

THE DIRECT PRODUCTION OF MONOISOPINOCAMPHEYLBORANE BY THE
REDISTRIBUTION OF DIISOPINOCAMPHEYLBORANE WITH BORANE

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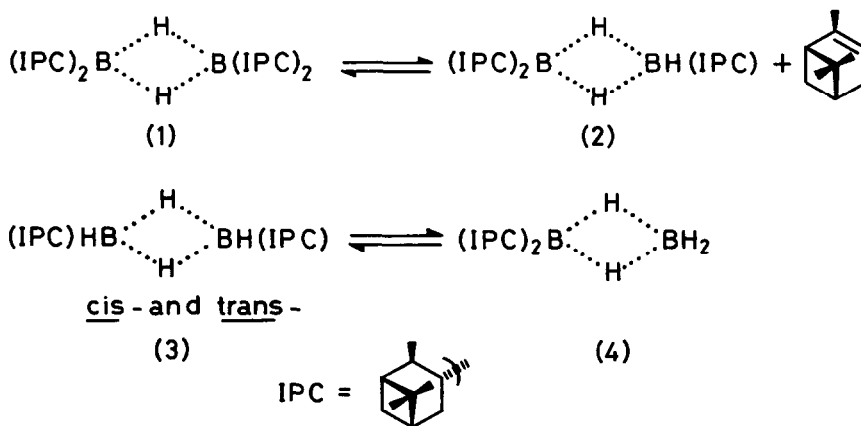
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Two simple and direct methods are outlined for the production of
monoisopinocampheylphenylborane, a valuable chiral hydroborating agent.

The introduction of generally applicable chiral reagents is a matter of the greatest importance for the future of organic synthesis. The chiral hydroborating agent, tetraiso-pinocampheyl-diborane (1)* is readily available from the reaction of $\text{BH}_3 \cdot \text{THF}$ and optically active α -pinene.¹ It reacts with cis-disubstituted alkenes with excellent chiral induction but with even moderately hindered alkenes it reacts in a complex fashion involving the displacement of α -pinene, to give species such as (2). As a result, the degree of chiral induction is dramatically lowered.²

It has therefore been a matter of high interest to synthesis sym-diisopinocampheyl-diborane (3), or its monomer stabilised as a complex, to test whether or not it would react rapidly and with chiral induction with alkenes that react with (1) with difficulty. Moreover as a bifunctional hydroborating agent it may be used to hydroborate dienes to yield boracyclic compounds which can be converted to carbocycles. As with other dialkylboranes,³ it is to be expected that (3) will exist in equilibrium with (4), and also that (4) will be a relatively poor chiral hydroborating agent.



The reaction of α -pinene with $\text{BH}_3 \cdot \text{THF}$ in equimolar proportions (the "1:1 reagent")

* For convenience, in the text monomeric structures such as $(\text{IPC})_2\text{BH}$ will be used where applicable.

From this work two convenient procedures for the preparation of $(IPC)_2BH$ have emerged, together with two alternative methods for its utilisation for hydroboration. In each procedure equimolar proportions of $BH_3 \cdot THF$ and (+)- α -pinene (ca 93% optical purity) are mixed together in THF so that the solution is 0.7M in both reagents. In the first procedure the reagents are mixed at 25° and the solution set aside for a period. The result of one such study is shown in Table 1.

Table 1.

Ratios of BH_3 , $(IPC)BH_2$ and $(IPC)_2BH$ obtained by equilibration at 25°C of equimolar proportions of borane and α -pinene in THF.

Time (h)	BH_3	$(IPC)BH_2$	$(IPC)_2BH$
24	13.80	72.40	13.80
48	8.25	83.50	8.25
76	5.65	88.70	5.65
96	4.75	90.50	4.75
120	4.50	91.00	4.50

About 96h. would seem to be a convenient optimum time. Alternatively the solution may be heated to 50°C for 3½ - 4h, after which time the mixture contains ca 86% $(IPC)BH_2$ (average of six runs.)

The THF is removed at the pump and replaced by pentane. Addition of the appropriate amount of tetramethylethylenediamine (TMEDA) equivalent to the $BH_3 \cdot THF$ present leads to precipitation of $TMEDA \cdot 2BH_3$. This complex is not an active hydroborating agent and if direct hydroboration is envisaged it need not be removed from the supernatant, which contains >95% $(IPC)BH_2$ for the room temperature equilibration and 92.5% $(IPC)BH_2$ for the 50°C equilibration. Moreover, at the temperature used for hydroboration, $(IPC)_2BH$ reacts extremely slowly with trisubstituted alkenes so that the alkene reacts essentially only with the $(IPC)BH_2$ present. Hydroboration of 1-methylcyclopentene with a mixture produced by equilibration at 50° gave, after oxidation, trans-2-methylcyclopentanol of 74.9% optical purity (corresponding to 80.5% optical purity if optically pure α -pinene had been used.)

A different procedure is to filter off the $TMEDA \cdot 2BH_3$ and then add sufficient TMEDA to bring out $TMEDA \cdot 2(IPC)BH_2$ as a white solid m.p. 139 - 40° (ex. Et_2O).¹² For hydroboration the solid complex may be dissolved in THF and sufficient quantity of $BF_3 \cdot Et_2O$ added to completely generate $(IPC)BH_2$. The hydroboration of 1-methylcyclohexene for 2.5h at 0°C with the resultant mixture, followed by oxidation, gave 71.5% optically pure trans-2-methylcyclohexanol (equivalent to 76.8% optical purity using pure (+)- α -pinene.)

Monoisopinocampheylborane is now a readily available chiral hydroborating agent. It should find wide synthetic application for the hydroboration of those alkenes that react slowly, or not at all, with (1). Other applications of the reagent for asymmetric reductions are under investigation.

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