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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$_4$NBF$_4$ 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 β-keto carboxylic acids (**2a**-**2e**) in yields of 28-77%. © 1998 Elsevier Science Ltd. All rights reserved.

It has been reported by Silvestri[1,2] and Perichon[3,4] 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 γ-substituted β,γ-unsaturated carboxylic acids,[5] allenic acids,[6] and 3-methylene-4-pentenoic acid[7] by the electrochemical carboxylation of γ-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 α,β-unsaturated carboxylic acids.[8] We also found that electrochemical carboxylation of alkyl-substituted vinyl bromides occurred in high yields to give the corresponding α,β-unsaturated carboxylic acids when the electrochemical carboxylation was carried out in the presence of 20 mol% of NiBr$_2$•bpy complex.[9] On the other hand, quite recently, Jutand reported similar electrochemical synthesis of α,β-unsaturated carboxylic acids by palladium-catalyzed electrochemical carboxylation of vinyl triflates.[10] Their paper prompted us to publish our recent results on a new electrochemical carboxylation of vinyl triflates giving β-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.[11] 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.[12] A 4:1 mixture of two isomeric vinyl triflates (**1e** and **1f**) was obtained in the reaction of β-tetralone.

Electrochemical carboxylation of vinyl triflates **1** (6 mmol) in a DMF solution containing 0.1M Bu$_4$NBF$_4$ (15 ml) under an atmospheric pressure of carbon dioxide gave the corresponding β-keto carboxylic acids **2** in

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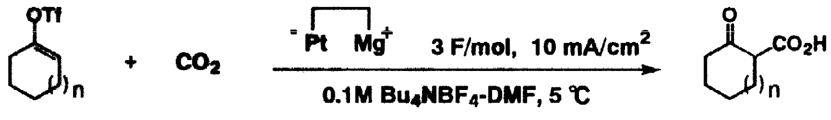
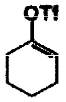
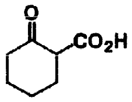
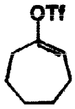
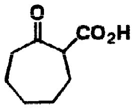
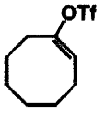
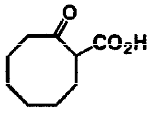
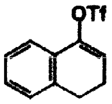
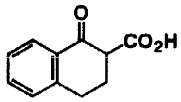
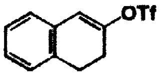
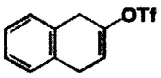
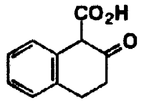
good yields (Scheme 1). Electrolysis was carried out at 5 °C at a constant current of 10 mA/cm$^2$ in a one-compartment cell equipped with a platinum plate cathode (2x3 cm$^2$) and a magnesium rod anode (3 mmφ). Electricity of 3 Faradays per mol of **1** was passed in these carboxylations. Usual acid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



**1a-1e** **2a-2e**

Scheme 1

Table 1. Electrochemical Carboxylation of Vinyl Triflates (**1a**-**1f**) [a]

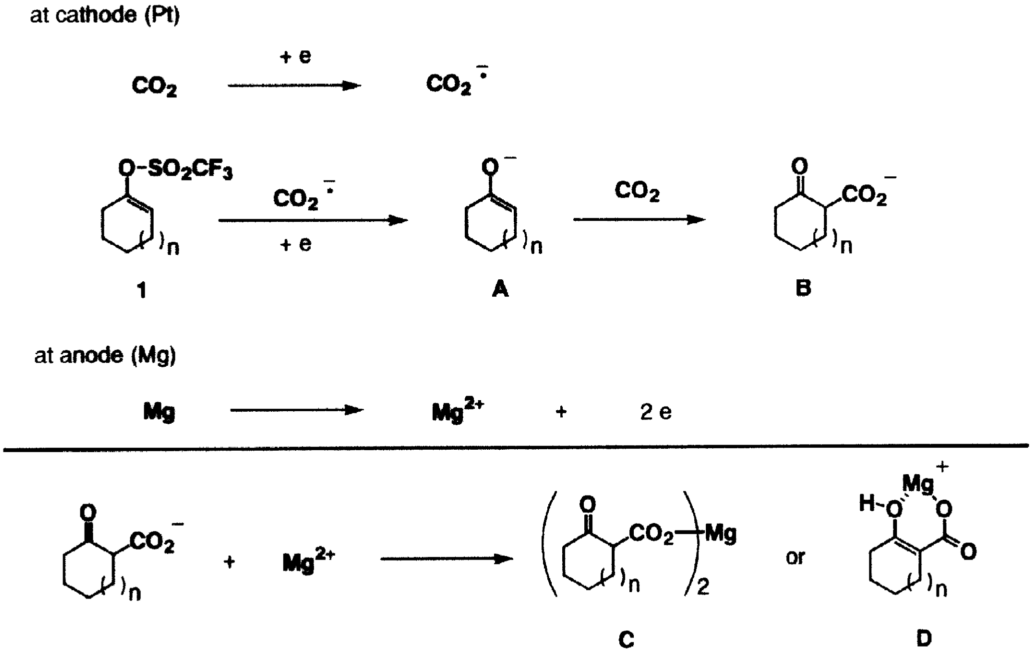
| Substrate | | Product | | Yield of 2 (%)[b] |
|---|---|---|---|---|
|  | **1a** |  | **2a** | 75 (100) |
|  | **1b** |  | **2b** | 56 (89) |
|  | **1c** |  | **2c** | 28 (59) |
|  | **1d** |  | **2d** | 71 (81) |
| <br>4 : 1<br> | **1e**<br><br>**1f** |  | **2e** | 77 (87) |

a) Vinylic triflate (**1a**-**1f**)(6 mmol) in 0.1M Bu$_4$NBF$_4$-DMF (15 ml) was electrolyzed at 10 mA/cm$^2$ 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 β-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[8] and alkyl-substituted vinyl bromides.[9]

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 β-keto acid **2a**. Even in the presence of electrogenerated magnesium bromide,[13] electrochemical carboxylation of **1a** with a platinum cathode and anode also gave no **2a**. Therefore, the present electrochemical carboxylation of vinyl triflates giving β-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.[5] 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 **1a** was almost recovered. Cyclic voltammetry of **1a** showed no reduction peak at > -2.9 V *vs* $Ag/Ag^+$. On the other hand, the reduction peak potential of carbon dioxide in DMF containing 0.1 M $Bu_4NBF_4$ is -2.6 V *vs* $Ag/Ag^+$. 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 $CO_2$, which induces the cleavage of an oxygen-sulfur bond of **1** by a nucleophilic attack at sulfur or by an electron transfer reaction.[14] An enolate **A** thus generated is trapped by atmospheric carbon dioxide to give β-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 β-keto carboxylate (**B**) to give the stable magnesium carboxylate **C** or **D**. Acid treatment of **C** or **D** gives β-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.**[14] **A detailed study on the reaction mechanism of the present electrochemical carboxylation is now in progress.**

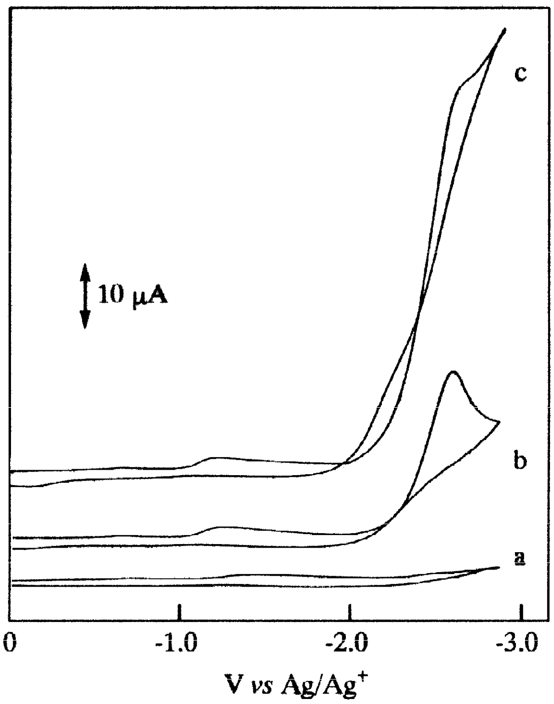


Fig. 1. Cyclic voltammograms of $CO_2$ and **1a** in 0.1M $Bu_4NBF_4$-DMF (Au disc electrode (1.6 mmϕ); scan rate=0.1 $Vs^{-1}$)
a) 0.1 M $Bu_4NBF_4$-DMF; b) $CO_2$; c) $CO_2$ + 8.9 mM **1a**

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## REFERENCES AND NOTES

1. Silvetsri, G.; Gambino, S.; Filardo, G.; Gulotta, A. *Angew. Chem. Int. Ed. Engl.*, **1984**, *23*, 979-980.
2. Silvetsri, G.; Gambino, S.; Filardo, G. *Acta Chem. Scand.*, **1991**, *45*, 987-992.
3. Sock, O.; Troupel, M.; Perichon, J. *Tetrahedron Lett.*, **1985**, *26*, 1509-1512.
4. Chaussard, J.; Folest, J. C.; Nedelec, J. Y.; Perichon, J.; Sibille, S.; Troupel, M. *Synthesis*, **1990**, 369-381.
5. Tokuda, M.; Kabuki, T.; Katoh, Y.; Suginome, H. *Tetrahedron Lett.*, **1995**, *36*, 3345-3348.
6. Tokuda, M.; Kabuki, T.; Suginome, H. *DENKI KAGAKU*, **1994**, *62*, 1144-1147.
7. Tokuda, M.; Yoshikawa, A.; Suginome, H.; Senboku, H. *Synthesis*, **1997**, *in press*.
8. Kamekawa, H.; Senboku, H.; Tokuda, M. *Electrochimica Acta*, **1997**, *42*, 2117-2123.
9. Kamekawa, H.; Kudoh, H.; Senboku, H.; Tokuda, M. *Chem. Lett.*, **1997**, 917-918.
10. Jutand, A.; Négri, S. *Synlett*, **1997**, 719-721.
11. Ritter, K. *Synthesis*, **1993**, 735-762.
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 1,2-dibromoethane 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.