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Novel Method for Hydroboration of Olefins Using Electrolysis

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A first example of electrochemical hydroboration of olefins was found. Anodic oxidation of sodium borohydride in the presence of olefins in diglyme followed by conventional oxidation gave the corresponding alcohols regio- and stereoselectively in good yields.

Hydroboration has been well recognized as one of most important and useful methods in organic synthesis, and applied to numerous types of selective transformations of organic compounds.[1] In this study, we wish to report a new method for hydroboration of a variety of olefins **1** using electrolysis, which may be initiated by anodic oxidation of borohydride anion to borane (Eq. 1).

$$\underset{\mathbf{1}}{R\text{-}CH{=}CH_2} \xrightarrow[NaBH_4,\ \text{electrolyte}]{\text{electrolysis}} \xrightarrow[H_2O_2,\ NaOH]{} \underset{\mathbf{2}}{R\text{-}CH_2\text{-}CH_2\text{-}OH} \quad (1)$$

The typical procedure for preparation of cis-myrtanol (**2e**) is as follows: (-)-β-pinene (**1e**) (2.72 g, 20 mmol) was dissolved in 50 ml of anhydrous diglyme containing sodium iodide (2.98 g, 20 mmol) and sodium borohydride (0.37 g, 10 mmol). The electrolysis was carried out under the constant-current conditions (0.2 A, current density 50 mA/cm^2) using a beaker-type undivided cell equipped with a platinum foil (2 cm X 2 cm) as an anode and a stainless plate as a cathode (2 cm X 2 cm). The solution was magnetically stirred at room temperature under nitrogen

atmosphere until 2 F/mol of electricity based on **1e** passed through the system The reaction mixture was filtered through glass wool,[2] and was subsequently oxidized with a mixture of 3 mol dm^{-3} sodium hydroxide (5 ml) and 30% hydrogen peroxide (5 ml) for 2 h at room temperature. Usual work-up followed by fractional distillation gave (-)-cis-myrtanol[3] (**2e**) as a single product in an 81% yield.

It was noteworthy that the yield of **2e** was strongly dependent on the nature of a supporting electrolyte, as shown in Table 1. Sodium iodide gave the best result among the supporting electrolytes examined (entry 1 in Table 1). The absence of alkali metal iodide required 2 equiv. mole of sodium borohydride for the effective transformation of **1e** to **2e** (entry 6 in Table 1). It was interesting that only half equivalent mole of sodium borohydride based on **1e** was enough when sodium iodide was used as a supporting electrolyte (entry 2 in Table 1).

Table 1. Effect of Supporting Electrolytes on Electrochemical Hydroboration of **1e**

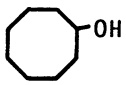
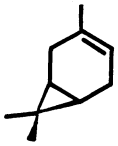
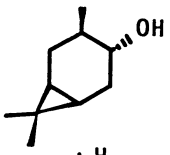
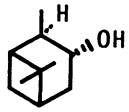
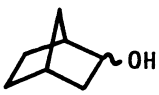
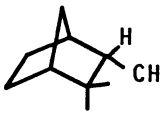
Entry	Supporting electrolyte	$NaBH_4$ /mmol	Yield[a]/% of **2e**
1	NaI	25	82
2	NaI	10	81
3	KI	25	71
4	LiI	25	82
5	LiI	10	0
6	-	40	71
7	-	25	0[b]
8	$NaBF_4$	40	44
9	$LiClO_4$	25	12
10	LiBr	25	0[b]

a) Isolated yield based on **1e** 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.

The similar electrochemical methods under these optimum conditions brought about regio- and stereoselective transformation of a variety of olefins **1** to the corresponding alcohols **2**, and the results are summarized in Table 2.

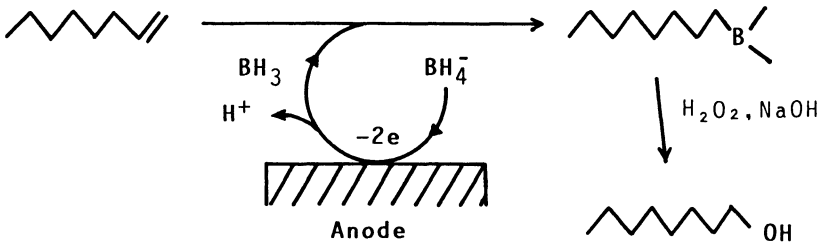
Table 2. Electrochemical Hydroboration of Olefins[a)]

Substrate 1		Product 2[b)]		Yield[c)] / %	
	1a		2a[d)]	81	(80)[e)]
	1b		2b	72	
	1c		2c	70	(98)[e)]
	1d		2d	78	(89)[e)]
	1e		2e	82	(81)[e)]
	1f		2f	72[f)]	(85)[e)]
	1g		endo 2g	75	(77)[e)]

a) The reaction was carried out under similar reaction conditions to those described for the preparation of **2e** from **1e**. b) All the products were identified by comparison of their spectroscopic (IR, ^{1}H-NMR, and MS) and gas chromatographic behaviors with those of authentic samples. c) Isolated yield based on a substrate used. d) 2-Octanol (4-5%) was also formed as was found by a conventional method.[4)] e) Reported yields by a conventional method.[4)] f) exo/endo = >99/1.

Cyclic voltammetry of sodium borohydride showed the oxidation peak potential(Ep) at -0.045 V (vs. SCE), indicating that borohydride anion is quite readily oxidized. Although a detailed reaction mechanism for the present electrochemical hydrobration has not been clear as yet, the initial two-electron

transfer from borohydride anion (BH_4^-) to an anode may generate borane species,[5] which readily reacts with olefins to give the corresponding alkylborane,[6] as shown in Scheme 1.



Scheme 1.

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References

1) G. Zweifel and H. C. Brown, "Organic Reactions," John Wiley & Sons, New York (1963), Vol. 13, Chap.1; H. C. Brown, "Organic Synthesis via Boranes," John Wiley & Sons, New York (1975); A. Pelter, K. Smith, and H. C. Brown, "Borane Reagents," Academic Press, London (1988).

2) Some pieces of sodium metal generated by cathodic reduction of sodium cation was easily removed by filtration.

3) **2e** : bp 78-82 °C (3 mmHg); $[\alpha]_D$ -18.8° (c 1.28, EtOH); IR (neat) 3300(OH), 2950, 1460, and 1045 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ = 0.92 (3H, s, $-CH_3$), 1.19 (3H, s, $-CH_3$), 3.57 (2H, dd, J=6 and 3Hz); m/z (rel intensity) 154 (M^+;0.6), 136 (15), 123 (100), 93 (77), 81 (70), 69 (85), and 67 (78).

4) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover, and G. Zweifel, J. Am. Chem. Soc., 82, 4233 (1960); H. C. Brown and G. Zweifel, ibid., 83, 2544 (1961); H. C. Brown and A. Suzuki, ibid., 89, 1933 (1967); R. Dulou and Y. Chretien-Bessiee, Bull. Soc. Chim. Fr., 1959, 1362.

5) This electrochemically generated borane species may include borane and its complex with diglyme (BH_3-diglyme).

6) Electrochemical reactions of trialkylborane were reported : T. Taguchi, M. Ito, and A. Suzuki, Chem. Lett., 1973, 719; T. Taguchi, Y. Takahashi, and A. Suzuki, ibid., 1974, 1021; Y. Takahashi, M. Tokuda, M. Ito, and A. Suzuki, ibid., 1975, 523; Y. Takahashi, M. Tokuda, M. Ito, and A. Suzuki, Synthesis, 1976, 616; Y. Takahashi, M. Tokuda, M. Ito, and A. Suzuki, Chem. Lett., 1977, 999; Y. Takahashi, K. Yuasa, M. Tokuda, M. Ito, and A. Suzuki, Bull. Chem. Soc. Jpn., 51, 339 (1978); Y. Takahashi, M. Tokuda, M. Ito, and A. Suzuki, Chem. Lett., 1980, 461.

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