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ANODIC OXIDATION OF TRIALKYLBORANES.
A NEW PROCEDURE OF ALKYL COUPLING REACTION OF ORGANOBORANES

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Trialkylboranes are readily electrolyzed by using two platinum plates as electrodes in methanol containing potassium hydroxide to give alkyl group coupling products.

The reaction of trialkylboranes with silver nitrate in aqueous potassium hydroxide solution is well known in that it provides a convenient means of bringing about the dimerization of alkyl groups in trialkylboranes.1) On the other hand, it has been reported that aryl groups2) and alkyl groups3) in borates can be dimerized electrochemically. In addition, Schäfer and Koch4) have recently described the same type of anodic oxidation of trihexylborane in the presence of butadiene to transfer the hexyl group from trihexylborane to butadiene. It therefore appears to be of interest to explore the possibility of bringing about alkyl group coupling reaction of trialkylboranes themselves by anodic oxidation.

We wish to report here that trialkylboranes can be oxidized electrochemically in potassium-methanol solution to yield alkyl group dimerization products in good yields by using two platinum plate electrodes. A typical run of the electrolysis is as follows. Trioctylborane (1.0 mmol) which was prepared from 1-octene and diborane in THF by the usual procedure,5) was dissolved in 3 ml of methanol containing 1.4 g of potassium hydroxide in a 50 ml-cylindrical tube (diameter, 2.0 cm) equipped with a reflux condenser and a magnetic stirring bar. By using two platinum plates (1 x 1 cm^2) 6 mm apart from each other without separation of the anodic compartment from the cathodic, the solution was electrolyzed at 25°C for one hour under a current of 0.4 - 2.0 A at a terminal voltage of 20 V under nitrogen atmosphere. The reaction mixture was oxidized with 1 ml of 3N sodium hydroxide and 1 ml of 30% hydrogen peroxide. Potassium carbonate was added until the aqueous layer was saturated. Analysis of the organic layer by glpc indicated that 1.03 mmol (69 %) of hexadecane and 0.54 mmol (18 %) of octanol had formed respectively. Formation of 1.5 mole of the coupling product was calculated as 100% per mole of trialkylborane. From the yield of the alcohol, the conversion of organoborane was calculated. The results are summarized in Table 1.

Table 1. Alkyl Group Coupling Reactions

Organoborane R_3B	Current, A	Coupling product, R-R	Yield[a] of R-R, %	Conversion of R_3B, %
n-Octyl	2.0 - 0.4	Hexadecane	69	82
n-Hexyl	2.0 - 0.7	Dodecane	56	93
n-Pentyl	2.1 - 0.6	Decane	46	98
Cyclohexyl	0.8 - 0.5	Bicyclohexyl	23	95

a) Formation of 1.5 mole of R-R is calculated as 100% per mole of R_3B.

Table 2. Alkyl Group Cross Coupling Reactions

Organoborane		Yield of coupling products, %			Conversion of		Φ[b]
R^m_3B	R^n_3B	R^m-R^m	R^m-R^n	R^n-R^n	R^m_3B	R^n_3B	
n-Octyl	n-Hexyl[c]	15	27	13	38	36	1.94
n-Octyl	n-Hexyl[d]	33	25	1	30	32	-
n-Hexyl	n-Pentyl[c]	14	19	8	47	47	1.80

b) $\Phi = k_{mn}/(k_{mn}k_{nn})^{1/2}$

c) Molar ratio, 1:1

d) Molar ratio, 2:1

Since our efforts were mainly directed toward the practical application of organic synthesis using organoboranes, we have not undertaken a mechanistic investigation of this reaction. The coupling reaction of alkyl groups, however, may be rationalized in terms of the following explanation. It is well known that trigonal coplanar boron compounds form 1:1 complexes with a variety of nucleophilic reagents.[6] The complex (I) thus formed should be subjected to one electron discharge at an anode with subsequent formation of alkyl radical and dialkylhydroxyborane (II) (eq. 1).

$$R_3B + OH^- \longrightarrow \underset{\text{I}}{R_3B^-(OH)} \xrightarrow{-e} R_3\dot{B}(OH)$$

$$\longrightarrow R\cdot + \underset{\text{II}}{R_2B(OH)} \qquad (1)$$

$$\text{II} + OH^- \longrightarrow R_2B^-(OH) \xrightarrow{-e}\longrightarrow R\cdot + \underset{\text{III}}{RB(OH)_2} \qquad (2)$$

$$\text{III} + OH^- \longrightarrow RB^-(OH)_3 \xrightarrow{-e}\longrightarrow R\cdot + B(OH)_3 \qquad (3)$$

According to the experimental results revealed in Table 1, not only the first alkyl group of trialkylborane but also the second and third alkyl groups should be considered to be involved in this reaction, contrary to general features of organoborane reactions. These reactions may be regarded to proceed through eqs 2 and 3.

Mixed coupling products were obtained from two trialkylboranes. The coupling gave a nearly statistical distribution of products, as summarized in Table 2. If it is desired to couple an alkyl group of the organoborane prepared from an expensive olefin with a less expensive organoborane, an excess of the latter may be used to increase the conversion of the more valuable material.

The present procedure may accommodate a wide variety of functional groups.[7] Although it is known that the organoboranes constitute a versatile new source of free radicals by the oxygen, peroxide and photochemical induced procedures,[8] the present study showed that the anodic oxidation of organoboranes is also useful for generation of alkyl radicals from such boron derivatives.

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