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Novel Reduction of Carboxylic Acids and Hydroboration of Olefins by Electrolysis of Sodium Borohydride[1]

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Electrochemical oxidation of sodium borohydride in diglyme containing aliphatic or aromatic carboxylic acids followed by acid-catalyzed hydrolysis afforded the corresponding primary alcohols in good yields. Furthermore, similar electrochemical oxidation in the presence of a variety of olefins instead of carboxylic acids, followed by treatment with alkaline–hydrogen peroxide, brought about novel electrochemical hydroboration to give the corresponding alcohols regio- and stereoselectively in good yields.

Reductive transformation of carboxylic acids into the corresponding primary alcohols is one of the most important reactions in organic synthesis. Many reactions such as reduction by metallic hydrides,[2] electrochemical reductions,[3] and catalytic hydrogenation[4] have been known as conventional methods.

Among them, a method[5] using diborane has been recognized to possess interesting selectivity and high efficiency although its usefulness in organic synthesis is considerably limited because of troublesome procedure and special caution in treatment of the reagent, and difficulty in expansion of the reaction scale.[6]

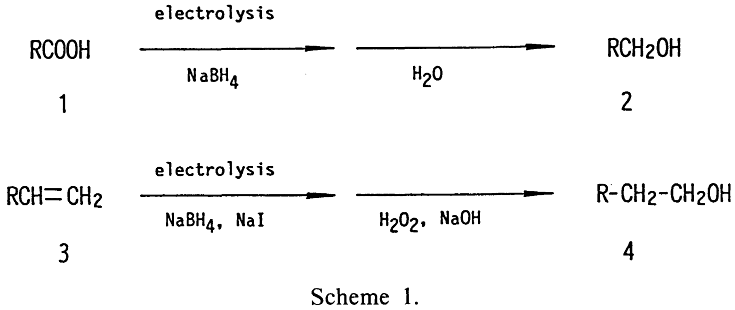
In this study, we wish to report selective and efficient electrochemical transformation of aliphatic and aromatic carboxylic acids into the corresponding primary alcohols through predominant generation of diborane by electrochemical oxidation of sodium borohydride. Furthermore, the present method was applied to development of the first example of electrochemical hydroboration of various olefins to give the corresponding alcohols high selectively in good yields after treatment of the reaction mixture with alkaline–hydrogen peroxide (Scheme 1).

Results and Discussion

Reduction of Carboxylic Acids. Although aromatic and unsaturated carboxylic acids were found to be electrochemically reduced to the corresponding benzyl alcohols,[3] none of electrochemical methods for reductive transformation of aliphatic carboxylic acids to the corresponding primary alcohols have been so far reported to our best knowledge.

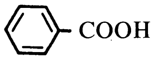
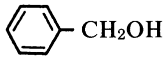
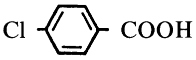
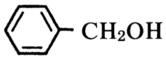
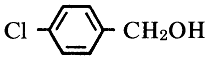
In this study, aliphatic primary alcohols were obtained in moderate to good yields through electrolysis of anhydrous diglyme containing sodium borohydride and the corresponding carboxylic acids followed by acid-catalyzed hydrolysis of the resulting mixture. In general, the electrolysis was carried out in an undivided cell equipped with a platinum foil electrode as the anode and a stainless steel plate as the cathode at 20—25 °C under nitrogen atmosphere applying the constant current conditions (current density: 40—50 mA cm^{-2}) until 2 F mol^{-1} of electricity based on the starting carboxylic acids passed through the system. The results are summarized in Table 1, accompanying with the results for aromatic carboxylic acids (Table 1).

It may be quite noteworthy that a carboxyl group was selectively reduced, but an ester group, usually more reducible than a carboxyl one, was quite inert in the present electrolysis of dicarboxylic acid monoesters (Entries 4 and 5). This unique reactivity and selectivity may remind us of generation of "diborane" in the present electrolysis since it has been already known that "diborane" can reduce carboxylic acids to the corresponding primary alcohols, but it is unreactive for carboxylic esters.[7] Thus, cyclic voltammetry of sodium borohydride in diglyme showed an oxidation peak

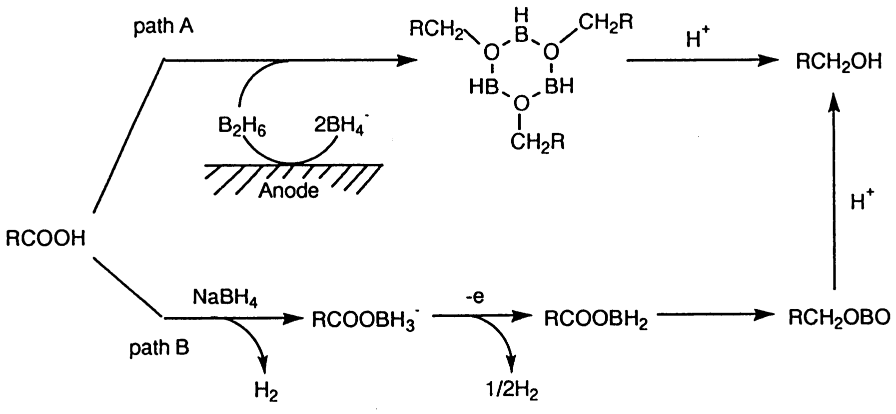


Scheme 1.

Table 1. Hydroboration of Carboxylic Acid by Electrolysis

Entry	Substrate 1		Products[a] 2		Yield[b]/%
1	$CH_3(CH_2)_6COOH$	**1a**	$CH_3(CH_2)_7OH$	**2a**	70
2	$CH_3(CH_2)_8COOH$	**1b**	$CH_3(CH_2)_9OH$	**2b**	72
3	$Br(CH_2)_{10}COOH$	**1c**	$CH_3(CH_2)_{10}OH$	**2c**	52
4	$H_3COOC(CH_2)_4COOH$	**1d**	$H_3COOC(CH_2)_5OH$	**2d**	49
5	$H_3COOC(CH_2)_{13}COOH$	**1e**	$H_3COOC(CH_2)_{14}OH$	**2e**	63
6	 COOH	**1f**	 CH_2OH	**2f**	65
7	 Cl COOH	**1g**	 CH_2OH	**2f**	60
			 Cl CH_2OH	**2g**	10

a) All the products were indentified by comparison of their spectroscopic (IR, ^1H NMR, and MS) data and gas liquid chromatographic behaviors with those of the authentic samples. b) Isolated yield.



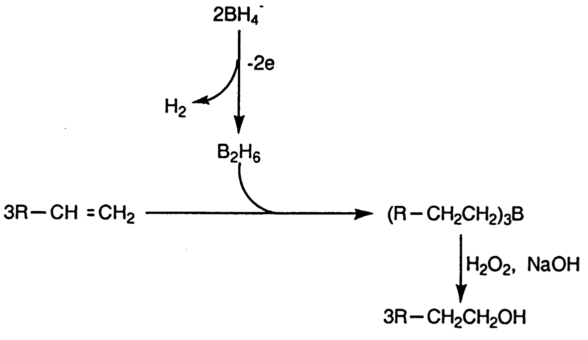
Scheme 2.

potential (E_p) at −0.045 V (vs. SCE), indicating that a borohydride anion is quite readily oxidized to give borane (or diborane in diglyme).

It was also found that electrochemical oxidation of a species such as $[RCOOBH_3]^-Na^+$ generated from the reaction of RCOOH with $NaBH_4$, gave the corresponding alcohol to some extent.[8] Thus, 1-decanol was obtained in a 33% yield from electrooxidation of the diglyme solution containing only $[n\text{-}C_9H_{19}COOBH_3]^-Na^+$ while the yield of the primary alcohol increased to 72% when the diglyme solution of $[n\text{-}C_9H_{19}COOBH_3]^-Na^+$ (20 mmol) and $NaBH_4$ (60 mmol) was electrochemically oxidized under the same conditions.

From these experimental results, carboxylic acids may be reduced to the corresponding alcohol through dual pathways, direct reduction route (path A) of B_2H_6 generated by two-electron oxidation[9] of BH_4^-, and the one involving electrooxidation of $RCOOBH_3^-$ (path B), shown in Scheme 2.

Formation of 1-undecanol and benzyl alcohol from 11-bromoundecanoic acid and *p*-chlorobenzoic acid may be explained by further electroreduction of the carbon–halogen bond at a cathode in addition to reduction of the carboxyl group (Entries 3 and 7) (Fig. 1).



Scheme 3.

The present method may possess high potentiality and usefulness as an practical method for efficient transformation of aliphatic and aromatic carboxylic acids into the corresponding primary alcohols.[10]

Electrochemical Hydroboration of Olefins. Facile generation of diborane by anodic oxidation of sodium borohydride in diglyme tempted us application to electrochemical hydroboration of olefins. Thus, electroly-

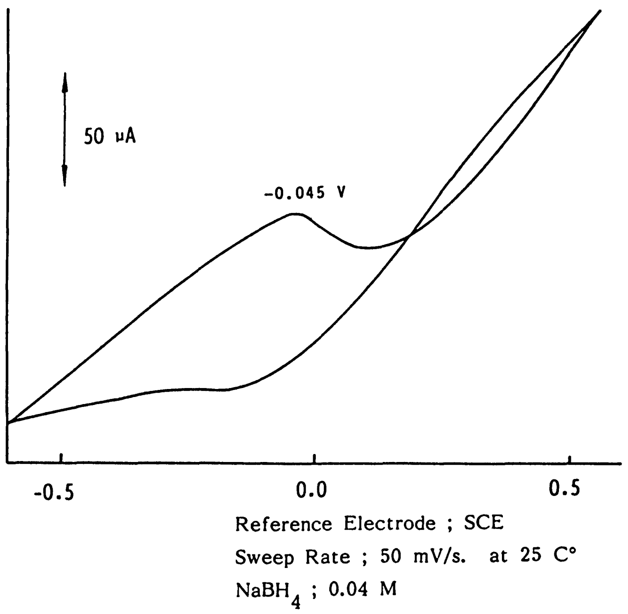


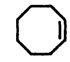
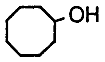
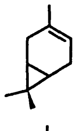
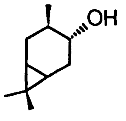
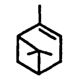
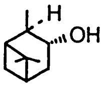
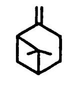
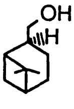
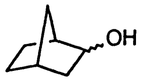
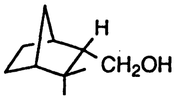
Fig. 1. Cyclic Voltammetry of $NaBH_4$ in Diglyme.

Table 2. Effect of Supporting Electrolyte on Electrochemical Hydroboration of (—)-2(10)-Pinene (**3h**)

Entry	Supporting electrolyte	$[NaBH_4]$/**3h**	Yield[a]/% of **4h**
1	NaI	1.25	82
2	NaI	0.5	81
3	KI	1.25	71
4	LiI	1.25	82
5	LiI	0.5	0
6		2.0	71
7		1.25	0[b]
8	$NaBF_4$	2.0	44
9	$LiClO_4$	1.25	12
10	LiBr	1.25	0[b]
11	Et_4NOTs	1.25	0[b]

a) Isolated yield based on **3h** used. b) In a little while after electrolysis was started, the terminal voltage of the system increased so much that the reaction could not continue further.

Table 3. Electrochemical Hydroboration of Olefins

Substrate 3		Product 4[a]		Yield[b]/%	
	**3a**		**4a**	81	(80)[d]
	**3b**		**4b**	69	
	**3c**		**4b**	64	
	**3d**		**4d**	28	
			**4d'**	42	
	**3e**		**4e**	72	
	**3f**		**4f**	70	(98)[d]
	**3g**		**4g**	78	(89)[d]
	**3h**		**4h**	82	(81)[d,f]
	**3i**		**4i**	72[e]	(85)[d]
	**3j**		**4j** endo	75	(77)[d]

a) All the products were identified by comparison of their spectroscopic (IR, ^1H NMR, and MS) and gas chromatographic behaviors with those of authentic samples. b) Isolated yield based on a substrate used. c) 2-Octanol (4—5%) was also formed as was found by a conventional method.[11] d) Reported yields by a conventional method.[12—15] e) *exo*/*endo*>99/1. f) The yield of **4h** was 75% from the reaction of 0.20 mole of **3h**.

sis of anhydrous diglyme solution of an olefin **3**, sodium borohydride and a supporting electrolyte was carried out under the constant-current conditions (current density: 40—50 mA cm^{-2}) in an undivided cell equipped with a platinum foil electrode as the anode and a stainless steel plate as the cathode. This mixture was stirred at 25 °C under nitrogen atmosphere until 2 F mol^{-1} of electricity based on the starting olefin passed through the system (see Scheme 1). After the reaction, the usual oxidation of the resulting mixture with alkaline-hydrogen peroxide selectively gave the corresponding alcohol **4**. Yield of the obtained alcohol **4** was found to be influenced by nature and amount of a supporting electrolyte, as shown in Table 2, in which (−)-2(10)-pinene (**3h**) was transformed to (−)-*cis*-myrtanol (**4h**). It was interesting that more than uni-equivalent mole of sodium borohydride was required for the effective transformation of **3h** to **4h** when a salt other than sodium iodide was used as a supporting electrolyte. However, just half equivalent mole of sodium borohydride based on **3h** was enough when sodium iodide was used as a supporting electrolyte (Entry 2 in Table 2).

Table 3 shows the results of the present electrochemical hydroboration of a variety of olefins **3a**—**j** under the optimum conditions. It was found that the products **4a**—**j** were formed regio- and stereoselectively in good yields, as observed in conventional methods. It was also found that some functional groups of the starting olefins such as a hydroxyl and an acetoxy group (transformed to a hydroxy group after hydrolysis) don't give important disturbance to the present electrooxidation while a chlorine atom was also reduced to some extent.

Although a detailed reaction mechanism for the present electrochemical hydroboration has not been clear, the initial two-electron transfer from borohydride anion to an anode may generate borane species, which readily reacts with olefins to give the corresponding alkylborane, as shown in Scheme 3.

Experimental

Materials. Diglyme was dried over sodium hydride and distilled. Commercially available (−)-2-pinene (**3g**) and (−)-2(10)-pinene (**3h**) were washed with dilute aq Na_2CO_3, then with water, and dried (Na_2SO_4). These were distilled through a spinning band precision distillation column under a reduced pressure to provide freshly distilled **3g** and **3h**, respectively by Nacalai Tesque Co., Lit.; **3g**: $[\alpha]^{23}_{D}$ −50.2 (*c* 1.7, $CHCl_3$); **3h**: $[\alpha]^{23}_{D}$ −16.9 (*c*1.0, $CHCl_3$). Other starting materials were used of commercially available samples.

Analytical Methods. Column chromatography was performed with Wako C-300 silica gel. Melting points were determined with a Yanagimoto MP-S3 instrument and are uncorrected. GLC analysis was conducted with a Hitachi 163 gas liquid chromatograph system equipped with an HFID (hydrogen flame ionization detector) and PEG 20M glass column (ϕ3 mm×3 m). Optical rotations were measured with a JASCO DIP-140 spectrophotometer. IR spectra were taken on a JASCO A-3 Grating spectrometer. Mass spectra were taken on a JEOL JMS-HX100 (with a JEOL JMA-DA5000 mass data system) high-resolution instrument and are given in terms of *m*/*z* (rel intensity) compared with the base peak. ^{1}H NMR spectra were recorded in $CDCl_3$ (with TMS as internal standard) with a JEOL FX-90Q (90 MHz for ^{1}H) and a JEOL GSX-270 (270 MHz for ^{1}H) at 27 °C.

Cyclic Voltammetry. Cyclic voltammetry of $NaBH_4$ (0.04 M, 1 M=1 mol dm^{-3})-diglyme solution at 25 °C was performed with a Hokuto Denko HA-303 potentiostat equipped with a platinum foil electrode (1 cm×1 cm) (vs. saturated calomel electrode) at sweep rate 50 mV s^{-1}.

General Procedure for the Reduction of Carboxylic Acids. Sodium borohydride (1.48 g, 40 mmol) was dissolved in 40 ml of anhydrous diglyme. Electrolysis of this solution was carried out under the constant-current condition (current: 0.2 A, current density: 50 mA cm^{-2}) in an undivided cell equipped with a platinum foil electrode (2cm×2 cm) as the anode and a stainless steel plate (2 cm×2 cm) as the cathode. The carboxylic acid **1** (10 mmol) dissolved in anhydrous diglyme solution (10 ml) was dropwisely added to this electrolysis solution at 25 °C for 30 min under nitrogen, and the mixture was stirred until 2 F mol^{-1} of electricity based on the corresponding alcohol **2** passed through the system (see Scheme 1). The reactant was filtered through glass wool, and was subsequently quenched with 10 ml of methanol. The filtrate was washed with 10% HCl solution (100 ml) and extracted with ether (3×70 ml). The combined extracts were washed with aq 5% NaOH, then with water, dried ($MgSO_4$), and evaporated in vacuo to give the reactant oil. The crude product **2** was carefully purified by distillation under a reduced pressure or silica-gel column chromatography. Yield of the product from each starting material is summarized in Table 1.

1-Octanol (2a), 1-Decanol (2b), 1-Undecanol (2c), Methyl 6-Hydroxyhexanate (2d), Methyl 15-Hydroxypentadecanate (2e), Benzyl Alcohol (2f), and *p*-Chlorobenzyl Alcohol (2g) : EI MS and ^{1}H NMR, identical with those of the authentic sample.

Electrooxidation of a Salt, *n*-$C_9H_{19}COOBH_3^-Na^+$, Generated from the Reaction of Decanoic Acid with Sodium Borohydride. Into 40 ml of anhydrous diglyme containing 0.74 g (20 mmol) of sodium borohydride, 3.44 g (20 mmol) of decanoic acid dissolved in 10 ml of anhydrous diglyme was added dropwise. Evolution of 20 mmol of hydrogen was observed. Electrolysis of the resulting solution of a salt, *n*-$C_9H_{19}COOBH_3^-Na^+$ was carried out under the constant-current conditions (current: 0.05 A, current density: 50 mA cm^{-2}) using an undivided cell with a platinum foil electrode (1 cm×1 cm) as the anode and a stainless steel plate (1 cm×1 cm) as the cathode. After the electrolysis and the usual work-up, 1.04 g (*Y*=33%) of 1-decanol (**2b**) was obtained. Employment of 80 mmol of sodium borohydride in this procedure brought about considerable increase in yield of the product to 72%.

General Procedure for the Electrochemical Hydroboration of Olefins. Olefin **3** (20 mmol) was dissolved in 50 ml of anhydrous diglyme containing sodium iodide (20 mmol) and sodium borohydride (10 mmol). Electrolysis of this solution was carried out under the constant-current condition (current: 0.2 A, current density: 50 mA cm^{-2}) in an undivided cell equipped with a platinum foil electrode (2 cm×2 cm) as the anode and a stainless steel plate (2 cm×2 cm) as the cathode. This mixture was stirred at 25 °C under nitrogen until 2 F mol^{-1}

of electricity based on the corresponding hydroboration product passed through the system (see Scheme 1). The reactant was filtered through glass wool, and the filtrate was subsequently oxidized with a mixture of 3 mol dm^{-3} sodium hydroxide (5 ml) and 30% hydrogen peroxide (5 ml) at 25 °C for 2 h. The reactant was poured into brine (100 ml) and extracted with ether (3×50 ml). The combined extracts were washed with water, dried ($MgSO_4$), and evaporated in vacuo to give the reactant oil. The crude product **4** was carefully purified by distillation under a reduced pressure or silica-gel column chromatography. Yield of the product from each starting material is summarized in Table 3.

1-Octanol 2a (4a), 2-Octanol (4a′), 1,6-Hexanediol (4b), 6-Chloro-1-hexanol (4d), 1-Hexanol (4d′), and Cyclooctanol (4e): EI MS and ^1H NMR, identical with those of the authentic sample.

(−)-4-Isocaranol (4f): Bp 87—90 °C (35 mmHg, 1 mmHg=133.322 Pa) [lit,$^{12)}$ bp 89—90 °C (35 mmHg)]; IR (neat) 3330, 2900, 1450, 1040 cm^{-1}; ^1H NMR (90 MHz), δ=0.90 (3H, s, Me), 0.95 (3H, s, Me); MS m/z 152 (M^+, 2%), 136 (65), 121 (85), 107 (33), 93 (100), 81 (35).

(−)-Isopinocamphenol (4g): Mp 55 °C; $[\alpha]_D^{23}$ +31.4 (c 0.8, $CHCl_3$) [lit,$^{13)}$ mp 54—56 °C, $[\alpha]_D^{20}$ −32.4 (c 4, benzene)]; IR (KBr) 3400, 2925, 1470, 1455 cm^{-1}; ^1H NMR (270 MHz), δ=0.92 (3H, s, *gem*-Me), 1.13 (3H, d, J=7.0 Hz, Me), 1.22 (3H, s, *gem*-Me), 1.59 (1H, brs), 1.66—1.75 (1H, ddd, J=14.0, 5.0, and 2.5 Hz), 1.77—1.84 (1H, td, J=6.0 and 2.0 Hz), 1.89—1.99 (2H, m), 2.32—2.42 (1H, m), 2.45—2.58 (1H, m), 4.02—4.11 (1H, m); MS m/z 136 (M^+-H_2O, 10%), 121 (13), 110 (12), 98 (15), 95 (27), 84 (55), 81 (33), 70 (100), 55 (44).

(−)-*cis*-Myrtanol (4h): Bp 78—82 °C (3 mmHg); $[\alpha]_D^{23}$ −18.8 (c 1.28, EtOH) [liit,$^{13)}$ bp 70—72 °C (1 mmHg), $[\alpha]_D^{23}$ −20.9]; IR (neat) 3300, 2950, 1460, 1045 cm^{-1} ^1H NMR (270 MHz), δ=0.97 (3H, s, *gem*-Me), 1.19 (3H, s, *gem*-Me), 1.41—1.53 (2H, m), 1.86—1.98 (4H, m), 1.98—2.06 (1H, m), 2.18—2.29 (1H, m), 2.32—2.43 (1H, m), 3.57 (2H, dd, J=7.5 and 4.0 Hz); MS m/z 154 (M^+, 0.6%), 136 (15), 123 (100), 93 (77), 81 (70), 69 (85), 67 (78).

***exo*-Norborneol (4i):** Mp 126 °C [lit,$^{14)}$ mp 126—127 °C]; ^1H NMR (90 MHz), δ=0.92—1.70 (m), 2.10—2.90 (m), 3.75 (1H, brd, J=3 Hz); MS m/z 112 (M^+, 5%), 94 (100), 83 (20), 79 (88), 67 (67), 57 (18).

***endo*-Camphanol (4j):** Mp 80—82 °C [lit,$^{15)}$ mp 81—83 °C]; IR (neat) 3350, 2980, 1475 cm^{-1}; ^1H NMR (270 MHz), δ=0.86, 1.00 (3H each, s, *gem*-Me), 1.16—1.40 (m), 1.54—1.72 (m), 1.73 (1H, brs), 2.27 (1H, brs), 3.59—3.68 (2H, m); MS m/z 154 (M^+, 2%), 136 (38), 121 (50), 111 (54), 107 (37), 93 (100), 67 (75).

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References

1) A part of the results were reported to *Chem. Lett.*, **1989**, 2033, by R. Shundo, Y. Matsubara, I. Nishiguchi, and T. Hirashima.

2) J. Malek, "Organic Reaction," John Wily & Sons, New York (1986), Vol. 36, p. 249, and others cited therein.

3) a) M. J. Allen, "Organic Electrode Processes," Chapman and Hall, London (1958); b) D. Deprez, R. Margraff, J. Bizot, and J. -P. Pulicani, *Tetrahedron Lett.*, **28**, 4679 (1987); c) L. Horner and H. Honl, *Justus Liebigs Ann. Chem.*, **1977**, 2036.

4) a) H. S. Broadbent and W. J. Bartly, *J. Org. Chem.*, **28**, 2345 (1963); b) H. S. Broadbent, G. C. Campbell, W. J. Bartley, and J. H. Johnson, *J. Org. Chem.*, **24**, 1847 (1959).

5) a) G. Zweifel and H. C. Brown, "Organic Reaction," John Wiley & Sons, New York (1963), Vol. 13, Chap. 1; b) A. Pelter, K. Smith, and H. C. Brown, "Borane Reagents," Academic Press, London (1988).

6) In general, diborane is generated by the reaction of sodium borohydride with a Lewis acid, such as $BF_3\cdot Et_2O$ or $AlCl_3$, and requires some special caution because of high reactivity toward air. A THF-solution is commercially available although it is limited for small-scale reactions in a laboratory.

7) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960); N. M. Yoon, C. S. Pak, H. C. Brown, S, Krishnamurthy, and T. P. Stocky, *J. Chem.*, **38**, 2786 (1973).

8) The similar oxidative transformation of $RCOOBH_3Na$ to RCH_2OH by iodine was recently reported. See J. V. Bhaskar Kanth and M. Periasamy, *J. Org. Chem.*, **56**, 5964 (1991).

9) Variation in amount of the starting compound and the product vs. that of passed electricity showed that passage of 1 F mol^{-1} of electricity led to ca. 50% conversion of the starting compound and ca. 50% yield of the product in the reaction of decanoic acid (**1b**), as shown Fig. 2.

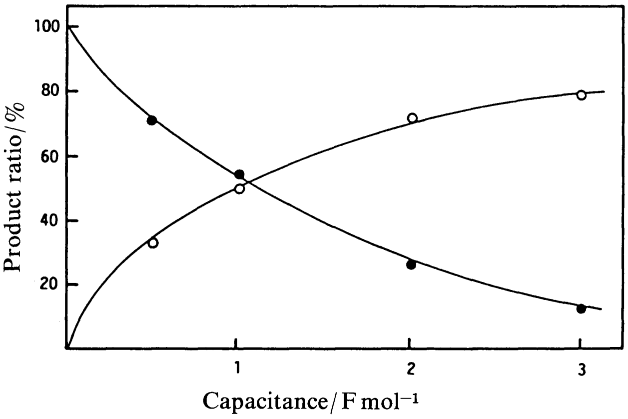

Fig. 2. Plots of product distribution of reduction of **1b** with passed electricity (F mol^{-1}): ○, **2b**: ●, **1b**.

10) Practical usefulness of the present method in organic synthesis may be shown by the fact that the yield of 1-decanol from the reaction of 0.20 mol of decanoic acid (**1b**) was almost same (69%) as that (72%) from the reaction of 0.01 mole of **1b**.

11) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover, and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4233 (1960).

12) H. C. Brown and A. Suzuki, *J. Am. Chem. Soc.*, **89**, 1933 (1967).

13) G. Zweifel and H. C. Brown, *J. Am. Chem. Soc.*, **86**, 393 (1964).

2544 (1961).

15) R. Dulou and Y. Chretien-Bessiere, *Bull. Soc. Chim. Fr.*, **1959**, 1362.