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Electrochemical Reaction of Organoboranes in the Presence of Propenoic Acid Esters. A Convenient Carboxylic Ester Synthesis from Organoboranes

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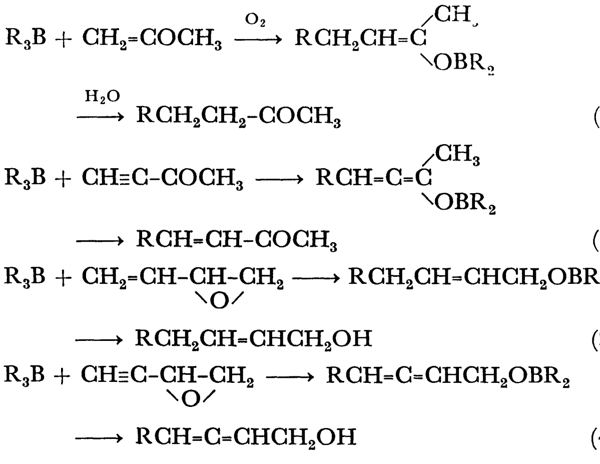
Synopsis. Electrolysis of trialkylboranes using two platinum electrodes in the presence of α,β-unsaturated esters in an acetonitrile solution containing tetraalkylammonium halide as a supporting electrolyte, produces the corresponding alkylated carboxylic acid esters in good yields.

Previously, we have reported that organoborane undergo spontaneous 1,4-addition reactions in the presence of oxygen to numerous α,β-unsaturated carbonyl compounds including methyl vinyl ketone[1] and acetylacetylene,[2] and to α,β-unsaturated oxiranes such as 1,3-butadiene monoxide[3] and 3,4-epoxy-1-butyne,[4] followed by hydrolysis to give corresponding alkylated compounds (Eqs. 1—4). However, it has been shown



$$R_3B + CH_2{=}COCH_3 \xrightarrow{O_2} RCH_2CH{=}C\begin{matrix}\diagup CH_3\\ \diagdown OBR_2\end{matrix}$$

$$\xrightarrow{H_2O} RCH_2CH_2\text{-}COCH_3 \qquad (1)$$

$$R_3B + CH{\equiv}C\text{-}COCH_3 \longrightarrow RCH{=}C{=}C\begin{matrix}\diagup CH_3\\ \diagdown OBR_2\end{matrix}$$

$$\longrightarrow RCH{=}CH\text{-}COCH_3 \qquad (2)$$

$$R_3B + CH_2{=}CH\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} \longrightarrow RCH_2CH{=}CHCH_2OBR_2$$

$$\longrightarrow RCH_2CH{=}CHCH_2OH \qquad (3)$$

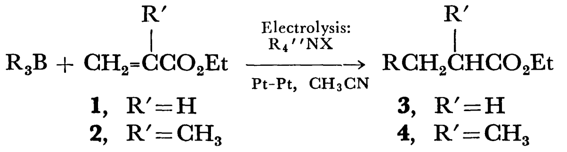
$$R_3B + CH{\equiv}C\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} \longrightarrow RCH{=}C{=}CHCH_2OBR_2$$

$$\longrightarrow RCH{=}C{=}CHCH_2OH \qquad (4)$$

that neither acrylonitrile nor ethyl acrylate (**1**) reacts with organoboranes under the same conditions. Although we have recently reported that the reaction of acrylonitrile or **1** with copper(I) trialkylmethylborates gives corresponding alkylation products,[5] this procedure has a disadvantage in that there is a difficulty in introducing secondary alkyl groups. On the other hand, the electrochemical reactions of trialkylboranes with compounds containing acidic hydrogens such as acetonitrile,[6] nitromethane,[7] and 1-alkynes[8] have also been reported by us to give the corresponding alkylated products such as cyanoalkanes, nitroalkanes and internal acetylenes, respectively.

In the present paper we wish to report that the electrochemical reaction of trialkylboranes with α,β-unsaturated esters such as **1** or ethyl methacrylate (**2**) in an acetonitrile solution containing tetraalkylammonium halide as a supporting electrolyte produces corresponding saturated carboxylic acid ester in good yields (Eq. 5).

The electrochemical reaction was carried out by means of controlled current electrolysis in an undivided



$$R_3B + CH_2{=}\overset{R'}{\overset{|}{C}}CO_2Et \xrightarrow[\text{Pt-Pt, }CH_3CN]{\text{Electrolysis: }R_4''NX} RCH_2\overset{R'}{\overset{|}{C}}HCO_2Et \qquad (5)$$

$$\begin{matrix}\mathbf{1},\ R'{=}H & & \mathbf{3},\ R'{=}H\\ \mathbf{2},\ R'{=}CH_3 & & \mathbf{4},\ R'{=}CH_3\end{matrix}$$

cell. The results of representative reactions are summarized in Table 1. As shown in the table, in this procedure there appears to be no difficulty in introducing secondary alkyl groups of organoboranes as well as primary alkyl groups. The effect of supporting electrolytes on the yield of **3c** in the reaction of tripropylborane with **1** was as follows: $(C_2H_5)_4NI$, 63; $(C_2H_5)_4NBr$, 17; $(n\text{-}C_4H_9)_4NI$, 77; $(n\text{-}C_4H_9)_4NBr$, 31; $(n\text{-}C_4H_9)_4NClO_4$, 0%. These results indicate that tetraalkylammonium bromide and iodide are effective as the supporting electrolyte in the reaction, whereas electrolysis using tetrabutylammonium perchlorate gives no detectable amount of the corresponding addition product.

Although the detailed reaction mechanism is not clear at present, several points must be noted. (a) The halide ion of a supporting electrolyte seems to play an important role in the reaction. (b) When a mixture of tripentylborane and **1** was electrolyzed in an undivided cell, small amounts of ethyl 2-pentyloctanoate (**6**; $R{=}C_5H_{11}$) and ethyl 2-methylheptanoate (**8**; $R{=}C_5H_{11}$) were obtained as by-products together with the normal product, ethyl octanoate. (c) When the electrolysis was carried out in a divided cell, the desirable reaction did not occur. By the use of a divided cell, electrolysis of a mixture of trialkylborane and **1** in an acetonitrile solution containing tetraalkylammonium iodide afforded the corresponding alkyl iodide at the anode and the dimer of **1** at the cathode as the main products. (d) Electrolysis of butyl iodide, instead of tributylborane, in the presence of ethyl acrylate under the same conditions described above gave ethyl heptanoate in a 22% yield. (e) The reduction potentials of

TABLE 1. ELECTROCHEMICAL REACTION OF TRIALKYLBORANES WITH **1** OR **2**

Organoborane, R_3B, R	Product	Yield of **3** (%)[a]	Product	Yield of **4** (%)[a]
$n\text{-}C_5H_{11}$	**3a**	86	**4a**	94
$n\text{-}C_4H_9$	**3b**	57	**4b**	64 (60)[b]
$n\text{-}C_3H_7$	**3c**	77	**4c**	85 (73)[b]
$s\text{-}C_4H_9$	**3d**	65 (59)[b]	—	—
$c\text{-}C_5H_9$	**3e**	51	**4e**	51

a) VPC yields based on organoborane used.
b) Isolated yields.

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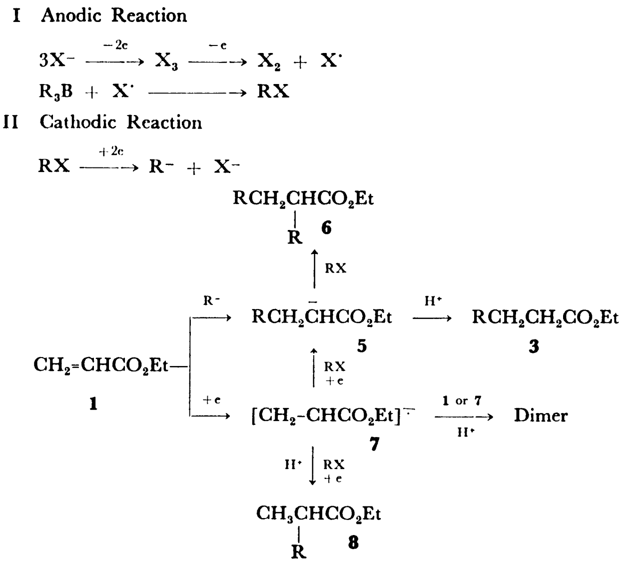

Scheme 1.

1 and **2** were observed at −2.28 and −2.41V *vs.* SCE, respectively, whereas those of alkyl iodide and alkyl bromide were reported to be around −1.63—−2.37V *vs.* SCE.[9,10] From these results the following mechanism involving two independent reaction pathways at the anode and the cathode may be proposed for the reaction of **1** (Scheme 1).

Experimental

Materials. Trialkylboranes were obtained by hydroboration of olefins.[11] Ethyl acrylate (**1**) and ethyl methacrylate (**2**) were distilled before use. Acetonitrile was dried over diphosphorus pentaoxide and distilled.

The IR and NMR spectra were taken on a Hitachi-Perkin-Elmer Model 125 spectrophotometer and a Hitachi R-22 spectrometer at 90 MHz using tetramethylsilane as the internal standard, respectively.

Quantitative analyses were carried out with Hitachi-063 gas chromatograph using a column of 15% Carbowax 20M on Uniport-B. Preparative VPC was done with JEOL JGC-20K gas chromatograph using the same type of column. The electrolyses were carried out with Yanagimoto VE-8.

General Procedure. The following procedure for the preparation of ethyl 2-methylhexanoate (**4c**) is representative. The electrolysis was carried out in the usual undivided cell equipped with two platinum plate electrodes (20×20 mm^2), a magnetic stirring bar and a reflux condenser. Tripropylborane (4.9 mmol) and 4.0 ml of **2** are dissolved in 17 ml of acetonitrile containing Bu_4NI (0.5 g, 1.35 mmol). The solution was electrolyzed at a constant current (0.5 A/cm^2) for 5 h under nitrogen atmosphere. After the electrolysis, the reaction mixture was oxidized by adding 3N aqueous sodium hydroxide (5.0 ml) and 30% hydrogen peroxide (5.0 ml) for 2 h at room temperature. The products were extracted with ether and dried over sodium sulfate. Distillation of organic layer gave 0.56 g (73%) of ethyl 2-methylhexanoate (**4c**), bp 50—52 °C/16 mmHg.

Identification of the Products. *Ethyl Octanoate (**3a**)*: n_D^{22} 1.4213. Found: C, 69.98; H, 11.88%. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70%. MS: m/e=172 (M$^+$). IR (neat): 1730 cm^{-1}. NMR (CCl_4): δ, 0.90 (3H, t, J=5.4 Hz), 1.15—1.80 (13H, m), 2.20 (2H, t, J=7.0 Hz), 4.08 ppm (2H, q, J=7.4 Hz). *Ethyl Heptanoate (**3b**)*: n_D^{22} 1.4137. Found: C, 68.03; H, 11.32%. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47%. MS: m/e=158 (M$^+$). IR (neat): 1735 cm^{-1}. NMR (CCl_4): δ, 0.91 (3H, t, J=5.2 Hz), 1.10—1.80 (9H, m), 2.22 (2H, t, J=7.4 Hz), 4.09 ppm (2H, q, J=7.2 Hz). *Ethyl Hexanoate (**3c**)*: n_D^{22} 1.4055. Found: C, 66.80; H, 11.38%. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18%. MS; m/e=144 (M$^+$). IR (neat): 1735 cm^{-1}. NMR (CCl_4): δ, 0.90 (3H, t, J=6.0 Hz), 1.23 (3H, t, J=6.4 Hz), 1.20—1.70 (6H, m), 2.21 (2H, t, J=7.4 Hz), 4.11 ppm (2H, q, J=7.2 Hz). *Ethyl 4-Methylhexanoate (**3d**)*: n_D^{22} 1.4152. Found: C, 68.11; H, 11.29%. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47%. MS; m/e=158 (M$^+$). IR (neat): 1735 cm^{-1}. NMR (CCl_4): δ, 0.92 (6H, m), 1.25 (3H, t, J=7.4 Hz), 1.20—1.80 (5H, m), 2.23 (2H, t, J=7.8 Hz), 4.05 ppm (2H, q, J=7.2 Hz). *Ethyl 3-Cyclopentylpropanoate (**3e**)*: n_D^{22} 1.4072. Found: C, 70.30; H, 10.68%. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66%. MS: m/e=170 (M$^+$). IR (neat): 1735 cm^{-1}. NMR (CCl_4): δ, 1.00—1.40 (2H, m), 1.24 (3H, t, J=7.4 Hz), 1.40—2.10 (9H, m), 2.24 (2H, t, J=7.0 Hz), 4.08 ppm (2H, q, J=7.2 Hz). *Ethyl 2-Methyloctanoate (**4a**)*: n_D^{22} 1.4168. Found: C, 70.50; H, 11.60%. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90%. MS: m/e=186 (M$^+$). IR (neat): 1735 cm^{-1}. NMR (CCl_4): δ, 0.89 (3H, t, J=5.6 Hz), 1.09 (3H, d, J=7.4 Hz), 1.10—1.80 (13 H, m), 2.31 (H, m), 4.08 ppm (2H, q, J=7.0 Hz). *Ethyl 2-Methylheptanoate (**4b**)*: n_D^{22} 1.4113. Found: C, 69.80; H, 11.77%. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70%. MS; m/e=172 (M$^+$). IR (neat): 1735 cm^{-1}. NMR (CCl_4): δ, 0.90 (3H, t, J=5.0 Hz), 1.11 (3H, d, J=7.0 Hz), 1.25 (3H, t, J=7.0 Hz), 1.10—1.80 (8H, m), 2.30 (H, m), 4.09 ppm (2H, q, J=6.6 Hz). *Ethyl 2-Methylhexanoate (**4c**)*: n_D^{22} 1.4072. Found: C, 68.55; H, 11.53%. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47%. MS: m/e=158 (M$^+$). IR (neat): 1735 cm^{-1}. NMR (CCl_4): δ, 0.91 (3H, t, J=6.0 Hz), 1.11 (3H, d, J=6.8 Hz), 1.25 (3H, t, J=7.8 Hz), 1.10—1.80 (6H, m), 2.31 (H, m), 4.08 ppm (2H, q, J=7.0 Hz). *Ethyl 3-Cyclopentyl-2-methylpropanoate (**4e**)*: n_D^{22} 1.4380. Found: C, 71.97; H, 11.03%. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94%. MS: m/e=184 (M$^+$). IR (neat): 1735 cm^{-1}. NMR (CCl_4): δ, 0.80—2.00 (11H, m), 1.11 (3H, d, J=7.2 Hz), 1.24 (3H, t, J=7.0 Hz), 2.38 (H, m), 4.08 ppm (2H, q, J=7.4 Hz).

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