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ANODIC OXIDATION OF TRIALKYLBORANES USING GRAPHITE AS THE ANODE. NOVEL REACTION OF ORGANOBORANES PROCEEDING THROUGH A CARBONIUM ION MECHANISM

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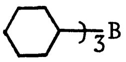
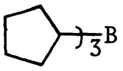
Trialkylboranes are readily electrolyzed by using graphite as an anode in a sodium perchlorate-methanol solution containing sodium methoxide or a sodium acetate-acetic acid solution to give corresponding alkyl methyl ethers or alkyl acetates in good yields, respectively.

Many reports have appeared recently dealing with a new application of organoboranes to the synthesis of a wide variety of organic compounds.1) Such organic syntheses may be classified into two types of reactions, in which the alkyl groups of organoboranes are used as carbanion or alkyl radical sources. However, for organic synthesis based on a reaction which proceeds through carbonium ion from organoboranes, no reports are available to date. We wish to report here a reaction in which alkyl groups of organoboranes are employed as carbonium ion sources.

We have previously reported that trialkylboranes are readily electrolyzed by using two platinum plates as electrodes in methanol containing potassium hydroxide to give alkyl group coupling products in relatively good yields,2) and the reaction was suggested to proceed through the same type of reaction path of the Kolbe electrolysis. It has been pointed that in the Kolbe reaction, a platinum or iridium anode should be chosen to obtain an optimum yield of the coupling product; on the other hand, at a carbon anode, many carboxylates give products derived almost exclusively from carbonium ions.3) Consequently, one can expect that the choice of anode material offers one possibility to obtain products formed from carbonium ions, even in an anodic oxidation reaction of organoboranes. In order to examine this possibility, we attempted electrolysis of organoboranes using a carbon anode. A typical run of the electrolysis is as follows.

Trioctylborane (2.19 mmol) which was prepared from 1-octene and diborane by the usual procedure,[4)] was dissolved in 7 ml of methanol containing sodium methoxide (13.1 mmol) and sodium perchlorate (3.28 mmol) in a 50 ml-cylindrical tube (diameter, 2.5 cm) equipped with a reflux condenser and a magnetic stirring bar. The solution was electolyzed at 25°C under nitrogen atmosphere using graphite (1X1 cm^2) as the anode and a platinum plate as the cathode without separation between the electrodes. During the electrochemical reaction, 3.3 equivalents of constant current (500 mA) were applied while the terminal voltage was 9.0-13.6V. Then 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 1.85 mmol (84%) of methyl octyl ethers and 0.365 mmol (33%) of hexadecane had formed respectively. The methyl octyl ethers were shown to be a mixture of 1-, 2-, 3- and 4-methoxyoctanes in a ratio of 8:66:25:1. The representative results are summarized in Table 1.

Table 1. Anodic Oxidation of Organoboranes in a $NaClO_4$-$NaOCH_3$-CH_3OH System.

Organoborane	Product and yield[a)] %			
R_3B	$ROCH_3$		R-R	
n-Oct_3B	Methyl octyl ethers[b)]	84	n-Hexadecane	33
n-Hex_3B	Hexyl methyl ethers[b)]	104	n-Dodecane	72
n-Pen_3B	Methyl pentyl ethers[b)]	83	n-Decane	88
2-Me-Bu_3B	Methyl pentyl ethers[b)]	102	3,6-Dimethyloctane	96
	Cyclohexyl methyl ether	92	Bicyclohexane	7
	Cyclopentyl methyl ether	95	Bicyclopentane	-

a) Based on organoborane used.

b) A mixture of corresponding alkyl methyl ethers.

Although the reaction mechanism is not clear at present, because our efforts were mainly directed toward the practical application of organic synthesis, the reaction seems to be rationalized in terms of the following explanation. Trigonal coplanar boron compound forms a 1:1 complex (I) with methoxide anion. The complex thus obtained is subjected to one electron discharge at an anode with subsequent formation of alkyl radical and dialkylmethoxyborane (eq. 1). According to the experimental results, not only the first alkyl group of trialkylboranes but also the second and third alkyl groups should be considered to be involved in the reaction. Consequently, this reaction is regarded to proceed through eqs. 2 and 3 to give alkyl radical, R· , as observed in the anodic oxidation of organoboranes using platinum as an anode in methanol containing potassium hydroxide.[2)]

$$R_3B + OCH_3^- \longrightarrow \underset{I}{R_3\bar{B}OCH_3} \xrightarrow{-e} R_3\dot{B}OCH_3 \longrightarrow R\cdot + \underset{II}{R_2BOCH_3} \tag{1}$$

$$II + OCH_3^- \longrightarrow R_2\bar{B}(OCH_3)_2 \xrightarrow{-e} \longrightarrow R\cdot + \underset{III}{RB(OCH_3)_2} \tag{2}$$

$$III + OCH_3^- \longrightarrow R\bar{B}(OCH_3)_3 \xrightarrow{-e} \longrightarrow R\cdot + B(OCH_3)_3 \tag{3}$$

$$2R\cdot \longrightarrow R\text{-}R \tag{4}$$

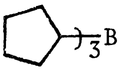
$$R\cdot \xrightarrow{-e} R^+ \xrightarrow{CH_3OH} ROCH_3 \tag{5}$$

The alkyl radical, R· , thus anodically formed underwent further oxidation to give carbonium ions, from which methyl ethers was derived(eq. 5). In spite of the fact that the Kolbe reaction is the oldest and probably most useful electrochemical synthetic procedure in organic chemistry, the detailed reaction mechanism is extremely complex and still subject to lively discussion.[5)] The mechanistic investigation of the present reaction, therefore, would be faced with many difficulties, but we are actively exploring in an attempt to elucidate the reaction mechanism.

Next, we attempted electrolysis of organoboranes in sodium acetate-acetic acid solution by using the same electrolysis cell. By this reaction, corresponding alkyl acetates were obtained in relatively good yields. The results of representative reactions are summarized in Table 2. The following procedure for the preparation of cyclopentyl acetate is representative. Tricyclopentylborane (1.76 mmol) prepared by the usual procedure was dissolved in 6 ml of acetic acid containing sodium acetate in the electrolysis cell described above. The solution was electrolyzed at 25°C by applying

6F per mole of the organoborane under a constant current of 0.1 A/cm^2 (terminal voltage, 21-25V). The reaction mixture was poured into an excess of water, and then extracted with ether. The combined extracts were washed with water and dried over anhydrous sodium sulfate. Analysis of the organic solution by glpc showed the formation of cyclopentyl acetate (1.22 mmol, 70%).

Table 2. Anodic Oxidation of Organoboranes in CH_3COONa-CH_3COOH System.

Organoborane R_3B	Product	Yield,[a] %
Oct_3B	Octyl acetates[b]	73
Hex_3B	Hexyl acetates[b]	54
Pen_3B	Pentyl acetates[b]	46
	Cyclopentyl acetate	70
$PhCH_2CH_2)_3B$	Phenethyl acetate	10
	1-Phenylethyl acetate	60

a) Based on organoborane used.

b) A mixture of corresponding alkyl acetates.

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