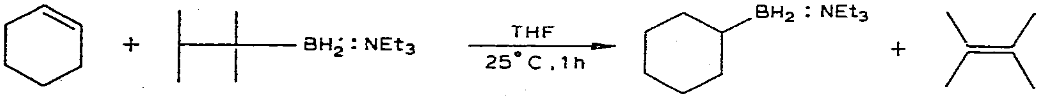
(2)

Thexylborane has made possible a two-step synthesis of monoalkylborane—triethylamine, from which the monoalkylborane can readily be obtained [4] (eq.3).



(3)

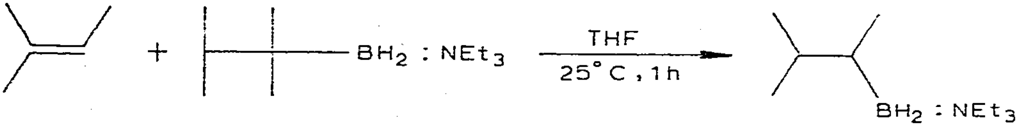
In the course of studies directed to other objectives, we observed that at 25° many olefins react rapidly, within one hour, with thexylborane—triethylamine to displace TME, giving the monoalkylborane—triethylamine directly. Thus, cyclohexene reacts to give the monocyclohexylborane derivative (eq. 4).



(4)

By removing the THF and TME under vacuum, the monoalkylborane—triethylamine adduct is readily recovered in yields of >90%. This development opens up a simple direct route to the monoalkylboranes and their derivatives.

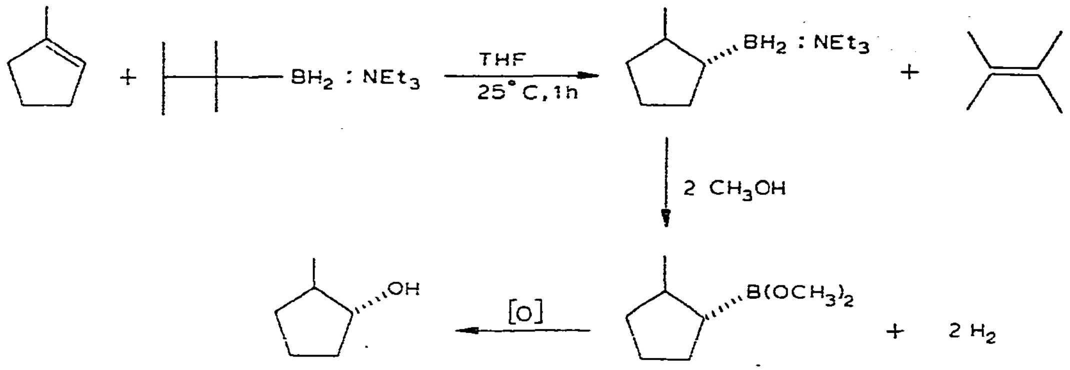
The reaction proceeds quite satisfactorily with 2-methyl-2-butene to yield monosiamylborane-triethylamine (eq. 5).



(5)

In the case of 1-methylcyclopentene, the product is the pure *trans* isomer (eq. 6), as established by oxidation of the methanolyzed product with alkaline hydrogen peroxide to pure *trans*-2-methylcyclopentanol.

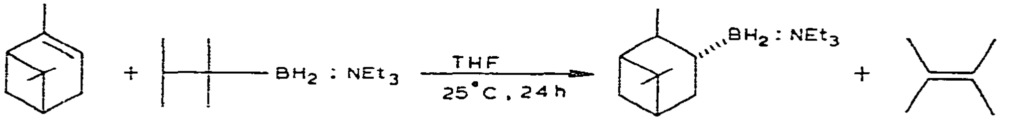
The reaction with 1-methylcyclohexene proved to be considerably slower. In 1 h, there is 50% residual thexylborane. The reaction is complete in 48 h



(6)

(utilizing four moles of triethylamine), but even here there is present in the product 7% of residual thexylborane, indicating the presence of 7--14% of bis(*trans*-2-methylcyclohexyl)-borane. Indeed, a precipitate is observed, presumably this highly insoluble by-product.

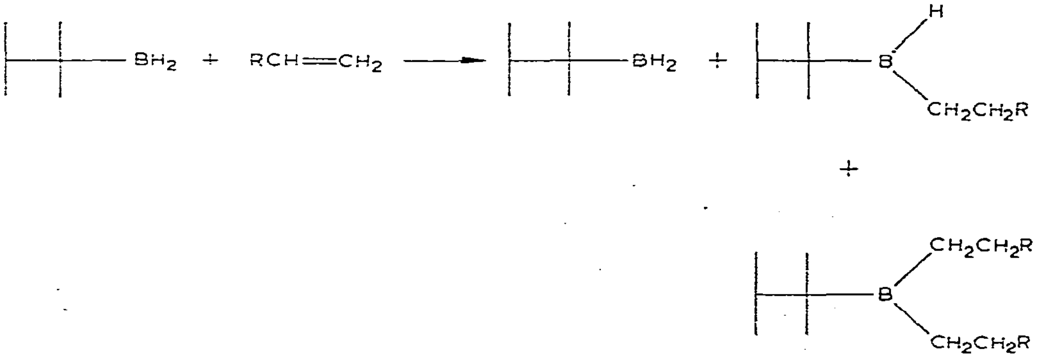
The reaction with α-pinene is also slow, showing 32% of residual thexylborane-triethylamine after 3 h. However, after 24 h, removal of the volatiles gives a product whose oxidation, following methanolysis, reveals the presence of only 3% of thexyl alcohol and 97% of isopinocampheol (eq. 7).



(7)

It is probable that the present one-stage synthesis proceeds through the two reactions shown in eq. 3. However, the present process works satisfactorily even in cases where the two-stage process has proved unsatisfactory. Thus, the reaction of α-pinene with thexylborane does not proceed cleanly [4]. Yet the present synthesis provides an excellent route to monoisopinocampheylborane—triethylamine.

It was previously established that the reaction of simple 1-alkenes with thexylborane is not simple and does not lead to the formation of the desired thexylmonoalkylboranes (eq. 8).



(8)

On this basis, there appears to be little prospect of utilizing this procedure for the synthesis of simple monoalkylboranes of this type and we did not explore this possibility.

The following procedure is representative. All operations were carried out under nitrogen [1]. A solution of thexylborane in THF was prepared by adding 5.9 ml of TME (50 mmol) to 20 ml of a 2.5 *M* solution of $BH_3 \cdot THF$ (50 mmol) at 0°C, following the standard procedure [1,4]. To this solution, maintained at 0°C, was added 14.0 ml of triethylamine (100 mmol, 100% excess), providing a 1.25 *M* solution of $ThexBH_2:NEt_3$ in THF. This solution was brought to 25°C and to it was added 5.0 ml of cyclohexene (50 mmol). The reaction mixture was stirred at 25°C for 1 h. The TME and THF (with the excess of triethylamine) were removed under the vacuum of an aspirator (15 mm Hg). Monocyclohexylborane—triethylamine was obtained as a colorless viscous liquid. Oxidation of the methanolyzed product with alkaline hydrogen peroxide provided a GLC analysis of 100% cyclohexanol and 3% thexyl alcohol. This analysis indicates the presence in the product of 94% monocyclohexylborane, 3% dicyclohexylborane, and 3% thexylborane.

The product can be used to hydroborate other olefins to produce mixed trialkyl- or dialkyl-boranes [4]. Alternatively, it can be treated with boron trifluoride to provide the free monoalkylborane [5]. Treatment with methanol, followed by distillation, provided 6.15 g of dimethylcyclohexylboronate, b.p. 72—73°C at 15 mmHg (lit. [4] 75—76°C at 17 mmHg), a yield of 79%.

Conclusion

The present development opens up a convenient synthetic route to the monoalkylborane-triethylamine adducts and to the many derivatives into which these can be transformed.

Acknowledgement

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5 Research in progress with A.K. Mandal.