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Preliminary communication

AN UNUSUALLY FACILE DEHYDROBORATION OF TRIORGANOBORANES FORMED BY TREATMENT OF ALKENYLTRIALKYLBORATES WITH HYDROCHLORIC ACID

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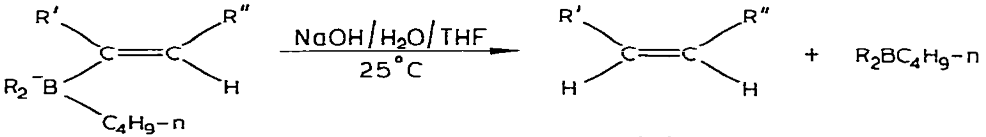
Summary

In contrast to the base hydrolysis of alkenyltrialkylborates(I) which involves a straightforward cleavage of the alkenyl carbon—boron bond, treatment of I with hydrochloric acid produces predominantly an olefin formed via the migration of an alkyl group from the boron atom to the alkenyl α carbon atom followed by an unprecedentedly facile dehydroboration of the trialkylborane intermediate.

We have recently found that the hydrolysis of alkenyltrialkylborates (I) with aq. sodium hydroxide produces the corresponding alkenes (II) in excellent yields, thereby providing a mild non-acidic procedure for the cleavage of alkenyl carbon—boron bonds [1] (eq. 1).

In marked contrast to these results, the hydrolysis of I under either neutral or acidic conditions yielded higher boiling olefins. Typically, treatment of lithium 5-decenylbis(3-methyl-2-butyl)(n-butyl)borate (III) with hydrochloric acid (1 *N*) at 25°C produced within several hours an 86% yield of 2,3-dimethyl-4-n-butyl-3-nonene (IV), ^{1}H NMR (CDCl$_3$, TMS) δ 0.6—1.0 (m with



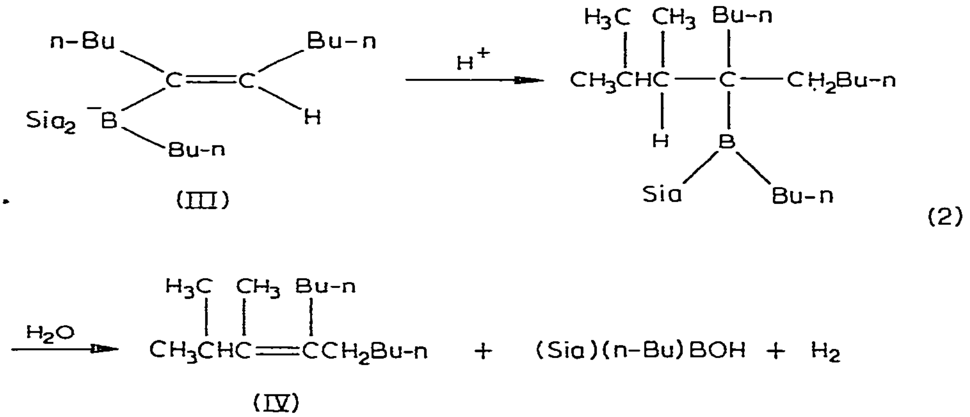
(1)

(I)

(II)

R, R', R'' = alkyl

peaks at 0.87 and 0.97 ppm, 12H), 1.0—1.6 (m with peaks at 1.27 and 1.49 ppm, 13H), 1.6—2.2 (m, 4H), and 2.81 (h, *J* 7Hz, 1H); Mass (70 eV) *m/e* 210 (M^+) (M:M+1:M+2 = 100:18:2); n_D^{23} 1.4538, and only a minor amount (< 5%) of 5-decene. The reaction was accompanied by a smooth evolution of a gas (presumably hydrogen, 95% based on eq. 2). After oxidation with 3 *N* sodium hydroxide and 30% hydrogen peroxide, 1-butanol and 3-methyl-2-butanol were obtained quantitatively (based on eq. 2) along with traces (< 2%) of 5-decanone and a few unidentified high boiling products. These results are consistent with the scheme shown in eq. 2. No other plausible schemes appear available.



(2)

Sia = $(CH_3)_2CH(CH_3)CH$

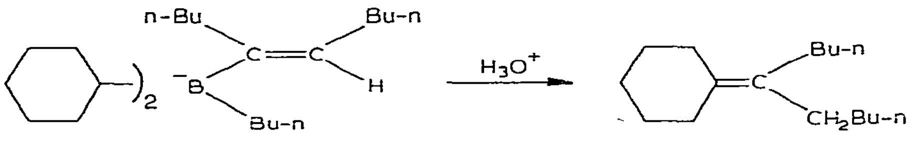
The results are unexpected in light of a recent publication [2] describing the reaction of similar alkenylborates with ethereal hydrogen chloride to produce carbinolic products in high yields. In fact, no mention of the dehydroboration of organoborane intermediates has been made in any of the previously reported studies of the acid treatment of alkenylborates [2] or alkynylborates [3]. To our knowledge, no previously known trialkylborane has exhibited such an extensive dehydroboration under these mild conditions, although hindered dialkylboranes which normally exist as dimers are known to undergo facile dehydroboration [4].

Similar results were obtained with V and VI. The assigned structures of the products are in agreement with their spectral properties (IR, ^{1}H NMR, and mass spectroscopy).

As demonstrated by these examples, the dehydroboration is highly regioselective in that the most substituted olefin is formed nearly exclusively. Another noteworthy feature is the preferential migration of the most hindered group in agreement with the previously reported results [2].

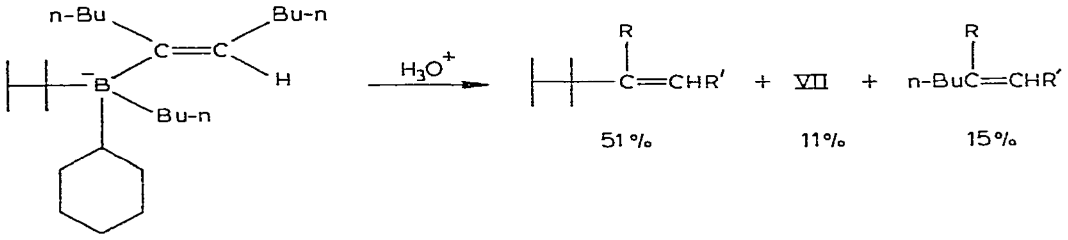
Further support for the intermediacy of trialkylboranes has been obtained in the acid hydrolysis of VIII and IX.

The reaction of VIII with 1 *N* hydrochloric acid over 16 h at 25°C produced, after oxidation, 1,2-dicyclohexylethanol as the major product (44%) along with cyclohexylethylene (37%) and only a small amount of 1-cyclohexyl-2-cyclo-



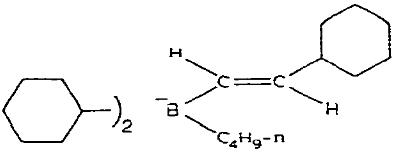
(V)

(VII) 73%

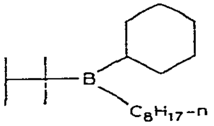


(VI)

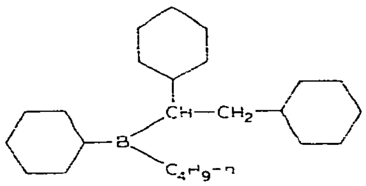
R, R′ = n-C_3H_7, n-C_4H_9, or n-C_5H_{11},  = 2,3-dimethyl-2-butyl



(VIII)



(IX)



(X)

hexylidenethane (XI) (< 2%). However, when the reaction mixture was refluxed for 24 h before oxidation, the yield of 1,2-dicyclohexylethanol decreased to less than 2%, and that of XI increased to 40%. Therefore, X must be the common intermediate for both the alkene and the alcohol products. These results prompted us to examine the acid hydrolysis of trialkylboranes containing hindered alkyl groups. Treatment of IX with 1 *N* hydrochloric acid at 25°C did not cause any significant change over 24 h. On refluxing the reaction mixture, however, 2,3-dimethyl-2-butene was formed in 45% over 24 h. Neither cyclohexene nor 1-octene was formed. We are currently attempting to develop this reaction into a simple procedure for the synthesis of "mixed" dialkylborane derivatives. Aside from such a synthetic potential, the novel findings reported here add to the rapidly growing knowledge of the chemical properties of organoboranes [5] and organoborates [6] which should prove significant in applying these organoboron compounds to organic synthesis.

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