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## New Electrochemical Carboxylation of Vinyl Triflates. Synthesis of β-Keto Carboxylic Acids

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Abstract: Electrochemical reduction of alicyclic vinyl triflates (1a-1e) in a DMF solution containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> under an atmospheric pressure of carbon dioxide with a platinum cathode and a magnesium anode resulted in the cleavage of an oxygen-sulfur bond of 1 to give the corresponding  $\beta$ -keto carboxylic acids (2a-2e) in yields of 28-77%. © 1998 Elsevier Science Ltd. All rights reserved.

It has been reported by Silvestri<sup>1,2</sup> and Perichon<sup>3,4</sup> that electrochemical carboxylation of organic halides or carbonyl compounds readily occurs under an atmospheric pressure of carbon dioxide to give the corresponding carboxylic acids in high yields when a sacrificial anode, such as a magnesium or aluminum metal, is used in the electrolysis. We recently reported the regioselective synthesis of  $\gamma$ -substituted  $\beta$ ,  $\gamma$ -unsaturated carboxylic acids, <sup>5</sup> allenic acids, <sup>6</sup> and 3-methylene-4-pentenoic acid<sup>7</sup> by the electrochemical carboxylation of  $\gamma$ -substituted allylic halides, substituted propargylic halides, and 2-bromomethyl-1,4-dibromo-2-butene, respectively, using a magnesium anode. We also reported the efficient electrochemical carboxylation of phenyl-substituted vinyl bromides to give the corresponding  $\alpha$ , $\beta$ -unsaturated carboxylic acids.<sup>8</sup> We also found that electrochemical carboxylation of alkyl-substituted vinyl bromides occurred in high yields to give the corresponding  $\alpha$ , $\beta$ -unsaturated carboxylic acids when the electrochemical carboxylation was carried out in the presence of 20 mol% of NiBr<sub>2</sub>-bpy complex.<sup>9</sup> On the other hand, quite recently, Jutand reported similar electrochemical synthesis of  $\alpha$ , $\beta$ -unsaturated carboxylic acids by palladium-catalyzed electrochemical carboxylation of vinyl triflates.<sup>10</sup> Their paper prompted us to publish our recent results on a new electrochemical carboxylation of vinyl triflates giving  $\beta$ -keto carboxylic acids.

The trifluoromethanesulfonate group is well known to be an excellent leaving group and, hence, a cleavage of the vinyl carbon-oxygen bond occurs in usual chemical reactions of vinyl triflates. Thus, vinyl triflates have been used as precursors of vinyl cations in various synthetic transformations.<sup>11</sup> On the other hand, the present electrochemical carboxylation of vinyl triflates is very unique since a cleavage of the oxygen-sulfur bond can take place to generate the corresponding enolates as an intermediate.

Vinyl triflates 1 were readily prepared in 73-98% yields from the corresponding ketones by their reactions with trifluoromethanesulfonic anhydride in the presence of 2,6-di-*t*-butyl-4-methylpyridine.<sup>12</sup> A 4:1 mixture of two isomeric vinyl triflates (1e and 1f) was obtained in the reaction of  $\beta$ -tetralone.

Electrochemical carboxylation of vinyl triflates 1 (6 mmol) in a DMF solution containing 0.1M  $Bu_4NBF_4$  (15 ml) under an atmospheric pressure of carbon dioxide gave the corresponding  $\beta$ -keto carboxylic acids 2 in

good yields (Scheme 1). Electrolysis was carried out at 5 °C at a constant current of 10 mA/cm<sup>2</sup> in a onecompartment cell equipped with a platinum plate cathode (2x3 cm<sup>2</sup>) and a magnesium rod anode (3 mm $\phi$ ). Electricity of 3 Faradays per mol of 1 was passed in these carboxylations. Usual acid treatment of the electrolyzed mixture gave  $\beta$ -keto carboxylic acids 2. The yields of products 2a-2e are summarized in Table 1.

Scheme 1	1
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Substrate		Product		Yield of <b>2</b> (%) <sup>b</sup>
от С	1a	CO2H	2a	75 (100)
	1b	CO <sup>2</sup> H	2b	56 (89)
ОТТ	1c	CO2H	2c	28 (59)
CTT.	1d	CO2H	2d	71 (81)
	10	C0₂H	2e	77 (87)
COLOTH 1	1f			

Table 1. Electrochemical Carboxylation of Vinyl Triflates (1a-1f)<sup>a</sup>

a) Vinylic triflate (1a-1f)(6 mmol) in 0.1M Bu<sub>4</sub>NBF<sub>4</sub>-DMF (15 ml) was electrolyzed at 10 mA/cm<sup>2</sup> under an atmospheric carbon dioxide with a platinum cathode and a magnesium anode. Electricity passed was 3 Faradays per mol of 1.

b) Isolated yields. Yields based on reacted vinyl triflates are shown in parentheses.

None of  $\beta$ -keto carboxylic acid arising from 1f was obtained in the electrochemical carboxylation of a mixture of 1e and 1f. In this case, 1f was almost recovered unreacted. This result shows that phenyl-substituted vinyl triflates are more reactive than alkyl-substituted ones. A similar tendency has been observed in the electrochemical carboxylation of phenyl-substituted<sup>8</sup> and alkyl-substituted vinyl bromides.<sup>9</sup>

The use of a magnesium anode and the presence of reduced species of carbon dioxide are necessary for efficient carboxylation of vinyl triflates. Electrochemical carboxylation of 1a by the use of a platinum cathode and a platinum anode did not give  $\beta$ -keto acid 2a. Even in the presence of electrogenerated magnesium bromide,<sup>13</sup> electrochemical carboxylation of **1a** with a platinum cathode and anode also gave no **2a**. Therefore, the present electrochemical carboxylation of vinyl triflates giving  $\beta$ -keto carboxylic acids can be achieved only when a reduction of carbon dioxide followed by a fragmentation of vinyl triflates and the formation of magnesium ion by dissolution of a magnesium anode take place at the same time and in the same compartment.<sup>5</sup> It was also confirmed that no reduction of 1a and no cleavage of the oxygen-sulfur bond occurred when the electrochemical reduction of 1a was carried out in the absence of carbon dioxide with a platinum cathode and a magnesium anode. In these electrolyses, the starting vinyl triflate la was almost recovered. Cyclic voltammetry of 1a showed no reduction peak at > -2.9 V vs Ag/Ag<sup>+</sup>. On the other hand, the reduction peak potential of carbon dioxide in DMF containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> is -2.6 V vs Ag/Ag<sup>+</sup>. Carbon dioxide is more readily reduced than vinyl triflate 1a. The probable reaction pathways of the present electrochemical carboxylation are shown in Scheme 2. A one-electron reduction of carbon dioxide generates an anion radical of CO<sub>2</sub>, which induces the cleavage of an oxygen-sulfur bond of 1 by a nucleophilic attack at sulfur or by an electron transfer reaction.<sup>14</sup> An enolate A thus generated is trapped by atmospheric carbon dioxide to give  $\beta$ -keto carboxylate ion (B). At the anode, on the other hand, a dissolution of magnesium metal takes place to give magnesium ions. The magnesium ion readily captures  $\beta$ -keto carboxylate (B) to give the stable magnesium carboxylate C or D. Acid treatment of C or D gives  $\beta$ -keto carboxylic acid 2. The exact mechanism of the step in which an enolate A is formed is unclear at the present stage. However, a study of cyclic voltammetry showed that the reduction current of carbon dioxide was considerably enhanced by the addition of 1a to a DMF solution containing carbon dioxide (Fig. 1). This result suggests that an anion radical of carbon dioxide actually induces the cleavage of an



Scheme 2

oxygen-sulfur bond of 1 to give A.<sup>14</sup> A detailed study on the reaction mechanism of the present electrochemical carboxylation is now in progress.



Fig. 1. Cyclic voltammograms of CO<sub>2</sub> and 1a in 0.1M Bu<sub>4</sub>NBF<sub>4</sub>-DMF (Au disc electrode (1.6 mmø); scan rate=0.1 Vs<sup>-1</sup>)
a) 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>-DMF; b) CO<sub>2</sub>; c) CO<sub>2</sub> + 8.9 mM 1a

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- 12. Jigajinni, V. B.; Wightman, R. H. Tetrahedron Lett., 1982, 23, 117-120; Stang, P.J.; Treptow, W. Synthesis, 1980, 283-284.
- 13. Magnesium bromide, which is soluble in a DMF solution, can be prepared by electrolysis of 1,2dibromoethane with a platinum cathode and a magnesium anode.
- 14. Magnesium ions generated by dissolution of a magnesium anode might play an important role in the cleavage of an oxygen-sulfur bond of 1, since the electrolysis of 1a using a platinum cathode and anode in the presence of  $CO_2$  gave no 2a, and 1a was almost recovered.