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Preliminary communication

OLEFIN—ALKYL GROUP EXCHANGE OF *B*-ALKYL-9-BORABICYCLO[3.3.1]NONANES. EVIDENCE FOR A DEHYDROBORATION—HYDROBORATION PROCESS

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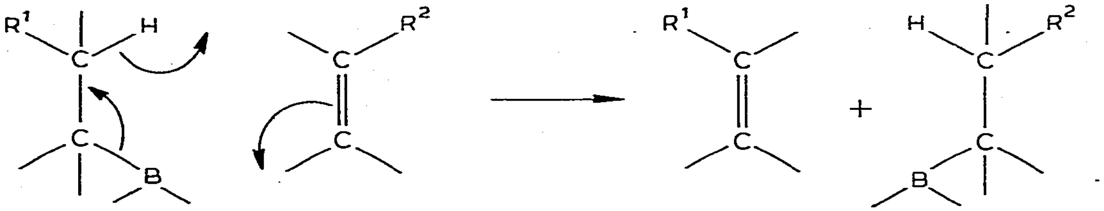
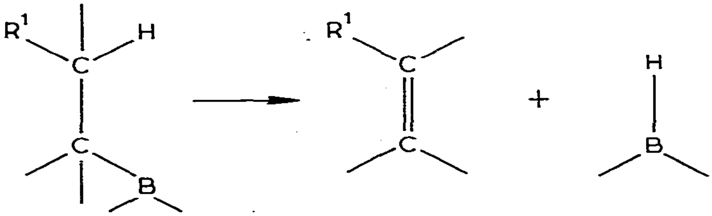
Summary

B-Alkyl-9-borabicyclo[3.3.1]nonanes (9-BBN) undergo a rather facile olefin—alkyl group exchange process when refluxed with an olefin in tetrahydrofuran. Kinetic and competition studies support a dehydroboration—hydroboration process.

Trialkylboranes are known to undergo an olefin—alkyl group exchange when heated with an olefin at elevated temperature (130—160° C) [1]. Two mechanisms have been postulated for this reaction. The first process involves a cyclic or concerted pathway [1a,b]:



The second postulated mechanism involves a two step dehydroboration—hydroboration process [1c—1e]:



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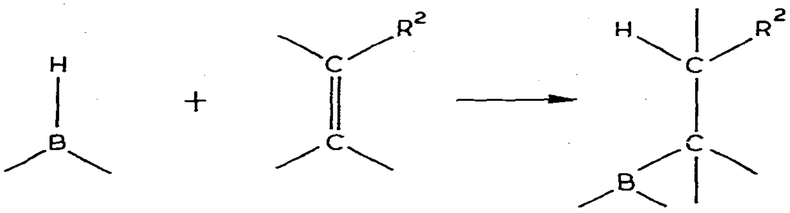

These two processes are analogous to the proposed mechanisms for the dealkylation of organoboranes by aldehydes. Mikhailov has proposed [2] and we have amply demonstrated [3] that the aldehyde dealkylation reactions occur by the cyclic process. The situation in the case of olefin—alkyl group exchange reaction is less clear. Evidence for a cyclic process for the exchange reaction includes the absence of B—H bonds in the reaction mixture, a greater selectivity for primary alcohol products from styrene and *p*-chlorostyrene during hydroboration than from olefin—alkyl group exchange, and retardation of the rate by a factor of two when the reaction is diluted fourfold [1a,1b]. On the other hand others [1d,1e] have found no effect on the rate by increasing the concentration of olefin. A fourfold decrease in concentration should lead to a much greater decrease in the rate for the bimolecular process. The discrepancy in product distributions could be explained by the fact that the hydroborations were done at room temperature while the exchange reaction was done at 130°C.

Previous investigations have been complicated by the fact that more than one alkyl group on boron may participate. As the reaction proceeds the original trialkylborane is converted into a mixed trialkylborane. Our observation that only the *B*-alkyl group of 9-BBN participates in the reaction with aldehydes [3] suggested that *B*-alkyl-9-BBN compounds might offer a simple method for studying the exchange process. However, it is reported that *B*-alkyl-9-BBN compounds are thermally quite stable [4]. We were thus surprised to find that these compounds do indeed undergo an exchange reaction under rather mild conditions. Furthermore, analysis of the products after oxidation gave no evidence for participation by the cyclooctyl portion of 9-BBN since there was a quantitative recovery of 1,5-cyclooctanediol. We have thus investigated further the details of this reaction.

Various *B*-alkyl-9-BBN compounds were refluxed in tetrahydrofuran with an olefin. The reactions were followed by monitoring the olefinic region of the NMR spectra or by VPC analysis. The results are presented in Table 1. In each case for a particular organoborane the initial reaction rate is essentially independent of the olefin structure. However, the half life of the reaction may vary as the reaction approaches equilibrium. For example the reactions of *B*-3-pinanyl-9-BBN with 1-octene, 2-methyl-1-pentene, cyclohexene and 1-methylcyclohexene proceed to 90, 90, 75 and 55% completion respectively. We thus concentrated on the less hindered olefins. The half life for the styrenes is slightly shorter than normal due to a small loss of styrene during the prolonged reactions.

The reaction rates do vary with the structure of the *B*-alkyl-9-BBN. The *B*-3-pinanyl-9-BBN is fast. The exceptional reactivity of this borane may reflect a relief of steric strain in the starting material. It should be noted that tetraiso-

TABLE 1

THE OLEFIN—ALKYL GROUP EXCHANGE OF *B*-ALKYL-9-BBN COMPOUNDS

B-Alkyl-9-BBN[a]	Olefin	$t_{1/2}$ (min)[b]
3-Pinanyl	1-Octene	500
	2-Methyl-1-pentene	540
	Cyclohexene	640
	1-Methylcyclohexene	1400
trans-2-Methylcyclopentyl	1-Octene (2 *M*)	6030
	1-Octene (0.5 *M*)	6360
	2-Methyl-1-pentene	5000
	Styrene	3630
	p-Methoxystyrene	4000
3-Methyl-2-butyl	1-Octene	5000
	2-Methyl-1-pentene	6000

[a] All reactions 1.0 *M* in *B*-alkyl-9-BBN and olefin unless otherwise indicated. [b] Time for 50% completion of the reaction.

pinocamphyldiborane is exceptionally prone to undergo dehydroboration [5]. However, that reaction is probably hydride catalyzed.

The reaction of *B*-3-pinanyl-9-BBN with 2-methyl-1-pentene followed first order rather than second order kinetics. In further support of the first order kinetics, the half life for the reaction of *B-trans*-2-methylcyclopentyl-9-BBN with 1-octene did not change appreciably on changing the concentrations from 2.0 *M* to 0.5 *M*.

Styrene and *p*-methoxystyrene may be distinguished kinetically by hydroboration with 9-BBN. At room temperature the *p*-methoxystyrene reacts 14 times faster [6], while in refluxing tetrahydrofuran it is 2.4 times faster. These two olefins react individually with *B-trans*-2-methylcyclopentyl-9-BBN at approximately the same rate. However, when an equimolar mixture of the two olefins is allowed to compete for either the *B-trans*-2-methylcyclopentyl- or *B*-3-methyl-2-butyl-9-BBN, the hydroboration product of *p*-methoxystyrene appears approximately 2.5 times faster than the styrene product. These results are consistent with a rate-determining dehydroboration followed by a product-determining hydroboration step.

Finally the reaction mixture of 2-methyl-1-pentene with *B*-3-pinanyl-9-BBN was oxidized and the 2-methyl-1-pentanol isolated. The alcohol had an optical rotation of $[\alpha]_D^{25}$ + 0.02 (lit. [7] $[\alpha]_D^{29}$ 12.9). The small observed rotation could be due to a trace of chiral impurity. The *B*-3-pinanyl-9-BBN has previously been shown to be an extremely effective asymmetric reducing agent in a reaction which proceeds through the cyclic mechanism [8]. Although the lack of optical purity in the present reaction does not exclude the cyclic process, it certainly is in accord with the dehydroboration—hydroboration mechanism.

In conclusion the data indicate that the concerted mechanism plays little if any role in the olefin—alkyl group exchange reaction of *B*-alkyl-9-BBN compounds. While the reaction is usually slow, certain structural features can greatly enhance the reactivity. Since the *B*-alkyl-9-BBN reagents are useful enantioselective [8] and chemoselective [9] reducing agents via a cyclic process, the rate of dehydroboration places an important lower limit on the reactivity of substrates. As the rate of reaction approaches the dehydroboration rate, competing reduction by 9-BBN may begin to interfere. Finally the reversibility of the olefin exchange may allow one to obtain thermodynamic equilibrium data to compare to kinetic data [10].

Acknowledgements

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