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# One Pot Electrooxidative Conversion of Benzyl Type Alcohols into the Corresponding Methyl Carboxylates

Mitsuhiro Okimoto<sup>a</sup>, Yuji Nagata<sup>a</sup>, Satoru Sueda<sup>a</sup> & Yukio Takahashi<sup>a</sup>

<sup>a</sup> Department of Applied Chemistry and Circumstance Engineering, Kitami Institute of Technology, Koen-cyo165, Kitami, 090-8507, Japan Published online: 18 Oct 2011.

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## One Pot Electrooxidative Conversion of Benzyl Type Alcohols into the Corresponding Methyl Carboxylates

#### Mitsuhiro Okimoto,\* Yuji Nagata, Satoru Sueda, and Yukio Takahashi

Department of Applied Chemistry and Circumstance Engineering, Kitami Institute of Technology, Kitami, Japan

#### ABSTRACT

One-pot conversion of several benzyl type alcohols into the corresponding methyl carboxylates was carried out by indirect electrooxidation using iodide ion as the electron carrier.

*Key Words:* Benzyl type alcohols; Electrooxidation; Methyl carboxylates; Iodide ion.

Oxidation of organic compounds using molecular iodine as the oxidizing agent has been limited due to the toxicity of iodine.<sup>[1-4]</sup> However, with the use

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<sup>\*</sup>Correspondence: Mitsuhiro Okimoto, Department of Applied Chemistry and Circumstance Engineering, Kitami Institute of Technology, Koen-cyo165, Kitami 090-8507, Japan; Fax: +81-157-24-7719.

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of catalytic amounts of iodide ion instead of the toxic iodine, these oxidation reactions have attracted renewed interest as useful synthetic methods.<sup>[5,6]</sup> Chemical oxidations of benzyl alcohols using various strong oxidizing agents, such as active manganese oxide,<sup>[7,8]</sup> chromium oxide,<sup>[9,10]</sup> and nitric acid,<sup>[11,12]</sup> are extensively reported in synthetic reactions. Although comparatively, a benzylic hydroxyl group is more readily oxidized to the corresponding carbonyl group than an aliphatic hydroxyl groups,<sup>[13]</sup> to the best of our knowledge, application of the electrochemical technique to the one-pot conversion of benzyl type alcohols (**1a–l**) into the corresponding methyl carboxylates (**2a–l**) has not been reported. We have previously reported on the indirect electrooxidation of aldehydes,<sup>[14]</sup> ketones,<sup>[15–17]</sup> and hydrazones<sup>[18,19]</sup> using halide ion as an electron carrier.

As a continuation in this series of studies, we have carried out one-pot conversion of 1a-l to the corresponding 2a-l through indirect electro-oxidation.

Benzyl type alcohols **1a–l** were oxidized electrochemically to afford the corresponding methyl carboxylates **2a–l** in good to excellent isolated yields (Table 1). Electrooxidation products **2a–g** and **2i–l** were isolated with yields of 80% or above, with the single exception for the electrooxidation of **4**-nitrobenzyl alcohol (**1h**), in which methyl **4**-nitrobenzoate (**2h**)was obtained in only 38% yield, along with unreacted **1h**.

We have observed a tendency that, remarkably, the ortho-substituted substrates (1c, 1e, and 1g) consumed significantly more quantities of electricity to complete the electrooxidation reaction than the para-isomers (1b, 1d, and 1f). We have also observed that several substrates that contain an electron-donating group on the aromatic ring (1b, 1c, 1d, 1e, and 1i) oxidized more readily than substrates bearing an electron-withdrawing group (1f, 1g, and **1h**). It is reasonable to assume that the electrooxidation of **1** proceeded via formation of the corresponding aldehydes as the reaction intermediate since detectable amounts of the aldehydes were usually confirmed by GLC analyses of the anolyte during the course of the electrooxidation. Furthermore, the conversion of 1 into the corresponding aldehydes appeared as the ratedetermining step, since several aromatic aldehydes were readily oxidized into the corresponding methyl carboxylates 2 with yields of 78-88% under the reaction conditions employed here.<sup>[14]</sup> The value of anode potential of the electrolysis was not dependent on that of oxidation potential of the substrate. In addition, the electrolysis could be achieved under 0.5 V or less vs. SCE of anode potential. These observations suggest that the oxidation proceeded by means of iodide cationic species which was formed from iodide ions.

As illustrated in Figure 1, the general reaction pathway of the electrooxidation involves a four-electron-oxidation reaction process with the iodide ion functioning as the electron carrier. However, we have observed that large

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#### **Conversion of Benzyl Type Alcohols**

	R —	CH <sub>2</sub> –OH – C 1 – KI-M	Dxidation eONa/MeOH	$\stackrel{O}{\rightarrow} R - \stackrel{  }{C} - OMe$	
			THE LAB AS	Bp(°C/mml	Hg) of (°C)
	Substrate R	Current passed (Fmol <sup>-1</sup> )	Yield <sup>®</sup> of 2 (%)	Obs.	Ref. <sup>c</sup>
1a	Ph	13	82	88-99 (19)	96-98 (24)
1b	$4-CH_3C_6H_4$	11	89	110-111 (23)	217
1c	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	18	81	98-99 (16)	97 (15)
1d	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	9	91	130-131 (14)	256
1e	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	16	85	128-129 (16)	245-246
1f	4-ClC <sub>6</sub> H <sub>4</sub>	15	90	40-42	44
				(MeOH) <sup>d</sup>	
1g	2-ClC <sub>6</sub> H <sub>4</sub>	27	83	114-117 (17)	234
1h	$4-NO_2C_6H_4$	15	38	96-97(EtOH) <sup>d</sup>	96
1i	4-iso-C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub>	12	83	120-122 (12)	126 (14)
1j	2-Furyl	18	73	104-106 (60)	181
1k	2-Thienyl	11	80	103-105 (27)	40 (0.5)
1l	1-Naphtyl	22	93	160-162 (12)	159–160 (11)

Table 1. Electrochemical indirect oxidation of benzyl type alcohols.<sup>a</sup>

<sup>a</sup>Substrate: 20 mmol; KI: 10 mmol; NaOMe: 5 mmol; MeOH: 80 mL; r.temp: ca 20°C. <sup>b</sup>Isolated yield. <sup>c</sup>Ref.<sup>[20]</sup>.

<sup>d</sup>Solvent for recrystallization.



Figure 1. Electrooxidation general reaction pathway involving a 4-electronoxidation reaction with iodine ion as the electron carrier.

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excesses in the quantity of electricity were consumed to complete the transformation of substrates 1 into products 2. We can assume that the chemical oxidation process of 1 to the aldehydes, through the action of iodonium ions formed on the anode is less efficient than the subsequent oxidation of the aldehydes to 2. In the case of the electrooxidation of 1a, the use of KBr or KCl instead of KI lowered the yields of 2a to 28% or 7%, respectively, with significant recovery of unreacted 1a. Higher reaction temperatures did not improve the yields of 2a; for example, by raising the reaction temperature from 15°C to 50°C, the yield of 2a decreased from 95% to 60%. However, in the cases of 1l, elevating the temperature from 15°C to 50°C was favorable for the formation of 2l. Furthermore, introduction of 0, 2.5, 5, and 10 mmol KI afforded 2a with yields of 6%, 43%, 70%, and 95%, respectively (GLC yield of 2a based on 1a). Addition of a stoichiometric (20 mmol) or excess amount of KI did not improve either the current efficiencies or the yields of 2a.

In summary, we have developed a convenient one-pot indirect electrooxidation method for the conversion of benzyl type alcohols into the corresponding methyl carboxylates in good to excellent isolated yields. This preparative electooxidation could be carried out under very mild conditions and without the use of strong and/or special oxidizing agents.

#### **EXPERIMENTAL**

All electrooxidation products 2a-l were identified by comparison of their physical and spectral data with those of authentic samples. Melting and boiling points were uncorrected. Substrates and other reagents were obtained from commercial suppliers, and used without further purifications. Preparative-scale electrooxidations were carried out in a tall 100-mL beaker equipped with a fine frit cup as the cathode compartment, a cylindrical platinum net anode (diameter, 33 mm; height, 40 mm), and a nickel coil cathode (diameter, 1 mm; length, 250 mm). Benzyl type alcohols **1a-1** were oxidized under conditions as follow: a solution of benzyl type alcohol 1a-l (20 mmol), KI (10 mmol), and NaOMe (5 mmol) in MeOH (80 mL) was electrooxidized under a constant current (0.5 A). During the course of the electrooxidation, while stirring the analyte with a magnetic stirring bar, the temperature of the cell was maintained at approximately 15°C. After completion of the electrooxidation, the reaction mixture was treated using a three-fold increase in the amount of the anolyte. After concentrating the combined anolyte solution in vacuo at approximately 30°C to about one-fifth of its original volume, the resulting residue was treated with water (60 mL), and the oily layer was extracted with ether (3  $\times$  50 mL). The combined ether extracts were washed with aqueous sodium thiosulfate solution (20 w%, 30 mL), and dried



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over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified by distillation in vacuo or by recrystallization from either MeOH or EtOH.

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