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# A NOVEL SYNTHESIS OF ALIPHATIC NITRILES FROM ORGANOBORANES BY ELECTROCHEMICAL REACTION

Yuzuru TAKAHASHI, Masao TOKUDA, Mitsuomi ITOH, and Akira SUZUKI*
Faculty of Engineering, Hokkaido University, Sapporo 060

Trialkylboranes are readily electrolyzed by using two platinum plates as the electrodes in an acetonitrile solution containing tetraalkylammonium halide to give corresponding aliphatic nitriles in good yields.

Previously we reported that trialkylboranes are readily electrolyzed by using two platinum plates as electrodes in methanol solution containing potassium hydroxide to give alkyl group coupling products.[1] It was also reported by us that such trialkylboranes are electrolyzed by using graphite as an anode in a sodium methoxide-methanol solution containing sodium perchlorate, or a sodium acetate-acetic acid solution to afford corresponding alkyl methyl ethers, or alkyl acetates in good yields, respectively.[2] In the course of studies on organic synthesis using organoboranes by electrochemical methods, we undertook a study on an electrochemical reaction of organoboranes in acetonitrile solution containing tetraalkylammonium halide as the supporting electrolyte by using two platinum plate electrodes. The reaction proceeded smoothly in the usual undivided cell to produce corresponding nitriles in good yields (eq. 1).

$$R_3B \quad + \quad CH_3CN \xrightarrow[\text{Pt-Pt}]{R'_4NX} RCH_2CN \qquad (1)$$

The following procedure for the preparation of octanenitrile is representative for the reaction described in this communication. The electrolysis was carried out in the usual undivided cell equipped with two platinum plate electrodes (1.0 x 1.0 $cm^2$), a magnetic stirring bar and a reflux condenser. Trihexylborane (0.96 mmol) was dissolved in 10 ml of acetonitrile containing tetraethylammonium iodide (1 mmol). The solution was electrolyzed at a constant current (500 $mA/cm^2$ of current density) for 1 hr at room temperature under nitrogen atmosphere. Then the reaction mixture was oxidized with 1.0 ml of 3N sodium hydroxide and 1.0 ml of 30% hydrogen peroxide for 2 hr at room temperature. Glpc analysis of the resulting organic layer indicated that 1.51 mmol (157%, based on trihexylborane) of octanenitrile had been formed.

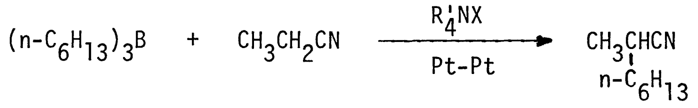
The results of representative reactions are summarized in Table 1.

Table 1. The Electrochemical Reaction of Trialkylboranes in Acetonitrile Solution Containing Tetraethylammonium Iodide[a]

| Organoborane<br>R | Product[b]<br>$RCH_2CN$ | Yield,[c] % |
|---|---|---|
| *n*-Octyl | Decanenitrile | 153 |
| *n*-Hexyl | Octanenitrile | 157 |
| *n*-Butyl | Hexanenitrile | 132 |
| *sec*-Butyl | 3-Methylpentanenitrile | 147 |
| *n*-Hexyl[d] | 2-Methyloctanenitrile | 80 |

[a] The reactions were carried out under the same conditions described in the preparation for octanenitrile from trihexylborane. [b] All the products were either compared with authentic samples or exhibited analytical data and spectra in accordance with the assigned structures. [c] Based on organoborane used. [d] Used propionitrile as the solvent.

In the reaction, there appears to be no difficulty in introducing secondary alkyl groups as well as primary groups. When propionitrile was used as the solvent instead of acetonitrile in the reaction of trihexylborane, the expected 2-methyloctanenitrile was obtained in a yield of 80% (eq. 2).



$$(n\text{-}C_6H_{13})_3B \quad + \quad CH_3CH_2CN \xrightarrow[\text{Pt-Pt}]{R'_4NX} \underset{\substack{| \\ n\text{-}C_6H_{13}}}{CH_3CHCN} \qquad (2)$$

Tetraalkylammonium halides and potassium iodide were found to be effective as the supporting electrolyte in the reaction, whereas the electrolysis using tetraalkylammonium perchlorate produced no detectable amount of corresponding nitriles. Such results are summarized in Table 2. Consequently, it may be said that halide ion seems to play an important role in this electrochemical reaction.

Table 2. The Electrochemical Reactions of Trioctylborane and Trihexylborane in Acetonitrile Solutions Containing Various Kinds of Supporting Electrolytes[a]

| Organoborane R | Electrolyte | Product $RCH_2CN$ | Yield,[b] % |
|---|---|---|---|
| _n_-Octyl | $Et_4NClO_4$ | Decanenitrile | 0 |
| | $Et_4NBr$ | | 145 |
| | $Et_4NI$ | | 153 |
| | _n_-$Bu_4NClO_4$ | | 0 |
| | _n_-$Bu_4NBr$ | | 126 |
| | _n_-$Bu_4NI$ | | 168 |
| _n_-Hexyl | KBr | Octanenitrile | trace |
| | KI | | 58 |

[a] Carried out under the same reaction conditions described in Table 1. [b] Based on the organoborane employed.

On the other hand, it was observed that no reaction occurs when the electrolysis was carried out in a divided cell. This fact suggests that the present synthesis needs the coupled chemical reactions at the anode and cathode. The formation of acetonitrile anion, $\overset{-}{C}H_2CN$, at the cathode is supported by the following evidences. (a) When the acetonitrile solution containing tetraethylammonium iodide only was electrolyzed, generation of hydrogen gas was observed at the cathode. This seems to show the formation of acetonitrile anion (I) through the reaction path indicated in eq. 3. (b) When the acetonitrile solution containing acetone and tetraethylammonium

$$CH_3CN \xrightarrow[\substack{\text{Pt-Pt} \\ Et_4NI}]{+e} \underset{\text{I}}{\overset{-}{C}H_2CN} + 1/2\ H_2 \qquad (3)$$

$$CH_3CN \xrightarrow[\substack{\text{Pt-Pt} \\ Et_4NI}]{+e} \underset{\text{I}}{\overset{-}{C}H_2CN} \xrightarrow{+\ CH_3COCH_3} \underset{\text{II}}{(CH_3)_2C(OH)CH_2CN} \qquad (4)$$

iodide was electrolyzed under the same conditions described above, 3-hydroxy-3-methylbutanenitrile (II) was obtained. This is explained by a nucleophilic attack of the initially formed acetonitrile anion (I) to acetone (eq. 4).

On the electrolysis of the acetonitrile solution containing trialkylborane and tetraethylammonium iodide, the corresponding alkyl iodide was found to be a main product at the anode in a divided cell, whereas the iodide was not detected at the cathode. The reaction is regarded to proceed through the first formation of iodine radical by anodic oxidation of iodide ion (eq. 5), followed by the reaction of the iodine radical with trialkylborane (eq. 6), although the latter reaction path can not be clearly stated to proceed via the same type of radical halogenation process reported by Lane and Brown,[3] or by a different mechanism. As shown in Table 2, when tetraalkylammonium perchlorate was used as the supporting salt, the expected nitrile derivatives were not obtained. This is understood by their oxidation potentials.[4]

$$3I^- \xrightarrow{-2e} I_3^- \xrightarrow{-e} I_2 + I\cdot \qquad (5)$$

$$R_3B + I\cdot \longrightarrow RI \qquad (6)$$

From these evidences observed in the anodic and cathodic parts of the present electrochemical reaction, it was concluded that nucleophilic attack of the acetonitrile anion (I) formed at the cathode to the alkyl iodide produced at the anode gives the corresponding nitriles.

Organic syntheses of aliphatic nitriles by the use of organoboranes have been already reported by Hooz et al.,[5] and Brown et al.[6] In those reactions, however, the intractable reagents such as diazoacetonitrile[5] and chloroacetonitrile[6] must be used. Further, in the present synthesis, not only the first alkyl group of organoborane but also the second alkyl group appears to be employed as the alkyl source, in contrast with usual organoborane reactions. Consequently, this reaction is considered to be a useful synthetic procedure for preparation of aliphatic nitriles from organoboranes under mild conditions.

## References

* Author to whom correspondence should be addressed.

1) T. Taguchi, M. Itoh, and A. Suzuki, Chem. Lett., 719 (1973).

2) T. Taguchi, Y. Takahashi, M. Itoh, and A. Suzuki, ibid., 1021 (1974).

3) C. F. Lane and H. C. Brown, J. Amer. Chem. Soc., 92, 7212 (1970).

4) W. M. Latimer, "Oxidation Potentials", Prentice-Hall, Inc., New York, 1952.

5) J. Hooz and S. Linke, J. Amer. Chem. Soc., 90, 6891 (1968).

6) H. C. Brown, H. Nambu, and M. M. Rogić, ibid., 91, 6584 (1969).

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