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THE SYNTHESIS OF MIXED GEMINAL ORGANOMETALLIC COMPOUNDS

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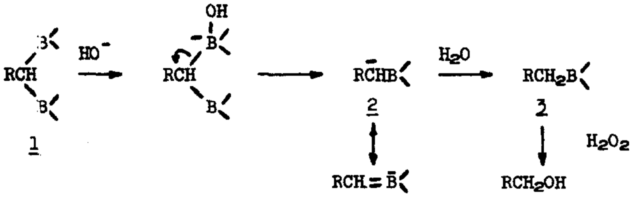
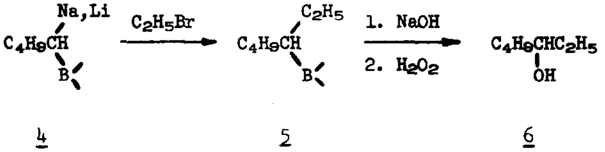
Until recently, the chemistry of geminal dimetallic compounds has received little attention.[1] The use of the hydroalumination[2] and hydroboration[3] reactions, however, has provided a new method for the preparation of difunctional organometallic compounds. We have shown that 1-alkynes are readily converted to 1,1-diboroalkanes when treated with diborane. Thus hydroboration of 1-pentyne or 1-hexyne with diborane in a 3 to 1 ratio gives 80% of the corresponding 1,1-diboroalkane. Use of dicyclohexylborane or 2,3-dimethyl-2-butylborane as hydroborating agents results in essentially quantitative yields of the geminal diboron compounds.[4] The structures of the dihydroboration products were established by their oxidation to n-pentanoic or n-hexanoic acid, respectively, when treated with m-chloroperbenzoic acid.[5]

In contrast to trialkylboranes, the geminal diboro derivatives (1) react rapidly with sodium hydroxide to give cleavage of one carbon-boron bond. The enhanced reactivity may be attributed to stabilization of the incipient carbanion (2) by interaction with the vacant p-orbital of boron.[4] Oxidation of the resulting intermediate organoboranes (3) with hydrogen peroxide gave 80% of primary alcohols.



We have now found that 1,1-diboropentane, derived from dihydroboration of 1-pentyne with diborane, undergoes a similar, facile cleavage with sodium methoxide, lithium methoxide, butyllithium and methyllithium to give the 1-boro-1-sodio and the 1-boro-1-lithio derivatives, respectively. The structures of these intermediates (4) were shown by their conversion to 3-heptylborane (5) when treated with ethyl bromide. This organoborane was not isolated but was oxidized directly to 3-heptanol (6).



The experimental results are summarized in Table I. The possibility that a 1,1-diboroalkane (1) was the precursor for the 3-heptanol is ruled out since heating 1,1-diboropentane with excess ethyl bromide for 4 hours at 60° followed by hydrolysis and oxidation gave only 1-pentanol. Moreover, evidence that 1,1-dilithiopentane was not formed[6] was shown by the following experiment: Treatment of 1,1-diboropentane in tetrahydrofuran at 0° with a 100% excess of methyllithium followed by hydrolysis with 3N sodium hydroxide and oxidation with hydrogen peroxide gave 80% 1-pentanol. Hydrolysis of a 1,1-dilithio derivative should have given only n-pentane. The fact that higher yields of 3-heptanol are obtained with increasing amounts of methyllithium (Table I) suggests that part of the reagent must react with the alkylborane to form lithium tetraalkylboron.

TABLE I

Yields of 3-Heptanol from 1-Sodio-1-boro- and 1-Lithio-1-boropentane

Reagent	Ratio Organoborane/ Reagent	Reaction Temp., °C.	3-Heptanol,[a,b] %
$NaOCH_3$	1:1	65	36
$LiOCH_3$	1:1	65	21
LiC_4H_9	1:1	25	55
$LiCH_3$	1:1	25	75
$LiCH_3$	1:1.5	25	83
$LiCH_3$	1:2	25	90

[a] Based on 1,1-diboropentane. [b] Determined by v.p.c. using an internal standard.

To the best of our knowledge these results provide the first evidence of the synthesis of a mixed geminal organometallic compound. Such derivatives, in which the two ligands exhibit large differences in reactivity, should be exceedingly useful in synthetic work. Experiments designed to establish the scope of this novel reaction and related transformations are currently underway.[7]

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7. Research performed under a grant by the National Science Foundation.