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ELECTROCHEMICAL REACTION OF TRIALKYLBORANES WITH ACETONE

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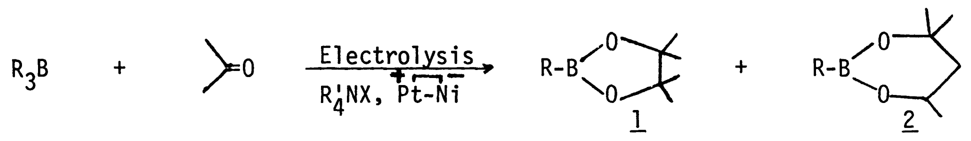
Trialkylboranes are readily electrolyzed in acetone solution, containing tetraalkylammonium salts to give corresponding 2-alkyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes (1) and 2-alkyl-4,4,6-trimethyl-1,3,2-dioxaborinanes (2) in good yields.

We have previously reported that electrochemical reactions of trialkylboranes with substrates having acidic hydrogens such as acetonitrile,$^{1)}$ nitromethane,$^{2)}$ 1-alkynes,$^{3)}$ piperidines,$^{4)}$ and ethyl phenylacetate$^{5)}$ proceed smoothly to provide convenient routes to nitriles, nitroalkanes, internal alkynes, N-alkylpiperidines, and ethyl 2-alkylphenylacetates, respectively, in good yields. In an attempt to apply these electrochemical alkylations to a synthesis of methyl ketones, we examined the electrochemical reactions of trialkylboranes with acetone. However, the expected alkyl methyl ketones could not be obtained. We wish to report here that trialkylboranes are readily electrolyzed in acetone to give the corresponding 2-alkyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes (1) and 2-alkyl-4,4,6-trimethyl-1,3,2-dioxaborinanes (2).



The electrolysis was carried out by means of controlled current method in the usual undivided cell equipped with a platinum plate as the anode and a nickel plate as the cathode. The results of representative reactions are summarized in Table 1. It appears that trialkylboranes are almost quantitatively converted to the corresponding cyclic boronates 1 and 2 with a preferential formation of 1. The results obtained by using several supporting electrolytes are shown in Table 2. Tetraalkylammonium halides were more effective than tetraalkylammonium perchlorates as a supporting salt.

Table 1. Electrolysis of Trialkylboranes in Acetone Solution Containing Tetra-n-butylammonium Iodide[a)]

Organoborane R	Yield of 1 + 2 (%)[b)]	Distribution of Products (%)	
		1	2
n-C_3H_7	94	97	3
iso-C_4H_9	79	68	32
sec-C_4H_9	89	>99	
n-C_5H_{11}	99	>99	
c-C_5H_9	95	>99	

a) The reactions were carried out under the same conditions described in the preparation for 1 and 2 from tri-n-propylborane.

b) Based on organoboranes used.

Products 1 and 2 were identified respectively by elemental analyses, ir, nmr, and mass spectra, and further confirmed by direct comparison with authentic samples. Product 1 was in good accordance with 2-alkyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes obtained by photochemical reaction of trialkylboranes with isopropyl alcohol.[6)] Product 2 was completely identical to 2-alkyl-4,4,6-trimethyl-1,3,2-dioxaborinanes prepared by esterification of monoalkylboric acid ($RB(OH)_2$)[7)] with 2-methyl-2,4-pentanediol.[8)]

Although the detailed reaction mechanism is not clear as yet, several points must be noted. (a) When the electrolysis was carried out in a divided cell, neither 1 nor 2 was produced. (b) The electrolysis of acetone containing tetra-n-butylammonium iodide as a supporting electrolyte produced 2,3-dimethyl-2,3-butanediol (3), 4-hydroxy-4-methyl-2-pentanone (4) and 2-methyl-2,4-pentanediol (5) at the cathode. The formation of pentanediol 5 was considerably slow when compared with that of 4. (c) When tri-n-propylborane was electrolyzed in the presence of diol 3 or 5 in dimethylformamide solution containing tetra-n-butylammonium iodide in an undivided cell, product 1 (R=n-C_3H_7) or 2 (R=n-C_3H_7) was obtained in a yield of 82 or 91%, respectively. Similar electrolysis in an divided cell gave the product 1 or 2 in a 83 or 47% yield, respectively, at the anode. Electrolysis of tri-n-propylborane in the presence of 4 in an undivided cell also gave dioxaborinane 2 in a lower yield (27%). (d) The ratio of 1 and 2 was found to vary by using different cathodes, 97:3 for a nickel cathode and 50:50 for a platinum cathode in the electrochemical reaction of tripropylborane with acetone. The similar effect was observed in the reaction of acetone alone; diols 3 and 5 were

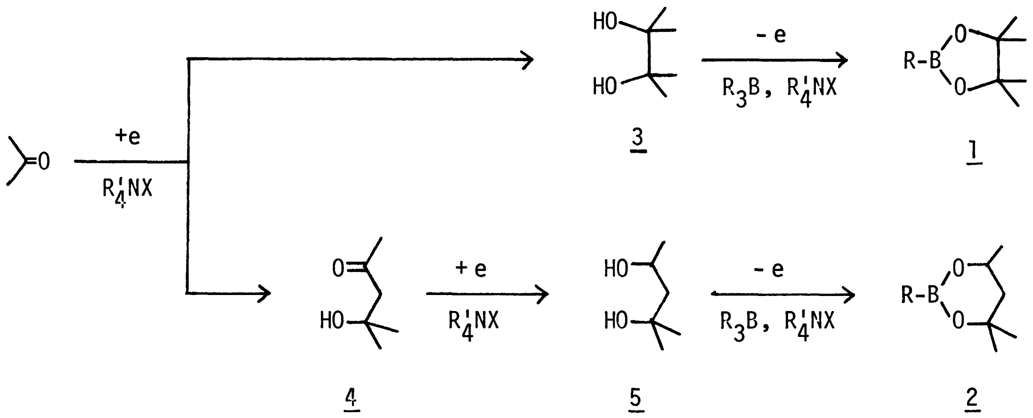
Table 2. Effect of Supporting Electrolytes on the Electrochemical Reaction of Tri-n-pentylborane with Acetone[a)]

Electrolyte	Yield of 1 + 2 (%)[b)]	Distribution of Products (%)	
		1	2
$(C_2H_5)_4NI$	58	69	31
$(C_2H_5)_4NBr$	59	71	29
$(C_2H_5)_4NClO_4$	10	44	56
$(n\text{-}C_4H_9)_4NI$	99	>99	
$(n\text{-}C_4H_9)_4NBr$	73	>99	
$(n\text{-}C_4H_9)_4NClO_4$	9	26	74

a) Carried out under the same reaction conditions described in Table 1.

b) Based on organoborane employed.

produced mainly by using nickel and platinum as cathodes, respectively. Consequently, we tentatively propose the following pathways for the formation 1 and 2 (Scheme 1). However, the different pathways involving a direct attack of acetone anion radical towards trialkylboranes may be considered since it was sometimes observed that the rates of formations of 1 and 2 were slightly faster than those of 3 and 5.



Scheme 1

The following procedure is representative. The electrolysis was carried out in the usual undivided cell equipped with a platinum plate (10 × 10 mm^2) as the anode and a nickel plate (10 × 10 mm^2) as the cathode, magnetic stirring bar and a reflux condenser. Tri-n-propylborane (2 mmol) was dissolved in 8.0 ml of acetone containing tetra-n-butylammonium iodide (1 mmol). The solution was electrolyzed at a constant current (0.5 A/cm^2 of current density) for 45 min at room temperature under nitrogen atmosphere. Then, the products were extracted with ether and dried over magnesium sulfate. Glpc analysis of the resulting organic layer indicated that 1.83 mmol (97%) of 1 ($R=n\text{-}C_3H_7$) and 0.06 mmol (3.0%) of 2 ($R=n\text{-}C_3H_7$) were formed. 1 ($R=n\text{-}C_3H_7$): n_D^{20} 1.4172; IR (neat), 1310 cm^{-1}; ^1H-NMR (CCl_4), δ 0.69 (t, 2H, J=7.1 Hz), 1.19 (s, 12H), and 1.2-1.6 ppm (m, 2H); ^{13}C-NMR ($CDCl_3$; ref. TMS), δ 16.9, 17.5, 24.8, and 82.8 ppm. Found: C, 63.55; H, 11.23%, Calcd for $C_9H_{19}O_2B$: C, 63.52; H, 11.17%. 2 ($R=n\text{-}C_3H_7$): n_D^{20} 1.4166; IR (neat) 1310 cm^{-1}; ^1H-NMR (CCl_4), δ 0.56 (t, 2H, J=7.4 Hz), 0.85 (t, 3H, J=6.6 Hz), 1.18 (d, 2H, J=7.2 Hz), 1.12 (s, 6H), 1.2-1.6 (m, 2H), 1.71 (d,d, 2H, J=3.5, 14 Hz), and 4.11 ppm (m, H); ^{13}C-NMR ($CDCl_3$; ref. TMS), δ 16.9, 17.7, 23.3, 28.1, 31.3, 46.1 64.4, and 70.2 ppm. Found: C, 63.34; H, 11.30%. Calcd for $C_9H_{19}O_2B$: C, 63.52; H, 11.17%.

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