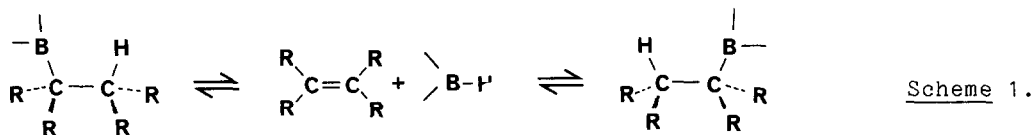


THE STEREOCHEMISTRY OF THE HYDROBORATION REARRANGEMENT.¹

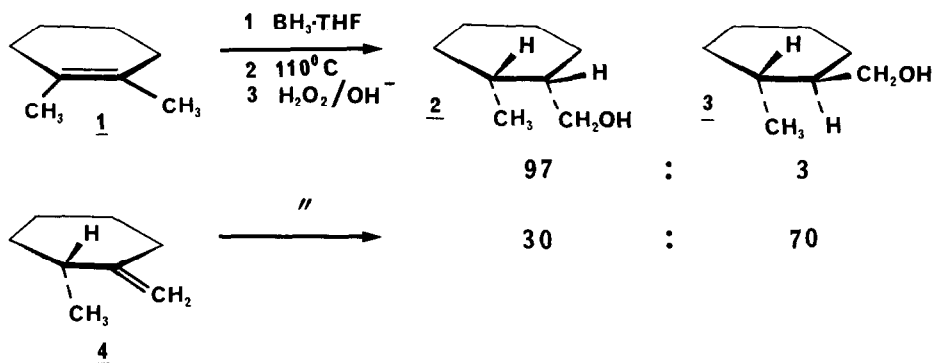
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Abstract : Hydroboration of 1,2-dimethylcyclopentene with $\text{BH}_3 \cdot \text{THF}$ affords a product in which boron migrates stereospecifically at low temperature into the cyclopentane ring. At higher temperatures subsequent (non-stereospecific) isomerisation occurs via a competing reaction mechanism.

Alkylboranes rearrange (on heating) to thermodynamically more-stable alkylboranes, typically with the boron atom attached to the sterically least hindered position on the alkyl chain. Brown et.al.²⁻⁶ have proposed that the hydroboration rearrangement proceeds by a series of reversible borane addition/elimination (ie. hydroboration/dehydroboration) steps involving an alkene intermediate (Scheme 1). There is strong precedent for such a mechanism since it is well established that alkylboranes intermolecularly exchange alkyl groups with free alkenes even under moderate conditions⁶⁻⁸.

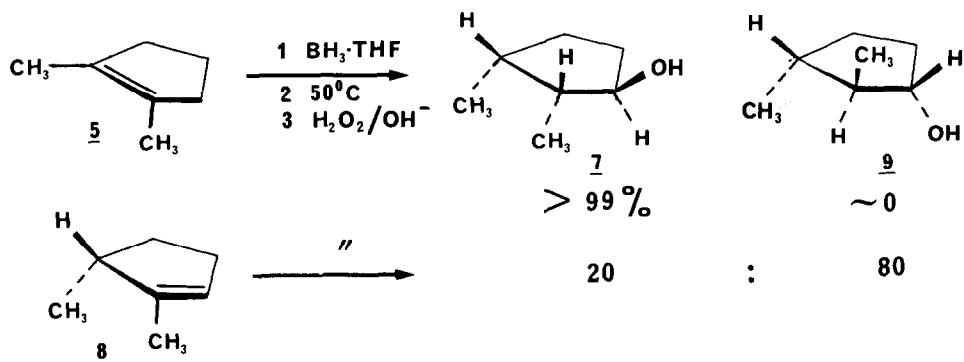


Rickbourne and Wood⁸ reported exceptionally high stereospecificity in the thermal rearrangement of the organoborane formed on in-situ hydroboration of 1,2-dimethylcyclohexene, 1. Under the conditions of their experiment (110°, THF solution) the rearrangement proceeded to give the primary alcohols 2 and 3 (after oxidative work-up) in the ratio 97:3. In contrast, direct hydroboration of the exocyclic olefin 4 (under the same experimental conditions) afforded 2 and 3 in the ratio 30:70, respectively. This result suggested that 4 could not be a discrete intermediate in the hydroboration rearrangement of 1 and that perhaps an intermediate which more stringently controlled the stereochemistry of the rearrangement eg. an olefin-boron π -complex^{9,10} or a three-centered intermediate¹¹⁻¹⁵ could be implicated.



Williams¹⁵ had earlier proposed boron migration in alkylboranes via B-C-H hydrogen-bridged intermediates by analogy with the mechanism of bridge-hydrogen tautomerism which is frequently observed in polyboranes and carboranes in solution. We report here the extremely facile stereospecific rearrangement of the organoborane obtained on hydroboration of 1,2-dimethylcyclopentene.

On treatment of 1,2-dimethylcyclopentene, 5, with excess (1.2 equivalents) of $\text{BH}_3\cdot\text{THF}$ at 25°C , for 5 minutes, the expected tertiary alcohol, 6, was obtained following an oxidative workup ($\text{H}_2\text{O}_2/\text{OH}^-/\text{H}_2\text{O}$ under N_2). If however the reaction mixture was left to stand for an extended period (several days) at room temperature or was heated to 50°C for ca. 2 hours, a single product, 7, resulting from stereospecific boron migration into the 5-membered ring was obtained in high yield ($> 90\%$). Products resulting from boron migration to the exocyclic carbon could be detected by NMR spectroscopy and GLC but constitute $< 1\%$ of the total product. Hydroboration of the potential intermediate, 1,5-dimethylcyclopentene, 8, under identical conditions afforded the alcohols 7 and 9 in the ratio 20:80 (ie. with 7 as the minor product) whilst 2-methylmethylenecyclopentane afforded solely the expected primary alcohols.



The progress of the rearrangement was monitored by removing aliquots from the reaction mixture and analysis by GLC following an oxidative work-up (Figure 1). The products resulting from the initially-formed tertiary borane decreased exponentially and the rate of rearrangement was independent of the concentration of $\text{BH}_3\cdot\text{THF}$ in the reaction mixture (at least over the range alkene:borane ratios ranging from 1.0 to 6.0).

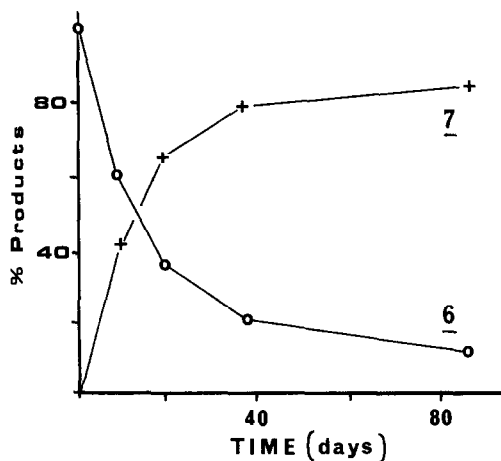


Figure 1 Products obtained on hydroboration of 5 with $\text{BH}_3\cdot\text{THF}$ (1.8 M, 1.2 equiv.) at 20°C .

When 1,2-dimethylcyclopentene was treated with $\text{BH}_3\cdot\text{THF}$ (1.2 eq.) at a higher temperature (110°C), 7 was formed rapidly but subsequently isomerised to 9. The ratio of 7:9 eventually matched that obtained by direct hydroboration of 1,5-dimethylcyclopentene and this is presumably the thermodynamic product ratio under the reaction conditions (Figure 2).

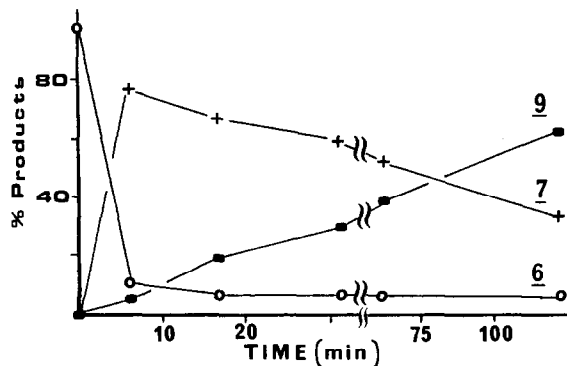


Figure 2 Products obtained on hydroboration of 5 with $\text{BH}_3\cdot\text{THF}$ (1.8 M, 1.2 equiv.) at 110°C .

The above results (taken with those of Rickbourn and Wood^{7,8}) suggest that the hydroboration rearrangement can proceed by two independent (and competing) mechanisms. Under mild conditions, a stereospecific boron migration leads to rearranged products with retention of configuration at the carbons at the migration origin and the migration terminus. At higher temperatures, a thermodynamic mixture of products is obtained, presumably via the accepted hydroboration/dehydroboration mechanism.

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